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

The Structure of Vinyl Copolymers

BY FREDERICK T. WALL

During recent years considerable work has been devoted to the study of vinyl polymers. These investigations have been carried out not only to find out more about methods of preparation, but also to learn something about the structures of the polymers. For example, Marvel and co-workers[1] have established the arrangements of the structural units in various polymers by studying their chemical properties and by carrying out quantitative experiments on the removal of substituents. They have also studied rates of formation of certain polymers,[2] and other investigators have carried out considerable research on viscosity and molecular weight determinations.[3] Most of the work, however, has been concerned with polymers of a single substance, so it seems appropriate now to look into the properties of copolymers.

In examining the properties of copolymers, we shall proceed with a theoretical treatment, and the results which we predict will be compared with the observed properties. Although the following treatment should be valid for many pairs of substances capable of undergoing copolymerization, we shall consider vinyl chloride and vinyl acetate as a typical pair of substances which can be polymerized together.

Theoretical Treatment.—Let us consider first the formation of a copolymer from the reaction mixture. For convenience in future discussion, let X represent one kind of molecule (*e. g.*, vinyl chloride) and Y represent another kind of molecule (*e. g.*, vinyl acetate). Suppose the original reaction mixture consists of n_{x_0} molecules of X and n_{y_0} molecules of Y. After the polymerization has proceeded to a certain extent, let n_x and n_y equal the number of unpolymerized X and Y molecules, respectively. Finally, define N_x and N_y as the number of X and Y units which have polymerized. Then evidently

$$N_x + n_x = n_{x_0}$$

and (1)

$$N_y + n_y = n_{y_0}$$

Now there is no general reason to suppose that the X and Y molecules will polymerize at the same rate even though they copolymerize. There is, however, a basis for assuming that the polymerizations will be first order, judging from the results of Marvel, Dec and Cooke[2] on the rates of polymerization of certain optically active vinyl esters. Assuming first order polymerizations, we arrive at

$$\frac{dN_x}{dt} = -\frac{dn_x}{dt} = k_1 n_x$$

and (2)

$$\frac{dN_y}{dt} = -\frac{dn_y}{dt} = k_2 n_y$$

Eliminating t from equations (2), we see that

$$\frac{dn_x}{dn_y} = \alpha \frac{n_x}{n_y} \quad (3)$$

where

$$\alpha = k_1/k_2 \quad (4)$$

It is obvious from equation (3) that unless $\alpha = 1$, the polymer which forms at any instant will not have the same composition as the reaction mixture. If we define x as the mole fraction of X units in the polymer forming at any instant, then

$$x = \frac{dN_x}{dN_x + dN_y} = \frac{\alpha n_x}{\alpha n_x + n_y} \quad (5)$$

If $\alpha > 1$, the first polymer that forms will be richer in X than the original reaction mixture. As the polymerization proceeds, the composition of polymer forming will change continuously until the last polymer will consist of nearly pure Y. The average composition of the completely polymerized products must, of course, be the same as that of the original reaction mixture. In case $\alpha < 1$, the same arguments prevail, except that the positions of X and Y must be interchanged in the discussion.

If $\alpha = 1$, the composition of polymer forming at any time will be the same as that of the reacting mixture. Accordingly the composition of polymer forming at any stage of the reaction (beginning, middle, or end) will be the same as the average. Such a polymer we shall call a "true copolymer." A true copolymer is one whose individual chains each have the same composition (within reasonable statistical fluctuations) as the mass of polymer. If the chains are short, the composition can vary appreciably from chain to

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(1) C. S. Marvel, J. H. Sample and Max F. Roy, THIS JOURNAL, 61, 3241 (1939); C. S. Marvel and J. C. Cowan, *ibid.*, 61, 3156 (1939).

(2) C. S. Marvel, Joseph Dec and Harold G. Cooke, Jr., *ibid.*, 62, 3499 (1940).

