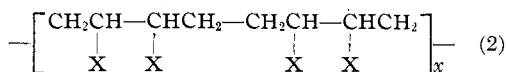# Intramolecular Reaction between Neighboring Substituents of Vinyl Polymers

BY PAUL J. FLORY

It has been demonstrated by Marvel and co-workers[1] that polyvinyl alcohol and the polymer of methyl vinyl ketone have their structural units joined in a "head to tail" manner in which consecu-

$$-\left[\begin{array}{c} CH_2CH-CH_2CH \\ | \quad\quad | \\ X \quad\quad X \end{array}\right]_x \quad (1)$$
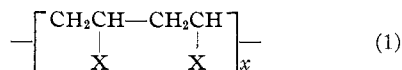
tive substituents X are 1,3 with respect to one another. The writer[2] pointed out a short time ago that upon the basis of the free radical chain reaction mechanism for vinyl polymerization, this type of structure is to be expected rather than either the "head to head, tail to tail" structure

$$-\left[\begin{array}{c} CH_2CH-CHCH_2-CH_2CH-CHCH_2 \\ | \quad | \quad\quad\quad | \quad | \\ X \quad X \quad\quad\quad X \quad X \end{array}\right]_x \quad (2)$$

or a mixture of these two arrangements, such as, for example, a polymer having its structural units oriented at random with respect to one another.

When X is a functional group of a character such that two neighboring X's may undergo condensation with one another or may jointly condense with another reagent, a unique and interesting circumstance arises. Random coupling of pairs of X's, such as should take place with polymers having the 1,3-structure (1), will occasionally leave single X's isolated between neighbors which have reacted. Because there are no neighboring groups with which such groups may react, the stoichiometric limit of the reaction cannot be reached. The calculation of the fraction of the groups which cannot react under these conditions is purely a statistical problem. In a polymer of type (2) the portion of the groups which may react will depend on the relative rates of 1,2- and 1,4-reactions, which rates depend on the ease of formation of the resulting rings, differing in size by two atoms. In a polymer having its structural units oriented at random, relative rates of 1,2-, 1,3- and 1,4-reactions must be considered.
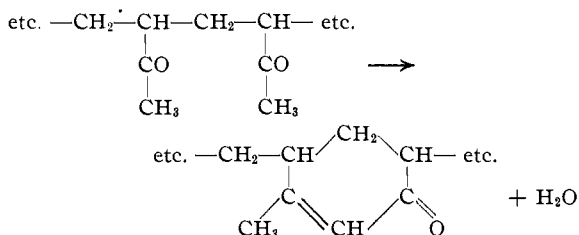
Two examples may be cited in which failure of the reaction to reach completion may be attributed to isolation of single unreacted substituents between reacted pairs.[3] Marvel and Levesque[1]

have shown that upon heating the polymer from methyl vinyl ketone around 300° the carbonyl group of one substituent condenses with the methyl group of the next substituent as follows

etc. $-CH_2-CH-CH_2-CH-$ etc.

$$\begin{array}{cc} | & | \\ CO & CO \\ | & | \\ CH_3 & CH_3 \end{array} \quad \longrightarrow$$

$$\text{etc. } -CH_2-CH\underset{\underset{CH_3}{\diagup}C\diagdown_{CH}}{\overset{\diagup CH_2\diagdown}{\diagup}}CH-\text{ etc.} \underset{\underset{O}{\diagup}C\diagdown}{} + H_2O$$

If condensation occurred regularly along the chain, one molecule of water would be eliminated for each carbonyl (the carbonyl at the end of the chain excepted). Pyrolysis for fifteen hours yielded an amount of water approximately equivalent to 79% of the carbonyl groups; the carbon–hydrogen analysis of the residue indicated a corresponding retention of oxygen[1] (p. 283). In another experiment 85% of the theoretically available water was obtained in twenty-four hours. The result of this latter experiment probably is nearer the true limit of the reaction.

Recently Marvel and Sample[4] have found that zinc removes chlorine from polyvinyl chloride, yielding a saturated product, which presumably contains cyclopropane rings. The removal of halogen is definitely not quantitative, which suggests that some of the substituents become isolated.

It is the purpose of this paper to present statistical calculations of the fraction of the functional substituents of vinyl polymers which may undergo reaction in pairs. In addition to clarifying such intramolecular polymer reactions, the results provide a means for differentiating between structures (1), (2) and the "random" structure.[5]

Intramolecular Reaction in 1,3-Polymers.—Reaction of an isolated substituent with another one farther removed than the next substituent or-

(1) C. S. Marvel and C. L. Levesque, THIS JOURNAL, **60**, 280 (1938); C. S. Marvel and C. E. Denoon, *ibid.*, **60**, 1045 (1938).

(2) Flory, *ibid.*, **59**, 241 (1937).

