passageway was not large enough to admit the additional group in the case of the naphthyl acetates.[3a]

With such a narrowed entrance the complexes of glycol and amine cannot easily reach the carbonyl carbon atom. Although the free amine molecules might gain access to the cationoid carbon, their number would be reduced to a value lower than in the absence of the glycol and for that reason we should expect a lowering of the rate by the glycol.

Further evidence for the steric factor can be seen from the order of amines in Table I. Piperidine and morpholine, in which hindrance is relieved by the folding back of the carbon chains by ring formation, have the greatest reaction rates of the secondary amines and in the case of morpholine the rates with and without glycol are nearly the same. As we pass down the series not only does the rate steadily diminish as the predicted steric hindrance increases, but we see also a general trend for a larger difference between the rates with and without ethylene glycol as a result of superimposing steric effects of amine and glycol.

Methyl lactate lies between methyl acetate and phenyl acetate in reactivity, to judge from the results obtained with morpholine. The relative activity of this ester in ammonolysis has been discussed in a previous paper.[3a] In every case shown in Table II, methyl lactate, although less reactive than phenyl acetate, shows catalysis by ethylene glycol, attesting to its freedom from steric hindrance.

The secondary amines are very much less reactive than primary amines. The attachment of the second alkyl group increases the screening of the nitrogen atom so greatly that the slight contribution to reactivity caused by augmenting the charge on the nitrogen is completely overshadowed. In general, basicity in this series has little effect on the order of activity unless the steric factors are practically identical for the amines being discussed. Such is the case with piperidine and morpholine and it will be noted that the more basic piperidine reacts much more rapidly.

Dimethylamine is the most reactive of the secondary amines studied. The only exception is its failure to react with phenyl acetate in the presence of ethylene glycol. This must mean that in the hydrogen-bonded complex which the amine forms with ethylene glycol the nitrogen atom must be effectively screened. Piperidine is a relatively basic amine and relatively unhindered. Morpholine is less basic than piperidine and also less reactive. Diethylamine, although slightly more basic than dimethylamine, is far less reactive as a result of increased steric hindrance. The severity of the steric restrictions is reflected in the failure to react with methyl lactate which is relatively unhindered. The order of the next three secondary amines, $(C_2H_5)_2NH > (n\text{-}C_4H_9)_2NH > (n\text{-}C_3H_7)_2NH$, suggests that a "delta effect"[3c] may be operative in the case of di-*n*-butylamine. Unfortunately, the precision of the measurements is insufficient to establish the existence of the effect in this case. The fact that the basicity constants are in the order di-*n*-butyl > diethyl > di-*n*-propyl, suggests that the delta effect may be more marked where the hydronium ion is the reference acid. The reactivity of diethanolamine is assumed to be due to hydrogen bonding between the hydroxyl groups, which would be expected to bend the carbon chains away from the nitrogen atom and thus reduce steric hindrance.

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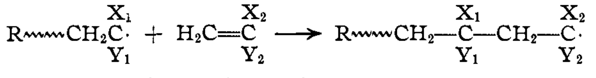
Rate Constants in Free Radical Polymerizations. IV. Methyl Acrylate[1]

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

The propagation and termination rate constants for methyl acrylate polymerization have been measured by the rotating sector method. With this monomer, under our experimental conditions, the increasing viscosity of the system causes chain termination to become diffusion-controlled even in the initial stages of polymerization. As a result, the rate of polymerization accelerates essentially at the beginning of the reaction. The rate constants for methyl acrylate have been compared with the results of Melville and Bickel on butyl acrylate, and also with the data previously obtained on methyl methacrylate, vinyl acetate and styrene. The comparison shows that, for vinyl polymerization, the frequency factors in chain propagation are low but in chain termination are nearly normal, and that the activation energies for propagation are 6-8 kilocalories, while the values for the termination reaction are somewhat lower, but not zero.

The study of polymerization rate constants yields an insight into the effects of structure on the reactivity of olefinic compounds (monomers) or of the derived radicals. From copolymerization studies one may obtain the ratio of the rate constants for the addition of two monomers to the same radical in the propagation reaction shown



$$R\sim\sim CH_2\underset{Y_1}{\overset{X_1}{C}}\cdot + H_2C{=}\underset{Y_2}{\overset{X_2}{C}} \longrightarrow R\sim\sim CH_2{-}\underset{Y_1}{\overset{X_1}{C}}{-}CH_2{-}\underset{Y_2}{\overset{X_2}{C}}\cdot$$

Such ratios have shown how monomer reactivity toward a given radical depends on the nature of the substituent groups X_2 and Y_2.[3,4] However, reactivities of different radicals toward a given monomer can only be deduced when the individual propagation rate constants are known. In recent years such absolute values have been obtained on several monomers, vinyl acetate,[5,6,7] methyl meth-

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[1] This work was carried out with the assistance of the Office of Naval Research under Contract N8 onr-544.

