CO$_2$ AS A MONOMER FOR POLYCARBONATE SYNTHESIS

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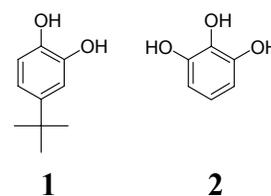
INTRODUCTION

The low cost and low toxicity of CO$_2$ make it an attractive industrial chemical reagent, and the utility of CO$_2$ is dramatically illustrated by the fact that 90 million tons of CO$_2$ are consumed per year in the industrial production of urea.[1]   Other methods for using CO$_2$ as a practical carbon feedstock are being aggressively investigated, and one of the most intensely studied processes involves the use of CO$_2$ in the synthesis of polymers, especially polycarbonates. The current industrial synthesis of polycarbonates is primarily based on the condensation of highly toxic phosgene and aromatic or aliphatic diols.   Because CO$_2$ would provide a less expensive, less toxic alternative to phosgene, considerable effort has gone into developing a polycarbonate synthesis based on CO$_2$.

FIRST GENERATION CATALYSTS

Zinc-Catalyzed Copolymerization of Epoxides and CO$_2$

In 1969, S. Inoue and co-workers discovered that CO$_2$ and propylene oxide copolymerize in the presence of ZnEt$_2$ and water to make a polycarbonate.[2] Following that report, the behavior of several zinc-based catalysts with different co-monomers was explored.[3-5]   The most successful and most intensively studied of the early catalysts were those based on ZnEt$_2$ and a co-catalyst having two or more labile hydrogen atoms, such as water, *tert*-butylcatechol (**1**), or pyrogallol (**2**).

The labile hydrogen atoms of the co-catalysts are believed to react in situ with the ZnEt$_2$ to form ethane and an oxygen-zinc bond.   Because the co-catalyst molecules each have at least two labile hydrogen atoms, they form a polymeric metal oxide structure with zinc in the backbone. Many epoxides and even some oxetanes were found to copolymerize with CO$_2$ in the presence of these catalysts, but because of its low cost and good reactivity, propylene oxide was the most studied co-monomer.   Unfortunately, these catalysts were usually insoluble and poorly defined, and they had rather low turnover numbers (TON).

Mechanistic Studies

On the basis of mechanistic studies, it is proposed that the epoxide ring is opened by nucleophilic attack from the backside. Several observations support this proposal: First, co-monomers which are susceptible to only cationic polymerization (tetrahydrofuran, 7-oxabicyclo[2.2.1]heptane, oxepane) do not copolymerize with CO$_2$, indicating that anionic attack is more likely.[4] Second, when the copolymer produced from *cis*-cyclohexene oxide and CO$_2$ was hydrolyzed, the resulting 1,2-cyclohexanediol was

found to have the *trans* configuration.[4] The inversion of one of the C-O bonds in the epoxide indicates that the ring-opening results from backside attack. Finally, studies with optically active epoxides established that the carbon atom which is favored for nucleophilic attack showed an inversion of configuration, again suggesting a nucleophilic mechanism.[6,7]

The alternating character of the copolymer suggests that epoxide insertion is the rate limiting step. It is important to note that the catalysts used in the copolymerizations are often very effective for the homopolymerization of epoxides if no CO_2 is added to the system.   However, in the copolymerization of CO_2 and epoxides, many of the systems produce nearly perfectly alternating copolymers.[4] If CO_2 insertion were the rate limiting step and epoxide opening were fast, the polymers would not be alternating, but instead, would have a high percentage of ether linkages resulting from the sequential addition of the epoxide monomers as in an epoxide homopolymerization. On the other hand, if CO_2 insertion were fast and the epoxide opening were slow, CO_2 insertion would nearly always precede a subsequent epoxide opening, which is consistent with the observed alternating copolymer.

Solvent effects in the polymerization imply that the mechanism involves coordination of the epoxide to the metal prior to insertion (Scheme 1). Polar, aprotic solvents that are weak Lewis bases were found to be the best solvents.[4] Strong Lewis bases inhibit the reaction, from which it was inferred that they compete with epoxide coordination to the metal center.

