[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY AND THE CRUFT LABORATORY OF HARVARD UNIVERSITY]

Rate Constants of the Steps in Addition Polymerization. II. Use of the Rotating-Sector Method on Liquid Vinyl Acetate

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Part I of this series[2] showed that in the polymerization of pure vinyl acetate the steady state is attained too rapidly to permit the detection of a "natural" induction period and its interpretation by the method of Flory,[3] although such interpretation in the case of peroxide-induced polymerization would have permitted evaluation of the absolute rate constants of the steps in the chain reaction. The high molecular weights of representative polyvinyl acetates indicate a low value of the ratio between termination and propagation velocity constants which determines the length of the natural induction period in comparison to some of the other common monomers polymerizable by peroxides. It follows that if we cannot measure the natural induction period in the polymerization of vinyl acetate there is little likelihood of this method being useful in the case of other common monomers.

Melville[4] in 1937 determined the mean lifetime of the free radicals in the polymerization of methyl methacrylate in the gas phase induced by hydrogen atoms photochemically produced. This was done by interrupting the exciting light by means of a slotted disc rotating at controlled speeds and yielding equal periods of light and darkness. By an analysis due originally to Briers, Chapman and Walters,[5] the dependence of the over-all rate of polymerization on the sector speed yields a determination of the average lifetime of the free radicals which control the polymerization rate. The application of this method to the liquid phase, though not without experimental and theoretical difficulties, now appears the best way of determining the absolute rate constants in the bulk polymerization of olefinic compounds.[6] The method is applicable in principle to any chain reaction in which the kinetic chains are broken by bimolecular reaction between the chain-carrying molecular species. The work described in this paper formed the basis of a preliminary communication[7] published in December, 1945. In the same month there appeared a similar communication[8] by Burnett and Melville, describing measurements on the same reaction under somewhat different conditions. The results from the two laboratories are compared in a later section of this paper.

Experimental

Vinyl Acetate.—Commercial vinyl acetate was distilled as described in Part I of this series.[2] The distillation and storage were in an atmosphere of oxygen-free nitrogen. The experiments were all done with vinyl acetate freshly distilled before use. Vinyl acetate prepared in this way underwent peroxide-induced polymerization without any detectable induction period.

Acetaldehyde, a likely impurity in vinyl acetate, has an absorption maximum[9] near 2900 Å. and has $\epsilon = 14$ for wave length 3000 Å. in hexane. It is a photosensitizer for the polymerization of vinyl acetate in this spectral region.[10] A sample of liquid vinyl acetate purified in the same manner as that used in these experiments, examined with a Beckman spectrophotometer in a 1-cm. cell against air, showed an absorption indistinguishable from zero at wave length 3000 Å. and equal to 1% ($\epsilon = 0.005$) at wave length 2900 Å., where acetaldehyde in hexane has $\epsilon = 15$. The maximal concentration of acetaldehyde in this material is therefore about 3×10^{-4} molar.[11] Although this is higher purity than was apparently had by Bagdassarian,[12] who reported 40% light absorption in a vessel the size of ours, the possibility exists that our reaction was initiated entirely by photodissociation products of the small amount of acetaldehyde present. If true, this would not otherwise affect the conclusions of this study.

Light Source.—The light source used was a General Electric Mazda A-H6 water-cooled 1000-watt mercury capillary arc. The luminous portion of this lamp was one inch high and one-sixteenth inch wide. The lamp was enclosed in a quartz water jacket and cooled by a flow of 8 quarts of tap water per minute. The power supply was 1500 volts d. c. from a special generator, the lamp being connected in series with a 650-ohm resistor. It was found advisable to start the lamp on alternating current and switch to the generator, as a precaution against an overdraft of current from the latter during the starting. During operation the lamp drew about one ampere, with a potential drop of 850 volts across its terminals.

The filtering system and dilatometer were designed to afford conditions close to those of Bagdassarian,[12] although our experiments turned out not to be comparable with his because of the much greater transparency of our vinyl acetate. Potassium chromate (0.0010 M in the first series of experiments and 0.0007 ± 0.0002 M in the others) was dissolved in the thermostat liquid surrounding the dilatometer. The effect of this is to eliminate light of wave length less than 2998 Å.

A stainless steel disc 10″ in diameter was divided into 24 equal sectors, and every fourth sector was cut out for a radial distance of two inches. The disc, interposed between the light source and the sample, was spun by a small variable speed motor and its speed, when too great for direct determination, was determined stroboscopically.

