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Effect of Supercritical CO₂ on the Copolymerization Behavior of Cyclohexene Oxide/CO₂ and Copolymer Properties with DMC/Salen-Co(III) Catalyst System

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ABSTRACT: The copolymerization of cyclohexene oxide (CHO) and carbon dioxide (CO₂) was carried out under supercritical CO₂ (scCO₂) conditions to afford poly (cyclohexene carbonate) (PCHC) in high yield. The scCO₂ provided not only the C1 feedstock but also proved to be a very efficient solvent and processing aid for this copolymerization system. Double metal cyanide (DMC) and salen-Co(III) catalysts were employed, demonstrating excellent CO₂/CHO copolymerization with high yield and high selectivity. Surprisingly, our use of scCO₂ was found to significantly enhance the copolymerization efficiency and the quality of the final polymer product. Thermally stable and high molecular weight (MW) copolymers were successfully obtained. Optimization led to excellent catalyst yield (656 wt/wt, polymer/catalyst) and selectivity (over 96% toward polycar-

bonate) that were significantly beyond what could be achieved in conventional solvents. Moreover, detailed thermal analyses demonstrated that the PCHC copolymer produced in scCO₂ exhibited higher glass transition temperatures ($T_g \sim 114$ °C) compared to polymer formed in dense phase CO₂ ($T_g \sim 77$ °C), and hence good thermal stability. Additionally, residual catalyst could be removed from the final polymer using scCO₂, pointing toward a green method that avoids the use of conventional volatile organic-based solvents for both synthesis and work-up. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *00*, 000–000

KEYWORDS: catalysis; copolymerization; polycarbonates; ring opening polymerization; supercritical CO₂

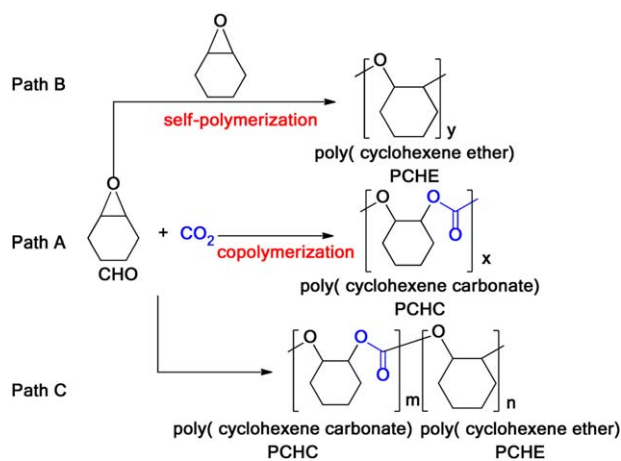
INTRODUCTION Societal and industrial development has led to a dramatic increase in the emission of CO₂ which contributes significantly to the greenhouse effect and leads to other detrimental effects. There is now a very strong push to reduce emissions of CO₂ and/or convert it into useful products. A particularly well studied reaction is the synthesis of polycarbonate via copolymerization of CO₂ with epoxides.^{1,2} Since the pioneering work on alternating copolymerization of CO₂/propylene oxide (PO) using a ZnEt₂/H₂O catalyst presented by Inoue in 1969, many studies have focused on finding efficient catalysts and using novel reaction process with improved activity and selectivity for the alternating copolymerization of CO₂ and epoxides (Scheme 1).^{3–12}

Alternatively salen-Co(III) complexes, first reported by Coates in 2003, have shown excellent selectivity toward poly(propylene carbonate) (PPC) formation with 99% carbonate linkages.⁹ Since 2003, significant effort has been devoted to the synthesis of more efficient salen cobalt com-

plexes.^{13–16} In 2006, Coats et al studied the copolymerization of gaseous CO₂ and CHO by salen-Co(III)X catalysts,¹⁷ in which they investigated the effect of pressure on the syndiotacticity of PCHC but at a very different pressure range. They found that catalyst syndiospecificity was pressure dependent, with the best selectivity realized employing high CO₂ pressure. PCHC with 81% *r*-centered tetrads was obtained. From these studies, a good catalytic system based on a chiral (R,R')-salen-Co(III) complex with *tert*-butyl substituents in the *ortho* and *para* positions of the aryl rings of the salen moiety has proven to be most effective.¹⁰ Although the salen-Co(III) complexes are now accepted as an ideal catalyst system to deliver polycarbonate linkages with high selectivity, they are hampered by low catalytic efficiency. Conversely, heterogeneous catalysts have also been investigated extensively. An ideal catalyst for CO₂/epoxide copolymerization is the DMC catalyst, originally reported by Kruper and Smart.¹⁸ These heterogeneous compounds were found to be extremely active for the copolymerization of CO₂ and

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SCHEME 1 Path A: Copolymerization of CHO and CO₂ to afford PPC; Path B: polymerization of CHO to afford polyether; Path C: CO₂/CHO random copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

epoxides. DMC catalysts such as zinc hexacyanoferrate(III) converted epoxides, EO, PO, 1-butene oxide, and CHO to polycarbonates (50–95% carbonate linkages and dispersity of 2–6) with turnover frequency (TOFs) of 4 h⁻¹.¹⁹ Although the high activity was attractive in industrialization production, the poor selectivity toward polycarbonate linkages hindered the application of DMC catalyst.

