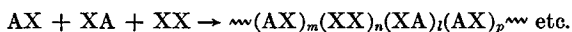


## Remarks on Copolymer Sequence Distributions\*

GARY VER STRATE, *Esso Research and Engineering Co.,  
Linden, New Jersey 07036*

### Synopsis

Distribution functions for the unit X in copolymers of the type



are given. These functions have been used to calculate the expected degree of crystallinity using the Flory theory of copolymer crystallinity. The calculations indicate that differences can be expected between polymers prepared from XA and XX on the one hand and A and X on the other when the kinetics constants of the polymer-forming reactions are identical. In addition, it has been shown that the Flory results carry over to the terpolymer case with the propagation probability given in its terpolymerization form. The addition of more than one comonomer can lead to increased or decreased crystallinity with a given constant melting point, depending on whether the noncrystallizable monomers tend to alternate or "block" with one another.

### INTRODUCTION

This discussion is concerned with several interrelated problems which arise in the calculation of sequence distributions of a particular unit in a copolymer or terpolymer. As an example of the use of the distributions obtained, the Flory theory<sup>1</sup> of copolymer crystallinity has been reworked to incorporate the situations described; however, the distributions so obtained could be used in other applications (e.g., interpretation of spectroscopic data).

In particular, expressions for the distribution of X units obtained in a copolymerization of XX with A or AX are derived. For the latter, two cases are considered, one where the AX unit enters the chain only as AX, not XA; and the other case permitting the XA unit to enter either way. This latter case amounts to a terpolymerization. Several terpolymer distributions are then discussed. The effect of the addition of two monomers, A and B, to a total concentration  $X_A + X_B = C$  is compared to the addition of a single comonomer A to the same concentration C.

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Some of these distributions have practical application in the interpretation of sequence distributions of ethylene- $\alpha$ -olefin copolymers and terpolymers which are currently commercially available.

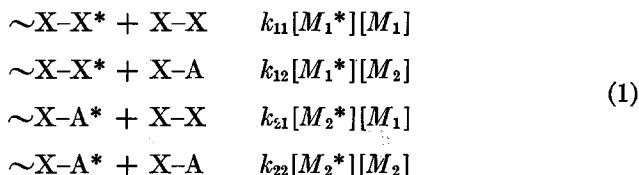
The purpose of performing these calculations is that kinetics analysis of the polymerization yields only the constants for addition of the more complicated XX and AX units, whereas it is the X and A unit distributions which are more fundamentally related to the properties of the materials.

## CALCULATION

### Case I

Given the propagation probabilities of an XA unit with an XX unit (terminal model, AX always adds XA), what is the frequency distribution for  $X_n$  sequences?

If the rates of the four fundamental growth reactions are expressed thus,<sup>2,3†</sup>



where the \* symbolizes an active chain end, letting

$$r_1 = \frac{k_{11}}{k_{12}}, r_2 = \frac{k_{22}}{k_{21}}, F = \frac{[\text{M}_1]}{[\text{M}_2]} \tag{2}$$

it is found that the propagation probabilities for the system are

$$\begin{aligned}
 P_{11} &= \frac{r_1 F}{r_1 F + 1}; & P_{12} &= 1 - P_{11} \\
 P_{22} &= \frac{r_2}{r_2 + F} = \frac{r_2/F}{r_2/(F + 1)}; & P_{21} &= 1 - P_{22}.
 \end{aligned} \tag{3}$$

The probability of observing sequences of one type of unit (e.g., X-X) of  $n$  units in length is

$$P(\text{X-X})_n = P_{11}^{n-1}(1 - P_{11}). \tag{4}$$

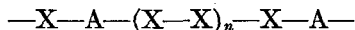
We also have the relationship

$$F = \frac{f - 1 + [(f - 1)^2 + 4r_1 r_2 f]^{1/2}}{2r_1} \tag{5}$$

where  $f$  is the ratio of monomer 1 to 2 in the copolymer.

† See these two references for a general review of the copolymer sequence distribution case.

Now, considering the distribution of X units, it is apparent that each  $-(X-X)_n-$  sequence will be lengthened by one X unit due to the presence of an X unit on the XA monomer:



Thus, the probability of observing even-numbered  $-X_n-$  sequences is zero while that for observing sequences of 3, 5, 7, . . .  $(2n + 1)$  units becomes that for observing the 1, 2, 3, . . .  $n$  length sequences of  $(X-X)$  units. Thus,

$$P(X_{2n+1}) = P_{11}^{n-1}(1 - P_{11}) \text{ number frequency} \quad (6)$$

$$W(X_{2n+1}) = \frac{(2n + 1)P_{11}^{n-1}(1 - P_{11})^2}{(3 - P_{11})} \text{ weight frequency} \quad (7)$$

The distribution of A and X units along the chain no doubt influences the polymer properties over the range from perfect alternation to block copolymers. As an example of how the above factors affect the relationships of kinetic parameters to properties, consider Flory's theory<sup>1</sup> of copolymer crystallinity.

