

## Emulsion polymerization of butadiene. 4. Effect of thiols

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## Emulsion polymerization of butadiene, 4<sup>a)</sup>

### Effect of thiols

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#### SUMMARY:

The role of thiols of low water solubility, commonly used in the emulsion polymerization of butadiene, has been considered. The following effects have become apparent: (1) dodecanethiols act as efficient chain transfer agents in limiting the formation of heavily cross-linked polymer networks; (2) the monomer concentration within the particles is not influenced by such thiols; (3) C<sub>12</sub>-thiol radicals do not desorb because of their extremely low water solubility. The 'promoting effect' of thiols in emulsion polymerizations of diene-hydrocarbons is still poorly understood, but it appears to be related to impurities present in the emulsifier, as it was found completely absent in emulsifier-free polymerizations.

#### Introduction

In earlier papers the *ab initio* emulsion polymerization of butadiene with Dresinate 214<sup>1)</sup> and sodium dodecylsulfate<sup>2)</sup> as emulsifiers, both in the presence of tertiary dodecanethiol as chain transfer agent, were discussed. Chain transfer agents are routinely used in diene-polymerizations to limit the extent of branching and cross-linking of the polymer, and thus the amount of heavily cross-linked insoluble gel. A limited gel content greatly facilitates processability of the crude polymer, such as in the compounding of synthetic rubbers.

However, chain transfer agents also exert other, sometimes less desirable effects in emulsion polymerization systems. It is well known they can promote radical desorption<sup>3,4)</sup>, thus lowering the rate of polymerization. Furthermore, slightly water-soluble thiols were found to be essential to bring about reaction at acceptable rates in persulfate-initiated polymerizations of butadiene(75 by weight)-styrene(25 by weight)<sup>5)</sup> or butadiene<sup>6)</sup>, a phenomenon referred to as the 'promoting effect'.

This article describes the various effects of the chain transfer agent tertiary dodecanethiol (t-DT) in the *ab initio* emulsion polymerization of butadiene, with regard to the process of gel formation as well as to the reaction kinetics.

#### Experimental part

*Materials and procedures:* All materials used are of high purity quality, except Dresinate 214 (from Hercules bv, Den Haag, Holland) which is a disproportionated mixture of abietic acid-type of derivatives, and tertiary dodecanethiol (from Pennwalt Chemicals, Rotterdam, Holland) which

<sup>a)</sup> Part 3: cf. P. A. Weerts, J. L. M. van der Loos, A. L. German, *Makromol. Chem.* **192**, 1993 (1991), preceding article.

is a crude mixture of C<sub>12</sub>-isomers. A well-defined mixture of two isomeric t-dodecanethiols (from Fluka AG, Buchs, Switzerland) was also used: (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>SH and (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C(CH<sub>3</sub>)(SH)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>. Unless stated otherwise, t-dodecanethiol (t-DT) refers to the commercial grade material supplied by Pennwalt. 1-Dodecanethiol (n-DT, 90%, from Merck, Darmstadt, FRG) was used as received.

The standard polymerization recipes and reaction conditions are given in Tab. 1, while further experimental details can be found in earlier papers<sup>1,2</sup>.

Tab. 1. Standard polymerization recipes in parts by weight<sup>a)</sup>

Ingredient	Recipe 1	Recipe 2
Water	230	230
Butadiene	100	100
Dresinate 214	7,6	
Sodium dodecyl sulfate (SDS)		7,6
K <sup>+</sup> /Na <sup>+</sup> carbonate <sup>b)</sup>	4,4	2,0
K <sup>+</sup> /Na <sup>+</sup> persulfate <sup>b)</sup>	0,8	0,7
t-Dodecanethiol	0,7	0,7

a) [Initiator] = 13 mmol · L<sup>-1</sup>, temp. = 62 °C, pH 10,5–10,8.

b) In recipe 1 potassium salts and in recipe 2 sodium salts were used.

The average particle diameters measured with dynamic light scattering (DLS) are weight-average diameters  $\bar{d}_w (= \sum n_i \cdot d_i^3 / \sum n_i \cdot d_i^2)$ , and those obtained with transmission electron microscopy (TEM) mean volume-average diameters  $\bar{d}_v (= \{\sum n_i \cdot d_i^3 / \sum n_i\}^{1/3})$ , unless stated otherwise. The particle number  $N$  (in mL<sup>-1</sup>) was calculated from the polymer content and the average particle volume. The polymerization rate  $R_{pol}$  (in g · mL<sup>-1</sup> · s<sup>-1</sup>) was taken as the slope of the linear portion of the conversion vs. time curve, i. e., interval II.

