$$x_{PX} = \frac{(r-1)[\{(1+\lambda)(r-1)+2\}^2 - 2(1-\lambda^2)(r-1)]}{r\{(1+\lambda)(r-1)+2\}^2} \quad \text{(B17)}$$

$$x_{XPX} = \frac{(1-\lambda^2)(r-1)^2}{r\{(1+\lambda)(r-1)+2\}^2} \quad \text{(B18)}$$

The dependence of each fraction on $\overline{P}_n/\overline{P}_{n,o}$ is given in Figures 12 and 13 for the cases of $\lambda = 0$ and 1. As is apparent from eq B9 and B18, the w_{XPX} and χ_{XPX} values vanish when $\lambda = 1$ (disproportionation termination).

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Block Lengths of Step Copolymers formed by Coupling Identical Comonomer Functional Groups of Differing Reactivity

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ABSTRACT: Step copolymers formed by linking together comonomers of the type A_1–R_1–A_1 and A_2–R_2–A_2 in which A_1 and A_2 are identical functional groups having differing coupling reactivities due to the presence of R_1 or R_2 are predicted to form block copolymers. Number average block lengths are calculated by assuming the copolymerization to pass through three sequential stages: (1) self-coupling between the more reactive functional groups, A_1, (2) cross-coupling between the more and less reactive functional groups, and (3) self-coupling between the less reactive functional groups, A_2. The iterations required by the calculation may be circumvented by assuming the extent of conversion where the comonomers are polymerizing at an equal rate closely corresponds to the point where the more reactive monomer has attained its maximum number average block length. Numerical results based on assumed reactivity ratios show the block length to increase with an increasing difference in reactivity ratios. When both reactivity ratios are between 0 and 1, an azeotrope is predicted.

Most step polymerizations occur by the linking together of different functional groups (i.e., an acid and an alcohol) of bifunctional monomers. However, coupling reactions are known where functional groups of the same identity link together. Such an example, which has been employed as a polymerization system,[2] is the copper–amine catalyzed oxidative coupling of terminal diynes.

$$n\text{HC}{\equiv}\text{CRC}{\equiv}\text{CH} \xrightarrow[\text{amine}]{\text{Cu}} \text{H}(\text{–C}{\equiv}\text{CRC}{\equiv}\text{C–})_n\text{H} + (2n-2)\text{H}^+$$

A particularly interesting consequence of the functional groups having the same identity is the absence of a stoichiometric restriction for obtaining high polymer. In a copolymerization the identity of R can be varied such that the coupling reactivity of the comonomer functional groups is different.

$$\text{A}_1\text{–R}_1\text{–A}_1 + \text{A}_2\text{–R}_2\text{–A}_2 \rightarrow [(\text{–A}_1\text{–R}_1\text{–A}_1\text{–})_p(\text{–A}_2\text{–R}_2\text{–A}_2\text{–})_q]_n$$

From cross-coupling experiments with the acetylenic coupling system,[3] it has been shown that the identity of R can have a substantial effect on the reactivity of A. It would be expected in a copolymerization system that the coupling would pass through three stages: first where coupling is predominant between the more reactive functional groups followed by cross-coupling and finally where coupling is predominant between the less reactive functional groups. The copolymer chain would then be expected to consist of block sequences of the comonomers. The present objective is to derive an equation for predicting number average block lengths and to obtain numerical results for a range of coupling reactivity differences.

Computation

In a step copolymer system where identical functional groups of the same and differing reactivities can couple to form polymer, three possible kinds of linkages may be formed: (1) a self-coupling between the monomers possessing the more reactive functional groups, (2) a cross-coupling between comonomers, and (3) a self-coupling between the monomers possessing the less reactive functional groups. These three reactions may be represented as follows

$$\text{A}_1 + \text{A}_1 \xrightarrow{k_{11}} \text{P}(\text{A}_1\text{A}_1) \quad (1)$$

$$\text{A}_1 + \text{A}_2 \xrightarrow{k_{12}} \text{P}(\text{A}_1\text{A}_2) \quad (2)$$

$$\text{A}_2 + \text{A}_2 \xrightarrow{k_{22}} \text{P}(\text{A}_2\text{A}_2) \quad (3)$$

where A_1 is the more reactive functional group, A_2 is the less reactive functional group, and $P(A_nA_n)$ is a polymer of DP ≥ 2.