Flory's theory considers the crystallization process to proceed by the selective crystallization of the longest sequences first, etc., with a surface energy associated with the chain emerging from the end (*c*-axis of the crystallite). By following his derivation, one obtains expressions for melting points, degree of crystallinity, minimum crystallizable sequence length, etc., in terms of the propagation probability for crystallizable units (e.g., X units). In order to compare the predictions of his theory with the kinetics data from a A-X + X-X polymerization, his relationships must be recast in terms of the A-X + X-X propagation probabilities. (See Appendix for a summary of notation.)

The theory carries over directly until his relation (7). Then, since  $W_{\delta=\text{even}}^0 \equiv 0$ , the expressions for the probability of a unit being a crystallizable unit followed in sequence by at least  $(\delta - 1)$  crystallizable units must be rewritten as terms over  $W_{\text{ODD}}^0$  only. Note that relation (7) of this paper must be multiplied by the mole fraction X units to correspond to Flory's  $W_j$ . Thus:

$$\begin{aligned} P_{2\delta+1} &= \sum_{j=\delta}^{\infty} \frac{(2j - 2\delta + 1)}{(2j + 1)} \cdot W_{2j+1} \\ P_{2\delta+2} &= \sum_{j=\delta+1}^{\infty} \frac{(2j - 2\delta)}{(2j + 1)} \cdot W_{2j+1} \\ P_{2\delta+3} &= \sum_{j=\delta+1}^{\infty} \frac{(2j - 2\delta - 1)}{(2j + 1)} \cdot W_{2j+1} \end{aligned} \quad (8)$$

where the  $W_{2j+1}$  refer to sequences of  $(2j + 1)$  X units,  $W_{2j} \equiv 0$ . The first term of  $P_{2\delta+1}$  is  $W_{2\delta+1}/(2\delta + 1)$ , and the remaining terms of  $aP_{2\delta+1}$ ,

$bP_{2\delta+2}$ ,  $cP_{2\delta+3}$  cancel if  $a = 1$ ,  $b = 2$ ,  $c = 1$ . Thus Flory's eq. (8) remains valid.

Flory's eq. (9) carries over thus:

$$W_{2\delta+1}^e = (2\delta + 1)D^{-1}e^{-(2\delta+1)\theta}[(1 - e^{-\theta})^2]. \quad (9)$$

This quantity is the equilibrium concentration of sequences of the particular length in the melt. Now formulating Flory's eq. (11),

$$W_{2\delta+1}^0 = \frac{X_c(2\delta + 1)\nu_{2\delta+1}^0}{\sum_{\delta=1}^{\infty} (2\delta + 1)\nu_{2\delta+1}^0} = \frac{X_c P_{11}^{\delta-1}(2\delta + 1)}{\sum_{\delta=1}^{\infty} P_{11}^{\delta-1}(2\delta + 1)} \quad (10)$$

$$W_{2\delta+1}^0 = \left(\frac{X_c}{P_{11}}\right) P_{11}^{\delta} \frac{(2\delta + 1)(1 - P_{11})^2}{(3 - P_{11})} \quad (11)$$

Here,  $X_c$  represents the mole fraction X units in sequences of 2 or longer. The mole fraction X in sequences of 2 and longer is determined as follows:

X-X yields 2X

A-X yields X.

If the mole fraction of X-X is  $X_x$ , then

$$\text{total mole fraction X} = \frac{X_x + 1}{2} \quad (12)$$

Subtracting the fraction of the total polymer of X units between A units which is equal to

$$\frac{X_{xa}}{2} \sum_{i=2}^{\infty} (i - 1)P_{x2}^{i-1} (1 - P_{22})^2 = \frac{X_{xa}P_{22}}{2} \quad (13)$$

$$X_c = \frac{X_x + 1 - (1 - X_x)P_{22}}{2}. \quad (14)$$

Setting  $W_{2\delta+1}^0 = W_{2\delta+1}^e$ , it is found that the intersection occurs at

$$\delta^* = \frac{-\left[+\theta + \ln\left[\frac{X_c D}{P_{11}}\right] + \ln\frac{1}{(3 - P_{11})} + 2 \ln\frac{(1 - P_{11})}{(1 - e^{-\theta})}\right]}{2\theta + \ln P_{11}} \quad (15)$$

and substituting eq. (11) in eq. (8),

$$P_{2\delta+1}^0 = \frac{X_c}{P} \sum_{j=\delta}^{\infty} (2j - 2\delta + 1) P_{11}^j \frac{(1 - P_{11})^2}{(3 - P_{11})} \quad (16)$$

$$P_{2\delta+1}^0 = \frac{X_c}{P_{11}} \frac{(1 - P_{11})^2}{(3 - P_{11})} P^{\delta} (1 - P_{11}), \quad (17)$$

since

$$P_{2\delta+1}^e = D^{-1} \exp-(2\delta + 1)\theta, \quad (18)$$

we obtain the equivalent of Flory's eq. (14) for the melting condition:

$$\frac{X_c}{P} \frac{(1 - P_{11})^2}{(3 - P_{11})} (1 - P_{11}) P^{\delta_{11}} > D^{-1} \exp - (2\delta + 1)\theta. \quad (19)$$

Taking the limit  $\delta \rightarrow \infty$ , since this is true as  $T_m$  is approached,

$$\ln P_{11} > -2\theta \quad (20)$$

$$\theta_m = \frac{-\ln P_{11}}{2} = \frac{\Delta H\mu}{R} \left( \frac{1}{T} - \frac{1}{T_m^0} \right) \quad (21)$$

$$\frac{1}{T} - \frac{1}{T_m^0} = \frac{-R \ln P_{11}}{2\Delta H\mu}. \quad (22)$$

Therefore the melting point relationship is changed to a form with  $P_{11} \rightarrow P^{1/2}_{11}$  or  $\Delta H\mu \rightarrow 2\Delta H\mu$ , depending on how you want to think about it.

