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Controlled Polymerization of Methyl Methacrylate with Porphinatocobalt(II) Catalysts in Supercritical Carbon Dioxide

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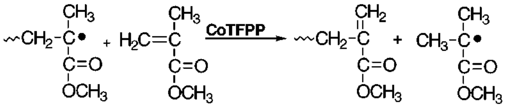
ABSTRACT



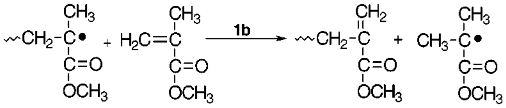
We report the successful controlled polymerization of methyl methacrylate in the presence of the catalytic chain transfer agents 5,10,15,20-tetraphenylporphinatocobalt(II) and 5,10,15,20-tetra(pentafluorophenyl)porphinatocobalt(II) (CoTFPP) in supercritical carbon dioxide ($scCO_2$). Low molecular weight polymers with narrow polydispersities have been prepared both at low and high monomer conversion and the chain transfer constant is found to be 1.3×10^3, which is comparable to the value obtained in traditional solvents.

Concern over the emission of volatile organic solvents, typically used in polymer synthesis, has prompted researchers to look for less harmful alternatives. Supercritical carbon dioxide has recently emerged as an environmentally benign, nontoxic, and inexpensive alternative to volatile organic solvents.[1]

DeSimone and co-workers have shown that $scCO_2$ is an ideal medium for both homogeneous and heterogeneous radical polymerizations.[2−7] However, homogeneous polymerization has been limited to those polymers soluble in $scCO_2$ such as amorphous fluoropolymers and poly(siloxanes).[5,6] As a result, the synthesis of poly(methyl methacrylate) in $scCO_2$ has been mainly limited to heterogeneous, i.e., dispersion, and precipitation polymerization techniques.[3,7]

Enikolopyan et al. first reported that porphinatocobalt(II) complexes behave as chain transfer agents in solution radical polymerization.[8] Since then numerous reports in this area have appeared in the literature.[9−12] It is now widely accepted that the process is catalytic, with transfer constants in the range 10^3−10^4 having been reported (Scheme 1).[8,9,12]

Scheme 1



Here we report the successful polymerization of methyl methacrylate in the presence of the transition metal catalysts

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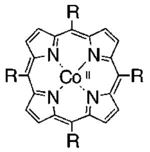
5,10,15,20-tetraphenylporphinatocobalt(II) **1a** and 5,10,15,20-tetra(pentafluorophenyl)porphinatocobalt(II) **1b** in $scCO_2$. The cobalt complexes **1a,b** (Scheme 2) were prepared according to previously published procedures.[13] Low molecular weight polymers with narrow polydispersities have been prepared both at low and high monomer conversion. The process is found to proceed by a catalytic chain transfer mechanism in $scCO_2$ with a chain transfer constant comparable to that for radical polymerization in conventional solvents.[8]

Scheme 2



1a; R = - C_6H_5
1b; R = - C_6F_5

Reactions performed in the absence of catalyst afforded moderately high molecular weight poly(methyl methacrylate) at low conversion (Table 1, entry A).[14] The polymer began precipitating from solution within 30 min of reaction, i.e. ~0.9% conversion with respect to initiator half-life.[2] A broad bimodal distribution curve was found by size exclusion chromatography (SEC) against polystyrene standards, indicating the lack of reaction control.

Table 1. Polymerization of Methyl Methacrylate[a] Initiated with AIBN[b] in the Presence of **1b**

entry	[(**1b**)]/[mma]	M_n[c]	M_w/M_n[c]
A	–	77 500	2.72
B	1.9×10^{-5}	7 100	1.87
C	3.3×10^{-5}	3 870	1.70
D	4.2×10^{-5}	3 690	1.38
E	6.0×10^{-5}	2 600	1.25
F	7.9×10^{-5}	2 250	1.32
G	9.5×10^{-5}	2 130	1.20
H	10.7×10^{-5}	1 930	1.18
I	12.5×10^{-5}	1 170	1.19
J[d]	6.1×10^{-5}	2 000	1.30

[a] Conditions: 60 °C, 3000–3500 psi for 2 h, 10-mL cell, methyl methacrylate 50 mmol. [b] AIBN 2.20×10^{-2} mmol. [c] SEC. [d] Conditions: 18 h, 40% yield.

Polymerization in the presence of the nonfluorinated 5,10,15,20-tetraphenylporphinatocobalt(II) **1a** afforded low molecular weight, monodisperse polymer at low conversion (M_n 3300 g mol^{-1}, M_w/M_n 1.33). The ^1H NMR spectrum indicated the presence of vinyl end groups (δ 5.5 and 6.2 ppm) which are indicative of a chain transfer mechanism having taken place in $scCO_2$, similar to that found in common organic solvents.[8]

The partial insolubility of the cobalt macrocycle **1a** in the binary monomer/$scCO_2$ mixture prompted us to search for a CO_2-soluble catalyst. The analogue **1b**, containing CO_2-philic pentafluorophenyl substituted moieties was found to be both soluble in liquid and $scCO_2$ at moderate pressures (1000–3500 psi) and temperatures (20–80 °C), giving highly red colored homogeneous solutions. A series of experiments was performed in the presence of varying concentrations of **1b** in relation to methyl methacrylate (Table 1, entries B–I).[15] Addition of the complex **1b** afforded low molecular weight, narrow polydispersity poly(methyl methacrylate) (Figure 1).

