Advances in Catalytic Chain Transfer Polymerisation mediated by Cobaloximes

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SUMMARY: Catalytic chain transfer copolymerisation of MMA and HEMA (70:30) has been carried out under semi-continuous emulsion polymerisation conditions, using CoBF as catalyst. It has been shown that macromonomers of low molar mass can be synthesised with an apparent chain transfer constant, C_S^E, of *ca.* 1300 down to a threshold value of *ca.* 20 ppm of CoBF. Below this value an initial 20% shot of monomer/catalyst mixture was necessary to prevent events involved in the catalytic chain transfer process becoming diffusion controlled and to prevent the reaction to proceed under monomer starved conditions. Analysis of the Co(II) species by SQUID has been carried out. CoBF shows a value for its effective magnetic susceptibility of $1.77\mu_B$. It was found that a correction for the response of the sample container is essential for reliable data to be achieved. Diffusion ordered 2D-NMR spectroscopy (DOSY) has been used as a method to study the catalyst diffusion dependence for the rate coefficient of chain transfer. However, the apparent values of the found diffusion coefficients are an order of magnitude above the natural limit for center of mass diffusion.

Introduction

Catalytic chain transfer (CCT) polymerization is a controlled radical polymerisation technique that allows for efficient production of ω-unsaturated (commonly C=C, also C=O[1]) polymers/oligomers.[2-4] Catalytic chain transfer polymerisation has emerged as a commercial route towards methacrylate containing/based macromonomers which find

applications in coatings, etc. Catalytic chain transfer polymerisation carried out under emulsion polymerisation conditions is of interest from a industrial point-of-view.[5,6]

Typically, organo-cobalt complexes (of similar structure to coenzyme B_{12}) are used as catalysts to induce chain-transfer, other metals have also been reported. Thus far, the most successful class of catalytic chain transfer agents is cobaloxime derivatives, *e.g.* CoBF (**1**). Addition of extremely low levels of **1** (ppm scale) to a free radical polymerisation of α-methyl vinylic monomers leads to dramatic reductions in molar mass.
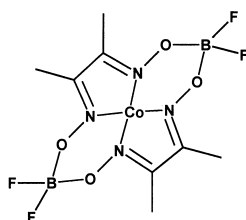

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An indicator of the effectiveness of a catalyst towards CCT is its spin-state, which can be determined via its magnetic susceptibility. For d^7 cobalt(II) complexes a low-spin state is characterised by an effective magnetic susceptibility (μ_{eff}) of 1.73 μ_B, whereas a high-spin state shows a theoretical value of 3.87 μ_B (calculated using $2[S(S+1)]^{\frac{1}{2}}$ and assuming complete quenching). play, at least, a transient role. A proposed mechanism for the catalytic chain transfer polymerisation of methacrylates is given in Scheme 1.

The chain transfer constant, C_S (k_{tr}/k_p), is commonly used as a measure for catalyst activity. Accurate values can be obtained from the molar mass distribution of the produced polymer using the classical Mayo equation, both $1/DP_n$ and $2/DP_w$ *vs.* [chain transfer agent]/[monomer], as well as the chain length dependent method. A typical C_S-value for the CoBF mediated bulk polymerisation of MMA is 40,000, which implies that the chain transfer process is very fast, and thus that diffusion may play a role in its overall rate coefficient. Reactions carried out in supercritical CO_2, a medium of extreme low

viscosity, indeed show that this is the case, as marked enhancements of C_S-values are observed.[7]
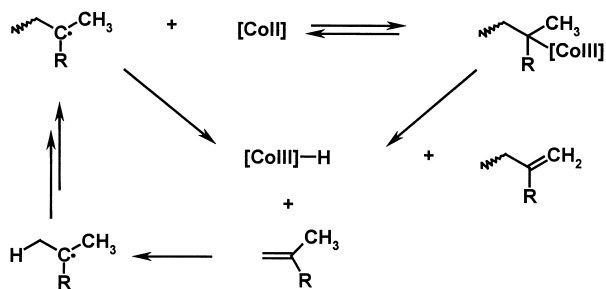
Scheme 1. *Proposed mechanism for the catalytic chain transfer polymerisation (CCTP) of methacrylates.*

In this paper we would like to report findings on the catalytic chain transfer copolymerisation of MMA with 2-hydroxyethyl methacrylate (HEMA) under emulsion polymerisation conditions, using **1** as the catalytic chain transfer agent. In addition our initial results on the use of SQUID to determine the magnetic properties of the cobalt complexes, *i.e.* **1** as function of temperature are presented. Moreover, preliminary results on the use of diffusion-ordered 2D-NMR spectroscopy (DOSY) to obtain accurate values for diffusion coefficients for the different species involved in the catalytic chain transfer process are discussed.

