725. *A Comparative Study of Persulphates and Benzoyl Peroxide as Initiators of Polymerization in Solution.*

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Polymerizations of styrene, methyl methacrylate, and methyl acrylate initiated by persulphates and benzoyl peroxide, as homogeneous solutions in glycols, have been compared. Persulphates are far more efficient catalyts than benzoyl peroxide, producing faster polymerization and also a polymer of higher molecular weight. Strong sensitivity to oxygen is also observed with persulphates. Polymerization by persulphates in homogeneous solutions therefore has many characteristics in common with emulsion polymerization. Two possible mechanisms are suggested for such difference in behaviour, and one of these is discussed quantitatively.

INORGANIC per-salts such as potassium persulphate have rarely been studied as catalysts of polymerization in solution, their use having been restricted almost entirely to emulsions. This is mainly attributable to the difficulty in dissolving persulphates in the monomers or in the organic solvents in which polymerization is generally carried out. However, the study of the kinetics of vinyl polymerization in homogeneous solution initiated by such catalysts is of interest, not only for its own sake but also because it may throw light on the well-known but unexplained peculiarities of emulsion polymerization (cf. Price, " Mechanism of the Reaction

of the Carbon–Carbon Double Bond," Interscience, 1946, Chap. VI; Harkins, *J. Amer. Chem. Soc.*, 1947, **69**, 1482). Further, a comparative study of the persulphates and benzoyl peroxide as catalysts is also of interest in order to assess how far the persulphates conform to the accepted theories of free-radical polymerization (Bawn, "The Chemistry of High Polymers," Butterworths, London, 1948; Gee and Melville, *Trans. Faraday Soc.*, 1944, **40**, 240).

With this end in view we have studied the polymerization of three monomers, styrene, methyl methacrylate, and methyl acrylate, initiated by potassium, sodium, or ammonium persulphate, and have compared the results with peroxide-catalysed polymerization under identical conditions. The solvents chosen were ethylene, propylene, and diethylene glycols, as we found that these dissolved sufficient both of the monomers and of the persulphates to give a conveniently measurable speed of reaction.

<div align="center">EXPERIMENTAL.</div>

Materials.—Monomers. Styrene was prepared by heating cinnamic acid in presence of quinoline (equal weight) and anhydrous copper sulphate (5% by weight), and a small quantity of quinol was added as inhibitor. Methyl methacrylate was prepared by pyrolytic decomposition of the polymer, and methyl acrylate was purified from the commercial product. Just before use, the monomers were fractionated repeatedly in an all-glass apparatus after the inhibitor had been removed by washing with alkali, and were redistilled.

Glycols. Commercial glycols were purified by two fractional distillations in a vacuum.

Catalysts. Benzoyl peroxide was prepared by Gambarjan's method (*Ber.*, 1909, **42**, 4008). AnalaR grades of persulphates were used as such after being dried in a vacuum-desiccator. Persulphates being very sparingly soluble in glycols, solutions were prepared by shaking, followed by filtration, and were standardized iodometrically just before use.

Polymerization Experiments.—Polymerization was done in Pyrex tubes sealed under vacuum while the contents were frozen in liquid air. The thermostat was kept constant to $\pm 0.1°$. The solvent : monomer ratio in all the solvents was 5 : 1. In polymerization of styrene, especially at high temperatures, there was some tendency for the polymer to be formed as a coarse colloidal suspension which could be separated only with difficulty by the usual method of precipitation with methyl alcohol. However, addition of ethyl alcohol saturated with sodium acetate brought about rapid coagulation of the polymer. This was washed with water and alcohol, redissolved in benzene, precipitated again with methyl alcohol, dried *in vacuo* at 45°, and weighed.

With methyl methacrylate, manipulation was simplified by the fact that the polymers coagulated readily on addition of methyl alcohol. From methyl acrylate the polymer separated as usual as a pasty mass, which caused some difficulty in obtaining it free from monomer.