For the degree of crystallinity,

$$W_c = \sum_{\delta=\delta^*}^{\infty} W^0_{\delta} - W^e_{\delta} \quad (23)$$

$$W_c = \sum_{\delta=\frac{\delta^*-1}{2}=\text{integer}}^{\infty} (W^0_{2j+1} - W^e_{2j+1}) \quad (24)$$

$$W_c = \sum_{\delta=\frac{\delta^*-1}{2}=\text{integer}}^{\infty} \frac{X_c}{P_{11}} P^{\delta} \frac{(2\delta + 1)(1 - P_{11})^2}{3 - P_{11}} - D^{-1} [1 - e^{-\theta}]^2 e^{-\theta} e^{-2\delta\theta} (2\delta + 1) \quad (25)$$

$$W_c = \sum_{\delta=\frac{\delta^*-1}{2}=\text{integer}}^{\infty} (Ap^{\delta} - B(e^{-2\theta})^{\delta})(2\delta + 1) \quad (26)$$

$$W_c = A \left[ \frac{P_{11}^{\delta^*+1}(1 - 2\delta^*) + P^{\delta^*}_{11}(2\delta^* + 1)}{(1 - P_{11})^2} \right] - B \left[ \frac{(e^{-2\theta})^{\delta^*+1}(1 - 2\delta^*) + (e^{-2\theta})^{\delta^*}(2\delta^* + 1)}{(1 - e^{-2\theta})^2} \right] \quad (27)$$

where

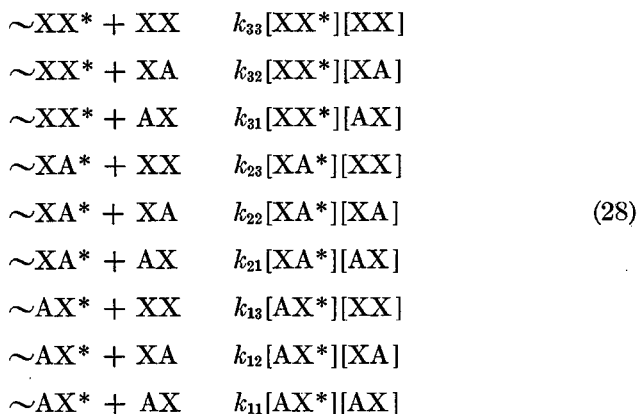
$$A = \frac{X_c}{P} \frac{(1 - P_{11})^2}{3 - P_{11}},$$

$$B = D^{-1} [1 - e^{-\theta}]^2 e^{-\theta}.$$

### Case II

The next more difficult situation to consider is one in which the XA unit can enter in both "normal" and inverted forms. This then becomes a somewhat degenerated terpolymerization; degenerated because the

concentrations of two components, i.e., AX and XA, are equal throughout the polymerization. There are three different growing units, however.



The expressions for the distributions of XX sequences have been given<sup>4</sup> as follows: The total  $(XX)_n$  sequences that are of length  $n$  in the following arrangements are proportional to the  $P_{ijk}$ :

$$\begin{aligned}
 \sim AX(XX)_n XA \sim & \quad P_{131} = n_1 p_{13} p_{33}^{i-1} p_{31} \\
 \sim AX(XX)_n XA \sim & \quad P_{132} = n_1 p_{13} p_{33}^{i-1} p_{32} \\
 \sim XA(XX)_n XA \sim & \quad P_{232} = n_2 p_{23} p_{33}^{i-1} p_{32} \\
 \sim XA(XX)_n AX \sim & \quad P_{231} = n_2 p_{23} p_{33}^{i-1} p_{31}
 \end{aligned} \tag{29}$$

where the  $p_{ij}$  are propagation probabilities and  $n_i$  represents the total number of  $i$  units in the polymer.

These units contain  $(X)_n$  sequences as follows:

$$\begin{aligned}
 P_{131}, & \quad (2n + 1) \text{ units} \\
 P_{132}, & \quad (2n + 2) \text{ units} \\
 P_{232}, & \quad (2n + 1) \text{ units} \\
 P_{231}, & \quad (2n) \text{ units}
 \end{aligned} \tag{30}$$

Therefore the fraction of X units in sequences of a given length from the  $P_{ijk}$  are,

for length  $2i$ ,

$${}_N P_{231}^{2i} = \frac{2i n_2 p_{23} p_{33}^{i-1} p_{31}}{N} \tag{31}$$

for length  $2i + 1$ ,

$${}_N P_{232}^{2i+1} + {}_N P_{131}^{2i} = \frac{(2i + 1)[n_2 p_{23} p_{32} + n_1 p_{13} p_{31}] p^{i-1, 33}}{N} \tag{32}$$

for length  $2i + 2$ ,

$${}_N P^{2i+2}_{132} = \frac{(2i + 2)[n_1 p_{13} p^{i-1}_{33} p_{32}]}{N} \tag{33}$$

