large excess of hydriodic acid employed is quite essential in order to produce the hydrocarbon with even moderate success.

Physical Properties of Tribenzylmethane

The melting point of the hydrocarbon prepared by Schmerda was given as 81°, Trotman gave 82–83°, while all the pure samples prepared in this Laboratory melted from 81.8–82°. The identity of the products of the syntheses given above was established by a series of mixed melting point determinations.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.30; H, 7.69. Calcd. for $C_{44}H_{42}$: C, 92.63; H, 7.36. Found: C, 92.07, 91.95, 91.97, 92.19, 92.49, Schmerda 92.35, Trotman 92.4; H, 7.68, 7.60, 7.73, 7.70, 7.85, Schmerda 7.04, Trotman 7.7.

Mol. wt. Calcd. for $C_{22}H_{22}$: 286; for $C_{44}H_{42}$: 570. Found: mol. wt. (depression in benzene), 278.5, 285.2, 293.7; (depression in acetic acid), 297.4, 287.7; (McCoy method) 276.3, 262.7; av. of all, 283.1; found by Schmerda, 560.6.

The Nitro Compound

This derivative of the hydrocarbon was prepared by Schmerda's method, nitration with fuming nitric acid. It is a yellow crystalline solid softening at 74°, decomposing on further heating; Schmerda reported 75°. Like Schmerda's compound, our product dissolved in alcoholic potash with a blue to violet color which became redder upon warming.

Anal. Calcd. for $C_{22}H_{19}O_6N_3$: N, 9.97. Found: (modified Kjeldahl method) N, 9.95, Schmerda (Dumas method) 9.55.

Mol. wt. Calcd. for $C_{22}H_{19}O_6N_3$: 421; for $C_{44}H_{36}O_{12}N_6$: 740. Found: mol. wt. (McCoy method), 472, 462, 444; (Rast method) 421, 421, 421, 408, 430, 425, 421; av. of all, 432.5.

Conclusions

1. The compound obtained by Schmerda and by Trotman, and believed by them to be hexabenzylethane, is in reality tribenzylmethane.
2. This conclusion is based upon analyses, molecular weight determinations, and three quite independent syntheses.
3. A nitro compound, hitherto believed to be hexanitrohexabenzylethane, has been prepared, and analyses and molecular weight determinations show it to be trinitrotribenzylmethane.

MIDDLETOWN, CONN. RECEIVED NOVEMBER 22, 1933

[CONTRIBUTION FROM RESEARCH LABORATORY, PACIFIC CHEMICAL INDUSTRIES]

The Mechanism of Macropolymerization Reactions

BY WILLIAM CHALMERS

General Introduction

This paper sets forth a theoretical study of a group of reactions by which simple substances are transformed into derivatives of high molecular weight. Such changes are classified at present under the two headings of "polymerization" and "condensation." Polymerization has been defined as the union of like molecules to form a product of the same composition.[1] Yet the tendency of unsaturated molecules to attain a higher degree of saturation by interaction is not confined to those of the same species. The "heteropolymerization" process described by Wagner-Juaregg[2] involves two or more different compounds. Polymerization in the broader sense is thus a class of addition reaction in which all reactant molecules are unsaturated. Polymerizations leading to polymers of considerable complexity will be designated as "macropolymerizations" in the following.

Processes in which the aggregation of molecules takes place by condensation present some formal analogies with polymerization. Condensation' it is now currently accepted, implies the elimination of another substance. Carothers[3] has proposed that it be regarded as a sub-class of polymerization and that the products be named "polymers." The writer does not concur in this view. It will be seen that macropolymerizations are quite different in mechanism from what will be referred to as "multicondensations." Multicondensations rarely elaborate molecules containing more than twenty-five structural units (see the numerous papers of Carothers and co-workers[3]) whereas the true high polymers may have an order of polymerization exceeding a thousand.

To these previously recognized divisions should be added a third, of which the so-called "polymerization" of formaldehyde is an example. This is intermediate in nature between multicondensation and polymerization proper and may resemble either under certain conditions. Consideration of these "pseudopolymerizations" will be reserved for a later article.

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(1) Staudinger, *Ber.*, **53**, 1073 (1920).

(2) Wagner-Juaregg, *ibid.*, **63**, 3213 (1930).

(3) Carothers, THIS JOURNAL, **51**, 2548 (1929), and later papers.

Part I. The Stepwise Reaction Mechanism

It has long been realized that macropolymerization is a composite process and that the development of a complex polymer must require a series of consecutive reactions. A number of authors[4] have maintained that it is made up of a repetition of the mechanism (simple addition, with hydrogen wandering) by which many known dimers are formed. It is of importance to determine with certainty whether the observed behavior may be so explained. If the introduction of any special hypothesis is to be avoided, it is necessary to assume that the first-formed polymers possess an ordinary double bond and are capable of being isolated. This scheme will be called "stepwise" to distinguish it from the "polymerization-chain" hypothesis (Part II) according to which the intervening stages have a peculiar structure and the simpler ones a transitory existence only.

On the basis of familiar facts it is possible at once to specify precisely the type of stepwise reaction which may occur. Invariably the structural units of the high polymers of a vinyl compound, $CH_2{=}CHX$, have been found to be joined in the same sense, so that the substituent X is attached to every alternate carbon atom. If the supposed dimeric stage is olefinic it may be either

$$CH_3CHXCH{=}CHX \text{ or } CH_2XCH_2CX{=}CH_2$$

In most cases the dimers (prepared by some special method) or substances related in constitution to these are quite stable under the same conditions by which the simpler substance is completely polymerized. Thus, unlike styrene, neither distyrene, $CH_3CH(C_6H_5)CH{=}CHC_6H_5$, nor β-methylstyrene, $C_6H_5CH{=}CHCH_3$, undergoes macropolymerization. While alpha-methyl styrene,[5] $C_6H_5C(CH_3)C{=}CH_2$, gives low polymers under some circumstances, it is quite inert to light and only slightly altered on heating. In general, therefore, the part played by the interaction of the polymeric molecules must be negligible. This leads to the deduction of the scheme put forward in detail by Whitby.[4b] There are two series of changes which may proceed in this manner, the derived complexes differing in the position of X in the terminal double bond. One of these (the most likely) is represented by way of illustration:

$$CHX{=}CH_2 + CHX{=}CH_2 = CH_2XCH_2CX{=}CH_2$$

$$CH_2XCH_2CX{=}CH_2 + CHX{=}CH_2 = CH_2XCH_2CHXCH_2CX{=}CH_2$$

$$H(CHXCH_2)_y{\cdot}CX{=}CH_2 + CHX{=}CH_2 = H(CHXCH_2)_y{\cdot}CHXCH_2CX{=}CH_2$$

Detailed Considerations.—A homogeneous process taking place at constant volume is characterized as follows. A substance M polymerizes to the dimer M_2 which again reacts (heteropolymerizes) with M to yield the trimer M_3. Similarly M_3 gives M_4 and M_4 gives M_5 and so on. It is further specified that the reactions are irreversible and that the polymers cannot themselves polymerize or react with each other (under the conditions selected). We shall use the symbols P, Q, R, S, T, ..., to represent the molecular concentrations of M, M_2, M_3, M_4, M_5, ..., respectively, at any time t, P_0 being the initial concentration of monomer. If the reaction

$$M + M = M_2$$

were isolated, its rate would be given by the bimolecular equation

$$dP/dt = -kP^2$$

where k is the velocity coefficient. M_2 will be formed from M at the rate $kP^2/2$.