*Gel analysis:* Although the gel content of a cross-linkable polymer is theoretically well defined as the fraction of material of "infinite" molecular weight, experimental criteria are usually more arbitrary, and depend strongly on the experimental procedure. The same holds for the gel point, i. e., the conversion at which the first insoluble polymer network makes its appearance. Therefore, the procedures followed to determine the gel content and gel point in this study will be described in some detail.

The first method is based on *toluene extraction* of the soluble fraction of polybutadiene (PB). The insoluble residue is considered the gel. The polybutadiene is isolated from the latex by precipitation in acidic methanol, followed by repeated washing with water and methanol. The polymer is dried under nitrogen at 50 °C. Toluene (100 mL) is pipetted to 1 g of an accurately weighed PB sample in a stoppered flask. After gentle shaking for at least 48 h at room temperature, the content is passed over a 100 mesh filter, and 50 mL of the filtrate evaporated to dryness in a weighed aluminium dish.

The gel content is simply calculated according to  $(w_{PB} - 2 w_F) / w_{PB}$ , where  $w_{PB}$  is the weight of the PB sample and  $w_F$  is the weight of the dried filtrate. Linear extrapolation to zero of the gel content as a function of conversion gives the experimental gel point. This can be markedly different from the theoretical gel point, since any possible gel structures of latex particle dimensions or smaller (i. e., microgel) that persist after coagulation remain undetected by this method, as they pass through the filter. It is assumed that during isolation of PB from the latex the microgel agglomerates completely.

The so-called *vistex method* is based on measurements of the intrinsic viscosity  $[\eta]$  of diluted latex solutions. The procedure is a slightly modified version of the one described by Henderson and Legge<sup>7</sup>. One gram of latex is dissolved in 100 mL toluene-isopropyl alcohol (80:20 by vol.), and diluted with pure toluene, successively. The viscosity was measured with an Ubbelohde viscometer at 25 °C, and  $[\eta]$  in pure toluene is obtained by extrapolation of the reduced or inherent

viscosity to zero concentration. A plot of  $[\eta]$  versus conversion has a pronounced maximum, taken as the gel point.

Initially  $[\eta]$  increases with conversion, as molecular weight increases through branching and cross-linking. Although the presence of toluene-swollen microgel may still raise  $[\eta]$  somewhat, as the amount of microgel and the cross-link density therein increases, the contribution to  $[\eta]$  inevitably decreases and a maximum in the  $[\eta]$  vs. conversion curve occurs.

## Results and discussion

### Thiol as chain transfer agent

The gel points were determined with the vistex and extraction procedures for polymerizations with Dresinate 214 (recipe 1) as emulsifier (Fig. 1). Agreement between these techniques is good; in both cases toluene was used as solvent/diluent. Results with varying amounts of t-DT are summarized in Tab. 2.

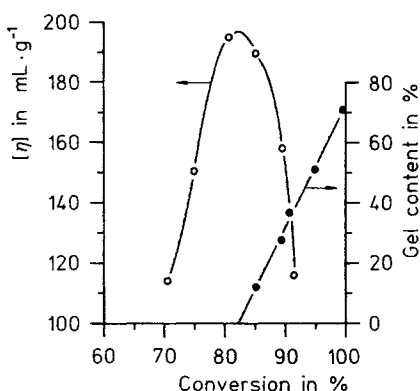


Fig. 1. Determination of the gel point and gel content with the vistex (○) and toluene extraction procedure (●)

Tab. 2. Gel points for polymerizations with Dresinate 214 (recipe 1) and different amounts of t-dodecanethiol (t-DT)<sup>a)</sup>

$10^3 \cdot C_{t-DT}$ <sup>b)</sup> g · g <sup>-1</sup>	Gel point in %		% Conversion after				$10^5 \cdot R_{pol}$ g · mL <sup>-1</sup> · s <sup>-1</sup>
	vistex	extraction	2h	4h	6h	8h	
0,0	25 26	28	16	42	69	85	1,6
3,5	68 73	72	18	42	68	87	1,6
7,0	83 84	83 84	15	43	71	89	1,7

a) The particle number was  $1,0 (\pm 0,05) \cdot 10^{15} \text{ mL}^{-1}$  in all experiments.

b)  $C_{t-DT}$  expressed in grams t-DT per gram of butadiene.