[2] Argonne National Laboratory, Chicago, Illinois.

[3] F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, **70**, 1529 (1948).

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

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

[6] (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); (c) H. Kwart and P. D. Bartlett, *ibid.*, **72**, 1060 (1950).

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

acrylate,[8,9] styrene,[10,11] butyl acrylate[12] and vinylidene chloride[13] by the rotating sector method, also on the first three of these monomers and on *p*-methoxystyrene by the viscosity method of Bamford and Dewar,[14] and on styrene in emulsion polymerization by the particle counting method.[15] Methyl acrylate rate constants have now also been measured by the rotating sector method and the results compared with our previous data on styrene, methyl methacrylate and vinyl acetate. The rate constants of these four monomers in combination with reactivity ratios from copolymerization yield several individual propagation constants of copolymerization, and from these conclusions relating the structure and reactivity of radicals have been drawn.[4]

Experimental

Purification.—Methyl acrylate (Rohm and Haas) was distilled and collected by the procedure previously described for vinyl acetate[7] (b.p. uncor. 44.0° at 193 mm., n^{20}_D 1.4025). To avoid polymer formation in the distillation column a shorter column (25 plates) and 10 instead of 5% takeoff were used. Furthermore, the dried nitrogen (Linde 99.99% min. purity) used in the distillation was not passed over hot copper as in previous work, since traces of oxygen appeared to be necessary to inhibit polymer formation in the column. The monomer was not prepolymerized as no induction period in polymerizations by either light or initiator was observed if the methyl acrylate was thoroughly degassed to remove oxygen.

Biacetyl[8] and α-azo-bis-isobutyronitrile[7] were purified as previously described. The former was used as a photosensitizer in all rotating sector experiments and the latter as the initiator in rate of initiation experiments. Eastman Kodak Co. *n*-butyl mercaptan was distilled under nitrogen at low pressure, and then degassed and fractionated on the vacuum line before use.

Apparatus and Procedure.—These have been described,[7,8] but the behavior of this monomer introduced certain experimental differences. To avoid undesirably high rates of reaction in the sector experiments, the light intensity used was only about 1% that used for methyl methacrylate.[8] Thus, in Run 25 Corning Glass filters were combined as follows: 2 no. 738, 1 no. 5840, 1 no. 5113 and 2 no. 5860. The light absorption of the experimental cells was always less than 12% at 3660 Å. The polymer radical lifetimes were so long for some of the experimental rates of reaction that rather low sector speeds[16] were used and 2 to 3% monomer was often polymerized in the determination of one sector rate ratio (Table II for definition), so that only a limited number of rate ratios could be obtained in a given run. Further, the very high molecular weight polymer formed in our experiments yielded a highly viscous reaction medium which posed experimental and theoretical problems. For example, the dark reaction could not be measured by allowing the reaction to proceed overnight, since popcorn polymer sometimes formed and broke the cells. Further, the dark rate probably varied with the conversion, and did not necessarily correspond at the time of measurement to the actual dark rate of the sector experiments.

Densities.—In Table I are the data necessary for calculation of rates of polymerization from the rates of contraction. Since the polymer shows some flexibility at room temperature and since the second order transition is near 0°[17] the apparent density of the polymer dissolved in monomer is probably close to the solid polymer density[7] and the data of the table were used as given.

TABLE I

DENSITY OF METHYL ACRYLATE AND POLYMETHYL ACRYLATE

Temp., °C.	Monomer[a] (in air)	Polymer[b] (*in vacuo*)
10	0.9607	1.2300
15	.9547	
30	.9362	1.2138
50	.9120	1.1985

[a] For methyl acrylate d^{20}_4 0.9535 and d^{40}_4 0.9276 (C. E. Rehberg, private communication from Eastern Regional Research Laboratory). [b] G. W. A. Kahlbaum, *Ber.*, **13**, 2348 (1880), for polymethyl acrylate d^{20}_0 1.222.

Rates of Initiation.—The procedure used has been described in the earlier paper on vinyl acetate. However, to prevent the high viscosity of the polymerizing system from deforming the meniscus in the capillary early in the reaction, the upper part of the capillary was kept at room temperature and the volume of reaction was taken as the volume of the system submerged in the bath.

