

# Dispersion Catalytic Chain Transfer Polymerizations of Methyl Methacrylate in Supercritical Carbon Dioxide

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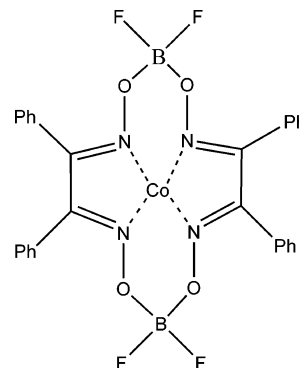
This paper describes a successful dispersion catalytic chain transfer polymerization (CCTP) of methyl methacrylate (MMA) in the presence of a transition-metal catalyst (tetraphenylcobalt-oxime boron fluoride, CPhBF (I)) in supercritical carbon dioxide (scCO<sub>2</sub>) using poly(dimethylsiloxane) monomethacrylate (PDMS-ma) macromonomer as a stabilizer. The final product is a dry, fine powder with controlled molecular weight and a narrow molecular weight distribution. It was found that the dispersion polymerization could reduce the activity of CCT catalyst, which can lead to facile and controlled preparation of high molecular weight vinyl-terminated macromonomers.

## Introduction

In recent years, there has been a significant increase in the use of scCO<sub>2</sub> as a reaction medium for free-radical dispersion polymerizations. ScCO<sub>2</sub> is environmentally friendly, relatively inexpensive, has tunable properties, and leaves no toxic solvent residues.<sup>1,2</sup> DeSimone et al. reported the first dispersion polymerization of methyl methacrylate in scCO<sub>2</sub> using a highly soluble amorphous fluorinated polymer (poly(dihydroperfluorooctylacrylate), PFOA) as a stabilizer.<sup>3</sup> Since then, the successful dispersion polymerizations of a very wide range of vinyl monomers have been reported, including methyl methacrylate,<sup>4–10</sup> 2-hydroxyethyl methacrylate,<sup>11</sup> styrene,<sup>12–15</sup> vinyl acetate,<sup>16</sup> acrylonitrile,<sup>17</sup> *N*-vinyl pyrrolidinone,<sup>18,19</sup> glycidyl methacrylate,<sup>20,21</sup> and copolymerization of methyl methacrylate and ethyl methacrylate.<sup>22</sup>

Controlled/living polymerizations allow for the synthesis of well-defined and complex macromolecular architectures. Recently, controlled/living radical polymerization has attracted much attention since radical polymerization is generally more tolerant toward polar functionalities and impurities than ionic and coordination polymerizations. Among the approaches developed, transition-metal-catalyzed chain transfer polymerization has been extensively studied. Catalytic chain transfer (CCT) reactions that employ low-spin Co<sup>II</sup> complexes as catalysts are the most efficient routes to molecular weight reduction in homogeneous<sup>23–34</sup> and heterogeneous systems without the use of stoichiometric chain terminators.<sup>28,35–39</sup> CCT reactions usually lead to the synthesis of a large variety of structured monofunctional macromonomers that are terminated by a vinylic functionality.<sup>40–44</sup> This terminal group creates the potential for synthesizing a wide variety of polymeric products which may be used to develop novel structured materials. This versatility has led to the application of CCT polymerization in the automotive, paper, and printing industries where materials with high-quality

## Scheme 1



finishes are required.<sup>40–44</sup> However, so far there have been very few reports about CCT polymerization in CO<sub>2</sub>. Davis et al.<sup>45</sup> reported the precipitation CCTP of MMA using CPhBF (I) (Scheme 1) as a catalyst in scCO<sub>2</sub>. The precipitation CCTP of MMA using porphinatecobalt(II) complexes as a catalyst in scCO<sub>2</sub> was also reported by Holmes et al.<sup>46</sup> Low molecular weight polymers with narrow polydispersities were prepared in both reactions. As part of the effort toward applying controlled radical polymerization in a more environmentally friendly medium, in this paper we report our work on CCT polymerization carried out in CO<sub>2</sub>. We demonstrate that the successful dispersion CCTP of MMA was achieved in the presence of a transition-metal catalyst CPhBF (I) in scCO<sub>2</sub> using a poly(dimethylsiloxane) monomethacrylate (PDMS-ma) macromonomer as stabilizer. The high molecular weight macromonomer can be produced with controlled molecular weight (from 20 000 to 60 000 g/mol) and narrow polydispersity (<1.5).

