The GR-S was prepared with added hydroquinone as a shortstop. Subsequent acetone and alcohol extractions may not have removed all traces of this inhibitor. It is possible that the presence of hydroquinone or of quinone derived therefrom could vitiate some of the conclusions to be drawn. However, at 2537 Å. calculations using the extinction coefficients of ethyl benzene and *p*-benzoquinone show that the absorption of the phenyl groups in GR-S is many orders of magnitude greater than that of the quinone which would be present even if all of the added hydroquinone were converted to benzoquinone. At 3660 and 3130 Å., one can only say that the highest amount possible of benzoquinone accounts for only a very small fraction of the observed absorption.

The low quantum yield of oxidation of GR-S as in rubber indicates that chains do not immediately follow the primary reaction with oxygen. The phenyl group is the effective absorbing group, and it seems likely that the photon energy is not so readily transferred from the benzene nucleus to the adjacent carbon-hydrogen grouping as from the double bond in rubber. Such an effect would explain the lower quantum yields of GR-S as compared with rubber. At all three ultraviolet wave lengths GR-S shows rates increasing with time of absorption which again may be due to photodecomposition of the peroxide first formed. Due to the high extinction coefficient of GR-S, a large proportion of the oxidation will occur near the front surface of the film and near this surface the per cent. oxygen added will be much higher than the average reported in Table II. Thus sufficient peroxides for autocatalysis may be quickly formed. The discrepancy of the dark reaction in GR-S at 2537 Å. in relation to total oxygen absorbed may be due to the formation of an oxygen-impermeable surface film or to the formation of phenolic type inhibitors during oxidation. Larsen, Thorpe and Armfield[25] have shown that alkyl substituted benzenes form inhibitors during thermal oxidation at 110°.

Summary

The initial quantum yields of photoöxidation for purified Hevea rubber have been measured for various mercury arc lines in the wave length region 2537–17,400 Å. All experiments were carried out at room temperature and at an oxygen pressure of one atmosphere. At the outset of irradiation all quantum yields of combined oxygen are less than unity, although the quantum efficiency rises above 1.0 at 2537 and 3130 Å. as photoöxidation proceeds. The low quantum yield suggests that in its initial stages (less than 0.1% oxygen combined on the rubber) photooxidation is not a chain reaction. It is postulated as the first step in rubber photoöxidation that the light activated rubber group reacts with oxygen to give a relatively stable intermediate which does not immediately dissociate to give a free radical reaction chain.

The quantum yields of photoöxidation of purified GR-S were also measured under the same conditions as used for rubber. At each wave length the quantum yield was lower than for rubber, indicating formation of a stable intermediate in the initial reaction also.

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[25] R. G. Larsen, R. E. Thorpe and F. A. Armfield, *Ind. Eng. Chem.*, **34**, 183 (1942).

PASSAIC, NEW JERSEY RECEIVED AUGUST 22, 1947

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies of Retarders and Inhibitors in the Emulsion Polymerization of Styrene. I. Retarders[1a]

BY I. M. KOLTHOFF AND F. A. BOVEY

Typical retarders of polymerization processes are defined as substances which retard the polymerization throughout the entire reaction period, without giving rise to induction periods. On the other hand, ideal inhibitors are defined as substances which cause a well-defined induction period, after which polymerization starts with its normal rate. There are substances the behavior of which is intermediate between that of compounds in either of these two classes.

Inhibitors and retarders both exert their effect by reacting with free radicals to produce reaction products which are either slow in propagating chains (oxygen is an example of this type of inhibitor) or unreactive so far as further chain propagation is concerned. The rate of reaction of inhibitors with free radicals is much greater than that of retarders. Ideal inhibitors react with such a rate that all the free radicals produced in the system are made inactive. Thus a typical induction period is observed, during which the inhibitor is consumed by reaction with the free radicals.

A typical retarder reacts with free radicals with such a rate that only a fraction of the free radicals produced can initiate normal polymerization. In addition, the growing polymer chains can react with the retarder. Thus a retarder acts as a typical chain-breaker. If this concept is correct, a retarder should reduce the molecular weight of the polymer, although this effect may not be large when effective chain transfer agents are present.

[1a] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government's synthetic rubber program.

Also, a fraction of the retarder added to the charge should be consumed during the polymerization and should be found in the polymer.

In the literature the terms "inhibitor" and "retarder" are often used synonymously. If added in large enough quantities, a retarder will virtually prevent the start of polymerization, and if added to a polymerizing mixture will virtually stop further reaction. Such an effect may be easily confused with the occurrence of an induction period. Actually, a large amount of a retarder does not give rise to a typical induction period, but causes the polymerization to be extremely slow at the beginning, and to remain slow throughout the entire reaction period. In this respect, it is of interest that much smaller quantities of an ideal inhibitor than of a typical retarder are required to shortstop a reaction. The shortstopping effect of a small amount of an inhibitor is only temporary, the length of the period of shortstopping increasing in proportion to the quantity of inhibitor initially present.

If the rate of reaction of a substance with free radicals is intermediate between that of an ideal inhibitor and a typical retarder, such a substance will give rise to an extremely small initial rate of polymerization, this rate increasing continually with time as more and more of the substance is consumed. In the presence of such a substance, the initial reaction-time curve approaches that found in the presence of an ideal inhibitor. After an ill-defined induction period, a retarded polymerization is observed, the retardation decreasing as the reaction progresses.

If the reaction product formed by reaction of an inhibitor with free radicals during the induction period acts as a retarder, a well-defined induction period is observed, followed by a retarded polymerization. Thus, such a substance combines the effect of an ideal inhibitor and a typical retarder. Similar behavior might be expected of a compound having functional groups characteristic of both an inhibitor and a retarder (*e. g.*, a nitroquinone).

In Fig. 1 are presented time-conversion curves typical of the effects we have described.

