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Communication

Metal Salen Derivatives as Catalysts for the Alternating Copolymerization of Oxetanes and Carbon Dioxide To Afford Polycarbonates

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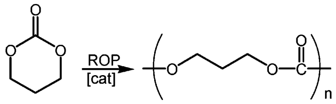
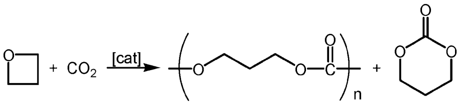
Metal salen derivatives of chromium and aluminum, along with *n*-Bu_4NX (X = Cl or N_3) salts, have been shown to be effective catalysts for the selective coupling of CO_2 and oxetane (trimethylene oxide) to provide the corresponding polycarbonate with only trace quantities of ether linkages. The formation of copolymer is suggested, based on circumstantial evidence, *not* to proceed via the intermediacy of trimethylene carbonate, which was observed as a minor product of the coupling reaction. For a reaction catalyzed by (salen)CrCl in the presence of *n*-Bu_4NN_3 as the cocatalyst, both matrix-assisted laser desorption ionization time-of-flight mass spectrometry and infrared spectroscopy revealed an azide end group in the copolymer.

The alternating copolymerization of CO_2 and epoxides in the presence of heterogeneous metal catalysts to provide polycarbonates, along with cyclic carbonates, was pioneered by Inoue and co-workers in the late 1960s.[1] Since that time, the development of discrete metal catalysts for this process has led to greatly enhanced catalytic activity and selectivity, for both *alicyclic* and *aliphatic* epoxides.[2] Nevertheless, the synthesis of polycarbonates from these latter epoxides has been a real challenge because of the propensity of aliphatic epoxides to couple with CO_2 to afford cyclic carbonates, either via a direct route or by copolymer degradation.[3] An alternative process for the synthesis of aliphatic polycarbonates is the ring-opening polymerization (ROP) of six- and seven-membered cyclic carbonates. Indeed, we recently reported upon the use of metal salen derivatives as effective homogeneous catalysts for the ROP of the six-membered cyclic carbonate trimethylene carbonate (TMC or 1,3-dioxan-2-one; eq 1).[4] This process was found to occur with complete retention of CO_2 in the polycarbonate; i.e., there were no ether linkages in the copolymer. Aliphatic polycarbonates, such as poly(TMC), can be utilized to modify the properties of the brittle biodegradable polyesters (polylactide or polyglycolide).[5] Importantly, poly(TMC) can be hydrolyzed both in vivo and in vitro.[6] Hence, these resulting biodegradable thermoplastic elastomers have a variety of potential applications in biomedical areas, such as surgical sutures, drug-delivery devices, and body or dental implants.



(1)

Four-membered cyclic ethers have only slightly less ring-strain energy than epoxides; e.g., the heat of polymerization of ethylene oxide ($-\Delta H_p = 104$ kJ/mol) differs from that of oxetane (trimethylene oxide) by only 23 kJ/mol.[7] Hence, it is anticipated that active catalysts for the CO_2/epoxide coupling process, such as (salen)MX complexes in the presence of a cocatalyst, would be effective at coupling CO_2 and oxetanes (eq 2). Importantly, in this instance, the byproduct, cyclic carbonate, unlike that in the epoxide process, can ultimately be transformed into the completely alternating copolymer by way of reaction (1). Surprisingly,



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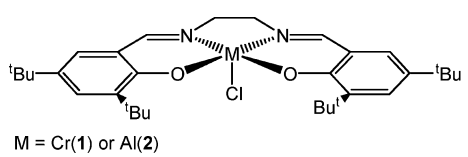


Figure 1. Structure of metal salen catalysts utilized for the copolymerization reactions in eq 2.

Table 1. Copolymerization of Oxetane and CO_2 in the Presence of Complex **1**[a]

cocatalyst	% TMC[b]	% poly(TMC)[b]
n-Bu_4NCl (1 equiv)	22.4	77.6
n-Bu_4NCl (2 equiv)	18.4	81.6
n-Bu_4NN_3 (1 equiv)	6.6	93.4
n-Bu_4NN_3 (2 equiv)	0	100

[a] Copolymerization conditions: 17 mg of catalyst **1** (0.15 mol %), M:I = 675:1, 10 mL of toluene, 35 bar CO_2, 110 °C, 24 h of reaction time. [b] Product distributions were determined by ^1H NMR measurements for polymerization processes carried out for 24 h.

the reaction in eq 2 has received very limited attention. Indeed, earlier reports of this process employing organotin halides or tetraphenylstibonium iodide as catalysts have suffered from very low selectivity for copolymer formation and/or the formation of low-molecular-weight copolymers (~1000 Da).[8]

In this Communication, we report our preliminary findings utilizing chromium(III) and aluminum(III) salen derivatives as catalysts for the coupling of oxetane and CO_2 to provide copolymer along with small quantities of TMC.

