# A Theoretical Interpretation of Reactivity Ratio Products in Copolymers Formed from Two Fractions Differing in Composition

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## Synopsis

Reactivity ratio products for ethylene-propylene copolymerization over catalysts with two sites differing in incorporation and/or reactivity ratio product have been theoretically derived. It is shown that combination of the polymer fractions resulting from two sites can lead to large dyadic reactivity ratio products as determined by nuclear magnetic resonance. The dyadic reactivity ratio product is calculated at several different monomer ratios in the reactor, and compared to the reactivity ratio product obtained from a least-squares fit of the copolymerization equation. When the polymers are compositionally heterogeneous, the reactivity ratios derived from kinetic measurements are not meaningful.

## INTRODUCTION

The characterization of ethylene-propylene (EP) copolymers by ^{13}C nuclear magnetic resonance (NMR) is important for determining their sequence distribution. The peaks occurring in the spectra of EPs produced over soluble or heterogeneous catalysts are quite complex, but the major peaks have been resolved, so that the ethylene content and dyad and triad fractions can be calculated.[1,2] Under the assumptions of invariant kinetics and constant monomer ratio during polymerization, the reactivity ratio product (RRP) for a single catalyst species producing polymer is given in terms of dyad fractions EE, PP, and EP as*

$$r_E r_P = 4 \frac{EE \cdot PP}{(EP)^2} \tag{1}$$

This dyadic reactivity ratio product obtained through NMR represents the "blockiness" of the polymer, and is correlated with industrially significant properties such as the crystallinity. For EPs produced over soluble vanadium catalysts, which are used commercially for production of ethylene-propylene rubbers, the dyadic reactivity ratio product generally falls in the range 0.8–1.0, while for polymers produced over heterogeneous catalysts, the dyadic reactivity ratio product is generally greater than 1 (e.g., 1.5–6). However, fractionation of these polymers either by successive extractions or by precipitation of a polymer solution with isopropanol yields fractions, some of which exhibit reactivity ratio products considerably less than that determined from

*See Appendix.

the original polymer.[3] These fractions also differ in ethylene content. Thus, the effect of compositional heterogeneity, or the presence of more than one mode in the polymer, complicates the interpretation of the reactivity ratio product observed by NMR.

Another important question relates to the discrepancy between values of the reactivity ratio product observed by NMR and those obtained from kinetic measurements, namely fitting of polymer composition data at several monomer ratios to the copolymerization equation to obtain the individual $r_E$ and $r_P$ values. For soluble vanadium catalysts, reactivity ratio products in line with the typical values from NMR (0.8–1.0) have been obtained in some cases, but in many cases, much smaller reactivity ratio products of 0.3–0.6 have resulted from the kinetic technique.[4] This trend of lower RRP from the copolymerization equation has also been found by Cozewith for soluble titanium catalysts,[3] and for heterogeneous titanium-based catalysts by other workers.[5,6] The discrepancy has not been adequately explained.

In this communication, a simple two-site model is considered and it is shown that the presence of fractions differing in composition and/or RRP results in "broadening" of the sequence distribution (analogous to the broadening of MWD (molecular weight distribution) due to multiple catalyst species).[7] Also, the occurrence of multiple modes in the polymer will be seen to provide a convincing explanation of the discrepancy between reactivity ratio product values obtained from NMR and from fitting of copolymerization data using the standard Fineman-Ross plot.

## DERIVATIONS

Using the well-known relations[2]

$$E = EE + 1/2EP \tag{2}$$

$$P = PP + 1/2EP \tag{3}$$

(where E, P are the mole fractions of ethylene and propylene in the copolymer), (1) becomes

$$r_E r_P = 4\frac{(E - 1/2EP)(1 - E - 1/2EP)}{(EP)^2} \tag{4}$$

In the case of a simple two-site catalyst producing a polymer blend with two modes, the average values composition and of the dyad fractions are:

$$E = f^1 E^1 + (1 - f^1)E^2 \tag{5}$$

$$EE = f^1 EE^1 + (1 - f^1)EE^2 \tag{6}$$

$$PP = f^1 PP^1 + (1 - f^1)PP^2 \tag{7}$$

$$EP = f^1 EP^1 + (1 - f^1)EP^2 \tag{8}$$

where $EE^i$ represents the fraction of EE dyads produced at site $i$ ($i = 1, 2$), etc., and $f^1$ is the mole fraction of monomers polymerized over site 1. If Eqs. (5) and (8) are substituted into (4), the following general expression is obtained:

$$r_E r_P = 4 \frac{\left[ f^1 E^1 + (1 - f^1) E^2 - \frac{1}{2} f^1 EP^1 - \frac{1}{2}(1 - f^1) EP^2 \right] \cdot \left[ f^1(1 - E^1) + (1 - f^1)(1 - E^2) - \frac{1}{2} f^1 EP^1 - \frac{1}{2}(1 - f^1) EP^2 \right]}{\left[ f^1 EP^1 + (1 - f^1) EP^2 \right]^2} \quad (9)$$

The dyad fractions in the individual modes can be calculated if the composition of the mode and reactivity ratio product for each catalyst site are known. Thus, writing Eq. (4) for each mode and solving for $EP^i$ yields

$$EP^i = \frac{1 - \sqrt{1 - 4(1 - r_E r_P^i) E^i (1 - E^i)}}{1 - r_E r_P^i} \quad (10)$$

when $r_E r_P^i$ is not equal to 1 (the other solution of the quadratic yields impossible values of $EP^i$). When $r_E r_P^i = 1$,

$$EP^i = 2 E^i (1 - E^i) \quad (11)$$

Thus, if the reactivity ratio products for the two sites and the composition and amount of each fraction are known, the dyadic RRP of the blend can be obtained using Eqs. (10) or (11) and (9).

