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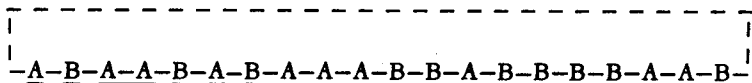
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THE CHARACTERIZATION OF SEQUENCE DISTRIBUTION IN COPOLYMERS

Theoretical predictions of sequence distribution in copolymers were included in the earliest treatments of copolymerization (1-3), and many theoretical papers on this subject have appeared in recent years (4-9). Unfortunately, experimental work has not kept pace with theoretical developments, possibly due to difficulties involved in measuring sequence distributions. However, experimentalists may have been discouraged from entering this field by the relatively complex mathematical approaches taken in the theoretical treatments. There is, at present, no uniform way to express sequence distribution results and experimental results have been treated differently in almost every paper published on this subject.

The purpose of this paper is to propose a convenient parameter for characterizing sequence distribution in copolymers. This parameter provides a useful mental picture of sequence distribution and its use simplifies sequence distribution calculations considerably. The average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units can be used to characterize its sequence distribution. This quantity, termed the run number, R , can be related through elementary stoichiometric and statistical considerations to any measurable feature of copolymer structure that depends on sequence distribution.

Consider, for example, the portion of a copolymer chain shown below. The chain contains twenty monomer units arranged in 12 alternating runs (underlined) or sequences. The run number associated with this structure is, therefore, 60.



In relating the run number to measurable features of sequence distribution, it is convenient to dispense with endgroup effects by considering the polymers to be cyclic and it is convenient to consider, at least initially, only linkages which occur to the right (or left) of a given monomer unit. To calculate the percentage of A-B linkages in a copolymer (number of A-B linkages per 100 monomer units), one must note that every run of A's is followed by an A-B linkage. Since there are as many A runs as B runs in the copolymers,

$$\% \text{ A-B linkages} = R/2$$

Similarly,

$$\% \text{ B-A linkages} = R/2$$

and

$$\% (\text{AB} + \text{BA}) \text{ linkages} = R$$

Now, the number of B units which have B neighbors on their right is obviously equal to the total number of B units present minus the number which have A neighbors. Thus,

$$\% \text{ B-B linkages} = \% \text{ B} - R/2$$

and similarly,

$$\% \text{ A-A linkages} = \% \text{ A} - R/2$$

where % A and % B refer to the molar percentages of monomer units in the copolymer.

The number-average length of a given type sequence, $\langle A \rangle$ or $\langle B \rangle$, is frequently encountered in theoretical treatments. This is simply the total number of the given type monomer units divided by the number of runs of that type present, so that

$$\langle A \rangle = \% \text{ A} / (R/2) \text{ and } \langle B \rangle = \% \text{ B} / (R/2)$$

The probability that a given B unit has an A unit on its right (or left) is equal to the number of B units which satisfy this condition divided by the total number of B units present. Basing a count on 100 monomer units,

$$P_{\text{B-A}} = (R/2) / \% \text{ B} = R/2 \% \text{ B}$$

Similarly,

$$P_{\text{A-B}} = R/2 \% \text{ A}$$

$$P_{\text{B-B}} = (\% \text{ B} - R/2) / \% \text{ B}$$

and

$$P_{\text{A-A}} = (\% \text{ A} - R/2) / \% \text{ A}$$

The probability that a given B unit has A units on both left and right

sides is the product of the separate probabilities, so that

$$P_{ABA} = P_{BA}^2 = \frac{R^2}{4. \% B^2}$$

Similarly,

$$P_{BBB} = P_{BB}^2 = \frac{(\% B - R/2)^2}{\% B^2}$$

and

$$(P_{BBA} + P_{ABB}) = \frac{R (\% B - R/2)}{\% B^2}$$

In essence, these probabilities are the fractions of B units which are centered in the three possible triadic sequences (f_{ABA} , f_{ABB} , f_{BBB}). Of course, similar calculations can be made for A-centered triads. This approach can also be extended for the calculation of the fractions of units centered in various pentadic or heptadic sequences. For example, the fraction of A units centered in BAAAB type pentads is given by the following relationship.