During these experiments it was noticed that, when persulphates were used as catalysts, the polymers were formed homogeneously throughout the ampoule, but with benzoyl peroxide, they tend to form lumps. This is comparable with Heuser and Perry's observation (*J. Phys. Coll. Chem.*, 1949, **52**, 1175) that the lumps are produced when oil-soluble catalysts are used in emulsion polymerization. Owing to the strong inhibition caused by the residual oxygen in the system, some of the experiments were performed in as complete absence of oxygen as practicable. This was achieved by cooling the ampoules in liquid air, evacuating the tubes, flushing them with nitrogen (washed free from oxygen by passage through towers filled with alkaline pyrogallol solution), and then warming them to room temperature, cooling again, evacuating and then flushing again with nitrogen, the procedure being repeated three times before sealing.

As the reaction we have studied is quite fast, and as some time is required for the monomer to dissolve completely when placed in the thermostat, the yields for low conversions are subject to greater error, as shown by the lower reproducibility of the results in this range.

Viscosity Measurements.—The viscosity was measured of solutions of less than 1% concentration in an Ostwald viscometer with an influx time of about 200 seconds with acetone. The temperature of the thermostat was checked to $\pm 0.02°$. The intrinsic viscosity, $[\eta]$, was obtained by graphical extrapolation to zero dilution of $\eta_{sp.}$/concentration plotted against concentration.

Results.—Styrene. Some typical results of experiments with styrene are summarized in Figs. 1—3. Full lines in all the figures represent results with persulphates, and the broken lines those with benzoyl peroxide. In Figs. 1 and 2 are shown the yield curves for experiments at 80° and 70° with diethylene glycol as solvent, and Fig. 3 represents experiments carried out at 61° (solvent, propylene glycol), all the residual air having been replaced by nitrogen before the ampoules were sealed. Our results show the following features.

(1) The persulphates are far stronger initiators than benzoyl peroxide; *e.g.*, our experiments at 80° (Fig. 1) show that potassium persulphate is about 50 times more efficient than benzoyl peroxide. This is evident on comparing curves 2 and *A* which show nearly equal speed, but the former contains 2.2×10^{-3}M-persulphate whereas the latter contains 110×10^{-3}M-peroxide. However, at lower temperatures, this marked disparity tends to diminish; *e.g.*, at 61° (Fig. 3; *cf.* curves 1 and *D*) the ratio of efficiencies is only about 30.

(2) The intrinsic viscosity of the polymers formed by the persulphate initiation is greater than that of those obtained by use of benzoyl peroxide; *e.g.*, at 80° seven samples of polymers chosen at

random prepared from persulphate catalysis gave [η] values of 0·82, 0·56, 0·55, 1·17, 0·885, 0·99, 1·17, average = 0·88; and the corresponding [η] values for benzoyl peroxide polymer are 0·21, 0·20, 0·21, 0·29, 0·40, average = 0·26. Similarly, at 61°, the corresponding ranges of [η] are *ca.* 1·25 and 0·35— 0·65, respectively. Hence, the viscosities of the persulphate-initiated polymers are roughly 3 times those of the peroxide-initiated polymers. When calculated in molecular weights according to the Staudinger–Mark equation (Goldberg, Hohenstein, and Mark, *J. Polymer. Sci.*, 1947, **2**, 503), *viz.*, [η] =
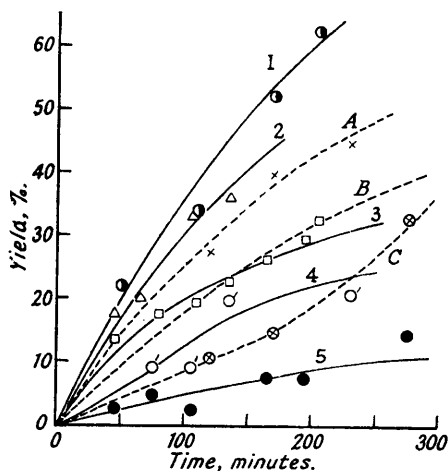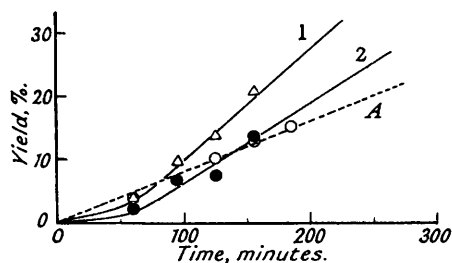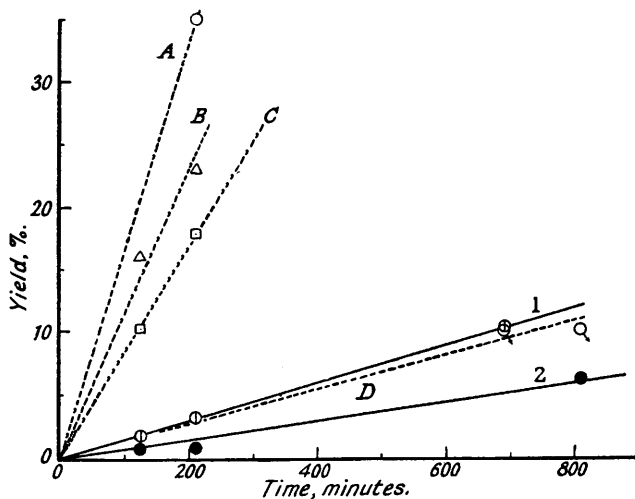
Fig. 1.