CCT Emulsion Polymerisation of MMA/HEMA

Catalytic chain transfer polymerisation has been developed under semi-continuous emulsion polymerisation conditions, whereby a monomer and catalyst mixture is fed into the reactor.[5,6] It has been found that high monomer conversions are reached to yield a macromonomer product with a polydispersity of *ca.* 2. The overall activity of the catalyst is approximately one order of magnitude lower than in bulk or solution reactions. Under emulsion polymerisation conditions the catalyst activity can be expressed as an apparent

chain transfer constant, C_s^E. Tentative explanations for the lower C_s^E-values are catalyst partitioning, diffusion controlled chain transfer, and catalyst destruction by acid hydrolysis. When functional oligomers of relatively high molar mass are desired, an *ab initio* monomer shot is often essential to prevent the reaction to proceed under starved conditions. High conversion during polymerisation causes a high viscosity in the loci of polymerisation restricting catalytic chain transfer events and reducing catalyst efficiency.

Use of the water-soluble monomer HEMA in a polymerisation allows the incorporation of hydroxyl groups into polymer backbones. Figure 1 shows the macromonomer product that should be formed by performing CCTP with a mixture of MMA and HEMA.
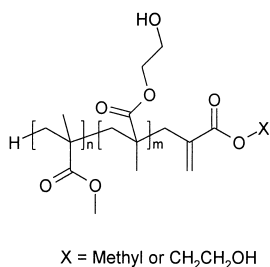

X = Methyl or CH$_2$CH$_2$OH

Figure 1: *Structure of MMA/HEMA statistical macromonomer.*

Table 1 - End properties of MMA/HEMA (70:30) CCT polymerisations in emulsion.

Reaction	CoBF/ g	CoBF/ ppm	Feed Conditions	$<M_n>/$ g mol^{-1}	PDI	Inst. Conv.	Cs^E
MH1	0.040	45.23	100% fed	1850	1.48	1.022	1302
MH2	0.028	35.54	100% fed	2540	1.72	1.016	1209
MH3	0.024	30.19	100% fed	2730	1.61	1.017	1323
MH4	0.020	19.54	100% fed	16600	1.98	1.032	336
MH5	0.009	11.77	100% fed	25200	2.02	1.039	367
MH6	0.009	11.77	20% shot/ 80% fed	7780	1.75	0.983	1187

Catalytic chain transfer emulsion copolymerisation was performed using a monomer 70:30 mixture of MMA and HEMA. The experimental conditions used were similar to those reported previously.[5,6] All experiments yielded stable emulsions without a marked presence of coagulum. Details and end properties of the products are given in Table 1.

^{1}H NMR analysis confirmed a statistical mixture of products in a ratio of 71.6:28.4 calculated from the HOCH_2CH_2O at 4.14 and 3.87 ppm, and the methoxy resonances at 3.74 (terminal unit) and 3.62 ppm respectively. This indicates that CCT copolymerisation of MMA and HEMA at this composition is successful. No detailed analysis on composition drift, primarily induced by monomer partitioning, was undertaken. Figures 2 and 3 show the <M_n> and the instantaneous overall monomer conversion as function of time. Note that the polydispersity of the molar mass distribution, PDI, was *ca.* 2 for all samples taken.
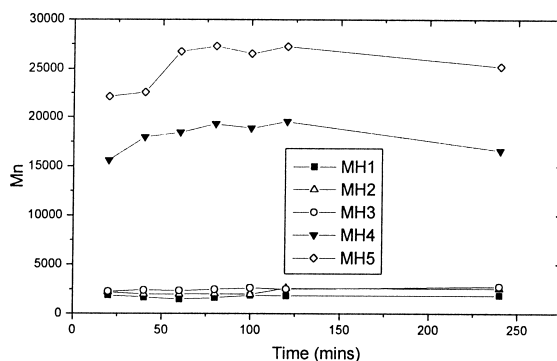

