proximately 30 and 35% of the carbon of the coal and coke, respectively, is found as aromatic acids.

It has been shown that good recoveries of oxalic and aromatic acids can be obtained by direct electrolytic decomposition, in a three compartment cell, of the potassium salts resulting from the oxidation. Oxalic plus aromatic acids recovered in this way were 88 and 98 g. per 100 g. of coal and coke, respectively.

Esterification followed by distillation of the esters in a special molecular fractionating still resulted in the isolation of no crystalline material other than dimethyl oxalate. Separation of the acids on the basis of varying salt solubilities, followed by liberation of the free acids from the salt fractions, and esterification and fractionation of the esters, resulted in the isolation of small amounts, usually less than 2 g. per 100 g. of coal or coke, of various benzene carboxylic acids. The presence of a large fraction, approximately 50%, of esters which are not distillable, under conditions where it was shown that the esters of known carboxylic acids distil rapidly, has led to the conclusion that a significant part of the acids from this coal and coke are more complex than benzene carboxylic acids. The persistent yellow color of the acids and low volatility of the esters indicate that they may be condensed aromatic acids containing carbonyl oxygen. It is pointed out that the failure to recover hydrocarbons more complex than diphenyl, by decarboxylation, does not necessarily preclude the possibility of the presence of acids with condensed aromatic nuclei containing carbonyl oxygen, since drastic alkaline decomposition is known to split the nuclei of such aromatic acids.

PITTSBURGH, PENNA. RECEIVED NOVEMBER 27, 1936

[CONTRIBUTION NO. 173 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

The Mechanism of Vinyl Polymerizations[1]

BY PAUL J. FLORY

Nearly all compounds containing non-benzenoid carbon–carbon double bonds are capable of undergoing polymerization when subjected to suitable conditions. High molecular weight polymers may be formed from many such compounds, notable examples of which are styrene, vinyl acetate, acrylic acid and its esters, butadiene, and chloroprene. The closely similar characteristics of the conversion of monomer to polymer in these vinyl polymerizations has led to the conclusion that all of them proceed by essentially the same mechanism.

An abundance of evidence has been accumulated to show that typical vinyl polymerizations are chain reactions.[2,3] Except in the presence of certain polymerization catalysts, it may be assumed that the chain is propagated through the successive addition of monomer molecules to a free radical, *i. e.*

$$\text{---}(CH_2\text{—}CHR)_x\text{—}CH_2\text{—}CHR\text{—}\xrightarrow{+\ CH_2=CHR}$$
$$\text{---}(CH_2\text{—}CHR)_{x+1}\text{—}CH_2\text{—}CHR\text{—}\xrightarrow{+\ CH_2=CHR}$$
etc.[4,5]

In support of this free radical chain mechanism Taylor and Jones[6] have found that ethylene is polymerized by free radicals released in the thermal decomposition of metal alkyls, and Rice and Sickman[7] induced the polymerization of ethylene with methyl radicals from decomposing azomethane. The mechanisms of the equally important processes of chain initiation and termination have remained more obscure. From the limited experimental results available at the present time it is possible to draw certain general conclusions pertaining to the mechanisms of these processes, and upon the basis of these conclusions the theoretical treatment of the kinetics of vinyl polymerizations presented in the following pages has been developed.

---

(1) The term "vinyl polymerizations" is used here to include not only polymerizations of derivatives of vinyl alcohol such as vinyl acetate or vinyl chloride, but all polymerizations involving olefinic double bonds and leading to products of high molecular weight.

(2) Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, Oxford, 1935, p. 444.

(3) Chalmers, THIS JOURNAL, **56**, 912 (1934).

(4) Staudinger and Frost, *Ber.*, **68**, 2351 (1935).

(5) Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936).

(6) H. S. Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

(7) O. K. Rice and Sickman, *ibid.*, **57**, 1384 (1935).

General Discussion

There are two pertinent characteristics of vinyl polymerization which must be accounted for by an acceptable mechanism for the process: the apparent autocatalytic character of the conversion of monomer to polymer, *i. e.*, the increase in rate during the first stage of the process,[8] and the approximate constancy of the average molecular weight during the polymerization.[4,5,9] Dostal and Mark[10] have proposed a mechanism based on two processes, chain initiation brought about by a relatively slow "activation" of monomer, and subsequent rapid successive addition of monomers to the activated molecule as indicated above. It was originally assumed that activated molecules continue to "grow" (add on monomers) indefinitely. More recently Dostal[11] has appended to the equations derived on the basis of this mechanism a correction to allow for an "isomerization" reaction whereby the actively "growing" molecule reverts to an inactive polymer molecule incapable of adding on more monomers. The equations of Dostal and Mark are unnecessarily obscure due to their use of an abstract quantity, the "eigenzeit" ($= {}_0\int^t x\, dt$ where x is the fraction of the material which is monomeric at time t), instead of an explicit expression of time.[12] Although the theories of Dostal predict an increase in rate during the early stages of the polymerization in agreement with experiment, they also predict an increase in the molecular weight during the course of the polymerization, which is not in accord with observation.

Staudinger and Frost[4] conceive of the polymerization process as consisting of the three steps: chain initiation, chain propagation, and chain termination. The latter step, whereby an "active" polymer molecule is "deactivated," is incorporated as one of the main reactions. Schulz[13] concludes that inasmuch as according to this mechanism the average molecular weight must be proportional to the ratio of the rate of chain propagation to the rate of chain termination, the constancy of the average molecular weight throughout the course of the polymerization is to be explained by a constancy in this ratio. From this conclusion he derives size distribution equations which are in agreement with the approximate distribution of sizes which he found experimentally in polyisobutylene. This mechanism offers a satisfactory explanation of molecular weight constancy during the polymerization and of the distribution of molecular sizes, but fails to account for the acceleration of the rate at the outset of the polymerization.[14] Thus, neither the theory of Dostal nor that of Schulz is in satisfactory accord with experiment.

Before attempting to formulate a preferable mechanism, let us examine the facts pertaining to the formation and termination of the polymerization chains. Both the formation and annihilation of free radicals (active centers) in the polymerizing monomer, in the absence of extraneous substances such as (negative) catalysts, is subject to a highly significant restriction, namely, that *the free radicals can be formed or destroyed in pairs only*. For example, the free bond terminus of an "active" polymer molecule may be destroyed through saturation of the free bond with a univalent group or a hydrogen atom, or through the formation of a double bond in place of the free radical end group with concurrent loss of a univalent group or a hydrogen atom. In any case the disappearance of the free bond on the chain molecule would require the appearance of a free radical or hydrogen atom elsewhere. Thus, although the active centers can, in effect, be transferred from one molecule to another, they can be destroyed only in pairs by reaction with each other. Consequently, the destruction of active centers must be bimolecular. Furthermore the rate of destruction of active centers must be proportional to the *square* of their concentration, and the length of a particular chain from initiation to destruction must be inversely proportional to the first power of their concentration.

In photopolymerizations a manifold increase in the rate of production of active centers is brought about without directly affecting the other proc-

---

[8] See for example, Mark and Raff, *Z. physik. Chem.*, **B31**, 275 (1936).

[9] It has been found in this Laboratory recently that the average molecular weight of methyl methacrylate polymer at less than one per cent. conversion does not differ significantly from the average molecular weight of the polymer when polymerization is nearly complete.

[10] Dostal and Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

[11] Dostal, *Monatsh.*, **67**, 1 (1935); **67**, 63 (1935).

[12] Gee, *Trans. Faraday Soc.*, **32**, 656 (1936), has simplified the abstract and approximate equations of Dostal and has shown the consequences of chain deactivation mechanisms of several sorts. He has attempted to apply his theories to polymerizations in general without differentiating between the various types [Carothers, *Chem. Rev.*, **8**, 378 (1931)] which involve unlike mechanisms. See Gee and Rideal, *Trans. Faraday Soc.*, **31**, 969 (1935), and **32**, 666 (1936).

