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NONHOMOGENEOUS COPOLYMERIZATION KINETICS: FIRST-ORDER MARKOVIAN SYSTEMS*

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ABSTRACT

Equations correlating sequence distributions of nonhomogeneous first-order Markovian copolymer systems have been derived. For systems where (r_1r_2) differs by a factor of 2 from unity, a cubic power series approximation in polymer composition is necessary to predict triads to a standard deviation of ~0.001–0.003. This precision holds over fairly broad ranges of (r_1r_2) and distribution function moments. Prediction of kinetic factors from sequence distribution data requires such precision that any derived data are questionable. Where two catalysts are involved, at least one of which is non-Bernoullian, there does not appear to be a practical way to derive kinetic data from triad sequences. Such systems can simulate homogeneous Bernoullian systems very closely.

INTRODUCTION

Kinetic modeling of polymerization reactions is becoming increasingly sophisticated. More powerful computers are allowing more parameters to be studied in greater detail than was possible only a few years ago [1]. The predictions of these models, however, do not always agree with

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*Fourth in a series on statistics of nonhomogeneous systems.

certain experimental results (though logically they should be expected to), yet agree with other hard experimental data.

This situation does arise in copolymerization where basic kinetic parameters are linked to polymer sequence distributions. Several cases have been solved that yield satisfactory predictions of sequences from kinetics and vice versa:

Homogeneous, steady-state 0–3-order Markovian
Nonhomogeneous, zero-order Markovian

The general case, however, has not been solved.

Previous papers in this series [2–5] developed kinetic models for nonhomogeneous Bernoullian, i.e., zero-order Markovian, copolymer systems. Dyad, triad, and tetrad copolymer distributions were derived and compared to experimental copolymer distributions.

Extension of these models to nonhomogeneous first-order Markovian systems was briefly considered in these papers but not developed. Factors relating first-order to zero-order probabilities were treated as constants, calculated at average copolymer composition, and not the functions of copolymer composition that they really are. This assumption simplified the mathematics but left the meaning of the data in doubt.

In this paper the nonhomogeneous model is extended to include first-order Markovian copolymer systems where the factors are expanded as power series in composition prior to summing the independent probability functions over all species present.

Two cases are developed. In the first, nonhomogeneity arises because of physical factors such as diffusion or varying comonomer composition. In the second, two catalyst species are the cause of nonhomogeneity.

TRIAD DISTRIBUTIONS

Probability equations for nonhomogeneous first-order triads had previously been derived in terms of three parameters, (m), (r_1/α), and $(r_2\alpha)$ [2]:

$$P_{111} = m^3F_{111}, \quad \text{where } F_{111} = (r_1/\alpha)^2/[1 + (r_1/\alpha - 1)m]^2 \tag{1a}$$

$$P_{112} = 2m^2(1 - m)F_{112}, \quad \text{where } F_{112} = (r_1/\alpha)/[1 + (r_1/\alpha - 1)m]^2 \tag{1b}$$

$$P_{212} = m(1 - m)^2F_{212}, \quad \text{where } F_{212} = 1/[1 + (r_1/\alpha - 1)m]^2 \tag{1c}$$

Similarly:

$$P_{121} = m^2(1 - m)F_{121}, \quad \text{where } F_{121} = 1/[1 + (r_2\alpha - 1)(1 - m)]^2 \tag{1d}$$

$$P_{122} = 2m(1 - m)^2F_{122}, \quad \text{where } F_{122} = (r_2\alpha)/[1 + (r_2\alpha - 1)(1 - m)]^2 \tag{1e}$$

$$P_{222} = (1 - m)^3F_{222}, \quad \text{where } F_{222} = (r_2\alpha)^2/[1 + (r_2\alpha - 1)(1 - m)]^2 \tag{1f}$$

Here,

$$\begin{aligned}\alpha &= [m/(1 - m)]/[(1 - M)/M] \\ &= r_1[1 + (r_1 - 1)M]/[r_1r_2 + (r_1 - r_1r_2)M]\end{aligned} \tag{2}$$

Some simplification is immediately possible. Equation (2) can be rearranged to yield

$$[1 + (r_1/\alpha - 1)m] = [1 + (r_2\alpha - 1)(1 - m)] \tag{2'}$$

so that all the denominators in Eqs. (1) are the same.

In previous papers, first-order Markovian systems were treated by calculating the six triad functions, F_{111} to F_{222}, at average polymer composition, m_0, for given values of r_1 and r_2. Then, the pseudotriads P_{ijk}/F_{ijk} etc. were correlated as if they followed nonhomogeneous Bernoullian kinetics; that is, the functions F_{111} etc. were regarded as constants for each m_0 and (r_1r_2) product.

