

## Free radical suspension polymerization kinetics of styrene up to high conversion

*Nurelegne Tefera*

Martin-Luther-Universität Halle-Wittenberg, Fachbereich Verfahrenstechnik,  
Geusaerstraße, D-06217 Merseburg, FRG

*Günter Weickert*

Twente University of Technology, Department of Chemical Technology,  
P. O. Box 217, 7500 AE Enschede, The Netherlands

*Robert Bloodworth, Johannes Schweer\**

Bayer AG, Central Research and Development, D-51368 Leverkusen, FRG

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### SUMMARY:

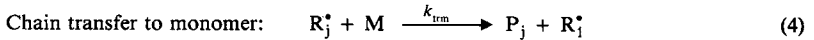
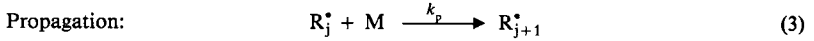
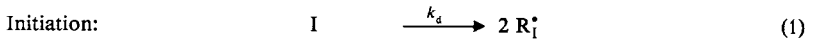
Styrene was polymerized using different amounts of azoisobutyronitrile as initiator at temperatures of 70 °C, 75 °C and 80 °C in suspension. The course of reaction up to almost complete conversion was modeled within a classical kinetic framework. Optimal simultaneous descriptions of both conversion and average degree of polymerization data were possible using two sets of values for the variation of the overall termination rate coefficient  $k_t$  with conversion. One explanation for this is that  $k_t$  is chain length dependent. Evidence for this necessity was derived by considering all kinetic parameters, except the termination rate coefficient, as reliable absolute values.

### Introduction

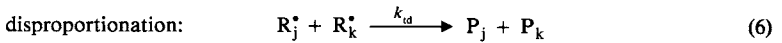
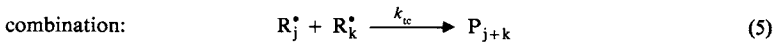
In general, the conversion-time curves, heats of polymerization, and the dependencies of the initial reaction rates on initiator concentrations in suspension polymerization are in good agreement with bulk phase kinetics. Particle sizes, type and concentration of stabilizers, and agitation conditions normally have little influence on the polymerization rates in suspension processes. Hence, mass transfer phenomena between the two phases in an oil-in-water suspension do not significantly affect the overall process<sup>1)</sup>. Thus, the polymerization occurring in the suspension droplets is conveniently considered as a small scale bulk polymerization.

The kinetics of free radical suspension polymerization have been widely investigated, and these efforts have recently been documented in a comprehensive review by Ray and coworkers<sup>1)</sup>. The present article deals with the modeling of suspension polymerization of styrene up to high degrees of conversion. Special emphasis is given to the optimal simultaneous descriptions of both the conversion/time curves and the changes in the number-average and weight-average molecular weights with conversion within the simple classical kinetic framework of initiation, propagation, transfer to monomer, and chain length independent termination.

The overall kinetic scheme for the free radical polymerization of styrene adopted here is given as follows:



Termination by



where I and M represent molecules of initiator and monomer, respectively.  $\text{R}_1^*$  is an initiator-derived radical, while  $\text{R}_j^*$  is a primary radical. The number of monomer units contained in propagating free radicals  $\text{R}^*$  or polymer molecules P, i. e., the chain length, is indicated by positive integral numbers  $j$  and/or  $k$ . The initiating reaction (2), which is characterized by the rate coefficient  $k_i$ , is normally considered to be very rapid in comparison to the initiator decomposition (1), which is described by the decomposition constant  $k_d$ . In other words, the overall rate of initiation is assumed to be controlled by the rate of the initiator decomposition. The chain transfer to monomer is characterized by the rate coefficient  $k_{trm}$ . It is assumed that chain transfer to polymer is negligible. The propagation rate coefficient  $k_p$  and especially the termination rate coefficients  $k_{tc}$  and  $k_{td}$  are assumed to be independent of the lengths of growing radical chains undergoing termination. Experimentally it has been established repeatedly that there is no discernible chain length dependence of  $k_p$  for long radical chains (see for instance<sup>2-4</sup>). On the other hand, a dependence of the termination rate coefficients on chain length has been shown both experimentally (e.g.<sup>2,5</sup>) and theoretically (e.g.<sup>6,7</sup>). Nevertheless, the termination coefficients were assumed to be chain length independent within the present investigation, i. e., they have been applied as chain length averaged values. We have assumed this simplified termination mechanism in an effort to test this model as to its ability to generate optimal simultaneous descriptions of rate data and molecular weight changes during polymerization.

## Model

For well stirred batch reactors, the following differential equations may be derived to describe the progress of the reaction and the molecular weight development with time  $t$  in bulk polymerization<sup>8</sup>):

$$dx/dt = k_p c_M c_R^S M_M / \rho_{rm} \quad (7)$$

$$dy_n/dt = (T' + 0,5 k_{tc} c_R^S) / \rho_{rm} \quad (8)$$

$$dy_w/dt = \{2k_p c_M (T' + 1,5 k_{tc} c_R^S) / (T' + k_{tc} c_R^S)^2\} dx/dt \quad (9)$$

where  $x$ ,  $c_M$ ,  $M_M$  and  $\rho_{rm}$  are the conversion, concentration and molecular weight of the monomer, and the density of the reaction medium, respectively,  $T' = k_{trm} c_M + k_{td} c_R^S$  and  $c_R^S = (2f k_d c_I / k_t)^{0.5}$ . With  $c_M M_M / \rho_{rm} = 1 - x$ , the right hand side of Eq. (7) may be turned into the form  $(1 - x) k_p c_R^S$ . The termination rate coefficient  $k_t = k_{tc} + k_{td}$  is derived from the equation  $dc_R/dt = -k_t c_R^2$ , where  $c_R$  is the total concentration of radicals and is assumed to be an average over all radical chain lengths. The stationary state concentration of radicals  $c_R^S$  is attained when the rate of initiation and the overall rate of loss of free radicals by termination  $dc_R/dt$  are equal. The concentration of the initiator is described by  $c_I$  and the dimensionless initiator efficiency by  $f$ , which is the number of initiator-derived end-groups in the polymer per initiator-derived primary radical within the present study. The cumulative number-average and weight-average degrees of polymerization at conversions  $x$  are calculated as  $P_n = x/(y_n M_M)$  and  $P_w = y_w/x$ , respectively. The dependence of  $k_t$  and  $f$  on molecular weight and/or volume fraction of polymer is considered according to<sup>8)</sup>

$$k_t = \{1/k_t^0 + (M_w/g_1) \exp(g_2 X_{vf})\}^{-1} + a k_p c_M \quad \text{and} \quad (10)$$

