



The Copolymerization of CO₂ and Cyclohexene Oxide, Catalyzed by a Tridentate Schiff Base Chromium(III) Complex

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Abstract

The catalytic copolymerization reaction of carbon dioxide and cyclohexene oxide (CHO) using the single-site chromium(III) Schiff base catalyst, [Cr(k³-C₂₄H₂₉NO₂)Cl] (complex 1) has been investigated according to gravimetric, IR and NMR spectral and GPC analysis of the resulting poly(cyclohexene carbonate) polymers (PCHC). Typical copolymerization reactions were carried out in bulk CHO monomer, utilizing a 25- ml stainless steel autoclave reactor, pressurized to 52 bar in CO₂ and maintained at 80°C. Complex 1 proved to be selective toward production of polymer and exhibited an average turnover frequency of TOF = 12.8(±1.1) hr⁻¹. Nevertheless, limited CO₂ incorporation was observed, resulting in polymers that were ~40-50% polycarbonate at most. Introduction of a neutral phosphine (tricyclohexylphosphine, PCy₃) was observed to increase CO₂ incorporations to as high as 82% based on ¹H NMR analysis. GPC analysis showed the polymers exhibited number-average-molecular-weights with a mean value of Mn = 2.6(±0.4) kDa under optimal copolymerization conditions (with 1 equivalent PCy₃ relative to chromium) and fairly broad molecular weight distributions with polydispersity indices (PDI) ranging from 3.6 to 12.0.

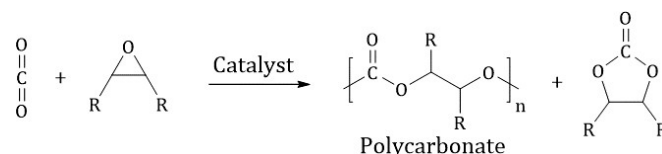
Keywords: CO₂ Capture; CO₂ Utilization; CO₂ Epoxide Copolymerization; Polycarbonate; Homogeneous Catalysis

Abbreviations: Carbon Dioxide (CO₂); Cyclohexene Oxide (CHO); (1S,2R)-1-[(3,5-di-tert-butyl salicylidine)imino]-2-indanol (H₂L); 1-[(3-tert-butyl-5-bromosalicylidine)imino]-2-indanol (H₂L'); Turnover Frequency (TOF); Poly(cyclohexene carbonate) (PCHC); Tricyclohexylphosphine (PCy₃); Polydispersity Index (PDI)

Introduction

Carbon dioxide has long been considered a major contributor to climate change due to its behavior as a “greenhouse gas” and its accumulation in the atmosphere [1]. Indeed, atmospheric CO₂ levels have increased from approximately 315 ppm in 1960 to 415.67 ppm as of February 10, 2020 [2]. Further, the rise in anthropogenic CO₂ emissions is expected to continue and to expand over the next several decades [1]. One of the possible measures which may mitigate this growing problem is CO₂ capture and utilization [1, 3-8]. In this context, the use of CO₂ as a renewable, raw material holds tremendous potential and has, therefore, been a goal of synthetic chemists for many years [9-11]. For these reasons, the metal-catalyzed coupling of CO₂ and epoxides to produce cyclic carbonates [12-15] and polycarbonates [16-32] is the subject of considerable

interest (Scheme I). This is particularly so in the preparation of aliphatic polycarbonates as possible alternatives to petrochemical materials in end uses such as films, packaging and rigid plastics applications [33].



Scheme I: Catalytic coupling of CO₂ and epoxides to form polycarbonate.

