

# High-Temperature Redox-Initiated Emulsion Polymerization of Butadiene

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## Synopsis

The kinetics of the ferric ethylenediaminetetraacetate (EDTA)-diisopropylbenzene hydroperoxide (DIBHP)-sodium formaldehyde sulfoxylate (SFS) redox system were determined. The rate constant is a function of the ionic strength  $\mu$ . A plot of  $\log_{10}$  (rate constant), for the rate-limiting second-order iron-SFS reaction, vs.  $\mu^{1/2}$  has a slope of 1.3 with a limiting rate constant of  $295 \pm 15 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$  at  $\mu = 0$ . The slope of this plot decreases to essentially zero for  $\mu > 0.06M$ . Incorporation of these results into the Smith-Ewart model for emulsion polymerization correctly predicts the dependence of latex particle size on Fe and DIBHP concentration, but a much lower dependence on SFS concentration is observed.

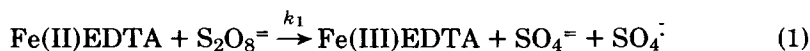
## INTRODUCTION

The emulsion polymerization of 1,3-butadiene and its copolymerization with styrene to produce a synthetic rubber has been known for many years.<sup>1</sup> The principal thrust of synthetic rubber latex research has been to produce molecular structures containing low levels of crosslinking or "gel",<sup>1</sup> a critical molecular parameter required for a major use of rubber, namely, tires. This led to low polymerization temperatures (0–50°C) and, therefore, the use of redox initiation systems.

However, in the manufacture of rubber-modified thermoplastics and thermosets, e.g., impact polystyrene, acrylonitrile-butadiene-styrene (ABS), and rubber-modified epoxies, the latex rubber particles are ultimately crosslinked; hence, it is not necessary for the rubber particles to be gel-free. The restriction of low polymerization temperature to produce a gel-free rubber no longer applies. This fact, combined with facilitated removal of the heat of polymerization at higher temperatures, is the impetus for this work.

In addition to their high reactivity at low temperatures, redox systems allow control of the rates of free radical formation provided that the kinetics of the initiating system is known. The use of redox systems at high temperatures still allows precise control over radical formation rates, a parameter necessary for description of the emulsion polymerization kinetics.<sup>2</sup>

Previous studies<sup>3–5</sup> have modelled the kinetics of iron-based redox systems, with kinetic schemes ranging from simple to very complex. These systems have been reviewed.<sup>6</sup> Equations (1) and (2) were adequate to describe a redox system based on ferric ions complexed with ethylenediaminetetraacetic acid (EDTA), persulfate anion as the oxidant, and sodium formaldehyde sulfoxylate (SFS) as the reductant<sup>3</sup>:





The radical species generated in reaction (2) was postulated. It is not clear whether this reaction product is an ion or a radical.<sup>6</sup> In either case, there is no change in our kinetic description of this system. The assumption of an ionic or radical species will change the number of radicals generated per minute by a factor of 2.

Early studies of reaction (1), with cumene hydroperoxide as the oxidant,<sup>7</sup> showed the reaction to be pH-insensitive over the range 3.7–10.3, with a second-order rate constant of about  $7 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$  at 25°C, the highest temperature studied.

Reaction (2) has been studied,<sup>3-5</sup> determining the rate constant to be about  $25 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ , significantly lower than reaction (1). The kinetics of this reaction have also been investigated at low temperatures.

The definition of the kinetics of this type of redox system at higher (70°C) temperatures requires the study of the rate limiting reaction (2). The kinetics are then integrated into an emulsion polymerization model, enabling prediction of latex particle size and the ability to "tailor" a latex formulation. This report will focus on (1) kinetic definition of the initiation system and (2) its incorporation into the Smith–Ewart emulsion polymerization model<sup>2</sup> applied to the emulsion polymerization of 1,3-butadiene at 70°C.

