[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A Redetermination of the Absolute Rate Constants in the Polymerization of Liquid Vinyl Acetate[1,2]

BY HAROLD KWART,[3] H. SMITH BROADBENT AND PAUL D. BARTLETT

Two almost simultaneous determinations of the rate constants of the steps in the polymerization of liquid vinyl acetate by the rotating sector method[4,5,6,7] yielded propagation rate constants in reasonable agreement but rate constants for termination which differed by a factor of 38. Swain and Bartlett[7] suggested that the reason for this discrepancy was the use by Burnett and Melville of rather strongly absorbing solutions which localized the reaction largely in the first portion of the vessel to be reached by the light. Although subsequent developments[1,7] have tended to confirm this explanation, there were certain sources of error in the experiments of Swain and Bartlett which we felt should be reexamined and minimized in view of the discordant results obtained. We have therefore made an extensive general study of the rotating sector method as applied to systems of this kind and have greatly refined the apparatus and procedure. While this project was in its early stages we learned that Dr. M. S. Matheson[8] was engaged in an extensive program with a similar purpose. In view of the importance and generality of the method we have continued with our redetermination of the rate constants in vinyl acetate polymerization. We have profited greatly by discussions with Dr. Matheson and have adopted several important features of his apparatus. We believe, however, that there are enough points of difference in the apparatus itself, in the method of determining the initiation rate and in the treatment of the measurements to justify a description of our apparatus and experiments.

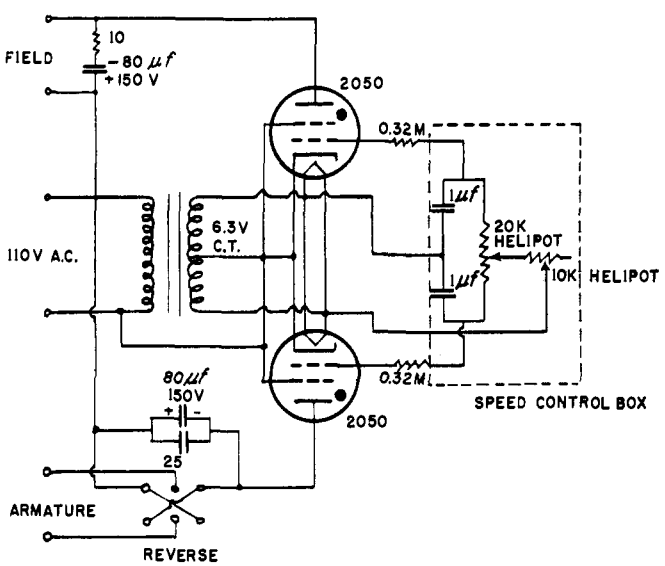

Fig. 1.—Thyratron motor control circuit for sector speed regulation.

Apparatus

The Disk.—A 12-in. stainless steel disk was divided into three equal sectors one of which was exactly cut out. The disk was balanced for high speed rotation by fastening small weights around the hub of the disk. The disk was spun by a small motor equipped with both gear-reduced and directly driven shafts and controlled by an electronic regulator (Fig. 1) similar to the General Electric Thymatrol. The speeds corresponding to selected resistances were determined either by direct timing when slow or by a calibrated General Radio Strobatac. Speed regulation was constant to ±3% for speeds over 300 r. p. m. and ±1% for lower speeds.

Light Source and Optical System.—The glass envelope of a Hanovia AH-8 (or General Electric AH-3) 85-watt mercury arc lamp was cut away and replaced by a clear quartz tube fastened to the base. The output intensity was regulated within ±2% of the set value by a Hanovia voltage regulator built originally for use with the Hanovia modulating arc lamp in sound-recording equipment. An additional phototube and bridge-balanced amplifier (Fig. 2) were mounted behind the reaction cell in such a way as to permit monitoring of the light intensity and also, by movement across the circle of illumination, determination of the uniformity of the field. A large insulated box which could be lowered over the optical system and light source acted as an air thermostat and served to shield the burner from drafts. The control device allowed any given lamp to be operated at an approximately fourfold range of intensities. The variation in characteristics from lamp to lamp was often very great but the intensity could be reproduced on changing lamps with the aid of the monitoring system.

The optical system is illustrated in Fig. 3. The lamp B is mounted in the horizontal plane so that its image, projected through the lenses to K, presents a thin cross section to the rotating sector. The lenses D and E are 9-cm. crystal quartz of about 12 cm. focal length and can be easily positioned to focus a small image of the arc at K. The iris diaphragm H is adjusted to remove stray reflections and shadows from this image. The image at the focus is less than $^1/_{16}$-in. in the important dimension cut by the sector. This means that the transition from light to dark occurs in about 0.2% of a flashing cycle, minimizing the penumbra effect which was commented on in the work of Swain and Bartlett. The lens F is a duplicate of D and E and when properly set produces a well collimated beam passing through the reaction cell. The light source is located about 6 ft. from the reaction cell and about 3 ft. from the lens F. L and L′ are polished

(1) Support of this work by a contract with the Office of Naval Research is gratefully acknowledged by the authors and the University. Much of the apparatus was constructed under a grant from the Milton Fund of Harvard University.