Since M_2, M_3, M_4, etc., are substitution products of the monomer of increasing complexity and are constituted analogously, it would be contrary to experience if the velocities of the subsequent reactions increased. We would expect them actually to decrease. To give every possible advantage to the theory under investigation we may first consider an "ideal" case where the coefficients are identical. That is, the rate of formation of M_3 from M_2 will be $kPQ/2$, of M_4 from M_3 will be $kPR/2$ and so on. The chief problem to be solved is that of the proportions of each polymer in the final product when M has disappeared completely.

Composition of Polymer: Exact Partial Solution.—The rate of variation of the dimer (M_2) concentration is equal to the difference of the velocities of formation (from M) and of conversion (into M_3). Thus

$$\frac{dQ}{dt} = \frac{kP^2}{2} - \frac{kPQ}{2} \qquad (1)$$

The concentration of M_3 alters at the rate

$$\frac{dR}{dt} = \frac{kPQ}{2} - \frac{kPR}{2} \qquad (2)$$

Similarly for M_4

$$\frac{dS}{dt} = \frac{kPR}{2} - \frac{kPS}{2} \qquad (3)$$

and so on for M_5, M_6, etc.

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(4) (a) Ostromuisslenskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 1937 (1915); (b) Whitby, *Trans. Inst. Rubber Industry*, **5**, 184 (1929); (c) Meyer and Mark, "Der Aufbau der hochpolymeren org. Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, p. 69.

(5) Staudinger and Breusch, *Ber.*, **62**, 443 (1929).

Now P is a function of P_0, k and t of the form, $P = P_0f(P_0kt)$. This is a consequence of the conditions that $P = P_0$ and $\mathrm{d}P/\mathrm{d}t = -kP_0^2$ when $t = 0$, and that $P = 0$ when $t =$ infinity. In any particular instance only t varies, P_0 and k being fixed. For convenience let us place $P_0kt = z$, whence also $\mathrm{d}t = \mathrm{d}z/P_0k$. Substituting $P = P_0f(z)$ and changing the independent variable in equation (1)

$$\frac{\mathrm{d}Q}{\mathrm{d}z} = \frac{P_0}{2}f^2(z) - \frac{Q}{2}f(z)$$

Using the integrating factor $e^{1/2\int f(z)\mathrm{d}z}$ we get

$$Q = \frac{P_0}{2}\, e^{-1/2\int f(z)\mathrm{d}z}\int f^2(z)\, e^{1/2\int f(z)\mathrm{d}z}\,\mathrm{d}z$$

When this solution for Q is placed in (2) we find

$$R = \frac{P_0}{4}\, e^{-1/2\int f(z)\mathrm{d}z}\int f(z)\int f^2(z)\, e^{1/2\int f(z)\mathrm{d}z}(\mathrm{d}z)^2$$

Similarly, from (3)

$$S = \frac{P_0}{8}\, e^{-1/2\int f(z)\mathrm{d}z}\int f(z)\int f(z)\int f^2(z)\, e^{1/2\int f(z)\mathrm{d}z}\,(\mathrm{d}z)^3$$

and so on for T, U, etc.

For the proportions by mass each expression must be divided by P_0 and multiplied by the number of molecules of monomer which enter into the polymer. On integrating from zero to infinity the final values are obtained, *e. g.*, for the dimer this is

$$\frac{2Q_{t=\alpha}}{P_0} = \frac{2}{2}\, e^{-1/2\int_0^{\alpha} f(z)\mathrm{d}z}\int_0^{\alpha} f^2(z)\, e^{1/2\int_0^{\alpha} f(z)\mathrm{d}z}\,\mathrm{d}z$$

and similarly for the higher polymers.

Let $\int_0^{\alpha} f^2(z)\mathrm{d}z = A$ and $\int_0^{\alpha} f(z)\mathrm{d}z = B$,

$$\text{then } \frac{2Q_{t=\alpha}}{P_0} = 2A\left(\frac{1}{2}\right)$$

$$\frac{3R_{t=\alpha}}{P_0} = 3A\left(\frac{1}{2}\right)^2 B$$

$$\frac{4S_{t=\alpha}}{P_0} = 4A\left(\frac{1}{2}\right)^3 B^2$$

$$\frac{nX_{t=\alpha}}{P_0} = nA\left(\frac{1}{2}\right)^{n-1} B^{n-2}$$

The terms of this sequence do not contain kP_0, so that the limiting fractions are independent of the actual reaction rate (hence, also, of the temperature) and of the initial concentration of monomer.

Taking the sum for all polymers, we have

$$1 = 2A\left(\frac{1}{2}\right) + 3A\left(\frac{1}{2}\right)^2 B + 4A\left(\frac{1}{2}\right)^3 B^2 + \ldots\; nA\left(\frac{1}{2}\right)^{n-1} B^{n-2} + \ldots$$

which simplifies to

$$1 + B/A = (1 - B/2)^{-2}$$

If either A or B can be found, the entire series will be determined. It should be noticed that A is identical with the dimer fraction.

Reverting to a consideration of the molecular proportions we see that if the ratio of the limiting total to the initial molecular concentration is symbolized by D, then

$$D = A/2 + A/2 \times B/2 + A/2 \times (B/2)^2 + A/2 \times (B/2)^3 + \ldots A/2 \times (B/2)^{n-2} + \ldots$$

Since $A/2$ and $D/2$ must be less than 1, the final molecular proportions will decrease regularly as the series is ascended.