scCO₂ is an attractive solvent as it combines environmentally benign characteristics with favorable physico-chemical properties for chemical synthesis and exhibits unique low density, high diffusivity, and variable solvating strength.^{20–23} Indeed, a large body of work has shown that scCO₂ presents very distinct advantages as a solvent for the synthesis of a wide range of polymers.^{24–26} Earlier work has shown that aliphatic polycarbonates can be prepared by precipitation polymerization²⁷ and that copolymerization to form polycarbonates is viable in scCO₂.^{28–30} However, the copolymerization of CO₂ and epoxide in scCO₂ has not been much studied. The precipitation copolymerization of CO₂ and PO in scCO₂ has been reported using zinc glutarate with carbonate linkage of over 90% at 1500 psi.³¹ The yields were generally increased 10–20%. Beckman observed that zinc oxide and a highly fluorinated carboxylic acid derived from a monoester of maleic acid was active for the alternating copolymerization of CHO with scCO₂, facilitating PCHC formation with TOF of 8.8 h⁻¹ at 1450 psi and 100 °C.³²

In this work, the copolymerization of CO₂ and CHO was investigated in scCO₂ to explore the effect of scCO₂ on copolymerization behavior and the properties of copolymer. It has been very clear that the CO₂ was used not only as the monomer, but also the solvent. Mixing these two different individual catalyst types (heterogeneous DMC and homogeneous salen-Co(III) acetate) *in situ* during copolymerization has been found to deliver both high activity and high selectivity through a possible synergistic effect. A scCO₂ flushing experiment was also designed to find an environmentally

friendly way of PCHC extraction. This work focused on the recycle and utilization of greenhouse gas CO₂, and turned it into economical product: degradable plastics. This research could not only improve the eco-environment but also generate immense economic value.

EXPERIMENTAL

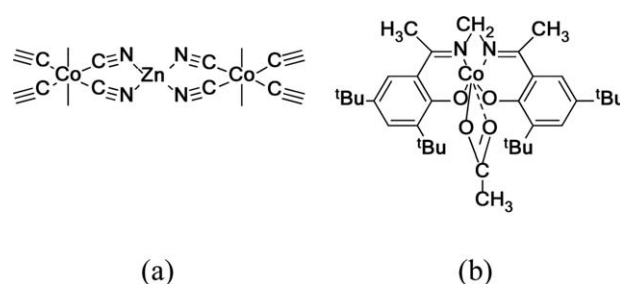
Materials

All chemicals were purchased from Sigma-Aldrich Corporation. Zinc chloride (ZnCl₂), potassium hexacyanocobaltate(III) (K₃[Co(CN)₆]), *tert*-butyl alcohol (*t*-BuOH), acetic acid (CH₃COOH), dichloromethane (CH₂Cl₂), sodium hexanitrocobaltate(III) (Na₃[Co(NO₂)₆]), bis(triphenylphosphine)iminium chloride ([PPN]Cl), diethyl ether, and hexane were of analytical purity and directly used. Salen-Co(II) of 98% was directly used. Nitrogen purity of 99.99% and oxygen purity of 99.999% were used as received. The purity of carbon dioxide was more than 99.99%. CHO (98%) was refluxed with calcium hydride (CaH₂, 99.9%) with a protective nitrogen atmosphere for more than 12 h at 160 °C before used.

Synthesis and Characterization of Catalyst

Synthesis of DMC Catalyst

First, 9.96 g (30 mmol) K₃[Co(CN)₆] was dissolved in 40 mL aqueous solution, and 20.45 g (150 mmol) ZnCl₂ was dissolved in a mixture of 100 mL water and 50 mL *t*-BuOH. The prepared ZnCl₂ solution was transferred into a 500 mL three-necked round-bottomed flask with a stirring speed of 6000 rpm. The prepared 40 mL K₃[Co(CN)₆] solution was added dropwise into the ZnCl₂ solution flask at a speed of one drop per 10 s, maintained the reaction flask at 30 °C and stirring speed of 6000 rpm. After 4 h reaction, the resultant suspension was centrifuged at room temperature to separate the solid product, then the precipitate was washed by 200 mL *t*-BuOH (heated at 50 °C) for six times to ensure that no ZnCl₂ or KCl was left in the solid product. The potassium reagent Na₃Co(NO₂)₆ was used to check the content of K⁺, ensuring that K⁺ could not be detected in the filtrate. The solid product was filtered and dried under vacuum conditions at 55 °C for 12 h. The proposed structure of Zn₃[Co(CN)₆]₂ is shown in Scheme 2 (a).³³ Yield: 72%. ELEM. ANAL. calcd (wt %) for Zn₃[Co(CN)₆]₂: Zn, 31.33, Co, 18.82, C, 23.01; N, 26.84, K < 0.01. Found: Zn, 22.03; Co, 12.55; C, 22.41; N, 19.17; H, 2.06.



SCHEME 2 Structures of Zn₃[Co(CN)₆]₂ (proposed) and salen-Co(III) acetate.

Synthesis of Salen-Co(III) Catalyst

A mixture of CH₃COOH (0.24 g, 4.0 mmol) and CH₂Cl₂ (40 mL) was added to the stirred mixture of salen-Co(II) (the structure refer to Supporting Information Fig. SI-2) complex (2.32 g, 4.0 mmol) with 300 mL CH₂Cl₂ in a 1 L round bottom flask. The mixed solution was stirred at a speed of 3000 rpm under a dry oxygen atmosphere at ambient temperature for 60 min. The solvent was then evaporated, leading to a crude dark green solid with close to 100% yield. The resulting solid was further treated with a mixture of 50 mL diethyl ether and 50 mL hexane for three times, and then dried at 60 °C under vacuum for 24 h. The structure of salen-Co(III) acetate is shown in Scheme 2 (b).

