The possibility of investigating the change in the rate constant at lower pressures has been considered and some experiments have been performed in the 4–10 mm. range. However, since the reproducibility of the experiments seems to become worse at the lower pressures, presumably as a result of more interference from heterogeneous processes, a detailed study of the rate at low pressures in the present apparatus did not appear to be worthwhile.

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman for making the infrared absorption measurements.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Inhibition of Polymerization. I. Methyl Methacrylate*

BY JOHN L. KICE

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The effect of nine compounds on the 2,2′-azo-bis-isobutyronitrile-catalyzed polymerization of methyl methacrylate has been studied kinetically by a dilatometric method. Where possible the data have been analyzed using a new equation, derived from a reasonable kinetic scheme, which permits a quantitative evaluation of the extent to which wastage of inhibitor takes place through "copolymerization." The results for benzoquinone and chloranil show that copolymerization is small for the former but almost 80% of the chloranil molecules disappear in this fashion without terminating kinetic chains. The rate constants obtained for the aromatic nitro compounds are compared with those previously reported for vinyl acetate and are found to be 10^5 smaller in methyl methacrylate. In addition it is found that even the stable free radical, 2,2-diphenyl-1-picrylhydrazyl, does not totally suppress the polymerization of methyl methacrylate during the induction period.

Introduction

Most of the quantitative information in the literature regarding inhibition of polymerization has been obtained with styrene and vinyl acetate. Thus Bartlett and Kwart[1] conducted a careful investigation of the effect of eleven compounds on the benzoyl peroxide-catalyzed polymerization of vinyl acetate, and a number of workers[2–4] have studied the action of various substances on the polymerization of styrene, both catalyzed and thermal. However, no extensive investigation of the behavior of inhibitors in methyl methacrylate polymerization has been reported, although Melville and co-workers[5,6] have studied the effect of quinone. The present investigation has been an attempt to partially rectify this situation.

To this end, the effect of nine inhibitors of various chemical types on the 2,2′-azo-bis-isobutyronitrile (AIBN) catalyzed polymerization of methyl methacrylate has been investigated using a dilatometric technique similar to that employed by Bartlett and Kwart.[1] All experiments were carried out at 44.1° in order to afford easy comparison with the data previously obtained at 45° with vinyl acetate.[1]

Experimental

Purification of Materials. Methyl Methacrylate.—Commercial monomer (Rohm and Haas) was washed repeatedly with 5% sodium hydroxide; it was then washed with water, followed by two washings with a saturated solution of sodium bisulfite in water. It was then washed twice more with water, dried over either Drierite or sodium sulfate and was then fractionally distilled under nitrogen at reduced pressure, only the middle cut being retained, b.p. 43° (90 mm.). After purification the monomer samples were stored in the dark at −20° in a desiccator until used. Freshly purified monomer was thus prepared every few weeks, and in addition the uninhibited polymerization rate of each batch of monomer was checked periodically during this period. In all cases these agreed with each other within the experimental error.

2,2′-Azo-bis-isobutyronitrile.—This was recrystallized from methanol until it showed a melting point of 103° dec. It was then stored at −20° under desiccation.

2,2-Diphenyl-1-picrylhydrazyl.—Material which had been prepared by the method of Goldschmidt and Renn[7] was recrystallized twice from chloroform–ether.

Benzoquinone.—This was recrystallized once from Esso octane, sublimed twice and then recrystallized again from octane, m.p. 114–115° (sealed tube).

Furfurylidene Malononitrile.—A sample was kindly supplied by Dr. R. N. Haward of Petrochemicals, Ltd. It was used as received.

Benzhydrilidene Malononitrile.—This was prepared according to the method of Schenk, *et al.*[8] Recrystallized twice from ethanol it melted at 138–139°.

Trinitrotoluene.—This was recrystallized once from methanol, m.p. 81–82°.

***m*-Dinitrobenzene.**—This was recrystallized from methanol, m.p. 89–90°.

***p*-Nitrotoluene.**—This was recrystallized once from methanol water, m.p. 50–51°.

Sulfur.—Reagent grade sulfur was recrystallized once from toluene.

Diphenylamine.—Eastman Kodak white label diphenylamine was recrystallized once from Esso octane, m.p. 50.5–51.0°.

The Dilatometer.—The dilatometers were similar in design to those employed by Bartlett and Kwart.[1] They were calibrated with mercury in the usual fashion to known marks in each capillary. From the density data of Fox and Loshaek[9] for monomer and polymer in monomer the volume change for complete polymerization at 44.1° was calculated to be 24.22%. From this and the volumes and capillary radii of the three dilatometers it was possible to ascertain the percentage polymerization for an over-all fall of 1 cm. in the capillaries. This was found to be 0.134, 0.138 and 0.142% for dilatometers 1, 2 and 3, respectively.

The procedure for a run was as follows. The proper amounts of initiator and inhibitor were weighed into a glass stoppered flask; a weighed amount of cold methyl methacrylate was quickly added, and solution was effected. About

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[*] Presented in part before the Division of Polymer Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

(1) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950); **74**, 3969 (1952).

(2) G. V. Schulz, *Makrom. Chem.*, **1**, 94 (1947).

(3) F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948).

(4) J. W. Brietenbach and H. L. Brietenbach, *Ber.*, **75**, 505 (1942).

(5) H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948).

(6) E. Bonsall, L. Valentine and H. W. Melville, *ibid.*, **49**, 686 (1953).