(3) The author gratefully acknowledges indebtedness to Professor C. S. Marvel of the University of Illinois for bringing these examples to his attention.

(4) Private communication.

(5) It should be pointed out that the analysis presented here does not apply when the reverse reaction occurs at an appreciable rate compared with the rate of the forward reaction, *i. e.*, when the reaction proceeds under conditions not far from those of equilibrium. Under such circumstances the distribution of isolated groups will rearrange continually and, depending on the equilibrium constant, the number of isolated groups may decrease below the statistical value calculated here.

dinarily may be disregarded because of the difficulty of forming rings of more than six members. Choice of experimental conditions such that intermolecular reactions are avoided is obviously essential.

If it be assumed that the probability of reaction of each adjacent pair of unreacted substituents is the same and independent of the status of neighboring substituents, the fraction of the X's which become isolated, and therefore remain unreacted at the termination of the reaction, can be calculated in the following manner. Consider a group of polymer molecules each containing n structural units (and n substituents) in the "1,3" configuration (1). The average number of unreacted X's per molecule at the end of the reaction will be termed S_n. Obviously, $S_0 = 0$, $S_1 = 1$, $S_2 = 0$ and $S_3 = 1$. If $n = 4$, the first reaction may link any one of three pairs, which may be designated 1-2, 2-3 and 3-4. If either the 1-2 or the 3-4 pair is joined, the unreacted portion is equivalent to an $n = 2$ molecule; if the 2-3 pair is joined, there remains the equivalent of two $n = 1$ molecules. Hence

$$S_4 = (2S_2 + 2S_1)/3$$

If $n = 5$ the first reaction may join any one of four different pairs. Two of these yield an $n = 3$ remainder; each of the other two possibilities yields both an $n = 2$ and an $n = 1$ remainder. Hence

$$S_5 = (2S_3 + 2S_2 + 2S_1)/4$$

Continuing in this manner, one obtains the general equation

$$S_n = \left(\frac{2}{n-1}\right)(S_1 + S_2 + \ldots S_{n-2}) \tag{3}$$

Subtracting the expression for $(n - 2)S_{n-1}$ from the expression for $(n - 1)S_n$ and setting $S_n - S_{n-1} = \Delta_n$

$$(n - 1)\Delta_n = S_{n-2} - \Delta_{n-1}$$

Subtracting $(n - 2)\Delta_{n-1} = S_{n-3} - \Delta_{n-2}$ from this equation and rearranging

$$\Delta_n - \Delta_{n-1} = \left(\frac{-2}{n-1}\right)(\Delta_{n-1} - \Delta_{n-2})$$

or

$$\Delta_n - \Delta_{n-1} = \frac{(-2)^{n-1}}{(n-1)!}(\Delta_1 - \Delta_0) \tag{4}$$

The proper value for $\Delta_1 - \Delta_0$ may be obtained as follows. Recalling the values of S_0, S_1 and S_2, $\Delta_1 = 1$ and $\Delta_2 = -1$. From (4)

$$\Delta_2 - \Delta_1 = -2(\Delta_1 - \Delta_0) = -2$$

and therefore $\Delta_1 - \Delta_0$ must equal unity, and

$$\Delta_n = 1 - \frac{2}{1!} + \frac{4}{2!} - \frac{8}{3!} + \ldots \frac{(-2)^{n-1}}{(n-1)!} \tag{5}$$

This series, which converges very rapidly beyond eight or ten terms, becomes the series expansion for $1/e^2$ when $n = \infty$; i. e.

$$\Delta_\infty = 1/e^2$$

For a high molecular weight polymer where n is large

$$S_n \cong n/e^2$$

The fraction of the substituents which become isolated is therefore very nearly $1/e^2 = 0.1353$, or 13.53%. The experimental data cited above for intramolecular reaction in methyl vinyl ketone polymer are in satisfactory accord with this figure.

For molecules of shorter chain length the average number of isolated substituents *per molecule* can be calculated from the following expression derived from (5)

$$S_n = n - 2(n - 1) +$$
$$\frac{4(n - 2)}{2!} - \ldots + (-2)^{n-1} \frac{[n - (n - 1)]}{(n - 1)!} \tag{6}$$

Intramolecular Reactions in "Random" Polymers.—The fraction of the functional groups which would become isolated at termination of the reaction also can be calculated for a polymer molecule in which the structural units are oriented at random relative to each other, provided suitable assumptions are accepted regarding the reactions which 1,2-, 1,3- and 1,4-pairs of substituents may undergo. In the intramolecular condensation of a random methyl vinyl ketone polymer, 1,2-substituents probably would form a furan ring
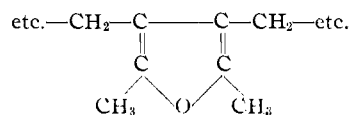
in preference to forming a cyclopentene ring analogous to the six-membered ring structure actually obtained from the 1,3-polymer. Reaction of 1,2-substituents should therefore be at least as rapid as the reaction of 1,3-substituents. Reaction of 1,4-substituents would be negligibly slow because of the necessity of forming a sterically unfavorable seven-membered ring. Intramolecular condensation in polyacrylamides,