The Dilatometer.—The rates of polymerization were measured by a dilatometer consisting of a 30-cc. spheroidal quartz bulb, connected by twin vertical capillaries (for convenience in filling) to a blackened 60-cc. reservoir at the

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(1) Pittsburgh Plate Glass Fellow, 1944-1945.

(2) Nozaki and Bartlett, THIS JOURNAL, **68**, 2377 (1946).

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

(4) Melville, *Proc. Roy. Soc.* (London), **A163**, 511 (1937).

(5) Briers, Chapman and Walters, *J. Chem. Soc.*, 562 (1926).

(6) The independent method of the double light beam used by Jones and Melville, *Proc. Roy. Soc.* (London), **A175**, 392 (1940), in the gas phase, does not appear so promising applied to liquids, where the mean free path is so much shorter.

(7) Bartlett and Swain, THIS JOURNAL, **67**, 2273 (1945).

(8) Burnett and Melville, *Nature*, **156**, 661 (1945).

(9) Schou, *J. chim. phys.*, **26**, 77 (1929).

(10) H. W. Melville, private communication, March 2, 1946.

(11) We thank Dr. John D. Roberts for determining the absorption spectrum of our vinyl acetate, and Mr. Harold Kwart for providing the purified sample which was used for this purpose.

(12) Bagdassarian, *Acta Physicochem. U.R.S.S.*, **19**, 266 (1944).

top, so inclined that after the sample had contracted below the bottom of the capillaries, more material could be added from the reservoir without opening the apparatus. The total measurable contraction of 20 cm. in the capillaries corresponded to about 1.7% polymerization.[13] It was possible with the same filling of vinyl acetate to replenish the capillaries from the reservoir twice and thus follow the rate to a total polymerization of about 6% without the material becoming inconveniently viscous.

Pure vinyl acetate was introduced into the reservoir and degassed by evacuation ten times over a period of five hours. An atmosphere of oxygen-free nitrogen was then introduced to retard gaseous diffusion within the apparatus, and the assembly was sealed. The dilatometer was kept in a thermostat at 25.0 ± 0.02° having a 2 × 4.5 cm. quartz window, the light passing through 1.8–2.4 cm. of the aqueous chromate solution between the window and the dilatometer. The lamp was located 30 cm. from the center of the dilatometer bulb, and the disc 2 cm. before the thermostat window. This arrangement prevented the shadow of the edge of a sector from being as sharp as it should have been, and the resulting periods of partial illumination affected the character of the curve of polymerization rate against sector speed. This effect is discussed below.

Nitrogen.—Commercial nitrogen containing 0.5% hydrogen and not over 0.001% oxygen was passed through a hot copper furnace at 675°. Nitrogen from this treatment was used for all purposes described.

Procedure.—After the dilatometer had been filled as described and brought to the temperature of the thermostat the lamp was started and kept running throughout a series of experiments, isolated from the rest of the apparatus by transite panels between runs. Positions of lamp, cell, and disc were not touched during the series. The disc was brought to the desired speed, then the screening panel was removed from the light and a stopwatch started. After a measured interval, usually exactly ten minutes, the panel was replaced. The dilatometer reading continued to change rapidly for five to eight minutes as the heat produced by the polymerization was dissipated. At a definite time after interruption of the light (ten minutes for Series 1 and 2, fifteen minutes for Series 3, and seventeen minutes for Series 4, 5 and 6) the dilatometer readings were taken to the nearest millimeter. Then the disc was immediately started at a different speed and the process repeated. The increase in waiting time for thermal equilibrium after Series 2 was due to the observation of a 5-mm. blank contraction in a further ten-minute interval in the early series.

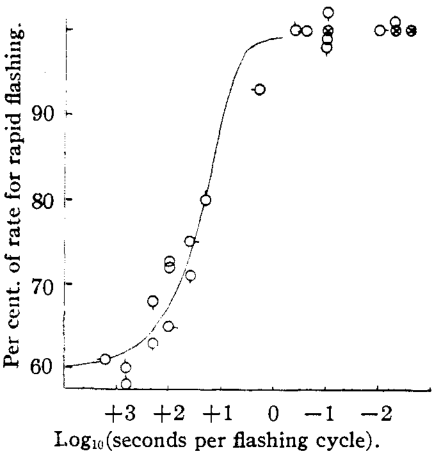

Fig. 1.—Rate of polymerization of vinyl acetate at different frequencies of flashing. Points of the same type represent experiments in the same series.

