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Copolymerization Kinetic Constants and Their Prediction from Dyad/Triad Distributions

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ABSTRACT

When any degree of inhomogeneity exists in a copolymer–regardless of source–distributions of dyads and triads will deviate from values calculated under the assumption of homogeneity. For copolymer systems described by the Wall equation ($r_1 r_2 = 1$), the triads (111) and (222) will always be higher than predicted; (112 and (121) will be less than predicted at $m_1 < 0.33$; greater when $m_1 > 0.33$. The triads (221) and (212) will be less when $m_1 < 0.67$, greater at $m_1 > 0.67$. When nonhomogeneity is taken into account, and the probability equations adjusted accordingly, monomer distributions can be predicted accurately from simple Markovian statistics. Further, in the presence of inhomogeneity, pseudoreactivity ratio products calculated from dyads will always be fallaciously high. Published data for olefin copolymerizations using heterogeneous Ziegler-Natta catalysts confirm that these systems follow the Wall equation but are nonhomogeneous.

The basic kinetic constants which describe the copolymerization behavior of a binary system include the kinetic reactivity ratios r_1, r_2, and/or their product (r_1r_2). These constants and their ramifications can be calculated in principle by two independent methods:

Kinetic, using average compositions of monomer and polymer phases only.

Probabilistic, using polymer dyad/triad distributions as well as monomer compositions.

KINETIC APPROACH

The kinetic approach was the first to be employed in elucidating the mechanism of binary copolymerization. In 1941, Wall developed the simple kinetic equation for the case where each monomer enters a growing chain uninfluenced by what has already happened [1]. For this case, Wall derived the single parameter equation

$$m_1/m_2 = r_1(M_1/M_2) \tag{1}$$

Although this simple equation holds for many systems, it fails to give an adequate description of a host of others.

In 1944, Mayo and Lewis accounted for the influence of the terminal monomer molecule already incorporated in the chain on the relative rates of monomer addition [2]. They derived the two constant equation

$$(m_1/m_2) = (M_1/M_2)(r_1M_1 + M_2)/(M_1 + r_2M_2) \tag{2}$$

Their equation readily reduces to Wall's when (r_1r_2) equals unity.

The Mayo-Lewis equation has been demonstrated valid for an extremely wide variety of polymerizations. Further complications to the mathematical models were made in 1946 by Merz, Alfrey, and Goldfinger with their four constant equation that accounts for the influence of the penultimate molecule in the chain [3]. The pen-penultimate model was derived by Ham in 1960 [4] and corrected by Ito et al. in 1965 [5]. These mathematically elegant models have never been adequately tested against experimental data. This is at least partially because the number of parameters increases geometrically with each posited molecular influence and there is a corresponding loss in statistical degrees of freedom. But at least part of the reason for their development was the apparent failure of simpler models in predicting observed monomer sequences.

PROBABILISTIC APPROACH

An alternate method of calculating kinetic parameters utilizes the sequences of monomer units in the polymer. These sequences are determined by NMR, IR, or even wet chemical methods. Sequences were used to elucidate kinetics as early as 1942 by Marvel et al. [6]. This approach was given a basis in probability theory by Stockmayer in 1945 [7]. The mathematics of this approach have been much published and refined over the past 40 years. This approach has been the subject of voluminous data since the development of proton and ^{13}C-NMR, which allows the determination of various monomer sequences within the polymer with accuracy and speed.

In one method based on this approach, dyad ratios are employed to calculate the $(r_1 r_2)$ product. This effectively reduces the number of parameters by one so that the Mayo-Lewis equation may be solved to give a unique set of r_1 and r_2 values for each datum.

Alternately, dyads and monomer compositions are employed to give reactivity ratios [8]. But mathematically, these two approaches are equivalent.

AGREEMENT BETWEEN METHODS

When the two approaches yield the same numerical values for r_1, r_2, and/or $(r_1 r_2)$, they tend to confirm the validity of both the experimental data and the assumed mechanisms. However, there are cases where the two approaches yield widely divergent results. For example, Kakugo et al. presented NMR dyad and triad data for the system ethylene-propylene polymerized by Ziegler-Natta catalyst [8]. They proposed r_1 values that varied between 9.3 and 4.2, r_2 that varied from 0.4 to 0.7, and $(r_1 r_2)$ products from 4.2 to 2.9 as polymer ethylene content varied from 0.15 to 0.75.

