# Inhibition of Polymerization.   II.   Methyl Acrylate

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In a previous communication[1] we presented the results of an investigation of the behavior of various terminators in the 2,2'-azobisisobutyronitrile (AIBN) initiated polymerization of methyl methacrylate. The present paper deals with a study of the behavior of these same terminators in the AIBN initiated polymerization of methyl acrylate; two additional compounds, 2,6- and 2,5-dichlorobenzoquinone, have also been studied in both monomers. All of these investigations have been carried out at the same temperature, and they consequently permit a direct comparison of terminator effectiveness in the two monomers, enabling one to draw some tentative conclusions regarding the factors influencing the pertinent reaction rates.

The most noteworthy feature of the bulk polymerization of methyl acrylate is a rapid acceleration of the rate, almost from zero conversion, due to the formation of an immobile crosslinked network.[2,3] This phenomenon renders an accurate measurement of the initial rate in bulk exceedingly difficult. To avoid this complication the present rate measurements were carried out in methyl propionate solution at a methyl acrylate concentration of 3 M. Under such conditions there is no acceleration of the initial rate below 12% conversion. This change to solution polymerization should not affect the results significantly since the chief radical formed by chain transfer with solvent will be I which, being similar in structure to a growing methyl acrylate chain, II, would be expected to have comparable reactivity toward monomer and inhibitor.
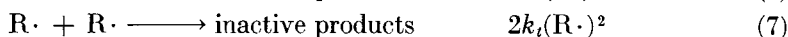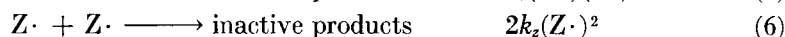
$$CH_3—CH \cdot$$
$$\overset{|}{C}OOCH_3$$
$$(I)$$
$$\sim\!\!\sim CH_2—CH \cdot$$
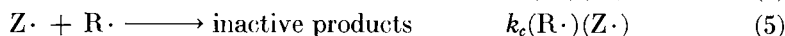$$\overset{|}{C}OOCH_3$$
$$(II)$$
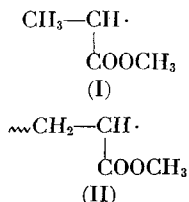
The rate measurements on the two dichloroquinones in methyl methacrylate were carried out as before[1] in bulk monomer.

KINETICS OF INHIBITION

The following scheme has again been assumed to be representative of the mode of action of most terminators (inhibitors and retarders). Here X is

the added terminator, and $Z\cdot$ is the radical formed by reaction of an initiator or polymer free radical, $R\cdot$, with X:

$$I \longrightarrow 2R\cdot \qquad\qquad 2k_d f(I) \qquad\qquad (1)$$
$$R\cdot + M \longrightarrow R\cdot \qquad\qquad k_p(R\cdot)(M) \qquad\qquad (2)$$
$$R\cdot + X \longrightarrow Z\cdot \qquad\qquad k_x(R\cdot)(X) \qquad\qquad (3)$$
$$Z\cdot + M \longrightarrow R\cdot \qquad\qquad k_0(Z\cdot)(M) \qquad\qquad (4)$$
$$Z\cdot + R\cdot \longrightarrow \text{inactive products} \qquad\qquad k_c(R\cdot)(Z\cdot) \qquad\qquad (5)$$
$$Z\cdot + Z\cdot \longrightarrow \text{inactive products} \qquad\qquad 2k_z(Z\cdot)^2 \qquad\qquad (6)$$
$$R\cdot + R\cdot \longrightarrow \text{inactive products} \qquad\qquad 2k_t(R\cdot)^2 \qquad\qquad (7)$$

Following the derivation given in the previous paper[1] it is possible to obtain from the above scheme the following equation relating rate and terminator concentration:

$$\frac{\phi^2(X)}{1 - \phi^2}\left[1 + \left(1 + \frac{c(1 - \phi^2)}{\phi^2}\right)^{1/2}\right] =$$

$$\frac{2k_t R}{k_p k_x}\left(1 + \frac{c(1 - \phi^2)}{\phi^2}\right)^{1/2} + \frac{2k_t}{k_x}\cdot\frac{k_0(M)}{k_c} \qquad (8)$$

where $R \equiv (-d\ln(M)/dt)$ = rate of polymerization in presence of terminator, $R_0 \equiv (d\ln(M)/dt)_{\text{uninhibited}}$ = rate of polymerization in absence of terminator at same initiator concentration, $\phi = R/R_0$, and $c = 4k_tk_z/k_c^2$.
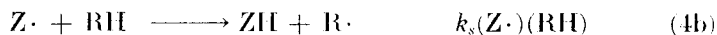
From equation (8) it is evident that a plot of:

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

for the various runs with a given terminator should be a straight line of slope $2k_t/k_pk_x$ and intercept $2k_tk_0(M)/k_xk_c$. Since k_t and k_p for methyl acrylate have been measured by Matheson and coworkers,[2] k_x and k_0/k_c for a terminator in methyl acrylate may be evaluated from the slope and intercept, respectively, of the plot. The data obtained with the two dichloroquinones in methyl methacrylate may be analyzed in similar fashion using the values of k_p and k_t for that monomer employed earlier.[1]

In order to make the plot described above it is necessary to assume a value of c for the terminator-monomer system in question. As in the previous paper[1] plots of the data for each terminator-monomer pair were made using different assumed values of c. 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 k_0/k_c were obtained from the slope and intercept of this "best" straight line.

