DOI: 10.1002/masy.200751346

Molecular Weight Control in Emulsion Polymerization by Catalytic Chain Transfer: A Reaction Engineering Approach

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Summary: For the application of catalytic chain transfer in (mini)emulsion polymerization, catalyst partitioning and deactivation are key parameters that govern the actual catalyst concentration at the locus of polymerization and consequently the final molecular weight distribution. A global model, based on the Mayo equation, catalyst partitioning and deactivation was developed. The influence of several reaction parameters on the instantaneous number average molecular weight was quantified.

Keywords: catalytic chain transfer; catalyst deactivation; CoBF; emulsion polymerization; modeling; partitioning

Introduction

The molecular mass distribution amongst others governs the end use properties of polymeric materials, e.g. coatings. High molecular weight material is often desired for the product's strength. On the other hand low molecular weight material enhances the ease of polymer processing. Robust molecular mass control is therefore a key issue in polymer production. Smirnov and co-workers reported that certain low spin cobalt(II) compounds are able to catalyze the chain transfer to monomer reaction and thereby offer the possibility for molecular weight control.[1–3] The overall reaction of catalytic chain transfer to monomer in the case of methyl methacrylate presented in Scheme 1.

Catalytic chain transfer with Co(II) complexes has demonstrated to be a versatile method to produce polymers with a predefined molecular weight distribution.[4–6]

The molecular weight of the polymer formed can be predicted fairly accurately by the Mayo equation in bulk and solution polymerization, which relates the catalyst activity and the amount of catalytic chain transfer agent (CCTA) to the instantaneous number-average degree of polymerization, see Equation (1). [7]

$$DP_{\mathrm{n}}^{-1} = DP_{\mathrm{n},0}^{-1} + C_{\mathrm{T}}\frac{C_{\mathrm{Co},0}}{C_{\mathrm{M}}} \tag{1}$$

In Equation (1) DP_{n} and $DP_{\mathrm{n},0}$, denote the instantaneous number-average degree of polymerization with and without CCTA, respectively. C_T, $C_{\mathrm{co},0}$ and C_{M} are the chain transfer coefficient, the concentration of CCTA and monomer concentration, respectively.

Bulk as well as solution polymerizations are homogeneous reactions, the CCTA concentration at the locus of polymerization is simply the overall catalyst concentration $C_{\mathrm{co},0}$. However, due to the heterogeneity of the reaction mixture has some important issues for the application of CCT in

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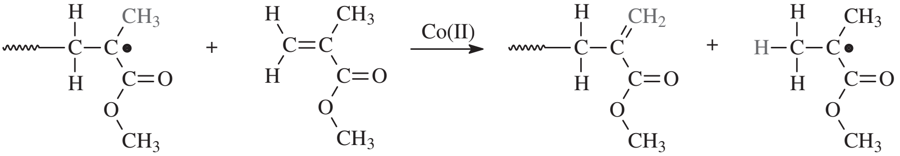


Scheme 1.
The overall reaction of catalytic chain transfer to monomer.

emulsion polymerization have to be addressed:

- Partition coefficients as well as phase ratios govern the actual 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, i.e. the loci of polymerization.
- CCTA deactivation in the aqueous phase during polymerization.

For an accurate prediction of the molecular weight distribution in CCT mediated emulsion polymerization, partitioning, mass transfer and aqueous phase deactivation have to be taken into account.

Figure 1 clearly illustrates the effect of the heterogeneity of a (mini)emulsion polymerization system. Since the ratio of $C_{co,0}$ and C_M continuously increases with increasing conversion, a decrease of DP_n is expected, see Equation (1). In general this decrease is not observed experimentally.[8–10] The observed molecular weights remain virtually unchanged throughout the course of polymerization. Only one study by Kowollik and Davis, actually reported a decrease of DP_n at higher monomer conversion.[11] In (mini)emulsion polymerization, however, two deviations from DP_n, as predicted by the Mayo equation (using overall concentrations), can be observed. Firstly, there appears to be an offset between the predicted and experimentally obtained DP_n and secondly DP_n appears to increase with conversion.

