Seeded emulsion polymerization of butadiene. 1. The propagation rate coefficient
Published in:
Macromolecules

DOI:
10.1021/ma00054a004

Published: 01/01/1993

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

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

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 21. Dec. 2018
Seeded Emulsion Polymerization of Butadiene. 1. The Propagation Rate Coefficient

Edwin M. Verdurmen, Erik H. Dohmen, John M. Verstegen, Ian A. Maxwell, and Anton L. German*

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

Robert G. Gilbert

School of Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia

Received April 6, 1992; Revised Manuscript Received September 6, 1992

ABSTRACT: The kinetics of the emulsifier free seeded polymerization of butadiene at 60 °C in Smith–Ewart interval III was investigated using sodium peroxodisulphate as initiator. The aim of this work was to measure the propagation rate coefficient ($k_p$) of butadiene at 60 °C in emulsion polymerization. Model-independent techniques to measure propagation rate coefficients like spatially intermitted polymerizations1–3 (“rotating sector” and “laser flash” photolysis) have not been used for butadiene so far since network formation prevents acquiring the necessary data from GPC. All experiments were conducted in the presence of tert-dodecylmercaptan, as it is usual in industrial practice. The fractional conversion was based on gravimetric analysis, calibrated on-line densitometry and was found to be highly accurate. By analogy with the well-known Ugelstad plots, the product of the propagation rate coefficient ($k_p$) and the average number of radicals per particle ($n$) versus seed latex particle diameter clearly shows Smith–Ewart case I and case II regimes. From a constancy in values of $k_p/n$ (case II regime) in this plot, a value for $k_p$ could be calculated that was 3 times larger than the current literature value. It was found that negligible “thermal background initiation” is present in the butadiene system. Two linear regions in polymerization rate are observed in interval III. Model calculations are presented in excellent agreement with the experimental data. From these calculations a value of the rate coefficient for transfer to monomer, $k_{tr}$, could be estimated.

Introduction

Despite the enormous volume of polybutadiene produced annually (use of SBR latex, and polybutadiene: 1.378 000 metric tons in 1990; ABS expected use 1.4 billion pounds in 19938) very little is reported in open literature on the emulsion polymerization of butadiene. Important papers on the subject have been published following the synthetic rubber program5 and by Morton et al.6–9. The latter reported work on cross-linking and kinetics assuming Smith–Ewart case II behavior. Wendler et al.10–13 reported on the emulsion polymerization of butadiene in the presence of large amounts of bis(alkoxythio)carbonyl]-disulfanes in order to prepare low molecular weight polymer. The results indicated a strong deviation from ideal Smith–Ewart case II behavior. Bhakuni14 concluded that the nature of the emulsifier influences the polymerization kinetics and also that network formation within the polymer has no influence on the saturation monomer solubility in the polymer. Radical desorption from the particles was proposed. These conclusions were confirmed and largely complemented by the work of Weerts et al.15–21. These papers deal with a wide range of parameters such as: concentration and type of emulsifier (Rosin acid soap and SDS), electrolyte concentration, initiator concentration, degree of agitation, monomer to water ratio, and the tert–dodecylmercaptan concentration. On the basis of these experimental studies, important conclusions were made about the kinetics of the emulsion polymerization of butadiene.

The available literature value for the propagation rate coefficient ($k_p$) at 60 °C reported by Morton et al.8 is highly questionable inter alia because (1) the measurements were done on ab inito polymerizations at low temperatures (0–30 °C); the value for $k_p$ at 60 °C is therefore an extrapolation, (2) particle sizing on latexes with broad particle size distributions was performed by the soap titration method, and (3) in the modeling of the data, Smith–Ewart case II kinetics were assumed.

Model-independent techniques to measure propagation rate coefficients like “spatially intermitted polymerizations”1–3 (“rotating sector” and “laser flash” photolysis) have not been used so far since the network formation of butadiene prevents acquisition of the necessary data from GPC. The aim of this paper is to evaluate the propagation rate coefficient of butadiene at 60 °C by seeded emulsion polymerizations of butadiene in interval III, by an attempt to see a clear indication of case II ($\eta = 0.5$) conditions. Knowing $n = 0.5$ and from the observed rate and particle number, $k_p$ can be found unambiguously.

