

## Effect of Concentration of Inhibitors and Retarders on the Catalyzed Polymerization of Styrene\*

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### INTRODUCTION

Although much literature concerned with regulation of vinyl polymerization is available, quantitative data, which permit a comparison or a contrast of the effects of common retarders and inhibitors on a given vinyl polymerization system, are not often found. This investigation was initiated to provide such information in the hope that an analytical method could be developed to detect types of inhibitors and retarders contained in natural materials. Such a technique could conceivably indicate the presence of stable free radicals, independently of electron-spin resonance spectral measurements. The applications of the findings described herein to natural systems will be the subject of another communication.

The effects of varying concentrations of several inhibitors and retarders in modifying the polymerization of styrene, initiated by benzoyl peroxide, are reported in the following. Kinetic measurements were made by a dilatometric method.

### EXPERIMENTAL

#### Description of the Apparatus

The dilatometer used was of the stopcock type similar to that described by Bartlett and Trifan.<sup>1</sup> A mineral oil bath was used which was heated by means of a hotplate with a self-contained thermostat and an immersed coil of nichrome wire which was regulated through a powerstat. A small pump circulated the oil through a glass jacket surrounding

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the capillary. A mechanical stirrer in the oil bath also helped to keep the heating uniform. Such an assembly made manual control of the temperature possible to within  $\pm 0.2^\circ\text{C}$ . by infrequent minor adjustments. The temperature for individual runs was maintained near  $86^\circ\text{C}$ .

Standard-taper joints were used to attach the capillary to the bulb and the loading assembly to the dilatometer. Fisher Nonaq stopcock grease, insoluble in organic solvents, was successfully used on all joints. Since precision-bore capillary tubing was not employed to make the dilatometers, they were calibrated by filling the tubing with mercury and weighing the amount drained from given intervals marked on the capillary tubing.

The apparatus was degassed by aspirating the air and filling with nitrogen three successive times.<sup>1,2</sup> Before charging the dilatometer the styrene was also deoxygenated by bubbling commercial grade tank nitrogen through it for 30 min.

#### Zero Time Problem

Establishing zero time<sup>3,4</sup> for dilatometric measurements has always been a problem since the inception of the method. Many investigators<sup>5</sup> have devised elaborate dilatometers to eliminate the issue. It has been our purpose to obtain data which are as accurate as possible without elaborate methods. With this aim in mind the time of mixing has uniformly been designated as zero time. Satisfactory *relative* inhibition times have thus been obtained, even though they do not represent the absolute duration of inhibition. Bartlett and Trifan<sup>1</sup> also approached the problem in this manner. This meant that control runs in which no inhibitor was added showed a zero point greater than zero. With inhibited runs the time for attainment of maximum height and therefore temperature equilibrium, was 12-14 min. after loading. With uninhibited runs the drop of the capillary meniscus

began after 8–11 min. and therefore prior to temperature equilibration. Thus, when inhibition times were involved a standard 9 min. was subtracted in an attempt to approximate the time when reaction began. This same 9-min. correction was made for both inhibited and uninhibited runs.

### Materials

Benzoyl peroxide was twice precipitated from a saturated chloroform solution by pouring into methanol, m.p. 105–106.5°C.

1,1-Diphenyl-2-picrylhydrazine was prepared by the method of Poirier, Kahler, and Benington,<sup>6</sup> m.p. 172–174°C.

1,1-Diphenyl-2-picrylhydrazyl was prepared by the method of Poirier, Kahler, and Benington<sup>6</sup> from 1,1-diphenyl-2-picrylhydrazine and processed as described by Lyons and Watson,<sup>7</sup> m.p. 131–135°C.

1,3,5-Trinitrobenzene was recrystallized once from 80% ethanol, m.p. 121°C.

1,4-Benzoquinone was recrystallized once from petroleum ether, m.p. 113–115°C.

*N*-(3-*N*-Hydroxyanilino-1,3-dimethylbutylidene)-aniline *N*-oxide (Banfield's hydroxide) was prepared by the method of Banfield and Kenyon,<sup>8</sup> m.p. 133–134°C.

Banfield's Free Radical was prepared from Banfield's hydroxide, m.p. 84–85°C.

### Purification of Styrene

Eastman white-label styrene containing *tert*-butylcatechol was distilled once under nitrogen at 10–30 mm. mercury pressure and collected in 55 ml. portions. The first and last 20% of each batch was discarded. Each 55 ml. portion was stored in a separate stoppered test tube under nitrogen in a refrigerator kept at –18°C. The rate of polymerization of samples stored for several weeks did not change perceptibly. This procedure and the subsequent degassing were found to eliminate essentially any inhibition period which might be caused from residual inhibitors or oxygen.