It should be noted that the inclusion in the above kinetic scheme of the two additional reactions shown below does not alter the general

$$Z\cdot \longrightarrow R\cdot + X \qquad\qquad k_y(Z\cdot) \qquad\qquad (1a)$$
$$Z\cdot + RH \longrightarrow ZH + R\cdot \qquad\qquad k_s(Z\cdot)(RH) \qquad\qquad (1b)$$

form of equation (8) since it merely replaces k_0 by the expression $(k_0 + k_s(RH)/(M) + k_y/(M))$, which under our conditions is itself a constant. The first of these reactions is suggested by the recent work of Hammond,[4] which indicates such a process may occur more generally in radical reactions than had previously been supposed. The probable structure of some of the $Z \cdot$ radicals renders hydrogen abstraction from methyl propionate of sufficient likelihood relative to reaction (4) that reaction (4b) may be of measurable importance for some of the terminators in the runs with methyl acrylate. Unfortunately our present knowledge does not permit quantitative assessment of the relative importance of reactions (4), (4a), and (4b). Consequently the values of k_0/k_c obtained from the intercepts of the plots are probably more correctly taken to be k_0'/k_c, where:

$$k_0' = k_0 + k_s \frac{(RH)}{(M)} + \frac{k_y}{(M)}$$

RESULTS

All of the runs were carried out *in vacuo* on carefully degassed solutions following the procedure described in the experimental section.
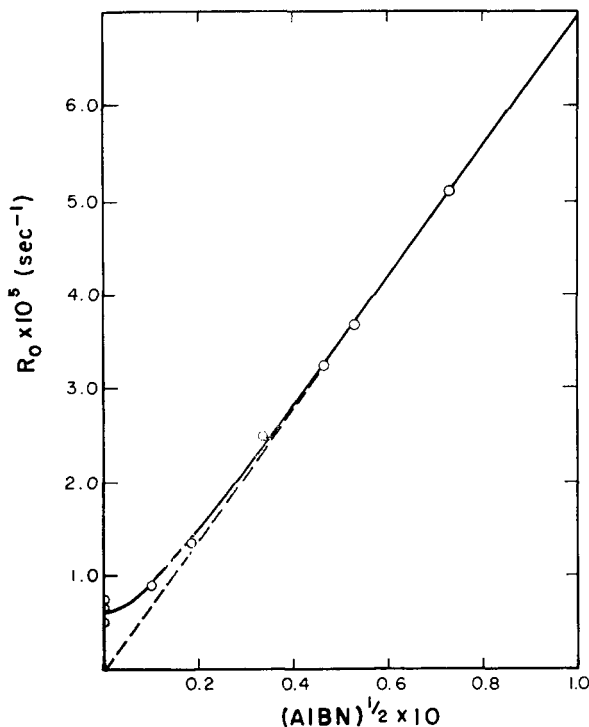

Fig. 1. Plot of the uninhibited rate of polymerization, R_0, vs. $(AIBN)^{1/2}$ for methyl acrylate (3 M) in methyl propionate solution. Solid line corresponds to the relation, $R_0 = 69.4 \times 10^{-5} [(AIBN) + 8 \times 10^{-5}]^{1/2}$.

The uninhibited rate of the AIBN-initiated polymerization of methyl methacrylate at 44.1° has already been measured.[1]   The uninhibited rate of polymerization of methyl acrylate at the same temperature in methyl propionate solution was determined, using azobisisobutyronitrile as initiator, over a fifty fold range of initiator concentration at a constant monomer concentration of 3 M (Fig. 1).   The results at very low initiator concentrations showed a slight positive deviation from the expected half-

TABLE Ia

RESULTS IN METHYL ACRYLATE FOR TERMINATORS AT 44.1°

Compound	(Terminator) $\times 10^3$, moles/liter	(AIBN) $\times 10^3$, moles/liter	$\phi \times 10^2$
Benzoquinone	2.70	1.87	3.95
	2.44	4.83	5.84
	2.18	11.7	8.62
	1.38	4.72	9.24
	0.44	4.65	23.6
2,6-Dichlorobenzoquinone	1.40	12.2	0.81
	0.72	12.4	1.57
	0.45	12.7	2.53
	0.45	5.99	1.80
2,5-Dichlorobenzoquinone	1.51	12.1	1.07
	0.76	12.3	2.34
	0.51	12.4	3.55
	0.50	5.89	2.49
Chloranil	2.55	4.21	3.30
	1.26	4.22	5.65
	0.49	5.07	13.6
	1.26	10.2	8.20
	1.25	1.77	5.12
Furfurylidene malononitrile	1.60	5.36	2.95
	1.60	12.4	4.11
	1.56	2.62	2.25
	0.79	5.63	5.61
	0.40	5.21	10.56
Sulfur	2.19	1.96	5.14
	0.92	4.09	12.6
	1.07	8.80	14.8
	1.61	5.71	8.67
Trinitrotoluene	12.9	2.32	6.40
	6.46	2.26	12.6
	3.57	2.25	20.9
	6.00	5.02	19.4
	6.35	7.54	21.4
m-Dinitrobenzene	18.8	2.61	8.96
	9.34	2.59	17.0
	5.58	2.61	26.4
	9.14	6.39	24.9
	8.86	1.29	13.8
Diphenylamine	9.23	3.37	97.1
	4.50	3.10	98.0