Doi et al. [9] reported similar data for propylene-ethylene copolymerization using a different Ziegler-Natta catalyst. They report variable r_1 values from 5.5 to 10, r_2 from 0.34 to 0.18, and $(r_1 r_2)$ products of 1.8-2.0 as polymer ethylene content varied from 0.70 to 0.45. Kinetically, variations of this magnitude in what are supposed to be constants is sufficient to invalidate a proposed mechanism. Thus both the Kakugo and Doi data superficially indicate that the Mayo-Lewis equation does not adequately describe the copolymerization of ethylene-propylene by Ziegler-Natta catalyst.

On the other hand, in Table 4 of their paper, Kakugo et al. present

TABLE 1. Kinetic Copolymerization Constants, Ethylene/Propylene (Ziegler-Natta Catalyst) (calculated from data of Kakugo et al. [8], Table 4)

Calculation method	r_1	r_2	$r_1 r_2$
Fineman and Ross [10]:			
Slope = r_1	3.0 ± 0.4[a]	0.27 ± 0.07	0.8 ± 0.3
Slope = r_2	3.3 ± 0.7	0.31 ± 0.02	1.0 ± 0.2
Behnken [11], nonlinear	3.2 ± 0.5	0.28 ± 0.03	0.9 ± 0.3
Assume $r_1 r_2 = 1$	3.3 ± 0.4	-	-
Weighted average	3.2 ± 0.5	0.3 ± 0.05	1.0 ± 0.3

[a]Standard deviation.

monomer-polymer phase compositions that allow calculating r_1 and r_2 values by the kinetic approach. When this is done using the methods of Fineman and Ross [10] or Behnken [11], their data are represented by $r_1 = 3.2$, $r_2 = 0.3$, $(r_1 r_2) = 1.00$. A summary of these calculations is given in Table 1. A similar analysis of Doi gas-phase compositions shows that, except for their Polymer 5, the data are best fit statistically by $r_1 = 3.7$, $r_2 = 0.14$, $(r_1 r_2) = 0.50$. However, if a 1% analytical error in gas composition is assumed, their data are not inconsistent with $r_1 = 4.9$, $r_2 = 0.2$, $(r_1 r_2) = 1$ at the 95% confidence level.

These data show that both systems can be described not only by the Mayo-Lewis but also by the simpler Wall equation.

This basic discrepancy between the results obtained from the two approaches cannot be dismissed as due to faulty data, mathematical errors, or inapplicable mechanism. As is shown below, the disagreement between the two approaches is adequately explained by polymer nonhomogeneity. Discrepancy arises because equations used to predict kinetic constants from distribution data are nonlinear. For nonlinear systems, in general, the average value of a function is not equal to the value of the function at the average value of a parameter (i.e., $\bar{f}(x) \neq f(\bar{x})$).

When there is a variation from one chain to another chain, or even in one chain segment to another segment, the Wall or Mayo-Lewis kinetic equations (being essentially linear in polymer distribution) describe the overall or average kinetics while the dyad/triad distribution based equations do not. In the Appendix to their paper, Cozewith and VerStrate [12] show that the Mayo-Lewis equation can describe

overall copolymerization kinetics regardless of local variations. As shown below, the probability equations used to predict dyads or triad distributions must be adjusted to account for local variations in the polymer. Use of average monomer concentrations in these equations does not yield the true average.

DERIVATION

To derive the equations that average the theoretical probability equations so as to interpret actual sequence data correctly, it is perhaps most simple to begin with triad distributions.

Following the derivation and nomenclature of Uebel and Dinan [13], the six triads are related to monomer composition for systems that obey the Mayo-Lewis relationship by the following equations:

$$(111) = m_1 \left[\frac{r_1 M_1}{1 + (r_1 - 1)M_1} \right]^2 \tag{3}$$

$$(212) = m_1 \left[\frac{M_2}{1 + (r_1 - 1)M_1} \right]^2 \tag{4}$$

Correcting the obvious error in Uebel and Dinan's Eqs. (9) and (10),

$$(112) = \frac{2m_1 r_1 M_1 M_2}{[1 + (r_1 - 1)M_1]^2} \tag{5}$$

Similarly,

$$(121) = m_2 \left[\frac{M_1}{1 + (r_2 - 1)M_2} \right]^2 \tag{6}$$

$$(221) = \frac{2m_2 r_2 M_1 M_2}{[1 + (r_2 - 1)M_2]^2} \tag{7}$$

$$(222) = m_2 \left[\frac{r_2 M_2}{1 + (r_2 - 1)M_2} \right]^2 \tag{8}$$

Investigating first the Wall model, where $(r_1 r_2) = 1$, and letting $m_2 = (1 - m_1)$, $M_2 = (1 - M_1)$, the following equations are readily obtained by substitution into Eqs. 3-8, and rearranging:

$$(111)_o = (m_1)^3 = m^3 \tag{9}$$

$$(212)_o = m_1 m_2 = m(1 - m)^2 \tag{10}$$

$$(112)_o = 2m_1^2 m_2 = 2m^2(1 - m) \tag{11}$$

$$(121)_o = m_1^2 m_2 = m^2(1 - m) \tag{12}$$

$$(221)_o = 2m_1 m_2^2 = 2m(1 - m)^2 \tag{13}$$

$$(222)_o = (m_2)^3 = (1 - m)^3 \tag{14}$$

When there is any inhomogeneity in the polymer, for any given segment of the copolymer: $m_i = m_o + \delta_i$, or for the polymer sample as a whole:

$$m = (1/n) \sum_i (m_i) = (1/n) \sum_i (m_o + \delta_i) \tag{15}$$

where m_o is the average monomer concentration in the polymer.

Considering first the triad (111):

$$(111) = m^3 = (1/n) \sum_i (m_i)^3 = (1/n) \sum_i (m_o + \delta_i)^3$$
$$= m_o^3 + 3m_o^2 [(1/n) \sum_i \delta_i] + 3m_o[(1/n) \sum_i \delta_i^2] + (1/n) \sum_i \delta_i^3 \tag{16}$$

To simplify nomenclature, let

$$X_j = (1/n) \sum_i (\delta_i)^j$$

where $X_1 = 0$, by definition

$X_2 > 0$, if any $\delta_i \neq 0$ ($X_2 = 0$ only if all $\delta_i = 0$)

$X_3 < X_2$, and may be $>$, $=$, < 0 depending on distribution of δ_i

Then,

$$(111) = m_o^3 + 3m_oX_2 + X_3 \simeq m_o^3(1 + 3X_2/m_o^2) \tag{17}$$

Similarly,

$$(212) = m_o(1 - m_o)^2 \left[1 + \frac{(3m_o - 2)X_2}{m_o(1 - m_o)^2} \right] \tag{18}$$

$$(112) = 2m_o^2(1 - m_o) \left[1 + \frac{(1 - 3m_o)X_2}{m_o^2(1 - m_o)} \right] \tag{19}$$

$$(121) = m_o^2(1 - m_o) \left[1 + \frac{(1 - 3m_o)X_2}{m_o^2(1 - m_o)} \right] \tag{20}$$

$$(221) = 2m_o(1 - m_o)^2 \left[1 + \frac{(3m_o - 2)X_2}{m_o(1 - m_o)^2} \right] \tag{21}$$

$$(222) = (1 - m_o)^3 \left[1 + \frac{3X_2}{(1 - m_o)^2} \right] \tag{22}$$

Letting the triad $(XYZ)_o$ represent the triad (XYZ) at m_o using Eqs. (9)-(14),

$$(111) = (111)_o \left[1 + \frac{3X_2}{m_o^2} \right] \tag{17'}$$

$$(212) = (212)_o \left[1 + \frac{(3m_o - 2)X_2}{m_o(1 - m_o)^2} \right] \tag{18'}$$

$$(112) = (112)_o \left[1 + \frac{(1 - 3m_o)X_2}{m_o^2(1 - m_o)} \right] \tag{19'}$$

$$(121) = (121)_o \left[1 + \frac{(1 - 3m_o)X_2}{m_o^2(1 - m_o)} \right] \tag{20'}$$

$$(221) = (221)_0 \left[1 + \frac{(3m_0 - 2)X_2}{m_0(1 - m_0)^2} \right] \qquad (21')$$

$$(222) = (222)_0 \left[1 + \frac{3X_2}{(1 - m_0)^2} \right] \qquad (22')$$

In the presence of nonhomogeneity, the triads (111) and (222) are always greater than predicted for homogeneous systems. The triads (121) and (112) are greater than predicted for $m_0 < 0.33$ and less than predicted for $m_0 > 0.33$. The triads (212) and (221) are greater than predicted at $m_0 < 0.67$ and less than at $m_0 > 0.67$. These deviations are inherent for all nonhomogeneous systems that obey the Wall relationship, $(r_1 r_2) = 1$.