Scheme 1.
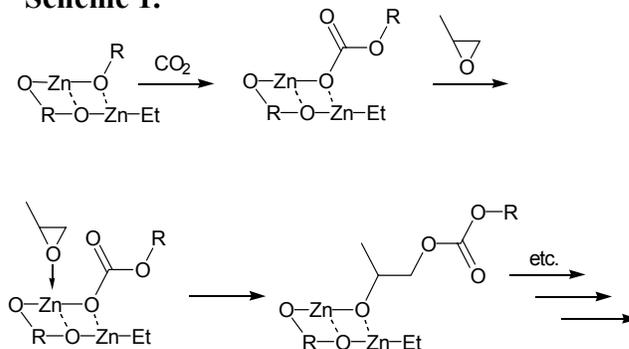
Effective catalyst systems are based on $ZnEt_2$ and a co-catalyst with two acidic hydrogen atoms. When a co-catalyst with only one acidic hydrogen atom is used, the primary product is a cyclic carbonate, and some cyclic carbonate forms even with highly active copolymerization catalysts. This cyclic carbonate has been proposed to form through a back-biting reaction, as shown in Scheme 2.[8] Because the polymeric Zn species formed from co-catalysts with two or more labile hydrogen atoms is large, it may sterically favor insertion of the rather small CO_2 molecule rather than the back-biting coordination of the relatively large chain end, thus favoring polymerization.[9]

Scheme 2.

R, R' = alkyl, aryl

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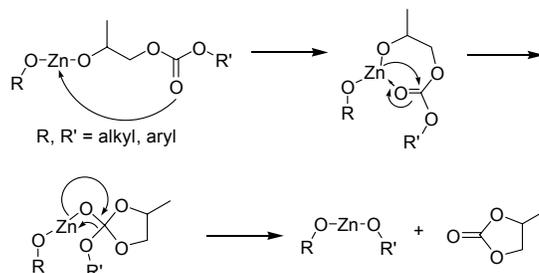
SECOND GENERATION ZINC CATALYSTS

Well Defined Zinc Bis(Phenoxide) Catalyst

While work with the first generation of catalysts led to successful copolymerization of CO_2 and epoxides, the catalyst turnover was low, and the lack of a well defined catalyst made it difficult to rationally design improved systems. A major step in understanding and improving the zinc-catalyzed polymerization of CO_2 and epoxides was made in 1995 by Darensbourg and co-workers with well-defined zinc bis(phenoxide) catalysts (**3**) based on 2,6-diphenylphenol and similar 2,6-disubstituted phenols.[10,11] These complexes were found to crystallize with two Lewis base ligands, and crystallography showed the catalyst to have a distorted tetrahedral arrangement of the ligands around the zinc center. When placed in a solution of cyclohexene oxide with added CO_2, the catalyst produced high yields of the desired polycarbonate (Table 1), whereas it gave primarily cyclic propylene carbonate when propylene oxide was employed as a monomer. The steric bulk of the chain formed from cyclohexene oxide was claimed to prevent the back biting required for cyclic carbonate formation as shown in Scheme 2. In spite of being more costly, the tendency of cyclohexene oxide to favor polymerization over cyclization has made it the most common monomer for copolymerization with CO_2 in recent polycarbonate studies. Another advantage of poly(cyclohexene carbonate) is its relatively high glass transition temperature (135 ºC) compared with poly(propylene carbonate) (33 ºC).[3]
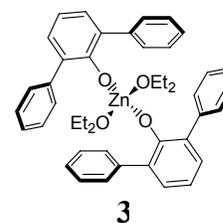
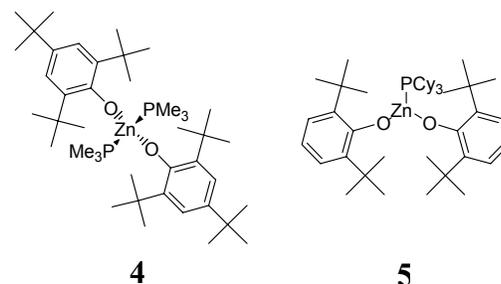**Table 1. Polycarbonate synthesis from CO_2 and cyclohexene oxide.**