Results on Methyl Acrylate

Auto-acceleration of Rate.—When pure methyl acrylate was polymerized in our experiments, using either biactyl as a photosensitizer or α-azo-bis-isobutyronitrile as a thermal initiator, the rate of polymerization accelerated continually from the first stages of the reaction. A similar acceleration of rate was observed in methyl methacrylate but only after high conversions were reached, and was attributed by Norrish and Smith[18] to a decrease in the termination rate constant in the highly viscous reaction medium. Their interpretation was quantitatively confirmed by us.[8] Acrylic acid, whose behavior might be expected to resemble that of methyl acrylate, shows this acceleration to an even more marked degree than methyl methacrylate.[19] The notable rate acceleration observed in methyl acrylate at the beginning of the reaction may also be explained by the effect of viscosity on termination, as is indicated by two facts. First, a gel-like state is attained very early in the polymerization of this monomer, but in the presence of a small amount of the transfer agent, *n*-butyl mercaptan, the system remains quite fluid and the rate acceleration is eliminated. Second, Bagdasaryan[20] has also shown that in the presence of 50% or more ethyl acetate as a solvent the viscosity increase is diminished and the photopolymerization rate remains constant with time. Thus, either a transfer agent or a solvent may lower sufficiently the molecular weight of the polymer formed by methyl acrylate, so that in the resulting relatively low viscosity systems termination is not diffusion-controlled and no rate acceleration is observed.

Sector Experiments.—Table II presents a summary of our measurements of kinetic chain lifetimes in methyl acrylate. The observed lifetimes are long compared with those of other monomers[7,8,10]; indeed, the decay of the polymerization rate (somewhat modified by cooling effects) after irradiation may be easily followed in the dilatometer. The lifetime calculated from the measured decay of the rate at 50° (72 sec. in expt. 14) agrees within a factor of 2 with the value

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(8) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **71**, 497 (1949).

(9) M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.*, **45**, 323 (1949).

(10) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

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

(12) H. W. Melville and A. F. Bickel, *ibid.*, **45**, 1049 (1949).

(13) J. D. Burnett and H. W. Melville, *ibid.*, **46**, 976 (1950).

(14) (a) M. J. S. Dewar and C. H. Bamford, *Nature*, **158**, 380 (1946); (b) C. H. Bamford and M. J. S. Dewar, *ibid.*, **157**, 845 (1946); (c) *Proc. Roy. Soc.* (*London*), **A192**, 309 (1948); "The Labile Molecule," Discussions of the Faraday Soc., No. 2, 310 (1947); (d) C. H. Bamford, *ibid.*, p. 317; (e) G. Dixon-Lewis, *ibid.*, p. 319; (f) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **A197**, 356 (1949); (g) G. Dixon-Lewis, *ibid.*, **A198**, 510 (1949); (h) D. W. E. Axford, *ibid.*, **A197**, 374 (1949).

(15) W. V. Smith, THIS JOURNAL, **70**, 3695 (1948).

(16) With slow sectors the dilatometric rate of reaction, although lagging behind the sector cycle because of slight heat of reaction effects, rose and fell during the light:dark cycle. The average rate in such case should be calculated only from a set of readings with exactly one cycle period between observations. Of course, by taking several readings during each cycle several such sets are obtained.

(17) (a) E. Jenckel, *Z. physik. Chem.*, **A190**, 24 (1941); (b) R. H. Wiley and G. M. Brauer, *J. Polymer Sci.*, **3**, 455 (1948).

(18) R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).

(19) G. V. Schulz and G. Harborth, *Die Makromoleculare Chemie*, **1**, 106 (1947).

(20) K. S. Bagdasaryan, *J. Phys. Chem.* (*U. S. S. R.*), **22**, 1181 (1948).

of τ_s obtained in the usual sector experiments (37 sec. in expt. 14).

TABLE II

KINETIC CHAIN LIFETIME IN Me ACRYLATE POLYMERIZATION

Expt.	No. of sector rate ratios	Rate, % contraction per hr.	τ_s[a] sec.	2 × fast sector ratio[b]	τ_s sec. at 0.8% cont./hr.
			30°		
14	2	1.485	11.55	1.067	21.4
25	4	0.65	31.1	1.075	25.3
				Av.	24.2
			30° Regulated		
25	4	0.55	11	0.933	8
			50°		
14	5	1.00	37	1.098	46
25b	4	0.80	22.5	1.123	22.5
25d	4	0.80	20.0	0.979	20.0
				Av.	29.5

[a] Lifetime measured for experimental rate in previous column. [b] The "sector rate ratio" is defined as the rate of polymerization under interrupted illumination divided by the rate under steady illumination. The fast sector ratio is the limiting ratio using high speed sectors.

Our observations in these experiments may be correlated with the idea that termination is diffusion-controlled. Thus, the rates for *steady* illumination increased steadily during *sector* runs, by about 20% increase at 30° and 10% at 50° between 0 to 5% conversion. If the polymer molecular weight in these experiments is controlled by transfer,[20] then a lower polymer molecular weight at 50° would be expected, and the effect of polymer size could combine with the usual effect of temperature on viscosity to explain the lesser acceleration at 50°.