Dyad concentrations can be calculated by a similar procedure:

$$(11) = (111) + (112)/2 = m_0^2 + X_2 = (11)_0 + X_2 \qquad (25)$$

$$(22) = (1 - m_0)^2 + X_2 = (22)_0 + X_2 \qquad (26)$$

$$(12) = (21) = 2 \left[m_0(1 - m_0) - X_2 \right] = (12)_0 - 2X_2 \qquad (27)$$

Dyads (11) and (22) will always be greater than predicted from simple Markovian probabilities where there is nonhomogeneity, and dyad (12) will be less.

It is obvious that tetrads and pentads may also be calculated for nonhomogeneous copolymers by considering an additional parameter, $X_4 = (1/n) \Sigma \delta_i^4$. This parameter will always be positive but less than X_2.

Further, a pseudoreactivity ratio product may be defined:

$$(r_1 r_2)' = 4(11)(22)/(12)^2 = \frac{[m_0^2 + X_2][(1 - m_0)^2 + X_2]}{[m_0(1 - m_0) - X_2]^2} \qquad (28)$$

which, by simple algebraic manipulation, becomes

$$(r_1 r_2)' = 1 + \frac{X_2}{[m_0(1 - m_0) - X_2]^2} \qquad (29)$$

The value $(r_1 r_2) = 1$ was assumed in deriving Eqs. (27) and (28). It is therefore obvious that pseudoreactivity ratio products are without physical significance, save as a measure of nonhomogeneity. In all cases, the pseudoproduct will fallaciously be greater than unity. The apparent singular points at $X_2 = m_o (1 - m_o)$ are illusory because as explained below, $X_2 < m_o$ or $(1 - m_o)$.

EXTENSION OF MODEL

The present model may be extended to incorporate the Mayo-Lewis equation where $(r_1 r_2) \neq 1$.

Their equation may be rearranged for a binary system:

$$[m/(1 - m)]/[M/(1 - M)] = \alpha = r_1 \left[\frac{1 + (r_1 - 1)M}{r_1 r_2 + (r_1 - r_1 r_2)M} \right] \quad (30)$$

where

$$M = \frac{m}{\alpha - (\alpha - 1)m} \quad (31)$$

From Eq. (3), before considering nonhomogeneity,

$$(111) = m \left[\frac{r_1 M}{1 + (r_1 - 1)M} \right]^2 = m \left[\frac{r_1 M}{\alpha - (\alpha - 1)m} \right]^2 \left[1 + \frac{(r_1 - 1)m}{\alpha - (\alpha - 1)m} \right]^2 \quad (32)$$

$$= m^3 \left[\frac{r_1}{\alpha + (r_1 - \alpha)m} \right]^2 = (111)_0 \left[\frac{(r_1/\alpha)^2}{(1 + (r_1/\alpha - 1)m)^2} \right] \quad (32')$$

where $(111)_0$ is defined by Eq. (9).

Similarly:

$$(212) = m(1 - m)^2 \left[\frac{1}{1 + (r_1/\alpha - 1)m} \right]^2 = (212)_0 \left[\frac{1}{1 + (r_1/\alpha - 1)m} \right]^2 \quad (33)$$

$$(112) = 2m^2 (1 - m) \left[\frac{r_1/\alpha}{[1 + (r_1/\alpha - 1)m]^2} \right] = (112)_0 \left[\frac{r_1/\alpha}{[1 + (r_1/\alpha -)m]^2} \right]$$

(34)

By symmetry, the other three triads can be obtained.

