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ARTICLE

Mass Transport Limitations and Their Effect on the Control of the Molecular Weight Distribution in Catalytic Chain Transfer Mediated Emulsion Polymerization

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ABSTRACT: The existence of mass transport limitations in catalytic chain transfer mediated emulsion polymerization of methyl methacrylate (MMA) using bis[(difluoroboryl)dimethylglyoximato]cobalt(II) (COBF) was investigated. The rate of mass transport of COBF from the aqueous phase toward the polymer particles proved to depend strongly on the viscosity of the polymer particles and consequently on the instantaneous conversion. At high instantaneous conversion the exchange of COBF between the particles and the aqueous phase is severely hindered. As a result, the control of the molecular weight distribution is hampered. At low instantaneous conversion COBF is readily transferred between the aqueous phase and polymer particles, resulting in immediate molecular weight control. The chain transfer activity of COBF inside the polymer particles during the polymerization was successfully quantified using the chain length distribution method. The results of this work show that the presence of a catalytic chain transfer agent can severely affect the course of the emulsion polymerization. Furthermore, it was demonstrated that molecular weight control during the final stages of an emulsion polymerization is affected by the increasing viscosity of the polymer particles.

Introduction

Robust molecular mass control is a key issue in polymer production. Catalytic chain transfer has proven to be a promising technique to control the molecular weight distribution in free radical polymerization.[1−7] The most widely accepted mechanism suggests that radical activity of a propagating polymeric radical is transferred to a monomer molecule, resulting in a dead polymer chain with an unsaturated end group and a monomeric radical (see Scheme 1).

In homogeneous polymerizations, i.e., bulk and solution polymerization, the instantaneous degree of polymerization is directly related to the concentration of the chain transfer agent in the reaction mixture and can be calculated directly with the Mayo equation.[8] In emulsion polymerization, however, the reaction mixture is heterogeneous by nature, which has important consequences for the application of CCT:[9−16]

- Partition coefficients and phase ratios govern the equilibrium catalyst concentration in the locus of polymerization.
- Transport of the catalytic chain transfer agent (CCTA) from the monomer droplets via the aqueous phase to the particles is a prerequisite for effective molecular weight control.
- CCTA deactivation during polymerization by aqueous phase species lowers the overall amount of CCTA and by that increases the molecular weight.

For effective molecular weight control, it is desired to have a predetermined catalytic chain transfer agent concentration in the loci of polymerization, i.e., the polymer particles. Furthermore, for successful application of catalytic chain transfer in emulsion polymerization, a finite aqueous phase solubility is required to allow transport of the CCTA from the monomer droplets, through the aqueous phase, to the polymer particles.[10]

Aqueous phase solubility of the CCTA results in partitioning of the catalyst complex between the different phases present in the emulsion polymerization reaction mixture.[9,10,15] Partitioning of the catalytic chain transfer agent results in a lower actual concentration in the loci of polymerization and consequently a lower apparent chain transfer activity.[15] The presence of a CCTA in the aqueous phase might eventually also result in aqueous phase decomposition of the active complex, thereby reducing the absolute amount of active catalytic chain transfer agent in the system.[16] The heterogeneous nature of the emulsion polymerization system has comparable implications for living/controlled radical polymerization techniques.[17−21]

For a typical MMA emulsion polymerization recipe applied in our studies, i.e., 15% w/w methyl methacrylate (MMA), using a typical amount of catalytic chain transfer agent, i.e., 5.0 ppm of COBF, and correcting for partitioning, the average number of catalyst molecules per polymer particle can be calculated as a function of the particle diameter (see Figure 1). From Figure 1 it can be concluded that, for the experimental window of typical emulsion polymerizations in our studies, the number of COBF molecules per polymer particle is in the range of roughly 0.1−1. Therefore, a single COBF molecule often has to be able to mediate multiple reacting polymer particles to ensure that in all the particles chain stoppage occurs by COBF-catalyzed chain transfer. This can only be achieved if the COBF molecules can efficiently leave and enter the polymer particles. Hence, ideally no mass transport limitations between the different phases in the emulsion polymerization system should be present; i.e., the

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characteristic time for COBF exchange should be significantly shorter than the characteristic time for chain growth.

In the present study we evaluate the possible existence of mass transport limitations in the COBF mediated ab initio and seeded emulsion polymerizations of MMA. First, the impact of the instantaneous addition of a fairly water-soluble catalytic chain transfer agent on the course of the emulsion polymerization is demonstrated. Second, the rate of COBF exchange and the existence of mass transport limitations are investigated using the chain length distribution (CLD) method.