TABLE Ib

RESULTS IN METHYL METHACRYLATE FOR TERMINATORS AT 44.1°

Compound	(Terminator) × 10³, moles/liter	(AIBN) × 10², moles/liter	$\phi \times 10^2$
2,6-Dichlorobenzoquinone.................	3.27	2.56	1.02
	1.62	2.46	1.85
	1.05	2.94	2.89
	1.10	1.10	2.08
2,5-Dichlorobenzoquinone...	3.08	2.53	2.98
	1.52	2.51	5.88
	0.99	2.57	8.36
	1.06	1.25	6.38
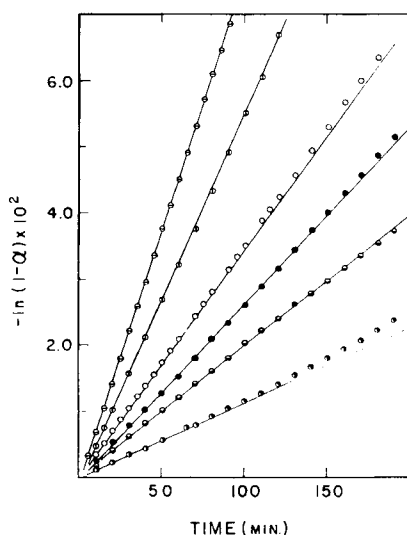
Fig. 2. Plots of conversion, ln $(1 - \alpha)$, *vs.* time for some typical runs in methyl acrylate with the various terminators: ⊖; (TNT) = 6.35×10^{-3}, (AIBN) = 7.54×10^{-3}. ⊙; (dinitrobenzene) = 5.58×10^{-3}, (AIBN) = 2.61×10^{-3}. O; (chloranil) = 1.26×10^{-3}, (AIBN) = 10.2×10^{-3}. ●; (benzoquinone) = 1.38×10^{-3}, (AIBN) = 4.72×10^{-3}. ◉; (FMN) = 1.60×10^{-3}, (AIBN) = 12.4×10^{-3}. ◑; (2,6-dichloroquinone) = 0.45×10^{-3}, (AIBN) = 12.7×10^{-3}.

order dependence on catalyst, corresponding to the relation:

$$R_0^2 = 4.80 \times 10^{-7} \text{ (AIBN)} + 4 \times 10^{-11} \text{ (sec.}^{-2})$$

or:

$$R_0 = 69.4 \times 10^{-5} [\text{(AIBN)} + 8 \times 10^{-5}]^{1/2} \text{ (sec.}^{-1})$$

Subsequent experiments in which no initiator was used demonstrated the presence of a small and somewhat erratic "thermal" rate of polymerization, possibly due to the presence of small amounts of peroxidic impurities in either the monomer or the methyl propionate.

In order to minimize errors due to the slightly erratic nature of the "thermal" rate all of the inhibited methyl acrylate runs were carried out at initiator concentrations sufficiently higher than 8×10^{-5} M that any variation in the "thermal" rate had a negligible effect on the overall rate of polymerization.

The data for the inhibited methyl acrylate runs are shown in Table Ia. The data for the inhibited methyl methacrylate runs with the two dichloroquinones are shown in Table Ib.   In all cases the initial rates were constant over a long enough period of time to permit their accurate determination. Figure 2 shows some typical runs in methyl acrylate.

The data for the various compounds were plotted according to equation (8) using the method outlined in the preceding section and described in full earlier.[1]   As in the previous study[1] it was found that in each case the least deviation of the experimental points from a straight line was obtained when c was sufficiently small that the second term under the square root was essentially negligible for all runs with a given terminator.   It has been pointed out[1] that this indicates reaction 5 is the predominant mode of $Z \cdot$ termination.

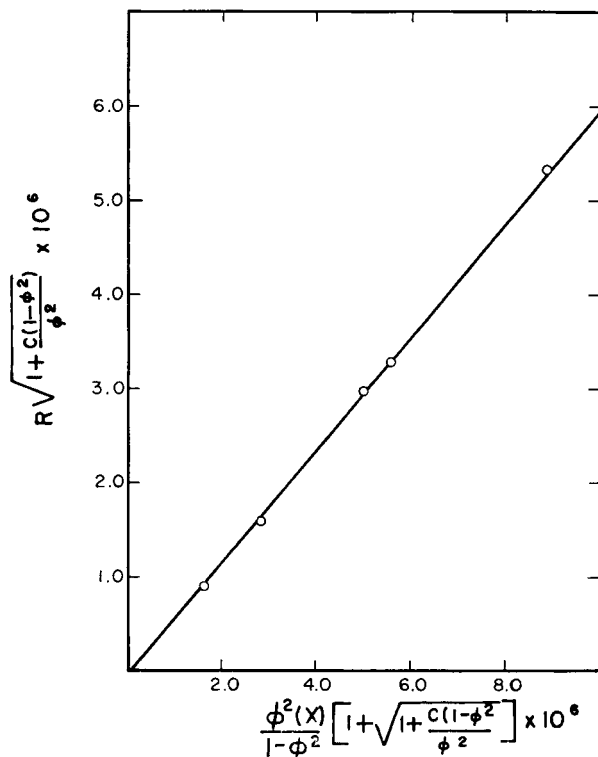Plots of the methyl acrylate data for some of the terminators according

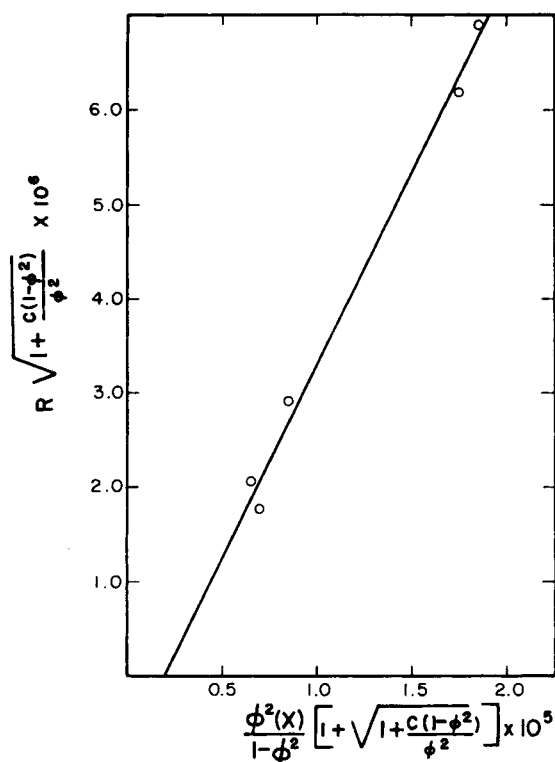Fig. 3. **Results for furfurylidene malonitrile plotted according to equation (8) for $c = 10^{-4}$.**

Fig. 4. Results for chloranil plotted according to equation (8) for $c = 10^{-3}$.

to equation (8) are shown in Figures 3–7. From the slopes and intercepts of such plots values for the pertinent rate constants were determined using values of k_p and k_t calculated for 44.1° from the data of Matheson et al.[2] ($k_p = 1280$; $2k_t = 6.2 \times 10^6$). The results are shown in Table II.

