

Redox Recipes. X. A Recipe with Ferric Versenate, Sodium Dithionite, and Hydroperoxide as Activating System (Veroxathionite Recipe)*

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INTRODUCTION

Initiation of emulsion polymerization at low temperature usually is based upon the production of free radicals in the reaction between ferrous iron and an organic hydroperoxide. The rate of this intrinsically very rapid reaction may be kept at a suitable level (thus preventing exhaustion of either ferrous iron or of hydroperoxide) by supplying ferrous iron continuously by reduction of ferric iron. Among inorganic reducing agents, hydrazine,¹ sulfide ion,² and sodium formaldehyde sulfoxylate³ have been found suitable for the reduction of ferric versenate. This paper describes the use of sodium dithionite as a reductant for ferric versenate. The name Veroxathionite is proposed for recipes containing the above redox system plus a hydroperoxide.

Sodium dithionite has been used in emulsion polymerization to remove traces of oxygen ("scavenger" for oxygen) thus eliminating induction periods.^{2,4} A small amount (*ca.* 0.01 part per 100 parts monomer) is sufficient. It has been used also as a shortstopping agent,⁵ the amount required being 0.2-0.4 part.

An accelerating effect of sodium dithionite on polymerization is mentioned in the patent literature.^{6,7} In connection with the investigation as oxygen scavenger,⁴ it was noted that some activation appeared to be caused by dithionite, and it was suggested that dithionite and hydroperoxide might form a redox pair. It has been found also⁸ that dithionite exerts a specific accelerating effect in a redox recipe containing diethylenetriamine. In both investigations,^{4,8} it was observed that the use of too large an amount of dithionite caused polymerization to come to a dead-stop.

In this laboratory dithionite was first tried as

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reductant in redox recipes several years ago.¹ Polymerization occurred, but the rate was not so great as with hydrazine or sulfide. The early experiments were done with cumene hydroperoxide (CHP) and similar hydroperoxides. After *p*-menthane hydroperoxide (PMHP) and phenylcyclohexane hydroperoxide (PCHP) became available, the experiments were repeated. Extremely rapid recipes could be developed with these hydroperoxides.

An indication of the relative rates of reaction of sodium dithionite with CHP and with diisopropylbenzene hydroperoxide (Diox D) was obtained some years ago in this laboratory.⁹ When an aqueous solution, 0.03 *M* in sodium dithionite, 0.04 *M* in sodium hydroxide, was shaken at 30°C. with an equal volume of benzene 0.01 *M* in hydroperoxide, 50% of the CHP and Diox D reacted in 20 minutes and in 250 minutes, respectively. The rate of reaction was not dependent on the rate of shaking. The rate of reaction of Diox D was accelerated in the presence of either soluble ferric pyrophosphate complex or of fatty acid soap. Thus, when the aqueous phase was 0.0007 *M* in the ferric complex, 50% of the hydroperoxide reacted in 150 minutes; when 0.1 *M* in soap, there was 25% reaction in 15 minutes; in presence of both iron and soap, complete reaction took place in less than 15 minutes. The ferric pyrophosphate is reduced by dithionite with the formation of ferrous iron which in turn reacts rapidly with the hydroperoxide (CHP). Soap makes the distribution of hydroperoxide much more favorable toward the water phase; in other words, soap increases the effective (distribution) concentration of hydroperoxide in the water phase. Also, in butadiene-styrene latex containing iron, the reaction between sodium dithionite and Diox D was complete in less than 15 minutes at 30°C. In a latex, the polymer

particles make the distribution of hydroperoxide more favorable toward the aqueous layer.

The above results account for the shortstopping action of a large amount of dithionite by destruction of hydroperoxide.

An approximate estimate of the rate of reaction between sodium dithionite and ferric versenate has been made in this laboratory by N. Tamberg. In alkaline medium at room temperature the reaction is stoichiometric (oxidation to sulfite and practically instantaneous, and can be used for the amperometric titration of dithionite.¹⁰ At 0°C. and in dilute solution, the reaction has a measurable velocity. The rate of the reaction could be obtained by making a record of the change of the current of ferric versenate at the dropping mercury electrode after the addition of sodium dithionite. The reaction appears to be complete at 0°C. in 10–20 seconds at pH 9 in a solution initially 0.001 *M* in each reactant. Because of experimental complications it was not possible to make precise measurement of the rate, but the reaction appeared to be first order to each reactant, which indicates that a free radical derived from dithionite must be an intermediate.

On the other hand, at the same pH, temperature, and concentration, the reaction between ferric versenate and sodium formaldehyde sulfoxylate is very slow, no measurable decrease in concentration of ferric versenate occurring within several hours after the addition of sulfoxylate. In spite of this large difference in reaction rate between the two systems, the rate of the Veroxathionite recipe under optimum conditions is no more than twice that of the corresponding sulfoxylate recipe (v.i.). This tends to indicate that the efficiency of the radicals formed in the Veroxathionite recipe is considerably less than that of those formed in the sulfoxylate recipe.

EXPERIMENTAL

The following reagents were as described before:^{1,2,11} monomers, water, soaps, ferric nitrate, versene, CHP, Diox D, Diox 8, mercaptans, potassium pyrophosphate. *p*-Menthane hydroperoxide (PMHP) and phenylcyclohexane hydroperoxide (PCHP) (Hercules Powder Co.), had hydroperoxide contents of 49% and 21%, respectively (iodometric titration), and were used as received. Since commercial samples of hydroperoxides vary considerably in purity, the amount of each is expressed as millimoles of pure hydro-

peroxide per 100 parts monomer; 0.66 mmole corresponds to 0.1 part of pure CHP.

Most of the experiments were carried out with two samples of sodium dithionite from Malinckrodt, used as received. (Both contained about 82% Na₂S₂O₄ and about 18% Na₂SO₃.) With both samples the results were the same as with an Eastman sample, P533. The preparation and storage of the solutions are of critical importance (v.i.). One-tenth part of pure sodium dithionite is 0.57 mmole. Sodium formaldehyde sulfoxylate was Eastman P1080, and formaldehyde was Fisher 40% reagent, NF grade. Other chemicals were usual laboratory chemicals.

Preparation of latices, polymerization, and determination of conversion were conventional.¹¹

Stability of Dithionite Solutions

The first experiments gave poorly reproducible results because of the instability of dithionite solutions. In the presence of air, dithionite is oxidized rapidly to sulfite; in the absence of air the decomposition products are mainly sulfite and thiosulfate, the rate being greatly increased with increase of temperature and decrease of pH. Experiments with sulfite as reductant in redox recipes with ferric versenate and hydroperoxide were carried out in this laboratory in 1951. At 5°C., the maximum rate of conversion (0.001 *M* ferric versenate, 0.6 mmole Diox D) was 8% in 12 hours. Similarly, no rapid low temperature recipe could be developed with thiosulfate.

