A Decrease in Effective Acrylate Propagation Rate Constants Caused by Intramolecular Chain Transfer

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Introduction. Latices prepared by semibatch emulsion polymerization are widely used in a variety of applications such as adhesives, coatings, and synthetic rubbers. These processes are usually carried out under starved conditions because of heat removal limitations or to avoid compositional drifts. The mathematical modeling of semibatch emulsion polymerization processes has been reported.[1−4] These models require, between other kinetic parameters, the propagation rate constant. The IUPAC Working Party "Modeling of Kinetics and Processes of Polymerization"[5] has devoted considerable effort to obtain consistent values for the propagation rate constants of several monomers. The method recommended by the IUPAC Working Party to determine propagation rate constants is the pulsed laser polymerization (PLP), which is linked to the analysis of the molecular weight distribution (MWD) of the polymer produced by size exclusion chromatography (SEC). For some monomers such styrene[6] and methyl methacrylate,[7] benchmark k_p values have been provided. For other monomers such as *n*-butyl acrylate, BA, the implementation of PLP has encountered some difficulties. Thus, Lyons et al.[8] calculated k_p values for BA finding that the consistency checks for the PLP experiments were fulfilled from −65 to −7 °C, but not at higher temperatures. Lyons et al.[8] suggested that side reactions such as intramolecular transfer to polymer that affects SEC separation can cause such difficulties. Beuermann et al.[9] provided k_p values for BA up to temperatures about 30 °C. In addition, they found that their data could be combined with the data obtained by Lyons et al.[8] in a lower temperature range to obtain a reasonable Arrhenius plot of the combined data set. Beuermann et al.[9] pointed out that the failure in getting k_p values at temperatures above 30 °C was due to the chain transfer to monomer, which becomes the predominant termination mechanism at higher temperatures. They suggested that high-temperature k_p values could be obtained by running PLP experiments at higher pulse repetition rate or by using a solvent with a significantly less transfer activity than BA. The feasibility of the first suggestion was supported by simulations carried out by Busch and Wahl,[10] but no experimental confirmations were reported. Recently, Beuermann et al.[11,12] carried out PLP/SEC experiments for BA in supercritical fluid CO_2 under different temperature and pressure ranges, but always below 30 °C, finding that k_p decreased as CO_2 concentration increased. Thus, the k_p of BA reduces a 40% with respect to the corresponding value in bulk.[8,9] According to Beuermann et al.,[11,12] the local concentration of the monomer in the vicinity of the chain end radical differs when bulk and CO_2 solutions are used due to polymer−solvent interaction, which might change the polymer coil size.

k_p values obtained from PLP/SEC analysis for BA are 2 orders of magnitude larger than those used before the development of the PLP/SEC technique. The new values of k_p do have mechanistic implications in emulsion polymerization. Thus, BA emulsion polymerization has been considered to proceed under pseudobulk conditions,[13−15] but the use of the PLP−SEC value[8−9,16] led to the conclusion that the emulsion polymerization of BA was a zero-one system.[17] However, such a conclusion might be premature.

In the present work, it is shown that the evolution of the instantaneous conversion, sol MWD, gel content, and extent of branching during the emulsion polymerization of BA are not consistent with a zero-one system, but with an average number of radicals per particle close to or greater than 0.5. This means that the effective propagation rate constant should be significantly lower than the propagation rate constant value calculated by PLP/SEC.

Experimental Section. *n*-Butyl acrylate and acrylic acid, sodium hydrogen carbonate (Panreac), potassium persulfate (Fluka), and DDI water were used as received throughout the work. Seeded semicontinuous polymerizations were carried out in a 1 L glass reactor at 75 °C using a set of three pitch blade impellers at 200 rpm. The seed ($d_p = 97$ nm, solids content = 20.5 wt %, and prepared using SLS (Merck)), the surfactant (provided by Rhodia), the initiator, and the water were initially charged into the reactor. The feed was divided in two streams: one was a preemulsion and the other an initiator solution. The final solids content was about 40 wt %. Samples were withdrawn from the reactor, and conversion was measured gravimetrically and particle size by dynamic light scattering and by capillary hydrodynamic fractionation, CHDF. The sol molecular weight distributions were determined by gel permeation chromatography using a dual detector system formed by a differential refractometer and a viscometer. The amount of gel was determined by means of an extraction process under reflux conditions in THF. The level of branching was measured by solid-state ^{13}C NMR by analyzing the percentage of quaternary carbons in the spectrum as reported in the literature.[18,19]

