Probing the mechanistic aspects of the chromium salen catalyzed carbon dioxide/epoxide copolymerization process using in situ ATR/FTIR

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Abstract

Studies of the copolymerization of CO_2 and epoxides have been the staple of our group's research program for the better part of a decade now. During that time, the incorporation of attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectroscopy has greatly enhanced the kinetic and mechanistic investigations performed. However helpful, there are some difficulties, e.g., phase partitioning, that we have discovered and overcome in that same time period. The greatest step forward was achieved by the incorporation of 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane (TMSO) as an epoxide for performing accurate kinetic studies. Herein, we discuss the development of this technique into one of the mainstays within our laboratories, highlighted by our most recent catalyst system that utilizes (salen)Cr^{III}X/cocatalyst where salen: N,N'-bis(salicylidene)-1,2-ethylenediimine, X: Cl^- or N_3^- and cocatalyst: N-methylimidazole, phosphines and PPN^+ salts. Through altering the cocatalyst, ligand architecture and initiator, this catalyst system has proven to be one of the most industrially viable catalysts currently being studied.

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1. Introduction

Progress in the transition metal-mediated catalysis of epoxide/CO_2 coupling to provide polycarbonates and cyclic carbonates has steadily occurred over the past 35 years. While the process traces its lineage back to the classical studies of Inoue utilizing heterogeneous catalysts consisting of diethyl zinc and a polyhydric source [1], over the last decade academia and industry alike have focused primarily on the development of highly active homogeneous catalysts. Studies within our research group in the mid to late 1990s produced the first truly homogeneous zinc catalyst for the coupling of epoxides and CO_2, zinc bis-phenoxides [2–6]. By employing phenoxide ligands with sterically bulky substituents at the 2 and 6 positions, it was possible to solubilize the normally insoluble zinc phenoxide system creating a catalyst that selectively coupled alicyclic cyclohexene oxide and CO_2 to give high molecular weight polycarbonate. When applied to propylene oxide, a more

industrially relevant monomer, as is often seen, cyclic carbonate was favored, except at lower temperatures. A major step forward was achieved with the development of Coates' zinc β-diiminate complexes, which copolymerize CO_2 and cyclohexene oxide at extremely high rates and impart impressive molecular weight control on the resulting polycarbonate, despite their relatively high sensitivity to moisture and temperature [7–9]. Coates' catalysts presently represent the most effective homogeneous system for polycarbonate formation. More recent studies have shifted away from the use of zinc and towards early transition metals utilizing planar tetradentate ligand systems. The early development of these systems can be traced back again to the rudimentary studies of Inoue on aluminum tetraphenyl porphyrin (TPP) catalysts that coupled epoxides and CO_2 to give oligomeric carbonates in the presence of a Lewis base cocatalyst, such as N-methylimidazole (N-MeIm) or 4-(dimethylamino)-pyridine (DMAP) [10–12]. Other active metalloporphyrins include the Cr(TPP)Cl complex used by Kruper to synthesize cyclic carbonates [13] and the chromium(III) perfluorinated porphyrinate complex developed by Mang and Holmes which imparted solubility in

supercritical CO_2 [14]. As was found for the aluminum system, both the Kruper and Holmes catalysts required the addition of a Lewis base cocatalyst.