TABLE II

RATE CONSTANTS FOR TERMINATORS IN METHYL ACRYLATE AT 44.1°

Compound	k_x, l. mole^{-1} sec.$^{-1}$	$(k_0'/k_c) \times 10^{10}$
Benzoquinone	1,200	1.5
2,6-Dichlorobenzoquinone	16,700	0.07[a]
2,5-Dichlorobenzoquinone	10,200	0.04[a]
Chloranil	2,000	2.0
Furfurylidene malononitrile	2,900	0.2[a]
Sulfur	1,100	2.3
Trinitrotoluene	105	0.7[a]
m-Dinitrobenzene	58	1.0
Diphenylamine	Too small to be measured	

[a] The magnitude of the intercept of the equation (8) plot is sufficiently small in these cases that the k_0'/k_c value must be regarded as only very approximate.

DISCUSSION

Since data are available for the reactivity of these same terminators in methyl methacrylate polymerization, a comparison of the methyl methacrylate values with those in Table II should prove informative. The results of reference 1 and those obtained in methyl methacrylate with the two dichloroquinones in the present study are shown in Table III.
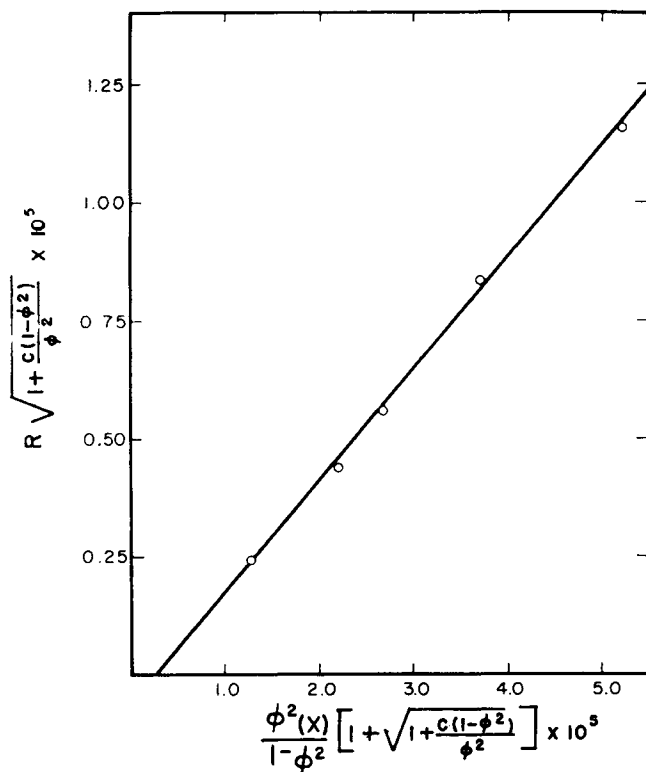

Fig. 5. Results for benzoquinone plotted according to equation (8) for $c = 5 \times 10^{-3}$.

Comparison of k_x Values in Methyl Methacrylate (MMA) and Methyl Acrylate (MA). When making a comparison of the rate constants in the two monomers it is important to remember that the experimental data yield directly a value of $k_t/k_p k_x$, and consequently the accuracy of the absolute values of k_x in Tables II and III is dependent on the accuracy of the values of k_t and k_p employed. For consistency we have used Matheson and co-workers' values for both monomers[2,5] (correcting in the case of methyl methacrylate for termination by disproportionation[6]). However, for the reasons outlined in the *Note* below, it is felt that, while k_p and k_t for methyl methacrylate are substantially correct, the values of k_p and k_t for methyl acrylate are subject to sufficient uncertainty that the k_x values in Table II

TABLE III

RATE CONSTANTS FOR TERMINATORS IN METHYL METHACRYLATE
AT 44.1°

Compound	$k_x,$ mole^{-1} sec.$^{-1}$	$(k_0'/k_c) \times 10^{10}$
Benzoquinone	2,400	0.05[a]
2,6-Dichlorobenzoquinone	16,500	0.1
2,5-Dichlorobenzoquinone	5,500	0.2
Chloranil	120	40
Furfurylidene malononitrile	550	0.05[a]
Sulfur	40[b]	—
Trinitrotoluene	23	3.5
m-Dinitrobenzene	2.2	4.5

[a] See footnote a of Table II.
[b] Value less reliable than other k_x values since low solubility of sulfur in methyl methacrylate precludes accurate measurement.

may all be in error by a constant factor (probably they are up to 1.4 times too high). For this reason any quantitative conclusions drawn from a direct comparison of the absolute values of k_x for a given terminator in acrylate and methacrylate are open to error. Comparisons based on the
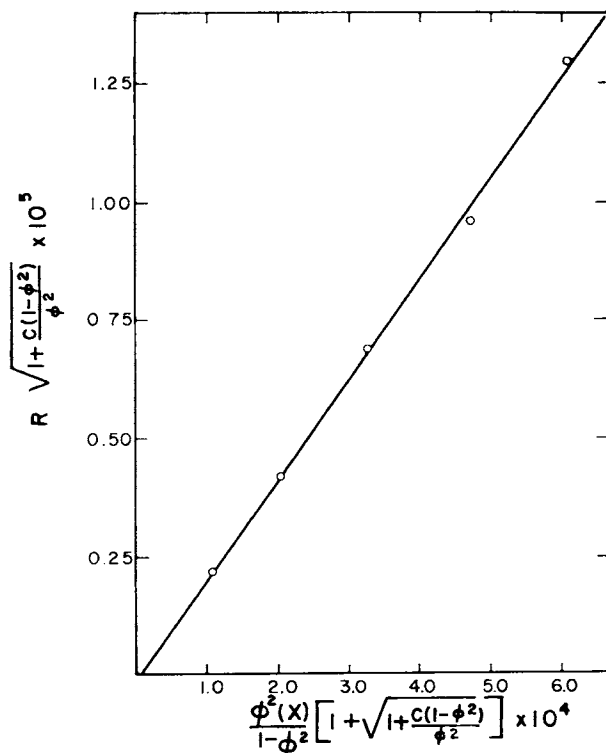