Figure 2: *<M_n> vs. time for emulsion polymerisations MH1-MH5.*

Figure 2 shows that MMA/HEMA macromonomers are successfully synthesised. Reactions MH1-MH3 show the formation of polymers of low molar mass consistent with effective CCT in emulsion as reported previously. Polymerisations MH4 and MH5 exhibit much higher molecular weights than for the other reactions and the overall apparent chain transfer constant, Cs^E, for these reactions ($Cs^E \approx 300$) is noticeably lower than for reactions MH1-MH3 ($Cs^E \approx 1300$), Table. 1.
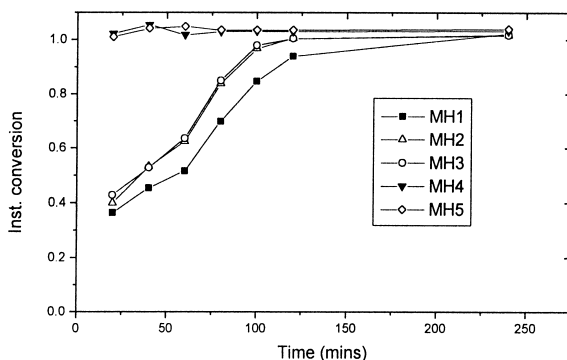
Figure 3: *Instantaneous conversion versus time graph for emulsion polymerisations MH1-MH5.*

The instantaneous conversion for reactions MH1-MH3 show very similar rates of polymerisation to MMA homopolymerisation with polymerisation proceeding under *non-starved fed* conditions allowing efficient macromonomer synthesis. Thus **1** has the effect of lowering the rate of polymerization. For reactions MH4 and MH5 the instantaneous conversion is much higher at the early stages of the reaction and the polymerisation proceeds under starve fed conditions. It is observed that a threshold level of catalyst is reached, below which the transfer reaction does not proceed efficiently.[5,6]

An injection of a shot of 20% of the monomer/catalyst mixture at the start of the reaction allowed effective CCT to be carried out with lower levels of catalyst (< ~15 ppm) for MMA and for a BMA/MMA mixture.[5,6] The monomer shot had the effect of bringing the polymerisation from a starved fed to a non-starved fed state allowing the CCT reaction to proceed at full effectiveness. For the MMA/HEMA polymerisations the reactions with high Cs^E are all at low instantaneous conversions early in the polymerisation and so it is expected that the addition of a monomer shot would allow lower catalyst concentrations to be employed. Figures 4 and 5 show that an initial addition of a 20% shot of monomer / catalyst mixture allows CCT to be carried out at under a wider range of catalyst concentrations and hence permits the synthesis of a wider mass range of MMA/HEMA co-polymers. Figure 4 shows a marked reduction in $<M_n>$ for reaction MH6, using the

monomer shot, as opposed to MH5. Furthermore, MH6 has a much slower rate of polymerisation over the first 100 minutes of polymerisation than for the other experiments with low catalyst levels. The observed reduction in the rate indicates that the monomer shot achieved the change from starve fed to non-starve fed conditions that was desired.
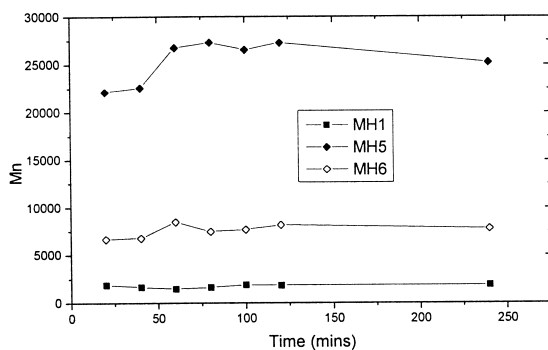

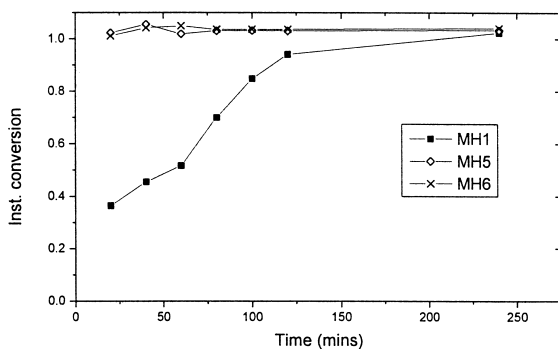**Figure 4**; *M_n versus time graph for emulsion polymerisations MH1,MH5 and MH6.*

