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# Catalytic Chain Transfer in Miniemulsion Polymerization

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ABSTRACT: The influence of cobalt catalytic chain transfer agents to control molecular weight in the miniemulsion polymerization of methyl methacrylate has been studied. The solubility of the cobalt catalyst was found to have a large influence on the mechanism of the reaction. Two catalysts were selected for study: cobaloxime boron fluoride (COBF), which partitions approximately equally between the water and oil phases, and tetraphenylcobaloxime boron fluoride (COPhBF) which resides exclusively in the oil phase. The COBF-mediated reaction was found to be extremely sensitive to the selection of initiator, displaying poor catalytic activity in the presence of oxygen-centered radicals (derived from potassium persulfate). In contrast, the COPhBF catalytic activity proved to be independent of initiator type, as the catalyst does not come in direct contact with the initiator-derived radicals. The results are consistent with a mechanism whereby the cobalt catalyst is poisoned or deactivated in the presence of oxygen-centered radicals. In miniemulsion polymerization the catalyst can effectively be isolated from the initiator radicals, thereby allowing a batch reaction to proceed without significant loss of catalytic activity. The conclusions are supported by comparison of chain transfer constants obtained in miniemulsion and bulk polymerizations.

## Introduction

Emulsion polymerization[1] is widely used as a commercial process to produce a variety of latexes for a range of industries. Emulsion polymerization processes are typically used to produce high molecular weight polymers; however, in recent times, the advantage of generating much lower molecular weights for specific product applications has become evident. The versatility of emulsion polymerization can be extended by the use of chain transfer agents to regulate molecular weight. Catalytic chain transfer has been shown to be a highly effective synthetic tool for reducing molecular weight in free-radical solution/bulk polymerization[2−4] and emulsion polymerization.[5−7] Cobaloximes are extremely effective catalytic chain transfer agents with transfer constants, $C_S$, on the order of $10^3$−$10^4$.[8,9] Under ideal conditions the reaction is catalytic and a mechanism has been proposed where the cobalt terminates and reinitiates chains in a cyclic process with a cobalt hydride assumed to be the key intermediate.[10]

In previous work,[5,6] some limitations to catalytic chain transfer in emulsion were identified. These emulsion polymerization studies were conducted in semibatch mode, where the cobalt complex was fed into the reaction to compensate for a loss of catalytic activity with time. In addition, it has been noted that oxygen-centered peroxide radicals have a detrimental effect on the reaction, causing deactivation of the catalyst.[11] Similar behavior has also been seen for oxygen-centered persulfate radicals in emulsion polymerization.[12] This latter problem is highly inconvenient for commercial application of the technology, as peroxides and persulfates are often the initiators of choice.[13] These problems can be overcome if the cobalt catalyst can be separated form the primary initiator radicals. To achieve this, we decided to operate the reaction under miniemulsion conditions.

A miniemulsion can be formed from an emulsion by ultrasonification or high shear mixing[14] and stabilized by the presence of a highly water-insoluble compound (hydrophobe). The role of the hydrophobe is to minimize the Ostwald ripening effect (diffusion of the oil phase from small to large droplets to reduce the interfacial free energy of the system).[15] In miniemulsion polymerization,[15−21] the initial monomer droplet size, ~100 nm, is much smaller than that in conventional emulsion polymerization,[1] ~1 $\mu$m. Due to this size difference, particle formation often occurs predominantly in the monomer droplets as opposed to creating a new particle phase.

A major advantage of miniemulsion polymerization is that highly water-insoluble ingredients are present directly in the monomer droplets, which are the locus of polymerization, whereas in conventional emulsion polymerization, monomer and other reaction components need to diffuse from the droplets via the water phase to the locus of the reaction (the particles). This can be exploited by dissolving highly water-insoluble catalytic chain transfer agents directly into the monomer droplets, the loci of reaction.

In this work, methyl methacrylate (MMA) is polymerized under miniemulsion conditions in a series of experiments designed to explore catalytic chain transfer in miniemulsion polymerization. To illustrate the features, we utilized two different catalytic chain transfer agents of varying hydrophobicity: cobaloxime boron fluoride (COBF), which partitions approximately equally between the oil and water phase,[5,6] and tetraphenylcobaloxime boron fluoride (COPhBF), which resides exclusively in the oil phase.[5] Furthermore, two different initiators were used: azobis(isobutyronitrile) (AIBN), which produces carbon-centered radicals, and potassium persulfate (KPS), which produces oxygen-centered radicals. The experiments were all conducted in batch mode.

