Acknowledgment.—Drs. W. V. Smith, R. H. Ewart and Ellen B. Bevilacqua of this Laboratory have materially assisted the authors through discussions, suggestions and assistance in calculations.

SCHENECTADY, N. Y. RECEIVED JULY 10, 1950

[CONTRIBUTION NO. 108 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Rate Constants in Free Radical Polymerization. III. Styrene[1]

BY MAX S. MATHESON,[2] E. E. AUER, ELLEN B. BEVILACQUA[3] AND E. J. HART[2]

By use of the rotating sector technique, the average lifetimes of growing polystyrene radicals in the photosensitized polymerization of the liquid monomer have been determined at 10, 30 and 50°. Rates of initiation have also been determined by three methods which agree closely: (1) from variation of polymer molecular weight with rate of polymerization, (2) from the rate of decomposition of the initiator, 2-azobisisobutyronitrile, and (3) from the rate of consumption of the inhibitor, 2,2-diphenyl-1-picrylhydrazyl. Comparison of the three methods gives strong evidence that termination occurs mostly by coupling of radicals. From the above experiments, the propagation rate constant, k_p, is found to be $2.16 \times 10^7 e^{-7760/RT}$, and the termination rate constant, $2k_t$, to be $2.59 \times 10^9 e^{-2370/RT}$. The propagation constant is in fair agreement with literature values, but the termination constant is 20-fold that reported by Bamford and Dewar. Reasons are given why our result is to be preferred. At 60° the propagation constant for styrene is one-half that for methyl methacrylate and one-twentieth that for vinyl acetate, while the termination constant for styrene is four times that for methyl methacrylate and one-half that for vinyl acetate. In the initial stages of polymerization the rate constants are found to be independent of radical length. At 40% conversion the termination constant decreases somewhat, but the decrease is less than that found in methyl methacrylate.

Introduction

In the first two papers of this series the application of the rotating sector technique to the measurement of the polymerization rate constants of methyl methacrylate[4] and vinyl acetate[5] was described. In this paper, application of this method to styrene polymerization is reported and discussed. The rate constants obtained are compared with those of Bamford and Dewar,[6] who investigated this monomer with their viscosity method, with those of Melville and Valentine[7] obtained also by the rotating sector method, and with the propagation rate constant found by Smith[8] for the emulsion polymerization of styrene.

Experimental

Purification of Materials.—Dow styrene was distilled under nitrogen through a 50-plate column to give a product, $n^{20}D$ 1.5465, b.p. 44.5° at 18 mm. The product was then recrystallized five times under dry nitrogen with an overall yield of 50%. The recrystallized material was stored in evacuated glass tubes in the dark at −25°. Since biacetyl gave such a low photosensitized rate of polymerization, 2-azobispropane was used as a sensitizer in the styrene experiments. The resulting rate was about twice the rate with biacetyl for equal absorbed intensities at 3660 Å. The 2-azobispropane was synthesized by the method of Lochte, Noyes and Bailey.[9] From the fractionated material a middle cut was retained, b.p. 89.5–90.5 (762 mm.), $n^{20}D$ 1.3903; (lit.,[9] b.p. 88.5° (750 mm.), $n^{23}D$ 1.3890). The α-azobisisobutyronitrile, obtained from the Naugatuck Chemical Division of this company, was recrystallized three times from redistilled C.P. toluene. The ultraviolet absorption curves for 2-azobispropane and α-azo-bis-isobutyronitrile as measured by Mr. M. D. Allen of this Laboratory are given in Fig. 1. A sample of 2,2-diphenyl-1-picrylhydrazyl generously sent by Professor P. D. Bartlett was used without further purification.

Apparatus and Procedure.—The experimental apparatus and procedure were essentially those described in refs. (4) and (5). Irradiations were all at 3660 Å. as in ref. (4). The cells were filled as for methyl methacrylate and vinyl acetate, 2-azobispropane being distilled (and α-azo-bis-isobutyronitrile being weighed) into the reaction cells. The main experimental differences were due to the fact that the polymerization of styrene by light is much slower than that of methyl methacrylate or vinyl acetate, while the thermal polymerization (in the dark) is much faster than with the other monomers. Because of the low rates of photopolymerization, the cells used at 10° and at 30° in sector experiments were surmounted with 1 mm. capillaries instead of 2 mm., except for those reactions photosensitized by α-azo-bis-isobutyronitrile. For accurate results rates had to be measured over a longer period. Further, because of the high thermal or dark rates of polymerization, accurate measurements on the dark rate were necessary. Because the dark rate increased more rapidly with temperature than did the light rate, experiments could not be made at temperatures much above 50° with the available light intensities using 2-azobispropane as a sensitizer. In the experiments at 10° some difficulty was experienced with erratic measurements of rates. This was due to the low rate of polymerization and to the fact that the water in the Dewar surrounding the top of the cell capillary was warmer than the bath and was not stirred by convection. A few degrees change in room temperature was found to affect the temperature of the capillary and the apparent rates. This difficulty was corrected in the vinyl acetate work by providing continuous circulation of water through the Dewar. Except as otherwise noted, no experiment was carried beyond 5–10% conversion.