$$P_{\text{B-A-A-A-B}} = P_{AA} P_{AB} P_{AA} P_{AB} = \frac{R^2 (\% A - R/2)^2}{4. \% A^4}$$

The various measurable features of copolymer structure which are related to sequence distribution ($\% AB$, $\% BB$, f_{BBB} , f_{BAAAB} , etc.) are thus simple functions of copolymer composition ($\% A$ or $\% B$) and of R . Knowledge of copolymer composition and R thus permits one to calculate any measurable feature of copolymer structure that is related to sequence distribution. Conversely, R can be evaluated experimentally by determining copolymer composition and the proportion of any one of these structural features present in the copolymer.

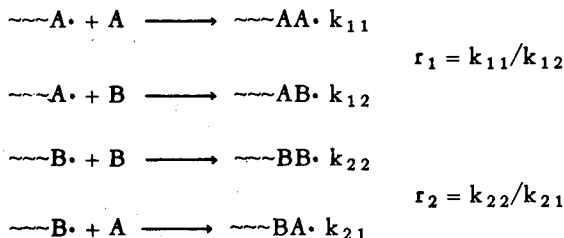
Prediction of Run Numbers

In using sequence distribution information to study polymerization mechanism, or in developing techniques for measuring sequence distribution in copolymers, it will prove useful to compare measured run numbers with run numbers predicted by polymerization models. Some copolymerization processes (e.g., polycondensation) can be expected to produce copolymers having monomer units distributed randomly along polymer chains. It can be shown that run numbers for such polymers are given by the following expression.

$$R_{\text{random}} = \% A \% B / 50$$

In general, if $R_{\text{expt'l}} > R_{\text{random}}$, the monomer units tend to alternate in the copolymer, whereas if $R_{\text{expt'l}} < R_{\text{random}}$ the monomer units tend to cluster in blocks of like units.

Most vinyl copolymerizations are believed to proceed through the following propagation steps:



It is possible, by invoking the steady-state assumption, to derive an expression which predicts the run number of polymer formed instantaneously from a given polymerization mixture. Thus, the rate at which monomer units are incorporated into the polymer is

$$\frac{d(A+B)}{dt} = k_{11} (A\cdot) (A) + k_{12} (A\cdot) (B) + k_{21} (B\cdot) (A) + k_{22} (B\cdot) (B)$$

and the rate at which sequences are generated in the copolymer is

$$dS/dt = k_{12} (A\cdot) (B) + k_{21} (B\cdot) (A)$$

By dividing the above two equations and by making use of the steady-state condition,

$$k_{12} (A\cdot) (B) = k_{21} (B\cdot) (A)$$

the average number of monomer units per run in the instantaneous polymer becomes

$$\frac{d(A+B)}{dS} = 1 + \frac{r_1}{2} \frac{\% A_f}{\% B_f} + \frac{r_2}{2} \frac{\% B_f}{\% A_f}$$

where $\% A_f$ and $\% B_f$ refer to the molar percentages of A and B in the initial copolymerization mixture (feed compositions). By definition,

$$R = 100 \frac{dS}{d(A+B)}$$

so that

$$R = \frac{200}{2 + r_1 (A_f/B_f) + r_2 (B_f/A_f)} \quad (1)$$

By a similar derivation, the following equation, which predicts run numbers for instantaneous polymers from penultimate reactivity ratios and feed composition data, can also be obtained.

$$R = \frac{200}{2 + \frac{1+r_1}{1+\frac{1}{r_1}} \frac{(A_f/B_f)}{(B_f/A_f)} + \frac{1+r_2}{1+\frac{1}{r_2}} \frac{(B_f/A_f)}{(A_f/B_f)}} \quad (2)$$

where r_1 , r'_1 , r'_2 , and r_2 have their usual significance, i.e., $r_1 = k_{111}/k_{112}$, $r'_1 = k_{211}/k_{212}$, etc.

By applying the above considerations, we have recently written a FORTRAN (IBM 1620) program for calculating run numbers, triad distributions, and pentad distributions of initial copolymers from feed composition data and either terminal or penultimate reactivity ratios. Copies of this program will be supplied upon request.