Results and Discussion

Determination of the CCTA Concentration in the Polymer Particles. The effects of COBF partitioning should be evident from examination of the molecular weight distribution, as the presence of COBF inside a polymer particle results in a lowering of the instantaneous degree of polymerization. To determine the amount of the catalytic chain transfer agent in the locus of polymerization, an approach comparable to that reported by Cunningham et al. was used.[22,23] The chain length distribution method (CLD method)[24,25] can be used as a tool to determine the amount of CCTA in the particles from the cumulative molecular weight distribution of the latex product at different conversions.

The concentration of COBF in the polymer particles follows from the high molecular weight slope, Λ_H, of a plot of $\ln(P(M))$ vs M (see eq 1). Note that an expression for $P(M)$ has been presented by Gilbert and co-workers[26] for a zero-one system, i.e., an emulsion polymerization obeying Smith−Ewart case 1 or case 2 kinetics,[27] without chain branching. In eq 1, M and M_0 are the molecular weight of the dead polymer chain and monomer, respectively, $[M]_p$ is the monomer concentration inside the polymer particle, and ρ stands for the total rate coefficient for entry of radicals into the polymer particles.[26,28]

$$\Lambda_H = \lim_{M\to\infty} \frac{d(\ln P(M))}{dM} = -\left(C_T \frac{[COBF]_p}{[M]_p} + \frac{\rho}{k_p[M]_p}\right)\frac{1}{M_0} \qquad (1)$$

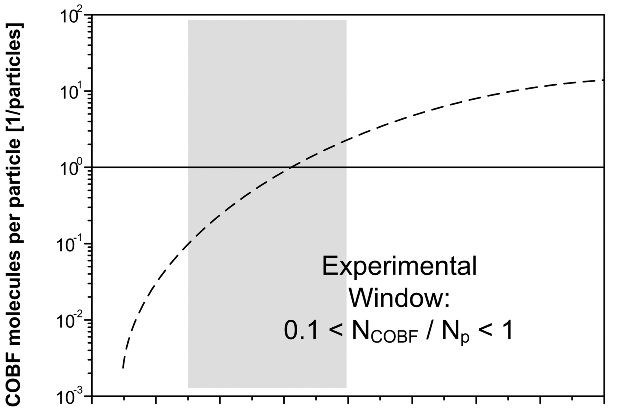


Figure 1. Average number of COBF molecules per polymer particle in a typical methyl methacrylate emulsion polymerization. Conditions for the calculation: 5.0 ppm of COBF (mol COBF per mol MMA). The partitioning of COBF is calculated based on a model published previously, using a partition coefficient $m_{Co} = [Co]_M/[Co]_W = 0.72$ $dm_W^3\ dm_M^{-3}$ and a phase ratio $\beta = V_M/V_W = 0.19\ dm_M^3\ dm_W^{-3}$.[15]

To circumvent effects of baseline correction errors, we used the slope in the peak region, Λ_{peak}, of the molecular weight distribution.[29,30] When chain transfer is the predominant chain stopping event, eq 1 can be simplified to determine the amount of catalytic chain transfer agent inside the polymer particles (see eq 2).

$$\Lambda_{peak} = \left(\frac{d(\ln P(M))}{dM}\right)_{peak} \approx -\left(C_T \frac{[COBF]_p}{[M]_p}\right)\frac{1}{M_0} \qquad (2)$$

The CLD method is often used to experimentally determine the chain transfer constant.[30−32] For the determination of the C_T value a number of samples with different [COBF]/[M] ratios are prepared. Consequently, the value of C_T can be determined from a linear plot of [COBF]/[M] vs Λ_{peak} (in the case of the CLD method) or DP_n^{-1} (in the case of the Mayo method). The reverse is also true: when the activity of the chain transfer agent is known, the value of [COBF]/[M] can be determined from experimental values of Λ_{peak} or DP_n^{-1}. It should be noted that eq 2 is only strictly valid for instantaneous molecular weight distributions (just as the Mayo equation is).