### Decomposition of Benzoyl Peroxide

The rate of decomposition of benzoyl peroxide at 86.6°C. was determined by iodometric titration of residual peroxide after measured reaction times. A potentiometric rather than colorimetric titration<sup>9</sup> with standard thiosulfate was used. This modification was necessary because of the small concentrations of peroxide (0.001–0.003*M*). Because insoluble polystyrene interfered with the

potentiometric titration, *p*-benzoquinone was added to minimize polymer formation during periods of 2½ hr. Rates of decomposition of benzoyl peroxide with or without the retarder for periods up to one hour were not measurably different.

### Preparation of Standard Solutions

Regulator solutions were prepared using distilled and deoxygenated styrene in volumetric flasks at room temperature. Every effort was taken to prevent decomposition and minimize dissolving oxygen in these solutions by storing each one at 0°C. for no longer than two weeks, and displacing the air in the top of the flask by nitrogen after each use of the solution. Concentrations of these solutions were approximately 0.055*M*. Varying amounts were used in the reaction system so that the concentrations of regulators varied between 0.0002 and 0.0027*M*.

### RESULTS

It is a well-established fact that the volume contraction observed in the polymerization of styrene is directly proportional to the extent of this reaction in its early stages. Complete polymerization of styrene at 80°C. results in 18.37% volume contraction.<sup>10</sup> The experiments described herein were conducted near 86°C. The per cent volume contraction at this temperature would be expected to be essentially the same as at 80°C. Accordingly, a total volume of 42 ml. of styrene, contained in the dilatometer assembly, would contract 7.7 ml. when complete polymerization of the monomer had occurred. In this investigation, the extent of polymerization was never carried beyond 10%.

In the control run (Fig. 1, curve *A*) in which no retarder was used, a decrease in height of the liquid of 1.78 mm./min. was observed. (All the dilatometric data were subjected to a least squares analysis to determine slopes.) This represented a rate of 1.39% volume contraction/hr. or 7.5% polymerization/hr. The average for all such control runs was 1.472% volume contraction/hr. with a standard deviation of 0.045. Thus the 95% confidence limits for this average became 1.472 ± 0.103. In such unretarded runs the initial rate began to fall off after 1 hr. This was attributed, in part, to a significant decrease in initiator concentration.

The concentration of benzoyl peroxide was maintained constant at 1.77 × 10<sup>-3</sup>*M* in all runs except those with diphenylpicrylhydrazyl in which