$$f = \{1 + (1/f^0 - 1) \exp(g_3 X_{vf})\}^{-1} \quad (11)$$

respectively, where  $M_w = M_M \cdot P_w$ ,  $a = 1 \text{ L} \cdot \text{mol}^{-1}$  and<sup>9)</sup>

$$\begin{aligned} X_{vf} &= 1/V_f - 1/V_f^0 & V_f &= \phi_M V_{fM} + \phi_P V_{fP} \\ V_{fM} &= 0,025 + 10^{-3} (T^{(c)} - T_{gM}^{(c)}) & V_{fP} &= 0,025 + 4,8 \cdot 10^{-4} (T^{(c)} - T_{gP}^{(c)}) \\ T_{gM}^{(c)} &= -30,6^\circ\text{C} & T_{gP}^{(c)} &= 100^\circ\text{C} \\ T^{(c)} &= \text{Celsius temperature} \end{aligned}$$

$$\phi_P = x \rho_{rm} / \rho_P \quad \phi_M = (1 - \phi_P)$$

$$\rho_{rm} = 1/\{(1 - x)/\rho_M\} + x/\rho_P\}$$

$$\rho_M/(\text{g} \cdot \text{L}^{-1}) = 924 - 0,918 T^{(c)}$$

$$\rho_P/(\text{g} \cdot \text{L}^{-1}) = 1084 - 0,605 T^{(c)}$$

Eqs. (10) and (11) are based on changes of the free volumes of monomer and polymer with the progress of polymerization. Superscripts "0" refer to zero conversion.  $V_f$ ,  $V_{fM}$  and  $V_{fP}$  denote the fractional free volume of the polymerization medium, of the pure monomer and of the pure polymer, respectively. To calculate  $V_f$ , additivity of free volume is assumed, while  $\rho_{rm}$  is calculated assuming additivity of monomer and polymer volumes and neglecting the weight fraction of initiator.  $\phi_M$  and  $\phi_P$  are the volume fractions of monomer and polymer, respectively. The free volumes  $V_{fM}$  and  $V_{fP}$  of pure styrene and pure polystyrene are given as functions of the polymerization temperature  $T^{(c)}$  and of the glass transition temperature  $T_{gM}^{(c)}$  or  $T_{gP}^{(c)}$  of styrene or polystyrene, respectively. The densities  $\rho_M$  and  $\rho_P$  of pure styrene and pure polystyrene are given in g/L as functions of the polymerization temperature  $T^{(c)}$  (in  $^\circ\text{C}$ ). The various values for the glass temperatures and densities contained in Eqs. (10) and (11) have been taken from different sources of literature by Weickert<sup>9)</sup>. It goes without saying that the choice of these values will be reflected in the adjusted absolute values

of  $g_1$ ,  $g_2$  and  $g_3$ . In any event it is not the validation of model equations (10) and (11) but only the simple representation of conversion-dependent absolute values of  $k_t$  and  $f$  with the aid of these equations which is intended within the present investigation. For a physical explanation of the above termination model, we refer the reader to the paper of Weickert and Tefera<sup>8)</sup> and references cited therein.

## Experimental part

### *Polymerization*

Polymerizations were performed in aqueous suspension using 88% hydrolyzed poly(vinyl alcohol) (Moviol 40–88; Hoechst AG) as the dispersing agent. Styrene was freshly distilled and the initiator azoisobutyronitrile (AIBN, Merck) recrystallized from methanol. Polymerizations were performed under nitrogen ( $N_2$ ) with concentrations of 0,15%, 0,30% or 0,45% initiator per gram of styrene at temperatures of 70 °C, 75 °C and 80 °C.

In a 3-L flat-bottomed polymerization vessel fitted with a reflux condenser, mechanical stirrer and inlet, an aqueous phase consisting of 25,1 g poly(vinyl alcohol) and 10,0 g  $NaH_2PO_3$  dissolved in 1200 mL deionized water was degassed and heated to the polymerization temperature. 600 g degassed styrene containing the initiator were added quickly, i. e., within approximately 1–2 min while stirring (stirring paddle at 600 rpm). Samples (10 mL) were removed at intervals of 30 min and quenched in a dry-ice bath at  $-20^\circ C$ .

### *Sample work-up and gel-permeation chromatography (GPC)*

After thawing the samples to 5 °C, methylene dichloride containing 200 ppm of inhibitor was added along with sufficient molecular sieves to absorb the water present in each sample. The polymer had completely dissolved within approximately 72 h at  $-4^\circ C$ . The methylene dichloride phase was analyzed by GPC. Two mixed-bed columns (Nucleogel GPC M5, Machery-Nagel) were used at a temperature of 298 K. The eluent was methylene dichloride at a flow rate of 0,66 mL/min. Signals from an ultraviolet (UV) detector (254 nm) and an infrared (IR) detector (6,24  $\mu m$ ) were used as a measure of the concentrations of polystyrene (PS) and styrene (S), respectively. The data were digitized and stored within a laboratory automation system (HP 3350 A, Hewlett Packard). Calibration was performed with methylene dichloride solutions of 16 narrow molecular weight standards of PS (Polymer Standard Service) in a molecular weight range from  $5 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$  to  $7 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ . A polynomial of order 5 was fitted to the calibration plot, so that molecular weights were recalculated within  $\pm 3\%$  deviation of the nominal molecular weights of the standards. The fractional conversions were determined from calibrated IR and UV signals.

### **Rate parameters**

Unless stated otherwise, all the model calculations within the present study were performed on the basis of the following rate parameters, all of which result from separate experimental work and thus are generally independent of the experiments under investigation.

### *Propagation rate coefficient*

Using the pulsed laser technique<sup>10)</sup> the propagation rate coefficient for the free radical polymerization of styrene was determined as  $77 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and 355

$\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  at temperatures of 25 °C and 60 °C, respectively. The corresponding temperature dependence of the propagation rate coefficient, which has been shown to be constant up to conversions of beyond 0,8<sup>11</sup>, is given as

$$k_p = 10^{8,21} \cdot \exp(-36,1 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (12)$$

in  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , where  $R$  and  $T$  are the gas constant and the absolute temperature (in K), respectively. The absolute  $k_p$  values calculable from Eq. (12) compare excellently with determinations of  $k_p$  by reliable methods<sup>12</sup>, i. e., both with spatially intermittent polymerization rate measurements of Mahabadi et al.<sup>13</sup> in the temperature range of 15 °C to 30 °C and with emulsion polymerization rate measurements of Lansdowne et al.<sup>14</sup> in the range of 45 °C to 65 °C. Moreover,  $k_p$ -values of 77,5  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , 72  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , and 78  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  were determined by Davis et al.<sup>15</sup>, Olaj et al.<sup>16</sup>, and Davis et al.<sup>17</sup> at 25 °C, using the pulsed laser technique. For temperatures of 70 °C, 80 °C, and 100 °C  $k_p$ -values of 480  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , 650  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and 1620  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  were determined on the basis of a combination of ESR spectroscopy and rate measurements by Yamada et al.<sup>11</sup>, Shen et al.<sup>18</sup>, and Yamada et al.<sup>19</sup>, respectively, which also compare very well with values of 519  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , 742  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , and 1435  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , calculable from Eq. (12).

