Catalytic Chain Transfer in a Miniemulsion Copolymerization of Methyl Methacrylate and *n*-Butyl Acrylate

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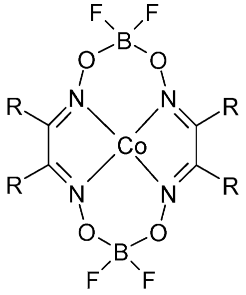
Introduction. In the past two decades catalytic chain transfer (CCT) has emerged as a useful, industrial applicable technique to prepare low molecular weight macromonomers[1−3] from methacrylates, α-methylstyrene, and styrenes[4−6] and from acrylates as comonomers.[7] Cobaloxime boron fluorides are typical examples of highly active CCT catalysts. Most studies on CCT have been performed in bulk or solution. However, many industrially relevant polymerization processes are carried out in heterogeneous systems, like emulsions.

When compared with homogeneous systems, many additional aspects play a role in emulsion (co)polymerization, like particle nucleation, monomer partitioning and colloidal stability.[8−10] The application of CCT in emulsion polymerization is disclosed in several patents by Janowicz[11,12] and Haddleton et al.[13−15] and in a few papers.[16−20] A few years ago, Kukulj et al.[21] published some interesting results on CCT in miniemulsion polymerization. The main difference between emulsion and miniemulsion polymerization is that in the latter initiation/nucleation takes place in the monomer droplets, which have about the same size as polymer particles in emulsion polymerization. To be able to produce such small monomer droplets, larger amounts of surfactant and cosurfactant are required, which is a disadvantage. However, controlled radical polymerizations in miniemulsions usually give better defined polymers than in regular emulsion polymerization.[22−25] Kukulj et al.[21] have demonstrated similar benefits for CCT in miniemulsion homopolymerization. This paper reports on the application of CCT in miniemulsion copolymerization.

Experimental Section. a. Materials. The monomers methyl methacrylate (MMA) (Merck, 99%) and *n*-butyl acrylate (BA) (Merck, 99%) and the initiator 2,2′-azobis(isobutyronitrile) (AIBN) were purified according to previously published procedures.[26] All other chemicals were used without further purification.

b. Syntheses. A modification of the procedures of Lance et al.[27] and Cervera et al.[28] was followed for the synthesis of 3,4-hexanedione dioxime.[29] The product was analyzed by elemental analysis. $C_6H_{12}N_2O_2$ experimental: C, 50.5%; H, 8.4%; N, 19.1%. Calculated: C, 50.0%; H, 8.39%; N, 19.4%.

Ethyl cobaloxime boron fluoride, **1** (Co(Et)$_4$BF) (R = C_2H_5), was synthesized according to a procedure of Bakac and Espenson.[30] The product was analyzed by elemental analysis. $C_{12}H_{20}N_4O_4B_2F_4Co\cdot 2H_2O$ experimental: C, 30.3%; H, 4.9%; N, 11.6%. Calculated: C, 30.2%; H, 5.1%; N, 11.7%.



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c. Determination of Chain Transfer Constant. The determination of the chain transfer constant (C_T) of Co(Et)$_4$BF in the bulk polymerization of MMA was carried out according to the procedure described previously.[26]

d. Miniemulsion Polymerizations. The recipe for the miniemulsion polymerizations was similar to the one presented by Kukulj et al.[21] The polymerizations were carried out in batch mode in a conically shaped, double-walled reactor, which is especially designed for the preparation of monomer miniemulsions. A magnetic stirrer bar is used to provide sufficient mixing. A typical recipe consisted of 80 g of demineralized water, in total 20 g of BA and/or MMA, 0.50 g of hexadecane, 0.80 g sodium dodecyl sulfate (SDS), 0.20 g of AIBN, and a varying amount of Co(Et)$_4$BF. Inside a glovebox a solution of catalyst, monomer, hexadecane, and initiator was prepared. SDS was added to the reactor. Subsequently, the reactor was purged with argon, and during all further steps care was taken to exclude oxygen. Water was deoxygenated and transferred into the reactor. After that, the monomer phase was added dropwise while stirring vigorously. After 15 min an ultrasound probe (750 W Sonics Vibra cell) was immersed into the reaction mixture. During sonication the reactor was cooled using a cryostat set at 5 °C. Sonication was carried out for 4 min at 60% amplitude, followed by additional stirring for 15 min. The reactor was connected to a preheated thermostated water bath set at 75 °C. Before and during the reaction samples were withdrawn by syringe to monitor conversion, MWD, and particle size distribution.

e. Analyses. Conversion was determined gravimetrically. Size exclusion chromatography was carried out as described previously.[26] Molecular weight distributions (MWDs) for copolymers were determined directly from the polystyrene calibration curve.