Experimental Section

Butadiene (DSM Chemicals, Geleen, The Netherlands) was distilled directly from a 27-L storage vessel into a cooled steel recipient. tert-Dodecylmercaptan (TDM), sodium peroxodisulfate (Fluka AG, Buchs, Switzerland), sodium dodecyl sulfate (p.a. Merck, Darmstadt, FRG), sodium carbonate (p.a. Merck, Darmstadt, FRG), and Aerosol MA 80 (80 % solution in methanol; Cyanamid B.V., Rotterdam, The Netherlands) were all used without further purification. Water was doubly distilled and purged with nitrogen to remove oxygen.

Emulsion Polymerizations. The seeded emulsion polymerizations were carried out in a cylindrical stainless steel reactor (1150 cm$^{3}$, diameter = 96 mm, height = 178 mm) fitted with four baffles plates located at 90° intervals and a 12-blade turbine type impeller (diameter = 60 mm, placed at a height of 1/3 of the liquid level). 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 into the density cell and back into the reactor. In this latex loop a thermosteal was installed to record the temperature of the passing liquid and thus to verify whether the latex flow was...
Seeded Emulsion Polymerization of Butadiene. I

Table I

<table>
<thead>
<tr>
<th>Component</th>
<th>Recipe Description</th>
<th>Recipe (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene</td>
<td>60% of max solid content</td>
<td>97.5</td>
</tr>
<tr>
<td>Butadiene</td>
<td>40% of max solid content</td>
<td>65</td>
</tr>
<tr>
<td>Water</td>
<td>90% of reaction mixture</td>
<td>877.5</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>$10^{-2}$ mol L$^{-1}$</td>
<td>0.93</td>
</tr>
<tr>
<td>Sodium peroxodisulfate</td>
<td>$10^{-2}$ mol L$^{-1}$</td>
<td>2.09</td>
</tr>
<tr>
<td>tert-Dodecylmercapto</td>
<td>1% on monomer</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The use of Anton Paar density meters in emulsion polymerization has been described elsewhere. The density meter was calibrated with six different liquids with density spanning the measured range. The calibration is incorporated in the computer program that records density data in 30-s intervals throughout the reaction. The signal of the density meter varies linearly with density within the measured range. The calibration is incorporated in the computer program that records density data in 30-s intervals throughout the reaction. The polymerizations were performed in a polymerization system comprising a reactor, a density meter, and a high-pressure proof syringe. From these samples the conversion was calculated via the following equation:

$$x(t) = \frac{DS^{(t)} - DS_{\text{minimal}}}{DS_{\text{maximum}} - DS_{\text{minimal}}}$$

where $x$ is the fractional conversion, $DS^{(t)}$ is the dry solid content determined at time $t$ of the reaction, $DS_{\text{minimal}}$ is the dry solid content at the start of the reaction, and $DS_{\text{maximum}}$ dry solid content at 100% conversion, both the last parameters being calculated from the recipe. Conversions assessed in this way were accurate to within 0.5%. Even though the gas cap is minimized a limited percentage of the butadiene is present as the gas phase in the reactor. This caused a systematic error for gravimetric conversion data; however, this error is of negligible importance compared to statistical errors involved in the sampling. Nevertheless, excessive sampling was avoided. Final conversions were measured by four gravimetric samples, all usually within 1% conversion. Recipes were weighed to within a 0.01-g accuracy, reducing recipe errors on the total reactor volume of 1180 cm$^3$ to negligible values. The densitometric technique seems well suited and accurate for this system, even when considering that the density of the reaction mixture is not ideal and that the mutual solubility of monomer and water is low enough to be ignored. Gravimetric conversion data are used to calibrate density data by plotting gravimetric conversion versus density at corresponding reaction times (see Figure 1). The correlation produced is used to transform the density data into conversion data ($x$). Gravimetric samples were collected using a high-pressure proof syringe. From these samples the conversion was calculated via the following equation:

$$\text{gel content} = (w_{\text{Pb}} - 2w_{\text{P}})/w_{\text{Pb}}$$

where $w_{\text{Pb}}$ is the weight of the Pb sample and $w_{\text{P}}$ is the weight of the dried filtrate. The factor 2 in eq 2 originates from the fact that 100 mL of Pb is used for extraction and only 50 mL of the filtrate is used.