(2) Presented before the Organic Division at the San Francisco Meeting of the American Chemical Society, March 27–April 1, 1949.

(3) Address: Bryn Mawr College, Bryn Mawr, Pennsylvania.

(4) G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945).

(5) G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (London), **A189**, 456 (1947).

(6) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945).

(7) C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946).

(8) M. S. Matheson, E. B. Bevilacqua, E. E. Auer and E. J. Hart, *ibid.*, **71**, 2610 (1949).

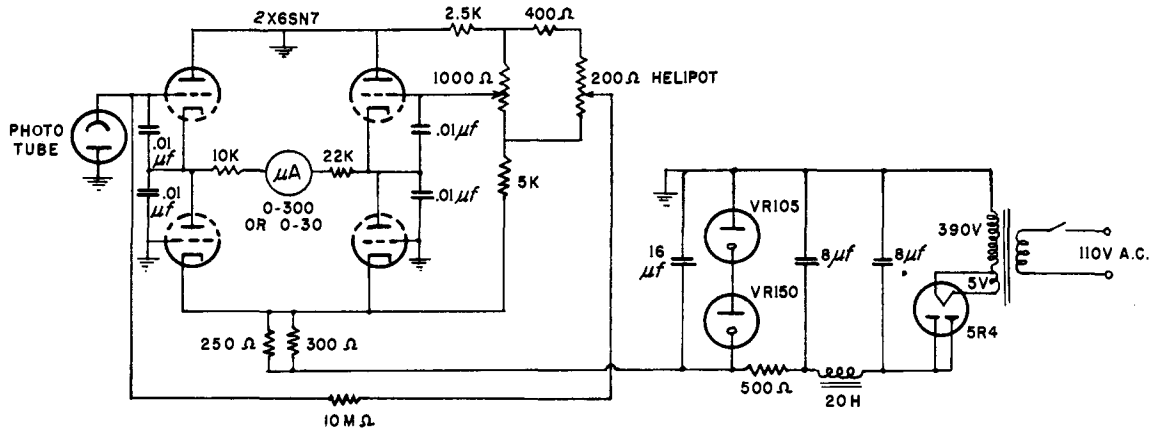

Fig. 2.—Bridge balanced phototube amplifier and power supply.

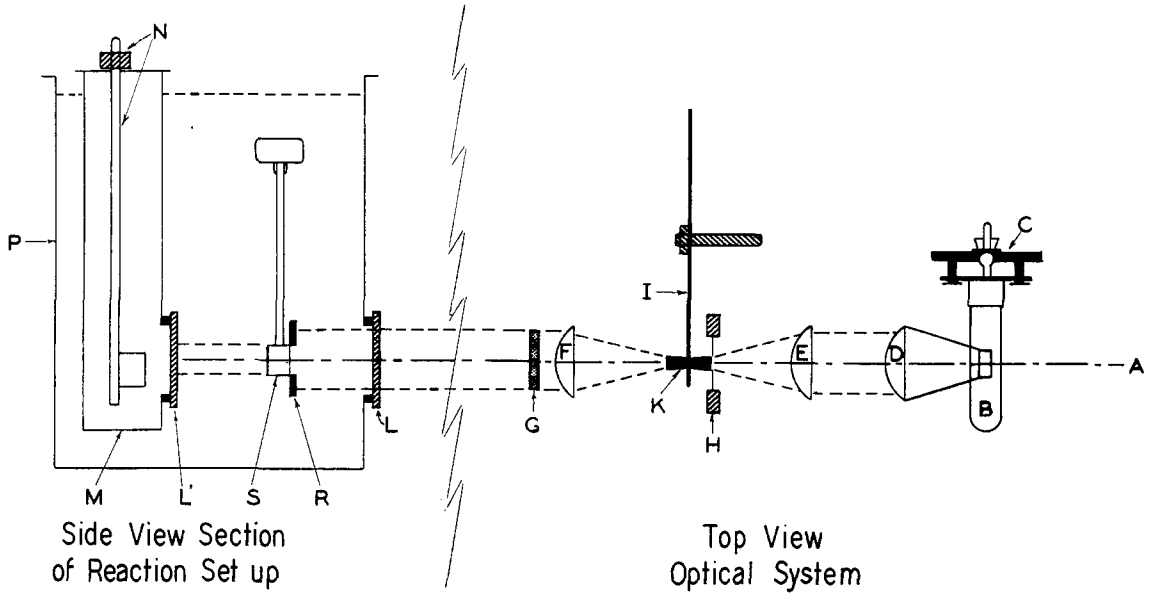

Fig. 3.—Schematic diagram of the optical system and reaction apparatus.