To calculate the amount of polymer produced at each site, one must further specify the ratio of the individual catalyst sites and their kinetic constants. Considering a single catalyst site, the quasi-steady-state approximation[8] (square brackets indicate monomer concentrations in reactor, asterisks indicate live chains ending in ethylene or propylene) is expressed as:

$$k_{EP} E_* [P] = k_{PE} P_* [E] \quad (12)$$

The reaction rates of ethylene and propylene are obtained as

$$R_E = k_{EP} E_* (r_E [E] + [P]) \quad (13)$$

$$R_P = k_{PE} P_* (r_P [P] + [E]) \quad (14)$$

where $E_*$ and $P_*$ are the concentrations of chains ending in ethylene and propylene, respectively. For polymers growing at any instant in time, the total concentration of live chains is

$$E_* + P_* = C_* \quad (15)$$

where $C_*$ is the concentration of catalyst sites, so from Eqs. (15) and (12) one

may solve for $E_*$ and $P_*$:

$$E_* = \frac{C_*}{1 + (k_{EP}/k_{PE})[P]/[E]} \tag{16}$$

$$P_* = \frac{C_*}{1 + (k_{EP}/k_{PE})[P]/[E]} \cdot \frac{k_{EP}}{k_{PE}} \cdot \frac{[P]}{[E]} \tag{17}$$

Then, from Eqs. (13), (14), (16), and (17) the total rate of reaction (mol/catalyst sites · sec) is given as

$$R = \frac{(r_E[E] + [P]) + (r_P[P] + [E])[P]/[E]}{1 + (k_{EP}/k_{PE})[P]/[E]} C_* k_{EP} \tag{18}$$

for a two-site case, (18) can be written with appropriate superscripts on $r_E$, $r_P$, $k_{EP}$, $k_{PE}$, and $C_*$ for each type of site. Here, to simplify the treatment, the following assumptions were made:

$$M = [E]/[P] = \text{const.} \tag{19}$$

$$C_*{}^1/C_*{}^2 = C = \text{const.} \tag{20}$$

Assumption (19) is applicable to some types of semibatch polymerization, as well as continuous polymerization in a CSTR. With these assumptions, the ratio of the steady-state rate of consumption of monomers over sites 1 and 2 becomes

$$\frac{R^1}{R^2} = \frac{r_E^1 M^2 + 2M + r_P^1}{r_E^2 M^2 + 2M + r_P^2} \cdot \frac{M + k_{EP}^2/k_{PE}^2}{M + k_{EP}^1/k_{PE}^1} \cdot \frac{k_{EP}^1}{k_{EP}^2} C \tag{21}$$

from which the fraction of monomers polymerized from the first site is obtained as:

$$f^1 = \frac{\left(r_E^1 M^2 + 2M + r_P^1\right)C'}{\left(r_E^1 M^2 + 2M + r_P^1\right)C' + r_E^2 M^2 + 2M + r_P^2} \tag{22}$$

where

$$C' = \frac{M + k_{EP}^2/k_{PE}^2}{M + k_{EP}^1/k_{PE}^1} \cdot \frac{k_{EP}^1}{k_{EP}^2} C$$

The average composition of the whole polymer is obtained from Eq. (5), where $E^1$ and $E^2$ are determined from the copolymerization equation for each fraction

$$m^i = \frac{M\left(r_E^i M + 1\right)}{r_P^i + M} \tag{23}$$

in which

$$m^i = \frac{E^i}{P^i} = \frac{E^i}{1 - E^i} \quad (i = 1, 2) \tag{24}$$

Equation (23) can be solved for $E^i$ and $P^i = 1 - E^i$ to give:

$$E^i = \frac{M(r_E^i M + 1)}{r_E^i M^2 + 2M + r_P^i} \tag{25}$$

$$P^i = \frac{r_P^i + M}{r_E^i M^2 + 2M + r_P^i} \tag{26}$$

substituting these expressions into (10) or (11) gives the simple relation

$$EP^i = \frac{2M}{r_E^i M^2 + 2M + r_P^i} \tag{27}$$

Equations (22) and (25)–(27) can be substituted into (9) to yield (after some algebraic manipulations) an analytical expression for the dyadic RRP.

$$r_E r_P = \frac{(r_E^1 C' + r_E^2)(r_P^1 C' + r_P^2)}{(C' + 1)^2} \tag{28}$$

in which $C'$ was defined previously. Thus, assuming the kinetic constants for each site, one may calculate the dyadic reactivity ratio product from NMR at a given monomer ratio. In addition, the reactivity ratio product from a least-squares fit to the Fineman-Ross plot (a plot of the copolymerization equation (23), in for the form $M(1 - 1/m)$ versus $M^2/m$) for the whole polymer can be calculated using the "datapoints" from several values of M.

## RESULTS AND DISCUSSION

Numerous calculations of dyadic reactivity ratio products were performed, and comparisons to RRPs from fitting the copolymerization equation were made. In the following, cases which are representative of general concepts are discussed.