## Experimental Section

**Materials.** CPhBF was donated by Uniqema Company. CPhBF catalyst stock solution was prepared in methyl methacrylate monomer. The commercially available methacrylate-terminated poly(dimethylsiloxane) (PDMS-ma, *M<sub>n</sub>* ~ 10 000 g/mol, Aldrich) was used as received. Methyl methacrylate (MMA) monomer was

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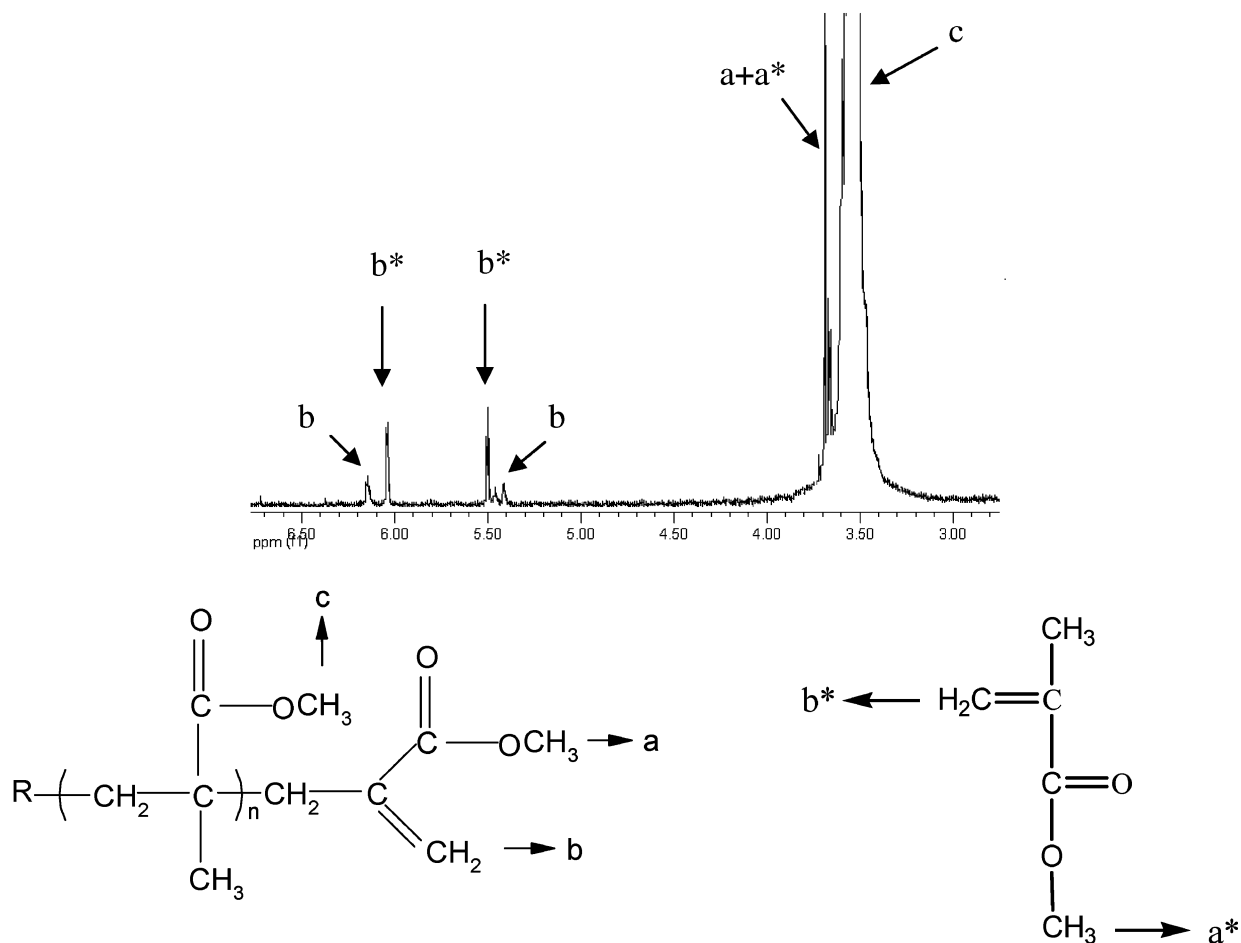
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**Table 1. Polymerizations of Methyl Methacrylate in scCO<sub>2</sub><sup>d</sup>**