The relative rate that the functional groups couple to form polymer is given by

$$\frac{dA_1}{dA_2} = \frac{k_{11}A_1^2 + k_{12}A_1A_2}{k_{22}A_2^2 + k_{12}A_1A_2} = \frac{r_1(A_1/A_2) + 1}{r_2(A_2/A_1) + 1} \quad (4)$$

$$r_1 = k_{11}/k_{12}, \qquad r_2 = k_{22}/k_{12}$$

where A_1 and A_2 represent concentrations of respective uncoupled functional groups.

The relative functional group reaction rate can be expressed as F_1, the instantaneous mole fraction of A_1 in the copolymer, and the relative unreacted functional group concentration as f_1, the mole fraction of A_1 in the feed. These quantities are defined as follows.

$$F_1 = \frac{dA_1}{dA_1 + dA_2} \quad (5)$$

$$f_1 = \frac{A_1}{A_1 + A_2} \quad (6)$$

The quantity F_1 may then be expressed as a function of f_1 by way of eq 4.

$$F_1 = \frac{f_1(r_1 - 1) + 1}{f_1(r_1 + r_2 - 2) + r_1/f_1 - 2r_2 + 1} \quad (7)$$

Copolymer Equation. As the polymeric coupling proceeds to higher extents of reaction, the feed composition drifts in favor of monomer 2. To obtain the feed composition as a function of extent of reaction, the differential equation is set up as follows.[4] The copolymer contains $F_1\,dA$ moles of A_1 and the feed contains $(A - dA)(f_1 - df_1)$ moles of A_1. Then

$$A_{1,\text{copolymerized}} = A_{1,\text{before reaction}} - A_{1,\text{after reaction}}$$

$$F_1 dA = Af_1 - (A - dA)(f_1 - df_1)$$

or

$$dA/A = df_1/(F_1 - f_1)$$

assuming $df_1\,dA$ to be negligible. This equation may be integrated after substitution from eq 7 to yield

$$\frac{A}{A^0} = \left[\left(\frac{\delta f_1 - 1}{\delta f_1^0 - 1}\right)\left(\frac{f_1^0 - 1}{f_1 - 1}\right)\right]^{\epsilon} \times \left[\frac{\Delta_2 - (\Delta_1 + 2\Delta_2)f_1 + (\Delta_1 + \Delta_2)f_1^2}{\Delta_2 - (\Delta_1 + 2\Delta_2)f_1 + (\Delta_1 + \Delta_2)(f_1^0)^2}\right]^{\mu}\left[\frac{f_1}{f_1^0}\right]^{\eta} \quad (8)$$

$$\Delta_1 = (1 - r_1), \qquad \Delta_2 = (1 - r_2), \qquad \delta = ((\Delta_2/\Delta_1) + 1)$$

$$\epsilon = \left(1 - \frac{1}{\Delta_1} - \frac{1}{2\Delta_2}\right), \qquad \mu = \left(\frac{-1}{2\Delta_2}\right), \qquad \eta = \left(\frac{1}{\Delta_2} - 1\right)$$

where A^0 is the initial total functional group concentration and f_1^0 is the initial feed mole fraction.