First, the simple blending of two fractions of known RRP will be considered. Figure 1 illustrates blending of a 50 mol% (40 wt%) ethylene content fraction, typical of a completely amorphous rubber, with fractions of ethylene content ranging from 0.1 to 0.9. Each fraction has RRP equal to 0.5. The plots are symmetrical with respect to the ethylene content of the second fraction (more accurately, the difference in ethylene contents of the two fractions), namely, the curves for $E^2 = 0.1$ and $E^2 = 0.9$ superimpose. However, the maximum in the dyadic RRP for the whole polymer occurs at different values of $f^1$ for each $E^2$. From this plot, it is evident that when the second fraction differs in composition from the first by less than 10 mol%, there is negligible change in the reactivity ratio product. However, as the difference in composi-
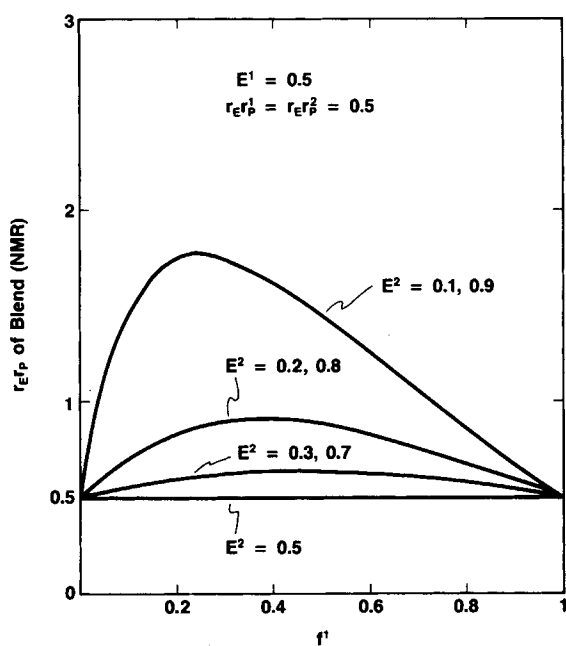
Fig. 1. Calculated reactivity ratio product for a polymer blend with fraction 1: $E^1 = 0.5$, $r_E r_P^1 = 0.5$, fraction 2: $r_E r_P^2 = 0.5$, ethylene content = various.
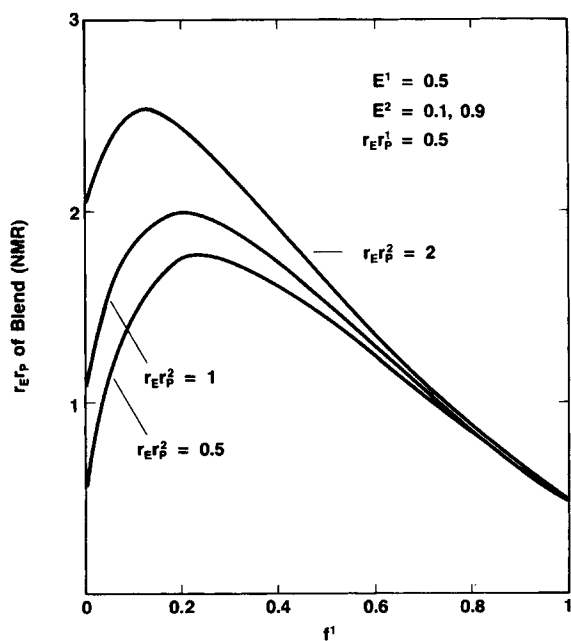


Fig. 2. Calculated reactivity ratio product for a polymer blend with fraction 1: $E^1 = 0.5$, $r_E r_P^1 = 1.0$, fraction 2: $r_E r_P^2 = 1.0$, ethylene content = various.

tion between the fractions increases, the dyadic RRP for the whole polymer increases significantly over the RRP values for the fractions, (i.e., the sequence distribution is noticeably broadened).

It is possible to show, as stated by Ross,[9] that the reactivity ratio product for the blend is always greater than the reactivity ratio products for the individual fractions when these are equal. It is also true that when the reactivity ratio products for the individual sites differ, the dyadic RRP for the blend is always greater than the minimum of the actual RRPs for the individual sites, as was seen in all the calculations. Clearly, the presence of a catalyst site which selectively polymerizes either ethylene or propylene can result in a large dyadic reactivity ratio product due to compositional heterogeneity even if the reactivity ratio products for the individual sites are low. In fact, the RRP of the blend can easily be three times that of the original fractions when a fraction of very high or low ethylene content is present. This point is reiterated in Figure 2, which shows a case similar to Figure 1 but with $r_E r_P = 1$ for each fraction. The positions of the maxima of the curves are the same as in Figure 1, but one should note that the blend RRP is not directly proportional to the RRP of the fractions.

Figures 1 and 2 suggest that the broad sequence distributions typical of EPs produced over heterogeneous catalysts may be adequately explained in terms of a two-catalyst site model, in which each site produces essentially random polymer, but the two sites differ significantly in selectivity toward ethylene. The effect of adding a second mode which already has broad sequence distribution to a mode with $r_E r_P = 0.5$ is illustrated in Figure 3. Here, the dyadic RRP of the whole polymer is seen to increase as the RRP of the
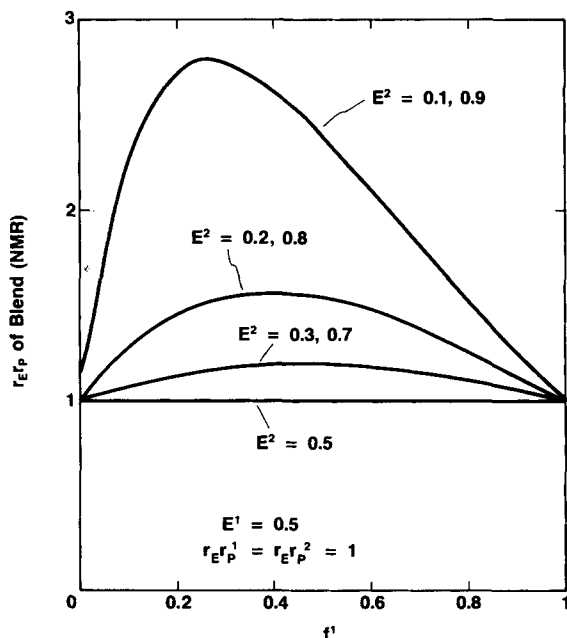


