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Homopolymerization and Copolymerization of Cyclohexene Oxide with Carbon Dioxide Using Zinc and Aluminum Catalysts

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ABSTRACT: Homopolymerization of cyclohexene oxide and copolymerization of cyclohexene oxide and carbon dioxide using zinc and aluminum catalysts having the same type of substitution were studied. The aluminum derivatives are more active, in both homopolymerization and copolymerization of cyclohexene oxide and carbon dioxide. From ^{27}Al NMR spectra it was observed that aluminum catalysts consist of both penta- and hexacoordinated species but after reaction with monomer predominantly become pentacoordinated. During initiation the equilibrium between five and six hypercoordinated species is shifted toward lower coordination. The nature of the catalysts and their symmetry influence the yield in the copolymerization of CHO and CO_2 and the amount of carbon dioxide inserted. The yield obtained with aluminum derivatives during the copolymerization of CHO and CO_2 ranged between 41.2 and 93.6% (149.85−340.4 g of polymer/g of metal).

Introduction

The polymerization of cyclohexene oxide (CHO), as previously reported in the literature, has been performed primarily with zinc-, aluminum-, or titanium-based catalysts. Cyclohexene oxide should be a very reactive alicyclic epoxide, according to the reactivity order estimated by Bacskai,[1] who polymerized CHO cationically with aluminum alkyls at −70 °C; amorphous polymers were obtained in high yields. Some research has also been directed toward the stereospecific polymerization of this oxirane. Vandenberg,[2] for example, polymerized cyclohexene oxide with R_3Al-H_2O with or without a chelating agent (acetyl acetone), but only small amounts of crystalline polymer were obtained. Tsuruta[3] studied the stereospecific polymerization of oxiranes with (ROZnOR)/(EtZnOR) systems as initiators and made the assumption that methoxypropoxy groups are responsible for initiation. Hasebe and co-workers[4] obtained a predominantly syndiotactic poly(CHO) using an alkoxy zinc catalyst. Sepulchre et al.[5,6] studied the stereospecific polymerization of cyclohexene oxide with achiral and chiral zinc initiators and observed that only some of the chiral systems induced the formation of significant optically active polymers. They assumed that at least three different types of active sites were involved in the polymerization reaction. Fukuchi et al.[7] showed that the polymerization of cyclohexene oxide initiated by titanium alkoxides occurs with very low yield, probably because the basicity of the epoxide is too weak to facilitate coordination to the titanium; if a phenol or naphthol is added to the metal alkoxide, the reaction is fast and high yield is obtained in short time.

Following the first report on carbon dioxide/propylene oxide copolymerization,[8,9] the copolymerization of CO_2 and cyclic ethers has been investigated by various groups over the past three decades. Most of the research has been directed toward propylene oxide/CO_2 copolymerization, and it has been shown that, in the presence of carbon dioxide, both polycarbonate and cyclic carbonate are formed.[8,10−15] Rokicki and Kuran[16] suggested that the reactivity of monosubstituted oxiranes during copolymerization with carbon dioxide is enhanced by increasing the electron-donor character of the substituent group. For alicyclic epoxides the reactivity order is the same as in homopolymerization, where the strain in the transition state during propagation was presumed to govern the rate of the copolymerization reaction.[1] The opening of the oxirane ring could take place with CH_2-O or $CH-O$ bond breakage, according to the substituent's nature, suggesting nucleophilic attack of the cyclic ether in the copolymerization reaction.[17−20] It was also shown that cyclohexene oxide polymerization occurs with inversion of configuration at the carbon atom of the broken C−O bond.[3,4,21]

The catalysts for the reaction between epoxides and carbon dioxide have been recently reviewed by Darensbourg and Holtcamp.[22] The most studied catalysts for the copolymerization of oxiranes and carbon dioxide can be divided into two classes: (a) organometallic compounds of Zn, Cd, or Al, among them the most active being synthesized from dialkyl zinc and a modifier having at least two labile hydrogen atoms, and (b) coordination metal complexes.[16]

The active catalysts belonging to the first class have repeating Zn−O units in their structure, formed during the reaction of diethyl zinc and difunctional alcohols, phenols, or carboxylic acids.[8,10,23,24] Although the zinc derivatives are highly active,[25,26] only a low number of available metal atoms comprise active sites.

The coordination catalysts are less active than those organometallics where a Zn−C bond is present. Aluminum-based catalysts tend to produce low molecular weight polymers that contain both ether and carbonate linkages.[26,27] The catalytic activity of aluminum compounds is dependent on the degree and strength of association, which affects the coordination at the aluminum atom.[28] Pentacoordinated aluminum−porphyrin compounds were found to generate alternating copolymers of epoxides and carbon dioxide,[29,30] but the reaction rate was observed to be very slow. Chromium porphyrinates, on the other hand, are good catalysts only for the formation of cyclic carbonates from epoxides and

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carbon dioxide.[31] Recently, Kuran et al.[32] reported a pentacoordinated aluminum complex, (25,26-dimethoxy-*p-tert*-butylcalix[4]arene-26,28-diolato)aluminum chloride, that was used for homogeneous oxirane homopolymerization and copolymerization with carbon dioxide. Here, however, only low molecular weight products were obtained. The proposed reaction mechanism is a simultaneous participation of two molecules and a rearward attack of the nucleophilic substituent onto the coordinated monomer. The copolymerization process produced low molecular weight polycarbonate and significant amounts of cyclic carbonate as well.

