Inquiry into the Formation of Cyclic Carbonates during the (Salen)CrX Catalyzed CO_2/Cyclohexene Oxide Copolymerization Process in the Presence of Ionic Initiators

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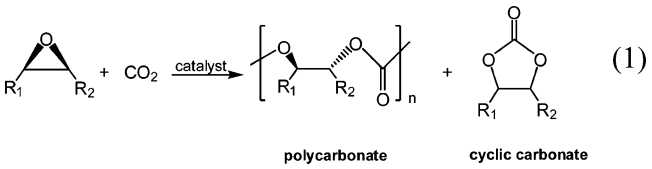
Introduction

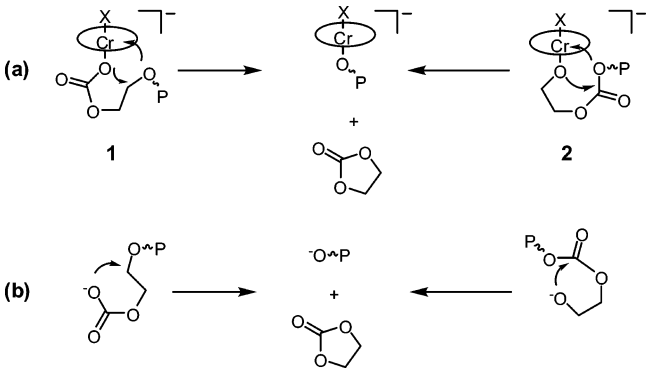
The coupling of carbon dioxide and epoxides catalyzed by metal complexes in general provides two products in varying relative quantities, polycarbonates and/or cyclic carbonates (eq 1). The extent of formation of these two materials incorporating CO_2 depends critically on the nature of the epoxide, the metal catalyst, and the reaction conditions.[1] We and others have been investigating the use of robust Schiff base metal (III) complexes as catalysts in the presence of anionic initiators for the selective production of either the polymeric or monomeric organic carbonates.[2] In our early studies in this area we reported that the difference in activation energies for copolymer vs cyclic carbonate formation was much greater and positive for cyclohexene oxide/CO_2 copolymerization than for the corresponding process involving propylene oxide.[3,4] This observation accounts for the generally noted fact that *alicyclic* epoxides couple with CO_2 to selectively afford copolymers at much harsher reaction conditions than *aliphatic* epoxides. Furthermore, it was also apparent that (salen)CoX derivatives were more effective for copolymerizing propylene oxide/CO_2, whereas, (salen)CrX derivatives were more efficient at copolymerizing cyclohexene oxide and carbon dioxide.[5] Nevertheless, (salen)CoX complexes have shown significant activity as well for this latter process, specifically providing syndiotactic poly(cyclohexylene carbonate).[6]

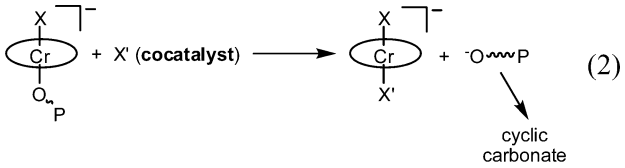


(1)

The formation of cyclic carbonate is thought to occur via two concurrent backbiting mechanisms, one aided by the metal (a) and one taking place on the free anionic polymer chain (b) (Scheme 1). The latter process is believed to have a lower activation barrier and to be assisted in the presence of an excess of neutral and ionic Lewis bases (cocatalysts) which serve to displace the growing polymer chain from the metal center (eq 2).[7,8] At this time, we wish to report on our studies to examine the activation barriers for cyclic carbonate formation from metal-bound polymer chains in *isolated* (salen)Cr intermediates. Importantly, the effect of excess, i.e., beyond 1 equiv, of ionic cocatalyst on the rate of cyclic carbonate production will be investigated.

Scheme 1





(2)

Experimental Section

Materials and Methods. Unless otherwise stated all synthesis and manipulations discussed were carried out on a double-manifold Schlenk vacuum line under an argon atmosphere or in an argon filled glovebox. Methanol and dichloromethane were freshly purified by a MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. Cyclohexene oxide was purchased from TCI America and freshly distilled from CaH_2. (Salen)CrCl (H_2salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-di-*tert*-butylethylenediimine) was synthesized according to the previously published procedure.[9] Bone dry carbon dioxide was purchased from Scott Specialty Gases equipped with a liquid dip-tube. ^{1}H and ^{13}C NMR spectra were acquired using Unity+ 300 MHz and VXR 300 MHz superconducting spectrometers.

