

# Control of the Molecular Weight Distribution in Continuous Emulsion Polymerization in a Pulsed Sieve Plate Column

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**Summary:** Control of the molecular weight distribution in continuous emulsion polymerization in a pulsed sieve plate column (PSPC) is experimentally studied. A global model, based on the Mayo equation, incorporating catalyst partitioning and deactivation was used to quantitatively illustrate the effect of the COBF addition on the instantaneous degree of polymerization in a batch reactor and the PSPC. Operating conditions have a strong influence on the cumulative molecular weight distribution of the latex product produced in the PSPC.

**Keywords:** catalytic chain transfer; COBF; continuous emulsion polymerization; molecular weight distribution; pulsed sieve plate column

## Introduction

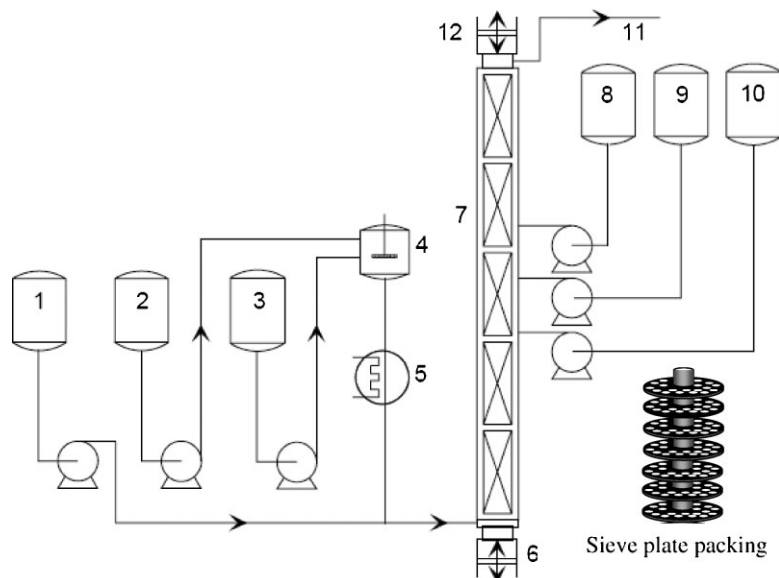
Emulsion polymerizations are frequently carried out in (semi-) batch processes. Demands for improved process control and narrow product specifications make that continuous operation may become an interesting alternative. For emulsion polymerization in continuously operated reactors, product properties, such as conversion, particle number, particle size distribution and the molecular weight distribution are strongly dependent on the residence time distribution. A single continuously operated stirred tank reactor (CSTR) has a broad residence time distribution. As a consequence the nucleation and the rest of the emulsion polymerization proceed simultaneously. The conversion level and number of particle in the product stream of a CSTR are much lower than for a

batch process. In a plug flow reactor nucleation and the rest of the polymerization are spatially separated. If the reaction time in an ideally mixed isothermal batch reactor is equal to the residence time in a plug flow reactor, the product properties in terms of the conversion, particle number, particle size distribution and molecular weight distribution are the same for both reactor types. A disadvantage, however, is that plug flow in a tubular reactor demands for turbulent flow and as a consequence for high liquid velocities. For high monomer conversions impractical reactor dimensions are required. Turbulent flow is also necessary for proper emulsification and for a low resistance against transfer of the heat of polymerization to the reactor wall. A combination of low net flow rates, limited backmixing, high local flow rates and intensive radial mixing is achieved with the pulsed packed column, see Meuldijk et al.<sup>[1]</sup>, Meuldijk and German<sup>[2]</sup> and with the Pulsed Sieve Plate Column, see Meuldijk<sup>[3]</sup> et al. and Scholtens et al.<sup>[4]</sup> Figure 1 shows the Pulsed Sieve Plate Column (PSPC) equipment as used in this study.