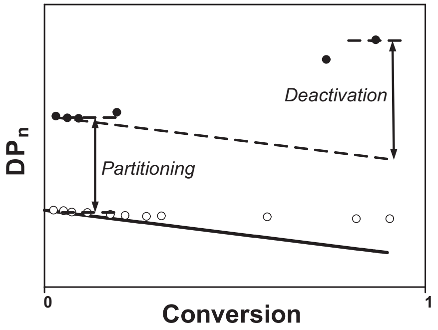
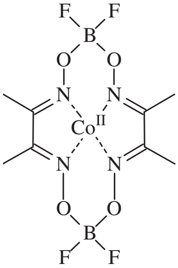


Figure 1.
DP_n as a function of conversion as predicted by the Mayo equation (Equation (1)) for solution polymerization (—), solution polymerization experiments (○)[12] and miniemulsion polymerization experiments (●).

The aim is to achieve control of DP_n at the locus of polymerization, i.e. the polymer particles. Some water solubility is required to limit the resistance against transport of CCTA from the monomer droplets via the aqueous phase to the polymer particles. Note that this (moderate) water solubility is also responsible for CCTA partitioning between the monomer droplets, the polymer particles and the aqueous phase. So a substantial amount of CCTA is not available for molecular weight control which implies an apparent poor control of the polymerization. The offset between the predicted and experimentally obtained values of DP_n can be attributed to the effects of CCTA partitioning.

The most commonly used CCTA's are transition metal complexes, which are susceptible towards deactivation if present in water. Catalyst deactivation will effectively reduce the amount of CCTA available for catalytic chain transfer, continuously decreasing the ratio of $C_{co,0}$ to C_M with time resulting in increasing molecular weights. The increase of DP_n can be attributed to the effects of CCTA deactivation in the aqueous phase.

In this paper we present the results of a modeling study on the effects of CCTA partitioning and deactivation in the aqueous phase for bis[(difluoroboryl) dimethylglyoximato]cobalt(II) (CoBF, **1**). A global model, based on the Mayo equation and CCTA partitioning, is used to illustrate the effect of partitioning on DP_n in CCT mediated miniemulsion polymerization. Furthermore CCTA deactivation in the aqueous phase is quantified. The results of the deactivation study are used to extend the global model, for predicting the trend in DP_n in CCT mediated (mini)emulsion polymerization.



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Experimental Part

Materials

The bis(methanol) complex CoBF was prepared as described previously.[13,14] For all experiments, one single batch of catalyst was used. The intrinsic activity of the catalyst was determined by measuring the chain transfer constant in bulk polymerization of methyl methacrylate (MMA) at 60 °C: $C_T = 30 \cdot 10^3$.

Partitioning

A catalyst stock solution was prepared by dissolving an accurately weighted amount of CoBF (approximately 6 mg) in 75.0 mL deoxygenated MMA. The required amount of catalyst stock solution and deoxygenated water were added to a reactor using a gas-tight syringe. The mixture was stirred for 30 minutes at the desired temperature, after which the reactor content was transferred into the separation funnel. After phase separation, samples from both the aqueous and monomer phase were taken and analyzed using UV-VIS spectrometry. The extinction coefficients were obtained from calibration lines or from literature, see Table 1.

Rate of Deactivation

An accurate amount of CoBF was dissolved in water containing a pre-determined amount of oxygen, initiator or buffer. If necessary, the solution was de-oxygenated by a repeated vacuum-argon cycle. The solution was then transferred into a quartz cuvet, while maintaining an argon atmosphere. The sealed cuvet was subsequently placed in a thermostated water bath, and the CCTA deactivation was monitored by UV-VIS spectroscopy.