In the first experiments with dithionite, the solid was added to air-free water at room temperature, and the solution was added to the remainder of the charge. Such solutions deteriorate rapidly and do not give reproducible results unless they are used within a few minutes after preparation. The stability is improved when the solutions are kept at 0°C., and improved still further when they are made alkaline. Polarographic work¹⁰ showed that a 0.1 *M* solution of sodium dithionite in 0.02 *M* sodium carbonate, kept air-free and stored at below 10°C., decomposed less than 3% in 12 hours. Numerous polymerization experiments confirmed that solutions prepared and stored in this manner maintained their polymerization activity unchanged for at least 2 days.

At 25 to 30°C. the stability is less. Fresh, air-free solutions made up at room temperature in 0.02 *M* sodium carbonate, in 0.02 *M* sodium hydroxide, or in 0.02 *M* borax, gave the same results

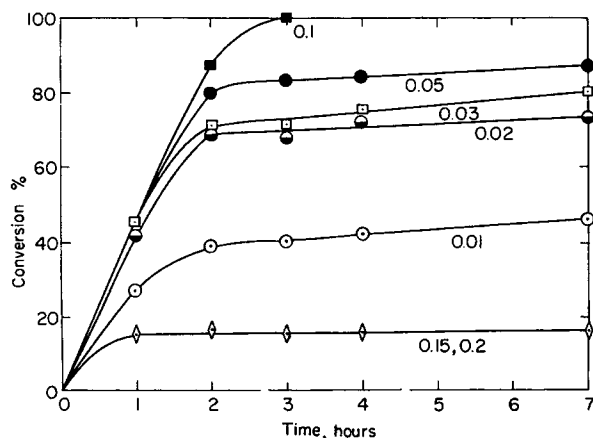


Fig. 1. Veroxathionite recipe; 0.001 *M* ferric versenate, 0.66 mmole PCHP, and sodium dithionite varied.

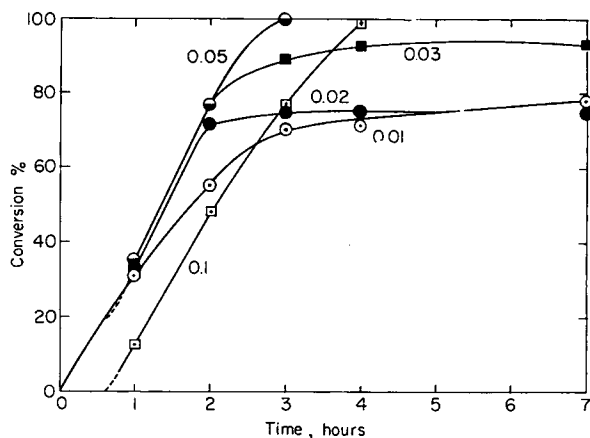


Fig. 2. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.33 mmole PCHP, and sodium dithionite varied.

as solutions made up at 0°C. After standing 12 hours in capped bottles at room temperature, all the solutions had deteriorated and gave dead-stop at 60–70% conversion; after 2 days at room temperature, no polymerization occurred with any of the solutions. Other stock solutions were made up as above, except that they were not air-free. Such solutions gave markedly poorer results after standing only one hour.

It may be mentioned that sodium dithionite in the solid state deteriorates when it is kept exposed to a humid atmosphere.

In summary, if the stock solution of sodium dithionite is made up about 0.1 *M* in 0.02 *M* sodium carbonate, is kept air-free, and is stored at below 10°C., it maintains its polymerization activity for at least 2 days.

Presence of Air

This is another factor affecting reproducibility. In the usual laboratory procedure for the emulsion polymerization of butadiene-styrene,¹¹ air is removed from the vapor space and the organic layer by the addition of an excess of butadiene, the excess being allowed to evaporate. Some air may be dissolved in the aqueous layer. Usually it is unnecessary to remove the dissolved air, since the induction periods caused by it are negligibly small. However, in the Veroxathionite recipe, the presence of dissolved air causes irregular results at low levels of dithionite due to the rapid reaction with oxygen. The amount of oxygen in 180 parts of water saturated with air at 25°C., 1 atm., is equivalent to 0.015 part of sodium dithionite (oxidation to sulfite).

Polymerization Recipe

The experiments were carried out with stable solutions of dithionite, the following recipe being used.

Veroxathionite Recipe (Temperature, 0°C.; Rotation, 35 rpm)

Butadiene	75 parts
Styrene	25 "
Water	180 "
Potassium myristate ^a	Varied (5 parts unless specified)
Potassium pyrophosphate ^b	1 part
Sulfole mercaptan	0.3 "
Sodium dithionite	Varied
Ferric nitrate	"
Versene ^c	"
Hydroperoxide	"

^a In some experiments as noted other soaps were used.

^b In some experiments as noted replaced by potassium chloride.

^c Equimolar to iron unless specified.

The above recipe with 5 parts potassium myristate, 0.001 *M* ferric versenate, 0.66 mmole PCHP, and 0.1 part sodium dithionite gave 45, 87, and 100% conversion in 1, 2, and 3 hours, respectively.

POLYMERIZATION VARIABLES AND RESULTS

Variation of Amount of Dithionite

Figure 1 shows typical conversion-time data obtained with 0.001 *M* ferric versenate, 0.66 mmole PCHP and varied amounts of dithionite. Negligible polymerization occurred in 12 hours with less than 0.002 part of dithionite, whatever

the variation of the recipe. Dead-stop occurred with 0.15 part or more. Similar results were found with other amounts of hydroperoxide (Figs. 2-5). The relation between initial rate of conversion and amounts of dithionite and hydroper-

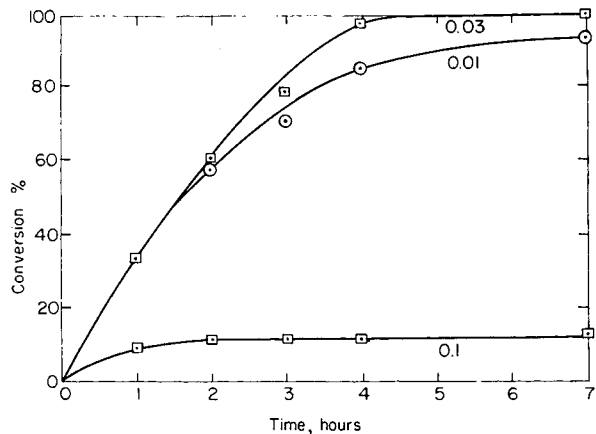


Fig. 3. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.132 mmole PCHP, and sodium dithionite varied.

