456. *The Mechanisms of Inhibition and Retardation in Radical Polymerizations. Part IV.* The Effects of Diphenylpicrylhydrazine and a Condensation Product of Acetone with Phenylhydroxylamine upon the Sensitized Polymerization of Styrene.*

By J. C. Bevington and N. A. Ghanem.

Both diphenylpicrylhydrazine (I) and *N*-(3-*N*-hydroxyanilino-1 : 3-dimethylbutylidene)aniline *N*-oxide (II) retard the radical polymerization of styrene at 60°. By using labelled retarders it has been shown that both substances become chemically incorporated in the polymers; if the concentration of retarder is sufficient, the number of initiator fragments combined in each polymer molecule is approximately 1 and the number of retarder molecules is approximately 0·5. The use of these retarders in the determination of rates of initiation in radical polymerizations is discussed; it is concluded that the *N*-oxide (II) could be used for this.

Apart from the mechanism by which they act, retarders of radical polymerizations are of interest since they might be used for determining rates of initiation in certain polymerizations. Rates of initiation in sensitized polymerizations can be determined by using labelled sensitizers,[1] but this cannot be done for other types of radical polymerization. For example, a reliable method is needed for measuring rates of initiation in graft copolymerizations and in studies of branching reactions, and here labelled retarders might be used.

A retarder which functions by becoming attached to the growing end of a polymer chain and completely deactivating it was sought. The number of monomer units associated with one retarder molecule could be determined by analysis of the polymer and would be the kinetic chain length (ν) in the polymerization; the rate of initiation is then the ratio of the overall rate of polymerisation to ν. Substances which might behave as such retarders include stabilized radicals which can react with other radicals but not with monomer molecules. If the retarder did not combine with the polymer radical, its action might be represented as

$$R\cdot + X\cdot \longrightarrow P + Y \qquad \ldots\ldots\ldots \quad (1)$$

where R· is a growing polymer radical, X· a stabilized radical, P a dead polymer molecule, and Y a stable product derived from X. In this case, it would be necessary to determine the quantity of Y produced instead of the quantity of retarder incorporated in the polymer, but no suitable stabilized radical was discovered.

Another possibility is to use a substance, such as a quinone, which can add to the end of a growing polymer radical to form a new radical so stabilized that it is incapable of further growth. *p*-Benzoquinone behaves thus during the polymerization of methyl methacrylate;[2] the product of the interaction of a polymer radical and a quinone molecule can be represented as (III) where P represents a poly(methyl methacrylate) chain. Almost all these radicals disappear by combination with another polymer radical to give the molecule (IV). In this case, one molecule of combined retarder represents two polymer radicals. With other monomers, different effects occur[3] and so *p*-benzoquinone could not be used generally for measuring rates of initiation.

A substance X·H whose hydrogen atom is easily removed by polymer radicals can be regarded as a transfer agent; if however the radical X· is so stabilized that it cannot re-initiate a polymer chain and can only combine with a second polymer radical, then the

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* Part III, Bevington and Ghanem, *J.*, 1956, 3506.

[1] Bevington, *Trans. Faraday Soc.*, 1955, **51**, 1392.

[2] Bevington, Ghanem, and Melville, *Trans. Faraday Soc.*, 1955, **51**, 346.

[3] Bevington, Ghanem, and Melville, *J.*, 1955, 2822.

substance X·H is then a retarder and not a transfer agent. Each molecule, as represented by equations (2) and (3), terminates two growing chains and on the average each polymer

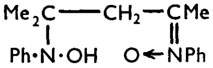
$$P\cdot + X\cdot H \longrightarrow P\cdot H + X\cdot \qquad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$P\cdot + X\cdot \longrightarrow P\cdot X \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

molecule contains half a molecule of retarder. If transfer to solvent or monomer occurs each kinetic chain contains on the average half a molecule of retarder, and it is still possible to measure the rate of initiation.

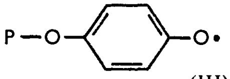
$Ph_2N\cdot NHPc$

(I)



$Me_2\underset{\underset{Ph\cdot N\cdot OH}{|}}{C}-CH_2-\underset{\underset{O\leftarrow NPh}{\|}}{C}Me$

(II)

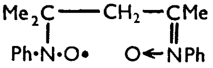


(III)

Pc = Picryl

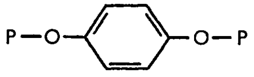
$Ph_2N\cdot\dot{N}Pc$

(V)



$Me_2\underset{\underset{Ph\cdot N\cdot O\cdot}{|}}{C}-CH_2-\underset{\underset{O\leftarrow NPh}{\|}}{C}Me$

(VI)



(IV)

The substances (I) and (II) can quite easily lose hydrogen atoms and so be converted into the radicals diphenylpicrylhydrazyl (V) and (VI) which are stabilized and inhibit radical polymerizations.[4] The substances (I) and (II) are retarders for certain polymerizations, and it seems quite likely that their action might be according to equations (2) and (3).