Results and Discussion. Figure 1 presents the evolutions of the instantaneous conversion and the percentage of branches of the final latexes for the different initiator concentrations. Figure 2 shows the effect of initiator concentration on the weight-average molecular weight and cumulative gel content. These figures show that the polymerizations were carried out under rather starved conditions, and about 55−60% of

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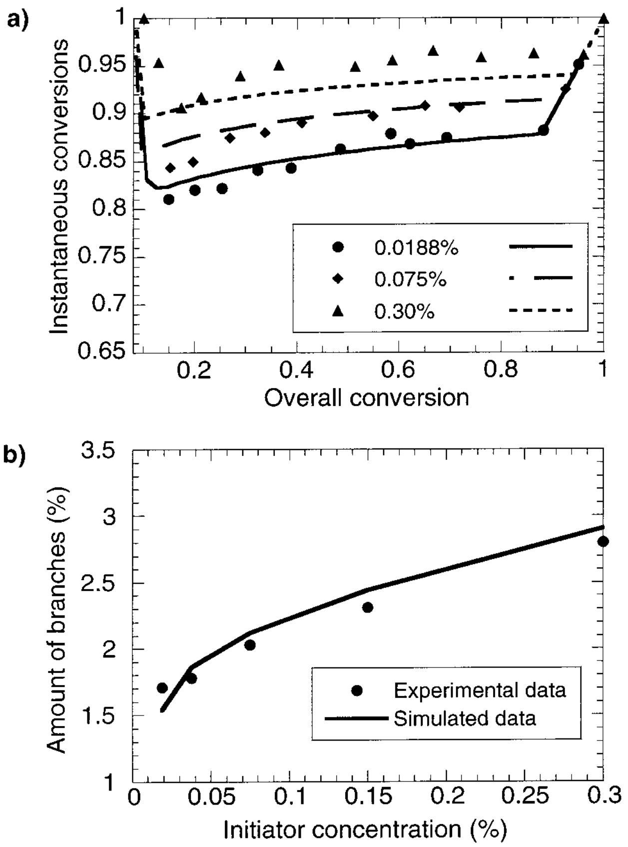


Figure 1. Evolution of the experimental (points) and simulated (lines) data for latexes prepared with different initiator concentrations: (a) instantaneous conversion; (b) final level of branches.

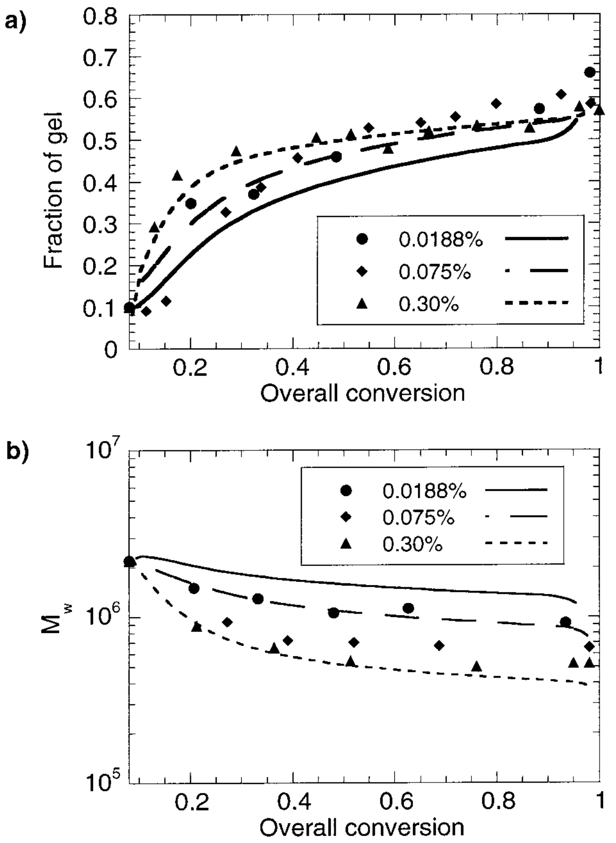


Figure 2. Evolution of the experimental (points) and simulated (lines) data for latexes prepared with different initiator concentration: (a) fraction of gel; (b) weight-average molecular weights.

gel was obtained at the end of the processes. In addition, the percentage of branches ranged from 1.7 to 2.8%.