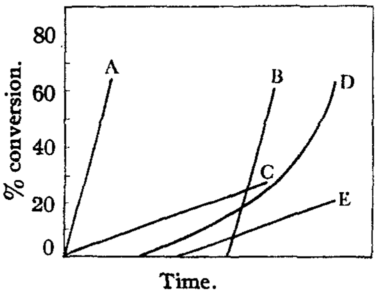

Fig. 1.—Typical time-conversion curves for various inhibitory and retarding effects: A, normal polymerization; B, ideal inhibition; C, typical retardation; D, non-ideal inhibition; E, ideal inhibition, followed by typical retardation.

No kinetic studies of the effect of retarders in emulsion polymerization are to be found in the literature. The present paper deals with the effect of retarders on the emulsion polymerization of styrene. In a subsequent paper, studies on the effect of inhibitors on the emulsion polymerization of styrene will be described.

Quite generally, the interpretation of the action of inhibitors and retarders in emulsion polymerization may be expected to be identical with that found in bulk or solution polymerizations. However, as far as the kinetics is concerned, interesting differences between bulk and solution polymerizations on the one hand and emulsion polymerization on the other may be expected under certain conditions. In emulsion polymerizations, we are dealing with typical heterogeneous systems. In order to act like a retarder, the substance must be at the locus of reaction. Thus, studies with retarders may give some insight into the locus of activation and of propagation. (See the "Discussion" section.)

Experimental Technique

Materials

***m*-Dinitrobenzene.**—A product with a melting point of 88.5–89.5° (lit. 90°) was used in part of this work. In the remainder, a sample recrystallized from ethanol (m. p. 90–91°) was employed.

3,5-Dinitrobenzoic Acid.—A product with a melting point of 201–202° uncor. (lit. 204°) was employed.

1,4-Pentadiene.—The 1,4-pentadiene used was supplied by Prof. C. S. Marvel of the University of Illinois.

Styrene.—Dow styrene with a purity of at least 99.5% was used. This material was distilled *in vacuo* just before use, although it may be safely stored for one or two days at 0 to 10°.

Water.—Conductivity water was used throughout.

Soap Flakes.—Commercial (S. F.) soap flakes (designated as S. F. flakes) supplied by Procter and Gamble were employed. This material is largely composed of the sodium salts of stearic, palmitic, and oleic acids, and contains only very small amounts of soaps of polyunsaturated fatty acids. The same lot of this material was used throughout this work.

Dodecylamine Hydrochloride.—Dodecylamine hydrochloride (designated as DDA·HCl) was prepared by neutralizing a solution of one mole of Armour dodecylamine dissolved in one liter of ethanol with concentrated hydrochloric acid, using methyl red indicator. Five hundred milliliters of ethyl ether was then added, and the hydrochloride was crystallized at about 0°, collected by suction filtration, washed with cold ether, and dried *in vacuo* for twelve hours at 25°.

Potassium Persulfate.—Reagent grade potassium persulfate was twice recrystallized from conductivity water, and the crystals dried *in vacuo* at room temperature.

Polymerization Technique.—The polymerizations were carried out in screw-cap bottles of 130-ml. capacity, sealed with pierced caps containing Buna-N self-sealing gaskets. The bottles were rotated end-over-end at about 35 r. p. m. in a thermostat and were sampled with hypodermic syringes in the same manner as described by Kolthoff and Dale.[1b] The 2-ml. samples thus obtained were expelled into weighed aluminum dishes containing 10.0 ml. of 0.02% aqueous hydroquinone solution, evaporated to dryness, and the residue dried for twenty–twenty-four hours at 80°. Per cent. conversion was calculated as previously described.[1b] The ingredients of the charge were added as described below.

(1b) I. M. Kolthoff and W. J. Dale, THIS JOURNAL, 69, 441 (1947).

Polymerization Recipe.—The following recipe, in which the amounts of several of the constituents were varied systematically, was used: styrene, 35.6 g. (39.3 ml. at 25°), designated as 100 parts; water, 65.7 ml., or 185 parts; emulsifier, 1.78 g. or 5 parts, based on the styrene. This quantity of emulsifier is designated as $1 - X$, and other quantities as fractions or multiples thereof. (Thus "$^1/_2 - X$" means 2.5 parts per 100 g. of styrene, or 0.89 g. per bottle.) When recipes containing dodecylamine hydrochloride were employed, the emulsifier was dissolved in water which had been flushed with nitrogen. No special effort was made to remove oxygen completely. Consequently, short and well-defined induction periods were observed, due to residual oxygen. In recipes with fatty-acid soap flakes, a given amount of oxygen causes a considerably larger induction period than in a dodecylamine hydrochloride recipe. To make the induction periods as short as possible, the dry soap flakes were brushed into the bottle while a current of nitrogen was passed into it, in the manner previously described.[1b] In both types of recipe, the styrene and aqueous persulfate solution were flushed with nitrogen while in the bottle. Potassium persulfate: 0.107 g. or 0.3 part, based on styrene. This quantity of persulfate is designated as $1 - X$ and other quantities as fractions or multiples thereof. The potassium persulfate was added as a solution in water. For $1 - X$ persulfate, 15.7 ml. of a 0.68% solution was added to each bottle. Retarders: the concentration of retarding substances is expressed as millimoles per 100 g. of styrene. The *m*-dinitrobenzene and 1,4-pentadiene were added as solutions in styrene. The 3,5-dinitrobenzoic acid was added as a water solution.

Experimental Results

Retardation by *m*-Dinitrobenzene.—Experiments were carried out with concentrations of *m*-dinitrobenzene varying between 0.052 and 0.830 millimole per 100 g. of styrene, employing both the DDA·HCl and soap flakes recipes. The conversion data obtained with the DDA·HCl recipe are plotted in Fig. 2, and the rates of conversion are presented in Table I. The results obtained with the soap flakes recipe are presented in Fig. 3 and Table II.

