Macromolecules **1983,** *16,* 121–127

tended by Koningsveld and Kleintjens is suitable for calculating cloud point curves at high pressure if a pressure dependence is introduced in the interaction parameter. The particular pressure dependence for systems of linear polyethylene + ethylene has been evaluated and is given in an analytical form. Thus the calculation of the phase behavior of any system of linear polyethylene + ethylene is now possible if the molecular weight distribution of the linear polyethylene is known.

Experimental work on systems of branched polyethylene + ethylene indicates a strong effect of the degree of branching on the cloud point curves.[19] This effect cannot be described by the model in the present form. Proper modification of the model taking into account the degree of branching is in progress.

Acknowledgment. We are indebted to Dr. R. Koningsveld and Dr. L. A. Kleintjens (Central Laboratory, DSM) for stimulating discussions.

Registry No. Polyethylene, 9002-88-4; ethylene, 74-85-1.

References and Notes

(1) de Loos, Th. W.; Poot, W.; Diepen, G. A. M. *Macromolecules*, preceding paper in this issue.
(2) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(3) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(4) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(5) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(6) Bonner, D. C.; Maloney, D. P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13*, 91.
(7) Harmony, S. C.; Bonner, D. C.; Heichelheim, H. R. *AIChE J.* **1977**, *23*, 758.
(8) Bogdanović, V.; Djordjević, B.; Tasić, A.; Krnić, Z. *Adv. Sep. Sci.* **1978**, 185.
(9) Bogdanović, V.; Tasić, A.; Djordjević, B.; Krnić, Z. *Chem.-Ing.-Tech.* **1980**, *52*, 149.
(10) Bogdanović, V.; Tasić, A.; Djordjević, B. *Fluid Phase Equilib.* **1981**, *6*, 83.
(11) Liu, D. D.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 205.
(12) Kleintjens, L. A. Ph.D. Thesis, Essex, 1979.
(13) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(14) Koningsveld, R.; Diepen, G. A. M.; Chermin, H. A. G. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 504.
(15) Swelheim, T.; de Swaan Arons, J.; Diepen, G. A. M. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1.
(16) de Loos, Th. W. Ph.D. Thesis, Delft, 1981.
(17) Šolc, K. *Macromolecules* **1970**, *3*, 665.
(18) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Part A-2* **1968**, *6*, 305.
(19) de Loos, Th. W.; Poot, W.; Lichtenthaler, R. N., to be published.

Equilibrium Polymer Size Distributions

John L. Spouge

Trinity College, Oxford OX1 3BH, England. *Received March 30, 1982*

ABSTRACT: In this paper, we give general methods of determining the equilibrium distribution of polymer sizes. Our methods apply to any closed system, subject to the following conditions: (1) the structural units composing the polymers are identical, (2) the forward reaction rates of aggregation a_{ij} depend only on the sizes (and not the structures) of the reacting species, and (3) intramolecular reactions do not occur. In 1943, Stockmayer determined a particular equilibrium distribution of polymer sizes by maximizing statistical mechanical entropy. In our paper, we use another statistical mechanical quantity, our so-called polymer partition function Z. Using Z, we give general formulas for polymer size distributions and gelation conditions. These formulas admit numerical solution for any form of a_{ij}. On the other hand, when $a_{ij} = A + B(i + j) + Cij$, the polymer partition function Z is determined by an ordinary differential equation. By solving the differential equation and applying Lagrange's expansion to the resulting functional equation, we give explicit size distributions for Flory's f-functional random polycondensation (RA$_f$) model and for the ARB$_{f-1}$ model, along with the size distributions in the limiting case as f tends to infinity. These distributions agree with classical results. We give explicit gelation conditions for the A$_g$RB$_{f-g}$ model of polymerization. Donoghue and Gibbs gave asymptotic series (as the system size approaches infinity) for the distribution of polymer sizes in the RA$_f$ model. In statistical mechanics, this is equivalent to applying Darwin and Fowler's method of mean distributions (steepest descents method) instead of the method of most probable distributions (Lagrange multipliers). Knowing this, we can state that our results will apply only if the system has not gelled. In addition, the discussion announces new results concerning the agreement between models of reversible and irreversible polymerization, while the Appendix gives some solutions for reversible polymerization in cases other than $a_{ij} = A + B(i + j) + Cij$.

I. Introduction

This paper concerns itself with the determination of equilibrium polymer size distributions, and its methods are quite general. Here is a list of sections in the paper, along with a resumé of each section:

Section II: The Different Models

We introduce some classical models for polymerization reactions. These models can be characterized by their forward reaction rates for aggregation (which we call the a_{ij}'s). In a crucial step, we relate these forward reaction rates to the number of polymeric isomers of size k (which we call w_k).