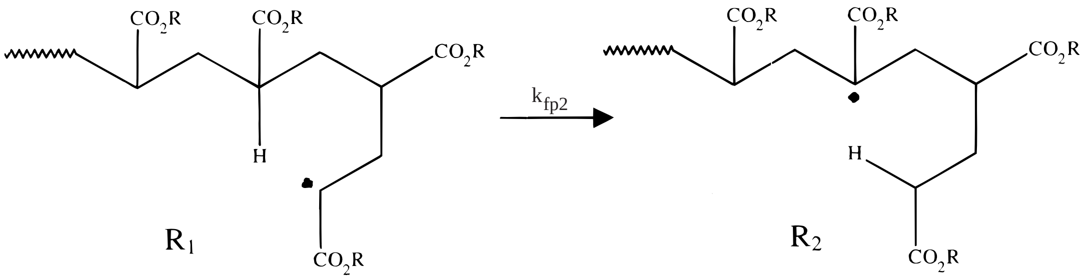
One must be cautious about the meaning of the experimentally determined gel. This is the polymer fraction that cannot be dissolved by THF. An indication of the minimum molecular weight that cannot be dissolved by THF can be obtained from the maximum molecular weight obtained in the GPC trace of the soluble polymer. For these reactions, no polymer was observed over a molecular weight of 7×10^6. Therefore, polymer exceeding this value was considered to be gel.

These results were analyzed by means of a mathematical model that included the calculation of gel and sol molecular weight distribution[20] in the framework of the partial distinction approach[21] to account for the compartmentalization of radicals in the polymer particles. In addition, the model was modified to consider the polymer with molecular weights over 7×10^6 to be gel.

Molecular weights high enough to give apparent gel, i.e., higher than 7×10^6 g/mol, can in principle be produced by several mechanisms: (1) intermolecular chain transfer to polymer, (2) propagation to terminal double bond, and (3) termination by combination. On the other hand, the number of branches is affected by inter- and intramolecular (backbiting) chain transfer to polymer.[22,23]

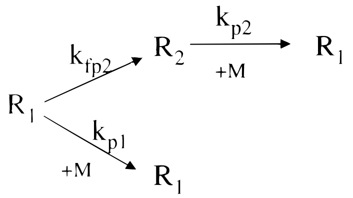
The model described above was used in an attempt to fit the data reported in Figures 1 and 2. Combination of the k_p values reported by Beuermann et al.[9] for bulk polymerization in the range 5−30 °C with those obtained by Lyons et al.[8] in the temperature range −67 °C $\leq T \leq$ −7 °C allows to estimate a value of k_p of 44 290 L mol^{-1} s^{-1}. Under these circumstances $\bar{n} \approx 0.1$, and hence termination by combination was not significant. Using $k_p = 44\,290$ L mol^{-1} s^{-1}, monomer conversion was relatively easy to fit, but fitting of the sol MWD, gel content, and percentage of branches was more challenging. In particular, when only intermolecular chain transfer was considered, the gel content was in general lower than that obtained experimentally (Figure 3a), and the percentage of branches was too low for the values of C_p (k_{fp}/k_p) in the range given by the literature ($0.1 \leq C_p \times 10^{+4} \leq 10$).[24,25] In addition, the model predictions for the gel fraction were much more sensitive to the initiator concentration than the experimental results, and the sol molecular weights were too high (solid lines in Figure 3a,b). When both intermolecular chain transfer to polymer and propagation to terminal double bonds were considered, the model predicted a substantial effect of initiator concentration on the amount of gel (not observed experimentally, Figure 3a), the percentage of branches was too low (2 orders of magnitude lower), and the molecular weights were too high (Figure 3b). Finally, when intramolecular chain transfer to polymer was also included, gel content and level of branches for a single experiment were well fitted, but the model predictions were still too sensitive to variations in the initiator concentration and the molecular weights were too high. These results showed that the model was not consistent with the experimental results. Exploratory simulations showed that the model could be made consistent with the experimental data if termination by combination played a significant role in the gel formation. This requires $\bar{n}$ being close to or greater than 0.5, namely, a k_p substantially lower than

Scheme 1



that obtained from PLP/SEC.[8,9] Obviously, one wonders about the reasons for this low k_p.

