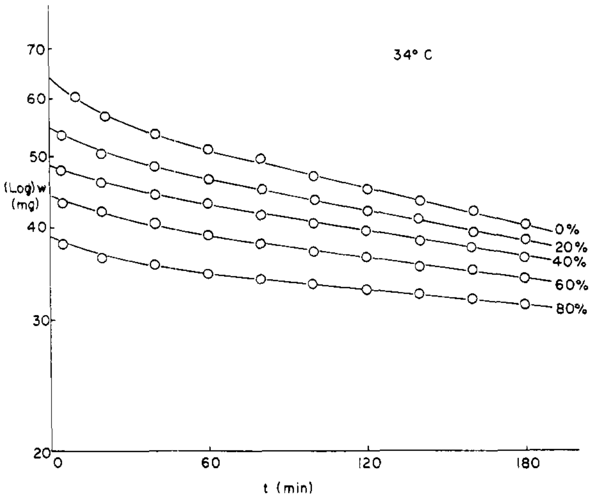

Figure 5. Diffusion experiments with dissolved polymer blends, prepared with the indicated content of the high molecular weight component; experimentation with frit I.

centrated with respect to the high molecular weight constituent. It should be mentioned that the differences in the extrapolation values of w_0 must not be misunderstood to reflect on differences in density alone. Although the solutions of polymers with different molecular weight are capable of showing different densities, these effects are expected to be quite small.

The individual diffusion plots of polymer blends are expected to be curved and concave upward if the low molecular weight constituents were depleted within the frit significantly faster than high molecular weight fractions. As shown in Figure 5, this behavior has not been encountered at the frit thickness employed and under the particular conditions of the experiments. Because of the absence of fractionation effects, it appears that our experiments provide a measure of an average diffusion coefficient that applies to each polymer blend as a whole. As shown in Figure 6, the determined diffusion coefficients are described well by a linear function of the weight composition for the prepared blends

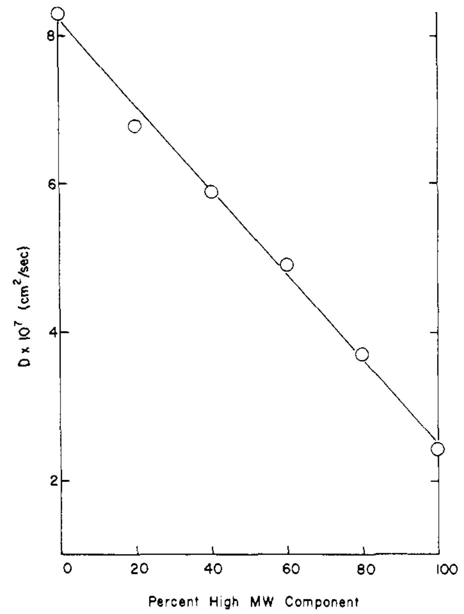

Figure 6. The effect of the composition of dissolved polymer blends on the effective diffusion coefficient.

Multicomponent Polymerization. I. Integration of the Rate Equations

K. F. O'Driscoll and R. Knorr

Chemical Engineering Department, State University of New York at Buffalo, Buffalo, New York 14214.

Received May 6, 1968

ABSTRACT: The equation describing instantaneous copolymer composition in free-radical vinyl copolymerization has been known and verified for many years. Although this equation has been integrated to give composition as a function of conversion, no analytical expression has been presented which gives conversion as a simple function of time. In this paper a derivation and experimental verification of such an equation is presented. Applications of this equation to problems in copolymerization kinetics are also considered. Extension of the equation to systems of more than two monomers is postulated.

In order to describe completely the course of a copolymerization it is necessary to know both monomer feed and polymer composition as functions of conversion and time.