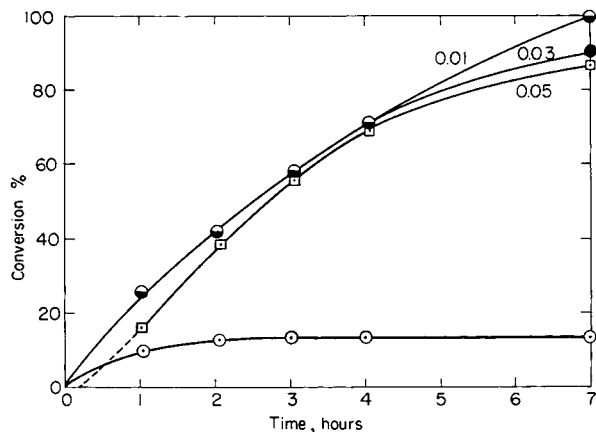


Fig. 4. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.066 mmole PCHP, and sodium dithionite varied.

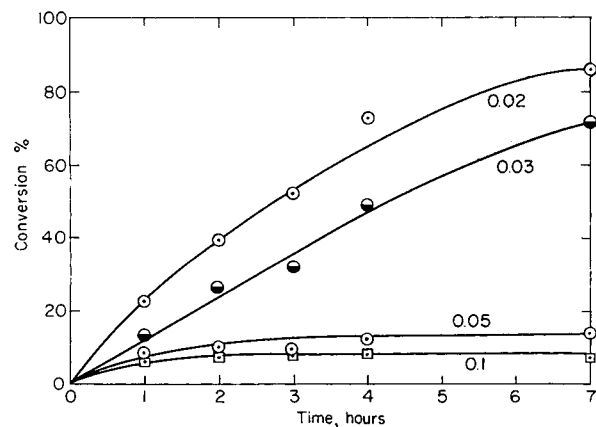


Fig. 5. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.033 mmole PCHP, and sodium dithionite varied.

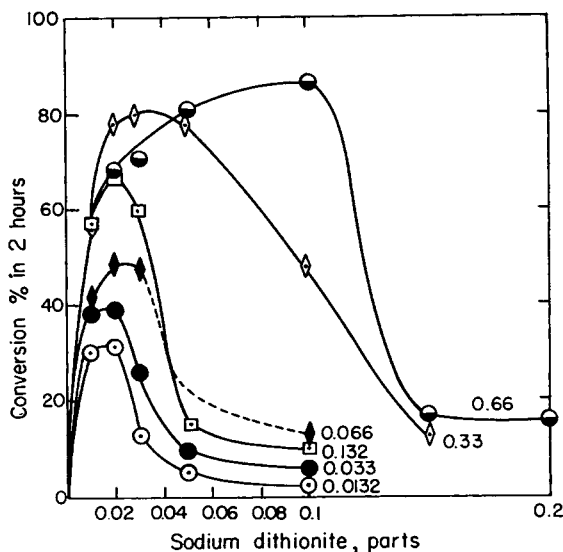


Fig. 6. Veroxathionite recipe: 0.001 *M* ferric versenate; amounts of PCHP (mmole) shown by figures on curves.

oxide is shown in Figure 6. The maximum rate was found at approximately the 1:1 mole ratio. Polymerization with PMHP was almost as rapid as with PCHP (Tables I and II).

TABLE I
Variation of Dithionite Concentration. Use of PMHP.
(0.66 mmole PMHP, 0.005 *M* ferric versenate)

Sodium dithionite, parts	Conversion, %, in hours				
	1	2	4	7	12
0.01	13	21	20	22	23
0.05	15	40	76	100	—
0.1	20	31	56	100	—
0.2	10	11	17	21	26
0.5	5	5	5	5	5

Variation of Amount of Ferric Versenate

Typical results (PMHP) are given in Table II. The 4-hour conversions are plotted in Figure 7. Similar results were found with PCHP.

TABLE II
Variation of Ferric Versenate Concentration
(0.66 mmole PMHP, 0.1 part sodium dithionite)

Ferric versenate concn., <i>M</i>	Conversion, %, in hours				
	1	2	3	7	12
0.005	20	31	56	100	—
0.002	26	36	83	100	—
0.001	17	35	100	—	—
0.0005	16	28	68	100	—
0.0002	9	11	24	61	75
0	3	7	11	15	18

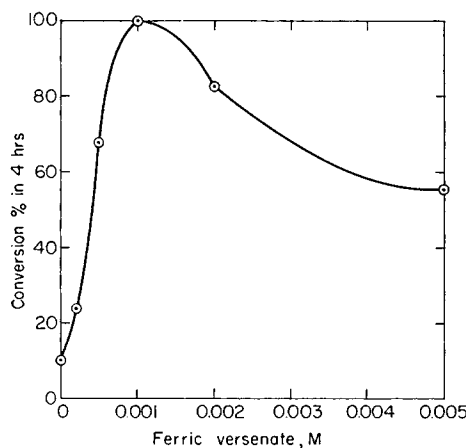


Fig. 7. Veroxathionite recipe: 0.1 part sodium dithionite, 0.66 mmole PMHP, and various levels of ferric versenate.

Relatively rapid polymerization occurred, even at very low concentrations of iron (Table III). With the optimum amount of dithionite and only 10^{-4} M ferric versenate (1.1 mg. iron per 100 parts monomer), 71% conversion was reached in 12 hours.

Variation of Amount of PCHP

The general nature of the results is evident from Figures 1-6. Additional experiments at various levels of activator ingredients may be summarized as follows.

Ferric versenate concn., M	Sodium dithionite, parts	Optimum PCHP level, mmole	Conversion at optimum PCHP level
0.005	0.1	ca. 0.66	100% in 4 hours or less
0.001	0.1	0.5-0.7	90% in 2 hours
0.0005	0.05	0.3	60% in 2 hours

Use of CHP

Systematic wide variations did not yield a rate comparable with the rate found with either PCHP or PMHP. Results given in Table IV display the feature of pronounced retardation by large amounts of CHP. As a matter of fact, practically no polymerization occurs when the amount of CHP added to the charge corresponds to 6.6 mmoles per 100 parts of monomer. At this high concentration the dithionite is probably rapidly oxidized.

Use of Ferric Pyrophosphate Instead of Ferric Versenate

When versene was omitted and 0.01 M potassium pyrophosphate was used, the resulting ferric

TABLE III
Low Iron Level
(0.66 mmole PCHP)

Ferric versenate concn., M	Sodium dithionite, parts	Conversion, %, in hours				
		1	2	4	8	12
0.0001	0.01	—	—	—	—	0
	0.02	14	19	25	29	31
	0.03	16	30	44	56	58
	0.04	15	34	45	55	61
	0.06	11	19	49	66	71
	0.08	11	17	41	58	72
0.00005	0.01	—	—	—	—	0
	0.02	16	22	24	33	36
	0.03	15	25	35	48	50
	0.04	14	19	33	49	53
	0.06	10	17	19	44	53
	0.08	11	17	19	47	52
0.00001	0.05	7	12	20	22	26
	0.1	7	12	19	19	20

pyrophosphate recipe gave slower polymerization than the ferric versenate recipe (Table V). The addition of either potassium citrate or sodium tartrate up to 0.005 M to the ferric pyrophosphate recipe (no versene) had no effect on the rate.

