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Rate Constants in Free Radical Polymerizations. I. Methyl Methacrylate

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Until recently, the absolute rate constants of vinyl polymerization have not been measured. Now, however, Burnett and Melville[1] and Swain and Bartlett[2] have applied the rotating sector method of Briers, Chapman and Walters[3] to the measurement of the absolute rate constants of vinyl acetate addition polymerization in the liquid phase. A new and elegant method has recently been devised by Bamford and Dewar[4] and applied to the measurement of the absolute rate constants of polymerization of styrene and methyl methacrylate. In their method, changes in intrinsic viscosity of a photopolymerizing system during and after irradiation and knowledge of the molecular weight of a thermal or photopolymer permit the evaluation of all the rate constants. A further very ingenious method applicable to emulsion polymerization has been developed by Smith and Ewart[5] for the measurement of the propagation rate constant. In this Laboratory, we have studied several monomers with the rotating sector method and this paper reports the work on methyl methacrylate.

Theoretical

The usual studies on polymerization yield the ratios of rate constants rather than their individual values. This is made clear by consideration of the mechanism below, which includes simultaneous initiation by a free radical source such as benzoyl peroxide and by monomer.

Free Radical Initiation	*Rate*
$\mathrm{Init.} \xrightarrow{k_d} 2\mathrm{R}\cdot$	$2k_d\,(\mathrm{Init.})$
$2\mathrm{R}\cdot \xrightarrow{k_r}$ Stable product	$2k_r\,(R\cdot)$
$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{M}_1\cdot$	$2k_a(\mathrm{R}\cdot)\,(\mathrm{M})$
Initiation by Monomer	
$\mathrm{M} + \mathrm{M} \xrightarrow{k_i} \cdot\mathrm{M}_2\cdot$	$2k_i(\mathrm{M})^2$
Propagation	
$\mathrm{M}_r\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_{r\dot{+}1}$	$k_p(\mathrm{M}_r\cdot)(\mathrm{M})$
$\cdot\mathrm{M}_r\cdot + \mathrm{M} \xrightarrow{k_{p1}} \cdot\mathrm{M}_{r\dot{+}1}$	$k_p(2[\cdot\mathrm{M}_r\cdot])(\mathrm{M})$
Termination	
$\mathrm{M}_r\cdot + \mathrm{M}_s\cdot \xrightarrow{k_t} \mathrm{M}_{r+s}$	$2k_t(\mathrm{M}_r\cdot)(\mathrm{M}_s\cdot)$
$\mathrm{M}_1\cdot + \cdot\mathrm{M}_s\cdot \xrightarrow{k_{t1}} \mathrm{M}_{r\dot{+}s}$	$2k_t(2[\cdot\mathrm{M}_s\cdot])(\mathrm{M}_r\cdot)$
$\cdot\mathrm{M}_r\cdot + \cdot\mathrm{M}_s\cdot \xrightarrow{k_{t2}} \cdot\mathrm{M}_{r\dot{+}s}$	$2k_t(2[\cdot\mathrm{M}_r\cdot])(2[\cdot\mathrm{M}_s^{\cdot}])$
Transfer with Monomer	
$\mathrm{M}_r\cdot + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_r + \mathrm{M}_1\cdot$	$k_{tr}(\mathrm{M}_r^{\cdot})(\mathrm{M})$
$\cdot\mathrm{M}_r\cdot + \mathrm{M} \xrightarrow{k_{tr1}} \mathrm{M}_r\cdot + \mathrm{M}_1\cdot$	$k_{tr}(2[\cdot\mathrm{M}_r\cdot])(\mathrm{M})$

where

Init. = initiator or source of free radicals
R· = radical from initiator
M = monomer
$\mathrm{M}_r\cdot$, $\cdot\mathrm{M}_r\cdot$ and M_r = respectively, monovalent polymer radical, bivalent polymer radical and stable polymer molecule of *r* monomer units
k's = rate constants. Rates are given for formation or consumption of free valencies in initiation or termination, and for consumption of monomer in propagation or transfer.

Implicit in the mechanism are the following assumptions: (1) Although the "Cage" mechanism[6] is given, the essential assumption is that free radical induced initiation is proportional to (Init). Further, monomer initiation gives a biradical.[7] (2) The rate constants of propagation, termination, and transfer are independent of the length[8] or bivalent character of the polymer radicals. (3) The growing polymer radicals terminate by combining.[9] It is further assumed that: (4) Kinetic chains are long. (5) The monomer concentration is constant. In our work, except where specifically stated, no polymerization was carried beyond 5 to 10%. (6) A steady state is attained.

On the basis of the above, one obtains

$$R_i = 2k_d f(\mathrm{Init.}) + 2k_i\,(\mathrm{M})^2 \qquad (1)$$

where R_i = rate of initiation of polymer radicals, $2k_d f(\mathrm{Init.})$ = rate of initiation by initiator, and $f = k_a(\mathrm{M})/(k_r + k_a(\mathrm{M}))$ = constant if (M) held constant.

$$R_p{}^2 = [k_p{}^2(\mathrm{M})^2/k_t]\,[k_d f(\mathrm{Init.}) + k_i(\mathrm{M})^2] \qquad (2)$$

where R_p = rate of polymerization = $-\mathrm{d}(\mathrm{M})/\mathrm{d}t$.

$$\frac{1}{\bar{P}} = \frac{k_d f(\mathrm{Init.})}{R_p} + C \qquad (3)$$

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[1] (a) G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945); (b) *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

[2] (a) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945); (b) C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946).

[3] F. Briers, D. L. Chapman and E. Walters, *J. Chem. Soc.*, 562 (1926).

