from those of collagenous fibers with respect to the exhibition of large spacings transverse to the fiber axis. With the former group the pronounced evidences of lateral spacings indicate that the denser layers distributed along the fibrils (every 145 Å. in the case of clam muscle) in turn are composed of denser and less dense concentrations of electrons distributed transversely in each layer. In such instances two-dimensional (corresponding to radially symmetrical fibrils) or three-dimensional density distributions will be required to explain the diffraction effects, whereas for collagen the one-dimensional longitudinal plots are all that present diffraction data require.

Summary

Studies of the X-ray diffractions exhibited at small angles by feather and porcupine quill keratins and by clam muscle fibers have disclosed for these materials two principal kinds of large spacing: one represents the repeated pattern along the fiber axis and the other is a prominent spacing transverse thereto. The measured values are, respectively, 95 and 34 Å. for feather, 198 and 83 Å. for porcupine quill, and about 725 and 325 Å. for clam muscle. The observation that silk fibers lack discrete small-angle diffractions has been confirmed.

The keratin and clam muscle fibers exhibit in their wide-angle diffractions phenomena which suggest that the diffuse short-spacing spots are in reality clusters of higher diffraction orders of the large fundamental structural pattern. Fibers whose wide-angle patterns at low angular resolution are almost identical (porcupine quill and clam muscle) may differ considerably in their diffraction effects at small angles, hence also in their wide-angle fine structure.

A comparison of existing data regarding the complete diffraction patterns of protein fibers indicates that as chemical complexity increases wide-angle patterns deteriorate and the structures responsible for low-angle diffraction increase in size. It is tentatively suggested that the complex fibrous proteins possess local regions of two or more kinds differing in the degree of crystalline or quasi-crystalline order. Only a fraction of the better ordered regions contribute predominantly to the wide-angle diffractions, while larger structural patterns, embracing a number of the smaller regions of all kinds, are in evidence in the small-angle systems of interferences.

Astbury's keratin–myosin class of fibrous proteins is recognizable at small diffraction angles by the following general characteristics: the possession of both longitudinal (fiber-axis) and lateral (transverse) large spacings, and the predominant intensification of meridional diffraction orders higher than the first (in contrast to collagenous fibers which possess a distinctively different wide-angle pattern, lack a definite lateral macroperiod, and intensify the first meridional order most strongly).

The remarkable clam muscle diffractions at small angles exhibit a striking near repetition of layer lines in index cycles of five, the meridional orders whose indices are multiples of five being most intense (through the fortieth order). This is evidence for the location of dense layers of matter (relative to background) every 145 Å. along the muscle fibrils. Prominent row lines to either side of the meridian suggest that these layers in turn possess structure laterally.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Copolymers. II[1]

BY FREDERICK T. WALL

When dealing with the structure of ordinary polymers (those obtained from a single kind of monomer unit), one does not usually encounter any serious problems with respect to chemical composition, except possibly from the effect of end groups. In the case of copolymers, however, the question of composition becomes one of great importance. This is true not merely because the average monomer ratio in a copolymer can be varied, but also because different polymer molecules obtained from the same batch can have quite different compositions for various reasons to be set forth later.

A simple quantitative theory which recognized this possibility was given earlier by the author.[1] The important point is that when a mixture of monomers undergoes polymerization, the polymer formed at any instant does not necessarily have the same composition as the monomer mixture from which it is derived. Accordingly if one starts with a given monomer charge and carries the polymerization to completion, the resulting copolymer will in general exhibit substantial heterogeneities in composition.

The theory originally advanced[1] has not been found to be entirely satisfactory on a quantitative basis although the work of Marvel and coworkers[2] has given qualitative support to the theory. Moreover, certain patents have been issued[3] which indicate that cognizance has been

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(1) For the first paper of this series see F. T. Wall, THIS JOURNAL, **63**, 1862 (1941).

(2) Marvel, Jones, Mastin and Schertz, *ibid.*, **64**, 2356 (1942); Marvel and Schertz, *ibid.*, **65**, 2054 (1943).

(3) Finkentscher and Hengstenberg, U. S. Patent 2,100,900 (1937).

taken of the qualitative factors involved. To bring the theory into better quantitative agreement with observation certain improvements need to be made. Some improvements have been considered and carried out by Mayo and Lewis[4] as well as by Jenckel.[5] It is the purpose of this paper to treat the problem in more detail and to formulate the different kinds of copolymers that can be expected.

Recently Alfrey and Goldfinger[6] dealt with the mechanism of copolymerization and obtained results consistent with those reported here. Simha and Branson[7] also worked on the theory of chain copolymerization reactions employing postulates similar to those of Alfrey and Goldfinger and of the present author. Although the various theories have started out quite alike, the directions of emphasis have varied considerably. In this paper there is predicted the existence of "azeotropic" copolymers which can have considerable importance in practice.

Simple Theory.—Letting X and Y represent the amounts of each of two kinds of monomers present in a reaction mixture, it was assumed in the theory mentioned above[1] that each monomer disappeared in accordance with first order kinetics.

$$\mathrm{d}X/\mathrm{d}t = -kX \qquad (1)$$

$$\mathrm{d}Y/\mathrm{d}t = -k'Y \qquad (2)$$

Taking the quotient of equations (1) and (2) there was obtained

$$\frac{\mathrm{d}X}{\mathrm{d}Y} = \frac{kX}{k'Y} = \alpha\frac{X}{Y} \qquad (3)$$

where α is the ratio of the specific reaction rate constants. If α is different from unity, it follows from (3) that the composition of polymer forming at any instant will not be the same as that of the reaction mixture. Although equation (3) does not quantitatively describe the behavior of many systems, it can nevertheless be regarded as an ideal from which deviations may be observed. Equation (3) is in fact identical with the differential equation describing the boiling of a mixture of liquids which obey Raoult's law. Hence equation (3) may be considered the copolymerization counterpart to Raoult's law of vapor pressures.

