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General Treatment of Equilibrium Copolymerization of Two or More Comonomers Deduced from the Initial State of the System

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ABSTRACT: A mathematical approach was developed to account for equilibrium copolymerization, a process involving the pertinent propagation and cross-propagation steps, as well as their respective depropagations, but free of termination and chain transfers. The treatment leads to the determination of the equilibrium concentrations of the comonomers, the molecular weight distribution of the resulting copolymers, the average composition of *n*-mers as a function of *n*, the probability of having a specified comonomer at *m*-th segments of *n*-mers, etc. This information is deduced from the knowledge of the initial state of the system and the required equilibrium constants. The treatment applies to low as well as to high molecular weight polymers and is designed to handle any number of comonomers.

The problem of monomer–polymer equilibrium was explored initially by Dainton and Ivin.[1] Such an equilibrium is of considerable interest when one deals with living polymer systems[2] since the permanent capacity of those polymers to grow is coupled with their capacity to degrade. Consequently, living polymers eventually have to be in equilibrium with their monomers. The treatment of such an equilibrium in living homopolymers was outlined by Tobolsky and Eisenberg[3] and later by Wheeler et al.[4]

A reversible copolymerization was studied less thoroughly. Calculation of the free energy of conversion of two infinitely long homopolymers, ...AA... and ...BB..., into an infinitely long copolymer of a desired composition was reported by Sawada[5] and later by Theil.[6] Kinetics of copolymerizations involving propagation and depropagation was developed by Lowry,[7] and similar treatments were discussed by other investigators.[8-12] The complexity of the problem, set in conventional kinetic form, limits this approach to copolymerizations involving a reversible addition of only one comonomer.

The stochastic approach, developed by O'Driscoll and his associates,[13] permits handling copolymerizations with all four basic steps reversible, i.e.

$$-\mathrm{A}^* + \mathrm{A} \underset{b_{11}}{\overset{k_{11}}{\rightleftharpoons}} -\mathrm{AA}^*$$

$$-\mathrm{A}^* + \mathrm{B} \underset{b_{12}}{\overset{k_{12}}{\rightleftharpoons}} -\mathrm{AB}^*$$

$$-\mathrm{B}^* + \mathrm{A} \underset{b_{21}}{\overset{k_{21}}{\rightleftharpoons}} -\mathrm{BA}^*$$

$$-\mathrm{B}^* + \mathrm{B} \underset{b_{22}}{\overset{k_{22}}{\rightleftharpoons}} -\mathrm{BB}^*$$

In such schemes the propagation rate is assumed to be determined by the nature of the last unit of the growing polymers and the monomer's nature, while the rate of depropagation is determined by the nature of the last two units.[18] This treatment, in common with the previous ones, deals with copolymerizations proceeding at constant, although arbitrary, concentrations of the comonomers. Under such conditions the distribution of the monomeric segments in the copolymer chains becomes virtually constant as their length becomes sufficiently long, approaching the limiting distribution of infinitely long chains. Such a distribution obeys the first-order Markov statistics; i.e., probabilities of finding the segments A or B at any location in the chain, as well as the respective conditional probabilities of A being preceded by A or B preceded by B, all become constant, independent of location. Let it be stressed that the steady-state conditions result in constant probabilities of finding A or B at the *ends* of growing polymers; howowever, these probabilities are, on the whole, different from those determining the chances of having these units at any other arbitrary location in the chain.

Let us summarize the important achievements gained through this work. The composition of long copolymers

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and the conditional probabilities of various diads describing the distribution of the segments are all determined by the eight forward and backward rate constants and the arbitrarily chosen concentrations of the comonomers. However, the nature of the approach–handling copolymers of high molecular weight only—does not allow one to inquire about the molecular weight distribution of the products. It excludes also any inquiries about the nature or quantity of low molecular weight oligomers, which could be, in fact should be, formed in the process, especially when the rate of depropagation becomes comparable to the rate of propagation. Finally, this approach deals with the dynamic process of copolymer formation and not with the equilibrium eventually established between living copolymers and their comonomers. This kind of equilibrium was discussed in the later paper of O'Driscoll et al.[15] that extends the stochastic treatment to copolymerizations of any number of comonomers. The critical discussion of such an approach to copolymerization equilibrium is presented in Appendix I.

