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Particle growth in butadiene emulsion polymerization, 4^{a)}

The promoting effect of mercaptans

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SUMMARY:

The observation that butadiene emulsion polymerizations in the presence of fatty acid emulsifiers need minimal amounts of tertiary or *n*-dodecanethiols to polymerize at a reasonable rate is often referred to as the *promoting effect of mercaptans* and is evaluated in this paper. Experimental evidence is presented which shows that fatty acid emulsifiers can actively reduce the average number of radicals per particle. In this paper it will be shown that three components are necessary for retardation of the rate of polymerization in the absence of dodecanethiol to occur: 1) Only diene monomer polymerizations show retardation. 2) Only peroxodisulfate-initiated polymerizations show retardation. 3) Retardation of the rate of polymerization only occurs in the presence of fatty acid emulsifiers. These three components are combined for the first time in a reaction scheme which is an extension of a reaction scheme proposed by Kolthoff in 1951. Experimental evidence justifies the suggestion that reactions between a fatty acid radical and butadiene play an important role in the *promoting effect*.

Introduction

Chain transfer agents or modifiers like thiols have always played a crucial role in reducing the molecular weight of the polymers formed during the process of butadiene and styrene-butadiene emulsion (co)polymerization¹⁾. It was noted that the presence of thiols had a complex effect on the polymerization kinetics as well. Important observations were reported by Kolthoff et al.^{2–5)}. The latter published a series of papers on the effect of C₁₂ thiols on the rate of polymerization and their possible effect on the dissociation rate of peroxodisulfate. This series of papers was induced by the observation that a minimal amount of dodecanethiol was necessary to obtain a reasonable rate of polymerization in peroxodisulfate-initiated butadiene emulsion polymerization in the presence of saturated carboxylic acid soaps of the rosin acid type. This effect has become known as the *promoting effect of mercaptans*. The dodecanethiols are commonly used as modifiers of the molecular weight, but due to the *promoting* effect they serve two purposes. The pursuit of the effect of dodecanethiols is of considerable importance, since in industrial practice butadiene rubbers are often polymerized in the presence of dodecanethiols. However, the effects of thiols on the general kinetics of emulsion polymerization are not solved as yet and hamper the unraveling of standing problems like the peroxodisulfate initiating efficiency discussed elsewhere⁹⁾.

a) Part 3: cf. ref. 27).

This paper reports on well characterized emulsifier-free experiments and experiments in the presence of fatty acid emulsifiers performed in an effort to elucidate the effect of tertiary dodecanethiol (TDM) on the rate of nucleation in butadiene emulsion polymerization.

Experimental part

Materials

Butadiene (DMS Chemicals, Geleen, The Netherlands) was distilled directly from a 27-L storage vessel into a cooled steel recipient. A two-isomer mixture of tertiary dodecanethiol (TDM) was used (Fluka AG, Buchs, Switzerland): $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{SH}$ 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, FRG), sodium carbonate (p.a. Merck, Darmstadt, Germany), stearic acid (z.s. Merck-Schuchard, Darmstadt, Germany) and diethyl ether (Genfarma b.v., Maarsen, The Netherlands) were all used without further purification. Water was doubly distilled and purged with nitrogen to remove oxygen. NMR samples were dissolved in deuterated chloroform (Aldrich Chemicals Company Inc., Milwaukee, USA).

Ab initio polymerizations

Experimental details and recipes are elaborately explained elsewhere⁶⁻⁸. The emulsion polymerizations were carried out in a stainless steel reactor vessel (2,4 L, K. K. Juchheim, Bernkastel-Kues, Germany) fitted with four baffle plates located at 90° intervals and a twelve-bladed turbine-type impeller. The reactor was charged at room temperature with all ingredients under nitrogen, except for the butadiene. The head space was cleared of inert gases by flushing through gaseous butadiene followed by evacuation. The amount of butadiene prescribed by the recipe was added last to the reactor. After adding all the ingredients, the mixture was emulsified. The rise of temperature was taken as the starting point of the polymerizations.