Fig. 6. Results for trinitrotoluene plotted according to equation (8) for $c = 10^{-3}$.

relative order of effectiveness of the terminators in the two monomers do not suffer from this difficulty. Accordingly, we shall confine our discussion chiefly to these latter considerations.
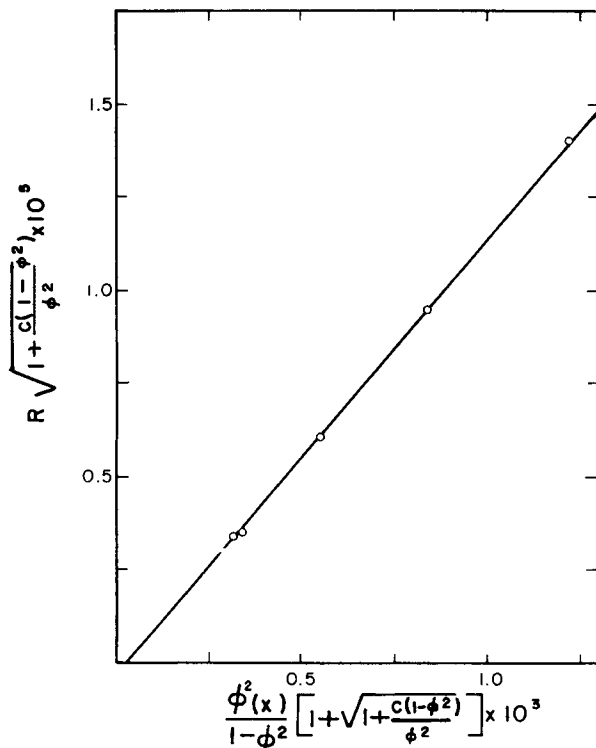

Fig. 7. Results for m-dinitrobenzene plotted according to equation (8) for $c = 10^{-3}$.

(*Note:* When the adopted values of k_p and k_t for methyl methacrylate[5,6] and k_d for AIBN[7] are substituted into the expression for the uninhibited rate of polymerization of that monomer given in reference 1, they require that f, the apparent efficiency of initiation, be about 0.5, a reasonable value in light of the results of Melville[6] and Arnett.[8] However, when a similar substitution is made in the methyl acrylate rate equation given earlier, the adopted values[2] of k_p and k_t require f be equal to one, a value which seems too high. Consequently k_p^2/k_t as calculated for this temperature from Matheson's data[2] is probably too low by a factor of up to two, which is not surprising since Matheson[2] states that his values of k_p and k_t for methyl acrylate are somewhat uncertain. Of course, the ratio, k_p/k_t, is not necessarily incorrect since k_p and k_t might both be too low by the same factor. However, in the absence of this particular compensating error, the k_x values in Table II are probably up to 1.4 times too large. When more accurate values of k_p and k_t for methyl acrylate become available the present k_x values will require multiplication by a suitable correction factor.)

Before discussing the specific differences shown in Tables II and III it is pertinent to review briefly the factors which might be expected to influence the rate of reaction (3). The relative reactivities of the methacrylate and

acrylate radicals toward a terminator should depend chiefly on three factors —the relative stabilities of the two polymer radicals; the polarization, polarizability, and electron donating-accepting properties of the radical and the terminator; and the extent of steric hindrance in the transition state.

The available data[9,10] on the stabilities of methyl methacrylate and methyl acrylate radicals indicate the acrylate radical to be less stable. Consequently, all else being equal, its rate of reaction with a given terminator should be greater than that for the methacrylate radical. However, the order of effectiveness of the various terminators in one monomer will not be changed in another monomer as a result of the difference in stability of the two polymer radicals since this difference will have the same effect on all terminators. Changes in the order of effectiveness, such as those evident from an examination of Tables II and III, can result only from polar and steric effects.

Previous work[10-12] has amply demonstrated the importance of polar effects in radical reactions, and accordingly the relative effectiveness of a terminator in the two monomers would be expected to vary from terminator to terminator due to the varying terminator polarities and the somewhat different polarities of the acrylate and methacrylate radical. Those terminators which are strongly electron attracting or accepting should react relatively less rapidly than expected with methyl acrylate since this monomer is somewhat more electron accepting than methyl methacrylate (the Price-Alfrey[13] e parameters are $+0.6$ for MA and $+0.4$ for MMA[14]).

Steric effects in radical reactions have not been extensively investigated, although such effects are claimed to be responsible for the extremely low values of k_p and k_t found for butyl acrylate[15] and for the low frequency factors observed for the methyl methacrylate rate constants.[5] In the present studies steric effects would be expected to be much more evident for reactions involving the tertiary methacrylate radical than for those involving the less hindered methyl acrylate radical.

