Each of the low temperature isotherms exhibits a flat maximum at 163–170 atmospheres. The magnitudes of the Joule–Thomson cooling effects at the several maxima are as follows: 25.7° for the 64° isotherm; 21.8° for the 69° isotherm; 19.9° for the 75° isotherm and 16.9° for the 80° isotherm. The maxima are somewhat flatter than those observed for hydrogen. The 64° curve lies above that for hydrogen, in the high pressure region, but the relative positions of the curves is reversed for the 75 and 80° isotherms.

The 25° isotherm rises with a slight upward inflection with an average Joule–Thomson coefficient of approximately 2.1° warming per 68 atmospheres of pressure drop.

A table of heat contents, as a function of pressure and of temperature, is computed from the smooth isotherms of our data.

The accuracy of the measurements made with deuterium exceeds that obtained with hydrogen. This is due principally to better temperature control obtained through the use of liquid nitrogen as cryostat bath liquid.

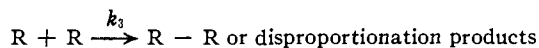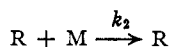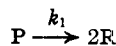# Rate Constants of the Steps in Addition Polymerization. I. The Induction Period in the Polymerization of Vinyl Acetate

BY KENZIE NOZAKI[1] AND PAUL D. BARTLETT

Introduction.—The term, "natural induction period," used in this paper refers to the time required for the establishment of the steady state in a chain reaction. In an important paper in 1937, Flory[2] showed that for thermal polymerization the fractional conversion of the monomer to polymer at the end of the natural induction period is directly related to the ratio, k_3/k_2, between the rate constants for chain termination and chain propagation in the scheme below.

Recent developments in the study of the chain-initiating process in peroxide-induced polymerization have raised the hope that the separate rate constants themselves might be evaluated, once the ratio k_3/k_2 was known. This follows from the fact that in all probability the rate of chain initiation is identical with the rate of spontaneous (as opposed to radical-induced) decomposition of the peroxide[3] and therefore for peroxide-induced polymerization we have a direct way of measuring the rate of chain initiation, a way which does not exist in thermal or photochemical polymerization. If the steps in peroxide-induced polymerization are those of the following scheme, (R = radical, M = monomer, P = peroxide)

$$P \xrightarrow{k_1} 2R$$

$$R + M \xrightarrow{k_2} R$$

$$R + R \xrightarrow{k_3} R - R \text{ or disproportionation products}$$

then the usual steady-state approximation yields

$$R = \sqrt{k_1 P / k_3} \qquad (1)$$

and

$$\frac{\left(\dfrac{-\mathrm{d}M}{\mathrm{d}t}\right)}{M} = k_2 \sqrt{\frac{k_1 P}{k_3}} \qquad (2)$$

The capital letters in the chemical equations denote molecular species, in the mathematical equations the concentrations of those species. The last combination of constants can be determined by a simple measurement of the rate of polymerization after the steady state has been reached. If this can be combined with an evaluation of k_3/k_2 from the measurement of the natural induction period, the two composites can be multiplied

$$\left(\frac{k_3}{k_2}\right)\left(k_2 \sqrt{\frac{k_1 P}{k_3}}\right) = \sqrt{k_1 k_3 P} \qquad (3)$$

Since k_1 and P can both be determined experimentally, a direct evaluation of k_3 would thus be afforded, and accordingly an evaluation of k_2 as well. In a later section we show the necessary modifications of Flory's derivation to permit these calculations for peroxide-induced polymerization.

The possible utility of this method rests upon the crucial question of whether any instance of peroxide-induced polymerization has a measurable natural induction period or not. The lower the ratio k_3/k_2, the longer is the natural induction period; therefore the most favorable case in which to measure this period would be the polymerization with the greatest kinetic chain length. We have chosen vinyl acetate for investigation and have found that the purest vinyl acetate is polymerized in the presence of benzoyl peroxide without any measurable induction period. This confirms indications reported by Bagdassarian.[4]

Experimental

Purification of Vinyl Acetate.—To determine the effect of the method of purification upon the rate of polymerization and the presence or absence of an induction period, four methods of purification and two methods of degassing were employed. The methods of purification were: A partial polymerization. Samples of vinyl acetate were heated with benzoyl peroxide until the mixture had be-

(1) Pittsburgh Plate Glass Fellow, 1943–1945; present address, Shell Development Co., Emeryville, California.