The density of polybutadiene at 60 °C was measured in the form of a latex using a Anton Paar DMA 55 internal density cell,
combined with the determination of the solid content of the latex, and found to be 880 kg m$^{-3}$ independent of particle size and gel content (see Table II). This is an important result since the density of polybutadiene at the reaction temperature is used to calculate the monomer concentration in the particles.

**Latex Particle Characterization.** The average particle diameter and the particle size distribution were determined using transmission electron microscopy (TEM; Jeol 2000 FX) in combination with OsO$_4$ staining techniques. Typically, some 1000 particles were counted (Zeiss TGA-10 particle analyzer) on a micrograph taken from various parts of the TEM sample grid. Calibration of the measured particle diameters was performed with a specimen of known diameter. The particle diameters measured in this paper are weight-average diameters $d_w$ and number-average particle diameters $d_n$. Particle size distributions of the seed latexes used were extremely narrow (typically polydispersity $= 1.01$). Polydispersity ($P$) is defined as $d_w/d_n$.

The number concentration of particles, $N$, is calculated from

$$N = \frac{8(M/W)p_w}{\pi \rho_{PB} d_n^3}$$

where $(M/W)$ is the monomer to water weight ratio, $p_w$ is the density of water at 60 °C, and $\rho_{PB}$ is the density of polybutadiene at 60 °C. Special care was undertaken to inspect the particle size distribution of both the seed latex and the final product by TEM for secondary nucleation or coagulation, neither of which ever occurred during the polymerizations as used here. The monomer concentration in the particles at the start of the polymerization in interval III (a constant) was calculated according to

$$C_{m0} = \frac{M_{\text{but}}^{\text{init}}}{M_{\text{but}} + M_{\text{PB}}^{\text{init}}}$$

where $M_{\text{but}}^{\text{init}}$ is the initial mass of butadiene utilized (see Table I), $M_{\text{but}}$ is the molecular weight of butadiene, $\rho_{PB}$ is the density of butadiene at 60 °C, and $M_{\text{PB}}^{\text{init}}$ is the initial mass of polybutadiene utilized. The slight volume contraction occurring when mixing polybutadiene and butadiene is not compensated for, causing a small systematic error in $C_{m0}$.

**Theory**

Seeded emulsion polymerizations were performed in the Smith–Ewart interval III regime. An interval III analysis is relatively straightforward: the monomer concentration in the particles is described by

$$-d \ln (1 - x) = k_p N_{n0} C_{m0} N = \frac{k_p n_{n0} d_n^3}{N_{n0} d_n^3}$$

where $k_p$ is the propagation rate coefficient, $n$ is the average number of radicals per particle, $N_{n0}$ is Avogadro’s constant, and $n_{n0}$ is the number of moles of monomer present per unit volume of the water phase at the beginning of interval III (a constant). From the steady-state regime of a plot of $-\ln (1 - x)$ versus time the product of $k_p n$ can be calculated since all other variables on the right-hand side of eq 5 are known (e.g, Figure 3). Note that a value for $k_p$ cannot be calculated from such a plot until the value of $n$ is known. For this reason several important results deduced from ab initio interval II and III analyses of the emulsion polymerization of butadiene need to be evaluated. From ab initio interval II analysis it was shown that the polymerization kinetics depend solely on particle size: there is a decrease in the rate per particle with decreasing particle size. Using the estimate for the value of $k_p$ of 100 L mol$^{-1}$ s$^{-1}$ reported by Morton et al.,$^6$ implies that $n \ll 0.5$. Ab initio interval III analysis,$^{15,21}$ showed that plots $-\ln (1 - x)$ versus time under various initiator and electrolyte concentrations and over a wide range of particle sizes are linear. However, bimolecular termination rate coefficients are expected to vary significantly with the weight fraction of polymer (w$_p$) in interval III. Therefore, the following conclusions were reached:

1. Termination is not rate determining and thus instantaneous upon entry of free radicals into particles. This leads to the conclusion that butadiene is a Smith–Ewart case I or II system at 62 °C and at particle diameters below 200 nm. This is an important consideration, since in the limit of $n = 0.5$ a value for $k_p$ can be calculated from the steady-state regime of the plot of $-\ln (1 - x)$ versus time and the eq 5.