, with the formation of imide

rings,[6] and the formation of ketal, or acetal, from a ketone, or aldehyde, and polyvinyl alcohol,[7] are other examples where one would expect isolation of substituents to occur. In both of these ex-
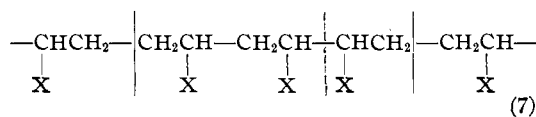
(6) H. Staudinger and E. Urech, *Helv. Chim. Acta*, **12**, 1132 (1929).

(7) C. Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, N. Y., 1935, Vol. II, pp. 1060, 1063.

amples reaction of 1,2-, 1,3- and 1,4-pairs of substituents would yield, respectively, five, six and seven-membered rings. As in the case of methyl vinyl ketone polymer, therefore, reaction between the 1,4-pairs of the random polymers should be very much slower than reactions between 1,2- and 1,3-pairs.

In the analysis of random polymer intramolecular reactions presented here, reaction between 1,4-substituents will be assumed not to occur. With regard to the relative occurrence of 1,2- and 1,3-reactions, three circumstances will be discussed: (1) equal rates of reaction for 1,2- and 1,3-pairs, (2) 1,2-reaction much more rapid than 1,3-reaction and (3) 1,3-reaction much more rapid than 1,2-reaction.

For statistical treatment of the first case it is convenient to imagine the random polymer molecule divided into groups of structural units, each group consisting of the portion of the molecule between two pairs of consecutive structural units so oriented that their substituents are 1,4 with respect to each other. For example, one such group is represented by the portion of the molecule between the solid vertical lines below.

$$-CHCH_2-|CH_2CH-CH_2CH-|CHCH_2-|-CH_2CH-$$
$$\quad | \qquad\quad | \qquad\quad | \quad | \qquad\qquad |$$
$$\quad X \qquad\quad X \qquad\quad X \; | X \qquad\qquad X$$
$$\hspace{11cm}(7)$$

Within each group there will be one 1,2-pair, an undetermined number of 1,3-pairs and no 1,4-pairs. Reaction of any pair of adjacent substituents within a group is considered equally probable, but inter-group reactions are forbidden according to the above assumption regarding the reaction of 1,4-pairs.

Since random orientation of the structural units is assumed, the probability that any arbitrarily selected group will have n units (i. e., n substituents) is[8]

$$P_n = (n-1)(1/2)^n \qquad\qquad (n > 1)$$

In a very long molecule, the ratio of the number of groups which contain n units each to the total number of groups is given by P_n. The number of isolated substituents in an n-group at termination of the reaction equals S_n as given by (6). Consequently, the average number of isolated substituents per group is

$$\sum_{2}^{\infty} S_n P_n$$

(8) This equation may be derived readily from considerations similar to those set forth in a previous paper, THIS JOURNAL, **58**, 1877 (1936).

The average number of units per group is four. Thus, the fraction of the substituents which become isolated is

$$\frac{1}{4}\sum_{2}^{\infty} S_n P_n = \sum_{2}^{\infty} S_n(n-1)\left(\frac{1}{2}\right)^{n+2}$$

Substituting equation (6) for S_n and collecting terms gives

$$\sum_{1}^{\infty} n(n-1)\left(\frac{1}{2}\right)^{n+2} - \sum_{2}^{\infty}(n-1)(n-1)\left(\frac{1}{2}\right)^{n+1} +$$
$$\frac{1}{2!}\sum_{3}^{\infty}(n-1)(n-2)\left(\frac{1}{2}\right)^{n} -$$
$$\frac{1}{3!}\sum_{4}^{\infty}(n-1)(n-3)\left(\frac{1}{2}\right)^{n-1} + \ldots$$

Or

$$\sum_{1}^{\infty}\left(\frac{1}{2}\right)^{n+2}\left[n(n-1) - n^2 + n\left(\frac{n+1}{2!}\right) - n\left(\frac{n+2}{3!}\right) + \ldots\right]$$
$$= \sum_{1}^{\infty} n^2\left(\frac{1}{2}\right)^{n+2}\left(\frac{1}{2!} - \frac{1}{3!} + \frac{1}{4!}\ldots\right)$$
$$+ \sum_{1}^{\infty} n\left(\frac{1}{2}\right)^{n+2}\left(-1 + \frac{1}{2!} - \frac{2}{3!} + \frac{3}{4!}\ldots\right) \quad (8)$$