Our initial foray at examining the copolymerization reaction of oxetanes and CO_2 involved the utilization of the metal salen derivatives shown in Figure 1 as catalysts. These particular metal complexes, along with anions as cocatalysts, were previously determined to be among the most active for selective coupling of cyclohexene oxide and CO_2 to poly(cyclohexylene carbonate).[9,10] Table 1 contains data for reaction (2) carried out in toluene at 110 °C. We employed as cocatalysts highly purified alkylammonium salts instead of the hydrophobic bis(triphenylphosphine)iminium (PPN) salts because these latter salts are only sparingly soluble in toluene. As is readily seen from Table 1, formation of poly(TMC) is favored using either 1 or 2 equiv of the cocatalyst *n*-Bu_4NCl or *n*-Bu_4NN_3, with the latter salt being more selective toward the formation of the copolymer.

For technical reasons, we have thus far not been able to monitor the copolymerization of oxetane and CO_2 utilizing in situ infrared spectroscopy.[11] Therefore, several bulk polymerization reactions were carried out under the same reaction conditions as a function of the reaction time. Table 2 and Figure 2 contain the results of this study, where it is apparent that the high selectivity of reaction (2) for poly(TMC) formation (98.5%) catalyzed by complex **1** in the presence of 2 equiv of *n*-Bu_4NCl exhibits no time dependence. In an effort to ascertain whether the copolymer was formed directly via reaction (2) or originated from subsequent ROP of the first formed TMC, we have examined the rate of this latter process under identical reaction conditions.[12] Consequently, the ROP of TMC in toluene was found to proceed to completion in less than 4 h (Figure 2), or on a much shorter time scale than the formation of poly(TMC) from CO_2/oxetane. Hence, from these preliminary kinetic studies alone, it is not possible to discern if poly(TMC) formed from reaction (2) is a primary product from the coupling of CO_2 and oxetane, with a concomitant backbiting process providing trace quantities of TMC, or a secondary product from a facile ROP process involving preformed TMC. That is, does the copolymerization reaction in eq 2 proceed in part or exclusively by way of the intermediate formation of TMC (eq 3).

Table 2. Time-Dependent Copolymerization Runs of Oxetane and CO_2 Catalyzed by Complex **1** in the Presence of 2 equiv of *n*-Bu_4NCl[a]

entry	time (h)	% convn	% TMC[b]	% poly(TMC)[b]	% CO_2 content of copolymer[b]
1	4	20.4 (21.4)[c]	1.5 (4.9)[c]	98.4 (95.1)[c]	90.3 (82.4)[c]
2	10.5	42.3	1.6	98.4	89.5
3	18	57.3	1.4	98.6	91.4
4	24	72.7	1.2	98.6	91.8

[a] Copolymerization conditions: 17 mg of **1**, M/I = 675, 3 mL of toluene, 35 bar CO_2, 110 °C. [b] Respective average values with standard deviations for the four entries are 1.5 ± 0.2, 98.5 ± 0.2, and 90.8 ± 1.1. [c] Reaction temperature elevated to 130 °C.

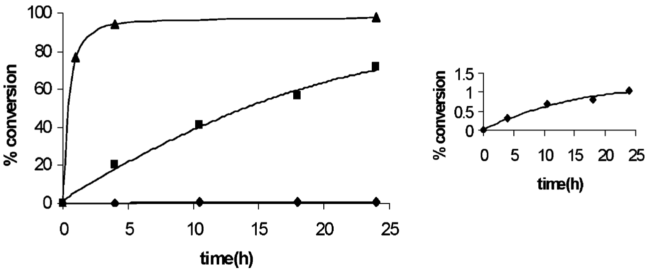
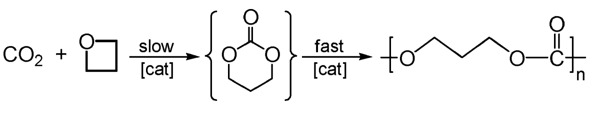


Figure 2. Time dependence of poly(TMC) formation: (■) poly(TMC) and (◆) trace TMC produced by way of CO_2 and oxetane (shown as well in the inset); (▲) poly(TMC) produced from the ROP of TMC. Reaction conditions are described in Table 2.