(7) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

(8) R. Schenk and H. Finken, *Ann.*, **462**, 267 (1928).

(9) T. G Fox and S. Loshaek, *J. Polymer Science*, in press.

40 ml. of this solution was then rapidly pipetted into the side reservoir, A, of the dilatometer (see diagram of dilatometer in reference 1). From this point on the experimental procedure was similar to that employed in reference 1.

After the dilatometer had come to thermal equilibrium in the constant temperature bath (44.1 ± 0.005°), the height of the liquid in the two capillaries was read to ±0.01 cm. by means of a small cathetometer at suitable time intervals.

For the uninhibited runs the procedure was similar except, of course, that only initiator and monomer were used.

Theoretical

It is generally accepted that any substance which arrests or retards the polymerization of a vinyl monomer does so by reaction with either initiator or polymer free radicals, R·, to yield a new free radical, Z·. This new radical, being relatively unreactive toward monomer, is chiefly consumed by reaction with other free radicals, resulting in chain termination. However, from elementary considerations it is apparent that there also exists the possibility that a fraction of the Z· produced is instead removed by reaction with monomer as in true copolymerization or chain transfer.

Consequently the following kinetic scheme has been modified from those previously given[1,6] in order to take into account this possibility.

Reaction		Rate	
Initiation	$I \rightarrow 2R\cdot$	$2k_d f(I)$	(1)
Propagation	$R\cdot + M \rightarrow R\cdot$	$k_p(R\cdot)(M)$	(2)
Transfer (or addition)	$R\cdot + X \rightarrow Z\cdot$	$k_x(R\cdot)(X)$	(3)
Copolymerization	$Z\cdot + M \rightarrow R\cdot$	$k_0(Z\cdot)(M)$	(4)
Termination	$Z\cdot + R\cdot \rightarrow$ inactive prod.	$k_c(R\cdot)(Z\cdot)$	(5)
	$Z\cdot + Z\cdot \rightarrow$ inactive prod.	$2k_z(Z\cdot)^2$	(6)
	$R\cdot + R\cdot \rightarrow$ inactive prod.	$2k_t(R\cdot)^2$	(7)

In this scheme X is the added inhibitor or retarder, hereafter called terminator, and Z· is the radical formed by the reaction of R· with terminator. Z· may be formed either by addition of R· to X or by transfer of an atom or group to R· from X. Whichever happens cannot be distinguished kinetically.

It has been assumed that the usual steady state assumptions with regard to the concentrations of radicals may be applied, and that one may therefore write

$$\frac{d(R\cdot)}{dt} = 2k_d f(I) + k_0(Z\cdot)(M) - k_x(R\cdot)(X) - 2k_t(R\cdot)^2 - k_c(R\cdot)(Z\cdot) \cong 0 \quad (8)$$

$$\frac{d(Z\cdot)}{dt} = k_x(R\cdot)(X) - k_0(Z\cdot)(M) - k_c(R\cdot)(Z\cdot) - 2k_z(Z\cdot)^2 \cong 0 \quad (9)$$

$$k_x(R\cdot)(X) = k_0(Z\cdot)(M) + k_c(R\cdot)(Z\cdot) + 2k_z(Z\cdot)^2 \quad (9a)$$

It is obvious from an examination of equations 1–7 that of the Z· produced by reaction 3 some disappear by reaction 4, some by reaction 5 and the rest by reaction 6. The fraction which disappears by reaction 5, Ω, is equal to

$$\Omega = \frac{k_c(R\cdot)}{k_0(M) + k_c(R\cdot) + 2k_z(Z\cdot)} \quad (10)$$

Similarly the fraction which is consumed by reaction 6, β, is equal to

$$\beta = \frac{2k_z(Z\cdot)}{k_0(M) + k_c(R\cdot) + 2k_z(Z\cdot)} \quad (11)$$

From equation 9a it is easy to see that the total number of Z· consumed in unit time must equal the number produced, which is $k_x(R\cdot)(X)$. Therefore the number of Z· disappearing in unit time by reaction 5 is $k_x(R\cdot)(X)\Omega$, and similarly for reaction 6, $k_x(R\cdot)(X)\beta$. Now each Z· which disappears by reaction 5 stops in all two kinetic chains while each Z· which is consumed by reaction 6 stops only one chain. Consequently the total number of chains stopped by Z· radicals in unit time is equal to $2k_x(R\cdot)(X)\Omega + k_x(R\cdot)(X)\beta$. Our assumption of a steady state in both Z· and R· radicals may alternatively be expressed by saying that the number of kinetic chains started in unit time must equal the number stopped since the addition of equations 8 and 9 yields

$$2k_d f(I) = 2k_c(R\cdot)(Z\cdot) + 2k_t(R\cdot)^2 + 2k_z(Z\cdot)^2 \quad (12)$$

From the preceding argument it is seen that equation 12 may be rewritten as

$$2k_d f(I) = 2k_x(R\cdot)(X)\Omega + k_x(R\cdot)(X)\beta + 2k_t(R\cdot)^2 \quad (13)$$

Substitution of the expressions for Ω and β into equation 13 gives

$$k_d f(I) = k_x(R\cdot)(X)\left[\frac{k_c(R\cdot) + k_z(Z\cdot)}{k_0(M) + k_c(R\cdot) + 2k_z(Z\cdot)}\right] + k_t(R\cdot)^2 \quad (14)$$

