Catalytic Chain Transfer Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide: Evidence for a Diffusion-Controlled Transfer Process

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ABSTRACT: The mechanism of catalytic chain transfer polymerization with methyl methacrylate was studied in a range of media. The chain transfer reaction in supercritical CO_2 was found to be significantly enhanced compared with similar experiments in toluene or in bulk methyl methacrylate. The results are consistent with a diffusion-controlled rate-determining step in the transfer process with cobaloxime catalysts. The gaslike viscosities in the supercritical medium result in an approximate chain transfer coefficient (k_{tr}) of 10^8 L mol^{-1} s^{-1}: an order of magnitude higher than values obtained in conventional organic solvents.

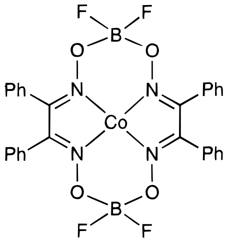
Introduction

The controlled synthesis of low molecular weight polymers is assuming greater importance as applications in the coatings, detergents, and water treatment industries continue to develop. There is a driving force to decrease molecular weight in oligomeric additives to detergents, dispersants, and scale inhibitors as biodegradability is facilitated as molecular weight decreases.

One standard approach to molecular weight reduction involves the use of chain transfer agents such as mercaptans. This strategy has two major disadvantages; viz., the mercaptan is incorporated in the small chains adversely affecting the oligomer properties, and also the malodorous nature of the mercaptans is often a problem. Another approach is to use high initiator concentrations which is often uneconomic and therefore impractical. Molecular weight reduction can also be effected in semicontinuous solution polymerization, which can result in high organic solvent emissions and problems in isolation of the oligomeric product. In many practical instances a combination of these approaches is taken.

Two technologies have emerged in recent years that may lead to a step change in green oligomer synthesis. First, catalytic chain transfer (CCT) polymerization is now well-known as a highly efficient method for producing oligomers.[1,2] CCT has many favorable characteristics; the catalysts are used in low concentrations and are generally nontoxic, and the free-radical nature of the reaction means that many conventional monomers can be polymerized without special plant requirements. The other new technological area, i.e., polymerization in supercritical fluids (SCF) such as carbon dioxide, has two primary advantages for oligomer synthesis: the elimination of organic solvent emissions and facile oligomer isolation.[3] The limited solubility of common polymers in supercritical CO_2 is also overcome to some extent by targeting a low molecular weight product. Dada et al. (Rohm & Haas)[4] have patented a high-temperature process for oligomer synthesis in supercritical CO_2, which demonstrates the potential commercial utility of a successful CCT/SCF approach.

This paper describes initial experiments performed to test the potential of CCT in supercritical carbon dioxide, for the synthesis of acrylic oligomers.



(I)

Experimental Section

Materials. The bis(methanol) complex of COPhBF (**I**) was prepared according to the method described by Bakac et al.,[5] replacing dimethylglyoxime in the described procedure with diphenylglyoxime. Methyl methacrylate monomer was passed through a column of activated basic alumina (ACROS, 50−200 μm) and was purged with high-purity nitrogen (BOC) for 1.5 h prior to use. AIBN (Dupont) was recrystallized twice from methanol and used as initiator. Toluene, used without further purification, was purged with high-purity nitrogen (BOC) for 1.5 h prior to use. The CO_2 (99.5%) was supplied by CIG.

General Polymerization Procedure. The basic polymerization procedure (in conventional organic media) has been described previously.[6−8] Two stock solutions were prepared: (i) an initiator stock solution and a (ii) catalyst stock solution. (i) The initiator stock solution was prepared by dissolution of approximately 200 mg of AIBN into 50 mL of monomer. (ii) The catalyst stock solution was prepared by dissolution of 2−3 mg of catalyst into 10 mL of solution (i). Three reaction mixtures were prepared by the addition of between 2 and 3 mL of solution (ii) to 24 mL of solution (i). For the supercritical reactions a Jerguson sight gauge (50 mL), equipped with a recirculating pump, was purged with CO_2 before reaction mixture was introduced. The reaction mixture (7 mL) was introduced via a glass syringe to the reactor. The experiments were performed at 150 bar, and the temperature was maintained at 50 °C as the entire sight gauge was immersed in an

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isothermal water bath. The control reaction mixture (7 mL) was diluted with toluene (43 mL) and charged to a Schlenck vessel which was then immersed in a 50 °C water bath. Conversions were maintained below 5%.

