Catalytic Activity of Zinc(II) Phenoxides Which Possess Readily Accessible Coordination Sites. Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide

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Received June 16, 1995
Revised Manuscript Received August 16, 1995

Inoue and co-workers first reported the alternating copolymerization of carbon dioxide and epoxides using $Zn(CH_2CH_3)_2$ and H_2O in 1969.[1,2] Since then a variety of other catalysts and catalyst precursors have been investigated for this polymerization process,[3] with the most active being those prepared by the reaction of zinc oxide with dicarboxylic acids.[4] The formation of condensed Zn(II) species is considered necessary for copolymer chain propagation, where polymer formation is proposed to occur on adjacent zinc centers.[5] Although some of these catalyst systems operate under mild conditions (ambient temperature and modest pressure), these processes have been plagued by low turnovers, broad molecular weight distributions, and often low reproducibility.

The accepted mechanism for this copolymerization reaction involves epoxide coupling to a metal alkyl carbonate (or carboxylate) with subsequent CO_2 insertion into the thus formed metal alkoxide. In an effort to establish reaction precedent for carboxylate/epoxide coupling at group 12 metal centers, we recently reported the isolation and characterization of η^3-HB(3-Phpz)$_3$Cd(carboxylate)·epoxide complexes.[6] These derivatives were observed to react with excess epoxide to homopolymerize the epoxide to provide polyethers with carboxylate end groups and to react in the presence of CO_2/epoxide to provide exclusively cyclic carbonates. The analogous zinc(II) complexes were found not to bind epoxides; hence monomeric zinc(II) complexes with more accessible coordination sites were sought. An established synthon to well-defined, mononuclear Zn(II) phenoxide derivatives has been reported using bulky *tert*-butyl moieties in the 2 and 6 positions of phenol.[7] We have expanded upon this methodology to synthesize 2,6-disubstituted phenol derivatives from the reaction of 2,6-diphenylphenol with a solution of Zn^{II}(bis-(trimethylsilyl)amide)$_2$ in tetrahydrofuran or diethyl ether. The resulting acid−base reactions afforded high yields of (2,6-diphenylphenoxide)$_2$Zn^{II}(THF)$_2$ (**1**) or (2,6-diphenylphenoxide)$_2$Zn^{II}(diethyl ether)$_2$ (**2**) upon crystallization from concentrated ether solutions.[8] Herein, we describe the remarkable catalytic activity of these Zn(II) complexes for the copolymerization of CO_2 and epoxides.

In a typical copolymerization or terpolymerization run, 0.125 g of **2** was dissolved in the appropriate amount of cyclohexene oxide and/or propylene oxide. The solution was loaded *via* an injection port into a 300 mL autoclave which had previously been dried *in vacuo* at 90 °C. The autoclave was placed under 800 psi of carbon dioxide and heated to 80 °C. After 69 h the autoclave was allowed to cool to room temperature and the polymer was extracted, dissolved in dichloromethane, and reprecipitated with methanol. Table 1 displays the results obtained from our initial polymerization attempts. High-yield conversions of cyclohexene oxide to high molecular weight poly(cyclohexenylene carbonate)s were obtained with greatly improved turnover numbers, i.e., >350 g of polymer/g of Zn over a 69 h period. In all instances, except run no. 4, the catalyst displayed a high efficiency, with the moles of polymer/mole of catalyst exceeding 0.6. As anticipated, the catalytic activity decreased upon lowering the temperature or CO_2 pressure. Nevertheless, catalyst efficiency was still quite high, i.e., 88 g of polymer/g of Zn (40 °C/800 psi) and 98 g of polymer/g of Zn (80 °C/400 psi). An additional reaction carried out for 6 days has provided over 1200 g of polymer /g of Zn. By way of contrast, the reaction of propylene oxide and CO_2 catalyzed by **2** formed predominantly cyclic carbonates under reaction conditions identical to those above. It is not surprising that the bulk of copolymerization studies have focused on propylene or ethylene oxide and CO_2 because of the low cost of these oxides. Nevertheless, these copolymers have much lower glass transitions than the corresponding polymer derived from cyclohexene oxide.[9] Relevant to these issues we have investigated the preparation of terpolymers containing both cyclohexenylene carbonate and propylene carbonate linkages. Indeed we have found that the catalyst precursor, **2**, is highly effective for terpolymerization. Apparently, the back-biting reaction (eq 1), which is extensive in poly(propylene carbonate) formation, is negligible in poly(cyclohexenylene carbonate) formation. Hence, the tendency of cyclohexene oxide and CO_2 to copolymerize minimizes the extent of back-biting which occurs readily in the propylene oxide and carbon dioxide reaction. Evidently, k_2 (eq 2) is greater than k_1 since cyclic carbonates are hardly

