

(Salen)Cr^{III}X Catalysts for the Copolymerization of Carbon Dioxide and Epoxides: Role of the Initiator and Cocatalyst

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The copolymerization of CO₂ and cyclohexene or propylene oxide has been examined employing (salen)Cr^{III}Nu complexes (Nu = Cl or N₃) as catalysts. The addition of various cocatalysts, including phosphines and PPN⁺ or Bu₄N⁺ Cl⁻ salts serves to greatly enhance the rate of copolymer production. In these instances, the mechanism of the initiation step appears to be unimolecular in catalyst concentration, unlike the bimolecular process cocatalyzed by *N*-methylimidazole. The copolymers were produced with >95% carbonate linkages with TOFs in the range 39–494 mol epoxide consumed/mol Cr·h. In the presence of phosphine cocatalysts, no cyclic carbonate was produced as a byproduct.

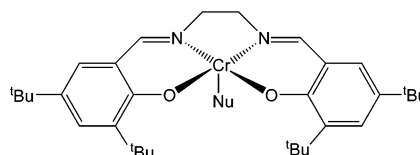


Figure 1. Typical (salen)Cr^{III}Nu (**1**), Nu = Cl (**1a**), N₃ (**1b**), catalyst for the copolymerization of epoxides and carbon dioxide.

Furthermore, this catalyst system has been shown to be equally effective at copolymerizing carbon dioxide and epoxy functionalized silanes, such as 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, to afford potentially industrially useful polycarbonates.³ That is, cross-linking of the silane units leads to very tough polymeric materials, and a blending of cyclohexene oxide with these epoxy silanes in a terpolymerization process should provide an effective approach for modifying the polymer's physical properties.

The initiation step for the copolymerization process utilizing (salen)Cr^{III}Nu catalysts is akin to the mechanism for the asymmetric ring opening (ARO) of epoxides which has been defined to proceed via a dinuclear transition state.⁴ This is illustrated in Scheme 1 (second order pathway), whereby the nucleophile on one chromium center attacks an epoxide bound to a second chromium center. On the other hand, the monomer enchainment steps were found to be first order in catalyst concentration and to be greatly enhanced in the presence of a cocatalyst, e.g., *N*-methylimidazole or (dimethylamino)pyridine.^{2,5} Since the cocatalyst is assumed to bind to the metal center at the vacant site *trans* to the nucleophile, i.e., the site for epoxide binding, the initiation step should be highly sensitive to the nature and concentration of the cocatalyst. In this communication, we wish to report quantitative studies on the influences of the nature of the nucleophile, cocatalyst, and ligand on the activity of (salen)Cr^{III}(Nu) catalysts for the copolymerization of epoxides and CO₂.

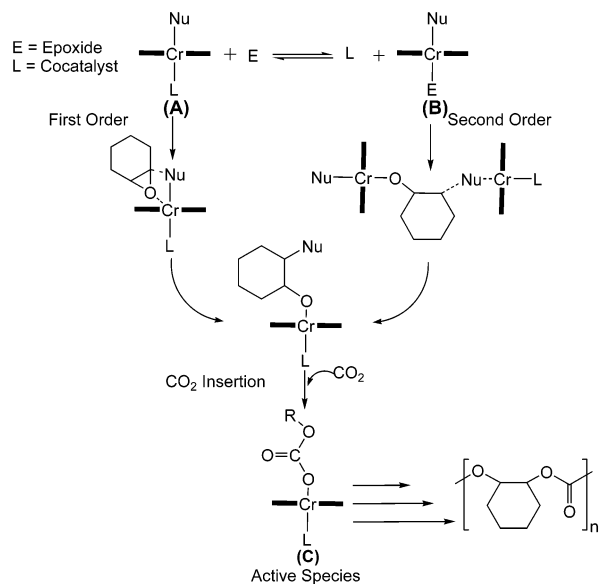
Over the past decade a variety of efficient catalysts or catalyst precursors for the copolymerization of cyclohexene oxide and carbon dioxide have been reported.¹ These processes represent environmentally benign synthetic routes to polycarbonates, biodegradable thermoplastics which are mostly prepared by the interfacial polycondensation of diols and phosgene. In this connection we have described a very active, robust catalyst for the coupling of cyclohexene oxide and CO₂ based on salen derivatives of chromium(III).² One such catalyst is depicted in Figure 1, where the H₂salen ligand is *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine.