## Experimental Section

**Synthesis of Catalytic Chain Transfer Agents.** COBF was synthesized according to a modification of the method of

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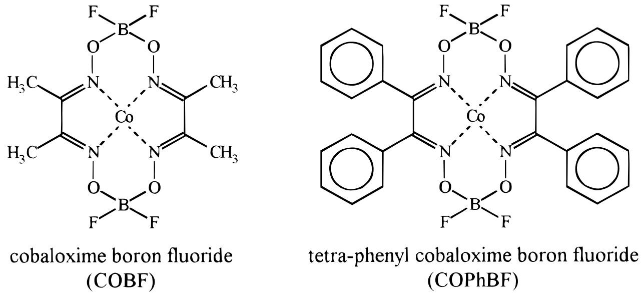

cobaloxime boron fluoride (COBF) tetra-phenyl cobaloxime boron fluoride (COPhBF)

**Figure 1.** Structures of catalytic chain transfer agents used in this work.

**Table 1. Typical Recipe**

| component | mass /g |
|---|---|
| water | 80 |
| sodium dodecyl sulfate | 0.80 |
| methyl methacrylate | 20 |
| hexadecane | 0.50 |
| initiator (AIBN or KPS) | 0.20 |
| catalyst (COBF or COPhBF) | see Table 2 |

Bakac and Espenson.[8,22] COPhBF was prepared by a similar procedure except dimethylglyoxime was replaced by diphenylglyoxime. The structures of the catalysts are shown in Figure 1.

**Materials.** All chemicals were purchased from Aldrich and used as received, with the exception of MMA, which was purified by passing through a column of activated basic alumina, to remove inhibitor, and AIBN, which was obtained from DuPont and purified by recrystallization from methanol.

**Polymerizations.** The miniemulsions were prepared according to the following general procedure. Care was taken at all steps to exclude oxygen from the system as the catalysts are sensitive to oxygen once in solution. A typical miniemulsion recipe is given in Table 1. The surfactant, sodium dodecyl sulfate (SDS), was dissolved in deionized water that was previously deoxygenated by purging with argon for 1 h. The catalytic chain transfer agent was dissolved in the organic components, MMA and the hydrophobe (hexadecane), that were previously degassed by three freeze−pump−thaw cycles. The monomer solution was then transferred via a cannula to the aqueous solution, and initial emulsification was achieved using a magnetic stirrer. The miniemulsion was generated by ultrasonification of the emulsion for 15 min using an ultrasonic bath (180 W, Ultrasonics FX 12P). The formation of the miniemulsion was confirmed by measuring the particle size with a Malvern PCS2 photon correlation spectrometer at 25 °C. It needs to be noted that measuring droplet size distribution using photon correlation spectroscopy is not quantitatively reliable because the sample needs to be diluted enormously. It is, however, a useful check, as it clearly indicates the possible presence of large droplets, >300 nm, remaining from inefficient miniemulsification (the droplet size before ultrasonification is greater than 1 $\mu$m). A typical miniemulsion particle size distribution is shown in Figure 2. The miniemulsion, once formed, is stable for several weeks.

When AIBN was used as initiator, it was added to the water phase with the SDS, prior to the formation of the emulsion. KPS was predissolved in water and added to the miniemulsion at the reaction temperature.

The reactions were controlled isothermally at 65 °C in a flask fitted with a nitrogen purge and a magnetic stirrer. Samples were removed periodically for conversion (by gravimetry) and molecular weight analyses. A summary of the experimental runs is given in Table 2.

**Analyses.** Molecular weight distributions were measured by size exclusion chromatography (SEC) on a modular system, comprising an autoinjector, guard column, two mixed bed columns (60 cm mixed C, and 30 cm mixed E, Polymer Laboratories) and a differential refractive index detector. The eluent was tetrahydrofuran at 1 mL/min.

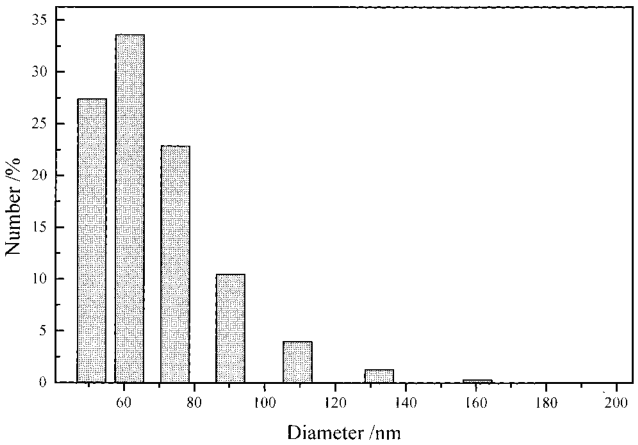

**Figure 2.** Particle size distribution of a typical miniemulsion before polymerization (measured by photon correlation spectroscopy).