It is known that intramolecular chain transfer to polymer occurs in the polymerization of BA[19] following Scheme 1. According to McCord et al.,[23] the reactivity of tertiary carbon radicals originated by backbiting, R_2, is much lower than that of secondary radicals, R_1.[9,26] Furthermore, experimental studies indicate that increasing the size of the alkyl side chain on a monomer reduces activity; the polymerization rate of methyl ethacrylate is 1 order of magnitude lower than that of methyl methacrylate.[27,28] Thus, it is reasonable to expect that the activity of the alkylated acrylate radical, R_2, originated from the backbiting mechanism in the polymerization of BA will be much lower than that of an acrylate radical, R_1. This leads to the following reaction scheme:



where k_{fp2} is the intramolecular chain transfer reaction and k_{p1} and k_{p2} are the propagation rate constants of radicals R_1 and R_2, respectively. In addition, $k_{p1} \gg k_{p2}$. According to this scheme, the effective polymerization rate constant, $\overline{k_p}$, is given by

$$\overline{k_p} = k_{p1}P_1 + k_{p2}P_2 \tag{1}$$

where P_1 and P_2 are the probabilities of having a radical of type R_1 and R_2, respectively. These probabilities are given by

$$P_1 = \frac{k_{p2}[M]}{k_{fp2} + k_{p2}[M]};\quad P_2 = 1 - P_1 \tag{2}$$

where it is implicitly assumed that the rates of termination and transfer to monomer by radicals of type R_2 are negligible. Equations 1 and 2 show that for a given system, i.e., given values of k_{p1}, k_{fp2}, and k_{p2}, the effective propagation rate constant depends on monomer concentration. Thus, in starved semicontinuous emulsion polymerization, the effective propagation rate constant, $\overline{k_p}$, will be lower than that in the initial stages of bulk polymerization. In the frame of the present model, PLP provides values for the effective polymerization rate constant, which would coincide with k_{p1} only if P_1 approaches unity. However, even at the initial stages of bulk polymerization there is no guarantee that $P_1 = 1$. Therefore, in this work, k_{p1} was considered to be unknown and was estimated together with k_{p2} and k_{fp2} by fitting the data in Figures 1 and 2 with the model. Figures 1 and 2 show a comparison between experimental results and model predictions using the parameters presented in Table 1. It can be seen that a fairly good agreement between experimental results and model predictions was achieved. It is also noticeable that when eqs 1 and 2 are used with data in Table 1 for bulk conditions ([M] = 7.4 mol/L), the effective propagation

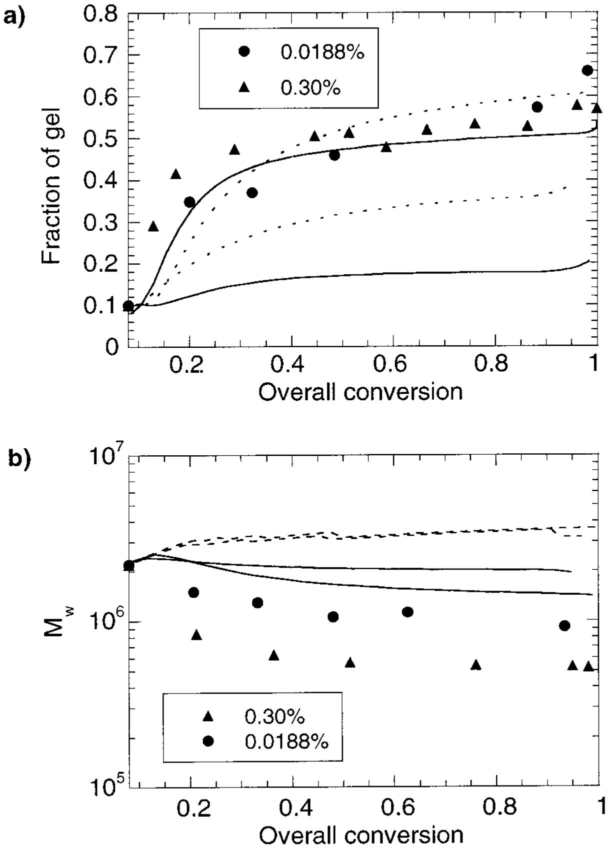


Figure 3. Comparison between experimental (points) and simulated (solid lines) data of (a) the fraction of gel and (b) the weight-average molecular weight Legend: (—) only intermolecular chain transfer to polymer; (- - -) intermolecular chain transfer to polymer and propagation to terminal double bonds.

