

INHIBITION AND RETARDATION OF VINYL POLYMERIZATION¹

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Ideal inhibitors are defined as substances which cause an induction period in the polymerization of monomers, during which the inhibitor is consumed and after which polymerization starts at its normal rate.

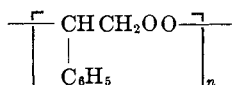
Typical retarders are defined as substances which cause retardation during the entire polymerization, without giving rise to an induction period.

A review is given of the literature concerning the effects of inhibitors and retarders on the uncatalyzed and catalyzed bulk polymerization of various monomers, chiefly styrene. Less information appears to be available concerning the kinetics of catalyzed than of uncatalyzed bulk polymerization in the presence of inhibitors and retarders. It is concluded that both inhibitors and retarders exert their effects by reacting with free radicals produced in the system. Inhibitors react with practically all the free radicals produced, but retarders are less efficient and permit some polymer chains to be initiated. They react with these growing chains and terminate them, thus acting like chain-breakers and reducing the molecular weight of the polymer.

Oxygen exerts opposing effects upon the bulk polymerization of monomers. It reacts with the free radicals initially produced (thermally, photochemically, or catalytically), forming peroxides which are more or less unstable. Depending upon the monomer and the temperature, this peroxide may catalyze polymerization or, if the peroxide is stable, its preferential formation may result in inhibition.

Inhibition and retardation effects in emulsion polymerization are discussed. In general, the effects are comparable to those found in bulk polymerization. In emulsion polymerization "catalysts" are always employed. Owing to the heterogeneous nature of the reaction mixture, it is possible to separate a retarder (such as 3,5-dinitrobenzoate in alkaline medium) from the locus of chain propagation (the soap micelle), in which case the retarder hardly affects the molecular weight of the polymer. Evidence is given that in emulsion polymerization with water-soluble "catalysts", activation occurs mainly in the "true" water phase and not in the soap micelle.

Oxygen inhibits the emulsion polymerization at 50°C. of styrene, of butadiene, and of butadiene (75)-styrene (25). In styrene emulsion polymerization a copolymer of styrene and oxygen is formed:



It is suggested that this same substance is formed during bulk polymerization of styrene in the presence of oxygen, and is responsible for the catalytic effect of oxygen at high temperatures (80°C. or above). At lower temperatures (55°C. or below) it is fairly stable, and its formation in preference to normal polymerization gives rise to the observed inhibitory effect of oxygen upon the polymerization of styrene at these temperatures.

Brief mention is made of some of the practical aspects of the inhibition and retardation of vinyl polymerization.

¹ Experimental work done in this laboratory and briefly described in this review was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the synthetic rubber program of the United States Government.

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I. INTRODUCTION

Ideal inhibitors are defined as substances which cause an induction period in the polymerization of monomers. During this induction period, the inhibitor is consumed and no normal polymerization occurs. After the induction period, polymerization starts with the normal rate, i.e., the rate which would have been observed in the absence of the inhibitor. If the reaction product formed during the induction period acts as a retarder, the polymerization after the induction period will be retarded.

Typical retarders are defined as substances which cause retardation during the entire polymerization without giving rise to an induction period. If present in large enough quantities, retarders may virtually prevent the initiation of polymerization. If added to a reaction mixture at any degree of polymerization, these substances retard further polymerization. If added in large enough quantities, they virtually stop further polymerization and thus act as "short-stops." Inhibitors can also be used as shortstops.

From a theoretical viewpoint, inhibitors are of special interest. A study of the induction periods produced by ideal inhibitors furnishes a means of measuring the rate at which free radicals are produced in the system, a measurement most difficult to arrive at by any other means. Moreover, the strongest evidence that the polymerization is a chain reaction is the fact that even traces of inhibitors prevent the occurrence of normal polymerization for long intervals.

In the next section is presented a review of the literature concerning the effects of inhibitors and retarders on bulk polymerization, and the interpretation of these effects. This work has dealt mainly with uncatalyzed polymerization, although a few studies have recently been made of peroxide-catalyzed polymerization in the presence of certain inhibitors and retarders.

In Section III, a review is given of similar effects in emulsion polymerizations. This type of polymerization is always catalyzed.

In Section IV, brief mention is made of some of the practical aspects of the inhibition and retardation of vinyl polymerization.

Most of this work has been carried out with styrene, although a few other monomers, notably methyl methacrylate and vinyl acetate, have been used.

II. INHIBITORS AND RETARDERS IN BULK POLYMERIZATION

A. *Effect of quinones, nitro compounds, etc.*

It has been known for some time that certain substances, particularly quinones and nitro compounds, inhibit or retard the polymerization of vinyl monomers. The existence has been observed of an induction period during which the rate of polymerization is very slow or nil, followed either by an increasing or nearly constant rate of polymerization. The length of this induction period is not always well defined. In other cases, induction periods are not observed, but the polymerization is retarded over its entire course. These effects have been observed in supposedly pure monomers (50), and have been attributed to the presence of traces of certain impurities.

The most comprehensive study yet made of the effect of various substances on vinyl polymerization is that of Foord (20), who observed the effects of a large variety of compounds on the uncatalyzed bulk polymerization of styrene at 60°, 90°, and 120°C. For convenience, these studies were carried out by observing the rate of increase of viscosity of the styrene sample, using a sealed viscometer which served as a reaction vessel as well. The sample was introduced and sealed *in vacuo*, oxygen being thus excluded. Viscosity measurements were made by inverting the vessel and measuring the time required for a definite volume to flow through the orifice. This method is applicable only to the early stage of conversion, but this was the stage that was of most interest. At later stages, the degree of polymerization was measured by alcohol precipitation and weighing of the polymer.

In general, such viscometric procedures are not the best means of following the polymerization process, because the viscosity increases with the molecular weight as well as with the concentration of the polymer. The assumption that the former is constant is not always warranted.

One hundred and thirty compounds were tested. In each case, the induction period (if any) was noted, and the rate of relative viscosity increase over at least the early stages was measured. Results obtained with *p*-benzoquinone at 90°C. are shown in figure 1 and represent the behavior of a typical inhibitor.

The rates of consumption of quinone during the induction period and of polymerization of styrene following the induction period were, in moles per liter per hour:

TEMPERATURE	STYRENE	BENZOQUINONE
°C.		
90	0.117	2.2×10^{-4}
120	0.840	4.2×10^{-3}

We shall return later to these results in discussing the explanation of these effects.

It was observed during these experiments that the yellow color of benzoquinone fades during the induction period and has nearly disappeared at the end of the induction period.

Following the induction period, the rate of polymerization is apparently that

of the control, where no quinone was present. In those runs containing the largest quantities of quinone, some retardation of the rate of viscosity increase was observed, but this was thought to be largely due to the fact that the molecular weight of the product was somewhat reduced, and not to a decrease in the rate of conversion. In order to account for the decrease in molecular weight we

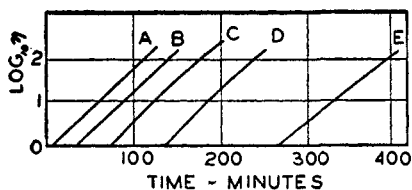


FIG. 1

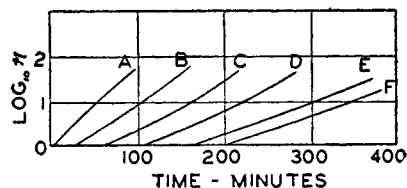


FIG. 2

FIG. 1. Polymerization of styrene at 120°C. in presence of *p*-benzoquinone

CURVE	<i>p</i> -BENZOQUINONE	
	Per cent	Millimoles per 100 g. styrene
A.	0	
B.	0.02	0.185
C.	0.05	0.463
D.	0.10	0.925
E.	0.20	1.850

FIG. 2. Polymerization of styrene at 120°C. in presence of phenanthrenequinone

CURVE	PHENANTHRENEQUINONE	
	Per cent	Millimoles per 100 g. styrene
A.	0	
B.	0.026	0.125
C.	0.050	0.240
D.	0.120	0.575
E.	0.187	0.895
F.	0.240	1.15

suggest that a reaction product formed during the induction period retards the polymerization proper. Foord's results are inconclusive in this regard.

The lengths of the induction periods increase linearly with the quantity of quinone initially present.

In figure 2 are shown the results obtained with a somewhat less effective inhibitor, phenanthrenequinone. Here it will be observed that the induction periods are still fairly well defined, but that a gradually increasing rate of polymerization is observed, rather than a linear rate.

In addition to substances which behave in this way, which will be referred to as typical or nearly typical *inhibitors*, Foord recognized another class of substances, which produced little or no induction period but retarded the rate of polymerization in varying degrees, the effect continuing throughout the course of the polymerization. These substances will be called *retarders*. Certain substances seemed to have the properties of both classes to some degree.

The following classification of the compounds tried was made by Foord. In arriving at this classification, those substances which acted as retarders were generally tested at 60°C. in a qualitative manner, by noting visually the rate of flow in small sealed tubes at various times.

(1) *Accelerators*: These substances increase the rate of polymerization over that observed for pure styrene.

(2) No appreciable effect.

(3) *Retarders*: Some of these substances also produced short induction periods.

(4a) *Inhibitors* giving induction periods of not more than 240 hr. in concentrations of about 1.0 per cent at 60°C., after which the normal rate of polymerization is observed.

(4b) *Inhibitors* giving induction periods of at least 600 hr. in 1.0 per cent concentration at 60°C. Only to members of class 4b was the semiquantitative viscometric method described above applied.

The substances tested were classified as follows (omitting classes 1 and 2):

Class 3: Aromatic nitro compounds make up the bulk of this class. Particularly effective are *o*-nitrophenol, 2,4-dinitroaniline, *m*-dinitrobenzene, dinitro-*o*-cresol (location of nitro groups not specified), 2,4-dinitrophenylamine, 2,4-dinitrophenol, 2,4-dinitrophenylhydrazine, 2,4-dinitrotoluene, picric acid, naphthalene picrate, and 1,3,8-trinitronaphthalene. It will be noted that the nitro groups in these substances are in general located in meta positions with respect to each other.

Certain nitroso compounds fall in this class. Most effective is nitroso- β -naphthol. Hydrazobenzene also falls in this group.

Class 4a: 1-Aminoanthraquinone, acenaphthenequinone, benzidine, 2,4-diaminoazobenzene, methylaniline, *p*-phenylenediamine, phenyl- α - and phenyl- β -naphthylamines. Anthraquinone itself is ineffective; 1-aminoanthraquinone probably acts largely by virtue of the amino group. These substances are intermediate in properties between typical inhibitors and retarders.

Class 4b: This class is composed, with the exception of *p*-nitrosodimethylaniline, entirely of quinones of relatively high oxidation potential: *p*-benzoquinone, *p*-toluquinone, phenanthrenequinone, and chloranil.