Most of the early work in the catalytic coupling of CO₂ and epoxides focused on zinc compounds [25, 34-39] stemming from

Inoue's findings in 1969 [40]. Since then, several other metals have been reported for this application. Among these are numerous chromium (III) and cobalt (III) coordination compounds based on the well-known Schiff base "salen" ligand and derivatives thereof (salen = N, N'-bis (salicylidene)-1, 2- ethylene diamine). The first example of a chromium (III) salen catalyst used for the copolymerization of CO₂ and epoxides was reported in the patent literature by Jacobsen and coworkers [41]. In this account, there was little reported in the way of relevant details regarding copolymerization beyond stating that poly(propylene carbonate) was prepared under 1 atm CO₂. Independently, and unaware of the work detailed in patent literature, Darensbourg and Yarbrough, inspired by Jacobsen's work on asymmetric epoxide ring-opening, reported the use of a salen chromium(III) chloride catalyst which exhibited high activity toward copolymerization of CO₂ with CHO, resulting in polymer with very uniform molecular weight distributions [42]. Around this same time Nguyen and coworkers at Northwestern University independently reported similar results with Jacobsen's salen chromium (III) chloride catalyst [43]. This sparked a new direction in the investigation of CO₂/epoxide copolymerization from zinc to chromium (III) and cobalt (III) salen and porphyrin catalysts and related derivatives. Indeed, these have become the basis for nearly all of the CO₂/epoxide work conducted since 2001 as detailed in the literature, including numerous comprehensive reviews on the subject [17, 30, 39, 44-52].

In spite of the inherent versatility in the synthesis of Schiff base ligands, tetra dentate salens, porphyrins and their derivatives represent the bulk of the chromium (III) and cobalt (III) catalysts employed for this purpose [46]. Relatively few chromium species have been investigated with markedly different ligand architectures. Notable exceptions include the work of Duchateau and coworkers concerning the use of chromium(III) iminopyrrole, aminopyrrole and aminophosphine complexes [53] as well as that of Kazak and coworkers who have developed chromium(III) diaminebisphenolate catalysts for this purpose [54]. Here in we report the activity toward CO₂/CHO copolymerization of a chromium(III) catalyst using a tridentate Schiff base ligand, (1S,2R)-1-[(3,5-di-*tert*-butylsalicylidene)imino]-2-indanol (H₂L) the synthesis of which has been published previously [55,56]. We report its effectiveness as a catalyst for the bulk, solvent less copolymerization of CO₂ and CHO with and without the assistance of a neutral phosphine donor, tricyclohexyl phosphine (PCy₃).

Materials and Methods

Unless otherwise indicated, all manipulations were carried out under inert conditions using standard Schlenk and dry box techniques. Additionally, all reagents were purchased from Sigma Aldrich and used as received unless otherwise stated. Prior to use, THF was distilled from sodium/benzophenone ketyl still and stored over 3 Å molecular sieves. CHO was purchased from Across

Organics and freshly distilled over CaH₂ prior to use. Sure/Seal™ a hydrous ethanol was purchased from Sigma Aldrich and used as received. The ligand (1S, 2R)-1-[(3,5-di-*tert*-butylsalicylidene)imino]-2-indanol, C₂₄H₃₁NO₂(H₂L) was purchased from Sigma Aldrich and used as received. Complex 1, [Cr(k3O,N,O-L)Cl] was prepared according to a previously published procedure [56]. All 1H and 13C NMR spectra were recorded using a Bruker Avance III HD Spectrometer (Ascend™400 Magnet) at ambient temperature. FTIR spectra were recorded on a Nicolet iS5 spectrometer. Much of the syntheses and data collection described herein was recently reported in the MSc. Thesis of Adrian Pap at West Texas A&M University [57]. GPC analysis was performed by EAG Laboratories (Maryland Heights, MO, USA).

