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Chain-Transfer-Dependent Termination in Emulsion Polymerization

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SUMMARY: The influence of chain transfer agent, *tert*-dodecyl mercaptan, on the kinetics of semi-batch seeded emulsion (co)polymerizations has been studied. Due to the very low water-solubility of *tert*-dodecyl mercaptan, the radical resulting after transfer to this chain transfer agent is not likely to exit the growing polymer particles and the kinetics should not be affected by this radical loss route. This has been confirmed experimentally for styrene–butadiene and butyl acrylate systems. However, increasing the level of *tert*-dodecyl mercaptan at large (final) particle sizes for styrene–butadiene led to a reduced rate of polymerization. This only can be attributed to an increased rate of termination.

Introduction

Emulsion polymerization is a complex process, with many different interacting mechanisms determining the emulsion polymerization kinetics. A good understanding of these kinetics allows control over the polymerization in emulsion systems and the resulting product quality. Nowadays, more fundamental knowledge about these processes is available[e.g. 1)] and many fundamental mechanisms have been described. However, so far not many kinetic studies have been devoted to semi-batch, seeded emulsion (co)polymerization. Although the principles derived for batch homopolymerizations can be used, it is often difficult to directly use this information or insight due to the extra complication of having one or more monomers being fed into the system. Therefore, we set out to investigate some aspects of the semi-batch, seeded emulsion (co)polymerization to obtain a better understanding of this process.

For varying (final) particle sizes, we have varied the amount of chain transfer agent, *tert*-dodecyl mercaptan (TDM), for the monomer systems styrene–butadiene and butyl acrylate. The experiments have been performed in a reaction calorimeter. This allows the determination of the rate of polymerization from the measurement of the heat of reaction, but also the average number of radicals per particle, $\bar{n}$, can been determined as a function of time for each experiment from this rate, as the particle number is known.

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Experimental

Seeded semi-batch emulsion polymerizations were performed in reaction calorimeters. To maximize use of the kinetic information, the experiments were performed isothermally. Both heat flow and heat balance calorimetry can be used isothermally, although for the methods this is not absolutely necessary. Heat-flow calorimetry, which is based on the measurement of the temperature difference between the reaction mixture and the jacket, is in principle more accurate than heat-balance calorimetry. However, this method requires known heat transfer coefficients and heat transfer areas. With changing filling levels, viscosities and fouling factors, heat flow calorimetry becomes difficult for semi-batch emulsion polymerizations. These difficulties can be eliminated using heat balances of the cooling/heating medium of the reactor, using the temperature difference between jacket inlet and outlet. This temperature difference is usually large enough for emulsion polymerization processes with reasonable heat flows2). Two reaction calorimeters — a 2 L bench-scale calorimeter and a 150 L pilot plant reactor — have been used, both based on a design by Moritz3).

The styrene–butadiene semi-batch emulsion copolymerizations were performed at 85 °C with a styrene/butadiene ratio of 2/1 with 1.5 wt-% (based on total monomer) acrylic acid and a constant initiator concentration of 1.1 wt-% (based on total monomer) sodium persulphate. The monomers were fed to the pilot plant reactor in 5¾ hours, resulting in a dispersion with a solid content of 50 wt-%. Texapon NSO was used as emulsifier. The amount of TDM (which was added to the monomer feed) has been varied between 0 and 1.5 wt-% (based on total monomer). The amount of seed has been varied to yield final particle sizes (measured as particle diameter) between 125 and 200 nm.

The semi-batch emulsion polymerizations of butyl acrylate were performed at 80 °C in the 2 L bench-scale reaction calorimeter. Here, the initiator concentration was 0.6 wt-% (based on total monomer) sodium persulfate. A 40 wt-% solids dispersion was obtained after feed times of 2 hours. Sodium dodecyl sulphate was used to stabilize the latex. The TDM level was varied between 0 and 1 wt-% (based on total monomer). The chosen seed levels yielded final particle sizes between 115 and 229 nm.