[4] (a) C. H. Bamford and M. J. S. Dewar, *Nature*, **157**, 845 (1946); (b) *Proc. Roy. Soc.* (*London*), **A192**, 309 (1948); (c) Discussions of the Faraday Soc. No. 2 (1947), The Labile Molecule, p. 310; (d) M. J. S. Dewar and C. H. Bamford, *Nature*, **158**, 380 (1946).

[5] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

[6] M. S. Matheson, *ibid.*, **13**, 584 (1945).

[7] P. J. Flory, THIS JOURANL, **59**, 241 (1937).

[8] F. R. Mayo, *ibid.*, **70**, 3689 (1948); R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948).

[9] J. H. Baxendale, S. Bywater and M. G. Evans, *Trans. Faraday Soc.*, **42**, 675 (1946), and M. G. Evans, private communication, give evidence for combination in methyl methacrylate; M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945), show a large proportion of $\mathrm{MeOC_6H_4\underset{\cdot}{C}HCH_2CH_3}$ radicals dimerize with no evidence of disproportionation.

where $\bar{P}$ = number average degree of polymerization, C = transfer constant = k_{tr}/k_p.

These equations show that if R_p and $\bar{P}$ are studied as a function of (Init.) the quantities k_p^2/k_t, $k_d f$, and C may be obtained. A further relation to evaluate k_p, k_t and k_{tr} individually may be obtained by measuring τ_s, the time average lifetime of the growing polymer radical.

The theory of the rotating sector is fully presented elsewhere.[10] However, some monomers, especially styrene, exhibit "dark" reactions, and we have extended the theory to cover these systems using the mechanism below and following the procedure of Dickinson.[10]

Initiation	*Rate*	*Definitions*
$S + h\nu \xrightarrow{I_a} 2R\cdot$	$2qI_a$	S = sensitizer
$2R\cdot \xrightarrow{k_r} S$	$2k_r(R\cdot)$	$h\nu$ = quantum of frequency ν
$R\cdot + M \xrightarrow{k_a} M\cdot$	$2k_a(R\cdot)(M)$	I_a = absorbed light intensity
Propagation		
$M\cdot + M \xrightarrow{k_p} M\cdot$	$k_p(M\cdot)(M)$	$R\cdot$ = radicals from sensitizer
Termination		
$M\cdot + M\cdot \xrightarrow{k_t}$ Polymer	$2k_t(M\cdot)^2$	q = quantum yield of dissociation of S
		M, M·, and k's as previously defined

The Assumptions for Photopolymerization in Intermittent Light.—(1) Initiation: The essential assumption is that the rate of initiation, R_i, is proportional to the absorbed light intensity, I_a. In our work thermal initiation during light periods in all sector experiments was negligible compared to the photosensitized initiation. During dark periods it is assumed that there is a "dark reaction," whose magnitude is equal to that which would be caused by stray light of intensity nI_a (the dark rate, of course, is induced either by thermal initiation by the monomer as in styrene or by "catalysts" such as peroxides as in methyl methacrylate) where I_a corresponds to the total initiation in the cell when the sector is open and n equals a quantity less than one. Evidence for the mechanism as given has been found by Schulz and Husemann,[11] Schulz and Blaschke[12] and Mark and Josefowitz.[13] (2) Assumptions 2, 4, 5 and 6 of previous mechanism held valid. (3) The irradiating light is absorbed in the cell uniformly, both as to space and as to time during light periods. (4) The magnitude of the "dark" rate of initiation is unaffected by light. (5) The dark–light and light–dark transitions in the cell are instantaneous at the beginning and end of a light flash; precautions to insure the correctness of assumptions 3 to 5 will be found under Experimental Procedure.

From the assumptions about the initiation

$$d(M\cdot)/dt = 2qfI_a - 2k_t(M\cdot)^2 \qquad (4)$$

is derived for the light period while during the dark period the following is derived

$$-d(M\cdot)/dt = 2k_t(M\cdot)^2 - 2qfnI_a \qquad (5)$$

Following Dickinson, we obtain as the final result

$$\frac{(\overline{M\cdot})}{(M\cdot)_s} = \frac{1}{p+1}\cdot\frac{1}{b}\left\{ b + n^{1/2}\,pb + \ln\left[\frac{1+\dfrac{(M\cdot)_2}{(M\cdot)_s}}{1+\dfrac{(M\cdot)_2}{(M\cdot)_s n^{1/2}}}\right]\left[\frac{1+\dfrac{(M\cdot)_1}{(M\cdot)_s n^{1/2}}}{1+\dfrac{(M\cdot)_1}{(M\cdot)_s}}\right]\right\} \qquad (6)$$

where

$(\overline{M\cdot})/(M\cdot)_s$ = the ratio of R_p in intermittent light to R_p in steady light

since

$(\overline{M\cdot})$ = the time average concentration of M· in intermittent light

and

$(M\cdot)_s$ = the concentration of M· in steady light,

and where

p = ratio of the dark period to the light period = 3 in our work

b = ratio of the time of flash, t_1, to the time average duration of growth, τ_s, where τ_s is the lifetime of the kinetic chain from the initiation of a chain to its termination by mutual interaction with another growing radical