Replacement of Potassium Pyrophosphate by Potassium Chloride

In the Veroxathionite recipe, as in most low temperature recipes, the presence of an electrolyte is necessary for the formation of latex of suitable viscosity. Polymerization in the absence of electrolyte yields latex which coagulates at relatively low conversion. The use of potassium pyrophosphate or chloride gave practically the same rate of conversion. However, the viscosity of the latex made with 1 part of pyrophosphate at 2 hours was noticeably smaller than that of the latex made with the same amount of the chloride. In the presence of either electrolyte, the latex was free of pre-coagulation up to 80% conversion.

Effect of Concentration of Versene

The data are in Table VI. In the absence of versene the rate was relatively small (cf. Table V). The addition of versene caused a pronounced acceleration, but an excess of versene over iron had little or no effect; the rate depended on the concentration of ferric versenate. Note in Table VI that the rate for the recipe containing 0.001 M iron and 0.0005 M versene was the same as that for the recipe containing 0.0005 M iron and 0.0005 M versene.

TABLE IV
Polymerization with CHP^a

Ferric versenate concn., <i>M</i>	Sodium dithionite, parts	CHP level (relative) ^b	Conversion, %, in hours				
			1	2	4	7	12
0.005	0.1	0	—	—	—	—	6
		1	6	17	24	31	52
		2	6	7	9	9	12
		5	5	—	—	—	7
		10	—	—	—	—	5
0.001	0.1	20	—	—	—	—	1
		0	—	—	—	—	2
		1	—	—	—	—	5
		2	5	7	12	14	23
		5	6	6	7	8	15
0.001	0.05	10	—	—	—	—	9
		20	—	—	—	—	3
		0	—	—	—	—	1
		0.2	6	6	6	6	7
		0.5	10	18	24	26	40
0.001	0.02	1	5	8	13	16	24
		2	5	8	10	12	21
		5	2	3	4	7	10
		0	—	—	—	—	2
		0.2	14	18	18	19	28
0.001	0.02	0.5	7	7	7	12	16
		1	4	6	8	10	18
		2	3	3	6	8	13
		5	1	1	2	4	7
		0	—	—	—	—	2
0.0005	0.05	0.2	5	—	—	—	6
		0.5	12	13	19	21	42
		1	6	7	10	15	22
		2	4	6	7	9	16
		5	4	4	6	7	12
0.0005	0.02	0	—	—	—	6	10
		0.2	4	14	17	17	23
		0.5	6	—	6	7	12
		1	4	6	6	7	13
		2	3	4	6	6	13
5	0	—	—	—	3		

^a Most results are averages of duplicates.
^b One unit (1) corresponds to 0.66 mmole.

In respect to the effect of versene, the Veroxathionite recipe resembles the Veroxasulfide recipe² and the Sulfoxylate recipe,³ in which an excess of versene over iron is harmless. It differs from the Veroxazine recipe,¹ in which an excess of versene definitely reduces the rate of polymerization.

Comparison with Sodium Formaldehyde Sulfoxylate: Effect of Formaldehyde

The use of sodium formaldehyde sulfoxylate (SFS) as reductant with ferric versenate and hydroperoxide was introduced by Howland et al.³ At pH 9 or greater, formaldehyde reacts rapidly with sodium dithionite to form formaldehyde

TABLE V
Ferric Pyrophosphate Recipe (Fundamental Recipe without Versene)
(0.01 *M* K₄P₂O₇; 0.66 mmole PCHP)

Ferric nitrate concn., <i>M</i>	Sodium dithionite, parts	Conversion, %, in hours				
		1	2	4	7	12
0.001	0	0	0	0	0	1
	0.02	25	25	28	24	30
	0.05	20	23	37	37	45
	0.08	18	21	35	39	47
	0.10	19	20	30	38	48
0.0005	0.15	19	18	23	22	20
	0	0	0	0	0	0
	0.02	21	21	25	26	30
	0.05	20	28	45	50	59
	0.08	20	27	48	47	60
0.0005	0.10	17	21	23	28	40
	0.15	17	20	25	24	29

TABLE VI
Effect of Concentration of Versene (Fundamental Recipe)
(0.66 mmole PCHP, 0.05 part sodium dithionite)

Fe(III) concn., <i>M</i>	Versene concn., <i>M</i>	Conversion, %, in hours				
		1	2	4	7	12
0.001	0	13	23	28	34	34
	0.0005	28	69	75	100	—
	0.0008	26	83	100	—	—
	0.001	38	85	100	—	—
	0.0015	37	87	—	—	—
0.0005	0.002	36	89	—	—	—
	0	12	29	42	56	57
	0.0002	17	64	68	82	—
	0.0004	24	63	73	97	—
	0.0005	31	72	74	89	—
0.0005	0.001	31	89	—	—	—
	0.002	29	78	—	—	—

sulfoxylate plus formaldehyde sulfite. The latter substance is inactive in polymerization.³ In separate experiments it was shown that formaldehyde did not affect the rate of the formaldehyde sulfoxylate recipe. Thus, it is to be expected that addition of an excess of formaldehyde (more than 2 moles per mole) to a veroxathionite recipe should yield reaction at a rate the same as that with the equivalent sulfoxylate recipe. This is confirmed by the data in Table VII. The experiments were carried out by mixing solutions of sodium dithionite and formaldehyde and adding the mixture to the rest of the charge. Other experiments showed that when less than 2 moles of formaldehyde was added per mole dithionite, the rate was intermediate between the two extremes. The result with 0.2 part of dithionite may be noted.

The polymerization stopped at low conversion, undoubtedly due to exhaustion of the hydroperoxide. The addition of an excess of formaldehyde prevented this dead-stop.

TABLE VII
Effect of Formaldehyde
(0.66 mmole PCHP; 0.001 *M* ferric versenate)

Sodium dithionite, parts	Formaldehyde, moles/mole sodium dithionite	SFS, ^a parts	Conversion, %, in hours				
			1	2	4	6	8
0.03	0	0	43	69	85		
	4	0	9	18	45	67	85
	10	0	1	11	30	58	89
0	0	0.03	3	16	45	69	87
	0.05	0	45	70	86		
0	4	0	15	30	53	91	
	10	0	11	27	51	84	
	0	0.05	5	19	51	79	
0.1	0	0	28	65	100		
	4	0	22	40	75	98	
0	10	0	17	36	62	91	
	0	0.1	15	42	73	89	
0.2	0	0	16	18	20	21	21
	4	0	43	67	100 ^b		
0	0	0.2	40	60	90		

^a Expressed as the equivalent of sodium dithionite.