entry	AIBN <sup>a</sup> (%)	COPhBF (ppm <sup>b</sup> )	stabilizer <sup>a</sup> (%)	yield (%)	<i>M<sub>n</sub></i>	PDI	sample description
A	1	NA <sup>c</sup>	NA <sup>c</sup>	29	26 700	1.98	sticky solid and viscous liquid
B	1	1	NA <sup>c</sup>	39	7300	1.30	viscous liquid
C	1	NA <sup>c</sup>	PDMS-ma, 5%	93	228 100	1.34	free-flowing white powder
D	1	1	PDMS-ma, 5%	91	45 600	1.35	free-flowing white powder
E	2	1	PDMS-ma, 5%	93	51 800	1.44	free-flowing white powder
F	3	1	PDMS-ma, 5%	93	49 700	1.44	free-flowing white powder
G	3	2	PDMS-ma, 5%	91	20 700	1.25	free-flowing white powder

<sup>a</sup> Weight percentage based on monomer. <sup>b</sup> 1 ppm is defined as 10<sup>-6</sup> mol of catalyst per mole of monomer. <sup>c</sup> NA: not applicable. <sup>d</sup> Reaction conditions: reaction temperature = 65 °C, reaction time = 7 h, reaction pressure = 3600 psi, stirring rate = 300 rpm.



**Figure 1.** <sup>1</sup>H NMR spectrum of MMA macromonomer (entry G in Table 1), *M<sub>n,NMR</sub>* = 25 000 g/mol. MMA macromonomer is a fine powder, which was directly collected for NMR analysis after CO<sub>2</sub> venting. From the spectrum, it can be clearly seen that there is some residual monomer in the product.

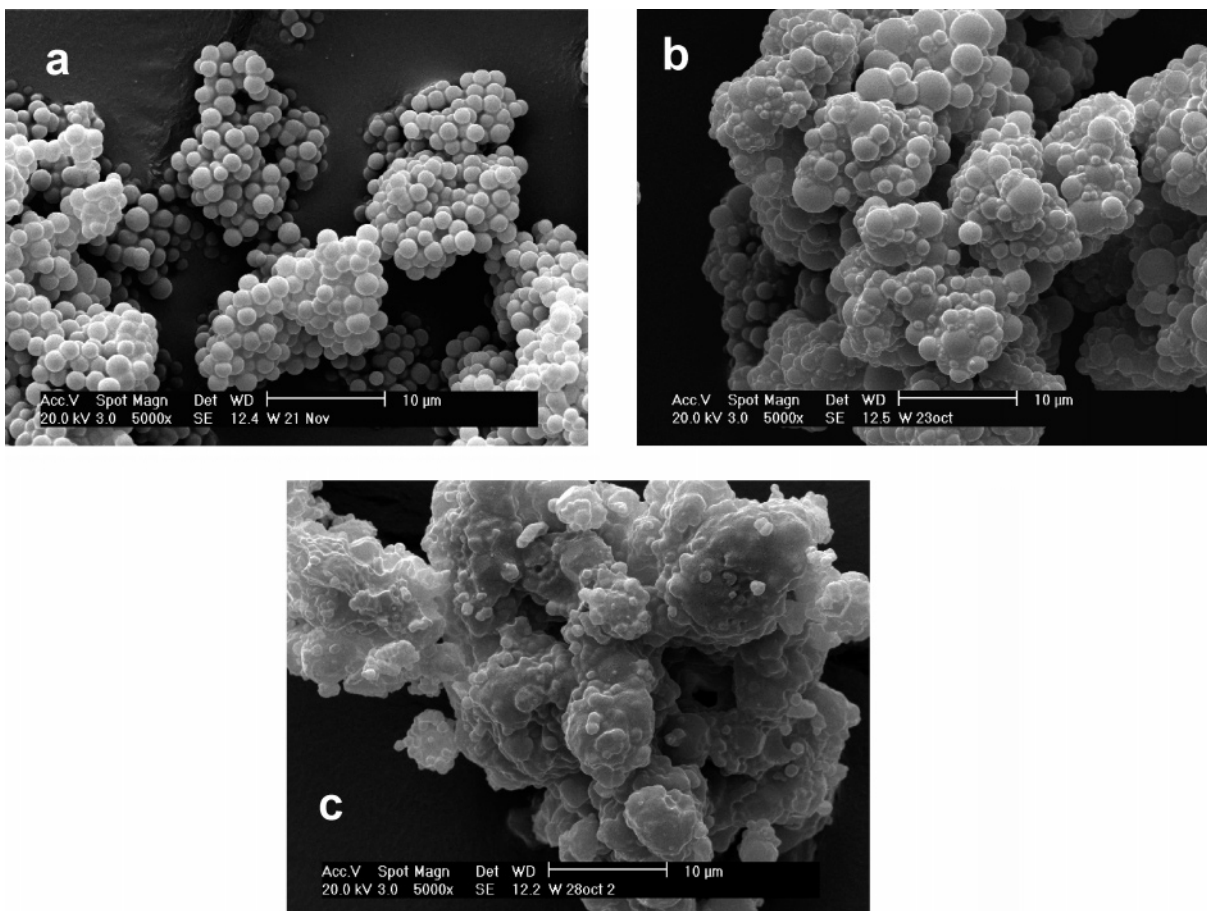
passed through a column of activated basic alumina (ACROS) and was purged with high-purity nitrogen for 1 h prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Fisher Chemicals) was purified via recrystallization from THF.