Dynamic light scattering was performed on a Malvern 4700 light scattering apparatus equipped with a Malvern 7032 correlator at a scattering angle of 90° at a temperature of 25 °C. For monomer miniemulsions the resulting droplet size distributions should be interpreted with caution.[31] Reproducible results were obtained when the samples were diluted with monomer saturated water to prevent dissolution of the monomer droplets.

Results and Discussion. The catalytic activity of Co(Et)$_4$BF was determined in the bulk polymerization

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Table 1. Experimental Data and Results for Co(Et)$_4$BF Mediated Homo- and Copolymerizations

expt	f_{MMA}	[Co(Et)$_4$BF] (ppm)[a]	conv[b] (%)	M_n[b] (10^3 g mol^{-1})	PDI[b]	initial D_z (nm)	final D_z (nm)
1	1	0	99.0	546	2.43	148	125
2	1	4.7	95.6	2.39	1.72	151	188
3	0.5	0	100	358	3.00	238	93
4	0.5	68	88.1	14.6	3.13	445	180

[a] 1 ppm is defined as 10^{-6} mol of catalyst per mole of monomer. [b] Final latex properties.

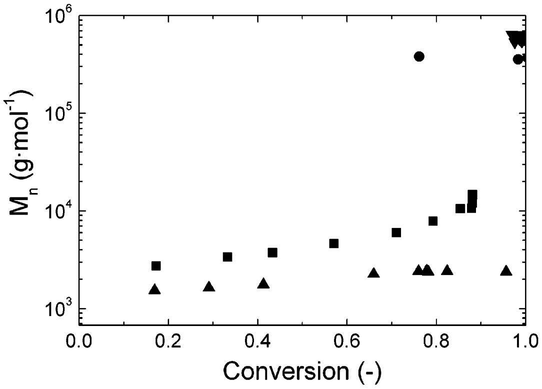

Figure 1. Evolution of M_n with conversion for four miniemulsion polymerizations initiated by AIBN. Downward triangles: MMA, no Co(Et)$_4$BF; upward triangles: MMA, 4.7 ppm of Co(Et)$_4$BF; circles: MMA−BA, no Co(Et)$_4$BF; squares: MMA−BA, 68 ppm of Co(Et)$_4$BF.

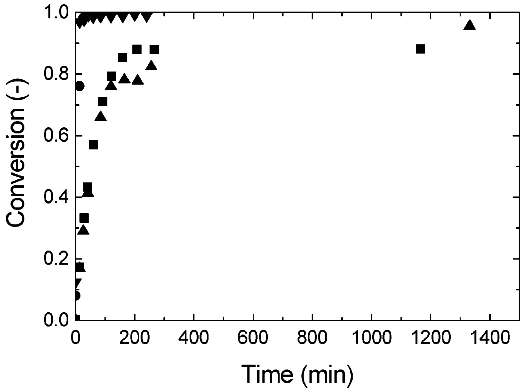

Figure 2. Conversion−time plots for four miniemulsion polymerization initiated by AIBN. Downward triangles: MMA, no Co(Et)$_4$BF; upward triangles: MMA, 4.7 ppm of Co(Et)$_4$BF; circles: MMA−BA, no Co(Et)$_4$BF; squares: MMA−BA, 68 ppm of Co(Et)$_4$BF.

of MMA at 60 °C. C_T was found to be 32×10^3 compared to 18×10^3 reported earlier.[32] For the corresponding cobaloxime with four methyl side groups (CoBF) C_T's around 40×10^3 are generally reported.

A total of four polymerizations have been performed: two MMA homopolymerizations and two MMA−BA copolymerizations at 50 mol % of MMA. One of each is carried out in the presence of Co(Et)$_4$BF. Experimental data and results are collected in Table 1. It appeared to be rather difficult to produce a monomodal droplet size distribution (DSD) of monomer droplets. In general, over 90% particles of small size, less than 100 nm, and a small amount of larger particles, between 300 and 500 nm, are produced. Final particle size distributions (PSD) are generally more narrow having D_z between 100 and 200 nm. This change in PSD means that not all droplets were nucleated. Incomplete nucleation may well affect apparent catalyst activity.