It is assumed[10] that the rate of polymerization may be defined as

$$R \equiv \left[\frac{-d \ln (M)}{dt}\right] = k_p(R\cdot);\ \frac{R}{k_p} = (R\cdot) \quad (15)$$

In the absence of terminator the steady state assumption would give at the same initiator concentration

$$k_d f(I) = k_t(R\cdot)_0^2 \quad (16)$$

where $(R\cdot)_0$ is the concentration of radicals in the absence of terminator. This is in turn related to the rate of polymerization in the absence of terminator (uninhibited rate), R_0, in the same way that R is related to $(R\cdot)$, *i.e.*

$$R_0 \equiv \left[\frac{-d \ln (M)}{dt}\right]_{\text{uninhib.}} = k_p(R\cdot)_0;\ \frac{R_0}{k_p} = (R\cdot)_0 \quad (17)$$

From equations 16 and 17 one obtains

$$k_d f(I) = k_t R_0^2/k_p^2 \quad (18)$$

Substitution of equations 15 and 18 into equation 14 gives

$$k_x R(X)\left[\frac{\frac{k_c R}{k_p} + k_z(Z\cdot)}{k_0(M) + \frac{k_c R}{k_p} + 2k_z(Z\cdot)}\right] = \frac{k_t}{k_p}(R_0^2 - R^2) \quad (19)$$

It is also advantageous to make a similar substitution of R and R_0 into equation 12 which is then solved for (Z·) by the quadratic formula, giving

$$(Z\cdot) = \frac{k_c}{2k_z k_p}\left(\sqrt{R^2 + \frac{4k_t k_z}{k_c^2}(R_0^2 - R^2)} - R\right) \quad (20)$$

It is now convenient to define two new symbols

$$\phi = \frac{R}{R_0} \text{ and } c = \frac{4k_t k_z}{k_c^2}$$

Equation 20 may then be rewritten as

$$(Z\cdot) = \frac{k_c R}{2k_z k_p}\left(\sqrt{1 + \frac{c(1 - \phi)^2}{\phi_2}} - 1\right) \quad (21)$$

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[10] This assumption appears to be valid since it can be easily shown that if $k_0(Z\cdot)(M)$ constituted an important source of monomer consumption the concentration of X would have to change far more rapidly with time than was observed for any terminator studied.

The result of equation 21 may then be substituted into equation 19, and after simple algebraic manipulation it is possible to obtain

$$\frac{\phi^2(\mathrm{X})}{1-\phi^2}\left[1+\sqrt{1+\frac{c(1-\phi^2)}{\phi^2}}\right] = \frac{2k_\mathrm{t}R}{k_\mathrm{p}k_\mathrm{x}}\sqrt{1+\frac{c(1-\phi^2)}{\phi^2}}+\left(\frac{k_0}{k_\mathrm{c}}\times\frac{2k_\mathrm{t}(\mathrm{M})}{k_\mathrm{x}}\right) \quad (22)$$

Equation 22 will be of experimental value only for those cases in which the following conditions hold: first, the concentration of X must remain effectively constant at its initial value for a long enough period of time to allow an accurate measure of the initial rate, and second, the initial rate must be large enough to be accurately measurable. (In terms of popular usage, the polymerization must be "retarded" rather than "inhibited".) For an easily inhibited monomer such as vinyl acetate it would be difficult to satisfy both conditions simultaneously, but with methyl methacrylate it is usually possible to adjust experimental conditions so as to satisfy both requirements, and the data may be treated by equation 22.

From an examination of equation 22 it is apparent that a plot of

$$\frac{\phi^2(\mathrm{X})}{1-\phi^2}\left[1+\sqrt{1+\frac{c(1-\phi^2)}{\phi^2}}\right] \; vs. R\sqrt{1+\frac{c(1-\phi^2)}{\phi^2}}$$

for the various runs with a given terminator should be a straight line of slope $2k_\mathrm{t}/k_\mathrm{p}k_\mathrm{x}$ and intercept $2k_0k_\mathrm{t}(\mathrm{M})/k_\mathrm{x}k_\mathrm{c}$. Since $k_\mathrm{t}/k_\mathrm{p}$ is known from the work of Matheson, *et al.*,[11] k_x may be readily evaluated. Similarly it is possible to ascertain from the intercept, with somewhat less accuracy, k_0/k_c, using k_t as reported in reference 11 and k_x as found from the slope.

In order to make the plot described above it is necessary to assume a value of c for the terminator in question. Thus plots of the data for each terminator were made according to equation 22 using different assumed values of c ranging from one[12] to a number so small that for the observed values of ϕ the terms containing c were negligibly small. It was then determined which value of c gave the least deviation of the experimental points from a straight line, and the values of k_x and of k_0/k_c were determined from the slope and intercept, respectively, of this "best" straight line.

