

## Particle growth in butadiene emulsion polymerization. 3. Radical adsorption and desorption rate coefficients

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## Particle growth in butadiene emulsion polymerization, 3<sup>a)</sup>

### Radical adsorption and desorption rate coefficients

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

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#### SUMMARY:

The kinetics of the emulsion polymerization of butadiene at 60 °C in Smith-Ewart interval III were investigated using peroxodisulfate as initiator. The aim of this work was to obtain insight in the radical adsorption and desorption rate coefficients through monitoring non-steady state kinetics. The acquired data shows an initiator concentration dependence of the desorption rate coefficients. This dependence explains the independence of the rate of butadiene emulsion polymerization of the peroxodisulfate concentration in the presence of tertiary dodecylthiols.

#### Introduction

The aim of this work was to obtain insight in the radical absorption (entry) and desorption (exit) rate coefficients in the butadiene emulsion polymerization by monitoring non-steady state kinetics. 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 known<sup>1)</sup>. The parameters that determine  $\bar{n}$ , like the rate coefficients for entry of radicals into particles,  $\rho$ , and the rate coefficient for exit of radicals out of particles,  $k$ , can be determined from the steady state slope and the intercept with the conversion axis utilizing the 'slope and intercept method'<sup>1,2)</sup>. 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. Three methods of monitoring non-steady state kinetics were applied by the current authors to allow the use of the 'slope and intercept method': 1) gamma radiolysis<sup>3)</sup>, 2) using a uniquely water soluble radical scavenger, Fremy salt<sup>4)</sup>, and 3) monitoring the start-up of chemically initiated polymerizations. The latter is described in this paper. The drawbacks and advantages of each method are discussed elsewhere<sup>4)</sup>.

#### Experimental part

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 dodecanethiol (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) and sodium carbonate (p.a. Merck, Darmstadt, Germany) were used without further purification. Water was doubly distilled and

<sup>a)</sup> Part 2: cf. <sup>3)</sup>

purged with nitrogen to remove oxygen. Experimental details and recipes of the emulsion polymerizations are elaborately explained elsewhere<sup>5-7</sup>. 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 and 60, Graz, Austria). 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 elsewhere<sup>6</sup> and is used for all polymerizations unless stated otherwise. The preparation of the seed latex is discussed in detail elsewhere<sup>8</sup>. 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. Particle sizing is described elsewhere<sup>5</sup>.

## Results and discussion

The proper monitoring of non-steady state kinetics in the chemically initiated method depends on the creation of a step function in radical production. This is approximated by injecting the initiator into the system. The reaction mixture, except for the initiator, was allowed to reach the reaction temperature (60 °C). The on-line conversion monitoring signal was established, and the initiator was injected when the on-line signal was maintained at a constant value for a short period of time. Conversion and time were defined zero at injection time. In Fig. 1 an example of a  $-\ln(1-x)$  versus time curve, from which the slope and intercept can be obtained, is shown (the injection of peroxodisulfate is indicated by the arrow).

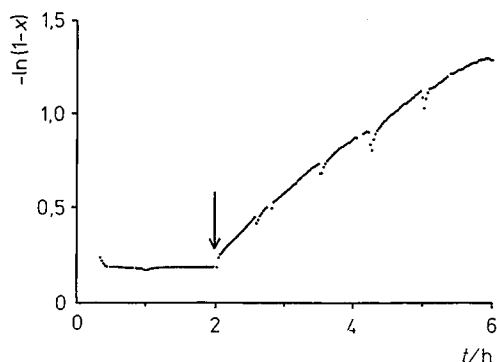


Fig. 1.  $-\ln(1-x)$  versus time plot with extremely short approach to steady state (peroxodisulfate injection indicated with the arrow) ( $x$  = conversion)

The intercept data is hard to obtain within reasonable accuracy, as will be evident from the very short approach to steady state in Fig. 1. However, under experimental conditions leading to low values of  $\rho$  (low  $[I]$  and high number of particles), the approach to steady state is longer and can be measured more accurately. The results of this method are shown in Tab. 1. The values are calculated using the  $\alpha = 1$  and  $\alpha = 0$  models described elsewhere<sup>1,7</sup> and are therefore model dependent data!

