Statistical Mechanics of Reversible Reactions of Neighboring Pairs of Substituents in Linear Polymers

BY PAUL J. FLORY

Non-reversible reactions of pairs of adjacent substituents in linear polymers have been treated in a fairly exhaustive manner through the efforts of various investigators.[1,2,3,4] In the simpler cases, each substituent X of the chain is capable of reacting with only one of its neighboring substituents X; the pair of groups may react directly with one another or jointly with a monomeric reactant A as indicated below

$$+B$$

where X–A–X represents the condensation product formed in the reaction between $2X + A$, and B is the by-product of that reaction.[5] For a random non-reversible reaction between adjacent pairs of substituents on an infinitely long polymer chain it was shown[1] that the fraction of the X groups remaining intact owing to isolation between reacted pairs is $1/e^2$ when all available adjacent pairs have reacted. The theory was extended by Wall[2] to include random copolymers, and by Merz, Alfrey and Goldfinger[4] to include non-random vinyl copolymers. Alfrey, Lewis and Magel[6] recently presented a treatment of intramolecular condensations in non-random vinyl copolymers of the type

in which X may condense with Y. Although their treatment actually applies only to non-reversible condensation, they suggest its application to the

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

(2) F. T. Wall, ibid., **62**, 803 (1940); **63**, 821 (1941).

(3) R. Simha, ibid., **63**, 1479 (1941).

(4) E. Merz, T. Alfrey and G. Goldfinger, J. Polymer Sci., 1, 75 (1946); see also C. Lewis and H. Haas, ibid., 4, 665 (1949).

(5) The case in which each substituent bears a pair of complementary reacting groups, as in poly-(methyl vinyl ketone)

(see C. S. Marvel and C. L. Levesque, THIS JOURNAL, **60**, 280 (1938)) has also been treated. See P. J. Flory, ibid., **64**, 177 (1942); F. T. Wall, ibid., **64**, 269 (1942).

(6) T. Alfrey, C. Lewis and B. Magel, ibid., **71**, 3793 (1949).

intramolecular lactonization of vinyl alcohol–maleic anhydride copolymers, a reaction which may be susceptible to interchange, in which case the reacted pairs would not be permanently fixed.

Most of the known reactions involving neighboring pairs of substituents in chain polymers are easily reversible and subject to interchange. Examples include the formation of polyvinyl acetals from polyvinyl alcohol and aldehydes

imide formation on heating polyacrylamides

and intramolecular lactonization referred to above. It was noted in the first paper on this subject[7] that the calculation of the fraction of the groups which remain isolated at completion of the reaction of all available adjacent pairs was predicted on the assumption that the process is not subject to reversal, i.e., that once two adjacent functional groups react they remain permanently paired. The same applies to all subsequent extensions of the theory, although this requisite does not always appear to have been fully appreciated.

If under the conditions prevailing during the intramolecular reaction between pairs of substituents the reverse process may also take place, a reacted pair which is adjacent to an isolated substituent now may dissociate and the other pair of the sequence of the three substituents may then react. The same result may be achieved through interchange between an unreacted functional group and a neighboring reacted pair. Repeated occurrence of such processes causes the array of reacted pairs to change continually, and in particular it provides a mechanism whereby two previously isolated functional groups may "diffuse" along the chain until they are adjacent to one another whereupon they

(7) See footnote (5) of ref. 1.

become susceptible to reaction. Thus, the array indicated by

may be converted to

which possesses a potentially reactive pair of substituents. So long as the indefinitely long polymer chain possesses unreacted substituents, any mechanism which permits alteration of the array obviously offers the possibility that two unreacted groups may come into juxtaposition. Hence there can be no finite limit to the extent of reaction which is possible. However, as will be shown below, the ordinary mass action law does not apply and attainment of close approach to complete conversion will be far more difficult than for the analogous reaction of a bifunctional compound.

The following symbols will represent the numbers of the various species and groups participating in a reaction of the type indicated by (1) above.

a = initial number of molecules of A
b = initial number of product molecules B
n = initial number of regularly recurring substituents X in the polymer chain
p = number of reacted pairs X–A–X *at equilibrium*

The reaction of a given pair of neighboring substituents will be assumed to contribute a factor to the partition function of the system which is independent of whether or not other nearby substituents along the chain have reacted. In other words, the energy change per reacted pair is assumed constant, as is also the entropy change associated with internal degrees of freedom in the vicinity of the reacting pair. A standard state free energy change ΔF° may be defined in the conventional manner, therefore, as the free energy change per mole associated with the transformation of pure reactants into pure products. In the hypothetical reference reaction p consecutive pairs of substituents may be considered to be formed, the sequence being interrupted only by the infrequently occurring ends of polymer chains; or, any other uniquely specified arrangement of the reacted pairs among the unreacted groups could be assumed for the reference state.