Section III: Polymer Partition Functions

In 1943, Stockmayer determined the equilibrium distribution of polymer sizes for one particular model of polymerization (Flory's RA$_f$ model). He did this by maximizing the entropy of the size distribution, a quantity that involved the w_k's. Because his methods generalize, we summarize them. We then show that his results are simplified by the use of the exponential generating function of the w_k's, which we call the polymer partition function Z. Hence, *we reduce the calculation of polymer size distributions to the calculation of the polymer partition function Z.*

Section IV: Specific Polymer Partition Functions

In this section, we show how several classical models can be handled by our methods. When $a_{ij} = A + B(i + j) + Cij$, we can manipulate the relationship between the a_{ij}'s and w_k's (at the end of section II) into an ordinary dif-

0024-9297/83/2216-0121$01.50/0

ferential equation for Z. In most cases, the differential equation produces a functional equation for Z to which Lagrange's expansion applies. In these cases, we obtain explicit forms for the w_k's. These, in turn, yield explicit forms for the polymer distributions. In all cases, we give explicit expressions for Z and its derivatives.

Please note that *our formalism is not limited to producing explicit formulas.* For models where a_{ij}'s have more complicated forms than $A + B(i + j) + Cij$, *our methods may be used to generate numerical results.*

Section V: Moments of the Size Distribution and Gelation

In this section, we give general expressions for the number- and weight-average molecular weights of a polymer distribution. These involve Z and its derivatives. From the expressions, we posit the divergence of any derivative of Z is a sufficient condition for gelation to occur. From this, *we derive new gelation results* for a classical model of polymerization (Flory's A_gRB_{f-g} model).

Section VI. Discussion

Here we clarify the physical basis for the mathematical results. In particular, we show that *the solutions obtained are indeed equilibrium solutions.* Statistical mechanical methods allow some simple observations to be made. In addition, we announce a result concerning the concurrence of kinetic and equilibrium distributions.

Appendix

Some additional equilibrium solutions are displayed.

II. The Different Models

In this section, we introduce five models which will serve as paradigms of polymerization.

(1) The RA_f Model. This was introduced by Flory[6] and is 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. The units react subject to three conditions:

(a) Functional groups of the type A react with one another to form bonds between the units.

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

(c) Flory's principle of equireactivity: subject to conditions a and b, all unreacted functional groups are equally reactive.

Let us call a polymer of k units a k-mer. Let a_{ij} be the number of different bonds that may be formed between an i-mer and a j-mer. For the RA_f model (Stockmayer,[12] Appendix)

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

The proof is as follows: the i-mer contains a total of fi functional groups. Of these, $2(i - 1)$ have been consumed in the formation of the $i - 1$ bonds of the i-mer (recall (b): all polymers are noncyclic). a_{ij} is the number of different bonds that could connect the $2 + (f - 2)i$ unreacted groups of the i-mer and the $2 + (f - 2)j$ unreacted groups of the j-mer. (Here, and throughout this paper, we make the assumption of classical statistics for the functional groups: though they may be chemically identical, they are distinguishable.)

(2) The RA_∞ Model. This is the limiting case of the RA_f model as f tends to infinity. Here

$$a_{ij} = ij \tag{2}$$

since this is, within a constant proportionality factor, the most significant term in (1).

(3) The ARB_{f-1} Model. In this model, each structural unit has one functional group of the type A, and $f - 1$ groups of the type B. This model is like the RA_f model, except that condition (a) is replaced by the following:

(a′) Functional groups of the type A react only with those of the type B, and vice versa.

For this model (see Ziff[16])

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

The derivative of (3) is similar to that of (1).

(4) The ARB_∞ Model. This is the limiting case of the ARB_{f-1} model as f tends the infinity. Here

$$a_{ij} = i + j \tag{4}$$

(5) The A_gRB_{f-g} Model. In this model, each structural unit has g functional groups of the type A and $f - g$ of the type B. The other conditions on this model are the same as for the ARB_{f-1} model.

Here

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

This model is not as well understood as the other models, because it is mathematically less tractable.

All of these models are cases of

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

the "bilinear case".

For each of the RA_f, ARB_{f-1}, and A_gRB_{f-g} models, let w_k be the number of ways of forming a k-mer from k distinguishable units with distinguishable functional groups. For all these models, the w_k's are related to the a_{ij}'s by

$$2(k - 1)w_k = \sum_{i=1}^{k-1} \binom{k}{i} w_i w_{k-i} a_{i,(k-i)}; \qquad w_1 = 1 \tag{6}$$

where

$$\binom{k}{i} = \frac{k!}{i!(k - i)!}$$

is a combinatorial coefficient, the number of ways of choosing a set of i objects from a set of k objects. (Percus[8] serves as a combinatorics reference.)

The left side of (6) is the number of ways of assembling a k-mer, choosing one of its $k - 1$ bonds (noncyclic polymers) and then painting one of the two polymers on either side of the chosen bond black. The right side of (6) is the sum over i of the number of ways of starting with k units, painting i of them black, assembling a painted i-mer and an unpainted $(k - i)$-mer, and then choosing a bond through which to combine them into a k-mer. Clearly, the two sides are equal.