Fig. 3.   Calculated reactivity ratio product for a polymer blend with fraction 1: $E^1 = 0.5$, $r_E r_P^1 = 0.5$, fraction 2: $E^2 = 0.1, 0.9$, $r_E r_P^2 = $ various.

Dyadic $r_E r_P$ of Blend

$r_E^1 = 5,\quad r_P^1 = 0.1$

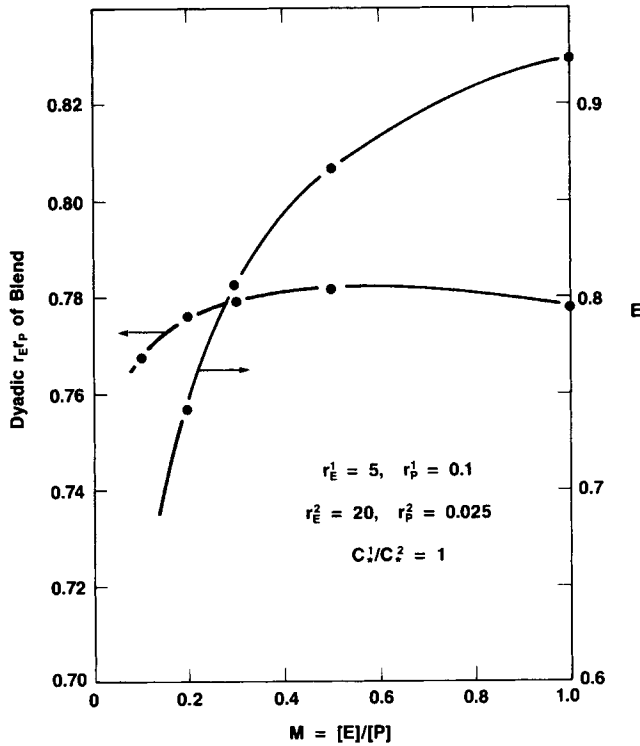$r_E^2 = 20,\quad r_P^2 = 0.025$

$C_*^1/C_*^2 = 1$

E

M = [E]/[P]

Fig. 4. Reactivity ratio product and polymer E/P ratio for polymer produced over two-site catalyst at various monomer ratios M = [E]/[P] in reactor. $k_{EP}^1 = k_{PE}^1 = 5$; $k_{EP}^2 = 2.5$, $k_{PE}^2 = 10$.

M(1-1/m)

Least-Squares Fit:
$r_E = 11$
$r_P = 0.024$
$r_E r_P = 0.27$

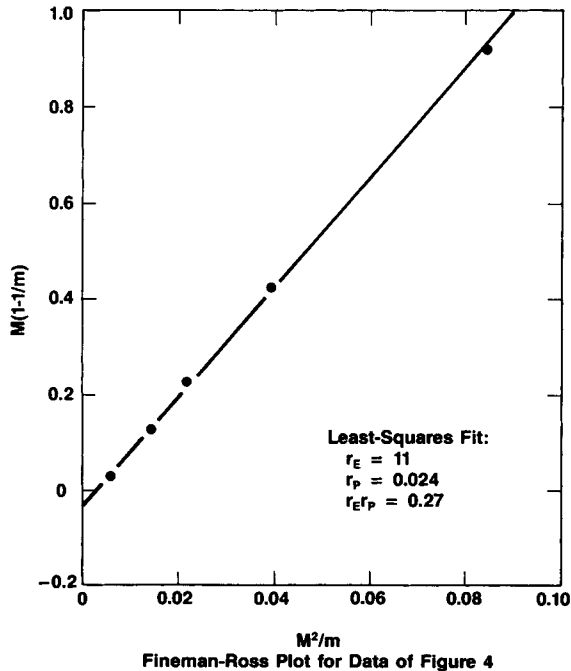$M^2/m$
Fineman-Ross Plot for Data of Figure 4

Fig. 5. Fineman-Ross plot for polymerization data of Figure 4 illustrating excellent fit to copolymerization equation which yields low reactivity ratio product of 0.27.

second fraction is varied from 0.5 to 2. Thus, at $f^1 = 0.2$, the fraction with $r_E r_P = 0.5$ causes a dyadic RRP of 1.75, while increasing the RRP of the second fraction to 2 changes the dyadic RRP to 2.45. This example mimics a multiple-fraction case, where several fractions combine to form the second fraction with reactivity ratio product equal to 2. It may be inferred that presence of multiple fractions (beyond 2) will not necessarily result in broadening of the sequence distribution. Specifically, as a third fraction equal in composition to the blend of the first two is added, at some point the combined RRP for the triblend must fall below the combined RRP of the first two. This conclusion agrees with that found in a study of MWD broadening in polyolefins.[7]