The treatment of copolymerization equilibrium determined by the initial state of the system was outlined by Tobolsky and Owen.[16] However, the authors could not solve the problem for a general case of reversible copolymerization involving four *different* equilibrium constants, namely K_{11}, K_{12}, K_{21}, and K_{22}. They limited, therefore, their solution to a very restricted and on the whole improbable case when $K_{11} = K_{21}$ and $K_{12} = K_{22}$, i.e., when the rate of propagation is determined only by the nature of the monomer, and of depropagation only by the last unit of the growing copolymer.

These shortcomings of the previous treatments of equilibria in living copolymerization systems induced us to develop a more general approach to those problems. It considers the initial conditions of the copolymerizing systems, it is applicable to low as well as to high molecular weight copolymers, and it leads to the previously reported results in the limit of infinitely long polymers. Moreover, the treatment reported here allows the calculation of the equilibrium concentrations of the comonomers, the molecular weight distribution of the resulting copolymers, the average composition of n-mers as a function of n, the probability of finding a specified comonomer at m-th segments of n-mers, etc. The outlined mathematical approach is applicable to any number of comonomers, although it is presented first for two comonomers and thereafter generalized for many comonomer systems. For the sake of compactness the vector notation is used throughout the derivations.

Statement of the Problem

Consider a system resulting from copolymerization of monomers A and B initiated by XA* and XB*. The latter two symbols denote the respective activated monomers that can grow but cannot degrade; e.g., XA* cannot dissociate into X + A. The copolymerization is assumed to be a living type; i.e., it involves propagation and depropagation but not termination or chain transfer. Moreover, we assume the propagation constants to be determined by the nature of the added monomer and of the last active unit of the polymers, whatever their size, even for XA* or XB*, whereas the depropagation constants are determined by the nature of the last two units. Thus, the respective equilibrium constants

$$\mathrm{X}(n-1)\mathrm{A}^* + \mathrm{A} \rightleftarrows \mathrm{X}(n-1)\mathrm{AA}^*, \qquad K_{11} \qquad \text{(a)}$$

$$\mathrm{X}(n-1)\mathrm{A}^* + \mathrm{B} \rightleftarrows \mathrm{X}(n-1)\mathrm{AB}^*, \qquad K_{12} \qquad \text{(b)}$$

$$\mathrm{X}(n-1)\mathrm{B}^* + \mathrm{A} \rightleftarrows \mathrm{X}(n-1)\mathrm{BA}^*, \qquad K_{21} \qquad \text{(c)}$$

$$\mathrm{X}(n-1)\mathrm{B}^* + \mathrm{B} \rightleftarrows \mathrm{X}(n-1)\mathrm{BB}^*, \qquad K_{22} \qquad \text{(d)}$$

are assumed to be independent of n for $n \geq 1$, where n represents the number of monomeric segments inserted between X and the end group. Note, X(0)A* denotes XA*, etc. Introduction of size-dependent equilibrium constants complicates the mathematics without providing any further insight into the problem. This justifies the simplification proposed here.

After a sufficiently long time, during which all the polymers have had a chance to be degraded down to their smallest unit, XA* or XB*, and to be rebuilt many times, the system attains the state of its ultimate equilibrium. At this stage the concentrations of the monomers are constant, namely a and b, as well as the concentrations of any n-mers, whether starting with XA or XB, or whether ended by A* or B*. Of course, the *initial* concentrations of XA* and XB*, denoted by A_0 and B_0, are freely chosen for each system, but their equilibrium concentrations, denoted by ${}^\circ A_1$ and ${}^\circ B_1$, are determined by the pertinent equilibrium constants, K_{11}, K_{12}, etc., and the initial conditions of the system, namely A_0 and B_0 and a_0 and b_0. The last two symbols refer to the initial concentrations of respective monomers, including those in XA* and XB*.

As will be shown in the following sections, the detailed description of the ultimate state of the system is determined by the four unknowns, the equilibrium concentrations of the monomers a and b, and the equilibrium concentrations of the *activated* monomers XA* and XB* denoted by ${}^\circ A_1$ and ${}^\circ B_1$. These have to be calculated from the known initial concentrations of the activated monomers, A_0 and B_0, and the initial concentrations of the monomers, a_0 and b_0.

