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James F. Ross[a]
[a] Norchem Inc., Morris, Illinois

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SEQUENCE DISTRIBUTIONS OF NONHOMOGENEOUS COPOLYMERS*

JAMES F. ROSS

Norchem Inc.
Morris, Illinois 60450

ABSTRACT

Sequence distributions of nonhomogeneous copolymer systems can be correlated by equations which recognize that catalyst sites are statistically independent of each other. Dyad, triad, and tetrad distributions each provide a single characteristic parameter in the correlation equations. Even partial resolution of NMR peaks serves to estimate these parameters. In the case of two-component homopolymer or copolymer blends, these parameters can identify the composition and amount of blend components from triad distributions.

INTRODUCTION

Earlier papers in this series developed a logical basis and appropriate equations to explain deviations from low-order Markovian statistics in nonhomogeneous copolymer systems [1, 2]. Such systems contain many individual statistically independent catalyst sites. Because of this independence, conditional probabilities that may apply at each site individually cannot be applied to the polymerization as a whole. Approximate equations were derived that contain only a single parameter, X_2, to reflect the effects of nonhomogeneity on copolymer sequence distribution data. Excellent agreement with

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*Third in a series on statistics of nonhomogeneous systems [1, 2] experimental triad distribution data was obtained for several olefin copolymers made with Ziegler-Natta catalysts.

Now, further work shows that the previous approximations are unnecessary. Exact equations derived here give even better agreement with data, albeit by introducing one additional parameter X_3.

Exact equations for frequency distributions of nonhomogeneous copolymers are derived on the assumptions that: 1) low-order Markovian statistics are valid at each catalyst site individually at any given time, 2) the appropriate order of these statistics is determined unambiguously from coexistent monomer phase and copolymer compositions, and 3) the sites are statistically independent of each other.

DYAD DISTRIBUTIONS

To illustrate the derivation of nonhomogeneity equations, consider a copolymer of Components 1 and 2. For the dyad (11), the first assumption states that at the *i*th site.

$$P(11)_i = m_i^2, \tag{1}$$

where $P(11)_i$ is the probability of forming the dyad (11) when the instantaneous probability of Monomer 1 is m_i [3]. Equation (1) is exact only for Bernoullian mechanisms but can be modified for first-order Markovian mechanisms [1].

The second assumption implies that coexistent monomer-copolymer composition data yield valid reactivity ratios because reactivity ratios are linear functions of composition [1, 2].

The third assumption means that

$$P(11)_0 = (1/n) \sum_i m_i^2, \tag{2}$$

where the subscript *o* refers to the polymerization as a whole, considered over *n* independent microdomains.

Letting $m_i = (m_o + \delta_i)$ and defining

$$X_j = (1/n) \sum_i \delta_i^j, \tag{3}$$

and noting that $X_1 = 0$, Eq. (2) becomes

$$P(11)_o = (1/n)\Sigma(m_o + \delta_i)^2 = m_o^{\,2} + 2m_o[(1/n)\Sigma\delta_i] + (1/n)\Sigma\delta_i^{\,2} \tag{4}$$

or

$$P(11)_o = m_o^{\,2} + X_2. \tag{5a}$$

Similarly,

$$P(22)_o = (1 - m_o)^2 + X_2 \tag{5b}$$

and

$$P(12)_o = 2m_o(1 - m_o) - 2X_2. \tag{5c}$$

Equations (5a), (5b), and (5c) do not yield three independent estimates of X_2 because the sum of probabilities must be unity. It is easy to demonstrate that a simple average of the three estimates given by Eqs. (5a), (5b), and (5c) is equivalent to Eq. (5c) alone.