Recent work of importance to this study includes the development by Darensbourg[33] of a phenoxy−zinc, single-site type catalyst which allows the generation of over 400 g of polycyclohexene carbonate per gram of zinc. Despite the use of the single-site type catalyst, the copolymers still exhibited broad molecular weight distributions. Further work revealed that the nature of substituents on the phenolate ligands of the zinc catalyst influences the yield; the less bulky trimethyl derivative provides 1441 g of polymer per gram of zinc in 69 h at 80 °C.[34] A highly active catalyst for the copolymerization of CHO and carbon dioxide was developed by Coates and colleagues;[35] this β-diimine zinc-based catalyst produced monodispersed polymer containing over 95% carbonate linkages in a very short reaction time. In addition, Super et al.[36] developed a fluorinated (and thus highly CO_2-soluble) zinc-based catalyst which also produced over 400 g of high molecular weight polycyclohexene carbonate per gram of zinc (here CO_2 is both monomer and solvent), yet which also displays broad molecular weight distributions. Further, it was eventually determined that high CO_2 solubility of the catalyst (and thus the fluorinated ligand) is probably not necessary.[37] At lower pressures, the CO_2−cyclohexene oxide binary exhibits liquid−liquid phase separation, leading to formation of a dilute phase (less than 5 mol % CHO) and a concentrated phase containing relatively similar amounts of CHO and CO_2.[38] The CHO comonomer acts as a cosolvent for CO_2, allowing solubilization of relatively larger amounts of the catalyst in the concentrated phase than in the CO_2-rich phase. Because the copolymerization was found to exhibit equilibrium characteristics with respect to [CHO], polymerization in a phase relatively concentrated in CHO is favored. As such, what is required for homogeneous polymerization is a catalyst that dissolves preferentially in concentrated mixtures of CHO in CO_2.

This study is focused on the homopolymerization of cyclohexene oxide and its copolymerization with carbon dioxide using a family of organozinc and organoaluminum compounds as catalysts, to gain a better understanding of the differences in reactivity between the above-mentioned systems.

Experimental Section

Materials. Cyclohexene oxide (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure over CaH_2. Chloroform ($CHCl_3$, J.T. Baker, Phillipsburg, NJ) was stirred overnight over concentrated H_2SO_4, washed to neutral pH, dried over $CaCl_2$, and distilled over CaH_2. Toluene (Aldrich Chemicals, Milwaukee, WI) was distilled over CaH_2. Hexane (Aldrich Chemicals, Milwaukee, WI) was distilled prior use. Zinc oxide and diethyl zinc (1.0 M in hexanes or 1.1 M in toluene), all from Aldrich Chemicals, were used without further purification. Diethylaluminum chloride (from Aldrich Chemicals, Milwaukee, WI) 25 wt % (1.8 M) in toluene, was used as received. Tridecafluorooctanol and 1,1,2-trichlorotrifluoroethane (TCTFE), both from Aldrich Chemicals, were used without further purification. 1-Octanol (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure, and the middle fraction was collected. Cyclohexanol, from Aldrich Chemicals, was used without further purification. Maleic anhydride briquettes and phthalic anhydride (both from Aldrich) were used as received. 2,6-di-*tert*-Butyl-4-methylphenol (Aldrich) was used without further purification. Anhydrous methyl alcohol (Mallinckrodt Baker Inc., Paris, KY) was used without further purification to stop the polymerization reaction and to separate the reactor products. Argon (Praxair, Pittsburgh, PA) was passed through a 21 in. purifier and then distributed to the reaction system. Carbon dioxide (Praxair, Pittsburgh, PA, 99.99% purity) was passed through a high-pressure purifier before use.

Synthesis of the Catalysts. The catalysts have been synthesized under argon, in glass flasks that were heated to 200 °C and then evacuated and flushed with inert gas three times. Some of the zinc catalysts were synthesized from a hemiester of maleic anhydride and either zinc oxide, zinc chloride, or diethyl zinc. The hemiester was prepared via the reaction of maleic anhydride and 1-octanol or perfluorooctanol, in toluene, 24 h at 55 °C, using procedures similar to those described elsewhere.[36,39,40] The perfluorinated hemiester was obtained at 61% yield as a white solid that can be isolated by filtration. The nonfluorinated analogue, synthesized from 10.6 g of maleic anhydride and 13.94 g of 1-octanol in 10 mL of toluene, is filtered, to remove unreacted maleic anhydride, and then processed in a rotary evaporator under reduced pressure. An oily product that solidifies in 2−3 days to a white wax is obtained with 88−90% yield. In some experiments the nonfluorinated hemiester was synthesized from the reaction of maleic anhydride and 1-octanol without solvent in the initial stage, 1 h at 80 °C, and then diluted with hexane and reacted with stirring for an additional 19 h. After removing the solvent under reduced pressure a white, waxy solid was obtained at yields of 92.5% or greater. The products were stored under an argon blanket.