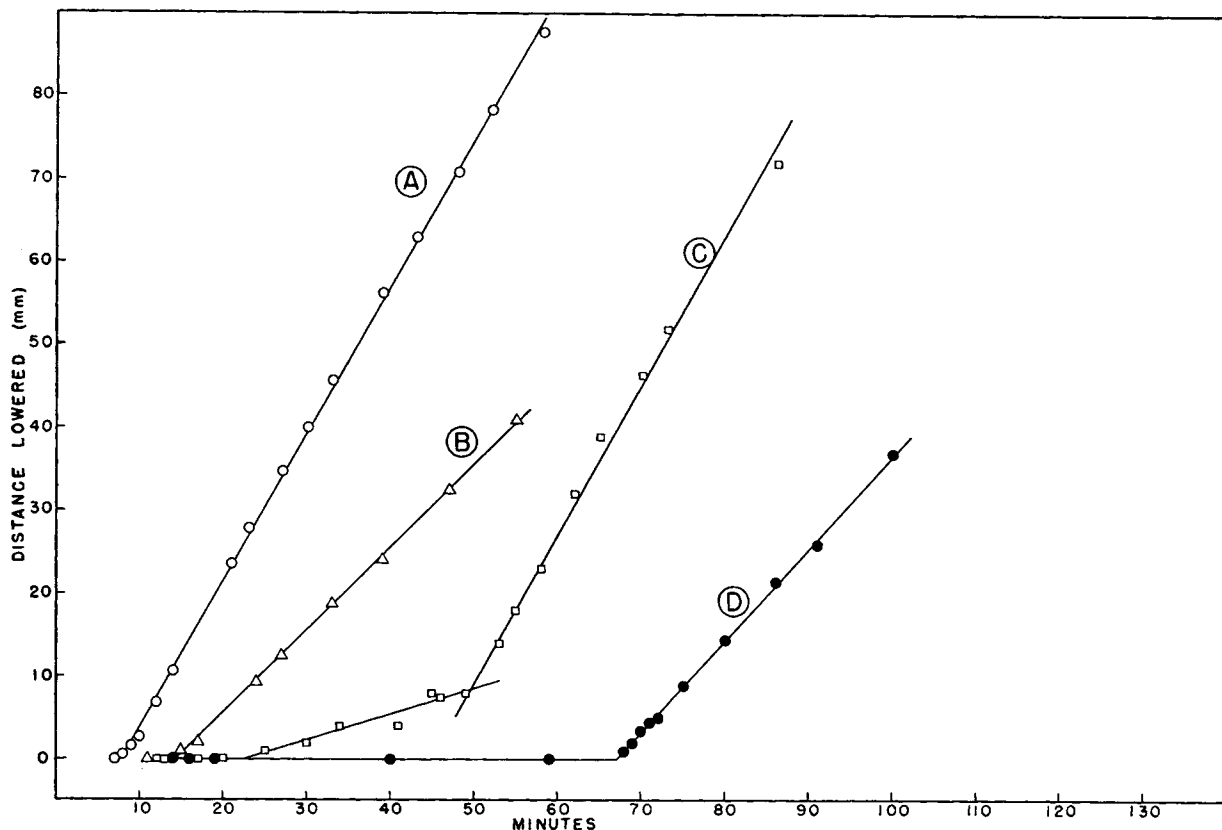


Fig. 1. Bulk polymerization of styrene at 86.6°C. catalyzed by  $1.77 \times 10^{-3}M$  benzoyl peroxide with various additives, followed dilatometrically: (A) control run without additives; (B)  $0.865 \times 10^{-3}M$  Banfield's hydroxide; (C)  $0.534 \times 10^{-3}M$  benzoquinone; (D)  $1.46 \times 10^{-3}M$  Banfield's radical.

the concentration was raised to  $2.65 \times 10^{-3}M$ . The change was made to permit the collection of reliable data after the long inhibition periods found with DPPH. The additional benzoyl peroxide would of course shorten the inhibition periods and increase the subsequent polymerization rates.

The rate of polymerization of styrene is proportional to the square root of the initiator concentration.<sup>11</sup> During the course of an experiment carried over a period of more than 1 hr. at a temperature of 86°C., a considerable portion of the benzoyl peroxide initially introduced was decomposed. Thus a reasonably accurate measure of the decomposition rate was necessary to correct data derived in those runs in which two or more polymerization rates were involved. The rate constant determined for decomposition at 86°C., was  $36.5 \times 10^{-6} \text{ sec.}^{-1}$ . This figure compares with Bevington's<sup>12</sup> value of  $2.1 \times 10^{-6} \text{ sec.}^{-1}$  at 60°C. and Cohen's<sup>13</sup> value of  $19.3 \times 10^{-6} \text{ sec.}^{-1}$  at 74°C. in a benzene solution.

Several investigators<sup>14-16</sup> have indicated that the length of the inhibition period resulting when *p*-benzoquinone is present in the thermal polymerization of styrene is proportional to the initial concentration of benzoquinone. This is also true of the catalyzed reaction. However, in the catalyzed case benzoquinone does not completely inhibit the polymerization reaction.<sup>17,18</sup> Figure 1, curve C shows a period of slow polymerization followed by an increased rate. Experimental points obtained for the second phase of the reaction fell on a straight line, indicating a constant polymerization rate. The points for the first phase were considerably more random and reflected a continually changing polymerization rate. However, when least-squares lines were drawn for both slopes, a definite intersection point was found which indicated the time necessary for the quinone to be consumed. Bevington<sup>17</sup> found that at this intersection point less than 1% of the original quinone was present. Variation of the concentration of

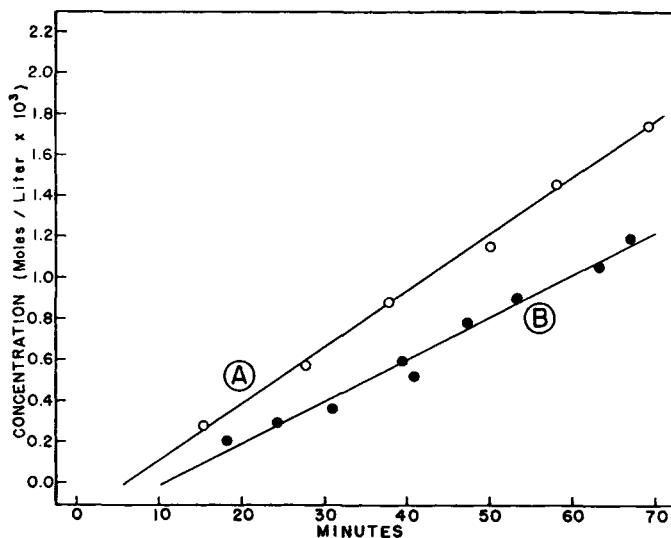


Fig. 2. Concentration dependence of: (A) the inhibition period caused by Banfield's radical (Table I); (B) the intersection point of the two slopes existing when diphenylpicrylhydrazine is the additive (Table IV).