General Procedures for Cyclohexene Oxide/CO_2 Copolymerization. First, 50 mg (0.086 mmol) of (salen)CrCl and 1 equiv of PPNCl (PPN^+ = bis(triphenylphosphoranylidene)ammonium) were dissolved in a one-to-one mixture of CH_3OH/benzene and the solution was taken to dryness under vacuum over a 3 h period. Then 20 mL of freshly distilled cyclohexene oxide was added, and the solution was cannulated into a stainless steel reactor which had been dried under vacuum at 80 °C for over 6 h. The reactor was loaded with 500 psi of CO_2 and set to the desired temperature for 4 h. Subsequently, the reactor was vented in a fume hood and the product was recovered with the minimum quantity of methylene chloride. The copolymer was precipitated from methanol in the presence of HCl. The copolymer was isolated and dried at 100 °C under vacuum overnight, weighed, and analyzed by ^{1}H NMR spectroscopy.

Results and Discussion

In order to ascertain that the specific catalytic system under study displayed behavior typical for these processes, a control experiment was carried out under the normally practiced conditions. Characteristic of these copolymerization processes, a reaction performed at 80 °C for 4 h at 500 psi with a monomer/catalyst/PPNCl loading of 2300:1:1 afforded a copolymer with 1% ether linkages, a M_n of 12 000 (PDI = 1.09), and a TOF

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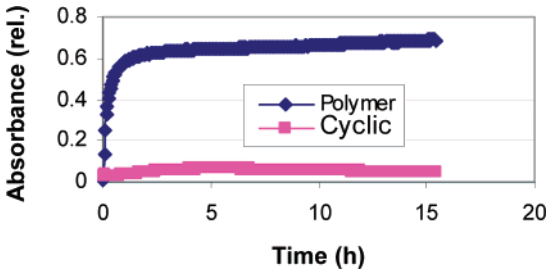


Figure 1. Reaction profile for formation of poly(cyclohexylene carbonate) and cyclohexylene carbonate as a function of time. Reaction carried out at 80 °C in 500 psi CO_2 with a monomer/catalyst/PPNCl loading of 100:1:1 in methylene chloride.

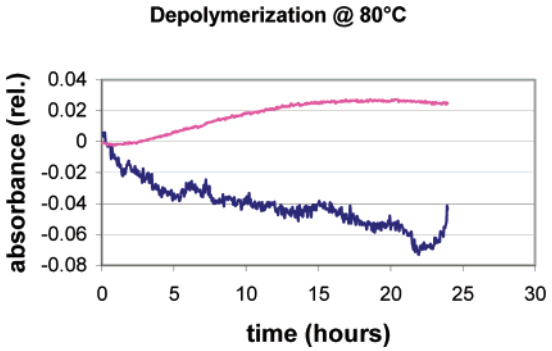


Figure 2. Depolymerization of metal-bound copolymer chain with accompanying formation of cyclic carbonate at 80 °C in CH_2Cl_2: (black line) copolymer disappearance; (red line) cyclic appearance.

Table 1. Initial Rate Data for the Formation of Cyclohexylene Carbonate from Copolymer Degradation

T (K)	rate (abs/time)	$\Delta E^{\ddagger}_{act}$[a] (kJ/mol)
343.15	0.0058	105 ± 7
353.15	0.0135	
363.15	0.0359	
373.15	0.1149	

[a] Obtained from the slope of the plot in Figure 3.

(mol of epoxide consumed)/(mol catalyst·h) of 211. These observations are representative of previously reported data.[10]

To investigate the degradation step of the metal-bound polymer chain in the absence of other concurrent chemical processes it is desirous to carry out the copolymerization reaction to completion, i.e., to consume all of the epoxide monomer. Under the typical solventless copolymerization conditions, the reaction mixture becomes too viscous to achieve 100% conversion. Hence, for the purpose of this study the copolymerization process was carried out at a low monomer/catalyst/PPNCl ratio of 100:1:1 and with a methylene chloride cosolvent. In a prototypical experiment performed in a stainless steel Parr reactor modified to accommodate an ASI ReactIR SiCOMP probe, the reaction was monitored in the ν_{CO_3} region *in situ* for copolymer and cyclic carbonate production (Figure 1). The isolated, purified copolymer obtained by this protocol exhibited 0−2% ether linkages with a M_n value of 3500−4200 and a PDI of 1.2−1.4. Furthermore, there was only a trace of cyclic carbonate formed and cyclohexene oxide was completely consumed.