Improved Theory.—Assuming a free radical mechanism of chain growth, Norrish and Brookman[8] recognized that four different growth reactions are possible during copolymerization. These reactions are

$$\mathrm{R_x} + \mathrm{X} \xrightarrow{k_1} \mathrm{R_x}$$

$$\mathrm{R_y} + \mathrm{X} \xrightarrow{k_2} \mathrm{R_x}$$

$$\mathrm{R_x} + \mathrm{Y} \xrightarrow{k_3} \mathrm{R_y}$$

$$\mathrm{R_y} + \mathrm{Y} \xrightarrow{k_4} \mathrm{R_y}$$

where X and Y represent the two kinds of monomers and $\mathrm{R_x}$ and $\mathrm{R_y}$ represent the two kinds of free radicals which can be characterized by the last added monomer units. Assigning specific reaction rate constants k_1, k_2, k_3 and k_4 to the reactions and letting the symbols also represent amounts of material (in moles), then the rate equations can be written

$$\mathrm{d}X/\mathrm{d}t = -k_1R_xX - k_2R_yX \qquad (4)$$

$$\mathrm{d}Y/\mathrm{d}t = -k_3R_xY - k_4R_yY \qquad (5)$$

$$\mathrm{d}R_x/\mathrm{d}t = -\mathrm{d}R_y/\mathrm{d}t = k_2R_yX - k_3R_xY \qquad (6)$$

Equations (6) obviously are not exact since no account has been taken of radical concentration changes due to catalyst activity, chain transfer and chain termination processes. Nevertheless the most important factors contributing to interchange of radical types are given by (6), from which it is seen that

$$R_x + R_y = R \text{ (a constant)} \qquad (7)$$

Assuming further that a steady state with respect to free radicals is soon attained, there can be written as a first approximation

$$\mathrm{d}R_x/\mathrm{d}t = 0 = k_2R_yX - k_3R_xY \qquad (8)$$

From (8) in conjunction with (7) it is seen that

$$R_x = \frac{k_2XR}{k_2X + k_3Y} \qquad (9a)$$

$$R_y = \frac{k_3YR}{k_2X + k_3Y} \qquad (9b)$$

Although equations (9) are not in general exact, it can be shown that they are a good approximation. Differentiating the first approximation to R_x with respect to t and eliminating all the derivatives by use of equations (4), (5) and (6), a second approximation to R_x can be obtained in the form

$$R_x = \frac{k_2XR}{k_2X + k_3Y}\{1 + \mathrm{O}(R/X)\} \qquad (10)$$

In obtaining (10) it is assumed that all the k's are of the same order of magnitude and that Y is of the same order as X. Since the total radical concentration is very small compared to the monomer concentration under ordinary conditions, it follows that $\mathrm{O}(R/X) \ll 1$; hence the second approximation is only slightly different from the first. The third approximation would involve correction factors with order $\mathrm{O}(R^2/X^2)$, etc.

Further evidence for the usefulness of equations (9) is provided by the following considerations. Rearranging (6) and making use of (7) it is seen that

$$\frac{\mathrm{d}R_x}{\mathrm{d}t} = (k_2X + k_3Y)\left\{\frac{k_2XR}{k_2X + k_3Y} - R_x\right\} \qquad (11)$$

Hence, if

$$R_x < \frac{k_2XR}{k_2X + k_3Y}, \text{ then } \mathrm{d}R_x/\mathrm{d}t > 0$$

and *vice versa*. This means that if R_x is smaller than assumed, it will tend to increase, and if R_x is too large, it will tend to decrease. This fact, though plausible, is not obvious since it is conceivable that the differential equations could

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[4] Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

[5] Jenckel, *Z. physik. Chem.*, **190A**, 24 (1941).

[6] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[7] Simha and Branson, *ibid.*, **12**, 253 (1944).

[8] Norrish and Brookman, *Proc. Roy. Soc.* (London), **A171**, 147 (1939).

give rise to an instability in which there is divergence from rather than convergence toward certain values.

Relative Polymerization Velocities.—Introducing expressions (9) into (4) and (5), one obtains

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{-k_1k_2RX^2 - k_2k_3RXY}{k_2X + k_3Y} \tag{12a}$$

and

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \frac{-k_2k_3RXY - k_3k_4RY^2}{k_2X + k_3Y} \tag{12b}$$

Let us now define relative reaction velocities V_x and V_y by means of the equations

$$V_x = -\frac{1}{R(X + Y)}\frac{\mathrm{d}X}{\mathrm{d}t} \tag{13a}$$

$$V_y = -\frac{1}{R(X + Y)}\frac{\mathrm{d}Y}{\mathrm{d}t} \tag{13b}$$

Equations (13) put the velocities on a fractional basis, the fractions being determined in relation to the total amount of monomer, $X + Y$. Moreover, equations (13) give these velocities per unit free radical concentration, thus removing (in part at least) the dependence on amount of catalyst. From (12) and (13) it follows that

$$V_x = k_2x\left\{\frac{k_1x + k_3y}{k_2x + k_3y}\right\} \tag{14a}$$

and

$$V_y = k_3y\left\{\frac{k_2x + k_4y}{k_2x + k_3y}\right\} \tag{14b}$$

where

$$x = \frac{X}{X + Y} \text{ and } y = \frac{Y}{X + Y}$$

so that $x + y = 1$.[9] It will be noted that equations (14) give the velocities of polymerization only insofar as they depend upon the specific reaction rate constants and upon the composition of the monomer mixture.