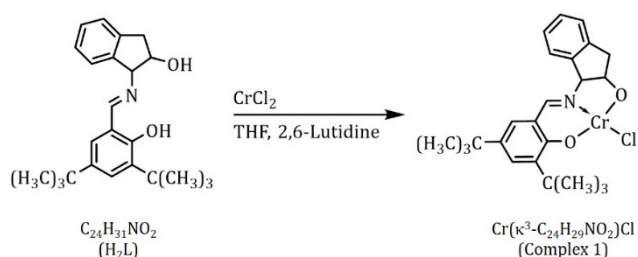
Typical Copolymerization of CO₂ and Cyclohexene Oxide

In a typical copolymerization experiment approximately 11-12 g of freshly distilled CHO monomer is charged into a 25-ml, stainless-steel reactor equipped with a magnetic stirring bar, a two-way inlet valve and a pressure gauge. To this, an appropriate amount of complex 1 (typically 15 mg) is added along with tri cyclohexylphosphine (typically between 0 and 18 mg). The reactor is then sealed, removed to a fume hood, connected via inlet valve to a purged, "bone dry" CO₂ line and placed in a temperature-controlled oil bath. The reactor is then pressurized to approximately 34.5-37.5 bar in CO₂ and heated to temperature (typically 80°C). At 80°C a pressure of approximately 50-57 bar is achieved. The reactor is then maintained at these conditions with stirring for a reaction time of 17-18 hours. Following each copolymerization a small aliquot to the crude reaction mixture is removed and analyzed by FTIR spectroscopy to determine the presence of either polycarbonate (ν(CO₂) = 1742-1748 cm⁻¹) or the cyclic carbonate, 7,9-dioxabicyclo[4.3.0]nonan-8-one (ν(CO₂) = 1802 cm⁻¹). The reaction mixture is then diluted in dichloromethane and precipitated in cold methanol and the crude polymer is then dried in vacuo to constant mass to determine turn over numbers and frequencies and analyzed by 1H and 13C NMR spectroscopies.

Results and Discussion

The ligand (1S, 2R)-1-[(3, 5-di-*tert*-butylsalicylidene) imino]-2-indanol, C₂₄H₃₁NO₂ (H₂L) contains 2 chiral centers at the first and second position of the indanol moiety and can be prepared according to a previously published procedure [56]. As such, a chiral ligand environment may be a source of stereo control in the ring-opening and enchainment of the CHO monomer during polymerization. A point of investigation described later in this treatment. Complex 1, [Cr(k3O, N, O-L)Cl], was readily synthesized from the ligand, H₂L, as described previously in the literature and depicted in Scheme II [56]. The reaction of H₂L with 1 equivalent of CrCl₂ produced the dark brown, air-stable catalyst (complex 1) in reasonable yield. Further, a previously published XRD characterization of an analogous compound reported by Jacobsen

and coworkers in the same 2002 publication[56], exhibited two hexacoordinate, octahedral chromium(III) ions in a dimeric complex $[\text{Cr}(\text{H}_2\text{O})(\text{k}3\text{-O,N,O-m-O-L})\text{Cl}]_2$ (wherein $\text{H}_2\text{L}' = 1\text{-}[(3\text{-tert-butyl-5-bromosalicylidine})\text{imino}]\text{-2-indanol}$, $\text{C}_{20}\text{H}_{22}\text{NO}_2$) [56]. Given the preference of Cr (III) for octahedral coordination geometry, this structure provides sound precedent for the suggestion of a dimeric structure for complex 1 in the solid state. However, to our knowledge, no structural determination of complex 1 has yet been reported in the literature.



Scheme II: The synthesis of Complex 1, $[\text{Cr}(\text{k}3\text{-C}_{24}\text{H}_{29}\text{NO}_2)\text{Cl}]$, was carried out according to the procedure reported by Eric Jacobsen and coworkers in 2002[56].