Densities.—Since the rates were followed dilatometrically, the densities of monomer and polymer must be known as a function of temperature. Further, since monomer and polymer volumes may not be additive in solution,[10] the apparent density of polystyrene in styrene must be determined in the proper concentration range. The polystyrene sample for density experiments was prepared as follows: 200 cc. of styrene plus 0.2 cc. of biacetyl was irradiated *in vacuo* to form a hard polymer. This polymer was cut in strips of 2 mm. square cross section and then heated 20 hours at 120° under continuous evacuation with an oil diffusion pump. Spectroscopic analysis showed less than

---

[1] In this paper half of the experiments and all of the preparation for publication were carried out with the assistance of the Office of Naval Research under Contract N8onr-544.

[2] Argonne National Laboratory, Chicago, Illinois.

[3] 193 Airmount Avenue, Ramsey, New Jersey.

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

[5] Matheson, *et al.*, *ibid.*, **71**, 2610 (1949) (G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945) and P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945) have previously reported application of this method to vinyl acetate).

[6] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **192A**, 309 (1948); *Nature*, **157**, 845 (1946).

[7] H. W. Melville and L. Valentine, *Trans. Faraday Soc.*, **46**, 210 (1950).

[8] W. V. Smith, THIS JOURNAL, **70**, 3695 (1948).

[9] H. L. Lochte, W. A. Noyes and J. R. Bailey, *ibid*, **44**, 2556 (1922).

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

TABLE I

DENSITY OF POLYSTYRENE IN STYRENE

Cell	1	2	3
Wt. % polystyrene	None	5.46	10.86
20° Density styrene	0.9058(0.906)[a]	....	....
20° Density polystyrene	....	1.073(±0.008)	1.080(±0.004)
50° Density styrene	0.8789(0.878)[a]	....	....
50° Density polystyrene	....	1.052(±0.008)	1.062(±0.004)

[a] *Cf.* [a] in Table II.

0.5% monomer left in the polymer. Using this polymer and purified styrene the solutions of Table I were made up by weight in 50-cc. glass-stoppered calibrated volumetric flasks. The necks of the flasks were made from sections of a 50-cc. buret. The liquid levels were determined at 20 and 50° for each flask for 3 successive days, at the end of which period the levels showed no change and the solutions appeared homogeneous. The flasks were kept in constant temperature baths in the dark except when readings were made in dim red light. Each cell contained 0.05 g. of benzoquinone to inhibit polymerization, calculated as 0.038 cc. at all temperatures.

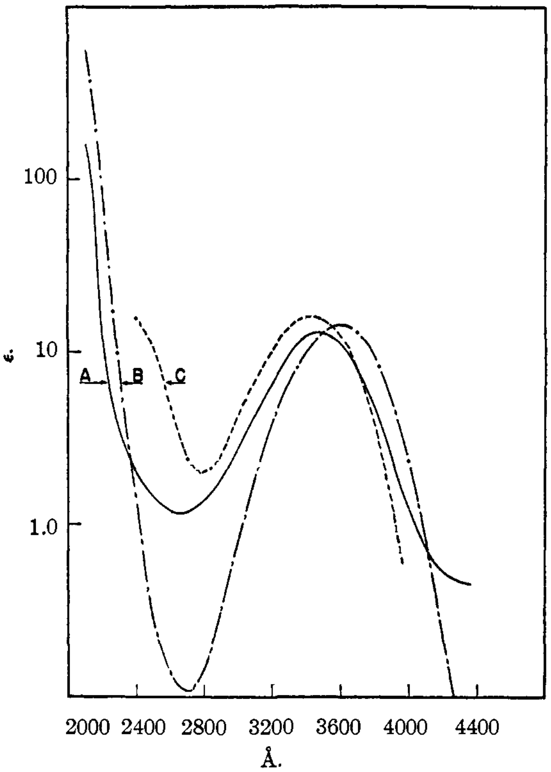

Fig. 1.—Ultraviolet absorption spectra of sensitizers: A, α-azo-bis-isobutyronitrile (in absolute ethanol); B, 2-azobispropane (in cyclohexane); C, azomethane in water [Kortüm and Finckh, *Z. physik. Chem.*, **B48**, 32 (1940)].

$\log I_0/I = \epsilon cl$ I_0 = incident intensity
I = transmitted intensity
ϵ = molar extinction coefficient
c = concn. moles/l.
l = cm. depth

Overberger, O'Shaughnessy and Shalit [THIS JOURNAL, 71, 2661 (1949)] give a curve for α-azo-bis-isobutyronitrile corresponding to extinction coefficients 93% of those plotted in curve A.

Table II shows the densities used in this work, rates being calculated from the second and fourth columns.

TABLE II

DENSITIES OF STYRENE MONOMER AND POLYMER

T, °C.	Monomer[a]	Solid polymer[b]	Polymer in monomer Average[c]	Literature
10	0.915	1.055	1.0830	
20	.906		1.0780	
25	.901		1.0750	1.073[d]
30	.897	1.052	1.0723	
38.4	.889		1.0680	1.075[e]
50	.878	1.049	1.0617	
56.4			1.0580	1.059[e]
60	.869	1.0475	1.0563	1.060[f]
70	.860	1.046	1.0510	1.050[e]

[a] Patnode and Scheiber, THIS JOURNAL, 61, 3449 (1939), in agreement with data of Goldfinger and Lauterbach.[e] [b] Our data. [c] Averaged from data of Table I and our point marked *f* at 60°, next column. [d] Estimated from data Giguère, *J. Polymer Sci.*, 2, 296 (1947). [e] Estimated from data Goldfinger and Lauterbach, *ibid.*, 3, 145 (1948). [f] Calculated from Table VI, ref. (11).