Gravimetric samples were collected using a high pressure proof syringe. From these samples the conversion was calculated. Conversions assessed in this way were accurate to within 0,5%⁷. The rate per particle, R_p/N , was determined by linear regression from the linear part of the conversion-time plots.

Seeded emulsion polymerizations

Experimental details and recipes are elaborately explained elsewhere⁷⁻⁹. 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 slope of the linear part of these plots is determined by linear regression.

The recipe used is reported elsewhere⁷ 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 under the section *ab initio* polymerizations⁶. 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. The beginning of polymerization was taken as the time when the temperature

began rising from room temperature to 60 °C. No retardation was noticed in any of the polymerizations.

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 OsO₄ 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 .

Results and discussion

The role of thiols is not restricted to modification of the molecular weight. The effects of sparingly water-soluble TDM on the kinetics of an emulsion polymerization are numerous. The following section will summarize the possible effects of TDM on the kinetics and the experimental evidence reported in literature.

In theories on exit of radicals from latex particles, transfer of radical activity from the polymer chain to a mobile and short molecule, usually the monomer molecule, is often introduced¹⁰⁻¹³. The short and mobile radical thus formed is then suggested to be capable of desorbing from the particle. Therefore, it is conceivable that the addition of some chain transfer agents could induce exit of radicals from latex particles, thus seriously retarding the polymerization rate. This has been discussed elsewhere⁹, where it has become clear that tertiary dodecanethiol in fact causes the reverse: it may reduce radical desorption. It was shown⁹ that the independence of the rate of polymerization (R_{pol}) from the initiator concentration, [I], is caused by the presence of TDM. It was reported^{6,9} that the effect of TDM in emulsifier-free polymerizations is restricted to low initiator concentrations. At high initiator concentrations the presence of TDM has no effect on the emulsifier-free emulsion polymerization of butadiene. The reports on the promoting effect, however, show that there is a strong effect of TDM at high initiator concentration in the presence of saturated fatty acid emulsifiers^{5,14}. The reduction of radical desorption therefore cannot explain the promoting effect but will nevertheless occur concurrently.

Various investigations were dedicated to the problem of the minimum concentration of TDM necessary to polymerize diene monomers at a reasonable rate in the presence of fatty acid soaps. Close examination of the available data reveals requirements for retardation in the absence of TDM to occur.

1) Retardation only occurs in the emulsion polymerization of diene monomers like butadiene and isoprene^{5,14,15}. Styrene can readily be polymerized using a variety of emulsifiers including saturated fatty acid soaps and initiators, and without thiols⁴.

2) The differences between rates of polymerization and nucleation in the presence and absence of TDM, at high peroxodisulfate concentration, only occur in the presence of emulsifier^{6,15}.

3) The observed retardation in the absence of TDM is only observed when peroxodisulfate is used as initiator. When an oil-soluble initiator like AIBN is used, the presence of TDM has little effect on the rate of polymerization¹⁵.

In an effort to elucidate these puzzling phenomena several authors suggested explanations for the effects of dodecanethiols. The following sections are a summary of the explanations given in literature and of experimental evidence in favour of, or in contradiction with, the explanations.

The enhancement of peroxodisulfate dissociation by dodecanethiols

It has been suggested by Blackley¹⁶⁾ in his well known book that the following reaction scheme describes the reaction of TDM to form a redox couple with peroxodisulfate, thus enhancing the dissociation rate of peroxodisulfate and introducing a non-charged radical for which no barrier exists against entry into a charged latex particle:

Overall stoichiometry:

However, it is not clear who reported the redox couple effect, and it definitely has not been reported by Kolthoff et al.³⁾ in 1947, although this is suggested between the lines in Blackleys book. The effect of TDM on the dissociation rate coefficient, k_d , is well described in literature. Kolthoff et al.⁴⁾ report that dodecanethiol does not enhance the dissociation rate of peroxodisulfate in the emulsion polymerization of styrene and by direct determination in emulsifier solutions³⁾. Kolthoff et al. never reported an enhancement of the dissociation rate of peroxodisulfate by dodecanethiols. Weerts et al.¹⁷⁾ report measurements of the k_d of peroxodisulfate in the presence of TDM during actual emulsion polymerizations as a function of the dresinate 214 concentration. At low dresinate 214 concentrations the value of k_d compares excellently to the value of Kolthoff et al.²⁾ measured in water (0,1 M NaOH). Apart from the experiments cited, the redox couple model also fails to explain why TDM does not influence the rate of styrene emulsion polymerizations. Moreover, the emulsifier-free emulsion polymerizations reported by Weerts et al.¹⁵⁾ and in this paper show that the rate of polymerization is unaffected by the presence of TDM at high peroxodisulfate concentrations in the absence of emulsifier. The literature evaluation given above leaves only one conclusion: TDM has no effect on the dissociation rate of peroxodisulfate, and the existence of a redox couple does not lead to a satisfactory explanation of the promoting effect.

The enhancement of radical absorption by dodecanethiols

It is proposed that peroxodisulfate radicals, being negatively charged and water soluble, have no driving force for diffusion into the organic phase of monomer-swollen

negatively charged micelles or particles. This was first recognized by Priest¹⁸⁾, whereas Vanderhoff¹⁹⁾ first proposed that sulfate radicals grow in the aqueous phase to surface-active oligomers before they are adsorbed on the particle surface and subsequently enter the particle. Recently Maxwell et al.²⁰⁾ reported a new entry model on the basis of this concept. This model suggests that the rate-determining step for radical entry is the growth of the water-soluble sulfate radical to a oligomeric radical of a degree of polymerization, z , at which this oligomer becomes surface active and enters the particles instantaneously.

The general entry theory is extended to incorporate the effect of sparingly water-soluble thiols like TDM²¹⁾. In addition to the termination and propagation possibilities of the oligomeric radical, a possible transfer of radical activity to TDM is proposed. This seems unlikely given the reported low water solubility of TDM, $[TDM]_{aq}$. On the other hand, Kolthoff et al.³⁾ report a value of $[TDM]_{aq} = 3 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. This value is reported to be strongly enhanced by the presence of fatty acid soaps³⁾. Maxwell et al.²¹⁾ use the value of $3 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. It elegantly explains the observation that only a minimal amount of dodecanethiol is necessary, since it involves water phase kinetics and, due to the low water solubility of dodecanethiols, a very small amount is needed to saturate the water phase. In the presence of a monomer-swollen polymer phase, the dodecanethiols will be partitioned mainly in the polymer phase, but individual dodecanethiol molecules will be transferring rapidly between the particle and aqueous phase. Although the dodecanethiol concentration in the water phase might be significantly below its saturation value, this will still be orders of magnitude higher than the average radical concentration in emulsion polymerizations: $[T^*]_{aq} = 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ ¹⁰⁾. Consequently, it is argued by Maxwell et al.²¹⁾ that a mercaptyl radical has no barrier against radical absorption into a latex particle and entry will therefore be instantaneous. It is argued that this model offers an explanation for the observed difference between butadiene and styrene emulsion polymerization in the absence of TDM. During the growth of the sulfate radical to become a surface-active oligomeric radical, a portion of the radicals will be terminated. Thus the higher the value of z , the less efficient entry of radicals will be. The proposed values of z for styrene and butadiene are 2 and 3, respectively. Although the values seem practically the same, it explains a large difference in initiator efficiency (the value of z is in the power of the initiator efficiency). If, however, chain transfer to TDM would take place in the aqueous phase, the initiator efficiency would be strongly enhanced. Whether the difference in z between styrene and butadiene is large enough to generate the difference in behaviour between the two monomers in the absence of TDM is questionable. Weerts et al.¹⁵⁾ and Verdurmen et al.⁹⁾ reported that the emulsifier-free emulsion polymerizations of butadiene shows no difference between the rates of polymerization with or without TDM at high peroxodisulfate concentration. However, it was reported⁹⁾ that the presence of dodecanethiol makes a strong difference at low peroxodisulfate concentration, whereas Maxwell et al.²¹⁾ predict a large influence at high peroxodisulfate concentration. Moreover, it has been proved⁹⁾ that the difference in rate of polymerization is not due to enhanced entry of radicals by dodecanethiol, since it would require higher entry rates than peroxodisulfate dissociation allows for. The extended model incorporating the

effect of TDM in predicting rates of entry of radicals in latex particles is therefore not successful, although the basic model does seem to hold for styrene²⁰⁾ as well as butadiene^{7, 9)}.