[13] Schulz, *Z. physik. Chem.*, **B30**, 379 (1935).

[14] Schulz has mentioned in a footnote that perhaps an occasional "branching" of the chain to bring about initiation of one or two new chains at the moment of deactivation might explain the acceleration in rate.

esses involved. With the resultant increase in the concentration of active centers the chain length must decrease and so, according to the conventionally accepted identity of chain length and degree of polymerization, a decrease in molecular weight would be expected. In conflict with this latter deduction, photopolymerized methyl methacrylate[20] (methyl α-methyl acrylate) is not of appreciably lower molecular weight than polymer prepared in the absence of light at the same temperature. Staudinger and Schwalbach[15] obtained their highest molecular weight polyvinyl acetate by photopolymerization at 20°. Although no polymer was prepared by thermal polymerization at this temperature, extrapolation of data at higher temperatures (*cf. seq.*) indicates approximate equality of the molecular weights of photo and thermal polymers at 20°. Staudinger and Schwalbach also found that introduction of oxygen retarded the rate of the photopolymerization much more than it reduced the molecular weight.

It is evident from these results that an increase in the number of active centers does not decrease the molecular weight, nor does impedance of the reaction through the destruction of active centers by a negative catalyst necessitate a corresponding reduction in molecular weight. These facts suggest that the reaction which limits the growth of a particular molecule, *i. e.*, the reaction which determines the molecular weight, and the reaction which destroys active centers are not one and the same reaction, but are entirely independent processes. This concept has been embodied in the following scheme for the mechanism of vinyl polymerizations

$$M_1 + M_1 \longrightarrow 2M^* \qquad (1)$$
$$M^*_n + M_1 \longrightarrow M^*_{n+1} \qquad (2)$$
$$M^*_n + M \longrightarrow M_n + M^* \qquad (3)$$
$$M^*_n + M^*_m \longrightarrow M_n + M_m, \text{ or } M_{n+m} \qquad (4)$$

where M_1 denotes a monomer molecule, M_n a polymer molecule composed of n units, and M a molecule containing an unspecified number of units; a molecule bearing an active center is marked with an asterisk. Reaction (1) has been written to imply the simultaneous formation of two active centers; as will be shown later, both of them are very probably on the same molecule (dimer or trimer). The active centers created in (1) undergo the chain propagation reaction (2) repeatedly until at some stage the "chain transfer" reaction (3) intervenes, whereupon the polymer molecule loses the active center and ceases to grow. The molecule M* which inherits the active center grows by the repeated occurrence of reaction (2) until (3) again intervenes, etc. At a favorable collision of two of the active centers, which will be relatively rare since the active centers must be present in such minute concentrations, mutual deactivation (4) will occur. The production of each active center will, on the average, bring about the formation of many polymer molecules before the effect of the active center is finally ended by reaction (4). (It is assumed that the absolute rate of (3) is much greater than that of (4).)

The principal feature of the above mechanism in contrast to previous theories is the concept of distinctly separate processes for the interruption of the growth of a particular molecule and for the destruction of active centers. As the following discussion shows, this mechanism is capable of explaining in a quantitative manner the acceleration of the rate which occurs at the outset of the polymerization, the approximate constancy of molecular weight during the course of the process, and the molecular weight dependence on temperature and independence of rate of polymerization.

Kinetics of Conversion of Monomer to Polymer

The following analysis of polymerization kinetics will be restricted to non-catalytic and homogeneous processes, *i. e.*, to polymerizations carried out under catalytically aseptic conditions. It will be assumed that the rate constants of reactions (2), (3) and (4) are independent of the size of the polymer molecule bearing the active center. Hence, the probability either of chain transfer or of chain termination at any particular stage of growth of the polymer will be the same as for any other stage of growth. If the molecular weight of the polymer is disregarded and only the conversion of monomer to polymer is considered, then reactions (1), (2) and (4) will suffice as a basis for a kinetic interpretation of the process. As discussed above, it is apparent that both (2) and (4) must be second-order processes. Chain initiation (1) cannot be first order (in the absence of catalysts) because as shown in a following section the energy requirement for such a process is too great, but it may be either second or third order. In the following treatment (2) and (4) will be taken as second order, and equations will be derived for both a second order and a third order initiation process.

---

(15) Staudinger and Schwalbach, *Ann.*, **488**, 8 (1931).

Polymerization Kinetics Assuming Second Order Chain Initiation.—The following notation will be used

n = concentration of monomer
N = concentration of active centers
k_1, k_2 and k_4 = velocity constants of reactions (1), (2) and (4), respectively.

If (1), (2) and (4) are all second order[16]

$$dN/dt = k_1n^2 - k_4N^2 \quad (5)$$

$$dn/dt = k_2Nn \quad (6)$$

Dividing equation (5) by (6), integrating and supplying the boundary condition, $N = 0$ when $n = n_0$, gives

$$N = \left(\frac{k_1}{k_4 - k_2}\right)^{1/2} [n^2 - n_0^2(n/n_0)^{2r}]^{1/2} \quad (7)$$

where $r = k_4/k_2$. Substituting (7) in (6) and letting $n/n_0 = x$ and $n_0(k_1k_2)^{1/2} = K$

$$\frac{dx}{dt} = -Kx^2\left(\frac{1 - x^{2r-2}}{r - 1}\right)^{1/2} \quad (8)$$

Equation (8) and some of the equations derived therefrom are indeterminate at the point $r = 1$.

The relation of x, the fraction of the original material which is unpolymerized, to t is completely determined according to (8) by two parameters, K and r. Since K occurs conjugate with t, a change in K merely has the same effect as an alteration of the time units; the fundamental characteristics of the variation of x with t are entirely determined by r. The solid curves in Fig. 1A represent solutions of (8) for the several values of r indicated above each curve, time being expressed in arbitrary units equal to $1/K$; in Fig. 1B a magnified scale has been used to show the initial portions of the curves. Inasmuch as no general solution of (8) has been obtained, these solutions have been obtained by the special methods discussed in the following paragraphs.

When $r = 0$, *i. e.*, when no destruction of active centers occurs ($k_4 = 0$), the mechanism presented above and the original Dostal and Mark[10] mechanism in which second order chain initiation is assumed are identical with respect to conversion of monomer to polymer (although the two mechanisms predict different molecular weights). In this case (8) becomes[17]

$$dx/dt = -Kx(1 - x^2)^{1/2} \quad (8.1)$$

Integration of (8.1) gives

$$\ln [(1 + \sqrt{1 - x^2})/x] = Kt \quad (9.1)$$

The $r = 0$ curve in Fig. 1A was obtained from equation (9.1), which corresponds to Dostal and Mark's[10] approximate equation (20). As they have shown, the rate of polymerization accelerates, reaches a maximum corresponding to the inflection in the curve, and then decreases continuously.

As r increases to large values, *i. e.*, as the rate of destruction of active centers becomes relatively more rapid, the duration of the rate acceleration period becomes shorter, and when $r \gg 1$, (8) approaches the simple second order equation[18]

$$dx/dt = -(K/r^{1/2})x^2 \quad (8.2)$$

For $r = 2$, an intermediate case between these two extremes, equation (8) integrates to

$$Kt = (1 - x^2)^{1/2}/x \quad (9.3)$$

from which the $r = 2$ curve has been derived. The curves for $r = 10$, 25 and 100, have been obtained by graphical integration using the first form of the equation

$$Kt = 1/2\ (r - 1)^{-1/2}\int_1^x \frac{1}{x}\, d \ln \left[\frac{1 + (1 - x^{2r-2})^{1/2}}{1 - (1 - x^{2r-2})^{1/2}}\right]$$

$$= (r - 1)^{1/2}\int_1^x (1 - x^{2r-2})^{-1/2}\, d(1/x)$$

for values of x near unity and the second form for all smaller values of x.