Experimental Results and Calculations.—The data obtained were treated as described in the preceding papers in order to adjust all measurements in a given run to the same rate of polymerization, R_p, and to the same ratio of dark rate to steady light rate, $n^{1/2}$. From the adjusted experimental data a plot of 2 × (rate in sectored light/rate in steady light) *vs.* the log of the time of flash, log t_l, was made and fitted to the proper theoretical curve as previously described. A plot for a styrene run is shown in Fig. 2. It will be noted that in this run the dark rate was 10% of the continuous light rate and the theoretical curve was drawn accordingly.

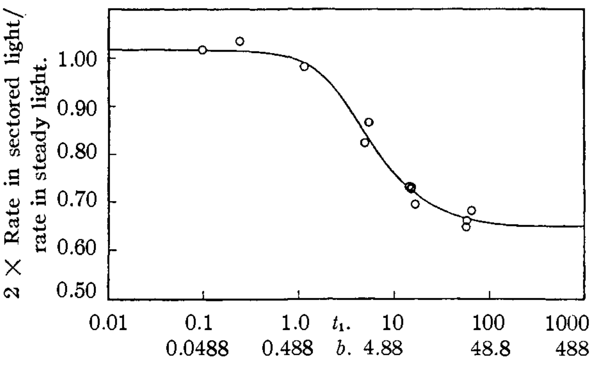

Fig. 2.—Rates of polymerization of styrene in intermittent light for different times of flash: curve, theory for dark rate 10% of steady light rate; points, Run 20 at 50°. $\tau_s = t_l/b$ = lifetime of polystyrene radicals in steady light; steady light rate = 0.05% contraction per hour.

The results of the experiments on lifetimes of polystyrene radicals are summarized in Table III. In averaging at each temperature, the

TABLE III

LIFETIMES OF POLYSTYRENE RADICALS

Expt.	No. of sector rate ratios	Approx. $n^{1/2}$	σ of ratios[a]	Contraction per hr., %	τ_s, sec.	Av. τ_s at 0.05% cont./hr.
10°						
21b	9	0.05	0.042	0.01	3.0	0.6
30°						
12	8	0.05	0.042	0.0275	3.85	2.12
20a	12	.05	.034	.0275	1.84	1.01
20b	12	.05	.037	.0275	2.10	1.16
						1.28
30° (fast rates)[b]						
21a1	4	0.15	0.054	0.15	0.40	1.20
21a2	4	.20	.035	.15	.65	1.95
						1.53
						1.33[c]
50°						
12	8	0.10	0.022	0.05	2.85	2.85
20	12	.10	.018	.05	2.05	2.05
						2.36

[a] This is standard deviation of sector rate ratios (ordinates in Fig. 2), from the theoretical curve at τ_s for the best least squares fit. [b] α-Azo-bis-isobutyronitrile sensitizer used in these experiments, 2-azobispropane in the others. [c] Average for all 30° runs.

logarithms of the τ_s values (τ_s = polystyrene radical lifetime for steady light rate or, the life of the kinetic chain from initiation by sensitizer fragments to termination by interaction with another growing chain), were weighted according to the number of sector rate ratios measured in each run and then averaged. As the experimental temperature was decreased the rate obtainable from 2-azobispropane sensitization decreased, increasing the errors in the measurement of the rates, as reflected in the σ values in column 4 of Table III.

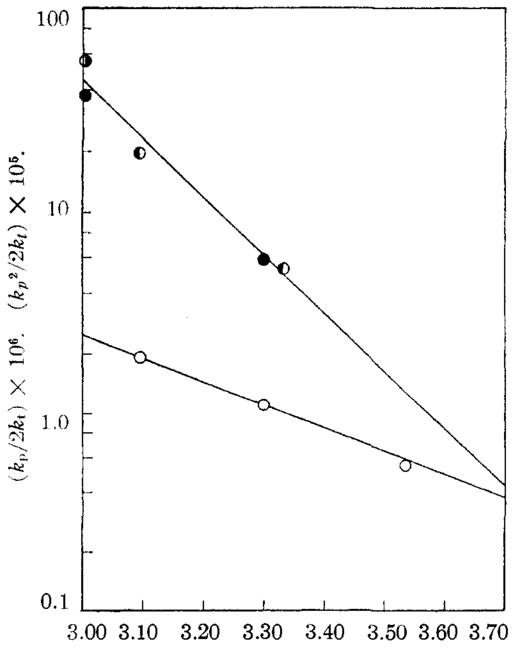

Fig. 3.—Rate constant ratios in styrene polymerization: ○, $(k_p/2k_t) \times 10^6$; ●, $(k_p^2/2k_t) \times 10^5$ from inhibitor; ◑, $(k_p^2/2k_t) \times 10^5$ from polymer mol. wt. ref. (11); ◐, $(k_p^2/2k_t) \times 10^5$ from polymer mol. wt. ref. (16).