For the RA_f, ARB_{f-1}, and A_gRB_{f-g} models, the w_k's have a combinatoric interpretation: they are the number of isomeric k-mers that can be constructed from k distinguishable units with distinguishable functional groups. For the RA_∞ and ARB_∞ models, there is no combinatoric interpretation for the w_k's of eq 6, though the equation still makes mathematical sense. We shall take (6) as the definition of w_k for any set of a_{ij}'s.

We are considering the reversible polymerization reaction

$$R_i + R_j \rightleftharpoons R_{i+j} \tag{7}$$

where R_i represents an i-mer. Then the a_{ij}'s of all five models are proportional to the forward reaction rate constants of the reactions.

Equation 6 is the most important relationship of this paper. It relates the w_k's, complicated expressions, but important for computation, to the a_{ij}'s, which are simple expressions. *For our purposes, all the information we will require about each specific model is contained in the appropriate* a_{ij}.

We now show how the w_k's can be used to compute polymer size distributions.

III. Polymer Partition Functions

Stockmayer[12] was the first to apply the methods of statistical mechanics to determine a polymer size distribution. His methods apply to all the models we have described in section II, so we summarize them here.

Denote the number of structural units in a closed system by N, and the number of k-mers by m_k. The polymer size distribution $(m_1, m_2, m_3, ...)$ (m_1 units, m_2 dimers, m_3 trimers, etc.) satisfies the constraints

$$\sum_{k=1}^{\infty} m_k = M \tag{8}$$

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

where M is the number of polymers in the system.

In passing, let us note that (8) is an energy constraint. This is apparent if we rewrite it as

$$\sum_{k=1}^{\infty} \epsilon(k-1) m_k = (N - M)\epsilon \tag{10}$$

where ϵ is the bonding energy between units. (Here Flory's principle of equireactivity ensures that all bonding energies are equal.) (A k-mer has $k - 1$ bonds.)

$\Omega(m_1,m_2,m_3,...,N,M)$ denotes the number of ways of producing the size distribution $(m_1, m_2, m_3, ...)$. Assuming the system is classical (i.e., all units and functional groups are distinguishable), Stockmayer showed

$$\Omega(m_1,m_2,m_3,...,N,M) = \frac{N!}{m_1!m_2!m_3!...}\left(\frac{w_1}{1!}\right)^{m_1}\left(\frac{w_2}{2!}\right)^{m_2}\left(\frac{w_3}{3!}\right)^{m_3}... \tag{11}$$

where w_k is again the number of ways of forming a k-mer from k distinguishable units with distinguishable functional groups. This result is general and holds for all the models of section II.

We give a proof: $\Omega(m_1,m_2,m_3,...,N,M)$ is the number of distinct ways of partitioning N units into subsets, with m_1 subsets of one unit, m_2 subsets of two units, etc., multiplied by $w_1^{m_1}w_2^{m_2}w_3^{m_3}...$, the number of ways of assembling the subsets of units into polymers. (See Percus.[8]) This gives (11).

Stockmayer then used Lagrange multipliers to determine $(m_1^*, m_2^*, m_3^*, ...)$, the most probable polymer size distribution. Set up the auxiliary function

$$F(m_1,m_2,m_3,...) = \ln \Omega - \gamma M - \beta N \tag{12}$$

where γ and β are Lagrange multipliers. (Maximizing $\ln \Omega$ is the same as maximizing Ω.) Using Stirling's approximation for large m_k ($\ln m_k! \sim m_k \ln m_k - m_k$) and setting the derivatives of F to zero, we get

$$\partial F/\partial m_k = \ln (w_k/k!) - \ln m_k^* - \gamma - \beta k = 0 \tag{13}$$

Hence

$$m_k^* = \frac{w_k}{k!}e^{-\gamma-\beta k} \tag{14}$$

Stockmayer did this for the RA_f model in 1943. Again, we emphasize: *all of these results hold for all the models we are discussing.*

We define the polymer partition function, Z (an exponential-generating function for the w_k's), by

$$Z = \sum_{k=1}^{\infty} \frac{w_k}{k!}e^{-\beta k} \tag{15}$$

The constraints (8) and (9) are equivalent to

$$Z = \sum_{k=1}^{\infty} \frac{w_k}{k!}e^{-\beta k} = e^{\gamma}\sum_{k=1}^{\infty} m_k^* = e^{\gamma}M \tag{16}$$

$$Z' = -\sum_{k=1}^{\infty} k\frac{w_k}{k!}e^{-\beta k} = -e^{\gamma}\sum_{k=1}^{\infty} k m_k^* = -e^{\gamma}N \tag{17}$$

where Z', Z'', etc. will denote successive derivatives of Z with respect to β.

We define μ, the separation of the system, to be

$$\mu = M/N, \qquad 0 \le \mu \le 1 \tag{18}$$

(The separation is one when all material is monomeric and decreases toward zero as the monomers aggregate.)