Yield: 90%. ELEM. ANAL. calcd (wt %) for C₃₆H₅₃CoN₂O: C, 67.90; H, 8.39; N, 4.40. Found: C, 67.75; H, 8.31; N, 4.36. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.13(s, 6H), 1.32(s, 18H), 1.75(s, 18H), 2.14(s, 2H), 4.13(m, 4H), 7.40(s, 2H), 7.48(s, 2H).

The detailed characterization of DMC and salen-Co(III) acetate were shown in Supporting Information Figures SI-2–SI-6.

Alternating Copolymerization of CO₂ and CHO

Alternating copolymerization of CO₂ and CHO was carried out in a 60 mL stainless steel autoclave equipped with a mechanical stirrer, and heated with heating jacket. Thirty mg DMC and 50 mg salen-Co(III) combined with 12 mg [PPN]Cl was dissolved in 10 mL CHO, stirred by a magnetic stirrer at room temperature for 5 min. The 10 mL DMC/salen-Co(III) catalyst solution was added *in situ* into the autoclave (salen-Co(III), homogenous; DMC, heterogeneous), followed by injection of another 10 mL CHO under vacuum. Temperature and pressures were then increased to 60 °C and 1000, 1500, 2000, 2500, and 3000 psi with stirring speed of 200 rpm. After 12 h reaction, the autoclave was cooled by dry ice from reaction temperature to 25 °C, depressurized and opened. Fifty milliliters of chloroform was used to dissolve the polymer product, and 200 mL methanol was added to precipitate and wash the obtained PCHC for three times. Then, the product was dried under vacuum at 55 °C for 12 h for further characterization.

Flushing Experiment

Five grams of PCHC (original copolymer without purification, obtained at 2000 psi and 60 °C) was added into a 60 mL stainless steel autoclave. ScCO₂ pressure was increased to 3000 psi and maintained for 5 min⁻¹. Open the decompression valve to release the pressure at a speed of 200 psi CO₂ s⁻¹. Meanwhile the CO₂ inlet valve was opened with a speed of 200 psi CO₂ s⁻¹ to maintain the scCO₂ pressure at 3000 psi of the flushing system. The PCHC was flushed for 15 min⁻¹ and then 2.0 g flushed PCHC was took out for further characterization. The PCHC left was flushed for another 15 min⁻¹ and then took out for further characterization.

Characterization Instruments and Methods

The selectivity, tacticity and polycarbonate linkage level were determined by using ¹H NMR and ¹³C NMR using a Bruker Avance 500 MHz with TMS as internal standard at 0 ppm

for ¹H NMR and against d-chloroform at 77.0 ppm for ¹³C NMR. The carbonate linkage content was calculated by ¹H NMR with the following equation:

$$W_{pc} = \frac{A_{4.71}}{A_{3.45} + A_{4.71}} \times 100\% \quad (1)$$

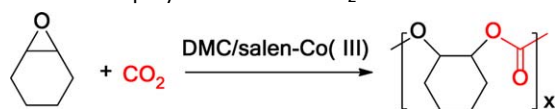
The weight percentage of Fourier transform infrared spectrometer (FTIR) with potassium bromide tablets were recorded on a Nicolet 6700 with scanning resolution of 4 cm⁻¹ and scanning speed of 10,000 Hz. The molecular weights (MW) and the dispersities ($\bar{D} = M_w/M_n$) of the copolymers were determined by gel permeation chromatography (GPC) on a GPC 50 from Polymer laboratories. The GPC columns were eluted with chloroform at 1.0 mL/min at 35 °C. The sample concentration was 0.3 wt % and the injection volume was 100 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular weight range from 580 to 460,000 Da. Glass transition temperature (T_g) was evaluated using Waters Q2000 differential scanning calorimeter from TA instruments at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 100 mL min⁻¹. Thermal gravity analysis (TGA) was used to detect thermal decomposition temperature using a TA Q500 SDT Thermal Gravimetric Analyzer from TA instruments (20–400 °C, under a protective nitrogen atmosphere of 100 mL min⁻¹ and a ramping rate of 20 °C min⁻¹). Elemental analyses was carried out by Vario Macro Cube—M336, which produced by Elementar Corporation of Germany. The physical properties of the polymer in scCO₂ were evaluated using an MCR Rheometer produced by Anton Parr Corporation (scCO₂ pressure: 1500, 2000, 2500, and 3000 psi, temperature: 60 °C). The concentration of catalyst residue in the polymer was determined by UV-Vis, using a Varian Cary 500 with acetone used as the solvent at room temperature.

RESULTS AND DISCUSSION

Copolymerization of CO₂ and CHO

ScCO₂ provides an ideal environment for the copolymerization, maximizing the concentration of CO₂ in the CHO and in the growing polymer phase and also facilitating good mass and heat transfer.^{34,35} The DMC/salen-Co (III) catalyst was deemed to be good choice to form the polycarbonate by alternating insertion of CO₂ and CHO. The DMC coordinates with the C—O bond of CHO central carbon while salen-Co(III) activates CO₂.^{36,37} (The copolymerization behaviors of individual DMC and salen-Co(III) under supercritical conditions were shown in Supporting Information Table SI-1)

The product PCHC was obtained under various conditions of pressure, temperature, and catalyst ratios (Table 1). At 1000 psi (145 psi = 1 MPa) CO₂ and 60 °C (subcritical conditions and low CO₂ density), the yield of obtained PCHC was 249–268 g polymer/g catalyst with only moderate carbonate linkage content of 59.2–60.8% to PCHC and MW of 0.87–0.91 × 10⁴ (\bar{D} : 4.61–4.78), which led to T_g of (74.8–79.6 °C) and T_{max} of (227.9–235.0 °C). When the pressure was raised, the CO₂ density increased and a significant improvement of