Hydroquinone and catechol produce some induction period, and the latter also has a retarding effect. Pyrogallol gives strong retardation with little induction period, but phenols in general have a weak effect. Phenol and the cresols are relatively ineffective.

A similar but much less extensive study has been made by Frank and Adams (21), who studied the effect of various inhibitors as 10 per cent solutions in styrene, 3,4-dichlorostyrene, and 5-ethyl-2-vinylpyridine. The last two polymerize more readily than styrene. The temperature was 100°C. They found that picric acid and trinitrobenzene protected the monomers from polymerization for the longest time, 299 hr. for styrene, 39 hr. for the dichlorostyrene, and 120 hr. for the vinylpyridine. The following substances studied are arranged in descending order of effectiveness: 2,5-dihydroxy-1,4-benzoquinone, 1,4-naphthoquinone, 1,4-benzoquinone, chloranil, 9,10-phenanthrenequinone, *tert*-butylcatechol. The following protected the monomers for periods (9 hr.)

not much longer than that observed for the pure styrene control: 4-amino-1-naphthol, hydroquinone, phenyl- β -naphthylamine. Triphenyl phosphite had no effect.

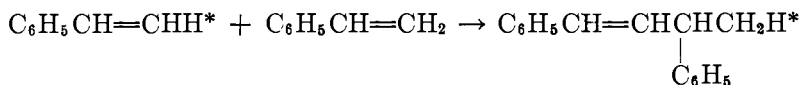
In these experiments no attempt was made to exclude air (oxygen), but approximately the same volume was present in each case. It will be observed that, in general, the compounds found by Foord to be most effective stand high also in the above list, although the experiments were not carried out in such a way as to allow any distinction between inhibitors and retarders to be made.

Since *p*-benzoquinone appears to possess the properties of a typical inhibitor, its effect on vinyl polymerization has been studied by a number of investigators. Breitenbach, Springer, and Horeischy (7) observed that hydroquinone does not stabilize styrene against polymerization in the absence of oxygen, but is very effective when oxygen is present. They believed benzoquinone to be the true inhibitor.

The effect of various quinones on the bulk thermal polymerization of styrene has been studied by Breitenbach and Breitenbach (4) and Breitenbach and Horeischy (5). In contrast to the results obtained by Foord, they claimed that during what Foord called the "induction period" a slow polymerization actually occurs, even in the presence of as much as 2 per cent quinone, leading to a polymer of so low a molecular weight (300-600) that polymerization could not be detected by Foord's viscometric method. They carried their experiments out at temperatures and quinone concentrations comparable to those used by Foord, but determined the polymer formed by volatilizing the unreacted styrene. The quinone disappears during the "induction period" and is partially converted to hydroquinone. Similar results were observed using chloranil. It is evident from their results that the authors were not justified in assuming a polymerization during the induction period. Actually, as will be shown below, their "polymer" is very probably the reaction product of two molecules of styrene with one of quinone.

Using the series of methylated *p*-benzoquinones from monomethyl- to tetramethyl-quinone, they found that the efficiency of the quinones in suppressing polymerization was proportional to their normal potentials. Thus, the strongest oxidant, *p*-benzoquinone itself, gave rise to the smallest rate of "polymerization," whereas with the weakest, tetramethylquinone, the greatest rate was observed. Confusion is caused here by the fact that these authors designate as "polymerization" both the reaction occurring between styrene and a typical inhibitor during the induction period, and the retarded chain propagation caused by the less effective methylated quinones.

It had been previously found by Dimroth (13) that the velocities of dehydrogenation of various reducing agents by these quinones were also proportional to their normal oxidation potentials. Breitenbach and Breitenbach interpreted their results as indicating that the initiation reaction consists in a labilization of a hydrogen atom on a styrene molecule, followed by reaction of this activated molecule with another styrene molecule:



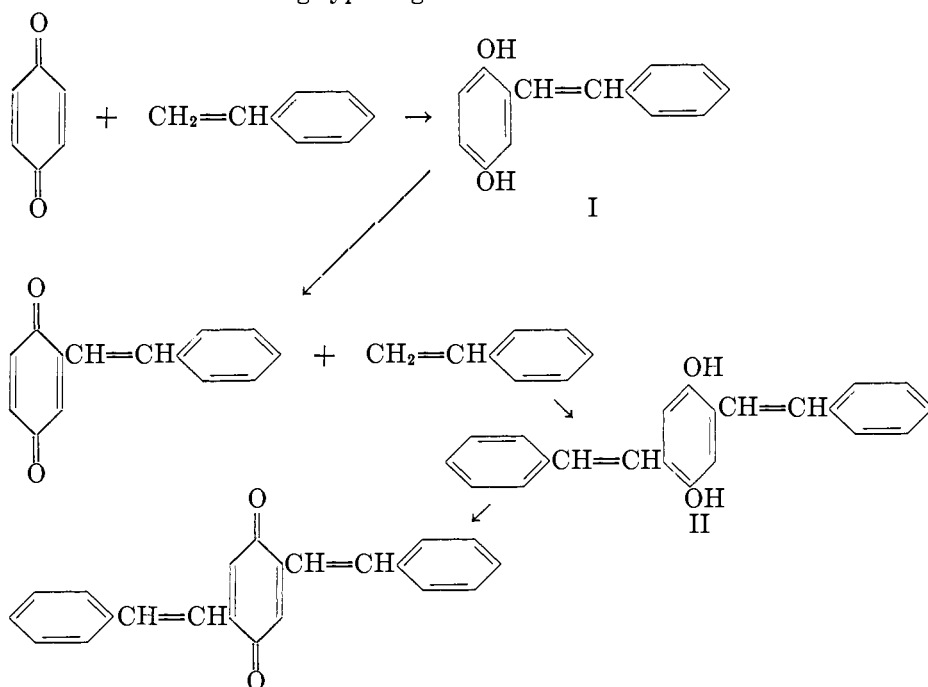
etc. The chain continues until broken by quinone, which abstracts the activated hydrogen atom.

This explanation is deficient in several respects. The nature of the "activation" of the hydrogen atom is not well explained. The peculiar effectiveness of quinones as inhibitors is not explained, since it appears that any strong oxidizing agent might serve equally well. Further, the reason for the effectiveness of several other classes of compounds, notably the aromatic nitro compounds, is not clear. It is especially difficult to explain on this basis the effectiveness of hydrazobenzene, methylaniline, and phenyl- α - and phenyl- β -naphthylamines, although admittedly these substances are not so efficient as the quinones.

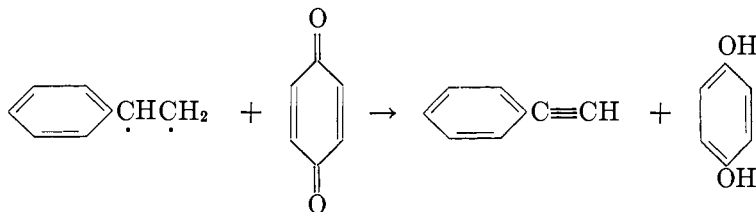
It had been suggested earlier by Springer (58) that polystyrene is first formed and then decomposed by the quinone, but, as pointed out by Foord (20), this suggestion is at once disposed of by the fact that polystyrene in benzene solution suffers no decrease in molecular weight on being heated with quinone.

Schulz (48) has also investigated the effect of *p*-benzoquinone on the thermal polymerization of styrene. The details of this investigation are not available, and the method used for the measurement of polymerization is not known. Schulz concurs with the finding of Foord that quinone produces induction periods, but finds the induction periods to be somewhat less than directly proportional to the initial quinone concentration, indicating that the quinone disappears also by some side reaction.

An attempt has been made by Kern and Feuerstein (29, 30) to identify the actual product formed by the reaction of *p*-benzoquinone with the activated styrene molecules. Reasoning by analogy to the known reactions of quinone with aniline, hydrochloric acid, and aromatic thiols (14), they suggested that reactions of the following type might occur:

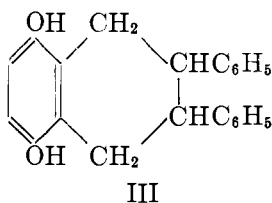


It was also thought possible that the production of hydroquinone might be due to the reaction of an activated styrene molecule with quinone as follows:



This latter reaction does not appear very probable.

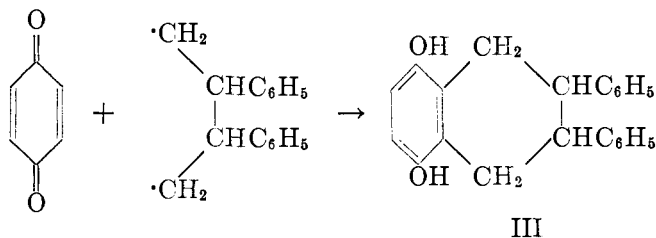
Experimentally, it was found that by heating styrene and quinone together in nearly equal mole ratio for several hours at 100–150°C., quinhydrone and hydroquinone are formed, as observed by Breitenbach and Breitenbach (4). In addition, on vacuum distillation of the mixture they obtained a residue which was shown to contain phenols. A product was isolated which gave an elementary analysis corresponding to the suggested structure:



On distillation of this substance with zinc dust, a stable hydrocarbon was produced. This hydrocarbon did not react with potassium permanganate, and thus appeared to have no aliphatic unsaturation. They concluded that structure III was probably correct for the reaction product and that I and II were unlikely.

No phenylacetylene was found. The production of hydroquinone was believed to be due to the oxidation of III by the *p*-benzoquinone, with consequent reduction of the latter. Since it is probable that the oxidation potential of III is lower than that of *p*-benzoquinone, this explanation is plausible.

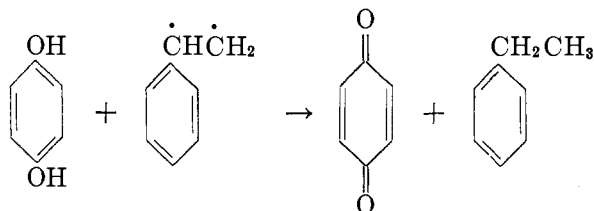
The formation of III was attributed by Kern to the reaction of the styrene dimer diradical with quinone:



More will be said later concerning this diradical formulation.

In this connection, it may be well to note the observation of Goldfinger, Naidus, and Mark (22) that on heating equimolar quantities of styrene and

hydroquinone for several hours at 150°C. quinone and ethylbenzene are formed, the reaction being formulated as proceeding through the monomer diradical:



It would be expected that the quinone formed would react further with the styrene in the manner postulated by Kern (29), thus producing hydroquinone again. It appears that styrene can react with quinone with the production of hydroquinone, or with hydroquinone to produce quinone. The processes involved are evidently irreversible, and their relative rates do not appear from the present data.