Actually, however, the functions F_{ijk} are very much functions of (m) as well as (r_1r_2). Their relationships is illustrated in Fig. 1, where they are plotted against polymer composition for $(r_1r_2) = 2.0$ and 0.5. Note that the three functions for Component 2 when plotted against $(1 - m)$ are exact mirror images of the functions shown.

Call [10] has derived the expression

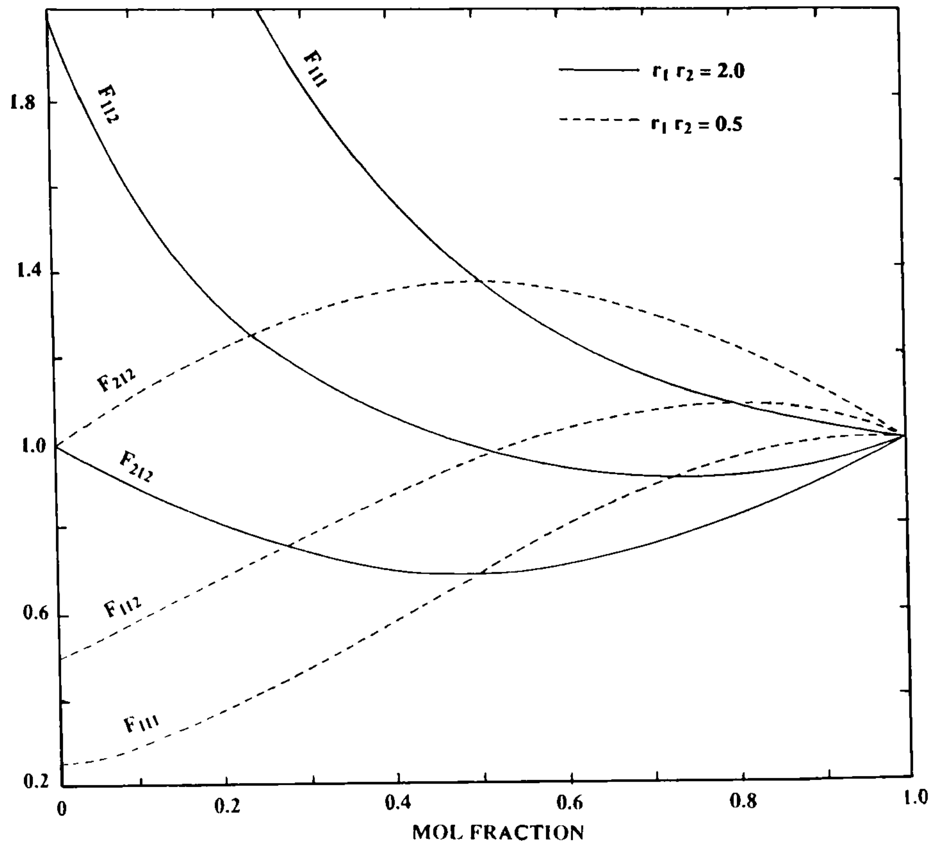

FIG. 1. Homogeneous first-order triad factors.

$$r_1/\alpha = \frac{(1 - m)}{2m}\left[\sqrt{\left(\frac{1 - 2m}{1 - m}\right)^2 + \frac{4m(r_1r_2)}{(1 - m)}} - \frac{(1 - 2m)}{(1 - m)}\right] \qquad (2'')$$

from Eq. (2). This equation together with Eq. (2′) demonstrates that F_{ijk} are not functions of (m), (r_1), and (r_2) individually, but rather are nonlinear functions of (m) and (r_1r_2) only. In principle, Eqs. (2) may be substituted into Eqs. (1) to permit direct calculation of probabilities, but the algebra becomes complicated.

However, these factors may be closely approximated by a power series expansion in composition for any given (r_1r_2):

$$F_{111} = (r_1/\alpha)^2/[1 + (r_1/\alpha - 1)m]^2 = a_0 + a_1m + a_2m^2 + a_3m^3 + \cdots \tag{3a}$$

$$F_{112} = (r_1/\alpha)/[1 + (r_1/\alpha - 1)m]^2 = b_0 + b_1m + b_2m^2 + b_3m^3 + \cdots \tag{3b}$$

. .

. .

. .

$$F_{222} = (r_2\alpha)^2/[1 + (r_2\alpha - 1)(1 - m)]^2 = f_0 + f_1m + f_2m^2 + f_3m^3 + \cdots \tag{3f}$$

Probably the simplest method of calculating the coefficients in Eqs. (3) for various values of (r_1r_2) is to compute the F_{ijk} at each 0.01 increment of m from 0.01 to 0.99 as input to a double precision statistical program. This is the procedure used throughout this paper.