The utilization of salen ligands with chromium was inspired by Jacobsen's success with chromium salen complexes to asymmetrically ring-open epoxides [15]. Mechanistically, Jacobsen showed the key reaction step to be the formation of a chromium–alkoxide bond through a bimetallic initiation process. With the ability of CO_2 to insert into this type of bond already established, the utilization of chromium(III) salen complexes as a copolymerization catalyst was the next logical step. Within the last couple of years, we have extensively utilized this catalyst system, Fig. 1, studying both cyclohexene oxide and propylene oxide as monomers [16–18]. These complexes have proven to be robust catalysts, producing completely alternating polycarbonate with very little cyclic carbonate and activities approaching that of the zinc β-diiminates as the most active homogeneous catalysts in the field. The chromium salen system also presents some intriguing mechanistic variations on the classical polycarbonate synthetic model, as the epoxide-binding site in this instance is located *trans* to the nucleophile, making concerted epoxide ring-opening difficult to envision. Similar to the Jacobsen process, it was determined that the initiation step for the copolymerization reaction was most likely second order with respect to catalyst concentration, while chain propagation had a first order dependence. Analogous to the metalloporphyrin systems, chromium salens require a cocatalyst to maximize activity. Upon variation of the cocatalyst from *N*-MeIm to phosphines and "free" halides, the initiation mechanism shifts from second to first order in [catalyst] with large increases in the rate of polymerization as a result [18]. Additional studies by Nguyen [19] and Rieger [20] have implicated more ionic character to the initiation and propagation steps based on results from reactivity studies. The most practical value of mechanistic studies comes from catalyst design, especially for systems that behave in seemingly anomalous ways. In this case, kinetic studies are highly valuable in determining the intimate mechanism of this process and allow for enhancement of the catalytic activity. While bulk studies can help identify the appropriate trends for increasing activity, such methods are limited to observation of product formation at the termination of a reaction. The development of in situ monitoring of high pressure and temperature reactions has been made practical by the application of attenuated total reflectance (ATR) technology. When coupled with Fourier transform infrared
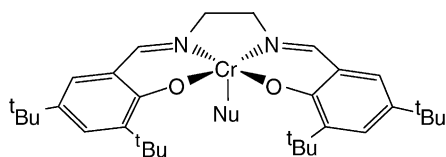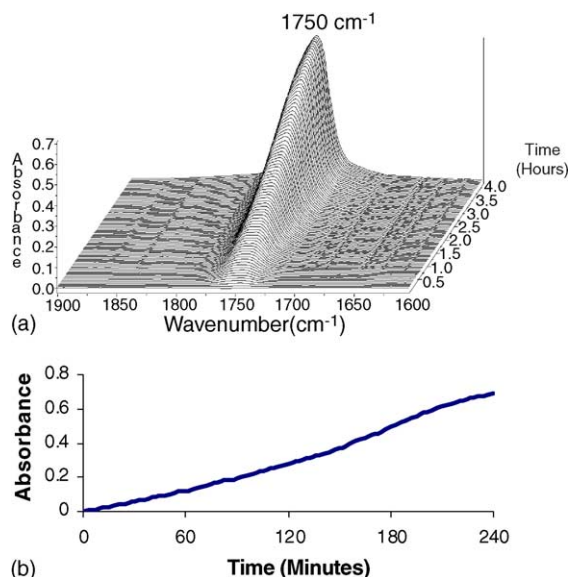

Fig. 2. (a) Three-dimensional stack plot of the infrared spectra collected every 3 min during the reaction of CO_2 and cyclohexene oxide (80 °C and 55 bar pressure). (b) Time profile of the absorbance at 1750 cm^{-1} corresponding to poly(cyclohexylene)carbonate.

spectroscopy (FTIR), it is possible to monitor the concentrations of infrared active species during the entire reaction, making it feasible to obtain rate information and mechanistic insight into the copolymerization reaction under extreme reaction conditions (see Fig. 2). Herein, we report on the integration of the ATR/FTIR technique as a tool for kinetic studies and catalyst design within our research group and its successful application to the chromium salen catalyst system for epoxide/CO_2 coupling.

2. Experimental section

Salen ligands, H_2(salen), were synthesized by the condensation of salicylaldehydes with diamines in methanol catalyzed by a small amount of aqueous formic acid. Chromium salen chloride complexes, Cr^{III}(salen)Cl, were synthesized using excess chromium(II) chloride mixed with H_2(salen) in tetrahydrofuran at room temperature with stirring overnight followed by oxidation in air over the course of the following day [21]. Product work-up yielded the complexes in high yields. The corresponding chromium salen azide complexes, Cr^{III}(salen)N_3, could then be prepared by chloride abstraction with silver perchlorate followed by addition of sodium azide in acetonitrile as described by Jacobsen [22]. While the azide complexes exhibit higher activities under all conditions, additional steps are necessary to remove unreacted chromium chloride/perchlorate starting materials.

High-pressure reaction kinetic measurements were carried out using a stainless steel Parr® autoclave modified with silicon crystal to allow for Fourier transform attenuated total reflectance (ATR) infrared spectroscopy (ASI®

Fig. 1. Structure of a highly active chromium salen, Cr(salen)Nu, complex (Nu: Cl^-, N_3^-).

Fig. 3. ASI® ReactIR 1000 reaction analysis system with stainless steel Parr® autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo).