Catalyst	P (psi)	T (ºC)	t (h)	%c[a]	M_n	pdi	TON	TOF (h^{-1})
ZnEt$_2$/**2** (2:1)	880	85	5	--	--	--	18	4.5
3	800	80	69	91	38000	4.50	168	2.4
5	800	80	62	95	--	--	322	5.2
ZFA[b]	2000	110	24	96	16200	4.20	203	8.4
6	100	50	2	96	31000	1.11	449	247.0
9	3300	95	18	97	3930	1.16	4147	230.4

[a] Percent carbonate linkages in the polymer backbone. [b] Zinc fluoroalkyl catalyst shown in Figure 2.

In contrast to the rather speculative mechanistic work done with the poorly-defined first generation catalysts, the well-defined nature of the second generation catalysts facilitated more direct mechanistic studies. For example, with the first generation systems, solvent effects were used to establish that the availability of coordination sites on the Zn atom plays a key role in the reactivity of the catalyst.[4] However, with the well-defined catalysts developed Darensbourg and co-workers, more sophisticated experiments could be done to more directly make a similar conclusion. They synthesized

catalysts such as **4** in which labile ether ligands were replaced with strongly binding phosphine ligands, thus resulting in a catalyst with four non-displaceable ligands and no available coordination sites. As predicted, this compound shows no reactivity toward epoxides in homopolymerizations or copolymerizations with CO_2.[11]

While epoxide opening requires an open coordination site on the metal, further work with the zinc bis(phenoxide) catalysts established that CO_2 insertion does not.[11] In the presence of pyridine (a strongly coordinating Lewis base), the zinc bis(phenoxide) catalysts were inactive for both homopolymerization of epoxides and copolymerizations of epoxides with CO_2. Thus, pyridine apparently binds so strongly to the metal that the epoxide cannot compete. However, ^{13}C NMR experiments in pyridine-d_5 solutions of zinc bis(phenoxides) showed that $^{13}CO_2$ nearly quantitatively inserted into one of the two zinc-phenoxide bonds to form a carbonate. If the oxygen atom of the phenoxide ligands was sterically crowded, this insertion was not observed. Thus, because the insertion of CO_2 is sensitive to the steric environment around the phenoxide oxygen atom and rather insensitive to the environment around the metal, the insertion seems to involve interaction of the electrophilic carbon of CO_2 with the phenoxide oxygen atom prior to insertion.

The importance of the exact number of available coordination sites was further elucidated with the synthesis of catalysts such as **5** which have only one site available for epoxide binding on each Zn center.[12,13] These catalysts were active in the copolymerization of epoxides and CO_2, but they significantly decreased the percentage of ether linkages incorporated into the polymer backbone. Based on this behavior, it appears that catalysts with only one available site for epoxide binding nearly always undergo CO_2 insertion prior to coordinating with another epoxide. However, catalysts with two sites available for epoxide coordination can have two simultaneously bound epoxides, and in that case, sequential epoxide opening to form an ether linkage is competitive with CO_2 insertion.

Zinc β-Diiminate catalyst

Coates and co-workers recently reported a soluble Zn catalyst (**6**) with a chelating β-diiminate ligand having an unprecedented TON and turnover frequency (TOF) (Table 1).[14,15] This high activity was achieved with mild conditions of only 100 psi of CO_2 at 50 °C for 2 h. Another feature of the β-diiminate catalyst is its remarkably low polydispersity, with indices near 1.1. The low polydispersity is suggestive of quantitative, rapid initiation and lack of significant chain transfer or termination during the polymerization.