Of the results in Tables II and III those with the four quinones seem most worthy of comment. Waters and co-workers[16,17] have found that the reaction of 2-cyanopropyl or 2-carbomethoxypropyl radicals with a large number of benzoquinones yields as products almost exclusively the mono and diethers of the corresponding hydroquinones. This would indicate that any changes in the relative reactivity of the various quinones apparent on comparison of their k_z values in methacrylate and acrylate must be ascribed to polar and steric effects rather than to differences in their mechanism for reaction (3). Moreover, the reasonable similarity of the attacking radicals employed by Waters *et al.* and those under study in this investigation suggests that in the present case radical attack also occurs primarily at the carbonyl oxygens, as shown below:

$$R\cdot + O = \!\!\!\bigcirc\!\!\!= O \longrightarrow RO - \!\!\!\bigcirc\!\!\! - O\cdot$$

Since the transfer in the transition state of an electron from an attacking radical to the quinone produces a canonical structure (III) in which the aromatization of the quinone ring has afforded a considerable gain in resonance energy, it seems reasonable to believe that the quinones are considerably more strongly electron attracting and accepting than any of the other

$$\left[R^+ \quad {}^-O\!-\!\!\left\langle\!\!\begin{array}{c}\diagup\diagdown\\\diagdown\diagup\end{array}\!\!\right\rangle\!\!-\!O\cdot \right] \qquad \text{(III)}$$
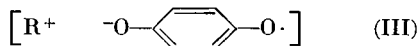
terminators we have studied. In view of the unfavorable situation with respect to electron donation by either methacrylate or acrylate radicals it is probable that structures of type III do not contribute greatly in either monomer. Nevertheless, because of the gain in stability provided by the aromatization of the quinone ring, they are doubtless of more importance than those (R$^+$ Inhibitor$\cdot$ $^-$) which would be formed by a similar electron transfer with the other terminators. Such structures (III) will be of lesser energy for methacrylate where the seat of the positive charge is a tertiary carbon than for acrylate where the charge is located on a secondary carbon. They will therefore contribute relatively more in methacrylate toward lowering the activation energy of reaction (3), and from such considerations it would be expected that the ratio $k_{z_{MA}}/k_{z_{MMA}}$ would be lower for the quinones than for the other compounds in Tables II and III. Examination of the data shows that this is indeed the case for three of the quinones— benzoquinone, 2,6-dichloroquinone, and 2,5-dichloroquinone—for which this ratio is 0.5, 1.0, and 1.9, respectively, as compared with values of from 4.5 to 27 for the other terminators. In marked contrast, however, the ratio for chloranil has a value of almost 17. Examination of any reasonable model for the chloranil-MMA transition state indicates that in all probability this different behavior is due to steric hindrance. Thus models show that the formation of the transition state from the tetrasubstituted quinone and the tertiary methacrylate radical may require deformation of normal bond angles and distances, and that rotation is extremely restricted. Further, while we are uncertain as to the steric requirements of the R$\cdot$ + quinone reaction, it is quite possible that maximum stabilization of the transition state is only achieved by coplanarity of the incipient radical-oxygen bond and the quinone ring. Such an orientation is, of course, sterically inhibited in the methyl methacrylate-chloranil case.

The presence of an "*ortho* effect" in the methyl methacrylate-chloranil reaction is not unexpected in view of the frequent occurrence of steric retardation in the reactions of *o*-substituted benzoates, benzoyl halides, benzonitriles, etc.[18] It is also historically interesting to recall that some of the earliest evidence for steric hindrance was afforded by Kehrmann's[19] demonstration that two *o*-substituents prevented (and one *o*-substituent hindered) oxime formation by the carbonyl group of a quinone.

Closer examination of the data for the four quinones suggests that the magnitude of the steric effect in the MMA-chloranil reaction is perhaps somewhat greater than is at first apparent. Thus the results with 2,5-

dichloroquinone in the two monomers indicate the possible existence of some slight steric hindrance for the reaction of this compound with methyl methacrylate radical. If this is actually the case, a slight steric retardation would also be expected in the chloranil-methyl acrylate reaction; and consequently the ratio for chloranil of $k_{x_{MA}}/k_{x_{MMA}}$ would give somewhat too low an estimate of the importance of steric factors in methyl methacrylate. Comparison of the k_x values for the three chloroquinones in methyl acrylate lends some support to this belief. However, we recognize that factors other than steric hindrance may be of equal importance in contributing to the relatively low value of k_x for chloranil in methyl acrylate.

In the course of a broad investigation of the effect of quinones on the polymerization of methyl acrylate Breitenbach and Fally[20] studied the four quinones used in the present work. With allowance for the probable lesser precision of their gravimetric technique, their results are in quite good agreement with those in Table II.

Let us now consider the results obtained with the other compounds that showed inhibitory activity—sulfur, dinitrobenzene, trinitrotoluene, and furfurylidene malononitrile. As none of these possess structural features which would lead to a driving force for electron donation by R· comparable to that existing in the quinones, it is not surprising that the ratio $k_{x_{MA}}/k_{x_{MMA}}$ is larger in all four cases than the ratios observed with the three unhindered quinones. The magnitude of the $k_{x_{MA}}/k_{x_{MMA}}$ values increases in the order, trinitotoluene $\leqq$ furfurylidene malononitrile $<$ dinitrobenzene $\leqq$ sulfur. Since it is easy to conceive of both the trinitro compound and the malononitrile being far more strongly electron accepting than sulfur the results for these three compounds are certainly qualitatively as expected. That sulfur is far less electron accepting than the nitro compounds is borne out by a comparison of the results in Table II with those obtained by Bartlett and Kwart[21] in vinyl acetate. In vinyl acetate k_x for sulfur is only about five times that for m-dinitrobenzene while in methyl acrylate the sulfur rate constant is nearly twenty times that of its dinitrobenzene counterpart.

The results for dinitrobenzene, however, seem somewhat out of line. For while one would expect the dinitro compound to be less strongly electron accepting than trinitrotoluene and therefore to have, as is found, a relatively larger increase in k_x on going from methacrylate to acrylate, one would not think the removal of only one nitro group could bring about as large a difference as that shown in Tables II and III. Actually the magnitude of the discrepancy is probably not greater than a factor of two. In view of this and the limited amount of data presently available it would seem somewhat presumptuous to speculate as to the cause of this behavior.