1/8-in. quartz plates serving as windows, respectively, for the thermostat P and phototube box M. R is a Bakelite mask serving as a light stop to prevent the light from striking the cell edges. The assembly N is a screw device controlling the movement of the phototube probe, an R.C.A. 935 tube enclosed in a blackened brass box pierced by a small, sharp-edged hole directly in front of the photosensitive surface of the tube. Before any experiments were performed it was verified by means of this device that the light intensity from top to bottom and from right to left of the field did not deviate by more than 10% from the average over the diameter of the cell. It was confirmed by a mathematical analysis[8a] that variation by this amount produces only a negligible error in the quantities being determined. The filter G was a 2-in. square Corning plate having a maximum transmission of about 75% in the region from 360–380 mμ and transmitting no detectable light below 306 mμ. Samples of vinyl acetate examined in the Beckman spectrophotometer showed no absorption above 280 mμ and were therefore not absorbing light directly in these experiments.

(8a) Office of Naval Research, Project No. NR-056-095, Harvard University. No. N5-ori-76, Tech. Rept. No. 1, June 1, 1949, Appendix 2.

Thermostatic Bath.—The bath was a tank of nickel-plated brass and plate glass, 36 × 43 × 65 cm. deep, of about 25 gal. capacity. A window of 1/4-in. polished quartz plate was cemented into one side at a point just opposite the position occupied by the dilatometer bulb. The bath was filled with distilled water. It was provided with conventional heating, cooling and regulating devices. Temperature regulation was within 0.002°.

The dilatometer rode upon a tinned brass carriage constructed with four grooved wheels which rested on guides milled in a heavy base plate in the bottom of the bath. This permitted the reaction cell to be moved toward or away from the light source in a straight line. The base plate was provided with leveling screws. The dilatometer mounting was a 10 × 32 cm. tinned brass plate to the back of which four small grooved pulleys were attached on adjustable screws as axles. These pulleys were set so as to engage two tinned brass uprights which in turn were part of the carriage mentioned above. The dilatometer could be slid into and out of the bath on the uprights. The adjustable screws bearing the pulleys provided for lateral displacement of the dilatometer with respect to the axis of the light beam entering the bath; for adjustment of the dilatometer carriage a rubber lined tinned brass cradle was affixed to hold the dilatometer cell. Attached to the

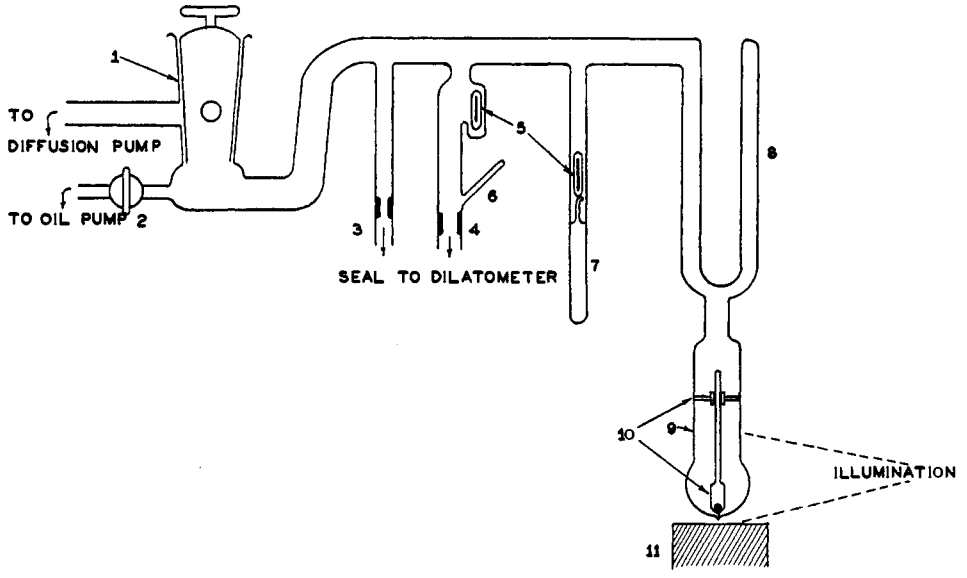

Fig. 4.—Schematic diagram of apparatus for degassing and prepolymerization.

bottom of the cradle was an adjustable, screw-mounted leg, which rested on the floor of the carriage carrying the uprights. By means of this the vertical displacement of the dilatometer could be altered so as to bring the dilatometer cell squarely into the path of the light beam. Running the length of the front of the dilatometer carriage was a 15-in. wide strip of mirror cemented on with litharge-glycerine to facilitate reading the menisci in the dilatometer capillaries, which were mounted directly in front of it. The whole mechanism was so located as to place the dilatometer bulb about 9 cm. from the bath wall. In this position the capillaries could be observed by the cathetometer, located some eight feet away, without any of the usual aberrations.

The bath was always sufficiently deep so that all the dilatometer was beneath the liquid level. This obviated the necessity of introducing an inert atmosphere to prevent distillation from the reservoir into the capillaries, or of making any correction for exposed capillaries.