It is certain that run numbers can be predicted for polymers formed by even more complex polymerization mechanisms, such as those involving Ziegler-Natta type catalysts. In this connection, most theoretical treatments on this subject provide expressions for number-average sequence lengths of polymers. As mentioned earlier, these expressions can easily be related to run numbers.

Use of Run Numbers To Determine Reactivity Ratios

In addition to being useful for characterizing the sequential structure of copolymers, run numbers are convenient quantities to manipulate, as for example, in the evaluation of monomer reactivity ratios from sequence distribution data. Thus, rearrangement of eq. (1) yields

$$2 \left(\frac{100}{R} - 1 \right) \frac{B_f}{A_f} = \frac{B_f^2}{A_f^2} r_2 + r_1 \quad (3)$$

which provides for the graphical determination of reactivity ratios from feed composition and sequence distribution data (Fig. 1).

Alfrey and Goldfinger (1), have related P_{AA} , P_{AB} , P_{BA} , and P_{BB} to monomer reactivity ratios and feed composition data through relationships given in Table I. Relations of these probabilities to the compositions and run numbers of instantaneous copolymers were derived in the present paper and these are also included in Table I. It is apparent that

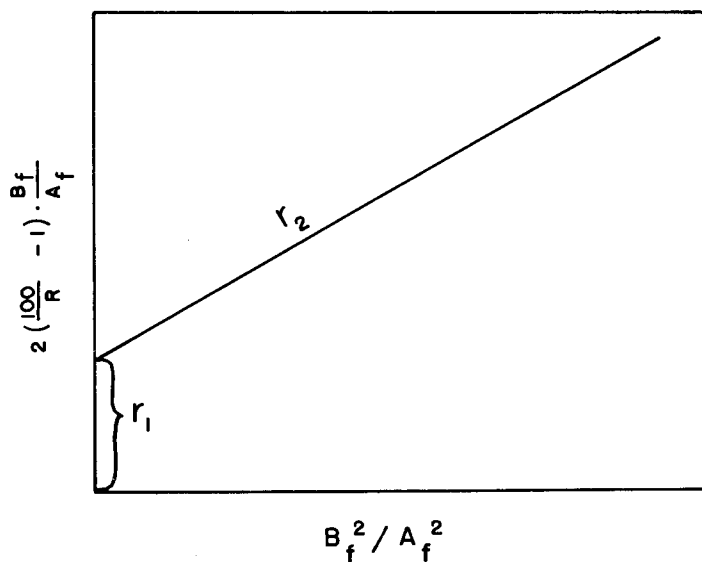


Fig. 1. Determination of monomer reactivity ratios from sequence distribution information.

TABLE I

Linkage Probabilities

Probability	Alfrey and Goldfinger	This work
P_{A-A}	$= \frac{r_1 \% A_f}{r_1 \% A_f + \% B_f}$	$= \frac{\% A - R/2}{\% A}$
P_{A-B}	$= \frac{\% B_f}{r_1 \% A_f + \% B_f}$	$= \frac{R}{2 \% A}$
P_{B-A}	$= \frac{\% A_f}{\% A_f + r_2 \% B_f}$	$= \frac{R}{2 \% B}$
P_{B-B}	$= \frac{r_2 \% B_f}{\% A_f + r_2 \% B_f}$	$= \frac{\% B - R/2}{\% B}$

the relationships given in Table I can be used to determine "instantaneous" monomer reactivity ratios as a function of feed composition, provided the compositions and run numbers of instantaneous polymers formed at various feed compositions are known. Such instantaneous reactivity ratios would be extremely valuable in studies on suspected penultimate effects in vinyl polymerizations.

Run numbers should be useful for characterizing stereoregular polymers and they may also find application in studies on terpolymers. While number-average run numbers were dealt with in this paper, weighted average run numbers may prove useful in some studies, although techniques for measuring these latter quantities are not immediately obvious.

The relationship of run number to feed composition and penultimate reactivity ratios was obtained in collaboration with Mr. T. L. Ang.

This paper was presented before the Division of Polymer Chemistry at the 147th National Meeting of the American Chemical Society, Philadelphia, April 8, 1964.

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