**Table 2. Summary of Runs**

| run | initiator | catalyst | concn[a] |
|---|---|---|---|
| A1 | AIBN | | |
| A2 | AIBN | COBF | 3.0 |
| A3 | AIBN | COBF | 18 |
| A4 | AIBN | COPhBF | 2.0 |
| A5 | AIBN | COPhBF | 9.3 |
| K1 | KPS | | |
| K2 | KPS | COBF | 17 |
| K3 | KPS | COPhBF | 2.0 |

[a] ppm mol/mol, equivalent to [S]/[M] × $10^6$.

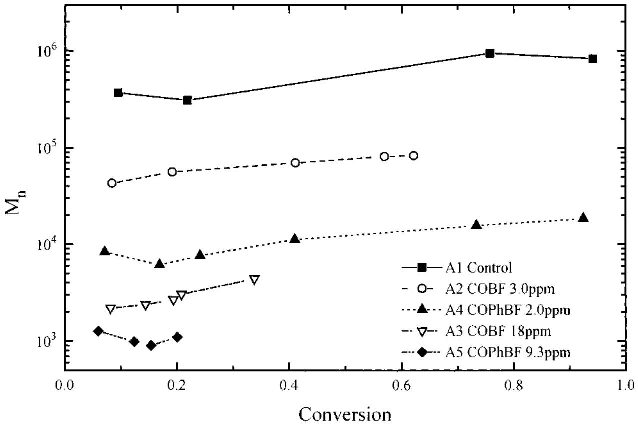

**Figure 3.** Dependence of $M_n$ vs conversion on the concentration of catalyst (COBF and COPhBF) for AIBN-initiated runs.

Final latex particle size distributions were measured using capillary hydrodynamic fractionation[23,24] on a Matec Applied Sciences CHDF-1100 particle size analyzer, calibrated with polystyrene latex standards.

## Results and Discussion

**Azobis(isobutyronitrile)-Initiated Polymerizations.** The influence of catalytic chain transfer agents on the miniemulsion polymerization of MMA initiated by AIBN can be seen in Figures 3 and 4. The control polymerization (run A1 with no catalytic chain transfer agent) produces a number average molecular weight, $M_n$, on the order of $10^6$, which is typical of a miniemulsion polymerization. Upon the addition of 3.0 ppm mol/mol (on monomer) and 18 ppm COBF, the molecular weight of PMMA is drastically reduced to 87.0 × $10^3$ and 4.41 × $10^3$, respectively. A similar trend is noted for the COPhBF-mediated reactions with an even greater reduction in molecular weight to 18.4 × $10^3$ and

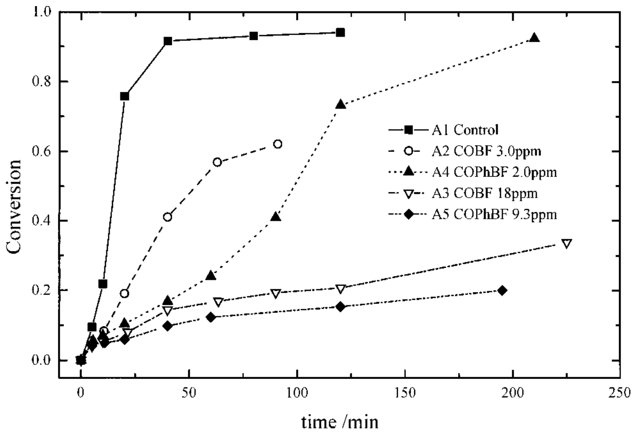

**Figure 4.** Dependence of conversion vs time on the concentration of catalyst (COBF and COPhBF) for AIBN-initiated runs.

**Table 3. Summary of Final Properties from Each Run**

| | | MWD[a] | | | PSD[b] | | | |
|---|---|---|---|---|---|---|---|---|
| run | conv[c] | $M_n$ | $M_w$ | PDI | $D_n$ | $D_w$ | PDI | $N_c$[d] |
| A1 | 0.94 | $828 \times 10^3$ | $2.12 \times 10^6$ | 2.6 | 81 | 96 | 1.19 | 6.14 |
| A2 | 0.65 | $87.0 \times 10^3$ | $171 \times 10^3$ | 2.0 | 96 | 135 | 1.41 | 3.69 |
| A3 | 0.34 | $4.41 \times 10^3$ | $10.8 \times 10^3$ | 2.4 | | | | |
| A4 | 0.92 | $18.4 \times 10^3$ | $116 \times 10^3$ | 6.3 | 85 | 125 | 1.47 | 5.23 |
| A5 | 0.20 | $1.10 \times 10^3$ | $3.76 \times 10^3$ | 3.4 | | | | |
| K1 | 0.99 | $900 \times 10^3$ | $2.30 \times 10^6$ | 2.6 | 77 | 86 | 1.12 | 7.15 |
| K2 | 0.96 | $157 \times 10^3$ | $436 \times 10^3$ | 2.8 | 71 | 76 | 1.07 | 9.12 |
| K3 | 0.93 | $17.0 \times 10^3$ | $52.3 \times 10^3$ | 3.1 | 77 | 84 | 1.09 | 7.15 |