The Dilatometer.—The dilatometer was of the general type recently described by Bartlett and Kwart.[9] From the data of Starkweather and Taylor[10] and polymer density measurements by Dr. M. S. Matheson[11] the relation between capillary fall in the dilatometer and extent of polymerization was determined. In one of our typical dilatometers a centimeter contraction corresponded to 0.304% polymerization.

Purification of Vinyl Acetate.—The vinyl acetate was purified as previously described.[9,12] As final insurance against the presence of traces of inhibitory materials the sample was degassed and prepolymerized in the apparatus of Fig. 4. Photosensitizer (10–30 mg. of di-*t*-butyl peroxide, see below) was carefully weighed out on a microbalance in a 0.5-cc. glass-stoppered vial. The weighed material was frozen thoroughly, degassed at 10^{-4} mm. for several hours and sealed off in the break-seal tube 7, preliminary to attachment on the line. After the dilatometer was sealed in place and the apparatus tested for leaks, up to 75 cc. of pure monomer was weighed into a volumetric flask together with 0.1% of its weight of benzil which serves as a non-volatile sensitizer in the prepolymerization. This material was introduced into flask 9 through a side-arm tube not shown. After half an hour of pumping, stopcock 2 was closed and the charge thawed. Chipped ice was loaded into the Dewar condenser 8 and on removal of the thawing bath around 9 the magnetic stirrer 11 was set in place. The monomer mixture was refluxed at about 0° with stirring. After fifteen minutes the vinyl acetate was again frozen and pumping resumed. On the fifth such cycle of freezing, thawing, and refluxing, the diffusion pump was switched in through cock 1 (Eck and Krebs precision-ground 20-mm. bore, plug type) and the system was exhausted to near 10^{-5} mm. of mercury as read on a calibrated ionization gage in the line. After closing cock 1 and melting the now thoroughly crystalline mass of monomer, illumination by an AH-8 lamp was begun. Polymerization in flask 9 proceeded with stirring and gentle refluxing at about 15–20°. After about five hours of such treatment the charge had polymerized to the extent of 6–10% and had become fairly viscous. At this point the contents of flask 9 was sometimes frozen and possible gases formed in the polymerization process were pumped out through 1. Thereafter the residual monomer was distilled into the dilatometer by placing a cold trap under the dilatometer reservoir. The break-seal 7 was then crushed with its glass-enclosed hammer 5 and the sensitizer condensed in E. When an inhibitor was used (see below) it was introduced in a thin-walled ampoule jutting from tube 6 into the larger tube 4. This ampoule was then crushed by a magnetic hammer (5) so that the fragments fell into the dilatometer reservoir. Sealing off at the constrictions 3 and 4 required the use of a thin, wax-coated brass paddle to sever the glass connection, since it was not possible to pull on the dilatometer. The exact amount of prepolymerization, and therefore the volume of pure monomer in the dilatometer charge, was determined by leaching out with acetone the polymer remaining in the prepolymerization vessel. After evaporation of the solvent acetone the polymer and benzil were weighed directly.

Light Absorption.—Figure 5 illustrates the absorption characteristics of the filter, Pyrex cell wall, and di-*t*-butyl peroxide used as photosensitizer at a concentration typical of that employed in the experiments. Only the mercury bands at 334 and 313 mμ were effective in decomposing di-*t*-butyl peroxide and the latter group was only weakly transmitted. As measured on the monitoring phototube the total light absorption by the cell contents never exceeded 15% and was usually about 5% of the light transmitted by the filter. This includes experiments in which small amounts of the inhibitor duroquinone were used for measurements of the initiation rate.

(9) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).
(10) H. W. Starkweather and G. B. Taylor, *ibid.*, **52**, 4708 (1930).
(11) Private communication, November 18, 1948.
(12) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 2377 (1946).

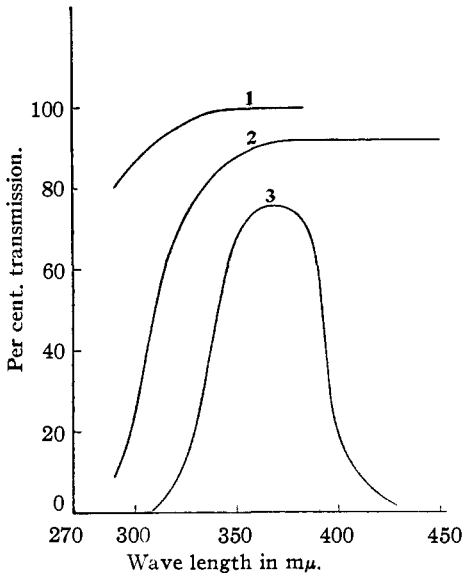

Fig. 5.—Transmission characteristics of a (1) di-*t*-butyl peroxide solution in vinyl acetate, (2) Pyrex plate and (3) Corning filter in the near ultraviolet.