$(M\cdot)_1$ = concentration of M· at the beginning of each dark period

$(M\cdot)_2$ = concentration of M· at the end of each dark period

Further

$$\frac{(M\cdot)_1}{(M\cdot)_s} = \frac{\tanh b + \dfrac{(M\cdot)_2}{(M\cdot)_s}}{1 + \dfrac{(M\cdot)_2}{(M\cdot)_s}\tanh b} \qquad (7)$$

and

$$\frac{(M\cdot)_2}{(M\cdot)_s} = \frac{-(1-n)\tanh b \cdot \tanh(n^{1/2}pb)}{2[n^{1/2}\tanh b + \tanh(n^{1/2}pb)]} + \frac{\sqrt{(1-n)^2\tanh^2 b\cdot\tanh^2(n^{1/2}pb) + 4[n^{1/2}\tanh b + \tanh(n^{1/2}pb)][n^{1/2}\tanh b + n\tanh(n^{1/2}pb)]}}{2[n^{1/2}\tanh b + \tanh(n^{1/2}pb)]} \qquad (8)$$

The curves obtained by the use of eqns. (6), (7) and (8) are plotted in Fig. 1 for various values of $n^{1/2}$. $n^{1/2}$ is the ratio of the steady dark rate to the steady light rate. The use of Fig. 1 in the measurement of the kinetic chain lifetime, τ_s, is illustrated under Experimental Procedure.

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(10) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 202.

(11) G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

(12) G. V. Schulz and F. Blaschke, *ibid.*, **B51**, 75 (1942).

(13) D. Josefowitz and H. Mark, *Polymer Bull.*, **1**, 140 (1945); Ph.D. Thesis of D. Josefowitz, Brooklyn Polytechnic Inst., 1945.

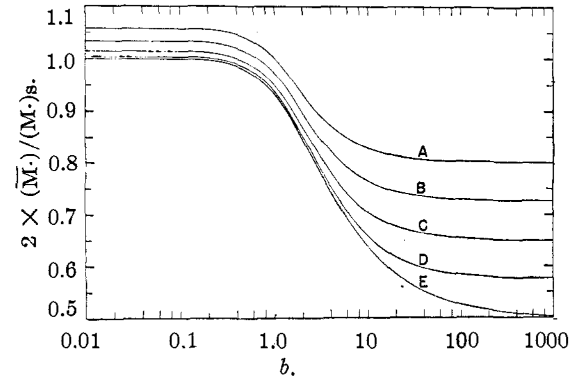

Fig. 1.—The ratio of intermittent light rate to steady light rate as a function of time of flash and dark rate: $A - n^{1/2} = 0.20$, $B - n^{1/2} = 0.15$, $C - n^{1/2} = 0.10$, $D - n^{1/2} = 0.05$, $E - n^{1/2} = 0.0$.

From the mechanism of photopolymerization, the following equations obtain in steady light

$$R_p = k_p(M\cdot)_s(M) \qquad (9)$$

$$(M\cdot)_s = R_i\tau_s \qquad (10)$$

$$R_i = 2k_t(M\cdot)_s^2 \qquad (11)$$

whence

$$R_p\tau_s/(M) = k_p/2k_t \qquad (12)$$

Thus, by measuring τ_s we can get $k_p/2k_t$ whereas by initiator studies we can get $k_p^2/2k_t$ and k_{tr}/k_p. The combination yields the individual values of k_p, k_t and k_{tr}.

Experimental

Purification of Materials.—Rohm and Haas methyl methacrylate was distilled through a 50-plate column under nitrogen: n^{20}D 1.4152, b. p. 45.0° at 105 mm. This product was kept in the dark at −25° until further use. Subsequently, this material was recrystallized five times under dry nitrogen to a constant freezing point 0.3°[13a] above that of the distilled material with an over-all yield for all recrystallizations of 50%. The recrystallized material was stored in an evacuated tube containing 0.1% hydroquinone at −25° in the dark. Recrystallization and all subsequent operations were carried out in a dark room. Earlier experiments showed the necessity for filling the reaction cells by distillation into the cells *in vacuo* and in the absence of light if high dark reactions were to be avoided. Therefore, the vacuum bench and rotating sector equipment were located in a dark room. Eastman Kodak Co. biacetyl was distilled through a Vigreux column and the middle cut retained. Mallinckrodt Chemical Works photographic grade hydroquinone was used without further purification.

Apparatus.—A plan view of the rotating sector apparatus is shown diagrammatically in Fig. 2.

This apparatus enables sector studies to be made on two pairs of cells simultaneously, each pair being at a different temperature. The arcs A are Hanovia constant intensity high pressure mercury arcs, Type AH-8 with photocell feedback, supplied from two Sola constant voltage transformers in cascade. Experimentally the intensity was found to be constant to ±1% after a half hour warmup. The a. c. ripple in the light output was shown to be less than 3% of the total intensity. The light was made monochromatic by filters at F, using Corning no. 5840 and no. 738 filters to isolate the 3660 Å. line, except for the slow 30° experiment where the following combination was used: one 5840 + one 738 + three 5113. All lenses were crystal quartz 10 cm. f. l. and 4.6 cm. diameter free aperture. The lenses L₁ focused the narrow arc image at the sectors S, so that the transition time from dark to light and *vice versa* was about 2% of the light period. The sectors were made of 11 in. diameter aluminum disks divided into eight equal sectors and every fourth sector cut out to a radial depth of 2 in. These disks were driven by readily interchangeable synchronous motors. By means of these motors the disk speeds could be varied in steps from $^1/_{60}$ to 1800 r. p. m., each step corresponding approximately to a fourfold change in speed. The lenses L_2 were placed close to the sectors and considered to be located at the arc image. These lenses focused the image of the L_1's in cells C to assure uniform light intensity over the cell and also to provide for simultaneous transition from dark to light throughout the cell. The images of the L_1's overlapped the front windows of the cells 3 mm. all around. However, at the front of the cell a diaphragm limited the beam to just fill the inside of the cell. These cells were cylindrical cells with plane-polished faces, American Instrument Company Grade 1, 1 cm. internal depth and 3.7 cm. internal diameter. They were surmounted by a 25 cm. length of 2-mm. precision bore capillary. Gaertner M930-342 cathetometers were used to read the liquid levels in the capillaries to 0.01 mm. The cells were placed in holders in the baths B, so designed that inverted clear Pyrex cylindrical Dewars could be placed over the capillaries, the lower end of the Dewar dipping into the bath. Water was drawn up into the Dewar to cover the capillary, and for bath temperatures above room temperature, convection currents within the Dewar kept the temperature at the top of the capillary within 2° of that of the bath, even at a bath temperature of 60°. However, for bath temperatures below room temperature the difference at the top of the capillary was greater, since convection no longer played such an important part in heat transfer up the Dewar, but even in this case a more constant capillary temperature was assured, and in all cases the Dewar served to prevent condensation of the monomer in the capillary tip. Liquid level readings were taken through the transparent Dewar and this arrangement enabled the use of baths of moderate depth.