Experiments on Rates of Initiation.—The cells used in these experiments were of approximately 20 cc. volume, being made from a length of 15 mm. Pyrex tubing surmounted by a 2 mm. precision bore capillary. The cells were filled by a device like that in Fig. 3 of ref. (4). Initiator and inhibitor were weighed directly into the bulbs of the cell-filling devices except in the case of the 30° cells. In the latter case, the inhibitor was added as 1 cc. of a benzene solution, and 1 cc. of pure benzene was also added to the 60° inhibitor cells and to a pair of control cells without inhibitor. The exact amounts of styrene necessary to fill each cell were measured and distilled into the filling devices *in vacuo*. Reactions were carried out in baths (±0.01°) under dim red light.

Results and Discussion

The many possible steps in the mechanism of styrene polymerization have been previously[11] considered. This paper reports measurements of the rate constants for the propagation and termination steps, and discusses conclusions which may be drawn from these measurements. The rate constants for propagation, k_p, and for termination, $2k_t$, are defined by the reactions

$$M\cdot + M \xrightarrow{k_p} M\cdot \qquad \text{rate} = k_p[M\cdot][M]$$

$$M\cdot + M\cdot \xrightarrow{k_t} \text{polymer} \qquad \text{rate} = 2k_t[M\cdot]^2 = -d[M\cdot]/dt$$

where M = monomer, and $M\cdot$ = the growing polymer radical. As already noted[5] k_p and $2k_t$ may be determined individually by means of two experiments: (1) a rotating sector experiment to measure the kinetic chain life at a given rate of polymerization, and (2) an experiment to measure the rate of initiation at a known polymerization rate.

In the sections following, the sector experiments are discussed first; rates of initiation by three different methods are then shown to agree closely; the k_p and $2k_t$ rate constants are calculated and shown to be more accurate than literature values; the rate constant for transfer with the monomer is calculated; the termination reaction is shown not to be affected by radical chain length and, finally, the termination reaction is found to be somewhat slower at high conversion.

Sector Experiments.—The ratio $k_p/2k_t$ is calculated from the kinetic chain life,[4] using Tables II and III, and is given in Table IV and plotted in Fig. 3. The 30° runs with fast polymerization were not included in deriving Table IV but, as seen in Table III, they change the average result only about 4%. Since the lifetime experiment at 10° is not considered as accurate as the experiments at 30 and 50°, the $k_p/2k_t$ line was drawn through the 30 and 50° points only. This procedure was simple and has little effect on the

TABLE IV

RATIO OF PROPAGATION AND TERMINATION RATE CONSTANTS IN STYRENE

$(k_p/2k_t) \times 10^6$	T., °C.
0.538	10
1.089	30
1.895	50

---

(11) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, 72, 1691 (1950).

results, since the 10° point would be weighted for fewer sector rate ratios and is quite close to the chosen line.

Rate of Initiation Experiments.—Three methods are available for the determination of rates of initiation in polymerization, and all have been found applicable to styrene. In one method the rate of initiation is taken as twice the rate of decomposition of initiator and the results obtained using two initiator concentrations at two temperatures are summarized in Table V (a). (The "uncatalyzed" thermal rate of initiation is negligible in these experiments.) The assumption that the radical derived from α-azo-bis-isobutyronitrile, $((CH_3)_2CCN)$, is essentially 100% efficient in initiation is justified by its equivalent efficiency in vinyl acetate,[5] and by its resemblance to the polymethacrylonitrile radical which is 70–80 times as reactive toward styrene as toward vinyl acetate.[12]

TABLE V

RATES OF INITIATION[a]

(a) From initiator decomposition[b]

	30°		60°	
Cell	5	9	37	54
$R_p \times 10^2$	0.627	1.218	4.06	7.96
Initiator × 10^2	4.568	18.27	0.3042	1.2168
$R_i \times 10^8$ from initiator	0.813	3.252	6.14	24.59
$(k_p^2/2k_t) \times 10^5$	6.53	6.06	38.6	37.1

(b) From inhibitor consumption[c]

	30°		
Cell	59	37	40
Styrene,[d] %	92.1	92.1	92.2
$R_p \times 10^5$	1.0875	Retard.	Retard.
Hydrazyl × 10^4	.....	1.991	4.904
Induction period, min.	.....	93	272
$R_i \times 10^8$ from hydrazyl	.....	3.567	3.005
$(k_p^2/2k_t) \times 10^5$	.....	5.28	6.27

	60°				
Cell	40[e]	61[e]	7	3	6
Styrene,[d] %	94.8	95.0	94.4	94.6	94.5
$R_p \times 10^5$	7.47	Retard.	7.27	Retard.	Retard.
Hydrazyl × 10^4	...	17.72	...	14.80	36.88
Induction period, min.	...	129	...	109	245
$R_i \times 10^8$ from hydrazyl	...	22.90	...	22.63	25.09
$(k_p^2/2k_t) \times 10^5$	...	38.8	...	37.8	34.1

[a] All rates in moles/liter/second and all concentrations in moles/liter. [b] 2-Azo-bis-isobutyronitrile used as initiator. Rate constant for unimolecular decomposition = k_d = 8.9 × 10^{-8} at 30° and 1.01 × 10^{-5} sec.$^{-1}$ at 60° measured in xylene (F. M. Lewis and M. S. Matheson, THIS JOURNAL, 71, 747 (1949)). [c] 2,2-Diphenyl-1-picrylhydrazyl used as inhibitor. In experiments under (b) the concentration of 2-azo-bis-isobutyronitrile was 0.1828 at 30° and 1.2168 × 10^{-2} at 60° in m./l. [d] Remainder is largely benzene although initiator amounts to about 2% at 30°. [e] Preliminary experiment made several weeks before other inhibitor experiments.