Copolymer and monomer feed composition are related by the well-known copolymer composition equation

$$F_1 = \frac{r_1f_1^2 + f_1f_2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2} \qquad (1)$$

where the mole fractions of monomer i in the feed and instantaneous copolymer are f_i and F_i, respectively. The variation of composition f_i, with conversion, m, is governed, in turn, by a simple material balance. This relationship, known widely as the Skeist equation, has been successfully integrated by Meyer and Lowry[1] to give

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(1) V. Meyer and G. Lowry, *J. Polym. Sci., Part A*, 3, 2843 (1965).

$$m = 1 - \left(\frac{f_1}{f_1^0}\right)^{\alpha} \left(\frac{1 - f_1}{1 - f_1^0}\right)^{\beta} \left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^{\gamma} \qquad (2)$$

where

$$\alpha = r_2/(1 - r_2)$$

$$\beta = r_1/(1 - r_1)$$

$$\gamma = (1 - r_1 r_2)/[(1 - r_1)(1 - r_2)]$$

$$\delta = (1 - r_2)/(2 - r_1 - r_2)$$

In contrast, the time dependence of copolymerization has not yielded to useful mathematical description.

Derivation

The commonly accepted rate equations are

$$-\frac{\mathrm{d}[\mathrm{M}_1]}{\mathrm{d}t} = k_{11}[\mathrm{P}_1][\mathrm{M}_1] + k_{21}[\mathrm{P}_2][\mathrm{M}_1] \qquad (3)$$

$$-\frac{\mathrm{d}[\mathrm{M}_2]}{\mathrm{d}t} = k_{22}[\mathrm{P}_2][\mathrm{M}_2] + k_{12}[\mathrm{P}_1][\mathrm{M}_2] \qquad (4)$$

where $[\mathrm{M}_i]$ and $[\mathrm{P}_i]$ are the concentration of monomer i and propagating chains ending in monomer i, respectively. The instantaneous rate of polymerization, the sum of eq 3 and 4, has been cast into useful form by Walling.[2] In principle this equation can be integrated to describe conversion as a function of time. This approach has been taken by deButts.[3] However, the assumed dependence of $[\mathrm{P}_1]$ and $[\mathrm{P}_2]$ on $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$ results in an expression so complex that its usefulness is very limited.

On the other hand, by manipulating the basic eq 3 and 4, instead of attempting to integrate the Walling equation, it is possible to derive a simple, general expression for conversion or composition as a function of time.

Rearranging eq 3 and 4 to the form

$$-\frac{\mathrm{d}\ln[\mathrm{M}_1]}{\mathrm{d}t} = [\mathrm{P}_T]\left[(k_{11} - k_{21})\frac{[\mathrm{P}_1]}{[\mathrm{P}_T]} + k_{21}\right] \qquad (5)$$

$$-\frac{\mathrm{d}\ln[\mathrm{M}_2]}{\mathrm{d}t} = [\mathrm{P}_T]\left[k_{22} + (k_{12} - k_{22})\frac{[\mathrm{P}_1]}{[\mathrm{P}_T]}\right] \qquad (6)$$

where $[\mathrm{P}_1] + [\mathrm{P}_2] = [\mathrm{P}_T]$, and multiplying eq 6 by

$$X \equiv \frac{k_{11} - k_{21}}{k_{12} - k_{22}} \qquad (7)$$

gives

$$\frac{\mathrm{d}\ln[\mathrm{M}_1]}{\mathrm{d}t} - X\frac{\mathrm{d}\ln[\mathrm{M}_2]}{\mathrm{d}t} = -(k_{21} - Xk_{22})[\mathrm{P}_T] \qquad (8)$$

Integration of eq 8 gives

$$\ln\frac{[\mathrm{M}_1]}{[\mathrm{M}_1]_0} - X\ln\frac{[\mathrm{M}_2]}{[\mathrm{M}_2]_0} = -(k_{21} - Xk_{22})\int_0^t [\mathrm{P}_T]\mathrm{d}t \qquad (9)$$