As expected, the gel point goes to higher conversions with increasing amounts of thiol. However, there appears to be no significant effect on the polymerization kinetics; both  $R_{pol}$  and  $N$  are identical within experimental error. The polymerization rate  $R_{pol}$  is usually expressed as:

$$R_{\text{pol}} = \frac{dc}{dt} n_{\text{M}}^{\circ} = k_{\text{p}} C_{\text{M}} (\bar{n}/N_{\text{Av}}) N \quad (1)$$

where  $c$  is the fractional conversion,  $n_{\text{M}}^{\circ}$  is the initial amount of monomer per unit volume of water,  $k_{\text{p}}$  is the propagation rate coefficient,  $C_{\text{M}}$  the monomer concentration within the latex particles,  $\bar{n}$  the average number of radicals per particle, and  $N_{\text{Av}}$  Avogadro's number.

Cross-linking and network formation may possibly affect the monomer concentration within the particles (and thus the kinetics). Even when monomer and polymer are completely miscible, the swelling of a particle is limited, because the free energy of mixing, which favours swelling, is counterbalanced by the resulting increase in interfacial energy. The monomer concentration at saturation swelling is described by the Morton-Kaizerman-Altier equation<sup>8)</sup>:

$$-H_{\text{v}} - H_{\text{v}}^2 \ln(1 - 1/H_{\text{v}}) = \chi + \frac{4 V_{\text{M}} \gamma}{d R T} H_{\text{v}}^{5/3} \quad (2)$$

where  $H_{\text{v}}$  is the volume swelling ratio,  $V_{\text{M}}$  the molar volume of the monomer,  $d$  the unswollen particle diameter,  $\chi$  the Flory-Huggins interaction parameter,  $\gamma$  the interfacial tension,  $R$  the gas constant and  $T$  the absolute temperature.  $H_{\text{v}}$  is related to the monomer volume fraction  $\phi_{\text{M}}$  by:  $H_{\text{v}} = 1/(1 - \phi_{\text{M}})$ .

For densely cross-linked latex particles, the contribution of the elastic energy in limiting the swelling capacity is given by the Flory-Rehner theory<sup>9)</sup>, and is expressed in Eq. (2) by an extra term on the left-hand side:

$$-(V_{\text{M}} \rho_{\text{p}}/M_{\text{c}})(H_{\text{v}}^{5/3} - H_{\text{v}}/2) \quad (3)$$

where  $\rho_{\text{p}}$  is the polymer density and  $M_{\text{c}}$  the average molecular weight of the segments between two cross-links.

Given the large variation in gel point (i. e., cross-link density) and the constancy of  $R_{\text{pol}}$  and final  $N$  in the experiments described above (Tab. 2), the effect of t-DT on  $C_{\text{M}}$  appears negligible. Even in the absence of t-DT the cross-link density is still too low (or alternatively  $M_{\text{c}}$  too large) to further restrict monomer solubility within the particles under the prevailing experimental conditions.

In interval III (i. e., the regime where polymerization is commencing in the latex particles in the absence of monomer droplets) the monomer concentration in the particles is decreasing continuously, so it is convenient to remove  $C_{\text{M}}$  from the right side of Eq. (1) and write the expression in terms of the fractional conversion in interval III,  $x$ , with  $x = (C_{\text{M}}^{\circ} - C_{\text{M}})/C_{\text{M}}^{\circ}$ , and  $C_{\text{M}}^{\circ}$  the initial monomer concentration in the particles<sup>10)</sup>:

$$-\frac{d \ln(1-x)}{dt} = \frac{k_{\text{p}} C_{\text{M}}^{\circ} \bar{n} N}{N_{\text{Av}} n_{\text{M}}} \quad (4)$$

where  $n_M$  is the amount of monomer present at the beginning of interval III. Since  $n_M = (1-x')n_M^0$ , with  $x'$  the conversion where interval III begins, we can easily calculate  $x'$  from the experimental values of interval II ( $R_{pol}$ ) and interval III rate ( $-d \ln(1-x)/dt$ ).