The fast sector ratios in the fifth column of Table II are generally high. This is not a temperature effect, since in Run 25 at 30° the temperature rise in the center of the cell was 0.5° in steady light but only 0.25° in interrupted illumination. Possible explanations are: that the longer chains in sectored irradiation diffuse together more slowly than the chains produced in steady irradiation, or that absorbed light produces a short-lived catalyst which increases the effective "dark" reaction over that actually measured. Both explanations indicate that the actual lifetime corresponding to the rate in steady illumination is slightly shorter than determined by sector experiments. To test this conclusion, the kinetic chain life was measured using 0.1 mole % of *n*-butyl mercaptan (transfer constant = 1.53 at 30°[21]) in the 30° regulated Run No. 25 to lower the degree of polymerization to a calculated value of ~700. In this experiment the reaction system remained at relatively low viscosity even up to 10% conversion and, further, the rate remained constant as would be expected. In Table II, the presence of regulator is seen to shorten the lifetime, but the value found is a lower limit for τ_s, since the fast sector ratio is low, indicating a direct retarding effect of mercaptan in addition to its indirect effect on termination. Since τ_s is inversely proportional to k_t at a given rate of polymerization, the result that the regulator decreases τ_s threefold indicates that diffusion lowers k_t not more, and probably less, than threefold in our unregulated experiments at 30°. The relative rates in sectored light are plotted as a function of time of flash and compared with theory in Fig. 1.

b, for solid theoretical curve, 5% dark reaction, unregulated, and broken theoretical curve, 5% dark reaction regulated.

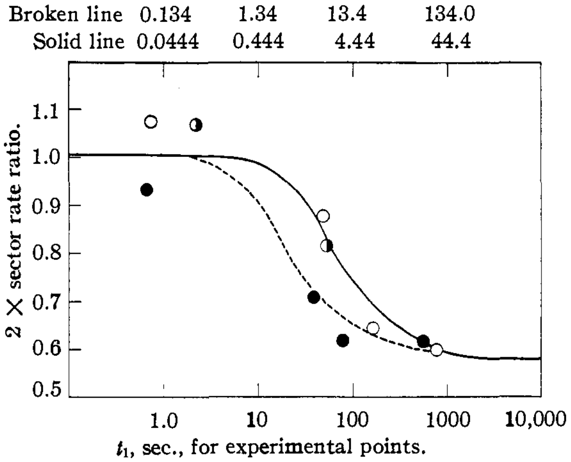

Fig. 1.—Rates of polymerization of methyl acrylate at 30° in intermittent light for different times of flash, t_1. Experimental points: ◑, Run 14; ○, Run 25 unregulated; ●, Run 25 regulated. All corrected to 0.86% contraction per hour at 5% dark reaction.

From equation (1)[7]

$$\frac{R_p\tau_s}{(\mathrm{M})} = \frac{k_p}{2k_t} \qquad (1)$$

and Tables I and II one can calculate $k_p/2k_t$ at 50 and 30° and this ratio is plotted in Fig. 2. Since experimentally the limiting slow sector ratio is equivalent to ($^1/_4$ the rate in steady illumination plus $^3/_4$ the dark rate)/(rate in steady illumination), the observed slow sector ratio should agree with theory regardless of the diffusion or retardation effects discussed above. Therefore, the slow speed sector rate ratio may be taken as correct, while the error for high speed sectors is measurable, and one may arbitrarily assume as an approximation that the error varies linearly with the value of the ratio. Applying this arbitrary correction to calculate τ_s changes $k_p/2k_t$ by less than 20%. Further, if it also be assumed that the increase in rate during lifetime measurements is solely due to the decrease in k_t, then the average decrease in k_t can be estimated and the initial value of $k_p/2k_t$ calculated. This correction is also small and the total estimated correction for sector rate ratio error and decrease in k_t is shown by the length of the arrows in Fig. 2. In the case of the regulated experiment, the correction for ratio error is positive and there is no correction for variation in k_t. The corrected results in Fig. 2 show that $k_p/2k_t$ at 30°