## EXPERIMENTAL

### Initiator Experiments

Initiator experiments were run at  $70 \pm 0.2^\circ\text{C}$ , in nitrogen-purged 5-L multi-necked flasks, using an electric heating mantle. Distilled water was used in all experiments, and all reactions were run in the absence of monomers.

Iron was added either by weighing out samples of solid ferric nitrate nonahydrate or pipetting a standard solution. A standard EDTA solution, which is reported to be stable,<sup>8</sup> was used.

A typical run recipe is as follows:

distilled water	2975 mL
Fe(NO <sub>3</sub> ) <sub>3</sub> solution	5 mL
EDTA solution	10 mL
diisopropylbenzene hydroperoxide (DIBHP), 50%	20 mL
SFS	1.0027
ORR soap	4.5

ORR (Office of the Rubber Reserve) soap flakes are a mixture of the sodium salts of ca. 25% stearic, 25% palmitic, and 50% oleic acids.

All concentrations are calculated as water phase concentrations, using an average molecular weight of 300 and 194 for ORR and DIBHP, respectively.

In a typical experiment, all components except SFS were charged. The SFS was charged at zero time. Samples (usually 10 mL) were removed and pipetted into a 125-mL flask containing 2 mL of 1 N CHI and 10 g of crushed ice and the SFS titrated with a permanganate solution. The flask was kept cold in an ice

bath. It was found that the presence of the ice and acid led to the rapid precipitation of the ORR soap from the solution and increased the sharpness of the titration end point, which slowly faded due to reaction of the permanganate with the hydroperoxide. Each sample was titrated immediately with a permanganate solution which was prepared fresh daily and standardized against arsenic trioxide.<sup>9</sup> Blanks containing no SFS were found to have essentially zero titer.

### Butadiene Polymerization Experiments

Polymerization of 1,3-butadiene (Bd) was carried out in  $N_2$  purged 1-gal glass-lined pressure reactors equipped with metering pumps for continuous adds of liquids. In a typical experiment, water, ORR soap, iron, and EDTA were charged (the EDTA/Fe mole ratio was maintained at 2). The reactor was adjusted to 70°C, and an initial charge of SFS was made. Simultaneously, additional metering of SFS was started, according to the calculated reaction rate, to maintain a constant concentration of SFS. ORR soap solution was added as required to maintain batch stability and, yet, not enough to initiate the formation of new particles.

Solids content was determined by vacuum drying an aliquot of the latex. Particle size was measured by turbidity using a previously described technique.<sup>10</sup>

SFS and DIBHP were commercial grades obtained from Nopco and Hercules Chemical, respectively, and had 99+ and ca. 50% assay. Ferric nitrate non-hydrate and arsenic trioxide were reagent grade (Fisher Scientific). EDTA was technical grade from Dow Chemical. ORR soap flakes were obtained from Proctor and Gamble. Co. 1,3-Butadiene, Phillips Petroleum rubber grade, was distilled prior to use.

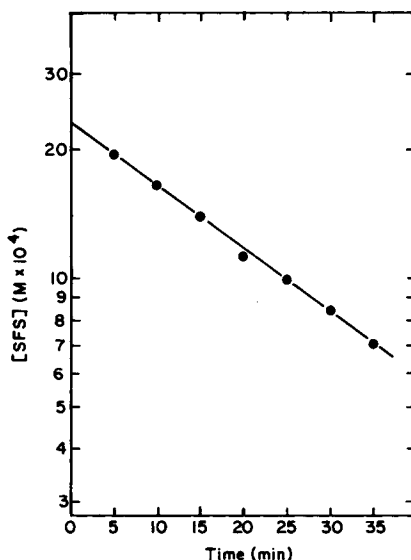


Fig. 1. Concentration of SFS vs. time at initial  $[SFS] = 2.17 \times 10^{-3}M$ ,  $[Fe^{+3}] = 1.00 \times 10^{-4}M$ ,  $[EDTA] = 0.88 \times 10^{-4}M$ .