The reactivity ratios may be obtained by measuring the relative amounts of self-coupling, $P(A_1A_1)$ and $P(A_2A_2)$, and cross-coupling, $P(A_1A_2)$, at low degrees of conversion and employing the following relations.

$$\frac{dP(A_1A_1)}{dP(A_1A_2)} = r_1\frac{A_1}{A_2} \simeq \left(\frac{P(A_1A_1)}{P(A_1A_2)}\right)_{\text{low conversion}}$$

$$\frac{dP(A_2A_2)}{dP(A_1A_2)} = r_2\frac{A_2}{A_1} \simeq \left(\frac{P(A_2A_2)}{P(A_1A_2)}\right)_{\text{low conversion}}$$

Alternately eq 7 may be rearranged to yield

$$\left[\frac{F_1 + f_1}{f_1^2(1 - F_1)}\right] = \left[\frac{F_1(f_1 - (1/f_1) - 2)}{f_1(F_1 - 1)}\right]\Delta_2 + \Delta_1 \quad (9)$$

Again at low conversion and approximating $f_1 \simeq f_1^0$ and $F_1 \simeq A_1'/(A_1' + A_2')$ (A_1' represents a reacted A_1 group), a plot of the first bracketed term against the second in eq 9 should yield a straight line of slope Δ_2 and intercept Δ_1.

Solution of the copolymer equation enables the copolymer composition at various extents of conversion to be obtained as the cumulative copolymer mole fraction, C.

$$C_1 = \frac{A_1'}{A_1' + A_2'} = \frac{A_1^0 - Af_1}{A^0 - A} \quad (10)$$

Copolymer Block Lengths. By constructing plots of the cumulative copolymer mole fractions, C_1 and C_2, against the extent of conversion, it can qualitatively be determined whether the comonomer sequence of the polymer is random or in blocks. Such a plot is illustrated in Figure 1. The more rapidly C_1 and C_2 converge, the shorter the blocks of monomer 1 and monomer 2 and the more random the placement in the copolymer. It can immediately be seen that as the difference in reactivity ratios becomes small, the monomer block lengths shorten.

A monomer block length, $\overline{X}_1$ corresponding to monomer 1, can be determined more quantitatively by employing a statistical method similar to that used by Flory for the degree of polymerization.[5]

$$\overline{X}_1 = 1/(1 - Q) \quad (11)$$

The quantity Q is the probability a linkage has been formed between functional groups of monomer 1.

$$Q = \frac{A_1'A_1'}{2A_1^0 + \phi A_2^0} \quad (12)$$

The concentration of linkages formed between two A_1 functional groups is represented by $A_1'A_1'$. The quantity ϕ is the ratio of the accumulation of A_2 into the copolymer relative to that of A_1 and is normalized to the relative quantities of comonomers initially present. The three possible ways that A_1 and A_2 accumulate in the copolymer are two self-couplings and one cross-coupling, that is an ~~A_1A_1~~, ~~A_2A_2~~, and ~~A_1A_2~~ linkage denoted by $A_1'A_1'$, $A_2'A_2'$, and $A_1'A_2'$, respectively. Only the $A_1'A_1'$ linkage is found within a monomer 1 block, and A_2 may accumulate in the copolymer as either an $A_1'A_2'$ or an $A_2'A_2'$ linkage. The quantity ϕ is then the ratio of linkages which cap the monomer 1 block to those inside a monomer 1 block.

$$\phi = \frac{A_1'A_2'}{A_1'A_1'}\cdot\frac{f_1^0}{f_2^0} = \frac{C_{12}}{C_{11}}\cdot\frac{f_1^0}{f_2^0} \quad (13)$$

The mole fraction of the various linkages within the copolymer is defined as follows.

$$C_{11} = \frac{A_1'A_1'}{A_1'A_1' + A_1'A_2' + A_2'A_2'}$$

$$C_{12} = \frac{A_1'A_2'}{A_1'A_1' + A_1'A_2' + A_2'A_2'}$$

To determine C_{11} or C_{12} it is necessary to obtain the concentrations of the various linkages in the copolymer. The differential equation for obtaining $A_1'A_1'$ can be set up as follows from eq 1.

$$dA_1'A_1'/dt = k_{11}A_1^2$$

or

$$dA_1'A_1' = k_{11}A_1^2\,(dt/dp_1)\,dp_1$$

where p_1 is the extent of reaction for monomer 1.