The quantities V_x and V_y can be likened somewhat to the vapor pressures of a pair of liquids in a binary mixture at a given temperature. In particular if

$$k_1 = k_2 \text{ and } k_3 = k_4 \tag{15}$$

then the counterpart of Raoult's law will be valid for

$$V_x = k_1x \tag{16}$$

and

$$V_y = k_4y$$

Under these conditions equation (3) of the elementary theory will apply with $\alpha = k_1/k_4$. If conditions (15) apply, the α concept and equations (16) are correct without making the approximation of equation (8).

A quantity of considerable importance in copolymer studies is the composition of the copolymer in relation to that of the monomer from which it is derived. If x' is the mole fraction of X monomer units in the polymer, then

$$\begin{aligned} x' &= \frac{\mathrm{d}X}{\mathrm{d}X + \mathrm{d}Y} = \frac{V_x}{V_x + V_y} \\ &= \frac{k_1k_2x^2 + k_2k_3xy}{k_1k_2x^2 + 2k_2k_3xy + k_3k_4y^2} \end{aligned} \tag{17}$$

Equation (17) can be rewritten

$$x' = \frac{\sigma x^2 + xy}{\sigma x^2 + 2xy + \rho y^2} \tag{18}$$

where

$$\sigma = k_1/k_3 \text{ and } \rho = k_4/k_2. \tag{19}$$

It will be observed that the dependence of x' on x involves only two ratios of reaction rate constants, here denoted by σ and ρ.[10] Hence we can conclude that the composition distribution functions to be expected for various copolymerization systems will depend only on σ and ρ, even though the velocities themselves involve the values of all the constants.

In general x' will not equal x; in order that they be equal for all values of x it is necessary and sufficient that

$$\sigma = \rho = 1 \tag{20}$$

This conclusion. like that of (16), does not depend upon the approximation (8). For if (20) is true, then it can be shown directly from (4) and (5) that

$$\frac{\mathrm{d}X}{\mathrm{d}Y} = \frac{X}{Y}, \text{ or } x' = x \tag{21}$$

A system which fulfills (20) can accordingly be regarded as forming a perfectly random copolymer, the significance of which has been previously considered.[1]

"Azeotropic" Copolymers.—Although the composition of a copolymer which is forming at any time is generally different from that of the monomer mixture, there can be particular compositions for which (21) holds even though $\rho \neq \sigma \neq 1$. Setting $x' = x$ in equation (18), the following three roots are found

$$x = 0 \tag{22a}$$

$$x = 1 \tag{22b}$$

$$x = \frac{\rho - 1}{\rho - 1 + \sigma - 1} \tag{22c}$$

The solutions $x = 0$ and $x = 1$ are trivial since they represent the two pure monomers, but the third root can have a real significance. The third solution has a new physical meaning, of course, only if $0 < x < 1$, which requires that

$$\rho > 1 \text{ and } \sigma > 1 \text{ simultaneously}$$

or

$$\rho < 1 \text{ and } \sigma < 1 \text{ simultaneously.}$$

Both possibilities can be incorporated into one statement which is

$$(\rho - 1)(\sigma - 1) > 0 \tag{23}$$

When the composition of the monomer is given by (22c), then the system forms a "constant polymerizing mixture" in analogy to constant boiling liquids. It will be seen later that when

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[9] The use of both x and y in equations (14) and subsequent equations is to emphasize symmetry of form although one of the two quantities can always be eliminated since $x + y = 1$.

[10] σ and ρ are identical with β and $1/\alpha$ of Alfrey and Goldfinger[6] and with σ and μ of Mayo and Lewis.[7]

ρ and σ are both greater than unity, the character of the "azeotropic copolymer" is quite different from that obtained when ρ and σ are both less than unity even if the monomer compositions are the same. This difference manifests itself in the intramolecular arrangement and distribution of monomer units.

Graphs of Velocity–Composition Functions.—In excellent analogy to the vapor pressure–composition diagrams which are plotted for liquid mixtures, it is convenient and instructive to plot relative polymerization velocities against composition. In the series of Figs. 1–8 are plotted V_x, V_y and $V = V_x + V_y$ as functions of x together with the corresponding x' values. The ordinate scales are perfectly arbitrary since the velocities are just relative quantities per unit free-radical concentration. In Fig. 1 is plotted a system for which $k_1:k_2:k_3:k_4 = 1:1:2:2$, thus satisfying equation (15). For this example, V_x, V_y and V are linear functions of x, but the polymer composition line is not linear. Taking any point M (for monomer) on the V curve, one can obtain the composition of polymer being formed by passing a horizontal line to a point P on the polymer curve and noting the corresponding abscissa (x') value. It will be observed that for this first example the polymer is relatively richer in constituent Y than is the monomer mixture, this being a consequence of the fact that Y tends to polymerize faster than X for all compositions. (It is assumed, of course, that equations (9) hold.) As the polymerization proceeds, the monomer residue becomes richer and richer in X until at the very end the last portion of the mixture to polymerize will approach pure X.