ReactIR 1000 in situ probe, Fig. 3). The ATR crystal is permanently fixed to the bottom of the reactor, allowing for monitoring of the reaction mixture without the complication of gas bubble accumulation, which often plagues data collection for in situ probes pointing downward into the solution. The infrared beam passes through several connecting arms, reflected by a mirror at each junction point, and then enters the ATR crystal. Upon reaching the crystal/solution interface at an angle larger than the critical angle, total reflectance of the beam takes place. By virtue of the resulting evanescent electrical field, the infrared light penetrates into the solution by a fraction of its wavelength where it can be absorbed by infrared active species. Signal enhancement occurs by repetitive reflections (30 bounces) into the reaction along the length of the ATR crystal, then exits into the connecting arms towards the MCT detector. Signal tuning is achieved through the adjustment of one movable mirror and the relative position of the detector. Although this technique allows for real-time monitoring of the reaction progress under extreme reaction conditions, some disadvantages exist when compared to routine infrared spectroscopic techniques. Most importantly, the pathlength light travels through the reaction mixture, a verifiable constant in normal infrared spectroscopic techniques, changes as a function of temperature and wavelength resulting in fluctuation of the spectrum baseline. In addition,

the index of refraction (which is related loosely to the density) of the reaction mixture also plays a role in attenuating the pathlength. While these effects represent only small deviations for the systems described herein, care must be taken when comparing absorbances at different wavelengths and temperatures as these may not have straightforward relationships as intimated by Beer's Law.

In order to obtain reproducible results, as demonstrated performing experiments with the highly moist air-sensitive zinc bis-phenoxides, it was necessary to dry the autoclave in vacuo overnight at 80 °C. Following that, 10 mL of solvent (neat epoxide or epoxide/solvent mixture) was loaded via a stainless steel cannula through an injection port into the reactor. After the background solvent reached the desired temperature, a single 128-scan background spectrum was collected. The specific catalyst and cocatalyst were dissolved together in 10 mL of solvent and injected into the autoclave, followed by immediate charging with CO_2 to the pre-selected pressure. When using PPN salts, the catalyst and cocatalyst are mixed together in 4 mL benzene and 1 mL methanol, stirred at least 30 min at room temperature, and dried in vacuo overnight prior to dissolution in epoxide. Maintaining the appropriate reaction temperature, a single 128-scan spectrum was collected every 3 min during a reaction period between 2 and 24 h. Profiles of the absorbance of polycarbonate and cyclic carbonate versus time were recorded after baseline correction (see Fig. 2). After cooling and venting in a fume hood, the polymer was extracted as a dichloromethane solution and dried under vacuum at 100 °C overnight. For bulk studies used in determining turnover frequencies, the same procedure is used except that catalyst and cocatalyst were dissolved in 20 mL of neat epoxide and added via injection port into a 300 mL autoclave.

The isolated polycarbonate was analyzed by ^{1}H NMR (300 MHz) in $CDCl_3$, where the relative amount of ether linkages was determined by integrating the peaks corresponding to the methine protons of the polyether and polycarbonate as shown in Table 1. The corresponding chemical shifts for monomeric cyclic carbonates give a quantitative measure of the amount produced relative to polymer formation. In the case of cyclohexene oxide, the cis- and trans-cyclohexylene carbonate can be distinguished by their differences in infrared absorption [23]. ^{13}C NMR can also be useful in that each of the carbonate species, be it cyclic or polymer, give a unique signal. Previous ^{13}C NMR studies by Nozaki [24] and Chisholm [25] have made it possible to identify the carbonate peaks corresponding to the different configurations within both the poly(cyclohexylene)carbonate and poly(propylene)carbonate chain, respectively. While the TMSO cyclic carbonate would be expected to have similar variation with regards to stereochemistry, these monomeric side products have yet to be isolated. Under identical conditions, TMSO has a smaller propensity to form cyclic carbonates when compared to cyclohexene oxide based on the reduction observed in the absorbance of

Table 1
Spectroscopic characterization of monomeric and polymeric carbonates from different epoxide monomers

Monomer	^1H NMR (ppm, $CDCl_3$)			^{13}C NMR(ppm, $CDCl_3$)		IR spectroscopy (cm^{-1}, CH_2Cl_2)	
	Polycarbonate	Polyether	Cyclic carbonate	Polycarbonate	Cyclic carbonate	Polycarbonate	Cyclic carbonate
CHO	4.2–4.6	3.2–3.6	3.96 [*trans*]	153.7[*iso*]	154.3[*cis*]	1750	1818(s), 1803 (sh) [*trans*]
			4.71 [*cis*]	153.3–153.1[*synd*]	155.1[*trans*]		1802(s), 1794 (sh) [*cis*]
PO	4.9–5.1	3.4–3.6	4.76	~154.7[TT]		1750	1800
	4.0–4.4		4.46	~154.2[HT]			
			3.92	~153.7[HH]			
TMSO	4.7–4.9	3.2–3.5	Not isolated			1750	Not isolated

the $\nu(C=O)$ stretch associated with the monomeric carbonates.