benzoquinone showed that the length of the first phase was directly proportional to the initial concentrations of benzoquinone in agreement with previous observations.<sup>17,18</sup>

An induction period occurred in the presence of Banfield's radical,<sup>19</sup> oxidized *N*-(3-*N*-hydroxyanilino-1,3-dimethylbutylidene)aniline *N*-oxide, in the polymerization system as illustrated in Figure 1, curve *D*. The duration of this induction period is proportional to the initial concentration of Banfield's radical, as shown in Figure 2, curve *A*. As previously stated, the same relationship applies to

TABLE I  
Inhibition by Banfield's Radical

Run no.	Radical concn., moles/l. $\times 10^3$	Inhibition time, min.	Corrected polymerization rate, %/hr.
112	0	0	1.46
114	0.29	15.4	1.44
113	0.58	27.7	1.36
111	0.89	37.8	1.28
107	1.16	50.0	1.11
123	1.46	58.0	1.01
124	1.75	69.1	0.944

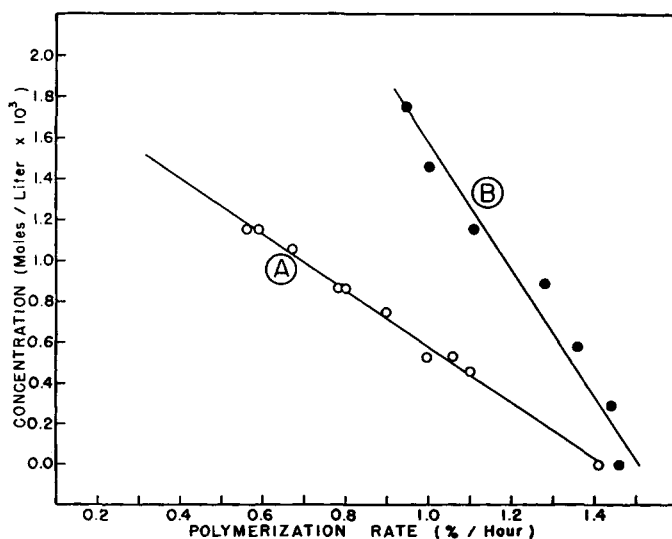


Fig. 3. Polymerization rate vs. initial concentrations: (A) Banfield's hydroxide (Table II); (B) Banfield's radical (Table I).

TABLE II  
Retardation by Banfield's Hydroxide

Run no.	Hydroxide concn., moles/l. $\times 10^3$	Corrected polymerization rate, %/hr.
95	0	1.41
94	0.27	1.34
96	0.46	1.10
83	0.53	1.06
90	0.53	0.998
133	0.75	0.897
97	0.865	0.783
132	0.865	0.803
129	0.865	0.780
85	1.06	0.671
103	1.15	0.590
104	1.15	0.561
92	1.38	0.321

benzoquinone. Thus the rate of disappearance of the radical during the inhibition period is independent of its concentration.<sup>20</sup> In the second phase, the retardation period (see Table I and Fig. 3, curve B), the rate of polymerization, corrected

for loss of benzoyl peroxide, was found to be inversely proportional to the initial concentration of the free radical. The same observations have been made<sup>14</sup> for benzoquinone for the second retardation period. Our findings are contrary to that reported by Bevington<sup>19</sup> who stated that the products of inhibition did not affect the rate of polymerization of styrene after the inhibition period.

Banfield's hydroxide *N*-(3-*N*-hydroxyanilino-1,3-dimethylbutylidene)aniline *N*-oxide, also investigated previously by Bevington,<sup>21</sup> is reported to act not as an inhibitor but rather as a retarder of polymerization. Figure 1, curve B indicates an apparent inhibition period of approximately 5 min. This variance was attributed to the observed instability of Banfield's hydroxide in the atmosphere. The straight line portion of the plot in Figure 1, curve B, with Banfield's hydroxide as retarder, shows a slope which proves to be inversely proportional to the retarder concentration (Fig. 3, curve A).