Figure 5: *Instantaneous conversion versus time graph for emulsion polymerisations MH1, MH5 and MH6.*
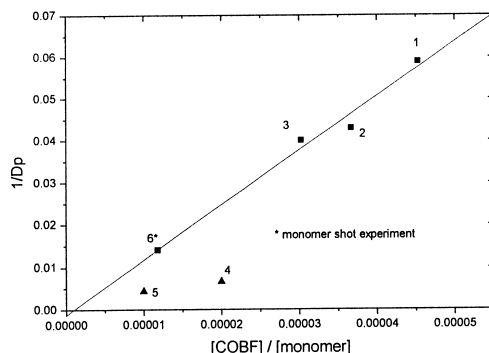
Figure 6: *Pseudo Mayo plot for MMA/HEMA (70:30 molar ratio) emulsion co-polymerisations using COBF as the transfer agent.*

Figure 6 shows a *pseudo* Mayo plot for the MMA/HEMA reactions. It gives a Cs^E (effective chain transfer constant in emulsion) of 1300 which is identical to that for pure MMA. It can be seen clearly that the monomer shot experiment now follows the general Cs^E value, allowing us to broaden the range of macromonomers of different molar masses which can be synthesised.

SQUID Analysis

Determination of magnetic moments is a valuable method to gain information on the spin state, ligand interactions and purity of organo cobalt catalysts. The magnetisation of a sample is measured as a function of temperature. The sample, **1**, is passed through a set of three superconducting detection coils while an external magnetic field is applied. This generates a current flow, which is detected by a SQUID (Superconducting Quantum Interference Device), which subsequently produces a proportional output voltage, *i.e.,* amplitude (V) *vs.* the position of the sample. From our experiments it has proven to be essential that the acquired raw data needs to be corrected for the response of the sample container, Figure 7.
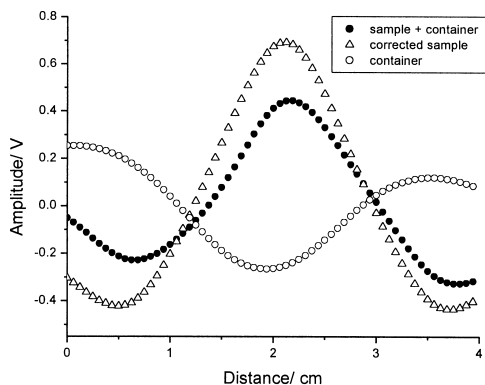
Figure 7: *Raw SQUID data for 1.*

This modified data is fitted, after applying a calibration factor which includes the amount and molar mass of the sample, using a response curve to finally produce a molar magnetisation, M, for a specific applied magnetic field, H, at a set temperature. The data aquired at different temperatures finally yields the magnetic susceptibility, χ = (M/H) *vs.* T. Data is normally acquired at different fields, *i.e.* H= 100, 1000, 6250 and 50000 Oe, to investigate if specific interactions between the molecules occur. The results for **1** are plotted in Figure 8.
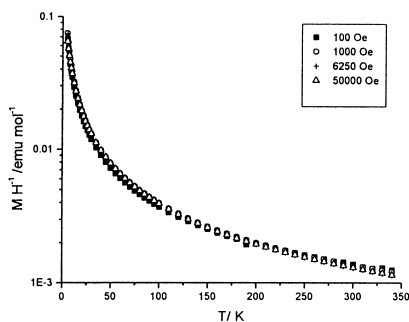

Figure 8: *Corrected magnetic susceptibility data of CoBF vs. temperature and measured at different fields.*

The magnetic susceptibility, χ, at different temperatures can for **1** be fitted with the Curie Law:

$$\chi = \chi_0 + \frac{C}{(T+\theta)}; \quad C = \frac{N_A \mu_B^2 \mu_{eff}^2}{3k}$$

In which χ_0 accounts for diamagnetic contributions and θ for sample interactions. Since the data at different applied fields are similar, this has only been carried out fot the data set acquired at H = 1000 Oe, see Fig 9.
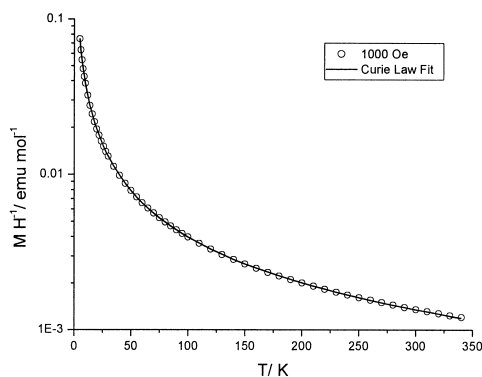