FIG. 2.

Polymerization of styrene in diethylene glycol at 70°.

(*A*) : Catalyst, Bz_2O_2—110 × 10^{-4} *mol.*/100 *c.c.* of monomer.
(1), (2) : Catalyst, $K_2S_2O_8$—2·5 × 10^{-4} and 2·2 × 10^{-4} *mol.*/100 *c.c.* of monomer, respectively.

FIG. 3.

Polymerization of styrene in propylene glycol at 61° (nitrogen atmosphere, under reduced pressure).

(*A*), (*B*), (*C*), (*D*) : Catalyst, Bz_2O_2—60 × 10^{-4}, 30 × 10^{-4}, 15 × 10^{-4}, and 3·8 × 10^{-4} *mol.*/100 *c.c.* of monomer, respectively.
(1), (2) : Catalyst, $K_2S_2O_8$—0·12 × 10^{-4} and 0·06 × 10^{-4} *mol.*/100 *c.c.* of monomer, respectively.

KM^a, where a = 0·62 and K = 3·7 × 10^{-4} for toluene, this means that the molecular weight of the former is $3^{1·6}$, *i.e.*, 5·8 times that of the latter. In fact, the viscosity-average molecular weight for one of the samples shown in Curve 2 in Fig. 1 is 64,000, which is unusually high for such dilute solutions of the monomer (1 : 5 by vol.) and with such a high rate of polymerization.

(3) At lower temperatures the differences in viscosity and speed are less marked, as shown by comparing the efficiency ratio and also [η] values for 80° and 61° as in section (2). It should be noted, however, that, although the intrinsic viscosity and hence the molecular weight of the polymer produced by persulphate is much higher than that produced by benzoyl peroxide, the variation in molecular

weight with different concentrations of the same catalyst is quite consistent, the slower the reaction the higher being the molecular weight.

(4) In Fig. 4 are plotted the square roots of the catalyst concentrations against the slopes of the yield curves obtained from Fig. 1. Both plots are straight lines, but that for the persulphate does not pass through the origin. This might be due to the slight inhibition caused by oxygen still present in the evacuated system, for Baxendale, Evans, and Kilham (*Trans. Faraday Soc.*, 1946, **42**, 668) found a

FIG. 4.

Plot of the rate of polymerization at 80° against the square root of catalyst concentration for polymerization of styrene in diethylene glycol.
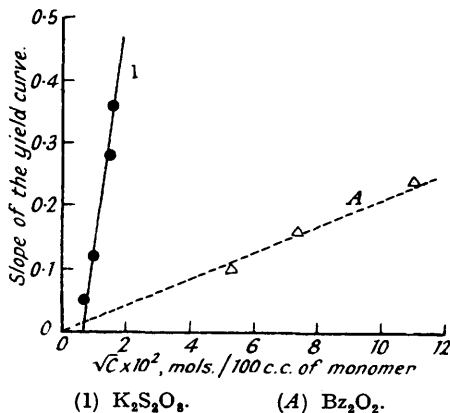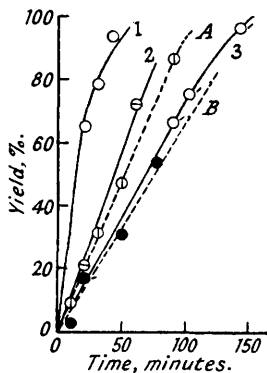

(1) $K_2S_2O_8$. (A) Bz_2O_2.