TABLE I  
Effect of  $\text{Na}_2\text{SO}_4$  on Rate Constant  $k_2$  with Initial  $[\text{SFS}] = 4.33 \times 10^{-3}M$

$\text{Fe}^{+3}$ ( $M \times 10^5$ )	EDTA $M \times 10^5$	$\text{Na}_2\text{SO}_4$ ( $M \times 10^3$ )	$k_2$ ( $L \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ )
10.0 <sup>a</sup>	8.80	0	354
10.0 <sup>a</sup>	8.80	4.70	419
10.0 <sup>b</sup>	8.80	9.40	506
7.20 <sup>b</sup>	75.0	0	505
7.20 <sup>b</sup>	75.0	7.50	497
7.20 <sup>b</sup>	75.0	15.0	608
7.20 <sup>b</sup>	75.0	30.0	663
7.20 <sup>b</sup>	7.50	37.4	707

<sup>a</sup>  $[\text{DIBHP}] = 8.6 \times 10^{-3}M$ .

<sup>b</sup>  $[\text{DIBHP}] = 1.7 \times 10^{-2}M$ .

## RESULTS AND DISCUSSIONS

### Initiator Kinetics in the Absence of Monomer

The Introduction showed that, for the reaction scheme depicted by reactions (1) and (2), and using DIBHP and SFS as the oxidant and reductant, respectively,  $k_1 \gg k_2$ . The measurement of the rate of disappearance of SFS is sufficient to define the rate of radical formation,  $\rho$ , as follows:

$$\rho = k_2 [\text{Fe(III)EDTA}] [\text{SFS}] \quad (3)$$

To simulate an aqueous phase typical of an emulsion polymerization recipe, ORR soap and sodium sulfate were used in addition to the redox components. In the experiments, the initial reaction pH was  $10.0 \pm 0.3$ . During the course of the reaction, the pH dropped to  $9.8 \pm 0.3$  depending upon the reaction conditions. No attempt was made to buffer the system since this would limit the lowest ionic strengths attainable.

The rate of SFS disappearance, in the absence of monomer, was followed by titrimetry. Figure 1 shows the results of a typical experiment. A first-order plot for SFS is linear over the entire reaction (up to 70% depletion of the SFS). Extrapolation to time zero provides a verification of the initial SFS concentration. The rate constant was calculated from the plot in Figure 1 by dividing the slope by the concentration of iron. Since  $k_1$  is generally much greater than  $k_2$  and the concentration of DIBHP greater than SFS, the iron exists essentially entirely in the ferric state. Thus, the concentration of iron used to calculate  $k_2$  was taken as the molar concentration of iron charged.

TABLE II  
Effect of DIBHP and ORR Soap on Rate Constant  $k_2$  with Initial  $[\text{SFS}] = 4.33 \times 10^{-3}M$

$\text{Fe}^{+3}$ ( $M \times 10^5$ )	DIBHP ( $M \times 10^3$ )	ORR ( $M \times 10^3$ )	$\text{Na}_2\text{SO}_4$ ( $M \times 10^3$ )	$k_2$ ( $L \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ )
10.0 <sup>a</sup>	8.60	50	0	347
10.0 <sup>a</sup>	8.60	5.0	0	350
7.20 <sup>b</sup>	8.60	15	37.4	681
7.20 <sup>b</sup>	17.2	15	37.4	626

<sup>a</sup>  $[\text{EDTA}] = 8.80 \times 10^{-5}M$ .

<sup>b</sup>  $[\text{EDTA}] = 7.50 \times 10^{-5}M$ .

TABLE III  
Effect of Other Components on Rate

Fe <sup>+3</sup> ( <i>M</i> × 10 <sup>5</sup> )	EDTA ( <i>M</i> × 10 <sup>5</sup> )	SFS ( <i>M</i> × 10 <sup>3</sup> )	Na <sub>2</sub> SO <sub>4</sub> ( <i>M</i> × 10 <sup>3</sup> )	<i>k</i> <sub>2</sub> (L · mol <sup>-1</sup> · min <sup>-1</sup> )
10.0 <sup>a</sup>	22.0	4.33	4.00	388
10.0 <sup>a</sup>	8.80	4.33	2.10	458
10.0 <sup>b</sup>	8.80	4.71	4.32	387
10.0 <sup>b</sup>	8.80	2.17	0	341
10.0 <sup>b</sup>	8.80	3.26	0	360
2.40 <sup>a</sup>	2.50	2.17	37.4	581
7.20 <sup>b</sup>	250	4.33	37.4	637
7.20 <sup>b</sup>	7.50	4.33	3.75	529

<sup>a,b</sup> see Table I for explanation.