The effect of Co(Et)$_4$BF on molecular weight can be seen readily from the results in Table 1 and from Figure 1, in which the evolution of M_n with conversion is presented. In the homopolymerizations M_n is reduced by more than 2 orders of magnitude, whereas in the copolymerization a 25-fold reduction is observed. From M_n of the first sample, taken at low conversion, an apparent C_T of 14×10^3 for MMA and of 6×10^2 for MMA−BA is determined from the Mayo equation. Using the equations and parameters reported earlier,[33] for the corresponding MMA−BA solution copolymerization C_T around 3×10^3 can be predicted. So for both miniemulsion polymerizations C_T is a factor of 3−5 lower than in the solution polymerization. In CCT emulsion polymerizations reduced catalyst activity has often been partially attributed to deactivation of the catalyst in the water phase.[17,19] Results from DLS measurements indicate that not all droplets have been nucleated. So, during transport of the catalyst from the nonnucleated droplets through the water phase, deactivation may also occur in these miniemulsion polymerizations. Partitioning studies of the catalyst[29,32] show that about 5% of the catalyst is present in the water phase. Though the direct effect of decreasing the catalyst concentration in the particles is small, this can also contribute to the amount of deactivation.

From the final sample an overall apparent C_T of 9×10^3 for MMA and of 1×10^2 for MMA−BA is calculated, which is still an order of magnitude higher than for conventional chain transfer agents.

As presented in Figure 2, the polymerizations without Co(II) catalyst reach nearly full conversion within half an hour. The rate of CCT mediated miniemulsion polymerizations is lower, which is likely to be expected from the increased generation of small radicals, followed by exit and finally termination, as is shown below. The exit rate coefficient for a monomeric radical, k_{dM}, and the probability of exit, P(exit), can be calculated from the following expressions[8]

$$k_{dM} = \frac{3D_w C_w}{r_s^{\,2} C_p} \tag{1}$$

$$P(\text{exit}) = \frac{k_{dM}}{k_{dM} + k_{p1} C_p} \tag{2}$$

in which D_w is the radical diffusion coefficient in the water phase, C_w and C_p are the solubilities in the water phase and particle phase, respectively, r_s is the particle radius, and k_{p1} is the propagation rate coefficient for the first propagation step. When the following general estimates $D_w = 1 \times 10^{-9}$ m^2 s^{-1}, $C_w = 0.15$ mol L^{-1}, $C_p = 5$ mol L^{-1}, $r_s = 100$ nm, and $k_{p1} = 2000$ L mol^{-1} s^{-1} are applied, P(exit) is around 0.5. So given the frequent chain transfer steps and the large probability of exit, the rate of polymerization will be affected.

The MWDs for the CCT-mediated polymerizations are presented in parts a and b of Figure 3 for MMA and MMA−BA, respectively. In the homopolymerization a slight shift to higher molecular weights is observed, where a slight decrease would be expected from a

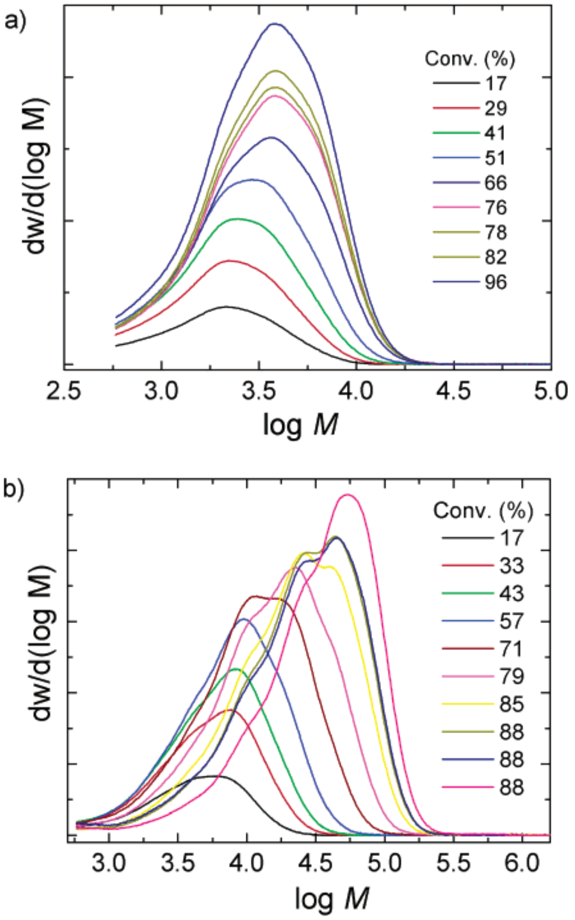

Figure 3. MWD measured at different conversions for the CCT miniemulsion polymerization of MMA (a) and MMA−BA (b) at 75 °C. The area under the distributions is proportional to the corresponding conversions.