Recently, the pulsed laser technique has been highly recommended for measuring  $k_p$  values for free-radical polymerizations<sup>20</sup>, because it seems to be free of model-based assumptions. The method comprises a pulsed laser polymerization at low conversion and a determination of the molecular weight distribution of the resultant polymer by means of GPC<sup>4</sup>). Its accuracy is therefore directly related to the accuracy of the GPC with respect to absolute molecular weights. Despite literature reports of pulsed laser technique based  $k_p$  values which deviate from Eq. (12) up to nearly 30% at 60 °C<sup>21</sup>, our value of 355  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  has recently been redetermined within 5%<sup>22</sup>). We therefore suggest that Eq. (12) yields correspondingly accurate values for the propagation rate coefficient of styrene at low conversion in the temperature range from 10 °C to 80 °C.

### *Initiator decomposition coefficient and efficiency*

The rate coefficient for the decomposition of AIBN used in this study is given as<sup>23</sup>

$$k_d = 10^{15,2} \cdot \exp(-128,96 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (13)$$

in  $\text{s}^{-1}$ . For example, at a temperature of 70 °C,  $k_d$  values of  $3,5 \cdot 10^{-5} \text{ s}^{-1}$  and  $3,7 \cdot 10^{-5} \text{ s}^{-1}$  were determined by monitoring the initiator decomposition via quantitative IR spectroscopy<sup>24</sup> or <sup>13</sup>C nuclear magnetic resonance spectroscopy<sup>25</sup>). Both values compare excellently with a calculation of  $k_d = 3,7 \cdot 10^{-5} \text{ s}^{-1}$  according to Eq. (13), which is thus estimated to give accurate decomposition rates for the temperature range under consideration, i. e., at temperatures from 70 °C to 80 °C.

In very good agreement with the findings of Moad et al.<sup>25</sup>, the zero conversion efficiency  $f^0$  at 70 °C was reported to be 0,61 by Schmid<sup>24</sup>). Assuming the weak tem-

perature dependence of  $f^0$  — which is only reported for a pressure of 1 000 bar — to be independent of pressure, a temperature dependent zero conversion efficiency  $f^0$  was extracted from the data of ref. <sup>24)</sup> as

$$f^0 = 89,91 \cdot \exp(-14,24 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (14)$$

Using  $f^0$  from Eq. (14) experimental data for the conversion-dependent AIBN efficiency during bulk polymerization of styrene at 70 °C were adjusted to Eq. (11), thus fixing the parameter  $g_3$  to a value of 0,1054 (cf. Fig. 3, see below).

### *Rate coefficient for chain transfer to monomer*

The rate coefficient  $k_{\text{trm}}$  for chain-transfer to monomer is calculated from the temperature dependence of the transfer constant  $C_M = k_{\text{trm}}/k_p$  according to the equation

$$C_M = 0,473 \cdot \exp(-24,3 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (15)$$

This relation is deemed to yield relatively accurate values of  $C_M$  because it was obtained by averaging over a large body of experimental data from different sources of literature <sup>26)</sup>. In accordance with recent theoretical considerations <sup>27)</sup>,  $C_M$  is assumed to be virtually independent of conversion (see below). Moreover, a new method for the accurate determination of the transfer coefficient to monomer has been recently reported <sup>28)</sup>. In this method,  $C_M$  is extracted from the high molecular weight tail of number molecular weight distributions from emulsion-polymerized polymers. Recent applications of this method yielded a mean  $C_M$  values of  $5,5 \cdot 10^{-5}$  for styrene at 50 °C <sup>29–31)</sup>, while a value of  $C_M = 5,6 \cdot 10^{-5}$  is calculated from Eq. (15) for this temperature.

## **Results and discussion**

### *A separate look at conversion/time curves*

Experimental conversion/time data are shown in Fig. 1: Fig. 1 a shows the variation of the conversion/time curves with the amount of initiator at constant temperature, while Fig. 1 b shows corresponding variations with temperature at the same level of initiator. Using the experimentally *fixed* values for  $k_p$  from Eq. (12), for  $k_d$  from Eq. (13) and for  $f$  according to Eq. (11) with  $g_3 = 0,1054$  (see above) and with  $f_0$  from Eq. (14), values of the termination coefficients  $k_t^0$  at zero conversion were *fitted* according to numerical integrations of Eqs. (7) and (9), while using Eq. (10) to estimate the termination coefficient. The limited range of temperature in the study prevents a certain determination of the energy of activation for  $k_t^0$  from these fits. In agreement with the literature <sup>5)</sup>, no significant trend in  $k_t^0$  with the amount of initiator was observed. Therefore, a mean value of  $k_t^0 = 1,70 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  was determined for a mean temperature of 77 °C. As shown in Fig. 2, this value compares well with recent measurements of Yamada et al. <sup>19)</sup> as well as with a linear extrapolation from Polymer Handbook data <sup>26)</sup>. Its temperature dependence is expressed as

Fig. 1a. Conversion vs. time for suspension polymerizations of styrene at 80°C. Dotted and full lines correspond to fits of the experimental data according to Eq. (7) with  $f$  according to Eq. (11) or according to Eq. (17), respectively. Edge-up triangles, circles, and edge-down triangles refer to amounts of initiator of 0,45%, 0,30% and 0,15%, respectively

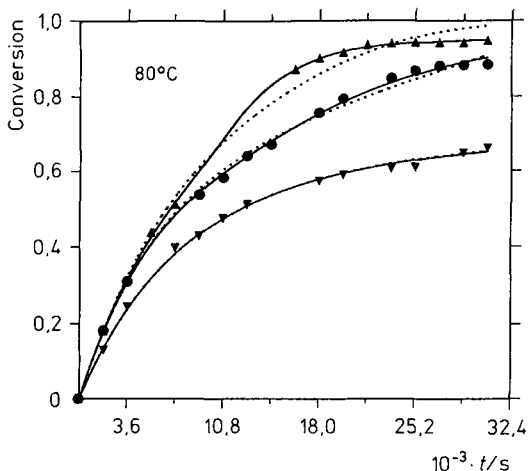
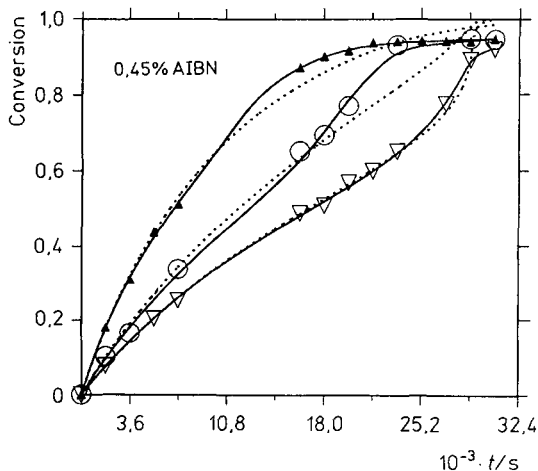