Complex 1 proved to be reasonably effective toward CO_2/CHO copolymerization (Scheme III) as indicated by the results detailed in Table 1. Typical copolymerizations were carried out with 7–15 mg complex 1, in bulk CHO monomer at 80°C , and at ~ 52 bar in CO_2

in a stainless-steel reactor, equipped with a magnetic stir bar and pressure gauge. Following each copolymerization reaction, the product was precipitated in cold methanol or hexane. The crude solid polymer precipitate was collected and dried in vacuo to constant mass, which was then used to calculate the turnover frequencies reported in Table 1. Complex 1 initially exhibited a turnover number of 236 mol $\text{CHO}/\text{mol Cr}$ and a corresponding turnover frequency (TOF) of 13.9 hr^{-1} (Table 1, entry 1). Further, following each polymerization and prior to isolation of the PCHC product, a sample of the crude reaction mixture was taken and analyzed by FTIR spectroscopy (in CH_2Cl_2) to determine the extent of cyclic carbonate formation. Based on the FTIR data, complex 1 appeared to be nearly 100% selective toward the production of polymer under the reported reaction conditions as evidenced by the intense absorbance observed at approximately $1742\text{--}1748 \text{ cm}^{-1}$ as seen in the FTIR spectrum illustrated in Figure 1. This is assigned to the $\nu(\text{C}=\text{O})$ stretching frequency of poly(cyclohexene carbonate) [45]. Very little if any signal was observed for the corresponding band assigned to the cyclic carbonate, 7,9-dioxabicyclo[4.3.0]nonan-8-one, at 1802 cm^{-1} (Figure 1). Additionally, selectivity toward polymer was further supported by the absence of the chemical shift assigned to the methine protons of the cyclic carbonate ($\delta = 3.99 \text{ ppm}$) in the ^1H NMR spectra recorded for the crude PCHC samples produced by complex 1 (Figure 2).

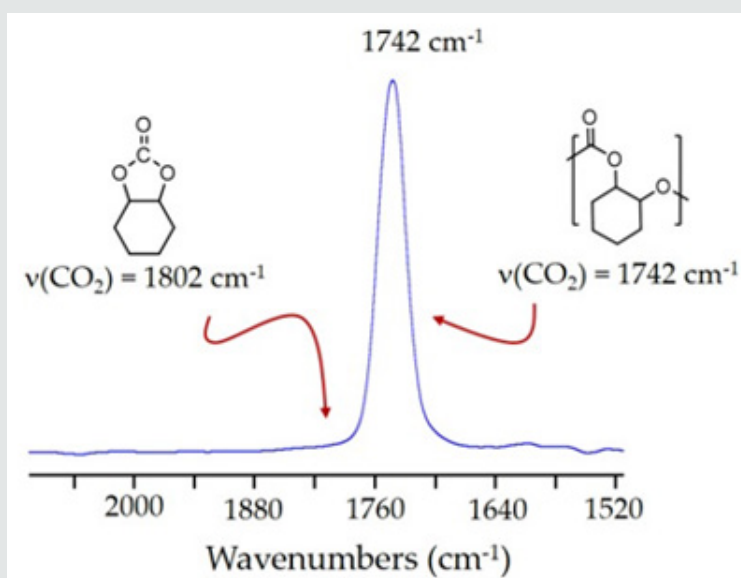
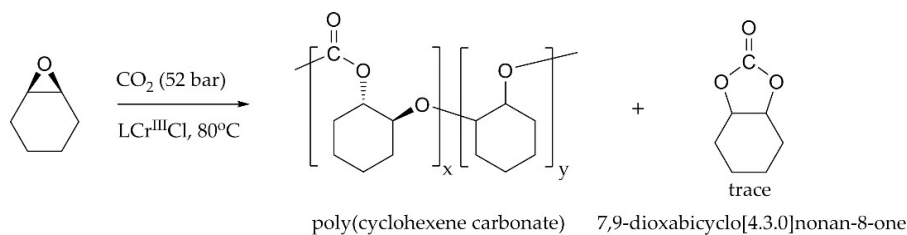


Figure 1: The $\nu(\text{C}=\text{O})$ region in a representative solution FTIR spectrum of poly(cyclohexene carbonate) prepared from copolymerization of CO_2 and CHO mediated by complex 1.

a Amounts of PCy_3 are given in molar equivalents relative to chromium. *b* The turnover frequency is reported as moles of CHO consumed per mole of chromium per hour. *c* CO_2 incorporation is determined by ^1H NMR spectroscopy. *d* GPC analysis was

conducted in THF against narrow molecular weight polystyrene standards. *e* The reactor pressure was observed to have reduced to ambient during the polymerization and the resulting polymer was predominantly CHO homopolymer.