**Dispersion Polymerization.** Polymerizations were performed in a 60-mL stainless steel autoclave equipped with a magnetically coupled overhead stirrer. The autoclave was first charged with high-purity nitrogen for 1 h prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Fisher Chemicals) was purified via recrystallization from THF.

Polymerizations were performed in a 60-mL stainless steel autoclave equipped with a magnetically coupled overhead stirrer. The autoclave was first charged with initiator (AIBN) and then was purged by flowing low-pressure CO<sub>2</sub> through the autoclave. After purging for 10 min, the monomer and catalyst solution were injected into autoclave under a flow of CO<sub>2</sub>. The autoclave was then filled with CO<sub>2</sub> (800 psi), stirred, and heated to the desired reaction temperature (65 °C) using a preheated thermocouple controlled aluminum block. Once the desired reaction temperature was reached, the required pressure (3600 psi) was attained by addition of CO<sub>2</sub>. The stirring rate (300 rpm) was kept constant throughout the reaction.

After 7 h, the heating was stopped and the reaction system was allowed to cool down to room temperature (ca. 30 min). The pressure was then slowly released to atmosphere and the polymeric product was recovered as a dry white powder, which was then characterized.

**Polymer Characterization.** The monomer conversion was measured gravimetrically. Molecular weight data were obtained by gel permeation chromatography (GPC) with two PLgel 5 μm Mixed-D columns (Polymer Laboratories, *M<sub>w</sub>* range: 200–400 000 g/mol) and an evaporative light scattering detector (PL-ELS 1000, Polymer Laboratories) using chloroform as the solvent at 30 °C. Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 mL/min. Scanning electron microscopy (SEM) data were collected using a JEOL 6400. Samples were mounted on an aluminum stub using an adhesive



**Figure 2.** SEM pictures of the product from the dispersion polymerizations of MMA in  $\text{scCO}_2$ , a: entry C in Table 1, b: entry F in Table 1, c: entry G in Table 1.

carbon tab and were coated with gold.  $^1\text{H}$  NMR data were collected on a Bruker 300 MHz spectrometer.

## Results and Discussion

As comparison, the polymerizations were initially carried out without stabilizer in  $\text{scCO}_2$ . Reactions performed in the absence of catalyst afforded high molecular weight poly(methyl methacrylate) with low monomer conversion (entry A in Table 1). A broad bimodal distribution curve was found by GPC against PMMA standards, indicating the lack of reaction control. Polymerization in the presence of CPhBF (I) without stabilizer afforded low molecular weight, monodisperse polymer at fairly high conversion (entry B in Table 1), compared to the polymerization in the absence of catalyst. The  $^1\text{H}$  NMR spectrum showed the presence of vinyl end groups which are indicative of a chain transfer mechanism having taken place in  $\text{scCO}_2$ , similar to that reported in previous papers.<sup>45,46</sup> In the absence of stabilizer, no stabilized polymerization was observed no particle of PMMA was produced, and the yield of polymer was quite low.