The dilatometric data obtained from a second

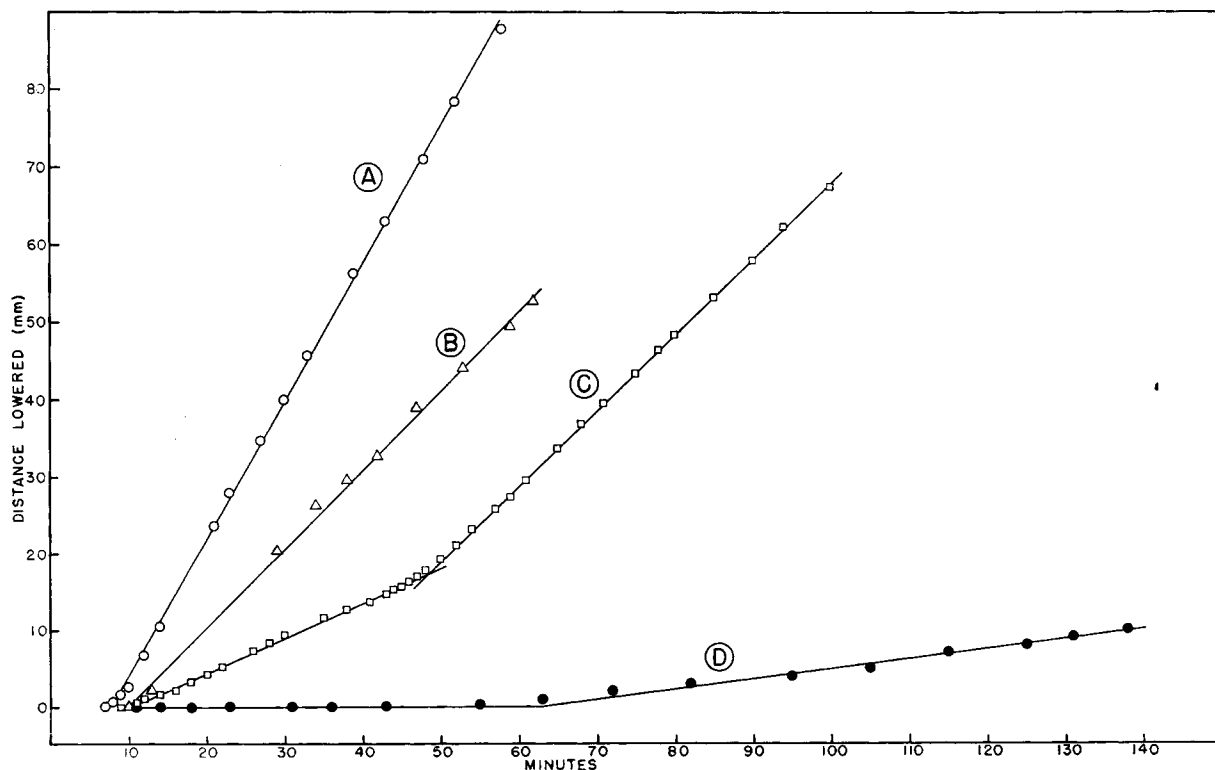


Fig. 4. Bulk polymerization of styrene at 86.6°C. catalyzed by  $1.77 \times 10^{-3}M$  benzoyl peroxide with various additives, followed dilatometrically: (A) control run without additives; (B)  $0.534 \times 10^{-3}M$  trinitrobenzene; (C)  $0.605 \times 10^{-3}M$  diphenylpicrylhydrazine; (D)  $1.65 \times 10^{-3}M$  diphenylpicrylhydrazyl (Curve D obtained using  $2.65 \times 10^{-3}M$  benzoyl peroxide).

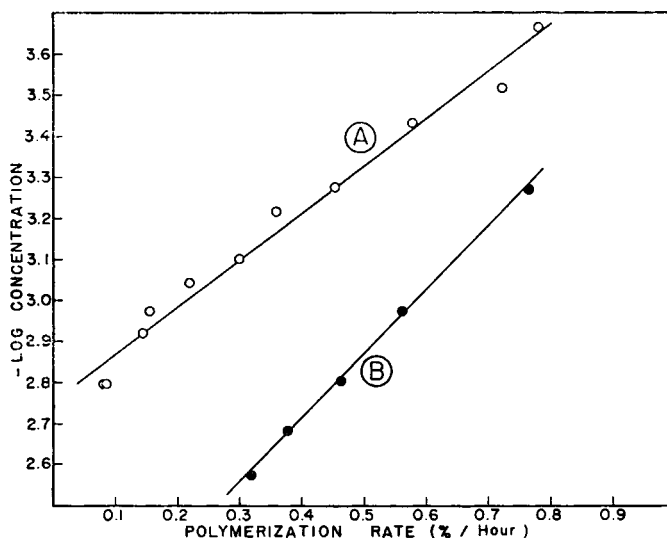


Fig. 5. Polymerization rate vs. logarithm of initial concentrations of: (A) diphenylpicrylhydrazine, first slope (Table IV); (B) trinitrobenzene (Table III).