TABLE I

RATES OF POLYMERIZATION OF STYRENE AT 50° IN 1*X* DDA·HCl, 1*X* PERSULFATE RECIPE, WITH VARYING AMOUNTS OF *m*-DINITROBENZENE, EXPRESSED AS MILLIMOLES PER 100 G. OF STYRENE

Concn. *m*-dinitrobenzene	Rate of poly., % per hr.
0.0	67
.0520	19
.104	13
.208	6.5
.415	3.2
.830	1.8

TABLE II

RATES OF POLYMERIZATION OF STYRENE AT 50° IN 1*X* S. F. FLAKES, 1*X* PERSULFATE RECIPE, WITH VARYING AMOUNTS OF *m*-DINITROBENZENE, EXPRESSED AS MILLIMOLES PER 100 G. OF STYRENE

Concn. *m*-dinitrobenzene	Rate of polym., % per hr.
0.0	65
.0520	27
.104	17
.208	10
.415	6.8
.830	3.5

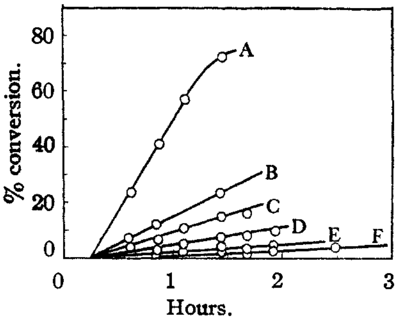

Fig. 2.—Effect of *m*-dinitrobenzene as retarder in emulsion polymerization of styrene: 1*X* dodecylamine hydrochloride, 1*X* persulfate, 50°, concentration of *m*-dinitrobenzene expressed in millimoles per 100 g. of styrene: A, 0.0; B, 0.052; C, 0.104; D, 0.208; E, 0.415; F, 0.830.

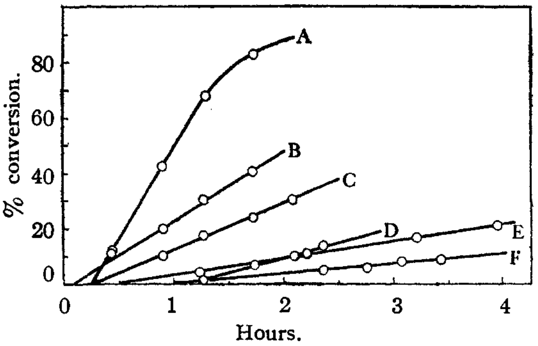

Fig. 3.—Effect of *m*-dinitrobenzene as retarder in emulsion polymerization of styrene: 1*X* S. F. flakes, 1*X* persulfate, 50°, concentration of *m*-dinitrobenzene expressed in millimoles per 100 g. of styrene: A, 0.0; B, 0.0520; C, 0.104; D, 0.208; E, 0.415; F, 0.830.

Since the smallest quantity of *m*-dinitrobenzene employed in the above experiments corresponds to only 0.0087% based on the styrene, it can be seen that *m*-dinitrobenzene is a very effective retarder. Its effectiveness is somewhat greater in the DDA·HCl recipe than in the S.F. flakes recipe. It produces no induction periods in either of the recipes, the small induction periods observed being caused by residual oxygen.

Effect of *m*-Dinitrobenzene on Molecular Weight of Polymer.—If *m*-dinitrobenzene exerts its effect in the soap micelle by terminating the growing polymer chains, the molecular weight of the polymer should be reduced. Accordingly, the experiments in Table II were repeated, the bottles being shortstopped with hydroquinone at times calculated to give approximately equal conversions in all cases. In addition, two more bottles were run, each containing 6.64 millimoles of *m*-dinitrobenzene per 100 g. styrene. These were shortstopped at 20% conversion (26 hr.) and 44% conversion (67.4 hr.). There appears in this case to be a considerable dependence of molecular weight on conversion.

The lattices obtained were coagulated with methanol and the polymer was dried *in vacuo* at 50°.

Intrinsic viscosities of 0.02% solutions in benzene were measured at 30°, using Ostwald pipets. The results obtained are summarized in Table III.

Table III

Effect of *m*-Dinitrobenzene on the Intrinsic Viscosity of Polystryene, Measured in Benzene at 30°. 1*X* Soap Flakes, 1*X* Potassium Persulfate Recipe at 50°

Concn. retarder, millimoles per 100 g. of styrene	% conversion when shortstopped	η_i^{30}, in benzene
0	39.7	13.8
.0520	33.1	9.1
.104	36.2	7.0
.208	32.4	6.0
.415	27.9	5.2
6.64	20.0	0.95
6.64	44.0	2.14

Effect of Large Concentrations of *m*-Dinitrobenzene at Varying Concentrations of Persulfate.—Polymerizations have been carried out in the presence of 0.415, 1.660, and 6.64 millimoles of *m*-dinitrobenzene per 100 g. of styrene, using different concentrations of persulfate. Figure 4 gives plots of the logarithm of the concentration of persulfate *versus* the logarithm of the observed rates of polymerization.

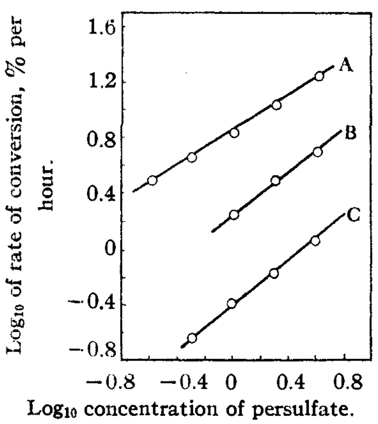

Fig. 4.—Log plots of rate of conversion *vs.* concentration of persulfate at three concentrations of *m*-dinitrobenzene, expressed in millimoles per 100 g. of styrene: A, 0.415; B, 1.66; C, 6.64.

The Disappearance of *m*-Dinitrobenzene during Polymerization.—If a retarder exerts its effect on the polymerization process by reacting with a fraction of the monomer and polymer radicals formed in the system, it appears that the retarder should become incorporated chemically into the polymer, and that the concentration of the free retarder in the reaction mixture should decrease during the polymerization. Experiments have been carried out to measure this decrease. The concentration of unconsumed *m*-dinitrobenzene was determined polarographically.