(2) Flory, THIS JOURNAL, **59**, 241 (1937).

(3) Nozaki and Bartlett, ibid., **68**, 1686 (1946).

(4) Bagdassarian, Acta Physicochim. U. R. S. S., **19**, 266 (1944).

come moderately viscous. The residual monomer was distilled under diminished pressure and used.

B. Fractional distillation through a Widmer column. The middle fraction of several having constant properties was used.

C. Fractional distillation through a 50-plate stainless steel Lecky-Ewell spiral screen column.

D. Fractional distillation through a 100–120-plate column with stainless steel Lecky-Ewell packing and a total reflux, intermittent take-off head designed to avoid any contact of the liquid or vapor with mercury, grease, metal other than the packing, or air.

Polymerization Measurements.—The kinetic measurements were carried out in sealed Pyrex tubes which were degassed prior to sealing by Method 1 in the exploratory experiments and by Method 2 in the kinetic study of the best samples. In Method 1 the sample was chilled in a Dry Ice-alcohol-bath and evacuated for ten minutes with an oil pump. In Method 2 the sample was chilled to Dry Ice temperature, evacuated with an oil pump for thirty minutes, warmed to room temperature, shaken to establish liquid–vapor equilibrium, and then the process repeated twice before sealing. Fractional polymerization was determined by bromometric titration of the sample, a separate sealed tube being opened for each point. The samples were dissolved in chloroform and were brominated in the dark, using bromide–bromate solutions and the all-glass brominating flask used in previously described work.[5] It was necessary to chill the reaction mixture in an ice-bath before the addition of potassium iodide to eliminate the debromination reaction.

Results

In order to determine the relative efficiencies of the different methods of purification and the effect of experimental conditions, samples of vinyl acetate purified by the several methods, containing $8.27 \times 10^{-3} M$ benzoyl peroxide, were degassed by Method 1, sealed *in vacuo* and heated for four hours at 45°. The percentage of polymerization was then determined. The results of these comparative tests are summarized in Table I, together with experiments in which the conditions were varied.

TABLE I

COMPARATIVE RATES OF POLYMERIZATION OF SAMPLES OF VINYL ACETATE

Method of purification	Conditions	% Polymerization in 4 hr. with 8.27×10^{-3} M benzoyl peroxide
B	Soft glass tube	0.77
A	Saturated with O_2	0.63
A	Vac., one drop water added	5.7
A	2 days' exposure to air before sampling	8.5
A	Vac., soft or Pyrex tube	9.6
C (Frac. 6)	Vac., soft or Pyrex tube	23.3

Tables II and III show a comparison of the rates of polymerization of the successive fractions in the 50-plate and 100-plate distillations. It is evident that removal of the inhibitor by distillation is accomplished quite slowly. All experiments described hereafter in this paper were carried out with Fraction 6 of the 50-plate distillation or

(5) Bartlett and Nozaki, THIS JOURNAL, **68**, 1495 (1946)

with the product of the 100-plate distillation (Method D).

The rates of polymerization in tubes of different sizes and shapes indicated that heating effects do not disturb experiments of this kind at 45°.

A few other experiments were carried out on Fraction 6 of the vinyl acetate. It was found that the monomer would not polymerize thermally at 100° in Pyrex but would do so in soft glass to an extent not reproducible.