The residence time distribution in the PSPC is quantified by the plug flow with

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**Figure 1.**

Pulsed Sieve Plate Column (PSPC) flow chart: storage vessels for respectively initiator solution (1), aqueous phase (2) and monomers (3, 8, 9, 10). (4), (5), (6), (7), (11), (12) represent the premixer, the preheater, the pulsation pump, the column packed with sieve plates, the product stream and the pulsation dampener, respectively.<sup>[5]</sup>

axial mixing model<sup>[2]</sup> in which axial mixing coefficient  $E [m^2 \cdot s^{-1}]$  is the key parameter. The dimensionless Peclet number ( $Pe_L$ ) quantifies the degree of axial mixing, see Eq. (1).

$$Pe_L = \frac{u \cdot L}{E} \quad (1)$$

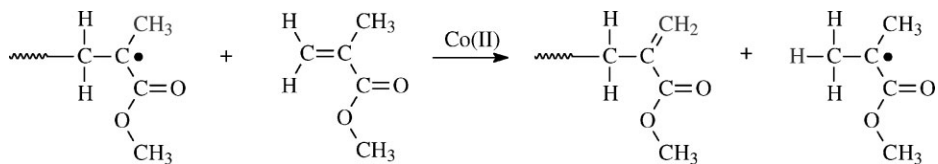
For a column with length  $L [m]$  and net liquid velocity  $u [m \cdot s^{-1}]$ , the Peclet number relates the residence time distribution in the column with that of a series of  $N$  equally sized tanks<sup>[6]</sup>, see Eq. (2).

$$N_{\text{tanks}} = \frac{Pe_L}{2} \quad (2)$$

For ab-initio styrene emulsion polymerization at 90 °C a reactor length of 5 m and a mean residence of about 20 minutes are sufficient for complete conversion and product properties not significantly different from those of a batch process.<sup>[3]</sup> The PSPC has proven to be a promising reactor for control of the intermolecular chemical composition in seeded emulsion copolymerization.<sup>[4,5]</sup>

For the application in e.g. waterborne coatings, the molecular weight distribution (MWD) of a latex is a key property. High molecular weight material is often desired for the product's strength, whereas low molecular weight material facilitates flow during processing and film formation in coating applications. Robust molecular mass control is therefore a key issue in polymer production. Catalytic chain transfer (CCT) is a promising tool to control the MWD in free radical polymerization.<sup>[7-12]</sup>

The most widely accepted mechanism for catalytic chain transfer involves a Co(II) complex that abstracts a hydrogen atom from the propagating polymeric radical, yielding a dead polymer chain with a vinyl end-group functionality and a Co(III)-H complex. The Co(III)-H intermediate can subsequently react with a monomer molecule, resulting in the regeneration of the active Co(II) species and the formation of a propagating monomeric radical. The hydrogen abstraction is assumed to be the rate determining step in this mechanism.<sup>[7,8]</sup> The overall reaction of catalytic chain

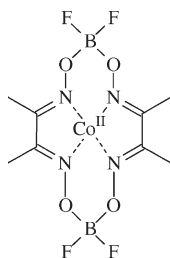
**Scheme 1.**

The overall reaction of catalytic chain transfer to monomer

transfer to monomer in the case of methyl methacrylate (MMA) is schematically presented in Scheme 1.

Recently, there is a growing interest for the application of controlled and living radical polymerization techniques in emulsion polymerization.<sup>[13]</sup> The emulsion polymerization system is heterogeneous by nature. This heterogeneity has major implications for the application of CCT and the control of the molecular weight distribution.<sup>[14–20]</sup> The catalytic chain transfer agent (CCTA) partitions over the phases present resulting in lower apparent activities,<sup>[16,20]</sup> lower rates of polymerization<sup>[17]</sup> and decomposition of the active complex.<sup>[21]</sup> Deviations from the intrinsic activity are governed by partition coefficients and phase ratios.<sup>[20]</sup> However, control of the molecular weight distribution in (semi-) batch emulsion polymerization can be achieved.<sup>[14–20]</sup>