2. Both $n$ and $k_p$ are constant during a particular polymerization up to $w_p = 0.85$, since it is highly unlikely that $n$ and $k_p$ would counterbalance each other under the wide range of experimental conditions. This is because the right-hand side of eq 5 consists of only constants within a particular polymerization. Thus for every separate seeded polymerization a unique value of the product of $k_p$ can be determined.

The aim of this work was to see if raising the particle diameter above 200 nm in seeded polymerizations could drive $n$ to the limiting Smith–Ewart case II value of $n = 0.5$. This would enable the calculation of $k_p$ at that limit. This strategy is slightly different from the one that has been successfully applied to the styrene system.$^{1,28}$ Here the initiator concentration was increased to raise $n$. In the butadiene case particle diameter is increased since it has been reported that the polymerization rate per particle in the butadiene case is insensitive to large changes in initiator concentration.$^{5,16-18,21,29}$

**Results and Discussion**

To convert the gravimetric conversion data and density data into conversion–time data, three plots were made for every polymerization (each polymerization was separately calibrated). Examples of such plots are depicted in Figures 1–3. In Figure 4 a plot of $k_p n$, calculated from eq 5 and with the use of slopes from curves for reactions with varying particle diameters, as in Figure 3, is presented. The data clearly show that $n$ is constant above particle sizes of 200 nm, strongly suggesting that this corresponds to $n = 0.5$. Below particle diameters of 200 nm the approach to the
from transforming density data into conversion data.


Figure 2. Conversion in interval III (%) versus reaction time (h). These plots consist of an average of 1000 data points gained from transforming density data into conversion data.

Figure 3. \(-\ln (1-x)\) versus reaction time (h) calculated from conversion-time data depicted in Figure 2. The plot shows an approach to steady state and a steady-state linear part. The slope of the linear part of such a plot is used in eq 5 to calculate the product of the propagation rate coefficient, \(k_p\), and the average number of radicals per particle, \(n\).

Figure 4. Product of the propagation rate coefficient, \(k_p\), and the average number of radicals per particle, \(n\), versus seed latex particle diameter (nm). The plot shows a plateau for particle diameters >200 nm and an approach to that plateau for particle diameters <200 nm.