(3) See H. Mark, Vol. II of "High Polymers," Interscience Publishers, New York, N. Y., for a complete discussion of these methods.

chain because of statistical variations. But if a chain of a true copolymer is long, for example containing 1000 members, then the probability of that chain's having a composition appreciably different from the average is almost nil.

If $\alpha \neq 1$, the product resulting from an ordinary polymerization of two substances will be a mixture of copolymers. This is in agreement with the observations of Staudinger and Schneiders,[4] who report the fractionation of vinyl chloride–vinyl acetate copolymers according to composition. Nevertheless, it should still be possible to prepare a true copolymer for such a pair of substances. In order to do this, start with a reaction mixture with a mole ratio of Y and X equal to $\alpha(1 - x)/x$ where x is the composition of the desired true copolymer. As the polymerization proceeds add more reactants in the ratio $1 - x/x$ just as fast as necessary to replace the reactants being used up. This method was approximated by Fikentscher and Hengstenberg,[5] who reported that the uniformity of copolymers could be increased by adding more of the faster reacting compound to the reaction mixture from time to time during the polymerization.

Composition Distribution Function.—Let us now investigate mathematically the composition distribution function for ordinary copolymers. Assuming α to be constant, equation (3) can be integrated immediately to give

$$\frac{n_x}{n_{x_0}} = \left(\frac{n_y}{n_{y_0}}\right)^{\alpha} \tag{6}$$

Eliminating n_y from equations (5) and (6), we find

$$x = \frac{\alpha\left(\frac{n_x}{n_{x_0}}\right)^{(\alpha-1)/\alpha}}{\alpha\left(\frac{n_x}{n_{x_0}}\right)^{(\alpha-1)/\alpha} + \frac{n_{y_0}}{n_{x_0}}} \tag{7}$$

Now define a new variable ξ as the fraction of the X molecules which have polymerized

$$\xi = \frac{N_x}{n_{x_0}} = 1 - \frac{n_x}{n_{x_0}} \tag{8}$$

and let

$$R = \frac{n_{y_0}}{n_{x_0}} \tag{9}$$

Substituting (8) and (9) into (7), we find the composition mole fraction x, of the polymer forming at any instant, in terms of the fraction of the X molecules already polymerized.

$$x = \frac{\alpha(1 - \xi)^{(\alpha-1)/\alpha}}{\alpha(1 - \xi)^{(\alpha-1)/\alpha} + R} \tag{10}$$

Solving equation (10) for ξ, we find

$$\xi = 1 - \left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)} \left(\frac{x}{1 - x}\right)^{\alpha/(\alpha-1)} \tag{11}$$

Now if N equals the total number of vinyl units which have polymerized, then

$$\mathrm{d}N = \mathrm{d}N_x + \mathrm{d}N_y = \frac{n_{x_0}}{x}\,\mathrm{d}\xi \tag{12}$$

Differentiating (11) and substituting into (12) we find that

$$\mathrm{d}N = -n_{x_0}\left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)} \left(\frac{a}{\alpha - 1}\right) \left(\frac{x}{1 - x}\right)^{(2-\alpha)/(\alpha-1)} \frac{\mathrm{d}x}{(1 - x)^3} \tag{13}$$

or

$$\frac{1}{n_0}\frac{\mathrm{d}N}{\mathrm{d}x} = -\frac{1}{(1 + R)}\left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)} \left(\frac{\alpha}{\alpha - 1}\right) \left(\frac{x}{1 - x}\right)^{(2-\alpha)/(\alpha-1)} \frac{1}{(1 - x)^3} \tag{14}$$

where

$$n_0 = n_{x_0} + n_{y_0} \tag{15}$$

Equation (14) is the desired distribution function, because $\left|\frac{1}{n_0}\frac{\mathrm{d}N}{\mathrm{d}x}\right|\mathrm{d}x$ equals the fraction of the copolymer with a composition between x and $x + \mathrm{d}x$.