TABLE 1 Copolymerization of CO₂ and CHO Under Different Temperature, Pressure, and DMC/Salen-Co(III)/[PPN]Cl Ratio

Ratio of DMC/ Salen-Co(III)/[PPN]Cl	Temperature	Pressure ^d	Yield g Polymer/g Catalyst	Carbonate Linkages ^a	M_n^b	M_w^b	T_g^c	T_{max}^c	PDI
Molar Ratio	°C	psi		%	$\times 10^4$	$\times 10^4$	°C	°C	Đ
3:1:1	60	1000	249.1	60.5	0.19	0.91	77.3	227.9	4.78
3:1:1	65	1000	267.6	59.2	0.17	0.79	74.8	231.6	4.65
3:1:1	70	1000	268.5	60.8	0.17	0.78	79.6	235.0	4.61
3:1:1	60	1500	622.8	93.6	2.05	4.18	84.5	256.6	2.04
3:1:1	60	2000	656.5	92.9	1.82	3.30	90.8	263.4	1.81
3:1:1	60	2500	564.9	95.1	1.68	3.24	92.1	280.7	1.93
3:1:1	60	3000	434.2	93.5	1.99	4.13	114.5	285.5	2.07
3:1:1	50	2000	–	–	–	–	–	–	–
3:1:1	55	2000	246.2	92.7	1.52	2.81	91.7	263.8	1.85
3:1:1	65	2000	519.6	93.7	2.32	3.97	110.3	266.9	1.71
3:1:1	70	2000	450.3	94.8	2.14	3.63	112.6	273.2	1.70
3:1:1	75	2000	329.0	94.2	1.96	3.28	109.8	270.8	1.67
3:1.5:1.5	60	2000	499.4	94.9	2.05	3.42	109.5	283.1	1.67
3:2:2	60	2000	367.1	96.6	2.26	3.61	115.7	285.8	1.76
3:3:3	60	2000	237.4	98.7	2.67	4.29	118.6	290.3	1.61

^aCarbonate Linkages is calculated by integration of methine resonances in ¹H NMR of unrefined product (CDCl₃, 500 MHz), as shown in eq 1. Molar ratio of polymer and cyclic carbonate.

^b M_n and M_w are determined by GPC, calibrated with PMMA standards in CDCl₃.

^c T_g is determined by DSC, and T_{max} is determined by TGA.

^d145 psi = 1 MPa.

catalyst activity was observed with yield rising to 656 g polymer/g catalyst. In addition, selectivity toward polycarbonate linkages proved to be excellent with hardly any byproduct of PCHE generated during CO₂/CHO copolymerization. This led to a significant increase in the T_g rising to a maximum value of 114.5 °C. Enhanced carbonate linkages also yields higher thermal stability with a peak T_{max} of 285.5 °C.

From Table 1, it is clear that increasing the scCO₂ pressure from 1500 to 2000 psi resulted an improved activity to copolymer, but further increasing proved to be deleterious with a sharp decrease as the yield dropped down to 434 g polymer/g catalyst. A possible reason for this could be that the increased solvating power of the scCO₂, at increased pressure, led to dissolution of part or all of the DMC/salen-Co(III) catalyst taking it away from the locus of polymerization in a polymer-rich phase. Evidence for this is presented later in this article with demonstrable extraction of catalyst components from the final polymer product using scCO₂. This was somewhat counterintuitive since we had hypothesized that higher CO₂ pressure would provide better heat and mass transfer and would in fact facilitate increased catalytic activity and selectivity rather than deactivating the DMC/salen-Co(III) catalyst. However, although the yield

decreased, the carbonate linkage content, T_g and MW of the obtained PCHC were in fact all improved at the highest pressure 3000 psi.

The reaction temperature also had a significant influence on scCO₂/CHO copolymerization (Table 1). The yield jumped to 656 g polymer/g catalyst at 60 °C but then dropped sharply to 329 g polymer/g catalyst at 75 °C, owing to the degradation of DMC/salen-Co(III) catalyst (see Supporting Information Fig. SI-6), while the selectivity remained very similar (from 92.4 to 94.8%). Higher temperature and scCO₂ pressure both strongly facilitate the formation of polycarbonate units of PCHC and hence an increase of MW, T_g and T_{max} . At lower temperature, almost no polymer was obtained at 50 °C because the catalyst system did not become active until 55 °C. From 55 to 75 °C, the selectivity toward carbonate linkage increases significantly from 89.2 to 95.5%.

However, the PCHC obtained at various scCO₂ pressures and reaction temperatures showed that scCO₂ pressure and reaction temperature influenced significantly the level of carbonate linkage (Table 2) and hence raised T_g . These data were in accordance with previous publications, demonstrating the effect of lowering concentration of CO₂.^{38,39} Comparing to the low copolymerization temperature of salen-Co(III), the

TABLE 2 Influence of Different Reaction Pressures and Temperatures on Carbonate and Ether Linkage

Pressure psi	Temperature °C	Carbonate Linkage %	Ether Linkage %
1,000	60	60.4	39.6
1,500	60	90.9	9.1
2,000	60	93.7	6.3
2,500	60	95.7	4.3
3,000	60	96.8	3.2
2,000	55	89.2	10.8
2,000	65	95.4	4.6
2,000	70	95.5	4.5
2,000	75	95.0	5.0

optimum temperature of 60 °C is a good balance for the best activity and selectivity as DMC catalyst tends to require a higher temperature of 60–100 °C.²²