3. Results and discussion

3.1. Inherent difficulties and their resolutions utilizing in situ ATR/FTIR methods for monitoring the coupling of CO_2 and epoxides

The incorporation of in situ real-time monitoring of polycarbonate formation has added a valuable dimension to catalyst design studies. Mechanistic investigation, prior to this technique, involved scaling down of the CO_2 pressure to near ambient pressures to allow for sampling at regular intervals without depressurization. A more time-intensive method involved running several copolymerization reactions under identical conditions and stopping the reactors at different times in order to obtain a crude profile of polymer formation as a function of time. Due to these previous constraints, mechanistic studies were limited to variation of polymer formation as a function of the metal–ligand environment. From a kinetic standpoint, it is most difficult to discern a reliable mechanism by monitoring only the final polymer yield.

The ReactIR 1000 reaction system and its newer versions modified for high-pressure applications, allows for collection of infrared spectra without disruptive sampling. Despite this advantage, some care must be taken when undertaking polymer kinetics. Most importantly, the ATR technique is susceptible to highly inflated absorbance values resulting from precipitation of polymer from the reaction mixture. Since the ATR light beam only penetrates into the reaction mixture on the scale of a fraction of a wavelength, even slight precipitation of polymer onto the crystal will cause large errors. This is particularly problematic when using propylene oxide as a monomer. The resulting poly(propylene)carbonate has very limited solubility in most organic solvents, including propylene oxide. As a result, no completely acceptable conditions have yet been found to accommodate reliable kinetic data collection using neat propylene oxide as a monomer.

Polymerization reactions were conducted utilizing a 4:1 toluene:propylene oxide mixture, hoping that the poly(propylene)carbonate would remain in solution. The catalyst/cocatalyst system used was one that does not form cyclic carbonate at low temperature (40 °C). The profile of the polymer formation is shown in Fig. 4 (top line). At the outset, the reaction was not stirred; but in the middle of the reaction, the stirrer was turned on for a short time. As can be seen, the absorbance was found to drop sharply, and then slowly begin to increase. This is indicative of the polymer falling out of solution, as it is being formed, and coating the crystal. When stirred, the polymer dissolved, thereby decreasing the effective absorbance. A control experiment was done under the same conditions except the reaction was continuously stirred. The profile of the polymer formation is drastically different (bottom line), with the maximum absorbance ending up being half the absorbance of the unstirred reaction, even though the amount of polymer formed was essentially the same for both experiments. This would indicate that the polymer is not plating out on the crystal when stirred. Although we are in the early stages of study, this could become a viable method for kinetic analysis of the propylene oxide/CO_2 reaction system.

Cyclohexene oxide has often been utilized as a monomer due to its relatively low cost and high selectivity towards polycarbonate rather than cyclic carbonate formation. Poly(cyclohexylene)carbonate has a relatively high solubility in the neat monomer in addition to moderate solubility in other non-coordinating solvents such as toluene. The inclusion of non-coordinating solvent is an important
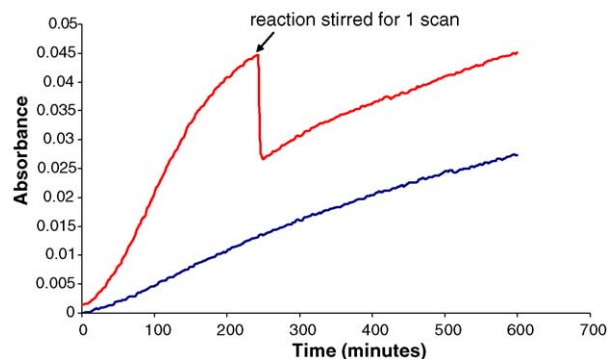

Fig. 4. Peak profiles for copolymerization of propylene oxide and CO_2 (40 mL of a 4:1 toluene:propylene oxide mixture, 35 bar CO_2, 40 °C) with and without stirring.

