Particle growth in butadiene emulsion polymerization. 1. The use of Fremy salt as aqueous radical scavenger

Citation for published version (APA):

Verdurmen, E. M. F. J., Geurts, J. M., & German, A. L. (1994). Particle growth in butadiene emulsion polymerization. 1. The use of Fremy salt as aqueous radical scavenger. *Macromolecular Chemistry and Physics*, 195(2), 621-633. <https://doi.org/10.1002/macp.1994.021950219>

DOI:

[10.1002/macp.1994.021950219](https://doi.org/10.1002/macp.1994.021950219)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Particle growth in butadiene emulsion polymerization, 1

The use of Fremy salt as aqueous radical scavenger

Edwin M. Verdurmen, John M. Geurts, Anton L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received: April 7, 1993)

SUMMARY:

The kinetics of the seeded emulsion polymerization of butadiene in combination with variable Fremy salt (potassium nitrosodisulfonate) concentrations was investigated in order to monitor non-steady state kinetics necessary for obtaining information on entry and exit of radicals from latex particles. Fremy salt is used because it is an entirely water-soluble stable radical that in principle can scavenge water-soluble radicals produced by a water-soluble initiator like peroxodisulfate, but allegedly will not interfere with radicals within latex particles. Adequate buffering of the pH is a prerequisite for stable Fremy salt concentrations in time. Emulsion polymerizations in the presence of Fremy salt showed that not all radicals in the aqueous phase of a swollen polybutadiene latex are scavenged. The use of Fremy salt to monitor non-steady state kinetics in the seeded emulsion polymerization of butadiene in the presence of tertiary dodecyl mercaptan yields no satisfying results. The use of Fremy salt seems to be restricted to systems where the rate of polymerization is strongly influenced by variation in initiator concentration, i. e. the styrene system or the butadiene system in the absence of tertiary dodecyl mercaptan.

Introduction

In an effort to elucidate the kinetic behaviour of the emulsion polymerization of butadiene, experiments were designed to monitor non-steady state kinetics. Experiments were performed in the presence of a uniquely water-soluble radical scavenger, potassium nitrosodisulfonate (Fremy salt, FS). The ability to stop and restart a polymerization offers possibilities to observe non-steady state kinetics. From the steady state conversion-time history, only an average number of radicals, $\bar{n}$, can be determined if the propagation rate coefficient, k_p , is known¹⁾. When certain conditions apply, a propagation rate coefficient can be determined^{2–4)} assuming $\bar{n} = 0.5$. The parameters that determine $\bar{n}$, like the rate coefficients for entry of radicals into particles, ρ , and the rate coefficient for exit of radicals out of particles, k , cannot be determined from steady state conversion-time history alone, since this only determines the ratio of ρ and k , in zero-one systems: $\bar{n} = \rho/(2\rho + k)$. The parameters ρ and k , which determine the behaviour of the emulsion polymerization in Smith-Ewart case I and II, can, however, be determined from the steady state rate of polymerization and the time needed to reach the steady state polymerization. Without fully describing the mathematics here it is intuitively clear that the values of ρ and k determine how fast a polymerization reaches its steady state. A measure of the latter observable is the intercept of the linear slope of the rate of polymerization with the y-axis. This method is commonly denoted as the 'slope and intercept method'^{1–5)}. A standard emulsion polymerization reaches a

steady state in a time scale of minutes. The accuracy to which an intercept can be determined is critical. Stopping and restarting the polymerization a number of times during a small time scale compared to the total reaction time offers an elegant method of acquiring more accurate data, since all other variables can be kept reasonably constant this way. The usual way to meet these preconditions is the use of gamma rays for the initiation of polymerizations⁶. One can simply remove a reactor vessel in or out of a gamma source to stop and restart the initiation of the polymerization. This method is discussed separately⁷.

In this paper the application of a uniquely water-soluble radical scavenger, potassium nitrosodisulfonate (Fremy salt), in combination with a water-soluble initiator like peroxodisulfate, is described as a possible substitute for gamma radiation facilities. The use of Fremy salt as water-soluble radical scavenger in emulsion polymerization has been described by Lacik et al.⁸ and Barton et al.^{9,10}.

A third alternative is monitoring the beginning of a chemically initiated polymerization and is discussed separately¹¹. The advantages and disadvantages of the methods are compared in the following section.