Table III

<table>
<thead>
<tr>
<th>(d_w) (nm)</th>
<th>(N_w \times 10^{-19}) (m²)</th>
<th>(C_m0 \times 10^{-3}) (mol m⁻³)</th>
<th>(n_m0 \times 10^3) (mol m⁻³)</th>
<th>slope (h_p) (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>0.79</td>
<td>5.39</td>
<td>1.408</td>
<td>0.0311</td>
</tr>
<tr>
<td>268</td>
<td>1.05</td>
<td>5.34</td>
<td>1.390</td>
<td>0.0392</td>
</tr>
<tr>
<td>268</td>
<td>1.22</td>
<td>5.26</td>
<td>1.338</td>
<td>0.0340</td>
</tr>
<tr>
<td>268</td>
<td>1.22</td>
<td>5.28</td>
<td>1.348</td>
<td>0.1415</td>
</tr>
<tr>
<td>234</td>
<td>1.98</td>
<td>5.30</td>
<td>1.381</td>
<td>0.0558</td>
</tr>
<tr>
<td>224</td>
<td>2.00</td>
<td>5.29</td>
<td>1.353</td>
<td>0.0599</td>
</tr>
<tr>
<td>216</td>
<td>2.30</td>
<td>5.28</td>
<td>1.351</td>
<td>0.0781</td>
</tr>
<tr>
<td>216</td>
<td>2.34</td>
<td>5.33</td>
<td>1.373</td>
<td>0.0983</td>
</tr>
<tr>
<td>216</td>
<td>2.34</td>
<td>5.31</td>
<td>1.362</td>
<td>0.1027</td>
</tr>
<tr>
<td>210</td>
<td>2.55</td>
<td>5.34</td>
<td>1.380</td>
<td>0.1171</td>
</tr>
<tr>
<td>207</td>
<td>2.64</td>
<td>5.29</td>
<td>1.0988</td>
<td>0.1288</td>
</tr>
<tr>
<td>207</td>
<td>2.65</td>
<td>5.50</td>
<td>1.488</td>
<td>0.0985</td>
</tr>
<tr>
<td>190</td>
<td>3.42</td>
<td>5.13</td>
<td>1.396</td>
<td>0.1062</td>
</tr>
<tr>
<td>166</td>
<td>5.17</td>
<td>5.40</td>
<td>1.418</td>
<td>0.1289</td>
</tr>
<tr>
<td>151</td>
<td>6.82</td>
<td>5.32</td>
<td>1.368</td>
<td>0.1277</td>
</tr>
<tr>
<td>90</td>
<td>31.8</td>
<td>5.23</td>
<td>1.350</td>
<td>0.3055</td>
</tr>
<tr>
<td>45</td>
<td>264</td>
<td>5.33</td>
<td>1.371</td>
<td>0.3350</td>
</tr>
<tr>
<td>45</td>
<td>275</td>
<td>5.31</td>
<td>1.365</td>
<td>0.3388</td>
</tr>
</tbody>
</table>

Table IV

<table>
<thead>
<tr>
<th>(d_w) (nm)</th>
<th>(N \times 10^{-19}) (m²)</th>
<th>(h_p) (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>216</td>
<td>2.34</td>
<td>180.4</td>
</tr>
<tr>
<td>216</td>
<td>2.34</td>
<td>187.8</td>
</tr>
</tbody>
</table>

* Pre-heat-treated seed latex.

The data reported by Weerts et al.18,21 Table III incorporates the values necessary to calculate the experimental values of \(k_p n\).

For the experiments performed the particle concentration is varied over 2 orders of magnitude while \(C_m0\) and \(n_m0\) are virtually constant. Note that the \(C_m0\) never surpasses the maximum reported18,21 solubility of butadiene in polybutadiene of \(C_m = 5.6\ \text{mol L}^{-1}\); hence, all polymerizations are performed in interval III. The constant value of \(n\) above particle diameters of 200 nm shows some scatter due to a combination of inaccuracies inherent in determining the slopes of \(-\ln (1-x)\) versus time curves (ca. 10%) and also in the latex particle concentrations (ca. 10%). The propagation rate coefficient can consequently only be calculated with limited accuracy, as is expected from such a model-dependent method. The value for the propagation rate coefficient determined from Figure 4 is \(k_p = 320 \pm 50 \ \text{L mol}^{-1} \ \text{s}^{-1}\). Note however that this new value is 3 times higher than the value reported by Morton et al.8 No model-independent value of the propagation rate coefficient is known for butadiene.

It is worthwhile noting that "background initiation" may originate, other than added persulfate, may fluctuate with, say, seed latex size and could be a cause of the scatter mentioned in the previous paragraph. The possible presence of a "thermal background initiation" rate in the butadiene system was checked by performing two seeded polymerizations on the same seed latex. In one of the experiments the seed latex was covered with 75% of the maximum SDS coverage (as was determined by tensiometric titration) and heated at 80 ⁰C for 16 h before swelling and polymerization. The other experiment was performed normally. The heating of the latex will hopefully decompose any radical, yielding substances like peroxides of residual persulfate. Table IV shows the results of both polymerizations. No significant difference in slopes or \(n\) is found, even though the particle diameter used is in the case II range was an effect of thermal background initiation on \(n\) should show up in the rate of polymerization. Therefore it was concluded that thermal background...
Model Calculations

In this section known theories for entry and exit of radicals from latex particles are combined in a model to elucidate the behavior of the average radical concentration in the particles of an emulsion polymerization of butadiene as a function of particle diameter.