TABLE III  
Retardation by Trinitrobenzene (TNB)

Run no.	TNB concn., moles/l. $\times 10^3$	$-\log$ TNB concn.	Poly- merization rate, %/hr.
61	0	—	1.48
72, 75, 78	0.534	3.272	0.762
70, 71	1.06	2.975	0.560
73	1.57	2.804	0.463
74	2.07	2.684	0.376
77	2.67	2.573	0.319

group of regulators are represented in Figure 4. Again the same control run (Curve A) is included as a reference. 1,3,5-Trinitrobenzene (TNB) has previously been reported<sup>5</sup> as a polymerization regulator but not at varying concentrations. It was rather surprising to note that the relationship of TNB concentration to polymerization rate did not fit the same pattern as was found with Banfield's radical and hydroxide and reported<sup>14</sup> for benzoquinone. Instead, the rate of catalyzed styrene polymerization in the presence of varying concentrations of TNB was determined to be proportional to the negative logarithm of the TNB concentration (Fig. 5, curve B).

A typical experiment with diphenylpicrylhydrazine gave the data plotted in Figure 4, curve C. This plot was treated in the same manner as previously described<sup>17</sup> for benzoquinone to provide two slopes and an intercept point. The rate of

styrene polymerization was found to be proportional to the negative logarithm of the diphenylpicrylhydrazine concentration in the initial phase of the measurement (Fig. 5, curve A; Table IV); however, in the second phase (Fig. 7, curve B; Table IV), the polymerization rate relates to the initial concentration of the retarder. The latter rate was corrected for benzoyl peroxide lost during the initial phase. The intercept point plotted against the initial concentration of diphenylpicrylhydrazine (Fig. 2, curve B; Table IV) provides a straight line. Bevington and Ghanem<sup>21</sup> consider diphenylpicrylhydrazine a nonideal retarder because of a continuous change in its ef-

TABLE IV  
Retardation by Diphenylpicrylhydrazine (DPPHn)

Run no.	DPPHn concn., moles/l. $\times 10^3$	Polymerization rate, %/hr.		Inter- section point, min.	$-\log$ DPPHn concn.
		Initial	Final		
115	0	1.44	—	—	—
119	0.215	0.778	1.12	18.2	3.676
125	0.37	0.576	1.05	30.9	3.432
128	0.529	0.452	0.952	40.9	3.276
120	0.794	0.299	0.782	47.3	3.103
122	1.06	0.154	0.400	63.2	2.974
117	1.59	0.080	—	—	2.798
131	1.59	0.085	—	—	2.798
158	1.20	0.143	0.290	66.9	2.9201
156	0.907	0.218	0.549	53.2	3.0423
154	0.605	0.356	0.842	39.4	3.2184
155	0.302	0.720	1.18	24.3	3.5194

iciency in modifying the polymerization rate. Our experimental data (Fig. 4, curve C; Table IV) clearly show that two different rates are involved in any given run.

Diphenylpicrylhydrazyl (DPPH), the free radical derived from  $PbO_2$  oxidation of diphenyl-

picrylhydrazine, differs from its reduced counterpart in that it behaves as a true inhibitor. The inhibition period plotted against the negative logarithm of DPPH concentration is a straight line (Fig. 6, Table V). The rate of polymerization subsequent to the inhibition period (Fig. 7,

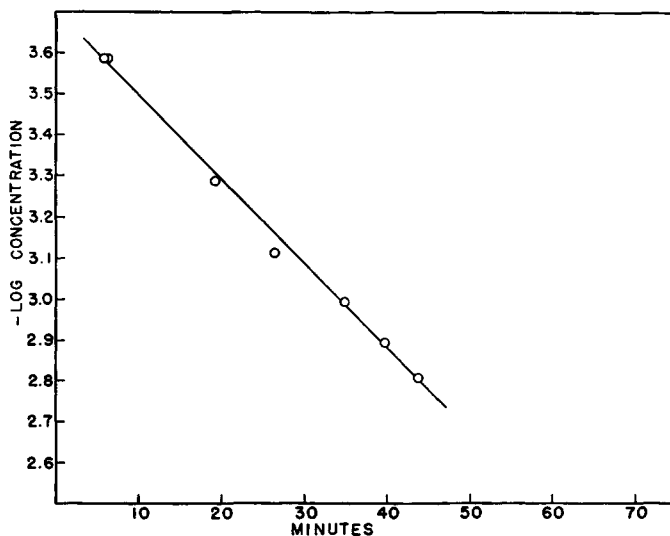


Fig. 6. Logarithm of diphenylpicrylhydrazyl concentration vs. length of inhibition period (Table V).