The advantage of gamma rays as initiator is that one can start and stop the initiation by simply moving the reactor, in and out the gamma source, respectively. This has three advantages: 1. It is possible to restart the polymerization after a steady state has been observed during the first insertion in the source, followed by removal from the source. The differences between the approaches to steady states (SS) before and after removal from the source will give information about any possible retardation during this approach. The steady state condition usually observed marks the disappearance of any retardation. Hence, during the second insertion the retardation is absent, and reliable information can be found about steady state slopes and intercepts, since approach to steady state is now only a function of the desired kinetic parameters. 2. The insertions can be frequently repeated during the same experiment, thus enhancing the number of data obtained. 3. When the reactor is moved out of the source, one is able to monitor the time needed for the rate of polymerization to reach a steady state, the decay time, which will give specific information on exit of radicals from particles (exit coefficient, k) and on the rates of thermal background initiation rates often present in emulsion polymerization. A serious disadvantage of gamma initiation is the fact that the initiating species, being predominantly $\text{OH}^\bullet$ radicals, are different from the sulfate radicals used in chemically initiated polymerization. This will have an effect on the entry of radicals in particles. Hence entry coefficients (ρ) determined from gamma radiolysis data can be compared neither with data from peroxodisulfate-initiated systems nor with model calculations specifically designed for peroxodisulfate-initiated systems²² like the model used elsewhere^{4,12}.

In theory, the aqueous radical scavenger method using Fremy salt should offer the same advantages as mentioned for gamma radiolysis. In addition, it offers the advantage of allowing the use of peroxodisulfate as initiator. Thus, sulfate radical absorption can be monitored and the resulting entry rate coefficient can be compared with model calculations. Moreover, insight is gained on which factors govern the peroxodisulfate initiating system.

The chemical initiation method offers the advantage of allowing peroxodisulfate initiation like the Fremy salt method, but the non-steady state kinetics can be monitored only once per experiment. Possible retardation of the polymerization will affect the data.

Experimental part

Material

Butadiene (DSM Chemicals, Geleen, The Netherlands) was distilled directly from a 27-L storage vessel into a cooled steel recipient. A two isomer mixture of tertiary dodecyl mercaptan (TDM) was used: $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{SH}$ and $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)(\text{SH})\text{CH}_2\text{C}(\text{CH}_3)_3$. Sodium peroxodisulfate (Fluka AG, Buchs, Switzerland), sodium dodecyl sulfate (p.a. Merck, Darmstadt, Germany), and sodium carbonate (p.a. Merck, Darmstadt, Germany) were all used without further purification. Water was doubly distilled and purged with nitrogen to remove oxygen. Potassium nitrosodisulfonate (Aldrich Chemie, Brussels, Belgium) was stored in a desiccator in the presence of calcium oxide lumps and ammonium carbonate, as described by Zimmer et al.¹³⁾. Potassium nitrosodisulfonate was used without further purification. The orange crystals were dissolved in water that was purged with argon under heating in order to remove oxygen. Fresh solutions were prepared for every polymerization prior to the introduction into the reactor by a syringe.

Emulsion polymerizations

Experimental details and recipes are elaborately explained elsewhere^{4, 12, 14)}. A summary of features important for this paper is presented below. The seeded emulsion polymerizations were carried out in a cylindrical stainless steel reactor. The reactor was connected with a remote density meter (Anton Paar DMA 401, Graz, Austria) linked to a registration unit (Anton Paar DMA 60, Graz, Austria) and a computer. The reaction mixture was pumped with a piston-membrane pump (Orlita KG, MK 10, Giessen/Lahn, FRG) from the reactor through the density cell and back into the reactor. Gravimetric conversion data is used to calibrate on-line density data. The density data converted into conversion data is transformed into plots of $-\ln(1 - x)$ versus time.

The recipe used is reported elsewhere⁴⁾ and is used for all polymerizations unless stated otherwise. The polybutadiene in the recipes is added in the form of a seed latex made by emulsifier-free emulsion polymerization. The preparation of this seed latex is discussed in detail elsewhere¹⁵⁾. All the seed latexes are prepared under comparable process conditions. The seed latexes used were dialysed until constant low serum conductivity ($< 20 \mu\text{S} \cdot \text{cm}^{-1}$) to remove traces of initiator. The monomer was allowed to swell the seed latex at 25 °C for 24 h. After swelling, the initiator was added as a 50-mL aqueous solution via a gas tight syringe through a valve.