FIG. 5.

*Polymerization of methyl methacrylate in diethylene glycol at 80°.*

Time, minutes.

(1), (2), (3) : Catalyst, $K_2S_2O_8$—3.7×10^{-4}, 2.8×10^{-4}, and 1.9×10^{-4} mol./100 c.c. of monomer, respectively.

(A), (B) : Catalyst, Bz_2O_2—35×10^{-4} and 17×10^{-4} mol./100 c.c. of monomer, respectively.

FIG. 6.

Polymerization of methyl methacrylate in ethylene glycol at 61° in an atmosphere of nitrogen under reduced pressure.

Time, minutes.
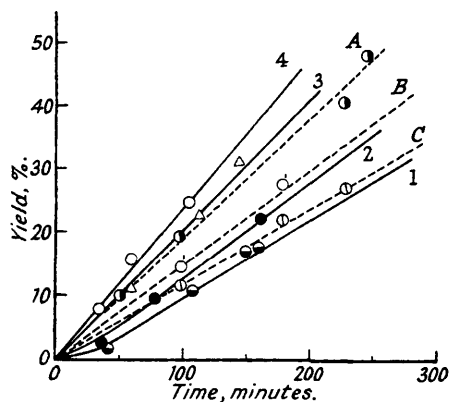
(A), (B), (C) : Catalyst, Bz_2O_2—1.1×10^{-4}, 0.84×10^{-4}, and 0.56×10^{-4} mol./100 c.c. of monomer, respectively.

(1), (2), (3), (4) : Catalyst, $K_2S_2O_8$—2.6×10^{-6}, 5.3×10^{-6}, 7.9×10^{-6}, and 10.6×10^{-6} mol./100 c.c. of monomer, respectively.

similar effect in the curve intended to describe the progress of polymerization of an oxidation–reduction-activated catalyst and attributed it to residual inhibition.

(5) We have found that the persulphate-initiated polymerization of styrene is fairly sensitive to oxygen. It is very difficult to obtain a yield curve which does not show an initial inhibition period, particularly at lower temperatures where the speed of polymerization is lower. With benzoyl peroxide catalysis the effect of oxygen is not marked, as seen from Fig. 2.

Methyl methacrylate. Some typical results with this monomer are presented in Figs. 5 and 6, Fig. 5 illustrating the results of the experiment in diethylene glycol at 80°. In order to show definitely that the inhibition periods in polymerization curves obtained during many preliminary experiments are due

to atmospheric oxygen, we performed a set of polymerization experiments (summarized in Fig. 6) in which the residual air was carefully displaced by nitrogen before sealing; this procedure practically eliminated the inhibition periods of persulphate-catalysed polymerization, though a slight inhibition was still noticeable at very small persulphate concentrations (curves 1 and 2).