Determination of the Equilibrium Concentrations

Denote by A^*_n and B^*_n the equilibrium concentrations of n-mers *terminated* by A* or B*, respectively, regardless of the nature of the preceding monomeric units, and by ${}^\circ A_n$ and ${}^\circ B_n$ the corresponding equilibrium concentrations of n-mers *started* by XA or XB, regardless of the nature of the following monomeric units. The equilibrium concentrations of XA* and XB* are therefore ${}^\circ A_1 = A^*_1$ and ${}^\circ B_1 = B^*_1$. Of course

$$\sum_1^\infty {}^\circ A_n = A_0 \quad \text{and} \quad \sum_1^\infty {}^\circ B_n = B_0 \tag{1}$$

whereas

$$\sum_1^\infty A^*_n = A^*_\mathrm{e} \quad \text{and} \quad \sum_1^\infty B^*_n = B^*_\mathrm{e} \tag{2}$$

A^*_e and B^*_e are the total equilibrium concentrations of all the polymers terminated by A* or B*, respectively, regardless of the preceding units.

The equilibria a–d are established at the ultimate state of the system. Hence

$$A^*_2 = K_{11}aA^*_1 + K_{21}aB^*_1 \tag{3}$$

and

$$B^*_2 = K_{12}bA^*_1 + K_{22}bB^*_1 \tag{4}$$

or more generally

$$A^*_{n+1} = K_{11}aA^*_n + K_{21}aB^*_n \tag{5}$$

$$B^*_{n+1} = K_{12}bA^*_n + K_{22}bB^*_n \tag{6}$$

Alternatively these relations can be cast in a vector-like notation

$$\begin{pmatrix} A^*_{n+1} \\ B^*_{n+1} \end{pmatrix} = \begin{pmatrix} K_{11}a & K_{21}a \\ K_{12}b & K_{22}b \end{pmatrix} \begin{pmatrix} A^*_n \\ B^*_n \end{pmatrix} \tag{7}$$

and denoting the matrix

$$\begin{pmatrix} K_{11}a & K_{21}a \\ K_{12}b & K_{22}b \end{pmatrix}$$

by **M**, we find

$$\begin{pmatrix} A^*{}_n \\ B^*{}_n \end{pmatrix} = \mathbf{M}^{n-1} \begin{pmatrix} A^*{}_1 \\ B^*{}_1 \end{pmatrix} = \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} \qquad (8)$$

Therefore, each $A^*{}_n$ and $B^*{}_n$ is determined by a, b, $A^*{}_1 = {}^\circ A_1$, and $B^*{}_1 = {}^\circ B_1$. Thus

$$\sum_1^\infty \begin{pmatrix} A^*{}_n \\ B^*{}_n \end{pmatrix} = \begin{pmatrix} A^*{}_e \\ B^*{}_e \end{pmatrix} = (1 - \mathbf{M})^{-1} \begin{pmatrix} A^*{}_1 \\ B^*{}_1 \end{pmatrix} \qquad (9)$$

where $A^*{}_e$ and $B^*{}_e$ denote the equilibrium concentrations of all n-mers terminated by A* or B*, respectively. Note in passing that $A^*{}_e + B^*{}_e = A_0 + B_0$ although on the whole $A^*{}_e \neq A_0$ and $B^*{}_e \neq B_0$.

In Appendix II we derive the expression for the matrix of conditional probabilities, i.e.

$$\mathbf{N}_{n,m} = \begin{pmatrix} r_{n,m} & 1 - s_{n,m} \\ 1 - r_{n,m} & s_{n,m} \end{pmatrix}$$

that converts the population of A and B segments in position m of living n-mers into their population in position $m + 1$. Thus

$$\begin{pmatrix} A^*{}_n \\ B^*{}_n \end{pmatrix} = \prod_{m=1}^{n-1} \mathbf{N}_{n,m} \begin{pmatrix} {}^\circ A_n \\ {}^\circ B_n \end{pmatrix} \qquad (10)$$

where ${}^\circ A_n$ and ${}^\circ B_n$ are the equilibrium concentrations of n-mers starting with A or B, respectively, while $A^*{}_n$ and $B^*{}_n$ are those ending with A or B. Note that on the whole ${}^\circ A_n \neq A^*{}_n$ and ${}^\circ B_n \neq B^*{}_n$ for $n > 1$, although ${}^\circ A_n + {}^\circ B_n = A^*{}_n + B^*{}_n$. However, ${}^\circ A_1 = A^*{}_1$ and ${}^\circ B_1 = B^*{}_1$—these are the equilibrium concentrations of the residual XA and XB, respectively. The product $\prod$ of noncommuting matrices always is formed by writing them in order of decreasing index, here m, from left to right. The matrices $\mathbf{N}_{n,0}$ and $\mathbf{N}_{n,n}$ are defined as unit matrix.