In general, cubic expansion of F_{111}, F_{112}, F_{122}, and F_{222} gave correlation coefficients in excess of 0.99. The functions F_{212} and F_{121} were represented to a similar accuracy by a second power correlation equation, i.e., $c_3 = d_3 = 0$.

Nonhomogeneous first-order triad probabilities are calculated by the technique used previously:

1. Equations (3) are substituted into appropriate Eqs. (1).
2. Individual molecular probabilities are accounted for by the substitution $m = (m_0 + \delta)$.
3. The power series are expanded term by term, then summed for all independent molecular species to obtain overall probabilities.

That is, for example,

$$P_{111} = \Sigma(m^3)(a_0 + a_1m + a_2m^2 + a_3m^3 + \cdots) \tag{4}$$

$$= \Sigma[a_0(m_0 + \delta)^3 + a_1(m_0 + \delta)^4 + \cdots] \tag{4'}$$

As previously defined, χ_n is the (n)th moment of the distribution function of δ about its mean value of zero, and F_{111_0} is the value of F_{111} at $m = m_0$. This yields

$$\begin{aligned}
P_{111} = {} & F_{111_0} m_0^3 \\
& + [3a_0 + 6a_1 m_0 + 10a_2 m_0^2 + 15a_3 m_0^3 + \cdots] m_0 \chi_2 \\
& + [a_0 + 4a_1 m_0 + 10a_2 m_0^2 + 20a_3 m_0^3 + \cdots] \chi_3 \\
& + [a_1 + 5a_2 m_0 + 15a_3 m_0^2 + \cdots] \chi_4 \\
& + [a_2 + 6a_2 m_0 + \cdots] \chi_5 + a_3 \chi_6 + \cdots
\end{aligned} \tag{5a}$$

Similarly:

$$\begin{aligned}
P_{112} = {} & F_{112_0} m_0^2 (1 - m_0) \\
& + [b_0 + 3(b_1 - b_0) m_0 + 6(b_2 - b_1) m_0^2 \\
& \quad + 10(b_3 - b_2) m_0^3 - 30 b_3 m_0^4 + \cdots] \chi_2 \\
& + [(b_1 - b_0) + 4(b_2 - b_1) m_0 \\
& \quad + 10(b_3 - b_2) m_0^2 - 20 b_3 m_0^3 + \cdots] \chi_3 \\
& + [(b_2 - b_1) + 5(b_3 - b_2) m_0 - 15 b_3 m_0^2 \cdots] \chi_4 \\
& + [(b_3 - b_2) - 6 b_3 m_0 + \cdots] \chi_5 - 2 b_3 \chi_6 + \cdots
\end{aligned} \tag{5b}$$

$$\begin{aligned}
P_{212} = {} & F_{212_0} m_0 (1 - m_0)^2 \\
& + [c_0 + 3(c_1 - c_0) m_0 + 6(c_2 - c_1) m_0^2 - 10 c_2 m_0^3 + \cdots] \chi_2 \\
& + [(c_1 - c_0) + 4(c_2 - c_1) m_0 - 10 c_2 m_0^2 + \cdots] \chi_3 \\
& + [(c_2 - c_1) - 5 c_2 m_0 + \cdots] \chi_4 - c_2 \chi_5 + \cdots
\end{aligned} \tag{5c}$$

$$\begin{aligned}
P_{121} = {} & F_{121_0} m_0^2 (1 - m_0) \\
& + [c_0 + 3(c_1 - c_0) m_0 + 6(c_2 - c_1) m_0^2 \\
& \quad - 10 c_2 m_0^3 + \cdots] \chi_2 \\
& + [(c_1 - c_0) + 4(c_2 - c_1) m_0 - 10 c_2 m_0^2 + \cdots] \chi_3 \\
& + [(c_2 - c_1) - 5 c_2 m_0 + \cdots] \chi_4 - c_2 \chi_5 + \cdots
\end{aligned} \tag{5d}$$

In setting up the equations for P_{121}, all $d_i = c_i$ by Eq. (2′).