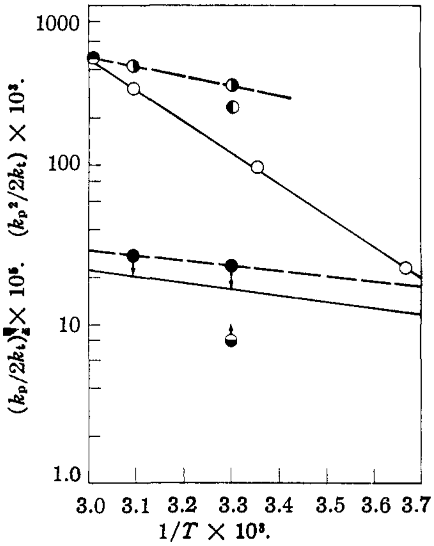

Fig. 2.—Rate constant ratios for methyl acrylate polymerization: ●, $k_p/2k_t$; ◓, $k_p/2k_t$ regulated; ◑, $k_p^2/2k_t$ from α-azo-bis-isobutyronitrile; ◐, $k_p^2/2k_t$ from benzoyl peroxide, all representing our data in pure monomer. Literature values: ○, $k_p^2/2k_t$ Bagdasaryan (ref. 20) 0.5 mole fraction monomer; ◒, $k_p^2/2k_t$ Walling (ref. 26) 0.5 vol. fraction monomer.

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[21] C. Walling, THIS JOURNAL, **70**, 2561 (1948).

in the absence of diffusion effects is in the neighborhood of 10 to 16 × 10^{-5}, and that even with the very long radicals found in methyl acrylate ($\bar{P}$ up to 40,000 or more)[20] k_t does not vary greatly with a 50-fold decrease in chain-length, at least in the initial stages of reaction.

Rates of Initiation.—The rate of initiation was calculated only from initiator decomposition, since the inhibitors tried, picric acid, benzoquinone, tetrachloroquinone, reduced only slightly the constant rate of polymerization induced by 5.1 × 10^{-4} mole/liter α-azo-bis-isobutyronitrile at 50°, with no evidence of an induction period.[22] Taking the rate with no inhibitor as 1.0, the relative rates were as follows for 1.5 × 10^{-5} mole/liter of inhibitor: picric acid 0.85, benzoquinone 0.77, tetrachloroquinone 0.62.

Two pieces of evidence support the assumption that twice the rate of decomposition of α-azo-bis-isobutyronitrile gives the rate of initiation of chains in methyl acrylate. (1) The decomposition of this initiator is independent of the solvent.[23] (2) The radicals from this initiator are 100% efficient in initiating chains in vinyl acetate and methyl acrylate is a more reactive monomer than vinyl acetate.[4]

TABLE III

RATES[a] OF INITIATION IN Me ACRYLATE

Expt.	Temp., °C.	R_p × 10^{5} [b]	($^1/_2$ R_i) × 10^{11} [c]	Conversion, %[d]	$k_p^2/2k_t$
1	25	5.53	1.96	4.25	0.66
2	30	26.9	94.8	0.9	.32
3a	30	5.61	3.67	0.4	.32
3b	30	14.67	13.8	3-4	.65
1	50	43.9	118	3.8	0.73
2	50	12.4	6.07	0.9	1.13[e]
3a	50	2.70	0.775	0.7	0.42
3b	50	5.05	2.71	1.3	0.42

[a] All rates in moles/liter/sec. and all concentrations in moles/liter. [b] Rate of polymerization. [c] R_i = rate of initiation calculated from initiator concentration and its rate constant for decomposition, k_d, where k_d = 8.9 × 10^{-8} at 30° and 2.3 × 10^{-6} at 50° in xylene.[23] $^1/_2 R_i = k_d$ (Initiator). [d] This is the per cent. polymerized at the point where the rate R_p in the third column was measured. [e] Upper limit as meniscus distorted early in experiment.

Table III presents our results on rates of initiation, $k_p^2/2k_t$ being calculated from eq. (2).[7]

$$R_p^2/R_i(\mathrm{M})^2 = k_p^2/2k_t \qquad (2)$$

In these experiments, as in the sector runs, the rate of polymerization increased from the beginning of reaction. This rate increase is again attributed to a decrease of k_t with increasing conversion and is reflected in the higher values of $k_p^2/2k_t$ calculated at higher conversions. The values of $k_p^2/2k_t$ for the initial stages of reaction (~ 1% reaction) are plotted in Fig. 2. In one experiment at 30° benzoyl peroxide was used as the initiator in undiluted monomer and the rate of initiation calculated using Nozaki and Bartlett's data on the rate of decomposition of the peroxide in vinyl acetate.[24] The result in Fig. 2 agrees well with results using azo initiator. Bagdasaryan[20] has evaluated the ratio by use of a photochemical technique, $k_p^2/2k_t$ for methyl acrylate in ethyl acetate solution. (See Fig. 2 for comparison with our results.) He found that the photochemical rate in the pure monomer increased continually, but that in solutions containing 50% or less of monomer, the initial rate remained constant with time, indicating that in solution the magnitude of k_t depends mainly on the reactivity of the radicals, not on their diffusion. Two facts support the accuracy of Bagdasaryan's results: (1) The same method applied to methyl methacrylate[25] gave $k_p^2/2k_t$ = 3.8 × 10^{-3} and $E_p - {^1/_2}E_t$ = 5.2 kcal. in fair agreement with the values 4.6 × 10^{-3} and 4.9 kcal.[8] we calculated from the data of Schulz, *et al.* (2) Further, in Fig. 2 Bagdasaryan's ratios agree very well with the value Walling[26] calculated in 50% ethyl acetate solution at 60° from the rate of α-azo-bis-isobutyronitrile decomposition. Comparison of $k_p^2/2k_t$ in Fig. 2 for pure monomer and solution indicates the difference becomes less at higher temperatures, being negligible at 60°. This is the expected effect of temperature since it has been shown for the undiluted monomer that the effect of diffusion on k_t is less at higher temperatures.