Goldfinger, Skeist, and Mark (23) carried out a study similar to that of Foord (20), using *p*-benzoquinone and styrene at 70°, 100.7°, and 130°C. in the absence of catalyst. They found, as did Foord, that induction periods were observed which were proportional to the initial concentration of quinone. However, the polymerization did not immediately set in with its normal rate (i.e., the rate in the absence of inhibitor) at the end of the induction period. It appeared (the data are sparse and apparently not very precise) that the rate immediately after the induction period was inversely proportional to the initial concentration of quinone.

It was also found that the molecular weight of the polymer formed was inversely proportional to the initial concentration of quinone. Some indication of this fact had also been obtained by Foord. This could be explained by assuming either that the reaction product formed during the induction period has properties of a retarder or that the inhibitor, when in the very small concentrations that are present toward the end of the induction period, does not react with all the free radicals before these are able to initiate polymerization. Thus the inhibitor might act at this stage as a retarder. Whether the termination of the growing chains is due to the quinone itself, or whether the quinone has been consumed and the effect is due to the retarding effect of its reaction product with the styrene, cannot be decided from the evidence at hand.

Breitenbach and Schneider (6) have studied the effect of *p*-benzoquinone and of chloranil in the thermal polymerization of styrene. Their purpose was to prepare polymers of such short chain length that their molecular weights could be determined by direct cryoscopic measurements. The values thus obtained were to be used to check Staudinger's viscosity relationship. They found that *p*-benzoquinone was too reactive and disappeared too rapidly by side reactions to serve their purpose. Chloranil was found to be more suitable. In its presence, polymers were obtained whose molecular weights from cryoscopic measurements were 360–600 (*cf.* Breitenbach and Breitenbach (4)). The chlorine analysis

indicated that there was probably more than one molecule of chloranil in each "polystyrene" molecule. Thus, the chloranil had apparently entered the chain, indicating that the radical formed by reaction of chloranil with a growing chain was still capable of propagating the chain. However, it appears that this conclusion must be received with considerable reservation. These authors found the apparent molecular weight of their "polymers" to vary widely with the solvent employed, being ten times lower in dibromocamphane than in benzene. The explanation of this effect is not established. Also, it is not certain that the "polymer" was freed from unreacted chloranil. The "polymer" was stated to be a brown, sticky mass which was soluble in methanol. Again, the term "polymer" may not be a correct description of this reaction product. (See above discussion of the work of Breitenbach and Breitenbach (4)).

The effect of chloranil has also been studied by Price (43, 47), who found that the chloranil entered into the polymer, but apparently only in the proportion of one chloranil residue per polystyrene molecule. In carrying out this experiment 5 g. of benzoyl peroxide, 4 g. of chloranil, and 25 ml. of styrene were heated at 100°C. for an interval of time not stated. Since the yield of polymer was 15.7 g., it was stated that chloranil did not act as a retarder.

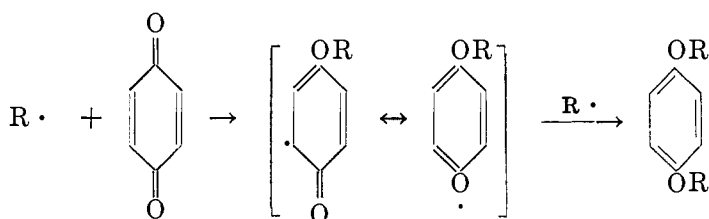
In establishing the molecular weight of the product formed, use was made of the solution viscosity relationship put forward for polystyrene of low molecular weight by Kemp and Peters (28). Since this relationship probably gives results that are much too low (1, 44, 16), it is probable that the true molecular weight found for the polymer prepared in the presence of chloranil is considerably higher than the reported value of 1300. This makes it appear that several chloranil residues must be present in each polystyrene molecule, provided it is certain that the polymer is free of unreacted chloranil. In this experiment it appears from blank runs that this was the case. It is emphasized that Price's experiments were carried out with unusually large concentrations of benzoyl peroxide and chloranil. Evidently, under these circumstances chloranil does not behave like a typical inhibitor. Kinetic studies are needed to decide this point. 3,6-Dichloroquinone was found to behave in the same way as chloranil.

Cohen (9) has recently studied the polymerization of 3.46 molar styrene in benzene at 64° and 74°C. in the presence of 0.0208 to 0.0714 molar benzoyl peroxide and 0.00444 to 0.00463 molar benzoquinone. Rates of polymerization were followed by methanol precipitation of the polymer. It was stated that if polymer had been determined by evaporation of the volatile material, residues would probably have been found quite early in the reaction. However, the nature of the product formed during the induction period was not established, and it can only be concluded that if it was polymeric in nature, its molecular weight must have been very low.

It was found by Cohen that induction periods were produced by quinone, as in thermal polymerization. These induction periods were approximately inversely proportional to the initial concentration of benzoyl peroxide, although the kinetics were complicated by the fact that the presence of quinone accelerated the decomposition of the benzoyl peroxide. Approximately equal molar quanti-

ties of quinone and peroxide were consumed during the induction period. The end of the induction period was not sharply defined, but instead a period of retarded rate was observed before the final linear rate was reached.

It was believed that the monomer free radicals react with quinone largely to produce diethers of hydroquinone, rather than to produce quinones or substances having free hydroxyls, since it was found that substances such as hydroquinone diethyl ether and diacetate had little or no retarding effect, whereas 2,5-di-*tert*-butylhydroquinone and 2,5-di-*tert*-butylquinone (which may be regarded as analogous to the compounds which would be produced by addition of radicals to the carbon-carbon double bond of the quinone) retarded polymerization more strongly than was actually observed after the induction period:



Melville and Watson (39) have found that whereas *p*-benzoquinone completely inhibited the thermal bulk polymerization of styrene and methyl methacrylate, when benzoyl peroxide was employed with these same monomers, *p*-benzoquinone produced no induction period but rather a retarded polymerization. The details of the experiments in which benzoyl peroxide was employed are not at present available, and it is therefore impossible to say whether or not these results actually conflict with those of Cohen.

The retardation of styrene polymerization by nitro compounds has been studied by Price, subsequent to the work of Foord (20). Price, Kell, and Krebs (46) observed that *m*- and *p*-nitrobenzoyl peroxides not only failed to initiate polymerization of styrene but actually stabilized it at temperatures at which thermal polymerization would normally have been appreciable. Price and Durham (45) studied the effect of nitrobenzene, 2,4-dinitrochlorobenzene, and nitromethane. In this work, benzoyl peroxide was employed as initiator, and rather large quantities of the nitro compounds were employed—for example, 5 g. of 2,4-dinitrochlorobenzene or 3 ml. of nitrobenzene per 25 ml. of styrene. Molecular weights and analytical evidence were presented tending to show that one retarder residue was present in each polystyrene molecule, but the molecular weight measurements are open to the same doubt as mentioned above.

Nitromethane was found to have no retarding effect, and in fact could be employed as a solvent in carrying out the polymerization. Thus it appears that the nitro group must be on a benzene ring to be effective.

Price (43) has also found that α -nitrothiophene acts as a retarder and reduces the molecular weight of the polymer. Again, it was believed that one nitrothiophene residue was present in each polystyrene molecule.

B. Effect of oxygen

The effect of oxygen on the polymerization of vinyl compounds has been such a vexed question as to deserve separate treatment from the compounds which have been grouped together in the preceding discussion. Oxygen has been found to exert a catalytic and an inhibitory effect, depending upon the monomer and the conditions employed.

Simon (53) first observed that the polymerization of styrene is accelerated by heat and by air. Stobbe and Posnjak (57) observed that samples of styrene which had been stored for several days at room temperature in the presence of oxygen polymerized much more rapidly at 200°C. than freshly distilled samples. They supposed that a catalyst was formed by the interaction of styrene and oxygen during storage, but did not investigate its nature. It was observed that the sample stored for 14 days polymerized immediately and rapidly, but that the other, after an induction period of about 7 hr., also polymerized quite rapidly, although not so rapidly as the stored sample. The temperature employed in this investigation was very high, and it does not appear that this induction period can be attributed to oxygen, in view of the results obtained by Medvedev and Zeitlin (37) which we shall discuss below. Possibly the catalyst formed during the 14-day period of storage destroyed some unknown inhibitor present in the monomer, while the 7-hr. induction period corresponded to the time necessary to destroy this inhibitor at 200°C.

Taylor and Vernon (59) studied the effect of oxygen on the photopolymerization of styrene and vinyl acetate. They allowed solutions of the monomers in ethylbenzene and ethyl acetate, respectively, to stand in contact with pure hydrogen and pure oxygen at room temperature for periods up to 144 hr., and then submitted the samples to photopolymerization at 100°C. They found that storage in oxygen accelerated the photopolymerization of styrene and produced no induction period. Photopolymerization occurred at an appreciable rate in the oxygen-free sample also. In the case of vinyl acetate, on the other hand, storage in oxygen resulted in a markedly decreased rate of polymerization.

Staudinger and Schwalbach (56) found that the thermal polymerization of vinyl acetate is accelerated by oxygen, without which no appreciable reaction occurs under 180°C. They confirmed the findings of Taylor and Vernon (59) for the photopolymerization, observing that whereas in an inert atmosphere the photopolymerization of vinyl acetate was nearly complete at room temperature in 6–12 hr. under their conditions, in the presence of air no change was observed after 6 hr., and only a small quantity of polymer was produced in 12 hr. They suggested that at low temperatures the activated styrene molecules formed by absorption of light quanta are removed by the formation of an inactive peroxide, whereas at high temperatures (absence of light) the peroxide formed is active and can initiate polymerization. However, in neither case could they find detectable quantities of peroxides.

It was found by Staudinger and Lautenschlager (55) that the polymerization of styrene at 80°C. (in the absence of added catalysts) is 2.5–3 times faster in the presence of oxygen than in its absence. They stated, on the basis of this experi-

ment, that peroxide catalysts function only through the release of molecular oxygen. This view, however, was entirely disproved by Houtz and Adkins (27), who showed that oxygen was a much less effective catalyst for the polymerization of styrene at 100°C. than an equivalent molar quantity of benzoyl peroxide or diisobutylene peroxide, and that furthermore the latter yielded only a trace of molecular oxygen on thermal decomposition. Oxygen is certainly therefore not to be regarded as a direct catalyst for vinyl polymerization.

Thompson and Burk (60) studied the polymerization of styrene at 118°C. in the presence and absence of oxygen, and found that oxygen produced an induction period of about 30 min., after which polymerization proceeded more rapidly than in its absence. They found that very highly purified styrene polymerized *in vacuo* at a measurable rate (although slower than in the presence of oxygen), and thus were really unable to prove their contention that thermal polymerization of styrene probably does not occur, and that polymerization, at least that of styrene, is always to be attributed to traces of catalysts. We shall return to this question in Section C.