In the present paper we report the preliminary results on the control of the molecular weight distribution in the PSPC reactor. The applicability of catalytic chain transfer in continuous emulsion polymerization, using a moderately water soluble catalytic chain transfer agent, i.e. bis[(difluoroboryl) dimethylglyoximate]cobalt(II) (COBF, **1**), is evaluated. The results

**1**

presented illustrate the feasibility of CCT to control the molecular weight distribution in continuously produced latex products

## Experimental Part

### Materials

The catalytic chain transfer agent, COBF, was prepared according to the method of Bakac and Espenson.<sup>[22]</sup> Distilled deionized water (DDW) was used throughout all experiments. Monomers, styrene (S, Aldrich, 99%) and methyl methacrylate (MMA, Aldrich, 99%) were either distilled or passed over a column packed with basic alumina to remove the inhibitor. The initiators, 2,2'-azobis(2-methylpropionamide) dihydrochloride (V50, Aldrich, 97%) and sodium persulfate (SPS, Aldrich), the surfactant, sodium dodecyl sulphate (SDS, Aldrich) and the buffer, sodium carbonate (SC, VWR, analysis grade), were used without any further purification.

### Experimental Set-Up

The Pulsed Packed Sieve Column (PSPC) is a tubular reactor with a length ( $L$ ) of 5 m and an internal diameter of 49.5 mm. Five stainless-steel jacketed segments, which can be thermostated separately, are placed on top of each other. The column contains a stacked stainless-steel sieve plate packing. The plates have a permeability of 34%. The distance between the sieve plates is 9 mm. A modified membrane pump is used for pulsation of the liquid in the column. Stroke length ( $s$ ) and frequency ( $f$ ) can be varied between 0 and 35 mm and 1 and 3.5 Hz, respectively. A schematic representation of the PSPC equipment is given in Figure 1.

### Seed Latex Production in the PSPC

Styrene and methyl methacrylate were mixed together in the monomer storage vessel (3) in a 1:1 molar ratio. The surfactant (SDS) and buffer (SC) were dissolved in water and stored in the aqueous phase storage vessel (2). An aqueous initiator (SPS) solution was prepared in the initiator solution vessel (1). All vessels were purged with argon prior to the polymerization. Before the start-up, the premixer and the column were filled with water. First, the continuous phase feed was started and one hour later the monomer and initiator feed. The complete recipe and operational conditions are presented in Table 1.

The properties of the produced seed latex are presented in Table 2. To completely decompose any remaining initiator residues, the seed latex was re-circulated through the column seven times for one hour at a temperature of 85 °C. Less than 1% of initiator should be present after this treatment.

### Catalytic Chain Transfer Mediated Emulsion Polymerization in the PSPC

Methyl methacrylate was stored in storage vessel (8). Seed latex, methyl methacrylate and water, in which surfactant (SDS) and

buffer (SC) were dissolved, were mixed together in the aqueous phase storage vessel (2). A solution of catalyst (COBF) and initiator (V50) in deoxygenized water was prepared in the initiator solution vessel (1). A solution of catalyst (COBF) in deoxygenized methyl methacrylate was prepared in a small monomer storage vessel (9). All vessels were purged with argon prior to the polymerization. First, the continuous phase feed was started and one hour later the monomer and initiator feed. Finally, the multiple side feeds were started. The complete recipe and reactor conditions are presented in Table 3.

### Size Exclusion Chromatography (SEC)

Size exclusion chromatography was performed using a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer. A set of two mixed bed columns (Mixed-C, Polymer Laboratories, 30 cm, 40 °C) were used. Tetrahydrofuran stabilized with 2,6-di-*tert*-butyl-4-methylphenol was used as the eluent, and the system was calibrated using narrow molecular weight polystyrene standards ranging from 600 to  $7 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ . Mark Houwink parameters used for the polystyrene standards:  $K = 1.14 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$ ,  $a = 0.716$ , and for poly(methyl methacrylate):  $K = 9.44 \times 10^{-5} \text{ dL} \cdot \text{g}^{-1}$ ,  $a = 0.719$ .