consideration for copolymerization reactions. Binding studies utilizing ^{113}Cd NMR have shown that epoxides are relatively weakly coordinating and would inadequately compete for metal binding with solvents such as tetrahydrofuran or acetonitrile [26]. Despite the favorable solubility properties, early kinetic experiments with cyclohexene oxide/CO$_2$ coupling produced results with poor reproducibility wherein the ν(C=O) stretch corresponding to copolymer showed sudden increases or decreases in absorbance. This phenomenon was traced back to the phase behavior of cyclohexene oxide and carbon dioxide as described by Beckman [27]. These studies showed that there exists, under certain conditions, a two-phase regime consisting of a higher density epoxide-rich phase, which presumably contains the catalyst, and a lower density carbon dioxide-rich phase. Fortunately, sampling occurs in the lower phase and this behavior can be effectively represented by the ATR technique by using different stirring modes. As shown in Fig. 5, the reaction was stirred for the first few hours and then discontinued, resulting in an apparent acceleration of polymer formation. This is due to the reformation of the biphasic system, which causes an increase in concentration of both synthesized polymer and the catalyst species. When stirring is resumed, an immediate decrease in polymer absorbance is observed corresponding to an abrupt dilution subsequent to phase mixing. Beckman's study included visual monitoring of the reactor and described a gradual merging of the two phases as polymer formation progressed, with eventual formation of a single phase. These observations indicate that the rate of formation of the dense polymer-rich phase will vary with the rate of polymerization, making quantitative rate studies quite difficult under these conditions. Alternatively, data can be obtained by not stirring the reaction which, because of its relatively slow rate, is not greatly affected by mass transfer processes. These problems can be reduced through the use of epoxide solutions in a non-coordinating organic solvent, specifically toluene, which keeps the reaction mixture in a single phase. However, the limited solubility of the copolymer in toluene dictates that small concentrations of
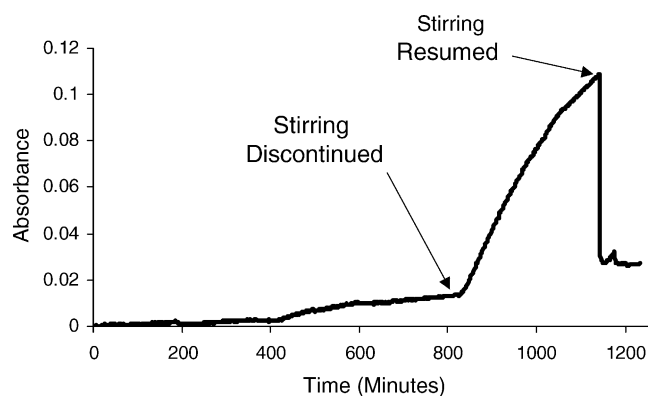
epoxide must be used to avoid polymer precipitation onto the ATR crystal, effectively reducing the epoxide concentration and decreasing the rate of polymerization. In order for viable kinetic studies to be performed under neat epoxide conditions, a new epoxide would have to be found that had similar reactivity, the correct solubility and suitable phase behaviors.

3.2. Copolymerization of TMSO/CO$_2$ to afford a CO$_2$-soluble copolymer

Concomitant with the search for a more favorable epoxide is the fact that poly(cyclohexylene)carbonate has inferior physical properties when compared to the more industrially relevant bis-phenol A polycarbonate [28]; it is of critical importance to not only find an active catalyst but also an epoxide monomer that will impart improved properties to the resulting polymer. One interesting example, 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane (TMSO, Fig. 7), has previously been described as giving a liquid CO$_2$-soluble polycarbonate that can be cross-linked [29]. As a consequence of this improved solubility, the neat monomer does not phase-partition under high CO$_2$ pressures, i.e., absorbance does not change as a result of stirring, and the resulting polycarbonate is highly soluble in neat TMSO, effectively overcoming cyclohexene oxide's shortcomings. As shown in Fig. 6, copolymerization runs using TMSO and cyclohexene oxide have very similar profiles with respect to polycarbonate formation, with slight differences most likely due to the catalyst partitioning into the lower phase in the CHO case. When determining rate data, however, the TMSO system benefits from the epoxide's relative phase stability, particularly in the initial few hours of the reaction (Fig. 8), allowing for more accurate determination of the initial rate
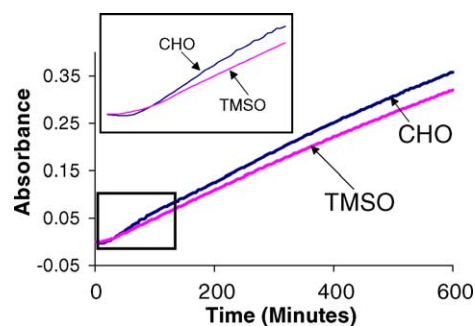
Fig. 6. Comparison of polycarbonate formation using cyclohexene oxide and TMSO as monomer. Inset: initial 2 h of reaction. Reaction conditions: 0.086 mmol Cr(salen)Cl, 2.25 equivalents *N*-MeIm, 20 mL epoxide, 50 bar CO$_2$, 80 °C.