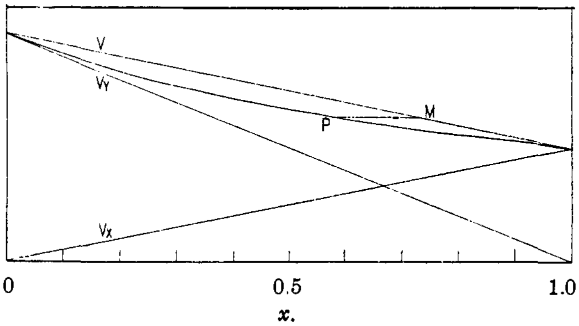

Fig. 1.—Velocity–composition diagram for ideal copolymerization system: $k_1:k_2:k_3:k_4 = 1:1:2:2$.

Figure 2 is illustrative of the situation that obtains when $\rho = \sigma = 1$ with $k_1:k_2 = 1:2$ (see equations (20) and (21)). The system is not ideal, taking (15) as the condition for ideality, but it does have the remarkable property that the polymer forming at any instant has the same composition as the monomer. This situation is unlikely to be encountered exactly in practice, but it may be approximated by some systems.

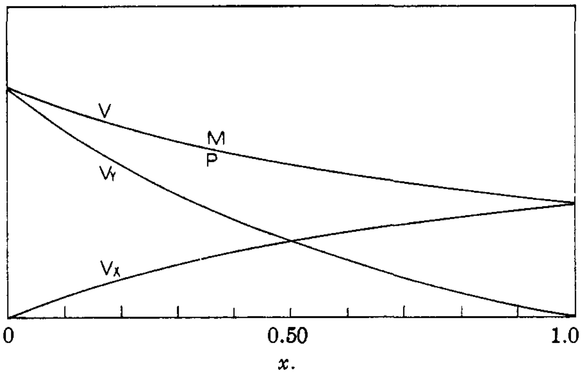

Fig. 2.—Velocity–composition diagram for copolymerization system for which $x = x'$: $k_1:k_2:k_3:k_4 = 1:2:1:2$.

Figure 3 illustrates another type of non-ideal polymerization which is of particular interest. For this case $10k_1 = k_2 = k_3 = 10k_4$. This system gives rise to a one to one azeotropic copolymer as is clear from the fact that the P and M curves meet at $x = 0.5$. Since k_2 and k_3 are considerably larger than k_1 and k_4, there is a definite tendency for the copolymer to have much alternation of monomer units to give molecules resembling -X-Y-X-Y-X-Y-, etc. Whenever the monomer composition is not 1:1, the polymer will have a composition nearer to that of the azeotrope than the monomer mixture. Accordingly the monomer residue approaches pure X or pure Y as the polymerization proceeds.

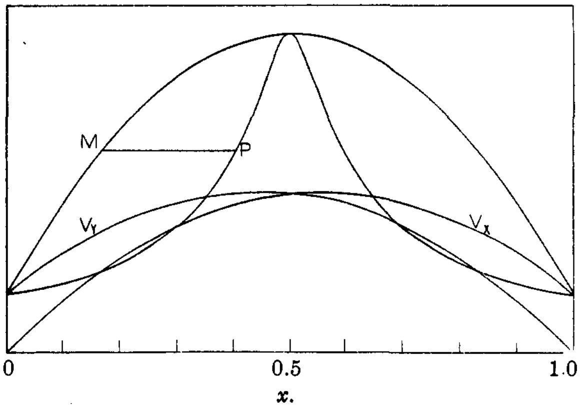

Fig. 3.—Velocity–composition diagram for copolymerization system with azeotrope at $x = 0.5$: $k_1:k_2:k_3:k_4 = 1:10:10:1$.

In Fig. 4, the numerical values of example 3 are interchanged to give a system in which $k_1 = 10k_2 = 10k_3 = k_4$. Here the polymer tends to have molecules with little alternation of monomer units so the chains will have relatively long sections of X's or of Y's in a row. Here too the system has a constant polymerizing mixture corresponding to $x = 0.5$, but that polymer will be quite different from the azeotrope of example 3. If the monomer composition is not 1:1, then the polymer tends to have a composition farther away from 1:1 than the monomer. Hence with increasing polymerization, the monomer residue

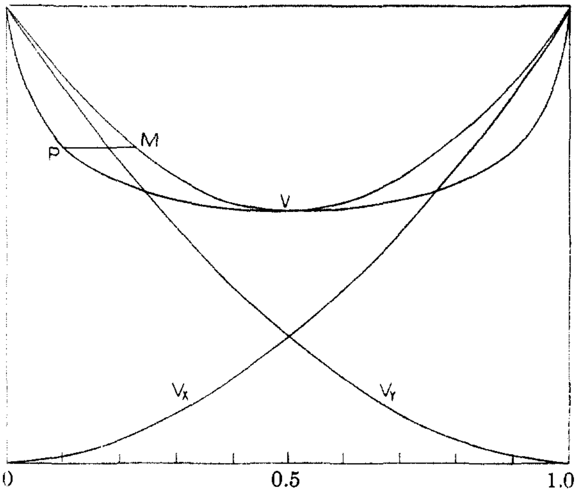

Fig. 4.—Velocity-composition diagram for copolymerization system with azeotrope at $x = 0.5$: $k_1:k_2:k_3:k_4 = 10:1:1:10$.

approaches nearer and nearer the constant polymerizing ratio.