If the left side of eq 9 is written in terms of mole fractions and fractional conversion using the relation

$$\frac{[\mathrm{M}_i]}{[\mathrm{M}_i]_0} = (1 - m)\frac{f_i}{f_i^0} \qquad (10)$$

then application of eq 2 leads to

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^{a}\left(\frac{1 - f_1}{1 - f_1^0}\right)^{b}\left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^{c}\right] = -(k_{21} - Xk_{22})\int_0^t [\mathrm{P}_T]\mathrm{d}t \qquad (11)$$

where

$$a = \alpha(1 - X) + 1$$

$$b = \beta(1 - X) - X$$

$$c = \gamma(1 - X)$$

Under the unique condition of azeotropic copolymerization, where $F_1/F_2 = f_1/f_2 = (r_2 - 1)/(r_1 - 1)$, there is no drift in f_1 or F_1 with conversion or time. Therefore, eq 2 and 11 are not applicable. Instead, since $f_i/f_i^0 = 1$ in eq 10, the terms $[\mathrm{M}_i]/[\mathrm{M}_i]_0$ reduce to $(1 - m)$ and eq 9 becomes

$$(1 - X)\ln(1 - m) = -(k_{21} - Xk_{22})\int_0^t [\mathrm{P}_T]\mathrm{d}t \qquad (9a)$$

In principle, then, eq 11 coupled with eq 1 leads to a complete description of the time dependency of copolymerization both with respect to composition and conversion. There are two restrictions to this.

(a) The value of $r_1r_2 = 1$ leads to the term $(k_{21} - Xk_{22})$ being zero and eq 11 cannot be used.

(b) It must be possible to evaluate the function

$$\int_0^t [\mathrm{P}_T]\mathrm{d}t$$

Application to Ionic Copolymerization. In many ionic systems $r_1r_2 = 1$ and eq 11 cannot be used. However when $r_1r_2 \neq 1$, and especially in those systems with rapid initiation and no termination where

$$\int_0^t [\mathrm{P}_T]\mathrm{d}t = [\text{initiator}] \times \text{time}$$

eq 11 may be quite useful.

Application to Free-Radical Copolymerization. Theoretical. When a copolymerization occurs with approximately equal initiation (R_i) and termination rates (R_t), the steady-state assumption on active chain ends is invaluable. For free-radical systems this is

$$R_\mathrm{i} = 2R_\mathrm{t} \qquad (12)$$

Since R_t is some function of $[\mathrm{P}_T]$, eq 12 permits calculation of $[\mathrm{P}_T]$ if the mechanism of termination and its dependence on $[\mathrm{P}_T]$ is known. In free-radical copolymerization the termination process is often represented as being chemically controlled. Three rate constants and two types of chain ends are specified. The work of North,[4] however, has shown that in most cases the termination reaction in copolymerization is better regarded as controlled by diffusion of chain segments of undefined length. As such, the termination rate constant represents an average value for the many different types of active chain segments present in solution. In practice, the termination rate constant

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(2) C. Walling, *J. Amer. Chem. Soc.*, **71**, 1930 (1949).

(3) E. H. deButts, *ibid.*, **72**, 411 (1950).

(4) (a) A. M. North, *Polymer*, **4**, 134 (1963); (b) J. N. Atherton and A. M. North, *Trans. Faraday Soc.*, **58**, 2049 (1962).

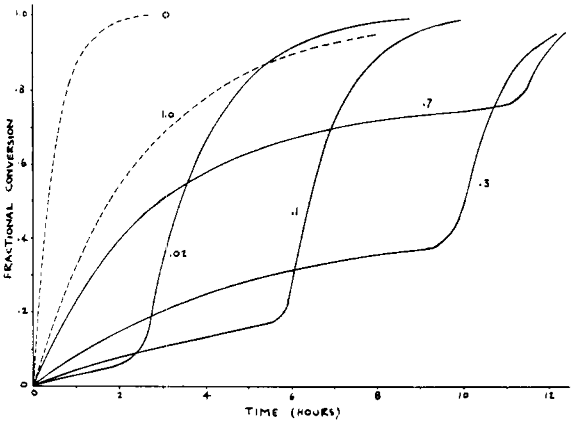

Figure 1. Theoretical conversion as a function of time for the bulk copolymerization of methyl methacrylate (M_1) with vinyl acetate (M_2) in various initial proportions (r_1/r_2 = 20/0.015, k_{11}/k_{22} = 705/3600, $k_t = 2.5 \times 10^7$, $[I]_0 = 0.06$, $k_d = 10^{-5}$; data from ref 4b and 6 for copolymerization at 60°). Numbers on curves refer to f_1^0.