The objects of the work now described were to discover the mechanism by which substances (I) and (II) retard, and to examine the possibility of using them to measure rates of initiation. The work involved the use of ^{14}C-labelled specimens of (I), (II), and αα′-azo*iso*butyronitrile.

EXPERIMENTAL

Materials and Methods.—The preparations of labelled azo*iso*butyronitrile[5] and labelled diphenylpicrylhydrazine[6] have been described. The labelled specimen of the *N*-oxide (II) was prepared by Banfield and Kenyon's method[7] from [1 : 3-$^{14}C_2$]acetone supplied by the Radiochemical Centre, Amersham. Experimental procedures have been described.[2] Polymerizations were allowed to go to about 6% conversion. In the results, the activities of the various materials are quoted in counts per min. (c./min.) for a fixed weight of carbon dioxide in a gas counter; these counting rates are directly proportional to the $^{14}C : ^{12}C$ ratios in the materials being assayed. For this method of assay, a counting rate of 14,000 c./min. corresponds to a specific activity of about 1μc/g. of carbon.

Results.—*Separation tests.* The removal from polymers of all traces of uncombined labelled reagents is very important in tracer studies of polymerizations. If polystyrene is prepared with αα′-azo*iso*butyronitrile as initiator,[5] virtually all traces of uncombined initiator can be removed by precipitating the polymer twice from benzene with methanol. Tests were made concerning the separation of polystyrene from the retarders (I) and (II). Unlabelled polymer was mixed in solution with labelled retarder; the polymer was recovered by precipitation and then assayed. The results (Table 1) show that two precipitations suffice to remove almost all traces of the uncombined hydrazine (I) from the polymer, but in the case of the *N*-oxide (II)

TABLE 1.

	Retarder (I)	Retarder (II)
Polystyrene (mg.)	164·3	625
Retarder (mg.)	11·5	103
Counting rate for retarder (c./min.)	56,200	161,000
Counting rate (c./min.) calc. for no separation	2200	18,400
Counting rate (c./min.) obs. for polymer after 1, 2, and 3 pptns. respectively	3, 1, 0	480, 17, 7

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[4] Bevington and Ghanem, *J.*, 1956, 3506.

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

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

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

three precipitations may be necessary; in routine experiments two and three precipitations respectively were used.

Experiments with the hydrazine (I) *as retarder.* Bulk styrene was polymerized at 60° by using a fixed concentration of the azo-compound as initiator and various concentrations of the hydrazine (I). Results of experiments with labelled initiator or retarder are summarized in Tables 2 and 3 and Fig. 1. For the unretarded polymerization the rate of polymerization is steady; when retarder is present, the rate gradually rises during the reaction. $N_{\rm i}$ and $N_{\rm r}$ are the numbers of molecules of initiator fragments or retarder molecules per polymer molecule.

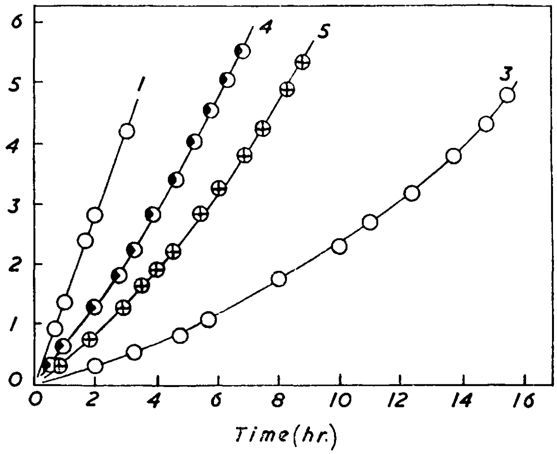

Fig. 1. *Conversion–time plots for sensitized polymerization of styrene at* 60° *in the presence of various concentrations of retarder* (I). *Curves are labelled with experiment numbers as in Tables* 2 *and* 3.