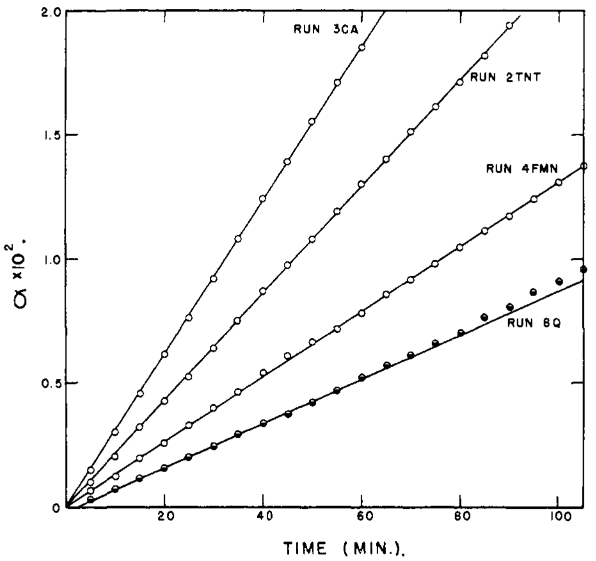

Fig. 1.—Plots of conversion, α, *vs.* time for some typical runs with various terminators.

Results and Discussion

All of the runs were carried out *in vacuo* on carefully degassed solutions as described in the Experimental section. Since it is necessary to know the uninhibited rate of polymerization for the application of equation 22, this was determined, found to be dependent on the half power of the initiator concentration, and could be expressed as

$$\left[\frac{-\mathrm{d}\ln(\mathrm{M})}{\mathrm{d}t}\right]_{\mathrm{uninhib.}} \equiv R_0 = 8.00\times10^{-5}\,(\mathrm{AIBN})^{1/2}\,(\mathrm{l.}^{1/2}\,\mathrm{mole}^{-1/2}\,\mathrm{sec.}^{-1})$$

TABLE I

EFFECT OF TERMINATORS ON METHYL METHACYLATE POLYMERIZATION

Terminator	(AIBN) $\times 10^2$, moles/l.	(Terminator) $\times 10^3$, moles/l.	$\phi \times 10^2$
Benzoquinone	2.56	5.89	3.25
Benzoquinone	2.37	3.34	5.32
Benzoquinone	2.46	2.49	7.14
Benzoquinone	2.49	1.59	11.3
Benzoquinone	1.46	2.51	5.96
Benzoquinone	0.79	3.02	3.47
Benzoquinone	0.49	3.35	2.72
Chloranil	0.74	4.94	74.2
Chloranil	0.74	2.67	83.0
Chloranil	2.38	2.50	86.2
Chloranil	0.30	5.16	71.1
Furfurylidene	2.25	12.9	5.15
Malononitrile	2.25	6.62	11.2
Malononitrile	2.31	2.65	25.0
Malononitrile	3.47	6.25	14.6
Malononitrile	0.79	5.94	6.05
Trinitrotoluene	2.37	76.7	29.3
Trinitrotoluene	2.35	39.5	44.4
Trinitrotoluene	2.42	7.70	82.9
Trinitrotoluene	3.60	40.5	47.5
Trinitrotoluene	0.87	45.3	34.7
Sulfur	2.11	2.96	85.8
m-Dinitrobenzene	2.13	239	59.6
m-Dinitrobenzene	2.06	171	68.4
m-Dinitrobenzene	2.38	96.0	78.6
m-Dinitrobenzene	0.80	121	67.5
m-Dinitrobenzene	0.34	128	58.2
Benzhydrilidene malononitrile	2.41	2.64	97.0

p-Nitrotoluene gave no measurable retardation in rate when present in concentrations up to 0.04 *M*. Diphenylamine was without retarding effect even at concentrations of 0.2 *M*.

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

[12] The upper limit of one was chosen because previous work in the field of copolymerization[13,14] has shown that cross-termination is usually a rather favored mode of termination for dissimilar radicals, *i.e.*, $k_\mathrm{c}^2/k_\mathrm{t}k_\mathrm{z} >> 1$.

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

[14] H. W. Melville and L. Valentine, *Proc. Roy. Soc.* (*London*), **A200**, 337, 358 (1950); H. W. Melville and E. T. Arlman, *ibid.*, **A203**, 301 (1950).

The data for the inhibited runs were obtained using the same technique, and the results are tabulated in Table I. The initial rates in all cases were constant over a long enough period of time to permit their accurate determination, as is evident from the typical plots shown in Fig. 1.

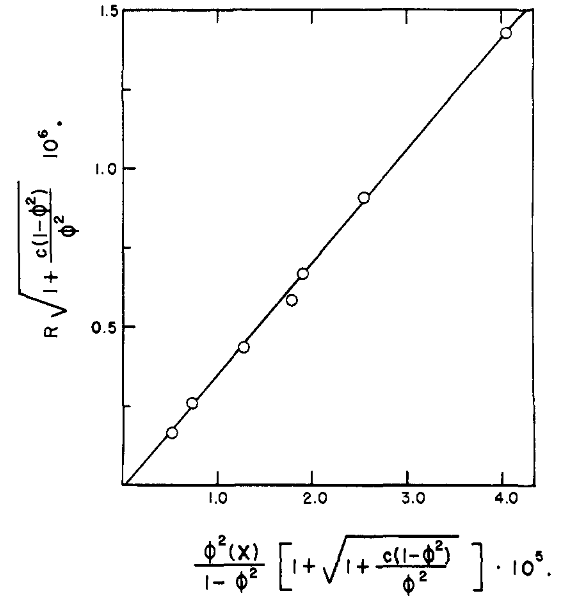


Fig. 2.—Results for benzoquinone plotted according to equation 22 for $c = 10^{-4}$.