CoBF Partitioning in Miniemulsion Polymerization

In emulsion polymerization, the concentration of CCTA in the particles strongly depends on the partitioning of the CCTA over the various phases, see Equation (2).

$$f_{CoBF,M} = \frac{N_{Co,M}}{N_{Co,0}} = \frac{m_{Co}(\beta+1)}{m_{Co}\beta+1}\left(\frac{\beta}{\beta+1}\right) \qquad (2)$$

In Equation (2) $f_{CoBF,M}$ denotes the ratio of the amount of CoBF in the organic phase ($N_{Co,M}$) and the overall amount of CoBF in

Table 1.
Extinction coefficients of CoBF in water and MMA.

	water	MMA		water	MMA
$\lambda_{max}[nm]$	456	454	$\varepsilon[dm^3 \cdot mol^{-1} \cdot cm^{-1}]$	4060[a)]	3640[b)]

[a)] taken from reference [14];
[b)] determined experimentally.

the reaction mixture ($N_{Co,0}$). The partition coefficient (m_{Co}) is defined as the ratio of the CCTA equilibrium concentrations in the organic and the water phase. The phase ratio (β) and m_{Co} govern the actual concentration of CCTA in the particles and consequently DP_n. Note that m_{Co} is independent of β. However, β controls the absolute amounts of CCTA in the organic phase as well as in the aqueous phase, see Figure 2.

With increasing values of β, the solid content of the miniemulsion increases and more CoBF partitions towards the particles, resulting in a higher fraction of the available CoBF residing in the particles, leading to a lower DP_n. The opposite effect occurs when extremely low solid contents are considered. The fraction of the available CCTA is then high in the aqueous phase and low in the particle phase As a consequence high DP_n polymer will be formed in the particles. Values of m_{Co} for CoBF in a MMA/H_2O and in a styrene/H_2O mixture are determined from a non-linear fit using Equation (2) and are equal to 0.72 $dm_W^3 \cdot dm_M^{-3}$ and 0.052 $dm_W^3 \cdot dm_M^{-3}$, respectively. and constant over the range of phase ratios investigated. Note that for (mini)emulsion polymerization, β normally varies between 0.10 and 0.60, which approximately corresponds to solid contents ranging from 10 to 55 wt%.

The results in Figure 2 demonstrate that the phase ratio is a key parameter in the control of the molecular weight of the polymer produced. Note that this result is probably counter-intuitive as one would probably assume that with an increasing amount of monomer, a lower effective ratio of $C_{\mathrm{Co},0}$ to C_{M} would occur and consequently a higher DP_n, see Equation (1).

We derived an expression for DP_n in the CoBF mediated miniemulsion polymerization of MMA which was found to describe the experimental data well, see Equation (3).[15]

$$DP_n = \frac{V_M C_{M,p}}{C_T} \frac{1}{N_{Co,0}} \left(\frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \times \left(1 + \frac{1}{\beta} \right) \tag{3}$$

In Equation (3), V_M and $C_{M,p}$ represent the volume of the organic phase and the monomer concentration in the particles, respectively. Equation (3) demonstrates that DP_n depends on (i) $C_{\mathrm{M,p}}$, (ii) the choice of CCTA (C_{T}, m_{Co}) and (iii) the recipe ($N_{\mathrm{Co},0}$, β, V_{M}).

Figure 3 presents the behavior of DP_n for CoBF as a function of β, with the overall amount of CCTA in the system ($N_{\mathrm{Co},0}$) and m_{Co} for CoBF as a parameter.

An increase in the total amount of CCTA in the system ($N_{\mathrm{Co},0}$) results, as