Procedure

The filled dilatometer was brought to temperature in the thermostat while the arc was being stabilized at some set intensity over a period of about an hour. The sector was kept running throughout a series, the light being isolated from the reaction cell by suitable panels in the optical path between rate determinations. The length of exposure was measured with a stopwatch to the nearest hundredth of a minute. For low flashing frequencies the period of exposure was made an integral number of sector revolutions. After an exposure the panel was replaced; the dilatometer reading continued to change as the heat produced by polymerization was dissipated. After about thirty minutes, periodic observations with the cathetometer were made until the meniscus was steady. The reading was recorded to the nearest 0.05 mm. The time of exposure was so chosen as to give a contraction of 0.75–1.0 cm. and the estimated error in any reading was about 0.1%. After each experiment the disk was changed to another speed and the process repeated.

Results

The Rate Constant for Chain Initiation.—The method of Bartlett and Kwart[9] was used to determine the rate of photoinitiation by means of duroquinone. These determinations were made with steady illumination and the results are plotted in Fig. 6, showing that the unimolecular rate constant for initiation of chains by di-*t*-butyl peroxide is proportional to the light intensity. The data leading to these values of the rate constant are shown in Table I. Here $(Q_0)/(P_0)$ is the ratio of initial concentrations of quinone and peroxide, and k_4/k_2 is the ratio of rate constants for chain termination by the inhibitor and chain propagation.

TABLE I

DATA FOR COMPUTATION OF INITIATION RATE CONSTANTS

Run	Rel. light intensity	$[(Q_0)/(P_0)]$ (10^2)	(10^4) intercept	k_4/k_2	$k_i(10^7)$ sec.$^{-1}$
Q1	26	0.970	3.98	152	3.09
Q2	41	1.311	3.04	154	5.54
Q3	54	1.567	3.07	158	6.71
Q4	12.5	1.405	10.7	157	1.72

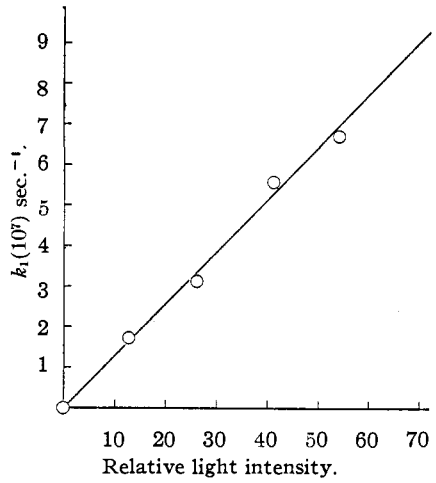

Fig. 6.—Initiation rate as a function of relative light intensity.

Di-*t*-butyl peroxide proved to be an excellent photoinitiator in these experiments. It affords adequate rates of initiation with low light absorption and with a rate of thermal decomposition which proved in our experiments to be negligible (not over $^1/_{150}$ of the light rate at the lowest light intensity). Any dark rate of initiation, due to the existence of thermal dissociation of the photoinitiator as in the experiments of the Matheson group,[8] could not be simply subtracted from the over-all rate of initiation. This is shown by the mathematical analysis of the rotating sector experiment.[7,12a] Though di-*t*-butyl peroxide has only a very small rate of dissociation at 25°[18] it was necessary to determine the maximum extent of thermal initiation that could be neglected in our experiment. An extension of the theory to include appropriate terms for initiation during the dark period is contained in Appendix 1 of Ref. (8a). It is demonstrated that even ten times the observed dark rate produces a maximum error of only 0.67% in the value of k_3 computed. Of the two rotating sector runs reported here, one was performed at a low light intensity for which the initiation rate constant had been measured; the second was run at the highest relative intensity attainable with our light source and the initiation rate for this intensity was calculated from the line of Fig. 6.

Evaluation of the Propagation and Termination Rate Constants.—Figure 7 shows for two runs the variation of rate of polymerization with sector speed. The mean life-time of the growing chains was derived from these data by comparison with the theoretical curve for intermit-

(12a) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

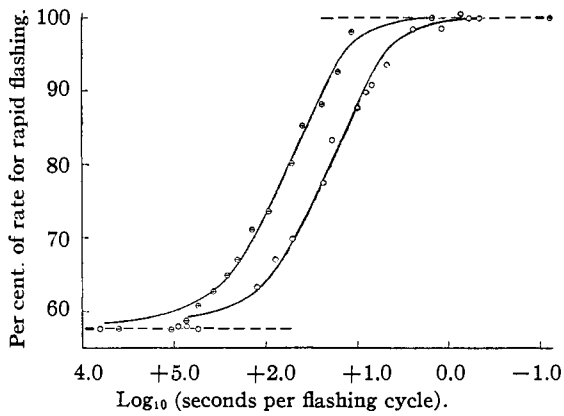

Fig. 7.—Experimental points, rate of polymerization of vinyl acetate at different flashing frequencies. The theoretical curves are also shown.

tent illumination with a light period equal to one-half the dark period by the method of Swain and Bartlett.[7] The experimental and derived quantities relating to these runs are assembled in Tables II and III.

