THE TERMINATION STEP IN THE POLYMERIZATION
OF METHYL METHACRYLATE AT 30° C

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Benzoquinone has been used as a retarder to the polymerization of methyl methacrylate, photo-initiated by 2-azo*bis*(*iso*butyronitrile), with a view to obtaining information about the mode of mutual termination in the unretarded reaction. By relating rate and molecular weight measurements for the retarded and unretarded polymerization, it is possible to distinguish between combination and disproportionation. Such a technique indicates that disproportionation is the predominating process for this system.

The study of addition polymerization in the liquid phase in the absence of retarder has revealed that termination occurs almost exclusively by the mutual interaction of radicals. The further problem has arisen as to whether the radicals combine or disproportionate.

A fairly comprehensive list of evidence for combination or disproportionation has already been given by Melville and Valentine.[1] Since then, more information has become available. Matheson *et al.*[2] have made use of the fact that the rate of initiation in a polymerization can be determined by three different methods, i.e. (i) by assuming the rate of initiation to be twice the rate of decomposition of the initiator, 2-azo*bis*(*iso*butyronitrile), assuming 100 % efficiency, (ii) by using inhibitors and assuming that one growing polymer chain is stopped by one inhibitor molecule, and (iii) by molecular-weight measurements. For the polymerization of styrene, Matheson *et al.* find that each method gives the same

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result only when combination is assumed. Baysal and Tobolsky [3] also relate initiator efficiency to the termination mechanism. When it is assumed to be disproportionation, the efficiency ranges from 26 % to 47 %, and correspondingly when it is combination, the efficiency varies between 52 % and 93 %. The authors state than an efficiency of 100 % is a much more probable occurrence, and so argue that termination by combination is the more important mechanism. Arnett [4] considers the azo*bis*(nitrile) to decompose in two steps, i.e.,

$$A - N = N - A \rightarrow A - N = N^* + A^*$$

$$A - N = N^* \rightarrow A^* + N_2$$
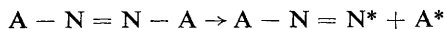
and maintains that for methyl methacrylate, only one type of free radical initiates polymer chains, but with a 100 % efficiency, whilst the other type is consumed by some other action, probably by reaction with itself. His kinetic scheme leads to the conclusion that combination is operating. Perhaps the most satisfactory method of tackling the problem is that of using a radioactive initiator. If comparison of the osmotic molecular weight and the amount of combined initiator fragments in a polymer indicates that there are two initiator fragments per polymer molecule, then clearly combination is occurring. The work of Arnett and Petersen [5] using this radioactive technique substantiates Arnett's previous results for methyl methacrylate. Taylor and Bevington [6] in these laboratories have also applied this technique to polymethyl methacrylates obtained at different temperatures, and they find that disproportionation predominates, being almost complete at 60° C. It is becoming increasingly clear that in any particular system both termination mechanisms are operating at the same time, and it is the temperature at which the reaction is carried out that determines which predominates, disproportionation being favoured at high temperatures.

In this paper the problem has been approached by studying a polymerization in the presence of a retarder. If a polymer molecule having reacted with a retarder molecule does not react further, either with monomer or another polymer molecule, this mode of termination is equivalent to that of disproportionation as far as molecular-weight measurements are concerned, since in each case one radical yields one polymer. This means that for 100 % disproportionation in a normal polymerization, reducing the rate by a factor of 10 using a retarder should result in the molecular weight being decreased tenfold, if the rate of initiation is kept constant. In the corresponding case for termination by 100 % combination, the molecular weight should be reduced by a factor of 20. Thus by studying the rate and molecular weight measurements for a retarded reaction in relation to those for an unretarded polymerization, some distinction can be made as to which termination mechanism is predominating in the latter. In this method it is essential that the retarder reduces the rate of polymerization by stopping the growing polymer chains, and not by acting directly on the initiator and thus cutting down the rate of initiation.