Latex particle characterization

The average particle diameter and the particle size distribution were measured using calibrated transmission electron microscopy (TEM, Jeol 2000 FX) in combination with OsO_4 staining techniques. Typically some 1000 particles were counted (TGA-10 particle analyzer, Zeiss, Oberkochen, Germany) on a micrograph taken from various parts of the TEM sample grid. Calibration of the measured particle diameters was performed with specimens of known diameter. The particle diameters mentioned in this paper are weight-average diameters d_w .

Theory

The proper monitoring of non-steady state kinetics depends on a step function in the presence of effective radicals capable of polymerizing monomer dissolved in the

aqueous phase. Ideally, the injection of a uniquely water-soluble radical scavenger reduces the efficient radical concentration in the aqueous phase from its steady state value to zero but should not interfere with the radicals or growing chains in the particle phase. This section describes the application of Fremy salt (FS) to serve as such a scavenger.

FS is a nitroxyl radical which has found widespread use as an ESR standard and as a selective oxidizer for some organic compounds¹⁶. The most important feature of FS is its extremely high stability. It is a long-lived radical, which makes it suitable for use as a scavenger of other radicals. It has been suggested by Lacik et al.⁸ that FS could be used as a scavenger in an emulsion polymerization when a water-soluble initiator is used. Several important advantages of the use of FS in an emulsion polymerization would be:

- 1) FS is highly water soluble and almost completely insoluble in organic solvents¹⁷, thus only radicals in the water phase are scavenged.
- 2) FS shows no interaction with SDS micelles^{17, 18}, consequently it seems reasonable to assume that FS will not enter SDS-stabilized latex particles and therefore will not interfere with the polymerization inside the latex particles.

The orange crystals of FS form a purple solution when dissolved in water. It has been observed that the decomposition of FS in water, among other things, depends on the pH of the solution. Murib et al.¹⁹ described this decomposition as summarized by Eq. (1):

Furthermore, Murib et al.¹⁹ described the reactions that occur at low pH as given by Eqs. (2), (3) and (4):

Lacik et al.⁸ described inhibition during an emulsion polymerization of styrene initiated by gamma radiation, thus by a combination of mainly $\text{OH}^\bullet$ and some $\text{H}^\bullet$ and $\text{e}^{-\bullet}$ radicals, in the presence of FS. This inhibition can probably be explained by Eq. (4).

Peroxodisulfate, a commonly used initiator in emulsion polymerization, dissociates in water producing $\text{SO}_4^{\bullet-}$ radicals. To be effective as a radical scavenger in such a system, FS should react with $\text{SO}_4^{\bullet-}$ or with active oligomeric radicals formed in water phase by $\text{SO}_4^{\bullet-}$. Wilson et al.²⁰ indicate that FS should be able to react with $\text{SO}_3^{\bullet-}$ radicals and that decomposition of FS in water is facilitated by SO_3^{2-} . The decomposition of FS, however, is not affected by SO_4^{2-} . Taking into account that these reactions took place in strongly alkaline solutions, it is still not unambiguously shown

that FS radicals react with $\text{SO}_4^{\cdot -}$ radicals, i. e. with the primary radicals formed during emulsion polymerization in the aqueous phase. The same uncertainty applies to organic oligomeric radicals in the water phase. There are some indications^{13,16)} that FS reacts with these species. It is, however, not known whether these reactions actually occur under emulsion polymerization conditions. Barton et al.⁹⁾ claim that the effectiveness of FS as a radical scavenger is based upon its reaction with oligomeric radicals rather than primary radicals in the water phase of a polymerizing latex.

After this literature survey some questions remain whether FS meets the requirements of the ideal radical scavenger defined earlier. Nevertheless, experiments were performed to verify the usefulness of FS.