Next, the reactivity ratio product was calculated as a function of monomer composition for sites with specified kinetics, using Eqs. (21)–(28). The following examples typify the results obtained. The first example shows calculated "datapoints" for a two-site catalyst with $r_E = 5$, $r_P = 0.1$ for the first site and $r_E = 20$, $r_P = 0.025$ for the second (i.e., the second site reacts preferentially with ethylene compared to the first). The resulting copolymer compositions and dyadic reactivity ratio products for the blend are shown in Figure 4. Here, $M = [E]/[P]$ was taken over a fairly typical range for solution polymeriza-
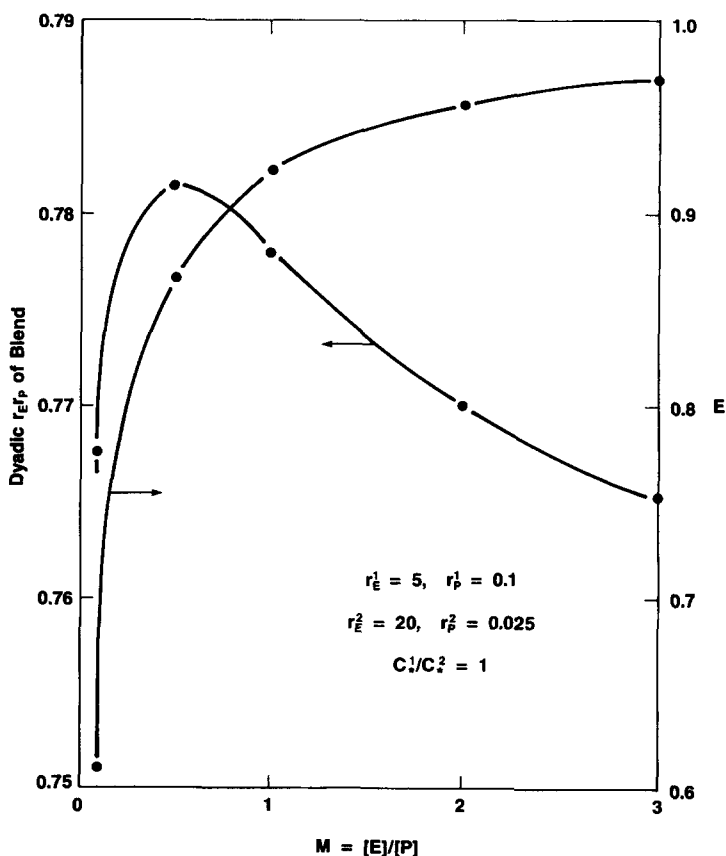


Fig. 6.  Reactivity ratio product and polymer E/P ratio for polymer produced over two-site catalyst at various monomer ratios $M = [E]/[P]$ in reactor. $k_{EP}^1 = k_{PE}^1 = 5$; $k_{EP}^2 = 2.5$, $k_{PE}^2 = 10$.
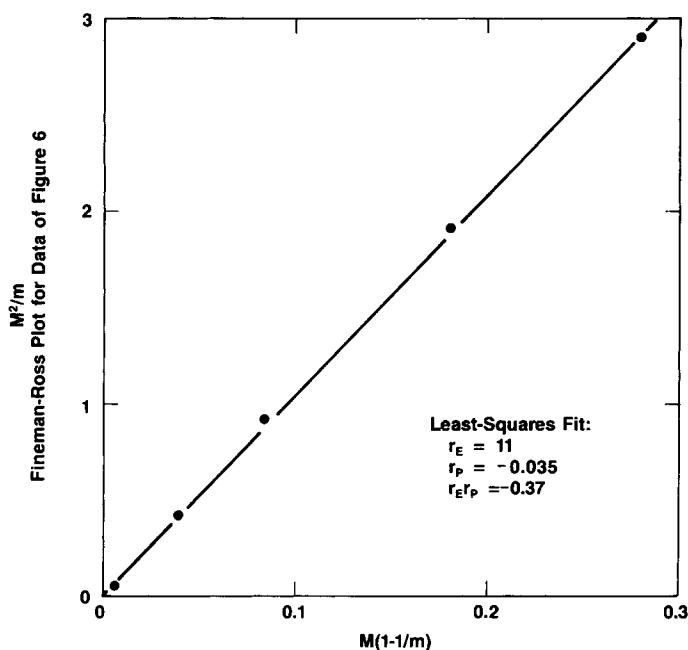
Fig. 7. Fineman-Ross plot for polymerization data of Figure 6 illustrating excellent fit to copolymerization equation which yields negative reactivity ratio product.

tion, 0.1-1. The dyadic RRP is almost constant at around 0.77, considerably greater than the reactivity ratio product of 0.5 for the individual sites, due to the compositional heterogeneity of the sample. On the other hand, as shown in Figure 5, the data at five different monomer ratios, fit to the copolymerization equation, yield $r_E = 11$ and $r_P = 0.024$, such that $r_E r_P = 0.27$. This value is much lower than any of the dyadic RRP values, and in fact is actually less than the minimum possible dyadic RRP of 0.5 (the reactivity ratio product for each site). However, the fit to the copolymerization equation is virtually perfect, which would undoubtedly lead the unwary investigator to conclude (in the absence of NMR data) that the simple copolymerization model for homogeneous copolymer is perfectly adequate to characterize the sequence distribution of this sample.