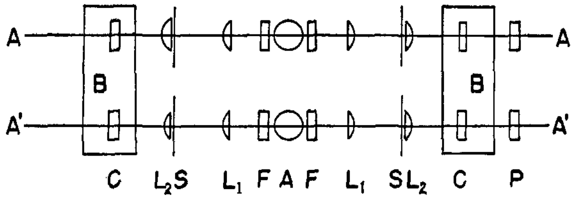

Fig. 2.—Apparatus for rotating sector studies.

During an experiment the constancy of the arcs was checked by the RCA935 photocells shown at P. A 6 cm. diameter quartz lens of 7.5 cm. focal length at the front of the photocell housing intercepted all of the light passing through the cell. The output of the 935 photocells was amplified by General Radio 715AE amplifiers and the amplified output recorded by Esterline Angus 5 ma. Model AW d. c. milliammeters. The output of the arcs was measured behind only one of the baths. The baths were fitted both front and rear with double windows of Corning no. 791 glass, having $^1/_4$″ of sealed air space. The double windows plus an air stream served to eliminate moisture condensation on the windows when the bath was operated at low temperatures. The temperatures of the baths were regulated to ±0.01°. Temperatures below room temperature were obtained by circulating an ethylene glycol-water mixture from an auxiliary American Instrument 4-86LE cooling bath through coils in the baths B. The optical paths in the diagram are designated AA and A′A′ and were thoroughly baffled and sealed against all stray light from other parts of the apparatus or originating externally.

[13a] F. p. of purified monomer −48.2° (Rohm and Haas Co. private communication). Using a thermocouple not absolutely calibrated we obtained a slightly higher value.

Procedure.—Filling of cells: Purified monomer was placed in a reservoir containing hydroquinone, and attached to a Pyrex glass vacuum system and degassed to a non-condensable gas pressure of 10^{-4} mm. while the monomer was at −80°. The process of melting, refreezing, and pumping on the monomer was repeated several times. The first 10% was distilled off *in vacuo* and rejected. Part of the remaining monomer was then distilled simultaneously into the bulbs B, as shown in Fig. 3. The volume of monomer in B was adjusted at 0° to a volume calibration mark on the bulb. The distilled biacetyl (the sensitizer used in all experiments) was also sealed to the vacuum system in a bulb containing hydroquinone. The required amount of biacetyl (calculated to give not more than 25% absorption in 1 cm. of depth when dissolved in the given volume of monomer in B) was distilled into a calibrated capillary for measuring at 0° and then into B. The apparatus of Fig. 3 was then sealed off at the constriction C_1. Next, the apparatus was inverted and the liquid level in the capillary of C adjusted to a suitable height. Both legs were cooled simultaneously to a few degrees above the freezing point of the monomer and the cell C sealed off at constriction C_2. The cell was stored at −25° in the dark until used.

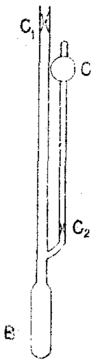

Fig. 3.—Device for filling cells.

Irradiation.—The cells were placed in the bath for a sufficient period before irradiation to get an accurate determination of the dark reaction, which in most cases was measured overnight. The cells were initially irradiated with the sectors in the open position to get the rate of polymerization in steady light. Then the sectors were started at known speeds and the rates of polymerization followed in intermittent light. The continuous and sectored irradiations were alternated during the day. Readings were taken at equal time intervals beginning a few minutes after the start of an irradiation so the method of Orthogonal Polynomials[14] could be used to get the least squares slope for the plot of liquid level *versus* time. Our method, it is believed, eliminates not only random reading errors but also errors due to slight heating and cooling effects in the cells at the beginning and end of a given irradiation as a result of the heat of reaction. If the experiments with a given cell were carried out over a period more than one day, the overnight dark reaction was checked each night. It was necessary to take the evening reading at least one hour after the end of an irradiation, otherwise the measured dark rate was affected by the decaying light-induced reaction.

Densities.—Since the rate was followed dilatometrically, the densities of monomer and polymer were determined as a function of temperature. The monomer used was freshly distilled, and the pyknometric determinations were carried out immediately in red light to avoid contamination by polymer. Constancy of the monomer density at 0° at the beginning and end of the experiment showed polymerization to be negligible. The polymer was prepared by allowing purified monomer to polymerize in sunlight in a pyrex flask in the presence of a trace of air. After apparent completion of polymerization the polymer was heated *in vacuo* at 100° for sixteen hours, after which the amount of monomer which could be pumped from shavings of the polymer at 100° was negligible. A portion of the polymer was cut to fit a mold and subjected to 2000 p. s. i. at 165° for one hour.