Curve A in Fig. 5 shows the reduction wave of 0.000880 *M* *m*-dinitrobenzene in 83% ethanol, the solution being 0.1 *N* in hydrochloric acid. It is seen that the reduction wave is composed of two waves, the first diffusion current being very poorly defined and not suitable for analytical purposes. On the other hand, the total diffusion current at potentials between −0.35 and −0.75 volt is well defined, and is suitable for analytical application. Assuming that the diffusion coefficient of *m*-dinitrobenzene is of the same order of magnitude as that of *p*-benzoquinone and benzaldehyde, it is found that the total diffusion current corresponds to a transfer of eight electrons per molecule. Since the height of the first wave is half that of the total wave, it may be concluded that *m*-dinitrobenzene is reduced at the dropping electrode in two steps, each corresponding to the reduction of the nitro group to a hydroxylamino group.

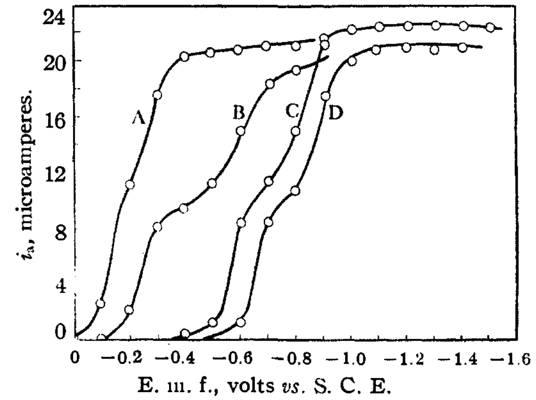

Fig. 5.—Polarographic reduction waves of 0.000880 *M* *m*-dinitrobenzene: A, in 83% ethanol, 0.1 *N* in HCl; B, same as A, but 1.5 ml. of styrene added to 25 ml. of solution in cell; C, in 90% ethanol, 0.1 *N* ammonium chloride plus ammonia, *p*H 8.5; D, same as C, but 1.5 ml. of styrene added to 25 ml. of solution in the cell.

From Curve B, it is seen that the presence of 6% styrene in the solution shifts the *m*-dinitrobenzene wave to more negative potentials, the first diffusion current becoming considerably more pronounced than in the absence of styrene. Unfortunately, the total diffusion current is no longer suitable for analytical purposes because of the appearance of the hydrogen wave.

By increasing the *p*H of the solution, the *m*-dinitrobenzene wave is displaced to more negative potentials. In Curve C is shown the wave of the nitro compound in 90% ethanol, the solution being 0.1 *M* in ammonium chloride, and containing enough ammonia to turn phenol red barely red (*p*H about 8.5). As is seen from Curves C and D the total diffusion current is now easily measurable, even though the presence of styrene shifts the wave to more negative potentials. The lowering of the diffusion current in Curve D is due entirely to dilution with styrene.

In preliminary work, about 20 g. of latex was coagulated in ethanol, and the *m*-dinitrobenzene determined. By adding known amounts of *m*-

dinitrobenzene to a 100% conversion polystyrene latex and coagulating in ethanol, it was found that a considerable amount of the *m*-dinitrobenzene was held in the coagulated polymer. Apparently the *m*-dinitrobenzene is soluble in polystyrene. After further investigation, the following procedure was adopted:

Approximately 25 g. of the latex was weighed into a 100-ml. beaker. In order to reduce the persulfate present, which interferes with the determination of the *m*-dinitrobenzene, 2.5 ml. of 6 *N* HCl and 5.0 ml. of a 5% aqueous solution of hydroxylamine hydrochloride were pipetted in. The contents of the beaker were heated to boiling to complete the reduction and allowed to cool. The polymer had now coagulated. Ammonia (about 3 *N*) was then added until phenol red turned red. The solution was decanted from the polymer through a coarse filter, the filtrate being caught in a 100-ml. volumetric flask. The polymer was washed in the beaker with alcohol and the washings were added to the filtrate. The polymer was extracted with 75 ml. of boiling 22:78 ethanol–benzene for three hours. It was established that by extracting with this solvent mixture, which swells the polymer considerably, 94% of a known quantity of *m*-dinitrobenzene added to a polystyrene latex could be recovered. To remove most of the benzene, the extracting liquid was boiled down on a steam-bath with frequent addition of ethanol. The ethanol solution was then added to the 100-ml. volumetric flask containing the filtrate, and the contents of the flask were diluted to volume with ethanol. This solution was then analyzed polarographically, using the diffusion current at −1.40 volt, and comparing to the current obtained with a known solution of *m*-dinitrobenzene in the same solvent.

This procedure was applied to a recipe containing 1*X* DDA·HCl, 1*X* persulfate, and 0.916 millimole of *m*-dinitrobenzene per 100 g. of styrene. After a reaction time of twenty-four hours, 33.5% conversion was obtained. This is a rate of about 1.4% per hour, or only about 2% of the normal rate in the absence of retarder. A control bottle containing no persulfate but the same quantities of the other ingredients was also run. No conversion occurred in this bottle.

m-Dinitrobenzene was determined after twenty-four hours in both bottles, two samples being taken from the bottle containing persulfate. The results obtained are summarized in Table IV.

TABLE IV

DISAPPEARANCE OF *m*-DINITROBENZENE DURING EMULSION POLYMERIZATION OF STYRENE, 1*X* DDA·HCl, 50°

Expt.	Concn. per sulfate	Conversion in 24 hours	Concn. *m*-dinitrobenzene, millimoles per 100 g. styrene initially present Initial	Final	Rate of *m*-dinitrobenzene disapp., millimoles/hour/liter of aqueous phase
1	1*X*	33.5	0.916	0.609 0.590	0.069 0.073
2	0	0	.916	0.916	0.0

In the last column, the rate of disappearance (assumed to be linear over the twenty-four hour period) of the *m*-dinitrobenzene is expressed as millimoles per hour per liter of aqueous phase, in order to facilitate comparison with the rate of disappearance of *p*-benzoquinone (see "Discussion").

It should be noted that the quantity of *m*-dinitrobenzene that has disappeared, and which we assume to have become chemically bound into the polystyrene molecules, corresponds to a nitrogen content in the polymer of only about 0.026%. While this quantity is determinable by refined methods, the method employed in this investigation appears to be more sensitive and precise, although of course it does not directly indicate the fate of the *m*-dinitrobenzene.