Another key controlling factor was the combination of DMC and salen-Co(III) catalysts. Different ratios of DMC and salen-Co(III) catalyst provided evidence that each individual part of the DMC/salen-Co(III) catalyst showed different catalytic trends (Table 1). For example, at a DMC: salen-Co(III) ratio of 3:1 the yield peaked at 656 g polymer/g catalyst with selectivity toward polycarbonate linkage approaching 92.9% and polymer molecular weight of 3.30×10^4 Da. However, increasing the ratio of salen-Co(III) (3: 1.5), decreased the yield to 237 g polymer/g catalyst but with increased selectivity of 98.7%. These results illustrate that DMC has a strong impact on activity and salen-Co(III) appears to control selectivity as has been noted elsewhere.^{4,15}

Our data also show that scCO₂ plays an important role during scCO₂/CHO copolymerization process by conferring excellent mobility, mass transfer, and high CO₂ concentration and likely creates a near homogeneous environment in the polymer-rich phase (vide infra) preventing CHO from copolymerizing with itself to form the unwanted byproduct polyether linkages.

Characterization of Copolymer PCHC Physicochemical Properties and Rheology of PCHC in scCO₂

To further probe the polymerization process under pressure, we utilized a view cell (a high-pressure autoclave with two windows) to observe the reactions (Fig. 1). DMC has been described as a heterogeneous catalyst whereas the salen-Co(III) system was considered to be homogeneous.¹⁷ The data we present clearly demonstrate that as a combined pair, the reaction characteristics of high yield and selectivity exceeded the values that each individual component can deliver, thus showing a possible synergistic effect.⁴⁰

When the catalyst was exposed to scCO₂ and CHO, both salen-Co(III) and DMC components appeared to dissolve in a CO₂ expanded monomer/polymer-rich phase. To understand the progress of the polymerization we evaluated the behavior of the PCHC product alone in scCO₂ (Fig. 1). From the coloring of the liquefied polymer sample, it was obvious that of some of the catalyst was still present in the polymer, and remained in the CO₂ expanded polymer phase. UV experiments presented later in the article show how such residual catalyst could be removed using scCO₂.

At ambient pressure and 60 °C, the PCHC was a light yellow solid. As CO₂ was introduced up to 800 psi the PCHC was partially liquefied (softened) as a small amount of CO₂ was

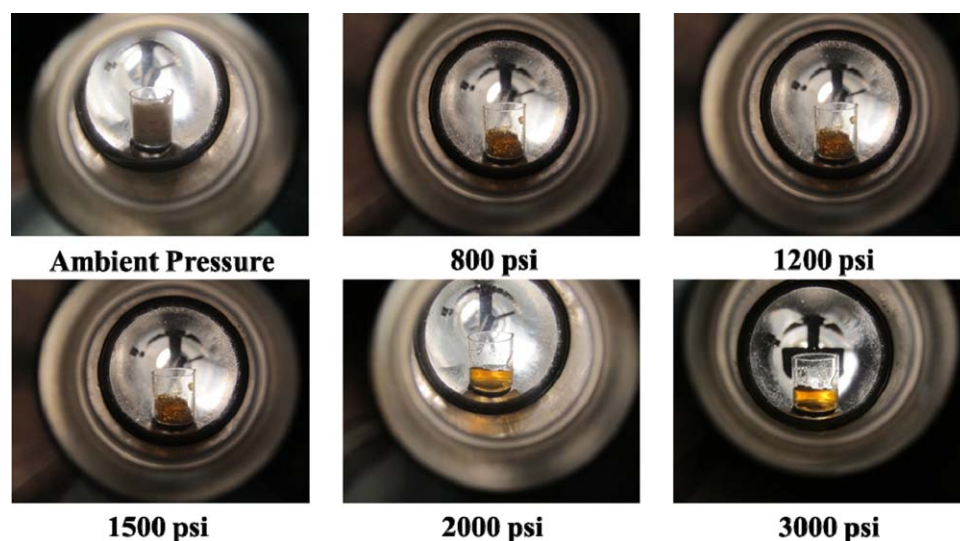


FIGURE 1 Behavior of PCHC under different pressures of CO₂ at a constant temperature of 60 °C. The data clearly show that CO₂ dissolves into the PCHC but only at 1500 psi do we begin to see any effect. At 2000 psi the polymer is completely liquefied. Note that in the reaction system we would see the same behavior—with a liquefied polymer-rich phase in which the polymerization reaction would be located. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

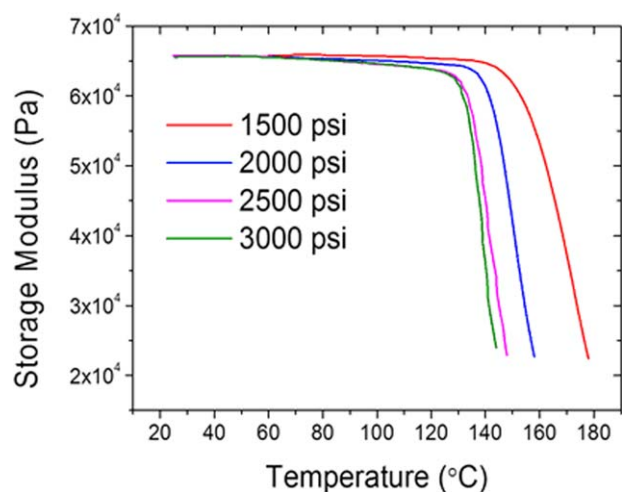


FIGURE 2 Temperature sweeps of PCHC using a high pressure rheometer showed that increasing scCO_2 pressure decreases glass transition temperature (as shown by the significant drop in storage modulus) and therefore had a strong effect upon the formed PCHC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbed. Increasing the pressure to 1500 psi appeared to have no immediate effect on the PCHC. However, when the pressure was raised to 2000 psi the PCHC completely liquefied presumably due to a sharp rise in CO_2 solubility in the polymer under these conditions. We speculate that under the reaction conditions the PCHC would be formed in a PCHC/ CHO/CO_2 phase and that the majority of the catalyst remained in this phase. Thus, the liquefaction of this phase provides a significant mass and heat transfer advantage that translates into improved reaction efficiency.