All of the curves meet at sufficiently small $1-x$ values, as shown in Figs. 1A and 1B. An increase in r retards the conversion and brings the inflection point, or point of the maximum rate, to a lower $1-x$ value; that is, a recession in the acceleration period occurs when r is increased.

The relation of x_m, the value of x at the inflection, to r can be derived from (8) as follows

$$\frac{d^2x}{dt^2} = \frac{K^2x^3}{(r - 1)}\,[2 - (r + 1)x^{2r-2}] = 0$$

$$x_m = ((r + 1)/2)^{1/(2-2r)} \quad (10)$$

Curve 2 of Fig. 2 expresses this relation graphically. Substituting (10) in (8) in order to obtain the rate at x_m

$$\left(\frac{dx}{dt}\right)_{\text{max.}} = -Kx_m^2\,(r + 1)^{-1/2} = \frac{-K}{\sqrt{2}}\left(\frac{2}{r + 1}\right)^{(r+1)/(2r-2)} \quad (8.8)$$

From a plot of experimental x *vs.* t data, both x_m and $(dx/dt)_{\text{max.}}$ can be determined. The value of r may be obtained by substituting x_m in (10), or by the use of Curve 2 in Fig. 2. Equation (8.8) can then be used to evaluate K from r and $(dx/dt)_{\text{max.}}$. Exact location of the inflection

---

[16] The term $-k_1n^2$, which represents the rate of consumption of monomers by reaction (1), has been omitted in (6). Except when the chain length is very short, this term is negligible compared with $-k_2Nn$.

[17] Equation (8.1) could have been derived directly from (5) and (6) by placing $k_4 = 0$ in the former.

[18] Equation (8.2) is the solution of (5) and (6) for the "steady state" condition $(dN/dt) = 0$.

point will, in general, be subject to a large uncertainty, although $(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$ may be determined quite accurately. When x_m is sufficiently near unity, *i. e.*, when r is large, the following approximate equation can be used satisfactorily.

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{\text{max.}} = -\frac{K}{r^{1/2}} = -n_0k_1{}^{1/2}\,k_2/k_4{}^{1/2} \qquad (8.9)$$

Although determination of r $(=k_4/k_2)$ and K $(=n_0(k_1k_2)^{1/2})$ is feasible, evaluation of the individual velocity constants from experimental determination of the course of the polymerization is impossible.

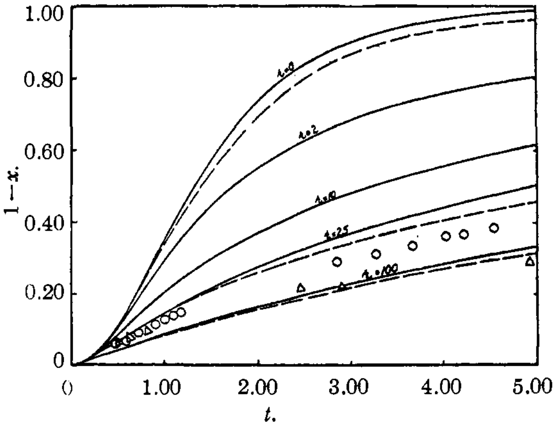


Fig. 1A.—Extent of polymerization *vs.* time for various values of r. Solid curves represent polymerization when chain initiation is second order with time expressed in units of $1/K$; dashed curves represent polymerization when chain initiation is third order, with t in units of $1/K'$. ○, experimental points for the polymerization of 60% vinyl acetate in toluene at 100.9°[19] △, experimental points for 22.5% styrene in toluene at 98.2°.[8]

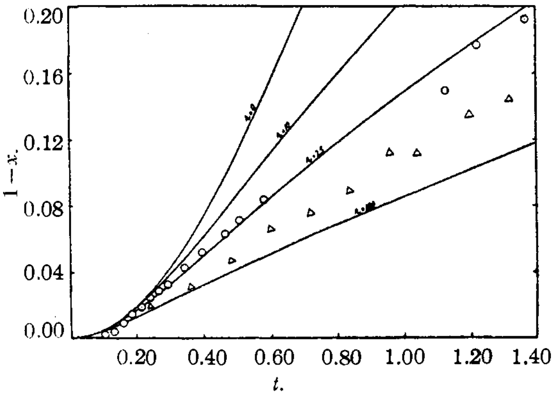


Fig. 1B.—Initial portions of curves shown in Fig. 1A. These are equally applicable to polymerization with second order chain initiation (t in $1/K$ units) or with third order chain initiation (t in $1/K'$ units). ○, 60% vinyl acetate in toluene at 81.8° [19]; △, undiluted styrene at 98.2°.[8]

Polymerization Kinetics Assuming Third Order Chain Initiation.—If reaction (1) is third order, equation (5) must be replaced by

$$\mathrm{d}N/\mathrm{d}t = k_1n^3 - k_4N^2 \qquad (11)$$

Solving (11) and (6) simultaneously gives

$$\mathrm{d}x/\mathrm{d}t = -K'x^{5/2}\left(\frac{1 - x^{2r-3}}{r - 3/2}\right)^{1/2} \qquad (12)$$

where $r = k_4/k_2$ as before, and $K' = n_0{}^{3/2}(k_1k_2)^{1/2}$. This equation closely resembles (8); x^2 in (8) has been replaced by $x^{5/2}$, the quantities in parentheses in the two equations differ only slightly, and n_0 in the K in (8) has been replaced by $n_0{}^{3/2}$ in K'. When r assumes large values (8) approaches a simple second order equation, whereas (12) approaches a five-halves order equation.

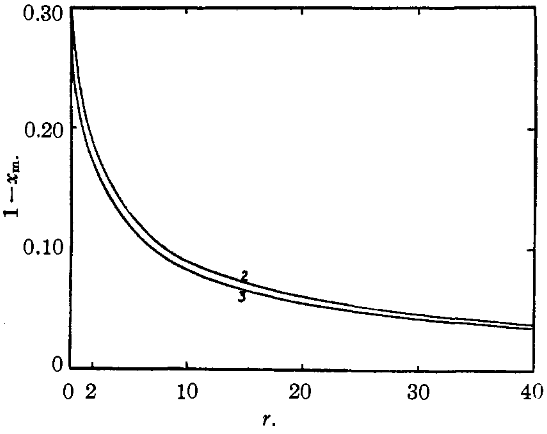


Fig. 2.—Relation of x_m, the value of x at $(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$, to r for second order initiation (curve 2) and for third order initiation (curve 3).

Several integrals of (12) are shown by the dashed curves in Fig. 1A. Each of these for values of x sufficiently near unity merges with the solid curve for the same r value; in the region shown in Fig. 1B the two sets of curves are substantially identical.

The $r = 0$ curve has been obtained from an integral solution of (12). The other curves have been obtained by the graphical evalution of the integrals in the equation

$$K't = 1/2\,(r - 3/2)^{-1/2}\int_1^x x^{-3/2}\,\mathrm{d}\ln\left[\frac{1 + (1 - x^{2r-3})^{1/2}}{1 - (1 - x^{2r-3})^{1/2}}\right]$$
$$= 2/3\,(r - 3/2)^{1/2}\int_1^x (1 - x^{2r-3})^{-1/2}\,\mathrm{d}(x^{-3/2})$$

the first integral being used for x values very close to unity, and the second for all smaller x values.

The relation of x_m to r, obtained by differentiating (12) and equating to zero, is

$$x_m = [2/5\,(r + 1)]^{1/(3-2r)} \qquad (14)$$

A comparison of the graph of (14), curve 3 of Fig. 2, with the graph of (10), curve 2 of the same figure, emphasizes the similarity of the two equations. The equation analogous to (8.8) for the maximum rate, obtained by substituting (14) in (12), is

$$(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}} = -K'x_m^{5/2}(r+1)^{-1/2} \qquad (12.8)$$

When r is large, $x_m \cong 1$, and

$$(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}} = -K'/r^{1/2} = n_0^{3/2}k_1^{1/2}k_2/k_4^{1/2} \qquad (12.9)$$

which is the same as (8.9) except for a factor $n_0^{1/2}$. Using (12.8) or (12.9) K' can be determined from a graph of x *vs.* t in the same manner as was discussed in connection with the corresponding equations in the preceding section. In view of the similarity of the two sets of equations, this method can be used for satisfactory evaluations of r and of K or K' without distinguishing the order of (1), unless r is of the order of unity or less.