The approach is by no means as simple as the above paragraph would suggest, especially when using benzoquinone as a retarder. A considerable amount of work has been carried out on this particular system by other investigators [7, 8] and it is certain that the polymer-retarder complex takes some further part in the reaction. This is to be expected as the complex is still a radical, although of reduced activity. It is interesting to note that for the peroxide initiated polymerization of methyl methacrylate at 80° C with benzoquinone as a retarder, Melville and Watson [8] found the rate to be dependent on the square root of the initiator concentration when the quinone concentration was kept constant. The square root dependence on initiator concentration was anticipated at all degrees of retardation, and so they considered the system as one of limited copolymerization. For the system to be of any use in solving the problem under investigation, it is essential that no such copolymerization takes place, and that when a quinone
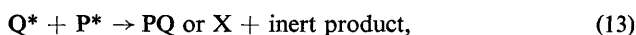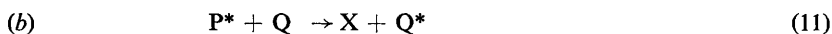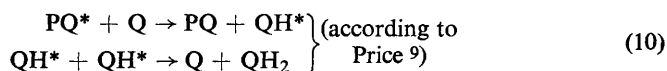
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molecule has attacked a growing polymer chain, the complex is removed by one further simple kinetic step. The chance of copolymerization occurring can be reduced to a minimum by adjusting the experimental conditions so that the dependence on light intensity, i.e. the intensity exponent of the system, is unity. Then it is probable that termination results through one radical chain being stopped by one retarder molecule, and not by mutual interaction between two growing polymer chains. The main immediate difficulty therefore concerns the behaviour of the polymer-quinone complex, and the following reaction steps are given as possible ways in which it may be removed from the system. The effect of transfer is considered later.

REACTION KINETICS.

The unretarded polymerization

$$M \rightarrow P^* \qquad I \tag{1}$$

$$P^* + M \rightarrow P^* \qquad k_p \tag{2}$$

$$P^* + P^* \rightarrow 2X \qquad k_{t_d} \tag{3}$$

$$P^* + P^* \rightarrow X_2 \qquad k_{t_c} \tag{4}$$

The retarded polymerization.—The growing radical P^* can react with the retarder Q in one of two ways, viz., (*a*) addition to form a radical PQ^*, or (*b*) transfer to form a dead polymer X and a small radical Q^*. If neither PQ^* nor Q^* reacts with a monomer molecule, then the only reactions possible are equivalent to those represented formally below.

(*a*)

$$P^* + Q \rightarrow PQ^* \qquad k_q \tag{5}$$

$$PQ^* + PQ^* \rightarrow 2X \qquad k_{xa} \tag{6}$$

$$PQ^* + PQ^* \rightarrow X_2 \qquad k_{xb} \tag{7}$$

$$PQ^* + P^* \rightarrow 2X \qquad k_{xc} \tag{8}$$

$$PQ^* + P^* \rightarrow X_2 \qquad k_{xd} \tag{9}$$

$$\left.\begin{array}{l} PQ^* + Q \rightarrow PQ + QH^* \\ QH^* + QH^* \rightarrow Q + QH_2 \end{array}\right\} \begin{array}{l}\text{(according to} \\ \text{Price }[9])\end{array} \tag{10}$$

(*b*)

$$P^* + Q \rightarrow X + Q^* \tag{11}$$

$$Q^* + Q^* \rightarrow \text{inert product} \tag{12}$$

$$Q^* + P^* \rightarrow PQ \text{ or } X + \text{inert product}, \tag{13}$$

where $P^* =$ radical obtained from monomer M

$Q =$ molecule of retarder

X, PQ $=$ dead polymer.

Also for the two separate polymerizations, there is the following relationship,

$$R_1/R_2 = \alpha = [P^*]_1/[P^*]_2$$

where $1 \equiv$ unretarded reaction and $2 \equiv$ retarded reaction.

THE UNRETARDED REACTION (intensity exponent $= 0.5$)

(*a*) *Disproportionation operating*, i.e. termination occurring only by eqn. (3).

$$d[P^*]_1/dt = 0 = I - 2k_{t_d}[P^*]_1{}^2$$

$$d[X]/dt = 2k_{t_d}[P^*]_1{}^2 = I$$

$$\text{rate} \equiv d[M]/dt = k_p[P^*]_1[M]$$

and $$\overline{DP_d} = -\,d[M]/d[X] = k_p[P^*]_1[M]/I,$$

where $\overline{DP} = $ degree of polymerization.