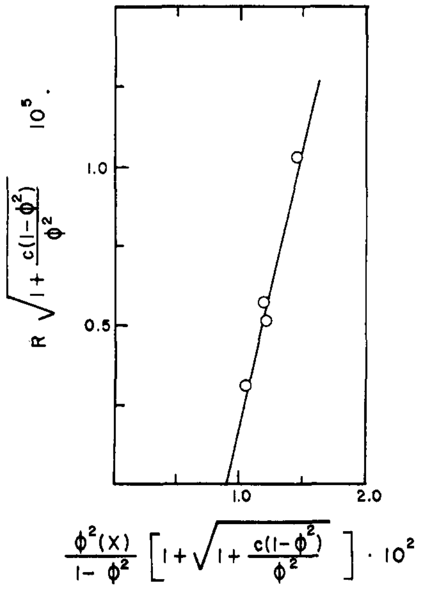


Fig. 3.—Results for chloranil plotted according to equation 22 for $c = 10^{-2}$.

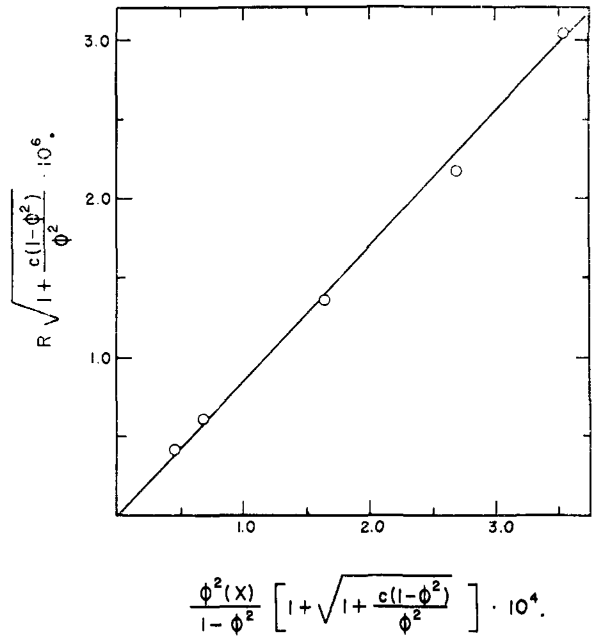


Fig. 4.—Results for furfurylidene malononitrile plotted according to equation 22 for $c = 10^{-4}$.

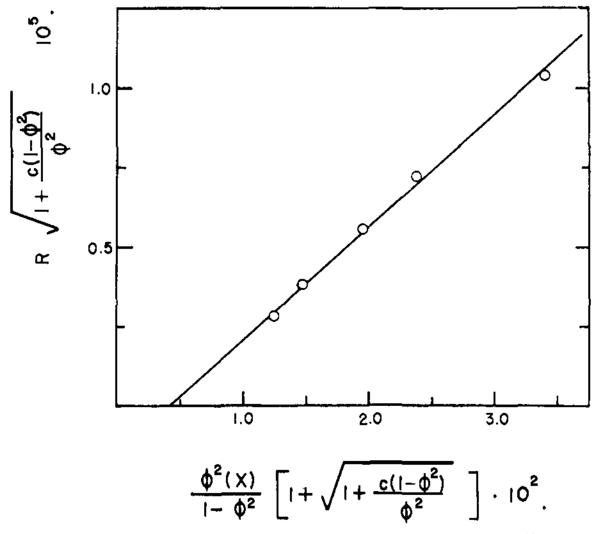


Fig. 5.—Results for trinitrotoluene plotted according to equation 22 for $c = 10^{-2}$.

As can be seen from Table I, the last three compounds were inactive within the sensitivity of our measurements. A fourth, sulfur, was so insoluble in methyl methacrylate as to preclude extension of the measurements to the higher sulfur concentrations necessary for an accurate determination of its k_x value. The data for the remaining compounds were treated according to equation 22 by the method described in the preceding section, and typical plots are shown in Figs. 2–5. In all cases it was easy to determine which value of c gave the least deviation of the experimental points from a straight line, and it is significant that in all five cases the best plots were obtained using values of c sufficiently small that the second term under the square root was effectively negligible for all runs with a given terminator. If this behavior is found to be generally observed it would be possible to simplify equation 22 to the form

$$\frac{\phi^2(X)}{1-\phi^2} = \frac{k_tR}{k_pk_x} + \frac{k_0(M)}{k_x}\,\frac{k_t}{k_0} \tag{22a}$$

Unless the present analysis is greatly in error, this indicates that reaction 5 (R· + Z·) is the predominant mode of Z· termination in all cases studied. While this might well have been expected for those runs with relatively high ϕ values, it is somewhat unexpected for those runs with low ϕ values where

(R·) is much smaller. Apparently cross-termination is even more favored in this case than the previous results[13,14] in the field of copolymerization would have led one to suspect. A possible but considerably less plausible alternative is discussed in the footnote below.[15]

From the slopes and intercepts of the plots the desired rate constants, k_x and k_0/k_c, were obtained using values of $2k_t$ and k_p calculated for this temperature from the data of reference 11 assuming termination to be by disproportionation[16] ($2k_t = 3.0 \times 10^7$, $k_p = 460$). The results are listed in Table II.