Equations have been worked out according to the above methods assuming first order chain initiation, in which case the mechanism becomes the same as assumed by Gee.[12] They too are similar to the equations for second order initiation. Thus, the character of the conversion of monomer to polymer is only slightly dependent upon the order of reaction (1). The kinetic orders of (2) and (4) are highly important, however, in determining the character of the conversion kinetics.

As mentioned before, the above treatment is intended for application to strictly non-catalytic polymerizations only. In general, catalysts may either accelerate reaction (1), ("positive" catalysts) or reaction (4) ("negative" catalysts or inhibitors), or both. If the action of the catalyst is limited to acceleration of (1), the above treatment can be expected to apply, although the order of (1) may be altered. If the catalyst causes chain termination, a term should be added to equation (5), or (11), and the polymerization kinetics will be materially affected. Nearly all catalysts (O_2, Na, $SnCl_4$, etc.) which are known to accelerate the polymerization are also effective chain terminators; the converse is not true.

Application to Experimental Data

Most of the experimental data pertaining to vinyl polymerization kinetics quoted in the following pages has been taken from one of the three following sources: the results of Starkweather and Taylor[19] on vinyl acetate, Mark and Raff's[8] results on styrene, and the work of Starkweather, Flory and Carothers[20] on methyl methacrylate. Starkweather and Taylor using a specially refined technique to prevent contamination (and using Pyrex glass) obtained consistently reproducible results on vinyl acetate. Mark and Raff's results on styrene were also quite reproducible, but the results referred to above on methyl methacrylate were erratic. In a study of catalysis of vinyl polymerizations, Breitenbach and Raff[21] found that, under their experimental conditions (using Jena or soft glass), the polymerization of acrylic ester definitely was catalyzed by the walls of the container, vinyl acetate was subject to the catalysis to a lesser extent, and styrene was free from catalysis. Irreproducibility seemed to accompany catalysis. Considering the reproducibility of the results referred to above on vinyl acetate, the polymerization results for this substance, as well as the results for styrene, must have been substantially free from the effects of catalysis. The polymerization of methyl methacrylate was probably catalytic.

In Figs. 1A and 1B representative experimental data on styrene and vinyl acetate have been included for comparison with the family of theoretical curves. Time units have been adjusted by a factor arbitrarily chosen to bring about the best possible fit with the curves. Considering the likelihood of accompanying secondary effects not taken into account by the simple theory given here, exact agreement with the theoretical curves is not to be expected. It is particularly significant that the theory describes satisfactorily the course of the polymerization during the acceleration period (Fig. 1B), which is so characteristic of most vinyl polymerizations. Although the points are more nearly in agreement with a third order chain initiation (dashed curves in Fig. 1A), a choice between the two mechanisms is scarcely justified by these results alone.

When, as in the case of the polymerization of indene,[22] the acceleration period is apparently absent, the theory leads to the conclusion that r is very large.

Apparent Energies of Activation.—Regardless of whether reaction (1) is second or third order, $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}}$ is proportional, according to (8.9) and (12.9), to $k_1^{1/2}k_2/k_4^{1/2}$ to a satisfactory approximation when r is sufficiently greater than unity. Upon

---

[19] Starkweather and G. B. Taylor, THIS JOURNAL, **52**, 4708 (1930). Drs. Starkweather and Taylor have kindly furnished the author with a detailed report of their results.

[20] Starkweather, Flory and Carothers, as yet unpublished.

[21] Breitenbach and Raff, *Ber.*, **69B**, 1107 (1936).

[22] Mark and Raff, *Z. physik. Chem.*, **B32**, 417 (1936).

substituting an Arrhenius expression, $k = Ae^{-E/RT}$, for each velocity constant

$$\log_{10}(\mathrm{d}x/\mathrm{d}t)_{\text{max.}} = B - E_a/2.303RT \qquad (15)$$

where B is a constant containing the A's and E_a is the "apparent energy of activation" defined by

$$E_a = 1/2\,E_1 + E_2 - 1/2\,E_4 \qquad (16)$$

E_1, E_2 and E_4 denoting the activation energies of (1), (2) and (4), respectively.

The $(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$ values in Table I for styrene, vinyl acetate and methyl methacrylate at various temperatures have been evaluated graphically from plots of experimental data. The data in Figs. 1A and 1B show that at least for styrene and vinyl acetate r is large enough (between 25 and 100) to permit assumption of the proportionality relation upon which (15) is based. In Fig. 3, $\log_{10}(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$ is shown to be a linear function of $1/T$ in agreement with (15). E_a values given in Table I have been calculated from the slopes of the lines in the figure. For styrene and vinyl acetate they are nearly the same, but E_a for methyl methacrylate is much lower.

TABLE I

MAXIMUM RATES OF POLYMERIZATION AND APPARENT ENERGIES OF ACTIVATION

Substance	Temp., °C.	$(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$ in min.$^{-1}$ $\times 10^4$	$\log_{10} (\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$	$1/T \times 10^3$ (T, °K.)	E_a, kcal.
Styrene[a]	60	0.211	−4.676	3.000	
Styrene[a]	70	0.494	−4.306	2.914	
Styrene[a]	80	1.64	−3.785	2.832	22.1 (±2)
Styrene[a]	98.2	4.90	−3.310	2.693	
Styrene[a]	130	34	−2.47	2.518	
22.5% styrene[a] in toluene	98.2	2.80			
Vinyl acetate[b]	81.8	8.9	−3.051	2.818	
Vinyl acetate[b]	100.9	46.7	−2.331	2.675	23.1 (±1)
Vinyl acetate[b]	111.2	112	−1.951	2.604	
60% Vinyl acetate[b] in toluene	81.8	5.82	−3.235	2.818	
	100.9	27.5	−2.560	2.675	22.3 (±1)
	111.2	56.0	−2.252	2.604	
Methyl methacrylate[c]	100	4.0	−3.398	2.681	
	132	10.7	−2.970	2.469	10.3 (±3)
	210	91	−2.041	2.070	

[a] The rates for styrene are based on the data of Mark and Raff. [b] The rates for vinyl acetate have been evaluated from the unpublished detailed measurements of Starkweather and G. B. Taylor.[19] [c] Unpublished work carried out by Starkweather, Flory and Carothers.[20]

Chain Lengths and Degree of Polymerization.—According to the proposed mechanism of polymerization two chain lengths must be differentiated: (ν, the average number of monomers caused to polymerize by one active center from its creation in reaction (1) to its annihilation by (4), and λ, the average number of monomers added to a particular chain free-radical from its formation by either (1) or (3) until its growth is arrested by chain transfer (3). According to the present theory many polymer molecules are formed for each active center created and so $\nu >> \lambda$.

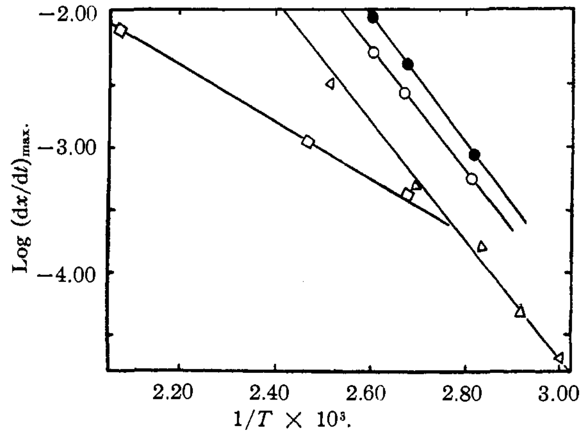


Fig. 3.—Decadic logarithm of maximum rate *vs.* the reciprocal of the absolute temperature: ○, 60% vinyl acetate in toluene; ●, undiluted vinyl acetate; △, styrene; □, methyl methacrylate (see Table I).