Retardation of the rate of polymerization caused by saturated fatty acid emulsifiers

In 1951 Kolthoff et al.³⁾ suggest an expanded reaction scheme for the transfer reaction of a sulfate radical to dodecanethiol involving fatty acid emulsifiers:

Considerable experimental evidence exists for the proposed reaction scheme. Again the mercaptyl radicals could be envisaged as the prime polymerization-initiating species, while at the same time the fatty acid soap radicals are considered incapable of initiating polymerizations.

Weerts et al.¹⁵⁾ report a decreasing retardation effect for different emulsifiers. The authors linked this to the presence of chemical impurities in the emulsifiers. Dresinate 214 (rosin acid soap), K-stearate, K-oleate and SDS gave less retardation in this order, and emulsifier-free emulsion polymerizations showed no retardation. What the effect of the impurities is, or on what exactly the impurities would have an effect, is not stated. Although the data suggests that the chemical purity of the emulsifiers used is an important parameter, it is not stated why the presence of TDM overcomes these problems. The reaction mechanism of Kolthoff and Miller³⁾ adequately explains the observations reported by Weerts et al. Especially the observation that emulsifier-free emulsion polymerizations are not affected by the presence of TDM is a strong indication of the validity of Kolthoff's reaction scheme: the emulsifier serves as a retarder for radical absorption and therefore emulsifier-free polymerizations are not retarded. On the other hand, the Kolthoff reaction scheme fails to explain why styrene emulsion polymerizations using fatty acid emulsifiers are not in need of TDM to occur at a reasonable rate. The Kolthoff scheme seems to rely on the fact that the fatty acid radicals are not reactive, which can be refuted on the basis of styrene polymerizations⁴⁾.

In order to clarify the effect of TDM on the kinetics of the emulsion polymerization of butadiene, several emulsifier-free experiments were performed. In Fig. 1 the conversion-time data of two *ab initio* emulsifier-free experiments are presented: one polymerized in the presence of TDM and one in the absence of TDM according to the standard recipe reported elsewhere⁶⁾ using an impeller speed of 750 rpm.

Obviously there is little difference in rate of polymerization or in length of the nucleation period as an effect of the presence of TDM. The average particle diameters, the particle numbers and rates per particle of both experiments are presented in Tab. 1. These experiments are in excellent agreement with experiments reported by Weerts et

Fig. 1. Conversion-time curves for standard polymerizations with ($\square$) and without TDM ($\triangle$), performed at an impeller speed of 750 rpm

Tab. 1. Average particle diameters, d_n and d_w , measured with TEM, particle size polydispersity, $P = d_w/d_n$, particle number, N , and rate per particle, R_{pol}/N , for the experiments shown in Fig. 1. [TDM] is 1% on monomer, reaction temperature = 80 °C

TDM	$\frac{d_n}{\text{nm}}$	$\frac{d_w}{\text{nm}}$	P	$\frac{N \cdot 10^{-17}}{\text{dm}^{-3}}$	$\frac{(R_{pol}/N) \cdot 10^{21}}{\text{mol} \cdot \text{s}^{-1}}$
With	157	162	1,032	2,0	2,2
Without	151	158	1,046	2,3	2,0

al.¹⁵⁾. However, the nucleation effects occurring in these experiments, depicted in Fig. 2, may render direct comparison ambiguous.