In the actual equilibrium state the p reacted pairs may be selected from the n substituents in a large number of ways which will depend on n, p and the chain lengths of the polymer molecules. If the polymer chains are very long, the number of arrangements may be approximated by the number of ways of arranging p pairs along a single linear sequence of n sites, which is given by

$$C_p^{n-p} = (n-p)!/p!(n-2p)! \qquad (2)$$

The error thus introduced into the entropy per

unit will be of the order of $R/\bar{x}_n$ where $\bar{x}_n$ is the average number of units per polymer chain.

Finally, account must be taken of the mixing of the polymer species with molecules of A and of B, and with a solvent if present. Employing for this purpose the lattice model, the total number of configurations for the mixture (assuming a particular arrangement for the reacted pairs) is given by[8]

$$W = [(\gamma - 1)/\Sigma x_i N_i]^{\Sigma(x_i - 1)N_i} (\Sigma x_i N_i)!/\Pi N_i! \qquad (3)$$

where γ represents the coördination number of the lattice and N_i is the number of molecules of species i and x_i is the number of lattice segments in a molecule i; the summations are over all species including A and B, and a solvent, if present, as well as polymers.[9] It is evident that W is the same for each arrangement of the p pairs among the substituents except insofar as the product $\Pi N_i!$ is affected. Furthermore, since there is no gain or loss of matter for the process considered and since the total number of molecules remains fixed, both $\Sigma x_i N_i$ and ΣN_i may be regarded as constants independent of the extent of reaction. Making the further assumption that the character of the lattice (*i.e.*, γ) does not change during the reaction, equation (3) may be written

$$W = H/\Pi N_i! \qquad (4)$$

where H is a constant.

The partition function for the mixture consisting of very long polymer chains bearing n regularly spaced substituents, p adjacent pair of which are reacted, plus A, B and solvent molecules is

$$Q = (HC_p^{n-p}/\Pi N_i!) \exp(-p\Delta F^\circ/RT) \qquad (5)$$

to the approximation that equation (2) affords a valid expression for the number of arrangements of the pairs. Inasmuch as the polymer chains are assumed to be very long, and hence relatively few in number, their contribution to the product of factorials may be ignored to a like approximation. Substituting from equation (2)

$$Q = H[(n - p)!/p!(n - 2p)!(a - p)!(b + p)!]$$
$$\exp(-p\Delta F^\circ/RT) \qquad (6)$$

Introducing Stirling's approximations and applying the equilibrium condition $d \ln Q/dp = 0$

$$-\Delta F^\circ/RT = \ln K \qquad (7)$$

where

$$K = (n - p)(b + p)p/(a - p)(n - 2p)^2 \qquad (8)$$

Letting $\alpha = 2p/n$

$$K = \frac{(1 - \alpha/2)(\alpha/2)(b + n\alpha/2)}{(1 - \alpha)^2(a - n\alpha/2)} \qquad (9)$$

(8) P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944).

(9) The lattice model is a convenience rather than a requisite for the treatment given. Through its use activities are replaced by appropriate concentrations. We might have started with the previous generalization[8] that, where polymeric species are involved, equilibrium constants should be formulated with concentrations expressed in moles per unit volume.

Equations (8) and (9) may be obtained by the application of the mass action principle to an infinite chain in which the unreacted substituents are distributed at random. The probability that a substituent which is adjacent to an unreacted substituent is also unreacted is $(n - 2p)/(n - p)$. Hence, the number of adjacent pairs of unreacted substituents is $(n - 2p)^2/(n - p)$, from which equation (8) follows at once.

The above treatment applied to the analogous reaction of a simple bifunctional compound

$$\overset{\frown}{X \quad X} + A \longrightarrow \overset{\frown}{X—A—X} + B \qquad (10)$$

yields, of course, the ordinary expression for the equilibrium constant

$$K' = \alpha(b + n\alpha/2)/(1 - \alpha)(a - n\alpha/2) \quad (11)$$

(In this case the partition function is

$$Q' = (H/\Pi N_i!) \exp(-p\Delta F^0/RT)$$
$$= [H/(n/2 - p)!(a - p)!(b + p)!p!]\exp(-p\Delta F^0/RT)$$

where the combinatory factor is that for an ideal liquid mixture.)