**Table 1.**

The recipe and the operational conditions for the seed latex production in the PSPC reactor.

Component	Mass [ $10^{-3} \text{ kg}$ ]	Feed rate [ $10^{-3} \text{ kg} \cdot \text{s}^{-1}$ ]	Operational variables	
Styrene	1290	0.72	Reactor volume [ $\text{dm}^3$ ]	8.7
Methyl methacrylate	1330	0.74	Residence time ( $\tau$ ) [s]	1800
Distilled deionized water	5830	3.06	$u$ [ $\text{m} \cdot \text{s}^{-1}$ ]	$2.8 \cdot 10^{-3}$
Sodium dodecyl sulphate	276	0.153	Temperature [ $^{\circ}\text{C}$ ]	85
Sodium carbonate	7.43	0.0041	Absolute pressure [bar]	2.7
Sodium persulphate	4.78	0.0027	Column Length (L) [m]	5.0
			Stroke length (s) [ $10^{-3} \text{ m}$ ]	7.0
			Frequency (f) [Hz]	3.2
			$E$ [ $\text{m}^2 \cdot \text{s}^{-1}$ ]	$0.12 \cdot 10^{-3}$
			Peclet number [-]	116

**Table 2.**

Properties of the seed latex produced in the PSPC.

Final conversion [-]	$\overline{M}_w$ [ $10^6 \text{ g} \cdot \text{mol}^{-1}$ ]	$d_p$ [nm]	$N_p$ [ $10^{18} \text{ dm}_w^{-3}$ ]
0.99	1.0	$64 \pm 4$	2.0

**Table 3.**

The recipe and operational conditions for the COBF mediated emulsion polymerization in the PSPC

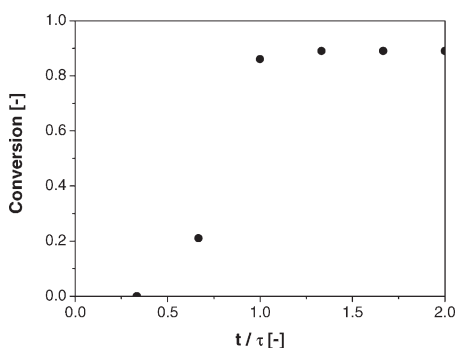
Component	Mass [ $10^{-3}$ kg]	Feed rate [ $10^{-3}$ kg $\cdot$ s $^{-1}$ ]	Operational variables	
Seed	2205	0.42	Reactor volume [ $dm^3$ ]	8.7
Methyl methacrylate <sup>a</sup>	1050	0.193	Residence time ( $\tau$ ) [s]	5400
Distilled deionized water	5420	0.93	$u$ [ $m \cdot s^{-1}$ ]	$0.93 \cdot 10^{-3}$
Sodium dodecyl sulphate	43.4	0.008	Temperature [ $^{\circ}C$ ]	65
Sodium carbonate	4.77	$8.8 \cdot 10^{-4}$	Absolute pressure [bar]	2.7
V50	8.55	0.0016	Column Length ( $l$ ) [m]	5.0
COBF feed $z = 0.0$ m	0.132	$4.12 \cdot 10^{-6}$	Stroke length ( $s$ ) [ $10^{-3}$ m]	15
MMA side feed $z = 1.4$ m		0.088	Frequency ( $f$ ) [Hz]	1.5
MMA side feed $z = 2.2$ m		0.058	$E$ [ $m^2 \cdot s^{-1}$ ]	$0.11 \cdot 10^{-3}$
MMA side feed $z = 3.2$ m		0.058	Peclet number [-]	42
COBF side feed $z = 1.4$ m		$4.12 \cdot 10^{-6}$		

<sup>a</sup>The amount represents the total amount of monomer added to the seed latex, vessel (2).**Molecular Weight Control in the PSPC**