Recently Schulz and Harborth[15] have found the apparent density of polymethyl methacrylate to be greater in solution than in the pure solid state. To check this result two experiments were carried out. In one, freshly distilled monomer containing 0.2% tetrachloroquinone was poured into 100-cc. volumetric flasks containing weighed amounts of polymer and the volume determined after solution of the polymer. In the second experiment the monomer was distilled into 100-cc. volumetric bulbs *in vacuo*, 0.2 g. of benzoquinone being used in each flask as the inhibitor. Air was then introduced into each flask to compress the bubbles formed in the viscous solution. In each case density results were corrected for the small amount of inhibitor present. All of our samples of polymer initiated polymerization of the monomer, probably because of peroxides in them, necessitating the use of considerable inhibitor. The solution density results are given in Table II.

TABLE I

DENSITY OF METHYL METHACRYLATE MONOMER AND POLYMER

(Equation for monomer density, $\rho = 0.9654 - 0.00109\,t - 0.00000097t^2$ (t = °C.)

Temp., °C.	Monomer density	Temp., °C.	Polymer density[a] Unmolded	Molded
0.38	0.9651	0.0	1.1903	1.1907
20.20	.9431	30.0	1.1834	1.1835
30.02	.9313	60.0	1.1756	1.1747
40.51	.9198			
49.74	.9088			
60.37	.8956			

[a] Rohm and Haas Co. has kindly informed us that they find a density of 1.182 ± 0.003 at 25°.

TABLE II

APPARENT DENSITY OF POLYMETHYLMETHACRYLATE AT 30°[a]

Experiment 1		Experiment 2	
Wt. % polymer	Density	Wt. % polymer	Density
5.26	1.195	16.09	1.227
10.39	1.213	26.93	1.224
15.40	1.213	39.72	1.219
38.78	1.218		

[a] Ref. 15 gives 1.213 at 25°.

Calculation of Results.—In cases where the dark rate amounted to more than 1% of the steady light rate, two corrections were made. First, least squares values of the rates were corrected for the dark reaction taking place in the unilluminated appendages to the cell, by subtracting the proper fraction of the dark rate, about 20%, from both continuous and sector rates. The ratio of the corrected sector rate to the corrected continuous light rate was then obtained. This is necessary since the theory considers the volume subject to illumination, and in the experimental setup the side tubes and capillary were completely shielded. For all cells used, both the volume in the barrel of the cell and the volume of monomer in the side tubes and capillary were measured. The effect of the dark reaction within the irradiated volume is considered next. By the use of the curves plotted in Fig. 1, the values of b corresponding to the corrected rate ratio were found for values of $n^{1/2}$ of 0, 0.05, 0.10, 0.15 and 0.20 and from these data a plot of b *vs.* $n^{1/2}$ was made ($n^{1/2}$, which will be called the fractional dark rate, is, as noted previously, the ratio of the steady dark rate of polymerization to the steady light rate of polymerization, both rates being

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[14] Tables of Orthogonal Polynomial Values Extended to N = 104: R. L. Anderson and E. E. Houseman Research Bulletin 297, April, 1942, Ames, Iowa.

[15] G. V. Schulz and G. Harborth, *Angew. Chem.*, **59A**, 90 (1947).

limited to the cell barrel). The value of b corresponding to the measured fractional dark rate which obtained during the experiment was then found by interpolation from the plot. The lifetime, τ_s, is the ratio of t_1, the time of flash for the given sector speed, to b. An example in which a sector speed of 1/15 r. p. m. was used in experiment 19L will make this calculation clear.

Rates	Cm./min.	Ratio	.315
Dark	0.000110	2 × Ratio	.630
Dark correction outside cell	.000024	t_1 sec.	112.5
		$n^{1/2}$	.021
Corrected dark rate in cell	.000086	b measured for $n^{1/2}$ = .021	11.5
11th continuous	.00396	τ_s	9.79
12th continuous	.00403	Rate % contraction per hr.	.0724
Av. continuous	.00400	τ_s @ 0.5% contraction per hr.	1.42
Corrected continuous	.00398	2 × ratio for $n^{1/2} = 0$	.625
8th sector	.001280		
Cor. sector	.001256		

In any run ratios were measured at several different sector speeds. In order to obtain an average value of τ_s from these results, the rate ratios were plotted against the log of the time of flash (log t_1) and the position of best fit with the proper theoretical curve of Fig. 1 found. As seen from Fig. 1 and from eqn. (12), the experimental results will depend on the fractional dark rate and the rate of polymerization; therefore, it is necessary to correct the results with each sector to the same $n^{1/2}$ and the same R_p before plotting as above. Further, if a series of experimental points is fitted to one of the curves shown in Fig. 1, the statistical weight for each point will depend in some manner on whether its abscissa corresponds to a flat or steep portion of the theoretical curve at the position of best fit. The points at the extremes of the curves have little effect on the average value of τ_s, but do test whether the theory is obeyed. In view of these considerations it was deemed advisable in adjusting results to a common basis to follow a procedure which would not change appreciably the position of a given point relative to the proper theoretical curve.

The rate ratios were first corrected to the nearest dark rate of Fig. 1. For methyl methacrylate, since the fractional dark rates were small, this meant correcting the given rate ratio to that corresponding to the same experimental value of b but at zero dark reaction ($n^{1/2} = 0$). In the example above the measured ratio for $n^{1/2} = 0.021$ is 0.630 and this is changed to 0.625 at $n^{1/2} = 0.00$, the value of b remaining unchanged at 11.5.