$$\begin{aligned}
P_{122} = {} & 2F_{122_0} m_0(1 - m_0)^2 \\
& + [(e_1 - 2e_2) + 3(e_2 - 2e_1 + c_0)m_0 \\
& \quad + 6(e_3 - 2e_2 + e_1)m_0^2 \\
& \quad + 10(e_2 - 2e_3)m_0^3 + 15e_3 m_0^4 + \cdots]\chi_2 \\
& + [(e_2 - 2e_1 + e_0) + 4(e_3 - 2e_2 + e_1)m_0 \\
& \quad + 10(e_2 - 2e_3)m_0^2 + 20e_3 m_0^3 + \cdots]\chi_3 \\
& + [(e_3 - 2e_2 + e_1) + 5(e_2 - 2e_3)m_0 + 15e_2 m_0^2 + \cdots]\chi_4 \\
& + [(e_2 - 2e_3) + 6e_3 m_0 + \cdots]\chi_5 \\
& + e_3\chi_6 + \cdots
\end{aligned} \tag{5e}$$

$$\begin{aligned}
P_{222} = {} & F_{222_0}(1 - m_0)^3 \\
& + [3k_0 + 6k_1 m_0 + 10k_2 m_0^2 + 15k_3 m_0^3 + \cdots]\chi_2 \\
& + [k_0 + 4k_1 m_0 + 10k_2 m_0^2 + 20k_3 m_0^3 + \cdots]\chi_3 \\
& + [k_1 + 5k_2 m_0 + 15k_3 m_0^2 + \cdots]\chi_4 \\
& + [k_2 + 6k_3 m_0 + \cdots]\chi_5 + k_3\chi_6 + \cdots
\end{aligned} \tag{5f}$$

where

$$\begin{aligned}
k_0 &= f_0 \\
k_1 &= f_1 - 3f_0 \\
k_2 &= f_2 - 3f_1 + 3f_0 \\
k_3 &= f_3 - 3f_2 + 3f_1 - f_0
\end{aligned}$$

Similarly for dyads:

$$\begin{aligned}
P_{11} &= m^2(r_1/\alpha)/[1 + (r_1/\alpha - 1)m] \\
&= m^2[A_0 + A_1 m + A_2 m^2 + A_3 m^3 + \cdots]
\end{aligned} \tag{6a}$$

$$\begin{aligned}
P_{12} &= 2m(1 - m)/[1 + (r_1/\alpha - 1)m] \\
&= 2m(1 - m)[B_0 + B_1 m^2 + B_2 m^2 + \cdots]
\end{aligned} \tag{6b}$$

$$\begin{aligned} P_{22} &= (1 - m)^2(r_2\alpha)/[1 + (r_2\alpha - 1)(1 - m) \\ &= (1 - m)^2[C_0 + C_1 m + C_2 m^2 + C_3 m^3 + \cdots] \end{aligned} \tag{6c}$$

Yielding

$$\begin{aligned} P_{11} &= F_{11_0} m_0^2 + [A_0 + 3A_1 m_0 + 6A_2 m_0^2 + 10A_3 m_0^3 + \cdots]\chi_2 \\ &\quad + [A_1 + 4A_2 m_0 + 10A_3 m_0^2 + \cdots]\chi_3 \\ &\quad + [A_2 - 5A_3 m_0 + \cdots]\chi_4 + A_3\chi_5 + \cdots \end{aligned} \tag{7a}$$

$$\begin{aligned} P_{12} &= F_{12_0} m_0(1 - m_0) \\ &\quad + [(B_1 - B_0) + 3(B_2 - B_1)m_0 - 6B_2 m_0^2 + \cdots]\chi_2 \\ &\quad + [(B_2 - B_1) - 4B_2 m_0 + \cdots]\chi_3 - B_2\chi_4 + \cdots \end{aligned} \tag{7b}$$

$$\begin{aligned} P_{22} &= F_{22_0}(1 - m_0)^2 \\ &+ [(C_2 - C_1 + C_0) + 3(C_3 - 2C_2 + C_1)m_0 \\ &\quad + 6(C_2 - 2C_3)m_0^2 + 10C_3 m_0^2 + \cdots]\chi_2 \\ &+ [(C_3 - 2C_2 + C_1) + 4(C_2 - 2C_3)m_0 + 10C_3 m_0^2 + \cdots]\chi_3 \\ &+ [(C_2 - 2C_3) + 5C_3 m_0 + \cdots]\chi_4 + C_3\chi_5 + \cdots \end{aligned} \tag{7c}$$

EXAMPLE I

The validity and accuracy of these equations may be tested for a first-order Markovian copolymerization where $(r_1 r_2) = 2.0$ and the polymer is a paper blend of 2 parts $(m_0 - 0.1)$ and 1 part $(m_0 + 0.2)$. Moments of this distribution function can be calculated directly from the definition.