Composition of Polymer: Complete Approximate Solution.—A solution for A is obtained by employing an approximation for $P = P_0f(z)$. This is arrived at by the assumption of a velocity which is the mean of those of bimolecular and quasi-unimolecular changes. That is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{-kP}{2}(P_0 + P)$$

The integrated form is

$$P = \frac{P_0}{2e^{P_0kt/2} - 1}$$

which may be regarded as that of a 1½ or "sesqui"-molecular reaction. Substituting for P in the primary equation (1), we have

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{kP_0^2}{2(2e^{P_0kt/2} - 1)} - \frac{kP_0Q}{2e^{P_0kt/2} - 1}$$

Let $2e^{P_0kt/2} - 1 = v$, then

$$\frac{\mathrm{d}Q}{\mathrm{d}v} = \frac{P_0}{v^2(1 + v)} - \frac{Q}{v(1 + v)}$$

Transposing and integrating, we find on the condition that $v = 1$ and $Q = 0$ when $t = 0$

$$Q = P_0\left(\frac{1+v}{v}\right)\left\{0.1931 + \frac{1}{1+v} - \ln\left(\frac{1+v}{v}\right)\right\}$$

Similarly

$$R = P_0\left(\frac{1+v}{v}\right)\left\{0.0866 + \frac{1}{1+v} - 1.1931\ln\left(\frac{1+v}{v}\right) + \frac{1}{2}\ln^2\left(\frac{1+v}{v}\right)\right\}$$

$$S = P_0\left(\frac{1+v}{v}\right)\left\{0.0222 + \frac{1}{1+v} - 1.0866\ln\left(\frac{1+v}{v}\right) + 0.5966\ln^2\left(\frac{1+v}{v}\right) - \frac{1}{6}\ln^3\left(\frac{1+v}{v}\right)\right\}$$

$$T = P_0\left(\frac{1+v}{v}\right)\left\{0.0041 + \frac{1}{1+v} - 1.0222\ln\left(\frac{1+v}{v}\right) + 0.5433\ln^2\left(\frac{1+v}{v}\right) - 0.1989\ln^3\left(\frac{1+v}{v}\right) + 0.04167\ln^4\left(\frac{1+v}{v}\right)\right\}$$

The limiting proportions by mass ($t =$ infinity), are compiled in the subjoined list

Dimer (A)— $2Q_{t=\alpha}/P_0 = 0.386$
Trimer— $3R_{t=\alpha}/P_0 = .260$
Tetramer— $4S_{t=\alpha}/P_0 = .089$
Pentamer— $5T_{t=\alpha}/P_0 = .020$
Total, 2-mer to 5-mer $= 0.755$

Clearly the higher polymers cannot together exceed a further 0.01. The sum of the percentages is thus about 76%. Yet the deficiency is not evenly distributed but lies to the greatest extent in the expressions for the higher polymers (compare with the table below). The dimer fraction may be accepted as being nearly correct and is certainly a minimum. The curve of the sesquimolecular equation (see accompanying graph, Curve 4) provides a lower limit to the space within which the actual reaction path of the monomer is confined. It is possible to make a maximum estimate of A from the bimolecular curve ($P = P_0/(P_0kt + 1)$, Curve 1) which bounds this area from above and to obtain another minimum value from a quasi-unimolecular curve ($P = P_0\,e^{-P_0kt}$ Curve 5), neither of which differs greatly from the one adopted.

From the equation derived from the series relationship it is found that $B = 0.9076$. The proportion by mass of a polymer formed by the union of n molecules of monomer is $nAB^{n-2}/2^{n-1} = n\,(0.386)(0.908)^{n-2}/2^{n-1}$. The results for polymers as high as the decamer are given in Table I. As n becomes large the ratio between any two consecutive polymers nears $B/2 = 0.454$.

TABLE I

APPROXIMATE COMPOSITION OF A THEORETICAL POLYMERIC MIXTURE

Polymer	% of whole	Polymer	% of whole
Dimer	38.6	Heptamer	2.60
Trimer	26.3	Octamer	1.34
Tetramer	15.9	Nonamer	0.686
Pentamer	9.00	Decamer	.345
Hexamer	4.90	Total, to decamer	99.6

The consequences of the mechanism may be demonstrated most concisely by the determination of the average order of polymerization. This is simply the reciprocal of the total relative molecular concentration, D. The series for the individual molecular concentrations reduces to

$$D = A/(2 - B)$$

whence

$$n\ (\text{average}) = (2 - B)/A = 2.83$$

Individual Reaction Paths.—In the neighborhood of the origin the Q-curve will have its maximum slope, $+\ kP^2/2$. On the other hand, the curves for the higher polymers start out with zero slope. It has been established that the limiting molecular concentrations of each polymer are higher than that of any polymer homolog of higher complexity. If the integrals be taken, not to t = infinity, but to any period of time, it can likewise be demonstrated that the molecular concentrations must follow this rule throughout the process of polymerization. Referring to the expressions deduced from the sesquimolecular equation we find that putting $R=Q$, $S=R$, etc., gives, other than $t = 0$, only imaginary values for t and the reaction paths of the polymers cannot intersect.

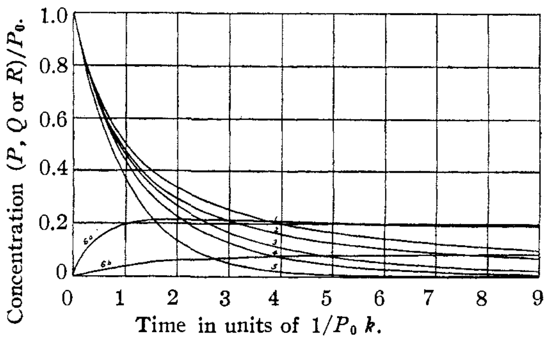

Fig. 1.—Graph of equations of the form—$P_0f(P_0kt)$: (1) bimolecular; (2) multicondensation; (3) derived approximate equation for hypothetical polymerization; (4) sesquimolecular; (5) quasi-unimolecular; (6) approximate theoretical reaction paths of (a) dimer, (b) trimer.

Not only do the rates of change of the various polymers become zero at infinite time but they would also be so if $R=Q$, $S=R$, etc. Since the latter conditions are not fulfilled except at the origin, the curves for trimer and higher polymers exhibit no intermediate maxima. Of course the curve of Q must cross that of P at a real point and this is a maximum. Briefly stated, the concentration of dimer rises to a value exceeding the limit, then drops toward it, whereas the curves of trimer, tetramer, etc., approach their asymptotes without alteration of sign of their slopes. These characteristics are illustrated by the approximate paths for dimer and trimer reproduced in the figure (Curves 6(a) and 6(b)).

It may be mentioned that an attempted systematic analysis, while incomplete, led to a more accurate (minimum) expression for the monomeric reaction path than that assumed, namely

$$P = P_0e^{-P_0kt/4}/(P_0kt + 1)^{3/4}$$

This lies slightly above the sesquimolecular curve and is shown in the figure (Curve 3). An upper boundary of the area within which the true curve must fall is supplied by an expression (Curve 2) for another type of stepwise mechanism applied to condensation processes (see later) and its position is, accordingly, limited to a comparatively narrow band and for over 50% change is known accurately. It suffices for the purpose of the present argument that the monomeric concentration-time graph corresponding to the stepwise scheme is quite distinct from a quasi-unimolecular one.