Returning to equation (10), we see again that the first polymer that forms (corresponding to $\xi = 0$) has the composition $x = \alpha/(\alpha + R)$. As ξ increases, however, x will change. If $\alpha > 1$, x will decrease until it reaches a value of zero (corresponding to $\xi = 1$). If $\alpha < 1$, on the other hand, x will increase until it reaches a maximum value of unity. We see, then, that the negative sign in equation (14) appears because x decreases (for $\alpha > 1$) as N, the number of polymerized molecules, increases.

In Fig. 1 are plotted the absolute values of $\frac{1}{n_0}\frac{\mathrm{d}N}{\mathrm{d}x}$ as a function of x for various values of α greater than unity and for $R = 1$. The curves all

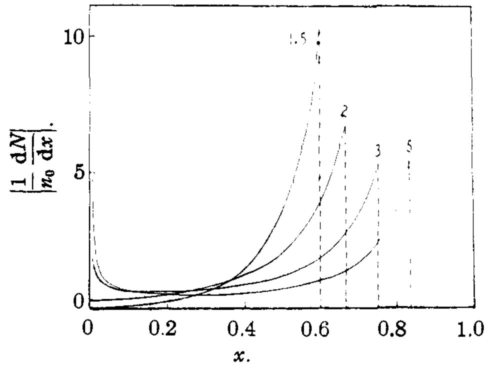

Fig. 1.—Copolymer composition distribution functions for $\alpha = 1.5, 2, 3$ and 5 with $R = 1$.

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[4] H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

[5] H. Fikentscher and J. Hengstenberg, U. S. Patent 2,100,900 (1937).

lie in the range $0 \leqslant x \leqslant \alpha/(\alpha + R)$ in accordance with equation (10). In case $R \neq 1$, the curves will still have the same shape, but will have different upper limits for x and different ordinate scales. Although the curves plotted all correspond to values of α greater than unity, similar curves would be obtained by replacing α with its reciprocal and x by $1 - x$.

It will be observed from the curves in Fig. 1 that when $\alpha = 1.5$, most of the polymer will have an X mole fraction between 0.5 and 0.6, but there will be enough polymer low in X to bring the average down to 0.5 as it must be for $R = 1$. The amount of polymer poor in X approaches zero as $x \rightarrow 0$, which is true as long as $1 < \alpha < 2$. When $\alpha = 2$, the theoretical distribution curve jumps up to a positive finite value for $x = 0$, the other end of the curve flattening out slightly as expected. When $\alpha > 2$, the function becomes infinite as $x \rightarrow 0$, meaning that the polymer will have a substantial fraction made up of nearly pure Y molecules. With α as large as 3 or 5, a copolymer formed by complete polymerization of X and Y molecules will tend to resemble a mixture of polymers with compositions $x = 0$ and $x = \alpha/(\alpha + R)$.

As long as $1/2 < \alpha < 2$, the properties of the complete polymer will not be very different from that of a true copolymer. For other values of α, the non-uniformity of product should become quite noticeable. If one desires a fairly uniform product without continuously adjusting the composition of the reaction mixture, one should introduce a suitable catalyst or set conditions in such a way as to keep α as near unity as possible.

In order for the foregoing considerations to be valid, it must be assumed that each polymer chain is long enough for statistical variations in composition to be negligible. It is also necessary to assume that each chain is small compared to the total amount of polymer and that each chain is completed in a time which is short compared to the time involved for complete polymerization. There is evidence that these conditions are fulfilled in actual processes.[3]

By integration of equation (14) one can determine the number of monomer units present in a portion of copolymer with extreme compositions x_1 and x_2.