 (3)

We have performed additional coupling reactions of oxetane and CO_2 in the absence of an organic solvent, i.e.,

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(12) It should be noted that the ROP of TMC by complex **1** does not require a cocatalyst.[4] However, this process takes place much faster in the presence of 2 equiv of *n*-Bu_4NCl than in complex **1** alone.

Table 3. Copolymerization of Oxetane and CO_2 with (salen)MCl (M = Al, Cr) Catalysts in CO_2-Expanded Oxetane[a]

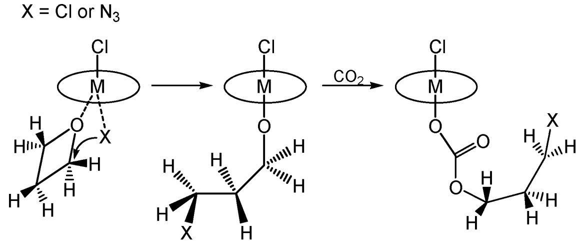
catalyst	cocatalyst[b]	% TMC	% poly(TMC)	% CO_2 content	TOF[c]	yield (%)
1	*n*-Bu_4NCl	2.9	97.1	96.7	41.2[d]	24.0
1	*n*-Bu_4NN_3	1.7	98.3	95.9	38.8[e]	19.5
2	*n*-Bu_4NCl	1.7	98.3	94.2	8.59[d]	5.0

[a] Copolymerization conditions: catalyst loading = 0.077 mol %, 4.0 g of oxetane, 110 °C, M/I = 1292, 35 bar CO_2. [b] 2 equiv of cocatalyst. [c] Measured in moles of oxetane consumed per mole of metal per hour. [d] Reaction time = 7.5 h. [e] Reaction time = 6.5 h.

in CO_2-expanded oxetane, for comparison with previously reported epoxide/CO_2 copolymerization reactions. These results are provided in Table 3, where both complexes **1** and **2** were employed as catalysts in the presence of anionic cocatalysts. As is apparent from the data in Table 3, the chromium salen derivative is much more effective than its aluminum analogue. This is consistent with observations for the epoxide/CO_2 copolymerization process.[10] Furthermore, the coupling of CO_2 and oxetane occurs at a reduced rate compared to propylene oxide or cyclohexene oxide and CO_2. This latter observation is not unanticipated based on the fact that ring opening of three-membered cyclic ethers is energetically favored by approximately 20 kJ/mol over their four-membered counterparts.

The molecular weights (M_n's) of the copolymers reported in Table 3 produced from catalyst **1** in the presence of cocatalysts *n*-Bu_4NCl and *n*-Bu_4NN_3 were determined by gel permeation chromatography (GPC) to be 10 100 and 7400 with corresponding polydispersity indices of 1.58 and 1.51, respectively.[13] Furthermore, a low-molecular-weight copolymer produced from a reaction catalyzed by complex **1** and 1 equiv of *n*-Bu_4NN_3 revealed an azide end group by matrix-assisted laser desorption ionization time-of-flight mass spectrometry.[14] Consistent with this observation, this copolymer possessed a ν_{N_3} vibrational frequency at 2102 cm^{-1} in CH_2Cl_2, which is representative of an organic azide. As is depicted in Scheme 1, the initiation step in the presence of an ionic cocatalyst has been shown to be first-order in both (salen)CrCl and PPNX.

Scheme 1



These latter observations, i.e., azide polymer end groups and molecular weights of about one-third to half their theoretical values, are earmarks of the CO_2/epoxide copolymerization process catalyzed by (salen)CrCl/$PPNN_3$.[15] By way of contrast, the ROP of TMC employing (salen)MX catalysts has provided *completely* alternating copolymers with molecular weights that track the monomer/initiator (M/I) ratio. Therefore, our current findings *suggest* that the copolymer produced in eq 2 results from the direct enchainment of oxetane and CO_2 following the initiation step in Scheme 1. What is extremely encouraging about these results is that the selectivity for copolymer formation from oxetane and CO_2 is very high (97%) in all instances, even at 110 °C, where the selectivity for propylene oxide and CO_2 is generally 100% in favor of monomeric propylene carbonate. This selectivity for copolymer formation might be anticipated because the six-membered cyclic carbonate has greater ring strain than its five-membered analogue.[16] Studies to further address these issues, as well as investigations into the mechanistic aspects of the oxetane/CO_2 coupling reaction, for a variety of oxetane derivatives in the presence of optimized metal catalysts are underway in our laboratories.

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Supporting Information Available: Experimental details of the copolymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) GPC measurements in THF were carried out at the New Jersey Center for Biomaterials, Rutgers University.

(14) We are extremely grateful to Dr. Shane Tichy of the Laboratory for Biological Mass Spectroscopy at Texas A&M University for this determination.

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