Results and discussion

Fremy salt aqueous solutions

The FS solutions as used in polymerizations were tested for radical activity. In Fig. 1 and ESR signal is plotted of a $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ solution of FS buffered with $10^{-2} \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{CO}_3$. The ESR signal is used here as a fingerprint of FS, which is used as an ESR standard and thus has a well known signal¹⁶⁾. To verify whether FS

Fig. 1. ESR signal of a $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ FS solution buffered with $10^{-2} \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{CO}_3$, frequency 9,67 GHz, modulator frequency 100 kHz, mid range 3470 G and scan range 100 G

Fig. 2. ESR signal of a $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ FS solution buffered with $10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{CO}_3$, heated for 4 min at 90°C

Fig. 3. ESR signal of a mixture of a $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ FS solution and a $5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8$ solution buffered with $10^{-2} \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{CO}_3$, heated for 4 min at 90°C

radicals react with sulfate radicals, a mixture of FS ($10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) from a stock solution and potassium peroxodisulfate ($5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) buffered with $10^{-2} \text{ mol} \cdot \text{dm}^{-3} \text{Na}_2\text{CO}_3$ were dissolved in water and heated for 4 min at 90°C . A reference solution of only FS from the same stock solution was treated likewise. In Figs. 2 and 3 the ESR signals of both solutions after heating are shown. From the intensity of the signals in the Figs. 1, 2 and 3 the concentrations of FS could be determined, and these are shown in Tab. 1.

Tab. 1. The relative intensity of the ESR signals of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ FS solutions after different treatment

Treatment of FS solutions	ESR relative signal intensity	FS radical concentration in $\text{mol} \cdot \text{dm}^{-3}$
$10^{-3} \text{ mol} \cdot \text{L}^{-1}$ FS, room. temp.	1	10^{-3}
$10^{-3} \text{ mol} \cdot \text{L}^{-1}$ FS, 90°C , 4 min	0,7	$0,7 \cdot 10^{-3}$
$10^{-3} \text{ mol} \cdot \text{L}^{-1}$ FS + $5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ peroxodisulfate, 90°C , 4 min	0,16	$0,16 \cdot 10^{-3}$

The difference in FS concentration after heating between the solution with peroxodisulfate and without peroxodisulfate is $0,53 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. This agrees acceptably with the amount of thermally created $\text{SO}_4^{\cdot-}$ radicals, assuming that all these radicals are scavenged by FS. In 4 min at 90°C the concentration of $\text{SO}_4^{\cdot-}$ radicals formed (in the absence of FS) would be $0,7 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ calculated utilizing Eq. (5) and a value for the peroxodisulfate dissociation constant, $k_d = 3,1 \cdot 10^{-4} \text{ s}^{-1}$ at 90°C ²¹).

$$\frac{[I]}{[I_0]} = e^{-k_d t} \quad (5)$$

where $[I]$ is the initiator concentration (in $\text{mol} \cdot \text{dm}^{-3}$), and t is time (in s). The deviation is within experimental error. Note that in the scanned range the ESR only detects signals of FS radicals. Sulfate radicals cannot be detected by ESR at room temperature because rapid termination ensures extremely low sulfate radical concentrations. The reactions leading to termination of FS radical activity are not clear. From these measurements one cannot unambiguously state that FS radicals scavenge sulfate radicals, since peroxodisulfate dissociation also produces $\text{OH}^{\cdot}$ radicals by means of reaction with water²¹:

There is some evidence that charged species like sodium dodecyl micelles are not affected or penetrated by FS due to electrostatic repulsion¹⁷). This might also prevent direct scavenging of sulfate radicals by FS, but does still allow for scavenging of products of the reaction²¹:

Some evidence exists for reaction of FS radicals with $\text{OH}^\bullet$ ^{8,19}). However, careful reading of the Lacik paper reveals that FS and gamma-initiated radicals are present simultaneously. In his paper a polymerization is described during which a reactor vessel is taken in and out of a gamma source. In the source gamma rays initiate the polymerization, out of the source the polymerization rate decays. It is stated that the polymerization comes to a full stop after the latex-FS mixture has been in and back out of the gamma source. This full stop of the polymerization is an effect ascribed to FS, since comparable polymerizations without FS decay to a slow but measurable background rate. Nevertheless, the latex-FS mixture polymerizes in the source, thus showing polymerization is possible in the presence of FS. The Figs. 1, 2 and 3 and Tab. 1 show that the FS solutions prepared in the current investigation contain active FS radicals, and these FS radicals terminate with whatever radicals are formed as a result of peroxodisulfate dissociation almost equivalently. The presence of monomer dissolved in the aqueous phase is a complicating factor. The following reaction is claimed to be diffusion controlled²²⁻²⁵):

The rate coefficient for this reaction k_{pi} equals $10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ²²). Whether the rate of the reaction between $\text{SO}_4^{\bullet-}$ radicals and FS is also diffusion controlled is not clear. In the presence of monomer, competition between the reaction of sulfate radicals with FS and the reaction of sulfate radicals with monomer is determined by the rate coefficients and the ratio of FS and monomer aqueous concentrations. After the oligomeric radicals are formed the following reaction is likely to happen:

For the kinetics of entry it makes little difference which radicals, $\text{SO}_4^{\bullet-}$ or oligomeric, are terminated by FS.