Effect of a Pulse-wise CCTA Addition on the Course of the Emulsion Polymerization. To investigate the effect of increasing viscosity of the polymer particles, COBF was added at different instantaneous conversions (i.e., $x \sim 0.10$, 0.20, 0.30, 0.40, and 0.70). From the observed conversion time histories, two different regimes can be observed: (i) at low conversion $x \leq 0.30$ and (ii) at higher conversion $x \geq 0.40$. Figure 2 presents the evolution of the conversion time history for the

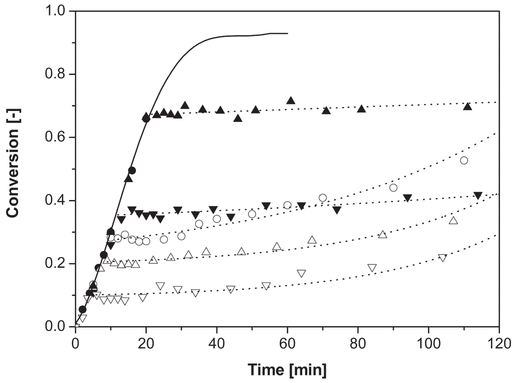
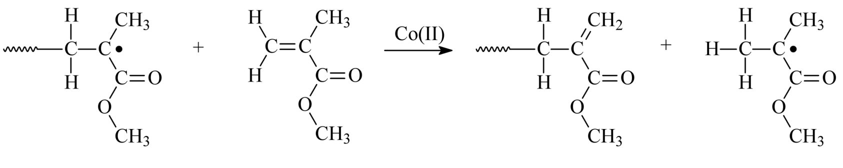


Figure 2. Ab initio emulsion polymerization of methyl methacrylate with instantaneous COBF addition at different instantaneous conversions. Ab initio emulsion polymerization without COBF (●). Ab initio emulsion polymerization with COBF added instantaneously at $x = 0.10$ (▽), $x = 0.20$ (△), $x = 0.30$ (○), $x = 0.40$ (▼), and $x = 0.70$ (▲).

Scheme 1. Overall Reaction of Catalytic Chain Transfer to Monomer



ab initio emulsion polymerizations with an instantaneous addition of COBF at a predefined conversion level. The polymerizations are performed at 50 °C to significantly reduce the rate of polymerization of the COBF-free free radical polymerization, allowing accurate and reproducible addition of the catalytic chain transfer agent at a certain conversion level. In the case of the COBF-free emulsion polymerization, approximately complete conversion is obtained within 45 min of polymerization.

The addition of the catalytic chain transfer agent has a severe impact on the rate of polymerization. Since the catalytic chain transfer agent used, COBF, has a fairly high aqueous phase solubility (a partition coefficient $m_{\mathrm{Co}} = 0.72$ $\mathrm{dm_W}^3$ $\mathrm{dm_M}^{-3}$),[16] upon the instantaneous addition to the aqueous phase, its aqueous phase concentration is increased momentarily to 9.4×10^{-6} mol $\mathrm{dm_w}^{-3}$. After partitioning of COBF over the aqueous and polymer particle phases, the equilibrium aqueous phase concentration is 8.2×10^{-6} mol $\mathrm{dm_W}^{-3}$. This would yield an instantaneous degree of polymerization of 1 of the polymer formed in the aqueous phase, estimated from the Mayo equation[8] with a C_{T} of 15×10^3 and an MMA concentration of 0.15 mol $\mathrm{dm_W}^{-3}$.[33] The outcome of this calculation illustrates that the presence of COBF, even in very low amounts, may severely affect the course of the polymerization in the aqueous phase. The most generally accepted mechanism for emulsion polymerization[26,27,34] suggests that oligomeric radicals formed in the aqueous phase will propagate until they become sufficiently surface active; i.e., they reach a length of z, at which instantaneous entry into a micelle or a polymer particle is possible.[35] However, in the presence of COBF a propagating oligomeric radical might undergo chain transfer before obtaining the required length for entry. In the latter case, a terminated water-soluble oligomer is formed and the radical activity is transferred to a monomer molecule. This aqueous phase chain transfer has two implications for the course of the emulsion polymerization:

- The frequency of entry is lowered, as fewer propagating oligomeric radicals reach the required z-length for entry.
- The rate of short−short termination in the aqueous phase is increased due to an accumulation of short oligomeric radicals.