[a] Molecular weight distribution averages. [b] Particle size distribution averages in nm. (Omitted samples did not go to high enough conversion to be measured by CHDF.) [c] Conversion at final sample taken. [d] Latex concentration in $10^{17}$ particles·L$^{-1}$.

$1.10 \times 10^3$, for slightly lower concentrations: 2.0 and 9.3 ppm, respectively. The first significant feature is that COPhBF appears to be a more effective catalyst than COBF under these conditions. This can easily be explained by the relative solubilities of the catalytic chain transfer agents in the two phases. In earlier work[5,6] we showed that COBF partitions approximately equally between the oil and water phase. Thus for the same overall catalyst concentration, the COBF concentration in the locus of polymerization is less than the COPhBF concentration that resides exclusively in the oil phase.[5] Another important point to make is that all these reactions were performed in batch and, in the case of COPhBF-mediated polymerization (run A4), the efficiency of the transfer process was maintained throughout the reaction to high conversion. This contrasts with previous emulsion[6] studies where the transfer efficiency rapidly waned and effective molecular weight control could only be maintained by the steady feed of catalyst throughout the reaction. Clearly, we have been successful in utilizing miniemulsion polymerization for effective compartmentalization of the catalyst, preventing its contamination and deactivation in the aqueous phase. The results of the reactions initiated with AIBN are given in Table 3. As previously noted in other studies,[5,6,8] the rate of polymerization is reduced by the presence of catalytic chain transfer agents. This is because the rate of exit and termination with short radicals is increased due the creation of monomeric radicals by the catalytic chain transfer reaction.[5,25]

**Potassium Persulfate Initiated Polymerizations.** The results for the KPS-initiated miniemulsion polymerizations of MMA are shown in Figures 5 and 6. The control polymerization (K1), without catalytic chain transfer agent, produced results very similar to those of the corresponding AIBN run (A1), indicating no specific influence of initiator type on the reaction in the absence of catalytic chain transfer agents. Upon the addition of 3.0 ppm mol/mol COPhBF the molecular weight is reduced from $900 \times 10^3$ to $17.0 \times 10^3$, which is comparable to the molecular weight reduction in the corresponding AIBN-initiated reaction (run A4 where $M_n = 18.4 \times 10^3$). This correlation shows that COPhBF maintains its efficiency as a catalytic chain transfer agent even in the presence of oxygen-centered persulfate initiator radicals. In the case of the COBF-mediated reaction (K2), the molecular weight is reduced to $157 \times 10^3$, a much smaller effect than the corresponding AIBN-initiated run (A3), which produced a molecular weight of $4.41 \times 10^3$, for similar catalyst concentrations. It is quite clear that in the case of COBF with KPS initiation there is a significant reduction in catalyst performance.

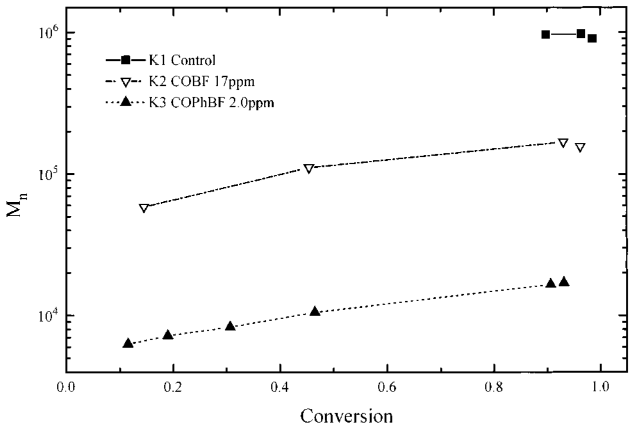

**Figure 5.** Dependence of $M_n$ vs conversion on the concentration of catalyst (COBF and COPhBF) for KPS-initiated runs.