To illustrate the ability to control the molecular weight distribution in continuous emulsion polymerization in the PSPC, a COBF mediated seeded emulsion polymerization was performed. The catalytic chain transfer agent used is known to partition to a large extend between the partially monomer swollen polymer particles and aqueous phase.<sup>[17,20]</sup> The nucleation stage was circumvented by feeding the reactor with a well defined number of seed particles. The seed latex was produced in the PSPC and consists of a styrene – methyl methacrylate copolymer. The properties of the seed latex are summarized in Table 2. To maintain a sufficiently low viscosity in the polymer particles and to allow for rapid diffusion of COBF, monomer was fed to the reaction mixture at three axial positions, i.e.  $z = 1.4, 2.2$  and  $3.2$  m. The catalytic chain transfer agent (COBF) was fed at the bottom of the reactor to control the molecular weight distribution of the freshly formed polymer.  $10^{-8} \text{ mol} \cdot \text{s}^{-1}$  COBF was fed to the reactor at the bottom ( $z = 0$ ). COBF was dissolved in the aqueous initiator solution. The COBF concentration was 5 ppm with respect to the amount of monomer present. A second feedstream of COBF to compensate for any catalyst deactivation was supplied to the reactor at  $z = 1.4$  m. Here COBF was dissolved in the monomer feedstream at  $z = 1.4$  m.

For proper mixing and negligible resistance against monomer transport from the side feed to the particles a stroke length of

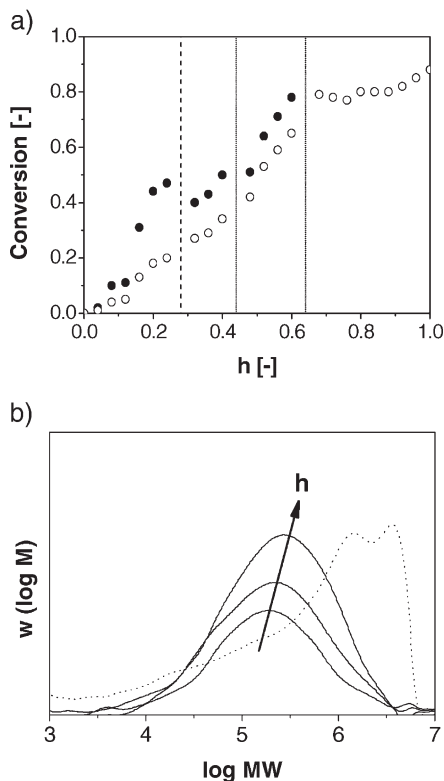
15 mm was chosen, to ensure that the liquid between two sieve plates was refreshed completely during one pulsation cycle. For the pulsation conditions applied ( $s = 15$  mm and  $f = 1.5$  Hz) the axial dispersion coefficient,  $E$ , is  $0.11 \cdot 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$ . The axial dispersion coefficient is evaluated from the pulsation velocity  $s \cdot f$  according to Scholtens et al.<sup>[4]</sup> The net liquid velocity ( $u$ ) is  $0.93 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$  which results in a Peclet number of 42. At the operational conditions used the column corresponds with 21 equally sized tanks in series, see Eq. (2). The performance of the column is expected to approximate the performance of a plug flow for seeded emulsion polymerization.<sup>[5]</sup> The conversion at the top of the column was monitored during the start-up of the polymerization, see Figure 2. The stationary state is reached after operation during less than 1.5

**Figure 2.**

Conversion at the top of the PSPC during the start-up of the seeded emulsion polymerization of MMA.  $\tau = 5400$  s,  $E = 1.1 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ ,  $Pe_L = 42$ .

times the mean residence time. This short time to approach steady state points to approximately plug flow for the operational conditions applied. The PSPC is beneficial with respect to grade changes: the amount of off-spec product is rather limited.