From eq. (33) we obtain

$$2i = {}_N P^{2i}_{132} = \frac{2i[n_1 p_{13} p^{i-2}_{33} p_{32}]}{N} \quad i \geq 2 \tag{34}$$

where sequences of 1 and 2X units between AX's are neglected, and  $N$  refers to the normalized  $P'_{ijk}$  as follows:

$$N = \sum_{i=1}^{\infty} 2n_2 p_{23} p_{31} i p^{i-1}_{33} + (n_2 p_{23} p_{32} + n_1 p_{13} p_{31})(2i + 1) p^{i-1}_{33} + \sum_{i=2}^{\infty} 2in_1 p_{13} p^{i-2}_{33} p_{32} \tag{35}$$

$$N = \frac{n_2 p_{23}(2p_{31} + 3p_{32} - p_{32} p_{33}) + n_1 p_{13} \times (3p_{31} - p_{31} p_{33} + 4p_{32} - 2p_{32} p_{33})}{(1 - p_{33})^2} \tag{36}$$

Expressions (31) + (34) and (32) give the fractions of X units in sequences of  $(2n)$  and  $(2n + 1)$  units, respectively.

As an example of the use of these functions, consider again Flory's copolymerization theory. Relationships through (10) in Flory<sup>1</sup> remain unchanged, and eq. (11) is replaced by:

$$W^0_{2n} = \frac{X_c}{N} \cdot Q \cdot p^{i-1}_{33}(2i) \tag{37}$$

$$W^0_{2n+1} = \frac{X_c}{N} \cdot R \cdot p^{i-1}_{33}(2i + 1)$$

The  $X_c$  refers to X in units of 2 and longer, and

$$Q = n_2 p_{23} p_{31} + n_1 p_{13} p_{32} p^{-1}_{33}$$

$$R = n_2 p_{23} p_{32} + n_1 p_{13} p_{33}$$

This fraction  $X_c$  can be obtained by the methods of eq. (13) above or by recognizing that XA units will not contribute to lengthening XX sequences only when they follow XA units or AX units. The fraction of the total polymer that XA units represent is

$$\frac{n_2 p_{22} + n_1 p_{12}}{n_1 + n_2 + n_3}$$

Similarly for AX units,

$$\frac{n_1 p_{11} + n_1 p_{12}}{n_1 + n_2 + n_3}$$

$$\therefore X_c = \frac{1 + X_3 - [X_2 p_{22} + 2X_1 p_{12} + X_1 p_{11}]}{2} \quad (38)$$

Equating eq. (37) with Flory's expression for  $W_\delta^e$  yields the minimum crystallizable sequence length,  $\delta^*$ :

$$\delta_{\text{even}}^* = \frac{- \left[ \ln \left( \frac{X_c Q}{p_{33} N} \right) - \ln C \right]}{(\ln p_{33} + 2\theta)} \quad \delta_{\text{odd}}^* = \frac{- \left[ \ln \left( \frac{X_c R}{P_{33} N} \right) - \ln C + \theta \right]}{(\ln p_{33} + 2\theta)} \quad (39)$$

Substituting eq. (37) in Flory's eq. (7) yields expressions for  $P_\delta^0$  of the form

$$P_\delta^0 = k p^{\delta/2}_{33} \quad (40)$$

where  $k$  contains  $X_c$ , the propagation probabilities, etc., but not  $\delta$ .

For the melting point condition,

$$k p^{\delta/2}_{33} > \frac{1}{D} \exp(-\delta\theta). \quad (41)$$

In the limit  $\delta \rightarrow \infty$ , the same result is obtained as eq. (22), with  $P_{11}$  replaced by  $p_{33}$ .

For the degree of crystallinity, using the odd and even limits appropriately,

$$W_c = \sum_{\delta^*}^{\infty} [2iQ + (2i + 1)R] P_{33}^{i-1} - C [2i + (2i + 1)e^{-\theta}] e^{-2i\theta}; \quad (42)$$

with  $C = D^{-1} [1 - e^{-\theta}]^2$ ,

$$W_c = \frac{X_c}{N(1 - P_{33})^2} 2Q [\delta_e^* (1 - P_{33}) + P_{33}] P_{33}^{\delta_e^* - 1} + R [2\delta_o^* (1 - P_{33}) + (1 + P_{33})] P_{33}^{\delta_o^* - 1} - \frac{C}{(1 - z)^2} \{ 2z [\delta_e^* (1 - z) + z] z^{\delta_e^* - 1} + z^{1/2} [2\delta_o^* (1 - z) + (1 + z)] z^{\delta_o^* - 1} \} \quad (43)$$

where  $z = e^{-2\theta}$ ,  $e$  in  $\delta_e^*$  = even, and  $o$  in  $\delta_o^*$  = odd.