$$p_1 = \frac{A_1^0 - A_1}{A_1^0} \text{ and } \frac{dp_1}{dt} = \left(\frac{1}{-A_1^0}\right)\frac{dA_1}{dt}$$

$$-\frac{dA_1}{dt} = k_{11}A_1^2 + k_{12}A_1A_2$$

Then

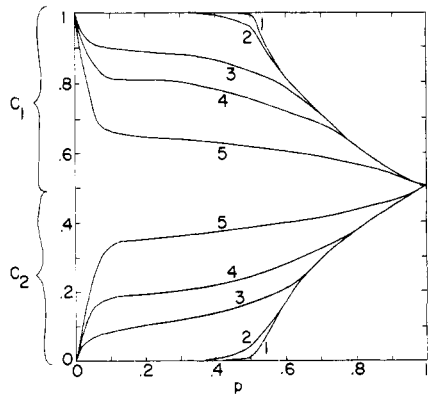

Figure 1. Dependence of cumulative copolymer mole fraction on extent of reaction where $A_1^0 = A_2^0 = 1M$. Curve 1, $(r_1, r_2) = (1000, 0.001)$; curve 2, $(r_1, r_2) = (100, 0.01)$; curve 3, $(r_1, r_2) = (10, 0.1)$; curve 4, $(r_1, r_2) = (5, 0.2)$; curve 5, $(r_1, r_2) = (2, 0.5)$.

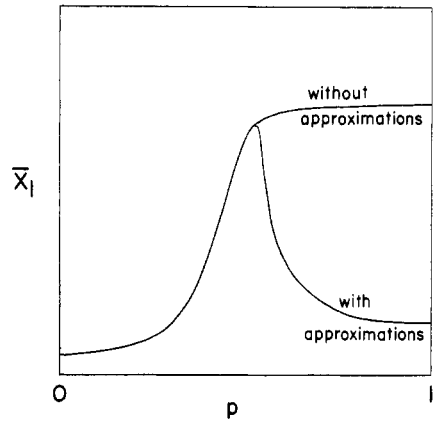

Figure 2. Schematic monomer block length vs. extent of conversion plot illustrating the effect of the approximations ($A_1'A_1' \gg A_1'A_2'$ and $A_1'A_2' \gg A_2'A_2'$).

$$dA_1'A_1' = A_1^0 \left[\frac{1}{1 + (A_2/r_1A_1)}\right] dp_1 \qquad (14)$$

To solve this differential equation A_2 must be expressed as a function of A_1 which is obtained by integrating eq 4 to yield the following equation.

$$A_2^{\omega}(\Delta_2A_2 - \Delta_1A_1)^{\sigma} = (A_2^0)^{\omega}(\Delta_2A_2^0 - \Delta_1A_1^0)^{\sigma}(A_1^0)^{\chi}(A_1)^{-\chi} \qquad (15)$$

$$\omega = \left(1 - \frac{1}{\Delta_1}\right), \qquad \sigma = \left(\frac{1}{\Delta_1} + \frac{1}{\Delta_2} - 1\right), \qquad \chi = \left(1 - \frac{1}{\Delta_2}\right)$$

To solve eq 15 for A_2 and substitute into and integrate eq 14 would require numerical values for r_1 and r_2 as well as complex iteration and graphical integration procedures. While the quantities $A_1'A_1'$, $A_1'A_2'$, and $A_2'A_2'$ cannot easily be computed, those of A_1' and A_2' can. The relation between these two groups of quantities is

$$A_1' = 2A_1'A_1' + A_1'A_2' \qquad (16)$$

$$A_2' = A_1'A_2' + 2A_2'A_2' \qquad (17)$$

If the relative coupling reactivities of the functional groups are substantially different ($r_1 \gg r_2$), the following approximations can be made between the different linkage concentrations

$$A_1'A_1' \gg A_1'A_2' \text{ and } A_1'A_2' \gg A_2'A_2'$$

The first approximation should be good throughout the whole extent of the reaction while the second will break down after the extent of reaction has passed the stage where cross-coupling is predominant.