^b At 5 hours.

The addition of acetone or of benzaldehyde in amounts up to 4 moles per mole of dithionite did not affect the rate (0.05 part sodium dithionite, 0.66 mmole PCHP, 0.001 *M* ferric versenate).

Comparison of Soaps

With KFA (potassium fatty acid) soap (a mixture of potassium stearate, palmitate, and oleate often

TABLE VIII
Comparison of Potassium Fatty Acid Soap and Potassium Myristate Soap
(0.66 mmole PCHP; 0.005 *M* ferric versenate)

Sodium dithionite, parts	Soap	Conversion, %, in hours		
		1	2	4
0.05	Potassium myristate	50	82	100
	Potassium fatty acid	25	49	100
0.1	Potassium myristate	54	90	100
	Potassium fatty acid	28	53	100

used in large-scale low-temperature, emulsion polymerization) polymerization was rapid, but slower than with potassium myristate (Table VIII).

With Dresinate 214 (potassium soap of dis-

proportionated rosin acids), rapid polymerization occurred (Table IX). The optimum amount of ferric versenate was about 0.002 *M*, somewhat larger than with myristate.

TABLE IX
Results with Dresinate 214
(0.66 mmole PCHP)

Dresinate 214, parts	Ferric versenate concn., <i>M</i>	Sodium dithionite, parts	Conversion, %, in hours					
			1	2	4	7	12	
3.8	0.0005	0.05	5	—	—	—	6	
		0.08	21	37	48	73	100	
		0.1	19	30	45	77	100	
3.8	0.001	0.15	8	8	11	11	12	
		0.02	7	8	8	10	11	
		0.05	16	26	26	29	37	
5	0.002	0.08	21	38	70	100		
		0.1	33	53	69	100		
		0.15	7	10	10	11	12	
5	0.002	0.04	21	21	25	25	28	
		0.06	41	42	50	53	53	
		0.08	46	57	70	100		
5	0.002	0.10	57	66	77	100		
		0.12	48	63	100			
		0.15	35	39	47	50	56	
5	0.005	0.06	27	30	30	34	37	
		0.08	41	41	46	52	55	
		0.10	40	47	57	68	69	
			0.12	36	42	45	56	62
			0.15	23	33	44	60	65

A commercial detergent, sodium dodecyl sulfate, was substituted for potassium myristate in the fundamental recipe in which 0.001 *M* ferric versenate, 0.66 mmole PCHP, and 0.05 part sodium dithionite were used. In borax buffer, pH 9, the initial rate was 14% per hour, but a dead-stop occurred at 40% conversion. In acetate buffer, pH 5, 24% conversion was reached in 27 hours, and in dodecylammonium chloride, pH 5, no conversion occurred in 51 hours.

Effect of Amount of Soap

With 4 or more parts of potassium myristate, polymerization proceeded normally to completion, but with 3 parts or less, dead-stops occurred. Such behavior has not been observed in any other recipe for emulsion polymerization of butadiene-styrene. It has been confirmed by repeated experiments at varied levels of iron and dithionite. Addition of sodium dithionite to the dead-stopped latices did not overcome the dead-stop. Qualitatively, the same results are found also with KFA soap and with Dresinate 214. Average results of several

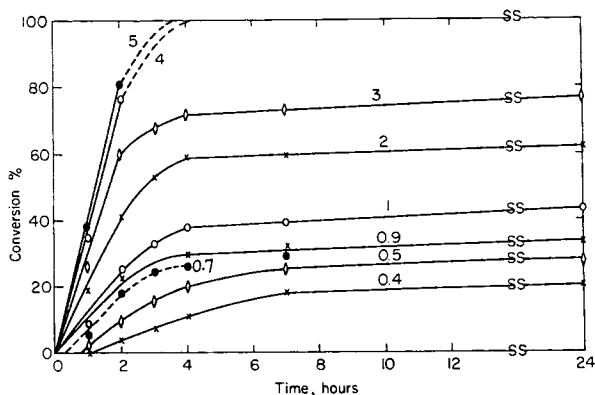


Fig. 8. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.66 mmole PCHP, 0.1 part sodium dithionite, and varied amounts of potassium myristate.

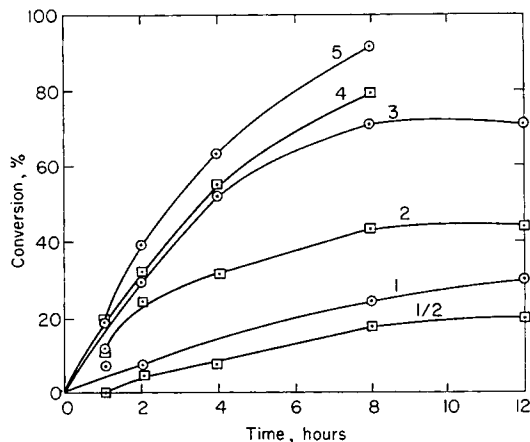


Fig. 9. Veroxathionite recipe: 0.0001 *M* ferric versenate, 0.66 mmole PCHP, 0.1 part sodium dithionite, and varied amounts of potassium myristate.

sets of experiments with myristate at 0.001 *M* ferric versenate are given in Table X and Figure 8. The initial rates in the last column of Table X were derived graphically, allowances being made for brief induction periods in some experiments. Figure 9 shows results for the Veroxathionite recipe with 0.0001 *M* ferric versenate.

TABLE X
Variation of Amount of Myristate
(0.001 *M* ferric versenate, 0.1 sodium dithionite, 0.66 mmole PCHP)

Potassium myristate, parts	Conversion, %, in hours						Initial rate, %/hr.
	1	2	4	7	12	24	
5	38	81					45
4	35	77		88			41
3	26	60	68	73		77	31
2	19	41	53	58	59	65	22
1	9	25	32	38	39	43	16
0.9	9	23		29	32	36	14
0.8	10	21	24	24	29	33	11
0.7	5	18	24	26	29	32	10
0.6	3	10	18	24	28	30	7.5
0.5	2	10	16	20	25	27	7.0
0.4	0	4	7	11	18	21	3.6
0.3	0	5	8	10	19	21	3.3

From solubilization data at 50°C.¹² it is estimated that the critical micelle concentration (c.m.c.) of potassium myristate at the electrolyte concentration of the recipe (1 part of potassium pyrophosphate, 0.067 *N*) is about 0.005 *M*. If it is assumed that the value is about the same at 0°C., the c.m.c. corresponds to 0.2–0.3 part of soap. The initial rate of polymerization (Fig. 10) is practically proportional to the amount of myristate above the c.m.c. up to about 1 part. The relation of the