The overall and instantaneous conversion time histories with side feeds of COBF and MMA are presented in Figure 3a. The instantaneous conversion at a dimensionless height  $h = z/L$  is based on the amount



**Figure 3.** Seeded COBF mediated emulsion polymerization of MMA in the PSPC a: Overall conversion (○) and the instantaneous conversion (●) as a function of the dimensionless axial position  $h$  (....) COBF side feed dissolved in monomer  $z = 1.4$  m and (----) monomer side feed at  $z = 2.2$  and  $3.2$  m. b: evolution of the molecular weight distribution as a function of  $h$  (....); the molecular weight distribution of the seed latex and (—) the cumulative molecular weight distribution for increasing axial position in the column ( $h$ ) determined at  $h = 0.18$ ,  $0.34$  and  $0.80$  without the contribution of the seed latex.

of monomer added until height  $z$ . The overall conversion is determined based on the total amount of monomer that is added to the reactor. The overall conversion is increasing gradually over the length of the reactor until a final conversion of 0.90 is reached. The instantaneous conversion time history is affected strongly by the monomer side feeds at  $h = 0.28$ ,  $0.44$  and  $0.64$ . However, throughout the course of the polymerization, the instantaneous conversion is increasing.

The evolution of the molecular weight distribution is presented in Figure 3b. The cumulative molecular weight distributions after the COBF addition are obtained by subtracting the contribution of the seed latex ( $h = 0$ ) from the cumulative molecular weight distribution at  $h > 0$ . The results collected in Figure 3b clearly demonstrate that as a result of the feeding of the catalytic chain transfer agent at  $h = 0$ , a decrease of the average molecular weight of the polymer is obtained. Approximately a ten-fold reduction in the weight average molecular weight is achieved. The COBF feed at  $h = 0.28$  did not lead to a significant decrease of the molecular weight of the polymer produced. It is assumed that catalyst deactivation occurred. The freshly supplied COBF at  $h = 0.28$  is hardly capable to compensate for this deactivation between  $0 \leq h \leq 0.28$ . Note that the metal surface per unit volume of the reaction mixture in the PSPC is much larger than in a batch reactor. In addition to deactivation of COBF by traces of oxygen,<sup>[11,23]</sup> adsorption of COBF at the metal surface of the sieve plates perhaps followed by redox reactions may lead to activity loss.

## Discussion

The instantaneous degree of polymerization ( $DP_n$ ) in catalytic chain transfer mediated bulk and solution polymerization can be predicted by the Mayo equation,<sup>[24]</sup> see Eq. (3). In Eq. (3)  $C_{Co,0}$  and  $C_M$  are the concentrations of catalytic chain transfer agent and monomer, respectively.  $C_T$  is the chain transfer coefficient reflecting the

intrinsic activity of the cobalt complex used.

$$DP_n^{-1} = DP_{n,0}^{-1} + C_T \frac{C_{Co,0}}{C_M} \quad (3)$$

However when applied in emulsion polymerization, the catalytic chain transfer agent will partition over the different phases present. In emulsion polymerization only the amount of catalytic chain transfer agent at the locus of polymerization, i.e. the polymer particles, is active in molecular weight control. The Mayo equation was modified to incorporate catalytic chain transfer agent partitioning, see Eq. (4).<sup>[20]</sup> In Eq. (4)  $V_M$  stands for the volume of the organic phase i.e. the polymer particles in this work,  $C_{M,p}$  for the monomer concentration inside a polymer particle,  $N_{Co,0}$  for the number of moles of COBF added,  $m_{Co} = C_{Co,M}/C_{Co,W}$  for the partition coefficient, and  $\beta$  for the phase ratio.