Application of the Analysis.—If the process is not carried out at constant volume (*i. e.*, in the absence of solvent), the limiting proportions remain unchanged since these are not a function of the concentration. The assumption that the velocity constants of the later reactions do not fall off permits the calculation of percentages of higher polymers which are larger than those to be anticipated in practice. In a non-ideal case the dimer would be produced in greater and the more complex polymers in smaller proportion than represented in the table. The average order of polymerization of the product of an "ideal" reaction is the highest allowable. The *P*-curve of a non-ideal process must be situated above the ideal and may rise as high as the bimolecular, with which it coincides when dimer alone is formed.

True macropolymerizations do not adhere to the generalizations derived above. Styrene, vinyl acetate, the acrylic esters, etc., give polymeric mixtures of which the complexity is so much higher than the limit fixed for the stepwise theory that this can no longer be entertained.

There are, admittedly, a few polymerizations which take place by an abbreviated series of "stepwise" reactions but these really serve to confirm the validity of this deduction. They are so far from ideal that, besides a predominant quantity of dimer and trimer, only inconsiderable amounts of tetramer and higher polymers are formed. The transformations undergone by unsaturated hydrocarbons in the presence of sulfuric acid and by acrylic, crotonic and related esters under the influence of alkaline catalysts are familiar examples.

Part II. The Polymerization-chain Reaction Mechanism

The deficiency of the first homologs in the various polymeric products shows that the velocity of addition of monomer to the transitory dimer, trimer, etc., must be very much greater than that of the initiative coupling of monomeric molecules. An even more striking proof of this assertion is the absence of appreciable proportions of the lower polymers at the beginning of and during macropolymerization.[6] In those processes in which the average order of polymerization, n, remains unaltered throughout their course, the following mechanism is indicated[7]

(I) $\mathrm{M} \longrightarrow \mathrm{M(activated)}$—comparatively slow

(II) $\mathrm{M(activated)} + (n - 1)\mathrm{M} \longrightarrow \mathrm{M}_n$—practically instantaneous

The activation of the monomer will be a reaction of the first order and its mathematical expression is

$$(\mathrm{d}x/\mathrm{d}t)_{\mathrm{I}} = k(a - x)$$

where a is the initial concentration and x molecules of monomer are transformed into polymer at the end of time, t. If the concatenation of the monomeric molecules progresses exceedingly rapidly in comparison with the primary activation, the velocity of the composite reaction will be

$$\begin{aligned}(\mathrm{d}x/\mathrm{d}t)_{\mathrm{II}} &= n(\mathrm{d}x/\mathrm{d}t)_{\mathrm{I}}\\ &= kn(a - x)\\ &= K(a - x)\end{aligned}$$

The gross change will be quasi-unimolecular. The velocity coefficient is the product of two factors which may vary independently from one compound to another.

Search of the literature revealed data on the quantitative course of polymerizations in several publications where no attempt had been made to ascertain the kinetic constants. Making allowances for their limited accuracy the figures collected in Table II show an approximate adherence to a quasi-unimolecular course. The constants have been calculated with the help of ordinary logarithmic tables and only the average values have been converted to the true unimolecular constants which are listed in Table III. For completeness the only previously determined thermal polymerization coefficient, that for vinyl acetate[8] has been added.

[6] Stobbe and Posnjak [*Ann.*, **371**, 269, 295 (1909)] recognized some years ago that only monomer and high polymer may be separated at any time during the gradual conversion of the liquid styrene into completely solid polymer. Stobbe and Lippold [*J. prakt. Chem.*, **90**, 336 (1914)] had expressed similar views with regard to ethyl itaconate. Lebedev and Mereshkovskii [*J. Russ. Phys.-Chem. Soc.*, **45**, 1357 (1913)] had likewise drawn attention to the non-existence of intermediates between dimer (formed by an independent side reaction) and rubber-like macropolymer in the polymerization of the diolefinic hydrocarbons.

[7] As already suggested by the author, *Can. Jour. Research*, **7**, 113 (1932).

[8] Starkweather and G. R. Taylor, THIS JOURNAL, **52**, 4708 (1930).

Velocity Coefficients of Thermal Polymerization of Various Ethylenic Compounds

TABLE II

DETAILED VALUES

Compound	Temp., °C.	Time, sec.	% Polymerization	$K \times 0.4343$
Styrene (Suter,[9] p. 96)	130	1 × 3600	21	2.85×10^{-5}
		3 × 3600	45	2.40×10^{-5}
				2.62×10^{-5} av.
p-Methylstyrene[9] (p. 100)	130	3 × 3600	50	2.79×10^{-5}
		6 × 3600	72	2.56×10^{-5}
				2.67×10^{-5} av.
p-Methoxystyrene[9] (p. 103)	130	3 × 3600	32	1.55×10^{-5}
		6 × 3600	52	1.48×10^{-5}
		15 × 3600	79	1.26
				1.43×10^{-5} av.
Styrene (Lautenschläger,[10] p. 27)	80	10 × 3600	10	(1.27×10^{-6})
		15 × 3600	18	1.60×10^{-6}
		20 × 3600	24	1.65×10^{-6}
		25 × 3600	26	1.46×10^{-6}
				1.57×10^{-6} av. (average of last three values only)
2,3-Dimethylbutadiene (Whitby and Crozier,[11] p. 204)	85	101 × 3600	10.5	1.33×10^{-7}
		154 × 3600	13.8	1.16×10^{-7}
		250 × 3600	19.6	1.05×10^{-7}
		900 × 3600	49.7	0.92×10^{-7}
				1.12×10^{-7} av.
[11]	45	2628 × 3600	19.25	9.845×10^{-9}
Indene (Whitby and Katz,[12] p. 1167)	200	1 × 86,400	22.7	1.29×10^{-6}
		2 × 86,400	38.7	1.23×10^{-6}
		3 × 86,400	49.1	1.13×10^{-6}
		4 × 86,400	76.3	1.81×10^{-6}
		8 × 86,400	89.3	1.41×10^{-6}
				1.38×10^{-6} av.
[12]	178	1 × 86,400	5.02	2.59×10^{-7}
		2 × 86,400	12.4	3.34×10^{-7}
		3 × 86,400	18.55	3.45×10^{-7}
		4 × 86,400	26.3	3.84×10^{-7}
		11 × 86,400	65.5	4.86×10^{-7}
		16 × 86,400	70.6	3.85×10^{-7}
		19 × 86,400	74.15	3.58×10^{-7}
		30 × 86,400	82.2	2.89×10^{-7}
				3.55×10^{-7} av.
[12]	140	25 × 86,400	15.9	3.49×10^{-8}
		70 × 86,400	45.35	4.34×10^{-8}
				3.92×10^{-8} av.
[12]	100	70 × 86,400	2.65	1.90×10^{-9}
Isosafrole (Whitby and Katz,[13] p. 491)	238	1 × 86,400	25.8	1.50×10^{-6}
		2.1 × 86,400	44.4	1.39×10^{-6}
		4 × 86,400	76.5	1.82×10^{-6}
		8 × 86,400	93.4	1.71×10^{-6}
				1.60×10^{-6} av.
	197	16 × 86,400	30.8	1.16×10^{-7}
		29 × 86,400	47.7	1.12×10^{-7}
		61 × 86,400	89.8	1.88×10^{-7}
				1.39×10^{-7} av.
Isoeugenol[13]	238	1 × 86,400	47.2	3.21×10^{-6}
		2.1 × 86,400	89.0	5.22×10^{-6}
				4.21×10^{-6} av.
Eugenol[13]	238	1 × 86,400	24.1	1.39×10^{-6}
		2.1 × 86,400	41.6	1.27×10^{-6}
		4 × 86,400	76.3	0.96×10^{-6}
		8 × 86,400	94.2	1.79×10^{-6}
				1.35×10^{-6} av.