Scheme III: The Copolymerization of CO₂ and cyclohexene oxide, mediated by complex 1. All polymerizations were performed in a 25-ml stainless steel reactor equipped with magnetic stir bar, at 80°C and under ~52 bar CO₂.

As suggested in Scheme III, the coupling of CO₂ and CHO at a ratio of 1:1 during the polymerization reaction is necessary for the realization of a purely polycarbonate product. The relative CO₂ incorporation in a particular polymer sample is determined by ¹H NMR spectroscopy and taken based on relative integrations of the methine chemical shifts centered at δ = 4.6 ppm and δ = 3.4 ppm corresponding to carbonate and ether linkages respectively (Figure 2) [45]. While there is some variability concerning CO₂ incorporation in the polymers reported here in, the result is noteworthy of remark. The initial CO₂ incorporation observed for polymers produced using complex 1 as a catalyst was approximately

~40-50% relative to CHO monomer enchainment (Table 1, entries 1 and 2). However, given the precedent in the literature for the use of N-heterocyclic amines, bulky phosphines (Tolman cone angles - 145°-185°)[58] and anions derived from PPN⁺, as well as R₄N⁺ salts[59-62], in concert with chromium (III) salen catalysts, we embarked on a study of the effect of the addition of various levels of tricyclohexylphosphine (PCy₃) on CO₂ incorporations as well as turnover frequency for the polymerizations mediated by complex 1. What was observed was a marginal impact on TOF but a significant effect on CO₂ incorporation.

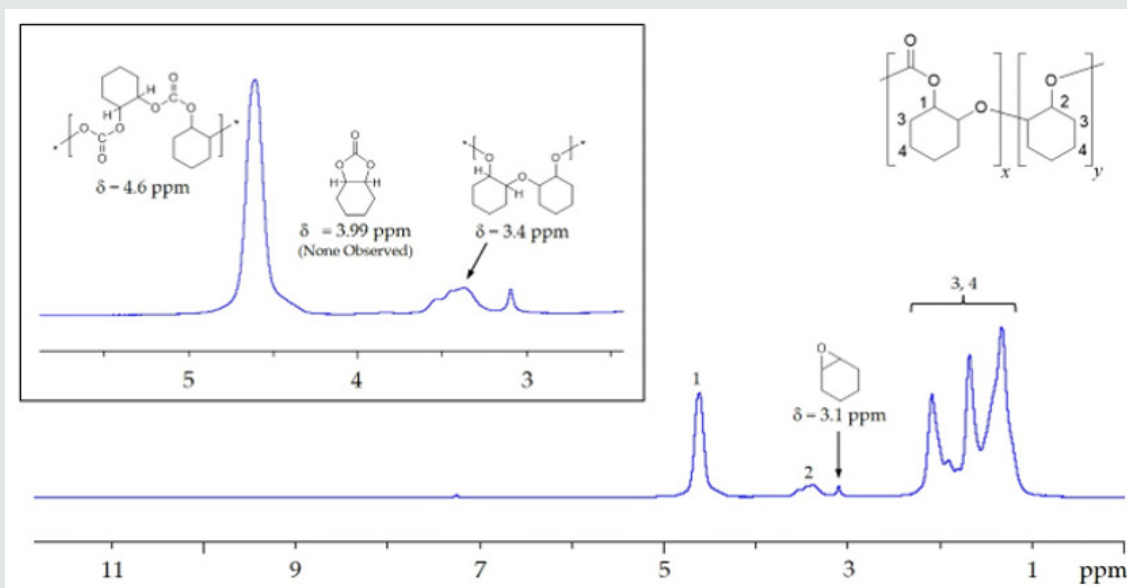


Figure 2: Are representative ¹H NMR spectrum of poly (cyclohexene carbonate) prepared from copolymerization of CO₂ and CHO mediated by complex 1.