Using (16–18), we derive the following equation, which gives β as a function of the system separation μ:

$$Z = -\mu Z' \tag{19}$$

For reasons given in the Discussion, we call this the steepest descent condition (SDC).

For future reference, we note that the derivatives of Z are related to the moments of the most probable size distribution by the formulas

$$Z^{(n)} = (-1)^n\sum_{k=1}^{\infty} k^n\frac{w_k}{k!}e^{-\beta k} = (-1)^n e^{\gamma}\sum_{k=1}^{\infty} k^n m_k^* \tag{20}$$

($Z^{(n)}$ denotes the nth derivative of Z with respect to β.)

IV. Specific Polymer Partition Functions

We shall be using our polymer partition functions as pivots for computation. In this section, we determine some.

Let us rewrite eq 6 for the bilinear case

$$2(k-1)\frac{w_k}{k!} = \sum_{i=1}^{k-1}\frac{w_i}{i!}\,\frac{w_{k-i}}{(k-i)!}a_{i,(k-i)} = \sum_{i+j=k}\frac{w_i}{i!}\,\frac{w_j}{j!}[A + B(i+j) + Cij] \tag{21}$$

We have rewritten the sum symmetrically and used our general expression for the a_{ij}'s of section II.

Multiply both sides of (21) by $e^{-\beta k}$ and sum over $k = 1, 2, 3, ...$. Using eq 16 and 17 for Z and Z' and the identity

$$\left(\sum_{k=1}^{\infty} a_k e^{-\beta k}\right)\left(\sum_{k=1}^{\infty} b_k e^{-\beta k}\right) = \sum_{k=2}^{\infty}\left(\sum_{i+j=k} a_i b_j\right)e^{-\beta k}$$

to multiply series, we see that

$$2(-Z' - Z) = AZ^2 - 2BZZ' + C(Z')^2 \tag{22}$$

Together with the initial condition $w_1 = 1$ (there is one way of forming a monomer), eq 22 determines the polymer partition function as a function of β.

In Table I, we give all our results for β, Z, Z', and Z'' in terms of the system separation μ, because μ has physical meaning in a wide variety of circumstances. We get Z as a function of μ by combining eq 22 with the SDC equation (19):

$$Z = \frac{2\mu(1-\mu)}{A\mu^2 + 2B\mu + C} \tag{23}$$

Table I
Specific Polymer Distributions for Any $a_{ij} = A + B(i + j) + Cij$:[a]

$$Z = \frac{2\mu(1-\mu)}{A\mu^2 + 2B\mu + C}; \quad Z' = -Z\frac{1}{\mu}; \quad Z'' = -Z'\frac{-A\mu^2 + 2A\mu + 2B + C}{(A + 2B)\mu^2 + 2C\mu - C}$$

	a_{ij} classes			
	$A + B(i + j) + Cij$ $B^2 = AC,\ C \neq 0$	Cij	$A + B(i + j)$ $A \neq 0$	$B(i + j)$
w_k	$\frac{2(B + C)}{B}\left[\frac{B(B + C)}{2C}\right]^{(k-1)}$ $\left[\frac{B + 2C}{B}k\right]^{(k-2)}$	$C(Ck)^{k-2}$	$\left(\frac{A}{2}\right)^{k-1}\left[\frac{A + 2B}{A}k\right]^{(k-1)}$	$(Bk)^{k-1}$
$e^{-\beta}$	$\frac{2C(1-\mu)}{(B + C)(B\mu + C)}\cdot$ $\left[\frac{B\mu + C}{B + C}\right]^{(B+2C)/B}$	$\frac{2(1-}{C}e^{-2(1-\mu)}$	$\frac{2(1-\mu)}{A\mu + 2B}\cdot$ $\left[\frac{A\mu + 2B}{A + 2B}\right]^{(A+2B)}$	$\frac{1-\mu}{B}e^{-(1-\mu)}$

	model			
	RA_f	RA_∞	ARB_{f-1}	ARB_∞
a_{ij}				
A	4	0	2	0
B	$2(f-2)$	0	$f-2$	1
C	$(f-2)^2$	1	0	0
w_k	$\frac{f^k(fk-k)!}{(fk-2k+2)!}$	k^{k-2}	$\frac{(fk-k)!}{(fk-2k+1)!}$	k^{k-1}
$e^{-\beta}$	$\frac{2(1-\mu)}{f(2\mu + f - 2)}\left[\frac{2\mu + f - 2}{f}\right]^{f-2}$	$2(1-\mu)e^{-2(1-\mu)}$	$\frac{1-\mu}{\mu + f - 2}\left[\frac{\mu + f - 2}{f - 1}\right]^{f-1}$	$(1-\mu)e^{-(1-\mu)}$