Figure 6 shows simulated "data" for exactly the same kinetic parameters for each site as in Figure 4, but with the monomer ratio varied over a broader range, M = 0.1 to 3 (it might be quite difficult to obtain such a broad range of values experimentally, at least in liquid-phase polymerization). Even in this range of concentrations, the dyadic RRP for the blend stays relatively constant. What is more striking about this example is the resulting Fineman-Ross plot shown in Figure 7. While the fit to the equation is well-nigh perfect, a physically meaningless negative value of $r_P$ is obtained. This situation can be taken as an indication that complications due to polymer heterogeneity are present, though of course there are other plausible reasons why the assumptions of the copolymerization equation may not be satisfied.[8]

In the third case considered, the RRPs of the individual sites are the same as in the previous two, but the individual kinetic constants are different, as
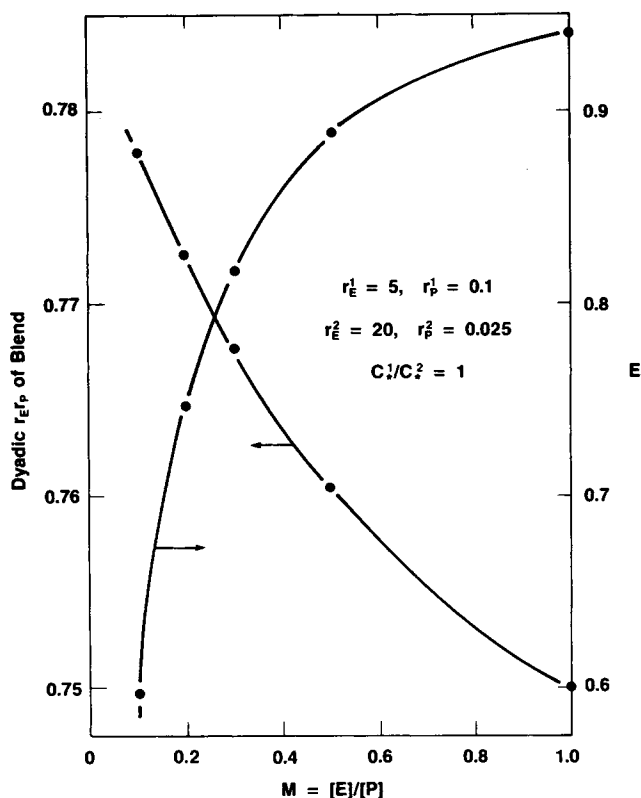
Fig. 8. Reactivity ratio product and polymer E/P ratio for polymer produced over two-site catalyst at various monomer ratios $M = [E]/[P]$ in reactor. $k_{EP}^1 = 1$, $k_{PE}^1 = 5$; $k_{EP}^2 = 2.5$, $k_{PE}^2 = 5$.

indicated in the figure captions [this changes the $C'$ factor in Eq. (21)]. Figure 8 illustrates the dyadic RRPs. As seen in Figure 9, in this case, the Fineman-Ross treatment yields a reactivity ratio product *greater* than the dyadic RRP from NMR ($r_E r_P = 1.2$). Again, this plot, taken in isolation from any NMR data, would undoubtedly lead one to conclude that the data were adequately fit by a random copolymerization-homogeneous polymer model, whereas actually, the polymer is blend formed from two sites with alternating tendencies. The excellent fits to the copolymerization equation indicate the virtual impossibility of detecting anomalies due to compositional hetero-geneity using the kinetic technique.

Many other examples were examined. Of particular note were certain cases in which the dyadic RRP was constant, that is, it did not vary with monomer ratio in the feed. In this case, the kinetic value agreed perfectly with the NMR value, which however was *not* equal to the RRPs of the individual sites. This occurs when the term $C'$ in Eq. (22) is not concentration dependent, a condition which is satisfied when

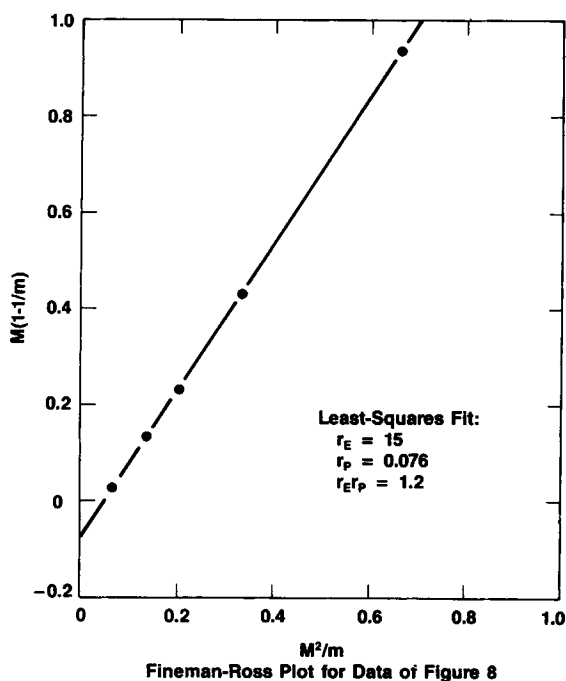$$k_{EP}^2/k_{PE}^2 = k_{EP}^1/k_{PE}^1 \qquad (28)$$

Fig. 9. Fineman-Ross plot for polymerization data of Figure 8 illustrating excellent fit to copolymerization equation which yields high reactivity ratio product of 1.2.