TABLE II

RATE CONSTANTS FOR TERMINATORS IN METHYL METHACRYLATE POLYMERIZATION

Compound	k_x(l. mole^{-1} sec.$^{-1}$)	k_x/k_p	$(k_0/k_c) \times 10^{10}$
Benzoquinone	2400	5.5	0.05
Chloranil	120	0.26	40
Furfurylidene malononitrile	550	1.2	0.05
Sulfur	(40)	(0.075)	...
Trinitrotoluene	23	0.05	3.7
m-Dinitrobenzene	2.2	0.0048	5.0
p-Nitrotoluene	Too small to be measured		
Diphenylamine	Too small to be measured		

Since the plots of the data seem to show that termination by reaction 6 can be neglected, one may estimate the extent of wastage of terminator through reaction 4 from the values of k_0/k_c. Thus the fraction of Z· which disappears by reaction 4, γ, is equal to

$$\gamma = \frac{k_0(\mathrm{M})}{k_0(\mathrm{M}) + k_c(\mathrm{R}\cdot) + 2k_z(\mathrm{Z}\cdot)} \cong \frac{k_0(M)}{k_0(\mathrm{M}) + k_c(\mathrm{R}\cdot)} \quad (23)$$

and substituting for (R·) and rearranging one obtains

$$\gamma = \frac{1}{1 + \left(\frac{R}{k_p(\mathrm{M})}\right)\left(\frac{k_c}{k_0}\right)} = \text{fraction of terminator molecules consumed which fails to stop chains} \quad (24)$$

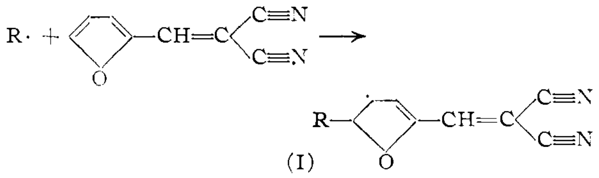
Benzoquinone and Chloranil.—It seems appropriate to discuss these two compounds together since, although closely related in chemical structure, their observed effect on methyl methacrylate polymerization is radically different.

In corroboration of Melville's results at 30°[6] benzoquinone was not found to copolymerize extensively (k_0/k_c only 0.5×10^{-11}). Such a value corresponds to 3% wastage of terminator through reaction 4 at a rate of polymerization of 6×10^{-7} sec.$^{-1}$ (a typical rate of polymerization observed in the runs with quinone). For comparison with the present investigation, Melville's[6] data yield a value of k_x, as defined here, of 1.8×10^3 at 30°, which is in reasonable agreement with the present value of 2.4×10^3 at 44.1°. It is also noteworthy that from molecular weight studies and other considerations Melville[6] was led to the conclusion that reaction 5 was the predominant mode of Z· termination, a conclusion also reached from kinetic evidence in the present investigation.

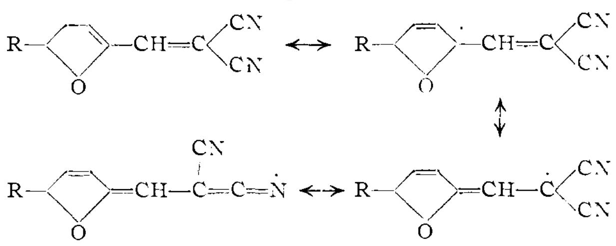
With chloranil one notices that k_x is less by a factor of 20, while k_0/k_c is almost three powers of ten greater. Evaluation of γ for a rate of polymerization of 5×10^{-6} sec.$^{-1}$ (a typical rate of polymerization observed in the chloranil runs) shows that in these experiments about 80% of the Z· radicals were being consumed through reaction 4. The observed behavior of chloranil in methyl methacrylate polymerization is thus similar to its action in styrene polymerization. In that case Brietenbach[17] was able to show by chemical degradation that styrene polymerized in the presence of large quantities of chloranil yielded essentially a 1:1 copolymer of the two compounds. Previous workers have also inferred from certain evidence[18] that benzoquinone behaved similarly in thermal styrene polymerization. However, the recent work of Russell and Tobolsky[19] demonstrates that in that case the rapid disappearance of quinone may be due to a totally different effect.

Certainly it is evident from the present investigation that in methacrylate polymerization the behavior of the two compounds is totally different, and consequently their action in other monomers is currently being investigated in an effort to determine the cause and generality of this phenomenon.

Furfurylidene Malononitrile.—This compound is reported to be a good inhibitor for styrene polymerization.[20] For that reason it was of interest to determine its effectiveness in arresting methacrylate polymerization. As can be seen from Table II it was approximately four times less efficient than benzoquinone. While no chemical evidence was secured on the exact nature of its action, it would seem reasonable to suppose that addition of R· to the compound by reaction 3



produces a radical which has enhanced stability by virtue of the resonance possibilities



Arguing for the above mechanism and against one postulating the formation of a stabilized radical through addition of the growing chain to the cyano group, is the fact that benzhydrilidene malononi-

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[15] It should be noted that in those cases in which the intercept is effectively zero (no wastage of Z· through reaction 4) it is also possible due to the nature of equation 22, to fit the data by assuming only Z· + Z· termination, *i.e.*, $c > 1$. However, when considered in the light of previous work[13,14] these values of c seem so high as to be unreasonable.

[16] J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Poly. Sci.*, **12**, 449 (1954).

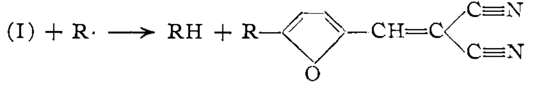
[17] J. W. Brietenbach and A. J. Renner, *Can. J. Research*, **28B**, 507 (1950).

[18] F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1285 (1948).

[19] K. E. Russell and A. V. Tobolsky, *ibid.*, **75**, 5052 (1953).