The superiority of the persulphates over the benzoyl peroxide is not so striking with this monomer as with styrene. The relative efficiency is of the order of 15, as can be seen by comparing any pair of curves having nearly equal speed, say curves *B* and 3 of Fig. 5. The molecular weight of the persulphate-
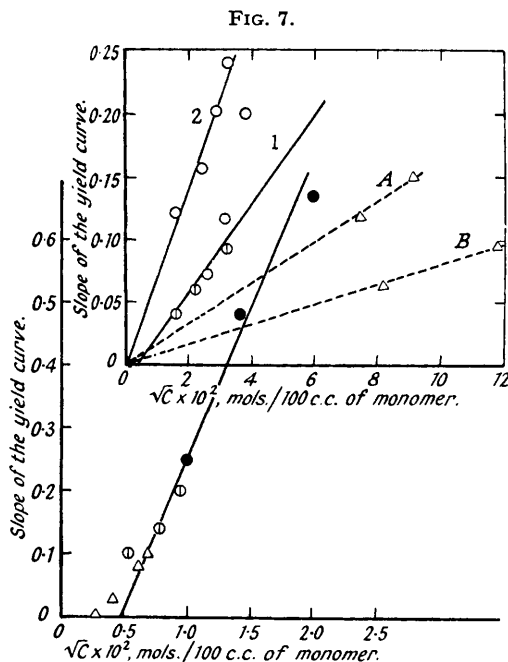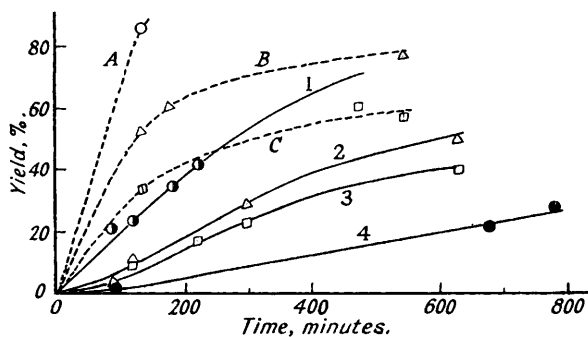
FIG. 7.

FIG. 8.

Polymerization of methyl acrylate in diethylene glycol at 66°.

(*A*), (*B*), (*C*) : Bz_2O_2—39×10^{-4}, 27×10^{-4}, and $15\cdot4 \times 10^{-4}$ *mol./100 c.c. of monomer, respectively.*
(1), (2), (3), (4) : $K_2S_2O_8$—$0\cdot8 \times 10^{-4}$, $0\cdot6 \times 10^{-4}$, $0\cdot3 \times 10^{-4}$, and $0\cdot15 \times 10^{-4}$ *mol./100 c.c. of monomer, respectively.*

catalysed products is also greater, for the [η] values of these polymers are 2·75, 3·1, 2·52, 1·85, 2·0, 2·22, 2·12, 2·24, 1·80, average = 2·28, whereas those for the peroxide-initiated polymers are 1·40, 1·20, 1·20, 1·24, 1·38, average = 1·28. The intrinsic viscosities of the former are therefore about twice those of the latter, indicating that the molecular weight is only $2^{1\cdot3}$, *i.e.* 2·46, times as great, as calculated as before but with $a = 0\cdot76$ (cf. Goldberg, Hohenstein, and Mark, *loc. cit.*).

The plot of the square root of the concentration of the catalysts against the slope of the yield curve (Fig. 7, inset; curves 1, 2, *A*, or *B*), like those of other free-radical-activated polymerizations, is a straight line.

Methyl acrylate. Fig. 8 gives some typical yield curves for methyl acrylate polymerized under conditions similar to those with styrene and methyl methacrylate, and the general results are the same, *viz.*, high speed and high oxygen sensitivity of persulphate-catalysed polymerization.

Viscosities of two samples of polymer were measured; one was prepared by using 1×10^{-4} mole of ammonium persulphate per 100 c.c. of monomer and isolated after 25·5% conversion, and the other with $1·5 \times 10^{-4}$ mole of benzoyl peroxide after 33·8% conversion, both polymerizations being carried out at 66° and with diethylene glycol as solvent. The former had an intrinsic viscosity of 0·5 in benzene but the latter had only 0·2.

An attempt was made to compare the relative efficiencies of the various persulphates among themselves. We have plotted in Curve 3 of Fig. 7 the rate versus the square root of catalyst concentration for the three persulphates studied. The results fall on a single curve, indicating that the activities of the three persulphates are closely similar if concentrations are expressed in molarities. This is not unexpected, for Green and Masson (*J.*, 1910, **97**, 2283) found that the various persulphates decomposed at essentially the same rate.