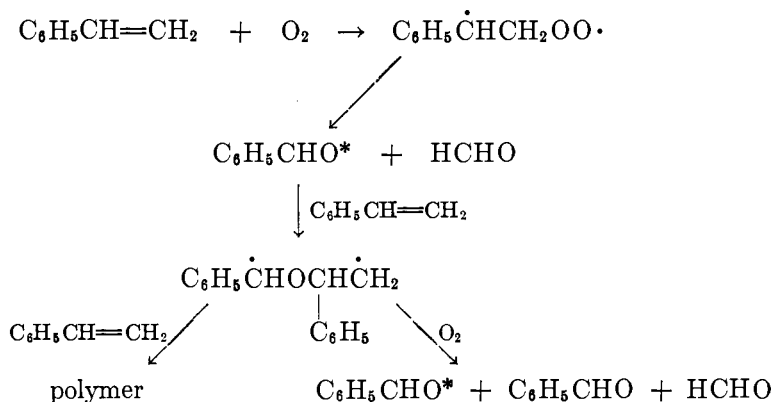
The effect of oxygen on the polymerization of methyl methacrylate has been studied by workers at E. I. du Pont de Nemours and Co. (15) (names not given). In the absence of light and oxygen, bulk polymerization of very pure methyl methacrylate was found to be exceedingly slow at 65°C., but proceeded at an appreciable rate at 170°C. and 210°C. With 0.01 atm. of oxygen (no agitation) polymerization at 65°C. was markedly accelerated, and in 0.1 atm. was faster yet. However, the photopolymerization at 35°C. was slower with 1 atm. of oxygen than with 0.1 atm., although faster in both cases than in the absence of oxygen. These results appear to indicate definitely that oxygen exerts competing effects, and destroys as well as generates active centers.

Melville (38) has found that the initial vapor-phase photopolymerization of methyl methacrylate is inhibited by traces of oxygen, although if solid polymer is once formed on the walls of the vessel, it was found that its continued growth was not retarded by the presence of several hundred millimeters of oxygen pressure.

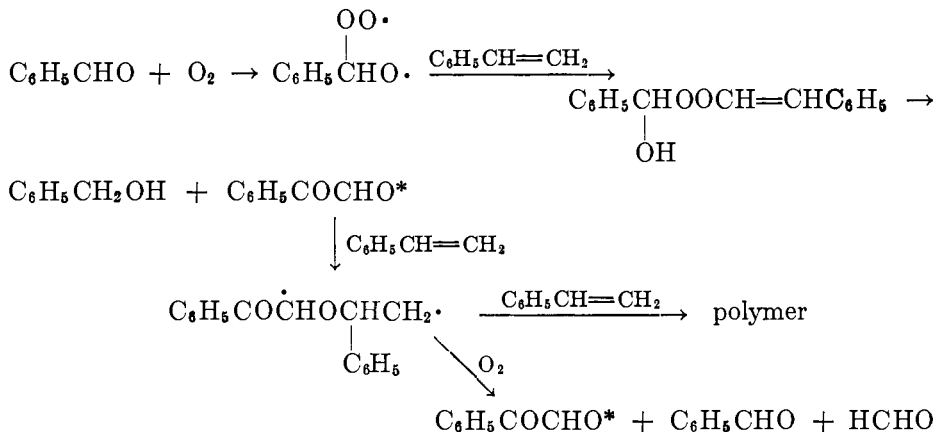
Barnes (2), studying the photopolymerization and thermal polymerization of vinyl acetate and methyl methacrylate in sealed tubes at 0°C., found that polymerization was completely inhibited in the presence of 1 atm. of oxygen, thus confirming the findings of Staudinger and Schwalbach (56) and Taylor and Vernon (59). In the case of methyl methacrylate, Barnes found that thermal polymerization at 65°C. is nearly completely inhibited by oxygen. This result is contradictory to that found by the du Pont workers (15). In neither study was the sample agitated while in contact with oxygen. Barnes explained this inhibitory effect as due to preferential reaction of the active centers produced by irradiation with oxygen to form peroxides, rather than with monomer to form polymer. The peroxides thus formed may also initiate active centers, but these also react preferentially with oxygen. Peroxides were detected experimentally. Their rate of formation in methyl methacrylate exposed to air at 27°C. was much faster when the sample was irradiated than when it was in the dark.

It was also found that the benzoyl peroxide-initiated polymerization of methyl methacrylate was retarded by the presence of oxygen.

Medvedev and Zeitlin (37) have studied the reaction of oxygen with styrene at 80°C. under conditions of very effective agitation, such that the liquid phase was always saturated with oxygen. They found no evidence of inhibition, but rather an acceleration of the polymerization. About 2.5 times as much styrene disappeared, with formation of benzaldehyde and formaldehyde (the amounts of which accounted nearly completely for the absorbed oxygen), as disappeared to form polymer. Further, they found no appreciable quantities of peroxide to be formed—at least so far as the acid potassium iodide test could detect. They concluded that if a peroxide were initially formed, which they conceded appeared very likely, it was immediately decomposed by reaction with the monomer to produce an active center which might then be oxidized further or react with monomer to form polymer:



In addition, they found that benzaldehyde had a pronounced accelerating effect on the oxidation-polymerization rate, and concluded that it also reacted with oxygen to form a labile peroxide which initiated another series of chain reactions:



The accumulation of benzaldehyde was thus believed to be the cause of the observed autocatalytic form of both the oxidation and polymer-formation curves.

It will be noted that in this rather elaborate scheme the formation of an initial active center by thermal activation, followed by reaction with oxygen or monomer, does not play a part. The active center is formed only by reaction of inactive styrene (or benzaldehyde) with oxygen. This recalls the view of Staudinger (55), who regarded molecular oxygen as a catalyst itself.

Although they did not analyze the polymer formed to see whether it contained oxygen—in particular, peroxide oxygen—it was found that it had no catalytic activity when added initially to a reaction mixture. Staudinger and Lautenschlager (55) found that polystyrene prepared in the presence of oxygen contained appreciable amounts of oxygen, but did not give a peroxide test. In the discussion of the inhibition of the emulsion polymerization of styrene, we shall see that a polymeric styrene peroxide is formed in that case also.

Kharasch and Nudenberg (31) have recently observed that at a temperature of 55°C. oxygen acts as an effective inhibitor for the bulk polymerization of styrene.

C. Nature of the inhibition process

In the previous discussion we have described inhibitory effects produced by several substances upon vinyl polymerization, in particular, the polymerization of styrene. At certain points, we have anticipated somewhat the discussion of this section in presenting the explanations of the authors for the phenomena observed. We shall now try to propose a general scheme for the explanation of these effects. On certain important points no definite decision can be made, and these points must be left for future experiments to decide.

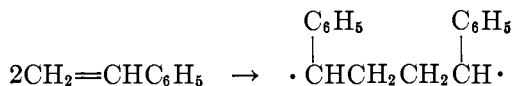
Of the kinetic studies which have been made of the effect of inhibitors and retarders on the bulk or solution polymerization of vinyl monomers, all but one (9) have dealt with either the photopolymerization or the thermal polymerization. At least, in those reactions which have been termed "thermal," no catalyst has been deliberately added. However, the important question remains whether the formation of active centers in these cases is due to a true thermal reaction or to initiation by traces of catalytic impurities, probably peroxides. It may well be imagined that the nature of the active centers which react with the inhibiting substances will depend upon the mode of activation.

Staudinger and Schwalbach (56) called attention to their difficulties in obtaining vinyl acetate sufficiently free of peroxides not to polymerize appreciably in an inert atmosphere. Conant and Tongberg (10), working at high pressure with vinyl acetate, decided that in this case the presence of peroxide catalysts was not essential, but that true thermal polymerization occurred, accelerated by the high pressure. With isoprene, they found that the pressure polymerization was not noticeably faster with a sample that had been shaken with oxygen for several hours than with a freshly distilled sample. However, Conant later found (11) that even the freshly distilled sample was not free of oxygen, since on storage with triphenylmethyl the rate of polymerization was reduced to one-tenth of that of the untreated sample. By no device were they able to prepare isoprene in so pure a state that it failed entirely to polymerize under their

conditions. Thus it appears that uncatalyzed polymerization may be possible, at least at high pressures.

Cuthbertson, Gee, and Rideal (12) found that carefully purified vinyl acetate was very resistant to polymerization.

Moureu and Dufraisse (40), who were the first to show that traces of peroxides and not oxygen itself were responsible for the air-induced polymerization of vinyl compounds (acrolein in the above paper), were strongly of the opinion that vinyl polymerization is never induced by the spontaneous thermal generation of active centers, even in the purest monomers that care and ingenuity can produce. A similar view has been expressed by Norrish and Brookman (41). Such a contention is, of course, difficult to disprove, but it is apparently believed by most workers in this field (for example, Mayo (35a, 36), Schulz (52), and Walling, Briggs, and Mayo (62)) that true thermal polymerization is possible, at least in the case of styrene and probably also in the case of methyl methacrylate (61). The kinetic studies carried out by these authors have indicated that thermal initiation occurs as a second-order reaction of two styrene molecules, presumably to form a dimeric radical. We have already seen that a similar diradical (but differing in the location of the phenyl groups) has been suggested by Kern and Feuerstein (29, 30) to account for the addition product of two styrene residues with quinone observed on heating these substances together:

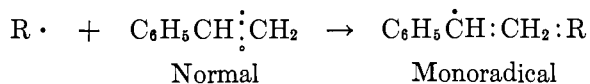


Activation of the double bond of vinyl compounds has been represented by Harman and Eyring (24) as proceeding by either of two mechanisms:

(a) By a rotational adiabatic (i.e., without change of electronic energy) transition from the singlet ground state (π electrons have opposite spins) to an upper singlet state, in which the electrons' spins are still opposed. This transition requires 40,000 cal. and is concerned in ionic polymerization, Friedel-Crafts reactions, etc.

(b) By a transition from the singlet ground state (π electrons have opposite spins) to a triplet state in which the spins of the electrons are the same. This transition requires only 25,000 cal., but the frequency factor (i.e., the probability of transition) is much lower than for mechanism (a). This is the mechanism concerned in the thermal and peroxide-initiated polymerization of vinyl compounds. (In both mechanisms, the products have the activity of free radicals.) Whether the monomer diradical formed then reacts with another molecule of styrene to produce a dimer diradical is not discussed by Harman and Eyring.