Table 1. Values of Parameters Used for the Model Predictions in Figures 1 and 2[a]

parameters	R_1	R_2
k_p (L/mol/s)	53460^b	100^b
k_{to} (L/mol/s)	6.55×10^9 [b]	6.55×10^9 [b]
k_{fp} (L/mol/s)	133^b	133^b
k_{fp2} (s^{-1})	924^b	
$k_{tr,M}/k_p = C_{tr,M}$	8.85×10^{-5} [29]	8.85×10^{-5} [29]
a_1	2.234^b	2.234^b

[a] $k_t = k_{to} \exp(-a_1\Phi_p^p)$. [b] Estimated parameters.

rate constant obtained is ca. 24 000 L $\mathrm{mol^{-1}\ s^{-1}}$. It is worth to compare this value with those estimated from PLP measurements. First of all, it should be pointed out that no PLP value at 75 °C has been published. Beuermann et al.[9] determined k_p in bulk in the temperature range 5 °C $\leq T \leq$ 30 °C, obtaining the following equation:

$$\ln[k_p\ (\mathrm{L\ mol^{-1}\ s^{-1}})] = (13.51 \pm 0.23) - (1157 \pm 68)/T\ (\mathrm{K}) \quad (3)$$

At 75 °C, eq 3 yields a value of the effective propagation rate constant of 26 500 L $\mathrm{mol^{-1}\ s^{-1}}$, which agrees well with the value predicted in the present work. On the other hand, Lyons et al.[8] estimated k_p in the temperature range −65 to −7 °C. They considered that quite a few data obtained in solution polymerization below −45 °C were reliable, whereas over −45 °C only one experiment obtained at −7 °C was retained. This single value largely determines the Arrhenius plot of k_p as it is far from the cloud of points in the range −67 °C $\leq T \leq$ −45 °C. Therefore, it is necessary to analyze carefully this point. Actually, at −7 °C, experiments in solution ([M] = 2.5 mol $\mathrm{L^{-1}}$)] and in bulk ([M] = 7.4 mol $\mathrm{L^{-1}}$) were performed, and the k_p values obtained in solution experiments were significantly lower (≈3600 L $\mathrm{mol^{-1}\ s^{-1}}$) than those obtained in bulk (≈6500 L $\mathrm{mol^{-1}\ s^{-1}}$). As the authors considered a classical kinetic model (completely separable kinetic equation), this difference was not analyzed further, and the value of 6500 L $\mathrm{mol^{-1}\ s^{-1}}$ was retained based on a lower variance of the experimental data. However, the experimental findings do agree with the prediction of eqs 1 and 2, and in the frame of the present model the values obtained in solution should be used in the Arrhenius plot. Otherwise, the activation energy, E_p, is overestimated as both the effect of temperature and monomer concentration are included in E_p. Using the solution values at −7 °C, the corresponding k_p value extrapolated to 75 °C is 16 300 L $\mathrm{mol^{-1}\ s^{-1}}$, which is lower than both that obtained in bulk by Beuermann et al.[9] (26 500 L $\mathrm{mol^{-1}\ s^{-1}}$) and that predicted in the present work (24 000). This is in agreement with the predictions of the present model. On the other hand, this value compares reasonably well with that predicted by eqs 1 and 2 using the parameters in Table 1 (11 500 L $\mathrm{mol^{-1}\ s^{-1}}$), in particular considering that a 82 °C extrapolation likely involves errors.

Conclusion. The seeded semicontinuous polymerization of *n*-BA was investigated at 75 °C. These polymerizations evolved at very high instantaneous conversions (high polymer concentration in the polymer particles), and the polymer produced contained about 55−60% of gel and a branching level of 2−4%. When these results were analyzed by using a mathematical model, it was found that most of the branches were short chain branches formed by backbiting, and termination by combination was necessary to account for the gel content. To have a significant termination by combination, $\bar{n}$ must be close to or greater than 0.5, namely, that the effective k_p must be lower than that obtained by combination of the PLP/SEC values produced in bulk and solution polymerizations. A mechanism involving secondary and tertiary radicals (the tertiary being much less active than the secondary) was proposed. This mechanism allowed a good fit of the experimental measurements. A consequence of this mechanism is that the effective k_p depends on the monomer concentration. Therefore, the values obtained by PLP/SEC are just effective values for the particular monomer concentration used in the PLP/SEC experiments. This also means that PLP/SEC propagation rate constants obtained in bulk at low polymer contents cannot be readily used in many practical situations, such as emulsion polymerization, where due to the low monomer concentration, the effective k_p is much lower. Although these conclusions are restricted to butyl acrylate, it is likely that they also apply to other alkyl acrylates.

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