TABLE II

COMPARATIVE RATES OF POLYMERIZATION OF FRACTIONS FROM DISTILLATION OF VINYL ACETATE (METHOD C)

Fraction	Boiling range, °C.	Reflux ratio	$n^{25}D$	Volume of fraction, cc.	% Polymerized in 4 hr. $P_0 = 8.27 \times 10^{-3} M$
1	64.5–70.5	45	1.3926	25	4.3
2	70.5–71.9	100	1.3931	20	5.2
3	71.9–72.0	100	1.3931	20	16.6
4	72.0	100	1.3934	25	16.6
5	72.0–72.1	100	1.3934	100	22.1
6	72.1	35		60	23.3

TABLE III

COMPARATIVE RATES OF POLYMERIZATION OF FRACTIONS FROM DISTILLATION OF VINYL ACETATE (METHOD D)

Fraction	Boiling range, °C.	Press.	$n^{25}D$	Volume of fraction, cc.	% Polymerized in 4 hr. $P_0 = 8.27 \times 10^{-3} M$
1	71.0–71.7	744	....	20	..
2	71.7–72.3	744–754	....	50	4.3
3	72.3	755.7	1.3932	60	9.7
4	72.3	757	1.3934	100	16.4
5	72.3	756	1.3934	200	25.1
6	72.3	756	1.3934	250	25.1

Polymerization of Fraction 6 from the 50-Plate Distillation.—Figure 1 shows the course of polymerization at 45 and 55° of Fraction 6, purified by Method C and degassed by Method 1. There is a well defined induction period in each case. Figure 2 shows the polymerization of vinyl acetate from the distillation through the 100–120-plate column with the special head, the second degassing procedure being employed. This material had b. p. 72.4° (760 mm.) and $n^{25}D$ 1.3934. There is no evidence of an induction period.

A further experiment tends to show that the inhibitor responsible for the induction periods of Fig. 1 is oxygen. A run was carried out on the most carefully distilled monomer in which, instead of evacuating, the samples were swept by a constant stream of nitrogen previously saturated with vinyl acetate vapor. The nitrogen contained not over 0.01% oxygen, but line D of Fig. 2 shows that the polymerization was sharply inhibited in comparison with the well degassed samples. The rate is also constant, as one would expect in the presence of an inhibitor maintained at constant concentration by the passage of a gas stream.
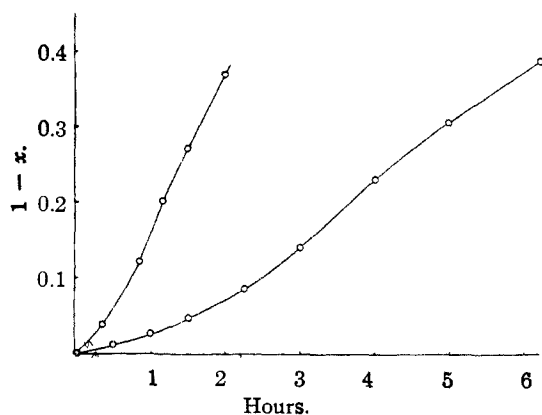
Fig. 1.—Polymerization of vinyl acetate (purification C, degassing procedure 1) at 55° (upper curve) and at 45° (lower curve).

The Effect of Temperature on the Polymerization of Vinyl Acetate.

—The upper line of Fig. 2 shows the polymerization of vinyl acetate at 54.9°. Here also there was no induction period. The over-all apparent energy of activation of the reaction between these two temperatures is 21.6 kcal.

The Effect of Peroxide Concentration on the Rate of Polymerization.

—Line C in Fig. 2 shows the polymerization of vinyl acetate at 45° with $2.07 \times 10^{-3} M$ benzoyl peroxide. The unimolecular rate constant is 4.13×10^{-2} hr.$^{-1}$ compared with 8.30×10^{-2} hr.$^{-1}$ for four times as high peroxide concentration. This variation of the rate of polymerization with the inverse square root of the peroxide concentration is typical of polymerizations whose chains are terminated by reaction between two free radicals.