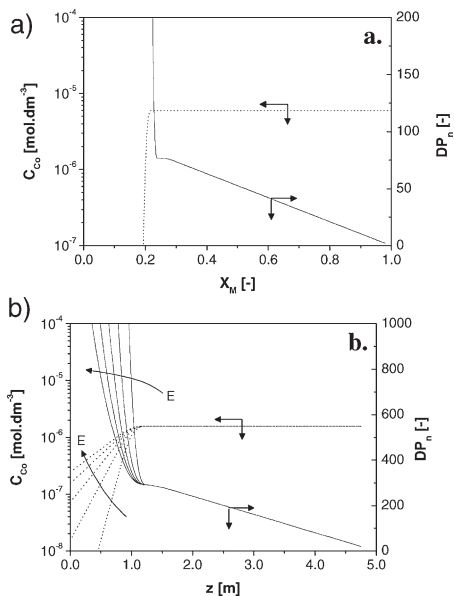
$$DP_n = \frac{V_M C_{M,p}}{C_T} \frac{1}{N_{Co,0}} \left( \frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \times \left( 1 + \frac{1}{\beta} \right) \quad (4)$$

with  $\beta = \frac{V_M}{V_W}$

Eq. (4) clearly demonstrates that the instantaneous degree of polymerization

$$DP_n = \left\{ \frac{V_M C_{M,p}}{C_T} \frac{1}{N_{Co,0}^0} \left( \frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \left( 1 + \frac{1}{\beta} \right) \right\} \times \exp(k_{dea}t) \quad (5)$$

depends on (i)  $C_{M,p}$ , (ii) the choice of CCTA ( $C_T$ ,  $m_{Co}$ ) and (iii) the polymerization recipe ( $N_{Co,0}$ ,  $\beta$ ,  $V_M$ ). The cobalt complexes used for molecular weight control are known to be susceptible to aqueous phase decomposition<sup>[21]</sup> as a consequence of oxidation in the presence of oxygen<sup>[11,23]</sup> or peroxide radicals<sup>[11,24,25]</sup> and hydrolysis in acidic aqueous media.<sup>[11]</sup> This results in a situation where the absolute amount of COBF is a function of the first order deactivation rate constant ( $k_{dea}$ ) and the polymerization time ( $t$ ), see Eq. (5).<sup>[21]</sup> However, under typical emulsion polymerization conditions the deactivation of the catalyst complex can be largely suppressed



**Figure 4.**

Simulation of the overall COBF concentration and the instantaneous degree of polymerization as a function of the monomer conversion for a batch emulsion polymerization (a) and continuous emulsion polymerization in the PSpC (b). (····)  $C_0/C_M$  and (–)  $DP_n$ .

when oxygen is excluded from the reaction system and when the presence of peroxide radicals and acidic media can be avoided.

Eq. (5) relates the instantaneous degree of polymerization directly to the emulsion polymerization recipe and operating conditions for a batch emulsion polymerization. Figure 4a shows the course of the instantaneous degree of polymerization in a batch emulsion polymerization of MMA. COBF is added to the reaction mixture as a pulse at 20% conversion. This COBF injection results in a stepwise increase of the COBF concentration in the particles and as a consequence in a stepwise decrease of the instantaneous degree of polymerization ( $DP_n$ ). After this stepwise decrease of  $DP_n$ ,  $DP_n$  gradually decreases as a result of the continuously decreasing monomer con-



centration in the particles when the monomer droplets are completely consumed ( $X_M > 0.27$ ), see Eq. (4).

For equal residence times the performance of a constant density plug flow reactor is equal to the performance of a constant density batch reactor. The instantaneous degree of polymerization in a plug flow reactor follows from Eq. (4) and (5) by replacing  $V_M$ ,  $V_W$ ,  $N_{Co,0}$  and  $t$  by  $\phi_{V,M}$ ,  $\phi_{V,W}$ ,  $\phi_{mol,Co,0}$  and  $\tau = V_r/\phi_{V,0}$ , respectively, see Eq. (6) and (7).  $\phi_{V,M}$ ,  $\phi_{V,W}$ ,  $\phi_{mol,Co,0}$  and  $\phi_{V,0}$  stand for the volumetric flow rate of the organic phase the volumetric flow rate of water, the molar flow rate of COBF and the total volumetric flow rate, respectively.