The second method involves the use of inhibitors to count chains. Until recently, no inhibitor was suitable for use in measuring initiation in styrene,[13] but Bartlett and Kwart[14] recently found 2,2-diphenyl-1-picrylhydrazyl to be an excellent inhibitor to count chains in vinyl acetate, one hydrazyl radical stopping one kinetic chain. Our results in Table V (b) and Fig. 4 show that the hydrazyl functions equally well for this purpose in styrene. Figure 4 shows that during an initial period the reaction is almost completely suppressed by the hydrazyl, and that following this period, the polymerization is much more rapid but still retarded. The breaks in the dilatometric curves in Fig. 4 are taken as the ends of the induction periods. The apparent induction periods in the control cells are due to delay in taking initial readings while cells attain temperature equilibrium. The end of the induction period in any given cell corresponded closely to the disappearance of the deep purple color of the inhibitor.[15] This behavior resembles very closely that in vinyl acetate, the retardation being ascribed by Bartlett and Kwart[14] to the nitro groups. In Fig. 4, as expected, the retarded rate is lower for higher inhibitor concentrations, showing that at still higher inhibitor concentrations the retarded rate will be so low that a break in the curve will not be detectable.

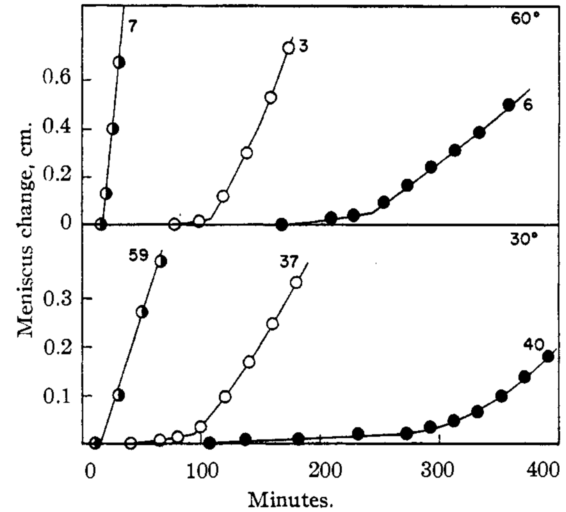

Fig. 4.—The inhibition of styrene polymerization by 2,2-diphenyl-1-picrylhydrazyl. Cell numbers as in Table V (b).

The question arises as to whether in the presence of the very reactive styrene molecule the hydrazyl radical, like the triphenylmethyl radical,[13] can initiate as well as stop chains. Assuming the usual reactions of polymerization, that one inhibitor radical stops one growing chain, and that the inhibitor radical may start a chain, by a reaction which is first order in both inhibitor and styrene, one can calculate the amount of the initiation by inhibitor from the data of Table V (b). At 60° the inhibitor ratio between cells 6 and 3 is 2.49 while the induction period ratio is 2.25. If the hydrazyl initiates no chains the above ratios should be identical. On the basis of our assumptions the actual ratios correspond to a consumption of about 8% of the inhibitor in starting chains and in *stopping chains started by the inhibitor* in cell 3. However, since the inhibitor is appreciably con-

---

[12] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[13] F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1284 (1948), for example have shown benzoquinone or triphenylmethyl are unsatisfactory.

[14] P. D. Bartlett and H. Kwart, *ibid.*, **72**, 1051 (1950).

[15] The absorption of this compound in benzene has been measured between 3500 and 8000 Å. A strong peak (molecular extinction coeff. = 10,600) at 5200 Å. should enable one to follow its disappearance by photometric means. For absorption data, order Document 2945 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

sumed faster at the *lower* concentration at 30°, and since the determination of the induction period in cell 6 at 60° is subject to some uncertainty, it can only be concluded that any effect of inhibitor in starting chains is small.

Considering now the $k_p^2/2k_t$ values calculated in Table V from the experiments we have been discussing, the consistency and close agreement between results calculated from initiator decomposition and from inhibitor consumption suggest that our assumptions and techniques are valid. As in the case of vinyl acetate,[5] the inhibitor values for $k_p^2/2k_t$ are taken as more precise and are plotted in Fig. 3.

In the third method, rates of initiation are calculated from molecular weights and rates of polymerization as illustrated in detail in the paper of Mayo, Gregg and Matheson.[11] Taking the data in Table III of that paper corresponding to C_m (transfer constant with monomer) = 6×10^{-5}, $\bar{M}_n = 167{,}000\ [\eta]^{1.37}$ ($\bar{M}_n$ = number average polymer molecular weight, $[\eta]$ = intrinsic viscosity based on g. polymer/100 cc. solvent), and all termination by combination of radicals, $k_p^2/2k_t$ is calculated to be 55.2×10^{-5} l./m./sec. at 60°. The procedure of these authors has also been applied to Tables 7 and 8 of Schulz and Husemann[16] which report data on the rates and degrees of polymerization for benzoyl peroxide initiation in pure styrene and in 3.85 molar styrene in toluene at 50 and 27°. At 50° $k_p^2/2k_t$ was estimated as 19.53×10^{-5} and at 27° as 5.23×10^{-5} l./m./sec. These are averaged from the results at the two styrene concentrations and are plotted in Fig. 3. In making these calculations, the transfer constant with the monomer was assumed as 4×10^{-5} at 50° and 2×10^{-5} at 27° to accord with the above value of 6×10^{-5} at 60° and assuming a temperature dependence similar to that found in methyl methacrylate.[4] Further, the transfer constant with toluene is 1×10^{-5} at 50° and 0.3×10^{-5} at 27°.[17] If transfer with monomer and solvent is ignored, $k_p^2/2k_t$ is little changed, being 18.53×10^{-5} at 50° and 4.87×10^{-5} at 27°.