Previously<sup>11)</sup> an average value of 0,60 was determined for  $x'$ , and this value was found to be independent of particle size between 30 and 150 nm. The values of  $x'$  at different levels of t-DT for polymerizations with SDS (Tab. 3) and Dresinate 214 were also found identical within experimental error, and in perfect agreement with our previous results.

Altogether, it can be safely concluded that the saturation monomer concentration  $C_M$  is constant and independent of the amount of t-DT in the present system.

Tab. 3. The conversion  $x'$  where interval III begins, for polymerizations with 32,4 g · L<sup>-1</sup> SDS and different amounts of t-DT

	10 <sup>2</sup> · C <sub>t-DT</sub> /(g · g <sup>-1</sup> )				
	0,0	0,0	0,7	1,4	2,8
Conversion $x'$	0,616	0,609	0,598	0,610	0,625

### Promoting effect of thiols

Another important effect of slightly water-soluble thiols is the so-called 'promoting effect'. At the time of the synthetic rubber program during World War II it was already known that the persulfate-initiated emulsion polymerization of butadiene(75 by weight)-styrene(25 by weight) or butadiene alone was extremely slow in the absence of an appropriate thiol. In the presence of such thiols,  $R_{pol}$  is virtually independent of the persulfate concentration within wide limits<sup>12)</sup>, and above a certain minimum level also independent of the amount of thiol<sup>5)</sup>. Similar results were found for the emulsion polymerization of isoprene<sup>13)</sup>. This rate-enhancing effect was commonly explained as being caused by a redox reaction between persulfate and thiol. Hydrogen abstraction by sulfate radical-anions gives uncharged, lyophilic thiol radicals, which supposedly are more efficient in entering a latex particle. Indeed, thiols containing 8 to 12 C-atoms solubilized in emulsifier solutions are oxidized by persulfate to disulfides<sup>14)</sup>. The latter compounds are easily envisaged as being formed by combination of thiol radicals.

The promoting effect is reconsidered here qualitatively, using as emulsifiers Dresinate 214, sodium dodecyl sulfate (SDS), potassium stearate and potassium oleate, and as initiators sodium (SPS) or potassium peroxydisulfate (PPS), 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and 2,2'-azoisobutyronitrile (AIBN). In a preliminary communication<sup>6)</sup> (Tab. 4) it was shown that the promoting effect was specific of persulfate-initiated polymerizations with Dresinate 214 as emulsifier. However, at lower

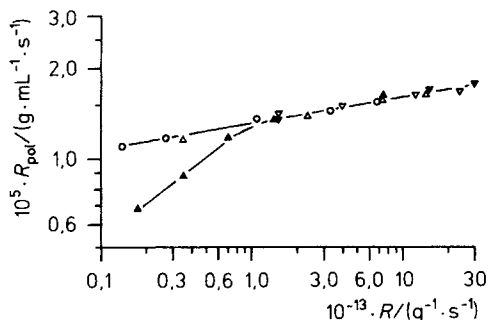


Fig. 2. Variation of polymerization rate  $R_{\text{pol}}$  with radical production rate per gram emulsion  $R$  for three initiators in the presence (open symbols) and absence (full symbols) of t-dodecanethiol (recipe 1): PPS ( $\circ$ ), ACPA ( $\triangle$ ) and AIBN ( $\nabla$ ). For details on  $R$  ( $= 2 k_d [I] N_{\text{Av}}$ ) see ref.<sup>1)</sup>

concentrations of ACPA, the polymerizations in the absence of t-DT also become markedly slower (Fig. 2, extension of Fig. 1 in ref.<sup>1)</sup>). The type and amount of initiator clearly plays an important role. The type of emulsifier also appears to be crucial in the promoting effect of t-DT, as Tab. 5 reveals large differences between the emulsifiers employed. It may be noted that Ishigure et al.<sup>15)</sup> found a similar increase in  $R_{\text{pol}}$  of about 30% with SDS in the radiation-induced emulsion polymerization of butadiene.