$$DP_n = \frac{\phi_{V,M} C_{M,p}}{C_T} \times \frac{1}{\phi_{mol,Co,0}} \left( \frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \times \left( 1 + \frac{1}{\beta} \right) \quad (6)$$

with  $\beta = \frac{\phi_{V,M}}{\phi_{V,W}}$

$$DP_n = \left\{ \frac{\phi_{V,M} C_{M,p}}{C_T} \frac{1}{\phi_{mol,Co,0}^0} \left( \frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \left( 1 + \frac{1}{\beta} \right) \right\} \exp(k_{dea}\tau) \quad (7)$$

The pulse wise addition of COBF in a (semi-) batch process corresponds with a COBF side feed in a plug flow reactor. Therefore, a side feed of COBF to a plug flow reactor leads to the same result as shown in Figure 4a. However, pulsation in the PSPC results in some backmixing. For a COBF feed stream at position  $z_i$ , a stationary axial COBF concentration profile establishes upstream of the feeding point, see Eq. (8).<sup>[4]</sup> Downstream the feeding point the COBF concentration is independent of the axial position, see Eq. (9).

$$C_{Co,z} = C_{Co,z_i} \exp\left(\frac{u(z - z_i)}{E}\right) \quad \text{for} \quad (8)$$

$$z < z_i$$

$$C_{Co,z} = C_{Co,z_i} \quad \text{for} \quad z \geq z_i \quad (9)$$

As result of backmixing a decrease of  $DP_n$  already starts upstream of the feeding position, see Figure 4b. Downstream the feeding point  $DP_n$  gradually decreases with  $h$  as a result of the continuously decreasing monomer concentration in the particles when the monomer droplets are completely consumed ( $X_M > 0.27$ ), see Eq. (6). However, due to catalyst deactivation a constant or slightly increasing instantaneous degree of polymerization is often observed, see Eq. (7).<sup>[14-20]</sup> Note that the final cumulative molecular weight distribution of the latex product of the PSPC will be broad and is most likely strongly tailing towards the high molecular weight end of the distribution. Our experimental results, see Figure 3b are qualitatively in line with these considerations about back mixing and catalyst deactivation downstream the feeding position at  $h = 0.28$ , see Figure 3a and 3b.

(a)  $DP_n$  calculated using Eq. (4). and  $m_{Co} = 0.72 \text{ dm}_W^3 \cdot \text{dm}_M^{-3}$ ;  $\beta = 0.20 \text{ dm}_M^3 \cdot \text{dm}_W^{-3}$ ;  $C_T = 15 \cdot 10^3$ ;  $V_M = 0.20 \text{ dm}^3$ ;  $C_{M,p}^{sat} = 6.9 \text{ mol} \cdot \text{dm}_M^{-3}$  and  $N_{Co} = 9.52 \cdot 10^{-6} \text{ mol}$ .

(b)  $DP_n$  calculated using Eq. (6 and 8). and  $m_{Co} = 0.72 \text{ dm}_W^3 \cdot \text{dm}_M^{-3}$ ;  $\beta = 0.20 \text{ dm}_M^3 \cdot \text{dm}_W^{-3}$ ;  $C_T = 15 \cdot 10^3$ ;  $\phi_{V,M} = 2.7 \cdot 10^{-4} \text{ dm}^3 \cdot \text{s}^{-1}$ ;  $C_{M,p}^{sat} = 6.9 \text{ mol} \cdot \text{dm}_M^{-3}$  and  $\phi_{mol,Co} = 2.53 \cdot 10^{-9} \text{ mol} \cdot \text{s}^{-1}$ . Operational conditions:  $u = 9.3 \cdot 10^{-4} \text{ m} \cdot \text{s}^{-1}$ ;  $E = 1.0 - 5.0 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ . The feed position is simulated at  $h = 0.2$  ( $z = 1 \text{ m}$ )

## Conclusion

The presented results indicate that control of the molecular weight distribution in latex products produced in the PSPC reactor is well possible.

Backmixing in the PSPC is a key factor in process design and operation.

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