The syntheses of $C_6F_{13}CH_2CH_2OCOCH{=}CHCOOZnOH$ and $C_8H_{17}OCOCH{=}CHCOOZnOH$ have been performed respectively from the reaction between the fluorinated hemiester and zinc oxide in TCTFE for 24 h at 55 °C and from the alkyl hemiester and zinc oxide for 3 days at 65 °C in toluene. Thus, 4.15 g of fluorinated hemiester and 0.73 g zinc oxide were reacted in 30 mL of TCTFE for 24 h at 50 °C and then filtered to yield the fluorinated catalyst that was purified by recrystallization from methylene chloride; a white solid was obtained in 86% yield. The nonfluorinated catalyst was purified by filtration and the solvent removed under reduced pressure. ^{1}H NMR spectra for the perfluorinated catalyst and its hemiester precursor, determined with a Bruker MSL 300 MHz instrument, are presented in Figure 1. The signal at 9.85 ppm, assigned to a COOH proton, does not appear in the catalyst, and the peak at 6.26 ppm for the double-bond proton in the hemiester is split into two signals at 6.08 and 6.45 ppm in the catalyst. Other asymmetric zinc catalysts have been synthesized from the reaction between diethyl zinc, the hemiester, and either an alcohol or sterically hindered phenol in two stages, in a manner similar to those described above. In a typical experiment 1.5076 g (0.015 mol) of cyclohexanol—as a solution in chloroform—was added dropwise, in 30 min at room temperature—over 1.85 g (0.015 mol) of diethyl zinc in 20 mL of hexane and left under stirring for 2 h. Then a solution of 3.424 g (0.015 mol) of maleic anhydride hemiester in 10 mL of chloroform was added dropwise in 60 min and stirred for 2 h at 40 °C. The solvent was removed in a vacuum at 50 °C. The ^{1}H NMR spectrum of the catalyst synthesized from diethyl zinc, maleic anhydride hemiester, and cyclohexanol shows a peak at 3.65 ppm, assigned to the ring proton adjacent to oxygen, and two signals at 6.21 and 5.98 ppm, for double-bond protons, more deshielded then in its hemiester precursor (Figure 2). Symmetric catalysts have been prepared from the reaction between diethyl zinc and either the hemiester or alcohol in a molar ratio of 1:2. The phthalic anhydride

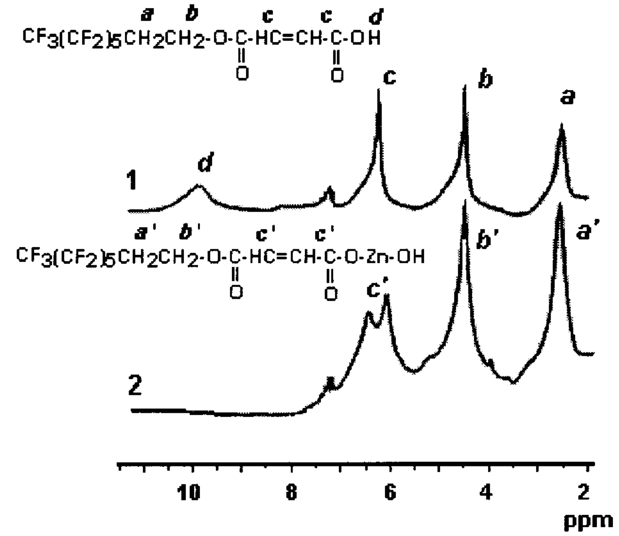


Figure 1. ^{1}H NMR spectra of perfluorinated hemiester (1) and zinc catalyst (2).

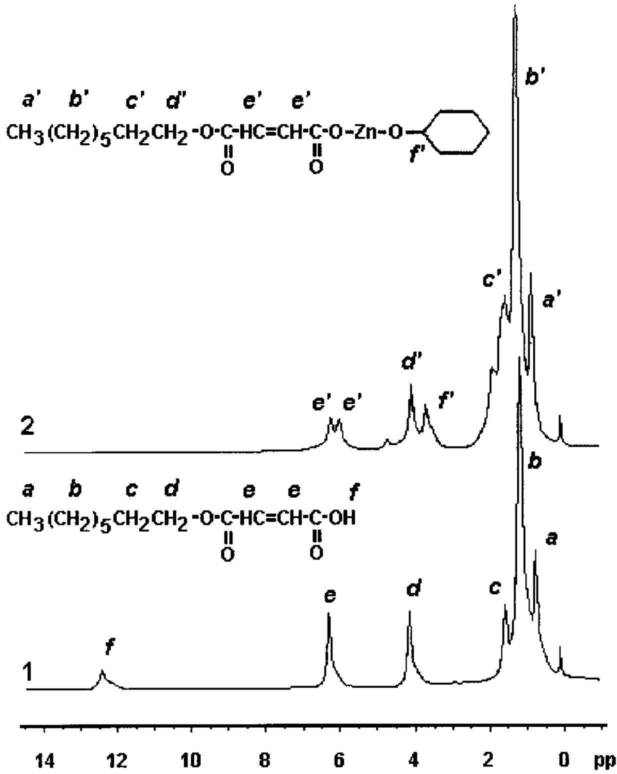


Figure 2. ^{1}H NMR spectra of hemiester (1) and asymmetric zinc catalyst (2).

hemiester and catalyst have been synthesized in a manner similar to the maleic analogue. The sterically hindered zinc phenoxide was synthesized from the reaction between diethyl zinc (1.23 g) and 2,6-di-*tert*-butyl-4-methylphenol (4.41 g) in hexane for 24 h at room temperature. The zinc catalysts used in the polymerization of cyclohexene oxide are presented in Table 1.

The aluminum-based catalysts have been synthesized from the reaction between diethylaluminum chloride and hemiester and/or cyclohexanol in one or two steps, in a manner similar to that employed for the zinc catalysts. They are presented in Table 2.

The ^{27}Al NMR spectra of the aluminum catalysts show that the substituent's nature strongly affects their structure. Thus, the catalyst **2c** (see Table 2) has the highest symmetry—half-line width $W_{1/2} = 567$ ppm—partly hexacoordinated, the δ value for this peak being 0.08 ppm (Figure 3). The broad peak at 81.94 ppm ($W_{1/2} = 1866$ ppm) can be assigned to pentacoordinated species. The catalyst **2a** consists of almost equal amounts of hexa (1.26 ppm)- and pentacoordinated species (69.87 ppm), but their symmetry degree is lower than **2c** (half-line width $W_{1/2} = 2404$ ppm and $W_{1/2} = 3384$ ppm, respectively). Catalyst **2b** presents three signals: one for hexacoordinated species and two signals (ratio 6:1) at 31.74 and 85.65 ppm assigned to pentacoordinated species, the predominant species having a higher degree of symmetry.