From eqn. (12) τ_s is inversely proportional to R_p, also $b = t_1/\tau_s$, therefore it is seen that if a certain ratio and value of b are measured for a given rate of polymerization, R_{PA}, and time of flash, t_{1A}, then this result is experimentally the same as obtaining the same ratio and same b at R_{PB} and t_{1B} where $R_{PA}/R_{PB} = t_{1B}/t_{1A}$. On the basis of this, all ratios for a given run were corrected to a common R_p adjusting the t_1's inversely. Then on semi-transparent paper the ratios were plotted *vs.* the log t_1 on the same scale as the proper curve of Fig. 1. The plot of ratios *vs.* log t_1 was placed over the theoretical curve with ordinates matching and moved back and forth horizontally to several different positions about the position which appeared to give the best fit. At each position the vertical deviations of the experimental points from the curve were measured and the sum of the squares of the deviations calculated. The sum of squares for each position was plotted *vs.* (t_1 on experimental curve)/(b on theoretical curve) and the position of the minimum taken as τ_s. The agreement between experiment and theory is indicated for a typical run (no. 17L-b) in Fig. 4. The t_1 and b scales are displaced with respect to each other so that the best statistical fit of $t_1/b = \tau_s$ is obtained.

The results of all lifetime runs on methyl methacrylate are summarized in Table III. While the samples are small it is believed that the table as a whole indicates that the average results are reproducible to within 25% or less of the indicated values.

TABLE III

LIFETIMES OF POLYMETHYLMETHACRYLATE RADICALS

Experiment	No. of sectors	Rate % contraction per hr.[a]	τ_s sec.	Av. τ_s at 1.0% contraction per hr.	Standard deviation, %
		5°			
17L-a	12	0.20	3.07		
17L-b	12	.20	2.95	0.603	2
		30°			
11L	4	.50	1.7		
15L-a	2	.50	2.2		
15L-b	6	.50	2.0		
16L-a	4	.50	1.8		
16L-b	4	.50	1.9		
18L-a	4	.50	1.43	0.906	14
18L-a	13	.10	11.5		
18L-b	12	.10	7.2		
19L-b	18	.10	7.25	0.831	24
		50°			
16L-b	4	1.0	1.40	1.40	
		60°			
11L	4	1.0	1.95		
15L-a	4	1.0	2.15		
15L-b	3	1.0	1.80		
16L-a	4	1.0	1.77		
17L-a	4	1.0	1.20		
17L-b	6	1.0	2.20	1.84	22

[a] Results in each experiment corrected to the same rate, the selected rate being very close to the experimental rates.

Results and Discussion

For the case where thermal initiation is rela-

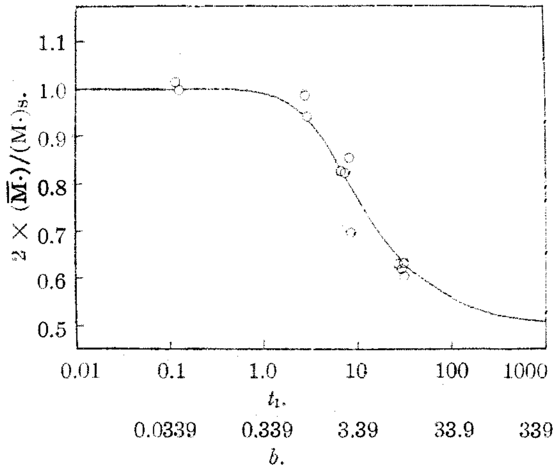

Fig. 4.—Rate of polymerization of methyl methacrylate in intermittent light for different times of flash: Curve, theory for zero dark rate; points, run 17L-b.

tively unimportant as in methyl methacrylate eqn. (2) reduces to

$$R_p = (k_p(M)/k_t^{1/2})\sqrt{k_d f\,(\text{Init.})} \qquad (13)$$

and eqn. (3) to

$$\frac{1}{\bar{P}} = \frac{\sqrt{k_d f\,(\text{Init.})}}{k_p(M)/k_t^{1/2}} + C \qquad (14)^{16a}$$

Schulz[11,12] has previously developed similar equations for this case and shown how by plotting R_p *vs.* $\sqrt{(\text{Init.})}$ and $1/\bar{P}$ *vs.* $\sqrt{(\text{Init.})}$ values of $k_p^2/2k_t$ and C may be obtained. We have combined the data of Schulz and Blaschke[12] with those of Schulz and Harborth[16] to obtain Table IV.

TABLE IV

	50°C.	70°C.
$k_d f \times 10^7$	8.76	119
$(k_p^2/2k_t) \times 10^3$	4.57	11.1
$C \times 10^5$	4.77	8.07

k's in this paper in moles, liters, seconds.

The results in Table IV differ from the average of those given in refs. 12 and 16 for three reasons. First, our calculations are based only on the results at different peroxide concentrations, ignoring the work in which the monomer concentration was varied as the experimental results are acknowledged by the authors to be less accurate at the lower monomer concentrations. Second, our least-squares plot of the data yields values differing slightly from those given for the peroxide studies. Third, although these authors assume termination by combination of radicals, their equation relating the degree of polymerization to kinetic chain length and the transfer constant corresponds to disproportionation. Because of this latter, our values of $k_p^2/2k_t$(or k_B^2/k_C) are very nearly half of those given by Schulz and coworkers. The revised values of Table IV constants recently published by Schulz and Harborth are considered by them to be more accurate. However, we have not used these values alone because (1) if only the studies in which the peroxide concentration is varied are used, $k_p^2/2k_t$ from the combined data is but little changed from that calculated from the same studies in ref. 12, (*e. g.* from ref. 12, we calculate $k_p^2/2k_t$ to be 4.52×10^{-3} at 50° and 11.2×10^{-3} at 70°); (2) a wider range of peroxide concentrations is used in ref. 12 as compared with 16.