Inversion of eq 10 gives

$$\begin{pmatrix} {}^\circ A_n \\ {}^\circ B_n \end{pmatrix} = \left(\prod_{m=1}^{n-1} \mathbf{N}_{n,m} \right)^{-1} \begin{pmatrix} A^*{}_n \\ B^*{}_n \end{pmatrix} \qquad (11)$$

and in view of eq 8

$$\begin{pmatrix} {}^\circ A_n \\ {}^\circ B_n \end{pmatrix} = \left(\prod_{m=1}^{n-1} \mathbf{N}_{n,m} \right)^{-1} \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} \qquad (12)$$

Since the sum

$$\sum_{n=1}^\infty \begin{pmatrix} {}^\circ A_n \\ {}^\circ B_n \end{pmatrix} = \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \qquad (13)$$

where A_0 and B_0 are the initial concentrations of XA* and XB*, we get

$$\sum_{n=1}^\infty \left(\prod_{m=1}^{n-1} \mathbf{N}_{n,m} \right)^{-1} \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} = \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \qquad (14)$$

Equation 14 describes the conservation of all living n-mers and provides two relations linking the unknown a, b, ${}^\circ A_1$, and ${}^\circ B_1$ to the known A_0, B_0, and the relevant K's.

An additional two equations involving the same four unknowns are derived from the condition of conservation of monomers supplied to the system, i.e., a_0 and b_0. The amounts of the monomeric units, A and B, in equilibrated n-mers, denoted by a_n and b_n, are

$$\begin{pmatrix} a_n \\ b_n \end{pmatrix} = \sum_{i=1}^{n} \left(\prod_{m=0}^{i-1} \mathbf{N}_{n,m} \right) \begin{pmatrix} {}^\circ A_n \\ {}^\circ B_n \end{pmatrix} \qquad (15)$$

The condition of monomer conservation demands

$$\begin{pmatrix} a_0 - a \\ b_0 - b \end{pmatrix} = \sum_{n=1}^\infty \begin{pmatrix} a_n \\ b_n \end{pmatrix}$$

and in view of (15) and (11)

$$\begin{pmatrix} a_0 - a \\ b_0 - b \end{pmatrix} = \sum_{n=1}^\infty \sum_{i=1}^{n} \left(\prod_{m=i}^{n-1} \mathbf{N}_{n,m} \right)^{-1} \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} \qquad (16)$$

Thus the four relations given by eq 14 and 16 allow us to calculate the four unknowns a, b, ${}^\circ A_1$, and ${}^\circ B_1$ from the knowledge of the initial conditions of the system, i.e., A_0, B_0, a_0, and b_0, and the pertinent K's.

It is beneficial to stress that the transformation by matrix **M** provides the *decreasing* number of ($n + 1$)-mers in equilibrium with the n-mers, whereas the matrix $\mathbf{N}_{n,m}$ converts the population of A and B in an m-th segment of n-mers into their population in the ($m + 1$)-th segment, without changing their total number.

Further Considerations

The procedure giving the equilibrium concentrations of the monomers, a and b, and of the residual XA* and XB*, i.e., ${}^\circ A_1 = A^*{}_1$ and ${}^\circ B_1 = B^*{}_1$, was outlined in the preceding section. Having their values, we may determine the other properties of the equilibrated system.

(a) Distribution of *n*-mers. The mole fraction of n-mers having A or B as their terminal units is given by

$$\begin{pmatrix} g_{A,n} \\ g_{B,n} \end{pmatrix} = \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} / (A_0 + B_0) \qquad (17)$$

The mole fraction g_n of n-mers, regardless of their starting or ending units, is

$$g_n = (1 \quad 1) \mathbf{M}^{n-1} \begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} / (A_0 + B_0)$$

This permits the evaluation of any moment of distribution and therefore allows us to calculate averages such as $\overline{\mathrm{DP}}_n$, $\overline{\mathrm{DP}}_w$, etc. Of course, $\overline{\mathrm{DP}}_n$ is given simply by

$$(a_0 + b_0 - a - b)/(A_0 + B_0)$$

(b) Probabilities of Finding A or B in Position *m* of *n*-mers. These probabilities, denoted by $P_{A,n,m}$ and $P_{B,n,m}$, are

$$\begin{pmatrix} P_{A,n,m} \\ P_{B,n,m} \end{pmatrix} = \left(\prod_{i=0}^{m-1} \mathbf{N}_{n,i} \right)^{-1} \begin{pmatrix} {}^\circ A_n / ({}^\circ A_n + {}^\circ B_n) \\ {}^\circ B_n / ({}^\circ A_n + {}^\circ B_n) \end{pmatrix} \qquad (18)$$