Only a reaction scheme in which the carbon atoms bound by the double linkage alone take part can be brought into accord with an almost instantaneous velocity of concatenation. A very plausible proposal made some time ago by Staudinger[14] is that each of the polymers has free terminal bonds (or trivalent carbons) so that no wandering of hydrogen is involved. For a representative ethylenic derivative we have

$$\mathrm{CHX{=}CH_2 + CHX{=}CH_2 = {-}CHXCH_2CHXCH_2{-}}$$
$$\mathrm{{-}CHXCH_2CHXCH_2{-} + CHX{=}CH_2 =}$$
$$\mathrm{{-}CHXCH_2CHXCH_2CHXCH_2{-}}\ \text{etc., etc.}$$

Other monomeric molecules add on in turn to give transitory intermediates of similar constitution. The building-up of the polymer can readily be imagined to proceed at a speed far greater than that of a reaction accompanied by atomic transfer. The macropolymerization of butadiene and other diolefins would be effected through the formation of quasi-molecules of the type of the dimer, $\mathrm{{-}CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2{-}}$.

More Complex Macropolymerization Processes.—In spite of the apparent simplicity of the reaction tabulated above, it cannot be denied that most macropolymerizations occurring at room temperature are much more complicated and often very erratic. Autocatalysis and the very variable effect of atmospheric oxygen, as well as other positive and negative catalysts which may be present, are evident even where quantitative studies are lacking. Usually it is only with rise of temperature (or pressure) that irregularities diminish and reproducible and consistent data are obtained.

It has been discovered by Staudinger and coworkers[15] that while the low-temperature polymers which appear at the beginning of the reaction are already very complex, at its termination they are still more so. Experiments bearing directly on this point have lately been described by Houtz and Adkins.[16] The explanation which would appear to follow naturally from the considerations

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(9) Suter (with Staudinger), Dissertation, Spamersche Buchdruckerei, Leipzig, 1920.

(10) Lautenschläger (with Engler), Dissertation, J. Langs Buchdruckerei, Karlsruhe, 1913.

(11) Whitby and Crozier, *Can. J. Res.*, **6**, 203 (1932).

(12) Whitby and Katz, THIS JOURNAL, **50**, 1160 (1928).

(13) Whitby and Katz, *Can. J. Res.*, **4**, 487 (1931).

(14) Staudinger, *Ber.*, **53**, 1081 (1920).

(15) Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli, *Ber.*, **62**, 245 (1929).

(16) Houtz and Adkins, THIS JOURNAL, **55**, 1617 (1933).

Table III

Average Values $K \times 10^6$

Compound	Temperature, °C.				
	80–85	100–101	130–140	197–200	238
Vinyl acetate[8]	18.3 (82°)	83.3 (101°)			
Styrene	3.61 (80°)		60.5 (130°)		
p-Methylstyrene			61.5 (130°)		
p-Methoxystyrene			32.9 (130°)		
2,3-Dimethylbutadiene	0.257 (85°)				
Indene		0.0019 (100°)	0.903 (140°)	3.17 (200°)	
Isosafrole				0.32 (197°)	3.68
Isoeugenol					9.70
Eugenol					3.11

already adduced would be that the addition of monomer takes place at a gradually decreasing rate. So long as the polymeric chain is prevented from exceeding a moderate length, either by some physico-chemical factor or simply by the rapid rate of the integrated reaction, the assumption of a constant n and of a negligibly small time of formation is valid. If, however, the process as a whole is very slow and the temperature conditions are such that giant molecules are stable, the addition may continue to a stage where this does not hold true. Under these circumstances a unimolecular reaction course can no longer be expected.[17]

In developing this reaction scheme we are hampered by an incomplete knowledge of the structure of the high polymers. The property possessed by some of these of increasing further in molecular magnitude has appeared to the writer to be compatible only with an "open-chain" arrangement of the carbon skeleton with free terminal valences. Instead of one[18] kind of structure alone for all purely polymeric bodies the possibility of any one of three should be taken into account, the tendency to the formation of each paralleling to a large degree, but not solely, the complexity of the product. The form with free bonds may be sufficiently stable to exist as such; if n is very small a rearrangement may occur to give an ethylenic derivative; or, if n is not too great, union of the ends may result (by virtue of the fields of force surrounding each). Ring closure would terminate abruptly the kinetic chain and fix the value of n.

Included in the tables above are indene and several related compounds for which n (average) approximately doubles during the progress of the reaction although originally it is very small in value. These changes have been cited[4b,12,13] as clear examples of the stepwise mechanism. That this is not so is proved not only by the nearness of their reaction paths to one of the first order but also by the non-appearance of dimer (seemingly also of trimer).[12,13] There is some evidence that the explanation of the increase in molecular weight is to be sought in the first appearance of a reactive olefinic polymer (after rearrangement of the form with free terminal bonds). This might dimerize, or enter once into a polymeric chain otherwise composed of simple units.

Catalytic Macropolymerizations.—It is a commonplace of organic chemical theory that unsaturated ("negative") substituents render labile the linkages of the carbon atoms to which they are attached. That the differing reactivities of the ethylenic carbon atoms of a mono-substituted compound such as styrene, $C_6H_5CH{=}CH_2$, would favor the creation of high polymers is most readily appreciated in a study of catalytic processes.