The result of these two above-mentioned effects would be a decreasing rate of polymerization as is confirmed by Figure 3, which shows a decrease of the average number of radicals inside the polymer particles ($\bar{n}$). The value of $\bar{n}$ follows from the observed rate of polymerization (R_{p}) and the global rate equation for emulsion polymerization (see eq 3)

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}]_{\mathrm{p}} \frac{\bar{n} N_{\mathrm{p}}}{N_{\mathrm{av}}} \tag{3}$$

where k_{p} stands for the rate coefficient of propagation, N_{p} for the particle number based on the number-average particle diameter, and N_{av} for Avogadro's number. In the COBF-free ab initio emulsion polymerization of MMA $\bar{n}$ values of ∼0.5 are found. For the experiments where a pulse of COBF is added to the reaction mixture, $\bar{n}$ drops severely (see Figure 3).

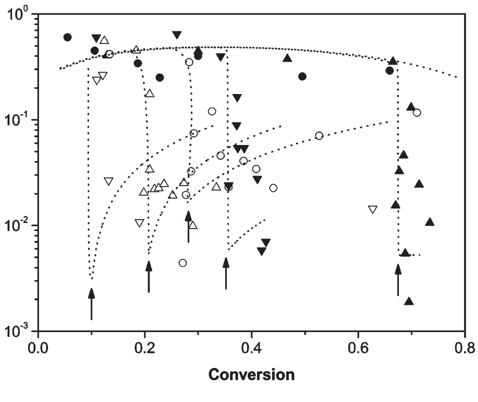


Figure 3. Evolution of $\bar{n}$ as a function of conversion. Ab initio emulsion polymerization without COBF (●). Ab initio emulsion polymerization with COBF added pulse-wise at at $x = 0.10$ (▽), $x = 0.20$ (△), $x = 0.30$ (○), $x = 0.40$ (▼), and $x = 0.70$ (▲). Arrows indicate the moment of the COBF addition.

At low conversion ($x \leq 0.30$), the polymerization is in interval II of the classic emulsion polymerization mechanism[27] and the monomer concentration in the polymer particles is equal to that for the saturation swelling, i.e., 6.6 mol $\mathrm{dm_p}^{-3}$.[33] Hence, a relatively low viscosity of the polymer particles is expected. Upon the addition of COBF, $\bar{n}$ quickly drops from approximately 0.5 to 0.5×10^{-3}, indicating that the system obeys Smith−Ewart case 1 kinetics. This 1000-fold decrease in $\bar{n}$ significantly retards the polymerization, but the polymerization still proceeds.

At higher conversion ($x > 0.30$), the polymerization is in interval III and the polymer particles are partially swollen with monomer. The concentration of monomer inside the polymer particles decreases with conversion, and the viscosity keeps increasing depending on the volume fraction of polymer. When COBF is added at higher conversions ($x > 0.30$), again a decrease in $\bar{n}$ is observed, retarding the polymerization. After the initial drop in $\bar{n}$ the polymerization apparently stops.

The observed results may conceivably be explained as follows. The instantaneous addition of COBF to the aqueous phase of the emulsion polymerization initially has a severe effect on the entry of surface-active oligomers. The rate of entry is lowered, and consequently $\bar{n}$ and the rate of polymerization decrease. When the viscosity of the polymer particles is still sufficiently low, the catalytic chain transfer agent will readily partition between the different phases. The partitioning only results in slight decrease in the aqueous phase chain transfer agent concentration, thereby hardly changing the probability of entry. However, even when the radical flux from the aqueous phase is constant, $\bar{n}$ is increasing as the polymer particles are slowly growing. The polymerizations obey Smith−Ewart case 1 kinetics, which implies that the value of $\bar{n}$ is governed by the rate of radical desorption from the polymer particles. As the particle size increases, the rate of radical desorption decreases and consequently $\bar{n}$ increases.[36,37] Although the rate of polymerization is still significantly lower than in the case for the COBF-free ab initio free radical polymerization, the polymerization proceeds.

When COBF is added in interval III, corresponding to high viscosity of the polymer particles, hardly any polymerization is observed after the pulse-wise addition of COBF, i.e., $\bar{n} \rightarrow 0$. There are three explanations for this phenomenon. First, even though the viscosity of the polymer particles is high, equilibrium partitioning will be achieved. As was mentioned before, this hardly affects the aqueous phase COBF concentration. The main difference with the polymerizations at low conversion is that the polymerizations at high conversion proceed in interval III. The polymer particles are only partially swollen with monomer, and as a consequence the aqueous phase monomer concentration is also below its saturation concentration (see e.g. ref 38). This affects the growth rate of water-soluble oligomers and consequently the rate of radical entry. Second, as the aqueous