(c) Average Composition of *n*-mers. The mole fractions, $f_{A,n}$ and $f_{B,n}$, and A's and B's in living n-mers are

$$\begin{pmatrix} f_{\mathrm{A},n} \\ \\ f_{\mathrm{B},n} \end{pmatrix} = \sum_{i=1}^{n} \left(\prod_{m=0}^{i-1} \mathrm{N}_{n,m} \right)^{-1} \begin{pmatrix} {}^{\circ}A_n/({}^{\circ}A_n + {}^{\circ}B_n) \\ \\ {}^{\circ}B_n/({}^{\circ}A_n + {}^{\circ}B_n) \end{pmatrix} \tag{19}$$

with ${}^{\circ}A_n$ and ${}^{\circ}B_n$ given by eq 12.

(d) Frequencies of Various Sequences of Monomers in Equilibrated Polymers. The probability of finding a sequence of monomers, say ABB, starting in position m of n-mers is given by the product of the probability of finding the first unit in that position and of the relevant conditional probabilities. Thus for ABB it is

$$P_{\mathrm{A},n,m}(1 - r_{n,m})s_{n,m+1}$$

The total number of ABB sequences in all the polymers is

$$\sum_{n=3}^{\infty} \sum_{m=1}^{n-2} P_{\mathrm{A},n,m}(1 - r_{n,m})(s_{n,m+1})(1 \quad 1)\mathrm{M}^{n-1} \begin{pmatrix} {}^{\circ}A_1 \\ \\ {}^{\circ}B_1 \end{pmatrix} \tag{20}$$

and their frequencies are given by the above value divided by the total number of triads

$$\sum_{n=3}^{\infty} (n - 2)(1 \quad 1)\mathrm{M}^{n-1} \begin{pmatrix} {}^{\circ}A_1 \\ \\ {}^{\circ}B_1 \end{pmatrix} \tag{21}$$

System Involving a Reversible Initiation by Initiator X

Consider reversible copolymerization of A and B, reversibly initiated by X, i.e.

$$\mathrm{X} + \mathrm{A} \rightleftarrows \mathrm{XA}^*, \qquad K_{\mathrm{A}}$$

$$\mathrm{X} + \mathrm{B} \rightleftarrows \mathrm{XB}^*, \qquad K_{\mathrm{B}}$$

The treatment of such a system is somewhat simpler than of the previous one. Denote by x_0 the initial concentration of X and by x_e its equilibrium value. Then

$$[\mathrm{XA}^*] = A^*_1 = K_{\mathrm{A}}x_e a \tag{22}$$

and

$$[\mathrm{XB}^*] = B^*_1 = K_{\mathrm{B}}x_e b \tag{23}$$

where a and b denote, like before, the equilibrium concentrations of the monomers A and B.

The initial conditions are given by x_0, a_0, and b_0. The concentrations of n-mers terminated by A* and B*, again denoted by A^*_n and B^*_n, are given by

$$\begin{pmatrix} A^*_n \\ B^*_n \end{pmatrix} = x_e\mathrm{M}^{n-1} \begin{pmatrix} K_{\mathrm{A}}a \\ K_{\mathrm{B}}b \end{pmatrix} \tag{24}$$

This equation provides the molecular weight distribution of the resulting polymers.

The three unknowns, x_e, a, and b, fully characterize the system. They are determined by the three equations: the first two resulting from the condition of conservation of monomers, i.e.

$$\begin{pmatrix} a_0 - a \\ \\ b_0 - b \end{pmatrix} = \sum_{n=1}^{\infty} \left(\sum_{i=1}^{n} \prod_{m=0}^{i-1} \mathrm{N}_{n,m} \right)^{-1} \begin{pmatrix} A^*_n \\ \\ B^*_n \end{pmatrix} =$$

$$x_e \sum_{n=1}^{\infty} \sum_{i=1}^{n} \left(\prod_{m=0}^{i-1} \mathrm{N}_{n,m} \right)^{-1} \mathrm{M}^{n-1} \begin{pmatrix} K_{\mathrm{A}}a \\ \\ K_{\mathrm{B}}b \end{pmatrix} \tag{25}$$

while the third one results from the condition of conservation of the initiator

$$x_e + \sum_{n=1}^{\infty} (A^*_n + B^*_n) = x_0 \tag{26}$$

the A^*_n and B^*_n being given by (24).