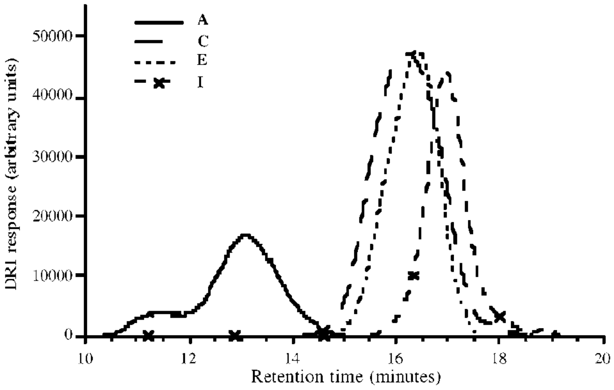


Figure 1. SEC analysis of poly(methyl methacrylate) prepared in the absence of **1b** (Table 1, entry A), and with various concentrations of **1b** in the reaction mixture (Table 1, entries C, E, I).

The use of the fluorinated catalyst **1b** avoided complications in kinetic measurements resulting from partial insolubility.[16]

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(15) **General Procedure for the Synthesis of Poly(methyl methacrylate) (PMMA):** A 10-mL Hastealloy steel reactor, equipped with a sapphire view window, was used for all reactions. Liquid carbon dioxide was delivered to the reactor using a Pickel PM 101 nitrogen-driven pump. The pressure in the reactor was measured with a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The internal temperature was measured with an Industrial Mineral Isolated thermocouple (type K, RS Electronics) and displayed on a temperature indicator (T 200, RS Electronics). A PTFE-coated magnetic stir bar was used to mix the contents of the reactor. In a typical polymerization, **1b** (3 μmol), AIBN (0.02 mmol), and methyl methacrylate (50 mmol) were added to the reactor. The solution was degassed by purging with CO_2 and then the reaction vessel was filled with liquid carbon dioxide to approximately three-quarter capacity. The solution was heated to 60 °C with stirring for 2 h. The carbon dioxide was vented into excess acetone to trap any residual monomer. Evaporation of the resultant solution afforded a viscous oil which was precipitated from excess hexane, to afford PMMA as a fine powder. The polymer was dried under vacuum to constant weight, and the yield was determined gravimetrically.

The molecular weight was found to be lowered with increasing catalyst concentration, as expected.

Polymerization control over an extended time period clearly suggests that the transfer agent was not being consumed during the reaction, in agreement with previous findings in conventional solvents (Table 1, entry J).[8,9]

The chain transfer constant (C_T) has been established from the high molecular weight limits of the number-molecular weight distribution (M_w/M_n) curves, at low initiator concentrations, using two methods.

First, the recently developed method of Gilbert and coworkers[17] [plot of ln $P(M)$ slopes against ratio of chain transfer agent to monomer concentration] afforded a linear relationship with a correlation coefficient of 0.99 (Figure 2).

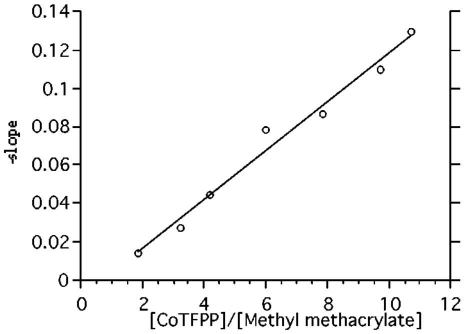

Figure 2. Negative slope of ln $P(M)$ versus M plots versus the relative concentration of **1b** to methyl methacrylate.

From the slope of Figure 2, C_T is found to be 1.3×10^3. This is in good agreement with previously reported literature values for porphinatocobalt(II) catalysts in solution polymerization,[8] which indicates that catalytic activity is not diminished in $scCO_2$.

The chain transfer constant was also measured by applying the commonly used Mayo equation.[18] When the inverse of the number average degree of polymerization was plotted against the ratio of the chain transfer agent to monomer concentration the slope of the resulting straight line afforded a value of $C_T = 550$. The discrepancy in the values measured by these two procedures is unusual, although recent comparisons of the two methods have shown that both methods are in principle identical.[19,20]

In summary, this study has shown that the well-known Co-mediated chain transfer polymerization of MMA occurs with comparable efficiency in $scCO_2$ to that in conventional solvents. This study demonstrates the continuing potential to achieve controlled polymer synthesis in environmentally benign solvents such as $scCO_2$.

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(16) A reviewer has suggested the measurement of cloud points of 5,10,15,20-tetra(pentafluorophenyl)porphinatocobalt(II) **1b** in the CO_2/methyl methacrylate binary mixture. This would be a useful additional measurement, but we are confident that all experiments have been conducted under initial conditions where the catalyst solubility was well above the limits.

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