Fig. 1b. Conversion vs. time for suspension polymerizations of styrene using 0,45% of AIBN. Dotted and full lines correspond to fits of the experimental data according to Eq. (7) with  $f$  according to Eq. (11) or according to Eq. (17), respectively. Edge-up triangles, circles, and edge-down triangles refer to polymerization temperatures of 80°C, 75°C and 70°C, respectively



$$k_t^0 = 10^{11,01} \cdot \exp(-18,66 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (16)$$

in  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , where a mean activation energy of  $18,66 \text{ kJ} \cdot \text{mol}^{-1}$  was adopted from the data of Yamada et al.<sup>19)</sup> and from the Polymer Handbook data<sup>26)</sup> (see Fig. 2). Eq. (16) is estimated to give reliable values with respect to the limited temperature range under study. Eq. (16) also compares well with determinations of  $k_t$  by a reliable method<sup>12)</sup> even at temperatures around  $25^\circ\text{C}$ <sup>13)</sup>. It should however be noted that termination coefficients are generally system-specific and may depend on the method of their determination<sup>28)</sup>. The chain length averaged quantities calculable from Eq. (16) may not be applicable under other experimental conditions.

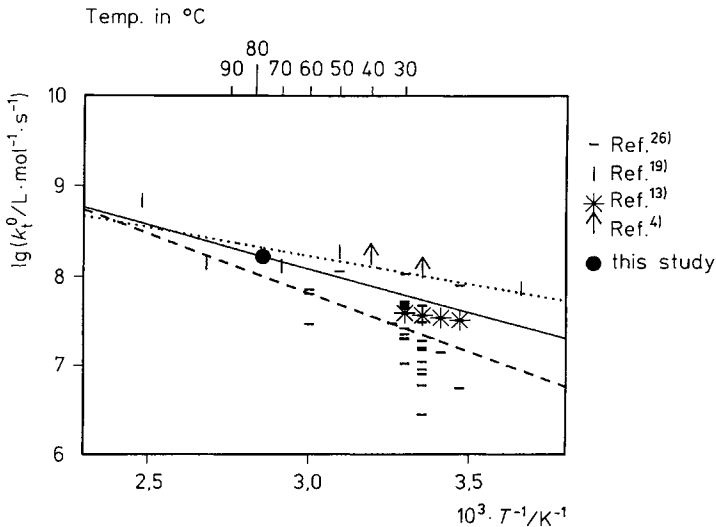


Fig. 2. Comparison of low conversion termination rate coefficients  $k_t^0$  for the free radical polymerization of styrene at different temperatures. The dotted and the broken lines correspond to linear regressions of the decadic logarithms  $\lg(k_t^0)$  versus the reciprocal absolute temperature  $1/T$  (lower axis) of the data of Yamada et al.<sup>19)</sup> and of the Polymer Handbook data<sup>26)</sup>, respectively. The full line corresponds to Eq. (16). For illustration purposes, temperatures are also given in °C (upper axis)

The experimental conversion/time curves in Figs. 1 a and 1 b may be optimally represented within experimental error by the above fit procedure up to conversions of at least, say, 0,7. However, some of the calculated fits — which appear as dotted lines in Figs. 1 a and 1 b — show significant deviations from the experimental data at higher conversions. In the 0,45% AIBN experiments at 80 °C and 75 °C, and to some extent at 70 °C, cessation of polymerization occurs at about  $x = 0,95$ , i. e., the conversion reaches a quasi plateau value below  $x = 1$ . This observation of a “glass effect”, which is commonly expected for radical polymerizations below the glass transition temperature of the polymer, is in close agreement with conversion/time measurements during polymerization of styrene up to high conversion of O’Driscoll and Huang<sup>32)</sup>.

An improved fit of the theoretical conversion/time curves might formally be achieved, both by a rapid decrease in propagation rate and/or in initiator efficiency at very high conversions. Although measurements of the AIBN efficiency as well as of the propagation rate coefficient during free radical polymerizations of styrene up to high conversions have been reported<sup>11, 18, 19, 24)</sup>, the data still appear somewhat uncertain at present for conversions around 0,8 or higher. Whereas measurements of Yamada et al.<sup>11)</sup> hint at a conversion-independent  $k_p$ , measurements of Shen et al.<sup>18)</sup> suggest a decrease of  $k_p$  beyond conversions around  $x = 0,7$ .



Theoretically, the origins for a vanishing rate of polymerization below complete conversion have recently been investigated by Russell et al.<sup>33)</sup>, who suggested that it is more likely the initiator efficiency that decreases dramatically beyond a certain weight fraction of polymer. Some subsequent experimental support for this conclusion may be seen in determinations of the stationary state free radical concentration during styrene polymerization in bulk<sup>11, 18)</sup>, which — after increasing to a maximum value — decrease again at high conversions.

In the absence of reliable measurements of  $f$  at the highest conversions (i. e., above about  $x = 0,7$ ) and relying — intuitively — on  $k_p$  remaining conversion independent<sup>11)</sup>, we prefer to attribute the observed fall off in the conversion/time curve in Fig. 1 a and 1 b solely to a decrease in  $f$  below values calculated according to Eq. (11) (with  $f_0$  from Eq. (14) and  $g_3 = 0,1054$ ). The full lines in Figs. 1 a and 1 b thus correspond to separate fits of the parameters  $g_1$  and  $g_2$  of Eq. (10), where the function

$$f = \{f_e + (1/f^0 - 1) \exp(g_3 X_{vr})\}^{-1} \quad (17)$$

together with the purely empirical  $f_e = 1 + g_4 (1 + x)^{g_5} (1 - x)^{(1-g_5)}$  with  $g_4 = 3,56 \cdot 10^{-6}$  and  $g_5 = 8,03$  was used instead of Eq. (11). Compared to the dotted lines, significantly improved fits of the experimental data resulted for all conversion/time curves over the whole conversion range in Figs. 1 a and 1 b. Values of  $g_1$  and  $g_2$  were of the order of  $10^{14}$  and 0,5, respectively.