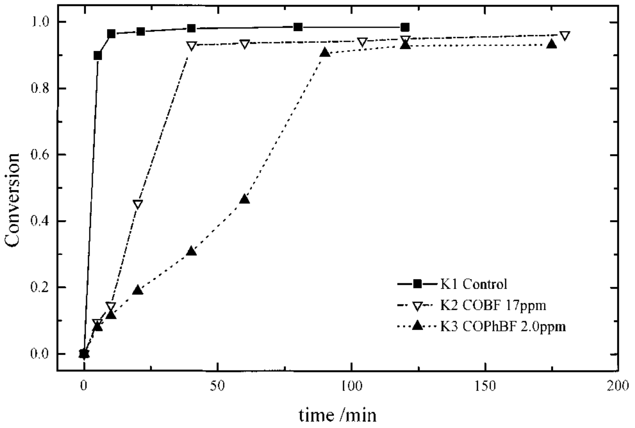

**Figure 6.** Dependence of conversion vs time on the concentration of catalyst (COBF and COPhBF) for KPS-initiated runs.

**Pathway for Catalyst Deactivation with Potassium Persulfate.** The main difference between COBF and COPhBF is the location of the catalysts in the polymerization system. This is illustrated in Figure 7. KPS is entirely water soluble, and the resulting anionic persulfate radical must first react with monomer in the aqueous phase to become sufficiently surface active to enter a miniemulsion monomer droplet (or latex particle). In the case of MMA polymerization, it has been shown that once the persulfate radical has reached a critical degree of polymerization of tetramer or pentamer it will enter the oil phase.[1]

COBF partitions approximately equally between the oil and water phases, which as mentioned earlier,

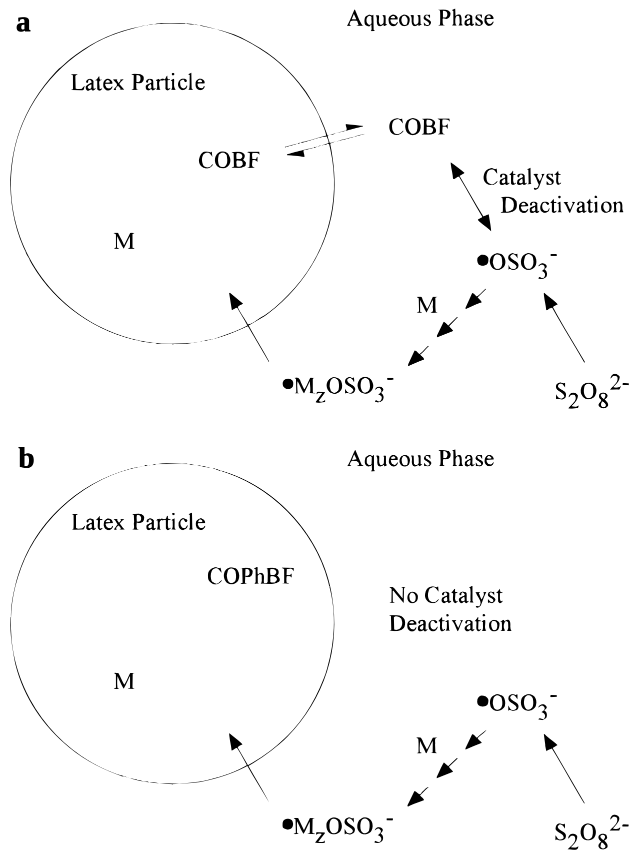

**Figure 7.** Location of important components in persulfate-initiated miniemulsion polymerization. *M* is monomer, $S_2O_8^{2-}$ is the persulfate anion, $O_3SO^{\bullet-}$ is the sulfate radical, and *z* is the critical degree of polymerization for the entry (4−5 in the case of MMA). (a) KPS with COBF: The oxygen-centered sulfate radical, $O_3SO^{\bullet-}$, can react directly with COBF in the water phase to deactivate it. (b) KPS with COPhBF: the sulfate radical cannot react directly with COPhBF, as they are in different phases. Only radicals that are able to enter the oil phase can react with COPhBF, and since these are carbon-centered, no catalyst deactivation occurs.

results in a lower concentration of catalyst in the locus of polymerization. Since an equilibrium exists between the aqueous and organic phases, COBF can migrate among droplets and also between phases. This is the primary reason why miniemulsion with COBF and KPS is ineffective. The oxygen-centered radicals deactivate the COBF in the aqueous phase, which is continually replenished with COBF from the oil phase, until most of the COBF is deactivated, severely reducing the catalytic chain transfer reaction. The COPhBF-mediated reaction maintains its efficiency as the catalyst resides entirely in the oil phase, isolating the catalyst from the aqueous phase oxygen-centered persulfate radicals.