The average kinetic chain length, or "ν chain length," is equal to the ratio of the rate of (2) to the rate of (4), *i. e.*

$$\nu = k_2n/k_4N \qquad (17)$$

Since according to (6) the rate of polymerization is proportional to N, ν is inversely proportional to the rate. Although $k_2/k_4 (= 1/r)$ can be estimated from the course of the polymerization, the absolute value of N cannot be determined from such data, and so ν also evades evaluation.

The average "λ chain length" is equal to the ratio of the rate of (2) to the rate of (3). It follows that

$$\lambda = (k_2/k_3)f \qquad (18)$$

where f is a function of n (and perhaps of the amount of solvent also; *cf. seq.*) depending on the kinetic orders of (2) and (3). Reaction (2) is obviously second order, but the kinetic order of (3), which will be discussed in a later section, is uncertain. Whatever is the exact mechanism of (3), at the same concentration of monomer λ should be proportional to k_2/k_3 according to (18). If no chain branching (*cf. seq.*) occurs, λ is equal to the average degree of polymerization $D. P.$ Upon introducing the Arrhenius equation into the above proportionality relation

$$\log_{10}\lambda = \log_{10}(D.\ P.) = C + (E_3 - E_2)/2.303RT \quad (19)$$

where C is a constant.

In Table II the available data on the *D. P.*'s of polymers prepared at two or more temperatures are given. These are all based on estimates of molecular weights obtained by the Staudinger viscosity method.[23] In Fig. 4 the log (*D. P.*) values (Table II) for styrene, vinyl acetate and methyl methacrylate are shown to be linear functions of $1/T$ in agreement with (19). This simple quantitative relation of observed molecular weights to temperature stands in excellent confirmation of the theory developed above. The $E_3 - E_2$ values in the last column of the table have been calculated from the slopes of the lines in the figure; in the case of ethyl acrylate, where data are available at two temperatures only, $E_3 - E_2$ values have been calculated directly from equation (19).

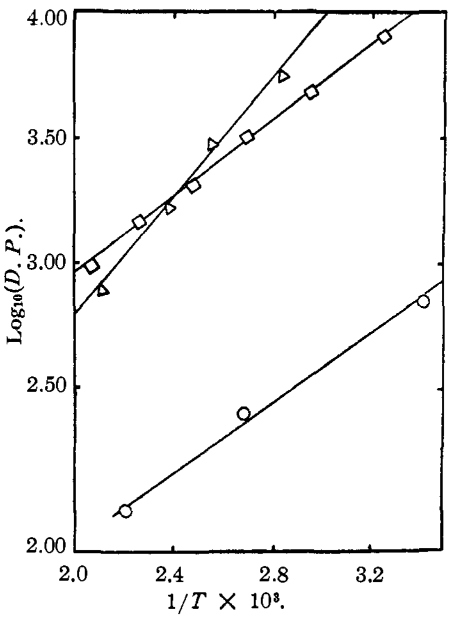


Fig. 4.—$\log_{10}$ (*D. P.*) *vs.* $1/T$: ○, vinyl acetate; △, styrene; □, methyl methacrylate (see Table II).

TABLE II

DEGREE OF POLYMERIZATION AND $E_3 - E_2$

Substance	T., °C.	$D.\ P.^a$	$\log_{10}$ ($D.\ P.$)	$1/T \times 10^3$ (T., °K.)	$E_3 - E_2$, kcal.
Styrene[b]	80	5880	3.769	2.833	
Styrene[b]	100	4130	3.616	2.671	
Styrene[b]	120	2900	3.463	2.545	5.4
Styrene[b]	150	1710	3.233	2.364	
Styrene[b]	200	827	2.917	2.114	
Vinyl acetate[c]	20[f]	700	2.85	3.413	
Vinyl acetate[c]	100	250	2.40	2.681	3.2
Vinyl acetate[c]	180	100	2.00	2.208	
Methyl methacrylate[d]	35[f]	8000	3.906	3.247	
Methyl methacrylate[d]	65	4750	3.677	2.959	
Methyl methacrylate[d]	100	3210	3.513	2.681	
Methyl methacrylate[d]	132	2020	3.305	2.469	3.5
Methyl methacrylate[d]	170	1480	3.170	2.257	
Methyl methacrylate[d]	210	980	2.991	2.070	
Ethyl acrylate[e], 1 *M* in	100	78	1.892	2.681	4.8
butyl acetate	190	22	1.342	2.160	
Ethyl acrylate[e], 2 *M* in	100	145	2.161	2.681	4.5
butyl acetate	200	40	1.602	2.114	

[a] These are relative values of *D. P.*, which may only roughly approximate the correct absolute values. [b] Staudinger and Husemann, *Ber.*, **68**, 1618 (1935). [c] Staudinger and Schwalbach.[15] [d] Starkweather, Flory and Carothers.[20] [e] Staudinger and Trommsdorff.[34] [f] The 20° vinyl acetate polymer and 35° methyl methacrylate polymer were obtained by photopolymerizations.

Photochemical Polymerization.—The experiments of Taylor and Vernon[24] on the photopolymerizations of styrene and vinyl acetate are of particular interest because of their bearing on activation energies. Radiation in the near ultraviolet region (3000 to 4000 Å.), such as Taylor and Vernon used, is absorbed by the double bond and not by other parts of the molecule. Consequently, the initial step consists of activation of the monomer at the double bond, and not formation of free radicals through the dissociation of C–C or C–H bonds. Although many of the optically excited monomers must lose their energy in collisions with other molecules, some of them evidently react with other unexcited monomers yielding active centers and thereby initiating polymerization chains. Since the initiation of chains must therefore be second (or third) order[25] and since it may be assumed that other processes occurring in the polymerization are unaffected by the light, the theory given above for thermal poly-

---

(23) Staudinger and Schulz, *Ber.*, **68**, 2320 (1935) have shown that for polystyrene the constant, K_m, in the Staudinger equation, $(\eta_r - 1)/C = K_m$ (M. W.), (η_r = relative viscosity of a dilute solution of polymer of concentration C) varies slightly with the temperature of polymerization, *e. g.*, from 0.61×10^{-4} at 80° to 0.41×10^{-4} at 200°. This behavior of polystyrene they attribute to chain branching (*cf. seq.*). Since it is the length of the chain (λ), rather than *D. P.*, which is primarily important in the evaluation of $E_3 - E_2$, and since according to Staudinger the viscosity molecular weight is fundamentally a measure of chain length, a constant value of K_m ($= 0.50 \times 10^{-4}$) has been preferred in calculating the *D. P.*'s for polystyrene in Table II from the $(\eta_r - 1)/C$ values given by Staudinger and Husemann. For the evaluation of $E_3 - E_2$, only relative values of M. W. at the various temperatures are required; hence, the absolute value of K_m is unimportant.

(24) H. S. Taylor and Vernon, THIS JOURNAL, **53**, 2527 (1931).

(25) In cases where all, or nearly all, of the incident light is absorbed, (1) may be first order because the amount of light absorbed is no longer dependent upon concentration.

merizations is equally applicable to photopolymerizations. Only the kinetic mechanism of reaction (1) differs in the two cases; E_a in equation (15) should be replaced by

$$E'_a = 1/2\,E'_1 + E_2 - 1/2\,E_4 \qquad (16.1)$$

where E'_1 is the activation energy which is required in addition to the photochemical excitation energy for the initiation of chains. E'_1 must be very small and within the limits of accuracy of the other E's, $1/2\,E'_1$ can be omitted in (16.1), *i. e.*

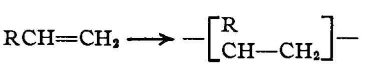
$$E'_a = E_2 - 1/2\,E_4 \qquad (16.2)$$

Taylor and Vernon found average 10° temperature coefficients of 1.30 for styrene in the range 30 to 100°, and 1.26 for vinyl acetate in the range 40 to 70°. For both substances the amount of light absorbed was independent of the temperature. The corresponding activation energies, E'_a, are 5.9 kcal. for styrene and 4.9 kcal. for vinyl acetate.