### Effect of Salt

In studying a reaction such as reaction (2), varying the components of the system affects both the concentration of that component as well as the ionic strength  $\mu$  of the system. Both of these factors are known to affect the kinetics of ionic reaction systems. An inert salt, sodium sulfate, was used to vary  $\mu$  independently. The results, shown in Table I, indicate a significant salt (ionic strength) effect. In order to study the effect of other variables, such as EDTA concentration, the salt and concentration effects must be considered simultaneously.

### Effect of DIBHP and ORR Soap

Table II shows that the ORR soap does not significantly affect the reaction kinetics and, therefore, must not add to the ionic strength of the system. This indicates that the reaction between SFS and Fe(III)EDTA occurs in the aqueous rather than micellar phase, as expected, and that the sodium ions from the surfactant are strongly bound to the micelles. Table II also shows that DIBHP level has no significant effect on the reaction rate, confirming reaction (2) to be rate limiting.

### Effect of Other Components

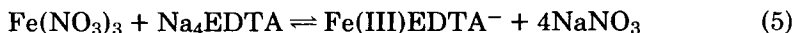
Other experiments performed during this study are summarized in Table III. Interpretation of these results follows.

### Effect and Calculation of Ionic Strength

For each of the experiments of Table I–III,  $\mu$  was calculated in the usual way:

$$\mu = \frac{1}{2} \sum c_i z_i^2 \quad (4)$$

where  $c_i$  is the molar concentration of each ion and  $z_i$  is the charge of the ion. In the calculation of  $\mu$ , contributions from DIBHP and ORR soap were taken to be zero, as previously discussed. For complexed species, i.e., Fe(III)EDTA, the following reaction takes place essentially quantitatively:



In cases where the Fe(III)/EDTA ratio is less than 1,  $\mu$  was calculated by assuming the EDTA concentration to be limiting, and the minor amount of potentially uncomplexed iron was ignored. Excess EDTA was assumed 100% ionized.

A plot of  $\log k_2$  vs.  $\mu^{1/2}$  is shown in Figure 2. At low ionic strength, the plot is linear as predicted from Brönsted's kinetic application of the Debye-Huckel limiting law.<sup>11</sup> The slope is 1.3 with a limiting ( $\mu = 0$ ) rate constant,  $k_2^0$ , of  $295 \pm 15 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ . At  $\mu > 0.06M$ , the slope decreases to essentially zero with a rate constant of  $660 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ . The straight line (nonhorizontal) portion of Figure 2 can be expressed as

$$\log(k_2/k_2^0) = a Z_a Z_b \mu^{1/2} \quad (5)$$

where  $Z_a$  and  $Z_b$  are the charges on the reacting species and  $a$  is a constant. At  $70^\circ\text{C}$ ,  $a$  ideally has a value of 0.88,<sup>12</sup> which results in a value of approximately 1.5 for  $Z_a Z_b$ . In the reaction scheme depicted by eq. (2), the reactant, SFS, has

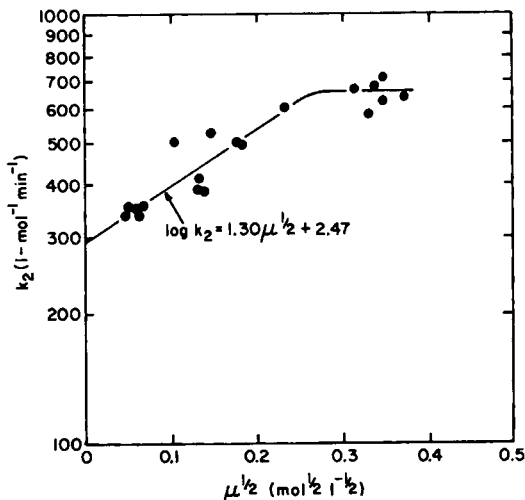


Fig. 2. Effect of  $\mu$  on the rate constant  $k_2$ .