(b) *Combination operating*, i.e. termination occurring only by eqn. (4) ; the following relation is obtained :

$$\overline{DP_c} \equiv d[M]/d[X] = 2k_p[P^*]_1[M]/I.$$

THE RETARDED REACTION (intensity exponent $= 1\cdot0$)

(c) for termination occurring by eqn. (5) and (6) only,

$$d[P^*]_2/dt = I - k_q[P^*]_2[Q] = 0$$

$$d[X]/dt = 2k_{x_a}[PQ^*]^2.$$

But

$$d[PQ^*]/dt = k_q[P^*]_2[Q] - 2k_{x_a}[PQ^*]^2 = 0$$

$$d[X]/dt = k_q[P^*]_2[Q] = I$$

and

$$\overline{DP_r} \equiv d[M]/d[X] = k_p[P^*]_2[M]/I.$$

The suffixes d, c, r (applied to the degree of polymerization) refer to disproportionation, combination, and retardation, respectively.

Thus, if I is kept constant, comparison of the different chain lengths for the unretarded and retarded polymerizations leads to the following relationships :

$$\overline{DP_d}/\overline{DP_r} = [P^*]_1/[P^*]_2 = \alpha = R_1/R_2$$

$$\overline{DP_c}/\overline{DP_r} = 2[P^*]_1/[P^*]_2 = 2\alpha = 2R_1/R_2.$$

(d) Similarly for termination by eqn. (5) and (7),

$$d[X]/dt = I/2$$

and

$$\overline{DP_d}/\overline{DP_r} = \alpha/2, \quad \overline{DP_c}/\overline{DP_r} = \alpha.$$

Extension of this treatment to the other possible modes of termination yields the following results :

$\overline{DP_1}/\overline{DP_2}$ for retardation according to equation

	6	7	8	9	10	12	13
disproportionation	α	$0\cdot5\alpha$	α	$0\cdot5\alpha$	α	α	α
combination	2α	α	2α	α	2α	2α	2α

Obviously if disproportionation and combination occur simultaneously, then intermediate values of $\overline{DP_1}/\overline{DP_2}$ will occur, e.g. for eqn. (6),

$$\overline{DP_1}/\overline{DP_2} = \alpha/(1 - \beta), \quad \text{where } \beta = k_{t_c}/2(k_{t_c} + k_{t_d}).$$

Thus, if disproportionation is the mechanism in the unretarded reaction,

$$\alpha/2 \leqslant \overline{DP_1}/\overline{DP_2} \leqslant \alpha,$$

whilst if combination occurs,

$$\alpha \leqslant \overline{DP_1}/\overline{DP_2} \leqslant 2\alpha.$$

Hence if a value of $\overline{DP_1}/\overline{DP_2} < \alpha$ is obtained, then some disproportionation is indicated, and if $\overline{DP_1}/\overline{DP_2} > \alpha$ some combination is indicated. The extreme possibilities are shown graphically in fig. 1. Curve A is a typical relative rate curve, calculated from the results given in table 2, whilst the dotted lines B and C show the extreme possibilities of the relative molecular weights when $\overline{DP_1}/\overline{DP_2} = \alpha/2$ and 2α, respectively. If the relative experimental molecular weights fall on either B or C, it can definitely be stated which mechanism is operating, but if they fall between B and C, it merely indicates that both are operating at the same time.