Solubilization of *m*-Dinitrobenzene in Solutions of Emulsifiers.—In connection with the problem of the locus at which a retarder exerts its effect, the solubilization of *m*-dinitrobenzene in 0.14 *M* solutions of dodecylamine hydrochloride and soap flakes (corresponding approximately to "1*X*" in the standard recipe) was measured.

An excess (about 1 g.) of *m*-dinitrobenzene was added to 100 ml. of the emulsifier solution in a screw-cap polymerization bottle. The bottle was rotated for twenty-four hours at 50°, and then a 5.0-ml. sample was removed with a pipet (carrying a glass wool filter on the end), 2.5 ml. of 1 *M* ammonium acetate was added, and the solution diluted to 25 ml. with ethanol. The concentration of *m*-dinitrobenzene was determined polarographically. A blank, using 0.14 *M* ammonium chloride solution instead of DDA·HCl solution, was also run. The results are shown in Table V.

TABLE V

SOLUBILIZATION OF *m*-DINITROBENZENE IN G. PER 100 ML. OF SOLUTION IN 0.14 *M* SOLUTIONS OF DDA·HCl AND S. F. FLAKES

(0.14 *M* NH_4Cl)	0.14 *M* DDA·HCl	0.14 *M* S. F. Flakes
0.147	0.270	0.310
.140	.250	
	.250	

The results indicate conclusively that *m*-dinitrobenzene is solubilized in solutions of the two emulsifiers.

Combined Effect of Oxygen and *m*-Dinitrobenzene.—It has been established[2] that during the induction period caused by oxygen in the emulsion polymerization of styrene, the oxygen is consumed by copolymerizing with the styrene to produce a polymeric styrene peroxide. The rate of this copolymerization is only about 0.1% of that of the normal polymerization in the absence of oxygen. The polymer produced has an average chain length of about 40 styrene peroxide  $-(-\underset{C_6H_5}{\underset{|}{C}}HCH_2OO-)-$ units. It appeared that if this chain process were interrupted by an effective retarder, for example, *m*-dinitrobenzene, the rate of consumption of the oxygen would be decreased, and the induction period caused by a given quantity of oxygen would be prolonged.

An experiment was carried out using 1*X* S. F. flakes, 2*X* $K_2S_2O_8$ and three concentrations of *m*-

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[2] F. A. Bovey and I. M. Kolthoff, THIS JOURNAL, **69**, 2143, (1947).

dinitrobenzene. In each bottle, 29 ml. of air and 101 ml. of liquid phase were present. The conversion curves obtained are shown in Fig. 6. It can be seen that the induction period caused by oxygen is not affected by the presence of *m*-dinitrobenzene.

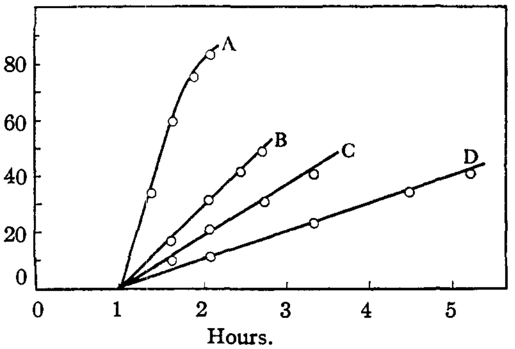

Fig. 6.—Effect of *m*-dinitrobenzene on induction period caused by 29 ml. of air per 101 ml. of charge in 1*X* S. F. flakes, 2*X* persulfate recipe, 50°; concentration of *m*-dinitrobenzene in millimoles per 100 g. of styrene: A, 0.0; B, 0.104; C, 0.208; D, 0.415.

Retardation by 1,4-Pentadiene.—This substance is an example of one type of retarder which may be encountered in commercial practice, since it is believed to occur as an impurity in technical butadiene. In addition, the structure —CH═CHCH$_2$CH═CH— which occurs in this compound also occurs in linoleic and linolenic acids. It is known from investigations carried out in this Laboratory that linoleic acid acts as an effective retarder when present as its sodium soap in commercial soap flakes. Linolenic acid has an even greater retarding effect. It was therefore of interest to compare equal molar quantities of 1,4-pentadiene and of a powerful retarder such as *m*-dinitrobenzene. In Table VI the rates of conversion with varying concentrations of 1,4-pentadiene are presented.

Table VI

Rates of Conversion with Varying Concentrations of 1,4-Pentadiene in Emulsion Polym. of Styrene at 50° 1*X* S. F. Flakes, 1*X* $K_2S_2O_8$

Concn. 1,4-pentadiene, millimoles per 100 g. styrene	Concn. 1,4-pentadiene, parts per 100 g. of styrene	Rate, %/hr.
0	0	78
0.415	0.028	74
0.830	.056	56
1.66	.113	43
3.32	.225	34

It is evident that 1,4-pentadiene is a much less effective retarder than *m*-dinitrobenzene.

3,5-Dinitrobenzoic Acid as Retarder.—If the locus at which a typical retarder, such as *m*-dinitrobenzene, exerts its effect is confined to the soap micelle and polymer particle, it appears that a compound having the structure of a retarder—for example, having two nitro groups in *meta* positions on a benzene ring—would be ineffective if it contained in addition a strongly polar functional group which confined it to the true water phase (*i. e.*, dissolved in water, but not in the micelles or in the polymer particles). Accordingly, 3,5-dinitrobenzoic acid, which has nitro groups meta to each other, was first tried in the alkaline recipe with S. F. flakes in order to compare its effect with that of *m*-dinitrobenzene. The acid is relatively strong ($K = 1.55 \times 10^{-3}$ at 25°), and at a *p*H of about 9, the concentration of free acid is vanishingly small.

In Figure 7 and Table VII are presented data for varying concentrations of 3,5-dinitrobenzoic acid in a 1*X* soap flakes, 1*X* persulfate recipe.