If $(R_p\tau_s)/(M)$ is calculated from the data of Table III, the monomer densities of Table I and polymer solution densities of Schulz and Harborth[15,17a] for each experimental temperature, then Table V is obtained. The log of $k_p/2k_t$ is plotted *vs.* $1/T$ in Fig. 5.

TABLE V

$(k_p/2k_t) \times 10^6$	°C.
7.78	5
10.94	30
16.06	50
20.60	60

The upper line was obtained by weighing each experimental point according to the number of

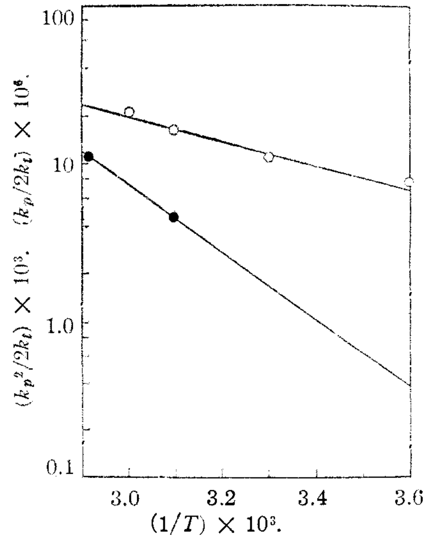

Fig. 5.—Rate constant ratios for methyl methacrylate polymerization: ●, $k_p^2/2k_t$ from data of Schulz and Blaschke[12] and Schulz and Harborth[16]; ○, $k_p/2k_t$, this paper.

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[16] G. V. Schulz and G. Harborth, *Die Makromolekulare Chemie*, **1**, 106 (1947).

[16a] The work of Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946), shows that with benzoyl peroxide induced polymerization of styrene, transfer with the initiator occurs, so that eqn. (14) should include a term for this effect. However, the data of Schulz, *et al.*,[12,16] show the plot of $1/\bar{P}$ *vs.* $\sqrt{(\text{Init.})}$ to be a good straight line with no hint of the upward curvature to be expected if transfer with the peroxide were important. F. R. Mayo has pointed out to us that polar effects would favor the transfer reaction of polystyrene radical with benzoyl peroxide as compared with polymethylmethacrylate radical plus the peroxide.

[17a] Use of the solid polymer densities of Table I would lower the calculated values of k_p about 4.8% and change E_p by 200 calories

runs made in obtaining that point (see Table III), and then calculating the least-squares line. The runs at the low rates of polymerization at 30° were not included in these calculations and would not affect the result much anyway. Also plotted in Fig. 5 is the line for $k_p^2/2k_t$ as obtained from Table IV. From Fig. 5 and a plot of C (Table IV) the values in Table VI have been calculated.

TABLE VI

	30°	60°	T
k_p	143	367	$5.13 \times 10^6 e^{-6310/RT}$
$2k_t$	1.22×10^7	1.87×10^7	$1.36 \times 10^9 e^{-2840/RT}$
k_{tr}	3.75×10^{-3}	22.9×10^{-3}	$2.75 \times 10^6 e^{-12280/RT}$

In our calculations on our lifetime results the value of (M) was varied from temperature to temperature according to the data of Table I while Schulz and Blaschke appear to have used the same concentration of monomer at all temperatures for the pure monomer disregarding the variation due to expansion with temperature. This means that their values of R_p and $k_p^2/2k_t$ need small corrections before they can be considered to correspond to the rate constants in terms of the actual moles per liter for a given temperature. This correction when made would, however, affect the log of the $k_p^2/2k_t$ *vs.* $1/T$ line only slightly.

The rate constants as represented by the last column of Table VI have the following ratios to the values found by Bamford and Dewar at 0°[4] for methyl methacrylate: for k_p 1.05, k_t 1.52, and for k_{tr} 0.59. The excellent agreement is well within the experimental precision of the two methods. Indeed, if we used termination by disproportionation as do Bamford and Dewar our values of k_p and k_t would double. A consideration of the experimental quantities involved in the determination of the rate constants indicates that the decreasing order of precision is k_p, k_t, k_{tr}. The quantities entering the k_p and k_t values are similar except that τ_s enters k_p to the first power and k_t to the second, so that the errors in the lifetime are doubled in effect in the determination of k_t. In k_{tr} the greatest source of uncertainty derives from the molecular weight measurements since C is determined as the intercept of $1/\bar{P}$ *vs.* $\sqrt{\text{(Init.)}}$

The activation energies in Table VI are of about the expected order of magnitude. The frequency factor for the termination reaction, which involves the interaction of two free radicals, approaches normality, whereas the factors for the propagation and transfer reactions, which involve a free radical plus an olefinic compound, are lower. The low frequency factor in the propagation reaction is in accord with the theories of Harman and Eyring.[17]

Effect of Chain Length on the Termination Constant.—The theory used in this work assumes the rate constants are independent of the radical chain length. However, Burnett and Melville[1] found that k_t decreased 20% when the radical chain length was doubled in vinyl acetate. Therefore, it seemed desirable to determine whether such an effect existed in methyl methacrylate. In Table III the results of such a test carried out at 30° are given.

The ratio between the experimental rates in the two series of experiments was 6. If k_t decreases 10% as the chain length is doubled it may be calculated that τ_s measured at the low rate of polymerization should be 40% longer than predicted by eqn. (12) from the value of τ_s at the high rate of polymerization. Actually, in Table III it is seen that the experimental τ_s is shorter, not longer, at the low rate of polymerization when the results are corrected to a common rate by eqn. (12). Applying statistics to these admittedly small samples, it is estimated that there is less than a 1% chance that the rate constant does decrease by as much as 10% when the polymer radical length is doubled. We conclude, therefore, that the rate constant for termination is independent of chain length at least up to about 10% conversion.