With these approximations ϕ and Q can be obtained at various extents of conversion from the following expressions.

$$\frac{C_2}{C_1} = \frac{A_2'}{A_1'} = \frac{A_1'A_2' + 2A_2'A_2'}{2A_1'A_1' + A_1'A_2'} \simeq \frac{A_1'A_2'}{2A_1'A_1'} = \frac{1}{2}\frac{f_2^0}{f_1^0}\phi \qquad (18)$$

$$Q = \frac{A_1'A_1'}{2A_1^0 + \phi A_2^0} \simeq \frac{A_1'}{A_1^0 + A_2^0(C_2/C_1)(f_1^0/f_2^0)} \qquad (19)$$

The breaking down of the second approximation will result in a negative deviation in $\overline{X}_1$. A plot of $\overline{X}_1$ against the extent of reaction, p, where the approximations are not made should yield a curve which rapidly approaches a constant value of $\overline{X}_1$ while a similar plot where the approximations are made will pass through an $\overline{X}_1$ maximum as the second approximation breaks down. Such a plot is illustrated in Figure 2.

This $\overline{X}_1$ maximum would represent a minimum monomer 1 number average block length but should be close to the actual monomer 1 block length since at the extent of reaction where the approximation of $A_1'A_2' \gg A_2'A_2'$ breaks down most of the monomer 1 oligomer blocks have been capped by monomer 2.

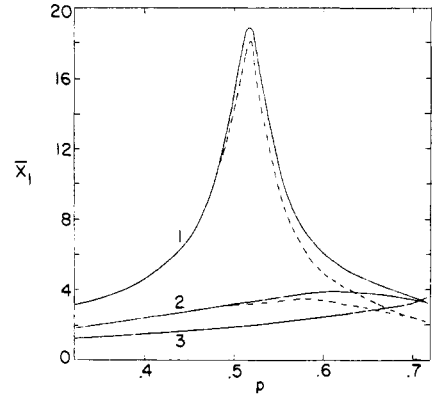

Figure 3. Dependence of monomer 1 block length on extent of reaction where $A_1^0 = A_2^0 = 1M$. The solid line is for $\overline{X}_1$, and the broken line is for $\overline{X}_1'$. Curve 1, $(r_1, r_2) = (100, 0.01)$, $\overline{X}_{1\,max} = 18.9$, $\overline{X}_{1'max} = 18.2$, $p_{max} = 0.519$, $p'_{max} = 0.518$; curve 2, $(r_1, r_2) = (10, 0.1)$, $\overline{X}_{1\,max} = 3.95$, $\overline{X}_{1'max} = 3.30$, $p_{max} = 0.608$, $p'_{max} = 0.574$; curve 3, $\overline{X}_n$ of system.

Just as $\overline{X}_n$ for a homopolymerization may be obtained directly from its definition without working through Flory's statistical method, so too can $\overline{X}_1$.

$$\overline{X}_1' = \frac{\text{no. of } M_1 \text{ units}}{\text{no. of } M_1 \text{ blocks}} = \frac{\text{initial concn of } M_1}{\text{half-concn of } M_1 \text{ block ends}}$$

The prime superscript distinguishes this $\overline{X}_1$ from that derived by Flory's method, and M_1 represents monomer 1 or A_1–R_1–A_1. A block end of an M_1 oligomer must be either an unreacted A_1 group or a reacted A_2 group.

$$\overline{X}_1' = \frac{M_1^0}{\frac{1}{2}(A_1 + A_2')} = \frac{A_1^0}{A_1 + A_2'} \qquad (20)$$

Inherent in this equation is that every A_2' functions as an M_1 block end which is another way of stating the approximation $A_1'A_2' \gg A_2'A_2'$. Thus, this $\overline{X}_1'$ will also go through a maximum with increasing extent of reaction. However, $\overline{X}_{1'max}$ will be different from $\overline{X}_{1\,max}$ since the former does not involve the approximation $A_1'A_1' \gg A_1'A_2'$. This difference should make $\overline{X}_{1\,max}$ slightly greater and occur at a slightly larger extent of reaction than $\overline{X}_{1'max}$ (see Figure 3). The number average monomer 1 block lengths may be expressed in terms of extent of reaction of each monomer as follows.