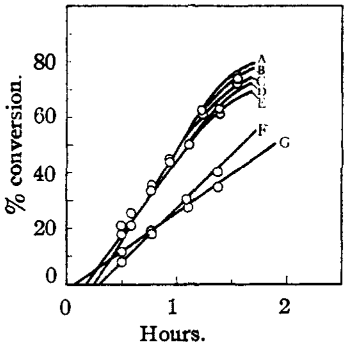

Fig. 7.—Effect of 3,5-dinitrobenzoic acid in emulsion polymerization of styrene: 1*X* S. F. flakes, 1*X* persulfate, 50°; concentration of retarder in millimoles per 100 g. of styrene: A, 0.0; B, 0.0415; C, 0.0830; D, 0.166; E, 0.332; F, 0.663; G, 1.33.

It will be observed that 3,5-dinitrobenzoic acid is very much less effective as a retarder in this recipe than an equal molar quantity of *m*-dinitrobenzene. Although the dinitrobenzoate is a very ineffective retarder, it was anticipated that the free acid would behave in a manner similar to that of *m*-dinitrobenzene, and that the retarding effect of the benzoate would increase with increasing hydrogen ion concentrations in the recipe. This was proved to be true. In Table VII are shown data obtained with a 1*X* DDA·HCl recipe in which the *p*H of the aqueous phase was made 3.3 (measured with the glass electrode) by adding acetic acid to a concentration of 0.3 *M* and sodium acetate to a concentration of about 0.03 *M*. The conversion curves are plotted in Fig. 8.

Table VII

Rates of Conversion with 3,5-Dinitrobenzoic Acid at Various *p*H's Compared to Effect of *m*-Dinitrobenzene at *p*H 9. Concn. Retarder in Millimoles per 100 G. of Styrene

Concn. of retarder → Retarder	*p*H	0	0.104	0.166	0.208	0.332	0.415	0.663	0.830	1.33
m-Dinitrobenzene	9.0	65	17	..	10	..	6.5	..	4	..
3,5-Dinitrobenzoic	9.0	65	..	58	..	58	...	40	..	30
acid	3.3	82	..	42	..	31	...	24	..	18
	1.0	66	..	21	..	11	...	4	..	1

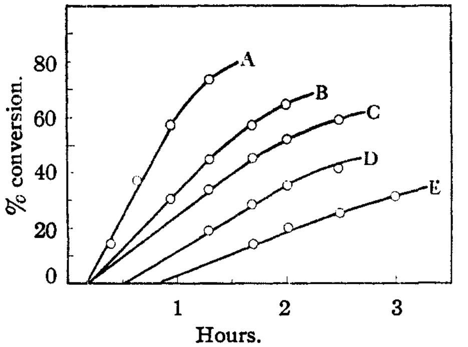

Fig. 8.—Effect of 3,5-dinitrobenzoic acid in emulsion polymerization of styrene: 1*X* S. F. flakes, 1*X* persulfate, sodium acetate–acetic acid buffer, *p*H 3.3, 50°; concentration of retarder in millimoles per 100 g. of styrene: A, 0.0; B, 0.166; C, 0.332; D, 0.663; E, 1.33.

This set of experiments was then carried out using the same recipe, except that instead of the sodium acetate–acetic acid buffer, the aqueous phase was made 0.1 *N* in hydrochloric acid, giving a measured *p*H of 1.0. The rates of conversion obtained under these conditions are also shown in Table VII, and plotted in Fig. 9.

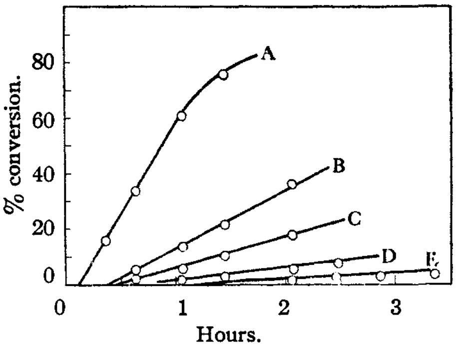

Fig. 9.—Effect of 3,5-dinitrobenzoic acid in emulsion polymerization of styrene: 1*X* dodecylamine hydrochloride, 1*X* persulfate, 0.1 *N* HCl; *p*H 1.0, 50°; concentration of retarder in millimoles per 100 g. of styrene: A, 0.0; B, 0.166; C, 0.332; D, 0.663; E, 1.33.

In Figure 10, the data of Table VII are plotted. It is evident from this plot that 3,5-dinitrobenzoic acid becomes equal in effectiveness to *m*-dinitrobenzene when the hydrogen ion concentration is high enough so that the acid is essentially un-ionized.

TABLE VIII

RATES OF CONVERSION AND INTRINSIC VISCOSITIES OF POLYSTYRENE IN PRESENCE OF 3,5-DINITROBENZOIC ACID; 1*X* $K_2S_2O_8$, 1*X* S. F. FLAKES, 0.03 *M* IN NaOH. CONCN. OF 3,5-DINITROBENZOIC ACID IN MILLIMOLES PER 100 G. OF STYRENE

Concn. of 3,5-dinitrobenzoic acid	Rate, %/hr.	η_i at 25°
0	67	13.2
1.33	46	12.0
2.65	47	12.5

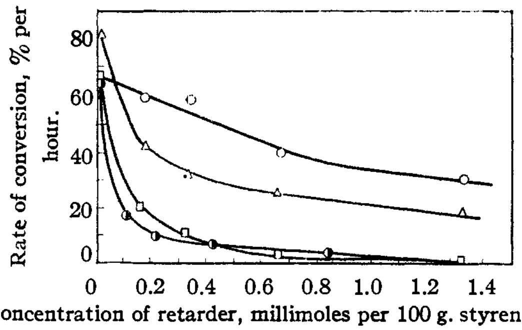

Fig. 10.—Effect of 3,5-dinitrobenzoic acid at varying *p*H compared to effect of *m*-dinitrobenzene at *p*H 9: ○, 3,5-dinitrobenzoic acid at *p*H 9.0; △, same at *p*H 3.3; □, same at *p*H 1.0; half-shaded circle, *m*-dinitrobenzene (*p*H 9).

Effect of 3,5-Dinitrobenzoate at High *p*H on Molecular Weight of Polymer.—An experiment was carried out with 1*X* $K_2S_2O_8$ and 1*X* S. F. flakes, using 1.33 and 2.65 millimoles of 3,5-dinitrobenzoic acid per 100 g. of styrene. The aqueous phase was made 0.03 *M* in NaOH. The rates of conversion and intrinsic viscosities of the polymers are shown in Table VIII.