Fig. 3 shows a comparison of  $f$  as calculated according to Eq. (11) and Eq. (17) with experimental data. Up to a conversion of about 0,6, both calculations are almost identical, matching the experimental data well. At higher conversions, the calculation according to Eq. (17) decreases more rapidly than the calculation according to Eq. (11), with a larger resulting deviation from experimental data. We would suggest that, in view of the significantly increased experimental error, the measurements of  $f$  at high

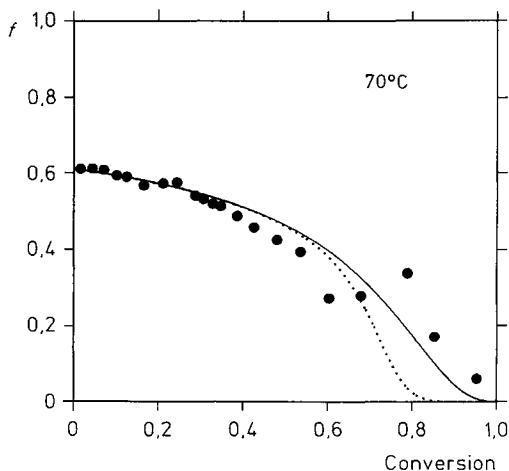


Fig. 3. Initiator efficiency  $f$  of AIBN vs. conversion at 70 °C. Experimental data (closed circles) correspond to bulk polymerization of styrene<sup>24)</sup>. The full and the dotted lines correspond to calculations of  $f$  according Eq. (11) or Eq. (17), respectively, using the parameters  $g_3 = 0,1054$  and  $f_0 = 0,61$  from Eq. (14) in both cases

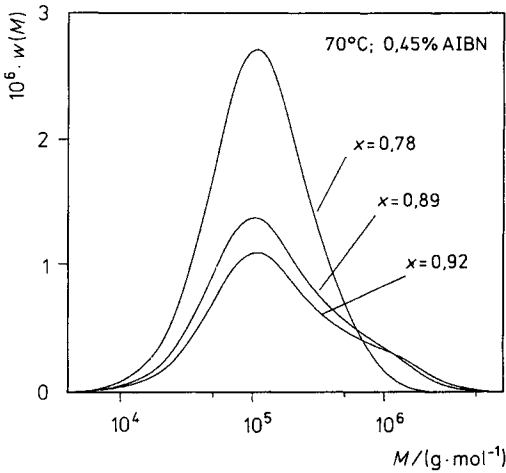


Fig. 4a. Experimental molecular weight distributions during free radical suspension polymerization of styrene up to different degrees of conversion  $x$  using 0,45% AIBN at 70 °C

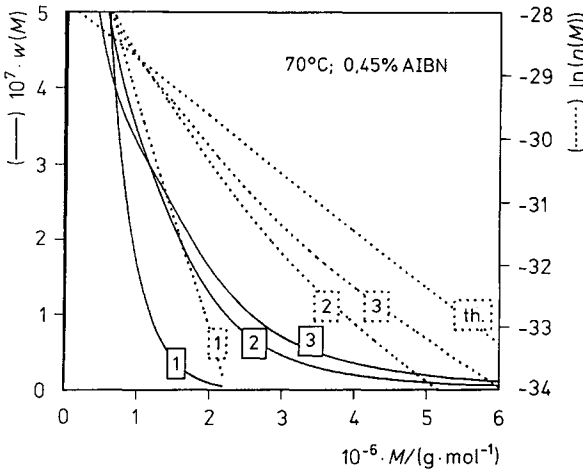


Fig. 4b. Experimental molecular weight distribution data of Fig. 4a plotted on a linear molecular weight scale. Curves 1, 2, and 3 correspond to conversions of 0,78, 0,89, and 0,92, respectively, while "th." refers to the theoretically limiting  $\ln(n(M))$ -vs.- $M$  curve at 70 °C

conversions may not rule out the behavior suggested by Eq. (17). An overestimation of the initiator efficiencies at high conversions, where polymerization has virtually ceased, would also appear to be plausible from an experimental point of view.

Further support for interpreting the decrease in polymerization rate at very high conversion in terms of a corresponding decrease in initiator efficiency comes from an examination of the molecular weight distributions (MWD's) at high conversion.

Fig. 4a shows three MWD's, which were measured at the highest conversions for the 0,45% AIBN/70 °C experiment. While the MWD is clearly monomodal at  $x = 0,78$  a second MWD with a maximum beyond  $10^6 \text{ g} \cdot \text{mol}^{-1}$  evolves at higher conversions, thus indicating a mechanistic change with respect to the polymer formation. This evolution of a bimodality in the MWD at conversions beyond around 0,9 is also observed for all other experimental conditions of the present investigation. Similar results have recently been published for the free radical polymerization of styrene in bulk<sup>3</sup>. In Fig. 4b, the high molecular weight tails of the MWDs of Fig. 4a are redrawn linearly with respect to molecular weight  $M$ . The weight fraction  $w(M)$  at molecular weight  $M$  was transformed into the number fraction  $n(M)$  according<sup>29</sup> to  $n(M) = w(M)/M$ . The natural logarithms of  $n(M)$ , which appear as dotted lines in Fig. 4b, approach the theoretical limit for transfer-determined growth of the polystyrene radicals — which was calculated according to Friis and Hamielec<sup>34</sup> using  $C_M$  from Eq. (15). The approach of  $\ln(n(M))$  to the theoretical limit with increasing conversion indicates enhanced polymer formation by the growth of isolated radicals.

A pronounced decrease in  $f$  should result in a corresponding decrease in the steady state radical termination rate  $2f k_d c_1$  and would thus ultimately lead to isolated radicals. However, a concomitant decrease in  $k_p$  would not be ruled out by this argument, and the validity of Eq. (15), even at the highest conversions, might be explained by assuming that an eventual rapid decrease of  $k_p$  is counterbalanced by a corresponding decrease in  $k_{\text{trm}}$ <sup>27</sup>.

#### *A separate look at degree of polymerization data*

Within the frame of the present investigation we wish to determine the feasibility of using an averaged termination rate coefficient, which is independent of the radical chain length, to obtain optimal simultaneous descriptions of conversion and molecular weight changes with time. To this effect, all model parameters, except for those contained in the expression for the termination rate coefficient, are assumed to be exactly known. With respect to this goal and in view of the significantly better fit of the experimental conversion/time curves, Eq. (17) was chosen over Eq. (11) as the “experimental” input for the conversion dependence of the initiator efficiency. The only remaining degree of freedom of the model up to this point is the ratio of termination by disproportionation and combination  $\gamma = k_{\text{td}}/k_{\text{tc}}$ .

Experimental polydispersities  $P_w/P_n$  did not vary significantly with temperature or the amount of initiator at conversions up to about 0,5, and have therefore been plotted in Fig. 5 without differentiating between the experimental conditions. An empirical function was fitted to these data, from which the mean polydispersity at low conversion of  $P_w/P_n = 1,6$  was deduced. This value appears to be in almost perfect agreement with measurements of O'Driscoll and Huang<sup>32</sup> at 60 °C and fixes the ratio  $\gamma$  to 0,1 within the present model. This value is estimated to be independent of temperature, amount of initiator and conversion, and to be accurate within approximately  $\pm 10\%$ .