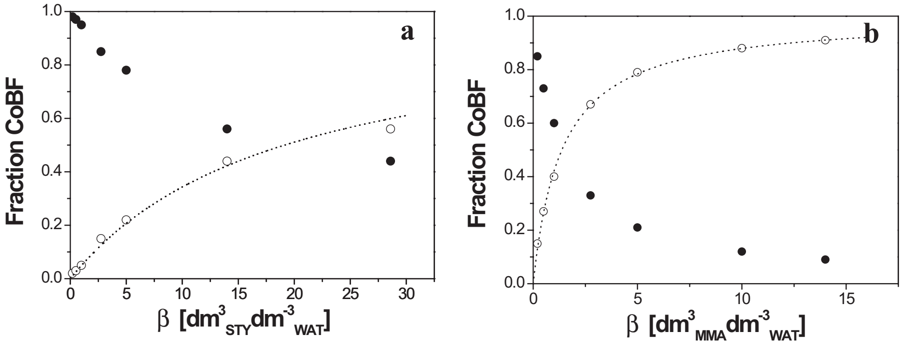

Figure 2.
The partitioning of CoBF in two water-monomer systems. a: The partitioning of CoBF in water (○) – styrene (●). b: The partitioning of CoBF in water (○) – methyl methacrylate (●). (····) best experimental fit obtained with Equation (2), $m_{\mathrm{Co}} = 0.72$ $dm_W^3 \cdot dm_M^{-3}$ for MMA/water and 0.052 $dm_W^3 \cdot dm_M^{-3}$ for styrene/water.

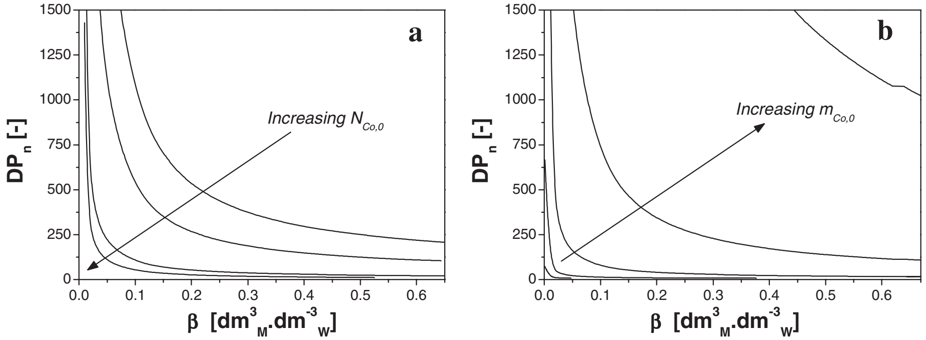

Figure 3.

Calculated values of DP_n as a function of the phase ratio. a. the effect of the overall amount of CCTA in the system (0.5, 1.0, 5.0 and 10.0 ppm respectively), $C_T = 30 \cdot 10^3$, $m_{Co} = 0.72\ dm^3_W \cdot dm^{-3}_M$. b. the effect of the partition coefficient (0.01, 0.10, 1.0, 10 and 100 $dm^3_W \cdot dm^{-3}_M$, respectively), $C_T = 30 \cdot 10^3$, $N_{Co,0} = 5$ ppm.

predicted by the Mayo equation, in lower values of DP_n, see Figure 3a. The effect of the partitioning decreases for larger amounts of CCTA and the value of DP_n converges faster to the bulk value, i.e. DP_n for $\beta \rightarrow \infty$ (bulk polymerization).

The effect of m_{Co} on DP_n is presented in Figure 3b. For $m_{Co} \rightarrow 0$, approximately all CCTA is in the aqueous phase. As a consequence no catalytic chain transfer occurs in the particles and polymer with high DP_n is produced. The opposite situation occurs for $m_{Co} \rightarrow \infty$: all catalyst is in the organic phase, resulting in a situation comparable to bulk polymerization. In both limiting cases, the effect of the phase ratio on DP_n is negligible. The examples discussed clearly illustrate how the recipe ($N_{Co,0}$) as well as m_{Co} and β govern DP_n.

CoBF Deactivation in Miniemulsion Polymerization

Determination of the Rate Constant of Deactivation

The complexes used for catalytic chain transfer are derivatives of cobaloximes, which are highly sensitive to hydrolysis and oxidation. CoBF has improved stability due to the BF_2 bridges, but despite this increased stability the complex is still readily oxidized by oxygen[5,16] or (peroxide) radicals.[5,17,18] Also hydrolysis in acidic media may have a significant contribution to deactivation.[5] The cobalt complex can be oxidized by radicals in the monomer phase, forming stable Co(III)-R complexes. Preliminary results of Heuts and co-workers indicate, however, that the active Co(II) species is regenerated *in-situ* during bulk polymerization.[19] Although catalyst deactivation in the monomer phase is not completely negligible,[9–11] our work focuses on the deactivation in the aqueous phase. In conclusion, since polymerizations are performed under exclusion of oxygen due to its high radical scavenging activity, three variables are found to affect the Co(II) deactivation: (i) the initiator concentration in the aqueous phase ($C_{I,W}$), (ii) the reaction temperature (T) and (iii) the pH of the aqueous phase.