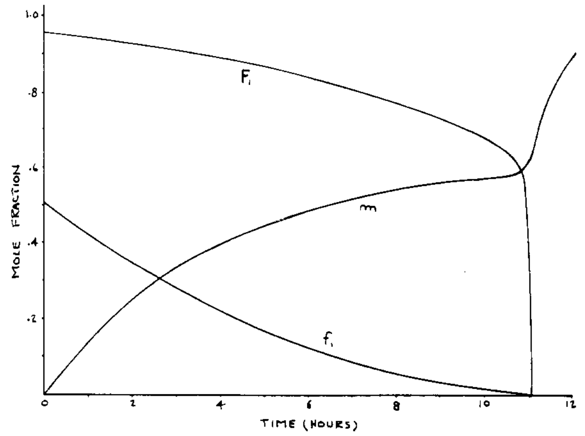

Figure 2. Theoretical conversion and instantaneous monomer feed and copolymer composition as functions of time for the copolymerization of an initially equimolar mixture of methyl methacrylate (M_1) and vinyl acetate (M_2). Rate parameters are as in Figure 1.

to be used can be considered as a single parameter which is dependent on the physics of the copolymer chains.

Although the authors feel strongly that the main body of evidence supports diffusion-controlled termination, it is not considered essential to the application of eq 11 for one or the other mechanism to be assumed.

If one wishes to accept the representation of the termination reaction as one which is chemically controlled, then the steady-state assumption would be written

$$R_i = 2[P_T]^2\left(k_{t_{11}}\frac{[P_1]^2}{[P_T]^2} + 2k_{t_{12}}\frac{[P_1][P_2]}{[P_T]^2} + k_{t_{22}}\frac{[P_2]^2}{[P_T]^2}\right) \tag{13a}$$

or

$$R_i = 2k_t'[P_T]^2 \tag{13b}$$

The k_t' in eq 13b is an apparent value representing the corresponding group of terms in eq 13a. An integration of $[P_T]$ then becomes feasible if k_t' is approximately constant over the desired range. This is a good approximation for cases where drift of monomer feed composition is not great or where there is a strong tendency for alternation ($r_1 \ll 1$, $r_2 \ll 1$, $F_1 \simeq 0.5$) or consecutive reaction of M_1 and M_2 ($r_1 \gg 1$, $r_2 \ll 1$, $F_1 \simeq 1$). In these cases, $[P_1]$ and $[P_2]$ would be nearly constant during a large portion of the polymerization reaction.

The steady-state assumption for diffusion controlled termination would be formally the same as eq 13b.

$$R_i = 2k_t''[P_T]^2 \tag{13c}$$

No general expression can yet be written for k_t'' but it is assumed that k_t'' depends on the physics of the chains as a whole rather than on the chemical nature of the chain ends. Good results are obtained by North[4b] using a weighted average of the two homopolymer termination constants

$$k_t'' = F_1k_{t_1} + F_2k_{t_2} \tag{14}$$

Whether termination is dominated by diffusive or chemical processes, results show that, for practical purposes in many systems, k_t is only slightly dependent on monomer composition over a wide range of compositions.

Thus, regardless of which mechanism is assumed, in free-radical copolymerization eq 11 can incorporate the steady-state assumption

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^a\left(\frac{1-f_1}{1-f_1^0}\right)^b\left(\frac{f_1^0-\delta}{f_1-\delta}\right)^c\right] = -(k_{21} - Xk_{22})\int_0^t\left(\frac{R_i}{2k_t}\right)^{1/2}\mathrm{d}t \tag{15}$$

If a first-order decay of initiator is assumed

$$R_i = 2ek_d[I]_0\exp(-k_dt) \tag{16}$$

where e is the efficiency of initiation. Equation 15 becomes

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^a\left(\frac{1-f_1}{1-f_1^0}\right)^b\left(\frac{f_1^0-\delta}{f_1-\delta}\right)^c\right] = 2(k_{21} - Xk_{22})\left(\frac{e[I]_0}{k_dk_t}\right)^{1/2}(\exp(-k_dt/2) - 1) \tag{17}$$

Equation 17 permits calculation of f_1 as a function of time under the assumptions made. The resulting values of f_1 may be used in eq 2 to obtain conversion *vs.* time, or in eq 1 to obtain F_1 *vs.* time. Equation 17 is, therefore, a key to the complete description of the time dependency of free-radial copolymerization. In the limit of infinite time eq 17 reduces to a "dead-end" equation analogous to that of Tobolsky,[5] with the added restriction that *neither* monomer is completely consumed before the initiator is depleted.