TRIAD DISTRIBUTIONS

The distribution of the six triads may be obtained in a similar manner. To illustrate with the triad (111),

$$P(111)_o = (1/n)\sum_i(m_i)^3 = (1/n)\sum_i(m_o + \delta_i)^3 = m_o^{\,3} = m_o^{\,2}\,[(1/n)\sum_i\delta_i^{\,2}]$$
$$+ (1/n)\sum_i\delta_i^{\,3} \tag{6a}$$

or

$$P(111)_o = m_o^{\,3} + 3m_oX_2 + X_3. \tag{6b}$$

Similarly:

$$P(112)_o = 2m_o^{\,2}(1 - m_o) + 2(1 - 3m_o)X_2 - 2X_3, \tag{6c}$$

$$P(212)_o = m_o(1 - m_o)^2 + (3m_o - 2)X_2 + X_3, \tag{6d}$$

$$P(121)_o = m_o^{\,2}(1 - m_o) + (1 - 3m_o)X_2 - X_3, \tag{6e}$$

$$P(221)_o = 2m_o(1 - m_o)^2 + (3m_o - 2)X_2 + 2X_3, \tag{6f}$$

$$P(222)_o = (1 - m_o)^3 + 3(1 - m_o)X_2 - X_3. \tag{6g}$$

In a prior paper, similar but approximate equations were obtained by setting $X_3 = 0$. This approximation is unnecessary, however, because X_2 is obtained exactly from dyad distributions. Triad data are employed to estimate X_3.

TETRAD DISTRIBUTIONS

By a similar procedure, tetrad distributions are obtained:

$$P(1111)_o = 1/n\Sigma m_i^4 = 1/n\Sigma(m_o + \delta_i)^4 = m_o^4 + 6m_o^2 X_2 + 4m_o X_3 + X_4. \tag{7a}$$

Similarly:

$$P(1112)_o = P(1121)_o = 2m_o^3(1 - m_o) + 6m_o(1 - 2m_o)X_2 + 2(1 - 4m_o)X_3 - 2X_4, \tag{7b}$$

$$P(1221)_o = P(2112)_o = m_o^2(1 - m_o)^2 + (6m_o^2 - 6m_o + 1)X_2 - 2(1 - 2m_o)X_3 + X_4, \tag{7c}$$

$$P(1122)_o = P(1212)_o = 2m_o^2(1 - m_o)^2 + 2(6m_o^2 - 6m_o + 1)X_2 - 4(1 - 2m_o)X_3 + 2X_4, \tag{7d}$$

$$P(2221)_o = P(2212)_o = 2m_o(1 - m_o)^3 - 6(1 - 2m_o)(1 - m_o)X_2 + 2(3 - 4m_o)X_3 - 2X_4, \tag{7e}$$

$$P(2222)_o = (1 - m_o)^4 + 6(1 - m_o)^2 X_2 - 4(1 - m_o)X_3 + X_4. \tag{7f}$$

Complete resolution of the tetrad peaks on an NMR trace is not necessary since X_4 can be obtained from any combination of Eqs. (7). An estimate can be obtained from as little as one accurately determined NMR tetrad peak and then used to predict the entire tetrad sequence.

The validity of this approach depends not only on the accuracy of the data, but also on the kinetic mechanism. For systems that follow Bernoullian statistics on a microscale, these equations are exact. But as shown in earlier papers, these equations are only approximations for systems following first-order Markovian statistics (as seen by the catalyst). For such systems, this approach is suspect.

Each additional level of sequences (dyads to triads to tetrads, etc.) requires no new assumptions and generates only one additional characteristic parameter. Thus, if pentad sequence data were available, even one peak on an NMR trace, the entire pentad distribution could be estimated from the value of X_5 so determined. Even without such data, the entire pentad distribution could be approximated by letting $X_5 = 0$ in the appropriate probability equations. Pragmatically, this would not be a bad approximation because differences in X_5 would probably be much smaller than errors in NMR measurements.

This simplicity is quite unlike traditional Markovian statistics where, at any level of insight, additional assumptions have to be made so that the number of relationships equals the number of unknowns. There is little doubt where Occam's razor would cut in any comparison of the two approaches.