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Scheme 1

Table 1. Copolymerization Data Using Different Cocatalysts^a

complex	cocatalyst (equiv)	TON ^b	TOF ^c	% carbonate
1a	<i>N</i> -methylimidazole (5)	95	24	69%
	PPh ₃ (3) ^d	157	39	96%
	PCy ₃ (3)	578	145	99%
	NBu ₄ Cl (1)	415	104	95%
	PPNCl (1) ^e	1004	251	>99%
1b	<i>N</i> -methylimidazole (5)	189	47	90%
	PPh ₃ (3)	284	71	96%
	PCy ₃ (3) ^f	391	98	97%
	NBu ₄ Cl (1)	721	180	98%
	PPNCl (1)	1022	255	>99%

^a 50 mg of catalyst was dissolved in 20 mL of cyclohexene oxide and injected into a 300 mL Parr autoclave. The reactor was charged to 55 bar CO₂ pressure and heated to 80 °C for 4 h. ^b Mol epoxide consumed/mol Cr. ^c Mol epoxide consumed/mol of Cr·h. ^d For a 24 h run, $M_n = 22\,700$ and PDI = 1.55. ^e For a 4 h run, $M_n = 5980$ and PDI = 2.05, whereas for a 12 h run, $M_n = 16\,800$ and PDI = 1.92. ^f For a 10 h run, $M_n = 10\,800$ and PDI = 1.54.

We have examined a wide variety of (salen)CrCl derivatives as catalysts for the copolymerization of epoxides and carbon dioxide;⁶ however, the majority of this report will focus on one of the more active derivatives thus far investigated, complex **1**. Under identical reaction conditions, the copolymerization of cyclohexene oxide and CO₂ catalyzed by complexes **1a** and **1b** exhibits similar rates for polymer production (Table 1). This is not unexpected since the nucleophile is only involved in the initial epoxide ring opening step. What does change significantly is the initiation time, which has a $t_{1/2}$ of about 5 min at 80 °C with a chloride initiator and <0.5 min with an azide initiator. In addition to azide being a better nucleophile than chloride, the azide ligand provides a useful infrared spectroscopic probe of the catalytic species in the solution. In weakly coordinating solvents such as toluene at -10 °C, complex **1b** exhibits an infrared stretching frequency due to the azide ligand at 2080 cm⁻¹, characteristic of the 5-coordinate species. Upon addition of a neutral donor ligand, the $\nu(\text{N}_3)$ band shifts to 2054 cm⁻¹, showing a change from 5- to 6-coordinate. When

the neutral donor is cyclohexene oxide, the initial shift to lower wavenumbers is followed by a shift back to higher frequency at 2098 cm⁻¹, indicative of a change from metal bound azide to an organic azide as has previously been observed.^{4b} In the presence of 2.25 equiv of *N*-methylimidazole, no change from the band at 2054 to 2098 cm⁻¹ was noted until the temperature was increased to 60 °C. If at this point CO₂ is introduced into the reaction system, a metal bound carbonate stretching frequency is observed at 1688 cm⁻¹ followed by formation of poly(cyclohexylene carbonate) as indicated by an infrared band at 1750 cm⁻¹.