The accuracy of the data can be estimated from the accuracy of the components used in the calculation of  $\rho$  and  $k$ . The three components required are the slope, the intercept and a set of recipe parameters<sup>1</sup>). The error in the slope is small and estimated to be 10%. The error in the recipe parameters with respect to the calculation of  $\bar{n}$  is mainly

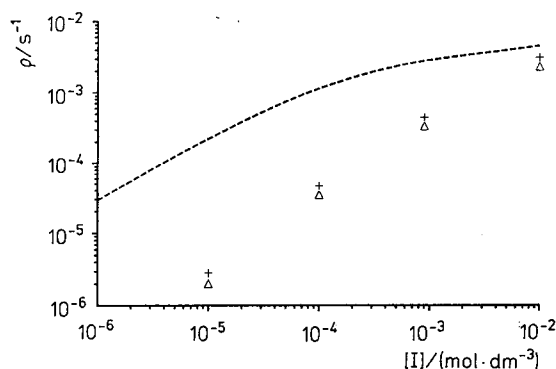
Tab. 1. Values for  $\rho$ ,  $k$  and  $\bar{n}$  obtained from the chemical initiation method, TDM was present in the recipes underlying these experiments

$10^3 \cdot [I]$ mol $\cdot$ dm <sup>3</sup>	$\rho(\alpha = 0)$ s <sup>-1</sup>	$\rho(\alpha = 1)$ s <sup>-1</sup>	$k(\alpha = 0)$ s <sup>-1</sup>	$k(\alpha = 1)$ s <sup>-1</sup>	$\bar{n}$
10	$3,1 \cdot 10^{-3}$	$2,3 \cdot 10^{-3}$	$1,8 \cdot 10^{-2}$	$5,0 \cdot 10^{-2}$	0,13
1	$4,5 \cdot 10^{-4}$	$3,4 \cdot 10^{-4}$	$2,2 \cdot 10^{-3}$	$5,8 \cdot 10^{-2}$	0,14
0,1	$4,7 \cdot 10^{-5}$	$3,5 \cdot 10^{-5}$	$3,3 \cdot 10^{-4}$	$1,1 \cdot 10^{-3}$	0,11
0,01	$2,9 \cdot 10^{-6}$	$2,0 \cdot 10^{-6}$	$6,6 \cdot 10^{-5}$	$5,9 \cdot 10^{-4}$	0,04
0	$3,4 \cdot 10^{-7}$	$2,4 \cdot 10^{-7}$	$2,7 \cdot 10^{-5}$	$7,7 \cdot 10^{-4}$	0,01

due to errors in the particle number ( $\approx 10\%$ ) and  $C_m$  ( $\approx 5\%$ ), and estimated to amount to 15%. The error in the intercept is large because the intercept itself is often very small ( $10^{-2}$  to  $10^{-6}$ ) as compared with the error in the slope. The maximum error in the intercept is estimated to be 1 to 2 orders of magnitude, which reduces the significance of all other errors. However, at lower peroxodisulfate concentrations the error in the intercept is much less than an order of magnitude and the range in  $\rho$  and  $k$  values spanned by the measurements is 3 orders of magnitude. Although the data is fairly inaccurate, it is the only  $\rho$  and  $k$  data currently available and will be discussed accordingly.

The data of Tab. 1 is depicted in the Figs. 2 and 3, together with model calculations elaborately discussed elsewhere<sup>5,6</sup>. The values  $k_{tr} = 5 \cdot 10^{-2} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $k_t = 2 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  are used in the model calculations.