Results and Discussion

From the heat balances, the heat of reaction can be determined. This can be converted into the rate of polymerization according to

$$\dot{Q}_r = \Delta H_{copol} \cdot R_p \tag{1}$$

with $\dot{Q}_r$ the heat of reaction in J s^{-1}, ΔH_{copol} the copolymerization enthalpy in J mol^{-1} and R_p the polymerization rate in mol s^{-1}. The copolymerization enthalpy depends on the homopolymerization enthalpies and the ratio of monomers being incorporated in the polymer. In principle, this ratio can (and usually will) be different from the monomer feed ratio and must be determined separately. However, since we performed the semi-batch styrene–butadiene copolymerization under almost starved conditions, the assumption that the monomer ratio being incorporated in the polymer equals the monomer feed ratio does not give rise to large deviations of the calculated rate of polymerization. This allows for an estimation of the average number of radicals per particle, $\bar{n}$, according to the equation

$$R_p = \frac{\bar{k}_p \cdot [\mathrm{M}] \cdot \bar{n} \cdot N_p}{N_A} \qquad 2)$$

where $\bar{k}_p$ is the overall copolymerization propagation rate coefficient in L mol^{-1} s^{-1}, [M] the monomer concentration in mol L^{-1}, N_p the number of polymer particles in the reactor and N_A Avogadro's number in mol^{-1}, in combination with the mass balance of monomer, given by

$$\frac{d[\mathrm{M}]}{dt} = -R_p + n_f \tag{3}$$

or for each monomer in a copolymerization

$$\frac{d[\mathrm{M}]_i}{dt} = -F_i \cdot R_p + n_{f,i} \tag{4}$$

with t the time in s, n_f the feed rate in mol s^{-1}, i the index for different monomers and F_i the (instantaneously) incorporated fraction of monomer i in the polymer.

For the semi-batch styrene–butadiene copolymerizations, the instantaneous conversion is given as a function of time in Fig. 1a and b for different final particle sizes and different levels of chain transfer agent. From Fig. 1a, we can see that, for the styrene–butadiene dispersions with a final particle size of 125 nm, there is no dependence of the instantaneous conversion on the TDM level. The apparent invariability of the polymerization mechanism can be explained by the fact that the water solubility of TDM is very low, therefore it is not likely that after transfer to this species, the resulting radical will exit the particles and affect the kinetics. However, repeating these experiments with less seed present at the start of the polymerization, leading to (larger) particles with a final particle size of 200 nm, clearly shows a difference between the instantaneous conversion with different TDM levels.

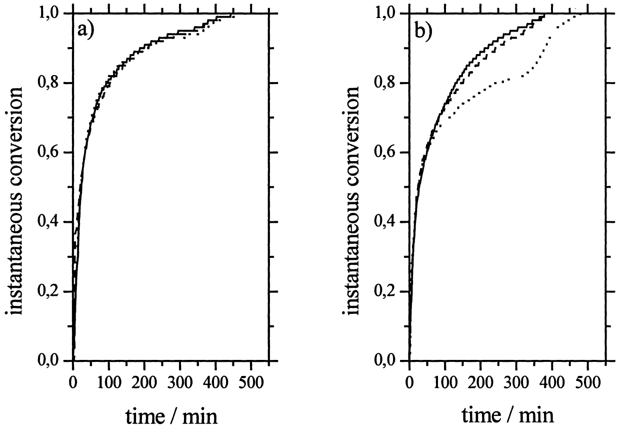

Fig. 1: The instantaneous conversion as a function of time for semi-batch, seeded styrene–butadiene emulsion copolymerizations with final particle sizes of a) 125 nm and b) 200 nm diameter for different TDM levels: —— 0 wt-% TDM; – – – 0.1 wt-% TDM; and - - - - 1.5 wt-% TDM.