TABLE II

DEPENDENCE OF POLYMERIZATION RATE ON SECTOR SPEED

Run 2 Duration of flashing cycle Seconds	Log10	% max. rate	Run 3 Duration of flashing cycle Seconds	Log10	% max. rate
1080	3.03	57.5	540	2.73	57.6
0.077	−1.11	100	23.5	1.37	77.5
540	2.73	60.7	8.0	0.90	89.8
11.5	1.06	98.1	6.92	0.84	90.8
24.5	1.39	88.2	900	2.95	58.0
40	1.60	85.3	79.5	1.90	67.1
206	2.31	67.0	51.6	1.71	69.9
263	2.42	64.9	12.5	2.10	63.3
141	2.15	71.1	18.5	1.27	80.3
369	2.57	62.7	98.2	0.99	86.7
93.5	1.97	73.6	4.77	0.68	93.5
52.5	1.72	80.2	2.47	0.39	98.4
720	2.86	58.7	1.20	0.08	98.4
1.54	0.18	100	0.75	−0.13	100.5
16.2	1.21	92.6	0.60	−0.22	100
40000	3.60	57.5	0.40	−0.34	100
			725	2.86	57.9
			6300	3.80	57.7

TABLE III

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

Run	2	3
Relative light intensity	12.5	64
$P_0(10^3)$ moles/liter	3.225	4.410
Av. λ_s,[a] sec.	4.00	1.50
$2k_3(10^7)$, liters/mole sec.	5.66	6.12
$k_2(10^{-8})$, liters/mole sec.	0.944	1.01
$V_s(10^4)$,[a] moles/liter-sec.	0.450	1.19
$2fI(10^9)$,[a] moles/liter-sec.	1.11	7.29

[a] λ_s = lifetime of a growing chain; V_s = rate of polymerization under steady illumination; $2fI$ = rate of initiation of chains by light.

Molecular Weight Determinations.—In a typical run the polymer was freed of residual monomer and initiator by the following procedure. The contents of the dilatometer cell after polymerization were introduced into an apparatus similar to that of Fig. 4 without the tubes 4 and 7. The apparatus was sealed off and flask 9 containing the product of the experiment was immersed in liquid air and pumping started by opening cock 1. The non-condensable gas pressure was reduced below 10^{-4} mm. Cock 1 was closed and the liquid-air trap removed from flask 9 to flask 3. After most of the residual monomer and initiator had been distilled into flask 3, flask 9 was warmed to room temperature, opened, and 50 cc. of reagent acetone was added. The acetone was then distilled off by a repetition of the procedure. After three such cycles the resulting unfractionated polymer solution in acetone was subjected to light scattering and osmotic pressure measurements to determine the weight average and number average molecular weights. The polymer concentrations in the several acetone solutions were determined with a differential refractometer.[13] The value of dn/dc, the increment of refractive index with concentration for polyvinyl acetate in acetone, was estimated from the refractive index of solutions whose concentrations in turn were determined by gravimetric methods. Osmotic pressure measurements were made with a Fuoss osmometer with non-waterproof cellophane membranes. The membranes were prepared by washing thoroughly with distilled water and gradually replacing the water by washing in successive aqueous acetone solutions of increasing acetone concentrations. Measurements were made by the procedure of Robertson, McIntosh, and Grummitt.[14] Observations of the height of the meniscus were made with a cathetometer to the nearest 0.05 mm.

Light scattering measurements were made with a Speiser and Brice apparatus[15] kindly made available to us by Professor P. M. Doty. The 90° scattering measurements recorded in Table IV

TABLE IV

DATA FROM LIGHT SCATTERING MEASUREMENTS

C = Concn. in g./cc.	$\frac{HC}{\tau}(10^{-5})$	$H = 1.012 \times 10^{-5}$ $dn/dc = 0.191$
0.0111	0.715	$M_w = 10^5/1.66 = 6.03 \times 10^5$
.00701	.491	$M_w/M_n = 1.62$
.00441	.389	$M_w/2 = M_n = 3.01 \times 10^5$
.00338	.327	

have been corrected by factors estimated from dissymmetry measurements at 45 and 135°. The molecular weight has been computed from the intercept of the graph in Fig. 8 and the relation

$$HC/\tau = 1/M_w + BC$$

(13) B. A. Brice and R. Speiser, *J. Opt. Soc. Am.*, **36**, 363 (1946).

(14) R. E. Robertson, R. McIntosh and W. E. Grummitt, *Can. J. Research*, **B24**, 150 (1946).

(15) R. Speiser and B. A. Brice, *J. Optical Soc. Am.*, **36**, 364 (1946)

where H and B are characteristic constants, C is the solution concentration in grams per cc. and τ the turbidity, a quantity computed from several characteristic constants and the intensity of the light scattered at 90° to the incident beam. Theoretically for an unfractionated polymer of the present type, $M_w = 2M_n$. In our case $M_w = 1.62\ M_n$. Of the two measurements, the one by light scattering is probably the more reliable since an osmotic membrane passes the molecules of low molecular size and thus creates a positive error in molecular weight. It seems best, therefore, to estimate our number average molecular weight as $M_w/2 = 3.01 \times 10^5$.