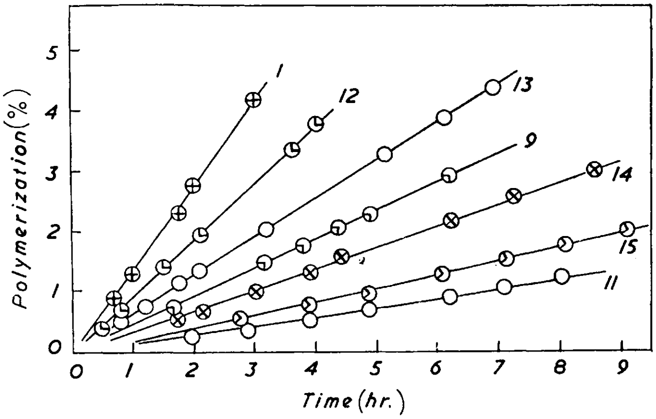

Fig. 2. *Conversion–time plots for sensitized polymerization of styrene at* 60° *in the presence of various concentrations of retarder* (II).

Table 2. *Labelled initiator, unlabelled retarder.*

Expt. no.	Initiator concn. (g./l.)	Retarder concn. (g./l.)	Rate (%/hr.)	Conversion (%)	M	c./min. for polymer	$N_{\rm i}$
1	0·300	0	1·37	5	264,000	200	2·03
2	0·300	0·102	*	6	117,500	287	1·30
3	0·300	0·203	*	6·5	72,000	395	1·09

* Acceleration during polymerization. c./min. for initiator = 500,000.

Table 3. *Labelled retarder, unlabelled initiator.*

Expt. no.	Initiator concn. (g./l.)	Retarder concn. (g./l.)	Rate	Conversion (%)	M	c./min. for polymer	$N_{\rm r}$
4	0·297	0·052	*	6·7	187,000	22	0·31
5	0·298	0·101	*	6·2	105,500	54	0·43
6	0·300	0·150	*	6	94,500	62	0·45

* Acceleration during polymerization. c./min. for retarder = 56,200.

Experiments with the N-*oxide* (II) *as retarder.* Similar experiments were performed (Tables 4 and 5, Fig. 2). There were no induction periods, and the rate of polymerization remained steady for at least 6% conversion. The retarder did not affect the polymerization of methyl methacrylate.

TABLE 4. *Labelled initiator, unlabelled retarder.*

Expt. no.	Initiator concn. (g./l.)	Retarder concn. (g./l.)	Rate (%/hr.)	M	c./min. for polymer	N_i
7	0·301	0·418	0·925	144,500	96	1·52
8	0·299	0·696	0·615	89,500	128	1·25
9	0·299	0·994	0·432	75,500	145	1·20
10	0·305	1·310	0·378	68,000	143	1·06
11	0·299	2·280	0·172	—	361	—

c./min. for initiator = 176,000.

TABLE 5. *Labelled retarder, unlabelled initiator.*

Expt. no.	Initiator concn. (g./l.)	Retarder concn. (g./l.)	Rate (%/hr.)	M	c./min. for polymer	N_r
12	0·298	0·406	0·915	151,000	90	0·36
13	0·300	0·752	0·667	99,000	166	0·44
14	0·306	1·510	0·369	58,000	338	0·52
15	0·300	2·000	0·210	44,000	475	0·55

c./min. for retarder = 161,000.

In expt. 16, an air-free solution of [^{14}C]azo*iso*butyronitrile (5·37 mg.) and the *N*-oxide (II) (26 mg.) in benzene (6 c.c.) was kept at 60° for 20 hr. It was then found by isotope dilution analysis that the solution contained 0·12 mg. of *iso*butyronitrile and 0·40 mg. of tetramethylsuccinodinitrile. If the *N*-oxide (II) had been absent from the reaction mixture, the expected yields of the nitrile and dinitrile would have been 0·40 mg. and 1·25 mg. respectively.[8]

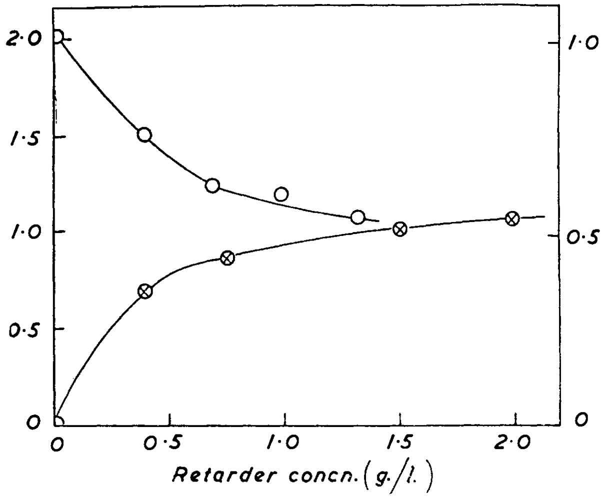

FIG. 3. *Variation of number of combined initiator fragments* ○ *and combined retarder molecules* ⊗ *in each polymer molecule with concentration of retarder.*