The stability of FS radicals as a function of pH of the solution was verified by monitoring the pH of several aqueous solutions of FS and sodium peroxodisulfate (NaPS). In Fig. 4 the pH is plotted versus time and shows that FS is degraded rapidly

Fig. 4. pH versus time of aqueous solutions; (+): $[\text{FS}] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, (Δ): $[\text{NaPS}] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, ($\circ$): $[\text{FS}] = [\text{NaPS}] = 0.5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

in pure water, probably via reaction (1). Peroxodisulfate is known to produce acidic components as a result of dissociation via reactions described by Eqs. (6) and (7). The pH of an FS solution buffered with potassium carbonate is monitored in time, and from the results shown in Fig. 5 it is clear that FS is stable and present at 60 °C in solution for at least 120 min, given an adequate buffering of the pH.

Fig. 5. Decrease of pH versus time in a buffered solution of: $[FS] = [NaPS] = 0,5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $[NaHCO_3] = 0,5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

Emulsion polymerizations

After testing the radical activity of FS solutions in time and as a function of pH, it was verified whether FS could actually meet the requirements defined for an ideal aqueous radical scavenger in order to obtain proper non-steady state kinetics upon injection of FS in a butadiene emulsion polymerization at 60 °C.

The polymerizations are performed using the recipe shown elsewhere⁴⁾. During polymerization 1, $0,9 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ FS was added to the reaction mixture twice. The initiator concentration used was $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$. The molar amount of FS added was calculated to be equivalent to the molar amount of peroxodisulfate radicals formed by dissociation during a time interval of 2 h using the straightforward Eq. (5) and a value for k_d of $6,3 \cdot 10^{-6} \text{ s}^{-1}$ at 60 °C²⁶⁾. Note that the thermal degradation of FS is not taken into account: from Fig. 5 it becomes clear that this is justified. In theory the FS radicals should scavenge the radicals formed by peroxodisulfate instantaneously. Bimolecular termination of small radical species in the water phase has been reported by several authors and found to be a diffusion-controlled process²⁷⁻²⁹⁾. In Fig. 6 the conversion-time history of polymerization 1 is shown. The injections of FS are indicated by the two arrows. The effect of FS on the rate of polymerization is negligible. This observation leaves a number of possible conclusions. Note that monitoring of the ESR signal of FS radicals, as depicted in Figs. 2 and 3, does suggest active radical scavenging by FS.

In polymerization 2 the injected amount of FS was drastically increased to verify whether the FS concentration was too low in polymerization 1 to have a noticeable effect. This resulted in a total inhibition of polymerization 2, no polymerization was observed (see Tab. 2). The observation of polymerization 2 suggests that radical

Fig. 6. *Polymerization 1:*

Conversion (x) in interval III versus reaction time: $[\text{NaPS}] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, particle diameter: $d_w = 45 \text{ nm}$. Two injections of FS as indicated by arrows: (1) $t = 0$, $[\text{FS}] = 0,19 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; (2) $t = 3,5 \text{ h}$, $[\text{FS}] = 0,19 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

scavenging was incomplete during polymerization 1, which can be compensated by adding more FS. However, this does not explain why the polymerization is inhibited long after the FS concentration drastically must have diminished, as can be deduced from the Figs. 2, 3 and 5.

In polymerization 3 a compromise in FS concentration between polymerization 1 and 2 was chosen. Fig. 7 shows the conversion-time history of two comparable experiments: polymerization 3 and a polymerization in which no FS was added. Obviously, the rate of polymerization and the average number of radicals per particle, $\bar{n}$, is reduced considerably by the presence of FS. However, the second injection of FS has no effect on the rate at all. This result is inexplicable with currently accepted ideas on entry of radicals into latex particles! The amount of FS added at the start of the reaction should have inhibited any polymerization for 5 h, according to Eq. (5).

In polymerization 4 yet another concentration of FS and peroxodisulfate was chosen. Fig. 8 shows the conversion-time history of the experiment. The first injection yields little or no effect, the second injection leads to an absolute stop of the polymerization. The polymerization does not restart after the calculated inhibition time of 15 h has expired for long.