Phase Behavior. Reactions in supercritical media are conducted at high pressure, and under these conditions the phase behavior of the reaction mixture can be complex. Subramaniam and McHugh[9] have noted that many studies fail to identify the phase behavior of the reaction mixture. The number and nature of extant phases have a direct impact on the progress of the reaction, and so knowledge of the phase behavior is essential for the proper interpretation of experimental data.

Prior to running the reaction experiments, the phase behavior of the CO_2/methyl methacrylate binary mixture was examined. This involved the determination of the transition pressure of the mixture at 50 °C. At pressures in excess of the transition pressure the mixture exists as a single, homogeneous phase which exhibits gaslike transport properties due to the presence of supercritical CO_2.[10,11]

Various quantities of methyl methacrylate (5−10 mL) were added to the Jerguson sight gauge. After purging the system with CO_2, the pressure was increased slowly with CO_2 so as to observe the behavior of the meniscus, visible along the length of the sight gauge. The addition of CO_2 was accompanied by a significant expansion of the liquid phase, especially once the critical pressure of CO_2 had been exceeded. At pressures in excess of 95 bar, the meniscus was no longer visible, thus indicating the formation of a homogeneous mixture.

It is noteworthy that when approximately 7 mL of methyl methacrylate was used, the position of the meniscus became stable toward the middle of the sight gauge. As the pressure was increased to around 95 bar, the meniscus became cloudy and eventually disappeared as the pressure was increased further. Such behavior typically indicates that the mixture critical point has been reached for a given mixture composition.[12,13] It was therefore concluded that operating at a pressure of 150 bar at 50 °C was sufficient to achieve a homogeneous reaction mixture.

Molecular Weight Analysis. Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10A autoinjector, a column set consisting of a Polymer Laboratories (PL) 3.0 μm bead size guard column (50 × 7.5 mm) followed by four linear PL columns(10^6, 10^5, 10^4, and 10^3) (300 × 7.5 mm), and a VISKOTEK duel detector model 250 differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as the eluent at 1 mL/min. Calibration of the SEC equipment was carried out with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range $200-1.6 \times 10^6$).

Matrix-Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry. Mass spectrometry analysis was carried out on a Biosystems, Voyager DERP instrument operated in reflectron mode. The mass scale was calibrated using substance P. The matrix used was 2,5-dihydroxybenzoic acid (DHB) with NaCl as the cation source and was dissolved in a 50:50 mixture of water and methanol. The polymer analyzed was dissolved in THF at a concentration of 5 mg/mL. The matrix solution was deposited onto a gold plated target and allowed to dry. The polymer was then deposited onto the matrix.

Results and Discussion

The preliminary experiments indicated that low molecular weight polymer could be synthesized, and the experiment was subsequently optimized to decrease the time taken for pressurization and thermal equilibration. The time taken for depressurization was also found to be important. In cases where a significant time interval passed in these initial and terminal stages, then high molecular weight material could be detected in the subsequent SEC analysis (see Figure 1). Results were only used when the reactions were observed to be homogeneous throughout the experiment.