### Case III

For purposes of comparison with cases I and II, consider the case of  $XX + A$ . Equation (9) is preserved while eq. (11) becomes

$$W_{2\delta}^0 = \left( \frac{X_c}{P_{11}} \right) \delta P_{11}^\delta (1 - P_{11})^2 \quad (44)$$

where  $X_c = \frac{2X_{zz}}{1 + X_{zz}}$ .



The  $P_{11}$  has the same meaning as in case I, with A replacing AX.

The melting point relation remains the same as in eq. (22).

The minimum crystallizable sequence length becomes

$$\delta^* = \ln [2CP_{11}/(1 - P_{11})^2 X_c] / [\ln P_{11} + 2\theta] \quad (45)$$

where  $c = D^{-1} [1 - \exp(-\theta)]^2$ .

The degree of crystallinity is given by

$$W_c = \sum_{\delta^*}^{\infty} \left[ \left( \frac{X_c}{P_{11}} \right) \delta P_{11}^{\delta} (1 - P_{11})^2 - 2C\delta \exp(-2\delta\theta) \right] \quad (46)$$

$$W_c = X_c [\delta^* (1 - P_{11}) P_{11}^{\delta^* - 1} + P_{11}^{\delta^*}] - 2Cz \frac{[\delta^* (1 - z) z^{\delta^* - 1} + z^{\delta^*}]}{(1 - z)^2} \quad (47)$$

where  $z = \exp(-2\theta)$ .

#### Case IV

Finally, a straight terpolymerization case is considered, where the unit of interest is monomer 3. We may adopt relations (29) from a previous section. These lead to relations for

$$P'(X_c)_j = jP_{33}^{j-1} [X_1 p_{13}(p_{32} + p_{31}) + X_2 p_{23}(p_{31} + p_{32})] \frac{1}{X_c} \quad (48)$$

where  $P'(X_c)_j$  is proportional to fractions of monomer 3 which occur in sequences of length  $j$ , and  $X_c = X_3$ .

It is noted that  $p_{32} + p_{31} = 1 - p_{33}$ . Also,

$$\frac{X_1 p_{13} + X_2 p_{23}}{X_c (1 - p_{33})} \quad (49)$$

is equal to the number of monomer 1 sequences becoming monomer 3 sequences plus the number of monomer 2 sequences becoming monomer 3 sequences, divided by the number of monomer 3 sequences becoming other sequences. This must be unity for high molecular weight polymers. Thus,

$$P(X_c)_j = jP_{33}^{j-1} (1 - P_{33})^2$$

is the normalized function. Considering again the degree of crystallinity, the  $W_{\delta}^0$  of Flory's paper is given by

$$W_{\delta}^0 = \delta \frac{X_c}{P_{33}} (1 - P_{33})^2 P_{33}^{\delta}$$

Thus, all of the relations of his paper remain unchanged. The answers depend only on the mole fraction and propagation probability of the crystallizable monomer. All questions as to the effects of adding a third monomer are directly interpretable in terms of the effects on  $X_c$  and  $P_{33}$ .

## RESULTS

Numerical values have been generated for the distribution functions and the expected degrees of crystallinity for various values of the parameters.

A comparison of the distribution functions is made in Figure 1, while the relation between the mole fraction  $X-X$  and  $X_c$  is given in Figure 2.

Degrees of crystallinity have been calculated for cases I, II, and III for the values of the parameters indicated in Table I. Typical results are

TABLE I  
Case I, Case III, and Normal X + A Copolymer<sup>a</sup>

$\sigma_c$ , cal/- mole units	$T_m^0$ , °K	$\Delta H\mu$ , cal/- mole	$r_1 r_2^*$	$T$ , °K	Mole Fraction crystallizable monomer
4000	415	1000	0.1	240	0.75
2700			0.55	—	—
			1.	400	0.95

<sup>a</sup> Case II same as above, except  $X_1 = X_2$ ;  $\frac{k_{33}}{k_{31}} = \frac{k_{33}}{k_{32}} = 20, 100, 1$ ;  $\frac{k_{22}}{k_{21}} = \frac{k_{11}}{k_{12}} = 1$ ;

$\frac{k_{22}}{k_{23}} = \frac{k_{11}}{k_{13}} = 0.05, 1$ .

presented in Figures 3 through 5.

Some typical results for case IV are presented in Table II. All of the results are presented in mole fractions.

## DISCUSSION

## Cases I, II, III

Questions which can be answered by a consideration of the data for cases I, II and III are:

Is there any significant difference in the shape of the distribution or the "degree of crystallinity" caused by adding the unit X in pairs? Here we compare the normal (A + X) with case III.

Is there any significant difference between the normal and cases I and II when the polymers are compared at the same total concentration of X?

In order to avoid repetitious plotting of the data, the crystallinity results are presented as a function of the quantity  $X_c$ . For the normal and case III polymers, this includes all X units; while for cases I and II, those X units which are in sequences (of 1 or 2 units) and which include no contribution from XX (added as XX) are excluded. Thus, for comparisons at constant total X for these latter cases, some interpolation must be done.