Only the experiments within one series are strictly comparable, and for this reason each series included at least one experiment at high sector speed, which was taken as the base of reference for that series. The actual value of the ten-minute contraction at high sector speed was 29 mm. in the first series and varied between 38.5 and 40 mm. in the subsequent series. Small deviations in the actual time of illumination were corrected for by multiplying the observed contractions by appropriate factors. The actual time never deviated by more than two minutes from the standard ten-minute interval except in the case of the one slowest speed, where it was twenty-six minutes (for one slot). All series were done on the same filling of vinyl acetate. In expt. 3 of Series 1, 3 mm. was added to the observed contraction to correct for the fact that the initial reading was an equilibrium reading and not the reading after a ten-minute waiting period from a previous run. All other experiments followed immediately termination of a previous waiting period. First experiments in each series were uniformly discarded, yielding contractions which were low by 7–15%.

The current drawn by the lamp fell off in a somewhat erratic fashion through this series of experiments from 0.98 to 0.89 ampere. However, no correction based on relative current values gave a sufficiently higher precision to the results to justify its use.

The results of the experiments with the rotating sector are summarized in Table I and plotted in Fig. 1.

TABLE I

DEPENDENCE OF RATE OF POLYMERIZATION ON RATE OF INTERRUPTION OF LIGHT

Series	Expt.	Duration of flashing cycle Seconds	Log	% of highest rate observed
1	1	0.13	−1.0	100
1	2	.0045	−2.3	100
1	3	.0026	−2.6	100
1	4	.13	−1.0	100
2	1	92.0	+2.0	72
2	2	0.0045	−2.3	101
2	3	92.0	+2.0	73
2	4	0.13	−1.0	99
3	1	0.13	−1.0	98
3	2	210.0	+2.3	63
3	3	42.0	+1.6	71
3	4	0.13	−1.0	102
3	5	210.0	+2.3	68
4	1	1600.0	+3.2	61
4	2	2.0	+0.3	93
4	3	0.25	−0.6	100
5	1	590.0	+2.8	58
5	2	22.0	+1.3	80
5	3	0.40	−0.4	100
5	4	590.0	+2.8	60
6	1	42.0	+1.6	75
6	2	92.0	+2.0	65
6	3	0.010	−2.0	100

The Peroxide-Induced Polymerization of Vinyl Acetate at 25°.—As is explained in the kinetic analysis below, the determination of the absolute rate constants from the mean lifetime of the free radicals involves an estimation of the rate of photochemical initiation of chains. Our method of doing this was to take advantage of a comparison with peroxide-induced polymerization which involved the measurement of the rate of polymeriza-

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[13] Based upon data of Starkweather and Taylor, THIS JOURNAL, 52, 4708 (1930).

tion and determination of the rate constants, k^1 and k_i, of spontaneous and radical-induced peroxide decomposition in a 0.105 M solution of benzoyl peroxide at 25°.[14] Under these conditions the rate of polymerization was found to be 8.4×10^{-5} mole/liter second. The other quantity required, k_1, was not determinable with as great accuracy as would be desirable. Not only are difficulties caused by the extreme slowness of the reaction and the viscosity of the polymerizing vinyl acetate, but also by the large proportion of induced decomposition of benzoyl peroxide at 25°. The value of k_1 at 25° was estimated from two runs in which the decomposition of benzoyl peroxide was followed at initial concentrations of 0.1054 and 0.0110 M. Points were selected (at 61 and 289 hours, respectively) before the logarithmic plots ceased to be linear. Since these times were not equal, the method of Nozaki and Bartlett[14] was not applicable in its simple form. Instead, the integrated equation for simultaneous first- and $^3/_2$-order reaction was thrown into the form

$$\frac{k_1}{k_i} = \frac{e^{k_1t/2} - 1}{\dfrac{1}{\sqrt{P}} - \dfrac{e^{k_1t/2}}{\sqrt{P_0}}}$$