The upper line shown in Fig. 3 was obtained by weighting each of the $k_p^2/2k_t$ points equally and determining a least squares line. All points lie fairly close to this line. Further, it may be noted that if the points based on molecular weights were to be recalculated assuming termination by disproportionation, their values would be at least twice those calculated by the other methods. The results from disproportionation would correspond to 50% initiator efficiency (possible but not probable), and to *two* hydrazyl radicals stopping *one* radical chain (see also ref. 11).

Rate Constants of Polymerization.—From the two lines in Fig. 3, Table VI is derived. Comparing first our propagation rate constant with that which Smith obtains by his elegant method for emulsion polymerization, it is seen that his value at 50° is about three times ours. This difference may be real and due to activity differences. Expressing the styrene propagation reaction, $M\cdot + M \rightarrow M\cdot$, in terms of the Brönsted equation, as has been done previously by Walling, *et al.*,[18] one obtains for the rate constant of propagation, $k_p{}^\circ f_M f_{M\cdot}/f_{MM\cdot}$, where f_M, $f_{M\cdot}$ and $f_{MM\cdot}$ are activity coefficients for the monomer, polymer radical and activated complex, respectively, and where $k_p{}^\circ$ is the propagation rate constant in the standard state where the f's are unity. In his emulsion particles at 50°, Smith found a limited solubility for styrene, indicating a monomer activity in the saturated polymer particles equal to that of bulk styrene. Since the concentrations in the emulsion particles corresponded to 39% conversion, f_M in Smith's work is about 1.5 times greater than in our own work.[19] If $f_{M\cdot}/f_{MM\cdot}$ is also greater than one the difference between k_p in the two cases is real. The activation energy of 11.7 reported by Smith is the activation energy for the over-all rate of polymerization per particle or per polymer radical. If the solubility of monomer in the polymer particle increases with temperature then the activation energy for the propagation reaction in the emulsion particle will be correspondingly less than 11.7.

TABLE VI

RATE CONSTANTS OF POLYMERIZATION IN STYRENE

	0°	25°	30°	50°	60°	$E_{act.}$
k_p	13.2	44	55	123	176	7.8
				(390)[a]		11.7[a]
	(6.91)[b]	(18.7)[b]			(59.5)[b]	(6.5)[b]
			(26)[c]			
$2k_t \times 10^{-7}$	3.32	4.75	5.05		7.2	2.4
	(0.183)[b]	(0.279)[b]			(0.46)[b]	(2.8)[b]
			(0.525)[c]			

$$k_p = 2.16 \times 10^7\, e^{-7760/RT}$$
$$2k_t = 2.59 \times 10^9\, e^{-2370/RT}$$

[a] W. V. Smith, ref. (8). [b] C. H. Bamford and M. J. S. Dewar, ref. (6). 60° values extrapolated. [c] H. W. Melville and L. Valentine, ref. (7), corresponding to termination by combination.

Considering now the results of Bamford and Dewar, Table VI shows that their rate constants for propagation as measured at 0 and 25° are about one-half our values. Compared with the 20-fold discrepancy in termination constants, the agreement in the k_p values is adequate. From their constants at 0 and 25°, one can calculate the ratios $k_p^2/2k_t$ and $k_p/2k_t$ for the two temperatures. Their $k_p^2/2k_t$ points are 3–5 times our values (Fig. 3) which are based on three independent methods, only one of which assumes termination by coupling. Further, their $k_p/2k_t$ ratios are 7–9 times as large as ours (Fig. 3) which are based on lifetime measurements and which are independent of whether termination is by coupling or disproportionation. Thus, their results, based on a single type of experiment and on the assumption that termination occurs by disproportionation, disagree with results from two different types of experiments. In the case of the $k_p/2k_t$ ratio, we believe our results to be accurate and reproducible well within a factor of 2. The use by Bamford and Dewar of an erroneous viscosity–molecular weight relation has already

---

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

(17) R. A. Gregg and F. R. Mayo, Discussions of the Faraday Soc., No. 2 328 (1947).

(18) C. Walling, E. R. Briggs and F. R. Mayo, THIS JOURNAL, **68**, 1145 (1946).

(19) Even in oil phase at 127° the monomer activity is nearly 1.0 at this conversion.[18]

been discussed.[11] In assuming termination by disproportionation, Bamford and Dewar[20] offer as the only supporting evidence the result that for high rates of photopolymerization the polymer molecular weight decreases as the rate increases. Two explanations are possible: (1) Initiation is not by biradicals as assumed but by monoradicals from impurities or from the monomer[21] itself while coupling occurs in termination. (2) Initiation is by biradicals but a small fraction of the chains are terminated by disproportionation. Equation (14) in ref. (11) shows that if Bz_2O_2 is set equal to zero and k_i multiplied by the (1 + AI) term of Bamford and Dewar to include photo-initiation, then the polymer molecular weight will depend on light intensity, even if termination is largely by coupling. It is possible that, since Bamford and Dewar assume disproportionation in their equations, their $2k_t$ is a measure of such termination. In such a case, since our termination constant represents the total of all bimolecular termination, and since their constant is about 5% as large as ours, disproportionation may occur in as much as 5% of the termination reactions.