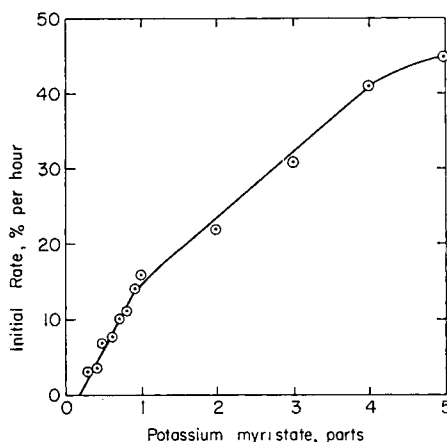


Fig. 10. Veroxathionite recipe: 0.001 *M* ferric versenate, 0.66 mmole PCHP, 0.1 part sodium dithionite, and various amounts of potassium myristate.

limiting or dead-stop conversion to the amount of myristate is similar to that of the initial rate.

Seeding Experiments

A charge prepared with the Veroxathionite recipe (5 parts myristate, 0.1 part dithionite, 0.001 *M* ferric versenate, 0.66 mmole PCHP) was polymerized 6 hours to 100% conversion. After removal of lumps of coagulated polymer, the polymer content of the latex corresponded to an 88% conversion, monomer-free latex. To a given weight of this latex (seed) there was added fresh charge prepared as above but with various amounts of soap. The mixtures were then polymerized as usual. The conversions given in Table X are those of the added monomer, exclusive of the original seed. (Example: mixture of 40 parts

seed, 88% conversion, and 60 parts fresh charge. Total polymer content, 71%; polymer due to seed, 35%; conversion of added monomers, 60%.)

TABLE XI

Seeding Experiments, Varied Soap Content

(Seed latex: 5 parts myristate, 0.001 M ferric versenate, 0.1 part dithionite, 0.66 mmole PCHP; conversion 88%. Seeded charges: as seed but with varied myristate)

Fresh charge, parts/100 total charge	Potassium myristate in fresh charge, parts	Total soap, parts	Conversion, % of fresh charge, in hours				
			1.5	3	4.5	7	24
60	10	8	28	58	68	73	82
	5	5	22	—	60	60	70
	2.5	3.5	17	—	57	57	72
	1.25	2.8	22	50	53	62	65
	0.63	2.4	20	53	62	75	77
80	0	2	25	52	60	73	75
	10	9	35	51	81	88	88
	2.5	3	9	19	21	25	34
	1.25	2	11	24	29	31	33
	0.63	1.5	11	23	26	27	30
100 ^a	0	1	8	20	30	40	41
	—	3	49	66	70	73	77
	—	2	30	49	55	58	65
—	1	18	30	33	39	43	

^a Cf. Table X.

It is interesting to note that the amount of soap added has no effect on the rate of conversion in the first set of experiments in Table XI (40 parts seed). Apparently, all of the added soap is adsorbed on the polymer particles, and the rate of polymerization is determined solely by the number of particles. The same is true in the second set of experiments (20 parts seed), when the amount of added soap is less than 4. However, with 9 total parts of soap there is an excess of free soap, and a considerable number of particles is formed in the early stages of polymerization. When all the added soap is adsorbed by the seed, the rate of conversion of the seeded charge closely corresponds to that of an unseeded charge with the same original soap content as the seeded charge (no extra soap added).

Polymerization at Subfreezing Temperatures

Results at -20°C . with methanol as antifreeze are summarized in Table XII.

At -20°C . and with 0.005 *M* iron, the use of 0.2 part of dithionite did not cause a dead-stop, as it did at 0°C . Apparently the reaction between

TABLE XII

Polymerization at -20°C .

(Fundamental recipe with 40 parts of water replaced by 40 parts of methanol and pyrophosphate omitted; 0.66 mmole hydroperoxide)

Ferric versenate concn., <i>M</i>	Sodium dithionite, parts	Hydroperoxide	Conversion, %, in hours				
			1	2	4	8	24
0.005	0.05	PCHP	6	8	12	18	18
	0.1	"	8	17	37	66	100
	0.2	"	0	5	16	36	65
	0.05	Diox 8	11	15	37	75	91
	0.1	"	1	2	10	43	<i>c</i>
	0.2	"	1	3	9	37	61
0.001	0.05	PCHP	2	19	37		<i>c</i>
	0.1	"	7	20	43		<i>c</i>
	0.2	"	4	8	8	9	
	0.05	Diox 8	2	15	31		<i>c</i>
	0.1	"	4	6	15		<i>c</i>
	0.2	"	2	4	23	24	

c = coagulated.

dithionite and hydroperoxide is sufficiently slow at -20°C to prevent exhaustion of the hydroperoxide in a relatively short time.

The veroxathionite recipe with methanol as antifreeze cannot be used at -30°C ., since the amount of methanol required for this temperature practically prevents polymerization, even at 0°C . (Table XIII).

TABLE XIII

Effect of Methanol at 0°C .

(Fundamental recipe, 0.001 *M* ferric versenate, 0.05 part sodium dithionite, 0.66 mmole PCHP)

Water, parts	Methanol, parts	Conversion, %, in hours				
		1	2	4	8	12
180	0	47	85	—	—	—
160	20	37	41	44	49	50
140	40	29	32	36	42	44
130	50	0	4	12	19	22
120	60 ^a	0	1	4	5	6

^a Freezing point -29°C .

In agreement with the conclusion of Table XIII, polymerization with systematic variation of the activating system at -30°C . with the use of 60 parts of methanol as antifreeze yielded negligible polymerization.

Effect of Quinone

The experiments were made either without iron or with 10^{-5} *M* ferric versenate. No polymeriza-

tion occurred in the absence of iron or in the presence of 0.05 part of quinone, while an extremely slow polymerization was observed in the absence of both constituents (Table XIV). In the presence of a trace of iron, quinone caused acceleration. If a 1:1 reaction ratio between dithionite and quinone (reduction to hydroquinone) is assumed, 0.1 part of dithionite is equivalent to 0.062 part of quinone. The limited data indicate that an excess of quinone over the 1:1 ratio may cause an induction period to occur (Table XIV).