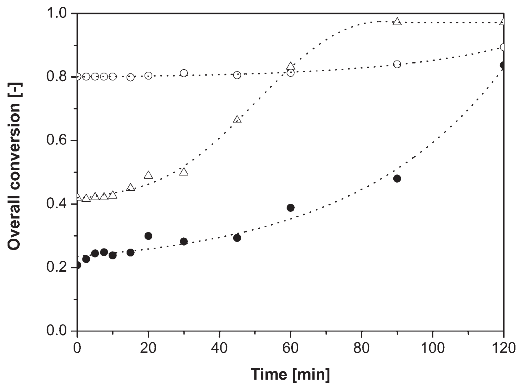


Figure 4. Conversion time history for the seeded emulsion polymerization of methyl methacrylate with an instantaneous COBF addition at different instantaneous conversions: (A) overall conversion and (B) instantaneous conversion. Seeded emulsion polymerizations swollen with monomer to mimic a conversion of $x = 0.20$ (●), $x = 0.40$ (△), and $x = 0.80$ (○).

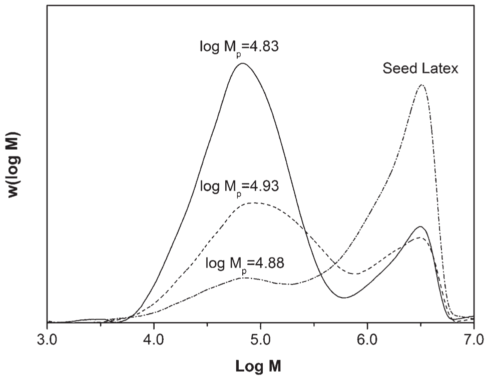


Figure 5. Final molecular weight distributions and log M_p values of the seeded emulsion polymerizations of MMA. Experimental conditions: $\beta = 0.20$ and $N_{CO}/N_{MMA} = 4.9 \times 10^{-6}$. COBF added at 20% conversion (—), COBF added at 40% conversion (---), and COBF added at 80% conversion (— · —).

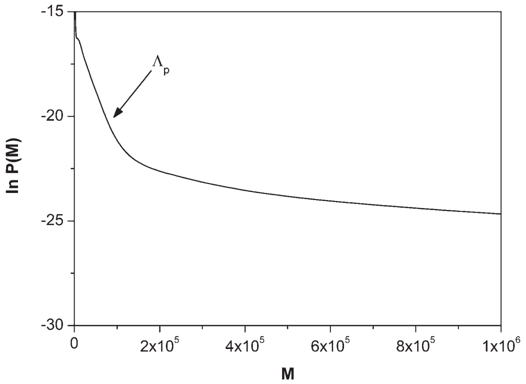


Figure 6. A CLD plot and an indication of the position of the peak molecular weight of the second-stage polymer at which Λ_p is determined from the final molecular weight distribution of the emulsion polymerization initiated at $x = 0.20$; see Figure 5 (—).

phase monomer concentration is below the saturation concentration, the ratio of the COBF concentration and the monomer concentration in the aqueous phase is higher when COBF is added at higher conversion. According to the Mayo equation, lower degrees of polymerization are obtained, thereby further affecting the rate of radical entry. Third, the polymerization is in interval III of the classic emulsion polymerization mechanism, and consequently particle growth is negligible for MMA emulsion polymerization. So $\bar{n}$ will remain constant at a very low value, and the polymerization apparently stops.

Monitoring of CCTA Partitioning in Seeded Emulsion Polymerization. The evolution of the molecular weight distribution can be used as a tool to monitor chain transfer activity at the locus of polymerization.[22,23] Instantaneous molecular weight distributions can be determined directly after the COBF addition to relate the decrease in the average molecular weight to the amount of COBF mediating the polymerization. The presence of COBF significantly retards the polymerization due to aqueous phase chain transfer effects. Directly after the COBF addition, an inhibition period occurs after which the polymerization eventually continues (see Figure 2). To ensure an acceptable rate of polymerization directly after the addition of COBF, seeded polymerizations are performed to allow for a higher reaction temperature (70 °C) in order to increase the radical flux and consequently increase the rate of entry. The seed latex was swollen with a certain amount of monomer to mimic a conversion of $x = 0.20$, 0.40, or 0.80. A pulse of the required amount of COBF was added prior to the initiator addition. The overall conversion time histories are presented in Figure 4. The trends observed in the conversion−time histories of the seeded emulsion polymerizations, collected in Figure 4, correspond to those obtained in the ab initio polymerization (see Figure 2).