An empirical approach was chosen to estimate the rate of deactivation in order to predict the increase in DP_n during (mini)-emulsion polymerization. Based on the preliminary results we have chosen a 2^3 full factorial experimental design to determine the pseudo-first order rate coefficient of deactivation (k_{dea}) of the CoBF catalyst. The parameter settings of the three critical parameters are collected in Table 2.

The rate of deactivation was measured with UV-VIS spectroscopy, at the specific wavelength of 456 nm, see Figure 4a.

The course of the decrease of the absorbance at 456 nm with time, see Figure 4b, reveals that deactivation obeys

Table 2.
The settings of the parameters used for the experimental design.

X_i	*Variable*	(−)	(+)
X_1	pH (-)	2	7
X_2	T^{-1} (10^{-3} K^{-1})	2.78	3.36
X_3	$-\log(C_{I,W})$	2.78	4.78
Y	$-\ln(k_{dea})$		

Table 3.
Results of the experimental design: estimated effects for the experimental variables.

X_i	*Variables*	*Coefficient*
X_2	T^{-1}	−1.530
X_1	pH	−0.666
X_3	$-\log(C_{I,W})$	−0.551
β_0	Mean value	−4.87
	R^2	0.983

a first order rate law in catalyst, see Equation (4).

$$k_{dea}t = -ln\frac{C_{Co,W}(t)}{C_{Co,W}(0)} = -ln\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) \quad (4)$$

The statistical evaluation showed that only the main effects were significant (for a confidence interval of 0.95). Note that the empirical model does not contain any interaction terms. The results of the experimental design are summarized in Table 3.

The statistical evaluation of the experimental design results in an empirical equation that can be used to predict the rate constant of deactivation of the CCTA in the aqueous phase, see Equation (5)., given in coded units.

$$Y = -4.87 - 0.666X_1 - 1.53X_2 - 0.551X_3 \quad (5)$$

The pseudo-first order rate constants of deactivation, as predicted by Equation (5), prove to be in good accordance with the experimentally obtained results, see Figure 5.

The model equation, obtained from the experimental design, allows for an estimation of the pseudo-first order rate constant of deactivation and consequently for a prediction of the increase of DP_n with time for a batch process.. The obtained kinetic information of deactivation can be used to further extend the global model, to incorporate CCTA in the Mayo equation, see Equation (3).

CoBF Deactivation in Miniemulsion Polymerization

The deactivation of the CCTA in the aqueous phase is assumed to be first order in the CCTA concentration in the aqueous phase, see Equation (6).

$$C_{Co,w}(t) = C_{Co,w}(0) \cdot e^{-k_{dea} \cdot t} \quad (6)$$

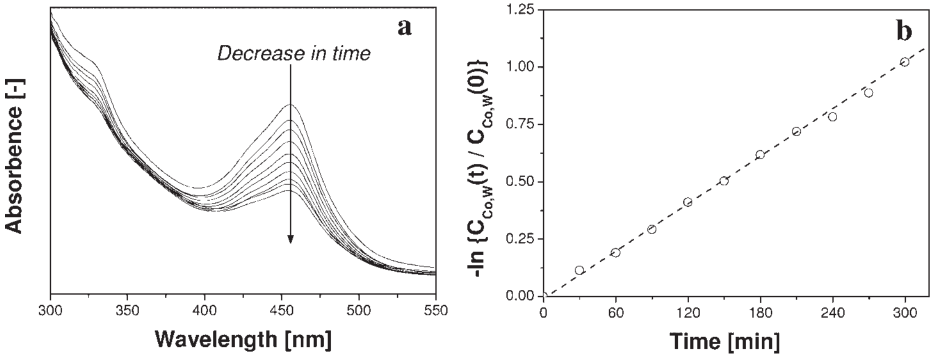

Figure 4.
Determination of the pseudo-first order rate coefficient of deactivation of CoBF with UV-VIS spectroscopy. a: The decrease in absorption of CoBF in water measured over 300 minutes, $T = 298$ *K*, *pH* = 7.0, $C_{Co,0} = 1.9 \cdot 10^{-4}$ $mol \cdot dm_W^{-3}$, $C_{I,W} = 1.9 \cdot 10^{-3}$ $mol \cdot dm_W^{-3}$. b: A linear fit of the relative decrease in absorbance in time according to Equation (4), $R^2 = 0.998$, absorbance at t = 0, $A_0 = 0.530$, for $t \to \infty$, $A_\infty = 0.122$.