If, for purposes of comparison, it is assumed that the standard state free energy changes for reaction (1) and for an equivalent monomeric reaction (10) are identical, then $K = K'$. Equilibrium degrees of conversion α may then be computed for the two analogous equilibria as functions of

$$K(a - n\alpha/2)/(b + n\alpha/2) = K[A]/[B]$$

Calculations based on the standard equilibrium expression (11) and on the one applicable to the linear polymer as given by equation (9) are shown in Fig. 1. Under corresponding conditions (i.e., for the same value $K[A]/[B]$) leading to low degrees of reaction α, the polymer reacts further
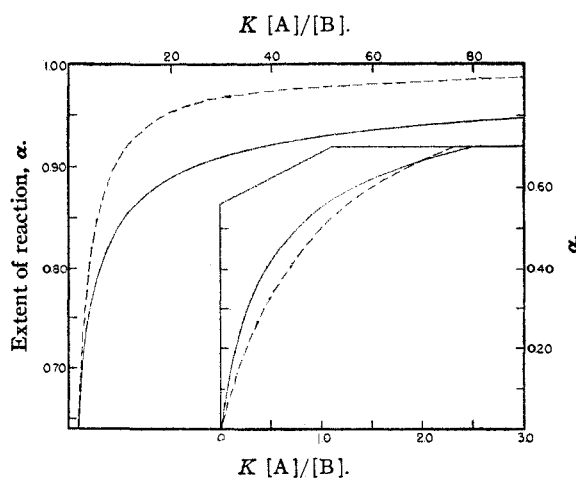
Fig. 1.—Extent of reaction α as a function of $K[A]/[B]$ for the reaction of pairs of a polymer chain (solid line calculated from equation (9)) and for the corresponding reaction of a bifunctional compound (dashed curve calculated from equation (11)). The lower range of conversion is covered in the inset.

than the monomeric compound. In the limit of $\alpha = 0$, $\alpha_{polymer}/\alpha_{monomer} = 2$, according to eqs. (8) and (11). This is an obvious consequence of the fact that for the same number n of functional groups X, the unreacted polymer presents twice as many potential sites for the reaction of a pair. As the reaction advances, the unreacted substituents of the polymer are segregated into sequences of decreasing average length. Sequences of one substituent offer no site for reaction, those of two substituents provide one site, and in general those of j substituents provide $j - 1$ sites. As is demonstrated in the upper part of Fig. 1, the polymer curve lags much behind the monomer curve at high conversions. While the polymer reaction may in principle be carried as near to completion as is desired, an excessively high "driving force" is required for attainment of anything approaching quantitative conversion.

Experimental evidence demonstrating the feasibility of carrying such a reaction substantially beyond the $\alpha = 1 - 1/e^2 = 0.865$ limit for the non-reversible random reaction is found in the literature on polyvinyl acetals where conversions exceeding 90% have been reported.[10] No quantitative studies of equilibria of this type appear to have been carried out, however. We have here the unusual circumstance that a reaction which proceeds under conditions such that reversal is possible (i.e., under conditions of dynamic equilibrium) may be carried further than one which is non-reversible.

It may be anticipated that the rates of such processes will display related anomalies. At low degrees of reaction, the rate should proceed approximately in proportion to the number of substituents. At high conversions under conditions not too close to equilibrium, the rate should depend on the one dimensional "diffusion" of isolated unreacted functional groups to adjacent positions along the chain. This "diffusion" occurs, of course, through dissociation of a pair adjacent to an isolated substituent, followed by combination of an adjacent pair of the resulting sequence of three substituents.

The problem treated here is the one dimensional analog of the adsorption of diatomic molecules each of which occupies two adjacent sites on a surface consisting of a uniform array of identical sites. Roberts and Miller[11] have dealt with this type of adsorption in some detail and have carefully distinguished random films from immobile films. They estimate that a maximum of about 92% of the surface sites in a square array may be covered in the latter case. If the film is mobile, the fraction of the surface

(10) G. O. Morrison and A. F. Price, U. S. Patent 2,179,051 (1939); J. G. McNally and R. H. Van Dyke, U. S. Patents 2,269,216 and 2,269,217 (1945).

(11) J. K. Roberts, Proc. Camb. Phil. Soc., 34, 399 (1938); J. K. Roberts and A. R. Miller, ibid., 35, 293 (1939); A. R. Miller, "The Adsorption of Gases on Solids," Cambridge University Press, New York, N. Y., 1949.

covered may, of course, approach unity even if the diatomic molecules are undissociated and retain their identity throughout the adsorption and subsequent surface diffusion processes. Thus, the results for the one- and the two-dimensional problems are similar.

Summary

Equilibria in reactions involving pairs of ad-

jacent substituents on indefinitely long polymer chains are treated statistically. Although it should be difficult to carry a reaction of this type close to completion, there is no finite limit on the fraction of the functional groups remaining unreacted, which is in contrast to the limit $1/e^2$ beyond which a non-reversible reaction of such pairs cannot be carried.