Experimental Verification

Kakugo et al. published NMR sequence distributions for ethylene-propylene copolymers produced by Ziegler-Natta catalysis [4]. They showed that their sequence distributions could not be fitted by low-order Markovian kinetics. However, Ross [1] has shown that their listed coexistent monomer and polymer compositions demonstrate that the $(r_1 r_2)$ product is unity and, therefore, microscale, but not macroscale, kinetics are Bernoullian. Taking Kakugo's Copolymer C as an example, we determine from Eqs. (5) and (6) that $X_2 = 0.0254$ and $X_3 = -0.0141$, from which we calculate the triad distributions listed in Table 1.

TABLE 1

Triad	(PPP)	(PPE)	(EPE)	(PEP)	(EEP)	(EEE)
Observed	0.67	0.17	0.02	0.07	0.03	0.04
Calculated	0.683	0.155	0.017	0.078	0.035	0.028
Bernoullian	0.636	0.207	0.017	0.104	0.034	0.003

TABLE 2

Triad	(*mmm*)	(*mmr*)	(*rmr*)	(*mrm*)	(*rrm*)	(*rrr*)
Observed	0.70	0.09	0.03	0.04	0.06	0.07
Calculated	0.696	0.093	0.032	0.046	0.062	0.071

Equivalent treatment of the sequences for Kakugo's Polymers D–H produces similar agreement. Nonhomogeneity per se is, therefore, an adequate model for Kakugo's data. It also resolves the discrepancy between the $(r_1 r_2)$ products obtained form coexistent monomer-copolymer compositions and those obtained from dyad distributions [1].

As a second example, Bovey [5] reports tacticity distribution data based on NMR analysis of his Polymer II. By use of a nonhomogeneous model, with $X_2 = 0.0701$ and $X_3 = -0.0277$, an excellent fit of the data is obtained (Table 2). The incompletely resolved tetrad data of Table 3 are also presented.

Peaks 1, 2, and 3 do not yield information on X_4 because this term cancels in summing the appropriate Eqs. (7). However, Peak 4 with Eq. (7f) yields $X_4 = 0.0354$, and Peak 5 with Eqs. (7c) and (7e) yields $X_4 = 0.0278$. The average estimate of X_4 (0.0316), when substituted back into Eqs. (7), predicts the following tetrad distribution:

(*mmmm*) = 0.676
(*mmmr*) = 0.041
(*mmrm*) = 0.041
(*mmrr*) = 0.052
(*mrrm*) = 0.026
(*rmmr*) = 0.026
(*mrmr*) = 0.052
(*rrmr*) = 0.010
(*rrrm*) = 0.010
(*rrrr*) = 0.066.

TABLE 3

NMR peak	Observed value	Components
1	0.75	(*mmmm*) + (*mmmr*) + (*rmmr*)
2	0.07	(*rmrr*) + (*mmrr*)
3	0.07	(*rmrm*) + (*mmrm*)
4	0.07	(*rrrr*)
5	0.04	(*mrrr*) + (*mrrm*)

From these we calculate Peak 1 = 0.74, Peak 2 = 0.06, Peak 3 = 0.09, Peak 4 = 0.07, and Peak 5 = 0.04, in good agreement with Bovey's observed values.

A nonhomogeneous Bernoullian mechanism is therefore an alternative explanation of these data. As shown earlier [1, 2], this ambiguity can be resolved by calculation of r_1 and r_2 from coexistent monomer-copolymer compositions.

POLYMER BLENDS

Numerical values of X_2, X_3, and X_4 can be calculated a priori for two-component copolymer blends or used to determine the amount and composition of each component.

Let a blend of two copolymers consist of only two components, (p) parts having average composition ($m_o + \delta_1$) and ($1 - p$) parts with composition ($m_o - \delta_2$).