Comparison of k_0'/k_c Values in Methyl Methacrylate (MMA) and Methyl Acrylate (MA). Since k_0' is composed of the sum of three different terms, it is difficult to draw any significant conclusions from the k_0'/k_c values of Tables II and III. It should be noted that the discussion in the *Note*

above is also pertinent in the present case; it indicates that the k_0'/k_c values for methyl acrylate are probably all too high by a constant factor of up to two.

The only results we shall discuss at the present time are those for the four quinones. First, one should note that the very high value of k_0'/k_c for chloranil in methyl methacrylate is consistent with our previous hypothesis regarding the importance of steric hindrance for this monomer-terminator pair. Thus steric considerations could lead to a considerably greater decrease in the magnitude of k_c than in that of k_0. However, if this alone were a sufficient explanation for the magnitude of the chloranil-MMA value, one would expect that the k_0'/k_c value for 2,6-dichloroquinone in methyl methacrylate would be somewhat larger than observed since termination of the $Z \cdot$ radical from this compound is similarly hindered. This fact seems to point toward the possible importance of reaction (4a) in the chloranil-MMA system, since, of the four quinones studied, only for chloranil might the steric strain in $Z \cdot$ be sufficient to provide appreciable driving force for this reaction. The results in methyl acrylate, where steric effects would be of less importance, are not in conflict with this picture. The increase from its value in methyl methacrylate of k_0'/k_c for benzoquinone suggests that perhaps reaction 4b is of some importance for the quinones in the monomer-methyl propionate solutions employed in this study.

Obviously, the complex nature of k_0'/k_c requires that a complete understanding of the differences in Tables II and III await extension of the present investigations to include such variables as monomer concentration, product composition, and molecular weight distribution.

In conclusion it is well to emphasize that the changes in both k_x and k_0'/k_c on going from methacrylate to acrylate show a wider variation from terminator to terminator than might have been expected for two such similar monomers. Attempts have been made to explain these variations in terms of polar and steric effects, and while these explanations seem reasonable they must be considered somewhat speculative since they are based on data for a relatively few compounds. However, it is hoped that the unexpected nature of some of the results will stimulate an extension of the present investigation to other terminators and monomers.

EXPERIMENTAL

Purification of Materials. *Methyl Acrylate.*—1.5 liters of monomer (Rohm & Haas ethylene cyanohydrin process) was washed with two 250-ml. portions of 2% ferrous sulfate solution. It was then washed twice with water followed by two washings with 250-ml. portions of a 2% solution of sodium hydroxide in water. The monomer was again washed with water and was then dried over either Drierite or anhydrous sodium sulfate. It was fractionally distilled twice at reduced pressure, only the middle cut being retained each time. The final product consisted of about 500 ml. of methyl acrylate, b.p. 31.4°/115 mm., $n_D^{25} = 1.4001$. This material was

stored under nitrogen in the dark at $-20°$ in a desiccator until used. Fresh monomer was purified by this procedure every few weeks.

Methyl Methacrylate. This was purified as previously described.

Methyl Propionate. Eastman Kodak White Label material was washed twice with dilute sodium bicarbonate, washed repeatedly with small portions of water, and finally dried over sodium sulfate. It was fractionally distilled at atmospheric pressure. The portion boiling 80.2–80.5° was used ($n_D^{25} = 1.3774$).

2,2'-Azobisisobutyronitrile. This was purified as previously described.[1]

Inhibitors. Benzoquinone, furfurylidene malononitrile, sulfur, trinitrotoluene, *m*-dinitrobenzene, and diphenylamine were all purified as in reference 1. Through an oversight the purification of chloranil was not described in the previous paper. For both investigations Eastman Kodak *Chloranil* was recrystallized from toluene, m.p. 289–290° (sealed tube).

2,6-Dichlorobenzoquinone. (Eastman Kodak) was recrystallized twice from ethanol, m.p. 120–121° (sealed tube).

2,5-Dichlorobenzoquinone. (Eastman Kodak) This was recrystallized twice from ethanol, m.p. 158–160° (sealed tube).

The Dilatometer. The dilatometers were those used in the previous investigation.[1] The use of these dilatometers with methyl methacrylate has already been described. For the methyl acrylate studies the density data of Matheson *et al.*[2] for methyl acrylate polymer and monomer were used to calculate the volume contraction expected for complete conversion. This was found to be 0.252 ml./g. of methyl acrylate at 44.1°, the temperature at which all the kinetic runs were carried out. Under our conditions this corresponded to about 0.5% polymerization for an over-all fall of 1 cm. in the capillaries of the dilatometer.

Procedure for a Run. *Methyl Methacrylate.* The runs were carried out using the previously described procedure.[1]

Methyl Acrylate. The desired amounts of initiator, inhibitor, and methyl propionate were weighed out and placed in the side chamber of the dilatometer (see reference 1 for design of dilatometer). The dilatometer was then attached to the vacuum line through a stopcock; the contents were frozen, and the inlet tube of the side chamber sealed off.

At the same time 0.04 g. AIBN, 0.04–0.2 g. of purified *n*-dodecyl mercaptan (b.p. 99.5°/1.5 mm.) and 20–25 g. of purified methyl acrylate were weighed into a ground glass jointed flask. The flask was attached to the vacuum line through a stopcock, and its contents were frozen.

The flask and the dilatometer were then alternately degassed twice by the usual procedure to a vacuum of 10^{-5} mm. After the second degassing the contents of the flask were heated at 45–50° until the increase in the viscosity of the solution showed that a significant amount of polymerization had taken place. During this time the dilatometer was degassed a third time.