$$\frac{\Delta N}{n_0} = -\frac{1}{(1+R)}\left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)}\left(\frac{\alpha}{\alpha-1}\right)\int_{x_1}^{x_2}\left(\frac{x}{1-x}\right)^{(2-\alpha)/(\alpha-1)}\frac{\mathrm{d}x}{(1-x)^3} \tag{16}$$

$$= -\frac{1}{(1+R)}\left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)}\left[\left(\frac{x}{1-x}\right)^{\alpha/(\alpha-1)} + \alpha\left(\frac{x}{1-x}\right)^{1/(\alpha-1)}\right]_{x_1}^{x_2} \tag{17}$$

If $x_1 = \alpha/(\alpha + R)$ and $x_2 = 0$ (with $\alpha > 1$) or $x_2 = 1$ (with $\alpha < 1$), then $\Delta N/n_0 = 1$, thus providing a check on equation (17).

The average mole fraction $\bar{x}$ will be given by

$$\bar{x} = \frac{\int_{x_1}^{x_2} x\,\mathrm{d}N}{\int_{x_1}^{x_2} \mathrm{d}N} \tag{18}$$

which upon integration yields

$$\bar{x} = \frac{\left(\frac{x_1}{1-x_1}\right)^{\alpha/(\alpha-1)} - \left(\frac{x_2}{1-x_2}\right)^{\alpha/(\alpha-1)}}{\left(\frac{x_1}{1-x_1}\right)^{\alpha/(\alpha-1)} + \alpha\left(\frac{x_1}{1-x_1}\right)^{1/(\alpha-1)} - \left(\frac{x_2}{1-x_2}\right)^{\alpha/(\alpha-1)} - \alpha\left(\frac{x_2}{1-x_2}\right)^{1/(\alpha-1)}} \tag{19}$$

In case $\alpha = 2$, equation (19) assumes a particularly simple form, namely

$$\bar{x} = \frac{\frac{x_1}{1-x_1} + \frac{x_2}{1-x_2}}{\frac{1}{1-x_1} + \frac{1}{1-x_2}} \tag{20}$$

Intramolecular Distribution.—Let us now investigate the distribution of monomer units within the copolymer chains. In a long copolymer chain, there will occur groups of X's and Y's of various lengths. These groups will not occur in any particular order, but the number of groups of given length can be determined for a long chain. In an earlier publication,[6] the distribution with respect to such groups was calculated for a true copolymer. If p_i equals the number of groups containing i members of the X variety and if x is the mole fraction of X in the true copolymer, then

$$p_i = N_x(1 - x)^2 x^{i-1} \tag{21}$$

where N_x is the total number of X units in the true copolymer. If one is dealing not with a true copolymer but rather with a mixture of copolymers such as one would expect according to previous considerations in this paper, then equation (21) is no longer completely valid as it stands. But equation (21) is still valid for each portion of

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[6] F. T. Wall, THIS JOURNAL, 62, 803 (1940).

polymer with composition x, so for the entire polymer we can write

$$dp_i = (1 - x)^2 x^{i-1} dN_x \tag{22}$$

or

$$dp_i = n_{x_0}(1 - x)^2 x^{i-1} d\xi \tag{23}$$

or

$$dp_i = n_{x_0} \left(\frac{R}{\alpha}\right)^{\alpha/(\alpha-1)} \left(\frac{\alpha}{\alpha - 1}\right) \left(\frac{x}{1 - x}\right)^{1/(\alpha-1)} \times x^{i-1} dx \tag{24}$$

Unfortunately, equation (24) cannot be integrated simply except when $\alpha = 2$ or $\alpha = {}^1/_2$. One interesting general conclusion can be deduced, however, without evaluating the general integral. Consider

$$p_i = n_{x_0} \int_0^1 (1 - x)^2 x^{i-1} d\xi \tag{25}$$

Then

$$\frac{\partial p_i}{\partial \alpha} = n_{x_0} \int_0^1 [(1 - x)^2 (i - 1) x^{i-2} - 2(1 - x) x^{i-1}] \frac{\partial x}{\partial \alpha} d\xi \tag{26}$$

Making use of equation (10) and setting $\alpha = 1$, we find upon integration that

$$\left(\frac{\partial p_i}{\partial \alpha}\right)_{\alpha = 1} = 0 \tag{27}$$

Equation (27) tells us that the total number of groups of given length in a copolymer will be at a maximum or minimum when $\alpha = 1$. It can be established that for small values of i, (27) corresponds to a maximum, and for large values of i to a minimum. This means that for α different from unity, the actual copolymer will have more long groups and fewer short groups than the corresponding true copolymer. This result could be anticipated from the distribution curves.