The depolymerization reaction via the production of cyclic carbonate was similarly monitored by in situ infrared spectroscopy. This was accomplished utilizing a low molecular weight metal-bound copolymer chain produced as described above and accompanied by the prior slow release of CO_2 from the reaction solution. Under these reaction conditions of 80 °C and a minimal

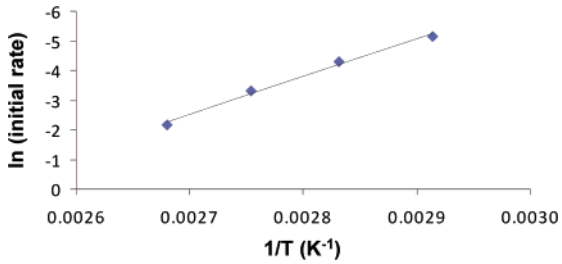


Figure 3. Arrhenius plot of rate data for copolymer → cyclic carbonate.

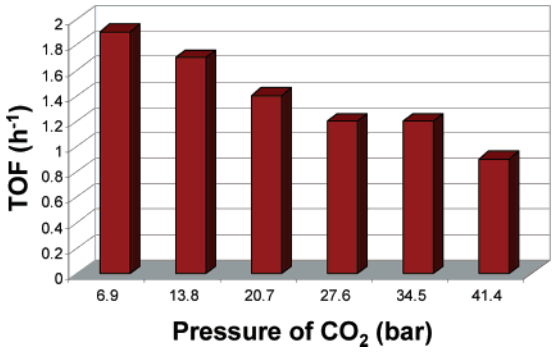


Figure 4. Production of cyclic carbonate as a function of CO_2 pressure. Data taken from ref 11.

quantity of CO_2, the resting state of the metal-bound copolymer chain is most likely species **2** in Scheme 1. Hence, the backbiting reaction would proceed by way of a metal alkoxide intermediate. Figure 2 depicted the traces of the infrared absorptions in the ν_{CO_3} region for the copolymer chain decomposition with concomitant cyclic carbonate production at 80 °C in methylene chloride. Initial rate data for the disappearance of poly(cyclohexylene carbonate) via formation of cyclohexylene carbonate as a function of temperature are provided in Table 1, along with the calculated Arrhenius activation energy obtained from the corresponding plot in Figure 3.

The rate of *trans*-cyclohexylene carbonate production during the copolymerization reaction performed in the traditional solventless manner was determined to have an $E^{\ddagger}_{act}$ of 133 kJ/mol.[4] Because of the high CO_2 pressure (55 bar), in this instance the backbiting process undoubtedly proceeds via the metal-bound carbonate species **1** in Scheme 1. The lower activation barrier for the backbiting reaction of 105 kJ/mol determined herein in the absence of CO_2 suggests the pathway to cyclic carbonate via species **2** is lower than that of species **1** by about 28 kJ/mol. This is consistent with the observations that the selectivity for copolymer vs cyclic carbonate production is greater at higher pressure of carbon dioxide. Figure 4 depicts the decrease in cyclic carbonate production with an increase in CO_2 pressure previously observed during the solventless copolymerization reaction.[11] Notwithstanding, computational studies have predicted that the backbiting elimination of cyclic carbonate occurs with a lower energy barrier via the carbonate intermediate **1** as compared to the alkoxide intermediate **2**.[7] At this point it is not possible to access whether this conclusion is incorrect or our comparison of the two processes carried out under different sets of conditions need further clarification. Studies are planned to better address this issue by kinetic measurements under more exacting reaction conditions for both *aliphatic* and *alicyclic* polycarbonates, as well as in the presence of more coordinating solvents where polymer chain dissociation would be favored.