The recipes all have the same phase ratio (β) and the same COBF to monomer ratio (N_{Co}/N_{MMA}). Keeping β and N_{Co}/N_{MMA} constant implies that the partitioning behavior of the catalytic chain transfer agent is comparable for all the experiments shown in Figure 4. The same partitioning behavior in combination with a constant COBF to MMA ratio for all the performed seeded emulsion polymerizations should also result in a comparable average molecular weight of the newly formed polymer if the system reaches equilibrium partitioning. This is confirmed experimentally where the peak molecular weights of the low molecular weight peak for the final latex coincide around log $M = 4.9$ ($\sim 80 \times 10^3$ g mol^{-1}) (see Figure 5).

An estimate of the catalytic chain transfer agent concentration inside the polymer particles can be obtained using the CLD method.[24,25] In principle, (pseudo)-instantaneous molecular weight distributions are required for accurate determination of the instantaneous COBF concentration in the polymer particles. However, the (pseudo)-instantaneous molecular weight distributions are very susceptible to baseline errors, especially for small conversion intervals and could therefore not be determined accurately. Therefore, in this work, we used the cumulative molecular weight distributions in combination with the CLD method. The slope Λ_{peak} is determined at the position of peak molecular weight of the molecular weight distribution of the second-stage polymer (see Figure 6).

The found values for Λ_{peak} directly reflect the value of $C_T[COBF]_p/[M]_p$, which is shown as a function of the overall conversion in Figure 7. When the viscosity of the polymer particles is relatively low at the beginning of the polymerization (i.e., the experiments with $x = 0.20$ and $x = 0.40$), the value of $C_T[COBF]_p/[M]_p$ rapidly increases to about 8×10^{-3}. After this initial increase the value of $C_T[COBF]_p/[M]_p$ gradually decreases to a value of $\sim 3 \times 10^{-3}$. At high conversion (i.e., the experiment with $x = 0.80$) and consequently at high viscosity of the polymer particles the value of $C_T[COBF]_p/[M]_p$ increases and reaches a plateau value of around 3×10^{-3} (see Figure 7). The value of

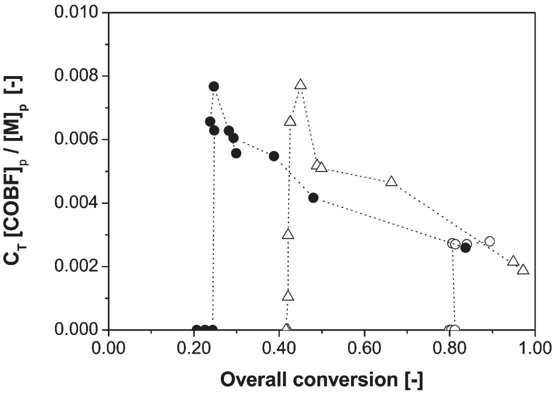


Figure 7. Evolution of C_T[COBF]$_p$/[M]$_p$ as a function of the overall conversion. Seeded emulsion polymerization with a pulse of COBF added at x = 0.20 (●), x = 0.40 (△), and x = 0.80 (○).

C_T[COBF]$_p$/[M]$_p$ changes during the course of the polymerization, and independent of the initial conversion comparable values are observed at high conversions.

The analysis of the obtained molecular weight distributions reveals a decrease in C_T[COBF]$_p$/[M]$_p$ as the reaction progresses. This change is unlikely to be attributed to a changing monomer concentration inside the polymer particles, as this concentration is constant in interval II and continuously decreasing in interval III. Hence, the decrease of C_T[COBF]$_p$/[M]$_p$ can only be attributed to either a change in the COBF concentration inside the polymer particles or a decrease in the chain transfer constant, or a combination of both.

Since no significant changes in partitioning behavior with increasing conversion are expected,[9,39] a possible decrease in the COBF concentration inside the polymer particles could be caused by aqueous phase decomposition of the catalyst. However, for the applied reaction conditions only a minor effect of decomposition is expected.[16] Hence, both the effect of COBF decomposition and a change in the partition coefficient seem to be insufficient to explain the significant decrease in C_T[COBF]$_p$/[M]$_p$.