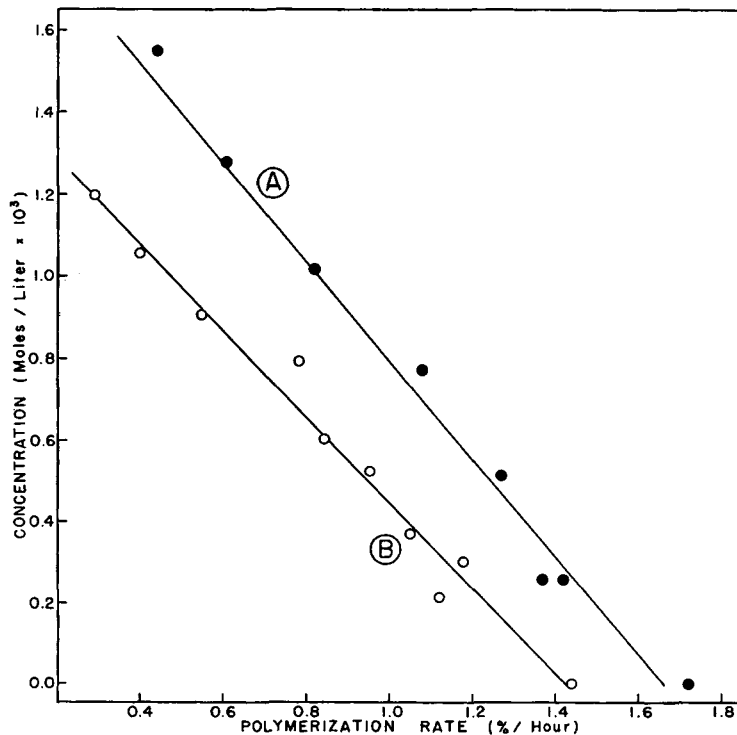


Fig. 7. Polymerization rate vs. initial concentrations: (A) diphenylpicrylhydrazyl (Table V); (B) diphenylpicrylhydrazine, second slope (Table IV).

TABLE V  
Inhibition by Diphenylpicrylhydrazyl (DPPH)

Run no.	DPPH concn., moles/l. $\times 10^3$	Inhibition time, min.	Polymerization rate (after inhibition), %/hr.	$-\log$ DPPH concn.
142, 143	0	0	1.72	—
150	0.258	5.8	1.37	3.588
149	0.258	6.2	1.42	3.588
144	0.515	19.3	1.27	3.288
148	0.773	26.4	1.08	3.112
145	1.02	34.8	0.82	2.992
146	1.28	39.7	0.61	2.893
147	1.55	43.7	0.44	2.810

curve A; Table V) is inversely proportional to the initial concentration of the DPPH. This rate was corrected for benzoyl peroxide lost during the inhibition period. Since a larger amount of benzoyl peroxide was used in each of the DPPH runs, the standard rate of polymerization of the system containing no inhibitor was different than that found for diphenylpicrylhydrazine.

### SUMMARY

The plots of the various runs (Figs. 1 and 4) demonstrate that trinitrobenzene and Banfield's hydroxide exhibit the same characteristics, in that the retarded rate remains constant during the early stages of polymerization. Diphenylpicrylhydrazyl and Banfield's free radical inhibit polymerization for a period of time, and this effect is followed by a decreased rate of polymerization as compared to the control. Benzoquinone and diphenylpicrylhydrazine provide the same type of data in which two different rates of polymerization are involved.

The relationships obtained by varying concentrations of inhibitors demonstrate that the length of the inhibition time is proportional to the concentration of Banfield's free radical (Fig. 2, curve A) but proportional to the logarithm of the concentration of diphenylpicrylhydrazyl (Fig. 6). Clearly, there are different mechanisms involved in these two cases.

The relationships obtained by varying concentrations of retarders show that the polymerization rate is proportional to the negative logarithm of the concentration of trinitrobenzene (Fig.

5, curve B). The same relationship prevails for diphenylpicrylhydrazine insofar as the first phase of the polymerization system is concerned (Fig. 5, curve A). A correlation of polymerization rates in all other instances was shown to be inversely proportional to the initial concentration of retarders and inhibitors, namely Banfield's hydroxide (Fig. 3, curve A), Banfield's free radical, and diphenylpicrylhydrazyl (following inhibition) (Fig. 3, curve B and Fig. 7, curve A), and diphenylpicrylhydrazine (second slope) (Fig. 7, curve B).

The length of time necessary to reach the point of intersection of the two slopes observed with diphenylpicrylhydrazine was found to be proportional to the concentration of retarder (Fig. 2, curve B) in the same manner as determined for the inhibitory action of Banfield's free radical.