Discussion

Improvements have been made in each of the sources of error recognized in the experimental conditions of Swain and Bartlett. These include irregularity in the light source, overheating in the dilatometer, indistinctness of the boundary between light and dark, uncertainty in the exact value of the initiation rate, limited accuracy in the determination of the over-all rate of polymerization, uncertainties arising out of increasing viscosity of the medium and optical imperfection of the reaction vessel.

Chain Transfer Constants.—The determination of molecular weights combined with a knowledge of the initiation and propagation rates permits a calculation of the rate constant k_5 for chain transfer by the following equations.

$$\bar{P} = \frac{k_2(\mathrm{R})(\mathrm{M})}{k_3(\mathrm{R})^2 + k_5(\mathrm{R})(\mathrm{M})} \qquad (1)$$

Defining ν = kinetic chain length = $k_2(\mathrm{R})(\mathrm{M})/2k_3(\mathrm{R})^2$, this equation can be rewritten

$$\frac{1}{\bar{P}} = \frac{1}{2\nu} + \frac{k_5}{k_2} \qquad (2)$$

Therefore

$$k_5 = k_2\left(\frac{1}{\bar{P}} - \frac{1}{2\nu}\right) \qquad (3)$$

These equations are based upon the assumption that chain termination involves the union of two growing radicals leading to a polymer of molecular weight 2ν. Since actually the molecular weight is determined almost entirely by chain transfer, the value of k_5 would be lowered only to 0.23 instead of 0.25 if it were assumed that the chains were terminated by disproportionation.

The Definitions of the Rate Constants.—The constants k_1 and k_3 in certain of our previous papers[7,12,16] have not been consistently defined. The equation

$$\mathrm{d(R)/d}t = k_1(\mathrm{P}) - k_3(\mathrm{R})^2 \qquad (4)$$

and the equation

$$-\mathrm{d(P)/d}t = k_1(\mathrm{P}) + k'(\mathrm{P})(\mathrm{R}) \qquad (5)$$

both from Reference (16), imply definitions of k_1 which differ by a factor of two, since two radicals appear every time one peroxide molecule undergoes unimolecular decomposition. Because d(R)/dt has usually been set equal to zero, so that the factor of two canceled out, no error has usually resulted. However, in Reference (12) a derivation occurs in which d(R)/dt is not set equal to zero. In that paper Eq. 9 should read

$$4\sqrt{r}\ \mathrm{K}t = \ln \frac{1 + (1 - x^{4r})^{1/2}}{1 - (1 - x^{4r})^{1/2}}$$

and Eq. 7, in which an exponent is incorrectly printed in the original, should read

$$R = \sqrt{\frac{k_1(\mathrm{P})}{k_3}}\left[1 - \left(\frac{M}{M_0}\right)^{4k_3/k_2}\right]^{1/2}$$

Similarly, in the equations of Swain and Bartlett k_1 from measurements of peroxide decomposition was erroneously equated to the rate of formation of free radicals (actually $2k_1$) in peroxide-induced polymerization. The quoted value of "k_3" in the work of Swain and Bartlett consequently also involves a factor of two.

In this paper we adhere to the definitions

$$\mathrm{d(R)/d}t = 2k_1(\mathrm{P}) - 2k_3(\mathrm{R})^2$$

and

$$\mathrm{d(R)/d}t = 2f(\mathrm{I}) - 2k_3(\mathrm{R})^2$$

for peroxide-induced and light-induced polymerization, respectively. These are the same as used by Matheson and co-workers. The k_3 of Swain and Bartlett in Table V has been correspondingly corrected to be experimentally comparable.

There are now available two further determinations of the absolute rate constants in the polymerization of liquid vinyl acetate.[8,17] Table V shows a comparison of the results of this paper with all four previously reported sets of constants. The agreement with the values of k_2 and k_3 of Matheson and co-workers is gratifyingly close and the agreement with those of Swain and Bartlett is closer than their discussion of errors would lead

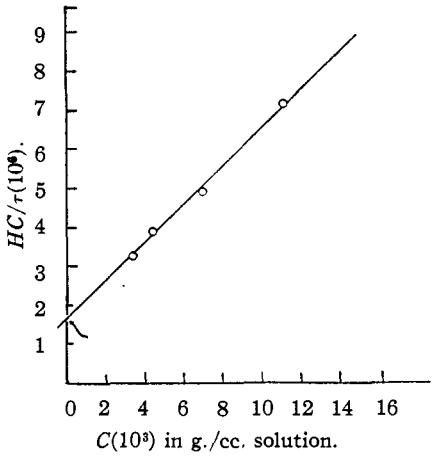

Fig. 8.—The variation of the scattered light function, HC/τ, with concentration of polyvinyl acetate in acetone solution.