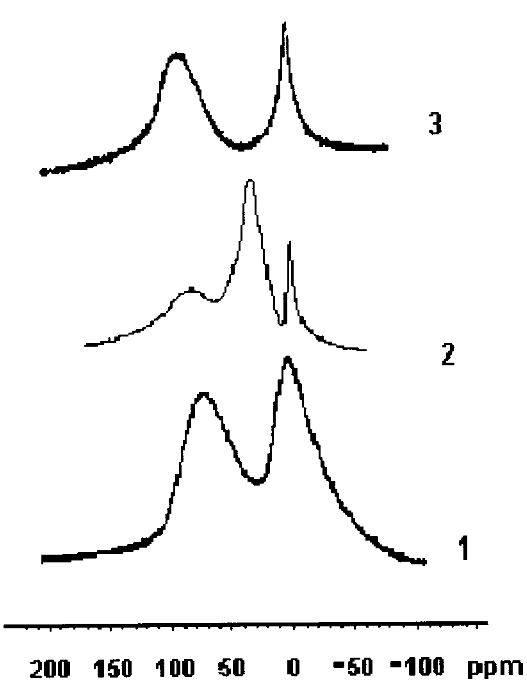


Figure 3. ^{27}Al NMR (75.468 MHz) spectra of the catalysts **2a** (1), **2b** (2), and **2c** (3).

Homopolymerization of CHO. The catalysts synthesized as described above have been tested in the homopolymerization of cyclohexene oxide in order to derive some basic information concerning their activity as initiators. Polymerization of cyclohexene oxide (CHO) has been performed under an argon blanket, in glass flasks purified as described above for catalyst synthesis, equipped with magnetic stirrer, condenser, and devices for adding reagents. The process was terminated with methanolic hydrochloric acid, the polymer solution was filtered using a 0.45 mm pore size Schleicher & Schuell membrane filter, and the solvent was then removed under vacuum.

Copolymerization of CHO and Carbon Dioxide. Polymerization of cyclohexene oxide in carbon dioxide was performed in a 25 mL high-pressure reactor equipped with magnetic stirrer and pressure and temperature indicators (Figure 4). Prior to the experiment the reactor is heated to 200 °C, evacuated, and then cooled to room temperature under an argon blanket. The catalysts were introduced with a syringe; the solid ones were previously dissolved in an appropriate solvent. The cyclohexene oxide was added alone using a syringe or as a mixture with CO_2 using a high-pressure syringe pump (High Pressure Equipment Co.). After injection of the reagents, the reactor was isolated and heated to the prescribed temperature. After the desired time the pressure was slowly released, and the reaction was then terminated with methanolic hydrochloric acid. The product was processed as described earlier.

Analyses. The ^{1}H NMR spectra of the catalysts and polymer solutions in $CDCl_3$ were recorded with a Bruker MSL 300 MHz spectrophotometer. TMS was used as the internal reference for all these runs. The ^{27}Al NMR (75.468 MHz) spectra of the aluminum catalysts as solutions in $CDCl_3$ were obtained at the following operating conditions: sweep width = 36 kHz, nondecoupling mode, pulse angle = 90°, pulse repetitions 40 μs, preaquisition delay = 10 μs, and number of scans = 20 000.

Table 1. $R_1-O-Zn-O-R_2$ **or a Mixture of** $R_1-O-Zn-O-R_2$ **and** $R_3-O-Zn-O-R_4$

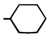
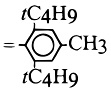
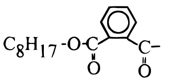
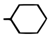
1a	$R_1 = C_6F_{13}CH_2CH_2OCOCH{=}CHCO$- $R_2 = H$	1b	$R_1 = C_8H_{17}OCOCH{=}CHCO$- $R_2 = H$
1c	$R_1 = C_8H_{17}OCOCH{=}CHCO$- $R_2 =$ 	1d	$R_1 = R_2 =$ 
1e	$R_1 = R_2 = C_8H_{17}OCOCH{=}CHCO$-	1f	$R_1 = R_2 =$  $R_3 = R_4 = C_8H_{17}OCOCH{=}CHCO$- (1 :1) mol
1g	$R_1 = R_2 =$  $R_3 = R_4 = C_8H_{17}OCOCH{=}CHCO$- (1 :1) mol	1h	$R_1 =$  $R_2 =$ 

Table 2. $R_1-O-Al(Cl)-O-R_2$ **or a Mixture of** $R_1-O-Al(Cl)-O-R_2$ **and** $R_3-O-Al(Cl)-O-R_4$

2a	$R_1 = C_8H_{17}OCOCH{=}CHCO$- $R_2 =$ 	2b	$R_1 = R_2 =$ 
2c	$R_1 = R_2 = C_8H_{17}OCOCH{=}CHCO$-	2d	$R_1 = R_2 =$  $R_3 = R_4 = C_8H_{17}OCOCH{=}CHCO$- (1 :1) mol

The FIDs were processed using an exponential multiplication and a line broadening of 10 Hz. For all measurements the chemical shifts were reported relative to a saturated solution of aluminum acetylacetonate in benzene-d_6 used as a standard.