EXPERIMENTAL

Dilatometry was used to follow the course of polymerization. The reaction vessels, made of Pyrex glass and of 5 ml capacity, were thoroughly cleaned and flamed *in vacuo* before being filled with initiator, retarder and monomer. Benzoquinone, purified by a process of steam distillation followed by sublimation, was introduced by pipetting in a known volume of a solution in benzene, and then carefully evaporating the solvent under low pressure at a water pump. When the tube was attached to the high-vacuum apparatus, the bulb was immersed in liquid air, and the system gradually evacuated, the full effect of the pumps never being used until the final degassing stage, after the monomer had been distilled. These precautions were necessary because of the great ease with which benzoquinone sublimed. 2-azo*bis*(*iso*butyronitrile) was always added before the quinone, the concentration of the initiator being kept constant at 0·5 g/l. throughout the series of experiments. Methyl methacrylate (Kallodoc), purified as previously described,[10] was
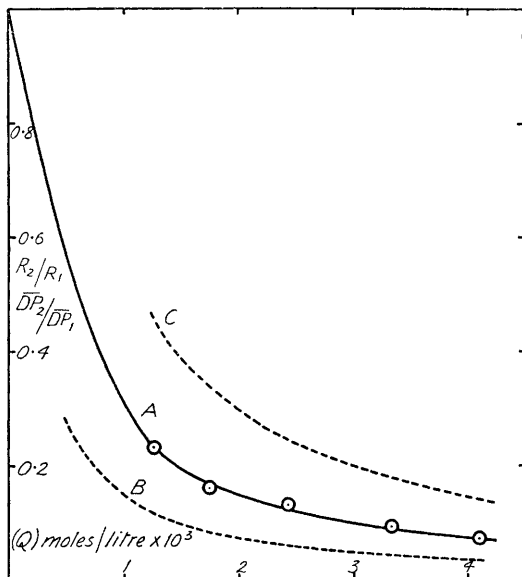

FIG. 1.—Variation of the relative rate (R_2/R_1) and the relative degree of polymerization (DP_2/DP_1) with the quinone concentration. A is an actual relative rate curve based on the results given in table 2. B and C are theoretical relative molecular-weight curves when $DP_1/DP_2 = \alpha/2$ and 2α, respectively.

distilled on the high-vacuum line, the volume being measured from the reaction tube dimensions. The amount distilled was regulated so that only the lower part of the stem was filled at the reaction temperature. Thus the volume measured and the actual volume irradiated were the same.

Polymerizations were carried out in a 5-l. Pyrex beaker maintained at 30° C, the temperature variation being estimated as $\pm 0.01°$ C. The light source was a 125 watt G.E.C. Osira mercury vapour lamp with the glass envelope removed. This was fed from the a.c. mains through a choke and condenser recommended by the makers. Although the Pyrex glass cut out light of wavelength < 3000 Å, there was still a considerable photo reaction for the pure monomer. Introduction of a Chance OX1 filter with a maximum transmission of 61 % at 3600 Å reduced this rate to about 0·1 % h. The filter was also ideal for the initiated reaction as the spectrum of 2-azo*bis*(*iso*butyronitrile) has its peak at 3400Å. Polymerization was followed by a cathetometer capable of reading to 0·01 mm. The yellow colour of the benzoquinone was retained throughout the time of reaction. As it was essential that the quinone did not affect the rate of initiation, the system was examined for internal filter effects. The spectrum of benzoquinone [11] at 3500 A has a molar extinction coefficient of 3. Under the experimental conditions, a concentration of quinone of $5·0 \times 10^{-3}$ (the highest value used) absorbed only about 3 % of the incident

light.   Thus it was safe to assume that there was no reduction in the light intensity for the retarded polymerization.

The polymers were isolated by precipitation with methanol, followed by further solution in benzene and precipitation, being finally dried in an oven at 100° C.   Osmotic pressures were measured in benzene solution at 25° C using a Fuoss and Mead [12] type of osmometer, as modified by Masson and Melville,[13] with bacterial cellulose as a membrane. The static method was used.

RESULTS AND DISCUSSION

As it was necessary, in the system investigated, that the intensity exponent n should be unity for the retarded reaction, a series of experiments was carried out with different quinone concentrations, in order to establish the most suitable conditions.   Table 1 shows the results obtained.