[a] At the top are the values of the polymer partition function Z and its derivatives Z' and Z'', given for a_{ij}'s of the form $A + B(i + j) + Cij$. These a_{ij}'s are then classed according to the values of A, B, and C. Under the classes are the corresponding values of w_k and $e^{-\beta}$. For the values of w_k, we have used the notation $x^{(k)} = x(x-1)\ldots(x-k+1)$ for falling factorials, along with the convention that $x^{(0)} = 1$ and $x^{(-1)} = (x+1)^{-1}$ (to accord with the recursion $x^{(k)} = x^{(k-1)}(x-k+1)$). Equation 14 then gives the polymer size distribution (system size determines $e^{-\gamma}$). Under each general class of a_{ij}'s, we give the representative classical model, along with the specific values of A, B, and C for the model (f is a positive integer). Under these values are the quantities w_k and $e^{-\beta}$. For the RA_f model, classical notation parameterizes by the extent of reaction α instead of the system separation μ. α is the proportion of functional groups that have reacted, so $\alpha = 2(N-M)/fN = 2(1-\mu)/f$. After this conversion our results agree with Stockmayer's distribution[12] for the RA_f model before gelation. All of these results have appeared in the literature. For reasons explained in the discussion, we do not give the A_gRB_{f-g} distribution.

The SDC (19) indicates Z' is merely this quantity divided by $-\mu$. We may derive Z'' by differentiating (22) with respect to β to give

$$Z'' = \frac{-AZZ' + B(Z')^2 - Z'}{1 - BZ + CZ'} = \frac{2(1-\mu)}{A\mu^2 + 2B\mu + C}\,\frac{-A\mu^2 + 2A\mu + 2B + C}{(A + 2B)\mu^2 + 2C\mu - C} \qquad (24)$$

The last equality follows from the expressions for Z and Z'. If necessary, higher derivatives of Z may be obtained by successive differentiation of (22), followed by back-substitution of the lower derivatives.

Explicit solution for $e^{-\beta}$ and w_k requires solution of the differential equation (22). To accomplish this, we establish two cases, according to whether C is zero or not:

Case 1: $C = 0$

$$Z' = -\frac{Z(Z + AZ)}{2(1 - BZ)} \qquad (25)$$

Rewrite this as

$$\int \frac{2(1 - BZ)}{Z(2 + AZ)}\,\mathrm{d}Z = -\int \mathrm{d}\beta \qquad (26)$$

The integral must be split into two cases, according to whether A is zero or not. Either case leads to a functional equation of the form (γ is a constant of integration)

$$Z = e^{-\beta}g(Z) \qquad A = 0,\quad g(Z) = \gamma e^{BZ} \qquad (27a)$$

$$Z = e^{-\beta}g(Z) \qquad A \neq 0,\quad g(Z) = \gamma(2 + AZ)^{(A+2B)/A} \qquad (27b)$$

$e^{-\beta}$ is easily expressed in terms of Z, and hence μ (by eq 23). To derive w_k, we require a version of Lagrange's theorem:

If $U = e^{-\beta}g(U)$ and $f(0) = 0$, then

$$f(U) = \sum_{k=1}^{\infty}\frac{\mathrm{d}^{k-1}}{\mathrm{d}U^{k-1}}\{f'(U)[g(U)]^k\}_{U=0}\frac{e^{-\beta k}}{k!}$$

where the subscript $U = 0$ indicates the derivative is to be evaluated at $U = 0$.

The full version of the theorem is in Whittaker and Watson.[14] Hence

$$w_k = \frac{\mathrm{d}^{k-1}}{\mathrm{d}U^{k-1}}\{f'(U)[g(U)]^k\}_{U=0} \qquad (28)$$

$$w_1 = f'(0)g(0) = 1 \qquad (29)$$

(The second equation is used to eliminate γ, the constant of integration in $g(Z)$.) In our cases, $f(U) = U$ (and $U = Z$). The results are in Table I.

Case 2: $C \neq 0$

$$Z' = \frac{-1 + BZ + [1 - 2(B + C)Z + (B^2 - AC)Z^2]^{1/2}}{C} \quad (30)$$

We have chosen the plus sign because Z' must go to zero when Z does.

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

$$\int \frac{C}{1 - BZ - [1 - 2(B + C)Z]^{1/2}}\, \mathrm{d}Z = -\int \mathrm{d}\beta \quad (31)$$

Apply the substitution

$$Z = f(U) = \frac{U(2 - U)}{2(B + C)} \quad (32)$$

Again, the integral must be split into two cases, according to whether B is zero or not. Either case leads to a function equation of the form

$$U = e^{-\beta}g(U) \qquad B = 0, \quad g(U) = \gamma e^{u} \quad (33a)$$

$$U = e^{-\beta}g(U) \qquad B \neq 0, \quad g(U) = \gamma\left[\frac{2C + BU}{2C}\right]^{(B+2C)/B} \quad (33b)$$

We apply Lagrange's theorem, with $f(U)$ from (32) and $g(U)$ from (33). Again, $w_1 = 1$ is used to eliminate γ. The results are in Table I.