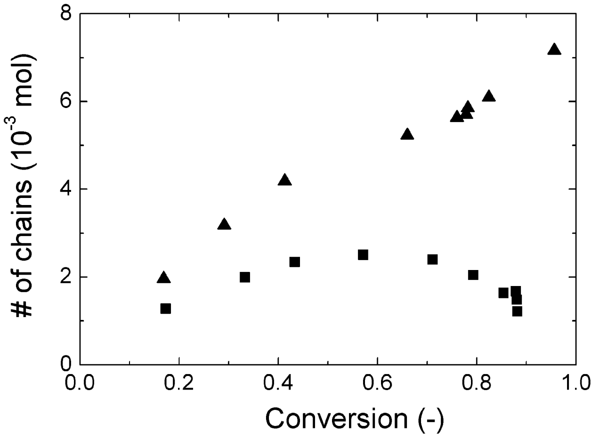

Figure 4. Evolution of the number of polymer chains with conversion in the CCT miniemulsion polymerizations of MMA (triangles) and MMA−BA (squares).

theoretical point of view. In solution or bulk CCT-mediated polymerizations similar behavior is often observed.[34] In a previous paper[35] possible reasons for such an increase have been discussed. In this case, hydrolysis of the Co(II) in the water phase is a plausible explanation.[17,19,35] All results and observations for CCT miniemulsion polymerizations of MMA are generally in line with results obtained by Kukulj et al.[21] However, it should be noted that with the catalyst applied in this work lower molecular weight polymer with a narrower distribution at higher final conversions is obtained at comparable amounts of catalyst. This can be explained from its partitioning behavior as it partitions less into the water phase than CoBF (**1**, R = CH_3). Furthermore, its activity in bulk is comparable to that of CoBF and about 3 times higher than that of $Co(Ph)_4BF$ (**1**, R = phenyl). Both CoBF and $Co(Ph)_4BF$ were studied by Kukulj et al.[21]

In the MMA−BA copolymerization a somewhat stronger increase in molecular weight compared to that in the MMA homopolymerization is observed initially. This can be explained by the effect of composition drift on C_T of the Co(II) complex.[33] Around 70% conversion low molecular weight material starts disappearing, and high molecular weight material is formed. After $3^1/_2$ h, 88% conversion has been reached. During the next 16 h no additional conversion was determined, but a significant shift in the MWD to higher molecular weights was observed. A similar shift in MWD has been reported previously[33] for the corresponding solution copolymerization. The evolution of the number of polymer chains with conversion can be used to obtain more information on the reactions that occur. The number of chains can be calculated from the initial amount of monomer, conversion, and M_n. For copolymers, especially when composition drift occurs, the calculation of M_n using a polystyrene calibration curve will result in a certain error in the absolute values of M_n. However, the calculated trends are expected to be correct. As can be seen in Figure 4, the number of polymer chains in the copolymerization decreases nearly 50% when going from 57 to 88% monomer conversion. The number of chains in the homopolymerization, on the other hand, shows a steady increase. For the copolymerization this has been explained by the incorporation of macromonomers into the growing polymer chain. The copolymerization of macromonomers can only occur with a BA radical chain end.[33] That is why macromonomer copolymerization becomes more pronounced at higher conversion when composition drift has occurred. Furthermore, the relative amount of monomer and macromonomer becomes more favorable. Chain transfer to polymer may and probably will occur simultaneously, but in a chain transfer event the number of chains remains the same. So far, it is not clear why this shift in MWD is accompanied by a dramatic drop in polymerization rate. A more predominant combination of butyl acrylate ended radicals with the Co(II) species at higher conversion when most MMA is consumed[7,33] is likely to occur, but that would also affect the rate of macromonomer incorporation.

In the miniemulsion polymerization the observed shift in molecular weight is more pronounced than in solution polymerization. A reason for the differences between miniemulsion and solution copolymerization may be found in the different water solubilities of MMA, viz. 0.15 mol L^{-1}, and BA, viz. 0.01 mol L^{-1}.[10] For this particular reaction this means that about 14 wt % of the total amount of MMA can be dissolved in the water phase. This has a significant effect on the ratio of MMA and BA in the particles, where the polymerization takes place. A smaller ratio of MMA and BA will favor macromer incorporation, as has been argued before.[33]

Conclusions. It has been found that $Co(Et)_4BF$ has a similar chain transfer activity in bulk as CoBF. CCT copolymerizations of MMA and BA can be performed in miniemulsion; large molecular weight reductions are achieved, and at high conversions significant macromer incorporation occurs.

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