Table I
Monomer 1 Block Lengths

$A_1^0 = A_2^0 = 1M$						$A_1^0 = A_2^0 = 1M$					
r_1	1000	100	10	5	2	r_1	1000	100	10	5	2
r_2	0.001	0.01	0.1	0.2	0.5	r_2	.5	0.5	0.5	0.5	0.5
$\overline{X}_{1\,max}$	128	18.9	3.95	2.82	2.10	$\overline{X}_{1\,max}$	21.6	7.00	2.84	2.39	2.10
$\overline{X}_1'_{max}$	127	18.2	3.30	2.15	1.33	$\overline{X}_1'_{max}$	21.3	6.63	2.30	1.77	1.33
p_{max}	0.503	0.519	0.608	0.686	0.890	p_{max}	0.502	0.518	0.636	0.732	0.890
p'_{max}	0.503	0.518	0.574	0.599	0.625	p'_{max}	0.502	0.511	0.554	0.580	0.625
$\overline{X}_{1\,F_1=F_2}$	128	18.9	3.86	2.68	1.82	$\overline{X}_{1F_1=F_2}$	21.6	6.97	2.72	2.22	1.82
$\overline{X}_1'_{F_1=F_2}$	127	18.2	3.30	2.15	1.33	$\overline{X}_1'_{F_1=F_2}$	21.3	6.63	2.30	1.77	1.33

$r_1 = 100, r_2 = 0.01$

A_1^0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
A_2^0	1.8	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2
$\overline{X}_{1max}$	3.89	6.64	9.80	13.7	18.9	26.2	37.7	59.5	119
$\overline{X}_1'_{max}$	3.29	6.00	9.14	13.0	18.2	25.5	37.0	58.7	119
p_{max}	0.120	0.222	0.322	0.421	0.519	0.616	0.713	0.810	0.906
p'_{max}	0.113	0.218	0.319	0.419	0.518	0.616	0.713	0.810	0.906
$\overline{X}_{1\,F_1=F_2}$	3.81	6.59	9.78	13.7	18.9	26.2	37.7	59.5	120
$\overline{X}_1'_{F_1=F_2}$	3.29	6.00	9.14	13.0	18.2	25.5	37.0	58.7	119

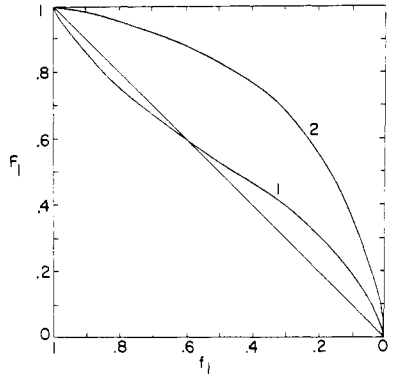

Figure 4. Dependence of instantaneous copolymer mole fraction on feed mole fraction where $A_1^0 = A_2^0 = 1M$. Curve 1, $(r_1, r_2) = (0.6, 0.4)$, azeotrope at $f_1 = F_1 = 0.6$; curve 2, $(r_1, r_2) = (5, 0.2)$, no azeotrope.

$$\overline{X}_1 = \frac{1 + r_C}{1 + r_C - p_1} \tag{21}$$

$$\overline{X}_1' = \frac{1}{1 + r_A p_2 - p_1} \tag{22}$$

where $r_A = A_2^0/A_1^0$, $r_C = C_2/C_1$, $p_1 = A_1'/A_1^0$, and $p_2 = A_2'/A_2^0$.

Azeotrope. Analogous to chain copolymerization an azeotrope should occur when the feed and copolymer compositions appproach a common value with increasing extent of reaction. Under such a condition $F_1 = f_1$ and with this substitution, eq 7 can be solved for f_1 to yield the following result.

$$f_1 = \frac{\Delta_2}{\Delta_1 + \Delta_2} = \frac{1 - r_2}{1 - r_1 + 1 - r_2} \tag{23}$$

Since f_1 can neither be greater than one nor less than zero, the following must hold for the existence of an azeotrope.