Most importantly, we showed that scCO_2 plasticizes the growing PCHC and lowers the viscosity ensuring good mass transfer and significantly lowering the viscosity of the growing polymer system and overcoming the issue of fouling of the autoclave stirrer which we found to be prevalent at low pressure and in the absence of scCO_2 .

The strong effect of scCO_2 on the PCHC was also demonstrated by the significant lowering of the T_g as measured using a modular compact rheometer. Temperature sweeps were performed on the synthesized PCHC to determine the effect of CO_2 on thermal transitions (Fig. 2) with increased pressure. The absolute values obtained were higher than those obtained by DSC, likely because of thermal lag caused by the geometry of the measurement. However, the data certainly correspond to the trend observed in the view cell experiments, where increasing the pressure from 1500 to 2000 psi had a significant effect on liquefying the PCHC (Fig. 1). In combination these factors led to a reaction system that was able to show significantly higher yield and selectivity of the DMC/salen-Co(III) catalyst, as well as higher MW and T_g of PCHC (See Table 1).

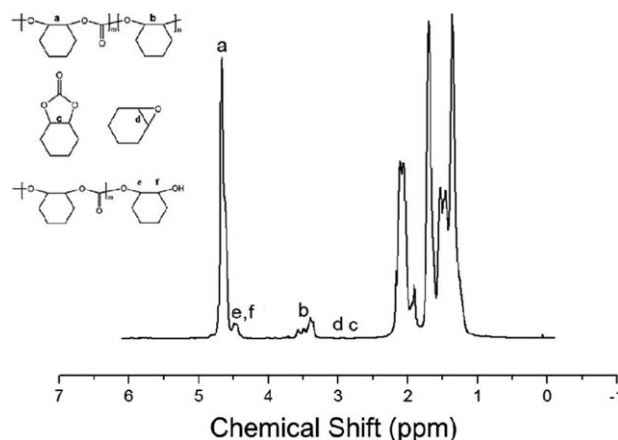


FIGURE 3 ^1H NMR spectra of PCHC obtained in scCO_2 (2000 psi, 60°C , 12 h). The integral of characteristic proton and other protons was very close to 1:4 (proton a: proton g).

PCHC Structure and Selectivity Toward Polycarbonate

^1H NMR confirmed that the PCHC obtained was predominantly formed of polycarbonate linkages in particular via the peaks at $\delta = 4.71$ ppm (Fig. 3 structure a). While a peak at $\delta = 3.45$ ppm was associated with the presence of small amounts of polyether (Fig. 3, structure b). The absence of a peak at a $\delta = 4.08$ ppm demonstrated that there was almost no backbiting processes leading to formation of the known byproduct cyclohexene carbonate (structure c).²² The NMR integrals concurred with the values we might expect for pure PCHC.

These data were further supported by ^{13}C NMR spectra (Fig. 4). The peaks at $\delta = 154.30$ – 154.06 ppm and $\delta = 153.51$ – 153.39 ppm can be ascribed to the isotactic and syndiotactic structures of the PCHC chain respectively (Fig. 7), allowing estimation of the tacticity of the polymer.⁴¹ Through

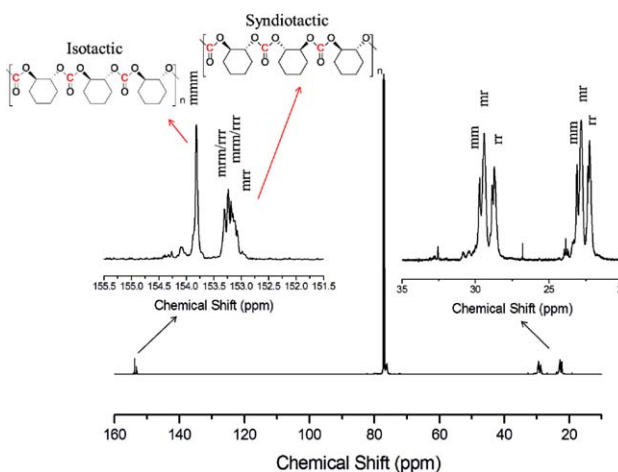


FIGURE 4 ^{13}C NMR spectra of PCHC obtained under scCO_2 (2000 psi, 60°C , 12 h). The data clearly show the presence of both isotactic and syndiotactic PCHC present in the final polymer product. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