Fig. 7. *Polymerization 3:*

Conversion (x) in interval III versus reaction time: $[\text{NaPS}] = 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, particle diameter: $d_w = 224 \text{ nm}$. Two injections of FS as indicated by arrows: (1) $t = 0$, $[\text{FS}] = 0,21 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; (2) $t = 18,9 \text{ h}$, $[\text{FS}] = 0,21 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

Fig. 8. *Polymerization 4*: Conversion (x) in interval III versus reaction time: $[\text{NaPS}] = 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, particle diameter: $d_w = 102 \text{ nm}$. Two injections of FS as indicated by arrows: (1) $t = 0$, $[\text{FS}] = 0,47 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; (2) $t = 5,3 \text{ h}$, $[\text{FS}] = 0,89 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

FS is capable of creating acidic components, therefore an investigation of the pH of the final latex samples was performed by introducing a calibrated pH-probe directly in the latex. In Tab. 2 the experimental results are compared. The polymerization 2 and 4 that suffered a complete stop of the polymerization seem to have developed a very low pH. Most likely the FS reactions with water lead to acidic components that, although a buffer was added (NaHCO_3), reduce the pH. It is well known that below $\text{pH} = 3$ the following reaction of peroxodisulfate increasingly contributes to its dissociation²¹⁾:

This suggests that the inhibition in polymerization 2 and the full retardation in polymerization 4 are due to degradation of peroxodisulfate caused by inadequate buffering of the pH. Barton et al.⁹⁾ describe comparable polymerizations using styrene in which none of the previously discussed problems occur. However, the effect of pH is not mentioned and no information about pH or the use of buffer is given in their work, although the concentrations used are comparable.

In literature many reports are available describing the near independence of the rate of peroxodisulfate-initiated butadiene emulsion polymerization in the presence of mercaptan^{12, 30–33)}. It is therefore conceivable that Fremy salt is capturing all but few of the produced radicals, whereas this would not show up in the rate which is virtually unvaried over two orders of magnitude in peroxodisulfate concentration¹²⁾. The rate of polymerization becomes sensitive to the peroxodisulfate concentration only in the absence of tertiary dodecyl mercaptan (TDM). A recipe without TDM and with adequate buffering is chosen for polymerization 5. The concentrations of Fremy salt and peroxodisulfate utilized are given in Tab. 2. In Fig. 9 the results of the polymerization 5 are shown. Obviously, experiments in the absence of TDM are adequately stopped by adding Fremy salt. This is again a strong confirmation of the data presented by Verdurmen et al.¹²⁾ where a strong influence of the rate of polymerization on the peroxodisulfate concentration was shown to occur by omitting TDM from the polymerization recipe. Two explanations are discussed:

Tab. 2. Overview of polymerizations on seed latexes of variable particle diameter, d_w , and the effect of Fremy salt concentrations, [FS], on the rate of polymerization and final latex pH

Number	$\frac{[I] \cdot 10^3}{\text{mol} \cdot \text{dm}^{-3}}$	$\frac{[\text{FS}] \cdot 10^3}{\text{mol} \cdot \text{dm}^{-3}}$	$\frac{d_w}{\text{nm}}$	pH	Effect on the rate of polymerization
1 (Fig. 6)	10	0,76 (1 st injection) 0,85 (2 nd injection)	45	a) 7,5	None None
2	0,1	0,15 (1 st injection)	45	3,3	Inhibition, no polymerization
3 (Fig. 7)	1,0	0,21 (1 st injection) 0,21 (2 nd injection)	224	7,3	Retardation
4 (Fig. 8)	1,0	0,47 (1 st injection) 0,89 (2 nd injection)	102	a) 2,4	None Reaction stops
5 (Fig. 9)	1,0	1,0 (1 st injection)	158	6	Decay and restart

a) Not measured, but expected to be approx. 7.

Fig. 9. Polymerization 5: $-\ln(1-x)$ in interval III versus reaction time: [NaPS] = $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, particle diameter: $d_w = 158 \text{ nm}$. One injection of FS as indicated by the arrow: $t = 9,5 \text{ h}$, [FS] = $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

- 1) TDM actively interferes with aqueous phase kinetics. However, this option is not likely in the light of the extremely low aqueous concentrations of TDM and of radicals in general as compared with the FS concentration.
- 2) TDM influences *in-particle* kinetics. This option is readily supported by data from Verdurmen et al.^{7,12)}.