For any two points in runs with different P_0 the values of the right-hand member may be equated. Solution of the resulting equation yields $k_1 = 0.02\, k_i = 0.00014$ hr.$^{-1}$ = 3.9×10^{-8} sec.$^{-1}$. The constant determined is uncertain by about a factor of two, but this value is reinforced by two extrapolations. At 45° the rates of benzoyl peroxide decomposition in vinyl acetate and in ethyl acetate are indistinguishable.[2] By the use of the activation energy E_1 = 28.3 kcal. which has been determined for ethyl acetate[15] we arrive at the extrapolated value $k_1^{25} = 3.4 \times 10^{-8}$. Independently in acetic anhydride, another solvent yielding a rate of decomposition of benzoyl peroxide close to that in vinyl acetate, extrapolation with the value E_1 = 28.3 yields $k_1^{25} = 2.3 \times 10^{-8}$. The directly measured value was adopted in making the calculations. Table II gives the data on the peroxide experiments at 25°.

TABLE II

POLYMERIZATION OF VINYL ACETATE AT 25° INDUCED BY BENZOYL PEROXIDE

Hr.	P	M
Initial Peroxide Concentration = 0.1054 M		
0	0.1054	11.31
26	.0994	5.53
61	.0912	1.91
128	.0809	...
216	.0745	0.55
449	.0754	.48
793	.0754	.46
Initial Peroxide Concentration = 0.0110 M		
0	.0110	11.58
25	.....	7.94
44	.....	6.58
168	.00960	...
288	.....	0.68
289	.00858	...
336	.00815	...

Evaluation of Constants

Mechanism and Notation.—It is assumed that the mechanism of polymerization by peroxides is adequately represented by the scheme used in Part I,[2] and that photopolymerization differs from it only in the nature of the initiating step. We shall further simplify the picture by confining attention to the polymerization of such a small fraction of the total monomer that the concentration of monomer and of photosensitizer, if any, may be treated as constant. It then becomes immaterial whether the chains are initiated by photoexcitation of vinyl acetate or by free radicals produced from photolysis of a sensitizer. (Kinetically it makes no difference whether one chain is growing at both ends or two chains are each growing at one end.) In either case the rate of initiation of chains will be proportional to the light intensity and the mechanism will be represented

$$\text{Light} \xrightarrow{\textit{via}\ \text{M or sensitizer}} 2\text{R}$$

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

$$2\text{R} \xrightarrow{k_3} \text{R–R or disproportionation products}$$

Here, as in Part I, M denotes monomer and R a free radical. P, the peroxide, enters in the peroxide-induced case. The following quantities, whose values as expressed follow from the above assumptions, will be used in the following derivation.

Light intensity = I
Rate of chain initiation = fI
Concentration of free radicals at the steady state under constant illumination = $R_s = \sqrt{\dfrac{fI}{k_3}}$
$R/R_s = y$
Average lifetime of growing chains at the steady state in photopolymerization = $\lambda_s = 1/k_3R_s = 1/\sqrt{fIk_3}$
Time in multiples of $\lambda_s = \tau = \dfrac{t}{\lambda_s}$
Velocity of polymerization with steady illumination = $V_s = k_2MR_s = k_2\sqrt{fI/k_3}\ M$
Concentration of free radicals at the steady state during peroxide-induced polymerization = $R_p = \sqrt{k_1P/k_3}$
Velocity of polymerization induced by peroxide = $V_p = k_2MR_p = k_2\sqrt{k_1P/k_3}\ M$

Evaluation of the Rate Constants for Chain Propagation and Termination.—Since the experimental quantity obtainable from experiments with the rotating sector is λ_s and this contains fI, the rate of chain initiation, as well as k_3, it is necessary to estimate the rate of chain initiation in order to determine the absolute rate con-

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[14] Nozaki and Bartlett, THIS JOURNAL, 68, 1686 (1946).

[15] K. Nozaki, unpublished results.