The last example illustrates a case where the sequence distributions of the individual sites are random ($r_E r_P = 1$) rather than alternating. Figure 10 illustrates that the dyadic RRPs are considerably greater than 1, as commonly observed in EPs produced over solid catalysts. One of the two sites polymerizes ethylene almost exclusively, while the other polymerizes ethylene and propylene at comparable rates (within an order of magnitude). In this case, the dyadic RRP also exhibits a strong dependence on monomer ratio, an effect which has been observed experimentally by the author. The fraction of monomers polymerized over site A (the ratio of A to B is 0.1) ranges from 9% at the lowest ethylene/propylene ratio in the feed to 22% at the highest [E]/[P]. This polymer formed over site A is 90–99% polyethylene. Qualitatively, this type of behavior is in accordance with results of simple fractionation of EP copolymers made over various solid catalysts, in which a soluble portion similar to amorphous EP and an insoluble portion which is higher in ethylene content are observed. It is noteworthy that although the RRP of the polyethylene site is 1, its selectivity toward ethylene results in the significant contribution of this site to sequence distribution broadening. As shown in Figure 11, the RRP from kinetics is 0.83.

A very dramatic example requiring no graphical illustration serves to highlight the fundamental difference between NMR measurement and kinetic measurement of the reactivity ratio product. Consider a two-site model in which one of the sites polymerizes only propylene, the other only ethylene. The two sites have equal reactivity and are present in the reactor at the same concentration. For this case, the average composition of the formed polymer is
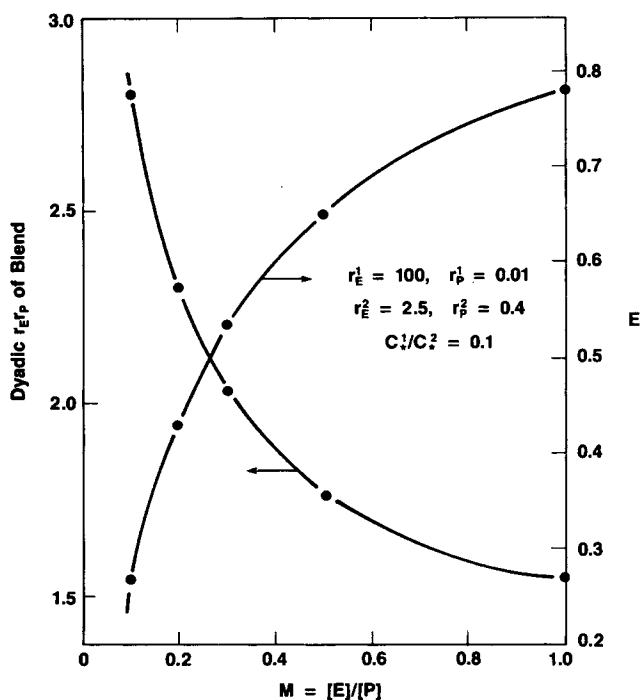
Fig. 10.   Reactivity ratio product and polymer E/P ratio for polymer produced over two-site catalyst at various monomer ratios M = [E]/[P] in reactor. $k^1_{EP} = 0.1$, $k^1_{PE} = 1$; $k^2_{EP} = 2$, $k^2_{PE} = 1$.

given by $m = M$, which gives a perfect fit to the copolymerization equation with $r_E = r_P = 1$. But from Eq. (1), from NMR, one will obtain $r_E r_P = $ infinity, since no EP dyads are present! From this example, we recognize that the essential characteristic of the kinetic measurement is that it is based on *average* compositions. Thus, the $r_E$ and $r_P$ values from kinetic measurements contain no quantitative information on sequence distribution or blockiness when compositional heterogeneity is present. Thus, these values are useful for little more than description of existing data. In contrast, the RRP obtained from NMR via Eq. (1) is a true indication of the *dyad* distribution in the polymer. Thus, these values generally do correlate with polymer crystallinity determined by techniques such as differential scanning calorimetry (DSC) or x-ray in the case of ethylene-propylene copolymers.

The above conclusions contradict those of Ross,[9,10] who considered the NMR reactivity ratio products to be "fallacious." However, Ross shows that observed triad distribution data of other workers are consistent with a two-site model in which the RRP for each site is 1. He goes on to conclude that this is a general feature of Ziegler-Natta polymerizations, but this conclusion is also not warranted since the work presented here makes it amply clear that observed RRP values can arise from an infinite number of possible combinations of fractions and reactivity ratio products. Indeed, it is rather fortuitous if the kinetic constants for a site happen to satisfy the relation $r_E r_P = 1$. Recently, Cozewith[3] has performed a detailed investigation of
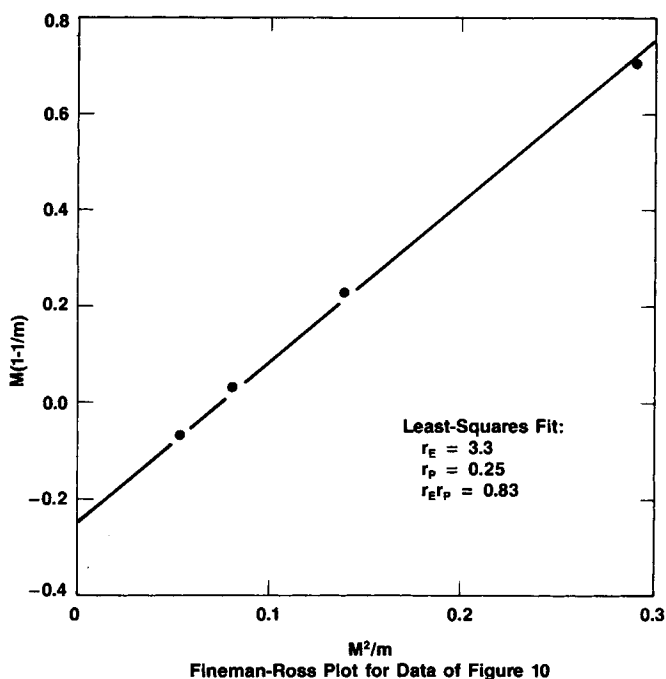
Fig. 11. Fineman-Ross plot for polymerization data of Figure 10 illustrating excellent fit to copolymerization equation which yields low reactivity ratio product of 0.83.