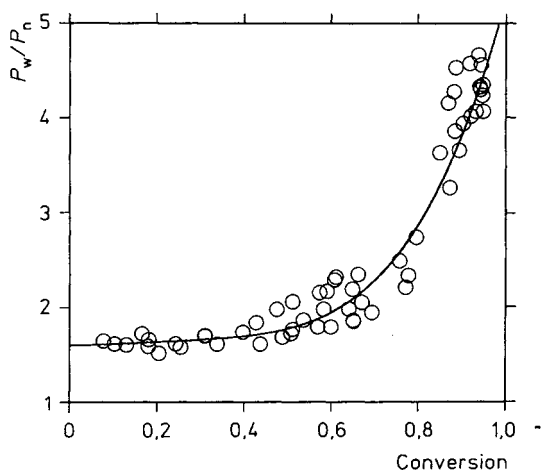


Fig. 5. Experimental polydispersities  $P_w/P_n$  not differentiated for experimental conditions. The full line corresponds to an adjusted monotonously increasing left-curved polynomial of order 4

The *separate* description of conversion/time curves on the basis of mean termination rate coefficients is beyond question. Thus, given a fixed value of  $\gamma$ , the model can be completed by fitting the time rate of conversion data. Preferably, one can test the fits of *simultaneous* representations of experimental conversion *and* average degree of polymerization data using a single set of model parameters. This may be accomplished by comparing the experimental average degrees of polymerization to those calculated using conversion/time optimized mean termination rate coefficients. Corresponding results are shown in Figs. 6a and 6b. Evidently, the model calculations, which were plotted according to conversion-adjusted variations of the termination coefficient, do not fit the experimental data. At low conversions, the calculations of  $P_w$  and  $P_n$  generally overestimate the experimental data by factors of around 2. Somewhat better agreement is obtained at higher conversions.

#### *Simultaneous description of conversion and average degrees of polymerization*

The overestimation of degrees of polymerization in Figs. 6a and 6b suggests the necessity for termination rate coefficients that are higher than those deduced from conversion/time curves at moderately low conversions. Similar hints may be inferred from the literature: Using  $k_p$  from Eq. (12),  $k_t$  values of  $0,97 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $1,37 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  have been calculated from the average molecular weight derived  $k_p^2/k_t$  values during free radical polymerizations of styrene in bulk at low conversions and temperatures of 25 °C and 40 °C<sup>4)</sup>, respectively. These values exceed  $k_t$  calculable from Eq. (16) by factors of about 2. Apparently, the molecular weight derived  $k_t$  values of Olaj et al.<sup>4)</sup> are much higher than those of Mahabadi and O'Driscoll<sup>13)</sup>, which are essentially derived from conversion data (cf. Fig. 2).

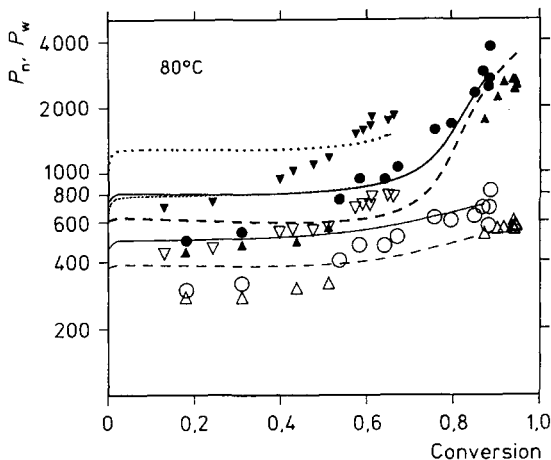


Fig. 6a. Comparison of experimental and calculated average degrees of polymerization at 80°C. Calculated lines correspond to conversion/time-adjusted termination rate coefficients. Edge-up triangles and broken lines refer to amounts of initiator of 0,45%, circles and full lines to 0,30%, and edge-down triangles and dotted lines to 0,15%. Filled symbols and bold lines indicate  $P_w$ , open symbols and thin lines indicate  $P_n$

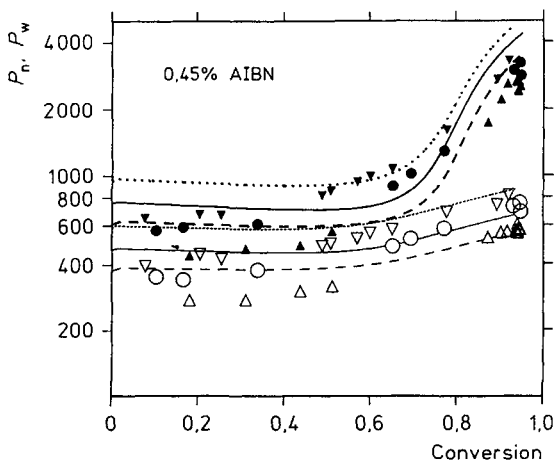


Fig. 6b. Comparison of experimental and calculated average degrees of polymerization using 0,45% of AIBN. Calculated lines correspond to conversion/time-adjusted termination rate coefficients. Edge-up triangles and broken lines refer to polymerization temperatures of 80°C, circles and full lines to 75°C, and edge-down triangles and dotted lines to 70°C. Filled symbols and bold lines indicate  $P_w$ , open symbols and thin lines indicate  $P_n$

One somewhat artificial way out of the dilemma is to use two different termination rate coefficients, i. e., one for the description of conversion, which fixes the concentration of propagating radicals during the course of polymerization, and one for the description of average degrees of polymerization. This procedure could be rationalized by assuming that the rate of termination depends on the chain length of terminating radicals. Chain length dependent termination rates would then be said to be different, depending on whether the average is taken from conversion or degree of polymerization. Correspondingly adjusted model calculations are shown in Figs. 7a and 7b, in which an average degree of polymerization derived termination rate coefficient

$$k_t^0 = 10^{11,45} \exp(-18,66 \text{ kJ} \cdot \text{mol}^{-1}/(RT)) \quad (18)$$

in  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  was obtained similarly to Eq. (16) from a mean value for the present experimental conditions and using an energy of activation of  $18,66 \text{ kJ} \cdot \text{mol}^{-1}$ . This  $k_t^0$  was used in

$$k_t^0 = \{1/k_t^0 + (M_w/g_1') \exp(g_2' X_{vf})\}^{-1} + a k_p c_M \quad (19)$$