$$\chi_n = \frac{1}{n}\Sigma(\delta)^n$$

$\chi_1 = 0$ $\chi_4 = 0.0006$

$\chi_2 = 0.02$ $\chi_5 = 0.0001$

$\chi_3 = 0.002$ $\chi_6 = 0.00002$

First-order factors are obtained as described previously. Their values in this example and the corresponding degree of correlation, as measured by squares of correlation coefficients, are

$$F_{111} = 3.761220 - 9.671216m + 12.438375m^2 - 5.626758m^3 \qquad (r^2 = 0.9963) \quad (8a)$$

$$F_{112} = 1.911619 - 3.745522m + 4.532010m^2 - 1.745908m^3 \qquad (r^2 = 0.9956) \quad (8b)$$

$$F_{212} = F_{121} = 0.962884 - 1.143912m + 1.143912m^2 \qquad (r^2 = 0.9875) \quad (8c, d)$$

$$F_{122} = 0.952199 - 0.080772m - 0.705715m^2 + 1.745908m^3 \qquad (r^2 = 0.9956) \quad (8e)$$

$$F_{222} = 0.901621 + 1.674739m - 4.441898m^2 + 1.745958m^3 \qquad (r^2 = 0.9963) \quad (8f)$$

Alternatively, these functions may be correlated by second power equations with some loss in accuracy:

$$F_{111} = 3.471386 - 6.278168m + 3.998239m^2 \qquad (r^2 = 0.9759) \quad (9a)$$

$$F_{112} = 1.821688 - 2.692704m + 1.913147m^2 \qquad (r^2 = 0.9811) \quad (9b)$$

$F_{121} = F_{212} =$ identical Eqs. (8c) and (8d) above.

$$F_{122} = 1.042130 - 1.133590m + 1.913147m^2 \qquad (r^2 = 0.9811) \quad (9e)$$

$$F_{222} = 1.191456 - 1.718309m + 3.998239m^2 \qquad (r^2 = 0.9759) \quad (9f)$$

Linear correlations may also be obtained, but they are considerably less precise. The squares of correlation coefficients drop to 0.7–0.8.

A comparison can be made to the previously described algorithm [2] where first-order factors are treated as constants.

These methods are compared in Table 1 for $r_1 = 4.0$, $r_2 = 0.5$, and $m_0 = 0.3$. In this case, triad functions are

$$F_{111_0} = 1.83052$$
$$F_{112_0} = 1.14830$$
$$F_{212_0} = F_{121_0} = 0.72034$$
$$F_{122_0} = 0.90374$$
$$F_{222_0} = 1.13386$$

EXAMPLE II

A similar analysis may be made when $(r_1r_2) < 1$. Here, for $r_1 = 2.0$, $r_2 = 0.25$, or $(r_1r_2) = 0.5$, comments as in Example 1 and $m_0 = 0.3$, data in Table 2 are obtained.

These data again indicate that the cubic correlation equations give excellent fits to the data. The square and linear approximations are not as precise, but superior to first- or zero-order Markovian kinetics and the original method.

The original method may be said to predict triad distributions more closely than homogeneous zero- or first-order equations, but gives little if any insight into compositional distribution parameters. In fact, what information it does yield is incorrect for first-order Markovian systems. For example, the original model yields $\chi_2 = 0.012$ and 0.033, respectively, vs 0.02 and $\chi_3 = 0.0006$ and 0.0039, respectively, vs 0.002, significantly misestimating the degree of nonhomogeneity really present.

Actually, triad distributions are quite insensitive to distribution function moments.

In Example I above, with the original method's estimates of $\chi_2 = 0.012$, $\chi_3 = 0.0006$, $\chi_4 = \chi_5 = \chi_6 = 0$, triads are predicted reasonably well ($\sigma = 0.0075$):

$$P_{111} = 0.0597 \qquad P_{121} = 0.0451$$
$$P_{112} = 0.1395 \qquad P_{122} = 0.2450$$
$$P_{212} = 0.0988 \qquad P_{222} = 0.4119$$

TABLE 1. Triad Distributions

	(111)	(112)	(212)	(121)	(122)	(222)	σ^a
“Experimental”	0.0691	0.1367	0.0942	0.0450	0.2352	0.4198	—
Cubic, Eqs. (8)	0.0678	0.1361	0.0944	0.0447	0.2324	0.4247	0.0026
Square, Eqs. (9)	0.0650	0.1372	0.0944	0.0447	0.2404	0.4331	0.0069
Linear approximation	0.0739	0.1350	0.0905	0.0454	0.2272	0.4065	0.0075
Original method	0.0443	0.1418	0.0997	0.0445	0.2501	0.4197	0.0134
First-order Mark	0.0494	0.1447	0.1059	0.0454	0.2657	0.3889	0.0223
Bernoullian	0.0270	0.1260	0.1470	0.0630	0.2940	0.3430	0.0536

[a] $\sigma = [\Sigma\,(\text{triad}_{\text{calc}} - \text{triad}_{\text{exp}})^2/5]^{1/2}$.