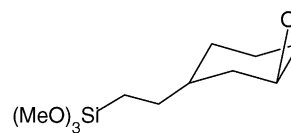Fig. 7. Schematic of 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane (TMSO).

Fig. 5. Profile of poly(cyclohexylene)carbonate as a function of time with and without stirring.
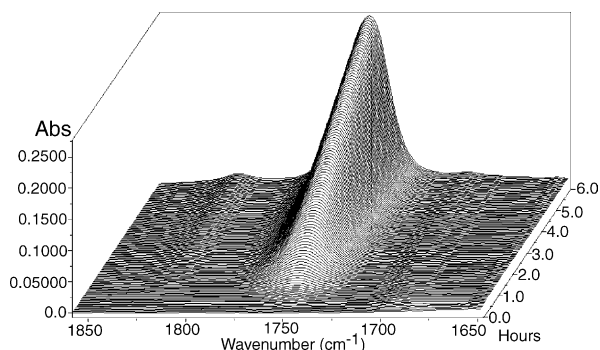
Fig. 8. Representative three-dimensional stack plot of the infrared spectra collected every 3 min during the reaction of CO_2 and TMSO (80 °C and 55 bar pressure).

values. Kinetic studies under neat epoxide and high CO_2 pressure conditions are dealt with as pseudo-first order systems, where excess epoxide and CO_2 concentrations (which are very difficult to quantify at any particular time in the reaction) remain approximately constant in the initial stages of the reaction. An unexpected benefit that came about because of TMSO polycarbonates' high solubility in liquid CO_2 was that it could be utilized for easy catalyst removal from the resulting polycarbonate. Shown in Fig. 9 are samples of TMSO polycarbonate before (left) and after (right) dissolution in liquid CO_2. As shown by the substantial color change, the process effectively removes a sizeable amount of the CO_2-insoluble catalyst species. This technique is being explored further as a benign method
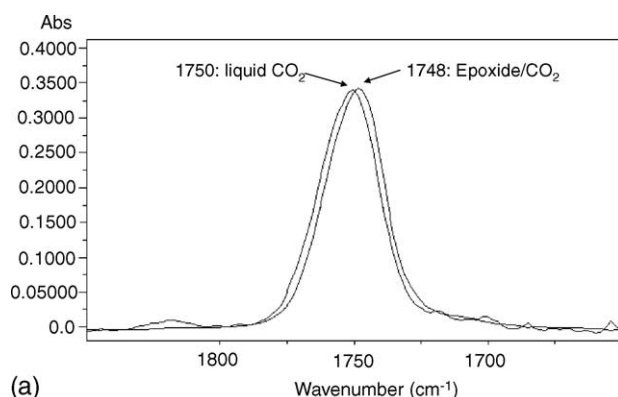
Fig. 9. (a) In situ infrared spectra of TMSO polycarbonate dissolved in epoxide/CO_2 and liquid CO_2. (b) Photos of TMSO polycarbonate before (left) and after (right) dissolution in liquid CO_2.

for extracting polycarbonate from a catalyst mixture without the use of organic solvents. By passing the CO_2 dissolved polymer through a high-pressure filter, allowing for purification at the extreme pressures required for liquid CO_2 to be present, followed by simple depressurization would give pure polycarbonate with potential recovery of CO_2 and the catalyst remains.

Polymer characterization is a major disadvantage of TMSO polycarbonate, since the silyl methoxy substituents have a ^{1}H NMR resonance almost identical to polyether linkages (∼3.4 ppm), making it difficult to accurately determine the relative amount of carbonate and ether linkages in the resulting copolymer. However, due to the many comparisons with cyclohexene oxide, we believe the carbonate content to be similar, if not the same, as in poly(cyclohexylene)carbonate. Additionally, in situ cross-linking is observed with prolonged contact with air or elevated temperatures, making it necessary to employ anhydrous conditions when removing solvent and utilizing sufficient reactor time to totally consume the high-boiling monomer. Molecular weight analysis also becomes problematic as the cross-linked polycarbonate loses solubility in common organic solvents. While analysis on the soluble portion of a polymer sample is possible, this is unlikely to be a representative sample and cannot be considered a quantitative measure of chain length.