Properly, the terms (r_1/α) and $(1 + (r_1/\alpha - 1)m)$ vary with monomer incorporation level and should be explicitly expressed as functions of m prior to making the substitution $(m = m_0 + \delta_i)$. When this is attempted, a series of nonlinear simultaneous equations is obtained. However, as a first approximation, both these terms may be assumed constant at the average incorporation level, m_0. This simplification is possible because both terms are ratios of sums rather than products. Both numerator and denominator increase as X_2 increases, so that there is a comparatively smaller variation in their ratio. Furthermore, both (r_1/α) and $[1 + (r_1/\alpha - 1)m]$ approach unity as $(r_1 r_2)$ approaches unity. For systems where $(r_1 r_2)$ is not too far from 1, this simplification is further justified. When the simplification is made, the same Eqs. (17')-(22') are obtained, except that the homogeneous triads $(XYZ)_0$ are now calculated using kinetically derived r_1 and r_2 values.

The present inhomogeneity model could probably incorporate the penultimate or pen-penultimate kinetic models, but the mathematical manipulations quickly bog down. Such models are probably of extremely limited utility in any event.

VALIDATION AGAINST EXPERIMENT

Kakugo's data can be recalculated by estimating the X_2 values that best fit their data, recognizing that triads numerically close to zero are relatively imprecise. Values of X_2 from 0.03 to 0.07 are obtained for their copolymers C–H. There are a priori reasons that X_2 must approach 0 as m_0 approaches 0 or 1. Physically and mathematically, X_2 must be less than m_0 or $(1 - m_0)$. This holds even for the extreme case of homopolymer blends. When the X_2 values of Kakugo et al. are plotted against m_0, as in Fig. 1, they appear to be adequately correlated by the simple parabolic relationship (with correlation coefficient of 0.990):
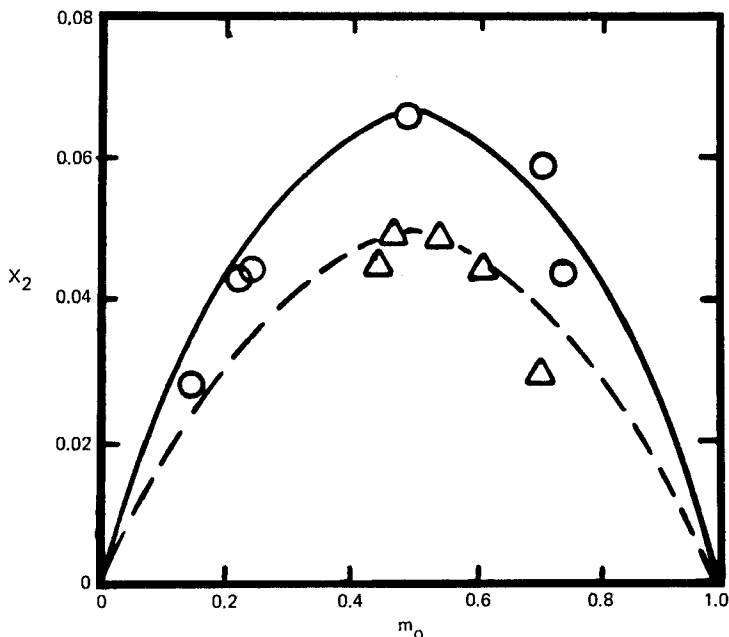
FIG. 1. Inhomogeneity factor as a function of the average polymer composition. System: Propylene-ethylene, Ziegler-Natta catalysts. (o) Data of Kakugo et al. [8]. (△) Data of Doi et al. [9].

$$X_2 = 0.259 \, m_o (1 - m_o) \qquad (23)$$

Similarly, the Doi et al. data, also plotted in Fig. 1, can be represented by

$$X_2 = 0.183 \, m_o (1 - m_o) \qquad (24)$$

where the correlation coefficient is 0.973.

A closer examination of probability distributions may provide a theoretical basis for the form of Eqs. (23) and (24). Until then, they may be accepted as empirical relationships that describe the data.

When Kakugo's data are recalculated by Eqs. (17)-(22) using X_2 from Eq. (23), the comparisons in Table 2 are obtained. Experimental and calculated triad concentrations are in good agreement—well within experimental error. Further, the calculated values are greater than or less than the homogeneous ideal values as predicted by the model.