<div align="center">DISCUSSION.</div>

The mechanisms of the various thermal, photochemical, and organic peroxide-catalysed polymerizations of vinyl compounds have been studied extensively, and the processes are believed to be initiated by free radicals [cf. *e.g.*, Jones and Melville, *Proc. Roy. Soc.*, 1946, *A*, **187**, 19; Bawn and Whitby, Faraday Soc. Discussion on Labile Molecules (Sept. 1947); Melville, *Proc. Roy. Soc.*, 1937, *A*, **163**, 511; 1938, **167**, 99; Baxendale, Evans, and Kilham, *Trans. Faraday Soc.*, 1946, **42**, 668]. Polymerizations of vinyl compounds initiated by stannic chloride (Williams, *J.*, 1940, 775; Pepper, *Nature*, 1946, **158**, 781), boron trifluoride, aluminium chloride, titanium tetrachloride, and silver perchloride (Evans and Polanyi, *J.*, 1947, 252; Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425; etc.) have also been shown to be chain processes which proceed *via* an ionic mechanism (see Price, *Ann. N.Y. Acad. Sci.*, 1943, **44**, 351).

In view of the structure of persulphates and of instability of the peroxide linkage, we conclude that persulphates also initiate polymerization *via* a free-radical process. This view has been taken by all workers on the persulphate-initiated emulsion polymerization and is supported by the high molecular weight of the polymers formed, the high sensitivity towards inhibitors, and the linear nature of the curve relating the speed of polymerization to the square root of catalyst concentration. Our comparison of the peroxide- and persulphate-initiated polymerization in homogeneous systems shows that the latter have many characteristics in common with the emulsion polymerization, so that any attempt to explain the high speed and high molecular weight of the emulsion process must take account of the ability of potassium persulphate to increase the chain length as demonstrated above.

A few alternative mechanisms can be suggested to account for this high efficiency of the persulphates. The simplest would be to attribute it to a higher rate of initiation of free radicals, but this is ruled out by the fact that, other things being equal, a higher rate of initiation would produce a lowering of the average molecular weight, which is contrary to our observation. This directly follows from the equation,

$$\gamma = -(d[M]/dt)/V_{init.} = k_p[M]/\sqrt{k_t V_{init.}}$$

where γ is the degree of polymerization, $d[M]/dt$ the rate of monomer consumption, $V_{init.}$ the initiation rate, and k_p and k_t are constants for the propagation and termination rates. There is no *a priori* reason to suppose that the rate of propagation has anything to do with the catalyst, and hence we conclude that this difference is to be accounted for by a low speed of termination of the growing chain by the activated free radical produced by the catalyst.
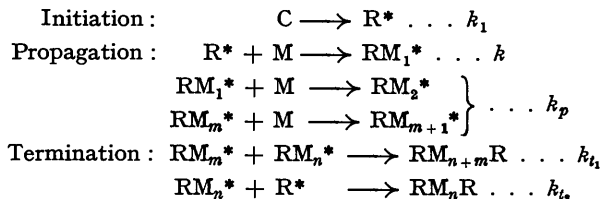
Of the usual processes of termination of free radicals, *viz.*,

(1) $M_n^* + M_s^* \longrightarrow M_{n+s}$; (2) $M_n^* + Cat.^* \longrightarrow M_n, Cat.$; and (3) $Cat.^* + Cat.^* \longrightarrow Cat._2$
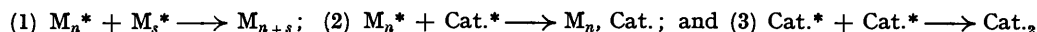
where Cat.* is the free radical produced by catalyst decomposition, we have to assume that reaction (2) probably predominates over reaction (1) in the case of benzoyl peroxide-catalysed polymerization, leading to a high wastage of the peroxide, whereas in the case of the persulphates this reaction is practically non-existent. This might be due to the low stationary concentration of the free radical produced by the persulphate, or to the inherent inertness of the persulphate radical towards such terminations.