Activation Energies of Individual Reactions.—Combining the E'_a with the E_a values (equation 16) for these two compounds one obtains values for E_1, namely, 32 kcal. for styrene, and 35 kcal. for vinyl acetate. Assuming any reasonable value of $E_2 - 1/2\,E_4$ for methyl methacrylate, E_1 must be less than about 20 kcal., *i. e.*, appreciably less than for styrene or vinyl acetate. If, as mentioned before, the polymerization of methyl methacrylate was catalytic, a low value for E_1 is in accord with expectation. E_4, the energy requirement for the inter-reaction of two free radicals (whether it be by combination or disproportionation, *cf. seq.*) must be very low, certainly less than 5 kcal. Hence, from the values of $E'_a = E_2 - 1/2\,E_4$, E_2 must be about 6 kcal. for styrene and about 5 kcal. for vinyl acetate.[26,27] Recalling the values of $E_3 - E_2$ in Table II, E_3 for styrene must be about 12 kcal. and for vinyl acetate about 9 kcal.

Heats of Polymerization

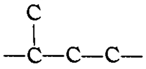
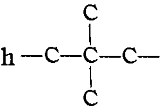
In a vinyl polymerization an unsaturated monomer is converted to a saturated (or less unsaturated) structural unit of a polymer molecule; that is



$$\mathrm{RCH{=}CH_2} \longrightarrow -\left[\begin{matrix}\mathrm{R}\\ \mathrm{CH{-}CH_2}\end{matrix}\right]- \qquad (20)$$

Rossini[28] has shown that the heat of formation in kcal. of a straight chain paraffin hydrocarbon in the gaseous state is given by the linear function of n

$$\Delta H^\circ_{298} = -7.91 - 5.55n$$

when n, the number of carbon atoms, is greater than four. When $n < 5$, the following corrections must be applied to this equation: −1.59 kcal. for $n = 2$, −0.83 kcal. for $n = 3$, and −0.46 kcal. for $n = 4$. Rossini's[29] comparisons of heats of combustion of isobutane and tetramethylmethane with the heats of combustion of their respective straight chain isomers suggest that the above formula may be used for branched chain hydrocarbons by applying the corrections, −1.63 kcal. for each  $\overset{\mathrm{C}}{\mathrm{-C{-}C{-}C-}}$ structure and −4.9 (±1) kcal. for each  $\mathrm{-C{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}C-}$ structure. With the aid of these corrections the heat of formation of any paraffin hydrocarbon can be calculated. The heat of formation of a structural unit of the polymer is

$$\Delta H_u = -5.55n + \Delta_u$$

where Δ_u is the sum of the corrections for each unit.

The very accurate determinations of heats of hydrogenation carried out by Kistiakowsky and co-workers[30] enable one to calculate the heats of formation of unsaturated hydrocarbons (monomer in (20)) using the formula

$$\Delta H_m = -7.91 - 5.55n - \Delta H_{hyd} + \Delta_m$$

where ΔH_m is the heat of formation of the gaseous unsaturated monomer, ΔH_{hyd} is the heat of hydrogenation to the corresponding saturated hydrocarbon, and Δ_m is the sum of the corrections for this saturated hydrocarbon. The heat of polymerization is then

$$\Delta H_p = \Delta H_u - \Delta H_m = 7.91 + \Delta H_{hyd} + \Delta_u - \Delta_m \qquad (21)$$

The very small correction necessary for conversion of ΔH_p to the liquid state will be overlooked. If the monomer is a diolefin (*e. g.*, if R in (20) is unsaturated), ΔH_{hyd} is the heat of hydrogenation of both double bonds and allowance must be made in Δ_u for the heat of hydrogenation of the single unsaturated group in the polymer unit (29.95 kcal. for $\mathrm{-CH{=}CH_2}$ and 27.80 kcal. for $\mathrm{-CH{=}CH-}$).

---

[26] Melville, *Trans. Faraday Soc.*, **32**, 258 (1936), has estimated that E_2 in the polymerization of gaseous acetylene is about 4 kcal.

[27] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 190, state that the addition of ethylene to an alkyl free radical probably requires less than 10 kcal. of activation energy.

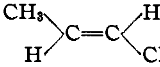
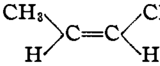
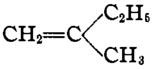
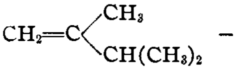
[28] Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[29] Rossini, *J. Chem. Phys.*, **3**, 438 (1935).

[30] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935); Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936).

Heats of polymerization calculated from the data of Rossini and of Kistiakowsky and co-workers using equation (21) are given in Table III.

TABLE III
HEATS OF POLYMERIZATION

Monomer	ΔH_{hyd}[a] (298°K.)	Δ_u	Δ_m	ΔH_p (298°K.)
C_2H_4	−32.57	0	−1.59	−23.07
C_3H_6	−29.86	−1.63	−0.83	−22.75
$C_2H_5—CH{=}CH_2$	−30.09	−1.63	−0.46	−23.35
	−27.37	−3.26	−0.46	−22.26
	−28.32	−3.26	−0.46	−23.21
$C_2H_5—CH{=}CH—CH_3$ (*cis* + *trans*)	−27.70	−3.26	0	−23.05
$C_5H_{11}—CH{=}CH_2$	−29.89	−1.63	0	−23.61
$CH_2{=}C(CH_3)_2$	−28.14	−4.9	−2.1	−23.0
 $CH_2{=}C\begin{smallmatrix}C_2H_5\\CH_3\end{smallmatrix}$	−28.24	−4.9	−1.63	−23.6
 $CH_2{=}C\begin{smallmatrix}CH_3\\CH(CH_3)_2\end{smallmatrix}$	−27.75	−6.5	−3.26	−23.1
$CH_2{=}CH—CH{=}CH_2$ (1,2-polymerization)	−56.57	28.32	−0.46	−19.88
$CH_2{=}CH—CH{=}CH_2$ (1,4-polymerization)	−56.57	27.80	−0.46	−20.40
$CH_2{=}CH—CH_2—CH{=}CH_2$ (1,2-polymerization)	−60.29	28.32	0	−24.06

[a] Kistiakowsky and co-workers give heats of hydrogenation at 355°K. These have been corrected to 298°K. by assuming that the correction for all olefins is the same as for ethylene, namely, +0.25 kcal. For diolefins 0.50 kcal. has been used.

It is significant that for all of the mono-olefins the heat of polymerization approximates −23.0 kcal. in spite of the wide variations in structure. For conjugated diolefins ΔH_p is about 20 kcal. For styrene there are no direct thermochemical data upon which to base a value of ΔH_p. However, Kharasch[31] in his calculations of heats of combustion from the principle of bond additivity uses a correction of −3.5 kcal. for an aryl-alkyl linkage and −6.5 kcal. for an aryl-vinyl linkage. It follows that the heat of polymerization of styrene should be about 3 kcal. less than the "normal" value of 23 kcal., which leads to a value the same as for conjugated diolefins.

Reaction Mechanisms

Chain Initiation.—The only conceivable unimolecular processes by which (1) might occur are the formation of free radicals through the spontaneous dissociation of a C–C or a C–H bond, or the opening of the double bond to yield a divalent free radical. The value for D_{C-C}, the heat of dissociation of a carbon-carbon bond, is about 75 kcal.[32] and D_{C-H} is about 95 kcal., although these values may be somewhat affected by substituent groups.[33] The opening of a double bond should require about 60 kcal. The much smaller experimental values for E_1 definitely rule out these unimolecular mechanisms of chain initiation.