Catalyst deactivation in the oil phase does not occur for either COBF or COPhBF with KPS initiation. The oxygen-centered persulfate radical needs to add 4−5 monomer units before becoming sufficiently surface active to enter the oil phase.[1] Once this occurs, the radical is carbon-centered and so catalyst deactivation does not occur.

Initiation with AIBN produces carbon-centered radicals and so is not a pathway for catalyst deactivation in the system.

**Catalytic Chain Transfer Efficiency in Miniemulsion.** The efficiency of the catalytic chain transfer reaction in miniemulsion was assessed by comparing the transfer constant obtained in miniemulsion to that under bulk polymerization conditions. The transfer constant, $C_S$, is the ratio of the transfer rate coefficient, $k_{tr}$, to the propagation rate coefficient, $k_p$. These two rate coefficients, and hence $C_S$, should be the same in miniemulsion and bulk polymerization. Any differences in the value of $C_S$ measured in miniemulsion compared to bulk reflects differences in the concentration of active catalyst in the locus of polymerization.

**Table 4. Data Used to Calculate COBF and COPhBF Transfer Constants in Miniemulsion Polymerization**

| run | initiator | catalyst | concn[a] | conv[b] | slope[c] |
|---|---|---|---|---|---|
| A1 | AIBN | | 0 | 0.095 | $-6.13 \times 10^{-7}$ |
| A2 | AIBN | COBF | 0.42 | 0.083 | $-2.15 \times 10^{-5}$ |
| A3 | AIBN | COBF | 2.5 | 0.081 | $-5.26 \times 10^{-4}$ |
| A4 | AIBN | COPhBF | 2.0 | 0.071 | $-1.28 \times 10^{-4}$ |
| A5 | AIBN | COPhBF | 9.3 | 0.059 | $-7.87 \times 10^{-4}$ |
| K1 | KPS | | 0 | 0.900 | $-7.22 \times 10^{-7}$ |
| K2 | KPS | COBF | 2.4 | 0.145 | $-2.04 \times 10^{-5}$ |
| K3 | KPS | COPhBF | 2.0 | 0.115 | $-2.36 \times 10^{-4}$ |

[a] Catalyst concentration in the oil phase (locus of polymerization) in ppm mol/mol, equivalent to [S]/[M] × $10^6$. [COBF]/[M] in oil phase = 0.14[COBF]/[M] overall (calculated from the volumes of the phases and $[\text{COBF}]_{\text{MMA}}/[\text{COBF}]_{\text{aq}} = 0.68$ since COBF partitions between the phases[6]). [COPhBF]/[M] in oil phase = [COPhBF]/[M] overall (COPhBF is located in the oil phase only). [b] Fractional conversion. [c] From eq 1, the slope = $-C_S[\text{S}]/([\text{M}]m_0)$.

$C_S$ was measured from the ln(number molecular weight distribution). For a transfer-dominated polymerization, the molecular weight distribution can be expressed as an exponential:[26−29]

$$P(M) \propto \exp\left(-C_S \frac{[\text{S}]}{[\text{M}]} \frac{M}{m_0}\right) \tag{1}$$

where [S] is the concentration of catalytic chain transfer agent, [M] is the monomer concentration, $m_0$ is the molecular weight of monomer, $C_S = k_{tr}/k_p$, and $P(M)$ is the number of chains of molecular weight *M*. The number distribution, $P(M)$, is obtained from the calibrated SEC distribution, $W(\log M)$, as follows:

$$P(M) = W(\log M)\frac{\log e}{M^2} \tag{2}$$

The procedure for obtaining the transformed SEC distribution, $W(\log M)$, from the raw SEC chromatogram is described elsewhere.[27,30]

Plotting ln $P(M)$ against *M* should yield a straight line for the transfer controlled region of the distribution. From the slope of this line, $C_S$ can be calculated. For a transfer-dominated reaction, it is best to measure the slope of the ln $P(M)$ distribution in the region of the maximum in the $W(\log M)$ distribution as this has the best signal to noise ratio.[31] Typical ln $P(M)$ vs *M* plots for each of the catalyst/initiator combinations are shown in Figure 8, the peak molecular weight being indicated for reference. In each case, the distribution is linear, except for K3, which shows some curvature. This curvature in ln $P(M)$ plots has been observed in several other instances where catalytic chain transfer agents have been used in bulk polymerization,[32−34] and in these cases the slope was taken in the region of the maximum in the SEC distribution. To obtain the chain transfer constant, the slope of the ln $P(M)$ distribution, for a series of runs, is plotted against [S]/[M], giving another slope equal to $-C_S/m_0$, as shown in Figure 9.