TABLE XIV
Effect of Quinone

Quinone, parts	Sodium dithionite, parts	Ferric versenate concn., M	PCHP, mmole	Conversion, %, in hours				
				1	3	5	7	25
0.05	0	0	0					0
0.05	0	0	0.66					0
0	0.05	0	0.66		6	11	14	
0.05	0.05	0	0.66					0
0.05	0	10^{-5}	0.66				14	26
0	0.05	10^{-5}	0.66	7	17	20	21	41
0.02	0.05	10^{-5}	0.66	10	29	34	40	64
0.05	0.05	10^{-5}	0.66	15	30	36	42	68
0.1	0.05	10^{-5}	0.66	5	14	25	34	56
0	0.1	10^{-5}	0.66	7	18	19	19	23
0.04	0.1	10^{-5}	0.66	—	8	14	35	72
0.06	0.1	10^{-5}	0.66	7	18	18	26	87
0.08	0.1	10^{-5}	0.66	8	22	27	44	69
0.1	0.1	10^{-5}	0.66	—	—	11	28	63

Miscellaneous Variables

To determine the effect of azobenzene and of diazonaminobenzene, each of these substances was added to an iron-free recipe and to a recipe containing $10^{-5} M$ ferric versenate, as described above for the experiments with quinone. In the absence of iron, neither substance affected the (small) rate of polymerization. In the presence of iron, each substance caused a slight reduction of the rate.

A set of experiments was carried out with the basic recipe except that ammonium vanadate was used instead of ferric nitrate. The other constituents were 0.66 mmole PCHP, 0.005 M versene, and either 0.05 or 0.2 parts sodium dithionite. In the absence of iron, polymerization was slow, the 12-hour conversion amounting only to 25 and 13%, respectively. The addition of ammonium vanadate dihydrate in varied amounts up to 0.4 part had almost no effect.

Similar experiments with potassium chromate

with 0 or 0.05 parts sodium dithionite and 0 or 0.005 M versene gave no conversion in 12 hours.

Replacement of ferric versenate by ferricyanide at 25°C. with the use of the system, ferricyanide-dithionite-Diox D, gave 52% conversion in 12 hours. This was larger than in the combination of ferricyanide with any other reducing agent tested, including hydrazine, arsenic(III) oxide, sulfide, thiosulfate, and sulfite.

DISCUSSION

Three reactions must be considered with respect to the rate of initiation. There are: (1) reaction of dithionite with ferric versenate to form ferrous versenate, (2) reaction of ferrous versenate with hydroperoxide to form hydroperoxide radical and ferric versenate, and (3) reaction of dithionite with hydroperoxide.

The direct reaction (3) undoubtedly involves two-electron transfer and does not lead to the formation of free radicals. This view is substantiated by the extremely slow polymerization when no iron is added. (Traces of iron may be present as impurity.)

Considering the above reactions, the recipe is unusual in two respects, first, the relatively great spread of reaction (1) compared to most reduction reactions used in redox polymerization and, second, the importance of reaction (3) under some conditions. It was mentioned in the introduction that, in the recommended recipe, the rate of reaction (1) is of the same order of magnitude as that of reaction (2) in homogeneous medium. The rate constant for the bimolecular reaction between ferrous versenate and cumene hydroperoxide in homogeneous aqueous solution at pH 9, 0°C., is 240 l./mole-sec.¹³ With equal initial concentrations of 0.001 M ferrous iron and hydroperoxide and under conditions such that the reaction ratio is unity, the half-time is about 4 seconds. Practically the same rate is found with other hydroperoxides in homogeneous medium. Naturally, when an organic layer is present, the concentration of hydroperoxide in the aqueous layer is decreased, and the reaction rate is decreased correspondingly.

Reaction (1) is faster by far than the reaction between hydrazine and ferric versenate. A detailed investigation of this reaction¹⁴ has shown that at 0°C., pH 9, the primary reaction producing ferrous versenate has a bimolecular rate constant of 0.089 l./mole-sec. When the concentration of hydrazine is 0.01 M and that of ferric versenate is 0.001 M , typical concentrations used in polymeriza-

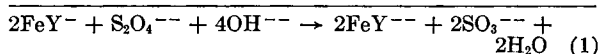
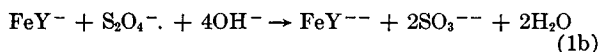
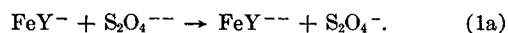
TABLE XV

Reducing agent	Dithionite	Sulfide	Hydrazine	SFS
Reaction with ferric versenate	Very rapid	Rapid	Slow	Very slow
Reaction with hydroperoxide	Fairly rapid	Fairly rapid (less so than with dithionite)	Very slow	—
Effect on polymerization rate of				
Excess of versene	None	Rate reduced	None	None
Excess of reductant	Dead-stop	Dead-stop	Rate increase	Rate increase
Concn. of ferric iron	Optimum concn.	Optimum concn.	Rate increase	Rate increase
Concn. of soap	Dead-stop at low soap	Not known	Rate $C_s^{0.7}$	Not known

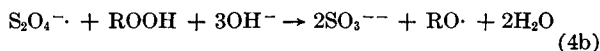
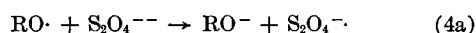
The assistance of Mrs. Marilyn Granbeck in the performance of the polymerization experiments is acknowledged.

tion, the reaction is pseudo-unimolecular with half-time of 780 seconds. The reduction of ferric versenate by sodium formaldehyde sulfoxylate is even slower. On the other hand, from semi-quantitative observations, the reduction by sulfide ion appears to be rapid.

Without further detailed studies it is not possible to give even a qualitative interpretation of the effect of all the factors involved in polymerization. The reason is not only our incomplete knowledge of rates of transfer of hydroperoxides from the organic to the aqueous layer, but also our ignorance of induced decomposition of hydroperoxide by both reactions (1) and (2). From studies of the kinetics of reaction (1) we conclude that it occurs in two steps:



The $\text{S}_2\text{O}_4^{\cdot-}$ is a free radical which can be oxidized not only by FeY^- but also by the hydroperoxide. The latter reaction should yield $\text{RO}\cdot$ free radicals which initiate polymerization. However, the $\text{RO}\cdot$ free radicals produced by this induced reaction and also in reaction (2) can react with $\text{S}_2\text{O}_4^{--}$ as follows



Reactions (4a) and (4b) constitute a chain reaction. Thus, both reactions (1a) and (2) can initiate a chain decomposition of the hydroperoxide, while the simultaneous occurrence of both reactions should yield a chain decomposition of hydroperoxide and dithionite. Stoichiometrically, the sum of reactions (4a) and (4b) is the same as the direct reaction (3), which is not a chain reaction.

An increase of the concentration of iron(III) in

the recipe results in an increased rate of production of iron(II) and of $\text{S}_2\text{O}_4^{\cdot-}$, and also in an increased rate of reaction (2). However, there is competition between reaction (4a) and the initiation for $\text{RO}\cdot$. Since the ratios of the rate constants of the various reactions are unknown, no definite statement can be made on the effect of the concentration of iron(III) on the rate of initiation and rate of polymerization.