Experiments at High Conversion.—Schulz and Blaschke[18] in investigating the benzoyl peroxide-induced polymerization of methyl methacrylate noted that the rate strongly accelerated after about 20% conversion was obtained at 70°. Trommsdorff[19] subsequently found this rate acceleration to be accompanied by a corresponding increase in the degree of polymerization, and suggested this effect is due to a decrease in the termination constant as the system becomes more viscous. Later, Schulz and Harborth[16] confirmed that even under isothermal conditions at 50 and 70° this strong acceleration persisted and that $\bar{P}$ increased approximately in the same ratio as the rate of polymerization, at least up to 40% conversion and where transfer was not too important. In their interpretation also the growing chains find it more difficult to diffuse together in the viscous medium.

Burnett and Melville[1] found this acceleration to occur at about 25% conversion in the photopolymerization of vinyl acetate and also to appear even earlier in vinyl acetate photopolymerized in a poor solvent such as n-hexane.[20] This "gel effect," as they call it, is also attributed by them to a decrease in k_t as the polymer–monomer mixture becomes more viscous. From sector measurements they estimated approximate values of k_t at some point in the gel stage. The results in n-hexane were explained as due to a coiling up of the molecule which prevented the active ends of the growing radicals coming together. However,

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(17) R. A. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).

(18) G. V. Schulz and F. Blaschke, *Z. physik. Chemie*, **B50**, 305 (1941).

(19) Trommsdorff, "Colloquium on High Polymers," Freiburg, 1944.

(20) Burnett and Melville, *Proc. Roy. Soc.* (*London*), **A189**, 494 (1947).

more plausible to us is the explanation Schulz and Harborth used to account for the results of Norrish and Smith[21] on methyl methacrylate polymerizations in poor solvents. They attribute the acceleration to precipitation of the polymer which then absorbs monomer to give an inhomogeneous mixture, portions of which correspond in composition to high conversion.

To test the effect of high conversion on the lifetime of polymethyl methacrylate radicals, two cells were prepared by the usual procedure and irradiated with steady light of the usual intensity at 30° until a conversion of ~37% was attained. At this point, sector measurements were made. Since the rate had increased so much on attaining this conversion, it was necessary to reduce the rate by reducing the light intensity 12.6-fold in order to make accurate measurements of the lifetime. Table VII summarizes the results.

TABLE VII

Cell	Init. rate contraction, %/hr.	Conversion at which rate increased, %	(Rate at 37% conv.)/(Init. rate), av.	Lifetime measurements		
				τ_s sec.	Rate contraction %/hr.	Conversion
1	0.496	16.0		111	0.755	33.9
			6.43	105	.946	36.3
2	.395	12.9		100	.746	36.5
Av.	.451	14.5	6.43	105	.816	35.6[a]

[a] Because irradiation and reaction occur in fixed volume, conversion of 35.6% of the original monomer in the irradiation zone yields a solution corresponding to 33.2% conversion as monomer enters from capillary.

In the work of Schulz and Harborth the increase in molecular weight fully accounts for the accelerated rate and the rate of initiation may be considered constant up to a considerable conversion. The theory of the "cage effect" indicates, however, that R_i may depend upon (M) and the following averages from three experiments enable us to make the assumption as to this dependence.

TABLE VIII

PHOTOPOLYMERIZATION METHYL METHACRYLATE AT 3660 Å. AND 30° BIACETYL SENSITIZER[a]

R_i	$\bar{P}$	Quantum yield R_p/I_a	C^b		qf
2.36×10^{-9} m./l./sec.	1963	43.1	2.6×10^{-5}	1.03×10^3	0.021

[a] These experiments yield $k_p/\sqrt{2k_t}$ 30% higher than Fig. 5. [b] From Table IV data. $\bar{\nu}$ = number av. kinetic chain length.

If q, the quantum yield for dissociation of biacetyl, is near 1.0 (experimentally we have found the quantum yield of biacetyl disappearance in ethyl alcohol was approximately 0.7), then f is seen to be low and is therefore $\simeq (k_a/k_r)(\mathrm{M})$. Thus, R_i may be assumed proportional to (M). The result of combining the lifetime data with either the assumption that R_i is constant or is proportional to (M) is given in Table IX.

TABLE IX

	(k_p initial)/(k_p at 33% conversion)	(k_t initial)/(k_t at 33% conversion)
R_i = constant	0.62	216
$R_i \alpha$ (M)	.89	151

We may conclude that at 33% conversion the propagation constant is unchanged while the termination constant has decreased over 100-fold. Thus, at low conversions we have found the termination constant to be independent of radical chain length while at high conversions the presence of a considerable amount of polymer has decreased the termination constant considerably. It is probable that in the presence of appreciable polymer the termination constant is no longer independent of chain length.

Acknowledgment.—The authors wish to express their appreciation to Dr. H. M. Smallwood for his advice and encouragement during the course of this work.

Summary

The average lifetime of growing polymethyl methacrylate radicals in the photosensitized polymerization of the liquid monomer has been measured as a function of temperature. Combining the lifetime data with studies by Schulz on the rate of polymerization and polymer molecular weight *vs.* free radical initiator concentration gives the rate constants for propagation, termination, and transfer with the monomer. In the initial stages the termination rate constant is independent of chain length. The accelerated polymerization rate occurring in the later stages is due to a decrease in the termination constant.

The theory of the rotating sector has been extended to include those cases having appreciable "dark" rates of polymerization.

PASSAIC, NEW JERSEY RECEIVED JUNE 7, 1948

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[21] R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).