TABLE 2. Triad Distributions

Triad	(111)	(112)	(212)	(121)	(122)	(222)	σ
"Experimental"	0.0306	0.1097	0.1597	0.0828	0.2635	0.3537	—
Cubic, Eqs. (8)	0.0306	0.1086	0.1595	0.0822	0.2642	0.3553	0.0010
Square, Eqs. (9)	0.0299	0.1064	0.1683	0.0734	0.2680	0.3574	0.0064
Linear approximation	0.0292	0.1053	0.1649	0.0818	0.2744	0.3608	0.0066
Original method	0.0465	0.1088	0.1442	0.0903	0.2393	0.3709	0.0166
First-order Mark	0.0126	0.0979	0.1895	0.0812	0.3144	0.3044	0.0357
Bernoullian	0.0270	0.1260	0.1470	0.0630	0.2940	0.3430	0.0194

Furthermore, if moments are assumed to be 10, 25, and 50% higher than in Example I, Eqs. (5) yield triad distributions with $\sigma = 0.0047$, 0.0082, and 0.0142 respectively.

The equations are not very sensitive to changes in (r_1r_2) product that are not too far removed from unity. For example, if (r_1r_2) is 10% higher than its true value in Example I above, triad distributions are predicted with $\sigma = 0.0062$ and 0.0114, respectively, for cubic and square approximations. For comparison, homogeneous zero- and first-order Markovian kinetics fit the "experimental" triads with $\sigma = 0.0181$ and 0.0536, respectively.

Errors in both reactivity ratio products and distribution function moments may cancel if one is positive and the other negative. If the data of Table 1 are recalculated with reactivity ratios each 5% higher and moments 10% lower than actual, a closer estimate than even the cubic correlation to "experimental" triads results ($\sigma = 0.0022$).

In dealing with nonhomogeneous first-order Markovian systems not too far removed from $(r_1r_2) = 1$, accurate estimates of reactivity ratio products and distribution function moments are not necessary to correlate or predict copolymer compositional distributions. Conversely, however, even accurate measurements of experimental triads may not yield accurate or unique reactivity ratio products or distribution function moments.

This situation does not exist when the nonhomogeneous system follows zero-order Markovian statistics. Previous papers and the equations discussed in this paper demonstrate that when $(r_1r_2) = 1$, all cross-product terms drop out of the equations and a series of unique relationships between moments and composition remains.

The cross-product or interaction terms assume greater and greater influence in the equations as (r_1r_2) differs more and more from unity. Even when (r_1r_2) differs by a factor of 2, as in Examples I and II, a large number of interaction terms are needed to replicate triad data closely. Even then, though results are close, they are not exact. At much larger (r_1r_2) values, the analysis of composition data fails to yield any meaningful kinetic data.

On the other hand, a theoretical model can be analyzed by the present model to predict compositional distributions of nonhomogeneous systems. An example would be a batch polymerization where monomer phase composition varies throughout a run, where catalyst activity varies with time, or the copolymerization is diffusion controlled. Here, however, agreement between model and experiment would not necessarily prove or test the model.

MULTIPLE CATALYST SYSTEMS

A previous paper [5] showed that copolymer triad distributions combined with coexistent monomer compositions readily yield estimates of reactivity ratios provided that (a) there are no more than two catalyst species and (b) each catalyst individually follows Bernoullian or zero-order Markovian kinetics. Subsequently, Floyd [6] showed in effect that the equations do not apply to mixtures of first-order Markovian catalysts. Calculated results could be quite misleading. There are several reasons for this.

Equations (5) and (6) in this paper need an estimate of (r_1r_2) product to define the power series coefficients in the single catalyst nonhomogeneous case. If two or more first-order Markovian catalysts are being dealt with, some average value of (r_1r_2) may be assumed to be the appropriate correlating parameter.

Cozewith and Ver Strate [7] showed that overall reactivity ratios in multicatalyst systems are weighted averages of individual reactivity ratios. Weighing factors are combinations of kinetic parameters that are generally not known *a priori*. Both overall reactivity ratios, $\bar{r}_1$ and $\bar{r}_2$, are averaged individually and so in general, their product will not be a simple average of individual (r_1r_2) products. In fact, for a two-component Bernoullian system, their Eqs. (A12a and A12b) reduce to (retaining their nomenclature):

$$R_1R_2 = 1 + \frac{(r_{1i} - r_{1i})^2(k_{12j}K_j)(k_{12i}K_i)}{(r_{1i}r_{1j})(k_{12i}K_i + k_{12j}K_j)^2} \tag{10}$$

which always exceeds unity.

Where first-order Markovian kinetics apply, the overall reactivity ratio product is a more complex combination of individual reactivity ratios.