TABLE 2. Propylene-Ethylene Triad Distributions. Data of Kakugo et al. [8]

Triad	PPP	PPE	EPE	PEP	EEP	EEE
Polymer C ($m_o = 0.15$, $X_2 = 0.033$):						
Observed, NMR	0.67	0.17	0.02	0.07	0.03	0.04
Calculated (Eqs. 17-22)	0.70	0.11	0.04	0.06	0.08	0.02
Ideal (Eqs. 9-14)	0.61	0.22	0.02	0.11	0.04	0.00
Polymer D ($m_o = 0.22$, $X_2 = 0.044$):						
Observed	0.57	0.18	0.03	0.10	0.06	0.06
Calculated	0.58	0.15	0.05	0.08	0.11	0.04
Ideal	0.47	0.27	0.04	0.13	0.08	0.01
Polymer E ($m_o = 0.25$, $X_2 = 0.049$):						
Observed	0.50	0.21	0.04	0.10	0.07	0.08
Calculated	0.53	0.16	0.06	0.08	0.12	0.05
Ideal	0.42	0.28	0.05	0.14	0.09	0.02

Polymer F ($m_0 = 0.49$, $X_2 = 0.065$):

Observed	0.22	0.21	0.08	0.11	0.15	0.23
Calculated	0.23	0.19	0.09	0.09	0.18	0.21
Ideal	0.13	0.25	0.12	0.13	0.24	0.12

Polymer G ($m_0 = 0.72$, $X_2 = 0.052$):

Observed	0.07	0.13	0.09	0.07	0.16	0.49
Calculated	0.07	0.13	0.09	0.07	0.17	0.49
Ideal	0.02	0.11	0.15	0.06	0.29	0.37

Polymer H ($m_0 = 0.75$, $X_2 = 0.049$):

Observed	0.04	0.10	0.11	0.05	0.17	0.52
Calculated	0.05	0.12	0.08	0.06	0.16	0.53
Ideal	0.02	0.09	0.14	0.05	0.28	0.42

Therefore, the NMR data are consistent with the Wall relationship with nonhomogeneities.

A similar treatment of Doi et al. data using Eqs. (17)-(22) and (24) produces the comparison of Table 3. As shown, the present method reproduces the experimental results extremely closely, and gives a significant improvement over the values calculated by Doi from his reported reactivity ratios. In fact, the residual sum of squares for the present model is 25% the sum of squares for Doi's calculations.

Values of X_2 from Eqs. (23) and (24) can be used to calculate expected dyads and pseudoreactivity ratio products for Kakugo's and Doi's copolymers. Comparisons between these calculated values and those reported in the original papers are shown in Tables 4 and 5. These data again indicate that the present model fits the experimental data well within experimental error.

Additional confirmation of the present model can be obtained from the Ziegler-Natta copolymerization of propylene and butene-1. Dyad-triad distributions reported by Randall [18] and Cheng [19] are compared in Tables 6 and 7 to values calculated by this model, assuming Wall kinetics. This comparison shows that the observed compositional distributions are not at all inconsistent with Wall kinetics and a nonhomogeneous product.

There are reasons to expect that polymer inhomogeneity is the rule in heterogeneous Ziegler-Natta polymerizations. Before 1960, Natta and co-workers [20-24] had found gross differences in copolymer composition on extracting various ethylene-propylene copolymers made with heterogeneous Ziegler-Natta catalysts. On the other hand, Phillips and Carrick [25] showed that ethylene-propylene copolymer prepared in a completely homogeneous polymerization—monomer, polymer and catalyst all dissolved in reaction medium—appears indeed to be homogeneous. A completely homogeneous system would appear to be the only route to homogeneous Ziegler-Natta olefin copolymers. Several recent papers [14-17] have shown that molecular weight distributions characteristic of heterogeneous Ziegler-Natta catalysis arise from diffusion of monomer within polymer particles to active sites. Relative monomer ratios, and therefore polymer ratios, will differ both from particle to particle and within individual particles, depending on the local histories of individual active sites. Diffusion as a major factor in these polymerizations may also be inferred from the much higher values of X_2 for ethylene-propylene compared to propylene-butylene (Table 6). The inherently larger polymerization rate of ethylene implies that its polymerization is more likely to be diffusion limited rather than reaction-rate limited.

Suzuki et al. [26] have found that chain lives are shorter than 5 s for propylene homopolymerization, so that diffusion as a factor begins to affect polymer homogeneity within a minute or so of initiating copolymerization.