Asymmetric Catalysts

In 1999, Nozaki and co-workers reported the first successful asymmetric copolymerization of CO_2 and cyclohexene oxide by using a catalyst derived from $ZnEt_2$ and a chiral amino alcohol (**7**).[16] The copolymer was hydrolyzed, and the resulting 1,2-cyclohexanediol was formed with 73% enantiomeric excess. Because only one enantiomer of the chiral alcohol **7** was used, only the enriched R,R-diol was reported.
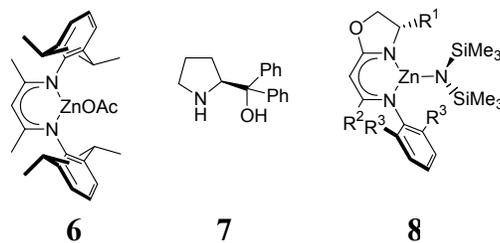
Coates and co-workers subsequently reported a system for asymmetric catalysis with even greater activity and selectivity.[17] Attempts to modify the previously reported β-diiminate catalyst **6** by synthesizing a bisoxazoline system with C_2 symmetry did not produce an active catalyst. However, by synthesizing a hybrid imine-oxazoline ligand, they were able to generate an active asymmetric catalyst (**8**). Furthermore, by varying the substituents on the oxazoline group (R^1), imine group (R^2), and N-phenyl group (R^3), they found an optimized catalyst that displayed up to 76% ee with higher conversions and milder conditions than those reported using the chiral alcohol **7**. These asymmetric catalytic systems have been proposed to serve not only for the production of chiral polymers, but also as an alternate route to asymmetric ring opening of epoxides via hydrolysis of the copolymers.

Unintentionally, Nozaki and co-workers' efforts toward the development of an asymmetric catalyst led to an interesting spectroscopic insight. Previous work had shown that the carbonyl carbon of isotactic and syndiotactic diads in polycyclohexene carbonate appeared at different chemical shifts in the ^{13}C NMR spectra (Figure 1). These isotactic and sydiotactic peaks were assigned by using the diastereomers of 2,2'-oxydicyclohexanol as model compounds.[9] The ^{13}C NMR peak assignments based on that model were accepted in subsequent literature, and as a result, it was claimed that the polycyclohexene carbonate from certain catalysts was primarily syndiotactic.[11] When Nozaki and co-workers first synthesized the asymmetric copolymer, the ^{13}C NMR showed that that copolymer must be syndiotactic if the previously reported peak assignments were correct.[16] However, a polymer with a high degree of optical purity cannot be syndiotactic because that would require adjacent repeat units to have opposite chirality. As a result of this realization, Nozaki and co-workers conducted a more thorough investigation with better model compounds and found that the previously accepted peak assignments indeed needed to be reversed.[18] Consequently, the enantiomerically enriched copolymer tends to be isotactic, as expected.
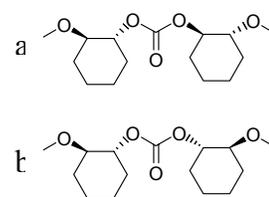
Figure 1. Isotactic (a) and syndiotactic (b) diads of poly(cyclohexene carbonate)

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CO₂ as a Monomer and Solvent

The use of liquid and supercritical CO_2 as solvents in chemical processes is a rapidly emerging field,[1] so the use of CO_2 as a solvent for the copolymerization of CO_2 and epoxides was a natural step. Beckman and co-workers synthesized a CO_2-soluble zinc fluoroalkyl catalyst (ZFA) from ZnO and the monoester of tridecafluorooctanol and malaeic acid (Figure 2).[19] A crystal structure of this catalyst could not be obtained, and it was assumed that it had structural variations. At the time the catalyst was reported, its TON and TOF were higher than any other zinc-based catalyst (Table 1). The activity of the catalyst was very sensitive to the conditions at which the reaction was performed. Temperature, pressure, and the mole ratio of cyclohexene oxide and CO_2 were all found to play an important role in determining the amount of copolymer synthesized.
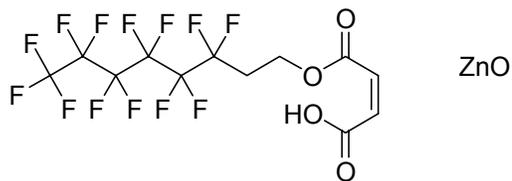
Figure 2. Components of a CO_2-soluble catalyst

PORPHYRIN CATALYSTS

After the initial discovery that Zn compounds are capable of catalyzing the copolymerization of CO_2 and epoxides, S. Inoue and co-workers began searching for other potential catalysts. Because of their structural similarity to chlorophyll, porphyrins were investigated to determine whether they had a similar ability to activate CO_2.[20] Certain porphyrin-based compounds were indeed active for the copolymerization of CO_2 and epoxides.[21] Based on these previous porphyrin catalysts, Holmes and co-workers developed a fluorinated porphyrin catalyst (**9**) that was soluble in supercritical CO_2.[22] Using