Ross [2] has shown that reactivity ratio products that are derived from coexistent monomer and copolymer compositions do not agree with those derived from dyad data whenever any nonhomogeneity exists—such as arises from two catalysts, but rather,

$$(r_1r_2) < 4P_{11}P_{22}/P_{12}^2 \tag{11}$$

Actually, for two Bernoullian catalysts

$$4P_{11}P_{22}/P_{12}^2 = 1 + \chi_2/[m_0(1 - m_0) - \chi_2]^2 \qquad (12)$$

The two approaches, Eq. (10) from consideration of individual rate constants and Eq. (12) from distribution function moments, are in principle interchangeable. They agree that the dyad ratio $4P_{11}P_{22}/P_{12}^2$ will exceed (r_1r_2) derived from kinetics or moments for nonhomogeneous systems. Because the term "reactivity ratio product" designates (r_1r_2) and has priority of usage, and because "dyadic reactivity ratio product" is awkward and intimates an equality that only exists as a limiting case (i.e., homogeneity), "dyad ratio" seems a more precise and less misleading term.

For more than two first-order Markovian catalysts, the relationship is even more complex and of limited utility when attempting to unravel the copolymerization kinetics.

A combination of two first-order Markovian catalysts can produce particularly misleading results if one catalyst follows $(r_1r_2) > 1$ and the other $(r_1r_2) < 1$. This is because the first will tend to produce higher than Bernoullian P_{111} and P_{222}, while the second enhances P_{121} and P_{212}. This is shown in Example III.

EXAMPLE III

In another thought experiment, the catalysts of Examples I and II are combined; these compositions are given in Table 3. They independently produce equal amounts of copolymers.

These data are correlated by the Fineman–Ross [8] technique to yield the values in Table 4. These values may be compared to the arithmetic mean of individual reactivity ratios for the two catalysts, $\bar{r}_1 = 3.0$, $\bar{r}_2 = 0.375$, $(\bar{r}_1\bar{r}_2) = 1.125$.

The triad distributions are compared to Bernoullian probabilities in Table 5.

It would be difficult not to conclude that this system follows classical homogeneous Bernoullian kinetics. Such a possible misinterpretation is also possible if one species is nonhomogeneous Bernoullian. This is shown in the next example.

EXAMPLE IV

An ethylene–propylene copolymer could be produced from a mixed Ziegler–Natta catalyst: $TiCl_3 + VCl_4 +$ DEAC in another thought experiment. The titanium and vanadium chlorides are assumed to react independently.

TABLE 3. Compositions, Mol Fraction

Monomer phase	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900
Polymer from I	0.208	0.400	0.556	0.677	0.769	0.840	0.895	0.938	0.972
Polymer from II	0.273	0.429	0.540	0.629	0.709	0.774	0.837	0.894	0.949
“Experimental”	0.241	0.414	0.548	0.653	0.739	0.807	0.866	0.916	0.960

TABLE 4.

	r_1 from slope		r_2 from slope	
	Value	Standard deviation	Value	Standard deviation
r_1	2.6563	0.0011	2.7454	0.0020
r_2	0.3081	0.0014	0.3451	0.0002
r_1r_2	0.8183	–	0.9474	–

The catalyst $TiCl_3$ + DEAC is nonhomogeneous but Bernoullian ($r_1 = 3.2$, $r_2 = 0.3$) as shown in Ross' [2] analysis of Kakugo et al. [9] data. The system VCl_4 + DEAC has been stated by Cozewith and Ver Strate [7] to be first-order Markovian: $r_1 = 5.9$, $r_2 = 0.029$.

If equal parts of polymer are produced with each catalyst where monomer phase composition is 0.504 mol fraction propylene (Kakugo et al., Polymer H), triad data can be obtained and compared to both homogeneous and nonhomogeneous Bernoullian predictions, listed in Table 6.

Agreement with Bernoullian kinetics is not exact, but close ($\sigma = 0.035$). Lacking other data, one could reasonably hypothesize a new Ti-V complex as the catalytic active site that produces copolymer by a homogeneous Bernoullian mechanism. One could even more reasonally hypothesize a nonhomogeneous Bernoullian system ($\sigma = 0.012$).

CONCLUSIONS

Equations have been derived that correlate triad distributions of nonhomogeneous first-order Markovian copolymers. These equations are nonlinear and require a cubic power series approximation to replicate triads to an order of magnitude closer than simple homogeneous Bernoullian statistics. They require prior knowledge of both reactivity ratio product and moments of the copolymer distribution function. In principle, triad distributions can predict kinetic parameters, but small errors in measured triads can lead to large errors in kinetic parameters. These equations would be most useful in predicting triad distributions of mathematical kinetic models.