As pointed out by other investigators<sup>5)</sup>, reproducibility of experiments without thiol is greatly affected by traces of impurities. Bhakuni<sup>16)</sup> showed that with peroxide-containing emulsifiers some polymerization occurs in the absence of thiol, whereas with peroxide-free emulsifiers no polymerization was observed. The results in Tab. 5 confirm the suggestion that impurities present in the emulsifier need to be considered in relation to the poorly understood promoting effect.

Altogether, the experimental data presented here qualitatively confirm the observations from early literature, but also gross quantitative differences become apparent, related to the nature and concentrations of emulsifier and initiator. This certainly is not helpful in clarifying the mechanistic role of thiols of low water solubility in the emulsion polymerization of butadiene. In an attempt to eliminate artifacts introduced by the emulsifier, *ab initio* emulsifier-free emulsion polymerizations with potassium persulfate as initiator were performed.

### Emulsifier-free polymerizations

Emulsifier-free polymerizations in the presence and absence of t-DT were performed; the monomer/water ratio was chosen low (i. e., 1/9 by weight) to reduce the polymerization time to an acceptable level (after 25 h a conversion of 90% was reached).

The kinetics in interval II of both emulsifier-free polymerizations, and of similar polymerizations with emulsifier and t-DT, were all found identical within experimental

Tab. 4. Effect of the type and concentration of initiator on reaction kinetics, both in the presence and absence of t-DT. Upper part with Dresinate 214 as emulsifier, and lower part with SDS ( $C_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ )

Initiator	$10^{-3} \cdot [I]$ $\text{mol} \cdot \text{L}^{-1}$	Polymerization with t-DT				Polymerization without t-DT				
		conversion in % after				conversion in % after				
		2 h	4 h	6 h	8 h	2 h	4 h	6 h	8 h	
		$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$				$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$				
PPS	13,0	15	39	63	80	3	6	7	7	—
ACPA	13,0	14	38	67	84	1,6	39	65	82	1,6
AIBN	13,0	14	37	62	80	1,6	40	63	79	1,6
SPS	13,0	11	29	55	79	1,82	11	25	43	1,38
ACPA	13,0	—	—	—	—	—	14	32	60	1,77
SPS	0,52	19	45	69	83	1,64	13	29	46	0,99
ACPA	0,52	—	—	—	—	—	13	33	55	1,31

Tab. 5. Effect of the type of emulsifier on reaction kinetics, both in the presence and absence of t-DT<sup>a)</sup>

Emulsifier	Polymerization with t-DT				Polymerization without t-DT					
	conversion in % after				conversion in % after					
	2 h	4 h	6 h	8 h	24 h	2 h	4 h	6 h	8 h	24 h
	$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$				$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$					
Dresinate	15	39	63	80	99	1,52	3	6	7	10
K-stearate	21	46	75	89	100	1,85	3	6	8	20
K-oleate	15	37	65	82	100	1,71	2	3	4	20
SDS	11	29	55	79	99	1,82	11	25	43	98

a) Initiator is persulfate;  $[I] = 13 \text{ mmol} \cdot \text{L}^{-1}$ .

b)  $R_{\text{pol}}$  determined between 20 to 35% conversion.



error, taking into account the variation of  $R_{\text{pol}}/N$  with particle size (Tab. 6). These data are consistent with the observation that  $R_{\text{pol}}/N$  is solely determined by particle size, and not by the parameters utilised to manipulate the final particle diameter<sup>11)</sup>. This behaviour strongly suggests that the promoting effect is indeed related to impurities present in the emulsifier, although experimental evidence is insufficient to draw definitive conclusions.

Tab. 6 Kinetic and particle size data for some emulsifier-free emulsion polymerizations of butadiene (for details see text)<sup>a)</sup>

$C_E$ g · L <sup>-1</sup>	$10^3 \cdot C_{\text{I-DT}}$ g · g <sup>-1</sup>	$10^5 \cdot R_{\text{pol}}$ g · mL <sup>-1</sup> · s <sup>-1</sup>	$10^{20} \cdot R_{\text{pol}}/N$ g · s <sup>-1</sup>	$\bar{d}_v/\text{nm}$ (at 90%)	$P$ (= $\bar{d}_w/\bar{d}_n$ )
0,0	0,0	0,19	4,7	173	1,26
0,0	7,0	0,18	3,9	167	1,16
4,0 <sup>b)</sup>	7,0	0,79	4,9	173	1,03

a) Experimental details of emulsifier-free runs:  $M/W = 1/9$  (w/w),  $[\text{PPS}] = 10 \text{ mmol} \cdot \text{L}^{-1}$ ,  $[\text{K}_2\text{CO}_3] = 10 \text{ mmol} \cdot \text{L}^{-1}$ .

b) Polymerization described in ref. 2).