It is of interest to note from Figures 1-6 that the polymerization soon comes to a dead-step when the number of millimoles of dithionite is approximately equal to or greater than the number of millimoles of hydroperoxide. Under this condition, the system rapidly becomes exhausted of hydroperoxide. No such rapid exhaustion occurs when the number of millimoles of hydroperoxide is greater than that of dithionite.

The induced decomposition of both dithionite and hydroperoxide results in a large waste of free radicals, as far as polymerization is concerned. This interpretation may account for the fact that the rate of polymerization of the Veroxathionite recipe is of the same order of magnitude as that of the Sulfoxylate recipe, although the rates of reaction of dithionite and sulfoxylate with ferric versenate differ greatly.

The correctness of the above qualitative interpretation is supported by the fact that the rate of polymerization of a recipe in which ferrous versenate and hydroperoxide are the sole reactants is considerably greater than the rate of the Veroxathionite recipe, in which the ferrous iron is formed very rapidly, but in which the dithionite inactivates a fraction of the $\text{RO}\cdot$ free radicals.

The induced reaction between hydroperoxide and reductant undoubtedly also occurs in redox recipes with a reductant other than dithionite. The occurrence of this induced reaction may account for differences in the effect of a given factor in different redox recipes. An illustration of the

variety of effects observed in emulsion redox polymerization is afforded by the comparison shown in Table XV. Further studies of kinetics and mechanism are required before all the facts can be interpreted.

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Synopsis

A new initiating system, named the Veroxathionite system, for the copolymerization of butadiene (75)-styrene (25) is described. At 0°C., with the recipe: butadiene, 75 parts; styrene, 25 parts; water, 180 parts; potassium myristate, 5 parts; potassium pyrophosphate, 1 part; sulfole mercaptan, 0.3 part; 0.66 mmole of phenylcyclohexane hydroperoxide, 0.001 M ferric versenate, and 0.1 part of sodium dithionite, conversions of 45, 87, and 100% were reached in 1, 2, and 3 hours, respectively. The rate can be varied within wide limits by changing the concentration of iron. With only 10^{-4} M ferric versenate and 0.06 part of dithionite, 71% conversion is attained in 12 hours. The amount of dithionite must be adjusted to the amount of hydroperoxide and, to a lesser extent, to the amount of iron. With much more than one mole of dithionite per mole of hydroperoxide, dead-stops occur at low conversion due to exhaustion of hydroperoxide. The rate is determined by the concentration of ferric versenate, and an excess of versene over ferric iron has no effect. The addition of potassium pyrophosphate yields a latex which is of normal fluidity and free of pre-coagulation up to 80% conversion. The effects of polymerization variables are described. With methanol as antifreeze, a recipe is described which yields 75% conversion in 8 hours at -20°C. The reaction mechanism is very involved. It is concluded that an induced reaction between hydroperoxide and dithionite is responsible for the low efficiency of the radicals produced in this recipe.

Résumé

Un nouveau système d'initiation, dénommé système Veroxathionite, est décrit pour la copolymérisation du butadiène (75) et du styrène (25). En travaillant à 0°C, et en employant le mode opératoire suivant: butadiène, 75; styrène, 25; eau, 180; myristate de potassium, 5; pyrophosphate de potassium, 1; mercaptan sulfolique, 0,3; 0,66 mmole d'hydroperoxyde de phényl-cyclohexane, 0,001 M de versénate ferrique et enfin 0,1 partie de dithionite de sodium, on obtient des conversions de 45, 87 et 100% en 1,2 et 3 heures. On peut faire varier la vitesse dans les larges limites en changeant la concentration du fer. On obtient 71% de conversion en 12 heures avec seulement 10^{-4} M de versénate ferrique et 0,06 partie de dithionite. On peut ajuster la quantité de dithionite à la quantité d'hydroperoxyde et, dans une moindre mesure, à la quantité de fer. En présence de plus d'une môle de dithionite par môle d'hydroperoxyde, la réaction s'arrête à faible conversion par suite de l'épuisement en hydroperoxyde. La vitesse est déterminée par la concentration en versénate ferrique; un excès de versène par rapport au fer ferrique n'a pas d'effet. L'addition de pyrophosphate de potassium donne un latex de fluidité normale et sans précoagulation jusqu'à 80% de conversion. Les différents effets de polymérisation sont décrits. En présence du méthanol pour éviter toute congélation un mode opératoire est décrit, qui donne 75% de conversion en 8 heures à -20°C. Le mécanisme de la réaction est très compliqué. On en conclut qu'une réaction induite entre l'hydroperoxyde et le dithionite est responsable de la faible efficacité des radicaux produits dans ce processus.

Zusammenfassung

Ein neues Startersystem für die Copolymerisation von Butadien (75)-Styrol(25), genannt Veroxathionit-System, wird beschrieben. Bei 0°C werden mit dem Rezept: Butadien, 75; Styrol, 25; Wasser, 180; Kaliummyristat, 5; Kaliumpyrophosphat, 1; Sulfolmerkaptan, 0,3; 0,66 Mmol Phenylcyclohexanhydroperoxyd, 0,001 M Ferriversenat und 0,1 Teilen Natriumdithionit, in 1, 2 und 3 Stunden Umsätze von 45, 87 und 100% erreicht. Die Geschwindigkeit kann innerhalb weiter Grenzen durch Änderung der Konzentration an Eisen variiert werden. Mit nur 10^{-4} M Ferriversenat und 0,06 Teilen Dithionit wird in 12 Stunden ein Umsatz von 71% erreicht. Die Menge des Dithionits muss der Menge des Hydroperoxyds und in einem geringeren Ausmass der des Eisens angepasst werden. Bei Anwendung eines hohen molaren Überschusses von Dithionit bezogen auf Hydroperoxyd, erfolgt ein Abstoppen bei niedrigem Umsatz wegen Verbrauches des Hydroperoxyds. Die Geschwindigkeit wird durch die Konzentration des Ferriversenates bestimmt und ein Überschuss von Versen über Ferriessen hat keinen Einfluss. Zusatz von Kaliumpyrophosphat ergibt ein Latex von normaler Fluidität, der bis zu 80% Umsatz keine Praekoagulation aufweist. Die Wirkungen verschiedener Variabler bei der Polymerisation werden beschrieben. Ein Rezept mit Methanol als Gefrierungsverhinderndem Zusatz wird beschrieben, das bei -20°C in 8 Stunden einen Umsatz von 75% liefert. Der Reaktionsmechanismus ist ziemlich kompliziert. Man kommt zu der Anschauung, dass eine induzierte Reaktion zwischen Hydroperoxyd und Dithionit für die geringe Radikalausbeute bei diesem Rezept verantwortlich ist.

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