To avoid particle nucleation effects, seeded emulsifier-free emulsion polymerizations are performed to verify whether the presence of TDM has any effect on the average number of radicals in the latex particles, $\bar{n}$. The seed latex used for these experiments was prepared emulsifier-free and in the absence of dodecanethiols to prevent the

Fig. 2. Particle size (d_n) distributions (TEM) of latexes of standard polymerizations with ($\square$) and without TDM ($\triangle$), performed at an impeller speed of 750 rpm

possibility of introducing TDM via the seed latex. Consequently, the gel content of the latex was high. However, the swellability of the latex was not affected, as was checked by swelling experiments described elsewhere⁹). The particle diameter was chosen in the Smith-Ewart case I regime⁷). In Tab. 2 the results of both seeded experiments are shown. Within the accuracy of the experiments no effect of TDM on $\bar{n}$ is observed.

Tab. 2. Values of the monomer concentration at the beginning of interval III in the particles, C_{m0} , initial amount of monomer per volume of aqueous phase, n_{m0} , the particle number, N , and average number of radicals per particle, $\bar{n}$, of standard seeded experiments with and without TDM. [TDM] is 1% on monomer, reaction temperature = 60°C

Experiments	C_{m0} mol · dm ⁻³	n_{m0} mol · dm ⁻³	$N \cdot 10^{-16}$ dm ⁻³	$\bar{n}$
With TDM	5,40	1,42	5,2	0,36
Without TDM	5,33	1,38	5,2	0,30

In order to verify the importance of particle number in polymerizations in the presence of fatty acid soaps, a seeded experiment was performed on a TDM-free seed latex which was covered with dresinate 214. In order to obtain a full coverage of the particle surface with dresinate 214, the seed latex was dialysed against a buffered dresinate 214 solution. This way *in situ* formed not covalently bonded oligomeric surfactant, located at the particle surface, can be exchanged with dresinate 214. Moreover, the water added to the recipe was saturated with dresinate under CMC conditions^{17, 22}).

In Tab. 3 the results of this experiment, a standard seeded emulsifier-free experiment with TDM and a comparable experiment with TDM but without initiator (thermal polymerization) are shown. The value for $\bar{n}$ obtained from the seeded experiment in the presence of dresinate 214, $\bar{n} = 0,09$, is considerably below the usual value for a comparable particle diameter, $\bar{n} = 0,35$. Moreover, a seeded emulsion polymerization in the absence of any initiator (thermal polymerization) has a comparably low $\bar{n}$.

Tab. 3. Values of the initiator concentration, [I], monomer concentration at the beginning of the polymerization in the particles, C_{m0} , initial amount of monomer per volume of aqueous phase, n_{m0} , the particle number, N , and average number of radicals per particle, $\bar{n}$, of a seeded experiment. [TDM] is 1% on monomer, reaction temperature = 60°C

Experiment	d_w nm	$[I] \cdot 10^3$ mol · dm ⁻³	C_{m0} mol · dm ⁻³	n_m mol · dm ⁻³	$N \cdot 10^{-16}$ dm ⁻³	$\bar{n}$
Dresinate without TDM	165	10	5,3	1,35	5,13	0,09
Dresinate with TDM	166	10	5,4	1,42	5,17	0,35
Dresinate with TDM (thermal)	102	0	3,8 ^{a)}	0,77 ^{a)}	22,3	0,01

^{a)} Seeded Recipe 2 is used (reported elsewhere⁹).

The experiment proves that dresinate 214 actively prevents radicals entry into latex particles, thus also indicates that radicals are prevented to enter dresinate 214 micelles. This is a strong indication that indeed the dodecanethiol is necessary to secure reasonable radical activity in the latex particles.

Retardation of polymerization caused by a combination of fatty acid emulsifiers and diene monomers

At this stage two of the observed essential components for the *promoting effect of mercaptans* are clarified:

1) The promoting effect only occurs when peroxodisulfate is used as initiator. When an oil-soluble initiator like AIBN is used in the presence of dodecanethiols, this has little effect on the rate of polymerization. This is readily explained by the fact that oil-soluble initiator fragments do not need to add monomer until surface activity develops in order to enter the organic phase inside a latex particle. Possibly initiation from within the particle occurs in this particular case. Also, radicals produced by these initiators may not transfer their radical activity to the fatty acid emulsifier molecules. These problems reach beyond the scope of this work.