stants which we seek. Measurements of light absorption cannot yield *fI*, since the fraction of activated molecules which actually produce radicals is unknown. The rate of chain initiation can be estimated by the use of an inhibitor,[8] together with a knowledge of the numerical relation between inhibitor molecules consumed and chains destroyed. Our method takes advantage of a relation which follows from the expressions above for V_s and V_p, namely

$$fI = k_1P\ (V_s^2/V_p^2)$$

The assumption involved is that the rate of spontaneous, unimolecular decomposition of peroxide is the rate of chain initiation in peroxide-induced polymerization. We thus have

$$k_3 = \frac{1}{\lambda_s^2 fI} = \frac{V_p^2}{k_1PV_s^2\lambda_s^2}$$

in which the right-hand member consists entirely of experimentally determined quantities. Knowing k_3, we obtain k_2

$$k_2 = \frac{V_p}{M}\sqrt{\frac{k_3}{k_1P}}$$

A knowledge of k_2 and k_3 permits, in turn, the calculation of R_s, R_p, and the kinetic chain length for the conditions of any particular experiment. Finally by equation (10) of Flory[3] we can calculate at what fractional polymerization and at what time the steady state should be established in the photopolymerization of vinyl acetate. By equation (11) of Part I of this series[2] we can make similar calculations for peroxide-induced polymerization with any particular concentration of peroxide. Table III lists the values of the experimental and derived quantities.

Evaluation of the Mean Lifetime of Growing Chains.—From the mechanism above and the analysis of Briers, Chapman and Walters,[5] the following equations are derived. During one of the periods of illumination

$$y = \tanh \tau \qquad (1)$$

in which τ and y are both zero at the moment when the light is turned on. During a period of darkness

$$y = \frac{1}{\tau + \frac{1}{y_2}} \qquad (2)$$

in which y_2 is the value of y when the light is cut off (taken as $\tau = 0$ in this equation). During any rhythmic alternation of steady light and darkness the system will so adjust itself that during illumination y rises by equation (1) from a minimum value y_1 to a maximum value y_2, and declines by equation (2) exactly to y_1 again. In combining equations (1) and (2) to determine the limits and average value of y during each interval, we may not start the time scale of equation (1) at $\tau = 0$, but must use a positive lower limit of τ, defined as τ_1 by the equation

$$y_1 = \tanh \tau_1$$

and an upper limit defined by

$$y_2 = \tanh \tau_2$$

The average value of y for any frequency of alternation of light and darkness is found by adding the integral

$$\int_{\tau_1}^{\tau_2} \tanh \tau\, d\,\tau \qquad (3)$$

for the light period to the integral

$$\int_{\tau_2}^{\tau_2+\delta} \frac{d\tau}{\tau + \frac{1}{y_2}} \qquad (4)$$

for the dark period of length δ and dividing by the total time for the cycle. The average value of y for equal light and dark periods is given accordingly by Briers, Chapman, and Walters as[16]

$$\bar{y} = \frac{\ln\cosh\tau_2 - \ln\cosh\tau_1 + \ln\,[(\tau_2-\tau_1)y_2 + 1]}{2(\tau_2-\tau_1)} \cdots \quad (5)$$

The corresponding equation for a dark period q times as long as the light period is

$$\bar{y} = \frac{\ln\cosh\tau_2 - \ln\cosh\tau_1 + \ln\,[q(\tau_2-\tau_1)y_2 + 1]}{(q+1)\,(\tau_2-\tau_1)} \quad (6)$$

Since for any flashing frequency a knowledge of y_2 allows determination of τ_2, thence τ_1 and y_1, equations (1) and (2) can be solved by successive approximations to yield these four quantities for each value of $(\tau_2 - \tau_1)$ that is of interest. Much time is saved in this stage of the calculation by use of the following graphical method. Equation (1) is plotted over the range $\tau = 0$ to 4. Equation (2) is plotted *backward, i.e.*, a plot is made of the equation

$$y = 1/(1 - \tau) \qquad (7)$$

over the range $\tau = 0$ to -4. This plot is made on transparent paper on the same scale as the plot of equation (1). If now the τ-axes of the two graphs are superposed and the second plot is slid from left to right over the first, the intersections of the two curves give sets of corresponding values of τ_1, τ_2, y_1, and y_2 for increasing "on" periods, and a table can be quickly constructed listing these quantities as a function of the illumination period $\tau_2 - \tau_1$. A slight modification, in which the second plot has a time scale shrunk by the factor q, being based on the equation

$$y = 1/(1 - q\tau) \qquad (8)$$

allows graphical determination of the y's and τ's for the more general case of unequal light and dark periods. Figure 2 shows a few representative intersections of the curves for $q = 3$, corresponding

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[16] According to Melville's statement of the equations used [*Proc. Roy. Soc.* (London), **A163**, 534 (1937)], he appears to have overlooked the importance of evaluating τ_1 in equation (3), for he replaced the correct equation (5 above) of Briers, Chapman and Walters by the equation

$$\bar{y} = \frac{\ln\cosh\tau + \ln(2\tau y_2 + 1)}{2\tau}$$

defining τ as the duration of the light period. This is tantamount to the assumption that whatever the value of y at the end of a dark period, y is zero at the beginning of each light period.