Figure 5 represents a system for which $k_1:k_2:k_3:k_4 = 1:20:2:10$. This example can be regarded as being somewhat intermediate between those of Figs. 3 and 4; it is closer to the former, however, with respect to qualitative composition relationships. The total velocity curve exhibits no maximum or minimum, but the P and M curves nevertheless cross at $x = 0.5$. Once again the 1:1 mixture constitutes a constant polymerizing mixture. It must not be supposed from the three last examples that the only azeotropic copolymers are of 1:1 composition. Any ratio might exist for such copolymers and innumerable examples might be constructed making use of equation (22c) to fix the composition.

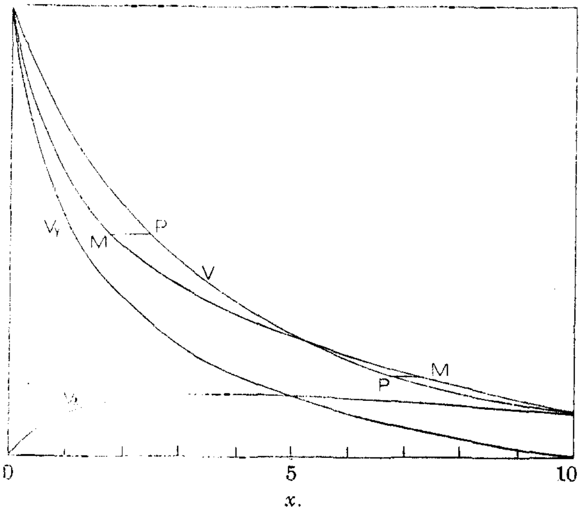

Fig. 5.—Velocity-composition diagram for copolymerization system with azeotrope at $x = 0.5$: $k_1:k_2:k_3:k_4 = 1:20:2:10$.

An interesting set of examples arises when one or more of the specific reaction rate constants is equal to zero. If k_2 or k_3 (but not both) is equal to zero, then one of the monomers will not polymerize according to the approximate equations. For example if $k_2 = 0$, then no R_y radicals can ever be converted into the R_x type although R_x can be turned into R_y. It follows that ultimately there will be no R_x radicals with the result that X cannot take part in the polymerization until all of Y is used up. This statement is not exact since no account has been taken of chain initiation or chain transfer processes which might give rise to new radicals with which X can react. Nevertheless the approximate statement is a good one since chain growth proceeds much faster than chain transfer or chain initiation.

More interesting is the situation when k_1 or k_4 equals zero. If $k_1 = 0$, then X cannot polymerize with itself and no copolymer of X and Y can have a composition with x greater than 0.5. Figure 6 provides an example for such a system in which $k_1:k_2:k_3:k_4 = 0:10:10:1$. The left-hand side looks much like that of Fig. 3, but the right-hand side shows a marked difference. Here as in example 3 there is a marked tendency for alternations in the polymer chain, but under no circumstances can there be two or more consecutive X's in a polymer molecule. The "azeotrope" of Fig. 6 corresponds to $x = 0.474$.

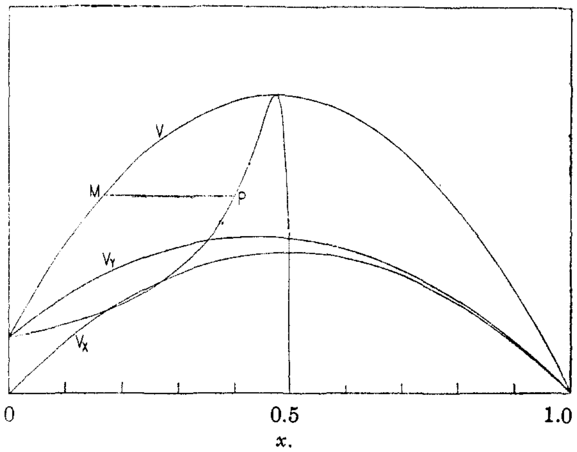

Fig. 6.—Velocity-composition diagram for copolymerization system with $\sigma = 0$ and with azeotrope at $x = 0.474$: $k_1:k_2:k_3:k_4 = 0:10:10:1$.

When $k_1:k_2:k_3:k_4 = 0:10:2:1$, one obtains the velocity composition diagram of Fig. 7, which also has a constant polymerizing mixture at $x = 0.474$. Although the monomer (M) and polymer (P) curves cross twice, only the crossing for which P and M coalesce (that is to say when $x = x'$) has the constant polymerizing significance. Another illustration is given in Fig. 8 which was calculated assuming $k_1:k_2:k_3:k_4 = 0:10:1:2$. In

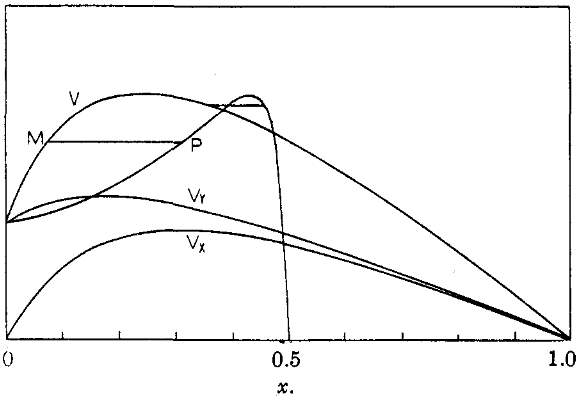

Fig. 7.—Velocity–composition diagram for copolymerization system with $\sigma = 0$ and with azeotrope at $x = 0.474$: $k_1:k_2:k_3:k_4 = 0:10:2:1$.

this example the constant polymerizing mixture has a composition $x = 0.444$. For the last three examples the analogy to vapor pressures does not hold completely.