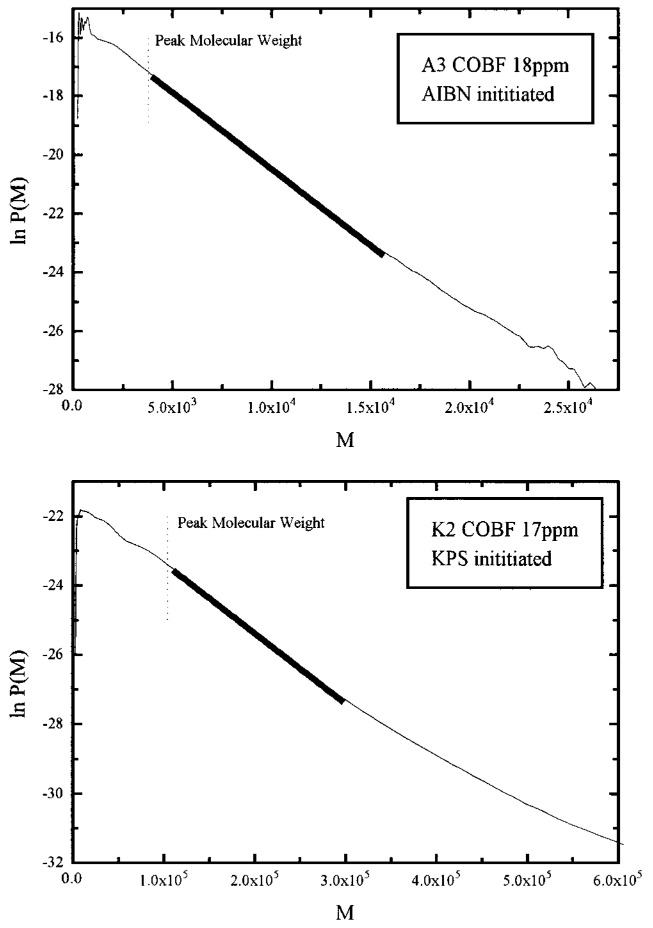

**Figure 8.** Typical molecular weight distributions, plotted as ln *P*(*M*) vs *M*, used for the determination of the apparent transfer constant ($C_S$). The highlighted region shows where the slope was measured. The location of the peak molecular weight in the SEC chromatogram is indicated for reference.

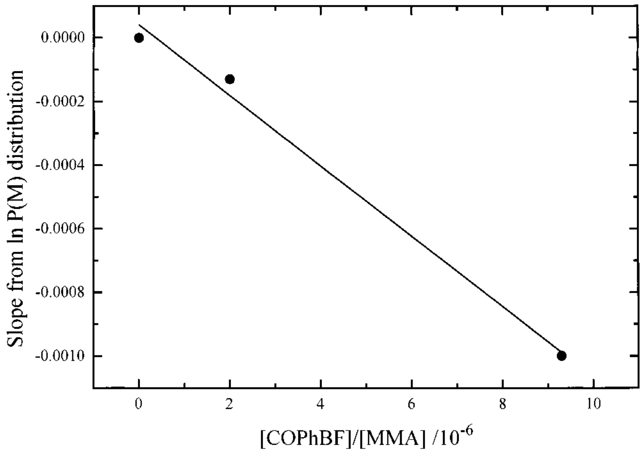

**Figure 9.** Typical plot of the slope from the ln *P*(*M*) distribution vs [catalyst] to [monomer] ratio used to determine the apparent transfer constant ($C_S$), data for the AIBN/COPhBF series (A1, A4, A5).

The data used to calculate the chain transfer constants are given in Table 4. The concentration of COBF in the oil phase (i.e., the locus of the polymerization) was estimated from the partitioning ratio,[6] and the ratio of the oil to water phase. The measured apparent transfer constants are listed in Table 5 alongside values obtained from bulk polymerization studies. As expected, the KPS/COBF system shows a significantly lower apparent $C_S$ value in miniemulsion than bulk because the catalyst is being deactivated. In the other cases, the $C_S$ in miniemulsion compares well to that in bulk.

**Table 5. Comparison of Apparent Transfer Constants for COBF and COPhBF with Methyl Methacrylate in Miniemulsion and Bulk Polymerization**

| initiator | catalyst | miniemulsion apparent $C_S$[a] | bulk $C_S$[b] |
|---|---|---|---|
| AIBN | COBF | $2.1 \times 10^4$ | $2.4 \times 10^4$ |
| AIBN | COPhBF | $1.1 \times 10^4$ | $1.4 \times 10^4$ |
| KPS | COBF | $0.083 \times 10^4$ | $2.4 \times 10^4$ |
| KPS | COPhBF | $1.2 \times 10^4$ | $1.4 \times 10^4$ |

[a] Apparent transfer constant measured in miniemulsion at 65 °C. [b] Transfer constant for COBF[33] and COPhBF[35] measured in bulk using AIBN at 60 °C.