Molecular weights and MWD of the polymers were measured using a Waters 150 CV gel permeation chromatograph,

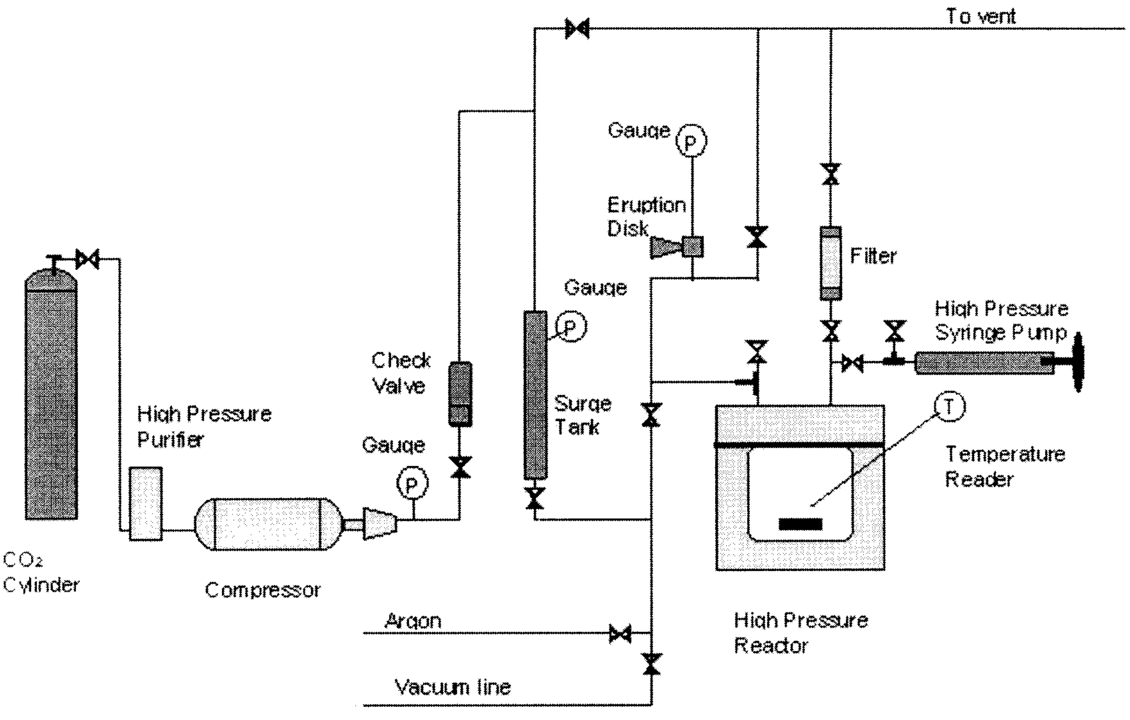


Figure 4. High-pressure equipment used in copolymerization of CHO and carbon dioxide.

Table 3. Homopolymerization of Cyclohexene Oxide with Zinc Catalysts

run	catalyst[a]	[M], mol/L	[I] × 10^2, mol/L	temp, °C	time, h	solvent	yield, %	M_n	MWD
CP-3	**1a**	4	4	35	24	TCTFE	19.8	5 696	1.99
CP-12	**1a**	4	4	38	24	TCTFE	21.4	6 115	2.18
CP-4	**1b**	4	4	35	24	$CHCl_3$	14.1		
CP-8	**1c**	4	2	35	24	$CHCl_3$	50.3	16 017	1.79
CP-9	**1d**	4	2	35	24	$CHCl_3$	33	15 696	1.83
CP-27	**1e**	4	4	50	24	$CHCl_3$	12.1	3 125	3.12
CP-10	**1f**	4	2 + 2	55	24	$CHCl_3$	35.2	20 253	1.57
CP-11	**1g**	4	2 + 2	55	24	$CHCl_3$	5.07		
CP-59	**1h**	4	4	40	72	$CHCl_3$	53.32	9 037	1.74

[a] Catalysts according to Table 1.

equipped with 10^4, 10^3, 500, and 100 Å Ultrastyragel columns. THF was used as eluent, and calibration was performed using polystyrene standards.

Results and Discussions

Homopolymerization of CHO. The data for the homopolymerization of cyclohexene oxide using zinc catalysts are presented in Table 3.

Table 4. Influence of the Synthesis Technique of Zinc Catalysts 1c on Activity in the Polymerization of Cyclohexene Oxide

run	cat.	[M], mol/L	[I] × 10^2, mol/L	temp, °C	time, h	solvent	yield, %
CP-28	**1c**[a]	4	4	55	24	$CHCl_3$	27.1
CP-37	**1c**[b]	4	4	52	24	$CHCl_3$	8.25
CP-50	**1c**[c]	4	4	50	24	$CHCl_3$	13
CP-57	**1c**[d]	4	4	55	70	$CHCl_3$	26.6

[a] Reversing reagent order, i.e., introduce the hemiester first, at room temperature, stir for 2 h, and then introduce the alcohol. Processed at low temperature in a vacuum (40 °C). The catalyst is yellow. [b] Short first stage and 16 h second one; the catalyst is gellike. [c] Catalyst synthesized from $ZnCl_2$ and the sodium alcoholate of cyclohexanol, followed by the addition of sodium salt of the hemiester and reacted 1 h. Processed in a vacuum at 60 °C. The catalyst is a white, soft solid. [d] From a toluene solution of $ZnEt_2$, and CH_2Cl_2 as solvent for alcohol and hemiester; 80 min at room temperature first stage and 60 min at room temperature second stage. Processed at 58 °C in a vacuum for 3 h. The catalyst is a white soft solid.

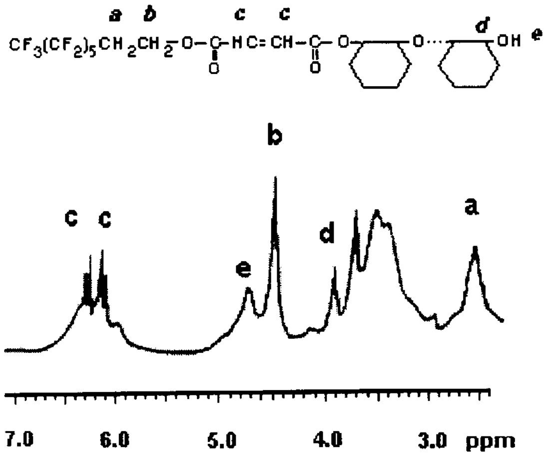


Figure 5. ^1H NMR spectrum of a cyclohexene oxide oligomer solution in trichlorotrifluorethane.