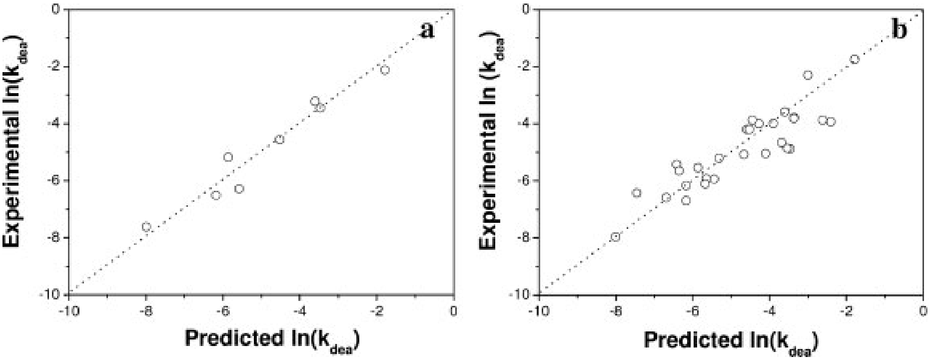

Figure 5.
Experimentally obtained rate constants of deactivation and calculated rate constants of deactivation. a: the experiments included in the experimental design. b: all deactivation experiments performed.

In Equation (6) $C^{t}_{Co,W}$, $C^{0}_{Co,W}$ and k_{dea} are the concentration of CCTA in the aqueous phase at time t, at time $t = 0$, and the first order rate coefficient of deactivation, respectively.

Equation (6) can be substituted into Equation (3), yielding a time dependent expression for DP_n, incorporating CCTA deactivation, see Equation (7).

$$DP_n = \left\{ \frac{V_M C_{M,p}}{C_T} \frac{1}{N_{Co,0}(0)} \left(\frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \times \left(1 + \frac{1}{\beta} \right) \right\} \exp(k_{dea} t) \tag{7}$$

The effect of temperature, pH and the initiator concentration on DP_n was evaluated. The results collected in Figure 6.

The reaction temperature has the strongest effect on the rate coefficient of deactivation, as determined by the experimental design, see Table 3. When an acceptable temperature range for (mini)-emulsion polymerization (i.e. 323–348 K) is considered, it is predicted that an approximate 3-fold reduction in the amount of CoBF in the system is obtained after 2 h of reaction, even for a low radical concentration and a high pH of the aqueous phase, see Figure 6a. However, when lower pH values are considered, the decrease in the activity is more severe. The model shows that acidic conditions at 348 K result in complete deactivation of the catalyst. As a consequence a DP_n then approaches the situation where no CTA is present in the system, see Figure 6b. Besides the strong effect of the pH of the aqueous phase, there also appears to be a strong effect of the initiator concentration in the aqueous phase, see Figure 6c. When generally accepted initiator concentrations are used, the deactivation results in DP_n values that increase excessively. Proper control of DP_n can be obtained, when suitable process conditions are chosen. From the Figure 6a–c, it is evident that at high pH and a low radical concentration in the aqueous phase hardly any catalyst deactivation occurs, even at a relatively high temperature.