An extreme case of vinyl polymerization where chain termination occurs solely by collision with catalyst fragment has been studied theoretically by the authors (*J. Indian Chem. Soc.*, 1949, **20**, 397). However, in actual practice we can hardly expect such an idealized condition

ever to be fulfilled. Consequently, we now give an analysis of a more complete case which is of particular interest for our present investigation, *viz.*, where the two types of termination, *i.e.*, combination by the two growing radicals (t_1) and termination by catalyst fragemnt (t_2), occur simultaneously. The kinetic framework considered is :

$$\text{Initiation :} \qquad \text{C} \longrightarrow \text{R*} \ldots k_1$$
$$\text{Propagation :} \qquad \text{R*} + \text{M} \longrightarrow \text{RM}_1\text{*} \ldots k$$
$$\left.\begin{array}{l} \text{RM}_1\text{*} + \text{M} \longrightarrow \text{RM}_2\text{*} \\ \text{RM}_m\text{*} + \text{M} \longrightarrow \text{RM}_{m+1}\text{*} \end{array}\right\} \ldots k_p$$
$$\text{Termination :} \quad \text{RM}_m\text{*} + \text{RM}_n\text{*} \longrightarrow \text{RM}_{n+m}\text{R} \ldots k_{t_1}$$
$$\qquad\qquad\qquad \text{RM}_n\text{*} + \text{R*} \longrightarrow \text{RM}_n\text{R} \ldots k_{t_2}$$

From the steady-state conditions $\text{d}[\text{R*}]/\text{d}t = 0$ and $\text{d}[\text{M*}]/\text{d}t = 0$, we obtain, on neglecting cubic terms in $[\text{M*}]^3$,

$$[\text{M*}] = \tfrac{1}{2}\sqrt{\frac{k_1[\text{C}]}{k_{t_1}}}\left\{\sqrt{\alpha^2 + 4} - \alpha\right\}$$

where

$$\alpha^2 = \frac{k_1[\text{C}]}{k_{t_1}}\frac{k_{t_2}{}^2}{k_i{}^2[\text{M}]^2}$$

Consequently,

$$\text{d}[M]/\text{d}t = k_p[\text{M}][\text{M*}] + k_i[\text{R*}][\text{M}]$$

$$= k_p\sqrt{\frac{k_1[\text{C}]}{k_{t_1}}}[\text{M}]\tfrac{1}{2}[\sqrt{\alpha^2 + 4} - \alpha] + k_1[\text{C}]$$

It will be seen that the maximum value of the term $[\sqrt{\alpha^2 + 4} - \alpha]$ is 2, and this occurs when $\alpha = 0$, *i.e.*, $k_{t_2} = 0$, and the rate expression then reduces to the ordinary form for t_1 termination alone. Under all other conditions $\text{d}[\text{M}]/\text{d}t$ is lower than this normal value, showing that t_2 termination has the effect of reducing the polymerization rate. It will also be noted that the term $[\sqrt{\alpha^2 + 4} - \alpha]$ decreases while [C] increases, showing that the polymerization rate should increase at a rate less than $\sqrt{[\text{C}]}$ and this should be more prominent the higher the value of [C]. The general observation of a square-root relation is due to the fact that under the conditions of most experiments α^2 is quite small, which makes the contribution of the term in brackets very small in comparison with that of the term outside the brackets, *i.e.*, $\sqrt{[\text{C}]}$. We can get an idea of the approximate value of α from the rate constants involved in it. Some of these are already known. Burnett (*Quart. Reviews*, 1950, **4**, 290) has collected all the available data. We know that for styrene at 30°, $k_p = 135$ l. mol.$^{-1}$ sec.$^{-1}$, $k_{t_1} = 1\cdot 7 \times 10^8$, and $k_p/k_{t_1} \simeq 10^6$, and this increases with higher temperature since the energy of activation of the termination reaction is comparatively small. In our experiments [C] has usually been less than 10^{-3}. We may justifiably assume k_p and k_i to be of the same order of magnitude, and k_{t_2} may have values of the same order of magnitude as k_{t_1}; k_1 for benzoyl peroxide is of the order of 10^{-3} in the range 60—80° (Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2229; Cass, *ibid.*, 1946, **68**, 1976) in solvents like alcohol, Cellosolve, etc., where the speed of decomposition is inordinately high. Hence,

$$\alpha^2 = \frac{k_1[\text{C}]}{k_{t_1}} \cdot \frac{k_{t_2}{}^2}{k_i{}^2[\text{M}]^2} \sim \frac{10^{-3} \times 10^{-3}}{1\cdot 7 \times 10^8} \times \frac{1\cdot 7 \times 10^8 \times 1\cdot 7 + 10^8}{135 \times 135 \times [\text{M}]^2} \sim \frac{10^{-2}}{[\text{M}]^2}$$

$< 0\cdot 01$ under usual experimental conditions

This shows the small order of magnitude of α^2 and hence its comparatively small effect on $\text{d}[\text{M}]/\text{d}t$ under the usual experimental conditions, *i.e.*, from pure monomer to about 1 : 10 dilution. The generally observed square-root relation is also due in no small measure to the uncertainty of experimentally obtaining an accurate value of $\text{d}[\text{M}]/\text{d}t$.