The activity of zinc catalysts as initiator in the polymerization of cyclohexene oxide varies significantly with the nature of the substituent groups. The perfluorinated catalyst (**1a**) exhibits a slightly higher activity in the homopolymerization of cyclohexene oxide than its unhalogenated analogue (**1b**) at 35 °C. The asymmetric catalysts (**1c** and **1h**)—having one alkoxy and another ester Zn—O bond—exhibit the highest catalytic activity. When a symmetric Zn catalyst is used—having only alkoxy metal—O bonds (**1d**) or ester ones (**1e**)—the polymer yield decreases, but the zinc alkoxide is more reactive than the carboxylated analogue. When an equimolar mixture of zinc alkoxide and ester is used (**1f**), the yield is higher than for symmetric catalysts but lower than for the asymmetric analogue. If the zinc alkoxide is replaced by a sterically hindered phenoxide (**1g**), the yield decreases significantly, suggesting that the Zn—O alkoxy bond is the primary site for insertion of the monomer. The molecular weights are much smaller for the polymers obtained with the perfluorinated catalysts, but the MWD are broader. The exception is the sample synthesized with catalyst **1e**, producing low molecular weight and the broadest distribution. This result suggests that the process is accompanied by strong termination reactions, as we suppose to be the case for the fluorinated catalyst as well. The high molecular weights of the polymers obtained with catalysts having at least one Zn—O alkoxy bond suggest that only a fraction of the zinc atoms are active. It is known that organozinc compounds containing Zn—O bonds tend to associate, from dimers to tetramers, depending on the nature and size of the substituents. This association involves changes in zinc atom hybridization. If only one coordination is formed, the structure of the complex is almost planar with a sp^2-hybridized zinc atom having an unoccupied valence orbital. But when both valence orbitals are used in coordination, the zinc atom will be tetrahedrally coordinated with its 3d shell filled. The initiation reaction involves first the coordination of a monomer molecule at the metal atom, and thus the metal atom should be accessible and able to coordinate. We suppose that rearrangements involving weak tetracoordinated zinc atoms can occur, too, and thus that the degree and the strength of association are responsible for the difference in catalytic activity of the studied complexes. According to our observations, the asymmetry of the active center enhances its reactivity. It was also observed that the catalytic activity is strongly influenced by the experimental technique used to prepare the catalyst; when compound **1c** is synthesized in different ways, the yield changes significantly (Table 4). This is similar to the behavior of zinc methoxide when used to catalyze oxirane polymerization, as explained by Tsuruta.[41] Because the ^1H NMR spectra of catalysts **1c** and **1c**[a] did not show any differences, the electron delocalization responsible for the change in the color of the latter material could be due to a different type of association of zinc atoms. Since the activity is also low for the catalyst synthesized from zinc chloride, sodium alkoxide, and the sodium salt of the maleated hemiester (exp. CP-50), we believe that Tsuruta's assumption concerning the available active sites and the asymmetry of the

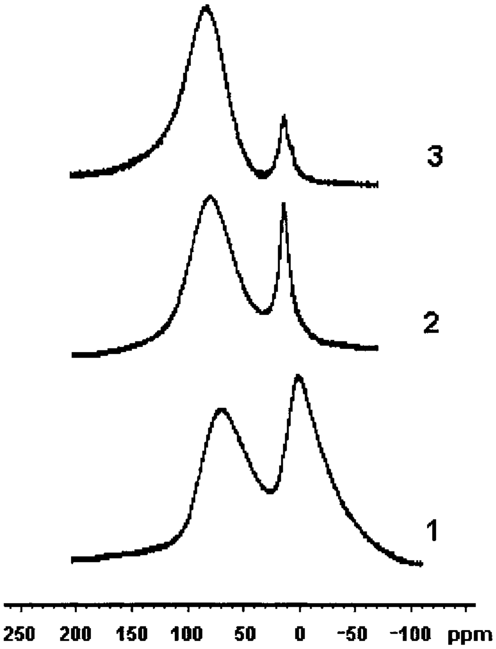


Figure 6. ^{27}Al NMR spectra of catalyst **2a** (1) and catalyst + CHO (1:1) after 15 min (2) and 24 h (3).

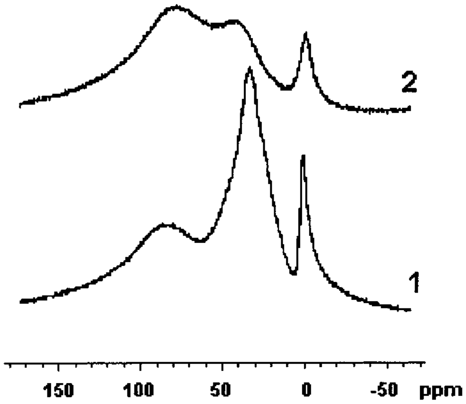


Figure 7. ^{27}Al NMR spectra of catalyst **2b** (1) and catalyst + CHO (1:2) after 1 h (2).