It will be observed that, although considerable retardation is produced by these concentrations of 3,5-dinitrobenzoic acid at this high *p*H, the molecular weight of the polymer is practically unaffected.

Discussion

1. From the viewpoint of the locus of reaction, the retarding effects of 3,5-dinitrobenzoate and of 3,5-dinitrobenzoic acid are very instructive. At a *p*H of 10, all of the dinitrobenzoate may be considered to be present in ionic form, and in the "true" aqueous solution (not the soap micelles). As mentioned in previous papers,[1,2] evidence has been obtained in this Laboratory that persulfate exerts its activating effect mainly in the true aqueous phase. Therefore, at a *p*H of 10 the dinitrobenzoate reacts with a fraction of the radicals produced in the aqueous phase. However, it cannot interfere with the chain propagation reaction, which takes place in the soap micelles during the early stages of conversion and in the polymer particles in the later stages of conversion.[3]

On the other hand, at a *p*H of 1, the dinitrobenzoic acid may be considered to be entirely in the un-ionized form and to be in the styrene phase and solubilized with the styrene in the micelles. The retarding effect of the 3,5-dinitrobenzoic acid is now comparable to that of *m*-dinitrobenzene. At a *p*H of 1 these substances have no opportunity to react with the free radicals produced in the true aqueous phase, but act rather as chain-breakers at the locus of propagation.

The above interpretation is substantitated by the results obtained in the measurement of the

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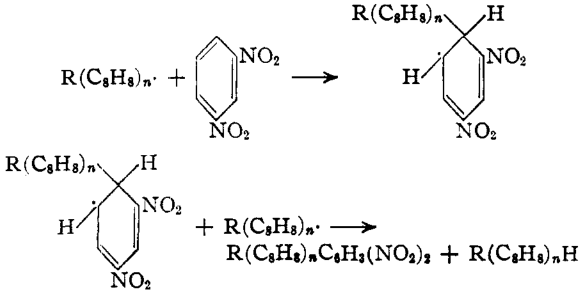
[3] W. D. Harkins, *J. Chem. Phys.*, **13**, 381 (1945); THIS JOURNAL, **69**, 1428 (1947).

intrinsic viscosities of the polymers. In the experimental part it has been shown that the polymer formed in the S. F. flakes recipe in the presence of dinitrobenzoate has practically the same intrinsic viscosity, and therefore molecular weight, as the polymer produced in the absence of this mild retarder. On the other hand, the molecular weight of the polymer formed is greatly reduced in the presence of *m*-dinitrobenzene in the same recipe (see Table III). It also has been shown that *m*-dinitrobenzene is solubilized in solutions of the two detergents used in this investigation. Hence this retarder should be present at the locus of the propagation reaction during the early stages of conversion. We also have shown that *m*-dinitrobenzene is soluble in the polystyrene particles. Therefore, it will also be present at the locus of the propagation reaction when the polymer particles become the locus of polymerization.

At higher concentrations of 3,5-dinitrobenzoate, some complex effects have been observed which are being studied further.

2. Following the suggestion of Price,[4] the reaction of the growing polymer chains with *m*-dinitrobenzene may be interpreted as follows



The adduct formed by addition of the radical to the aromatic ring is so much stabilized by resonance as to be unable to react further with monomer, although it can undergo disproportionation with another radical, as indicated.

The following kinetic scheme should be applicable to bulk polymerization and to emulsion polymerization in the presence of retarders. M represents 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:

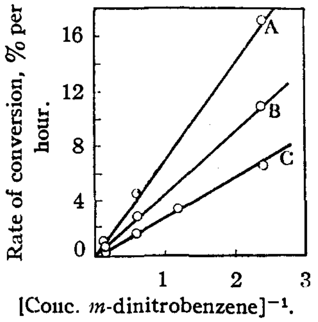


Fig. 11.—Reciprocal of *m*-dinitrobenzene concentration (millimoles per 100 g. styrene) *vs.* rate of polymerization at three concentrations of persulfate: A, 4*X*; B, 2*X*; C, 1*X*.

Initation: $\mathrm{M} + \mathrm{C} \longrightarrow \mathrm{R}\cdot \quad \mathrm{dR}\cdot/\mathrm{d}t = K_1(\mathrm{M})(\mathrm{C}) \quad (1)$

Propagation: $\mathrm{R}\cdot + \mathrm{M} \twoheadrightarrow \mathrm{R}\cdot \quad -\mathrm{dM}/\mathrm{d}t = K_2(\mathrm{M})(\mathrm{R}\cdot) \quad (2)$

Normal termination: $2\mathrm{R}\cdot \longrightarrow \mathrm{R}_2 \quad -\mathrm{dR}\cdot/\mathrm{d}t = K_3(\mathrm{R}\cdot)^2 \quad (3)$

Reaction with Retarder: $\mathrm{R}\cdot + \mathrm{r} \longrightarrow \mathrm{Rr}\cdot \quad -\mathrm{dR}\cdot/\mathrm{d}t = K_4(\mathrm{R}\cdot)(\mathrm{r}) \quad (4)$

$\mathrm{Rr}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{Rr} + \mathrm{RH} \quad -\mathrm{dR}\cdot/\mathrm{d}t = K_5(\mathrm{R}\cdot)(\mathrm{Rr}\cdot) \quad (5)$

Where the concentration of (r) is very large, as with the three largest concentrations of *m*-dinitrobenzene, 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

$$K_4(\mathrm{R}\cdot)(\mathrm{r}) + K_5(\mathrm{R}\cdot)(\mathrm{Rr}\cdot) = K_1(\mathrm{M})(\mathrm{C}) \qquad (6)$$

$$-\mathrm{dM}/\mathrm{d}t = K_2(\mathrm{M})(\mathrm{R}\cdot) = \frac{K_1K_2(\mathrm{M})^2(\mathrm{C})}{K_4(\mathrm{r}) + \mathrm{K}_5(\mathrm{Rr}\cdot)} \qquad (7)$$