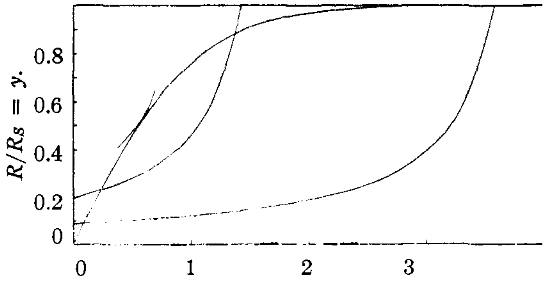

Fig. 2.—Rise and decline of radical concentration during intermittent illumination ($q = 3$).

to the design of the rotating disc used in our experiments.

With a table at hand of associated values of τ_1, τ_2, y_1, and y_2, the values of $\bar{y}$ are determined by substitution into equation (6). Figure 3 shows the resulting theoretical curves of $\bar{y}$ against logarithm of the duration of the light period for the three cases of $q = 1$, 1.81 and 3.

It is obvious that, if the rate of polymerization at an early stage is proportional to the free radical concentration, then the theoretical curve of relative $\bar{y}$ against log $(\tau_2 - \tau_1)$ should be identical with the curve of relative rate of polymerization against log $(\tau_2 - \tau_1)$. Since the midpoint of the former curve for $q = 3$ occurs where $\tau_2 - \tau_1 = 4$ and the mid-point of our experimental rate-frequency curve occurs where $t_2 - t_1 = 5$ seconds, it follows that $\lambda_s = 5/4$ or 1.25 seconds. A comparison of the experimental and theoretical curves, however, reveals that the limiting rates of polymerization for low and high flashing frequencies are in the ratio 0.60 instead of 0.50 as required by the theoretical curve. This might be due to one of two causes. If the polymerization chains were terminated by an inhibitor instead of by collision of radicals, the radical concentration would be independent of the flashing frequency, and if a portion of the chains were so terminated the sensitivity of the rate to the flashing frequency would be correspondingly impaired. Reasons were given in Part I, however, for believing that our vinyl acetate had been effectively freed of inhibitors. Alternatively, our optical system may have been at fault, through the periods of partial illumination referred to in the Experimental Section. Because the free radical concentration is built up more rapidly in the light than it decays in the dark, the net effect of the periods of partial illumination is in the same direction as that of a decreased value of q. We have calculated the theoretical curve for $q = 1.81$, the value which would give the ratio of limiting rates actually observed with sharp boundaries between light and dark. The midpoint of this curve occurs at $\tau_2 - \tau_1 = 5$, corresponding to $\lambda_s = 1$ second on the experimental curve. The fit of this curve to the experimental data when their midpoints are superposed is good except for a single point in Series 4. It therefore seems likely that the periods of partial illumination do not introduce an uncertainty greater than about 25% in the mean lifetime of the growing chains.

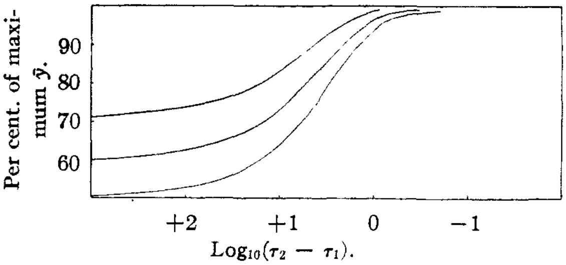

Fig. 3.—Theoretical curves of $\bar{y}$ as a function of duration of light period: upper, $q = 1$; middle, $q = 1.81$; lower, $q = 3$.