3.3. In situ kinetic studies employing TMSO as comonomer and solvent to assess mechanistic aspects of the copolymerization process

In situ kinetic studies, utilizing TMSO as monomer and solvent, have helped to clarify the nuances in reactivity of the chromium salen system as it applies to epoxide/CO_2 copolymerization to form polycarbonates. From a catalyst design standpoint, an early hurdle was encountered with the seemingly dichotomous role of N-methylimidazole. Although the presence of cocatalyst was required for polymerization and rate enhancement was observed by increasing cocatalyst loading, a drastic decrease in activity was observed at higher loadings (>5 eq.) [8]. This abrupt decline implicated N-methylimidazole as an inhibitor at high concentrations. However, in situ kinetic studies explained the observed behavior was actually due to the interplay between the maximum rate and initiation time or the time elapsed from beginning of reaction to the onset of the maximum rate (Fig. 10). As published previously, the increase in cocatalyst loading inhibits only the initiation step, i.e., Jacobsen bimetallic epoxide ring-opening [8]. However, after initiation is complete and propagation ensues, the rate of polymerization increases at higher cocatalyst loadings. Additional kinetic studies manipulating concentrations of catalyst, N-methylimidazole, and epoxide showed that equilibrium conditions, at both the initiation and propagation steps, control the rate of polymer formation. Based on these kinetic results, a mechanism for initiation
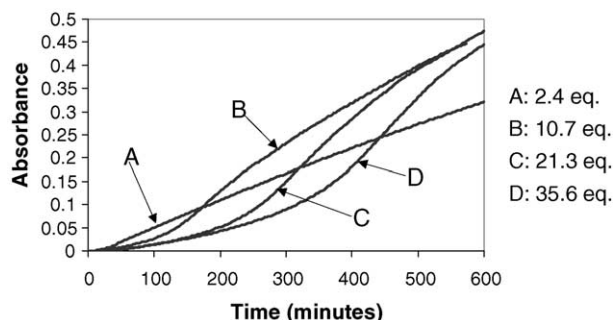
Fig. 10. Formation of TMSO polycarbonate at different *N*-methylimidazole loading. Reaction conditions: 0.086 mmol Cr(salen)Cl, 50 bar CO_2, 20 mL TMSO, 80 °C.

and propagation is proposed in Scheme 1. The chromium salen complex is in an initial equilibrium between epoxide (E) and imidazole (I) binding to the metal center, giving species A and B, respectively. Since *N*-MeIm is a better electron donor than epoxide, it would be expected that B would be the predominant species in solution. However, since this reaction takes place in neat epoxide, the large concentration of E would be expected to yield sufficient concentrations of A, the lifetime of which determines the length of the initiation step. The chloride from B is activated sufficiently towards nucleophilic attack on the activated epoxide bound to A, giving the initial ring-opened intermediate, exactly as the Jacobsen asymmetric ring-opening mechanism. Based on the consistently large amounts of CO_2 incorporation in the isolated copolymer, it is believed that CO_2 insertion into chromium–alkoxide
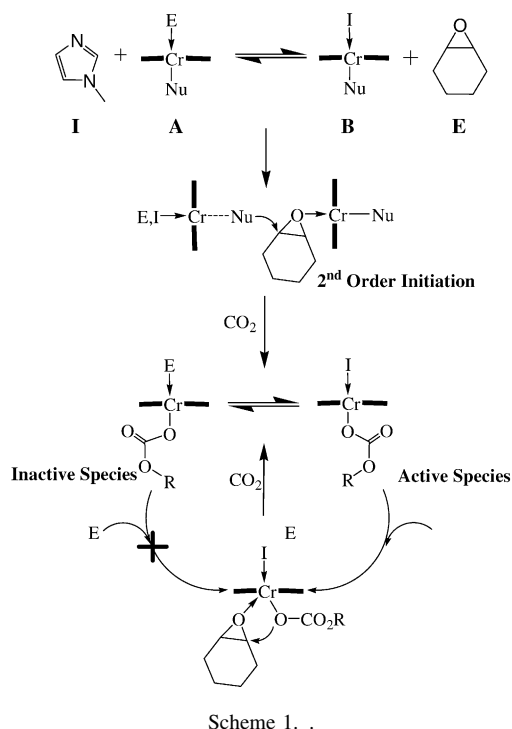
bonds is much faster than a second epoxide enchainment (causing a polyether linkage). The initiation step is dependent on significant concentrations of both A and B, which is consistent with the observed inhibition of initiation at high *N*-MeIm loadings. Such inhibition is inconsistent with a first order initiation whereby the epoxide is ring-opened by an initiator on the same metal center, since this pathway would be expected to be enhanced by additional cocatalyst. In this case, *N*-methylimidazole is a sufficient donor to activate the nucleophile for attack on an epoxide bound to a different metal center but inadequate for concerted ring-opening on the same metal center. The active species begins a second equilibrium in which epoxide and *N*-methylimidazole compete for the site *trans* to the growing polymer chain. When epoxide is bound, the catalyst is expected to have little to no activity, while the rate of polymerization accelerates upon coordination of imidazole. As a consequence of this condition, not all the metal centers are activated simultaneously and may continuously move between active and less active states depending on *trans* coordination of I or E.