The values of x_e, a, and b, resulting from the solution of (25) and (26), provide all the necessary information about the system through application of the previously discussed relations.

Extension of the Treatment to Copolymerization of *i* Monomers

The treatment outlined for the copolymerization of two monomers is readily generalized for copolymerization involving a greater number of monomers. For example, the system of three monomers is defined by their initial concentrations a_0, b_0, and c_0, by the initial concentrations of the activated monomers XA*, XB*, and XC*, denoted by A_0, B_0, and C_0, and by nine equilibrium constants $K_{i,j}$. We need to find the equilibrium concentrations of the residual activated monomers ${}^{\circ}A_1 = A^*_1$, ${}^{\circ}B_1 = B^*_1$, and ${}^{\circ}C_1 = {}^{\circ}C^*_1$, as well as the equilibrium concentrations of the monomers, a, b, and c. This is done by defining the 3 × 3 matrix

$$\mathrm{M} = \begin{pmatrix} K_{11}a & K_{21}a & K_{31}a \\ K_{12}b & K_{22}b & K_{32}b \\ K_{13}c & K_{23}c & K_{33}c \end{pmatrix}$$

and the 3 × 3 matrices of conditional probabilities

$$\mathrm{N}_{n,m} = \begin{pmatrix} r_{1,n,m} & r_{2,n,m} & r_{3,n,m} \\ s_{1,n,m} & s_{2,n,m} & s_{3,n,m} \\ q_{1,n,m} & q_{2,n,m} & q_{3,n,m} \end{pmatrix}$$

with

$$r_{1,n,m} =$$

$$(1 \quad 1 \quad 1)\mathrm{M}^{n-m-1} \begin{pmatrix} K_{11}a \\ 0 \\ 0 \end{pmatrix} / (1 \quad 1 \quad 1)\mathrm{M}^{n-m-1} \begin{pmatrix} K_{11}a \\ K_{12}b \\ K_{13}c \end{pmatrix}, \quad \text{etc}$$

The solution of the six equations describing the conservations of living polymers and of monomers, similar to eq 14 and 16, yields the desired unknowns, ${}^{\circ}A_1$, ${}^{\circ}B_1$, ${}^{\circ}C_1$, a, b, and c. These fully describe the equilibrated system, the molecular weight distribution, the average composition of the various n-mers, etc.

In the case of i components, one sets similar i-dimensional "vectors" and the respective $i \times i$ matrices and deduces the $2i$ equations for the $2i$ unknowns, analogously to the previous treatment.

Modification of the above treatment to systems involving equilibria between the initiator and the monomers may be accomplished by proceeding along the lines outlined in the preceding section. For copolymerization of i monomers, the solution of i equations analogous to (14) together with the balance equation $x_e + \sum A^*_n + \sum B^*_n + \sum C^*_n ... = x_0$ provides the values of x_e, a, b, c... required in characterization of the properties of the system.

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Appendix I

Consider a solution of very long living copolymers in equilibrium with their comonomers. In such a system the rate of each addition is equal to the rate of the corresponding depropagation; i.e.

$$K_{11}aA^* = [\mathrm{AA}^*]$$

$$K_{21}aB^* = [\mathrm{BA}^*]$$

$$K_{12}bA^* = [\mathrm{BA}^*]$$

$$K_{22}bB^* = [BB^*]$$

Here, K's are the pertinent equilibrium constants, a and b the equilibrium concentrations of the comonomers, and A^*, [AA*], B^*, [BA*], etc. the concentrations of the living copolymers possessing the respective end groups. Since [AA*] + [BA*] = A^* and [AB*] + [BB*] = B^*, we deduce

$$K_{11}aA^* + K_{21}aB^* = A^* \tag{A1}$$

$$K_{12}bA^* + K_{22}bB^* = B^* \tag{A2}$$

Solution of these homogeneous equations demands

$$\begin{vmatrix} K_{11} - 1/a & K_{21} \\ K_{12} & K_{22} - 1/b \end{vmatrix} = 0 \tag{A3}$$

thus providing a relation between the equilibrium constants and the equilibrium concentrations of the comonomers. Extension of such a treatment to systems composed of more than two comonomers is obvious.