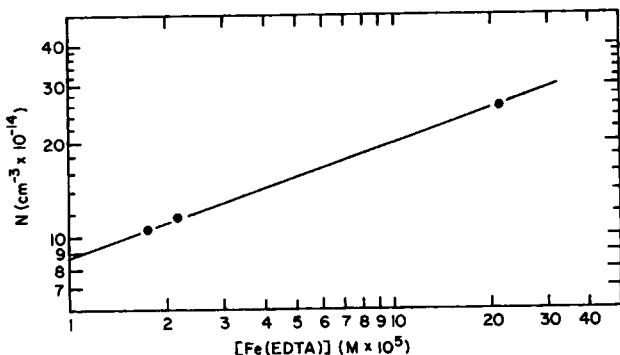


Fig. 3. Effect of Fe(EDTA) concentration on  $N$  at initial  $[\text{SFS}] = 4.80 \times 10^{-6}M$ ,  $[\text{ORR}] = 9.43 \times 10^{-2}M$ ,  $[\text{Na}_2\text{SO}_4] = 3.68 \times 10^{-2}M$ .

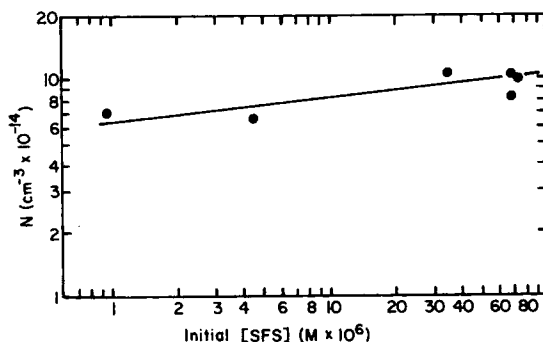


Fig. 4. Effect of initial SFS concentration on  $N$  at  $[\text{Fe}(\text{EDTA})] = 2.25 \times 10^{-5}M$ ,  $[\text{ORR}] = 9.43 \times 10^{-2}M$ ,  $[\text{Na}_2\text{SO}_4] = 3.68 \times 10^{-2}M$ .

a charge of  $-1$ ; therefore, the coreactant must be charged  $-1.5$ . Schwarzenbach<sup>13</sup> studied the hydrolysis of iron—EDTA complexes



and determined the  $\text{pK}$  to be 7.49 and 9.5 at  $25^\circ\text{C}$  for reactions (6) and (7), respectively. At  $\text{pH } 10$ , the equilibrium of reaction (6) lies far to the right. The second step in this hydrolysis, reaction (7) ( $\text{pK } 9.5$ ) also occurs to a significant extent yielding species of  $-3$  charge. The presence of these highly charged species will certainly increase the value of  $Z_a Z_b$  from 1.0 for univalent species to 3.0 for the univalent/trivalent reaction. The observed value of 1.5 is within this range.

This hydrolysis frees available ligand complexing sites and may allow the formation of polynuclear iron complexes. Therefore, reactions with  $\text{Fe}/\text{EDTA}$  ratios of slightly  $> 1$  respond to iron level in the usual first order way as do those cases with molar excesses of EDTA.

The leveling off of the  $\log k_2 - \mu^{1/2}$  plot at large  $\mu$  is expected and has been observed before. Brønsted et al.<sup>11</sup> found deviations from linearity at similar values of  $\mu$ .

A reaction scheme as shown by eqs. (1) and (2) describes the major features of the iron—EDTA—DIBHP—SFS redox initiation system at  $70^\circ\text{C}$  provided that proper consideration of ionic strength effects is made. Proposals for other methods to account for ionic effects have been made,<sup>12</sup> but ionic strength is adequate for the purposes of this work.