Discussion

For CCT mediated (mini)emulsion polymerizations the use persulfate initiators should be avoided due to severe deactivation of the Co(II) complex.[13] Therefore the use of (water soluble) azo-initiators is preferred. Especially in miniemulsion polymerization, AIBN is often a well suitable initiator. An important factor in the experimental design is the presence of initiator-derived radicals in the aqueous phase. Although AIBN is an oil-soluble initiator, with a solubility in the aqueous phase 0.04 wt%,[20] it is known that the

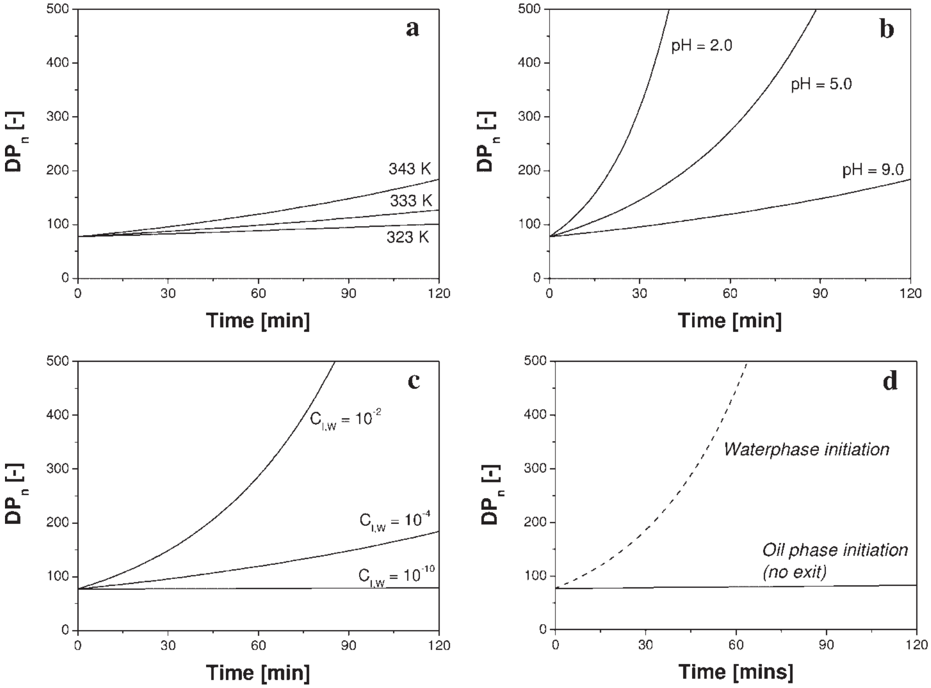

Figure 6.
The effect of the process variables on the normalized number-average degree of polymerization (Equation (7)). Model settings: $C_{Co,0} = 6 \cdot 10^{-6}$ $mol \cdot dm^{-3}$, $C_T = 15 \cdot 10^3$ [-], $m_{Co} = 0.72$ [-], $\beta = 0.20$ $dm_M^3 \cdot dm_W^{-3}$. Variable settings: $pH = 9$, $T = 343$ K, $C_{I,W} = 10^{-4}$ $mol \cdot dm_W^{-3}$ (AIBN) unless mentioned otherwise. a: Effect of the temperature, $T = 323$, 333 and 343 K. b: Effect of the pH of the aqueous phase, $pH = 2.0$; 5.0 and 9.0. c: Effect of the initiator concentration, $C_{I,W} = 10^{-10}$; 10^{-4} and 10^{-2} $mol \cdot dm_W^{-3}$. d: Model calculations: (····) $pH = 9.0$, $T = 343$ K and $C_{I,W} = 1.5 \cdot 10^{-3}$ $mol \cdot dm_W^{-3}$ and (—) $pH = 9.0$, $T = 343$ K and $C_{I,W} = 10^{-10}$ $mol \cdot dm_W^{-3}$.

AIBN-derived radicals desorb and partition towards the aqueous phase.[21,22] When it is assumed that virtually no radicals are present in the aqueous phase, a marginal increase in DP_n is predicted. On the other hand, if radical partitioning is considered, DP_n should show a strong increase, see Figure 6d. From a mechanistic point of view, it is important to elucidate the fate of alkyl radicals in the aqueous phase.

The effect of initiator concentration as found in the model deactivation experiments, i.e. in water without monomer, is diminished by the presence of monomer in the polymerization experiments, see Figure 7.