The relative *N*-methylimidazole loading also plays an important role in polymer formation. Upon increasing the concentration of cocatalyst for both **1a** and **1b**, the initiation time (measured from the beginning of the reaction to the onset of the maximum rate) lengthens while the maximum rate increases. Such behavior suggests additional amounts of Lewis base inhibit initiation yet enhance subsequent chain propagation. Consequently, if the reaction time is not sufficient, the catalyst would erroneously appear to be poisoned by excess cocatalyst. These observations would suggest that stronger donor ligands, such as phosphines, might severely inhibit the second order in catalyst concentration initiation step and concomitantly copolymer production. However, as indicated in Table 1 the addition of PPh₃ or PCy₃ enhanced catalytic activity. In addition, kinetic studies monitored via in situ infrared spectroscopy show that the more donating phosphine unexpectedly decreases the initiation time while increasing the maximum rate. Further studies have shown that additional equivalents of phosphine enhance this effect and saturation kinetics are observed above 5 equiv. Kinetic studies also show that the order in catalyst concentration decreases from a mixed order dependence when using *N*-methylimidazole as a cocatalyst to approximately first order with tricyclohexylphosphine. These results intimate a second pathway for catalyst activation for reactions carried out in the presence of strongly coordinating cocatalysts. Hence, Scheme 1 summarizes our findings with a more detailed mechanistic delineation.

Catalyst initiation is dictated by the preliminary equilibrium established between epoxide (**B**) and cocatalyst (**A**) binding to the metal center. When a strongly donating cocatalyst is present, the chromium–nucleophile bond is weakened suitably to allow concerted epoxide ring-opening to occur. Indeed, this step could involve some degree of ionic character. This pathway benefits kinetically from the shifting of the equilibrium toward **A**. *N*-Methylimidazole, a weaker donating Lewis base, can only adequately activate the nucleophile toward the second order pathway, which requires sufficient concentrations of both **A** and **B** for initiation, making the overall rate more sensitive to cocatalyst loading. Both first and second order initiation steps eventually result in the same active species, **C**, which will then alternately enchain cyclohexene oxide and CO₂ resulting in the polycarbonate chain. The rate enhancement gained from excess cocatalyst further suggests that the active species is affected by the competitive binding of cocatalyst and epoxide *trans* to the propagating chain, the latter species being much less active toward polymer formation.

(6) Unpublished results of Cindy C. Fang from our laboratories.

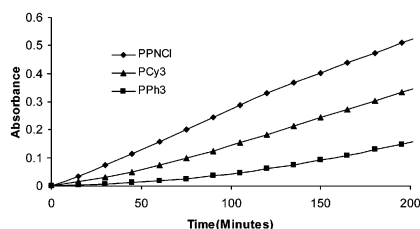


Figure 2. Comparison of cocatalysts using catalyst **1b**. Data taken from Table 1 for cyclohexene oxide/CO₂.

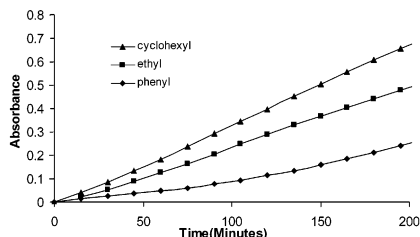


Figure 3. Comparison of different salen backbones employing PPNCl as cocatalyst for cyclohexene oxide/CO₂ copolymerization.