Table 1: Results of the copolymerization reactions of cyclohexene oxide and carbon dioxide catalyzed by complex 1.

Entry	Catalyst (mg)	CHO/Cr Ratio	PCy ₃ a(eq.)	Yield (g)	TOF ^b (hr ⁻¹)	%Carbonate ^c	Mn ^d (kDa)	PDI ^d
1	7	7800:1	0	0.439	13.9	49	1.1	12
2	16	3160:1	0	0.867	11.7	42	3.6	5.1
3e	30	3340:1	0	1.85	13.8	31	---	---
4	15	3260:1	0.5	0.699	9.6	55	---	---
5	15	2590:1	0.5	0.626	9.1	54	1.1	5.3
6	15	3530:1	1	0.592	7.4	82	3	3.6

7	15	3790:1	1	0.582	7.9	73	2.2	3.7
8	16	3310:1	1	0.563	6.7	75	---	---
9	15	3450:1	1.5	0.5	6.3	80	1.2	5.2
10	15	3560:1	1.5	0.62	8.5	70	---	---
11	16	3390:1	1.5	0.488	6.3	69	---	---
12	15	3640:1	2	0.519	7.1	73	---	---
13	15	3590:1	2	0.676	9.4	66	0.6	4.1
14	15	3410:1	2	0.65	8.9	73	1	4.3

As the addition of PCy₃ was increased, in successive polymerizations, from 0 to 2 molar equivalents relative to chromium, CO₂ incorporation was observed to increase from an average of 45.5(±3.5)% with no added phosphine (Table 1; entries 1 and 2), to 76.7 (s=3.9)% at 1eq. PCy₃ (Table 1; entries 6, 7 and 8), and as high as 82% in one instance (Figure 3). However, there appears to be no statistically significant change in the CO₂ incorporation with additional PCy₃ beyond 1 equivalent (Figure 4). While there is insufficient data for a definitive conclusion regarding mechanism, these observations are consistent with literature accounts which describe the direct attack of a single PCy₃ molecule on a bound, activated CHO molecule, generating an activated,

zwitterionic species [17, 39]. It is this species which can then bind the metal through its alkoxide oxygen donor, thus providing steric and electronic influence over the mechanism of CO₂ insertion and CHO enchainment. Darensbourg and coworkers have provided a detailed description of this mechanism in the literature concerning both Cr (III) and Co (III) salen catalysts [17, 39]. On such a basis, it isn't necessarily surprising that additional phosphine (beyond 1 equivalent) would have little additional impact on CO₂ incorporation, as the bulk of the CHO homopolymerization would likely occur prior to activation of the zwitterionic, phosphonium species.