A second order mechanism such as

$$2CH_2{=}CHR \longrightarrow CH_3—CHR— + CH_2{=}CR— \quad (1.1)$$

in which two free radicals are formed by the exchange of a hydrogen atom, also requires too much energy.

For the process in which two monomers are coupled to form a di-free radical, *viz.*

$$2CH_2{=}CHR \longrightarrow —CHR—CH_2—CH_2—CHR— \quad (1.2)$$

$\Delta H_{1\cdot 2} = D_{C-C} + 2\Delta H_p$; $\Delta H_{1\cdot 2} = 29$ kcal., when $R = H$. When the monomer is a substituted ethylene (*e. g.*, when $R = H$), $\Delta H_{1\cdot 2}$ will be lowered due to the effect of substituents in stabilizing free radical groups; *i. e.*, as Conant[33] has pointed out, D_{C-C} is lowered by the substituents on the carbon atoms separated on dissociation. Consequently, for styrene and vinyl acetate the estimate for $\Delta H_{1\cdot 2}$ should be less than the above value of 29 kcal., and compliance of this mechanism with the necessary condition, $\Delta H_1 < E_1$ (see above experimental values for E_1), is thus assured.

Although the above mechanism (1.2) appears quite plausible, it is open to the objection that reversal of (1.2) might occur with such ease that it should be written as an equilibrium. If this be the case the initiation of chains becomes third order, *viz.*

$$\begin{aligned}&2CH_2{=}CHR \rightleftarrows —CHR—CH_2—CH_2—CHR— +\\&CH_2{=}CHR \longrightarrow —CHR—CH_2—CHR—CH_2—CH_2—\\&\qquad\qquad\qquad CHR— \quad (1.3)\end{aligned}$$

E_1 according to this mechanism will be the sum of the heat of the first reaction and the activation of the second step. Since this second step is equivalent to (2), $E_{1\cdot 3} = \Delta H_{1\cdot 2} + E_2$. If $R = H$, $E_{1\cdot 3} \cong 35$ kcal.; if $R \neq H$, $E_{1\cdot 3}$ should be some-

---

(31) Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).

(32) As yet no reliable value has been obtained for the strength of a C–C or a C–H bond in an ordinary hydrocarbon. Rossini's[28] heats of formation of hydrocarbons and Schmid's [*Z. Physik*, **99**, 274, 281 (1936)] recent work on the heat of dissociation of CO can be combined to yield the heats of *complete* dissociation of hydrocarbons, but not to yield the heat of dissociation of a single bond without rupture of the other bonds in the molecule. The above values of D_{C-C} have been chosen largely on the basis of the activation energies for dissociation of ethane and propane into free radicals, given by Rice and Rice[27] (book, p. 78).

(33) Conant, *J. Chem. Phys.*, **1**, 427 (1933), has suggested that the reduction of D_{C-C} by substituents on the carbons joined by the bond dissociated is approximately an additive effect, D_{C-C} being lowered 6 kcal. by each alkyl group and 11 kcal. by each aryl group.

what less than this. These values are also in agreement with the experimental values of E_1, and choice between these similar mechanisms, (1.2) and (1.3), is impossible at present. For this reason two theoretical treatments, one for second order and one for third order chain initiation, have been presented above.

In either mechanism (1.2) or (1.3) the dimeric free radical having the substituted groups at its ends is the most likely to form since, according to Conant's conclusions, this is the most stable structure. The presence of substituents, especially negative substituents such as C_6H_5— and CH_3-OCO— on one of the carbons adjoining the double bond of the monomer should render the dimeric intermediate more stable[33] and consequently lower E_1 and facilitate the polymerization. This conclusion is in agreement with fact as shown by the tabulations of Staudinger (Tables I and II of reference 5); *e. g.*, $CH_2{=}C(CH_3)_2$ polymerizes more readily than either $CH_2{=}CH_2$ or $CH_2{=}CH{-}CH_3$, and $CH_2{=}CH{-}C_6H_5$ more readily than $CH_2{=}CH{-}CH_3$. By the same argument the coupling reaction (2) should nearly always take place between the free radical and the unsubstituted (or less substituted) carbon of the vinyl group, so that the "new" free radical will appear at the substituted end of the vinyl group. This leads to the formation of a chain having a preponderance of the substituents R on alternate carbon atoms.

Chain Transfer.—In order to explain the approximate constancy of molecular weight during polymerization, Schulz[13] has concluded that the process which causes cessation of polymer growth is of the same kinetic order as polymer growth. In the light of the present concepts, this means that reaction (3) is of the same kinetic order as (2), *i. e.*, second order. On the other hand, there is an abundance of evidence to show that the molecular weight of the polymer decreases on dilution of the monomer with an inert solvent. For example, Staudinger and Schwalbach[15] by polymerizing a 50% solution of vinyl acetate in benzene obtained a polymer of roughly half the molecular weight of a polymer prepared from undiluted vinyl acetate at the same temperature. The molecular weights of the polyethyl acrylates prepared by Staudinger and Trommsdorff[34] from undiluted monomer and solutions of various concentrations of monomer in butyl acetate are approximately proportional to the concentration. These results indicate that (3) is of lower kinetic order than (2), *i. e.*, that (3) is first order, in disagreement with Schulz's conclusion and equation (18). Any unimolecular mechanism for the process of chain transfer would of necessity consist of the expulsion of a free radical, or a hydrogen atom, from the chain bearing the free bond with simultaneous formation of a double bond in the chain molecule; for example

$$M_n{-}CH_2{-}CHR{-} \longrightarrow M_n{-}CH{=}CHR + H \quad (3.1)$$

where M_n denotes a sequence of n structural units preceding the terminal structural unit of the polymer. ΔH for this process is about 35 or 40 kcal., and for the expulsion of an alkyl group ΔH $(= -\Delta H_p)$ is about 20 kcal. Both values are so much greater than E_3 estimated from experimental data (13 and 9 kcal., see above) that it is necessary to reject unimolecular mechanisms.

Taylor and Jones[6] have proposed the bimolecular chain transfer reaction

$$M_n{-}CH_2{-}CHR{-} + CH_2{=}CHR \longrightarrow M_n - CH_2{=}CHR + CH_3{-}CHR{-} \quad (3.2)$$

in order to explain their results on the polymerization of gaseous ethylene. Another possible mechanism for (3) consists of saturation of the free radical with an atom from another molecule, for example

$$M_n{-}CH_2{-}CHR{-} + R'{-}CH_2{-}R'' \longrightarrow M_n{-}CH_2{-}CH_2R + R'{-}\overset{|}{C}H{-}R'' \quad (3.3)$$

The molecule $R'{-}CH_2{-}R''$ might be a monomer, a polymer or a solvent molecule. Rice and Rice[27] estimate that the activation energy for such a reaction is about 20 kcal. when the R's are alkyl groups and appreciably lower than this when either R′ or R″ is a negative group. Both of these bimolecular reactions (3.2) and (3.3) lead to constancy of molecular weight during polymerization. Participation of the solvent in (3.3) would provide an explanation of the decrease in molecular weight upon dilution with solvent. Choice of a definite mechanism for (3) is not possible at present, however.

Chain Termination.—The destruction of active centers by the inter-reaction of two of them may involve the coupling of the two radicals

$$M_m{-}CH_2{-}CHR{-} + M_n{-}CH_2{-}CHR{-} \longrightarrow M_m{-}CH_2{-}CHR{-}CHR{-}CH_2{-}M_n \quad (4.1)$$

or the disproportionation reaction

$$M_m{-}CH_2{-}CHR{-} + M_n{-}CH_2{-}CHR{-} \longrightarrow M_m{-}CH_2{-}CH_2R + M_n{-}CH{=}CHR \quad (4.2)$$

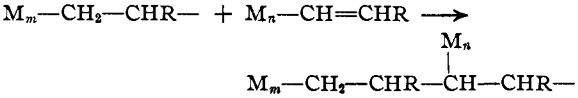
---

(34) Staudinger and Trommsdorff, *Ann.*, **502**, 201 (1933).