TABLE 1.—VARIATION OF THE INTENSITY EXPONENT WITH THE QUINONE CONCENTRATION

tube	n_1 n_2 $\bar{n}$	conc. of initiator g/l.	conc. of quinone moles/l. $\times 10^3$	$1/[Q] \times 10^{-3}$	rate % per h
M21	—	0·482	—	—	5·77
M40	0·84 0·85 0·84	0·502	1·02	0·98	2·17
M29	0·89 0·94 0·91	0·519	1·09	0·92	2·33
M39	0·79 0·84 0·81	0·507	1·44	0·695	1·60
M41	0·86 0·96 0·91	0·493	1·95	0·513	1·28
M34	0·87 0·94 0·90	0·504	2·02	0·495	1·04
M37	1·0 0·88 0·94	0·498	2·97	0·337	0·84
M35	1·04 — —	0·506	3·08	0·325	0·79
M36	1·03 0·90 0·96	0·497	4·0	0·25	0·53
M33	1·10 —	0·498	5·0	0·20	0·42

$\bar{n}$ is the mean of the two values n_1 and n_2, calculated from the rate with the screen inserted, and the rates under full illumination before and after inserting the screen, respectively.   A screen of transmission factor 0·44 was used for all tubes except M29.   For this tube the screen had a transmission factor of 0·484. As can be seen from table 1, the intensity exponent is unity when the quinone concentration is $> 3 \times 10^{-3}$ mole/l.   Conditions could therefore be chosen so that mutual termination was not operating in the reaction.   The rates recorded above are those for full light intensity.   Although there was a dark rate for the 2-azo*bis*(*iso*butyronitrile) initiated reaction (in absence of quinone), it was only of the order of 0·5 % per h for an initiator concentration of 0·5 g/l.   As it was less than a tenth of the photo-rate, it could safely be ignored.   It would also be reduced by the quinone to the same extent as in the photochemical reaction.

The series of experiments was repeated without making intensity exponent measurements, reaction being allowed to proceed to about 5 % conversion. Preliminary viscosity measurements had shown that for full illumination of the lamp the polymers obtained from tubes containing high quinone concentrations had molecular-weights $< 10^5$, a range not accurately covered by the osmometer available.   As it was essential that high quinone concentrations should be used for the intensity exponent to be unity, a screen of transmission factor 0·484 was permanently inserted into the optical system.   Thus by reducing the rate of polymerization, the molecular weights were correspondingly increased, and could

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be measured by the osmometer. As can be seen from fig. 2, the rates remain reasonably constant for the whole time of reaction, although there was a tendency for the rate to decrease slightly after 5 % conversion. Fig. 3 shows the π/C against C plots, whilst table 2 gives the rate and molecular weight measurements. The molecular weight of the polymer from M44 was too small to be measured accurately by the osmometer.
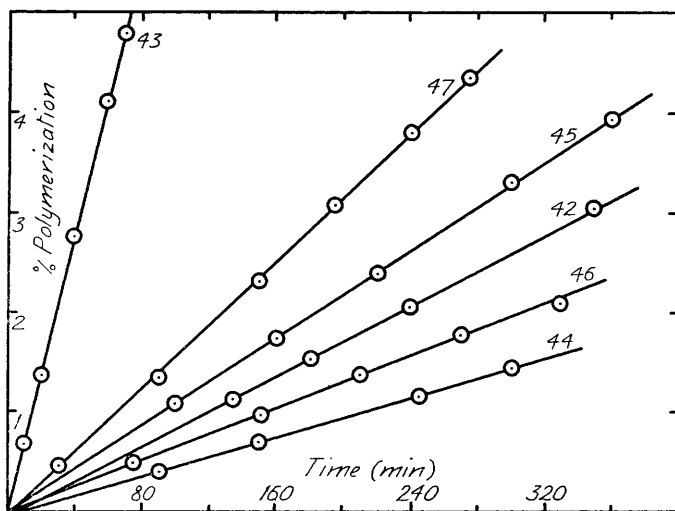

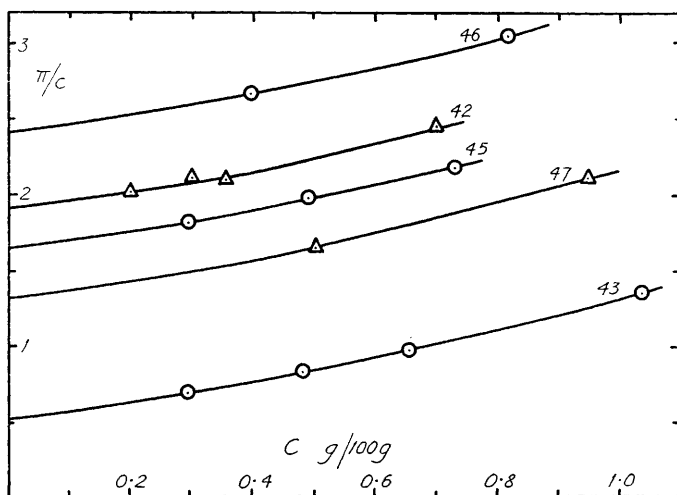FIG. 2.—The effect of benzoquinone on the rate of polymerization.