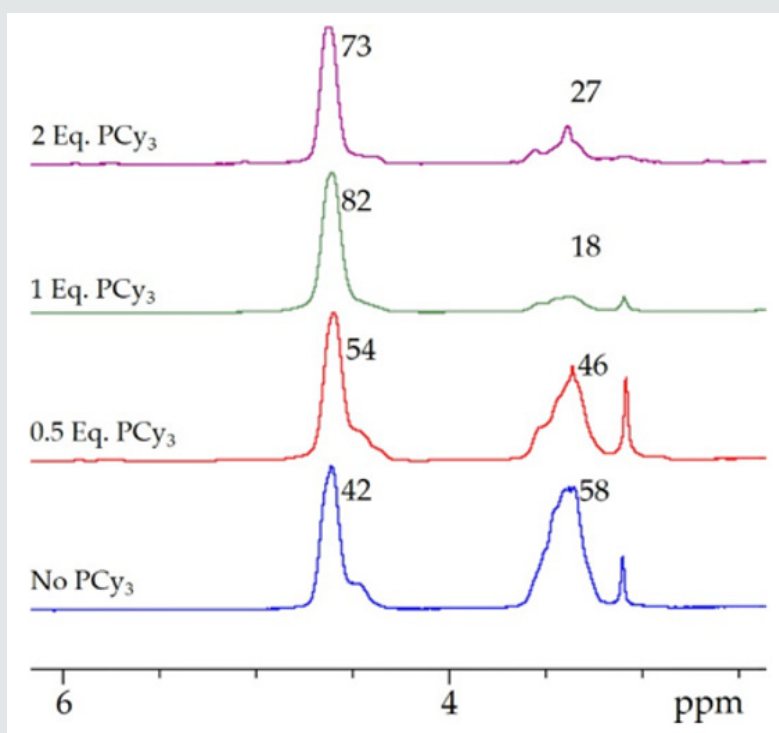


Figure 3: Stack plot of four representative ¹H NMR spectra. Integration of the shifts centered at $\delta = 4.6$ ppm and $\delta = 3.4$ ppm provide relative quantification of carbonate and ether linkages respectively. The numbers adjacent to each shift are relative integrations normalized to 100%.

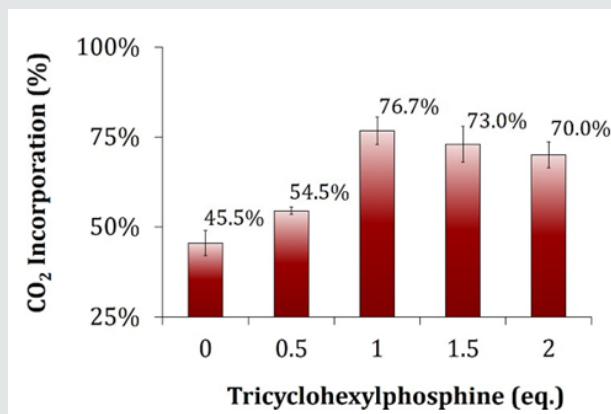


Figure 4: The average CO₂ incorporations as determined by ¹H NMR spectroscopy as described in Table 1 with increasing tricyclohexylphosphine (eq. = equivalents relative to chromium).

In order to establish the molecular weight distributions of the PCHC samples prepared using complex 1, a selection of polymer samples was analyzed by gel permeation chromatography (GPC). The data collected revealed number-average-molecular-weights (Mn) of the resulting polymers ranging between 0.6 and 3.6 kDa (Table 1). Additionally, the molecular weight distributions are broad with polydispersity's ranging from 3.6 to

12.0. This observation is not unprecedented in the coupling of CO₂ and epoxides and has been reported to be a possible indication of either slow initiation of the active species, multiple initiation mechanisms (perhaps mono- vs. dinuclear initiation sites), and/or the presence of trace amounts of protic impurities [39,63]. Among the PCHC samples analyzed by GPC, was a set of two samples (entries 1 and 2 in Table 1) each prepared by copolymerization at 80°C and 52 bar CO₂ and no added PCy₃. These polymers were found to each have number average molecular weights (Mn) of 1.1 and 3.6 kDa with corresponding PDI's of 12.0 and 5.3 respectively (Table 1). Further, number-average-molecular-weights were not observed to be significantly impacted from the addition of either 0.5 or 1

equivalent of PCy₃ relative to chromium during copolymerization (entries 5, 6 and 7 in Table 1). The corresponding PDI's were 5.3, 3.6 and 3.7 respectively. However, additional PCy₃ resulted in a fairly linear decrease in Mn from 1 eq. to 1.5 and 2 eq. of PCy₃ (Table 1). Therefore, just as observed for CO₂ incorporation, there appears to be an optimum loading of 1 eq. of PCy₃ in terms of its impact on Mn.