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^a\left(\frac{1-f_1}{1-f_1^0}\right)^b\left(\frac{f_1^0-\delta}{f_1-\delta}\right)^c\right] = -2(k_{21} - Xk_{22})\left(\frac{e[I]_0}{k_dk_t}\right)^{1/2} \tag{18}$$

(5) A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 5927 (1958).

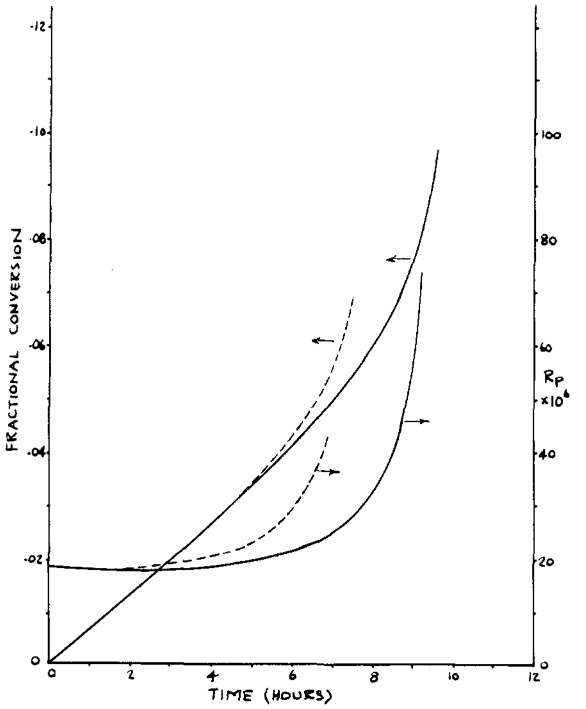

Figure 3. Experimental and theoretical conversion and rate of copolymerization as a function of time with AZ0 at 60° for a mixture of methyl methacrylate (M_1) and vinyl acetate (M_2) with an initial composition of $f_1^0 = 0.078$ ($r_1/r_2 = 20/0.015$, $k_1/k_2 = 705/3600$, $k_t = 7.5 \times 10^7$, $[I]_0 = 0.00112$, $k_d = 10^{-5}$). Rate constants are taken from ref 6 except k_t which is the value observed experimentally: – – – –, eyperimental; ——, theoretical.

For most monomer pairs eq 2 and 17 predict conversion–time curves similar to those of typical homopolymerizations. An exception, however, occurs in the case where $r_1 \gg 1$ and $r_2 \ll 1$. Such reactivity ratios describe a tendency for the two monomers to polymerize consecutively forming copolymer rich in monomer 1 in the early stages of reaction and copolymer rich in monomer 2 only when the supply of monomer 1 is nearly depleted. If the homopolymerization rate constants are such that $k_{11} \ll k_{22}$, then there will occur an acceleration in rate of reaction when the supply of monomer 1 is nearly depleted.

The results of calculations, using eq 2 and 17, show this behavior and are presented in Figures 1 and 2 for the monomer pair methyl methacrylate–vinyl acetate ($r_1/r_2 = 20/0.015$, $k_{11}/k_{22} = 705/3600$) at 60°. It was assumed that k_t/e was 2.5×10^7, $[I]_0$ was 0.06, and k_d was 10^{-5} (all units are liters, moles, and seconds). Reactivity ratios and other rate constants were selected from ref 6.

Experimental Section

Application to Free-Radical Copolymerization. The behavior predicted in Figures 1 and 2 has been implicitly described in earlier qualitative discussions of copolymerization rates.[7] However, the unique character of this type of copolymerization with its drastic increases in rate as the polymerization proceeds offers a rigorous experimental test of eq 17 and the assumptions associated with it. For this reason the copolymerization of vinyl acetate with methyl methacrylate was selected for study. Bulk copolymerizations were carried out at 60° with 2,2′-azobisisobutyronitrile as initiator, using very low mole fractions of methyl methacrylate. Conversion *vs.* time was measured using dilatometric data calibrated gravimetrically. Copolymer compositions were not measured. All polymerizations were carried out on freshly distilled monomer which was degassed by freeze–thaw cycles and then sealed under vacuum.