The present approach applies to inhomogeneity regardless of how it arises. It is not necessary to postulate multiple catalyst types to ex-

TABLE 3. Propylene–Ethylene Triad Distributions. Data of Doi et al. [9]

Triad	PPP	PPE	EPE	PEP	EEP	EEE
Polymer 1 ($m_o = 0.70$, $X_2 = 0.030$):						
Observed	0.07	0.10	0.14	0.08	0.21	0.40
Calculated (Eqs. 17–22)	0.05	0.13	0.11	0.07	0.23	0.41
Calculated by Doi[a]	0.05	0.15	0.11	0.05	0.26	0.38
Polymer 2 ($m_o = 0.60$, $X_2 = 0.045$):						
Observed	0.08	0.19	0.13	0.11	0.21	0.31
Calculated	0.12	0.17	0.10	0.09	0.21	0.31
Calculated by Doi	0.10	0.20	0.10	0.07	0.26	0.27
Polymer 3 ($m_o = 0.55$, $X_2 = 0.048$):						
Observed	0.15	0.16	0.13	0.11	0.21	0.25
Calculated	0.16	0.19	0.10	0.10	0.21	0.25
Calculated by Doi	0.14	0.23	0.09	0.08	0.25	0.21
Polymer 4 ($m_o = 0.48$, $X_2 = 0.049$):						
Observed	0.21	0.18	0.11	0.13	0.19	0.18
Calculated	0.22	0.20	0.10	0.10	0.20	0.18
Calculated by Doi	0.19	0.26	0.08	0.10	0.23	0.14
Polymer 5 ($m_o = 0.45$, $X_2 = 0.048$):						
Observed	0.23	0.21	0.11	0.12	0.18	0.15
Calculated	0.25	0.21	0.10	0.10	0.19	0.16
Calculated by Doi	0.21	0.26	0.08	0.10	0.22	0.13

[a]Using reactivity ratios as reported in original paper, q.v.

TABLE 4. Propylene-Ethylene Dyad Distributions and Pseudoreactivity Ratio Products. Data of Kakugo et al. [8]

Polymer		EE	PP	EP	$(r_1 r_2)'$
C	Observed	0.05	0.76	0.19	4.2
	Calculated (Eqs. 25-28)	0.06	0.76	0.19	4.7
	Ideal	0.02	0.72	0.26	-
D	Observed	0.09	0.66	0.25	3.8
	Calculated	0.09	0.65	0.25	3.7
	Ideal	0.05	0.61	0.34	-
E	Observed	0.11	0.61	0.27	3.7
	Calculated	0.11	0.61	0.28	3.6
	Ideal	0.06	0.56	0.37	-
F	Observed	0.31	0.33	0.37	3.0
	Calculated	0.31	0.33	0.37	2.9
	Ideal	0.24	0.26	0.50	-
G	Observed	0.57	0.13	0.31	3.1
	Calculated	0.57	0.13	0.30	3.3
	Ideal	0.52	0.08	0.40	-
H	Observed	0.61	0.10	0.29	2.9
	Calculated	0.61	0.11	0.28	3.6
	Ideal	0.56	0.06	0.37	-

TABLE 5. Propylene-Ethylene Dyad Distributions and Pseudoreactivity Ratio Products. Data of Doi et al. [9]

Polymer		EE	PP	EP	$(r_1 r_2)'$
1	Observed	0.52	0.12	0.36	1.9
	Calculated (Eqs. 25-28)	0.52	0.12	0.36	1.9
	Ideal	0.49	0.13	0.35	-
2	Observed	0.40	0.20	0.40	2.0
	Calculated	0.41	0.21	0.38	2.2
	Ideal	0.36	0.16	0.48	-
3	Observed	0.34	0.25	0.41	2.0
	Calculated	0.35	0.25	0.40	2.2
	Ideal	0.30	0.20	0.50	-
4	Observed	0.26	0.31	0.43	1.8
	Calculated	0.28	0.32	0.40	2.2
	Ideal	0.23	0.27	0.50	-
5	Observed	0.24	0.34	0.42	1.8
	Calculated	0.25	0.35	0.40	2.2
	Ideal	0.20	0.30	0.50	-

plain polymer dyad and triad compositions that superficially do not follow oversimplified Markovian statistics. In fact, by removing the apparent discrepancy, this model confirms the mutual validity of the kinetic and probabilistic approaches for inhomogeneous systems.

CONCLUSIONS

1. For a simple Wall copolymerization with polymer inhomogeneity, triads (111) and (222) will always be greater than calculated for a homogeneous system.