The summation $\sum_{1}^{\infty} n^2\left(\frac{1}{2}\right)^{n+2} = \frac{3}{2}$ and $\sum_{1}^{\infty} n\left(\frac{1}{2}\right)^{n+2} = \frac{1}{2}$. The series in parentheses in the first term in (8) is the common series expansion for $1/e$; the similar series in the second term can be reduced to $-2/e$. Substitution of these values in (8) yields the result

$$\frac{3}{2}\left(\frac{1}{e}\right) - \frac{1}{2}\left(\frac{2}{e}\right) = \frac{1}{2e} = 0.1840$$

For the discussion of the second case (reaction of 1,2-groups much more rapid than reaction of 1,3-groups) each of the groups of structural units discussed above will be divided into two groups as indicated by the dotted line in (7). Each resulting "Q" group is bounded at one end by a 1,4-pair and at the other by a 1,2-pair with a varying number of 1,3-pairs between. The probability that an arbitrarily selected Q group will contain n structural units is

$$Q_n = (1/2)^n \qquad\qquad (n > 0)$$

and the average number of units per group is two. Since 1,2-reaction in the present case is assumed to be very much more rapid than 1,3-reaction, all 1,2-pairs, each of which joins two Q groups, will react before the 1,3-pairs within the groups. After 1,2-reaction is completed but before appre-

ciable 1,3-reaction has occurred, each Q group which originally contained n substituents will contain $n - 1$ unreacted substituents. After the possibilities for 1,3-reaction have been exhausted, there will remain as isolated substituents a fraction given by

$$\frac{1}{2} \sum_{2}^{\infty} S_{n-1} Q_n = \sum_{1}^{\infty} S_n \left(\frac{1}{2}\right)^{n+2}$$

Upon substituting (6) for S_n this summation reduces readily to $1/2e$, the same result obtained above.

A somewhat similar analysis has been applied to the third case. The result is again $1/2e$. Since these three extreme cases all give the same result, it is probable that for all intermediate relative rates of reaction of 1,2- and 1,3-pairs the same result would be obtained. Thus, the fraction of isolated substituents remaining after intramolecular reaction of pairs of substituents of a random polymer will be $1/2e = 0.1840$ provided only that 1,4-pairs do not react. From precise quantitative determination of extent of reaction it should be possible to differentiate between a uniform 1,3-structure and a random structure by comparison with the above calculated result and with the result obtained for 1,3-polymers, 0.1353.

Summary

The condensation of pairs of consecutive substituents X of a high molecular weight polymer composed of —CH_2—CHX— structural units has been analyzed statistically. When the units are regularly oriented so that the X's occur on alternate atoms along the chain, 13.53% of them are prevented from reacting due to isolation between reacted pairs. Analogous condensations in polymers which have their substituents oriented at random have been discussed. If reaction between 1,4-pairs of substituents does not occur, 18.40% of the substituents of a random polymer remain isolated after the possibilities for 1,2- and 1,3-reactions have been exhausted.

Hydrogen Fluoride as a Condensing Agent. VI.[1] The Alkylation of Benzene with Compounds Containing an "Allylic" Group

BY J. H. SIMONS AND S. ARCHER

In the course of our investigations concerning the utility of hydrogen fluoride as a condensing agent, we have studied the reactions of compounds containing an "allylic" grouping in the molecule. Cinnamic acid, benzyl chloride, allyl alcohol, and allylbenzene were caused to react with benzene in the presence of hydrogen fluoride. In the case of the alcohol, reaction took place at both the double bond and the hydroxyl group. The other compounds studied contained only one reactive group.

Benzyl chloride reacted with benzene to produce diphenylmethane. As it is difficult to account for this reaction on any hypothesis that requires an olefinic compound as an essential intermediate, its occurrence presents strong evidence against the postulation of any such mechanism.[2]

When the proportion of cinnamic acid to benzene was small enough to prevent polysubstitution from taking place to any considerable extent, β,β-phenylpropionic acid was the only isolable product. That the α,β-acid was not formed is reasonable, as the carboxyl group is attached to the alpha carbon atom.

Two main products were formed in the reaction of allyl alcohol with benzene in the presence of hydrogen fluoride. Allylbenzene was identified as one of them by comparing the melting points and mixed melting point of a crystalline tribromide of the product with that of a tribromide of allylbenzene made through the Grignard reaction. The higher boiling product did not yield well-defined or reproducible derivatives, when treated with the usual reagents for such purposes. As it must be one of two possible isomers, 1,2- or 1,3-diphenylpropane, whose physical properties differ widely, a choice was made on the basis of the boiling point, density, and refrac-

(1) For the previous paper of this series see Simons, Archer and Passino, THIS JOURNAL, **60**, 2956 (1938).

(2) For postulated mechanisms of this type see McKenna and Sowa, *ibid.*, **59**, 470 (1937).