With an increase in reaction temperature the thus formed cyclic carbonate was found to undergo ring-opening polymerization, with the resultant polymer being a mixture of carbonate

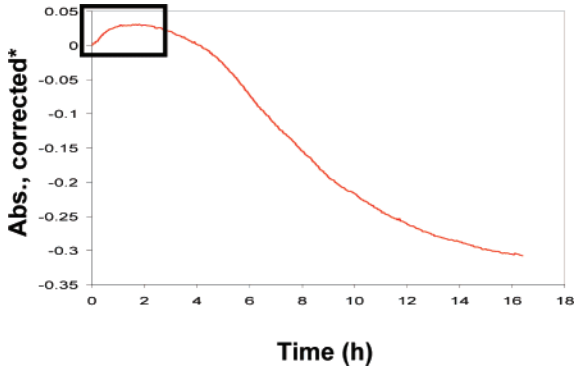


Figure 5. Depolymerization of poly(cyclohexylene carbonate) in CH_2Cl_2 at 90 °C followed by rapid ring-opening of cyclic carbonate to polyether and CO_2.

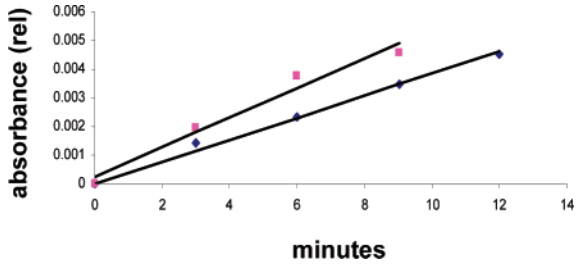
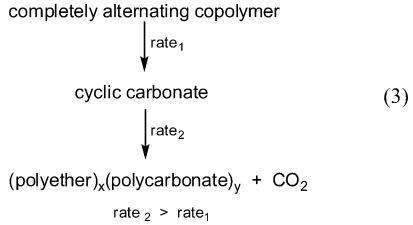


Figure 6. Rate of copolymer depolymerization via initial formation of cyclic carbonate: (blue ◆) 1 equiv PPNCl; (red ■) 2 equiv PPNCl.

units and the corresponding oxide units accompanied by CO_2 lost. This process is assumed to take place via a base-catalyzed process, where the anionic cocatalyst attacks the carbonyl carbon center of the cyclic carbonate.[12] For example, see the reaction profile at 90 °C in Figure 5, where the initially produced cyclohexylene carbonate shown in boxed area rapidly decomposes. For a temperature rise of 10 °C (90 → 100 °C), the ether linkages in the remaining polymeric material increased from 15% to 27%.

We anticipate, based on both experimental and theoretical studies,[7,8] that in the presence of an excess of the anionic initiator (cocatalyst) the activation barrier for the "free copolymer chain" depolymerization via the backbiting mechanism (Scheme 1, step b) would be less than that found for pathway a. When the cocatalyst loading was augmented to 2 equiv, it was readily apparent that this leads to faster cyclic carbonate production both during the polymerization and depolymerization steps. Unfortunately for the aims of this study, upon increasing the anionic cocatalyst the ring-opening of the cyclic carbonate leading to polyether and CO_2 was enhanced to a greater extent than the copolymer depolymerization to cyclic carbonate (eq 3). Nevertheless, it was apparent that the rate of copolymer degradation to cyclic carbonate was increased as the cocatalyst loading increased. Figure 6 depicted the 25% increase in copolymer depolymerization to cyclic carbonate upon increasing the concentration of PPNCl by a factor of 2.



(3)

Conclusions

We have shown from a model system designed to produce low molecular weight metal-bound copolymer chains from the completely alternating copolymerization of cyclohexene oxide and CO_2 that in the absence of these comonomers in methylene chloride, cyclic carbonate is produced via the backbiting mechanism with an activation energy of 105 ± 7 kJ/mol. This process is assumed to take place via a metal alkoxide (polymer chain) intermediate. This activation barrier is significantly lower than that previously reported for formation of cyclic carbonate during the copolymerization of cyclohexene oxide and CO_2 at 55 bar, a process presumably occurring by way of a metal−carbonate (polymer chain) intermediate. Additionally, this study revealed that the depolymerization reaction leading initially to cyclic carbonate was demonstrated to be enhanced in the presence of excess anionic cocatalyst, presumably by way of a metal displaced anionic copolymer chain (Scheme 1b). Unfortunately, subsequent ring-opening of the cyclic carbonate with concomitant formation of polyether and CO_2 was fast at these reaction temperatures (80−100 °C) such that it was not possible to adequately access the effect of increasing anion initiator concentrations on cyclic carbonate production.

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