678. *The Mechanisms of Inhibition and Retardation in Radical Polymerizations. Part III.* The Use of a Stable Free Radical as an Inhibitor.*

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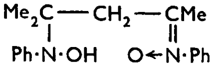
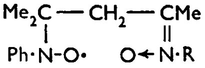
A stable free radical can be prepared by oxidation of a condensation product of acetone and phenylhydroxylamine. This radical is an inhibitor for the polymerization of styrene and of methyl α-methylacrylate. The induction periods are well defined, and the inhibitor is converted into products which do not affect the rate of polymerization; in these respects the radical is an ideal inhibitor, but the stoicheiometry of the reactions occurring during the induction periods is uncertain and therefore this inhibitor cannot be used for measuring rates of initiation in radical-chain reactions.

Banfield and Kenyon [1] showed that reaction of acetone with phenylhydroxylamine gave a crystalline product, *N*-(3-*N*-hydroxyanilino-1 : 3-dimethylbutylidene)aniline oxide (I). This material was oxidized by silver oxide to a red crystalline product (II), the free-radical nature of which was confirmed by physical measurements.[2,3,4] This radical appears to be stable at 0° but at room temperature in a period of a few weeks it becomes discoloured and loses its crystalline form. In this paper the effects of this radical on sensitized polymerizations and on the decomposition of αα′-azo*iso*butyronitrile are described.

(I)



$$\begin{array}{ccc} Me_2C & —CH_2— & CMe \\ | & & \| \\ Ph\cdot N\cdot OH & & O\leftarrow N\cdot Ph \end{array}$$



$$\begin{array}{ccc} Me_2C & —CH_2— & CMe \\ | & & \| \\ Ph\cdot N\cdot O\cdot & & O\leftarrow N\cdot R \end{array}$$

(II): R = Ph

(III): R = p-C_6H_4Me

Diphenylpicrylhydrazyl has been used as an inhibitor of polymerizations [5] and to measure the rate of generation of radicals from typical initiators of polymerization.[6] There

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* Part II, Bevington, Ghanem, and Melville, *J.*, 1955, 2822.

[1] Banfield and Kenyon, *J.*, 1926, 1612.

[2] Holden, Kittel, Merritt, and Yager, *Phys. Rev.*, 1950, **77**, 147.

[3] Van den Handel, *Physica*, 1952, **18**, 921.

[4] Chu, Pake, Paul, Townsend, and Weissman, *J. Phys. Chem.*, 1953, **57**, 504.

[5] Bartlett and Kwart, *J. Amer. Chem. Soc.*, 1952, **74**, 3969.

[6] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.

is evidence that one hydrazyl radical reacts with one radical but the mechanism of this reaction is uncertain.[7] There are other objections to the use of the hydrazyl in quantitative work; first, the products of the scavenging reaction can themselves react with free radicals and, secondly, it seems that the scavenger fails to react with all the radicals which are generated in solution by the dissociation of azo*iso*butyronitrile.[7] Radical (II) is less stable and presumably more reactive than diphenylpicrylhydrazyl, and also it does not contain nitro-groups which may be responsible for the reactivity of the products formed from the hydrazyl. For these reasons it was decided to examine the possibility of using the radical (II) as a radical scavenger.

The polymerizations at 60° of styrene and methyl α-methylacrylate sensitized by azo*iso*butyronitrile were studied, in presence of the radical (II) in various concentrations. The decomposition at 60° of the initiator in the presence of the radical (II) in benzene solution was also studied by using the ^{14}C-azo-compound so that products of the direct interaction of 2-cyano-2-propyl radicals could be determined by isotope dilution analysis.

FIG. 1. *Conversion–time plots showing the inhibitory effect of the radical* (II) *on the sensitized polymerization of styrene.* (*Numbers on curve are expt. nos.*)