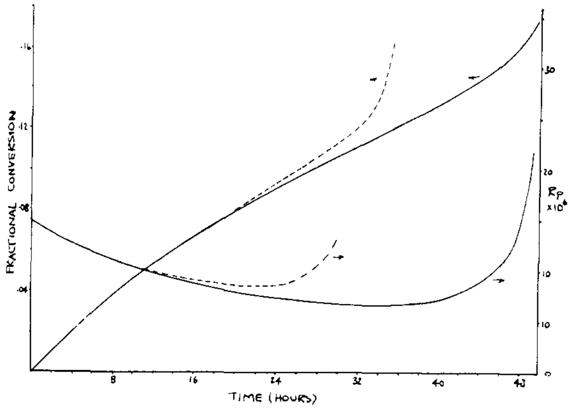

Figure 4. Experimental and theoretical conversion and rate of copolymerization as a function of time with AZ0 at 60° for a mixture of methyl methacrylate (M_1) and vinyl acetate (M_2) with an initial composition of $f_1^0 = 0.0225$ ($r_1/r_2 = 20/0.015$, $k_{11}/k_{22} = 705/3600$, $k_t = 6 \times 10^7$, $[I]_0 = 0.00184$, $k_d = 10^{-5}$, $e = 1$). Rate constants are taken from ref 6 except k_t which is the value observed experimentally: – – – –, experimental; ——, theoretical.

Figures 3 and 4 show the experimental conversion–time and rate–time plots for methyl methacrylate and vinyl acetate using mole fractions of methyl methacrylate of 0.0225 and 0.078. The calculated curves shown in Figures 3 and 4 were obtained using the same reactivity ratios and rate constants as in Figures 1 and 2, except that k_t/e was taken as 7×10^7.

Discussion

The qualitative agreement between the calculated time–conversion plots and the experimental data shown in Figures 3 and 4 can be improved quantitatively by varying the ratio k_t/e to account for the drift in f_1, and/or by varying the reactivity ratios, especially r_2, within their experimental errors.

At fixed values of reactivity ratios, the function X (eq 7), and therefore the rate of copolymerization, is somewhat insensitive to variations in the propagation rate constants.

While we have made (but do not show) improvements of the data in Figures 3 and 4 by varying reactivity ratios, it is beyond the scope of this paper to embark on the chimeric problem of fitting the experimental data with a large number of variables, since the data do conform sufficiently to the calculations to verify eq 17.

It should be noted that the upturn in rate in Figures 3 and 4 is due to an increase in the *relative* concentration of the more reactive of the two chain ends, and not due to an increase in the *absolute* concentration of

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(6) "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience Publishers, Inc., New York, N. Y., 1966.

(7) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

chain ends associated with the gel effect.[8] Comparison of the polymer concentration of Figure 3 where the upturn occurred with that of Figure 4 demonstrates that the data (at least in Figure 3) were obtained at concentrations of polymer below those which might cause the gel effect.

As a rigorous check on eq 17, eq 3 and 4 were numerically integrated using time intervals which were a small fraction (10^{-4} to 10^{-5}) of the over-all reaction time. The calculated results of the numerical integration were between those of eq 17 and of the experimental data. The difference between eq 17 and numerical integration is interpreted as arising from the steady-state assumption used in deriving eq 1 and 2.

$$k_{12}[P_1][M_2] = k_{21}[P_2][M_1] \tag{19}$$

This assumption is imprecise when only a few changeovers from P_1 to P_2 (or *vice versa*) occur during a chain lifetime. This imprecision becomes apparent only during the period of rate acceleration (*i.e.*, during the time when the system changes from one with most chain ends being P_1 to one with most chain ends being P_2). The error introduced by this imprecision is sufficiently small to be ignored in most cases.