By reducing radical desorption, TDM ensures that very small amounts of radicals produce a much higher rate of polymerization than expected. A reduction of three orders of magnitude in the peroxodisulfate concentration still has little effect on the rate of polymerization. This means that FS has to scavenge more than 99,9% of the created radicals to bring about a significant decrease in the rate of polymerization. From polymerization 1 to 4 it can be deduced that FS does not scavenge all created radicals. Omission of TDM from the recipe significantly increases the dependence of the rate of polymerization on the peroxodisulfate concentration. Combined with a much larger likelihood of radical desorption bringing monomeric radicals back into the realm of

the FS explains the full stop of the polymerization by FS in polymerization 5. The final pH of the latex resulting from polymerization 5 is in the required range for normal peroxodisulfate dissociation. This explains the restart of the polymerization after the FS concentration is diminished by reaction with water and the generated radicals.

From the polymerizations performed under a wide variety of particle sizes, initiator concentrations and FS concentrations, the following can be concluded. The rate of polymerization of seeded emulsion polymerization of butadiene is not affected by FS concentrations to a degree that can be expected according to the calculated production of sulfate radicals. Degradation of peroxodisulfate without the production of sulfate radicals at $\text{pH} < 3$ explains the retardation of polymerizations without adequate buffering of the pH. On the other hand, retardation is observed in polymerization 3 where adequate buffering of the pH is provided, and this leads to the conclusion that FS terminates a portion of the radicals formed by peroxodisulfate, $\text{SO}_4^{\cdot-}$ and oligomeric radicals, but not all the radicals formed in the aqueous phase of a swollen polybutadiene latex. A total scavenging of all radical activity is necessary to stop a butadiene emulsion polymerization in the presence of TDM. Explanation of these phenomena are found in the virtual initiator concentration independence of the rate per particle of butadiene emulsion polymerization. This is elegantly proven by polymerization 5 where an expected decay and restart of the polymerization is obtained in the absence of TDM. This is in excellent agreement with the findings revealed by Verdurmen et al.¹²⁾ indicating the peculiar and poorly understood role of TDM in the emulsion polymerization of butadiene.

The use of the Fremy salt method is somewhat dubious in obtaining kinetic information, since it is not clear to which extent the Fremy salt interferes with the normal emulsion polymerization kinetics. The ideal step function in radical activity from steady state activity to zero activity and vice versa, required for the slope and intercept method to be used, is probably not achieved. To what measure this will affect entry and exit rate coefficient data remains unclear as yet. This could be tested using the styrene system, which is sensitive to the peroxodisulfate concentration and for which entry and exit rate coefficients are known.

Conclusions

Indications are found for a reaction of PS radicals with radicals generated by peroxodisulfate dissociation. In aqueous FS solutions buffering of the pH is necessary to maintain a stable concentration of FS. If FS is added to a polymerization in such a way that the pH is reduced below $\text{pH} = 3$, then inhibition of the polymerization occurs via degradation of the peroxodisulfate. The use of FS to monitor non-steady state kinetics is unsatisfying. Only polymerization in the absence of TDM can be stopped and restarted. The FS radical does not seem capable of stopping all radicals formed.

The authors are indebted to *DSM Research*, Geleen, The Netherlands, for financially supporting with work.