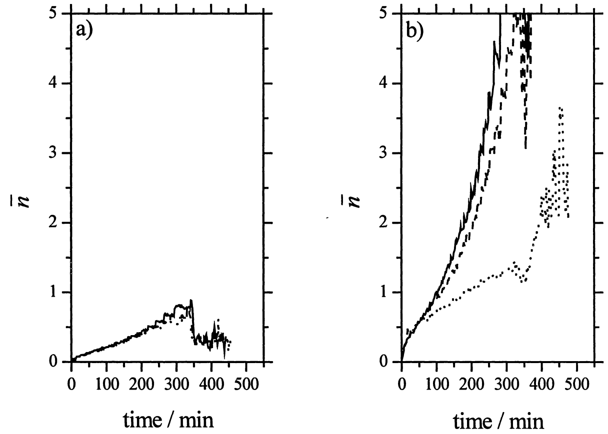

Fig. 2: The average number of radicals per particle, $\bar{n}$, as a function of time for semi-batch, seeded styrene–butadiene emulsion copolymerizations with final particle sizes of a) 125 nm and b) 200 nm diameter for different TDM levels: —— 0 wt-% TDM; – – – 0.1 wt-% TDM; and - - - - 1.5 wt-% TDM.

After some time, the polymerization rate drops with increasing TDM level. From Fig. 2, it can be seen that this effect is due to a decrease in $\bar{n}$, as has been estimated from the instantaneous conversion in Fig. 1 using Eq. (2) and (3) and the recipes used. A value for $\bar{k}_p$ has been used according to the terminal model4), with r_S = 0.82 and r_B = 1.38 and the homopropagation rate coefficients for styrene5) and butadiene6). It can be seen in Fig. 2, that as soon as $\bar{n}$ reaches a value of approximately 0.5, deviations start to occur. For lower $\bar{n}$ values, no effects can be seen, only when on average more than one radical exist in a particle, these termination effects become pronounced.

Changes in $\bar{n}$ can be understood in terms of the well described general mechanistic events, entry, exit and termination. Since within each series, the initiator concentration as well as the number of particles is kept constant, no entry effects are expected as long as entry is unaffected by TDM, which is certainly the case for the small particle results here. The same must be true for exit, as for the small particles, where exit would be higher, no such effect is seen when varying the TDM concentration. This only leaves an increment of the termination rate to explain the lower instantaneous conversion observed for the large particles with high TDM level. As termination is diffusion controlled, the diffusion in the latex particles must increase with increasing TDM level. A possible explanation lies in the fact that due to increased chain transfer agent concentrations, less network formation occurs. These networks can form because the second vinyl bond of butadiene monomer is still present after butadiene is incorporated in the main polymer chain. This (still reactive) double bond can act as a branch point when reacting with other growing radicals. This less dense network might increase the diffusion coefficient for growing polymer chains. However, the experiments are performed at 60 °C above the glass transition temperature of the polymer and there is still monomer present, further reducing the glass transition temperature. Another possibility can be that due to the existent abundance of possible branch points, the growing radicals are incorporated in the network and thus become very immobile. Highly mobile chain transfer agents will be able to 'find' these radicals, leading to transfer reactions. The resulting small radicals are more mobile and can terminate with other radicals present in the particle, on average increasing the termination rate. A third possible explanation lies in the fact that the diffusion at high instantaneous conversions is highly chain length dependent7,8,9). With an increase in chain transfer agent the average chain length decreases and on average the mobility of the chains increases and this automatically leads to higher termination rates.

Furthermore, from these experiments it can be seen that, if the level of TDM does not affect the rate of polymerization, the average number of radicals per particle must be low where the rate of termination is unimportant as in the classical 0-1 system.

The seeded, semi-batch emulsion polymerization of butyl acrylate data has been treated the same way. In Fig. 3 the instantaneous conversion as a function of time is shown for different TDM levels at a particle size of 185 nm. From the high instantaneous conversions it can be seen that the polymerizations are run at (almost) starved feed.