Case 2B: $C \neq 0, B^2 \neq AC$

$$\int \frac{C}{1 - BZ - [1 - 2(B + C)Z + (B^2AC)Z^2]^{1/2}}\, \mathrm{d}Z = -\int \mathrm{d}\beta \quad (34)$$

The integral on the left may be computed, albeit painfully, by standard methods described in Edwards.[4] The explicit result contains logarithms, trigonometric, and inverse trigonometric functions of Z into which μ is then substituted. Hence the calculation for $e^{-\beta}$ in this case is possible, though tedious.

All explicit results are summarized in Table I.

V. Moments of the Size Distribution and Gelation

A. General Results. In this section, we give general formulas for the number- and weight-average molecular weights, which involve the polymer partition function and its derivatives.

From eq 16 and 20 we get

$$\sum_{k=1}^{\infty} k^n \frac{m_k^*}{M} = (-1)^n \frac{Z^{(n)}}{Z} \quad (35)$$

Let M_1 be the molecular weight of a polymeric structural unit (we follow Tanford's notation;[13] do not confuse M_1 with M, the number of polymers in the system).

Then the number-average molecular weight is

$$\bar{M}_{\mathrm{n}} = \frac{\sum (kM_1)m_k^*}{\sum m_k^*} = -M_1\frac{Z'}{Z} = -M_1\frac{1}{\mu} \quad (36)$$

The last equality follows from the SDC, eq 19.

The weight-average molecular weight is

$$\bar{M}_{\mathrm{w}} = \frac{\sum (kM_1)km_k^*}{\sum km_k^*} = -M_1\frac{Z''}{Z'} \quad (37)$$

(Higher average molecular weights are computed analogously.)

Table I gives the values of Z, Z', and Z'' for the bilinear case $a_{ij} = A + B(i + j) + Cij$. Equations 36 and 37 allow us to use these values to compute number- and weight-average molecular weights. Conversely, if $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$ are known experimentally, these formulas may be used to fit values of A, B, and C to the data.

Ziff[16] has used the divergence of a moment of the mean polymer distribution (left side of (35)) as a gelation criterion. By virtue of (35), this means that *divergence of* $Z^{(n)}$, *for some n, is a sufficient condition for gelation.*

B. Specific Results. From Table I, for the bilinear case, divergence of Z'' occurs when

$$(A + 2B)\mu^2 + 2C\mu - C = 0 \quad (38)$$

Define μ_{C}, the critical separation of the system, as the value of μ at the gel point of the system. Then

$$\mu_{\mathrm{C}} = \frac{-C + [C(A + 2B + C)]^{1/2}}{A + 2B}, \qquad A + 2B \neq 0 \quad (39a)$$

$$\mu_{\mathrm{C}} = 0.5, \qquad \text{otherwise} \quad (39b)$$

If $C = 0$, then $\mu_{\mathrm{C}} = 0$, so that the system will never gel. This result is well-known.

The result also accords with Flory's result[5] for the RA_f model. Define the extent of reaction α (for the RA_f model) as the proportion of functional groups that have reacted. Then

$$\alpha = \frac{2(N - M)}{fN} = \frac{2(1 - \mu)}{f} \quad (40)$$

If α_{C} is the (critical) extent of reaction that produces gelation, then (1), (39), and (40) show that

$$\alpha_{\mathrm{C}} = (f - 1)^{-1}$$

This is Flory's 1941 result for the RA_f model.

Consider the $\mathrm{A}_g\mathrm{RB}_{f-g}$ model and its a_{ij}, given by (5). Substitution of values into (39) gives

$$\mu_{\mathrm{C}} = \frac{1}{1 + \left[\left(1 + \frac{1}{g - 1}\right)\left(1 + \frac{1}{f - g - 1}\right)\right]^{1/2}}, \qquad 2 \leq f - g,\ 2 \leq g \quad (41)$$

As f tends to infinity with g fixed

$$\mu_{\mathrm{C}} = \frac{1}{1 + \left(1 + \frac{1}{g - 1}\right)^{1/2}} \quad (42)$$

In Table II, we give numerical results based on eq 40–42 and make the following observations (all of which may be proved rigorously):

(1) $\mu_{\mathrm{C}} = 0$ for the ARB_{f-1} model, so that, in the $\mathrm{A}_g\mathrm{RB}_{f-g}$ model, gelation occurs if and only if there are at least two A's and two B's per structural unit.

(2) If g (the number of A's per structural unit) is fixed, then increasing $f - g$ (the number of B's per structural unit) increases μ_{C} (and decreases α_{C}), so that gelation occurs more easily.

(3) If f (the total number of functional groups per structural unit) is fixed, the closer the numbers of A and B groups, the higher μ_{C} (and the lower α_{C}) becomes.

All of these observations accord with intuition.