## Conclusions

This work has clearly shown that only ppm quantities of the catalytic chain transfer agents, COBF and COPhBF, need to be used in batch miniemulsion polymerization to significantly reduce the molecular weight. With AIBN initiation, both catalytic chain transfer agents are effective; however, with KPS initiation COBF is much less effective. A high transfer efficiency can be achieved with persulfate initiation if a highly water-insoluble catalytic chain transfer agent, such as COPhBF, is used, because the compartmentalization in the system prevents the oxygen-centered initiator radicals from degrading the catalyst in the aqueous phase.

This technology can be commercially exploited, as miniemulsions can be formed under high shear conditions (i.e., ultrasonification is not essential). Another potential application for this technology would be using a seed latex produced by miniemulsion polymerization with COPhBF as the first stage in a conventional semibatch emulsion polymerization process. The COPhBF would maintain its activity throughout the reaction, and the molecular weight could be controlled during the monomer feed stage by varying the instantaneous conversion (monomer to catalyst ratio) of the reaction via the monomer addition rate.

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## References and Notes

(1) See, for example: Gilbert, R. G. *Emulsion Polymerization, A Mechanistic Approach*; Academic Press: London, 1995.
(2) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365.
(3) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.
(4) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 879.
(5) Kukulj, D.; Davis, T. P.; Suddaby, K. G.; Haddleton, D. M.; Gilbert, R. G. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 859.
(6) Suddaby, K. G.; Haddleton, D. M.; Hastings, J. J.; Richards, S. N.; O'Donnell, J. P. *Macromolecules* **1996**, *29*, 8083.
(7) Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M., *Macromol. Symp.* **1996**, *111*, 13.
(8) Sanayei, R. A.; O'Driscoll, K. F., *J. Macromol. Sci., Chem*, **1989**, *A26*, 1137.
(9) Burczyk, A. F.; O'Drisscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255.
(10) Gridnev, A. A.; Ittel, S. D.; Wayland, B. B.; Fryd, M. *Organometallics* **1996**, *15*, 5116.
(11) Gridnev, A. A. *Polym. J.* **1992**, *24*, 613.
(12) Janowicz, A. H. *U.S. Patent 5 028 677*, 1991.
(13) See, for example: Blackley, D. C. *Emulsion Polymerisation*; Applied Science: London, 1975.
(14) Maxwell, I. A. Unpublished Results.
(15) Aizpurua, I.; Amalvy, J.; Barandiaran, M. J.; De la Cal, J. C.; Asua, J. M. *Macromol. Symp.* **1996**, *111*, 121.
(16) Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* **1995**, *28*, 2754.
(17) Reimers, J. L.; Schork, F. J. *J. Appl. Polym. Sci.* **1996**, *60* (2), 251.
(18) Reimers, J. L.; Schork, F. J. *J. Appl. Polym. Sci.* **1996**, *59* (12), 1833.
(19) Fontenot, K.; Schork, F. J. *J. Appl. Polym. Sci.* **1993**, *49* (4), 633.
(20) Rodriguez, V. S.; El-Aasser, M. S.; Asua, J. M.; Silebi, C. A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3659.
(21) Chamberlain, B. C.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 2*, **1982**, *78*, 59.
(22) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.
(23) Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1995**, *172*, 49.
(24) Dos Ramos, J. G.; Silebi, C. A. *Polym. Int.* **1993**, *30*, 445.
(25) Nomura, M.; Minamino, Y.; Fujila, K.; Harada, M. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1261.
(26) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133.
(27) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.
(28) Christie, D. I.; Gilbert, R. G. *Macromol. Chem. Phys.* **1996**, *197*, 403.
(29) Hutchinson, R. A.; Paquet, D. A.; McMinn, J. H. *Macromolecules* **1995**, *28*, 5655.
(30) Shortt, D. W. *J. Liq. Chromatogr.* **1993**, *16*, 3371.
(31) Moad, G.; Moad, C. L. *Macromolecules* **1996**, *29*, 7727.
(32) Suddaby, K. G.; Maloney, D. R.; Haddleton, D. M. *Macromolecules* **1997**, *30*, 702.
(33) Kukulj, D.; Davis, T. P. Submitted for publication.
(34) Heuts, J. P. A.; Kukulj, D.; Forster, D. J.; Davis, T. P. Submitted for publication.
(35) Forster, D. J.; Heuts, J. P. A.; Davis, T. P. To be published.

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