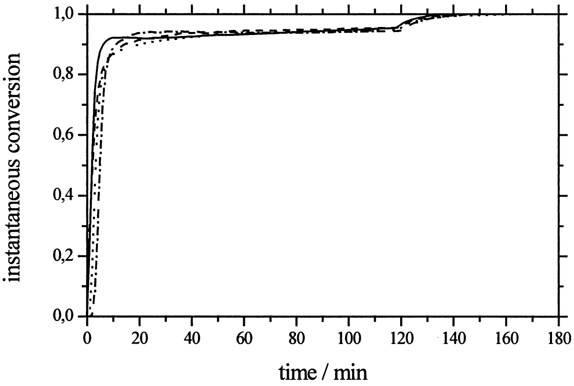

Fig. 3: The instantaneous conversion as a function of time for semi-batch, seeded butyl acrylate emulsion polymerizations with a final particle size of 185 nm diameter for different TDM levels: —— 0 wt-% TDM; – – – 0.01 wt-% TDM; - - - - 0.5 wt-% TDM; and – - – - 1.0 wt-% TDM.

No dependence on TDM can be observed in Fig. 3. The reason for this is we believe the very low $\bar{n}$, as is shown in Fig. 4, in which the average number of radicals per particle has been depicted. For the calculations of $\bar{n}$, a recently measured propagation rate coefficient of $49.1 \cdot 10^3$ L mol^{-1} s^{-1} from Lyons *et al.*[10)] has been used. Since the value of the rate coefficient of propagation is very high, we have to postulate that the very low $\bar{n}$ is a result of high radical exit and reentry resulting in termination. This postulate is well supported by the independence of the reaction rate on the very oil-insoluble chain transfer agent. The high exit rate, however, is difficult to reconcile with a high rate of propagation, especially since usually it is assumed that the propagation rate coefficient for the first few additions is even faster than the long-chain estimate as has been used above[1)]. In a model for exit[1)], it is assumed, that exit can only occur after transfer, since the monomeric radical formed is still rather water-soluble (the solubility is comparable to the water-solubility of the monomer). Furthermore, it is assumed that a dimer is already so water-insoluble — the dimer formed after transfer to monomer does not have a charged group, in contrast to dimers formed after persulphate initiator dissociation — that it cannot exit any more.

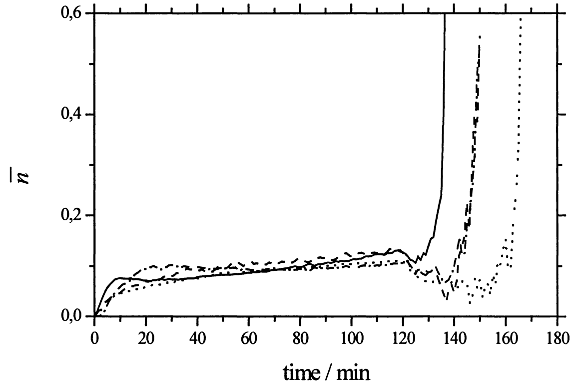

Fig. 4: The average number of radicals per particle, $\bar{n}$, as a function of time for semi-batch, seeded butyl acrylate emulsion polymerizations with a final particle sizes of 185 nm diameter for different TDM levels: —— 0 wt-% TDM; – – – 0.01 wt-% TDM; - - - - 0.5 wt-% TDM; and – - – - 1.0 wt-% TDM.

Thus, a comparison has to be made between the probability of a radical to propagate (equals $k_p^1 \cdot [\mathrm{M}]$) and to exit (equals k_{dM}). The rate of monomeric desorption, k_{dM}, is given by[1)]

$$k_{dM} = \frac{3D_w}{r_s^2}\frac{[\mathrm{M}]_w}{[\mathrm{M}]_p} \tag{5}$$

where D_w is the diffusion coefficient of the desorbing species in the water phase in $\mathrm{m}^2\ \mathrm{s}^{-1}$, r_s is the swollen particle radius in m and $[\mathrm{M}]_w$ and $[\mathrm{M}]_p$ are the monomer concentration in the water and particle phase respectively in mol^{-1} L. The dependence between $[\mathrm{M}]_w$ and $[\mathrm{M}]_p$ can be estimated according to the empirical relation[1)]