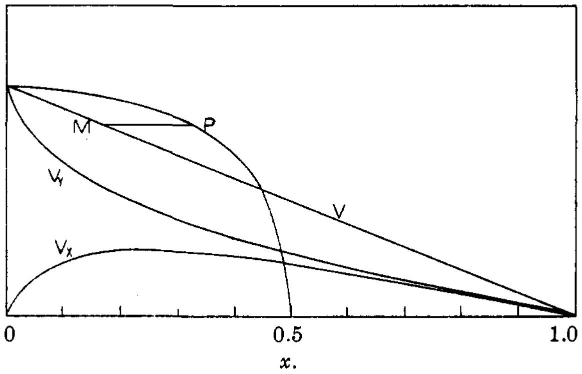

Fig. 8.—Velocity–composition diagram for copolymerization system with $\sigma = 0$ and with azeotrope at $x = 0.444$: $k_1:k_2:k_3:k_4 = 0:10:1:2$.

Another means for graphically representing some of the ideas already discussed is provided by Figs. 9 and 10. In these figures x', the composition of polymer, is plotted against x, the composition of monomer from which the polymer is being obtained. As mentioned earlier, the dependence of x' upon x involves only ρ and σ and not any other ratios of the specific reaction rate constants. Figure 9 deals with some cases where $\rho = \sigma$. The examples of Figs. 3, 4 and 5 correspond to curves labeled $\rho = 0.1$, 10 and 0.5 of Fig. 9. If $\rho = \sigma = 1$, then $x' = x$ for all values of x. It will be observed that all the curves of Fig. 9 pass through the point $x' = x = 0.5$ since that is a constant polymerizing point for these systems. Although curves for $\rho = 0.1$ and $\rho = 10$ appear somewhat symmetrical to each other, the polymers are quite different in character.

Figure 10 provides a similar plot for cases where $\sigma = 0$ (or $k_1 = 0$). The earlier examples of Figs. 6 and 7 correspond to $\rho = 0.1$ and Fig. 8 has its counterpart in the curve marked $\rho = 0.2$. When $\rho \geqslant 1$ the polymer can never be richer in X than the monomer. Of course, when $\sigma = 0$, x' can never exceed 0.5.

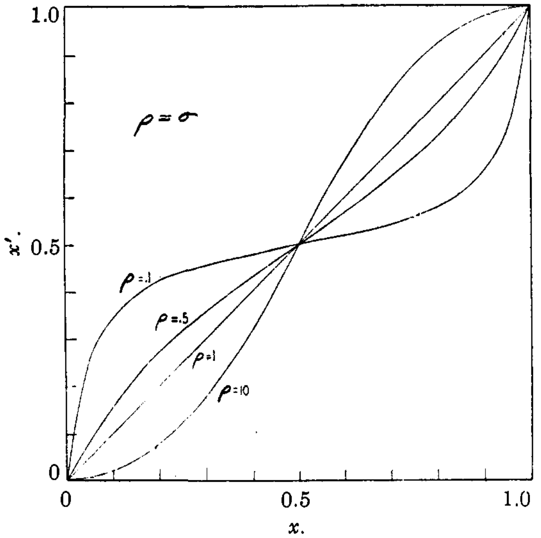

Fig. 9.—Graphs showing dependence of polymer composition (x') upon monomer composition (x) for systems with $\sigma = \rho$.

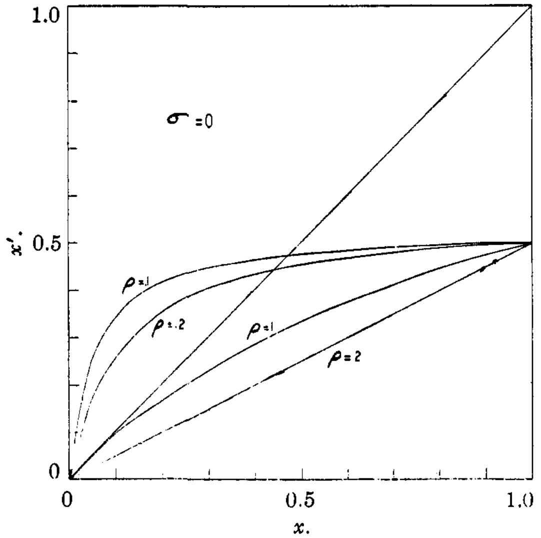

Fig. 10.—Graphs showing dependence of polymer composition (x') upon monomer composition (x) for systems with $\sigma = 0$.

Intramolecular Distributions.—It was indicated earlier that two or more azeotropic copolymers of the same composition can have quite different internal characteristics depending upon the actual values of ρ and σ. The examples of Figs. 3, 4 and 5 serve to demonstrate this proposition. We shall now consider quantitatively the effect of different values of ρ and σ on the distribution of monomer units within a given polymer chain.