The limiting rate constant  $k_2$  (for  $\mu > 0.06M$ ) is similar in magnitude to that predicted by extrapolation of other workers' data<sup>5</sup> obtained at high  $\mu$ .

TABLE IV  
Effect of DIBHP on Number of Latex Particles

SFS ( $M \times 10^4$ )	DIBHP ( $M \times 10^3$ )	$D$ ( $\mu\text{m}$ )	$N$ ( $\text{cm}^{-3}$ )
6.43	1.22	0.145	$5.22 \times 10^{14}$
6.98	12.2	0.145	$5.22 \times 10^{14}$

$[\text{Fe}(\text{EDTA})] = 2.33 \times 10^{-4}M$ ;  $[\text{ORR}] = 1.57 \times 10^{-2}M$ ;  $[\text{Na}_2\text{SO}_4] = 3.68 \times 10^{-2}M$

### Emulsion Polymerization of Butadiene

Classical emulsion polymerization kinetics defined by Smith and Ewart,<sup>2</sup> predicts the number of particles/cm<sup>3</sup> water,  $N$ , to be related to  $\rho$  and the total molecular area of the soap,  $A_t$ , by

$$N \propto \rho^{0.4} A_t^{0.6} \quad (8)$$

Substituting eq. (3),

$$N \propto \{k_2 [\text{Fe(III)EDTA}] [\text{SFS}]\}^{0.4} A_t^{0.6} \quad (9)$$

$N$  is related to the average particle diameter  $D$  ( $\mu\text{m}$ ) by

$$N = 6 \times 10^{12} R / d_R \pi D^3 \quad (10)$$

where  $d_R$  is the density of polybutadiene, taken to be  $0.89 \text{ g} \cdot \text{cm}^{-3}$  and  $R$  is the monomer to water weight ratio at the start of the polymerization. Typically  $R$  is 0.741.

Figure 3 is a plot of  $N$ , calculated from eq. (10), vs. the concentration of the iron—EDTA complex with the concentrations of ORR soap and SFS constant. The slope is 0.35, in agreement with the prediction of eq. (9). Similar experiments, varying  $A_t$ , gave a slope of 0.7 vs. the theoretical 0.6. Figure 4 is a plot of  $N$  vs. the concentration of SFS. The slope is 0.1, a very weak dependence on SFS concentration as compared to the theoretical slope of 0.4.

The low order of dependency on SFS has been observed in the 5°C emulsion polymerization of styrene by Suzuki and Ohishi.<sup>4</sup> They proposed the formation of an Fe—EDTA—SFS complex to explain this dependency. In their experiments, differences in polymerization rate were observed when the ratio of SFS to hydroperoxide was varied. We observe no such effect during the course of these experiments in either the rate of SFS reaction (in Table II, the less than 10% change in  $k_2$  with a twofold change in DIBHP concentration would, from eq. (9), result in a 4% change in  $N$  or a 1% change in  $D$ ) or the rate of polymerization. Table IV shows a comparison of two runs with a tenfold change in DIBHP level and no significant change in  $N$ .

Despite this low SFS dependence, the Smith—Ewart theory of emulsion polymerization is sufficient to predict the major kinetic features of the high temperature emulsion polymerization of butadiene. A more complex interaction of SFS exists than is predicted by the model described here. The efficiency of radical formation and capture should be further investigated to relate the initiator decomposition to the polymerization kinetics.

### CONCLUSIONS

A simple ionic reaction scheme for the rate of SFS disappearance in a redox initiating system composed a  $\text{Fe}^{+3}$  (EDTA), DIBHP, and SFS can account for both ionic strength and concentration effects.

This model, when incorporated into the Smith—Ewart emulsion polymerization model, and applied to 1,3—butadiene can predict latex particle size. However, the polymerization system does not respond to SFS concentration in a predicted fashion.

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