It has long been known that, in the presence of the alkali metals, the butadiene hydrocarbons[19] as well as styrene[20] undergo accelerated macropolymerization. The writer has more recently found that the polymerizations of acrylic and methacrylic nitrile and methacrylic ester are also catalyzed by sodium.[21] Recalling, on one hand, the inertness of ethylene itself and, on the other hand, the ready reactivity of stilbene[20] to sodium, it seems not unlikely that the metal unites with the alpha carbon of the vinyl derivatives to give a

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(17) The existence of the second stage in the polymerization-chain process provides an explanation of the autocatalysis found in all slow, low-temperature macropolymerizations to a greater or less degree. Nevertheless, it is not certain that this is the only or even the principal cause. The phenomenon may have, to some extent at least, also a "physical" origin, namely, the increase in internal pressure brought about by the presence of the colloidal polymer in the monomer.

(18) One of two opposing schools has championed the olefinic constitution and denied the free-bond and large-ring structures in all cases. The other, with as little justification, has sought to make it an invariable rule that double as well as free bonds are lacking. For orientating references see Carothers, *Chem. Reviews*, **8**, 378 (1931).

(19) See Schotz, "Synthetic Rubber," Benn, London, 1926, p. 77.

(20) See Houben, "Die Methoden der org. Chemie," Georg Thieme, Leipzig, 1925, Vol. IV, p. 966 and following.

(21) Unpublished experiments.

half-addition product such as $C_6H_5CHNaCH_2$—.[22] This could act as a "trigger" for a polymerization chain essentially identical with those started by other means.

As a result of their investigation of the addition of a potassium arylmethyl to butadiene, Ziegler and Kleiner[23] concluded that a dimetallic compound (*i. e.*, $KCH_2CHKCH{=}CH_2$ or $KCH_2CH{=}CHCH_2K$) initiated the polymerization of the diolefin. The growth of the polymeric structure was pictured as being "stepwise" with the intervention of a series of isolable alkali-metal addition products. Admittedly a process of this kind (resembling the pseudopolymerization of formaldehyde) could be completed with the production of only minute concentrations of the simplest intermediates, provided that the (effective) proportion of catalyst was small. Yet the most complex derivative prepared by Ziegler and Kleiner had only six molecules of butadiene combined in it, considerably short of the many hundred required for butadiene rubber.[24] We should assume the addition of one atom of metal to give a molecule with a free bond, *i. e.*, either

$$CH_2{=}CHCHKCH_2\text{—} \text{ or } CH_2KCH{=}CHCH_2\text{—}$$

The iodine polymerization of the vinyl ethers[25] may be explained by the momentary formation of mono-iodo ethers, $ROCHICH_2$—. The action of the volatile metallic halides on many vinyl compounds undoubtedly is similar although the linkage with the reactive carbon atom must necessarily be of an abnormal nature.

Individuality of the Polymerization-chain Process.—Macropolymerizations have already been described as chain reactions (7) owing to their resemblance to established examples of this type of change. The evolution of the polymeric molecule may indeed be regarded as a chain reaction of the "material"[26] sort in which the units produced (—CH_2CHX—) combine instead of maintaining separate existence. In this connection it should be borne in mind that while each link or set of links of a purely kinetic chain is identical (statistically) whether it be the second or the thousandth, this is not true of the polymerization chain. A less fortunate comparison is with the Christiansen–Kramers chain mechanism.

The latter theory states that the reaction products activate the reactants by a specific transfer of energy. We cannot at once put aside the possibility of adapting this hypothesis to the assumption of a regular olefinic structure of the intermediate polymeric stages.[27] Thus the end of the polymer might conceivably "hand on" a quantity of energy equal to or exceeding the heat of activation. However, by a consideration of the phenomenon of negative catalysis we are led to reject this hypothesis. According to Christiansen[28] certain foreign molecules are capable of taking up energy from the "hot" molecules which propagate the reaction chain. As the length is determined by the relative number of "effective" impacts, this becomes shorter as the proportion of the anticatalyst is increased. Theoretically, enough inhibitor may be added to make the chains on the average only two or three "links" long as well as to eliminate them almost entirely. Such behavior has never been observed in macropolymerizations. While the rate may be decreased practically to zero, there is no known instance where addition of an anticatalytic agent results in the appearance of a (previously absent) dimer or trimer. The fact that a high polymer is formed eventually even in the presence of anticatalyst is proof that low polymers have not intervened since an increase in complexity of these by homopolymerization (as a rule) is inadmissible.

It is not excluded that a non-macropolymerization may take place by a Christiansen–Kramers chain reaction. Pease[29] has indeed suggested a mechanism of this kind for the dimerization of ethylene.

Energetics of Macropolymerization Processes.—The constant of activation, k, of the kinetically simple processes is given by the quotient of the velocity coefficient of polymerization, K, by the complexity, n. A modified form of the integrated Arrhenius equation may be employed to ascertain the heat of activation, namely

$$\ln\left(\frac{K_1n_2}{K_2n_1}\right) = \ln\left(\frac{k_1}{k_2}\right) = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_1, K_2 and k_1, k_2 are the velocity coefficients of reaction and activation at the temperatures T_1

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[22] Compare the known behavior of unsymmetrical diphenyl ethylene, Ref. 20.

[23] Ziegler and Kleiner, *Ann.*, **473**, 57 (1929); see also Ziegler and Bähr, *Ber.*, **61**, 254 (1928).

[24] By analogy with isoprene rubber, Staudinger and Bondy, *Ber.*, **63**, 734 (1930).

[25] Chalmers, *Can. J. Res.*, **7**, 476 (1932).

[26] For detailed references to the literature of chain reactions see Kurt Clusius, "Kettenreaktionen," Gebrüder Borntraeger, Berlin, 1932.

[27] In this connection see (a) Starkweather and G. R. Taylor, THIS JOURNAL, **52**, 4714 (1930), also (b) Conant and Peterson, *ibid.*, **54**, 631 (1932).

[28] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

[29] Pease, THIS JOURNAL, **52**, 1160 (1930).

and T_2, n_1 and n_2 are the corresponding chain lengths or molecular weights of the polymers, and Q and R have their usual meaning. Table IV lists data for several compounds.

In the polymerization of indene and its analogs it is believed justifiable (for reasons briefly indicated above) to assume that the real length of the kinetic chain is fixed. The order of polymerization at the beginning is taken as n. The variation with temperature of the molecular weight of these polymers is so small as to be within the limits of the large experimental error so that it is impossible to distinguish between k_1/k_2 and K_1/K_2. As in several instances figures are available for one temperature only, a test of the Dushman expression[30] was considered desirable and the heats of activation calculated from it are given in the last column of the table. While the two equations give widely divergent results it is of interest that the Dushman values fall into two groups corresponding to the greater or lesser complexity of the polymers.