(16) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(17) G. Dixon-Lewis, "Discussions of the Faraday Soc.," no. 2, 319 (1947).

TABLE V

Investigators	Temp., °C.	$2k_3$ (10^{-7})	k_2 (10^{-3})	k_4
Burnett and Melville[5]	15.9	280 (av.)	0.72 (av.)	None
Swain and Bartlett[7]	25	4	.55	...
Dixon-Lewis[17]	0	20	1.8	0.123
Matheson, *et al.*[8]	25	5.88	1.012	5 (at 50°)
This paper	25	5.9	1.0	0.25[a]
				0.23[b]

[a] On the basis of union of radicals. [b] On the basis of disproportionation of radicals.

one to expect. The value of the chain transfer constant is not in good agreement with that from the other laboratories. The equations used by us neglect chain transfer to the initiator, a reaction which would have been important if benzoyl peroxide were being used but which does not seem to require consideration with either di-*t*-butyl peroxide[18] used by us or α-azo-bis-isobutyronitrile used by Matheson, *et al.*[19]

Summary

A much improved apparatus is described for determining absolute rate constants of liquid bulk polymerization by means of the rotating sector. Errors from previously recognized sources have been greatly curtailed. The results of a redetermination of the absolute rate constants for the steps in the polymerization of liquid vinyl acetate are reported and are compared in Table V with the results of other investigators.

(18) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 88 (1948).

(19) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE, LONDON]

Stereochemistry of the Cholesterol Dibromides[1]

BY D. H. R. BARTON[2] AND E. MILLER

The previous paper[3] in this series dealt with the elucidation of the stereochemistry of the two cholesterol dichlorides. Ordinary cholesterol dichloride, obtained by the addition of chlorine to cholesterol, was shown to be 5α,6β-dichlorocholestan-3β-ol, whilst the isomeric dichloride, obtained by the use of the iodobenzene dichloride reagent, was demonstrated to be 5α,6α-dichlorocholestan-3β-ol. In logical extension of this work the stereochemistry of the two cholesterol dibromides has now been investigated.

In the course of their extensive bromination studies Butenandt and Schramm[4] noted that dibromocholestanone, obtained by oxidation[4,5] of ordinary cholesterol dibromide, was monobrominated exclusively at the 4-position. Since cholestanone and coprostanone are brominated,[6] under comparable conditions, at the 2- and 4-positions, respectively, Butenandt and Schramm concluded that ordinary cholesterol dibromide probably had the coprostane configuration of rings A and B.

In actual fact this argument appears to be unsound because it is not based on a proper appreciation of the mechanism[7] of the bromination of ketones, the rate controlling step of which is the abstraction of a proton from the ketone by a base. Other factors being equal, the most acidic available proton will be removed. In the case under consideration here the powerful negative (acid strength increasing) inductive effect of the 5-bromine atom will clearly be dominant and thus lead to substitution at the 4-position irrespective of the nature of the A/B ring fusion.

The mechanism of the ionic type addition of bromine to olefinic linkages is generally accepted as comparable to that of chlorine, particularly in its stereochemical (*trans*-addition) implications.[8] It might be expected therefore, by analogy with the established[3] configuration of the dichloride, that ordinary cholesterol dibromide would be 5α,6β-dibromocholestan-3β-ol. This assignment of configuration is also suggested by the molecular rotation data summarized in Table I. Not only has ordinary cholesterol dibromide almost identical Δ values with those recorded[3] for 5α,6β-dichlorocholestan-3β-ol, but the absolute magnitudes of the optical rotations are similar. The 5α,-6β-configuration was finally confirmed chemically by treating the known cholesterol α-oxide with

TABLE I

Substance	$[M]_D$[a] Alcohol	Acetate	Benzoate	Ketone	Δ_1[b]	Δ_2	Δ_3
5α,6β-Dichlorocholestan-3β-ol[c]	−123	−145	−112	−123	−22	+9	±0
5α,6β-Dibromocholestan-3β-ol	−240	−271	−234	−245	−31	+6	−5

[a] All rotations in chloroform solution. [b] Δ_1 is the molecular rotation difference on acetylation, Δ_2 that on benzoylation and Δ_3 that on oxidation. [c] Data from Barton and Miller.[3]

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(2) Harvard University, Visiting Lecturer, 1949–1950.

(3) Barton and Miller, THIS JOURNAL, **72**, 370 (1950).

(4) Butenandt and Schramm, *Ber.*, **69**, 2289 (1936).

(5) Inhoffen, *ibid.*, **69**, 1134, 2141 (1936).

(6) Butenandt and Wo ff, *ibid.*, **68**, 2091 (1935); compare Butenandt and Mamoli, *ibid.* **8**, 1854 (1935); Djerassi and Scholz, *Experientia*, **3**, 107 (1947).

(7) *E. g.*, see Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 96 ff.

(8) Michael, *J. prakt. Chem.*, **52**, 344 (1893); McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912); Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925); Roberts and Kimball, *ibid.*, **59**, 947 (1937).