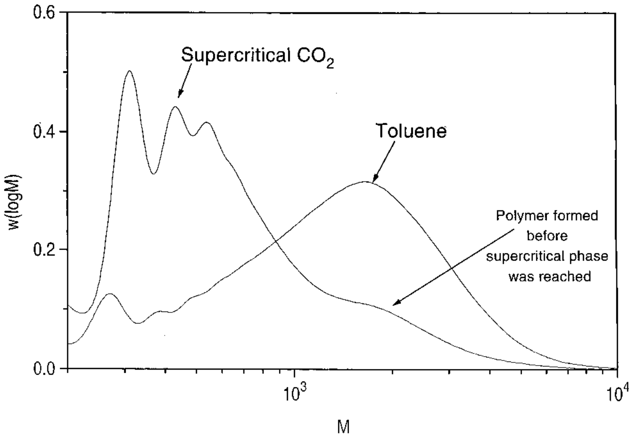


Figure 1. Molecular weight distributions obtained in supercritical CO_2 and in toluene solution.

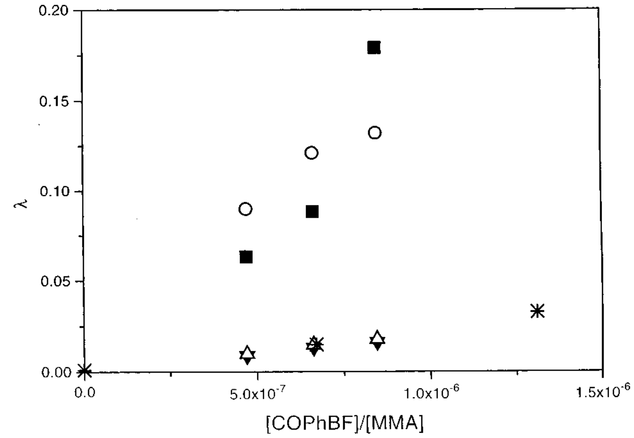


Figure 2. Mayo (■) and CLD (○) plots for MMA in supercritical CO_2 and Mayo (▼) and CLD (△) plots for bulk MMA. Also shown is the Mayo plot (*) for MMA solution (66% toluene).

To quantify the efficacy of the catalytic chain transfer reaction, we endeavored to measure the chain transfer constant of COPhBF in the MMA/CO_2 solution. The standard method for evaluating chain transfer coefficients is via the Mayo equation (eq 1).[14]

$$\frac{1}{\mathrm{DP_n}} = \frac{(1+\lambda)\langle k_t\rangle[\mathrm{R}^\bullet]}{k_p[\mathrm{M}]} + C_M + C_S\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad (1)$$

where $\mathrm{DP_n}$ is the number-average degree of polymerization, $\langle k_t\rangle$ is the average termination rate coefficient, $[\mathrm{R}^\bullet]$ is the total radical concentration, k_p is the propagation rate coefficient, [M] is the monomer concentration, C_M is the chain transfer to monomer constant, C_S is the chain transfer to transfer agent constant, λ is the fraction of chains undergoing disproportionation reactions, and [S] is the concentration of chain transfer agent. In this work, the chain transfer constant, C_S, was taken as the slope of the resulting straight line plot (Figure 2). The results were compared with control reactions performed either at the same concentration of MMA and [Co]/[MMA] ratio in toluene or in bulk MMA at ambient pressure, at 50 °C. The molecular weight distributions obtained in the different media are significantly different, as shown in Figures 1 and 3,