Another important question we set out to investigate regarding this catalyst was that of stereo control. As stated previously, the ligand, H₂L, contains two chiral centers and can be synthesized or purchased in an enantiomeric ally pure form [56]. To this point, ¹³C NMR spectroscopy was employed to evaluate the stereoregularity of the PCHC samples recovered from the polymerizations described herein. All ¹³C NMR spectra recorded for PCHC samples prepared in this study exhibited a set of chemical shifts centered at δ = 153.9 ppm and δ = 153.4 ppm which are assigned to isotactic, syndiotactic and heterotactic forms of the copolymer (Figure 5) [64]. As such, we observe all polymers to be atactic and therefore indicating no stereo control in the ring opening and enchainment of the CHO monomer.

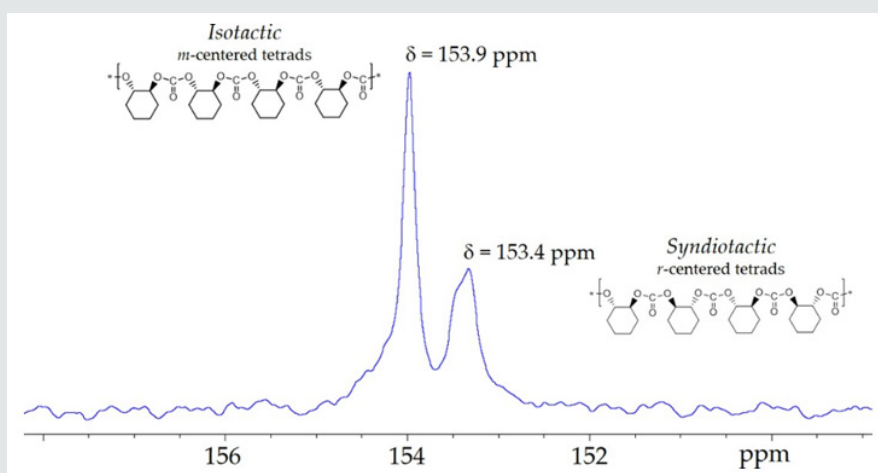


Figure 5: The carbonate chemical shifts in are representative ¹³C NMR spectrum of poly (cyclohexene carbonate) prepared from copolymerization of CO₂ and CHO, mediated by complex 1.

Conclusion

We have shown complex 1 to be an effective catalyst in the coupling of CO₂ and CHO to produce poly (cyclohexene carbonate) under reasonable conditions of temperature and subcritical CO₂ pressure. The air-stable complex 1 was easily synthesized and characterized in this study and found to be nearly 100% selective toward copolymer under the conditions reported, as evidenced by the lack of any cyclic carbonate observed in the FTIR or NMR spectral data. Addition of tricyclohexylphosphine was shown to enhance the degree of CO₂ incorporation, resulting in polymers which were found to be as high as 82% carbonate in contrast to initial values of ~40-50% carbonate for polymerization carried out in the absence of PCy₃. Further, number average molecular weights and CO₂ incorporations were highest for polymers prepared with addition of 1 equivalent of phosphine relative to chromium (Mn = 2.6 (±0.4) kDa; %CO₂ = 76.7 (s = 3.9)%). Given the results we report herein regarding the effect of PCy₃ on the polymerization reactions, it is likely similar effects might be observed with addition of PPN⁺ salts or N-heterocyclic compounds such as imidazole and pyridine derivatives. This is will be the subject of future studies as we seek to explore the activity of other catalysts for this purpose.

Acknowledgement

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Conflicts of Interest

The authors declare no conflict of interest.

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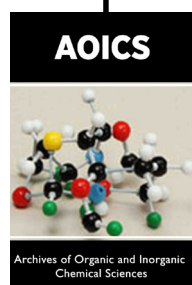
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