The above relations are only approximately correct. Depropagation of the smallest copolymers present in the high molecular weight material yields still smaller polymers, and their formation is not accounted for in the balance. Nevertheless the approximation inherent in (A3) is acceptable for high molecular weight material, although not for lower polymers.

Apart from this limitation, relation (A3), used by O'Driscoll for calculation of the equilibrium concentrations of the comonomers,[15] does not provide solution to the problem even if the initial state of the system is known. The approach proposed in ref 15 requires information about some properties of the *final* state of the system. However, this is a circular reasoning—the required properties should be determined by the initial state. This contrasts with the approach outlined in this paper, which provides the required equilibrium concentrations derived from the known K values and the description of the initial state, i.e., the initial concentrations of the monomers and of initiator.

Appendix II. Conditional Probabilities

Consider the subclass of all living n-mers possessing units A in positions m and $m + 1$, i.e., all $\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...A^*}_n$ and $\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...B^*}_n$. The thus specified n-mers are in equilibrium with the respective $(m + 1)$-mers, i.e., $\mathrm{X...A}_m\mathrm{A^*}_{m+1}$. In view of eq 8

$$\begin{pmatrix} \mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...A^*}_n \\ \mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...B^*}_n \end{pmatrix} = \mathbf{M}^{n-m-1} \begin{pmatrix} \mathrm{X...A}_m\mathrm{A^*}_{m+1} \\ 0 \end{pmatrix} \tag{A4}$$

Since $\mathrm{X...A}_m\mathrm{A^*}_{m+1}$ is in equilibrium with $\mathrm{X...A^*}_m$

$$\mathrm{X...A}_m\mathrm{A^*}_{m+1} = K_{11}a[\mathrm{X...A^*}_m] \tag{A5}$$

Hence

$$[\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...A^*}_n] + [\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...B^*}_n] = (1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} K_{11}a \\ 0 \end{pmatrix}[\mathrm{X...A^*}_m] \tag{A6}$$

Similar reasoning leads to an analogous expression for

$$[\mathrm{X...A}_m\mathrm{B}_{m+1}\mathrm{...A^*}_n] + [\mathrm{X...A}_m\mathrm{B}_{m+1}\mathrm{...B^*}_n] = (1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} 0 \\ K_{12}b \end{pmatrix}[\mathrm{X...A^*}_m] \tag{A7}$$

However, the ratio

$$\{[\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...A^*}_n] + [\mathrm{X...A}_m\mathrm{A}_{m+1}\mathrm{...B^*}_n]\}/\{[\mathrm{X...A}_m\mathrm{B}_{m+1}\mathrm{...A^*}_n] + [\mathrm{X...A}_m\mathrm{B}_{m+1}\mathrm{...B^*}_n]\}$$

is the ratio of conditional probabilities of A in position m of an n-mer being followed by A or B, respectively. Denoting these conditional probabilities by $r_{n,m}$ and $1 - r_{n,m}$, we find

$$r_{n,m}/(1 - r_{n,m}) = (1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} K_{11}a \\ 0 \end{pmatrix}/(1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} 0 \\ K_{12}b \end{pmatrix}$$

and

$$r_{n,m} = (1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} K_{11}a \\ 0 \end{pmatrix}/(1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} K_{11}a \\ K_{12}b \end{pmatrix} \tag{A8}$$

The same reasoning gives the conditional probability, denoted by $s_{n,m}$, of B in position of m of an n-mer being followed by B; namely

$$s_{n,m} = (1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} 0 \\ K_{22}b \end{pmatrix}/(1\quad 1)\mathbf{M}^{n-m-1}\begin{pmatrix} K_{21}a \\ K_{22}b \end{pmatrix} \tag{A9}$$

It is important to stress that the conditional probabilities depend on $n - m$ and are not constant. For example, for all polymers (with $n > m$), the conditional probability for the penultimate A being followed by the last active A is $K_{11}a/(K_{11}a + K_{12}b)$, whereas for the preceding A to be followed by the penultimate A (i.e., $n - m = 2$) the conditional probability is

$$(K_{11}a + K_{12}b)K_{11}a/\{(K_{11}a + K_{12}b)K_{11}a + (K_{21}a + K_{22}b)K_{22}b\}$$

Still more complex expressions give the conditional probabilities for $n - m = 3, 4, 5$, etc. Furthermore, let it be stressed that for $n - m > 1$ the conditional probabilities depend on all four K's as well as on the equilibrium concentrations of the monomers, a and b.