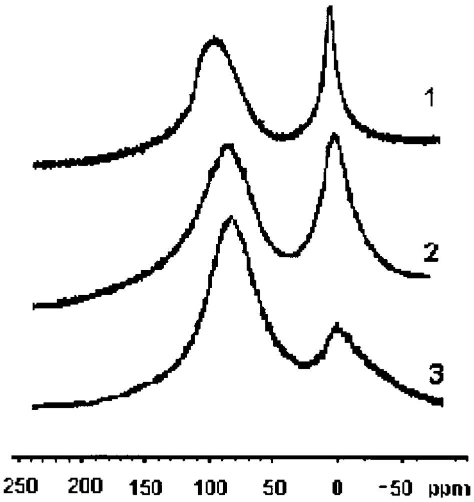


Figure 8. ^{27}Al NMR spectra of **2c** (1) and catalyst + CHO (1:2) after 15 min (2) and 11 h (3).

compound are the determining factors. The polymerization clearly takes place with ring opening and insertion of the monomer at Zn−O bond, as ^{1}H NMR spectra

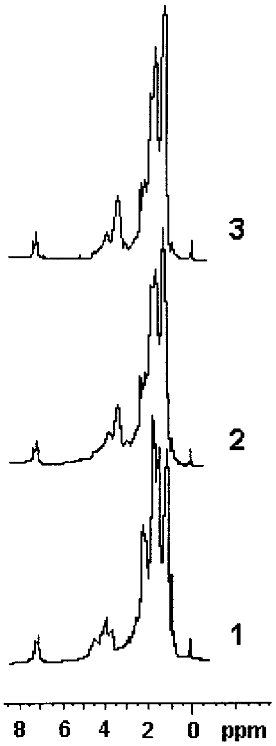


Figure 9. ^{1}H NMR spectra of **2b** (1) and catalyst + CHO (1:2) after 30 min (2) and 9 h (3).

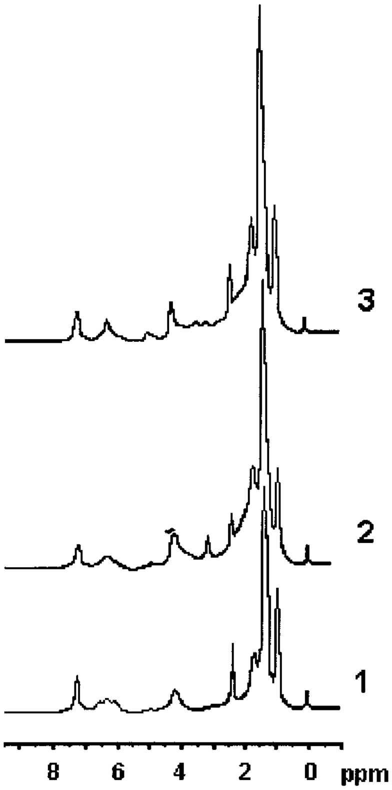


Figure 10. ^{1}H NMR spectra of **2c** (1) and catalyst + CHO (1:2) after 15 min (2) and 11 h (3).

performed on an oligomer of cyclohexene oxide obtained with the perfluorinated catalyst exhibit the signals at 6.14 and 6.26 ppm assigned for the double-bond proton (Figure 5) on to the catalyst.

Using aluminum catalysts, the homopolymerization of cyclohexene oxide gives higher yields, over 95% in 24 h at 55 °C (Table 5). The most active appear to be

Table 5. Polymerization of Cyclohexene Oxide with Aluminum Catalysts

run	catalyst[a]	[M], mol/L	[I] × 10^2, mol/L	temp, °C	time, h	solvent	yield, %	M_n	M_n
CP-100	**2a**	4	4	55	24	toluene	99.18	4652	2.58
CP-109	**2b**	4	4	55	24	toluene	95.5	4849	3.92
CP-110	**2c**	4	4	55	24	toluene	98.14	4522	2.41
CP-111	**2d**	4	2 + 2	55	24	toluene	98.8	5420	2.94

[a] Catalysts according to Table 2.

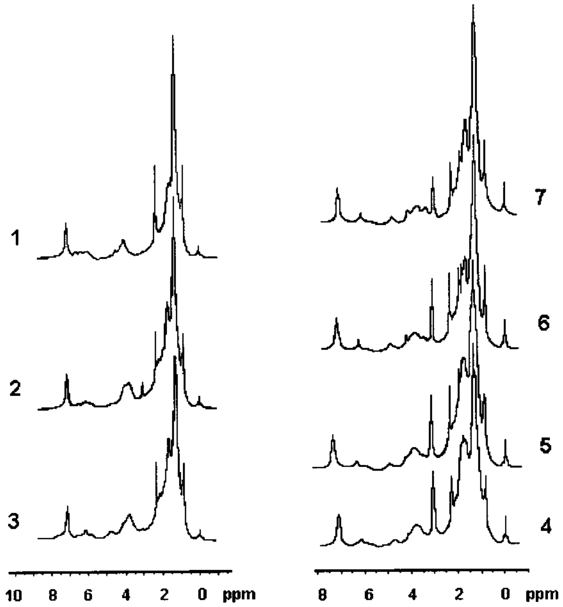


Figure 11. ^{1}H NMR spectra of catalyst **2a** (1), **2a** + CHO (1:1) after 15 min (2) and 24 h (3), and **2a** + CHO (1:2) after 15 min (4), 9 h (5), 32 h (6), and 5 days (7).