The particle size and size distribution of the final latexes of these emulsifier-free polymerizations (Fig. 3) reveal some other marked peculiarities. For the emulsifier-free emulsion polymerization of styrene, Goodwin et al.<sup>17)</sup> derived an empirical correlation between the particle diameter, initiator and monomer concentration, ionic strength, and temperature. From this relationship it follows that under the experimental conditions specified in Tab. 6, a monodisperse polystyrene (PS) latex with a diameter of 700 nm should be obtained. In contrast, the polybutadiene (PB) latexes prepared by us are highly polydisperse and of a significantly smaller diameter. The large polydispersity strongly suggests that (homogeneous) particle nucleation is not restricted to the very beginning of the polymerization, and that once formed, the PB particles appear highly stable towards coagulation. Consequently, the number of sulfate end-groups on these PB particles must be significantly larger than on PS particles prepared under identical conditions. This is fully consistent with the observation that the volume growth rate (which is mainly determined by  $k_p$  and  $\bar{n}$ ) of a PB particle is significantly smaller than the one for an equally sized PS particle<sup>11)</sup>.

Although the so-called promoting effect is far from being understood some aspects have become clearer, such as:

- The structure and purity of the emulsifier, as well as concentration and type of initiator, all play a crucial role.
- There is no apparent reason why sulfate radical anions (or oligomers thereof) should not initiate butadiene, as is shown in the persulfate-initiated emulsifier-free polymerizations in the absence of thiol.
- Although this does not disprove the involvement of thiol radicals in the initiation mechanism in polymerizations with emulsifier, a simple redox reaction between thiol and persulfate grossly oversimplifies the actual situation.

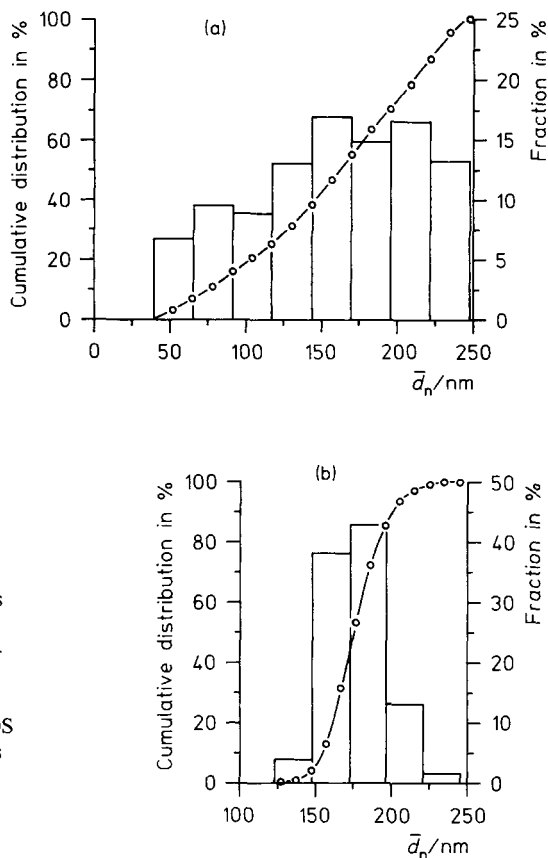


Fig. 3. Cumulative (○) and fractional particle size distributions vs. number-average diameter  $\bar{d}_n$  ( $= \sum d_i \cdot n_i / \sum n_i$ ) for the emulsifier-free polymerization without t-dodecanethiol (a), and the polymerization with 4,0 g · L<sup>-1</sup> SDS and t-dodecanethiol (b). For details see text

The most puzzling aspect yet remains to be solved: why is the promoting effect specific of diene-hydrocarbons, such as butadiene and isoprene, and not showing up when using other monomers. Styrene can readily be polymerized without a chain transfer agent, using any type of initiator or emulsifier (including Dresinate 214), both at widely varying concentrations.