Returning to an examination of Table VI, the frequency factor for the propagation step is low, while that for the termination step is more nearly normal, as found in the polymerizations of methyl methacrylate[4] and vinyl acetate.[5]

Comparison with Results of Melville and Valentine.—After this manuscript was completed a paper by Melville and Valentine[7] appeared reporting rate constant measurements on styrene at 30°. Their value of k_p (corrected to combination of radicals) is one-half ours (Table VI), while their $2k_t$ value is one-tenth ours.

Although their results are in fair agreement with those of Bamford and Dewar we believe our results to be more accurate and the following discussion shows some possible errors in their work. The discrepancy between the two sets of experiments, however, is best illustrated by comparison of the $k_p^2/2k_t$ and $k_p/2k_t$ ratios, since Melville and Valentine measure the first by determining the rate of initiation from over-all rates and molecular weights, and the second by use of the rotating sector method of measuring the kinetic chain life.

Melville and Valentine's $k_p^2/2k_t$ (corrected to combination) is twice our ratio. Melville and Valentine measure osmotic molecular weights in the range 48–83,000. In this range, diffusion of low molecular weight polymer through the membrane may give spuriously high molecular weights.[22], In this Laboratory,[11] molecular weights of about 50,000 by osmotic pressure have run 10–15% higher than those by end group analyses. If Melville and Valentine's molecular weights are 10–15% high, their $k_p^2/2k_t$ ratio is equally high. Further, their factor for converting rates of contraction to rates of reaction gives rates 13% higher than from our factor and their ratio would be lowered correspondingly. Corrected for the above sources of difference their $k_p^2/2k_t$ ratio is still 1.75-fold ours.

In determining our own ratio of $k_p^2/2k_t$ we found that ratios calculated from Schulz and Husemann's data on pure styrene and on 3.85 *M* styrene in toluene agreed very closely at 50°. However, at 27° (near the 30° used by Melville and Valentine), the agreement was not as good, the ratio calculated from the data on pure styrene being nearly twice the ratio calculated from the data on the toluene solution, and therefore nearly 50% higher than the average of the two ratios at this temperature. The average ratio is used in Fig. 3. However, because these authors had fewer data for pure styrene at 27° than for their other cases, and because the average of their results agrees so closely with our ratios at 30° by *two other* methods (see Fig. 3), we believe that our $k_p^2/2k_t$ ratio is in error by much less than 50%.

For $k_p/2k_t$ from sector measurements, Melville and Valentine get a ratio 4.5 times ours. This difference can be decreased by 13% by correcting the factor for converting dilatometric rates to monomer consumption rates. Further, Melville and Valentine use benzoyl peroxide as a photosensitizer, and from their data and the data of Schulz and Husemann, the dark reaction in their sector experiments may be as large as 10% of the rate in steady light. Such a dark rate uncorrected for would make their kinetic chain life about 20% too long. Such a dark reaction would not be easily detectable from the fast sector rate ratio, which is 0.711 for 10% dark reaction and 0.707 for zero dark reaction. At very low sector speeds the difference in sector rate ratios is appreciable, 0.55 against 0.50. The numbers given correspond to the use of sectors such that the light period equals the dark period. Using both corrections above the $k_p/2k_t$ ratio of Melville and Valentine is still 3.1 times ours.

A possible error which would make our own $k_p/2k_t$ ratio and kinetic chain life too small is the use of actinic light strongly absorbed in the front of the reaction cell. This is improbable because in no cell did the measured absorption exceed 25% at 3660 Å. Further, a Hanovia AH-8 lamp was used for a light source and the Nonex jacket on this arc reduces the 3130 Å. and shorter wave lengths to a negligible amount. The 5970 Corning filter used transmits 85% 3660 Å. and 5% 3130 Å., while the front faces of the Pyrex cells transmit 87% 3660 Å. and 40% 3130 Å. In addition the 2-azobispropane sensitizer has a molecular extinction coefficient of 14 at 3660 Å. and 2.4 at 3130 Å. Further, Melville and Valentine use wave lengths longer than 2940 Å., *i. e.*, a Pyrex filter in their work.

---

[20] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*) **197A**, 356 (1949).

[21] The initiation process in the photopolymerization of styrene has a very low quantum yield and the small amount of decomposition necessary for monoradical initiation would be difficult to detect, especially in the presence of the reactive styrene double bond. In thermal polymerization monoradical initiation is ruled out by energy requirements, but such is not the case in photopolymerization. Further, D. H. Johnson and A. V. Tobolsky (in a manuscript kindly sent us before publication) conclude from the experimental relation found between degree and rate of polymerization in styrene that termination is by combination of radicals and that monoradicals are involved in photopolymerization.

[22] H. W. Melville (private communication), however, found no diffusion of low molecular weight polymer through membrane according to precipitation tests.