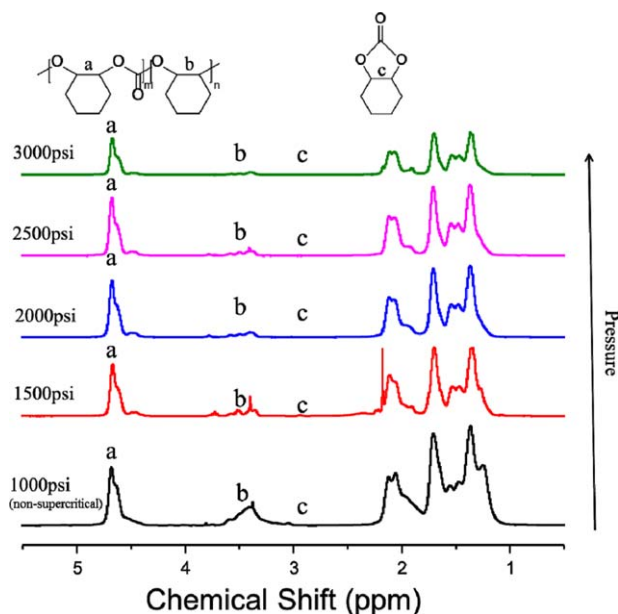


FIGURE 5 ^1H NMR spectra demonstrate the formation of both the main product PCHC (peak a) and the by-product PCHE (peak b). At higher scCO_2 pressures the PCHE content significantly decreases. (reactions conducted at $60\text{ }^\circ\text{C}$, 12 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

assignment of the sole contribution of r-centered tetrads ([rrrr], [rrm], [mrm]) were at $\delta = 153.9$ ppm, conversely the peaks at $\delta = 153.7$ ppm were assigned to the central carbonyl carbons of m-centered tetrads ([mmm]),^{42–45} with a series of lower intensity resonances at $\delta = 153.3$ – 153.1 ppm. The nonequivalent methylene carbons in the PCHC backbone at $\delta = 29.8$ and 23.2 ppm, corresponding to the mm triad, as reported in the literature.⁴⁶ The chain structure from the scCO_2 synthesized PCHC shows us that the combined DMC/salen-Co(III) catalyst system has poor stereo-control over CHO insertion into the main polymer chain,¹⁵ comparing to the obtained PCHC with 81% r-centered tetrads was obtained in Coates' work.¹⁷

^1H NMR spectra showed the very strong effect of CO_2 pressure upon the polymer produced (Fig. 5). The peak present at $\delta = 3.45$ ppm is attributed to the byproduct polyether and $\delta = 4.71$ ppm to the desired polycarbonate linkage. The data clearly show that carbonate linkage increases with CO_2 pressure and, the byproduct PCHE has almost disappeared at 3000 psi. These observations were also reinforced by DSC analysis discussed earlier (Table 1) which demonstrated increased T_g with the increase of the scCO_2 pressure. Again, the results could be explained by the enhancement of salen-Co(III) activity in the presence of a higher concentration of CO_2 .^{4–10} In CO_2/CHO copolymerization, the DMC catalyst dominates the ring-opening reaction of CHO, while the activation rate of CO_2 is slow, and hence, at low concentrations of CO_2 the activated CHO tends to coordinate with another CHO to form the unwanted byproduct PCHE. However, this

limitation appears to be removed under scCO_2 , likely because of the high concentration of CO_2 at the locus of polymerization and the catalyst system clearly delivers alternating copolymer PCHC at higher CO_2 concentrations.^{4–10} These same advantages also account for the increase in MW and narrower dispersity (Fig. 6) that is observed with increasing pressure. As shown in Table 1, PCHC obtained at 1000 psi CO_2 pressure has low MW and wide dispersity, and a high level of PCHE. A possible reason is that the DMC and salen-Co(III) catalyst were in different phase and the active sites could not synergize to form alternating copolymer. Large amount of low MW amorphous PCHE (selectivity toward ether units: 39.5%) was obtained as a result, broadening the MWD, especially in the low MW region. Moreover, 60.5% selectivity toward high MW polycarbonate retains the peaks of high MW part. Consequently, the MWD broadened compared to the uniform PCHC with high MW obtained under supercritical condition (selectivity toward carbonates: $>92\%$). Comparing to the narrow PDI (<2) obtained by salen-Co(III) catalyst in Coates' work,¹⁷ the reason for the broadening of obtained PDI in this work was mainly due to the use of DMC catalyst. In addition, we proposed that scCO_2 affected the chain transfer rate exceeding the chain growth rate of PCHC.

NMR analyses clearly show that ratio of carbonate to ether linkage has a strong impact on the T_g and T_{max} of PCHC⁴⁷ (Fig. 7). Table 1 shows that the T_g varies from 84.5 to 114.5 $^\circ\text{C}$ with increase of reaction pressures and temperatures. In addition T_{max} also increased, again in accordance with the increased carbonate linkage content (90.9–96.8%).