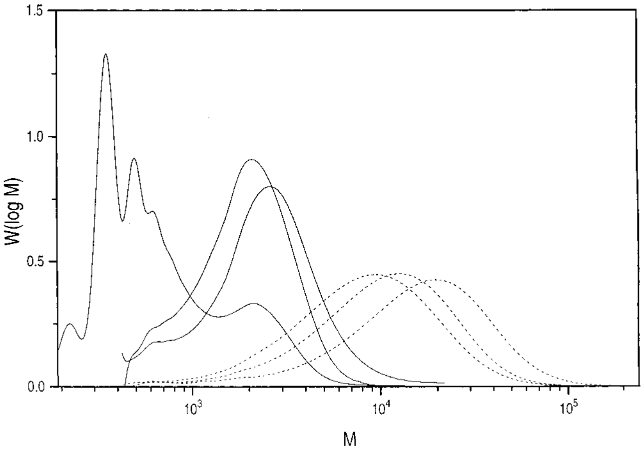


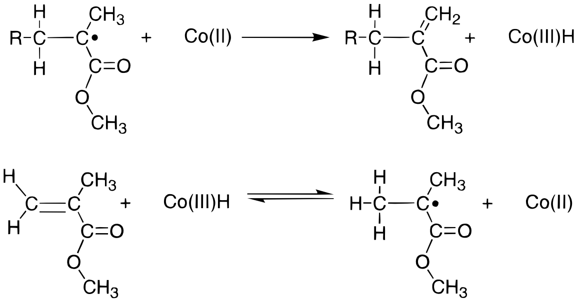
Figure 3. Molecular weight distributions obtained in supercritical CO_2 (solid line) and the control experiments run contemporaneously in bulk MMA (dotted line).

Table 1. C_S Values Obtained for CCT with MMA in Three Different Media, Using the CLD and Mayo Methods[a]

medium	Mayo C_S	CLD C_S
bulk MMA	20×10^3	21×10^3
toluene	23×10^3	26×10^3
supercritical CO_2	378×10^3	113×10^3

[a] The variation in the C_S value for MMA in supercritical CO_2 reflects the difficulty in accurately characterizing the molecular weight distribution at very low chain lengths, as discussed in the main text.

Scheme 1



where it is clear that extremely low molecular weights are generated in the supercritical CO_2. It is evident from Figures 1−3 that the CCT polymerization performed under supercritical conditions has a substantially higher apparent chain transfer constant; the actual C_S values obtained from the Mayo procedure are given in Table 1. The Mayo plots were generated assuming $DP_n = M_w/(2m_0)$. This assumption is generally applicable for a chain transfer dominated system, in which case M_w is equal to $2M_n$ (except for very low molecular weights).[15,16] The use of M_w is often more reliable, because M_w is much less sensitive to errors in analysis of the size exclusion chromatogram, as has been previously discussed in great detail. In this work, using M_w resulted in improved linearity of the Mayo plots; however, as such low molecular weights were generated, and hence $M_w \leq 2M_n$, some error is inevitable, and the C_S values should only be treated as indicative measures of the increased efficiency of transfer in the supercritical medium.

As monomer can be generated as part of the CCT reaction, as shown in Scheme 1, this can lead to an underestimate of C_S as this is excluded from the evaluation of the molecular weight moments, particularly when very low molecular weights are generated. In this regard the chain length distribution (CLD) method may be preferable for evaluating the true C_S value. The CLD procedure developed Gilbert and coworkers[17,18] is based upon taking the high molecular weight slope of the number distribution ($P(M)$) plotted as $\ln(P(M))$ vs M. The high molecular weight slope of this plot, denoted as Λ_{high}, is defined as follows:

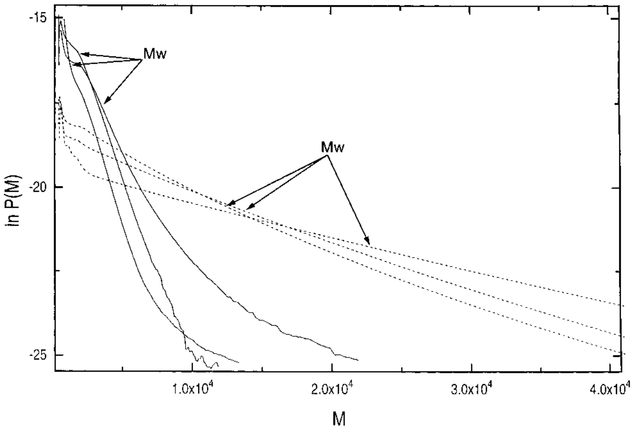


Figure 4. ln $P(M)$ distributions obtained in supercritical CO_2 (solid line) and the control experiments run contemporaneously in bulk MMA (dotted line).