With regard to the first question, it is apparent from Figure 1, plots 1 and 5, that identical kinetic constants need not yield distributions of the same shape. For this particular example where the reactivity ratio prod-

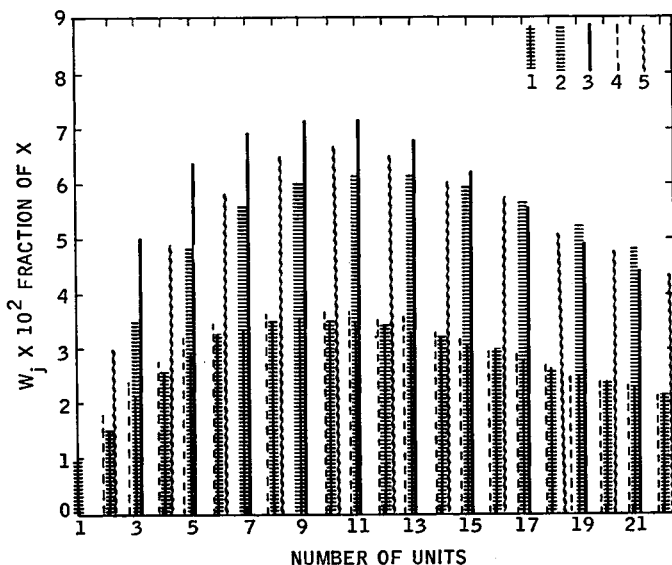


Fig. 1. Distribution functions for the unit. (1) Normal: mole fraction  $X = 0.9$ ;  $r_1r_2 = 1$ ;  $X_c = 0.9$ ;  $P = 0.9$ . (2) Case I: mole fraction  $X = 0.915$ ;  $r_1r_2 = 1$ ;  $X_c = 0.9$ ; mole fraction  $XX = 0.83 = P$ . (3) Case I: mole fraction  $X = 0.9$ ;  $r_1r_2 = 1$ ;  $X_c = 0.88$ ; mole fraction  $XX = 0.8 = P$ . (4) Case II: mole fraction  $X = 0.9$ ; all  $r_{ij} = 1$ ;  $X_c = 0.88$ ; mole fraction  $XX = 0.8 = P$ . (5) Case III: mole fraction  $X = 0.9$ ;  $r_1r_2 = 1$ ;  $X_c = 0.9$ ; mole fraction  $XX = 0.818 = P$ .

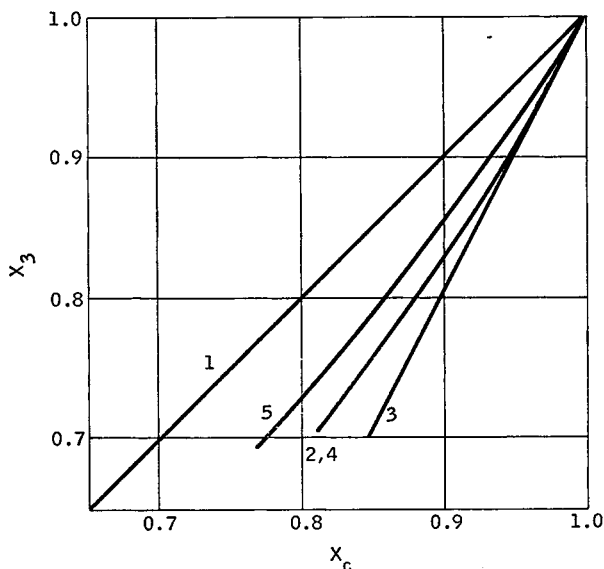


Fig. 2. Relationship of  $X_c$  to mole fraction  $X$ . (1)  $X + A$  Copolymer: all  $r_1r_2$ . (2) Case I:  $r_1r_2 = 1$ . (3) Case I:  $r_1r_2 = 0.1$ . (4) Case II: all  $r_{ij} = 1$ . (5) Case II:  $r_{12} = 1, r_{13} = 20, r_{21} = 1, r_{23} = 20, r_{31} = 0.01, r_{32} = 0.01$ .

TABLE II  
Terpolymer Crystallinity, Case IV

Feed $X_3/X_1$	Copolymer						Terpolymer								
	$r_{13}$	$r_{31}$	$r_{23}$	$r_{32}$	$r_{12}$	$r_{21}$	$r_{13}$	$r_{31}$	$r_{23}$	$r_{32}$	$r_{12}$	$r_{21}$	$P_{33}$	$X_3$	$X_2 = X_1$
0.725	1	0.01	0.986	0.969	1.45	0.01	0.01	1	1	0.05	0.986	0.977	0.986	0.977	0.0115
—	—	—	—	—	—	—	—	—	—	1	0.986	0.969	0.986	0.969	0.0157
—	—	—	—	—	—	—	—	—	—	20	0.986	0.826	0.986	0.826	0.087
0.725	1	1	0.420	0.420	1.45	1	1	1	1	1	0.420	0.420	0.420	0.420	0.29