The proposed mechanism in Scheme 1 suggests that overall activity is improved with cocatalysts that bind strongly enough to labilize the Cr–Nu bond. In the extreme case, a free anion might maximize nucleophile activation to effectively reduce the initiation time while increasing the rate of propagation. A suitable cocatalyst would require a noninteracting cation, a logical initial choice being bis-(triphenylphosphoranyl)ammonium (PPN⁺), with the positive charge delocalized over a large molecular volume. Using PPN⁺ Cl[−] as a cocatalyst, the initiation time was effectively reduced to zero for both **1a** and **1b** (presumably via first order initiation) resulting in significant gains in turnover frequency (Figure 2). Tetra-*n*-butylammonium chloride (NBu₄⁺Cl[−]) showed the same reduction in activation time but slightly lower activity. In the absence of catalyst, the PPN salts will couple cyclohexene oxide and CO₂ to form *cis*-cyclohexyl carbonate; however, only trace amounts of this side product are observed in the copolymerization reaction. The interplay between the first and second order processes has some significant consequences when using the anionic cocatalysts. Ligand design studies (using *N*-methylimidazole as cocatalyst) showed that steric crowding around the diimine moiety decreased activity regardless of the relative donating ability of the additional groups.⁶ These findings were consistent with a second order initiation step that would be inhibited by bulky groups in such close proximity to the metal center, making the unsubstituted ligand derived from ethylenediamine (precursor for **1a** and **1b**) the most active. However, the first order initiation step should relax the steric requirements and allow for incorporation of more electron donating groups along the diimine backbone. As shown in Figure 3, an increase in activity results from incorporation of the bulkier and more electron donating cyclohexyldiimine analogue as well as decreased activity from the electron withdrawing phenyl backbone. Further, a catalyst also incorporating donating groups to the phenolate moieties produces copolymer at an extremely high rate.⁷

Previous results from our group showed that Cr(salen)Cl complexes can also be utilized with propylene oxide as a

Table 2. Results Obtained for the Copolymerization of Propylene Oxide and CO₂^a

complex	PPh ₃ ^b	TOF ^c	% carbonate
2b	0.5	34	88
	1	69	92
	2	17	96
	3	7.5	98.5

^a 50 mg of catalyst was dissolved in 20 mL neat propylene oxide and injected into a Parr autoclave. The reactor was charged with 34.5 bar CO₂ and the reaction heated to 60 °C for 4 h. ^b Amount of phosphine measured in equiv/mol catalyst. ^c Mol PO consumed/mol Cr·h.

monomer.² These experiments were plagued by the fact that at high temperatures only cyclic carbonate was produced and at low temperatures the activity was greatly reduced. Rieger and co-workers have shown that by changing the salen diimine backbone from a cyclohexyl to phenyl group (i.e., in complex **2**, H₂salen = *N,N'*-bis(3,5-di-*tert*-butylsilylidene)-1,2-phenylenediimine) that the major product can be shifted from cyclic carbonate to polymer, yet a significant amount of cyclic carbonate was still produced.⁵ Herein we report attempts to apply phosphine and anionic cocatalysts as well as an azide initiator to propylene oxide/CO₂ copolymerization. While a more electron donating salen increases the rate of polymerization with cyclohexene oxide, this seems to have the opposite effect for propylene oxide and tends to decrease the rate of conversion for both cyclic and polymer. Although the use of a chloride initiator (**2a**) with PPh₃ cocatalyst produced little ring-opened products over a 4 h reaction period, a more nucleophilic initiator, azide (**2b**), proved to be ideal. The optimum reaction temperature was found to be 60 °C, where no cyclic carbonate was produced as compared to higher temperatures. As shown in Table 2, our results concur with Rieger in the respect that the addition of cocatalyst beyond 1 equiv. slows polymer formation; however, no concomitant increase in cyclic formation is observed. As previously stated, copolymerization using cyclohexene oxide is further enhanced through the use of anionic cocatalysts. However, when using a PPN⁺Cl[−] cocatalyst, this was not the case for propylene oxide as cyclic carbonate was the major product.

In conclusion, the catalytic systems reported herein for the coupling of either cyclohexene oxide or propylene oxide with CO₂ to provide polycarbonates with TOFs up to 494 h^{−1} are inferior in activity only to a selection of the highly active β-diimine zinc derivatives.^{1k}

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Note Added after ASAP: The word “only” was missing from the last paragraph of the version of this paper posted ASAP on February 13, 2004. The corrected version was posted on February 18, 2004.

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(7) Utilizing (1*R*,2*R*)-(−)-[1,2-cyclohexanediiimino-*N,N'*-bis(3-*tert*-butyl-5-methoxysilylidene)]chromium(III) azide and a PPN⁺Br[−] cocatalyst, a TOF of 494 mol CHO consumed/mol Cr·h is obtained.