Since it does not seem likely that a potential decrease in the COBF concentration inside the polymer particles with increasing conversion is responsible for the observed increase in molecular weight, the only plausible explanation would lie in a decreasing value of C_T. Although there still does not exist any hard evidence for a diffusion-controlled rate-determining chain transfer reaction, there are very strong indications that this may be the case. Heuts and co-workers found an inverse relationship between the transfer rate coefficient and the monomer viscosity,[40,41] suggesting that the reaction rate is governed by the microscopic viscosity (or monomeric friction coefficient).[41] This phenomenon is well-known in the diffusion literature for small-molecule probes (such as COBF in the present studies) in polymer/solvent systems: although the bulk viscosity may increase over several orders of magnitude with increasing polymer volume fraction, the diffusion coefficients remain approximately constant up to high polymer volume fraction. For higher volume fractions the diffusion coefficient of low molecular species decreases strongly.[42−46] The current situation for catalytic chain transfer is very similar, so it is conceivable that indeed C_T starts decreasing at a certain high polymer content.

The catalytic chain activity over the course of the polymerization can be evaluated from the results collected in Figure 7. High values for C_T[COBF]$_p$/[M]$_p$ correspond to a situation similar to bulk or solution polymerization. Low values for C_T[COBF]$_p$/[M]$_p$ indicate that the chain transfer reaction is severely hampered as a result of very slow mass transport. For the polymerization initiated at low viscosity (i.e., x=0.20 and x=0.40) the catalytic chain transfer activity inside the polymer particles rapidly increases, which is an indication for efficient catalytic chain transfer. The COBF complex can readily partition from the aqueous phase toward the polymer particles, and the chain transfer reaction is not hindered. As the polymerization proceeds, the chain transfer activity is continuously decreasing, indicating that chain transfer is becoming increasingly difficult. When COBF is added pulse-wise at a conversion of 0.80, a very low chain transfer activity is observed. Moreover, the observed chain transfer activities at high conversion in the individual polymerizations are consistent. The results collected in Figure 7 show that the efficiency of chain transfer severely changes throughout the course of an emulsion polymerization and that the polymer volume fraction inside the polymer particles is a key parameter governing the chain transfer reaction in emulsion polymerization.

Conclusions

The results of this work demonstrate that the pulse-wise addition of a fairly water-soluble catalytic chain transfer agent, i.e. COBF, severely affects the course of the emulsion polymerization. Aqueous phase chain transfer in combination with increased short−short termination competes with aqueous phase propagation, resulting in a situation where the entry frequency of radicals decreases. As the polymerizations strongly obey Smith−Ewart case 1 kinetics, radical desorption is significant and $\bar{n}$ is a function of the particle size. When COBF is added at low instantaneous conversion, $\bar{n}$ decreases while the polymerization still proceeds. At high instantaneous conversion, however, the polymerization apparently stops. The chain length distribution method was used to determine the catalytic chain transfer activity in the polymer particles from the obtained molecular weight distributions. When the polymer particles are at their monomer saturation concentration, there is hardly any resistance against mass transport and equilibrium partitioning is reached quickly. Below the saturation concentration, partitioning is slower due to mass transport limitations. The observed decrease in C_T[COBF]$_p$/[M]$_p$ indicates that during the course of the polymerization, i.e., as the weight fraction of polymer is increasing, the chain transfer constant is changing due to changes in the microscopic viscosity.

Experimental Section

Materials. The bis(methanol) complex COBF was prepared as described previously.[12,47] For all experiments, a single batch of catalyst was used. The intrinsic activity of the catalyst was determined by measuring the chain transfer constant in the bulk polymerization of MMA at 60 °C: $C_T = 30 \times 10^3$. Methyl methacrylate (MMA) (Aldrich, 99%) was purified by passing it over a column of activated basic alumina (Aldrich). Sodium bicarbonate (SBC) (Fluka, >99%), sodium dodecyl sulfate (SDS) (Fluka, 99%), potassium persulphate (KPS) (Aldrich, >98%), and 2,2′-azobis[*N*-(2-carboxylethyl)-2-methylpropionamide] hydrate (V57) (Wako) were used as received. Distilled deionized water (DDW) was used throughout this work. All experiments were conducted in a 1.2 dm^3 Mettler Toledo RC1e reaction calorimeter equipped with an anchor impellor, calibration heater, Tr sensor, and sample loop. The reactor was operated in isothermal mode.