The increase of \( n \) with increasing particle size is due to two phenomena: the increase of the entry rate caused by a decrease of the particle concentration in the various recipes and a simultaneous decrease of the exit rate because of an increase in the particle diameter.

1. The entry rate coefficient for radicals into particles (\( \rho \)) as reported by Maxwell et al. is given by eq 6:

\[
\rho = \left[ \frac{2k_d[I][N_{av}]}{N} \right] \left[ \frac{2k_i[T^*]}{k_M M_{eq} + 1} \right]^{-2}
\]  

where \( \rho \) is the entry rate coefficient, \( k_d \) is the dissociation rate coefficient of peroxydisulfate, \( I \) is the initiator concentration, \( k_i \) is the bimolecular termination rate coefficient of two radicals in the water phase, \( [T^*] \) is the total aequous phase radical concentration for which Ugelstad et al. used \( [T^*] = (k_d[I]/k_i)^{1/2}, M_{eq} = \) the butadiene water solubility, and \( z \) is the degree of polymerization that causes an oligomeric radical with a sulfate end group to be surface active. The values of the parameters are listed in Table V. The following brief discussion presents some information about the parameters used. The value for \( k_d \) used is reported in the literature and measured in the presence of butadiene in an emulsion system: \( 6.3 \times 10^{-6} \text{g}^{-1} \text{mol}^{-1} \text{s}^{-1} \). From the literature it is known that bimolecular termination rate constants \( k_i \) in aqueous media are on the order of magnitude of \( 10^{-9} - 10^{-10} \text{mol}^{-1} \text{L}^{-1} \text{s}^{-1} \). For \( M_{eq} \) the value of \( 37 \times 10^{-3} \text{mol} \text{L}^{-1} \) is taken since this value is measured at a saturation pressure of butadiene, comparable with polymerization conditions. The value for \( x \) used is 3 monomer units, calculated from a method described by Maxwell et al. Further work is being done on this subject and will be published separately.

2. The first-order exit rate coefficient is given by:

\[
k = k_{ex} C_m \left[ \frac{k_i}{k_{ex} + k_{po} C_m} \right]
\]

where \( k_{ex} \) is the rate coefficient for transfer to monomer, \( k_{po} \) is the propagation rate coefficient of a single monomeric radical with a monomer unit, and \( k_{es} \) is the escape rate coefficient of monomer from the particle given by

\[
k_{es} = 3D''/R_s q
\]

where \( R_s \) is the swollen radius of the latex particles, \( q \) is the partition coefficient of the monomeric radicals between the particle and water phases \( q = C_{m}/M_{eq} \), and \( D'' \) is the diffusion coefficient of the monomeric radical in water. \( D'' \) is calculated according to the Wilke and Chang equation and found to be \( 1.5 \times 10^{-7} \text{dm}^2/\text{s} \).
Introducing the expression for the first-order rate coefficient for escape in the final equation for the exit rate coefficient as proposed by Ugelstad and Hansen renders

\[ k = \frac{3D^*}{(2d_w)^3} \left( \frac{k_{20} C_m}{k_{p0} C_m + \frac{3D^*}{(2d_w)^3}} \right) \] (9)

Very little is reported on the value for \( k_p \) except for an estimation on kinetic grounds by Weerts et al.\(^{16,21}\) of \( k_p = 0.1 \text{ L mol}^{-1} \text{s}^{-1} \). The monomer concentration in the particles, \( C_m \), is reported\(^{16,21}\) to be 5.6 mol L\(^{-1}\). The value of \( k_{p0} \) may differ from the long-chain value of \( k_p \); however, for simplicity in the following discussion, \( k_{p0} \) is assumed to be identical to \( k_p \). \( d_w \) is the swollen weight-average particle diameter. Figure 6 shows the values of the exit rate coefficient predicted from eq 9 for various values of \( k_{p0} \) (actually \( k_p \)). It is apparent that the exit rate coefficients decrease with particle diameter although the decrease is less significant than the increase in entry rate coefficients. One of the curves in Figure 6 should reflect the actual exit rate coefficient of the experimental polymerizations, since at each particle size the experimental particle concentration was used to calculate the exit rate coefficient by eq 9.