Determination of k_1.—The value of k_1, the rate constant for spontaneous (as opposed to radical-induced) decomposition of benzoyl peroxide[3] in vinyl acetate at 45°, is involved in the calculation of the minimal rate constants. Because the decomposition of a small amount of benzoyl peroxide in vinyl acetate leads to a large amount of polymerization and a very viscous solution, accurate kinetic determinations of the peroxide decomposition at two dilutions[3] could not be made. As an approximation therefore a non-polymerizing solvent was chosen (ethyl acetate) in which the rate of decomposition of benzoyl peroxide was identical with that in vinyl acetate as far as it could be followed at the same concentration (Tables IV and V). The rate constants for spontaneous and induced decomposition in ethyl acetate were then evaluated by means of runs with $P_0 = 0.194$ and 0.00823, respectively (Table IV). This yielded $k_1 = 0.00393$ hr.$^{-1}$ and $k_i = 0.0367$ (liters/mole)$^{1/2}$ hr.$^{-1}$. It was assumed that the decomposition in vinyl acetate is composed of spontaneous and induced reactions in the same proportion as in ethyl acetate.

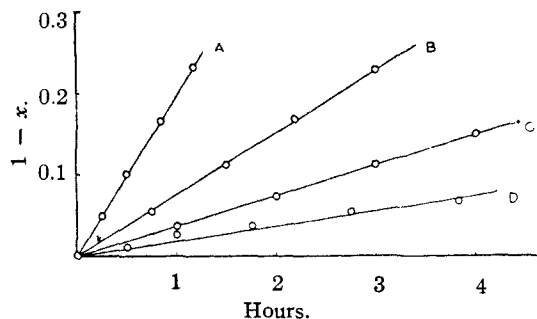From the values of k_1 and k_i at 45° in ethyl acetate it was possible to estimate the activation

Fig. 2.—Polymerization of vinyl acetate (purification D): A, at 54.9°; B, at 45°; C, at 45° with P_0 one-fourth as great as in other runs; D, at 45° in a stream of nitrogen.

energies for the two processes by combination with data at 80° previously obtained. These calculations yield $E_1 = 28.3$ kcal. and $E_i = 23.0$ kcal., somewhat lower in each case than in acetic anhydride or benzene.

TABLE IV

THE DECOMPOSITION OF BENZOYL PEROXIDE IN ETHYL ACETATE AT 45°

	Run 1				Run 2		
Time, hrs.	P M./L.	$1/\sqrt{P}$	$\frac{\ln(a+\sqrt{P})}{\sqrt{P}}$	Time, hrs.	P M./L.	$1/\sqrt{P}$	$\frac{\ln(a+\sqrt{P})}{\sqrt{P}}$
0.0	0.194	2.27	0.219	0.0	0.00823	11.03	0.779
12.0	.1583	2.51	.238	12.0	.00763	11.45	.800
27.5	.1261	2.81	.264	27.5	.00685	12.07	.830
47.0	.1056	3.08	.285	47.0	.00601	12.9	.867
71.0	.0868	3.39	.3075	71.0	.00503	14.08	.918
112.0	.0672	3.85	.345	112.0	.00384	16.15	1.004
164.0	.0521	4.38	.386	164.0	.00261	19.6	1.13

TABLE V

THE DECOMPOSITION OF BENZOYL PEROXIDE IN VINYL ACETATE AT 45°

Time, hr.	P M./L.
0.0	0.00818
2.00	.00803
4.00	.00793

Kinetic Equations for the Approach to the Steady State in Peroxide-Induced Polymerization.

—This derivation is simplified by certain assumptions. Changes in volume of the medium during reaction are ignored and the peroxide concentration is assumed to be constant. These conditions can be realized in the early stages of any polymerization which proceeds with high chain length, such as that of vinyl acetate. In addition, the assumption is made that all free radicals behave alike. If this assumption results in no trouble, it is because the radicals (benzoate and possibly phenyl) which differ greatly from the growing polymer radicals are invariably converted into the latter. The concentrations of free radicals and of monomer change according to the equations

$$dR/dt = k_1 P - k_2 R^2 \qquad (4)$$
$$-dM/dt = k_2 MR \qquad (5)$$

Combination of equations (4) and (5) yields

$$-\frac{dM}{M} = \frac{R dR}{\frac{k_3}{k_2}\left(\frac{k_1 P}{k_3} - R^2\right)}$$ (6)