Also

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

Thus instead of (7) we may write

$$-\mathrm{dM}/\mathrm{d}t = {}^1/_2\,\frac{K_1K_2(\mathrm{M})^2(\mathrm{C})}{K_4(\mathrm{r})}$$

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

$$-\mathrm{dM}/\mathrm{d}t = K(\mathrm{C})/(\mathrm{r})$$

It has been well established[5] that in the normal emulsion polymerization of styrene without retarder and with persulfate as catalyst, the following relation holds

$$-\mathrm{dM}/\mathrm{d}t = K(\mathrm{C})^n$$

in which the value of n is 0.5. This relationship has also been repeatedly observed for bulk and solution polymerization with oil-soluble catalysts. From the slopes of the plots (Fig. 4) of the logarithm of the rate of conversion *vs.* the logarithm of the concentration of persulfate, in the presence of large concentrations of *m*-dinitrobenzene, the exponents n are found to be

Concn. *m*-dinitrobenzene	*n*
0.0	0.50
0.415	.63
1.660	.76
6.64	.83

As the concentration of retarder is increased the exponent n approaches a value of unity as predicted by the above kinetic expression. From the fact that a value of $n = 1$ is not reached, even when the rate of polymerization is less than 1% of the normal rate, it appears that even under these conditions, some normal recombination of polymer radicals (Step 3) occurs, or that the mecha-

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(4) C. C. Price and D. A. Durham, This Journal, **65**, 757 (1943).

(5) I. M. Kolthoff and W. J. Dale, *ibid.*, **67**, 1672 (1945); C. C. Price and C. E. Adams, *ibid.*, **67**, 1674 (1945).

nism of the normal emulsion polymerization reaction needs revision.

Using the data of Tables II and Fig. 4, it is also possible to test the prediction of expression (8) that at a given persulfate concentration the rate of polymerization should be proportional to the reciprocal of the concentration of retarder at large concentrations of retarder. It is seen from Fig. 11 that this is actually the case at three different persulfate concentrations.

3. Assuming the rate of disappearance of *m*-dinitrobenzene to be constant during polymerization, we find (see Table IV) that this rate is 0.071 millimole per hour per liter of aqueous phase. In a subsequent paper, dealing with the behavior of inhibitors, it will be shown that the rate of disappearance of the ideal inhibitor *p*-benzoquinone is 0.057 millimole per hour per liter of aqueous phase in the same recipe. There is evidence, which is not conclusive, that each molecule of *p*-benzoquinone reacts with two monomer free radicals, but that this substance does not copolymerize with the styrene to any appreciable extent under the conditions of our experiments. Since the rate of disappearance of *m*-dinitrobenzene is about the same as that of *p*-benzoquinone, it is evident that *m*-dinitrobenzene does not copolymerize with styrene, and that the adduct formed by addition of the growing polymer chain to the retarder molecule is incapable of reacting with monomer.

4. From the fact that the induction period caused by oxygen is not affected by the presence of *m*-dinitrobenzene, it is evident that this substance has no retarding effect on the copolymerization of oxygen with styrene. Apparently, *m*-dinitrobenzene cannot compete effectively with oxygen for monomer free radicals, nor with monomer for the peroxide free radicals formed by reaction of monomer radicals with oxygen.

Acknowledgment.—The authors acknowledge the assistance of Miss Julie M. Schott, who performed the experiments in which rates of polymerization were measured.

Summary

An experimental study has been made of the effect of retarders on the emulsion polymerization of styrene with potassium persulfate as catalyst. It is postulated that in the presence of large concentrations of a retarder, such as *m*-dinitrobenzene, the rate of polymerization should be given by

$$-\frac{dM}{dt} = K\frac{(C)^n}{(r)} \quad (n = 1)$$

where (C) = concentration of catalyst
(r) = concentration of retarder

The value $n = 1$ has been approached but not attained.

m-Dinitrobenzene is nearly equally effective as a retarder in alkaline and acid recipes. It acts as a chain-breaker and reduces the molecular weight of the polymer formed. From its rate of disappearance, it is concluded that it does not act as a comonomer, but that it reacts with growing polymer chains to produce adduct radicals incapable of further chain propagation.

3,5-Dinitrobenzoate is a very ineffective retarder at a *p*H of 10, but the free acid becomes equal in effectiveness to *m*-dinitrobenzene at a *p*H of 1. The behavior of water-soluble and oil-soluble retarders is explained on the basis of the loci of the activation and propagation reactions.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 1, 1947

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES]

The Role of Bulk Cobalt Carbide in the Fischer–Tropsch Synthesis[1]

BY SOL WELLER,[2] L. J. E. HOFER[2] AND R. B. ANDERSON[2]

The Fischer–Tropsch synthesis involves formation of hydrocarbons by the passage of carbon monoxide–hydrogen mixtures over metallic catalysts, usually cobalt or iron, at elevated temperatures. With cobalt catalysts, the equation for the reaction may be written approximately as

$$x\text{CO} + 2x\text{H}_2 = (\text{CH}_2)_x + x\text{H}_2\text{O}$$

The hypothesis that the synthesis proceeds through the intermediate formation of a metal carbide was first suggested by Fischer and Tropsch[3] in 1926. It has been popular ever since in the scientific and the technical literature[4]; patents have even been granted based on the idea that carbiding of catalysts before synthesis is desirable.[5]

The concept of metal carbide as a synthesis intermediate has heretofore been used rather loosely. Distinction has rarely been made between bulk carbide and some sort of "surface" carbide as a possible intermediate. Craxford and Rideal,[4] for example, have done some of the important work on the mechanism of the synthesis and speak of "surface" carbide; they give as evidence for the carbide theory, however, only examples indi-

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[2] Physical chemist, Research and Development Division, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[3] Fischer and Tropsch, *Brennstoff Chem.*, **7**, 97 (1926).

[4] For example, Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939); Eidus, *Bull. Acad. Sci. URSS*, 447 (1946).

[5] Elian, U. S. Patent 2,369,548; Atwell, U. S. Patent 2,409,235.