From the definition of X_n given by Eq. (3):

$$X_n = (1/n)\Sigma(\delta_i)^n = p(\delta_1)^n + (1-p)(-\delta_2)^n = p[\delta_1{}^n - (-\delta_2)^n] + (-\delta_2)^n. \tag{8}$$

The first four moments of the distribution are calculated to be

$$X_1 = p(\delta_1 + \delta_2) - \delta_2 = 0, \tag{9}$$

$$X_2 = p(\delta_1{}^2 - \delta_2{}^2) + \delta_2 = \delta_1\delta_2 \tag{10}$$

$$X_2 = X_2(\delta_1 - \delta_2) \tag{11}$$

$$X_4 = X_2(\delta_1{}^2 - \delta_1\delta_2 + \delta_2{}^2) \tag{12}$$

where $p = \delta_2/(\delta_1 + \delta_2)$ from Eq. (9).

For blends of homopolymers or block copolymers, $\delta_1 = 1 - m_o$ and $\delta_2 = m_o$. Equations (10)-(12) reduce to

$$X_2 = m_o(1 - m_o), \tag{13}$$

$$X_3 = m_o(1 - m_o)(1 - 2m_o), \tag{14}$$

$$X_4 = m_o(1 - m_o)(1 - 3m_o + 3m_o{}^2).$$

In an earlier paper [1], data for real systems over a range of polymer compositions were correlated by equations of the form

$$X_2 = K_2(m_o)(1 - m_o). \qquad (15)$$

These equations were presented as empirical correlations that fit the data. It was noted that further examination might reveal a theoretical basis for this form of relationship.

Comparison of Eqs. (13) and (15) shows that K_2 represents an objective measure of nonhomogeneity, being zero for a homogeneous system and unity for maximum possible nonhomogeneity, a block copolymer or blend of homopolymers. This statement assumes that the factors that give rise to nonhomogeneities with the same catalyst, under the same process conditions, are not affected by monomer composition.

Experimental Verification

To verify these equations, let us first conduct a thought experiment in which different ratios of homopolymers are physically blended to obtain a set of products with different m_o values. The parameters X_2 and X_3 will be calculated from the blend ratios, then used in Eqs. (13) and (14), and finally used in Eqs. (6) to calculate the expected triads. The hypothetical data in Table 4 are obtained. Thus the equations developed here are valid even for blends of homopolymers.

As a second example, an impact-grade polypropylene was manufactured by blending homopolypropylene with an ethylene-propylene copolymer. When analyzed by ^{13}C NMR, this material gave the triad distribution shown in Table

TABLE 4

m_o	X_2	X_3	(111)	(112)	(212)	(121)	(221)	(222)
0.1	0.09	0.072	0.1	0	0	0	0	0.9
0.3	0.21	0.084	0.3	0	0	0	0	0.7
0.5	0.25	0	0.5	0	0	0	0	0.5
0.7	0.21	-0.084	0.7	0	0	0	0	0.3
0.9	0.09	-0.072	0.9	0	0	0	0	0.1

TABLE 5

Triad	(PPP)	(PPE)	(EPE)	(PEP)	(EEP)	(EEE)
By analysis	0.812	0.028	0.015	0.013	0.033	0.099
Calculation	0.813	0.026	0.016	0.013	0.033	0.100

5, which is compared to values calculated from Eqs. (5) and (6) for X_2 = 0.0947 and X_3 = - 0.0552. From Eqs. (14) and (15), we calculate δ_1 = 0.133 and δ_2 = 0.715. These data are consistent with a binary blend of 84% component containing 99 mol% propylene and 16% component containing 14 mol% propylene. Within the precision of the analysis, this interpretation of the triad data replicates the polymer as manufactured.

CONCLUSIONS

(1) Whenever there is nonhomogeneity, copolymer systems that follow low-order Markovian statistics at the catalyst site will not follow Markovian statistics in bulk.

(2) Correlation of comonomer distributions for these systems are obtained which recognize the statistical independence of each microdomain.

(3) Equations that correlate nonhomogeneous triad distributions yield variance and skewness parameters that adequately fit the data.

(4) The distribution of nonhomogeneous comonomer tetrads can be estimated from as little as one well-defined NMR peak.

(5) Nonhomogeneous statistics apply as well to copolymer (and even homopolymer) blends.

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