Rate Constants.—In view of the discussion above, individual rate constants, if calculated from Bagdasaryan's $k_p^2/2k_t$ results and our $k_p/2k_t$ values corrected for the fast sector error and to zero conversion, should correspond to a system in which termination is not diffusion-controlled. The constants so calculated are given in Table IV. The values in parentheses are calculated from our data for polymerization of the pure monomer using only the correction for the fast sector error. As seen in the table, the constants calculated at 60° are similar for pure monomer or solution, and therefore are estimated to be accurate within a factor of 2. Due to the uncertainty in the 30° values, not much significance can be attached to the last column in Table IV, but one may note that the parameters obtained are reasonable when compared with those for styrene, methyl methacrylate and vinyl acetate. For more precise values of the constants, measurements on this monomer should be made on solutions in an inert solvent (perhaps ethyl acetate) or using a transfer agent which does not affect the rate at which chains are propagated.

TABLE IV

RATE CONSTANTS IN METHYL ACRYLATE POLYMERIZATION

	30°	60°	T, °K.
k_p	720 (1730)	2090 (2000)	$10^8\ e^{-7100/RT}$
$2k_t$ × 10^{-7}	0.43 (0.94)	0.95 (0.85)	2.8 × $10^{10}\ e^{-5300/RT}$

Although there are no published values for the rate constants of methyl acrylate, our values may be compared with those obtained by Melville and Bickel[12] for butyl acrylate. Their measurements at 25 and 35° may be averaged for comparison with our 30° experiments. For k_p Melville and Bickel obtain 13.8 liters/mole/sec. at 30°, about one-fiftieth our methyl acrylate value, while for $2k_t$ they obtain 1.8 × 10^4 liters/mole/sec., about 1/240th of our value. From steric effects, the butyl acrylate constants might be expected to be lower, and the results are in agreement with this, especially as the $2k_t$ values, where the effect should be greater, do differ more than the k_p values. The effect of diffusion on k_t is probably less in butyl acrylate as Melville and Bickel find a constant rate of polymerization up to 8% conversion, whereas in methyl acrylate, acceleration occurs at less than 1% conversion.[27]

It is, however, more instructive to compare the ratios $k_p^2/2k_t$ and $k_p/2k_t$ in the two cases, since Melville and Bickel have measured rates of initiation and kinetic chain lifetimes to obtain these ratios just as we have. Such a comparison suggests the differences between methyl and butyl acrylate are less than indicated by the factors discussed above. In the case of $k_p/2k_t$ their ratio is fivefold ours. However, their experimental sector rate ratios decrease more rapidly with increasing time of flash than expected from theory (their Fig. 7), and if the middle rather than the upper portion of their experimental curve is taken to be correct then the difference in results disappears.

In the case of the $k_p^2/2k_t$ ratio, Melville and Bickel measure the rate of initiation by two methods. Their results based on molecular weight give a ratio $k_p^2/2k_t$ one-sixth of ours when corrected from the assumption of termination by disproportionation to termination by combination, and their results based on inhibitor are one-twelfth ours. These differences would be reduced if their molecular weights were too low and if the inhibitor, tetraphenylhydrazine, were used up in reactions other than stopping chains.

The most probable error in our own measurement of $k_p^2/2k_t$ is that the efficiency of the initiator is less than the

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(22) H. W. Melville and W. F. Watson (*Trans. Faraday Soc.*, **44**, 886 (1948)) found a similar behavior of inhibitors in methyl methacrylate.

(23) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(24) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946).

(25) K. S. Bagdasaryan, *J. Phys. Chem. (U. S. S. R.)*, **20**, 1415 (1946).

(26) C. Walling, THIS JOURNAL, **71**, 1930 (1949).