Seed Latex Preparation. The RC1e reactor was charged with MMA (240 g, 2.41 mol), distilled deionized water (DDW) (710 g), SDS (11 g, 3.8×10^{-2} mol), and SBC (0.74 g, 7.0×10^{-3} mol). The resulting emulsion was stirred vigorously, purged with nitrogen

Table 1. Properties of the Seed Latex Used for the Seeded Emulsion Polymerization Experiments

final x^a	$d_p(V)^b$ [nm]	poly^c	N_p [10^{18} dm_W^{-3}]
0.98	57.3	0.055	2.0

^{a} Conversion determined gravimetrically. ^{b} Volume average particle diameter as determined by dynamic light scattering using a Malvern Nanosizer. ^{c} Poly is the polydispersity of the particle size distribution as calculated by the Malvern software.

Table 2. Polymerization Conditions for the Seeded Emulsion Polymerization Experiments

x (%)	SEED [g]	DDW [g]	MMA [g]	COBF [mg]	$N_{Co,0}/N_{MMA}$ [10^{-6}]	solid content	β^a
20	70	385	64	1.65	4.9	0.16	0.20
40	140	328	48	1.65	4.9	0.16	0.20
80	280	220	16	1.65	4.9	0.16	0.20

^{a} The phase ratio (β) is defined as the ratio of the volume of organic phase and the volume of the aqueous phase.

for 1 h, and heated to the desired reaction temperature of 70 °C. Subsequently, the initiator (KPS) dissolved in 10 g of DDW was added instantaneously. After reacting for 1 h (conversion ~ 0.96), the temperature was raised to 90 °C to increase the decomposition rate of the initiator. The final latex was left stirring for 5 h, after which less than 0.5% of the initiator should remain. The latex was then dialyzed against DDW for 7 days, changing the DDW twice a day. The final properties of the seed latex are summarized in Table 1.

Ab Initio Catalytic Chain Transfer Mediated Emulsion Polymerization. SDS (2.75 g, 9.6 mmol) and SBC (0.42 g, 4.0 mmol) were dissolved in DDW (360 g) and added, under continuous stirring, to the reactor. Subsequently, MMA (70 g, 0.70 mol) was added, and the resulting emulsion was purged with nitrogen for 1 h. The reactor temperature was gradually raised to the final reaction temperature of 50 °C. The polymerization was initiated by the addition of the V57 initiator (0.131 g, 0.38 mmol). A catalyst stock solution was prepared by dissolving an accurate amount of COBF (~10 mg, 24×10^{-3} mmol) in DDW (66.7 g). At different conversion levels (x = 0.10, 0.20, 0.30, 0.40, and 0.70) 10 mL of the catalyst stock solution directly followed by a second addition of V57 (0.536 g, 1.57 mmol) dissolved in 10 g of DDW were added as a pulse injection to the reactor content. Samples were withdrawn periodically to monitor the gravimetric conversion, molecular weight, and the particle size distribution.

Seeded Catalytic Chain Transfer Mediated Emulsion Polymerization. SDS (0.25 g, 0.87 mmol) and SBC (0.40 g, 3.8 mmol) were dissolved in DDW and added to the reactor. Subsequently, the reactor was charged with the required amounts of seed latex and MMA. The latex was stirred gently overnight to allow swelling of the polymer particles. The temperature of the latex was set at 10 °C to prevent polymerization. After swelling, the resulting latex was purged with nitrogen for 1 h, and the reaction temperature was gradually raised to the reaction temperature of 70 °C. A catalyst stock solution was prepared by dissolving an accurate amount of COBF (~10 mg, 24×10^{-3} mmol) in DDW (61 g). After purging, 10 mL of the catalyst stock solution was added to the reactor, immediately followed by the addition of the V57 initiator (0.15 g, 0.44 mmol). The polymerization conditions are summarized in Table 2. Samples were withdrawn periodically to monitor the gravimetric conversion, molecular weight, and particle size distribution.

SEC Analysis. Size exclusion chromatography was performed using a Waters GPC equipped with a Waters model 510 pump and a Waters model 410 differential refractometer. A set of two mixed bed columns (Mixed-C, Polymer Laboratories, 30 cm, 40 8C) were used. Tetrahydrofuran (Aldrich) was used as the eluent, and the system was calibrated using narrow molecular weight polystyrene standards ranging from 600 to 7×10^6 g mol^{-1}. Mark–Houwink parameters used for the polystyrene standards are $K = 1.14 \times 10^{-4}$ dL g^{-1} and a = 0.716 and for poly(methyl methacrylate) are $K = 9.44 \times 10^{-5}$ dL g^{-1} and a = 0.719.

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