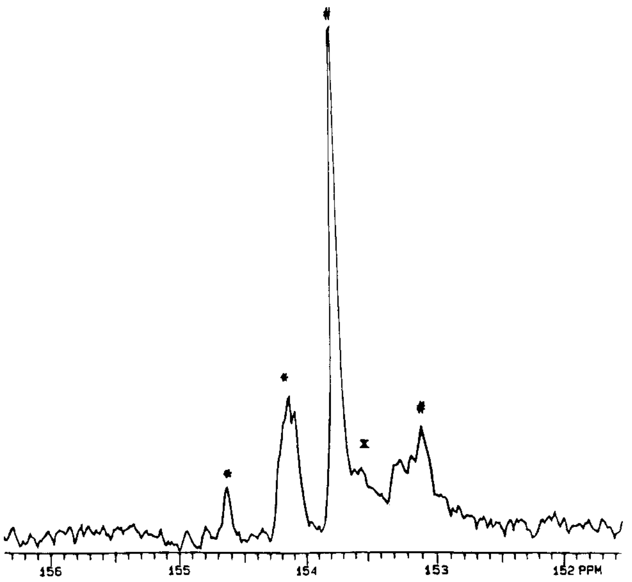
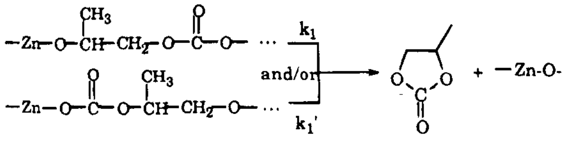


Figure 1. Natural-abundance ^{13}C NMR spectrum of polymer produced from terpolymerization of cyclohexene oxide, propylene oxide, and carbon dioxide: (*) tail-to-tail (154.6 ppm) and head-to-tail (154.1 ppm) propylene carbonate linkages; (#) syndiotactic (153.7 ppm) and isotactic (153.1 ppm) cyclohexene carbonate linkages; (×) various cyclohexene carbonate/propylene carbonate linkages (153.4−153.6 ppm).



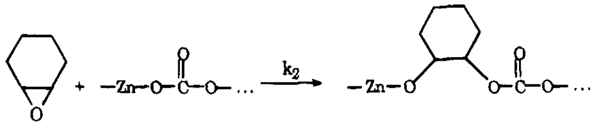
(1)

Table 1. Summary of Reaction Conditions and Results for the Copolymerization of Cyclohexene Oxide and/or Propylene Oxide with Carbon Dioxide via the Catalyst (2,6-Diphenylphenoxide)$_2$Zn(diethyl ether)$_2$ (0.125 g) at T = 80 °C (800 psi Initial Pressure) in a 300 mL High-Pressure Parr Reactor for 69 h

mol of cyclohexene oxide	mol of propylene oxide	% cyclohexene carbonate linkage	% propylene carbonate linkage	% polyether linkage	M_n[c]	M_w[c]	M_w/M_n	yield (g/g of Zn)	convn (%)
0.05	0	91		9	38 000	173 000	4.5	366	65
0.10	0.086	67	23	10	18 000	213 000	11.9	380	22
0.05[b]	0	90		10	18 000	45 000	2.5	357	64
0.05	0.071	66	18	16	4 000	17 000	4.5	421	36
0.020	0.043	73	19	8	23 000	67 000	2.9	50	25
0.15[a]	0	10		90	25 000	132 000	5.2	~300	~20

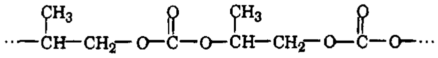
[a] Catalyst = (2,4,6-tri-*tert*-butylphenoxide)$_2$Zn(diethyl ether)$_n$, $n < 2$. Rapid homopolymerization occurred in this run before carbon dioxide was added. [b] Performed by Exxon Research with the catalyst (2,6-diphenylphenoxide)$_2$Zn(THF)$_2$ at 6500 psi CO$_2$. [c] Determined by GPC analysis.

formed until high concentrations of propylene oxide are introduced. That is, only trace quantities of cyclic carbonate were formed with a 1.1/1 ratio of cyclohexene oxide to propylene oxide. The resulting terpolymer contained ≈20% propylene carbonate linkages as determined by ^{1}H NMR with very little polyether, run 3. As expected, an increased amount of cyclic carbonate was formed with higher concentrations of propylene oxide.



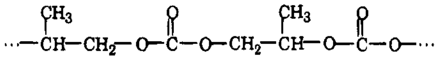
(2)

^{13}C NMR studies in the carbonate region reveal a complex pattern of lines (Figure 1). ^{13}C NMR spectra of poly(cyclohexenylene carbonate)[5,10] and poly(propylene carbonate)[11] have been previously reported. From a comparison of these data with Figure 1, we have been able to identify the ^{13}C NMR signals for the following carbonate linkages in poly(cyclohexenylene−propylene carbonate)s:



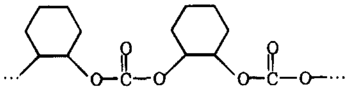
$$\cdots-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\cdots$$

*Head-to-Tail(154.1ppm)