(27) Bamford and Dewar (ref. 14c, p. 325) point out that the lower the velocity constant, the higher the critical viscosity above which viscosity becomes rate-determining. Their conclusion agrees with our statement that diffusion is less important in butyl acrylate if some of the difference between the methyl and butyl acrylate termination constants is real.

100% assumed. A lower efficiency would raise our $k_p^2/2k_t$ ratio so as to increase the difference with the butyl acrylate value of Melville and Bickel, and would also make our values still larger than Bagdasaryan's whose result we use at 30°.

Comparison of Monomers

While the individual rate constants for a given monomer are interesting in themselves, more important to an understanding of chemical behavior are the comparisons which may be made with the rate constants of the four monomers we have now studied. Therefore, we will first consider the propagation rate constants for the four monomers, and second, the termination rate constants and the effect of viscosity upon these.

Propagation Rate Constants.—Table V affords a comparison of the propagation rate constants of styrene, methyl methacrylate, methyl acrylate and vinyl acetate, and it will be noted that at 60° k_p increases as the general monomer reactivity (determined from copolymerization at 60°) decreases.[4] In the third column, the frequency factors are all found to be lower than the normal collision frequency by a factor of 10^3 or more. Methyl methacrylate has the lowest factor, which is readily understandable on steric grounds, since the polymethyl methacrylate radical is the only tertiary radical in the series. Two explanations may account for the consistently low frequency factors. Harman and Eyring[28] have proposed that in free radical addition to a double bond, a singlet–triplet transition of low probability is involved in the olefin. Baxendale and Evans,[29] however, also point out that the monomer molecule in entering the chain loses several degrees of freedom so that the entropy change is unfavorable, lowering the frequency factor.

TABLE V

PROPAGATION RATE CONSTANTS

Monomer	k_p at 60°	A	$E_{act.}$	$-\Delta H$
Styrene	176	2.2×10^7	7.8	17.5^a
Me methacrylate	367	5.1×10^6	6.3	13.0^b
Me acrylate	2090	(1×10^8)	(7.1)	18.7^c
Vinyl acetate	3700	2.4×10^8	7.3	21.3^c

[a] D. E. Roberts, W. W. Walton and R. S. Jessup, *J. Polymer Sci.*, **2**, 420 (1947). [b] L. K. J. Tong and W. O. Kenyon, THIS JOURNAL, **67**, 1278 (1945). [c] *Ibid.*, **69**, 2245 (1947).

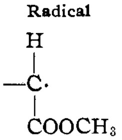
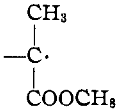
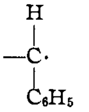
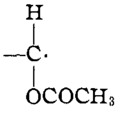
The activation energies of Table V do not differ greatly, the spread for singly substituted monomers being only 0.7 kcal. In the last column are heats of polymerization taken from the literature, which may be used to calculate activation energy differences by the method of Evans, Gergely and Seaman.[30] According to these authors, the difference in activation energy for two propagation reactions is proportional to the difference in the heats of reaction (this difference being mainly attributed to differences in resonance energies) with a proportionality factor of about −0.4, so that the styrene propagation step should have an activation energy 1.5 kcal greater than that for vinyl acetate. Since this theory makes the simplifying assumption (among others) that the different propagation reactions will not differ greatly in the extra resonance energy of the transition state, it may be considered that the agreement between theory and experiment is satisfactory, since in both cases the activation energy is slightly larger for styrene than vinyl acetate. For all the above monomers except methyl acrylate the activation energies are probably accurate within 1 kcal. However, since the predicted difference between reactivity extremes for singly substituted monomers above is only 1.5 kcal., it is apparent that an experimental precision of about 0.2 kcal. is necessary to make refinements of the theory worthwhile.

The disubstituted methyl methacrylate cannot be compared directly in this approximate theory with the other monomers, as it has the lowest activation energy whereas its low heat of polymerization would predict a high activation energy. However, Evans and Polanyi[31] estimate that steric hindrance reduces the heat of polymerization about 9 kcal. for isobutylene (with monosubstituted ethylenes the effect is negligible) and that the heat of polymerization is similarly lowered in methyl methacrylate. Since the steric effects would be less at the greater separation obtaining in the transition state, it is not surprising that the activation energy of methyl methacrylate corresponds to a higher heat of reaction than measured. Extra resonance in the transition state may also be greater for disubstituted ethylenes.