Within a given polymer chain, there are four kinds of monomer to monomer linkages, namely: X–X, X–Y, Y–X, and Y–Y. (X–Y and Y–X are, of course, equivalent, but they are considered separately here since they represent two different kinds of growth steps.) From equations (14) it is seen that the relative probabilities of attaining such linkages are $k_1k_2x^2$, k_2k_3xy, k_3k_2yx and $k_3k_4y^2$, respectively. Denoting the fractions of the total bonds which are of each variety by $f_{\mathrm{x-x}}$, $f_{\mathrm{x-y}}$, $f_{\mathrm{y-x}}$ and $f_{\mathrm{y-y}}$, it is seen that

$$f_{\mathrm{x-x}} = \frac{k_1k_2x^2}{k_1k_2x^2 + 2k_2k_3xy + k_3k_4y^2} = \frac{\sigma x^2}{\sigma x^2 + 2xy + \rho y^2} \tag{24a}$$

$$f_{\mathrm{x-y}} = f_{\mathrm{y-x}} = \frac{k_2k_3xy}{k_1k_2x^2 + 2k_2k_3xy + k_3k_4y^2} = \frac{xy}{\sigma x^2 + 2xy + \rho y^2} \tag{24b}$$

$$f_{\mathrm{y-y}} = \frac{k_3k_4y^2}{k_1k_2x^2 + 2k_2k_3xy + k_3k_4y^2} = \frac{\rho y^2}{\sigma x^2 + 2xy + \rho y^2} \tag{24c}$$

For a non-azeotropic polymerization, x is constantly changing so of course the intramolecular distribution of linkages will vary with the different stages of polymerization. If the polymerization is azeotropic, however, then from equation (22c) it follows that

$${}_{\mathrm{x-x}} = \frac{\sigma(\rho - 1)^2}{\sigma(\rho - 1)^2 + 2(\sigma - 1)(\rho - 1) + \rho(\sigma - 1)^2} \tag{25a}$$

$$f_{\mathrm{x-y}} = f_{\mathrm{y-x}} = \frac{(\sigma - 1)(\rho - 1)}{\sigma(\rho - 1)^2 + 2(\sigma - 1)(\rho - 1) + \rho(\sigma - 1)^2} \tag{25b}$$

$$f_{\mathrm{y-y}} = \frac{\rho(\sigma - 1)^2}{\sigma(\rho - 1)^2 + 2(\sigma - 1)(\rho - 1) + \rho(\sigma - 1)^2} \tag{25c}$$

It should be emphasized that equations (25) are valid only for constant polymerizing mixtures.

Other quantities of interest are the average lengths of groups of X's or groups of Y's in a copolymer. By a group we shall mean a series of monomer units of a given kind bounded at each end by monomer units of the other kind, and by the length of a group we shall mean the number of monomer units in the group. Letting $\bar{L}_{\mathrm{x}}$ and $\bar{L}_{\mathrm{y}}$ be the average lengths of such groups, it is seen that

$$\bar{L}_{\mathrm{x}} = \frac{f_{\mathrm{x-x}} + f_{\mathrm{x-y}}}{f_{\mathrm{x-y}}} \tag{26a}$$

$$\bar{L}_{\mathrm{y}} = \frac{f_{\mathrm{y-y}} + f_{\mathrm{y-x}}}{f_{\mathrm{y-x}}} \tag{26b}$$

The basis for the above formulas is that $f_{\mathrm{x-x}} + f_{\mathrm{x-y}}$ is proportional to the total number of X's in the chains under consideration and $f_{\mathrm{x-y}}$ is proportional to the number of groups of X's. Hence the quotients in equations (26) represent the averages specified.

If the copolymers are azeotropic, then combining (26) and (25) it is found that

$$\bar{L}_{\mathrm{x}} = \frac{\sigma\rho - 1}{\sigma - 1} \tag{27a}$$

$$\bar{L}_{\mathrm{y}} = \frac{\sigma\rho - 1}{\rho - 1} \tag{27b}$$

In Table I are summarized numerical values of the f's and $\bar{L}$'s for various values of ρ and σ.

TABLE I

INTRAMOLECULAR DISTRIBUTION OF BONDS FOR CONSTANT POLYMERIZING MIXTURES

Parameters			Bond types				Average group lengths	
ρ	σ	x	X–X	X–Y	Y–X	Y–Y	$\bar{L}_{\mathrm{x}}$	$\bar{L}_{\mathrm{y}}$
0.1	0.1	0.5	4.5%	45.5%	45.5%	4.5%	1.1	1.1
.5	.5	.5	16.7	33.3	33.3	16.7	1.5	1.5
1[a]	1[a]	.5[a]	25.0	25.0	25.0	25.0	2.0	2.0
5	5	.5	41.7	8.3	8.3	41.7	6.0	6.0
10	10	.5	45.5	4.5	4.5	45.5	11.0	11.0
.1	0	.474	0	47.4	47.4	5.3	1.0	1.11
.2	0	.444	0	44.4	44.4	11.1	1.0	1.25
.5	0	.333	0	33.3	33.3	33.3	1.0	2.00

[a] Not azeotropic, but perfectly random. (Assume x = 0.5.)