2. Triads (112) and (121) will always be greater than predicted for $m_o > 0.3$, less than predicted for $m_o < 0.33$.

TABLE 6. Propylene–Butene-1 Triad Distributions. Data of Randall [18] and Cheng [19]

Polymer	m_0	X_2	$\dfrac{X_2}{m(1-m)}$	PPP		PPB		BPB		PBP		BBP		BBB	
				Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc
							Randall								
A	0.77	0.006	.03	0.47	0.47	0.25	0.26	0.05	0.04	0.12	0.13	0.08	0.08	0.03	0.02
B	0.74	0.005	.03	0.38	0.42	0.26	0.27	0.10	0.05	0.13	0.14	0.10	0.10	0.03	0.02
C	0.70	0.006	.03	0.36	0.36	0.29	0.28	0.06	0.06	0.13	0.14	0.12	0.13	0.05	0.03
D	0.69	0.01	.05	0.36	0.35	0.24	0.27	0.09	0.07	0.14	0.14	0.13	0.13	0.04	0.04
E	0.68	0.025	(.11)	0.37	0.37	0.23	0.24	0.08	0.07	0.16	0.12	0.10	0.14	0.06	0.06
F	0.69	0.01	.05	0.32	0.35	0.28	0.27	0.11	0.07	0.15	0.14	0.12	0.13	0.04	0.04
G	0.64	0.03	(.13)	0.32	0.32	0.26	0.24	0.08	0.08	0.15	0.12	0.13	0.16	0.08	0.08
							Cheng								
C1	0.908	0.003	.04	0.757	0.757	0.114	0.141	0.007	0.010	0.068	0.071	0.022	0.020	0.002[a]	0.002
C2	0.800	0.012	.07	0.542	0.541	0.233	0.222	0.025	0.037	0.100[a]	0.111	0.083	0.074	0.017	0.015
C3	0.473[a]	0.007	.03	0.204	0.205	0.184	0.177	0.085	0.091	0.088	0.089	0.161	0.181	0.278	0.257

[a]Values reported in original article are incorrect. Values used here are based on triads.

TABLE 7. Propylene-Butene-1 Dyad Distributions and Pseudoreactivity Ratio Products. Data of Randall [18] and Cheng [19]

Polymer	PP Expt	PP Calc	PB Expt	PB Calc	BB Expt	BB Calc	$(r_3 r_4)'$ Original	$(r_3 r_4)'$ Calc
				Randall				
A	0.59	0.60	0.35	0.34	0.05	0.06	-	1.2
B	0.55	0.55	0.38	0.38	0.07	0.07	-	1.1
C	0.49	0.50	0.42	0.41	0.09	0.10	-	1.1
D	0.48	0.49	0.43	0.41	0.10	0.11	-	1.2
E	0.46	0.49	0.44	0.39	0.10	0.13	-	1.7
F	0.41	0.49	0.46	0.41	0.13	0.11	-	1.2
G	0.32	0.44	0.49	0.40	0.18	0.16	-	1.6
				Cheng				
C1	0.829	0.827	0.158	0.161	0.013	0.011	1.5	1.5
C2	0.659	0.652	0.283	0.296	0.059	0.052	1.9	1.5
C3	0.296[a]	0.294	0.345[a]	0.359	0.359[a]	0.348	4.2	3.2

[a]Values reported in original article are incorrect. Values used here are based on triads.

   3. Triads (212) and (221) will always be greater than predicted for $m_o < 0.67$ and less than predicted for $m_o > 0.67$.

   4. Pseudoreactivity ratio products, as well as reactivity ratios calculated from them, will always be fallaciously high in the presence of polymer inhomogeneity.

   5. Dyad/triad distributions on isolated samples in the absence of kinetic data that define $r_1 r_2$ are ambiguous and of themselves give no insight into possible mechanism.

   6. Dyad/triad distributions may be used to estimate the degree of nonhomogeneity in a copolymer system when kinetic parameters are determined independently.

   7. The above conclusions appear also to be valid for Mayo-Lewis systems.

   8. Olefin copolymerizations with Ziegler-Natta catalysts follow the Wall equation $(r_1 r_2 = 1)$. The polymers are inhomogeneous with a possible exception in completely homogeneous systems.

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