VI. Discussion

There is considerable confusion in the literature of polymer chemistry as to what constitutes an equilibrium

Table II
Gelation Values for A_gRB_{f-g} Models[a]

	f									
g	4	5	6	7	8	9	10	11		∞
					μ_C					
2	0.333	0.366	0.380	0.387	0.392	0.396	0.398	0.400	...	0.414
3			0.400	0.414	0.422	0.427	0.431	0.433	...	0.449
4					0.429	0.436	0.442	0.445	...	0.464
5							0.444	0.449	...	0.472
∞									...	0.500
					α_C					
2	0.333	0.254	0.207	0.175	0.152	0.134	0.120	0.109	...	0.000
3			0.200	0.167	0.144	0.127	0.114	0.103	...	0.000
4					0.143	0.125	0.112	0.101	...	0.000
5							0.111	0.100	...	0.000

[a] This table gives the critical values of μ_C (top) and α_C (bottom) for the A_gRB_{f-g} model of polymerization. Values of *f* are given horizontally and values of *g* vertically. Since the model is symmetric in *g* and $f - g$, we have taken $g \leqslant f - g$. Note that gelation does not occur for the ARB_{f-1} model.

polymer distribution, as opposed to a distribution produced by an irreversible kinetic polymerization reaction. This is because equilibrium solutions often determine corresponding kinetic solutions (and vice versa). The classic example is Stockmayer's determination of a kinetic RA_f distribution by equilibrium distributions coupled to a deterministically changing parameter.[12]

Let me emphasize that my method determines an equilibrium distribution. This paper's foundation, eq 6, is a statement based on equilibrium of the reactions (7). To see this, we make an appeal to the principle of detailed balance from statistical mechanics (Münster[7] and Whittle[15]). Applied to the reactions (7), it states the following: if the polymerizing system is in equilibrium, so is each individual reaction. Consider the reactions (7), with $i + j$ set to k, i running from 1 to $k - 1$. The left-hand side of (6) is proportional to the rate at which k-mers break up (there are $k - 1$ bonds in each of the w_k isomeric k-mers to break up), while the right-hand side is proportional to the aggregation rate. The missing constant of proportionality is supplied by the constraints (8) and (9) and ultimately determines the parameter β.

The equilibrium distributions of Table I have all appeared in print before. Indeed, all are implicit in the thorough review of the Smoluchowski coagulation equation[11] done by Drake.[3] This equation may be used to model irreversible polymerization (Ziff[16]). This author (unpublished work) has proven that the equilibrium distributions derived from eq 6 may be used to solve the coagulation equation for the cases $a_{ij} = A + B(i + j) + Cij$ and for these cases only. The equilibrium method can solve for the distribution of A_gRB_{f-g} polymers (corresponding to the case of bilinear a_{ij}'s ($A \neq 0$, $B^2 \neq AC$), but it requires numerical solution of recursion 6.

Explicit equilibrium solutions for some nonbilinear a_{ij}'s are given in the Appendix. The interested reader may verify that they do not satisfy the corresponding kinetic coagulation equations. The assumptions used are the same as those given by the Abstract (a constant rate of break up for each of the $k - 1$ bonds of a k-mer is also assumed).

Most of the issues raised here will be covered in later publications.

As Stockmayer[12] notes, his determination of polymer distribution for the RA_f model (section III) is in fact what Schrödinger[10] called the method of most probable distributions. Donoghue and Gibbs[1] and later Donoghue[2] produced a refinement of Stockmayer's approach to the RA_f model. (This approach actually used the polymer partition function for RA_f.) The refinement was equivalent to using the method of mean values in statistical mechanics. (See Schrödinger.[10]) The SDC, eq 19, arises by locating the saddle points of integrals required for the method of mean values.

For the RA_f model, Donoghue[2] showed that expression 14 is the first term of an asymptotic expansion as the system size N tends to infinity. He also showed this expansion is valid only when the system has not gelled. Though we do not prove it here, these results are general. Hence *eq 14 represents the sol distribution, but only before gelation has occurred.* After gelation, a different asymptotic expansion applies, and (14) is no longer its leading term.

Let σ_k denote the standard deviation of m_k, the number of k-mers. Another result of Donoghue and Gibbs generalizes:

$$\sigma_k / k m_k^* \propto N^{-1/2}$$

This, again, is readily understood in the light of a statistical mechanical analogy.

Acknowledgment. This work was supported by a Fellowship from the Medical Research Council of Canada.

Appendix

For completeness, the equilibrium distributions (i.e., the Z) corresponding to some nonbilinear a_{ij}'s are given. Pólya and Szegö[9] give other examples of the operator methods employed here.

Theorem 1: If b_k ($k = 1, 2, ...$) is any series such that $b_k \neq 0$ for all k and $Z = \sum_{k=1}^{\infty}(w_k/k!)e^{-\beta k}$ solves recursion 6, then $Z_b = \sum_{k=1}^{\infty} b_k(w_k/k!)e^{-\beta k}$ solves the same recursion with a_{ij} replaced by $a_{ij}(b_{i+j}/b_ib_j)$. (We ignore the initial condition $b_k = 1$ (so that $b_1w_1 = 1$), because this gives rise to factors easily absorbed into $e^{-\gamma}$ and $e^{-\beta}$.) The theorem essentially generates new solutions from known ones.