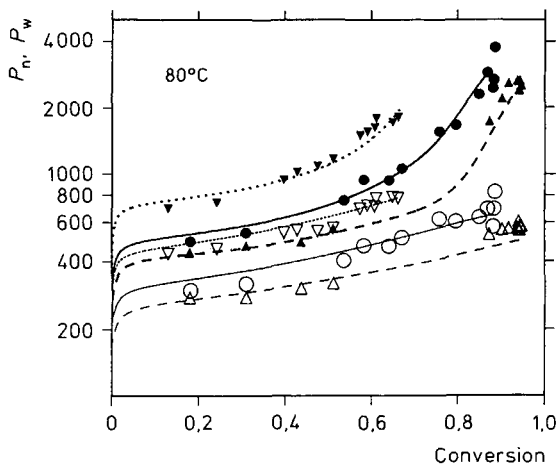


Fig. 7a. Comparison of experimental and calculated average degrees of polymerization at  $80^\circ\text{C}$ . Calculated lines correspond to simultaneous adjustments of conversion and weight-average degree of polymerization data using two different termination rate coefficients. Edge-up triangles and broken lines refer to amounts of initiator of 0,45%, circles and full lines to 0,30%, and edge-down triangles and dotted lines to 0,15%. Filled symbols and bold lines indicate  $P_w$ , open symbols and thin lines indicate  $P_n$ .

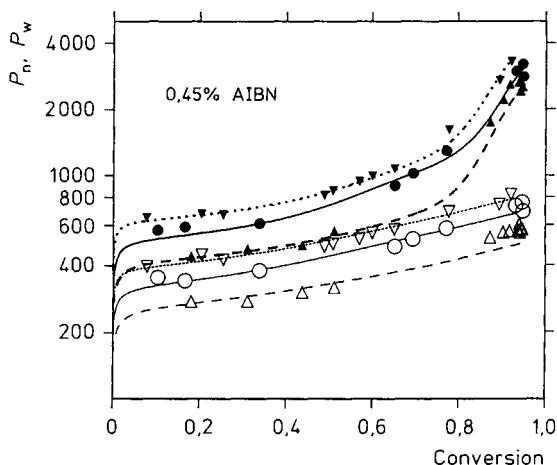


Fig. 7b. Comparison of experimental and calculated average degrees of polymerization using 0,45% of AIBN. Calculated lines correspond to simultaneous adjustments of conversion and weight-average degree of polymerization data using two different termination rate coefficients. Edge-up triangles and broken lines refer to polymerization temperatures of 80 °C, circles and full lines to 75 °C, and edge-down triangles and dotted lines to 70 °C. Filled symbols and bold lines indicate  $P_w$ , open symbols and thin lines indicate  $P_n$

for the representation of degrees of polymerization, while rate coefficients  $k_t^0$  calculated according to Eq. (16) were used in Eq. (10) for the representation of conversions. The resultant model parameters are summarized in Tab. 1. We do not seek to interpret the variation of these values, as it is our intention to concentrate on the representation of absolute  $k_t$  values using Eqs. (10) and (19).

The fit of experimental averaged degree of polymerization in Figs. 7a and 7b is much improved over that in Figs. 6a and 6b. The corresponding conversion/time curves are virtually identical to the full lines in Figs. 1a and 1b. The variations of the termination rate coefficients  $k_t$  and  $k_t'$  with conversion is shown in Figs. 8a and 8b. As expected from an examination of Figs. 6a and 6b,  $k_t'$  exceeds  $k_t$  by factors of around 2 at lower conversion, while the two termination rate coefficients approach and even intersect each other at intermediate conversions between 0,3 and 0,7. At conversions above about 0,7,  $k_t'$  is again larger than  $k_t$ , but it should be noted that the uncertainty in  $f$  at high conversions limits the reliability of any conclusions in the range above 0,7. On the whole, the variations of the termination rate coefficients in Fig. 6 — in particular the conversion-derived variations — appear to be remarkably small up to moderately high conversions, which is, however, not a new observation<sup>35,36</sup>.

The changes in the stationary state concentrations  $c_R^S$  with conversion appear in Figs. 9a and 9b. As a result of a corresponding decrease of  $k_t$ ,  $c_R^S$  increases rapidly above conversions of about 0,6 only to decrease again above conversions of about 0,9. This behavior is similar to that observed in experimental determinations of  $c_R^S$  during bulk polymerizations of styrene up to nearly 100% conversion by means of ESR<sup>11,19</sup>.

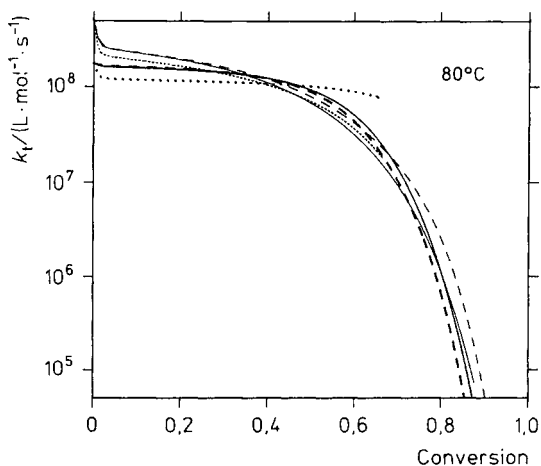


Fig. 8a. Curves of termination rate coefficients with conversion at 80 °C. Broken, full and dotted lines refer to amounts of initiator of 0,45%, 0,30% and 0,15%, respectively. Bold and thin lines indicate calculations of  $k_t$  according to Eq. (10) and  $k_t'$  according to Eq. (19), respectively, at which Eqs. (16) and (18) were used together with parameters of Tab. 1

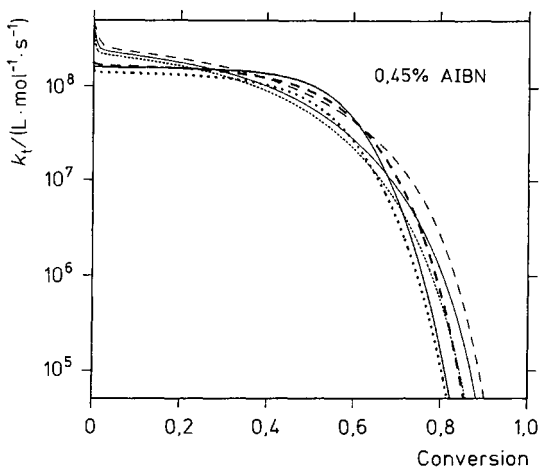


Fig. 8b. Curves of termination rate coefficients with conversion for 0,45% of AIBN. Broken, full and dotted lines refer to polymerization temperatures of 80 °C, 75 °C and 70 °C, respectively. Bold and thin lines indicate calculations of  $k_t$  according to Eq. (10) and  $k_t'$  according to Eq. (19), respectively, at which Eqs. (16) and (18) were used together with parameters of Tab. 1

According to Figs. 7a and 7b the calculations of  $P_w$  and  $P_n$  suggest a pronounced decrease in molecular weight at very low conversion. However, no experimental data were available in this conversion range, and the corresponding increase in  $k_t'$  is possibly artificial, although calculations according to Eq. (18) compare reasonably well with the low-conversion data of Olaj et al.<sup>4)</sup> Noteworthy is the very steep decrease of  $k_t'$  within a narrow conversion interval, as this would lead to somewhat lower experimental averages over that interval.