TABLE IV

VELOCITY CONSTANTS AND HEATS OF ACTIVATION

Q (Dushman) calculated at the upper temperature limit in each case.

Monomeric compound[31]	Temp., °C.	Approx. (av.) complexity (n) of polymer	Constant of activation $k \times 10^7$	Temp. coeff. (k_1/k_2) for 10°	Q in calories Arrhenius	Q in calories Dushman
Vinyl acetate	101	270[32a]	3.1	3.00	31,500[33]	36,000
	111	250[32b]	9.3			
Styrene	80	150[34]	0.25	1.90	18,000	38,500
	130	100[34]	6.1			
Indene	178	5[35]	1.6[36]	1.85	26,000	45,000
	200	5	6.3			
Isosafrole	197	4	0.64	1.82	28,000	48,500
	238	4	9.2			
Isoeugenol	238	4	24.0	..	....	47,500
Eugenol	238	4	7.8	..	....	48,500

Initiation of the Concatenation Process.—The kinetic data enable us to investigate to some extent the primary stages in the macropolymerization process. One is tempted on first thought to attribute to the trigger molecule a structure analogous to that of the later active polymers, that is one in which the double bond has "opened up." The untenability of this supposition is evident when the approximate heat of formation of such a substance is reckoned. While the values given in the literature for the various linkages differ somewhat, we may accept the energy content of the carbon–carbon single bond as being in the neighborhood of 71,000 calories and that of the double bond as about 125,000 calories.[37] The energies required in the transformation of the simple olefinic molecule into one with two free bonds, as well as into several lower polymers, are given in Table III. Some 17,000 calories are made available by each further addition of a monomeric molecule. This quantity should, in fact, roughly constitute the heat of polymerization when n is large.

TABLE V

HEATS OF FORMATION OF VARIOUS HYPOTHETICAL "TRIGGER" MOLECULES

Chain skeleton	Approx. heat of formation, cal.
—C—C—	−54,000
—C—C—C—C—	−37,000
—C—C—C—C—C—C—	−20,000
—(C—C)$_4$—	− 3,000
—(C—C)$_5$—	+14,000

While account must be taken of the influence of the negative radical in altering the thermal constants, there is no hope of reconciling that for a monomer with free bonds with the observed. The production of a dimer is admissible in the case of vinyl acetate and substances of the indene group if the substituent causes a (plausible) reduction of 6000 to 10,000 calories in the energy requirement. In the styrene polymerization the trimer is the first polymer of the type of structure proposed which the experimental data (which must be verified) will allow.

In view of the bimolecular or trimolecular course to be expected from these considerations we are confronted with the difficulty of explaining

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(30) See the chapter by Dushman in Taylor's "Treatise on Physical Chemistry," D. Van Nostrand, Co., New York, 1925, Vol. II, p. 1040.

(31) To these might be added approximate figures for 2,3-dimethylbutadiene. There are, unfortunately, no published measurements of the molecular weight of the high polymer which can be regarded as having any degree of accuracy. Without correcting for the differing orders of polymerization of materials formed at 45 and 85° (Tables II and III) a minimum temperature coefficient of 1.83 and heat of activation of 14,000 calories are obtained. The Dushman value reckoned with the aid of the value n = 40 (undoubtedly much too small) at 85° (Whitby and Crozier, Ref. 11, p. 204) is 37,300 calories.

(32) (a) Schwalbach (with Staudinger), Dissertation, Buchdruckerei Max Welzel, Köln-Kalk, 1930, p. 20. (b) This is a minimum estimate based on the data of Schwalbach (*ibid.*) for polymers obtained (in the presence of oxygen) at 100 and 150°.

(33) Starkweather and Taylor (Ref. 27(a), p. 4712) have already quoted a figure of 25,000 calories, taking K_1/K_2 = 2.7. The simple Arrhenius equation gives 28,300 and the corrected formula, 30,300. The value in the table has been calculated on the basis of a coefficient of 2.8.

(34) Staudinger and co-workers, Ref. 15. The molecular weight of a 75° polymer is 16,000 and at 80° has been estimated as about 15,000. The n_2/n_1 ratio for 10° is 1.09.

(35) The average orders of polymerization of the indene group have been taken from the papers of Whitby and Katz (Refs. 12 and 13).

(36) The true unimolecular constant of polymerization of indene at 178° is (from Table II), $K = 8.17 \times 10^{-7}$.

(37) See Meyer and Mark, Ref. 4c, p. 21.

the unimolecular reaction path found. This is the same problem encountered in photochemistry and in a number of thermal reactions with which the Christiansen–Kramers hypothesis makes an attempt to deal. As has been customary, we have postulated the existence of activated molecules of reactant in minute concentration, without specifying the actual character of these. In the Christiansen–Kramers and photochemical processes the reaction itself does not lead to a reduction in the number of active centers and, accordingly, the rate of deactivation must be identical with that of activation (for a "stationary" reaction). In the instantaneous stage of macropolymerizations, on the other hand, the rate of activation is equal to the rate of spontaneous deactivation plus that of reaction. These relations offer a valuable means of distinguishing between the two kinds of process.

Theory of Negative Catalysis in Macropolymerizations.—We assume that the activated monomer normally exists in a small concentration, m_0. This will be a steady state in which the formation of dimer is balanced by the effective activation (= activation minus deactivation). If an anticatalyst be added, the steady value for the activated monomer will be lowered. Let this be m in the presence of a very small concentration c of inhibitor. The effect of the latter will be measured by the product jmc where j is a constant for the particular anticatalyst chosen.

In the rapid stage of the polymerization-chain process

velocity of activation = velocity of reaction + velocity of deactivation (spontaneous + induced)

Representing the (constant) quantity on the left by v_a, the rate of reaction for any proportion of anticatalyst by v_r, and the velocity coefficients of reaction and spontaneous deactivation by k_r and k_d, then

$$v_a = v_r + k_d m + jmc \tag{1}$$

$$v_r = k_r m \tag{2}$$

whence

$$v_r = \frac{k_r v_a}{k_r + k_d + jc} \text{ (polymerization chain)}$$

Proceeding along similar lines on the basis of the Christiansen–Kramers mechanism, for which

velocity of activation = velocity of deactivation (spontaneous + induced)

we arrive at the expression[38]

$$v_r = k_d v_0/(k_d + jc) \text{ (Christiansen–Kramers)}$$

where v_0 is the velocity of the uninhibited reaction. Both equations may be written in the form given by Bäckstrom[39] and Alyea,[40] namely

$$v_r = k_1/(k_2 + kc) \text{ (empirical)}$$

In the Christiansen–Kramers processes, $k_2 = k_d = v_a/m_0$. Since $m_0 = v_a nT$, where T is the average life of an activated molecule and n is the chain length, then

$$k_2 = 1/nT$$

$1/k_2$ is a measure of the average life of a chain and, hence, of its length as recognized by Bäckstrom and by Alyea and co-workers.