It will be observed from Table I that azeotropes of the same composition have quite different intramolecular properties. The first five rows of the table all correspond to polymers of the same composition, that is with $x = 0.5$. Yet when $\rho = \sigma = 0.1$ only 4.5% of the bonds are of the X–X variety whereas when $\rho = \sigma = 10$, 45.5% of the linkages are of the X–X type. That there is considerable alternation of monomer type when $\rho = \sigma = 0.1$ is further demonstrated by the fact that the average group lengths are only 1.1. On the other hand when $\rho = \sigma = 10$, the average group lengths are equal to 11, suggesting that such a copolymer will tend to resemble an intimate mixture of the two separate polymers. When $\sigma = 0$, there can be no X–X bonds and of course $\bar{L}_{\mathrm{x}} = 1.0$.

Relationship of Theory to Known Copolymers.[11]—Up to the present time, little quantitative work has been done which would provide a check on the foregoing theory. Nevertheless, there is sufficient qualitative evidence available to support the general validity of the concepts set forth. Work by Marvel and co-workers[2] designed to test the simple theory (equation 3) did not give conclusive results. Among other things they worked on vinyl chloride–vinyl acetate systems and, although substantial differences in relative rates of reaction were observed, the experiments agreed only moderately well with the "Raoult's Law" counterpart of copolymerization. The more complete theory shows why deviations can be expected, so it can be concluded that vinyl acetate and vinyl chloride do not form an ideal polymerization pair. It is interesting that although vinyl acetate tends to polymerize faster by itself than does vinyl chloride, the latter monomer goes into the copolymer

[11] For a general discussion of synthetic copolymers, see Chapter 8 (by Marvel and Horning) in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

faster than the other for a wide range of concentrations.[12]

It should be emphasized that analytical determinations of copolymer composition as a function of conversion will yield information about ρ and σ only and not of any other parameters involved. To get the absolute values of the specific reaction rate constants it would be necessary to know something about the radical concentrations, which information is not readily available. A direct measurement of ρ and σ for the system methyl methacrylate and styrene has been carried out by Mayo and Lewis.[4] Their results indicate that $\rho = \sigma = 0.5$. This means that methyl methacrylate and styrene constitute a pair that is qualitatively similar to that illustrated by Fig. 3.

Numerous examples are available for systems in which σ (or ρ) is equal to zero. The early work of Wagner–Jauregg[13] on maleic anhydride and ethylene derivatives provides such examples. Maleic anhydride does not polymerize with itself but readily polymerizes with substances like styrene with a marked tendency to form a 1:1 polymer. It appears quite likely that maleic anhydride and styrene belong to a system similar to that of Fig. 6. The azeotrope will have a composition very nearly 1:1 but not exactly. If one starts with an excess of styrene, the first polymer will be close to the azeotrope, but the last polymer formed will be pure polystyrene. It would be incorrect to suppose, however, that no polymer chains could have intermediate compositions.

Other systems whose behaviors can be explained by setting σ (or ρ) equal to zero include ethylene derivatives in conjunction with sulfur dioxide[11] or with maleic imides.[14] In most cases sulfur dioxide appears to form approximately 1:1 azeotropes with the ethylene derivatives indicating that ρ is small compared to unity while $\sigma = 0$. On the other hand, vinyl chloride and sulfur dioxide may well form a 2:1 azeotrope,[11] suggesting that $\rho = 0.5$ while $\sigma = 0$.

Unless both ρ and σ are equal to zero one does not form exactly the so-called heteropolymers[13] which have regular alternations of monomer units. Many apparent heteropolymers are probably azeotropes for which $\rho = \sigma \neq 0$ or are systems for which $\sigma = 0$ and $0 < \rho \ll 1$.

Summary

Using the concepts of Norrish and Brookman,[8] a general theory of copolymerization is developed which involves relative polymerization velocities as functions of the monomer composition. The treatment is developed in analogy to vapor pressures of binary systems. The ideal systems[1] (corresponding to "Raoult's Law" type of behavior) are suggested as starting concepts from which deviations might be observed. Non-ideal copolymerization systems can sometimes lead to "azeotropic copolymers." The nature of such "azeotropes" together with their intramolecular distributions are considered. The behavior of certain polymerization systems, particularly those leading to so-called heteropolymers are accounted for by the theory.

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(12) Staudinger and Schneiders, *Ann.*, **541**, 151 (1939).

(13) Wagner–Jauregg, *Ber.*, **63**, 3213 (1930).

(14) Arnold, Brubaker and Dorough, U. S. Patent 2,301,356 (1942).

[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI AND THE CINCINNATI MILLING MACHINE COMPANY]

Action of *n*-Primary Alcohols as Metal Cutting Fluids—Alternating Properties with Chain Length

BY MILTON C. SHAW[1]

It is customary to introduce some form of cutting fluid at the chip–tool interface when metal is removed from a work-piece by means of a cutting tool. The purposes of the cutting fluid are to facilitate the removal of metal and to produce a smooth surface finish. A large variety of fluids have been used in the metal working industry in the past but little attempt has been made to correlate the efficiency of a cutting fluid with the physical and chemical properties of the liquid–metal combination. As part of a broad study of the mechanism of cutting fluid action, the metal cutting efficiency of pure *n*-primary alcohols has been investigated using a carefully controlled cutting technique.

All the normal, primary, monohydric alcohols from methanol to dodecanol were used in this investigation. The absolute methanol and absolute ethanol were used in their commercial form. The other alcohols were fractionated before using in a distillation apparatus with an efficiency of about nine theoretical plates. Pure distilled water was included as the first member of the series.

The manner in which the tests were made is shown diagrammatically in Fig. 1. A chip was cut from an aluminum work block using a high speed steel finishing-type planer tool having a

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