The probability of transition by mechanism (b) is increased by the presence of strong inhomogeneous magnetic fields, such as those present in aryloxy and acyloxy free radicals, triarylmethyls, etc. Such a free radical attacks the monomer by pairing its electron with the π electron of opposite spin in the monomer, thus producing a monoradical:



Thus, in thermal polymerization we evidently deal with diradicals, and in catalyzed polymerizations (as by peroxides, diazo compounds, and other free-radical generators) with monoradicals. According to Eyring's view, the activation energy should be about 25,000 cal. regardless of the nature of the catalyst, or whether any catalyst is present at all, provided transitions occur by reaction (b). This view appears to be supported by the following data, in which the rate constants for activation of styrene under various conditions are given:

$$K = Ne^{-E/RT}$$

where N is the frequency factor and E is the energy of activation.

	K	REFERENCE
Styrene under nitrogen (supposedly thermal only)....	$1.5 \times 10^4 e^{-23,300/RT}$	(53)
Styrene with benzoyl peroxide.....	$10^{10.85} e^{-23,700/RT}$	(52)
Styrene with free radicals.....	$10^{12.2} e^{-23,500/RT}$	(50)

From the temperature coefficient of the quinone induction period, Foord (20) obtained a value of 28,000 cal. for thermal activation of styrene.

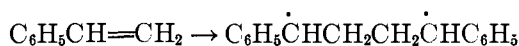
It should be borne in mind, however, that calculating energies of activation by measurement of the temperature coefficient of the rate is a questionable procedure when such catalysts as benzoyl peroxide are used, since what is actually measured may be the energy of activation for the cleavage of the catalyst itself. Barnett and Vaughan (2a) find that the energy of activation for the decomposition of benzoyl peroxide is from 28 to 32 kcal., depending upon the concentration of the peroxide. Thus, it is questionable whether the constant values of the activation energy tabulated above substantiate Eyring's view.

The question then arises whether substances which inhibit or retard thermal polymerization will react equally readily with the monoradicals produced in catalyzed polymerization. According to the study made by Cohen (9), it appears that they do. Furthermore, it has been found that the catalyzed emulsion polymerization of styrene is inhibited and retarded by the same types of compounds that are effective in bulk polymerization (see Section III).

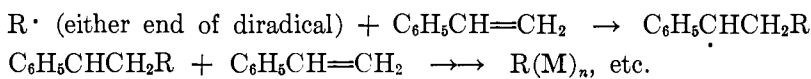
The reactions of typical inhibitors and retarders can probably be best formulated as follows (illustrated for styrene):

A. *Thermal polymerization:*

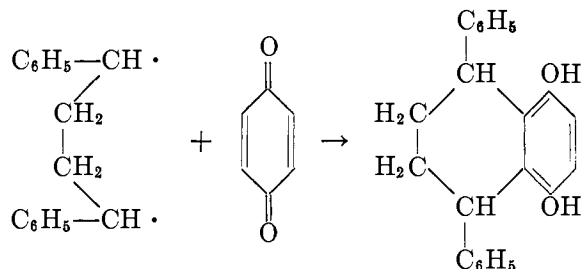
1. Initiation:



2. Propagation:



3a. Termination by inhibitor:



This adduct does not react readily with free radicals, but may have a slight retarding effect.

As we have seen, not all the quinone can be used for termination, as in 3a, since some appears as quinhydrone and hydroquinone. It seems reasonable to interpret the appearance of these products as Kern and Feuerstein (30) have done, as due to reduction of quinone by the substituted hydroquinone produced above.

That all the quinone is not consumed in termination reactions in bulk polymerization is also indicated by the relative rates of quinone disappearance during the induction period and styrene disappearance during subsequent polymerization, as determined by Foord (20). Taking the data for 120°C., Foord calculates the number-average molecular weight of the polymer formed after the induction period to be:

$$\bar{M}_N = \frac{\text{rate of propagation}}{\text{rate of activation}} = \frac{0.84 \times 104}{4.2 \times 10^{-3}} = 20,800$$

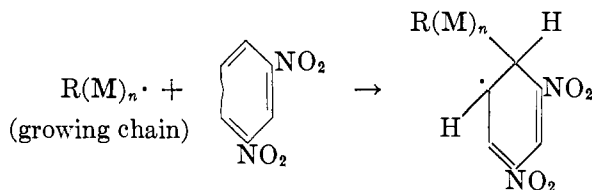
However, the actual number-average molecular weight is probably greater than 100,000, indicating that we have overestimated the true rate of activation, which is not so large as the rate of quinone disappearance.

The termination reaction is very rapid and occurs almost to the exclusion of the normal propagation reaction. That quinones and aryl nitro compounds react readily with free radicals appears to be indicated by the work of Fieser and Oxford (19) and Fieser, Clapp, and Daudt (18) on the methylation of these substances with lead tetraacetate.

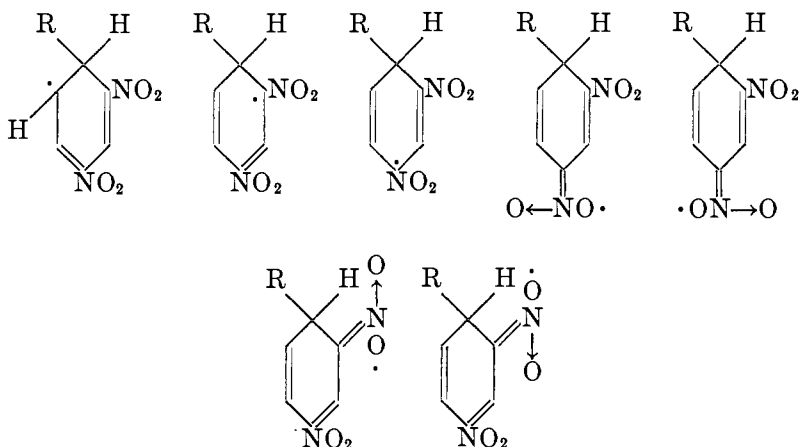
Very recently, Mayo and Gregg (36b) have obtained kinetic evidence tending to indicate that in the thermal polymerization of styrene at 100°C. the adduct produced by the reaction of *p*-benzoquinone with a styrene radical is not inactive, but is capable of continuing the chain, either by copolymerization or by transfer. The rate of disappearance of the quinone is not, therefore, a measure of the rate of activation under these conditions.²

² *Note added in proof:* In this laboratory, evidence has also been recently found which indicates that chloranil, and probably *p*-benzoquinone, actually copolymerizes with styrene under certain conditions.

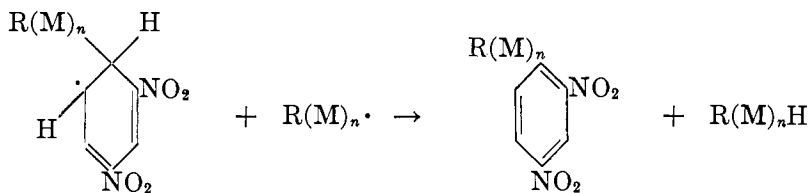
3b. Termination by retarder: The termination reaction of a typical retarder (*m*-dinitrobenzene) can be represented:



The resulting radical is too much stabilized by resonance to propagate the chain at an appreciable rate. This can be readily understood from a consideration of the following resonance forms:



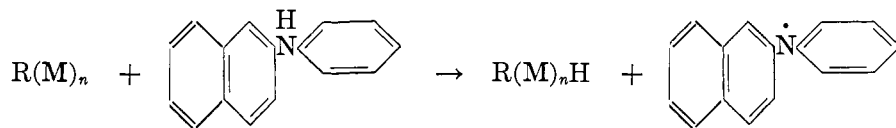
This radical will, however, react with another radical:



as suggested by Price (42, 45).

The reaction of free radicals with retarders such as *m*-dinitrobenzene does not occur so rapidly as with quinone. Therefore, many of the radicals formed are able to propagate chains of some length before reacting with the retarder. Thus, instead of complete or nearly complete absence of polymerization, there is observed instead a retarded rate, leading to a polymer of lower molecular weight than that formed in the absence of a retarder. A similar effect upon the molecular weight is produced by typical chain-transfer agents or modifiers, but since in the presence of these substances a new radical of equal reactivity is produced for each chain terminated, the rate of polymerization is not affected.

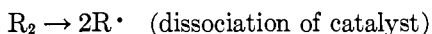
In addition, some substances, e.g., those in Foord's class 4a, react less readily with free radicals than typical inhibitors, but more readily than typical retarders. The reaction of such substances as phenyl- α - and phenyl- β -naphthylamines may possibly be explained by reactions such as:



The resulting radical cannot propagate the chain further but may be terminated by reaction with another polymer radical. These amines appear to be intermediate in activity between typical inhibitors and typical retarders.

B. Catalyzed polymerization:

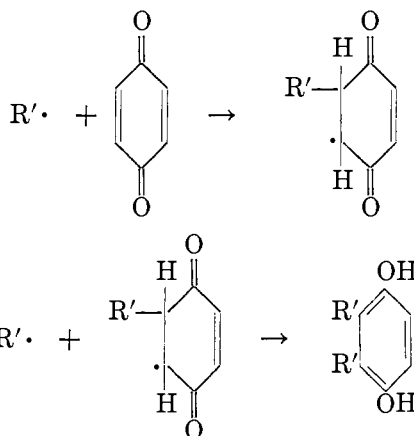
1. Initiation:



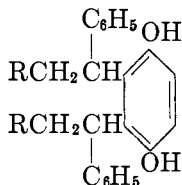
2. Propagation (same as under A):



3. Termination by inhibitor:

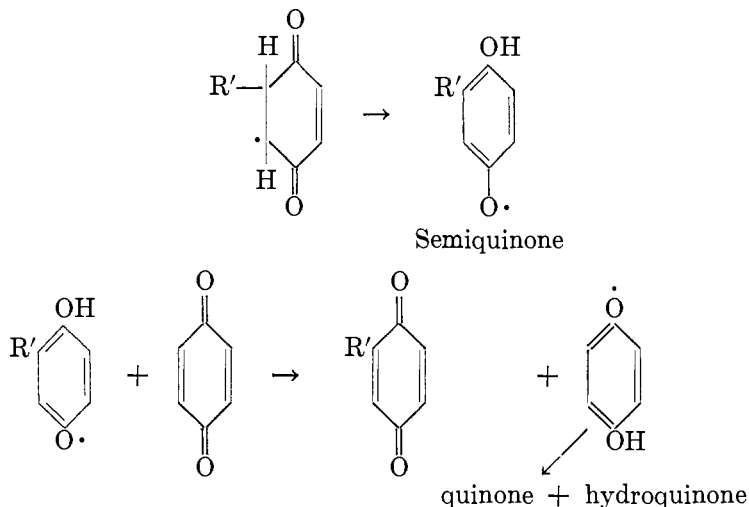


The final product in the case of styrene would evidently be, according to this formulation:



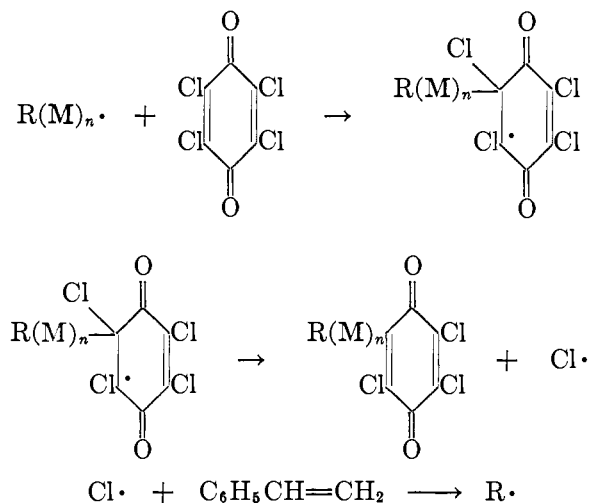
where R represents a fragment of the catalyst. According to Cohen (9) the final product should be represented as an ether of hydroquinone, as we have seen. Present unfinished work carried out in this laboratory tends to substantiate Cohen's formulation.