The calculations of Figs. 7a and 7b were actually performed by adjusting the parameters  $g_1$ ,  $g_2$ ,  $g_1'$  and  $g_2'$  of Tab. 1 to obtain optimized simultaneous fits of both conversion and of  $P_w$ , however not of  $P_n$ . The calculations of  $P_n$  are therefore to be



Fig. 9a. Curves of stationary state concentrations of radicals ( $c_R^S$ ) with conversion at 80 °C. Broken, full and dotted lines refer to amounts of initiator of 0,45%, 0,30% and 0,15%, respectively. Eq. (16) was used together with parameters of Tab. 1 for the corresponding calculations of  $k_t$  according to Eq. (10)

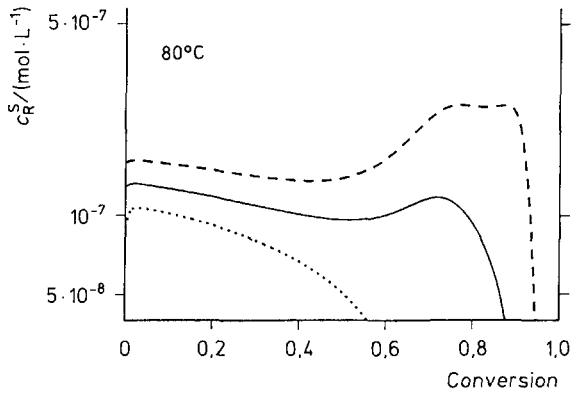
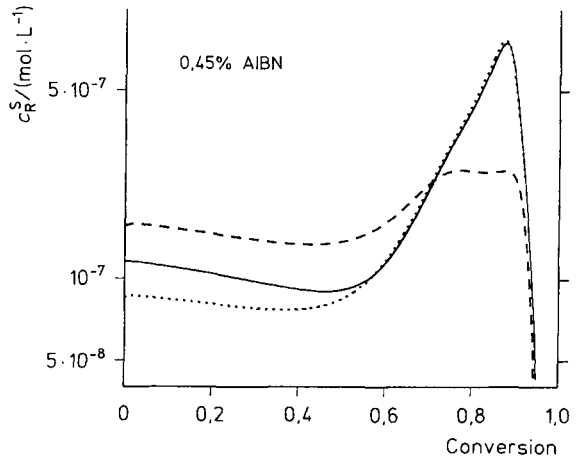


Fig. 9b. Curves of stationary state concentrations of radicals with conversion for 0,45% of AIBN. Broken, full and dotted lines characterize polymerization temperatures of 80 °C, 75 °C and 70 °C, respectively. Eq. (16) was used together with parameters of Tab. 1 for the corresponding calculations of  $k_t$  according to Eq. (10)



Tab. 1. Model parameters for different temperatures and amounts of AIBN while using  $k_t^0$  and  $k_t^{0'}$  according to Eqs. (16) and (18), respectively

Parameter	80 °C/0,15%	80 °C/0,30%	80 °C/0,45%	75 °C/0,45%	70 °C/0,45%
$g_1$	$2,69 \cdot 10^{13}$	$9,78 \cdot 10^{13}$	$1,00 \cdot 10^{14}$	$4,99 \cdot 10^{14}$	$1,81 \cdot 10^{14}$
$g_2$	$1,0 \cdot 10^{-5}$	0,393	0,481	0,601	0,501
$g_1'$	$2,67 \cdot 10^{13}$	$2,62 \cdot 10^{13}$	$2,15 \cdot 10^{13}$	$2,60 \cdot 10^{13}$	$3,03 \cdot 10^{13}$
$g_2'$	0,215	0,309	0,293	0,308	0,319

understood as predictions rather than as fits. We make this distinction to show that, contrary to a proposal of Zhu and Hamielec<sup>6)</sup>, and as was already evident from Figs. 6a and 6b, conversion-derived  $k_t$ -averages are not suitable for the description of  $P_n$  within the present system, whereas the  $P_w$ -derived  $k_t$ -averages effectively predict the behavior of  $P_n$  with conversion.

## Conclusions

The results of the present investigation suggest that optimal simultaneous descriptions of conversion/time curves and degree of polymerization or molecular weight changes with conversion during free radical polymerization of styrene in suspension are not possible on the basis of a single mean chain length independent termination rate coefficient. In the sense that some unsuspected reaction that influences the conversion-time kinetics but not molecular weights (or vice versa) is not identified yet, this hints at the necessity of using radical chain length dependent  $k_t$  values, which opens up the possibility of defining different averages of the termination rate coefficient. Whereas Zhu and Hamielec<sup>6)</sup> *theoretically* suggested a single average of the chain length dependent termination rate coefficients in free radical polymerizations for the representation of conversions and number-average degrees of polymerization and another  $k_t$  average for the weight-average degrees of polymerization, the present *experimental* results suggest one  $k_t$  average for the representation of conversions and another for the representation of  $P_w$  and  $P_n$ . Evidence for this necessity was unveiled by fixing all kinetic parameters except for the termination rate coefficient to reliable absolute values. Just to make this point more clear, we would repeat here that, with respect to the wide range of reported values for any particular rate parameter in free radical polymerization, *it is often possible that conflicting mechanistic suppositions can be supported with "evidence"*<sup>28)</sup>. This effect is expected, above all, for flexible models with many adjustable parameters.

The striking differences in the termination rate coefficients observed in this study were not obvious in a recent approach towards modeling high conversion free radical polymerization kinetics of styrene in bulk by Achilias et al.<sup>37)</sup>, mainly because these authors looked at simultaneous descriptions of conversion and polydispersity only. Because the kinetic analysis is based on reliable absolute values of the rate parameters, the two different averages of the termination rate coefficient determined in the present study may be useful in subsequent attempts to discriminate between different termination mechanisms up to moderately high conversions (approx. 0,7). At higher conversions more reliable measurements for the efficiency of the initiator and for the propagation rate coefficient are still needed. To take full advantage of the relatively costly measurements by GPC, which have reached a considerable level of accuracy during recent years, we suggest that a more sophisticated description of the whole MWD could yield more specific insights into the mechanistic peculiarities of chain length dependent termination during the free radical polymerization. Moreover, not only would academic knowledge be gained, but more importantly, from a reaction engineering point of view, the certainty of the model would be improved.

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