TABLE 5.

	m_0	(111)	(112)	(212)	(121)	(122)	(222)	σ
$M_0 = 0.1$:								
Experimental	0.241	0.014	0.085	0.141	0.047	0.273	0.439	
Bernoullian	—	0.014	0.088	0.139	0.044	0.278	0.438	0.003
$M_0 = 0.2$:								
Experimental	0.414	0.074	0.195	0.145	0.105	0.276	0.205	
Bernoullian	—	0.071	0.201	0.142	0.101	0.284	0.201	0.006
$M_0 = 0.3$:								
Experimental	0.548	0.168	0.264	0.116	0.139	0.217	0.096	
Bernoullian	—	0.165	0.271	0.112	0.136	0.224	0.072	0.005
$M_0 = 0.4$:								
Experimental	0.653	0.282	0.288	0.083	0.151	0.153	0.043	
Bernoullian	—	0.279	0.296	0.079	0.148	0.157	0.042	0.005

$M_0 = 0.5$:								
Experimental	0.738	0.403	0.280	0.055	0.145	0.098	0.019	
Bernoullian	—	0.401	0.286	0.051	0.143	0.102	0.018	0.004
$M_0 = 0.6$:								
Experimental	0.807	0.526	0.248	0.033	0.128	0.058	0.007	
Bernoullian	—	0.526	0.251	0.030	0.127	0.060	0.007	0.002
$M_0 = 0.7$:								
Experimental	0.866	0.649	0.200	0.017	0.102	0.030	0.002	
Bernoullian	—	0.649	0.201	0.016	0.101	0.031	0.002	0.001
$M_0 = 0.8$:								
Experimental	0.916	0.769	0.140	0.007	0.071	0.012	0.001	
Bernoullian	—	0.769	0.141	0.006	0.070	0.013	0.001	0.001
$M_0 = 0.9$:								
Experimental	0.960	0.886	0.073	0.002	0.037	0.003	0.000	
Bernoullian	—	0.886	0.073	0.002	0.036	0.003	0.000	0.000

TABLE 6. Triads

Triad	m_0	EEE	EEP	PEP	EPE	EPP	PPP
From Ti	0.75	0.52	0.17	0.05	0.11	0.10	0.04
From V	0.87	0.64	0.21	0.02	0.12	0.01	0.00
"Experimental"	0.81	0.58	0.19	0.03	0.12	0.05	0.02
Bernoullian	0.81	0.53	0.25	0.03	0.13	0.06	0.01
N—H	0.81	0.57	0.21	0.03	0.10	0.07	0.02

Analysis of multicatalyst systems is complex unless there are only two catalysts and they both follow Bernoullian kinetics. Furthermore, multicatalyst systems can mimic classical homogeneous Bernoullian kinetics rather closely.

Previous statements that coexistant polymer-monomer phase composition data yield unambiguous reactivity ratio products are clearly in error.

NOMENCLATURE

a_n	coefficient of *n*th power term in power series expansion of F_{111}
A_n	coefficient of *n*th power term in power series expansion of F_{11}
b_n	coefficient of *n*th power term in power series expansion of F_{112}
B_n	coefficient of *n*th power term in power series expansion of F_{12}
c_n	coefficient of *n*th power term in power series expansion of F_{212}
C_n	coefficient of *n*th power term in power series expansion of F_{22}
d_n	coefficient of *n*th power term in power series expansion of F_{121}
e_n	coefficient of *n*th power term in power series expansion of F_{122EI}
f_n	coefficient of *n*th power term in power series expansion of F_{222}
F_{ij}	ratio of first-order Markovian to Bernoullian probabilities for dyad *ij*
F_{ijk}	ratio of first-order Markovian to Bernoullian probabilities for triad *ijk*
k_n	combinations of f_i in Eq. (5f)
k_{ijk}	rate constants in Eq. (10) only
K_i	fraction component *i* species in Eq. (10) only
m	mol fraction component 1 in polymer
M	mol fraction component 1 in coexistant monomer phase

0	as subscript, value at average composition
P_{ij}	probability of finding dyad *ij* in polymer
P_{ijk}	probability of finding triad *ijk* in polymer
r	statistical correlation coefficient
r_i	reactivity ratio of component *i*
R_i	overall reactivity ratio of component *i* in Eq. (10) only
α	copolymer equivalent of distillation relative volatility. Defined by eq. (2)
δ	difference between individual and average mol fraction compound 1 in polymer
χ_n	the *n*th moment of the distribution function of δ about its mean value of 0
σ	standard deviation of calculated triads from experimental values, defined in the Table 1 footnote

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