Even for infinitely long polymers, i.e., for $n \to \infty$, the conditional probabilities depend on the distance of the unit in question from the growing end, i.e., on $n - m$. The conditional probabilities become constant for $n - m \to \infty$, i.e., when the unit in question is far from the growing end. The respective r_∞ and s_∞ are

$$r_\infty = 2K_{11}a/\{K_{11}a + K_{22}b + [(K_{11}a - K_{22}b)^2 + 4K_{12}K_{21}ab]^{1/2}\} \tag{A10}$$

$$s_\infty = 2K_{22}b/\{K_{11}a + K_{22}b + [(K_{11}a - K_{22}b)^2 + 4K_{12}K_{21}ab]^{1/2}\} \tag{A11}$$

We may form now the matrices of conditional probabilities

$$\mathbf{N}_{n,m} = \begin{pmatrix} r_{n,m} & 1 - s_{n,m} \\ 1 - r_{n,m} & s_{n,m} \end{pmatrix} \tag{A12}$$

that convert the population of A's and B's in m-th segment of n-mers into their population in the following $(m + 1)$-th segment. We shall need also in our treatment their reciprocals, which exist provided that $\mathbf{N}_{n,m}$ is not singular.

Such a matrix is singular when $r_{n,m} + s_{n,m} = 1$ and acquires then the form

$$\begin{pmatrix} r_{n,m} & r_{n,m} \\ 1 - r_{n,m} & 1 - r_{n,m} \end{pmatrix} \qquad \text{(A13)}$$

implying that the probability for A or B to be in position $m + 1$ is independent of the nature of the unit in position m.

Singularity of $\mathbf{N}_{n,n-1}$ in conjunction with eq A-10 and A-11 demands the relation

$$K_{11}K_{22} = K_{12}K_{21} \qquad \text{(A14)}$$

making **M** singular. For a singular 2 × 2 matrix $\mathbf{M}^i = \lambda^{i-1}\mathbf{M}$, where λ is the nonzero eigenvalue of **M**; i.e., $\lambda = K_{11}a + K_{22}b$. Singularity of **M** makes all the matrices $\mathbf{N}_{n,m}$ singular. Hence, the probability of having terminal A in any n-mer, for $n > 1$, is

$$q = K_{11}a/(K_{11}a + K_{12}b) = K_{21}a/(K_{21}a + K_{22}b) \qquad \text{(A15)}$$

and the probability of having A in any nonterminal place, but not the first one, of any n-mer is

$$r = K_{11}a/(K_{11}a + K_{22}b) \qquad \text{(A16)}$$

In view of these relations, the following balance equations are readily deduced

$$(1 \quad 1)\sum_1^{\infty}\begin{pmatrix} A^*_n \\ B^*_n \end{pmatrix} = (1 \quad 1)(1 - \lambda)^{-1}\mathbf{M}\begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} = (A_0 + B_0 - {}^\circ A_1 - {}^\circ B_1) \qquad \text{(A17)}$$

$$a_0 - a - A_0 = (1 \quad 1)\mathbf{M}\begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} \cdot \sum_2^{\infty}\lambda^{n-2}[(n-2)r + q] \qquad \text{(A18)}$$

$$b_0 - b - B_0 = (1 \quad 1)\mathbf{M}\begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_0 \end{pmatrix} \cdot \sum_2^{\infty}\lambda^{n-2}[(n-2)(1-r) + (1-q)] \qquad \text{(A19)}$$

Moreover, $(\mathbf{M} - \mathbf{N}') = (\mathbf{O})$, where

$$\mathbf{N}' = \begin{pmatrix} q & q \\ 1 - q & 1 - q \end{pmatrix}$$

because

$$\mathbf{M}\begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} = \begin{pmatrix} A^*_2 \\ B^*_2 \end{pmatrix} = \mathbf{N}'\begin{pmatrix} {}^\circ A_1 \\ {}^\circ B_1 \end{pmatrix} \qquad \text{(A20)}$$

leading to a relation such as

$$K_{11}a + K_{12}b = 1 \qquad \text{(A21)}$$

Thus, (A17), (A18), (A19), and (A21) provide the necessary four equations needed to determine ${}^\circ A_1$, ${}^\circ B_1$, a, and b.

References and Notes

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(18) O'Driscoll developed also a stochastic treatment of copolymerizations when the penultimate unit and the last one affect the rate of propagation, while the nature of the last three units determines the rate of depropagation.[13]