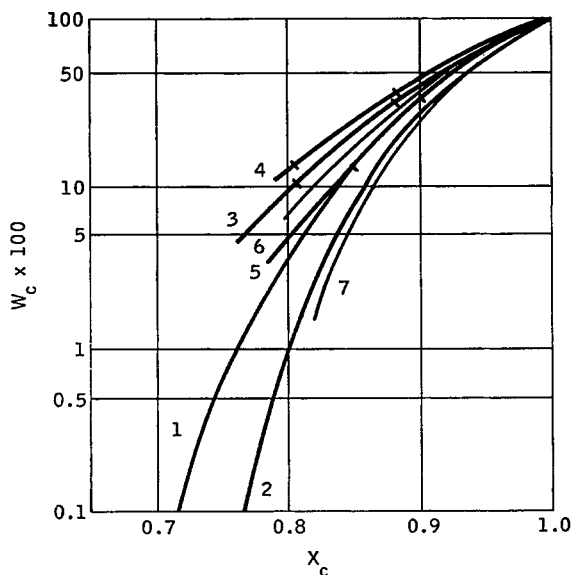


Fig. 3. Degree of crystallinity and composition:  $\sigma_e = 2700$  cal/mole,  $T_m^\circ = 415^\circ\text{K}$ ,  $\Delta H\mu = 1000$  cal/mole,  $T = 240^\circ\text{K}$ . (1) A + X Copolymer:  $r_1r_2 = 1$ . (2) A + X Copolymer:  $r_1r_2 = 0.1$ . (3) Case I:  $r_1r_2 = 1$ . (4) Case II: all  $r_{ij} = 1$ . (5) Case I:  $r_1r_2 = 0.55$ . (6) Case III:  $r_1r_2 = 1$ . (7) Case III:  $r_1r_2 = 0.1$ .

ucts are unity, the polymer formed by the addition of XX tends to have more longer sequences, at the same concentration of X, than does a polymer formed from A + X. A similar statement can be made about case II versus the normal if the comparison is made at constant  $X_c$  (plot 2); however, at constant total X (plot 3), the normal tends toward the larger fraction in longer sequences.

These differences bring about changes in the expected degree of crystallinity. For the particular set of parameters of Figure 3, A + XX polymers can be either more or less crystalline than A + X polymers for a given set of kinetics parameters. This can be seen by comparing curves 1, 6 and 2, 7. For the higher reactivity ratio product ( $r_1r_2 = 1$ ) the A + XX polymer is more crystalline, but as the product is lowered, this polymer should decrease in crystallinity faster. The per cent difference becomes larger as the degree of crystallinity is lowered.

A comparison with cases I and II is somewhat more complex because of the contribution of X from the AX monomer. If the comparison is made at constant  $X_c$ , these cases are even more crystalline than case III; however, if the comparison is made at constant total X, the normal appears much more like the AX + XX polymers. Conversion of  $X_c$  to X by use of Figure 2 permits this comparison. The intercepts on curve 1, Figure 3, at  $X_c$  values of 0.85 and 0.90 correspond to 0.88 and 0.805 mole fraction X in the AX and XX polymers when the reactivity ratio product is unity. As shown by the intercepts on curves 3 and 4, the case I poly-

mer is expected to be somewhat less crystalline and the case II polymer, somewhat more crystalline, than the normal.

Thus, it would appear that the sequence distribution of A + X polymers and AX + XX polymers with the same kinetic constants for monomer addition (equal to 1 for the reactivity ratio product) are similar enough so that one can expect the samples to behave similarly if compared at the same concentration of X.

The data presented in Figures 4 and 5 is reasonably self-explanatory and is offered to show that the effects persist over the whole temperature range and in the minimum crystallizable sequence length.

#### Case IV

Since the equations in this case degenerated to those for the normal copolymer case with the propagation probability redefined, the discussion is here confined to some observations as to how this probability can be modified.

In the copolymer case, the propagation probability can be written solely in terms of the polymer composition and the reactivity ratio product. For the terpolymer case, this is not so. Individual values for the reactivity ratios must be specified. If the reactivity ratios are unity, the propagation probability becomes equal to the mole fraction of the unit in the polymer, and the results are the same as those for a random copolymer of equal mole fraction crystallizable monomer.

Rather than consider many special cases of limited general interest here, those interested can use the relationships of Rabinovitch<sup>4</sup> to generate the appropriate feed ratios and polymer compositions, to give the propagation probabilities. Flory's results then carry over directly. As an example, consider the case where comonomers 1 and 2 are added to monomer 3 with a given set of kinetics constants, in comparison to the case where only monomer 1 is added to monomer 3 with the kinetics constants equal, where possible. These data are presented in tabular form in Table II.

If all the  $r_{ij} = 1$ , the copolymer and terpolymer have the same  $X_3$  and propagation probability in the polymer. If the  $r_{12} = r_{21}$  are permitted to differ from unity, however, it is found that either more or less of the crystallizable monomer must be in the polymer to get the same propagation probability. In particular, if cases A, C are considered, it is seen that for  $r_{12} = r_{21} \geq 1$  (the  $X_1, X_2$  units prefer to alternate) less of the crystallizable monomer must be added in the copolymer case to get the same propagation probability, and vice versa. Thus,  $W_c$  can vary, with  $T_m$  constant.

#### CONCLUSIONS

Distribution functions and expressions for degrees of crystallinity in the Flory<sup>1</sup> sense have been presented for particular copolymers and terpolymers. Particular numerical examples have been given to demonstrate the results of the calculations.