$f_1 = \frac{\Delta_2}{\Delta_1 + \Delta_2} > 0$	$f_1 = \frac{\Delta_2}{\Delta_1 + \Delta_2} < 1$
$\Delta_1 > -\Delta_2$	$\frac{\Delta_1}{\Delta_2} > 0$
$r_1 + r_2 < 2$	Either $r_1 < 1$ and $r_2 < 1$ or $r_1 > 1$ and $r_2 > 1$

The requirement on the left rules out the case $\{r_1 > 1, r_2 > 1\}$. Since by definition r_1 and r_2 are positive, the requirement for the existence of an azeotrope is

$$\left.\begin{matrix} 1 > r_1 > 0 \\ 1 > r_2 > 0 \end{matrix}\right\}$$

Numerical Results

To predict a monomer block length only three experimental quantities need be known, the monomer reactivity ratios of self-coupling to cross-coupling, r_1 and r_2, and the initial monomer composition, A_1^0 and A_2^0 or f_1^0. With these quantities the copolymer equation (eq 8) is solved for f_1 at various extents of conversion. From f_1 and the corresponding extent of conversion ($p = 1 - (A/A^0)$), values for C_1 and C_2 may be obtained from eq 10 and used to calculate $\overline{X}_1$ and $\overline{X}_1'$. The plot illustrating the maxima that $\overline{X}_1$ and $\overline{X}_1'$ pass through with increasing extent of conversion for two sets of reactivity ratios is presented in Figure 3. As the difference between reactivity ratios becomes small, $\overline{X}_{1\,max}$ and $\overline{X}_1'_{max}$ become smaller and occur at a later extent of conversion. The quantities $\overline{X}_{1\,max}$ and $\overline{X}_1'_{max}$ are obtained by two iterations. First the copolymer equation is solved by iteration for f_1 corresponding to a given extent of conversion. Then the particular extent of conversion corresponding to a maximum value of $\overline{X}_1$ or $\overline{X}_1'$ is iterated. Table I presents numerical results for assumed values of r_1, r_2, A_1^0, and A_2^0. In each case the agreement between $\overline{X}_{1\,max}$ and $\overline{X}_1'_{max}$ and the corresponding extents of conversion, p_{max} and p'_{max}, is found to be very good except where the difference between r_1 and r_2 is small. Also $\overline{X}_{1\,max}$ is always slightly greater than or equal to $\overline{X}_1'_{max}$, and the corresponding p_{max} is always slightly greater than or equal to p'_{max}. However, in the absence of experimental results or having performed the calculation without employing the approximation $r_1 \gg r_2$, agreement of a calculated $\overline{X}_{1\,max}$ with the actual $\overline{X}_1$ cannot be assessed.

It would intuitively be expected that the particular extent of conversion where the calculated monomer block length passes through a maximum would correspond closely to a point where both monomers are entering the copolymer at an equal rate ($F_1 = F_2$ or $dA_1 = dA_2$). Under this condition eq 4 is equal to unity. After substituting expressions of f_1 for A_1 and A_2 and solving eq 4 for f_1, the following result is obtained.

$$f_{1\,F_1=F_2} = \frac{r_2^{1/2}}{r_1^{1/2} + r_2^{1/2}} \tag{24}$$

When the corresponding extent of conversion is obtained from the copolymer equation and used to calculate $\overline{X}_1$ and $\overline{X}_1'$, the agreement with $\overline{X}_{1\,max}$ and $\overline{X}_1'_{max}$ is quite striking (see Table I). With the exception of high monomer 1 compositions (f_1^0

≥ 0.9), the agreement with $\overline{X}_{1\,max}'$ is exact to three figures and the value for $\overline{X}_{1\,F_1=F_2}$ is close to $\overline{X}_{1\,max}$ and always between $\overline{X}_{1\,max}$ and $\overline{X}_{1\,max}'$. Since this calculation requires no iterations, the necessary calculating power is reduced from a computer to a desk calculator.