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### Synopsis

The effect of varying concentrations of several common retarders and inhibitors on the polymerization of bulk styrene, catalyzed by benzoyl peroxide, was studied dilatometrically at a temperature of 86°C. At a benzoyl peroxide concentration of  $1.77 \times 10^{-3}M$ , the rate of volume contraction was found to be  $1.472 \pm 0.103\%/hr.$  or approximately 7.4–8.5% polymerization/hr. The rate constant for the decomposition of benzoyl peroxide in styrene was found to be  $36.5 \times 10^{-6} sec^{-1}$  at 86°C. At any given concentration for the several retarders and inhibitors, data were obtained which provided plots of extent of polymerization versus time of three different types. Trinitrobenzene and *N*-(3-*N*-hydroxyanilino-1,3-dimethylbutylidene)aniline *N*-oxide gave plots with single lines describing retarded rates of polymerization; diphenylpicrylhydrazyl and the free radical obtained from *N*-(3-*N*-hydroxyanilino-1,3-dimethylbutylidene)aniline *N*-oxide provided plots showing decreased rates of volume contraction following inhibition periods; and diphenylpicrylhydrazine and benzoquinone gave plots with two intersecting lines, suggesting two discrete steps. Concentrations of regulators were varied between 0.0002 and 0.0027*M*. In every instance plots of slopes of lines, inhibition times or intersection points versus concentration or logarithm of concentration provided straight lines.

### Résumé

Les effets de différentes concentrations de plusieurs retardateurs et inhibiteurs sur la polymérisation du styrène en bloc, catalysée par le peroxyde de benzoyle, ont été étudiés par dilatométrie à une température de 86°C. On a trouvé que pour une concentration en peroxyde de benzoyle de  $1,77 \times 10^{-3}M$ , la vitesse de contraction de volume était de  $1,472 \pm 0,103\%$  par heure, soit une polymérisation d'approximativement 7,4 à 8,5% par heure. On trouve que la constante de vitesse pour la décomposition de peroxyde de benzoyle dans le styrène était de  $36,5 \times 10^{-6} sec^{-1}$  à 86°C. A' une concentration quelconque donnée pour les nombreux retardateurs et inhibiteurs, on a obtenu des données fournissant des courbes de trois différents types donnant le pourcentage de polymérisation par rapport au temps. Le trinitrobenzène et le *N*-(3-*N*-hydroxyanilino-1,3-diméthylbutylidène) aniline *N*-oxyde fournissaient des diagrammes simples correspondant aux vitesses de retardement de la

polymérisation; le diphenylpicrylhydrazyl et le radical libre obtenu à partir du *N*-(3-hydroxyanilino-1,3-diméthylbutylidène)aniline *N*-oxyde fournissent des courbes montrant des vitesses décroissantes de contraction de volume après les périodes d'inhibition; et le diphenylpicrylhydrazyl et la benzoquinone fournissent deux droites qui se coupent suggérant ainsi deux étapes distinctes. Les concentrations des régulateurs variaient entre 0,0002 et 0,0027*M*. Dans chaque cas, les courbes des tangentes des droites, les temps d'inhibition ou les points d'intersection en fonction de la concentration ou du logarithme des concentrations fournissaient des lignes droites.

### Zusammenfassung

Der Einfluss verschiedener Konzentrationen einiger gebräuchlicher Verzögerer und Inhibitoren auf die durch Benzoylperoxyd katalysierte Polymerisation von Styrol in Substanz wurde bei einer Temperatur von 86°C dilatometrisch untersucht. Bei einer Benzoylperoxydkonzentration von  $1,77 \times 10^{-3}M$  ergab sich die Geschwindigkeit der Volumskontraktion zu  $1,472 \pm 0,103\%$  pro Stunde oder etwa 7,4–8,5% Polymerisation pro Stunde. Die Geschwindigkeitskonstante für die Zersetzung von Benzoylperoxyd in Styrol wurde zu  $36,5 \times 10^{-6} sec^{-1}$  bei 86°C ermittelt. Für die verschiedenen Verzögerer und Inhibitoren wurden bei mehreren Konzentrationen Ergebnisse erhalten, die drei verschiedene Typen von Zeit-Umsatz-Kurven lieferten. Trinitrobenzol und *N*-(3-*N*-Hydroxyanilino-1,3-dimethylbutyliden)-anilin-*N*-oxyd ergaben Diagramme mit einer einzigen, für verzögerte Polymerisationsgeschwindigkeit charakteristischen Kurve; Diphenylpicrylhydrazyl und das aus *N*-(3-*N*-Hydroxyanilino-1,3-dimethylbutyliden)-anilin-*N*-oxyd erhaltene freie Radikal lieferten Diagramme, die eine von einer verminderten Volumskontraktionsgeschwindigkeit gefolgte Inhibitionperiode zeigten; Diphenylpicrylhydrazin und Benzoquinon ergaben Diagramme mit zwei sich schneidenden Linien, was für zwei diskrete Stufen spricht. Die Reglerkonzentration wurde zwischen 0,0002 und 0,0027*M* variiert. In allen Fällen lieferte eine Auftragung der Neigung der Kurven, der Inhibierungsdauern oder Schnittpunkte gegen die Konzentration oder den Logarithmus der Konzentration gerade Linien.

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