In macropolymerizations such a simple interpretation cannot be given to the constant k_2, contrary to the statement of Jeu and Alyea.[41] It is true that the rate of spontaneous deactivation might be regarded as negligible so that the velocity equation is simplified to

$$v_r = k_r v_a/(k_r + jc) \text{ (polymerization chain)}$$

The k_r then coincides with Bäckstrom's k_2. That is, $k_2 = k_r = v_a/m_0$. But this does not make the cases analogous since m_0 is not equal to $v_a nT$ but simply to $v_a T$, or

$$k_2 = 1/T$$

Here $1/k_2$ is equivalent not to chain length but to the mean life of the activated monomeric molecules. It follows that Jeu and Alyea's[41] calculation of the "chain length" of the polymerization of vinyl acetate (given as 5000) is meaningless.

Mechanism of Multicondensation Reactions.—The arguments adduced in support of a unique mechanism of macropolymerization do not apply to multicondensations. Although surprisingly little is known about the latter there is no evidence which would lead us to doubt that they take place by simultaneous condensations of a normal nature.[42] This suggests a stepwise mechanism of a different kind from that considered with reference to polymerization. A mutual reactivity of the simpler derivatives comparable with that of the starting material makes possible their disappearance. The stages of a typical multicondensation may be illustrated symbolically as follows

$$\begin{array}{ccc} C_a + C_b = C_2 + W & & C_2 + C_2 = C_4 + W \\ C_2 + C_a = C_3 + W & \text{and} & C_2 + C_3 = C_5 + W \\ C_3 + C_b = C_4 + W & & C_3 + C_4 = C_7 + W \\ \text{etc., etc.} & & \text{etc., etc.} \end{array}$$

where C_a and C_b represent the simple substances (or substance) and C_2, C_3, C_4, etc., the derivatives

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[38] Compare this form with that deduced by Christiansen, *Trans. Faraday Soc.*, **24**, 600 (1928).

[39] See references given in Christiansen's paper.

[40] Jeu and Alyea, THIS JOURNAL, **55**, 575 (1933).

[41] *Ibid.*, p. 586.

[42] See (a) Kienle and Hovey, THIS JOURNAL, **51**, 518 (1929); **52**, 3643 (1930); (b) Carothers, *ibid.*, **51**, 2559 (1929).

of increasing complexity, W being eliminated. If the reactions are irreversible, or if W be removed as quickly as formed, the same considerations will hold as for a hypothetical stepwise polymerization in which the polymers are capable of interacting.

An "ideal" system in which C_a and C_b are taken in equivalent amounts and in which the velocity coefficients, k, are the same for all component processes would advance indefinitely in the direction of very complex substances. Each product would come to a maximum and then fall off to an infinitesimal concentration. The average order of complexity of the entire mixture at any time is given by

$$n \text{ (average)} = 1 + P_0kt/2$$

where P_0 is the original total concentration of C_a and C_b. The primary material would be subject to the relation

$$P = \frac{P_0}{\left(\frac{P_0kt}{2} + 1\right)\left\{\ln\left(\frac{P_0kt}{2} + 1\right) + 1\right\}}$$

The graph of this equation has been given in the figure above (Curve 2). There are as yet no experimental data[43] by which these can be checked so that their derivation will not be presented here.[44]

The progress of any real multicondensation is first retarded and then brought to a practical standstill as the products become decreasingly reactive. The composition of the limiting state and the time required to attain it will depend to a large degree upon the temperature and other conditions.

Decomposition of High Polymers a Type of Chain Process.—In conclusion attention is drawn to the surprising fact that the decomposition of high polymers has many features which suggest the existence of a chain mechanism of an inverse character to that involved in their generation. That the disruption of hemicolloidal polymers proceeds solely at the end of the molecule and is not distributed at random throughout their length (as in the degradation of multicondensation products[45]) is shown by the simple nature of the products of pyrolysis. Thus polystyrene when heated to a high temperature reproduces styrene alone.[46] Similarly, in the depolymerization of the polymer of butyraldehyde, products other than monomer are definitely absent in determinable proportions at all times.[47] The inability to obtain low polymers indicates further that the unraveling of the smaller polymeric aggregates at least is completed at a rate which is more rapid than that of the beginning of the decomposition sequence. In the case of polystyrene a closed structure would explain this behavior. Rupture of the large rings (requiring a minimum of *ca.* 71,000 calories) would be more difficult to effect than the disintegration of the opened-up chain (each step of which may possibly take as little as 17,000 calories).

The author wishes to express his thanks to Prof. W. F. Seyer of the University of British Columbia for the interest he has taken in the preparation of this paper.

Summary

1. An investigation has been made of the "stepwise" mechanism of macropolymerization supported by several writers. On the fundamental assumption that the rates of the consecutive reactions are not greater than that of the dimerization, it has been shown that the dimer and other low polymers would be formed in largest proportion.

2. On the basis, first, of the composition and complexity of the polymer and, second, of the reaction course of the monomer, the stepwise scheme has been rejected and a "polymerization-chain" mechanism adopted. The polymerization chain is made up of, (I) a primary activation of the monomer and (II) a subsequent process of concatenation which is rendered possible by the presence of free terminal bonds on all intermediate stages. The linking of the monomeric units proceeds initially at a rate which is almost instantaneous compared with that of activation but for very great chain lengths becomes increasingly slow.

3. The start and propagation of the chain have been studied from the viewpoint of energetics and of the phenomenon of negative catalysis.

4. It is suggested that in catalytic processes the "trigger" molecule is formed by union of the catalyst with only one unsaturated atom of the monomer, giving a half-addition product with a free bond.

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(43) The reactions of phthalic anhydride with glycol and glycerol which have been quantitatively investigated by Kienle and Hovey (Ref. 42a, **51**, 516; **52**, 3642) are not true multicondensations.

(44) Of more immediate applicability is the observation that this mechanism is identical in its fundamental features with that of the theory of coagulation of colloids. On comparing with the results of the present investigation, the formulas for single and complex particles deduced by Smoluchowski, *Z. physik. Chem.*, **92**, 146 (1917), were found to be incorrect, as will be shown elsewhere.

(45) See Kuhn, *Ber.*, **63**, 1503 (1930); Klages, *Z. physik. Chem.*, **159A**, 357 (1932).

(46) Stobbe and Posnjak, *Ann.*, **371**, 295 (1909).

(47) Ref. 27b, p. 634.