[20] R. N. Haward, private communication.

trile, $(C_6H_5)_2C{=}C(CN)_2$, was found to be essentially without retarding effect under similar conditions. Stabilization of radical I may well take place through the following reaction



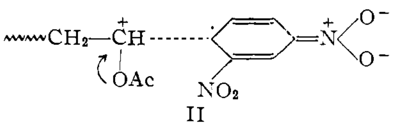
The Aromatic Nitro Compounds.—It is evident from the data in Table II that these compounds have but little effect in retarding the polymerization of methyl methacrylate. This is in striking but not wholly unexpected contrast to the results of Bartlett and Kwart[1] with vinyl acetate. For comparison their values of k_x/k_p have been converted to absolute values of k_x by multiplying by k_p for vinyl acetate (2320), evaluated at 45° from the data of other workers.[21]

	k_x (mole^{-1} l. sec.$^{-1}$) × 10^{-5}
s-Trinitrobenzene	20.5
m-Dinitrobenzene	2.46
p-Nitrotoluene	0.232

While the activity of the di- and tri-nitro compounds differs by approximately one power of ten in both monomers the absolute magnitude of the values for k_x decreases by about five powers of ten on changing from vinyl acetate to methyl methacrylate. This immense difference in activity is not unexpected in view of the chain transfer constants previously reported for the two monomers.[22–25] When these are multiplied by k_p to convert them into absolute values for the rate of reaction of polymer radical and transfer agent, the following results are obtained for several representative transfer agents for which data are available for both monomers. Also included in the table is sulfur, another terminator for which data are available in both monomers.

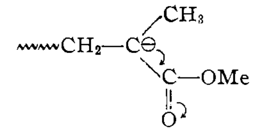
	k_{xVA}/k_{xMMA}	
n-Butyl mercaptan	3.6×10^2	ref. 25, 22
Tetrachloroethane	2.5×10^5	ref. 24, 22
Toluene	0.9×10^3	ref. 23, 22
Sulfur	1.5×10^4	ref. 1

While the difference is large in all cases, the nitro compounds appear to be somewhat less reactive toward methyl methacrylate radical than the majority of the compounds above. A possible explanation for this is available in terms of the concepts first enunciated by Mayo and Walling.[13] Thus the nitro compounds should certainly prefer to function as electron acceptors and the vinyl acetate radical as an electron donor, which could lead to structures of type II in the transition state and a consequent lowering of the activation energy.



II

With methyl methacrylate radical, which prefers a role as electron acceptor due to the possibility of the resonance structure



such an electron transfer with the nitro compound is not feasible, and there is no lowering of the activation energy due to such structures as II.

Picrylhydrazyl.—In addition to the compounds listed in Table II experiments were also carried out with 2,2-diphenyl-1-picrylhydrazyl as the added terminator. The use of this stable free radical as a polymerization inhibitor was first described by Bartlett and Kwart.[1] In discussing its action on polymerization one need take cognizance only of reactions 1–3 of the general kinetic scheme outlined earlier, since reaction of R· and hydrazyl yields a non-radical product. Consequently the kinetic equations are considerably simplified and, following the treatment of Bartlett and Kwart,[1] it is easy to derive equation 25

$$\ln(1-\alpha) = \frac{k_p}{k_x}\ln\left(1-\frac{t}{T}\right) \qquad (25)$$

where α equals the degree of conversion, T is the over-all length of the induction period and t is the time. For small α this reduces to

$$\alpha = -\frac{k_p}{k_x}\ln\left(1-\frac{t}{T}\right) \qquad (25a)$$

With picrylhydrazyl in vinyl acetate Bartlett

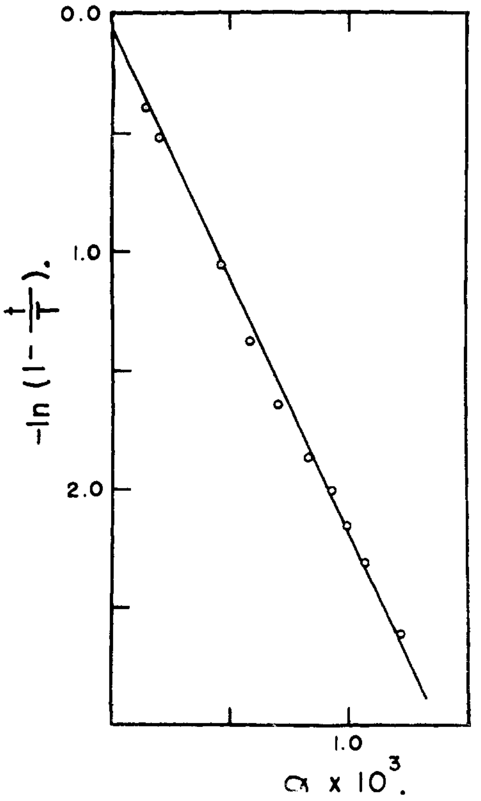


Fig. 6.—Data for run 2 with picrylhydrazyl plotted according to equation 25a.

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(21) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 2610 (1949); P. D. Bartlett, H. Kwart and H. S. Broadbent, *ibid.*, **72**, 1060 (1950).

(22) S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc.* (*London*), **A202**, 485 (1950).

(23) K. Nozaki, *Faraday Soc. Disc.*, **2**, 337 (1947).