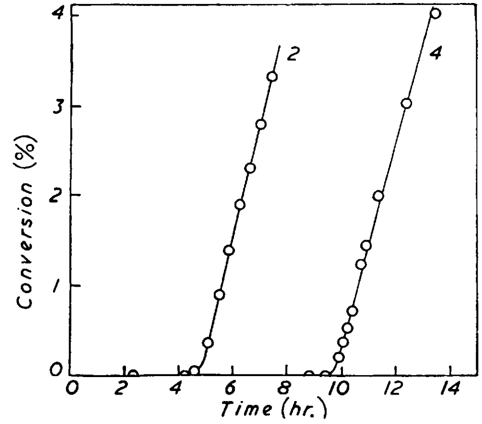
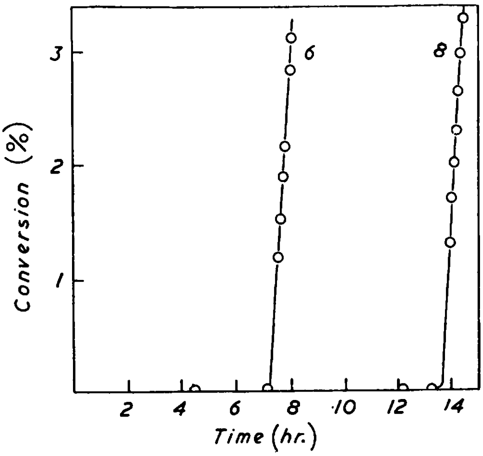


FIG. 2. *Conversion–time plots showing the inhibitory effect of* (II) *on the sensitized polymerization of methyl α-methylacrylate.*



EXPERIMENTAL

Materials and Methods.—The substances (I) and (II) were prepared by the methods of Banfield and Kenyon.[1] The preparations and purifications of the other substances and the experimental procedures have been described previously.[8,9]

An attempt was made to prepare the radical (III) from acetone and *p*-tolylhydroxylamine. The first product corresponding to the oxide (I) was isolated; oxidation of this product with silver oxide gave a red solution in light petroleum but a crystalline product could not be isolated.

Results.—Polymerizations of styrene in bulk at 60° in the complete absence of air were performed, with azo[^{14}C]*iso*butyronitrile at a concentration of 0·300 g./l. and various concentrations of the radical (II); typical conversion–time plots are shown in Fig. 1. The radical caused a well-defined induction period during which the colour disappeared completely; afterwards the rate rapidly attained a steady value. The induction periods were recorded as the intercepts on the time axis of the linear portions of the conversion–time plots. The polymers recovered from these experiments by precipitation in methanol showed no sign of coloration. Polymers were assayed after reprecipitation; the rates of initiation of polymerization were calculated from the specific activities of the polymers and the initiator, and the overall rates of polymerization. The results of these experiments are summarized in Table 1.

Similar experiments were performed with methyl α-methylacrylate in place of styrene, with initiator at a concentration near 0·200 g./l.; these experiments are referred to in Fig. 2 and

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[7] Bevington, *J.*, 1956, 1127.

[8] Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **12**, 449.

[9] Bevington, *J.*, 1954, 3707.

Table 2. The radical (II) introduced induction periods, followed by reactions at steady rates. The recovered polymers were white.

TABLE 1.

Expt. no.	Concn. of (II) (g./l.)	Induction period (min.)	Steady rate of polymn. (%/hr.)	Rate of initiation (10^{-8} mole l.$^{-1}$ sec.$^{-1}$)
1	0	0	1·37	2·26
2	0·199	290	1·29	2·11
3	0·355	464	1·20	2·06
4	0·509	585	1·11	1·71

TABLE 2.

Expt. no.	5	6	7	8
Concn. of (II) (g./l.)	0	0·102	0·198	0·206
Induction period (min.)	0	440	720	815
Steady rate of polymn. (%/hr.)	4·63	3·86	3·32	3·95

An air-free solution of azo[^{14}C]*iso*butyronitrile (2·83 mg.) and radical (II) (10·0 mg.) in benzene (2·15 c.c.) was kept at 60° for 16 hr. Subsequent analysis showed that 0·20 mg. of tetramethylsuccinodinitrile was present in the solution. From previous work,[9] about 0·48 mg. of the dinitrile would have been formed in this experiment if the radical (II) had been absent.