Figure 9: *Curie Law fit of magnetic susceptibility data at 1000 Oe for CoBF.*

The percentage deviations are all below 1.0%. The fit yields $\chi_0 = 3.4318 \times 10^{-5}$ emu mol^{-1} $\theta = 0.287$ K; C = 0.3945. The latter leads to a calculated experimental value of $\mu_{eff} = 1.77\mu_B$, which is close to the theoretical low-spin state value (1.73μ_B) of a Co(II) complex.

Diffusion Ordered 2D-NMR Spectroscopy (DOSY)

Diffusion ordered 2D-NMR spectroscopy is an FT-pulsed field gradient method. Using a LED pulse sequence [8] it is possible to measure diffusion coefficients and separate chemical species that diffuse at different rates, by means of acquiring a number of ^{1}H spectra measured at different gradients. The intensity of a specific resonance in a ^{1}H spectrum measured at a specific gradient, Gi/ G cm^{-1}, is related to a diffusion coefficient, D/ m^{2}s^{-1}:

$$ I \; = \; I_0 \, \exp\left[-D\left(2\pi\gamma\delta\right)^2\left(\Delta - \frac{\delta}{3}\right)Gi\right] $$

The set of ^{1}H NMR spectra acquired can then be used to calculate a real-time diffusion coefficient at a specific resonance, which for small molecules may directly relate to their centre of mass diffusion, as given by the Stokes-Einstein equation. Furthermore, this technique is able to separate mixtures of compounds on basis of their different diffusion coefficients. This is most clearly seen by composition of a 2D plot, in which one axis represents an ordinary ^{1}H-NMR spectrum and the other a diffusion scale (log D).

This method is illustrated with a solution of Co(II)(dmg)$_2$Cl.py in acetone-d_6 in the presence of a small amount of water. Sixteen ^{1}H NMR spectra were measured and five different resonances analysed, 8.229, 7.931 and 7.444 (axial pyridine ligand of cobalt), 2.851 ppm (water), 2.374 ppm (four methyl groups of the dimethylglyoxime ligands) and 2.082 ppm (d_6-acetone). Figure 10 shows the I/I$_0$ *vs.* the applied gradient (Gi) for these five resonances. It can be seen that the plots from the cobalt complex are well separated from the data of water and d_6-acetone, this illustrates the power of DOSY to separate compounds. The diffusion coefficients obtained by using a NLLS method on equation 1 are listed in Table 2.

Table 2. *Calculated Diffusion Coefficients from DOSY experiments on Co(II)(dmg)$_2$.py*

Resonance/ppm	$D \times 10^8 / m^2 s^{-1}$
8.229	1.292
7.931	1.309
7.444	1.309
2.851	2.536
2.374	1.136
2.082	2.378
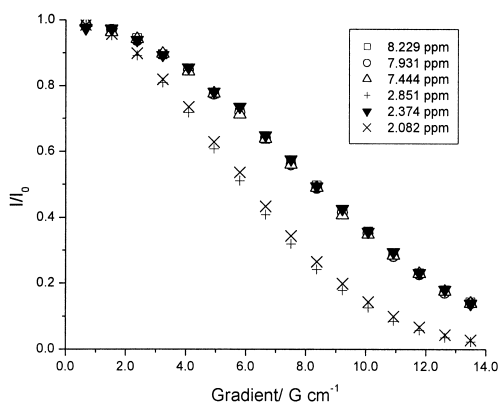
Figure 10: *I/I$_0$ vs. Gi obtained from DOSY experiments on Co(II)(dmg)$_2$.py.*

The cobalt complex diffuses approximately two times as slow as both water and d_6-acetone. An unanswered observation at present, however, is the validity of the absolute values of D. When we compare our data with the diffusion coefficients obtained for toluene in toluene, $D = 2.3 \times 10^{-9}$ m^2 s^{-1}, the present data shows a rate one order of magnitude higher, a rate coefficient for the diffusion in to order of 10^{10}, which is too high to be easily explained. Further studies are currently undertaken.

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