Although initiator-derived radicals are formed at the same rate as in the model experiments, their fate now is not necessarily catalyst deactivation. The presence of

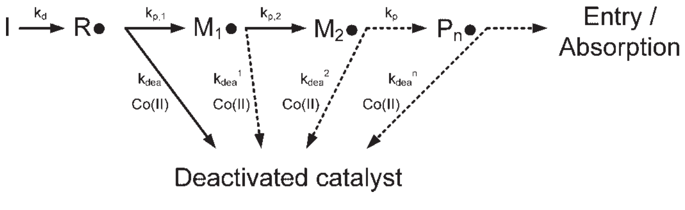

Figure 7.
Schematic representation of CoBF deactivation and aqueous phase propagation.

Table 4.
Estimated time constants for the reaction of an initiator-derived radical with MMA and CoBF at 70 °C.

	$k_i [dm_W^3 \cdot mol^{-1} \cdot s^{-1}]$	$C_{W,i} [mol \cdot dm_W^{-3}]$	*Time constant* [s]
MMA	$k_{p,1} = 16{,}8$ $k_p = 17.6 \cdot 10^3$ [23,25]	$1.5 \cdot 10^{-1}$ [24]	$4 \cdot 10^{-4}$
CoBF	$k_{dea} = 0.4 \cdot 10^3$ [a]	$6 \cdot 10^{-6}$	$4 \cdot 10^2$

[a] calculated based on the results of this work.

monomer in the aqueous phase will cause the initiator-derived radical to undergo a propagation reaction, turning the radical into a methacrylate propagating radical. This radical may grow until it becomes surface-active and enter a particle, thus reducing the steady-state radical concentration in the aqueous phase as compared to the model experiments. Furthermore, there is no reason to assume that the methacrylate propagating radicals do not cause any deactivation of the catalyst while in the aqueous phase, but the associated rate coefficients need not be the same as those associated with the initiator-derived radicals. For example, the reversible catalyst deactivation by Co-C bond formation is much stronger for AIBN-derived radicals (which are similar to those derived from cyanovaleric acid) than for MMA-derived radicals. In summary, the presence of MMA in the water phase may convert the initiator-derived radicals into other radicals (which may not cause as much deactivation) and which may grow to enter the particles, thus lowering the aqueous phase radical concentration. That this is indeed a plausible explanation can be concluded when considering the time constants associated with addition to monomer and catalyst deactivation by the initiator-derived radicals, see Table 4

$$t_{c,i} = \frac{1}{k_i C_{W,i}} \tag{7}$$

In order to calculate $k_{p,1}$, it is important to realize that the rate constant of propagation is strongly chain length dependent and can be calculated according to a model developed by Heuts et al.[25]

For k_{dea} a calculated value based on the results of this work is used. The difference in time constants is significant (the time for an alkyl radical propagating is 10^6 times faster then the deactivation of the Co(II) catalyst) and from this short calculation it can be concluded that the likelihood of a alkyl radical propagating with monomer is much larger than the deactivation of the active Co(II) complex. This result implies that the experimental design, used to predict the value of k_{dea}, most likely over-estimates the effect of alkyl radicals present in the aqueous phase. New deactivation experiments have to be performed in the presence of monomer to disclose the effect of alkyl radicals in the aqueous phase. Further insight will allow for a better understanding of this mechanism and an improved interpretation of the experimental design.

Conclusions

- The instantaneous number-average molecular degree of polymerization in CCT mediated miniemulsion polymerization is not only governed by the catalyst activity but also by CCTA partitioning and the phase ratio.
- A global model based on the Mayo equation and CCTA partitioning accurately describes the instantaneous number-average degree of polymerization at low conversion for miniemulsion polymerization of MMA.
- The global model was extended to incorporate CoBF deactivation in the aqueous phase.
- Aqueous phase deactivation of the CCTA plays a key role in proper molecular weight control in CCT mediated (mini)emulsion polymerization.

Acknowledgements: The authors wish to thank the Foundation Emulsion Polymerization (SEP) for financial support and the European Graduate School 'Microstructural Control in Free Radical Polymerization'

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