### Radical desorption

Regardless of complexity of the data presented above, one common characteristic is the observation that addition of t-DT never decreases the steady state  $R_{\text{pol}}$ , nor the average rate per particle  $R_{\text{pol}}/N$  (and thus  $\bar{n}$ ). If a chain transfer agent were facilitating desorption, a decrease in  $R_{\text{pol}}/N$  is anticipated, yet all experimental data indicate the reverse.

Nomura et al.<sup>3)</sup> investigated the effect of radical desorption by chain transfer agents in the emulsion polymerization of styrene. Carbon tetrachloride and tetrabromide,

1,2-ethanethiol, and 1-butanethiol were found to give extensive radical desorption; in contrast, 1-dodecanethiol (n-DT) did not affect the polymerization rate nor the particle number. The fact that n-DT radicals apparently do not desorb was attributed to their extremely low water solubility. The concentration of n-DT was varied between  $2,7 \cdot 10^{-5}$  and  $1,1 \cdot 10^{-4}$  mol  $\cdot$  g $^{-1}$  styrene, comparable with that in the present system, viz.  $3,5 \cdot 10^{-5}$  mol t-DT per gram butadiene.

A further check was made regarding the quality of the commercial grade t-DT (supplied by Pennwalt) used until now, being a crude mixture of C<sub>12</sub>-isomers which may also contain small amounts of lower and higher thiols. Polymerizations were performed with SDS as emulsifier (Tab. 7), and n-DT or a mixture of two tertiary C<sub>12</sub>-isomers (supplied by Fluka; for structures see *Experimental part*). Both polymerizations with t-DT were found identical, while the one with n-DT was only slightly faster. This latter observation is in accord with results reported by Kolthoff<sup>5</sup>). However, allowing for the difference in particle size and the dependence of  $\bar{n}$  on particle size<sup>11</sup>), the average rates per particle are equivalent for all three C<sub>12</sub>-thiols used. Radical desorption of dodecanethiol radicals is obviously negligible, regardless of the structure and composition of the dodecanethiol employed.

Tab. 7. Effect of the composition of dodecanethiol in polymerizations with 32,4 g  $\cdot$  L $^{-1}$  sodium dodecylsulfate (recipe 2)

Thiol	Conversion in % after				$\frac{10^5 \cdot R_{pol}}{g \cdot mL^{-1} \cdot s^{-1}}$	$\bar{d}_{90}$ <sup>a)</sup> nm	$x'$
	2 h	4 h	6 h	8 h			
t-DT <sup>b)</sup>	11	29	55	79	1,82	46	0,598
t-DT <sup>c)</sup>	11	29	56	79	1,82	44	0,613
n-DT	13	32	62	83	1,88	51	0,608

a) Weight-average particle diameter at 90% conversion.

b) t-DT supplied by Pennwalt.

c) t-DT supplied by Fluka.

## Conclusions

From a kinetic standpoint, t-dodecanethiol appears to behave as an 'ideal' chain transfer agent in the emulsion polymerization of butadiene; it regulates cross-linking efficiently, but otherwise does not influence the reaction kinetics:

- Even though the gel point varies widely with the initial amount of thiol,  $C_M$  and  $x'$  were both found to be constant within experimental error. Even in the absence of a chain transfer agent, the extent of cross-linking is still too low to restrict the monomer swelling of latex particles.
- Dodecanethiol radicals do not desorb, regardless of their structure and composition, as a result of an extremely low water solubility.

The promoting effect of slightly water-soluble thiols is specific of diene-hydrocarbon monomers, but the phenomenon is still poorly understood. Nevertheless, some aspect can now be placed in a better perspective:

- Sulfate radical anions (or oligomers thereof) are capable of initiating the emulsion polymerization of butadiene, as was shown in the emulsifier-free experiments, which polymerize with an  $R_{\text{pol}}/N$  identical to that of reactions with emulsifier and thiol rendering the same final particle size.
- Despite this observation, many authors (including the present ones) have reported on the retardation of butadiene emulsion polymerizations in the absence of an appropriate thiol, using different types of emulsifiers.
- The extent of retardation in the absence of thiol depends on the structure, concentration and chemical purity of the emulsifier and initiator employed.
- It has become clear that a simple redox reaction between a sulfate radical anion and thiol is inadequate to provide a satisfactory explanation.

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