Fig. 2.  $\rho$  versus  $[I]$  for a particle diameter of 101 nm. Model calculations<sup>5)</sup> using a value for the rate coefficient of radical transfer to monomer  $k_{tr} = 5 \cdot 10^{-2} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and a value for the termination rate coefficient in the aqueous phase  $k_t = 2 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ . (---): model calculations, (+): exp. data (Tab. 1,  $\alpha = 0$ ), ( $\Delta$ ): exp. data (Tab. 1,  $\alpha = 1$ )



The data and model calculations are not in good agreement, even when considering the inaccuracy of the data, which is not surprising since the model used was also incapable of fitting  $\bar{n}$  data versus peroxodisulfate concentration<sup>6)</sup>. Alas no entry or exit rate coefficient data of polymerizations without TDM is available. As suggested by Verdurmen et al.<sup>6)</sup>, a mechanism that would allow the exit rate coefficient to be influenced by the initiator concentration is needed to explain the anomalous behaviour of the butadiene emulsion polymerization in the presence of dodecyl thiols at different peroxodisulfate concentrations.

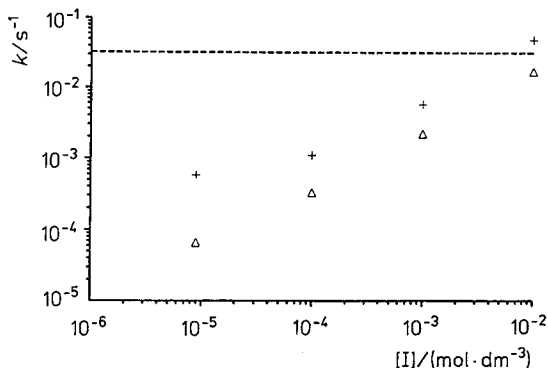


Fig. 3.  $k$  versus  $[I]$  for a particle diameter of 101 nm. Model calculations<sup>5)</sup> using a value for the rate coefficient of radical transfer to monomer  $k_{tr} = 5 \cdot 10^{-2} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and a value for the termination rate coefficient in the aqueous phase  $k_t = 2 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (Symbols as in Fig. 2)

The data in Fig. 3 does show a dependence of  $k$  on  $[I]$  (which is not accounted for in the currently used model) and is thus in agreement with the predictions by Verdurmen et al.<sup>6)</sup> Again these observations imply that the following issues should be considered in modelling the butadiene emulsion polymerization: 1) Exit and reentry of monomeric radicals. This would allow exit to depend on initiator concentration via termination of exited radicals involving initiator, or through the effect of  $\bar{n}$  on the fate of reentered radicals. 2) Other possible radical loss mechanisms unconsidered in the present modelling. It is noteworthy that the data of the Figs. 2 and 3 are close to the model calculations at high initiator concentration, which explains the good fit of  $\bar{n}$  versus particle diameter at this high initiator concentration, discussed by Verdurmen et al.<sup>5)</sup>

The data depicted in Fig. 2 cannot be completely explained. There is no obvious reason why the experimentally determined  $\rho$  data should not be fitted by the model prediction. This could, however, be caused by inaccurate data acquisition. The main problem of the chemical initiation method is that possible retardation or inhibition occurring after injection of the initiator will reduce the values of  $\rho$  and  $k$ . More accurate data of  $\rho$  and  $k$  should be obtained using recipes with and without TDM, together with incorporating reentry of exited radicals in the slope and intercept calculations, thus complying with the more complex kinetics of the butadiene emulsion polymerization.

Nevertheless, the models used<sup>5,6)</sup> should not be discarded. Although the models are simplifications of the mechanisms involved, the fit of two separate sets of accurate  $\bar{n}$  data still provides a powerful tool in description and control of butadiene emulsion polymerization. The kinetic regimes in which the system polymerizes can be derived as well as useful information on the peroxydisulfate initiating efficiency. Moreover, the complicated models taking into account reentry of desorbed radicals have a number of adjustable parameters or do not allow experimental determination of the rate coefficients by the slope and intercept method.

## Conclusions

The data obtained by this method shows an initiator concentration dependence of the exit rate coefficient. This explains the independence of the rate of butadiene emulsion polymerization of initiator concentration in the presence of tertiary dode-

canethiols. The exact mechanism for this phenomenon could not be elucidated. More accurate entry and exit rate coefficient data obtained in the presence and absence of tertiary dodecanethiols is needed.

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