Assuming that the Smith-Ewart case I and II approximations hold for the butadiene polymerization system at interest, \( n \) can be calculated in terms of the entry and exit rate coefficients.\(^{44}\)

\[ n = \rho/(2k + \rho) \] (10)

It is easily shown that as the particle diameter increases the corresponding increase in \( \rho \) and decrease in \( k \) results in the limiting value of \( n = 0.5 \). In practice this means that a plot of \( k_p \) versus particle diameter, in analogy with the well-known Ugelstad graphs,\(^{45,46}\) should show a constant value of \( k_p \) (in fact a constant value of \( n \) since \( k_p \) is assumed to be constant) above a certain particle diameter as long as the Smith-Ewart case II approximation holds. Figure 7 shows a graph of \( k_p \) versus particle diameter calculated with the use of the values for the calculated entry rate coefficient, \( \rho \), and exit rate coefficient, \( k \), of Figures 5 and 6. Comparison of the experimental data (\( \rho \) versus \( d_w \)) with the model prediction (Figure 7) indicates that the model predicts both the approach to the plateau and the existence of the plateau itself. Note that the \( k_p \) is varied over a small range compared to the usual inaccuracy in which propagation rate coefficients are known. The curve describing the experimental data includes two pieces of independent information:

1. The data show a plateau in \( n \) versus \( d_w \) from which a propagation rate coefficient can be determined. The assumptions necessary to reach this conclusion are as follows: (a) butadiene behaves like a Smith-Ewart case I or II system; (b) \( k_p \) and \( n \) are both constant throughout interval III; (c) \( n = 0.5 \) at the plateau value (case II approximation).

2. An approach to a plateau is expected as a consequence of the shift from case I to case II kinetics. It will be shown below that, given a value of the \( k_p \), determined by the plateau regime, a value of \( k_T \) can be deduced from the nonplateau regime of the \( k_p \) versus \( d_w \) plot.

The fact that both regimes discussed above can be fitted using the Smith-Ewart case II approximations (eq 10) and models for \( \rho \) and \( k \) is a strong indication that the use of these approximations for the butadiene system is justified.

The fit of model and experiment is extremely sensitive to variations in the values of \( k_T \) and \( k_p \). Figure 8 shows a plot of the calculated \( k_p \) versus particle diameter using \( k_T = 320 \text{ L mol}^{-1} \text{s}^{-1} \) for various values of \( k_{p0} \). Note that the \( k_{p0} \) is varied over a wide range. The best agreement between model and experiment is for a value of \( k_{p0} = 0.01 \text{ L mol}^{-1} \text{s}^{-1} \). We should note however that these values were found by assuming a value for \( k_T = 7 \times 10^4 \text{ L mol}^{-1} \text{s}^{-1} \).
Figure 9. Model calculations and experimental data of the product of the propagation rate coefficient, \(k_p\) (L mol\(^{-1}\) s\(^{-1}\)), and the average number of radicals per particle, \(n\) versus seed latex particle diameter \(d_w\) for \(k_p = 320\) L mol\(^{-1}\) s\(^{-1}\), the bimolecular termination rate coefficient \(k_t = 10^{10}\) L mol\(^{-1}\) s\(^{-1}\), and various values of the rate coefficient for transfer of radical activity to monomer, \(k_{t,2}\) (L mol\(^{-1}\) s\(^{-1}\)).

Figure 10. Model calculations and experimental data of the product of the propagation rate coefficient, \(k_p\) (L mol\(^{-1}\) s\(^{-1}\)), and the average number of radicals per particle, \(n\) versus seed latex particle diameter \(d_w\) for \(k_p = 320\) L mol\(^{-1}\) s\(^{-1}\), the bimolecular termination rate coefficient \(k_t = 10^{10}\) L mol\(^{-1}\) s\(^{-1}\), and various values of the rate coefficient for transfer of radical activity to monomer, \(k_{t,2}\) (L mol\(^{-1}\) s\(^{-1}\)).