Price (42) has suggested:



It is also possible that the semiquinone initially formed may lose a hydrogen atom to another R', in the same manner as that represented for *m*-dinitrobenzene (page 509).

We have seen that, according to Price (43, 47), chloranil and dichloro-*p*-benzoquinone present the special feature of acting as chain-transfer agents rather than inhibitors. This is supposed to occur as a result of chain initiation by a chlorine atom:



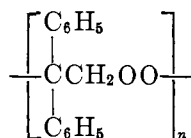
This hypothesis cannot be regarded as proved by the experimental evidence, nor is it in agreement with the observations of Foord (20) and of Frank and Adams (21) that chloranil is an effective inhibitor. This apparent contradiction may be caused by the fact that Price used unusually large quantities of benzoyl peroxide as catalyst. In general, a typical chain-transfer agent does not affect the over-all rate of polymerization, although it greatly reduces the molecular weight. This is true only if every free radical formed on termination of one chain initiates another chain. If this condition is not fulfilled, a retarding effect will result.

Oxygen: In the interpretation of the oxygen effects observed in uncatalyzed systems, it should be realized that even at room temperature oxygen reacts slowly with monomers, apparently with the primary formation of peroxides. The rate of this reaction undoubtedly varies with different monomers, and also varies with the temperature. The peroxides formed are more or less unstable and generally decompose at moderate temperatures (50°C. or below), with the formation of compounds which do not act as initiators of polymerization. The rate of polymerization after the induction period will be equal to the normal rate of uncatalyzed polymerization only when all the peroxides formed during the induction period are quantitatively decomposed, with the formation of substances which do not initiate polymerization. The rate of polymerization after the induction period will be in general greater than the "normal" rate if some undecomposed peroxide is still present, but when the rate of thermal or photo-induced formation of free radicals is large in comparison with the rate of formation of free radicals from the residual peroxide formed by reaction with oxygen, the rate of the thermal or photo-induced polymerization of the monomer after the induction period will not be greatly increased by the initial presence of oxygen. In this connection, it is of interest that chloroprene reacts readily with oxygen at room temperature to form a peroxide which is a powerful catalyst for its polymerization (8, 64). Oxygen has no inhibitory effect on this monomer, evidently because the chloroprene peroxide forms free radicals even at room temperature. The behavior of oxygen with chloroprene at room temperature is evidently comparable to that with styrene at 80°C. or higher temperatures.

In Section III it is shown that a polymeric peroxide of styrene is formed during the induction period caused by oxygen in the emulsion polymerization of styrene at 50°C., and that this substance is an effective catalyst for the bulk polymerization of styrene at 80°C. It is reasonable to suppose that this peroxidic polymer is formed also in bulk, and that its breakdown at higher temperatures (above 50–55°C.) is responsible for the accelerating effect of oxygen on the polymerization of styrene at higher temperatures. As we have mentioned, Medvedev and Zeitlin (37) found that the polystyrene produced in bulk at 80°C. in the presence of oxygen had no effect on the polymerization when added initially. However, they purified the polymer by four reprecipitations, as a result of which whatever remained of the polymeric peroxide was probably lost, since this material is of low molecular weight. At 80°C., little peroxide would be expected to remain, since it is unstable at this temperature. It appears probable

that the benzaldehyde and formaldehyde found by Medvedev and Zeitlin are decomposition products of the polymeric peroxide.

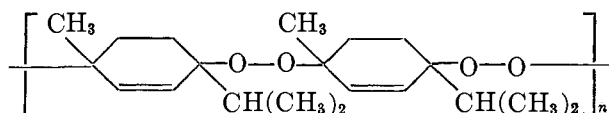
Although the peroxides formed when oxygen reacts with monomers may not always be polymeric, some instances of such polymeric peroxides are known. Staudinger (54) found that unsymmetrical diphenylethylene formed a peroxide of composition:



Staudinger and Lautenschlager (55) isolated polystyrene apparently containing some oxygen but never in a mole-for-mole proportion to the styrene.

Staudinger (54) also isolated a polymeric peroxide of diphenyl ketene.

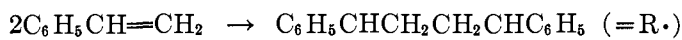
Farmer (17) reports that when α -terpinene is heated with oxygen, a polymeric peroxide is formed rather than the expected ascaridole:



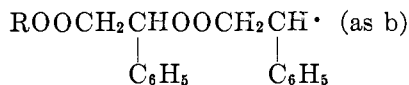
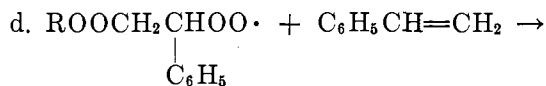
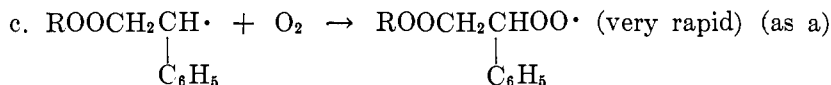
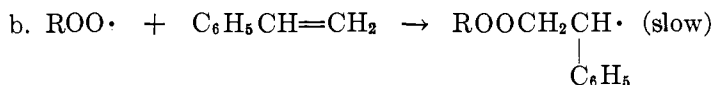
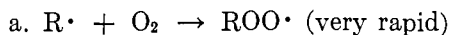
This substance was observed to be explosively decomposed by heating above 100°C.

The above considerations may account for the apparently contradictory effects exerted by oxygen under varying conditions, as described in the literature. In general, the following cycle of reactions accounts for the experimental observations; it is presumed in this scheme that the monomer (styrene) is initially free from catalytic impurities.

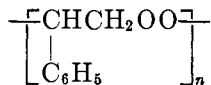
1. Thermal initiation:



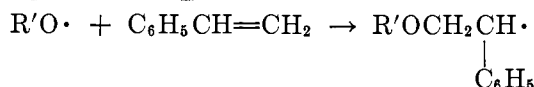
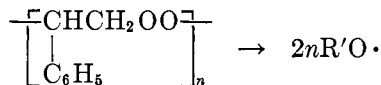
2. Peroxide formation:



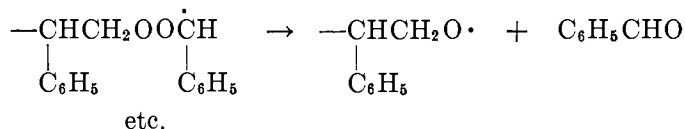
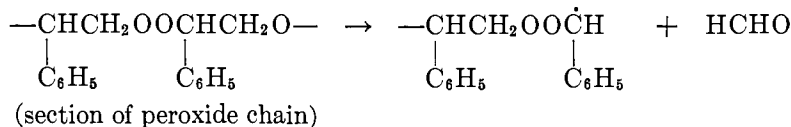
etc., plus termination steps, leading to:



3. Chain initiation by polymeric peroxide:

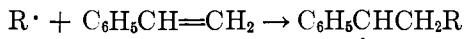


The peroxide may decompose according to the following series of reactions. Either the $\text{R}'\text{O}\cdot$ or the carbon radical may serve to initiate further polymerization:



In this way, the observed oxidation products, formaldehyde and benzaldehyde, may be produced while polymerization is taking place.

4. Normal propagation by thermal radical from 1; this will occur only if this radical escapes reacting with oxygen, which is improbable unless the concentration of oxygen is very small:



These chains may then react with oxygen.

At low temperatures, the polymeric peroxide formed is not cleaved rapidly enough to serve as an effective chain initiator. The stability of the peroxide and the rate of its formation no doubt vary widely with different monomers; probably that of isoprene is among the least stable, while that of styrene is stable at about 50°C . but unstable at 80°C . The chains initiated by other means (e.g., by ultraviolet irradiation) are in effect terminated by reaction 2a, since the radicals react more rapidly with oxygen, which may be regarded as a diradical, than with monomer, resulting in the much less reactive peroxide radical, and the succeeding steps b, c, d, etc. Since the over-all reaction under 2 is much slower than normal polymerization, and yet occurs nearly to the exclusion of normal polymerization, the oxygen is observed to cause nearly ideal inhibition.

At higher temperatures the peroxide breaks down rapidly with formation of

initiating radicals, according to 3. Of the radicals thus produced, some will react with oxygen again according to 2, but the polymer peroxide thus formed will again break down with formation of up to $2n$ radicals (n being the average number of peroxide links per polymer molecule) for each initiating radical. From the experiments discussed in section b, it appears that the rate of reaction of these radicals (or those produced thermally from the monomer) with monomer increases much more rapidly with increasing temperature than the rate of their reaction with oxygen. This appears reasonable, since the activation energy for reaction with oxygen is undoubtedly much smaller than that for their reaction with monomer. Thus, as the temperature increases, not all of the many radicals produced react with oxygen, and so the inhibitory mechanism 2 is overpowered by 3, resulting in polymerization even faster than normal polymerization.

III. INHIBITORS AND RETARDERS IN EMULSION POLYMERIZATION

A. Introduction

No studies on the inhibition and retardation of emulsion polymerization proper are to be found in the literature. Related studies on water-solution polymerization have been reported by Hohenstein and Mark (26). In these experiments, a small vessel of styrene was suspended above an aqueous phase containing potassium persulfate and small concentrations of hydroquinone, the whole system being flushed free of oxygen. Styrene vaporized from the small vessel and dissolved in the aqueous phase, where it polymerized. The appearance of a turbidity due to polymer was considerably delayed by the presence of hydroquinone in the aqueous phase. The induction period due to the hydroquinone (quinone under the conditions of the experiment) is considerably shortened by increasing the temperature or by adding emulsifiers. From the temperature coefficient of the induction period a value of about 25,000 cal. was obtained for the energy of activation of the formation of free radicals in the absence of emulsifiers.