FIG. 3.—The variation of Π/C with C for polymethyl methacrylates.

The ratios of the molecular weights and the rates for the unretarded to the retarded reaction were calculated for each tube, the results being given in table 3.

The steady decrease in the value of $\overline{DP}_1/(\overline{DP}_2 \cdot \alpha)$ as α increases can be explained on two counts. By reference to table 1, a drift would be expected because of the gradual change in the intensity exponent. The fact that the value falls below 0·5 is probably due to a slight decrease in the rate of initiation (thereby causing $\overline{DP}_2$ to be too high).

From the results of Mackay and Melville [7] on the pure photo polymerization of methyl methacrylate retarded by quinone, a value of $\overline{DP}_1/(\overline{DP}_2 \cdot \alpha) = 0\cdot53$ can be calculated. This is good confirmation of the reliability of the experimental procedure. Thus it appears that when consideration has been made for the slight change in the experimental conditions necessary to the kinetic scheme,

$$\overline{DP}_1/\overline{DP}_2 \simeq 0\cdot5\alpha.$$

For the retarded reaction, the rate is given by $R = k_p[M]I/k_q[Q]$. I can be found from the rate for the unretarded reaction using the expression $R = k_p[M](I/2k_t)^{\frac{1}{2}}$ and the known [14] values of k_p and k_t. Since it is found here that disproportionation is operating, the published values (based on combination) have been doubled.

TABLE 2.—RATE AND MOLECULAR WEIGHT MEASUREMENTS FOR DIFFERENT CONCENTRATIONS OF QUINONE

tube	conc. of initiator g/l.	conc. of quinone moles/l. $\times 10^3$	rate % per h	mol. $\times$ wt. 10^{-3}
M43	0·496	0·0	4·1	495
M47	0·505	1·25	0·95	191
M45	0·498	1·74	0·66	153
M42	0·486	2·43	0·54	133
M46	0·501	3·33	0·38	105
M44	0·498	4·1	0·29	—

TABLE 3.—VARIATION OF THE RATIO R_1/R_2 ($= \alpha$) WITH $\overline{DP}_1/\overline{DP}_2$

tube	R_1/R_2 ($= \alpha$)	$\dfrac{\text{mol. wt. (unretarded)}}{\text{mol. wt. (retarded)}} = \dfrac{\overline{DP}_1}{\overline{DP}_2}$	$\overline{DP}_1/(\overline{DP}_2 \cdot \alpha)$
M47	4·32	2·59	0·60
M45	6·21	3·24	0·52
M42	7·59	3·72	0·49
M46	10·8	4·71	0·44
M44	14·14	—	—

These data and a plot of R against $[Q]^{-1}$, using the data of table 2, enable k_q to be calculated; the result is $k_q = 3\cdot5 \times 10^3$ l. mole^{-1} sec^{-1}, which is in very good agreement with that found for the retardation of the direct photopolymerization [7] at 36°, viz., $k_q = 3\cdot7 \times 10^3$.