2) The promoting effect of TDM only occurs in the presence of emulsifiers capable of accepting radical activity, like fatty acid emulsifiers. This also explains why emulsifier-free experiments are not in need of TDM to polymerize monomer.

The last and most puzzling problem remains to be solved: The *promoting effect of mercaptans* seems specific of diene monomers when using fatty acid soaps but is not observed when polymerizing styrene⁴⁾ or any other monomer. In order to explain this behaviour, a reaction mechanism is proposed trying to combine the three elements leading to retardation of polymerization in the absence of dodecanethiols: peroxodisulfate, saturated fatty acid emulsifiers and diene monomers. The reaction starts with the dissociation of peroxodisulfate (Eq. (1)). The sulfate radicals subsequently react with the saturated fatty acid emulsifier to give a carboxyl radical following the reaction scheme reported by Kolthoff et al.³⁾ (Eq. (6)). This fatty acid emulsifier radical obviously is capable of forming polystyrene at a normal rate, as can be deduced from styrene emulsion polymerizations using fatty acid emulsifiers in the absence of dodecanethiol. Therefore, there is no reason to assume that the fatty acid-radical is incapable of polymerizing butadiene. It is now proposed for the first time that this fatty acid emulsifier radical might react with diene monomer via a *hetero Diels-Alder* or *concerted* reaction:

followed by:

The butadiene-fatty acid adduct **A** formed by reaction (9) is supposed to form polybutadiene at a low rate, as can be deduced from the low rates of peroxodisulfate-initiated butadiene emulsion polymerization using fatty acid emulsifiers in the absence of TDM. Diels-Alder reactions with double bonded oxygen are known²³⁾ but will only occur with diene monomers and not with styrene, thus explaining the difference in behaviour between the diene monomers and, for instance, styrene. The $\text{OH}^\bullet$ radical produced by reaction (10) will probably also transfer its radical activity to fatty acid, which is present in abundance in the aqueous phase as compared to free radicals. There are two ways of explaining the observed behaviour.

1) Dodecanethiol could enhance the radical entry into particles through radical transfer from the butadiene-fatty acid emulsifier adduct to dodecanethiol and subsequent radical entry. This explains the *promoting effect of mercaptan* as an effect of enhancement of radical adsorption. This is not in conflict with the suggestions ventilated by Verdurmen et al.⁹⁾ where an effect of radical absorption was refuted in that context. The polymerizations described currently involve high peroxodisulfate concentrations ($[\text{I}] \gg 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$), a region where enhancement of radical absorption is not in conflict with current ideas on initiator dissociation.

2) Fatty acid emulsifiers 'scavenge' radicals produced in the aqueous phase. The radical scavenging is presumably not complete, as can be deduced from the low rate of polymerization in the absence of TDM using fatty acid emulsifiers. This, together with the ability of TDM to reduce radical desorption⁹⁾, may lead to 'normal' high polymerization rates in the presence of TDM.

It is likely that both mechanisms occur concurrently. However, there is a striking resemblance in the conduct of dodecanethiol-free polymerizations between reactions with fatty acid emulsifier present and those in the presence of Fremy salt²⁴⁾. In both cases retardation of the polymerization only occurs in the absence of TDM, most likely via the same mechanism, i. e., radical scavenging in the aqueous phase by either Fremy salt or fatty acid emulsifier. The enhancement of radical entry by TDM might occur but is probably not the main effect deduced from the analogies in the conduct of butadiene emulsion polymerizations in the absence and presence of TDM at low initiator concentrations.