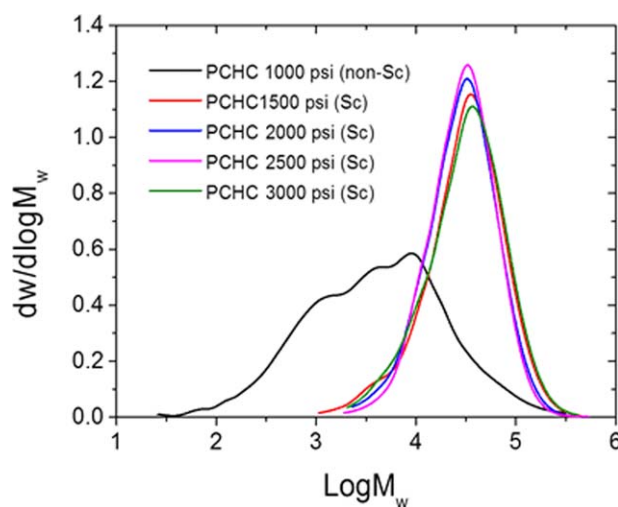


FIGURE 6 GPC traces of PCHC formed under various conditions. Very clearly the data showed that increased pressure led to higher quality polymer. (Reaction pressure: 1000, 1500, 2000, 2500, 3000 psi; reaction temperature: $60\text{ }^\circ\text{C}$, reaction time: 12 h) Key: Sc = supercritical, non-Sc = non-supercritical. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The residue of DMC/salen-Co(III) catalyst in the PCHC product was investigated by UV-VIS spectroscopy (see Supporting Information Fig. SI-10). scCO_2 extractions were carried out on the polymers prepared in our experiments to investigate if scCO_2 could extract the DMC/salen-Co(III) catalyst from PCHC and purify the obtained polymer *in situ*. The results clearly show that part of the combined DMC/salen-Co(III) dual catalyst was removed by scCO_2 and that this method provides a potential opportunity to treat the polymer products *in situ* by using scCO_2 to remove residual catalyst (Fig. 8). In addition, the data also provided an explanation for why a decrease of DMC/salen-Co(III) catalyst activity was observed at pressures greater than 2000 psi. The data clearly show that under these conditions the combined DMC/salen-Co(III) dual catalyst was partially dissolved and hence transferred to the CO_2 -rich phase—away from the locus of polymerization in the liquefied polymer-rich phase—effectively taking some of the catalyst out of the polymerization system. The use of methanol is not ideal, but

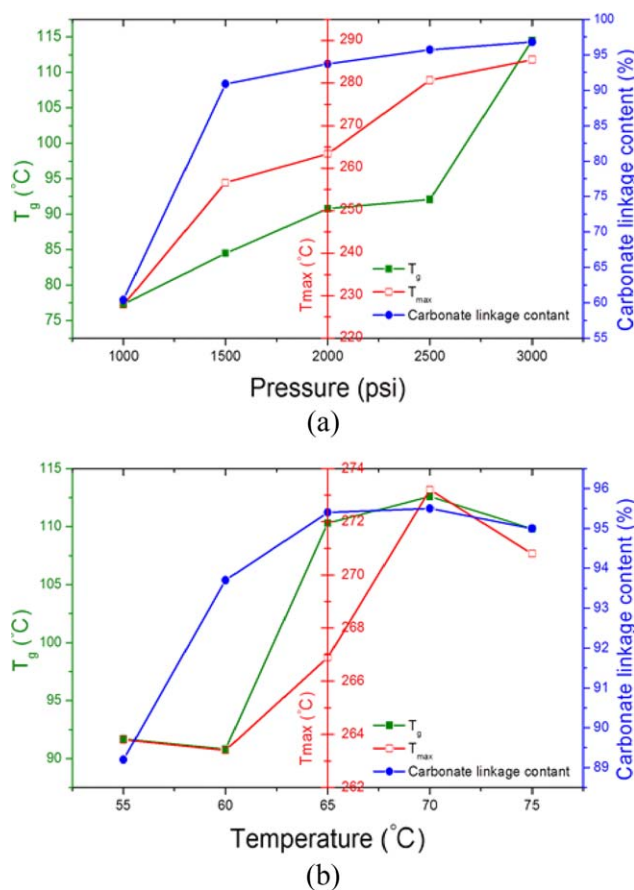
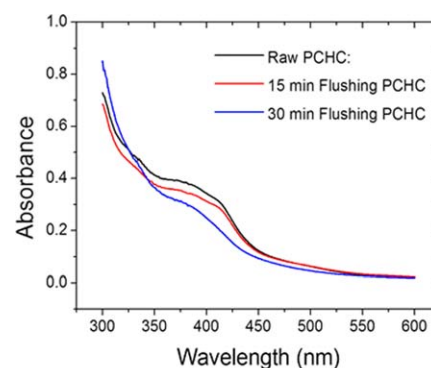


FIGURE 7 The evolution of carbonate linkage (as measured by NMR) and the effect upon T_g and T_{max} at: (a) various reaction pressures (reaction temperature: 60 °C) and (b) various temperatures (reaction pressure: 2000 psi). (CL = Carbonate Linkage) Increasing and decreasing trend of T_g and T_{max} closely associated with carbonate linkage content of PCHC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



PCHC	Absorbance Responses	Catalyst Concentration mg	Catalyst Reclamation mg
Raw	0.39	39.0	-
15 min Flushing	0.36	31.5	7.5
30 min Flushing	0.31	28.5	3.0

* PCHC was achieved at 60 °C, 2000 psi scCO_2 pressure and the reaction time of 12 h.

FIGURE 8 UV-VIS spectrum of combined DMC/salen-Co(III) dual catalyst residual in raw PCHC, the PCHC flushed by scCO_2 for 15 and 30 min. The data clearly show that scCO_2 can remove the combined catalyst from the PCHC polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was most practical and reliable at the time. Our future aim will be to use just scCO_2 and in a one pot process—but this will require considerable further development and also we must ensure the safety of a larger scale 200 mL scCO_2 process.

CONCLUSIONS

In summary, we show that scCO_2 effectively facilitates the heat and mass transfer of CO_2/CHO copolymerization. This supercritical reaction system has potential value for industrial application. The PCHC polymer product obtained in scCO_2 shows high MW, T_g , T_{max} , and narrow dispersity. Our data show that the reaction is controlled by both temperature and pressure and that these factors strongly influence the polymer-rich phase which is significantly swollen by CO_2 both reducing viscosity and providing a high concentration of CO_2 for CO_2/CHO copolymerization. These factors enhance mass and heat transfer to facilitate polymer chain growth rather than polymer chain transfer; as observed by the very low PCHE formation. scCO_2 did not significantly enhance stereocontrol as measured by polymer tacticity. Finally, along with the clear enhancements of the polymerization we also demonstrate that scCO_2 postprocessing could be exploited to remove the DMC/salen-Co(III) catalyst *in situ* and provide a cleaner methodology for work up of the final copolymer product.

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