Transfer with Monomer.—We take the transfer constant of polystyrene radicals with styrene at 60° as 6.0×10^{-5} [11] while Bamford and Dewar's value extrapolated to this temperature is estimated to be a factor of 2 greater. Transfer constants are not available at other temperatures, so that an activation energy for transfer with the monomer cannot be calculated. From the above value of k_{tr}/k_p and Table VI k_{tr} is 10.6×10^{-3} or about one-half the rate constant for transfer with the monomer found previously for methyl methacrylate at 60°.[4] Extrapolating the results of Bamford and Dewar to 60° one gets 8×10^{-3} for k_{tr}. This agreement is accidental in view of the discrepancy in k_{tr}/k_p.

Effect of Chain Length on Termination.—Burnett and Melville[23] report a decrease in the termination rate constant as the chain length is increased for vinyl acetate, even in the initial stages of polymerization. To see whether styrene exhibits a similar effect, two 30° runs were made at a high rate of polymerization, using α-azo-bis-isobutyronitrile as sensitizer. The fast rates were sixfold those in the normal experiments, and the molecular weights and average radical lengths were about one-sixth as large (actually 1/5.76 because of transfer with the monomer). As shown in the last column of Table III, when the measured lifetimes are corrected to equal rates, the lifetime is longer for the high experimental rate whereas if k_t decreased with increasing chain length the reverse should be true. Because of the few sector speeds used and the high dark rate (due to the use of α-azo-bis-isobutyronitrile as a photosensitizer) the fast rate runs are less accurate and the corrected lifetimes are the same within experimental error as those measured at the slower rates. It is concluded that in styrene, as in methyl methacrylate, the termination rate constant is independent of chain length at low conversion, at least for chains of 10–10^4 monomer units.[24]

Experiments at High Conversion.—Schulz and Blaschke[25] found the benzoyl peroxide initiated polymerization of methyl methacrylate to be strongly accelerated after about 20% conversion. Noting that this acceleration is accompanied by a corresponding increase in degree of polymerization, Trommsdorff[26] suggested that the termination rate constant decreases as the system becomes more viscous, a suggestion which has since been confirmed for this monomer.[4] Of several monomers examined by Trommsdorff, styrene alone did not show corresponding effects. However, since Smith's work in styrene emulsion polymerization involved monomer concentrations corresponding to about 40% conversion, measurement of polymer radical lifetimes at high conversion seemed desirable. A cell containing styrene and 2-azobispropane was prepared by the usual procedure and irradiated with light of constant intensity to nearly 30% conversion. At this point the previously constant rate of polymerization (or at least the rate of contraction) began to increase slightly. Lifetime measurements were begun at 30% conversion and continued to 50% conversion. During the course of these measurements the steady light rate of polymerization and the lifetime of the polystyrene radicals increased steadily, as shown in Table VII. The effects are not due to temperature, since a thermocouple inserted in a thin-walled capillary in the center of the cell showed negligible temperature increase (<0.1°) even at the highest conversion.

TABLE VII

LIFETIMES OF POLYSTYRENE RADICALS AT HIGH CONVERSION AT 50°.

Conversion, %	Rate % per hr.	τ_s, sec.
0.0	0.298	2.29[a]
32.7	.350	1.80
36.3	.382	9.1
39.5	.393	13.9
43.8	.434	18.8

[a] Estimated from Table II.

The trend in τ_s as shown in the table is believed to be well beyond experimental error. However, the following considerations suggest the actual increase may be less than shown. If the increase in τ_s is due to a decrease in k_t as termination becomes diffusion-controlled at high conversions, then it is reasonable to expect that in the diffusion-controlled reaction k_t will decrease as the radical chain length increases. Such an effect would yield measured lifetimes longer than those corresponding to the steady light rate, and would give a ratio higher than expected from simple theory for (rate in intermittent light)/(rate in steady light). The ratios measured in this experiment for very fast sectors were a few per cent. higher than the theoretical value (0.507 for 10% dark reaction).

Although the quantitative results to be calculated from Table VII depend on whether one assumes $R_i \alpha [M]$ or R_i = constant[27] (R_i = rate of initiation), and whether one assumes the rate of polymerization changes as shown or is constant,[28] the qualitative conclusion is the same: in the transition from 0 to 40% conversion, $k_p/2k_t$ increases about tenfold while k_p remains constant within a factor of about 2. This variation in $k_p/2k_t$ is very much smaller than that found previously for methyl methacrylate, and accounts for the previously reported absence of the Trommsdorff effect in styrene.

Acknowledgment.—Many helpful discussions with Dr. Frank R. Mayo are gratefully acknowledged. We also wish to thank Professor Paul D. Bartlett for the sample of 2,2-diphenyl-1-picrylhydrazyl so kindly sent us.

PASSAIC, NEW JERSEY RECEIVED JULY 10, 1950

---

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

(24) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948).

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

(26) Trommsdorff, Colloquium on High Polymers, Freiburg (1944); See B.I.O.S. Report No. 363, Item 22.

(27) The low initiating efficiency of 2-azobispropane (of the order of 1%) in styrene favors the assumption $R_i \alpha [M]$, although the high activity of the monomer in the presence of polymer presents complications.

(28) Some of the increase may be due to a change in the apparent density of the polymer at high polymer concentrations, although the apparent density of polymethyl methacrylate in methyl methacrylate is substantially constant from 5–40% conversion, ref. (4).