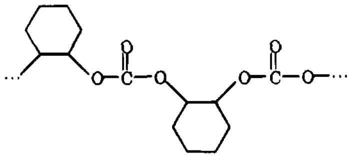


$$\cdots-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\cdots$$

*Tail-to-Tail (154.6ppm)

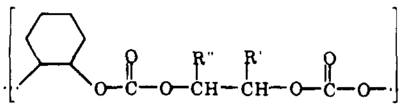


*Isotactic (153.1ppm)



*Syndiotactic (153.7ppm)

Head-to-head propylene carbonate peaks are reported to occur in the region from 153.5 to 153.7 ppm. However, these signals are normally less intense that the tail-to-tail signals. Therefore, we tend to believe the complex region between 153.4 and 153.6 ppm arises from carbonate carbon atoms of some combination of the various cyclohexenylene carbonate−propylene carbonate linkages as indicated below.



R'',R'=H,CH$_3$;R''≠R'

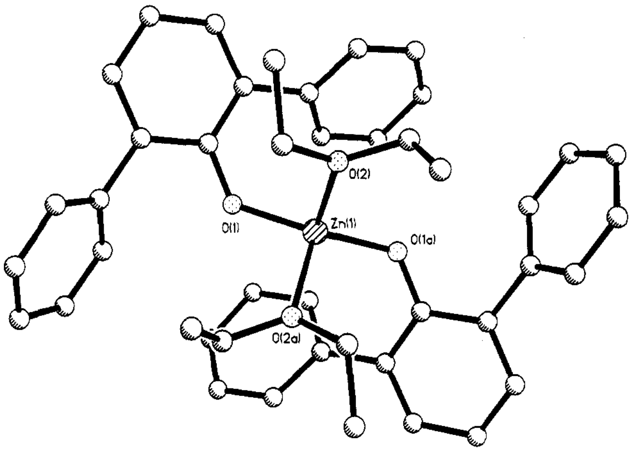


Figure 2. Ball-and-stick representation of complex **2**; ∠O(1)−Zn−O(1a) = 140.0° and ∠O(2)−Zn−O(2a) = 94.6°.

At present, we have limited this study to monomeric Zn(II) phenoxides with bulky substituents in the 2,6-positions. The structures of complexes **1** and **2** have been determined by single crystal X-ray diffraction studies (a ball-and-stick drawing of **2** is indicated in Figure 2). These complexes have highly distorted tetrahedral geometries which will be discussed in detail elsewhere. The ether ligands are quite labile as demonstrated by ^{1}H NMR,[7] with diethyl ether being more weakly bound than THF. Hence, a site for epoxide coordination is readily available in these zinc derivatives. The catalytic activity of (2,4,6-tri-*tert*-butylphenoxide)$_2$Zn(THF)$_2$ is also under investigation. Initial observations indicate that (2,4,6-tri-*tert*-butylphenoxide)$_2$Zn(THF)$_2$ homopolymerizes cyclohexene oxide in solution at room temperature even before the complex is stirred enough to completely dissolve (10 min), whereas **1** is dissolved into cyclohexene oxide without any significant homopolymerization in the same time frame. The high catalytic activity of complexes **1** and **2** is remarkable since it has previously been reported that complexes of the general formula Zn(OR)$_2$, where R is sterically nonencumbering and the complexes are aggregates, are inactive for epoxide/CO$_2$ copolymerizations.[9] Hence, we expect the availability of a coordination site on zinc for epoxide binding, as well as the role of *cyclohexene oxide* to be of paramount importance in this system. Literature precedent exists for the reactivity differences of metal complexes with propylene oxide and cyclohexene oxide.[12]

In conclusion, we have prepared well-characterized, mononuclear zinc catalysts or catalyst precursors which exhibit very high turnover capabilities for the copolymerization of cyclohexene oxide and CO$_2$.[13] Of equal significance is the observation that these zinc complexes are very effective at catalyzing the terpolymerization of cyclohexene oxide, propylene oxide, and carbon dioxide with concomitant retardation of cyclic propylene carbonate production. Future investigations will involve mechanistic studies of the homopolymerization,[14] copolymerization, and terpolymerization using these well-defined Zn(II) phenoxides as well as the optimization of reaction conditions.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE91-19737) is greatly appreciated. We are most grateful to Dr. Christine Costello and Mr. Joseph Sissano of Exxon Research and Engineering (Annandale) for molecular weight determinations of these polymers and a copolymerization run with our catalyst in supercritical CO_2.

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(8) A 77.8% yield of **1** was isolated as colorless crystals. ^1H NMR (CD_2Cl_2): δ 1.72 (m, *THF*, 8H), 3.46 (m, *THF*, 8H), 6.65–7.65 (m, 2,6-*Ph*$_2$*Ph*O, 26H). Free THF and bound THF are in equilibrium in solution and THF appears to be predominantly free in deuterated dichloromethane. Anal. Calcd for $C_{44}H_{42}O_4Zn$: C, 75.48; H, 6.05. Found: C, 73.91; H, 4.89. The inability to obtain a close match probably reflects the ease in which THF may be removed.[7]

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MA950849D