Then, a series of dispersion polymerizations (entries C–G in Table 1) were conducted with 5 wt % stabilizer (with respect to monomer). Using a high-pressure view cell, we observed the polymerization process under the conditions of our polymerization experiments. Before the polymerization started, the reaction system was orange and homogeneous, which indicates that CPhBF (I) is soluble in the polymerization medium. Thus, we are confident that all reactions were in a single phase at

the start of the polymerization. In the absence of stabilizer, although the reaction began as a single phase, it turned into heterogeneous and a liquid layer was observed on the bottom of autoclave during the polymerization. By contrast, in the presence of PDMS-ma stabilizer, the system turned into a stable milky emulsion system which lasted the duration of the polymerization. Under the dispersion polymerization conditions, the reactions produced high yields (>90%) of PMMA powder with high molecular weight and narrow polydispersity (entries C–G in Table 1). Comparison to the radical polymerization in the absence of metal catalyst (entry C in Table 1) clearly shows that the molecular weight of PMMA in the presence of CPhBF (I) (entries D–G in Table 1) has been dramatically reduced. Furthermore, it is clear that the molecular weight of polymers is independent of the initiator concentration (entries D–F in Table 1). The experiments were also performed using different concentrations of CPhBF (I) in relation to MMA (entries F and G in Table 1). The molecular weight was lowered with increasing catalyst concentration, as expected. The control over the polymerization period clearly suggests that the transfer agent was not being consumed during the reaction, in agreement with previous results.<sup>45,46</sup> The product was directly collected for NMR analysis after  $\text{CO}_2$  venting. The  $^1\text{H}$  NMR spectrum of the low molecular weight product (entry G in Table 1) shows vinyl resonances for macromonomers (peak b in Figure 1). From the spectrum, it can also be clearly seen that there is some residual monomer in the product. Integration of the vinyl



resonances of macromonomers against the bulk methoxy resonance of the PMMA chain (peak c) demonstrates that the molecular weight obtained from NMR ( $M_n$ , NMR = 25 000 g/mol) closely matches the GPC ( $M_n$  = 20 700 g/mol, entry G in Table 1). All these experimental data suggest that the dispersion radical polymerization of MMA is controlled and that CPhBF (I) enhances the chain transfer reaction. Figure 2 shows the scanning electron micrographs of the PMMA obtained from these reactions. SEM showed that the materials produced by dispersion CCTP indeed consisted of particles although the final product was partially flocculated (pictures b and c in Figure 2). Moreover, it can be clearly seen that the increase of catalyst concentration resulted in the more flocculated morphology. We think this is because the CCT catalyst greatly reduced the molecular weight of polymers, and they can easily be plasticized by scCO<sub>2</sub>. In the absence of CPhBF (I), the PMMA product has high molecular weight and is more likely to be discrete particles (picture a in Figure 2) as it is less plasticized.

In the previous research,<sup>45</sup> Davis et al. found that the chain transfer reaction in scCO<sub>2</sub> was significantly enhanced compared with similar experiments in normal organic solvents. However, for the dispersion CCTP, we found a contrary result. In contrast to CCTP without stabilizer (entry B in Table 1), the dispersion CCTP resulted in the higher molecular weight PMMA. This suggests that the activity of chain transfer reaction was significantly reduced rather than enhanced for the dispersion CCTP in scCO<sub>2</sub>. Further study is being carried out to explain this novel phenomenon. Thus, with easily accessible and measurable loadings of CPhBF (I) catalyst, it is very easy to generate high yields of high molecular weight macromonomers. By contrast, if the same molecular weight macromonomers are to be targeted in precipitation CCTP in scCO<sub>2</sub> or normal organic solvents, the concentration of catalyst required will need to be accurately measured to extremely low levels.

In summary, this study has shown the successful dispersion CCTP of MMA in the presence of a transition-metal catalyst CPhBF (I) in scCO<sub>2</sub>. It was found that the dispersion polymerization could reduce the activity of CCT catalyst, leading to facile and controlled preparation of high molecular weight vinyl-terminated macromonomers. This study demonstrates the continuing potential to achieve controlled polymer synthesis in environmentally benign solvents such as scCO<sub>2</sub>.

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