DISCUSSION

A significant amount of tetramethylsuccinodinitrile is produced from azo*iso*butyronitrile even when an excess of the radical (II) is present in the solution in which the azo-compound is decomposed; the quantity is similar to that formed in an experiment involving diphenylpicrylhydrazyl in place of the radical (II).[7] This confirms that only a part of the azo-compound decomposes to give radicals available for reaction with other substances in the solution. It is necessary to suppose that some sort of " cage effect " is operating or that part of the azo-compound decomposes by a mechanism not involving the liberation of free radicals.[10] In calculations involving the decrease in the concentration of the azo-compound, the first-order velocity constant for the decomposition at 60° is taken as $1{\cdot}20 \times 10^{-5}$ sec.$^{-1}$; in calculations requiring knowledge of the rate of production of *available* radicals, however, the smaller value of $1{\cdot}00 \times 10^{-5}$ sec.$^{-1}$ is chosen.

The steady rates of polymerization observed in experiments 2, 3, and 4 are less than that in expt. 1, probably owing to decomposition of initiator during the induction periods. The observed rates of polymerization can be corrected to those for an initiator concentration of 0·300 g./l. by assuming that the rate is proportional to (initiator concentration)$^{\frac{1}{2}}$ and that the velocity constant for the decomposition of the initiator is $1{\cdot}20 \times 10^{-5}$ sec.$^{-1}$. The corrected rates for expts. 2, 3, and 4 are respectively 1·43, 1·42, and 1·35%/hr.; these rates are quite close to that for expt. 1. It is concluded that products formed during the induction period are not retarders. The rates of initiation quoted in Table 1 are not corrected for decomposition of the initiator; if this correction is made, the rates of initiation for a concentration of initiator of 0·300 g./l. are 2·26, 2·59, 2·86, and $2{\cdot}53 \times 10^{-8}$ mole l.$^{-1}$ sec.$^{-1}$ for experiments 1, 2, 3, and 4 respectively. These figures suggest that products formed from the radical (II) during the induction period do not significantly interfere in the initiation of polymerization.

The corrected rates of polymerization for methyl α-methylacrylate at an initiator concentration of 0·200 g./l. are 4·63, 4·56, 4·37 and 5·27%/hr. for experiments 5, 6, 7, and 8 respectively. The agreement between these rates is not as good as that in the polymerizations involving styrene, but there is no evidence that retarders are formed during the induction period.

One of the objections to the use of diphenylpicrylhydrazyl as a radical scavenger is that products formed from it are reactive. In this respect, radical (II) is much superior to the hydrazyl.

The number of radicals generated from the initiator during the induction period can be

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[10] Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

calculated and then compared with the number of inhibitor radicals consumed. It is assumed that the inhibitor is completely used during the induction period. The results of the calculations are summarized in Table 3; 1 l. of reaction mixture is considered, and numbers of radicals are expressed in moles.

TABLE 3.

Expt. no.	2	3	4	6	7	8
No. of radicals generated (r) × 10^4	5·7	8·9	10·7	5·5	8·3	9·6
No. of inhibitor radicals consumed (i) × 10^4	6·7	12·0	17·1	3·4	6·7	6·9
i/r	1·18	1·35	1·60	0·62	0·81	0·72

For the experiments involving styrene, *viz.*, nos. 2, 3, and 4, the ratio i/r is considerably greater than 1. This indicates either that more than one inhibitor radical is needed to react with a 2-cyano-2-propyl radical, or that at 60° the inhibitor is gradually consumed by a reaction not involving the radicals generated from the initiator. The latter explanation seems the more likely since radical (II) is slightly unstable even at room temperature; further, it accounts for the fact that i/r increases with the length of the induction period. The results for styrene are at variance with those for methyl α-methylacrylate for which the ratio i/r is less than 1. This result is unexpected since the nature of the monomer should not affect the induction period during which the only reactions of significance are believed to be the decomposition of the initiator and the interaction of 2-cyano-2-propyl radicals with the inhibitor. The result could be explained by supposing that azo*iso*butyronitrile decomposes more slowly in methyl α-methylacrylate than in styrene, but there is no evidence to support this assumption. It is concluded that there is at present no satisfactory explanation for the difference between the experiments involving the two monomers.

Radical (II) is not regarded as an inhibitor suitable for quantitative study of radical-chain reactions. In kinetic work, inhibitors are used to evaluate rates of initiation and for this purpose it is necessary to know with certainty the relation between the number of radicals generated in the system and the quantity of inhibitor consumed. For radical (II) this relation varies from one system to another, and it varies also with the length of the induction period; the radical cannot therefore be used for measurements of rates of initiation except under special conditions.

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