Experimental evidence for the above predicted effect can be obtained by studying the removal of substituents (*e. g.*, chlorine) from the copolymers. It has been shown[1,6,7] that when vinyl polymers containing halogen are treated with zinc, part of the halogen is removed as zinc halide, leaving unsaturation or cyclopropane rings in the polymer. All of the halogen is not removed, the fraction remaining depending upon the structure and composition. If one has a true copolymer of vinyl chloride and vinyl acetate arranged so that substituents are all 1-3 with respect to each other, then the fraction of chlorine which can be expected to remain after treatment with zinc is given by[6]

$$f = e^{-2x} \tag{28}$$

If one does not have a true copolymer, but rather a mixture with a distribution given by equation (14), then equation (28) must be replaced by

$$f = \int_0^1 e^{-2x} d\xi \tag{29}$$

where ξ and x are related by equations (10) and (11). Just as p_i has a maximum or minimum for $\alpha = 1$, f also has a maximum for $\alpha = 1$. To prove this, note that

$$\frac{\partial f}{\partial \alpha} = -2 \int_0^1 e^{-2x} \frac{\partial x}{\partial \alpha} d\xi \tag{30}$$

Substituting for $\partial x/\partial \alpha$ and setting $\alpha = 1$, we find

$$\left(\frac{\partial f}{\partial \alpha}\right)_{\alpha = 1} = 0 \tag{31}$$

If $\alpha = 2$, equation (29) can be integrated immediately after substituting for ξ, to give

$$f = \left(\frac{R + 2}{2}\right)^2 e^{-4/(2+R)} - \left(\frac{R}{2}\right)^2 \tag{32}$$

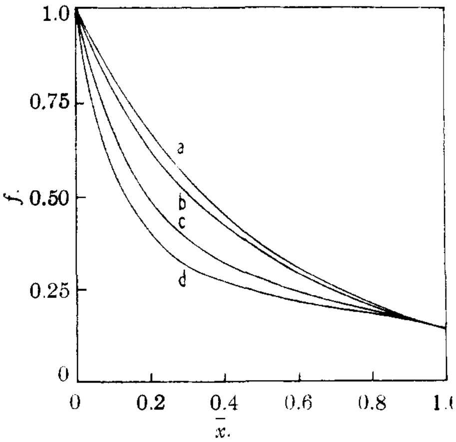

Fig. 2.—Halogen expectancy f as a function of average composition $\bar{x}$ for copolymers: a, $\alpha = 1$; b, $\alpha = 2$; c, $\alpha = 5$; d, $\alpha = 10$.

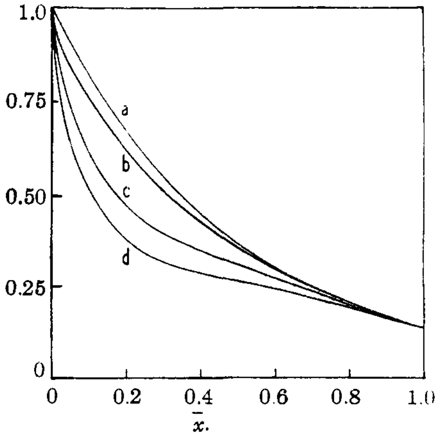

Fig. 3.—Halogen expectancy f as a function of average composition $\bar{x}$ for copolymers: a, $\alpha = 1$; b, $\alpha = {}^1/_2$; c, $\alpha = {}^1/_5$; d, $\alpha = {}^1/_{10}$.