The Infrared Spectra of Propargylic Alcohols and Bromides

BY JOHN H. WOTIZ, FOIL A. MILLER AND ROBERT J. PALCHAK

In a recent publication[1] dealing with the infrared spectrum of isomeric normal acetylenic compounds, it was noted that compounds containing a functional group on the carbon atom once removed from the triple bond ($C_4H_9C\equiv$ $C-CH_2X$; X equals OH, Cl, Br, CN) have a characteristic strong band near 1710 cm.$^{-1}$ (5.85 μ). Strong absorption at this position is quite unexpected, and the present investigation was undertaken to see whether this band is attributed to a carbonyl-containing impurity, or whether it is characteristic of such substances. Propargylic

$$R-C\equiv C-\overset{\overset{\textstyle R_1}{|}}{\underset{\underset{\textstyle R_2}{|}}{C}}-X,$$

compounds of the type R—C≡C—C—X, where X is OH or Br, R is hydrogen, alkyl, or phenyl, and R_1 and R_2 are hydrogen or alkyl groups, were synthesized and their infrared spectra determined. With the exception of the above-mentioned publication,[4] there is no record of infrared spectra of propargylic compounds in the literature. Table I contains the structural formulas and characteristic absorption bands of all the compounds considered in this study. Figures 1 and 2 contain the spectra of some of the more representative propargylic alcohols and bromides, respectively.

Experimental

Propargylic alcohols were prepared by the action of acetylenic Grignard reagents on aldehydes or ketones. Dimethyl-1-heptynylcarbinol (XVII) is a new compound.

Propargylic bromides were prepared by the reaction of phosphorus tribromide with an ether solution of the propargylic alcohol in the presence of pyridine. Compounds 2-bromo-3-octyne (X), 2-bromo-3-nonyne (XII), 3-bromo-1-heptyne (XIV), 2-bromo-2-methyl-3-octyne (XVI), and 2-bromo-2-methyl-3-nonyne (XVIII) have not been previously reported. The boiling point and refractive index of the alcohols and the bromides used for the infrared investigation are listed in Table I, together with references to previous preparations.

Spectroscopic Measurements.[2]—The infrared spectra were obtained with a Baird double beam spectrometer using a sodium chloride prism. The samples were studied

as pure liquids in 0.05 mm. cells. In Fig. 1 portions of some of the spectra are also given for other thicknesses.

The Raman spectrum was obtained for compound VI. The apparatus consisted of a spectrograph modeled closely after one designed by Prof. R. C. Lord,[3] and an illuminator unit similar to that of Crawford and Horwitz.[4] Exposures of one-half and one hour were used.

Discussion of Results

A number of the bands can be attributed immediately to corresponding modes of vibration, and need not be discussed explicitly. The monosubstituted acetylenes exhibit the $C\equiv C$ stretching frequency near 2100 cm.$^{-1}$ (4.76μ), whereas the disubstituted acetylenes have it at 2210 to 2280 cm.$^{-1}$ (4.52 to 4.38μ). Primary propargylic compounds $R-C\equiv C-CH_2-X$, where R is an alkyl group, show the band near 2260 cm.$^{-1}$ (compounds III through VI). When R is a phenyl group (compounds VII and VIII), the band is lowered to 2210 cm.$^{-1}$. These results agree with our earlier findings[1] and with observations on the Raman spectra of various acetylenic compounds.[5]

We turn now to the unsuspected band at 1740 to 1600 cm.$^{-1}$ which occurs in all but two of the compounds studied. The position depends upon whether the alcohol or bromide is primary, secondary, or tertiary, as shown in Table II. Within each of these classes there is a variation in intensity. However, as a group, the intensity diminishes in the order primary, secondary and tertiary. In general the band is more intense in the bromides than in the corresponding alcohols. The band is not observed for the two tertiary alcohols (compounds XV and XVII).

The following possible explanations for this band have occurred to us:

1. It May Be an Overtone or Combination Tone.—An overtone is out of the question because there is no strong fundamental at the proper position. Two arguments suggest that it cannot be a combination tone. First, for many

(1) Wotiz and Miller, THIS JOURNAL, **71**, 3441 (1949).

(2) The authors wish to thank Mr. R. B. Hannan for his able assistance in these determinations.

(3) Harrison, Lord and Loofbourow, "Practical Spectroscopy," Prentice Hall, Inc., New York, N. Y., 1948, p. 515 ff.

(4) Crawford and Horwitz, J. Chem. Phys., **15**, 268 (1947).

(5) Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publishing Corp., New York. N. Y., 1939, pp. 200-206.