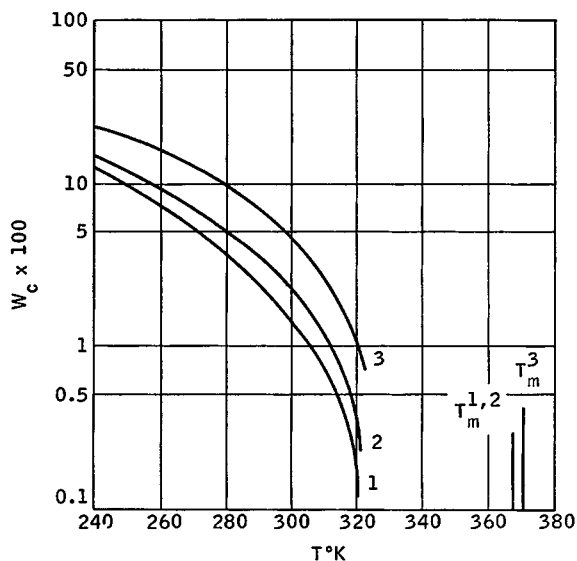


Fig. 4. Degree of crystallinity and temperature. (1) A + X Copolymer:  $X = X_c = 0.85$ ;  $r_1 r_2 = 1$ ;  $T_m = 366$ . (2) Case I:  $X_c = 0.853$ ;  $r_1 r_2 = 0.5$ ;  $T_m = 366$ . (3) Case II:  $X_c = 0.844$ ;  $r_{ij} = 1$ ;  $T_m = 371$ .

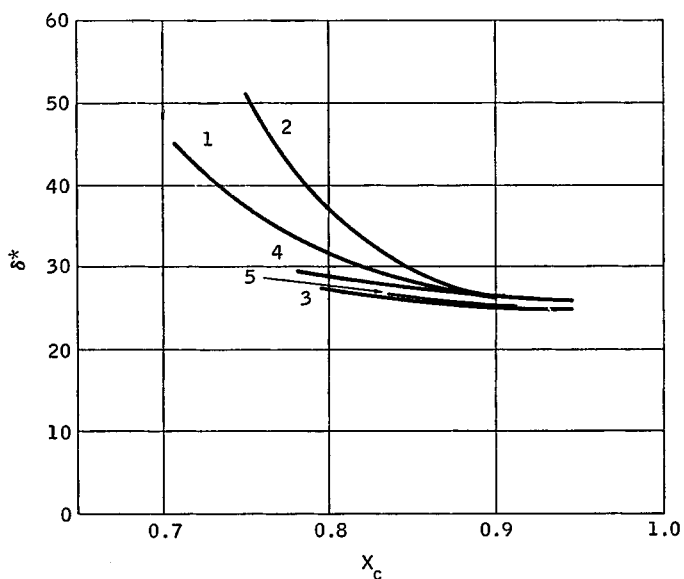


Fig. 5. Minimum crystallizable sequence length. (Same as Figure 3, except  $T = 280^\circ K$ ). (1) A + X Copolymer:  $r_1 r_2 = 1$ . (2) A + X Copolymer:  $r_1 r_2 = 0.1$ . (3) Case I Copolymer:  $r_1 r_2 = 1$ . (4) Case II Copolymer:  $r_{ij} = 1$ . (5) Case III Copolymer:  $r_1 r_2 = 1$ .

It appears that the detailed nature of the process of addition of the units of interest to the polymer chain must be considered both in the evaluation of the distribution functions and of the physical properties that can result.

In addition, terpolymerization should give considerable added flexibility over copolymerization with regard to properties that can be influenced by the sequence distribution of a particular monomer.

## APPENDIX

### Flory Nomenclature and Crystallinity Relationships for $X + A$ Copolymer.

- $X$  = mole fraction crystallizable unit  
 $\Delta H_{\mu}$  = heat of fusion/mole crystallizable units  
 $\sigma_e$  = excess free energy associated with a terminal crystallite unit  
 $T_m^0$  = melting point of perfect crystalline homopolymer degrees Kelvin
- $$\theta = (\Delta H_{\mu}/R) \left( \frac{1}{T} - \frac{1}{T_m^0} \right)$$
- $R$  = gas constant  
 $W_{\delta}^0$  = product of the mole fraction crystallizable units and the fraction of these units in sequences of length  $\delta$   
 $D = \exp(-2\sigma_e/RT)$   
 $p$  = propagation probability for crystallizable monomer  
 $\delta^*$  = minimum crystallizable sequence length  
 $= \{ \ln(DX/p) + 2 \ln[(1-P)/(1-\exp(-\theta))] \} / (\theta + \ln p)$   
 $W_c$  = mole fraction crystalline material  
 $= \frac{X}{p} (1-p)^2 p^{\delta^*} \{ p(1-p)^{-2} - e^{-\theta}(1-e^{-\theta})^{-2} + \delta^*[(1-p)^{-1} - (1-e^{-\theta})^{-1}] \}$   
 $P_{\delta}$  = probability that a site in the melt is an X unit and that it is succeeded in its chain by at least  $\delta - 1$  X units

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