TABLE III

VALUES OF QUANTITIES IN THE POLYMERIZATION OF VINYL ACETATE AT 25°

Quantity and units	Value
V_s moles/liter second	1.2×10^{-4}
V_p moles/liter second	8.4×10^{-5}
P moles/liter	0.105
k_1 seconds^{-1}	3.9×10^{-8}
Duration of light flash at mid-point of rate curve, seconds	5
λ_s seconds	1.25
k_2 liters/mole second	1.1×10^{3}
k_3 liters/mole second	8×10^{7}
R_s moles/liter	1×10^{-8}
Kinetic chain length with steady illumination	1.5×10^{4}
% Reaction at end of induction period in photopolymerization	0.007
Duration of induction period, sec.	7

Sources of Error.—Attention has been called in the experimental discussion to various sources of error in our experiments and calculations. These sources of error include irregularity in the light source, overheating in the dilatometer, unsharp boundaries between light and dark in the rotating sector, difficulty in obtaining an exact determination of k_1 at 25° due to much induced decomposition of peroxide, low rate and viscosity of the medium. In comparison to these, any errors in measuring sector speed and contraction in the dilatometer, and in chemical analyses, and troubles due to impurities, are negligible. The combined sources of error cannot have caused an error of more than a factor of two in the value selected for the mid-point of the curve of rate *vs.* flashing frequency, in V_s, k_1, or λ_s. The value of V_p cannot be in error by more than a factor of 1.5. Because of the way in which these constants are combined, some of them squared, in the determination of k_2, k_3, and other derived quantities, the corresponding uncertainty factors are larger, being taken as 5 for k_2, k_3, R_s, and the kinetic chain length. We believe that these factors represent liberal allowances for the errors possibly present.

Table IV compares our results with those of Burnett and Melville.[8] It will be seen that, whereas the values assigned to k_2 in the two laboratories differ by a factor of less than two, the values of k_3 are apart by a factor of 38, much more than our assigned uncertainty. Professor Melville has been kind enough to exchange information with us[10] concerning experimental detail. It appears that the most significant point of contrast between the two pieces of work (Table IV) is that the British investigators used light of frequencies which are rather strongly absorbed by liquid vinyl acetate, while we used light which is absorbed weakly if at all by this ester. According to absorption measurements made in this Laboratory, light of wave length 2600 Å. is half absorbed in a distance of 2.3 mm. of pure liquid vinyl acetate, and light of wave length 2500 Å. is half absorbed in a distance of only 0.16 mm. If most of Burnett and Melville's polymerization were localized in the first millimeter of a 4-cm. cell, so that the volume used in calculating concentrations was actually too large by an effective factor of 40, it can be shown that the corrected results would be in agreement with ours as to both k_2 and k_3. Indeed, a volume factor of even eight would reconcile the k_3 values within the uncertainty factor of 5 which we allow. It is certain that the results of Burnett and Melville require some such correction for the localization of the reaction.

TABLE IV

COMPARISON OF RESULTS OF BURNETT AND MELVILLE[8] WITH THOSE OF THIS PAPER

	B. and M.	This paper
Temperature, °C.	15.90	25
Exciting light, wave length, Å.	>2500[10]	>2998
λ_s, sec.	0.0225	1.25
k_2	5.86×10^2	1.1×10^3
k_3	3.04×10^9	8×10^7

If this is indeed the explanation for the deviation between Melville's k_3 and ours, then the agreement on k_2 attained by the two methods supports the assumptions (1) that chain propagation and hence probably chain termination, is by the same mechanism in photochemical and peroxide-induced polymerization, (2) that k_1 measures the rate of chain initiation in peroxide-induced polymerization, and (3) that the inhibitor method affords a valid measure of the rate of chain initiation by light.

In view of the uncertainties discussed, we question that the results of Burnett and Melville at two temperatures are accurate enough to justify the calculations of activation energies that they have made.

Acknowledgment.—We are grateful to Professor E. L. Chaffee, Director of the Cruft Laboratory, for allowing us the use of a special d. c. generator which served as a source of power, and for working space in the Cruft Laboratory.

Summary

The average lifetime of the growing chains in the photopolymerization of liquid vinyl acetate has been determined, using the rotating sector method of Melville and light of wave length greater than 2998 Å.

On the assumption that the chain propagating and chain terminating steps are identical for photochemical and peroxide-induced polymerization of liquid vinyl acetate, the rate of photochemical initiation of chains has been determined by appropriate combination of measurements upon these two types of polymerization. This makes possible the determination of the absolute rate constants for chain propagation and chain termination, and also the evaluation of such quantities as the concentration of free radicals at the steady state under any given conditions, the kinetic chain length, and the time required for establishment of the steady state.

The quantities determined are tabulated in Table III. A comparison is made with the recent results announced by Burnett and Melville, whose value of the chain termination constant does not agree with ours.

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