It is possible to use eq 17 in a variety of ways. The copolymerization termination rate constant k_t can be quantitatively assessed where propagation rate constants are known. As mentioned above, the work of North[4] has shown k_t to be a diffusion-controlled rate constant which is composition dependent. Quantitative determinations of k_t may shed light on the polymer chain physics involved in the termination process. The use of eq 18 under azeotropic or near-azeotropic conditions is especially attractive in this regard.

The effect of nonideal mixing in copolymerization reactors is being studied in detail and the results will be presented in a forthcoming publication.[9] In general, results for an imperfectly mixed continuous stirred tank reactor (CSTR) show that, for most monomer pairs, incomplete mixing has little effect on conversion and *average* copolymer composition but always produces broader distributions of copolymer composition. The sole exception to this is found to be monomer pairs where there is a strong tendency for consecutive reaction of the two types of monomer and where the propagation constants differ greatly (*e.g.*, methyl methacrylate–vinyl acetate). In the case of methyl methacrylate–vinyl acetate it was found that conversion increases dramatically with imperfect mixing and average copolymer composition may be as much as 10% lower than the ideal reactor product. The distribution of copolymer composition changes drastically from an ideal Poisson type to a U-shaped curve indicating large fractions of the two nearly pure homopolymers. Thus, rather than producing a true copolymer, an imperfectly mixed CSTR may actually yield a mixture of two homopolymers. The implications of such a composition distribution must be considered in attempting to describe the properties of copolymers produced in continuous reactors. For example, the "ionomers," whose properties have recently been described,[10] but whose polymerization has not, might be an example of such behavior.

It is also interesting to note the possibility of calculating addition schedules for batch reaction systems (designed to produce homogeneous copolymer) on a time basis rather than on a conversion basis.

Although this paper has been concerned only with binary copolymerization, the procedure leading to eq 9 is also applicable to multicomponent polymerizations of more than two monomers. General multicomponent rate equations, analogous to eq 3 and 4, can be written for a system of N monomers.

$$\begin{pmatrix} -\dfrac{1}{[M_1]}\dfrac{d[M_1]}{dt} \\ -\dfrac{1}{[M_2]}\dfrac{d[M_2]}{dt} \\ \vdots \\ -\dfrac{1}{[M_N]}\dfrac{d[M_N]}{dt} \end{pmatrix} = \begin{bmatrix} k_{11} & k_{21} \ldots & k_{N1} \\ k_{12} & k_{22} \ldots & k_{N2} \\ \vdots & \vdots & \vdots \\ k_{1N} & k_{2N} \ldots & k_{NN} \end{bmatrix} \begin{pmatrix} [P_1] \\ [P_2] \\ \vdots \\ [P_N] \end{pmatrix} \tag{20}$$

$$(D) = [K](P) \tag{20a}$$

This set of equations can be solved for $[P_i]$, $i = 1 \ldots N$.

$$(P) = [K]^{-1}(D) \tag{21}$$

Adding the solutions for the $[P_i]$'s indicated in eq 21 and collecting like terms gives the result

$$\sum_{i=1}^{N} K_i \frac{d \ln [M_i]}{dt} = \sum_{i=1}^{N} [P_i] = [P_T] \tag{22}$$

where K_i is the sum of the elements in the ith column of the inverse K matrix.

Finally, integrating eq 22 gives

$$\sum_{i=1}^{N} K_i \ln \frac{[M_i]}{[M_i]_0} = \int_0^t [P_T]dt \tag{23}$$

It is obvious that eq 9 is merely the special case of eq 23 when $N = 2$. Application of eq 23 should therefore follow the same forms as application of eq 9.

Acknowledgment. Support of this research by the National Science Foundation and by an unrestricted grant from the Chevron Research Corp. is gratefully acknowledged. The Computing Center at SUNY, Buffalo, whose facilities were so useful in this work, is partially supported by NIH Grant FR-00126 and NSF Grant GP-7318.

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(8) R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 566 (1942); E. Trommsdorff, H. Kohle, and P. Lagally, *Makromol. Chem.*, **1**, 169 (1947).

(9) K. O'Driscoll and R. Knorr, in preparation.

(10) F. C. Wilson, R. Longworth, and D. J. Vaughan, *Polym. Preprints*, **9** (1), 505 (1968), and following papers.