Experiments were performed in an attempt to isolate any reaction products created during a peroxodisulfate-initiated emulsion polymerization of butadiene in the presence of a fatty acid emulsifier. For this reason equivalent amounts of peroxodisulfate, stearate and butadiene were polymerized at 90 °C for 15,5 h in a dodecanethiol-free reactor. Tab. 4 shows the recipe used. Stearate was chosen as a model fatty acid

Tab. 4. Recipe utilizing equivalent amounts of fatty acid emulsifier, peroxydisulfate and butadiene; impeller speed: 300 rpm, temperature: 90 °C. The reaction temperature of 90 °C was chosen to maximize the amount of radicals produced

Ingredients	Description	Recipe
Water	Maximum reactor filling	1 100 g
Butadiene	Aqueous solubility + gascap	≈ 10 g
Potassium peroxydisulfate	$20 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$	5,96 g
Potassium carbonate	Equivalent to peroxydisulfate	7,6 g
Stearic acid	$20 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$	6,26 g

emulsifier to avoid effects of impurities in the dresinate 214 (natural product) which would seriously interfere with the analysis of the eventual latex.

Due to the low amount of butadiene utilized, insignificant particle formation occurred. The resulting latex was extracted with diethyl ether. The diethyl ether was separated, evaporated, and the obtained dry solid was dried under vacuum at room temperature. ^1H NMR in deuterated chloroform features the spectrum shown in Fig. 3. The signals belonging to polybutadiene (at $\delta = 5\text{--}6$ and 2 ppm)²⁵⁾ and stearate (at $\delta = 0,89, 1,29$, and 2,35 ppm)²⁶⁾ are manifest.

These limited experiments and analysis do not render unambiguous proof for the suggested reaction mechanism. However, the peaks in the ^1H NMR spectrum at $\delta = 4,65$ and 4,55 ppm offer an indication that reaction between stearate, peroxydisulfate and butadiene yields a reaction product other than polybutadiene and residual stearate, probably the final product, marked **B**, of reaction (10). The product **B** has, in the light

Fig. 3. ^1H NMR results of an analysis of a latex polymerized using the recipe of Tab. 4. On the right hand side an enlargement of the significant signals is given

of ^1H NMR, only two different ^1H signals as compared with a mixture of butadiene and stearate, namely, those from the ^1H atoms on the carbon atoms marked 1 and 4. The presence of the residual double bond shifts the signals to higher ppm values. The doublets at 4,65 and 4,55 ppm of carbon number 1 could originate from two possible configurations (*cis* and *trans*) of the C-2,3 double bond. The signal at 4,1 ppm is not explained, but on the left hand side of this rather large signal the presence of a smaller signal, probably from the H-atoms on carbon atom number 4, can be seen. The intensity of this signal is proportional to the signals of the H-atoms on carbon atom number 1.

With this experiment in mind and combined with the total evaluation of the *promoting effect* given above, it now seems justified to state that chemical reactions between fatty acid radicals and diene monomer play an important role in determining the *promoting effect of mercaptans* on the rate of butadiene emulsion polymerization in the presence of fatty acid emulsifiers. Additionally, it can be stated that no currently available model based on physical chemistry principles adequately describes the *promoting effect*.

Conclusions

Close examination of the *promoting effect of tertiary dodecyl mercaptan* (TDM) on the rate of emulsion polymerization in general reveals that three recipe components are necessary for retardation to occur: 1) fatty acid emulsifiers, 2) peroxodisulfate, 3) diene monomers. The reaction mechanism suggested by Kolthoff et al.³⁾ involving a radical transfer from sulfate radicals to fatty acid emulsifiers explains the necessary presence of the first two recipe components for retardation to occur. Concurrently, the observation that emulsifier-free butadiene emulsion polymerizations are not in need of TDM to polymerize at a reasonable rate is explained. The third component required for retardation to occur, diene monomers, is incorporated in a new mechanism involving a *Diels-Alder* or a *concerted* reaction between the fatty acid radical shown to be formed by Kolthoff et al. and diene monomers. Reaction products other than polybutadiene and residual stearate, and similar to the expected compounds, were detected by ^1H NMR. The *promoting effect of mercaptan* is explained as a decrease of radical desorption, caused by TDM.

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