Analogous studies with previously untested cocatalysts have shown interesting deviations in catalyst behavior as well as dramatically improved polymerization rates and will be summarized herein. Fig. 11 shows the relative rates of polycarbonate formation with the use of different cocatalysts at their optimized loadings. Surprisingly, better binding Lewis bases, i.e., phosphines, which would seem detrimental by the *N*-methylimidazole mechanism, increase the rate of polymerization, while simultaneously reducing the initiation time at higher loadings (Fig. 12). As a result, adding tricyclohexylphosphine (PCy_3) beyond 1 equivalent shortens the initiation time significantly, indicative of first order catalyst dependence for this step rather than the bimetallic pathway formulated for *N*-MeIm. The emergence of a first order initiation pathway allowed for the use of "free" anionic salts to act as external initiators for catalysis. In this case, the supplied cocatalyst could act as the polymer-chain initiator rather than binding directly to the metal center as postulated for the neutral Lewis base counterparts, requiring additional mechanistic aspects. The anion would require a minimal interaction to the corresponding cation, making bis(triphenylphosphoranylidene)ammonium (PPN^+) salts an
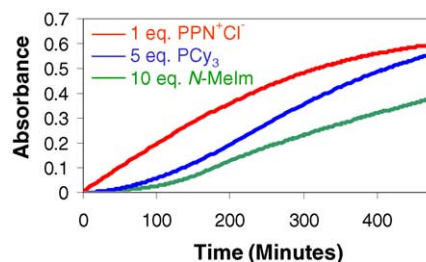

Scheme 1. .

Fig. 11. Formation of TMSO polycarbonate using different cocatalysts. Reaction conditions: 0.086 mmol Cr(salen)Cl, 20 mL TMSO, 50 bar CO_2, 80 °C.
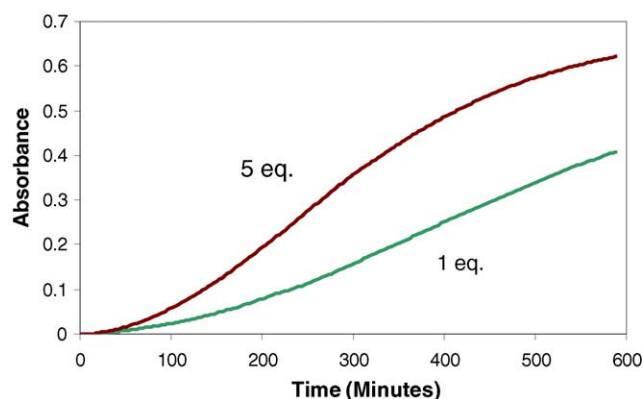
Fig. 12. Formation of TMSO polycarbonate using Cr(salen)Cl at different loadings of PCy₃. Reaction conditions: 0.086 mol Cr(salen)Cl, 20 mL TMSO, 50 bar CO₂, 80 °C.

ideal first choice. Kinetic studies on this anionic system show a significant reduction in initiation time (zero in most cases) while maintaining a high maximum rate. Tetra-*n*-butylammonium salts show similar initiation times, but inferior propagation rates, presumably due to an increased interaction of the cation with the anionic active species. Studies of the kinetics and optimization of chromium salen catalysts with phosphine or PPN salt cocatalysts are underway and will be presented in future publications.

4. Conclusions

The copolymerization of CO_2 and epoxides to produce polycarbonates represents a potentially less expensive and significantly "greener" route to these thermoplastics than the current commercial process, which involves condensation–polymerization of diols and phosgene or carbonates. In efforts to provide practical utility to this copolymerization process, we have performed detailed kinetic studies of these reactions utilizing both *alicyclic* and *aliphatic* epoxide monomers. Specifically, high pressure in situ infrared spectroscopy has proven to be a valuable tool for monitoring these reactions and thereby better defining the mechanistic aspects of the copolymerization process. This was illustrated employing chromium(III) salen derivatives as catalysts. These studies have clearly demonstrated that the effectiveness of this catalyst system is greatly enhanced via the nature of the Lewis base cocatalysts, with anionic bases such as halide ions being more efficient than phosphines which are better than *N*-MeIm.

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