Variation of \(k_t\) within the range discussed before has a dramatic effect as is shown in Figures 9 and 10. Therefore, \(k_t\) is presented as an order of magnitude value, \(k_t = 0.1 - 0.01\) L mol\(^{-1}\) s\(^{-1}\). This range is in accord with the proposed value for the \(k_t\) reported by Weerts et al.\(^{(5)}\),\(^{(21)}\)

From the \(k_pA\) versus \(d_w\) data the following three conclusions are reached.

1. The propagation rate coefficient can be calculated from the plateau region. The assumptions necessary to reach this conclusion are as follows: (a) butadiene behaves like a Smith–Ewart case I or II system; (b) \(k_p\) and \(n\) are both constant during the beginning of interval III; (c) \(n = 0.5\) at the plateau (case II approximation).

2. The nonplateau regime is a consequence of the shift from case I to case II kinetics and therefore a strong indication of the existence of case I and case II regimes in the butadiene system.

3. The excellent agreement of the model and experiment allows the calculation of an order of magnitude value for \(k_t\) from the nonplateau regime. The fitted value of \(k_t\) is the result of a model calculation using some (in certain limits adjustable) parameters and is therefore only calculated to within an order of magnitude. No value for the \(k_t\) for the butadiene system has been reported except a proposal\(^{(15,21)}\) mentioned earlier.

Conclusions

The emulsifier free seeded emulsion polymerization of butadiene could be performed at 60 °C in Smith–Ewart interval III without any coagulation or secondary nucleation. Gravimetrically calibrated densitometry is an extremely useful method for determining monomer conversion at high data acquisition rates with minimal disturbance of the polymerization system.

The density of polybutadiene at 60 °C was found to be independent of both the particle size and the degree of network formation in the particles (as was determined by the so-called toluene extraction method). The gel content of the seed latexes was moderate and did not affect the monomer solubility in the polymer nor the time needed to swell the polymer.

The plots of \(-\ln\ (1 - x)\) versus time show two linear regions. The last and steepest region is used to determine \(n\). From the data acquired by simultaneously varying the seed latex particle diameter (45-300 nm) and particle number concentration over 2 orders of magnitude, a plot of \(k_{t,2}\) versus seed latex particle diameter could be determined. This plot, an analogy to the well-known Ugelstad plots, clearly shows Smith–Ewart case I and case II regimes. From the constancy of \(n\) in this plot above a particle diameter of 200 nm, the propagation rate coefficient for butadiene polymerizations at 60 °C could be estimated to be 320 ± 50 L mol\(^{-1}\) s\(^{-1}\).

Known theories of emulsion polymerization kinetics are combined into a model that fits the experimental data extremely well and is capable of rendering an extra piece of information in the form of an order of magnitude value for the rate coefficient for transfer of radical activity to monomer. The rate coefficient for transfer to monomer is calculated to be in the range of 0.1-0.01 L mol\(^{-1}\) s\(^{-1}\).

Continuing research is being conducted to clarify the effects upon the emulsion polymerization of butadiene of (a) initiator concentration,\(^{(8)}\) (b) the addition of tert-dodecylmercaptan,\(^{(46)}\) and (c) the two regions of linear slope in plots of \(-\ln\ (1 - x)\) versus time.\(^{(21)}\) The results of these studies will be published separately.

Acknowledgment. The authors are indebted to DSM Research Geleen, The Netherlands, for financially supporting this work.

References and Notes

Seeded Emulsion Polymerization of Butadiene. 1


(22) Verduren, E. M. F. J.; Dohmen, E. H. M.; German, A. L., to be published.
(29) Verduren, E. M. F. J.; Verstegen, J. M. G.; Maxwell, I. A.; German, A. L., to be published.
(31) Verduren, E. M. F. J.; Gilbert, R. G.; German, A. L., to be published.