Subsequently the contents of the flask were frozen, and the flask was degassed. After melting, about half of the unpolymerized monomer was

distilled into a graduated tube attached to the vacuum system through another stopcock. After distillation the monomer in the tube was warmed to 0° and the volume noted. The desired quantity of methyl acrylate was then distilled from the tube into the side chamber of the dilatometer. After this distillation the contents of the dilatometer were degassed a final time, and the dilatometer was sealed from the system. From this point on the procedure was the same as that previously described for methyl methacrylate in reference 1.

If the prepolymerization of the monomer was omitted, a significant induction period occurred whose length was inversely proportional to the amount of initiator used in the run.

The amounts of methyl acrylate and methyl propionate used in the dilatometer were such as to give a methyl acrylate concentration of $3M$ (*i.e.*, propionate = 25.3–25.7 g.; acrylate = 10.2–10.4 g.).

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Synopsis

The effect of nine inhibitors on the 2.2'-azobisisobutyronitrile initiated polymerization of methyl acrylate in methyl propionate solution has been studied kinetically by a

dilatometric method.   The rate constants obtained are compared with those found for these same compounds in methyl methacrylate polymerization.   The ratio of the reactivity of an inhibitor toward methyl acrylate and methyl methacrylate radicals is found to vary considerably from inhibitor to inhibitor; these variations in behavior seem readily interpretable in terms of polar and steric effects.   Specifically, it is found that the three quinones—benzoquinone, 2,6-dichloroquinone, and 2,5-dichloroquinone— show a smaller increase in reactivity on going from methacrylate to acrylate than any of the other compounds studied.   This is consistent with the presumably strongly "electron-accepting" nature of the quinone ring.   On the other hand, the tetrachloroquinone, chloranil, shows a much larger increase in reactivity on going from methacrylate to acrylate.   Models indicate that this different behavior is due to the existence of considerable steric hindrance in the reaction of the bulky methacrylate radical with chloranil and not to any difference among these quinones as regards their mechanism of reaction with methacrylate and acrylate radicals.   With the other compounds which showed inhibitory activity—trinitrotoluene, furfurylidene malononitrile, dinitrobenzene, and sulfur—the relative magnitude of the increase in reactivity varies in a manner consistent with the differing polarities of these four compounds.

Résumé

L'effet de neuf inhibiteurs sur la polymérisation de l'acrylate de méthyle en solution dans le propionate de méthyle a été étudié cinétiquement au moyen d'une méthode dilatométrique; les polymérisations étaient initiées par le 2,2'-azobisisobutyronitrile. Les constantes de vitesse trouvées pour ces substances ont été comparées à celles trouvées pour ces mêmes produits dans la polymérisation du méthacrylate de méthyle.   Le rapport de réactivité d'un inhibiteur à l'égard des radicaux acrylates et méthacrylates varie considérablement; ces variations de comportement sont faciles à interpréter à la lumière d'effets stériques et effets polaires.   Particulièrement, on a trouvé que les trois quinones, la benzoquinone, la 2,6-dichloroquinone, et la 2,5-dichloroquinone, manifestent un accroissement moindre de réactivité en passant du méthacrylate à l'acrylate que les autres composés étudiés.   Ceci est en accord avec le caractère électrophile accusé du noyau quinonique.   D'autre part, la tétrachloroquinone (le chloranile) montre un accroissement plus considérable de réactivité en passant du méthacrylate à l'acrylate. Les modèles indiquent que ce comportement différent est dû à l'existence d'un empêchement stérique important qui se manifeste au cours de la réaction entre le radical méthacrylique encombrant et le chloranile, et non pas à quelque différence entre ces diverses quinones du point de vue de leur mécanisme de réaction avec les radicaux méthacryliques ou acryliques.   Avec les autres composés, qui montrent une activité inhibitrice—le trinitrotoluène, le furfurylidène-malononitrile, le dinitrobenzène, et le soufre—la grandeur relative de l'augmentation de réactivité varie conformément aux variations de polarités de ces quatre composés.

Zusammenfassung

Die Wirkung von neun Inhibitoren auf die durch 2,2'-Azo-bis-Isobutyronitril initierte Polymerisation von Methylacrylat in Methylpropionatlösung wurde kinetisch mittels einer dilatometrischen Methode untersucht.   Die erhaltenen Geschwindigkeitskonstanten werden mit den für die gleichen Verbindungen in Methylmethacrylat-Polymerisation gefundenen verglichen.   Es wird gefunden, dass das Verhältnis der Reaktivität eines Inhibitors gegen Methylacrylat-und Methylmethacrylat-Radikale erheblich von einem Inhibitor zum anderen variiert; diese Variationen im Verhalten scheinen gut durch polare und sterische Wirkungen erklärbar zu sein.   Insbesondere wird gefunden, dass die drei Chinone—Benzochinon, 2,6-Dichlorochinon und 2,5-Dichlorochinon—von Methacrylat zu Acrylat eine kleinere Zunahme der Reaktivität aufweisen, als die anderen untersuchten Verbindungen.   Dies stimmt mit der wahrscheinlich stark "Elektronen annehmenden" Natur des Chinonringes überein.   Anderseits zeigt das Tetrachloro-

chinon Chloranil eine viel grössere Zunahme der Reaktivität von Methacrylat zu Acrylat.
Modelle zeigen an, dass dieses verschiedene Verhalten durch die Gegenwart von er-
heblicher sterischer Verhinderung bei der Reaktion von massiven Methacrylat-Radi-
kalen mit Chloranil bedingt ist, und nicht durch einen Unterschied zwischen diesen
Chinonen in Bezug auf ihren Reaktionsmechanismus mit Methacrylat- und Acrylatra-
dikalen.   Bei den anderen Verbindungen, die Inhibitor-Aktivität zeigten—Trinitro-
toluol, Furfuryliden Malononitril, Dinitrobenzol, und Schwefel—variiert die relative
Grösse der Zunahme der Reaktivität in einer Weise, die mit den verschiedenen Polari-
täten dieser vier Verbindungen übereinstimmt.