Neither of these reactions should require a preactivation energy. Cramer[35] has concluded that in the recombination of ethyl radicals in benzene solution disproportionation (4.2) predominates over coupling (4.1).

Chain Branching and Molecular Weights.—That each polymer molecule has on the average one double bond has been shown by Staudinger and Steinhofer[36] for catalytically polymerized polystyrene, and by Whitby,[37] for polyindene. In both instances this observation has been advanced in an effort to prove particular mechanisms for the polymerization processes. Regardless of the mechanism of the polymerization, if extraneous substances (including solvents) are either completely absent or do not participate in the polymerization, and if no cyclic structures or triple bonds are formed, the polymerization of a monovinyl compound must yield a mixture of molecules having an average of one double bond each. Consequently, the formation of unsaturated polymer molecules in vinyl polymerizations is inevitable and not an indication of the mechanism involved.

Theoretically, a polymer molecule bearing a double bond is susceptible to reaction with a free radical according to (2), and thus a polymer molecule may be included as one member of a polymerization chain; thus, for example



$$\mathrm{M}_m\text{—CH}_2\text{—CHR— } + \mathrm{M}_n\text{—CH=CHR} \longrightarrow \mathrm{M}_m\text{—CH}_2\text{—CHR—}\overset{\overset{\mathrm{M}_n}{|}}{\mathrm{C}}\text{H—CHR—}$$

The frequency of the formation of branched chain molecules in this way must depend upon the relative reactivities with respect to (2) of the double bonds in polymers and those in monomers, and upon the relative numbers of polymers and monomers. If chain transfer proceeds according to (3.3), occasionally a free radical active center may be transferred to some point along the chain of a previously formed polymer molecule; subsequent growth from this center would also yield a branched chain. The possibility that inactive polymer molecules may participate in the subsequent polymerization is implied by both chain branching mechanisms. Houtz and Adkins[38] have presented experimental evidence to show that polystyrene added to polymerizing monomer actually does undergo further polymerization. The results of Staudinger and Frost[4] on the relative viscosities of solutions of polystyrene obtained at various stages of the polymerization show a slight increase as the reaction progresses, which may be an indication of an increase in molecular weight due to participation of "inactive" polymer in the subsequent polymerization. Staudinger and Schulz[23] have observed that a series of polystyrenes prepared at different temperatures deviate from strict adherence to the Staudinger viscosity law. They attribute this deviation to a particular type of chain branching reaction involving the disruption of the hexatriene bond structure of the phenyl group. Such a reaction would require a great deal of energy, and in the absence of definite evidence it seems preferable to avoid a specific mechanism in favor of the general explanation of chain branching given above.[39]

During the early stages of the polymerization when the quantity of monomer exceeds the quantity of polymer, branched chain molecules must be few. The average degree of polymerization should not differ appreciably from λ and the distribution of molecular sizes derived by Schulz[13,40] should prevail. At later stages of the polymerization the occurrence of chain branching may become appreciable. If so, *D. P.* will exceed λ and the distribution of molecular sizes will deviate from Schulz's distribution theory. If, as Staudinger claims, the viscosity of a dilute solution of polymer depends upon the length of the molecule and is independent of its lateral dimensions, the apparent viscosity molecular weight should no longer be proportional to *D. P.*

Since this article was submitted Schulz and Husemann[41] have published a comprehensive paper on the kinetics of styrene polymerization. Their basic concepts of the polymerization mechanism, the same as previously published by Staudinger and Frost[4] and by Schulz,[13] differ principally from those presented in this paper in that they do not include reaction (3). The kinetics of the conversion of monomer to polymer, which depends only upon (1), (2) and (4), should be essentially the same regardless of which interpretation is adopted. However, the equations given above

---

(35) Cramer, This Journal, **56**, 1234 (1934).

(36) Staudinger and Steinhofer, *Ann.*, **517**, 35 (1935).

(37) Whitby, *Trans. Faraday Soc.*, **32**, 315 (1936).

(38) Houtz and Adkins, This Journal, **55**, 1609 (1933).

(39) From measurements of streaming double refraction, Signer [*Helv. Chim. Acta*, **19**, 897 (1936)] has shown recently that Staudinger and Schulz's polystyrenes prepared at higher temperatures consist of molecules less nearly linear in shape than those prepared at lower temperatures.

(40) This distribution is identical with that obtained by the author [*ibid.*, **58**, 1877 (1936)] for linear condensation polymers, although the equations differ slightly in their form.

(41) Schulz and Husemann, *Z. physik. Chem.*, **B34**, 187–213 (1936).

differ a great deal from those given by Schulz and Husemann. The source of the dissimilarity lies in the different expressions obtained for the concentration of active centers, namely, equation (7) in this paper and their equation (12). The latter is incorrect for chain reactions in which the active centers are simultaneously created and destroyed.

From their experimental measurements they have derived 23.2 kcal. for the quantity herein designated as E_a. From the same data as quoted here, they obtain 5.7 kcal. for "Q," which according to the method of evaluation is equivalent to $E_3 - E_2$. These values are in good agreement with the ones given above. The present interpretation of these quantities is much different, however; *e. g.*, Schulz and Husemann regard E_a as equal to the activation energy of (1). Consistent interpretation according to the mechanism which they assume leads to $Q = 5.7$ kcal. $= E_4 - E_2$. That the activation energy E_4 for the reaction of two free radicals with one another should exceed the activation energy E_2 for the reaction of a free radical with a monomer molecule seems exceedingly unlikely.

The author is particularly indebted to Drs. Wallace H. Carothers and Elmer O. Kraemer for their valuable criticisms of this work.

Summary

A mechanism consisting of the four processes, (1) chain initiation, (2) chain propagation, (3) chain transfer and (4) destruction of active centers, has been proposed to account for the known characteristics of typical vinyl polymerizations. The free radical active centers must of necessity be both created (1) and destroyed (4) in pairs. The previously proposed process of coupling of monomers to the free radical through the opening of the double bond has been adopted for chain propagation (2). A chain transfer process (3), whereby the active center is transferred from one polymer molecule to another molecule, leaving the former "inactive" and endowing the latter with the ability to add on monomers successively (2), has been introduced in order to account for the independence of molecular weight on number of active centers.

Upon the basis of this mechanism, the kinetics of the conversion of monomer to polymer has been subjected to a theoretical analysis and equations have been derived to represent the course of the conversion. These are in satisfactory agreement with the limited available experimental data. The variation of relative molecular weight with temperature is in excellent agreement with the proposed mechanism for vinyl polymerizations.

Activation energies of the individual processes have been estimated from experimental data; the approximate values are: for styrene $E_1 = 32$ kcal., $E_2 = 6$ kcal., and $E_3 = 12$ kcal.; for vinyl acetate, $E_1 = 35$ kcal., $E_2 = 5$ kcal. and $E_3 = 9$ kcal.; for methyl methacrylate $E_1 < 20$ kcal. It has been assumed that $E_4 < 5$ kcal. in consideration of the ease with which two free radicals should inter-react. Heats of polymerization, ΔH_p, have been calculated for a number of unsaturated compounds from the recent thermochemical data of Rossini and Kistiakowsky and co-workers. For all types of mono-olefins $\Delta H_p = -23\ (\pm 1)$ kcal.; for conjugated diolefins (styrene included) $\Delta H_p = 20$ kcal.

In the light of their activation energies probable mechanisms for the individual reactions have been presented. The occasional formation of branched chain molecules is theoretically probable.

WILMINGTON, DEL. RECEIVED OCTOBER 26, 1936