$$\frac{[\mathrm{M}]_w}{[\mathrm{M}]_w^{sat}} = \left(\frac{[\mathrm{M}]_p}{[\mathrm{M}]_p^{sat}}\right)^{0.6} \tag{6}$$

where the index ^{sat} indicates the concentration at saturation conditions. With $[\mathrm{M}]_w^{sat}$ and $[\mathrm{M}]_p^{sat}$ equal to $6.2 \cdot 10^{-3}$ and 5.0 mol L^{-1} respectively, and D_w equal to $1.5 \cdot 10^{-5}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$, k_{dM} can be calculated and compared to k_p^1. The probability of successful exit of a monomeric radical formed by transfer, β, can be expressed by

$$\beta = \frac{k_{dM}}{k_{dM} + k_p^1 \cdot [\mathrm{M}]_p + 2\sum_{i=1}^{\infty} k_t^{1i} [\mathrm{R}_i]_p} \tag{7}$$

where k_t^{1i} is the microscopic termination rate coefficient between a monomeric radical and a radical of chain length i in L mol^{-1} s^{-1} and $[\mathrm{R}_i]_p$ the concentration of radicals with chain length i in mol L^{-1}. Ignoring the (unknown) termination rate, β is given in Fig. 5 for the experiment without TDM.

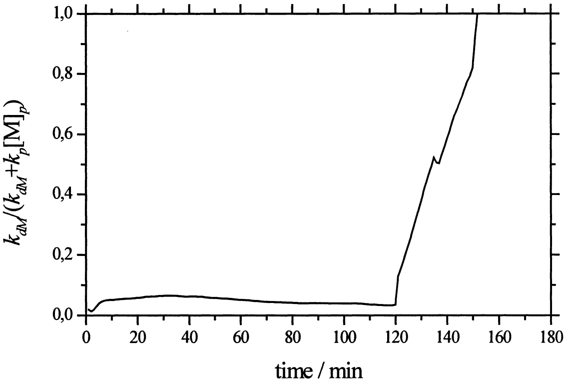

Fig. 5: The probability of successful exit of a monomeric radical formed by transfer ignoring the contribution of termination as function of time for the semi-batch, seeded butyl acrylate emulsion polymerization with a final particle size of 185 nm diameter without added TDM.

In Fig. 5, it can be seen that without taking into account termination, it is already unlikely that exit will occur. The low $\bar{n}$-values found for these experiments make it highly unlikely that after successful exit, reentry results in termination. Therefore, the postulate that the very low $\bar{n}$ is a result of high radical exit and reentry resulting in termination cannot be true.

Another observation that might explain the observed polymerization behavior is made by Plessis *et al.*,(11) who claim that, due to extensive (intra- and intermolecular) transfer to polymer under starved feed conditions, a relatively large part of the radicals is of a tertiary — and therefore rather stable — nature, reducing the effective k_p value as compared to the value determined in the low-conversion PLP/SEC experiments(10). They claim that $\bar{n}$ must be above 0.5 to explain the observed gel formation, and since the k_p value determined with PLP/SEC methods also results in values below 0.5 for their experiments, they assume a lower apparent k_p value. However, we did not observe a change in the rate of polymerization for our experiments depending on the amount of TDM added, indicating that $\bar{n}$ is indeed smaller than 0.5, even though we also find gel formation.

Conclusions

We have performed semi-batch, seeded emulsion polymerizations for the systems styrene–butadiene and butyl acrylate. For the copolymerization of styrene and butadiene, we have observed that there is a dependence on the level of chain transfer agent added to the system. This can be explained in terms of faster termination with added chain transfer agent, if $\bar{n}$ is higher than 0.5 and bimolecular termination becomes more pronounced. For the butyl acrylate homopolymerizations, we have found extremely low $\bar{n}$ values. Possible explanations have been found to be inconclusive and further explorations are necessary.

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