single-site and multiple-site models applied to $^{13}$C NMR data for ethylene-propylene copolymers. From analysis of sums of squares for the fits, he concludes that NMR data can sometimes distinguish between single-site and multiple-site cases. However, NMR is not sufficiently sensitive to detect subtle compositional heterogeneity, for example, in blends where the individual fractions differ by less than 20 mol% ethylene. Nevertheless, in several cases examined, it appeared that a two-site model with $r_E r_P = 1$ for each site gave a good description of experimental data, as also found by Ross.[10] In such cases, Cozewith's procedures yield quantitative estimates of the composition and amounts of the two fractions.

## CONCLUSIONS

It has been shown that compositional heterogeneity in ethylene-propylene copolymers can lead to larger values of the dyadic reactivity ratio product, as determined by NMR through Eq. (1), than those corresponding to the individual catalyst sites. The greater the compositional spread between fractions in the polymer, the larger is the dyadic reactivity ratio product of the blend. Compositional heterogeneity is thus a major reason for the large dyadic reactivity ratio products determined in catalyzed EP copolymerizations.

It has also been shown that the reactivity ratio product calculated from a least-squares fit to the copolymerization equation contains no information on sequence distribution when the copolymer is inhomogeneous. This is especially significant, since the fit to the copolymerization equation using the Fineman-

Ross plot is deceptively good in many cases. Indeed, even when the RRPs from NMR and kinetics are in good agreement, this is not a conclusive indication of absence of compositional heterogeneity, or of agreement with RRPs for individual sites. Nevertheless, the NMR values of the RRP, which contain information on the dyad distribution, are meaningful as an indication of the overall blockiness of the copolymer.

Needless to say, these conclusions are not restricted to EP copolymers, or to heterogeneously catalyzed systems. Even in polymerization systems other than Ziegler-Natta, where data have been satisfactorily analyzed via the copolymerization equation, a reexamination using structurally sensitive techniques such as NMR is essential to establish the validity of the reactivity ratios determined from kinetic measurements. In particular, fractionation of the polymer coupled with statistical analysis of the NMR spectra, using the techniques of Cozewith,[3] can be used to obtain reliable values of the reactivity ratio product for individual catalyst sites in heterogeneous systems.

## NOMENCLATURE

For each of the quantities below, the superscript represents site $i = 1, 2$.

| | |
|---|---|
| $C_*$ | mol. catalyst sites |
| E, P | ethylene, propylene content in polymer (mol fraction) |
| $E_*$, $P_*$ | live chains ending in ethylene, propylene |
| [E], [P] | ethylene, propylene content in reaction medium |
| EE, EP, PP | EE dyad fraction etc. |
| $f^i$ | mol. fraction monomers polymerized over site $i$ |
| $m = E/P$ | |
| $M = [E]/[P]$ | |
| $k_{ij}$ | rate constant for reaction of monomer $j$ with chain ending in monomer $i$ |
| $r_E = k_{EE}/k_{PE}$ | reactivity ratio for ethylene |
| $r_P = k_{PP}/k_{EP}$ | reactivity ratio for propylene |
| $R_E$, $R_P$ | reaction rate of ethylene, propylene |
| $R$ | total reaction rate (mol/catalyst · sec) |
| RRP | reactivity ratio product (in text) |

## APPENDIX

The number of EE dyads in the polymer chain is given as:

$$N_{EE} = \int_0^t k_{EE} E_* [E] \, dt \qquad (A1)$$

Thus,

$$\frac{N_{EE} \cdot N_{PP}}{N_{EP} \cdot N_{PE}} = \frac{\int_0^t k_{EE} E_* [E] \, dt \cdot \int_0^t k_{PP} P_* [P] \, dt}{\int_0^t k_{EP} E_* [P] \, dt \cdot \int_0^t k_{PE} P_* [E] \, dt} \qquad (A2)$$

Under the assumptions of time-invariant kinetics and constant monomer

concentration, Eq. (A2) becomes

$$\frac{N_{EE} \cdot N_{PP}}{N_{EP} \cdot N_{PE}} = \frac{k_{EE}[\dot{E}] \int_0^t \dot{E}_* \, dt \cdot k_{PP}[\dot{P}] \int_0^t \dot{P}_* \, dt}{k_{EP}[\dot{P}] \int_0^t \dot{E}_* \, dt \cdot k_{PE}[\dot{E}] \int_0^t \dot{P}_* \, dt} = r_E r_P \qquad (A3)$$

Under the long-chain hypothesis, the number of EP and PE sequences in the polymer must be equal. Hence,

$$N_{EP}/N_{tot} = N_{PE}/N_{tot} = 1/2EP \qquad (A4)$$

where $N_{tot}$ is the total number of dyads, while

$$N_{EE}/N_{tot} = EE, \quad N_{PP}/N_{tot} = PP \qquad (A5)$$

From (A3), (A4), and (A5):

$$r_E r_P = 4 \frac{EE \cdot PP}{(EP)^2} \qquad (A6)$$

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