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this catalyst, moderate polymer yields and narrow polydispersities were achieved with remarkably low catalyst loadings (Table 1). Unfortunately, in spite of the unprecedented TON for this system, it was plagued by the inability to produce high molecular weight polymers. The narrow polydispersity suggests a living polymerization, but the unexpectedly low molecular weights indicate that some mechanism is limiting the chain length. An unfavorable equilibrium between the polymer and monomers was suggested as a potential cause for the molecular weight limit. However, because the previously reported copolymerizations of CO_2 and epoxides with porphyrin catalysts are immortal polymerizations,[20] the low molecular weights are most likely caused by protic impurities introduced concurrently with the CO_2 that act as chain transfer agents. This hypothesis is supported by the fact that
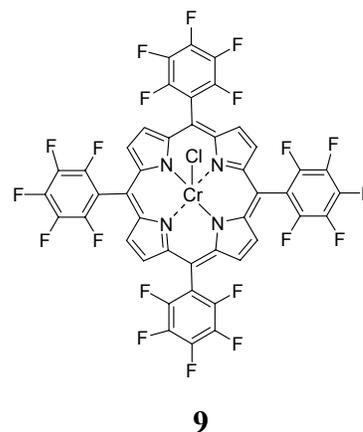
a copolymerization done with this catalyst under a carefully controlled atmosphere produced a nearly three-fold increase in molecular weight.[22] To further improve the system, the porphyrin catalyst was coupled to a polymer support.[23] The polymer-supported catalyst could be recycled, but a loss of reactivity was observed with each successive cycle.

CONDENSATION POLYMERIZATION TO FORM POLYCARBONATE

Soon after the first report of CO_2 as a monomer for polycarbonate synthesis, a system was reported for coupling dihalides, CO_2, and dialkoxides to form polycarbonate in a condensation reaction.[24] The work was not immediately pursued because the need for a strong base to form the alkoxide and the need to include crown ethers made the system impractical for scale-up. Y. Inoue and co-workers overcame those challenges with a recently reported one-pot approach to form polycarbonates by successive condensation of diols, CO_2, and dihalides that avoids the use of strong bases and crown ethers.[25] By mixing the diol, dihalide, and K_2CO_3 in a polar aprotic solvent under CO_2, an alternating polycarbonate was formed. The use of a base stronger than K_2CO_3 or the use of phenols instead of alcohols resulted in the formation of ether linkages rather than carbonate linkages. As a result, it was suggested that the reaction follows the mechanism shown in Scheme 3. K_2CO_3 is basic enough to deprotonate the carbonate, but not sufficiently basic to significantly deprotonate the diol, and this clever balance appears to be the key to the condensation polymerization of CO_2.

Scheme 3.
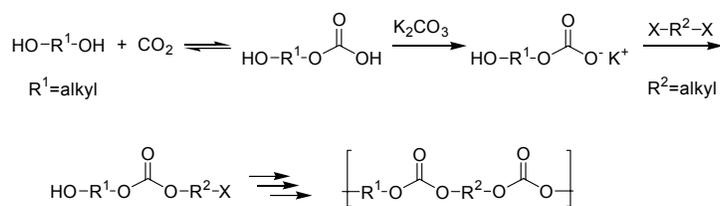
CONCLUSION

Over the past eight years, a new generation of catalysts has emerged for the synthesis of poly(cyclohexene carbonate) from CO_2. Unfortunately, poly(cyclohexene carbonate) does not have the same desirable physical properties as the aromatic polycarbonates being produced industrially, and further work must be done to find an industrially viable polycarbonate derived from CO_2.[26] However, the new catalytic systems have greatly improved activity, and they can produce polymer chains of well controlled molecular weight with relatively low CO_2 pressures. The fundamental knowledge gained through these systems will pave the way to finding an efficient use of CO_2 in the synthesis of industrial polycarbonates.

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