Finally, it was stated that when the reactivity ratios are both between 0 and 1, an azeotrope would exist. In Figure 4 a plot of F_1 against f_1 shows this to be the case.

In summary, for a step copolymer system where structurally identical comonomer functional groups having different reactivities couple to form polymer, a block copolymer is predicted. Once the reactivity ratios of self-coupling to cross-coupling are determined, comonomer block lengths may be calculated and are found to increase with an increasing difference between the reactivity ratios. The calculation can be greatly simplified by assuming that the extent of conversion where the comonomers are entering the polymer at an equal rate corresponds to the point where a sufficient but not excessive quantity of the less reactive monomer has coupled to terminate the oligomeric blocks of the more reactive monomer.

References and Notes

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Number of Contacts between Distant Segments of a Polymer Chain. A Solution of the Problem of Self-Avoiding Random Walk

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ABSTRACT: A new algebraic method is proposed for the rigorous study of the self-avoiding random-walk problem. This method allows the separate calculation of the number of configurations of n segments with fixed values of the number of contacts between neighboring segments and between distant segments.

A flexible chain that can assume all possible positions on a lattice without intersection of segments (self-avoiding random walk) has been used for a long time as a model of polymers in highly dilute solutions.

The present paper reinvestigates this problem in order to explain the experimentally observed difference of solubility between random and sequential copolymers of equal quantitative and qualitative composition. It seems intuitively evident that this difference is due to the nature of contact between distant segments of the chain.

A first method, based substantially on the form of the configurations up to a length of chain $n = 11$, has given predictions in good qualitative agreement with experience for the thermodynamic properties of copolymers in solution.[1,2]

The author has then looked for an algebraic method to determine the number of configurations with x primary contacts between nearby segments of a chain (segments p and $p + 3$), u primary contacts between distant segments (segments p and $p + i$, with $i > 3$), and y secondary contacts between nearby segments (segments p and $p + 2$). This number is denoted by the symbol $[N]_n^{u,x,y}$.

The calculation is made for cubic lattices of two and three dimensions. A primary contact takes place if two segments of the chain are on sites whose distance is the lattice parameter; a secondary contact happens if they are on two sites whose distance is the diagonal of the lattice cell.

The main basic ideas of this method were described in a previous article.[3] Recall that the method consists of decomposing the configurations with $x \neq 0$ into subchains with $x = 0$ primary contacts between neighboring segments. We have then derived a recursion equation which determines the number of chains with $x = 0$ for any n. y is considered as a variable. The form of this equation allows the recursive calculation, on the one hand, of the number of configurations to eliminate because they would correspond to the crossing of a site already occupied by a chain (excluded volume) and, on the other hand, of the number of primary or secondary contacts between distant segments, from the knowledge of these values for the chains with $n - 1$ to y, $n - 1$ to $y - 1$, and $n - 2$ to $y - 1$ secondary contacts between neighboring segments on the chain. These values $[N]_n^{x=0,y}$ are used for the subchains that occur in the computation of the configurations with $x \neq 0$. These values are thus already corrected for the excluded volume corresponding to the crossing, by the subchain, of a site already occupied by one of its segments. The number of contacts between distant segments which this subchain has within itself is also known. There remains the evaluation of the volume excluded due to the crossing by a subchain of a site already occupied by a segment of another subchain and the calculation of primary contacts that different subchains can have with each other. The elimination of the configurations corresponding to this volume excluded and the calculation of the number of configurations having primary contacts are done by means of recursive equations.[3] We shall recall further the principle of this type of calculation. We have tried and we think we have succeeded in obtaining accurate values for the number of configurations, none being included more than once or being wrongly excluded.

The numerical results of our equations for a cubic planar lattice were compared with those obtained by Professor Durup[8] of Orsay by exact computer enumeration up to $n = 13$, thus a method quite different from ours. He especially counted contacts between distant segments. Our results are identical.