Termination Rate Constants.—The summary of termination rate constants in Table VI shows variation by a factor of only 15. The last three values at 60° are considered accurate within a factor of two. The frequency factors are about in the order expected from steric effects, the tertiary methyl methacrylate radical having the lowest

TABLE VI

TERMINATION RATE CONSTANTS

Radical	$2k_t \times 10^{-7}$ at 60°	A^a	$E_{act.}$	$\bar{P}$
 $\text{H}-\dot{\text{C}}(-)-\text{COOCH}_3$	0.95	(3×10^{10})	(5)	>10,000
 $\text{CH}_3-\dot{\text{C}}(-)-\text{COOCH}_3$	1.87	1.4×10^9	2.8	6,500
 $\text{H}-\dot{\text{C}}(-)-\text{C}_6\text{H}_5$	7.2	2.6×10^9	2.4	4,000
 $\text{H}-\dot{\text{C}}(-)-\text{OCOCH}_3$	14.8	4.2×10^{11}	5.2	~2,000

[a] Since $2k_t$ is the rate constant for reaction of pairs of radicals $^1/_2\,A$ should be compared with collision frequency which is about 3×10^{11} in m./liter/sec.

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

(29) J. H. Baxendale and M. G. Evans, *Trans. Faraday Soc.*, **43**, 210 (1947); M. G. Evans, Discussions Faraday Soc., No. 2, 271 (1947).

(30) M. G. Evans, J. Gergely and E. C. Seaman, *J. Polymer Sci.*, **3**, 866 (1948).

(31) A. G. Evans and M. Polanyi, *Nature*, **152**, 738 (1943).

frequency factor. In all cases the frequency factors are 100–1000-fold larger than those for the corresponding propagation reactions. Either the theory of Harman and Eyring[28] or that of Baxendale and Evans[29] would predict higher factors in the termination reaction, as no singlet–triplet transition is involved and the loss of degrees of freedom is not as great. The latter authors estimate A for termination as 6×10^{10}.

Noteworthy in column 4 is the fact that the activation energies are not zero, even though termination has been clearly shown to occur by combination in the case of styrene[32] and probably is also by combination in the other cases.[33] Although these activation energies are of the magnitude to be expected for diffusion-controlled processes, the discussion in the next section indicates that only in the case of methyl acrylate is termination diffusion-controlled in the initial stages of reaction where these constants were measured. The error in activation energies is somewhat larger here than for propagation since the measured lifetime enters twice in the calculation of $2k_t$ and only once in the estimate of k_p. The error for the last three in the table is estimated to be ±1.5 kcal.

In the last column of Table VI are the degrees of polymerization, $\bar{P}$, for the polymer formed in steady irradiation in the lifetime experiments at or near 60°. As the value of $\bar{P}$ decreases, $2k_t$ in the second column increases. However, since it has been shown for styrene[10] and methyl methacrylate[8] that the rate constants are independent of chain length (at least in the initial stages of reaction), it must be concluded that the variation in $2k_t$ does not depend on the variation in $\bar{P}$, but that $\bar{P}$ at least in part depends on the termination constant.

Effect of Conversion on Rate Constants.—Trommsdorff[34] examined several monomers and found that the rates of polymerization accelerated after certain conversions were attained, styrene alone showing no such acceleration under his experimental conditions. He attributed this rate acceleration to a decrease in the termination rate constant with increasing viscosity of the system. The data of Table VII are in harmony with this thesis. Each monomer listed was irradiated at constant light intensity and the per cent. conversion at which the rate accelerated was noted. In the last column are the estimated degrees of polymerization for the polymer molecules formed in the initial stages of the irradiations.

TABLE VII

EFFECT OF % CONVERSION ON RATE CONSTANTS

Monomer	Temp., °C.	Transition point,[a] %	Ratios[b] k_p	$2k_t$	$\bar{P}$ Initial
Vinyl acetate	25	>40	..	....	2400
Styrene	50	30	0.67	0.075	4000
Me methacrylate	30	15	1.12	0.0066	5000
Me acrylate	30	0	..	....	>10,000

[a] Rate began to accelerate at conversion shown. [b] (Value at 35% conversion)/(Initial value).

The higher the initial molecular weight, the higher the viscosity should be for a given conversion and the earlier in the reaction should the rate accelerate, as is shown in column three. For styrene[10] and methyl methacrylate[8] the change in rate constants was measured during the accelerated polymerization. Within the experimental error the propagation rate constant remains unchanged, whereas the termination rate constants decrease as the systems become more viscous. The effect on the termination constant is less with styrene than with methyl methacrylate, as might be expected if termination is diffusion-controlled and depends on the viscosity of the system; the higher temperature and lower molecular weight in the case of styrene would both contribute to a lower viscosity. When termination becomes diffusion-controlled the rate constants may vary with radical size.

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[32] F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

[33] 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**, 394 (1945), show many small radicals similar to the radicals derived from methyl acrylate and methacrylate dimerize.

[34] Trommsdorff, "Colloquium on High Polymers," Freiburg, 1944. See B. I. O. S. Report No. 363, Item 22.