The effects of transfer have been completely ignored in the preceding treatment. Transfer will have the greater effect for the unretarded reaction as the larger molecular weight is involved. A correction can be made by applying the experimental molecular weight to the following equation,

$$I/R = (1/\overline{DP}) - (k_f/k_p),$$

where k_f is the transfer velocity constant. Taking $k_f/k_p = 2\cdot62 \times 10^{-5}$, as reported by Matheson et al.,[14]

$$I/R = (1/4,950) - 2\cdot62 \times 10^{-5} = 1\cdot758 \times 10^{-4}.$$

If there was no transfer. then

$$1/\overline{DP} = 1\cdot758 \times 10^{-4}, \quad \text{and} \quad M_n = 569,000.$$

A correction of this nature cannot be regarded as absolute, especially for the molecular weights obtained for the retarded reactions, but it is certainly in the right direction. Recalculating the ratio of the molecular weights using the above equation, it can be seen from table 4 that the conditions are satisfied when
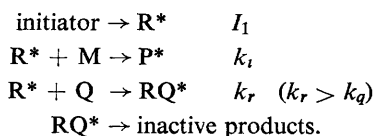
$$\overline{DP}_1/\overline{DP}_2 = 0\cdot5\alpha.$$

These results would indicate, therefore, that for the unretarded reaction, termination occurs by disproportionation, whilst for the retarded polymerization the mechanism is by combination.

TABLE 4.—THE EFFECT OF CORRECTING THE DEGREE OF POLYMERIZATION FOR TRANSFER

tube	$\overline{DP}$ uncorr. $\times 10^{-3}$	$\overline{DP}$ corr. $\times 10^{-3}$	$\overline{DP}_1/\overline{DP}_2$	$\overline{DP}_1/(\overline{DP}_2 . \alpha)$
M43	4950	5690	—	—
M47	1910	2010	2·83	0·66
M45	1530	1590	2·58	0·58
M42	1330	1370	4·04	0·53
M46	1050	1080	5·26	0·49

It is possible that the benzoquinone may be interacting with the initiator so as to reduce the rate of starting polymer chains. It is instructive to see if this phenomenon could account for the experimental finding that $\overline{DP}_1/(\overline{DP}_2 . \alpha) = 0.5$, on the basis that normal termination is by combination. The most likely way for the rate of initiation to be reduced is by a competition between monomer and retarder for the radicals formed from the initiator. Consider the effect of such a scheme on termination by eqn. (5) and (9):

$$\text{initiator} \rightarrow R^* \qquad I_1$$
$$R^* + M \rightarrow P^* \qquad k_i$$
$$R^* + Q \rightarrow RQ^* \qquad k_r \quad (k_r > k_q)$$
$$RQ^* \rightarrow \text{inactive products.}$$

Then $\quad d[R^*]/dt = 0 = I_1 - k_i[R^*][M] - k_r[R^*][Q],$

and $\qquad I_2 = k_i[R^*][M] = I_1 - k_r[R^*][Q] = I_1\left\{1 - \dfrac{[Q]}{[Q] + K[M]}\right\},$

where $\qquad K = k_i/k_r.$

Then $\quad \overline{DP}_c/\overline{DP}_r = \alpha I_2/I_1 = \alpha\left\{1 - \dfrac{[Q]}{[Q] + K[M]}\right\}.$

From table 4 it seems likely that $\overline{DP}_c/(\overline{DP}_r\alpha) = 0.5$ at $[Q] = 2.4 \times 10^{-3}$, and hence $K[M] = 2.4 \times 10^{-3}$. The ratio $\overline{DP}_c/(\overline{DP}_r . \alpha)$ can now be calculated for other values of $[Q]$, and the results are given below, together with the experimental values from table 4.

TABLE 5

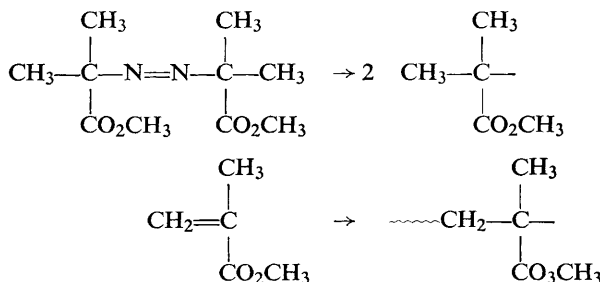| expt. no.	$[Q] \times 10^3$	$\left\{1 - \dfrac{[Q]}{[Q]+K[M]}\right\}$	$\overline{DP}_c/(\overline{DP}_r . \alpha)$ (expt.)
M47	1·25	0·66	0·66
M45	1·74	0·59	0·58
M42	2·43	0·50	0·53
M46	3·33	0·42	0·49
M44	4·1	0·37	?