$$\Lambda_{\text{high}} = \lim_{M\to\infty} \frac{d\ln(P(M))}{dM} = -\left(\frac{\langle k_t\rangle[R^\bullet]}{k_p[M]} + C_M + C_S\frac{[S]}{[M]}\right)\frac{1}{m_0} \quad (2)$$

where m_0 is the mass of the monomer. Measurement of C_S in this case involves the measurement of Λ_{high} as a function of [S]/[M], and a plot of $-\Lambda_{\text{high}}m_0$ vs [S]/[M] then yields a straight line with slope C_S. Two groups[19,20] have recently reported that optimal results are obtained when the slope at the peak of the molecular weight distribution is utilized, and this is often preferable to using Λ_{high}, provided the polymerization is truly transfer dominated. The ln $P(M)$ plots for polymerizations run in supercritical CO_2 and bulk MMA are shown in Figure 4, exemplifying the enormous difference in chain transfer activity in the two media. The C_S values derived from the CLD analyses are also reported in Table 1. It is clear that there is scatter in the data; this reflects the difficulties with analyzing very low molecular weight polymer. The main conclusion is that the transfer reaction is significantly enhanced in the supercritical medium, and all the results are consistent in this respect.

Mechanistic Interpretation. The mechanism of CCT has never been unambiguously proven. The generally accepted mechanism is shown in Scheme 1, where a transient cobalt hydride intermediate is generated. The chain transfer reaction is remarkably fast (compared with conventional chain transfer reactions), which has led to speculation that the reaction may be diffusion-controlled in some systems. A MALDI spectrum showing the molecular weight distribution of PMMA generated in a CCT reaction in supercritical CO_2 is shown in Figure 5. Each peak mass (m) is consistent with the expression $m = 100.1n + 23.0$, where n is the degree of polymerization, 100.1 is the mass of the repeat unit, and 23.0 is the mass of the sodium counterion. There are

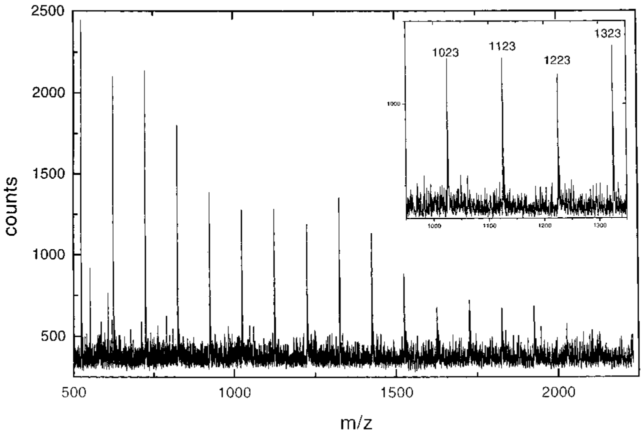


Figure 5. A MALDI-MS spectrum of PMMA synthesized using CCT in supercritical CO_2.

no chains evident with an AIBN initiator fragment (mass = 68). This result is concordant with a polymerization process dominated by catalytic chain transfer. The oligomer structure was also verified using NMR, which indicated the presence of the expected vinyl end groups.

Thus, it is clear that CCT polymerization of MMA with cobaloximes in supercritical CO_2 is more effective than the equivalent reaction in toluene or in bulk at ambient pressure. The raises the question as to why this should be. The first possibility to consider is that there is a significant solvent effect on the propagation reaction, as C_S is the ratio of the elemental transfer and propagation rate coefficients. Van Herk and co-workers[21,22] have shown that the propagation rate coefficient is virtually the same in supercritical CO_2 as in bulk. (There is a minor solvent effect, but this cannot account for the large change in C_S observed in the current work.) This leaves the second possibility, a significant solvent effect on the chain transfer reaction, as the basis of the reduced C_S. The solvent effect can be exerted conceivably via three different mechanisms: (1) complexation or ligation, (2) partitioning of the catalyst, and (3) viscosity of the reaction medium. In what follows, each of these possibilities will be discussed in turn.