DISCUSSION

The results in Fig. 1 show that the hydrazine (I) retards the polymerization of styrene. The retarder is not ideal, however, since the rate of polymerization gradually rises during reaction. Comparison of the results in Tables 2 and 3 shows that as the initial concentration of retarder is increased the number of initiator fragments combined in each polymer molecule falls towards 1; at the same time the corresponding number of retarder molecules rises to a value of about 0·5. These results would satisfy the mechanism implied in

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

equations 2 and 3, but they may be misleading since the concentration of retarder in the reaction mixture evidently falls appreciably during the reaction. Further, it is unlikely that the scavenging action of diphenylpicrylhydrazyl can be represented adequately as a simple combination between the hydrazyl and the radical.

The *N*-oxide (II) appears to be more satisfactory than the hydrazine (I); the rate of reaction remains steady over an appreciable extent of polymerization (Fig. 2), but as it does not retard polymerization of methyl methacrylate it cannot be of general application.

Results in Tables 4 and 5 have been used to construct Fig. 3. The numbers of combined initiator fragments and retarder molecules show the same trend as for the hydrazine (I), and again would be satisfied by eqns. (2) and (3). The *N*-oxide (II) might be used for measuring kinetic chain lengths and rates of initiation in at least some radical polymerizations; sufficient retarder to suppress all mutual termination of reaction chains would be needed. The kinetic chain length (ν) would be half the number of monomer units combined with one retarder molecule; for styrene,

$$\frac{\text{Counting rate for polymer}}{\text{Counting rate for retarder}} = \frac{18}{18 + 16\nu}$$

The retarder might react not only with growing polymer radicals but also with the primary radicals. If so, the rate of initiation measured with the retarder would be lower than the rate of production of radicals and also lower than the rate of initiation in a system not containing the retarder but otherwise identical. This possibility was examined by comparing the rates of initiation in those experiments involving labelled initiator and unlabelled retarder (Table 6); for all these experiments, the concentration of initiator was close to 0·300 g./l.

TABLE 6.

Expt. no.	1	7	8	9	10	11
Retarder concn. (g./l.)	0	0·418	0·696	0·994	1·310	2·280
ν	1250	917	687	607	615	244
10^8 × Rate of initiation (mole/l./sec.)	2·55	2·34	2·08	1·65	1·42	1·64

The rates of initiation of retarded polymerizations are appreciably lower than those of unretarded ones. Therefore if the *N*-oxide (II) were used in conjunction with styrene for measurement of the rate of production of radicals in a system, it would be possible only to fix a lower limit to this rate.

Experiment 16 showed that the yields of *iso*butyronitrile and tetramethylsuccinodinitrile formed during the decomposition of azo*iso*butyronitrile in benzene are appreciably decreased by the presence of the *N*-oxide (II). This result demonstrates that (II) can react directly with 1-cyano-1-methylethyl (2-cyano-2-propyl) radicals. It was shown previously [6] by similar experiments that the hydrazine (I) interferes in the decomposition of the azo-compound in benzene solution. By consideration of equations (2) and (3), it might be expected that the interaction of 1-cyano-1-methylethyl radicals and the *N*-oxide (II) could be represented by equations (4) and (5), where X represents the radical (VI).

$$\mathrm{Me_2\dot{C}{\cdot}CN + X{\cdot}H \longrightarrow Me_2CH{\cdot}CN + X{\cdot}} \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathrm{Me_2\dot{C}{\cdot}CN + X{\cdot} \longrightarrow Me_2CX{\cdot}CN} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Appreciable quantities of *iso*butyronitrile would then be expected in the reaction mixture, but this was not so. This result makes it uncertain that equations (2) and (3) accurately represent the mechanism of the retardation.

It is concluded that the *N*-oxide (II) can be used to measure rates of initiation in the polymerization of styrene, so long as enough retarder is used to suppress all mutual termination of reaction chains; at 60° for an unretarded rate of 1·4%/hr., which corresponds to a rate of initiation of about $2{\cdot}5 \times 10^{-8}$ mole/l./sec., *ca.* 1·5 g./l. is adequate. The kinetic chain length is then the number of monomer units equivalent to 0·5 molecule of *N*-oxide (II) incorporated in the polymer. For analysis of the polymer, it is necessary to use a tracer technique; if gas counting or other sensitive method of assay is used, the specific activity of the retarder (II) could be as low as about 10 μc/g. In view of the uncertainties referred to, this procedure must be regarded as empirical.

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