We are also interested here in the relation of the molecular weight of the polymer formed by the two mechanisms. If we denote by M_1 the mean molecular weight produced by a

termination process t_1 alone, and consider the case where the polymerization rates are the same in both the cases, *i.e.*, where

$$(d[M]/dt)_1 = (d[M]/dt)_2 \text{ and so } [M^*]_1 = [M^*]_2$$

we shall have,

$$\frac{\overline{M}_1}{\overline{M}_2} = \frac{[V_{\text{init.}}]_2}{[V_{\text{init.}}]_1} = \frac{[V_{\text{term.}}]_2}{[V_{\text{term.}}]_1} = \frac{k_{t_1}[M^*]_1{}^2 + k_1[R^*]_1[M^*]_1}{k_{t_1}[M^*]_2{}^2} = 1 + \frac{k_{t_2}}{k_{t_1}} \cdot \frac{[R^*]}{[M^*]}$$

Hence, we see that $\overline{M}_1$ is generally greater than $\overline{M}_2$, as we found, and their ratio depends on the ratio k_{t_2}/k_{t_1}. It may also be pointed out that $[R^*]$ and $[M^*]$ are generally of the same order of magnitude, and so the above equation is not incompatible with our experimental observations as far as the order of magnitude goes.

Another explanation for the diminished termination rate is possible.† The efficiency of chain termination in the case of the persulphates is diminished by the mutual repulsion of the growing radicals, for the persulphates yield charged radicals and this factor reduces the chances of mutual termination to a great extent. This repulsive effect is absent in benzoyl peroxide-catalysed polymerization.

It should be pointed out that in the above discussion we have not taken into consideration the possibility that some proportion of the radicals produced by persulphates may be diradicals and consequently tend to produce longer chains; *e.g.*, oxygen might be formed by the decomposition of persulphate and might behave as diradicals and these may play some part in our case, producing longer chains and higher speed, but there is no experimental support for such a mechanism.

It has been demonstrated by Nozaki and Bartlett (*J. Amer. Chem. Soc.*, 1946, **68**, 1686) that the decomposition of benzoyl peroxide is not a simple unimolecular reaction but is complicated by the concurrent 1·5-molecular decomposition of the peroxide by the catalyst radical. This leads to a wastage of the benzoyl peroxide without helping the polymerization and, in fact, Redington (*J. Polymer Sci.*, 1948, **3**, 503) has introduced the concept of a wastage factor to explain the relative efficiency of the different acyl peroxides in initiating styrene polymerization. Cooper's observations (*Nature*, 1948, **162**, 897, 927) also confirm this. It is probable that, unlike the unstable organic peroxides, the inorganic persulphates are stable enough successfully to withstand the onslaught of their own free radicals owing either to the mutual repulsion or to their inherent stability, and thus are able to prevent such wastage : this would partly account for their observed superiority. However, the concept of wastage alone is not sufficient, for we have shown (*loc. cit.*) that the " wastage factor " is a conception which tends to reduce only the effective catalyst concentration and this alone would not explain the higher molecular weight in our case.

Our general conclusions are supported by observations made recently by Bartlett and Cotman (*J. Amer. Chem. Soc.*, 1949, **71**, 1419), who measured the rate of decomposition of potassium persulphate in aqueous methanol. They found that, although persulphates decompose according to a free-radical mechanism, the phenomenon of induced decomposition of persulphates by free radicals is practically absent. This is the opposite of what is observed with benzoyl peroxide.

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† This was first suggested to the authors by Prof. Herman Mark in a private discussion.