The calculated and experimental values agree closely, except for the highest concentration of retarder, so that such a scheme is a possibility. $K[M] = 2.4 \times 10^{-3}$ yields $k_i/k_r = 2.5 \times 10^{-4}$, which is very reasonable. On the other hand, the fall in the values of $\overline{DP}_c/(\overline{DP}_r . \alpha)$ may well be due to mutual termination operating at the lower quinone concentrations.

Of the possible modes of interaction listed in the kinetics, only two involve the relationship $\overline{DP}_1/\overline{DP}_2 = 0.5\alpha$:

(5) and (7) $\qquad\qquad PQ^* + PQ^* \rightarrow X_2 \quad (P_2Q_2)$

(5) and (9) $\qquad\qquad PQ^* + P^* \rightarrow X_2 \quad (P_2Q).$

The work of Bickel and Waters [15] indicates that there is probably a mixture of (5) and (8), and (5) and (9). They have studied the free radicals formed by the decomposition of dimethyl 2 : 2'-azo*iso*butyrate in boiling toluene. By analogy with the chemical formulae,

$$CH_3-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-N{=}N-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad \rightarrow 2 \quad CH_3-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$

$$CH_2{=}\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \quad \rightarrow \quad {\sim}{\sim}{\sim}{\sim}CH_2-\underset{\underset{CO_3CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$

they suggested that the behaviour of a radical formed from the azo-compound would be similar to that of a growing polymethyl methacrylate radical. Equimolecular quantities of dimethyl 2 : 2'-azo*iso*butyrate and benzoquinone were refluxed together in toluene, and analysis of the reaction products showed the mono-ether and diether to be present in yields of 46 % and 27 % respectively. From these results they concluded that for the polymerization of methyl methacrylate retarded by benzoquinone, the mechanism involved the formation of a semiquinone radical (5), which interacted with a growing polymer chain by either disproportionation (8), or combination (9). Although caution must be exercised when comparing the action of large and small molecules, when each has an identical terminal group and therefore an expected identical reactivity, the results of Bickel and Waters do lend support to the assumed kinetic scheme.

Cohen [16] has also proposed that polymeric radicals add on to the O atom of benzoquinone, and that this adduct subsequently combines with another polymer radical. The sequence eqn. (5) and (9) is then chemically more plausible than the sequence eqn. (5) and (7), since the latter corresponds to the addition of two semi-quinone radicals to form a peroxide of the structure
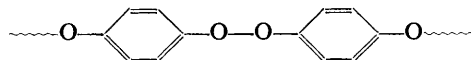
Taking all these factors into consideration, it seems likely that the sequence $P^* + Q \rightarrow PQ^*$, $PQ^* + P^* \rightarrow P_2Q$ is the most probable.

The problem of the termination mechanism has also been studied in this department using radioactive 2-azo*bis*(*iso*butyronitrile) as an initiator to the reaction.[6] For the polymerization of methyl methacrylate at 30° C, such a technique has indicated that the termination step is mainly by disproportionation, in agreement with what has been obtained here, but in complete disagreement with the work of Arnett and Peterson.[5] If the radioactive method could be extended to the use of radioactive benzoquinone, the mode of interaction of the polymer-retarder radical could be further distinguished, as the quantity of quinone incorporated into each polymer is dependent on which mechanism is assumed. For instance, eqn. (6), (8), (9) and (10) yield one quinone molecule per polymer molecule, (7) and (9) two quinone molecules per polymer molecule, and (11) to (13) either no quinone or one quinone molecule per two polymer molecules. Such a project presents considerable experimental difficulties as radioactive benzoquinone is not an easy compound to prepare. The method described in this paper is by itself rather limited and by no means unambiguous. For the particular reaction studied here, the method fortunately enables some distinction to be made regarding the termination mechanism, for the assumption of disproportionation leads to a straightforward interpretation of the experimental results, whereas combination does

not.   If, however, the method is used in conjunction with the radioactive-tracer technique, not only will the vexed problem of disproportionation or combination be solved, but also more information will become available concerning the exact role of a retarder in a polymerization.

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