- ¹⁾ R. G. Gilbert, D. H. Napper, "Polymerizations in Emulsions"; in "Comprehensive Polymer Science"; vol. 4, chapt. 11, G. C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt Vol. Eds., G. Allen, J. C. Bevington Eds., Pergamon, New York 1989, p. 171–218
- ²⁾ M. Buback, L. H. Garcia-Rubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. O'Driscoll, O. F. Olaj, Jiacong Shen, D. Solomon, G. Moad, M. Stickler, M. Tirrell, M. A. Winnik, *J. Polym. Sci., Part C: Polym. Lett.* **26**, 293 (1988)
- ³⁾ D. H. Napper, R. G. Gilbert, *J. Macromol. Sci., Rev. Macromol. Chem.* **C23**, 127 (1983)
- ⁴⁾ E. M. Verdurmen, E. H. Dohmen, J. M. Verstegen, I. A. Maxwell, R. G. Gilbert, A. L. German, *Macromolecules* **26**, 268 (1993)
- ⁵⁾ C. Y. Wang, D. H. Napper, M. J. Ballard, R. G. Gilbert, *J. Chem. Soc., Faraday Trans.* **78**(1), 1117 (1982)
- ⁶⁾ S. W. Lansdowne, R. G. Gilbert, D. H. Napper, D. F. Sangster, *J. Chem. Soc., Faraday Trans.* **76**(1), 1344 (1980)
- ⁷⁾ E. M. Verdurmen, R. G. Gilbert, A. L. German, *Macromol. Chem. Phys.* **195**, 635 (1994)
- ⁸⁾ I. Lacik, B. S. Casey, D. F. Sangster, R. G. Gilbert, *Macromolecules* **25**, 4065 (1992)
- ⁹⁾ J. Barton, V. Juranicova, *Makromol. Chem., Rapid Commun.* **12**, 669 (1991)
- ¹⁰⁾ J. Barton, *Makromol. Chem., Rapid Commun.* **12**, 675 (1991)
- ¹¹⁾ E. M. Verdurmen, J. M. Geurts, A. L. German, *Macromol. Chem. Phys.* **195**, 641 (1994)
- ¹²⁾ E. M. Verdurmen, J. M. Geurts, J. M. Verstegen, I. A. Maxwell, A. L. German, *Macromolecules*, accepted
- ¹³⁾ H. Zimmer, D. H. Lankin, S. W. Horgan, *Chem. Rev.* **71**(2), 229 (1971)
- ¹⁴⁾ E. M. Verdurmen, Ph. D. Thesis, Eindhoven University of Technology (1993), "Particle Nucleation and Growth in Butadiene Emulsion Polymerization"
- ¹⁵⁾ E. M. Verdurmen, J. G. Albers, E. H. Dohmen, H. F. Zirkzee, I. A. Maxwell, A. L. German, submitted to *J. Polym. Sci.*
- ¹⁶⁾ E. G. Rozantsev, "Free Nitroxyl Radicals", H. Ulrich, Ed., Plenum Press, New York-London 1970, p. 22–23, 242–243
- ¹⁷⁾ P. J. Bratt, H. C. Choudhury, P. B. Chowdhury, D. C. Gillies, A. M. L. Krebber, L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans* **86**(19), 3313 (1990)
- ¹⁸⁾ Y. Kotake, E. G. Janzen, *Can. J. Chem.* **66**, 1895 (1988)
- ¹⁹⁾ J. H. Murib, D. M. Ritter, *J. Am. Chem. Soc.* **74**, 3394 (1952)
- ²⁰⁾ B. J. Wilson, D. L. Fillmore, *Inorg. Chem.* **16**(6), 1404 (1977)
- ²¹⁾ E. J. Behrman, J. O. Edwards, *Rev. Org. Chem.* **2**, 179 (1980)
- ²²⁾ I. A. Maxwell, B. R. Morrison, D. H. Napper, R. G. Gilbert, *Macromolecules* **24**, 1629 (1991)
- ²³⁾ N. A. McAskill, D. F. Sangster, *Aust. J. Chem.* **32**, 2611 (1979)
- ²⁴⁾ N. A. McAskill, D. F. Sangster, *Aust. J. Chem.* **37**, 2137 (1984)
- ²⁵⁾ P. Maruthamuthu, *Makromol. Chem., Rapid Commun.* **1**, 23 (1980)
- ²⁶⁾ L. M. Kolthoff, I. K. Miller, *J. Am. Chem. Soc.* **73**, 3055 (1951)
- ²⁷⁾ D. F. Sangster, A. Davison, *J. Polym. Sci., Polym. Symp.* **49**, 191 (1975)
- ²⁸⁾ F. S. Dainton, D. G. L. James, *J. Polym. Sci.* **39**, 299 (1959)
- ²⁹⁾ H. Fischer, *Makromol. Chem.* **98**, 179 (1966)
- ³⁰⁾ F. A. Bovey, I. M. Kolthoff, A. I. Medalia, E. J. Meehan, "Emulsion Polymerization", Interscience Publishers, New York 1955, p. 344
- ³¹⁾ P. A. Weerts, J. L. M. van der Loos, A. L. German, *Makromol. Chem.* **190**, 777 (1989)
- ³²⁾ P. A. Weerts, J. L. M. van der Loos, A. L. German, *Makromol. Chem.* **191**, 2615 (1990)
- ³³⁾ P. A. Weerts, A. L. German, *Macromolecules* **24**, 1622 (1991)