Proof: Substitution of b_kw_k into recursion 6 after altering a_{ij}.

Corollary: If $b_i = P(i)$, a polynomial, then $Z_b = P(-\mathrm{d}/\mathrm{d}\beta)Z$ solves recursion 6 with a_{ij} replaced by $a_{ij}(b_{i+j}/b_ib_j)$, where $P(-\mathrm{d}/\mathrm{d}\beta)$ denotes the operator obtained by formal expansion of P in powers of $-\mathrm{d}/\mathrm{d}\beta$.

Proof: $-\mathrm{d}/\mathrm{d}\beta$ corresponds to termwise multiplication by k in the expansion for Z. The result follows in the obvious fashion.

These results can be extended to cases where b_k's contain terms like $(k + a)^{-m}$, by using integration instead of differentiation etc.

We now characterize all the a_{ij}'s that give rise to the polymer partition function

$$Z_1 = \sum_{k=1}^{\infty} e^{-\beta k} = (e^{\beta k} - 1)^{-1}$$

Theorem 2: If C_{ij} $(i, j = 1, 2, 3, ...)$ is any double sequence satisfying $C_{ij} \geq 0$ and $\sum_{i=1}^{k-1} C_{i,k-i} > 0$, then $Z_1 = \sum_{k=1}^{\infty} e^{-\beta k}$ solves recursion 6 when

$$a_{ij} = \frac{2(k-1)C_{ij}}{\sum\limits_{i=1}^{k-1} C_{i,k-i}}, \qquad i + j = k \tag{A1}$$

Proof: Z_1 corresponds to $w_k = k!$, $k = 1, 2, ...$ Substitution of these values into recursion 6 yields equality for the given values of a_{ij}.

Conversely, if Z_1 solves (6) for a given a_{ij}, then recursion 6 becomes

$$2(k-1) = \sum_{i=1}^{k-1} a_{i,k-i}$$

and so, if a_{ij} is substituted for C_{ij} in (A1), we get an identity. Hence, we have a complete characterization of a_{ij}'s producing the polymer partition function Z_1. This gives a complete characterization of a_{ij}'s producing an arbitrary polymer partition function Z with $w_k > 0$, $k = 1, 2, ...$: in theorem 1, take $Z = Z_1$ and $b_k = w_k/k!$.

As an example of these theorems, take in theorem 2

$$C_{ij} = \frac{(i + j - 2)!}{(i - 1)!(j - 1)!}$$

so

$$a_{ij} = 2^{-(k-3)} \frac{(k-1)!}{(i-1)!(j-1)!}$$

with solution Z_1. Use of theorem 1 with $b_k = 1/(k-1)!$ gives

$$Z = \sum_{k=1}^{\infty} b_k e^{-\beta k} = \sum_{k=1}^{\infty} \frac{e^{-\beta k}}{(k-1)!} = e^{-\beta} \exp(e^{-\beta})$$

as the solution for $a_{ij} = 2^{-(k-3)}$, as is rapidly verified.

These solutions are given to clarify the relationship between equilibrium and nonequilibrium distributions, which agree only for the bilinear case, $a_{ij} = A + B(i + j) + Cij$.

References and Notes

(1) Donoghue, E.; Gibbs, J. H. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 63*, 131.
(2) Donoghue, E. *J. Chem. Phys.*, to be published.
(3) Drake, R. L. In *Top. Curr. Aerosol Res.* 1972, Vol. 3, Part 2.
(4) Edwards, J. "A Treatise on the Integral Calculus"; Chelsea: New York, 1930; Vol. I, Chapter VIII, esp. pp 313–314.
(5) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
(6) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; Chapter 8.
(7) Münster, A. "Prinzipien der Statistischen Mechanik"; Springer: Berlin, 1959.
(8) Percus, J. K. "Combinatorial Methods"; Springer-Verlag: Berlin, 1971.
(9) Pôlya, G.; Szegö, G. "Problems and Theorems in Analysis"; Springer-Verlag: Berlin, 1976; Vol. I, p 8.
(10) Schrödinger, E. "Statistical Thermodynamics"; Cambridge University Press: New York, 1967.
(11) von Smoluchowski, M. *Phys. Z.* **1916**, *17*, 557, 585.
(12) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(13) Tanford, C. "Physical Chemistry of Macromolecules"; Wiley: New York, 1967.
(14) Whittaker, E. T.; Watson, G. N. "A Course of Modern Analysis"; Cambridge University Press: New York, 1978; p 133.
(15) Whittle, P. *Proc. Cambridge Philos. Soc.* **1965**, *61*, 475.
(16) Ziff, R. M. *J. Stat. Phys.* **1980**, *23*, 241.