Studies on the inhibition and retardation of emulsion polymerization are now being made in this laboratory. These investigations are confined at present to the emulsion polymerization of styrene and of butadiene, and the copolymerization of butadiene (75)–styrene (25). Persulfate has so far been used as “catalyst” in all these studies.

In emulsion polymerizations, “catalysts” are always used to initiate the polymerization. Everything that has been said for bulk polymerization would hold for emulsion polymerization if it were not for the fact that in emulsion polymerizations we are dealing with a heterogeneous system. In general, water-soluble “catalysts” (potassium persulfate, hydrogen peroxide, etc.) are used, these catalysts being completely or nearly completely insoluble in the monomer phase. In emulsion polymerization, the polymer always appears in the aqueous phase and not in the monomer phase. According to Harkins (25), the polymerization proper starts in the soap micelles, where the solubilized monomer becomes activated and where the polymer chain is propagated. After all the free soap has become adsorbed on the polymer particles, the latter are almost the sole loci of the further polymerization.

In order for a substance to act as an inhibitor or retarder in emulsion polymerization, it must be present at the locus where free radicals are formed, where they initiate polymerization, or where the polymer chains are growing. It is shown below that in this laboratory we have obtained good evidence that the activation of styrene by water-soluble catalysts occurs mainly in the "true" water phase and to a much lesser extent, if at all, in the soap micelles. The free radicals formed in the true aqueous layer must then be transferred to the soap micelle to initiate polymerization. If a substance which acts like an ideal inhibitor in bulk polymerization is water-soluble (e.g., oxygen, *p*-benzoquinone) it reacts in the "true" water phase with the free radicals formed there, and thus prevents the initiation of normal chain propagation. Such substances may react with radicals also at the soap micelle, and thus act like typical inhibitors even though their water solubility is low (e.g., chloranil).

A retarder is much less effective in its reaction with free radicals than is an inhibitor. If the retarder is water-soluble and insoluble in the monomer phase and in the micelles (e.g., nitrobenzoate in alkaline medium, nitrobenzenesulfonate, etc), it can react with some of the free radicals formed by the "catalyst" in the true aqueous layer, but it cannot interfere with the polymerization proper. It therefore exerts a retarding effect mainly by decreasing the rate at which free radicals reach the micelle, and hence the "effective" rate of activation. If the retarder is soluble in the monomer and in the micelles, it exerts the same retarding effect as in catalyzed bulk polymerization. Actually, experiments have substantiated this interpretation.

B. Experiments with retarders

It is shown in another paper (32) that 3,5-dinitrobenzoate in the emulsion polymerization of styrene with fatty acid soap as emulsifier and persulfate as "catalyst" acts like a mild retarder, its effect being very much less than that of an equimolar amount of *m*-dinitrobenzene. On the other hand, in acid medium (pH 1), with dodecylamine hydrochloride as emulsifier, practically all of the dinitrobenzoate is present in the form of the free acid in the organic phase and the soap micelles, only a negligible trace being present in the "true" aqueous phase. Therefore, at a pH of 1 3,5-dinitrobenzoate and *m*-dinitrobenzene are equally effective as retarders.

The mechanism of the retardation reaction has been discussed in the previous section under bulk polymerization. According to this mechanism, a retarder, which is present at the locus of the propagation reaction, should reduce the molecular weight of the polymer formed. This was found to be the case. An example is furnished by the effect of 0.052 and 6.64 millimoles of *m*-dinitrobenzene in the following recipe:

Styrene.....	100 g.
Water.....	185 g.
SF flakes.....	5.0 g.
Potassium persulfate.....	0.3 g.
Temperature.....	50°C.

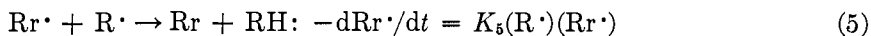
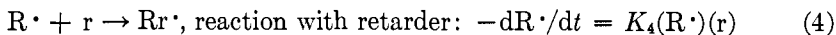
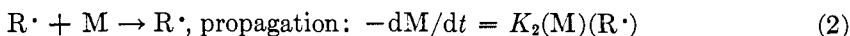
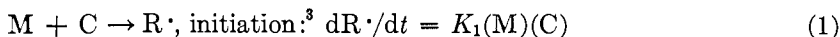
The observed rates of conversion and intrinsic viscosities (in benzene at 30°C.) are:

<i>m</i> -DINITROBENZENE	RATE OF CONVERSION	η_i AT 30°C.
<i>millimoles</i>	<i>per cent/hour</i>	
0	65	13.8
0.052	27	9.1
6.64	0.77	0.95

If the retarder is not present at the locus of propagation, but is present in the true aqueous phase where activation occurs, the molecular weight of the polymer is hardly affected. This is illustrated by the effect of 2.65 millimoles of 3,5-dinitrobenzoic acid in the above recipe, with the addition of sodium hydroxide to a concentration of 0.03 *M*:

3,5-DINITROBENZOIC ACID	RATE	η_i AT 25°C.
<i>millimoles</i>	<i>per cent/hour</i>	
0	67	13.2
2.65	47	12.5

The effect of a retarder on the kinetics of the polymerization reaction can be derived on the basis of the mechanism given in Section II. Let *M* represent monomer, *C* catalyst, *R*· a monomer or polymer radical, *r* the retarder, and *Rr*· the stabilized radical formed by addition of retarder to a monomer or polymer radical:



When the concentration of (*r*) is very large, we may assume as a first approximation that termination of growing polymer chains occurs largely by 4 and 5, and that 3 may be neglected. We then have at the steady state:

$$K_4(R\cdot)(r) + K_5(R\cdot)(Rr\cdot) = K_1(M)(C) \quad (6)$$

$$-\frac{dM}{dt} = K_2(M)(R\cdot) = \frac{K_1 K_2 (M)^2 (C)}{K_4(r) + K_5(Rr\cdot)} \quad (7)$$

³ It is quite possible that the initiation does not occur according to equation 1. The rate-determining step may be the rate of dissociation of the catalyst into free radicals, and the concentration of monomer will not then affect the rate of initiation.

Also, at the steady state the following relation holds:

$$K_4(\text{R}\cdot)(r) = K_5(\text{R}\cdot)(\text{Rr}\cdot), \text{ or} \quad (8)$$

$$K_4(r) = K_5(\text{Rr}\cdot) \quad (9)$$

Thus, instead of equation 6 we may write:

$$-\frac{dM}{dt} = \frac{1}{2} \frac{K_1 K_2 (M)^2 (C)}{K_4(r)} \quad (10)$$

In the presence of a separate styrene phase we find (M) constant, or

$$-\frac{dM}{dt} = K \frac{(C)}{(r)} \quad (11)$$

It has been well established (33, 44) that in the normal emulsion polymerization of styrene without retarder and with persulfate as catalyst, the following relation holds:

$$-\frac{dM}{dt} = K(C)^n$$

where $n = 0.5$. This relationship has also been repeatedly observed for bulk and solution polymerization with oil-soluble catalysts. In the presence of 6.64 millimoles of *m*-dinitrobenzene in the above recipe, but using dodecylamine hydrochloride instead of SF flakes, n becomes 0.83. Thus, the predicted value of unity is approached but not reached even where the rate of polymerization is only about 1 per cent of the normal rate.

The predicted dependence of the rate of polymerization upon the reciprocal of the retarder concentration has been found to hold well at high concentrations of retarder.

Polarographic measurements of the rate of disappearance of *m*-dinitrobenzene (32) during the emulsion polymerization of styrene in the above recipe, but with dodecylamine hydrochloride as emulsifier, have shown that it disappears at about the same rate as *p*-benzoquinone (see Section III,C). Since *p*-benzoquinone probably does not copolymerize with styrene under the conditions of our experiments, it is evident that *m*-dinitrobenzene also does not copolymerize, and that the adduct radicals are entirely unreactive toward monomer, as we have postulated in the mechanism proposed earlier.

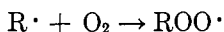
C. Experiments with inhibitors

For a study of the activation of a monomer in emulsion polymerization, it would be desirable to have available inhibitors which react with free radicals to produce finished molecules which do not affect the rate of polymerization after consumption of the inhibitor. The rate of consumption of such an inhibitor during the induction period would be equal to or would bear a simple ratio to the rate of activation of the monomer. Thus, the length of the induction period would be inversely proportional to the rate of activation. Unfortunately, benzoquinone and other quinones are not suitable inhibitors in emulsion polymer-

izations with fatty acid soaps, because the quinones are rapidly decomposed in the alkaline medium. However, we have found that in acid recipes at low pH (about 1), using cation detergents such as dodecylamine hydrochloride, *p*-benzoquinone behaves like an ideal inhibitor. These studies are still in progress, and the results will be reported at a later date. At this time, it may be stated that the induction periods caused by *p*-benzoquinone in the emulsion polymerization of styrene at pH 1, employing the recipe given above but with dodecylamine hydrochloride as emulsifier, are accurately proportional to the initial quantity of quinone (the curves resembling those of Foord (20; Fig. 1) for bulk polymerization), inversely proportional to the concentration of persulfate, and essentially independent of the concentration of emulsifier. The rate of disappearance of the quinone during the induction period is found to be 5.7×10^{-5} moles per hour per liter of aqueous phase at 50°C. in the above recipe, whereas at 90°C. in the bulk polymerization of styrene Foord found the rate of disappearance of quinone to be 2.2×10^{-4} moles per liter per hour. The rates of polymerization are 3.48 moles per liter per hour of aqueous phase for emulsion polymerization and only 0.117 mole per liter per hour for bulk polymerization. Since a much faster rate of polymerization is observed for emulsion polymerization in this recipe at 50°C. than for bulk polymerization at 90°C., although the rate of activation (as measured by the rate of quinone disappearance) is only about one-fourth as large, it appears that the rate of propagation and hence the molecular weight of the polymer must be very great in emulsion polymerization. This is actually the case. The intrinsic viscosities of the polymers formed during unretarded polymerizations (see Section III,B) probably correspond to molecular weights of at least 2-3 million.

In this laboratory, the induction period caused by oxygen in the emulsion polymerization of styrene according to the above standard recipe has been studied extensively, using fatty acid soap (SF flakes) as emulsifier and potassium persulfate as catalyst. It should be realized that qualitatively and quantitatively the effect of oxygen may vary with the type of catalyst (water- or oil-soluble, redox systems, etc.) used. Oxygen causes an induction period in the emulsion polymerization of styrene and of butadiene, and in the copolymerization of butadiene (75)-styrene (25). During the induction period the oxygen is consumed, and polymerization starts with its normal rate at the end of the induction period.