Complexation or Ligation. There has been some conjecture in the literature that CCT reactions can be strongly influenced by solvent. In recent work, we have shown that the solvent effect on CCT (with MMA and styrene) is not significant for solvents that are weak ligands, such as toluene and butyl acetate.[23] A solvent effect of this nature only becomes important for strong ligands such as pyridine—this has also been observed in previous studies. In the current case neither toluene nor CO_2 is a strong ligand, and therefore it seems unlikely that the strong effects we observe can be attributed to direct chemical interactions.

Partitioning of the Catalyst. An enhanced chain transfer process may be possible if the local cobaloxime concentration around the radical is increased. Despite the low solubility of phenyl compounds in supercritical CO_2,[24] the COPhBF was fully soluble at the very low concentrations required for efficient catalytic chain transfer. Klingler and Rathke[25] studied the hydrogenations of dicobalt octacarbonyl and dimanganese decacarbonyl in supercritical CO_2 over a wide temperature range and found no significant solvent effects in the supercritical medium in comparison to nonpolar organic solvents. Therefore, it seems unlikely that the increased transfer efficiency in supercritical CO_2 can be attributed to partitioning.

Viscosity of the Reaction Medium. As mentioned earlier in this paper, the chain transfer process may be diffusion-controlled, as indicated by the high chain transfer rate coefficient in the CCT polymerization of MMA in organic solvents. From the measured chain transfer constants and propagation rate coefficients a chain transfer rate coefficient of the order of $\sim 10^7$ dm^3 mol^{-1} s^{-1} is derived, which is similar to the rate coefficients for the bimolecular termination reaction between two radicals which are known to be diffusion-controlled. Furthermore, in concurrent work we have observed kinetic results from CCT reactions with methacrylates that seem to indicate a diffusion-controlled transfer reaction.[26] These results, that include Arrhenius parameters for the CCT reaction in a range of methacrylates, yield activation energies and frequency factors consistent with a diffusion-controlled process. In addition, the individual C_S values for the methacrylates can be correlated with monomer viscosity; i.e., the higher the viscosity, the lower C_S.

These findings are consistent with theories for a diffusion-controlled reaction, in which the rate coefficient is generally found to be proportional to the self-diffusion coefficients of the two reactants:

$$k_S \propto D_{Co} + D_i \tag{2}$$

Here D_{Co} is the diffusion coefficient of the cobalt catalyst and D_i the diffusion coefficient of an i-meric radical. Since diffusion coefficients are generally found to be roughly proportional to the inverse of the solvent viscosity η ($D \propto \eta^{-\alpha}$, where a lies generally between 0.5 and 1.0), the following relationship should approximately be valid for the chain transfer constant:

$$C_S \propto \frac{1}{\eta^a} \tag{3}$$

It is well-known that supercritical fluids are characterized by gaslike viscosities, and therefore we would predict an increase in the rate of transfer relative to propagation (which is chemically controlled) in the supercritical medium if the chain transfer reaction is indeed diffusion-controlled. Suarez et al.[27] have tabulated all the available data on diffusion coefficients in supercritical fluids; unfortunately, no cobaloximes appear to have been measured. Despite this, it is evident that diffusion coefficients of organic molecules in supercritical CO_2 are enhanced by an order of magnitude in supercritical CO_2 compared to ambient conditions in conventional organic media. Therefore, we would expect to see a proportionate increase in the diffusion coefficient of the cobaloxime leading to enhanced reaction rates provided the rate-determining step is diffusion-controlled. This is in qualitative agreement with our experimental observations.

Conclusions

This work provides further evidence that the rate-determining step of catalytic chain transfer polymerization of MMA with COPhBF is diffusion-controlled. In supercritical CO_2 the chain transfer rate is enhanced by an order of magnitude, and it is unlikely that this factor can be attributed to partitioning or direct chemical interactions. Catalytic chain transfer in supercritical

CO_2 thus represents an extremely efficient method for synthesizing oligomers using free-radical polymerization.

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