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(7) P. J. Flory, THIS JOURNAL, 61, 1518 (1939).

If $\alpha = {}^1/_2$, expression (29) can be integrated in series after replacing x by its equivalent in ξ and expanding the exponential function in a power series. Upon integration one obtains the following:

$$f = \frac{1}{R}\left\{ R - \log(1 + 2R) + \sum_{i=1}^{\infty} \frac{(-2)^i}{i(i+1)!}\left[\frac{1}{(1+2R)^i} - 1\right]\right\} \qquad (33)$$

For other values of α, f can be determined numerically for particular values of R by means of the trapezoidal rule or some other approximate method.

In Figs. 2 and 3 are plotted values of f as a function of the average composition $\bar{x}$ for various values of α. It is seen that regardless of whether α is greater or less than unity, the fraction of halogen left after treating a copolymer with zinc is less than it would be for a true copolymer of the same average composition. This is a natural consequence of the fact that the actual copolymers tend to resemble a mixture of polymers of extreme compositions. The curves for α = 1,2, and $^1/_2$ were calculated by use of equations (28), (32) and (33). The other curves were drawn through points for $\bar{x}$ = 0.25, 0.50 and 0.75, the corresponding values of f having been calculated by means of the trapezoidal rule using at least ten intervals for each numerical integration.

Discussion

Qualitative support for the theory presented here has already been obtained by Staudinger and Schneiders[4] as well as by Fikentscher and Hengstenberg.[5] Quantitative evidence in support of the theory is not yet available, but Professor C. S. Marvel and co-workers in the organic chemistry division of this Laboratory are now working on that problem. Preliminary results on copolymers of vinyl chloride and vinyl acetate are in agreement with the theory both as to rates of polymerization and as to removal of chlorine by means of zinc.

An important point to be recognized is that the average composition of a copolymer is not by itself sufficient to specify the properties of the polymer. This follows because a copolymer with a certain composition might consist of anything between a true copolymer and a mixture of polymers of extreme compositions, depending upon the value of α. It is to be expected that a true copolymer will be more uniform in its behavior than will a mixture of polymers.

The author is indebted to Professor C. S. Marvel for helpful discussions and for experimental information.

Summary

The structure of copolymers is considered theoretically and it is deduced that an ordinary copolymer consists of a mixture of polymers subject to a composition distribution function. It is found convenient to define a "true copolymer" as distinguished from an ordinary copolymer. The intramolecular distribution of monomer units within the polymer chains is also considered together with its effect on quantitative chemical experiments on the substances.

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Ternary Systems. VII. Sodium Phthalate, Sodium Carbonate and Water

BY STERLING B. SMITH AND ERICK I. HOEGBERG[1]

Phase rule studies of the solubilities in ternary systems involving the phthalates of the alkali metals have been carried on in this laboratory for several years. As a further step along this line, this investigation has been undertaken.

Experimental Part

Materials and Methods.—The sodium phthalate used was prepared by neutralizing phthalic acid with sodium carbonate and recrystallizing the product from water. Sodium carbonate decahydrate was prepared by recrystallization of reagent grade sodium carbonate from aqueous solution at zero degrees. Sodium carbonate heptahydrate was prepared by placing a saturated solution of reagent grade sodium carbonate in a water-bath kept at a temperature between 32 and 35.37° and allowing isothermal evaporation to take place. Sodium carbonate monohydrate was prepared by grinding purified sodium carbonate decahydrate to a fine powder and allowing the salt to stand in the atmosphere for about one week, occasionally grinding the lumps formed.

These hydrates, while not components of the system,

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[1] The material for this paper was taken from a thesis of Mr. Erick I. Hoegberg presented to the Graduate Committee of Trinity College in partial fulfilment of the requirements for the Master of Science degree.