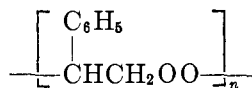
The reaction of styrene free radicals with oxygen is not so simple as their reaction with quinone. As we have mentioned in Section II of this paper, during the oxygen induction period in the emulsion polymerization of styrene with persulfate as catalyst (3), the free radicals formed in the activation reaction evidently react with oxygen with the formation of peroxide free radicals:



The peroxide free radicals then react very slowly (as compared to the reaction of monomer free radicals with oxygen or with monomer in the absence of oxygen) with monomer:



yielding a radical which then again rapidly reacts with oxygen, etc. A copolymer of styrene and oxygen is thus formed (polystyrene peroxide):



This copolymer has actually been isolated and gave the following elementary analysis: calculated for $\text{C}_8\text{H}_8\text{O}_2$: C, 70.50; H, 5.86; O, 23.60. Found: C, 71.05, 71.13; H, 6.04, 6.17; O (by difference), 22.9, 22.6.

This substance released iodine from potassium iodide in acetic anhydride (although not quantitatively), catalyzed the bulk polymerization of styrene at 80°C ., gave a characteristic reduction wave at the dropping-mercury electrode, and was found to decompose explosively at about 100°C . with formation of benzaldehyde and formaldehyde.

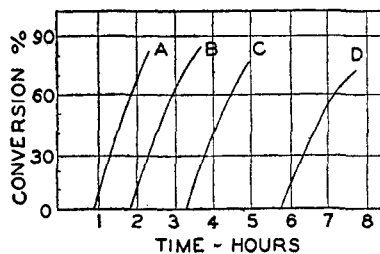


FIG. 3

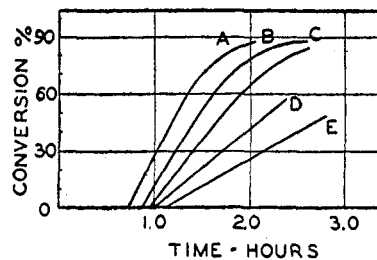


FIG. 4

Fig. 3. Induction periods produced by air in emulsion polymerization. Amounts of persulfate per 100 g. styrene: A, 0.6 g.; B, 0.3 g.; C, 0.15 g.; D, 0.075 g.

Fig. 4. Induction periods obtained using 0.6 part of persulfate and varying the concentration of the SF flakes emulsifier. SF flakes per 100 g. styrene: A, 5.0 g.; B, 2.5 g.; C, 1.25 g.; D, 0.625 g.; E, 0.313 g.

In the emulsion polymerization of styrene in bottles in the presence of oxygen, Kolthoff and Dale (34) have found:

(1) The induction period caused by oxygen in the emulsion polymerization of styrene with persulfate as "catalyst" is inversely proportional to the persulfate concentration, and proportional to the amount of oxygen provided the initial pressure of oxygen is constant, but not independent of the initial oxygen pressure when the initial volume is constant.

(2) The length of the induction period is hardly dependent upon the amount of soap in the charge, indicating that, as we have said earlier, the activation of the monomer occurs mainly in the "true" water phase and not in the soap micelles.

(3) Oxygen acts like a temporary shortstop when introduced into the mixture after the start of polymerization.

In figure 3 are represented the induction periods produced by 43 ml. of air in the polymerization of 210 ml. of emulsion made up according to the recipe on page 516, but employing varying amounts of persulfate, as indicated.

In figure 4 are represented the results obtained using 0.6 part of persulfate and varying the concentration of the SF flakes emulsifier.

The results shown in figures 3 and 4 closely resemble those found using quinone as inhibitor, except that much more oxygen than quinone is required to produce a given induction period. This more rapid rate of oxygen disappearance is a result of the chain reaction which it undergoes, and which quinone is capable of undergoing only to a much more limited extent if at all, under the conditions of our experiments.

Experiments by the present authors (3) have been carried out using a manometric apparatus by means of which the rate of oxygen consumption by the reaction mixture could be directly measured, and which allowed efficient mixing of the gas and liquid phases. It has been found that the rate of disappearance of the oxygen during the oxygen induction period in the emulsion polymerization of styrene is directly proportional to the persulfate concentration, but independent of the oxygen pressure. In the bottle experiments the induction period was not found to be independent of the initial oxygen pressure with a given volume of oxygen, apparently because under the conditions of agitation obtaining during bottle polymerizations, the oxygen does not attain solubility equilibrium.

These observations are consistent with a mechanism similar to that on page 513 but in which step 1 is an activation by persulfate rather than a thermal activation:



as in 2a, 2b, 2c, etc. Since step 2 is much more rapid than step 1, step 1, which is independent of the oxygen pressure, becomes the rate-controlling step; hence the rate of consumption of oxygen is independent of its pressure.

Again, the rate of oxygen consumption is found to be nearly independent of the concentration of the SF flakes emulsifier employed.

After very long induction periods in the emulsion polymerization of styrene at 50°C., a slight increase in polymerization rate over that normally found may be observed. However, the peroxide polymer formed is too stable to have an appreciable effect unless present in considerable concentrations.

Bottle polymerizations according to the standard recipe with butadiene and with butadiene (75)-styrene (25) are now being carried out in this laboratory by J. M. Honig. Again, oxygen causes a typical induction period, the length of which is not inversely proportional to the persulfate concentration but to the square root of the persulfate concentration. As was found in the emulsion polymerization of styrene, the induction period caused by oxygen decreases only slightly with increasing concentrations of soap. Thus, again, the activation reaction appears to occur mainly in the "true" aqueous phase. These studies so far appear to indicate striking differences between the activation of styrene by persulfate on the one hand and of butadiene and butadiene (75)-styrene (25) on the other.

IV. PRACTICAL ASPECTS OF THE INHIBITION AND RETARDATION OF VINYL POLYMERIZATION

Inhibitors and retarders are of practical importance in the manufacture of synthetic rubber. In this section, we shall limit our brief discussion chiefly to the effects observed in the emulsion copolymerization of butadiene (75)–styrene (25), which is generally carried out with 100 parts of monomers, 180 parts of water, 5 parts of soap flakes as emulsifier, 0.3 part of potassium persulfate, and 0.5 part of dodecyl mercaptan. In this process, inhibitors and retarders are important for the following reasons:

(1) They are used to stabilize monomers against premature polymerization during synthesis, distillation, shipment, and storage. Such premature polymerization would lead to great loss both through waste of monomer and through fouling of equipment. Compounds falling in Foord's class of ideal or nearly ideal inhibitors may be expected in general to be the most effective stabilizers. Substances falling in the class of retarders will be effective stabilizers if present in sufficient quantity. Although not mentioned by Foord, we have seen that oxygen is a good inhibitor for the bulk polymerization of styrene, and probably for other monomers as well, provided the temperature is not too high.

(2) They may interfere with the normal rate of polymerization. Traces of inhibitors or retarders are added to commercial monomers as stabilizers. These stabilizers may interfere with the emulsion polymerization and must be removed by distillation or by other means if present in harmful concentrations. Phenolic substances can be removed by caustic washing.

In addition, retarding substances occur in technical butadiene and in technical soap flakes. These substances probably act in essentially the same manner as aromatic nitro compounds, i.e., they react very readily with monomer radicals to produce adduct radicals having a very much lower order of reactivity. The structure:



which occurs in linoleic and linolenic acids (present in variable amounts in commercial soap flakes) and in 1,4-pentadiene (present in butadiene) has a particularly powerful retarding effect, although not so powerful as *m*-dinitrobenzene.

(3) They are employed to advantage to "shortstop" the polymerizing mixture when the desired conversion of monomer has been reached. Shortstops may function (a) by deactivating all or most of the free radicals produced in the system so that little or no normal chain propagation can occur, but without affecting the rate at which the radicals are produced, and (b) by destroying the "catalyst", and thus cutting off the supply of radicals at its source. Most shortstops used or proposed for use in commercial practice probably combine both actions, but action 1 is believed to be in general more important.

Hydroquinone, the most widely used shortstop, undoubtedly is first oxidized to *p*-benzoquinone, which is nearly an ideal inhibitor under suitable conditions. However, *p*-benzoquinone is not stable in alkaline medium but decomposes

fairly rapidly to degradation products of unknown structure, and it is probably these degradation products which actually react with the free radicals.

Some indication of the practical importance of Foord's work (20) is furnished by the fact that his studies provide the basis for patents relating to the stabilization of styrene and to the accurate control of the period of stabilization. Styrene polymerized *in situ* is of importance in the electrical industry, and the bulk polymerization of vinyl monomers is of course of fundamental importance in the plastics industries. It can be readily seen that ideal inhibitors would be useful in handling these substances, since they allow polymerization to occur only after a definite and predictable interval.

Stabilization of monomers has become a problem of considerable industrial importance, since the manufacture of synthetic rubber has been put in operation on a large scale. Undesirable polymerization with the formation of resinous products has proved to be a great nuisance in the polymer-manufacturing plants and in the final stages of the manufacture of butadiene.

The growth of a resinous polymer of butadiene has recently been studied by Welch, Swaney, Gleason, and Beckwith (63). This polymer, which has been designated in the literature as "cauliflower" polymer but is now called "popcorn" polymer, is a tough, insoluble, infusible substance which forms in and frequently fouls the columns used for the distillation of butadiene. The growth of this substance is initiated by peroxides in the presence of rusty iron and moisture. Once growth has been initiated, polymerization proceeds rapidly on the surface of the polymer formed, provided monomer (vapor or liquid) is supplied, and the presence of catalyst is no longer required. Polymer growth can be retarded by mercaptobenzothiazole, *p*-quinone dioxime, and other vulcanizing agents and accelerators for vulcanization. Typical antioxidants are ineffective in retarding its growth.

The resinous copolymer of butadiene and styrene has been studied by Kharasch *et al.* (31b). This substance resembles the popcorn polymer of butadiene, but is somewhat more soluble in organic solvents. It forms where butadiene and styrene are present together at relatively high temperatures (75–100°C.), as in the monomer recovery units of the GR-S manufacturing plants, and also presents a serious fouling problem. It shows ability to grow in the presence of monomer from "seeds" of initially formed polymer. Its growth can be initiated by any substance having α -methylene groups capable of forming peroxides. Butadiene and its polymers, after exposure to oxygen, are such substances. Peroxidized and polymerized tung oil serves equally well. The activity of the seeds can be destroyed by nitrogen dioxide or nitrogen trioxide, which decomposes the peroxides necessary for the polymerization and combines with the double bonds present. The growth of polymer, even when active seeds are present, can be arrested by aqueous solutions of sodium nitrite. Aqueous sodium nitrite was also found to be an exceedingly effective inhibitor for the thermal polymerization of styrene (even at temperatures as high as 100°C.), provided the aqueous and oil phases were effectively agitated.

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