Integration followed by application of the boundary condition, $R = 0$ when $M = M_0$, gives

$$R = \sqrt{\frac{k_1 P}{k_3}}\left[1 - \left(\frac{M}{M_0}\right)^{\frac{2k_3}{k_2}}\right]^{1/2}$$ (7)

Substituting into (5) the value of R from (7) and letting $M/M_0 = x$, $k_3/k_2 = r$, and $\sqrt{k_1 k_2 P} = K$, we obtain

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

This equation may be integrated again, yielding

$$2\sqrt{r}\, Kt = \ln\frac{1 + (1 - x^{2r})^{1/2}}{1 - (1 - x^{2r})^{1/2}}$$ (9)

When $r >> 1$, (8) approaches the steady-state equation

$$\frac{dx}{dt} = -\frac{Kx}{\sqrt{r}}$$ (10)

Equation (8) shows that, as in the thermal case, a plot of x against time will have an inflection point whose abscissa may be taken as a convenient arbitrary definition of the "time of establishment of the steady state." To locate this point, d^2x/dt^2 is equated to zero, yielding for x_m (the value of x at the inflection point)

$$x_m = \left(\frac{1}{r + 1}\right)^{1/2r}$$ (11)

Therefore

$$\left(\frac{dx}{dt}\right)_m = -K\left(\frac{1}{r + 1}\right)^{(r + 1)/2r}$$ (12)

When r is large x_m approaches unity and (12) reduces to (2).

A similar set of equations has been derived on the assumption (contrary to experience thus far) that chains are initiated by a bimolecular reaction between monomer and peroxide. In such a case, equation (11) is replaced by

$$x_m = \left[\frac{3}{2(r + 1)}\right]^{1/(2r - 1)}$$ (13)

Evaluation of Minimal Rate Constants.—By introducing the definition of r into equation (2) we get the expression

$$k_3 = \frac{(-dM/dt)^2 r^2}{M^2 k_1 P}$$ (14)

By the use of equations (11) and (14) and the necessary experimental quantities it is possible to construct Table VI, which shows the relation between the length of the natural induction period and the absolute rate constants k_2 and k_3 for chain propagation and chain termination. Although the natural induction period has turned out to be too short for measurement, Table VI can be used to estimate minimal values of the constants. Figure 2 makes it highly probable that x_m is greater than 0.977, so that k_2 must be greater than 4.9 and k_3 greater than 485. Actually, as will be shown in the following paper, the true constants are greater than these by a number of powers of ten, as measured by the method of the rotating sector.

TABLE VI

RELATION BETWEEN. LENGTH OF NATURAL INDUCTION PERIOD AND ABSOLUTE RATE CONSTANTS FOR PEROXIDE-INDUCED BULK POLYMERIZATION OF VINYL ACETATE AT 45°

Values taken when $M = 10.86$ and $P = 8.27 \times 10^{-3}$, $-dM/dt = 2.3 \times 10^{-4}$ sec.$^{-1}$ and $k_1 = 1.09 \times 10^{-6}$.

% reaction at point of maximum rate	x_m	r	k_2	k_3
12.0	0.88	9	0.45	4.0
2.3	.977	99	4.9	485
0.34	.9966	999	49.5	5×10^4
0.05	.9995	9999	496	5×10^6
0.007	.99993	99999	4960	5×10^8

Summary

It is shown that in the peroxide-induced polymerization of an olefinic compound it would be possible to determine the absolute rate constants for chain propagation and chain termination if the steady state were established slowly enough to produce a measurable "natural" induction period.

In the case of the polymerization of liquid vinyl acetate induced by benzoyl peroxide, it is shown that the measurable induction period is due to the presence of an inhibitor and can be eliminated by sufficient care in purification and degassing of the monomer.

From the experimental result that the "natural" induction period is over some time before 2.3% of the monomer has polymerized, it is calculated that the rate constants for chain propagation and chain termination of liquid vinyl acetate at 45° are greater than 4.9 and 485 liters/mole second, respectively. In the following paper they are shown to be actually far greater than this.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 29, 1946