(24) W. H. Stockmayer, J. T. Clarke and R. O. Howard, unpublished results.

(25) C. Walling, THIS JOURNAL, **70**, 2561 (1948).

and Kwart[1] found that no measurable amount of polymerization took place up to the end of the induction period. For this reason they were unable to determine the value of k_x/k_p. However, with methyl methacrylate a small but measurable amount of polymerization does take place prior to the end of the induction period, and after the end of this period the rate is found, within the experimental error, to be unretarded. The magnitude of k_x/k_p was obtained by plotting α *vs.* ln $(1 - (t/T))$ for the three runs with picrylhydrazyl; a typical plot is shown in Fig. 6. In addition the rate of decomposition of the initiator was calculated from the length of the induction period. The results obtained with picrylhydrazyl are summarized below in Table III.

From the average value of k_x obtained it is apparent that the hydrazyl is approximately 400 times more reactive toward methyl methacrylate radical than benzoquinone, the most active of the other terminators studied.

TABLE III

EFFECT OF DIPHENYLPICRYLHYDRAZYL ON METHYL METHACRYLATE POLYMERIZATION

Run	(AIBN) $\times 10^2$ (moles/l.)	(DPPH) $\times 10^4$ (moles/l.)	$k_d f$ for AIBN (sec.$^{-1}$), calcd. from induction period	k_x/k_p
2	2.50	5.4	6.9×10^{-7}	2100
3	2.33	2.6	7.9×10^{-7}	2000
4	3.16	4.2	7.2×10^{-7}	2000

Av. value of k_x = 920,000

A similar study of the behavior of terminators in methyl acrylate polymerization will be the subject of a future paper.

Acknowledgments.—The author wishes to thank Drs. T. G Fox and S. Gratch of these laboratories for their helpful comments and advice; the author is also indebted to Mr. C. A. Cooper for his assistance with the experimental portion of this investigation.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Side Chain Crystallization of *n*-Alkyl Polymethacrylates and Polyacrylates[1]

BY SIDNEY A. GREENBERG[2] AND TURNER ALFREY

RECEIVED MAY 17, 1954

In this study of side chain crystallinity, methacrylate and acrylate monomers, with *n*-alkyl groups containing from 12 to 18 carbon atoms, were synthesized, polymerized and copolymerized; dilatometric measurements were made on these polymers to determine the changes in specific volume with temperature and time; spacings were obtained from Debye–Scherrer patterns taken at small and wide angles. The following results were noted: the specific volume–temperature plots were S-shaped, typical of first-order transitions; crystallization was rapid and accompanied by very little supercooling; melting ranges were short except for the mixed long chain copolymers; long and short spacings were found in the X-ray patterns. The melting ranges of the polymers did not depend on the temperature of the cooling bath.

Introduction

In this paper there is described an investigation of the side chain crystallinity found in polymethacrylates and polyacrylates with *n*-alkyl groups from 12 to 18 carbon atoms in length. These crystalline polymers differ from crystalline polyethylene[3a] and natural rubber[3b] in that the crystallites are made up of the *n*-alkyl groups which extend from the backbone of the molecules, rather than of segments of the backbone itself.

Rehberg and Fisher[4] prepared a series of the polyacrylates and methacrylates and found that the brittle points of these polymers, beginning with polydodecyl methacrylate and polyoctyl acrylate, increase with the lengths of the *n*-alkyl groups. This increase in brittle points has been attributed[5] to the higher melting points of the polymers with longer alkyl groups.

Very little appears in the literature on the subject of side chain crystallinity. Barrer[6] predicted crystallization of long side chains, and in the same discussion Crisp stated that the properties of polyoctadecyl methacrylate surface films were affected by the interactions of the long side chains. Wiley and Brauer[7] found breaks in the index of refraction *versus* temperature curves of polyhexadecyl and polytetradecyl acrylates and of polyhexadecyl methacrylate. These breaks occurred in the same temperature ranges as the brittle points of the polymers. Similarly, polyvinyl palmitate and stearate and the copolymers of vinyl stearate and vinyl acetate were prepared by Swern and Jordan[8] and are hard wax-like solids, which indicates that the side chains have probably crystallized.

In this study of the structure and crystalline–amorphous equilibrium of the various polymers, the following experimental work was carried out.

(1) The long chain (12 to 18 carbon atoms) acrylate and methacrylate monomers were synthesized by the alcoholysis of methyl acrylate and methyl methacrylate.

(2) Monomers, thus synthesized, were polymerized in bulk, emulsion or solution, and co-

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[1] Abstracted in part from a dissertation presented by Sidney A. Greenberg to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Summaries of this work were presented before the Division of Polymer Chemistry, American Chemical Society Meeting, Chicago, Illinois, September, 1950.

[2] Johns-Manville Research Center, Manville, New Jersey.

[3] (a) E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945); (b) L. A. Wood and N. J. Bekkedahl, *J. Research Natl. Bur. Standards*, **36**, 489 (1946).

[4] C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

[5] H. S. Kaufman, A. Sacher, T. Alfrey and I. Fankuchen, THIS JOURNAL, **70**, 3147 (1948).

[6] R. M. Barrer and D. J. Crisp, *Trans. Faraday Soc.*, **38**, 431 (1942).

[7] R. H. Wiley and G. M. Brauer, *J. Polymer Sci.*, **3**, 647 (1948).

[8] D. Swern and E. F. Jordan, THIS JOURNAL, **70**, 2334 (1948).