the catalysts having at least one carboxylic group, different behavior than was observed for the zinc analogues. As was shown above from ^{27}Al NMR spectra, the aluminum catalysts tend to form associations involving either penta- or hexacoordination of the metal atom. It is known that a tetracoordinated aluminum is sp^3-hybridized and that pentacoordinated Al has sp^{3}d hybridization. From the half-line width ($W_{1/2}$) of the ^{27}Al NMR spectra we observed a high degree of symmetry of the studied systems. Therefore, we suppose that the structure of the pentacoordinated species is that of a trigonal bipyramid involving the dz^2-orbital. For this type of structure the coordination of a monomer molecule depends strongly on steric hindrance. Moreover, this involves a change in geometry, the arrangement becoming an octahedral one by the participation of the $d_{x^2-y^2}$ orbital. Our supposition made for zinc catalysts relative to rearrangements in association is supported here by the observation that the aluminum catalysts are more reactive despite their partial hexacoordination (and thus the apparent lack of an empty orbital able to coordinate the monomer). From ^{27}Al NMR spectra recorded on the reaction mixture using catalyst **2a** and CHO, we observed that the peak at 1.26 ppm decreased strongly and was shifted to 14.91 ppm, but the peak at 69.87 ppm increased significantly (Figure 6). The species **2b**, having Al−alkoxy substitution, reacts with CHO to give predominantly two types of asymmetrical structures with pentacoordinated aluminum (Figure 7). The most symmetrical catalyst (**2c**) changes its hypercoordination from six to five when it is reacted with CHO (Figure 8). The peak from 0.08 ppm, assigned to hexacoordinated aluminum, is shifted to 4.68 ppm after reaction with CHO, but in time it moves back, while

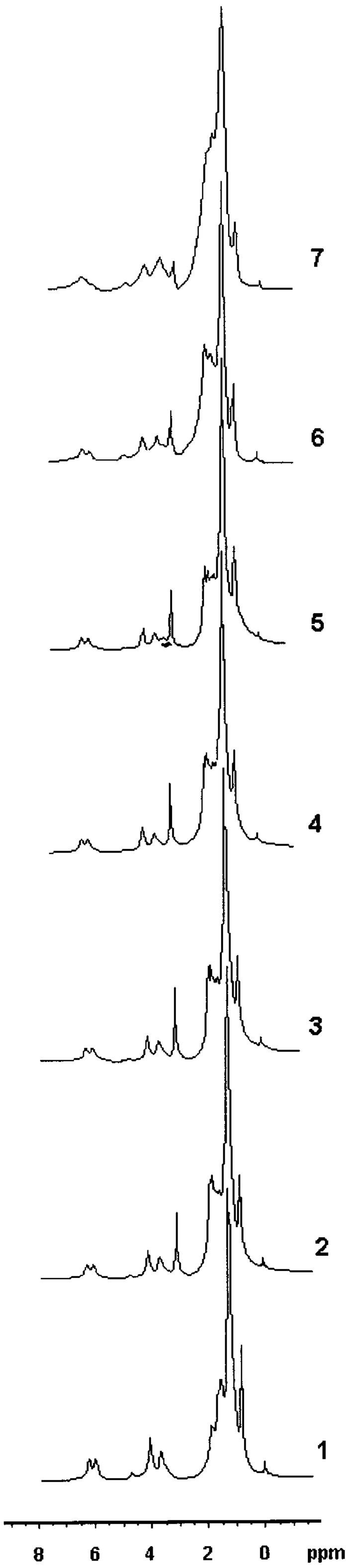


Figure 12. ^{1}H NMR spectra of **1c** (1) and **1c** + CHO (1:1) after 15 min (2), 1 h (3), 2 h (4), 24 h (5), 7 days (6), and 20 days (7).

Table 6. Copolymerization of Cyclohexene Oxide and Carbon Dioxide Using Zinc Catalysts

run	[M], mol/L	catalyst	[I] × 10^2, mol/L	$[CO_2]/[CHO]$	P_{CO_2}, psi	temp, °C	time, h	yield, g/g of Zn	M_n	MWD
SP-1	1.976	**1c**	0.99	0.62	1800	45	24	47.7	4328	1.64
SP-2	3.95	**1c**	3.95	0.545	1600	90	24	63.3	2147	4.35
SP-4	3.952	**1c**	3.96	0.73	2700	52	24	28.13	2312	2.62
SP-5	3.952	**1c**	3.96	0.57	1500	50	24	28.4	2475	4.29

Table 7. Copolymerization of Cyclohexene Oxide and Carbon Dioxide Using Aluminum Catalysts at Initial Carbon Dioxide Pressure $P_{CO_2} = 1200$ psi

run	[M], mol/L	catalyst[a]	[I] × 10^2, mol/L	$[CO_2]/[CHO]$	temp, °C	time, h	yield, g of polymer/g of Al	M_n	MWD	carbonate:ether units[b]
SP-49	1.976	**2a**	1.976	6.64	62	24	149.95	3274	4.15	1:11.7
SP-51	1.976	**2a**	1.976	6.56	62	24	180.69	4206	3.84	
SP-48	1.976	**2b**	1.976	6.98	60	24	340.4	4531	2.62	1:12
SP-52	1.976	**2c**	1.976	6.64	60	24	248.9	4985	2.89	1:3.6

[a] According to Table 2. [b] From ^1H NMR.

the signal at 82.7 ppm increases and becomes narrower, suggesting a high symmetry of these species.

To see where the monomer is inserted, we studied the variation of ^1H NMR spectra of catalyst–CHO reactions performed in probe tubes. When the catalyst **2b** is reacted with CHO, of the peaks (at 3.76, 3.93, and 4.39 ppm) assigned to CH ring protons bound to the Al–O bond, the latter two disappear, and a new peak appears at 3.34 ppm which can be attributed to the ether linked CH from the inserted cyclohexene oxide. The monomer insertion is fast because the peak at 3.06 ppm, corresponding to the CH proton from CHO, is insignificant after 30 min (Figure 9). The ^1H NMR spectra of the catalyst **2c**–CHO mixture show that the peaks at 6.05 and 6.27 ppm, corresponding to double-bond H, disappeared after 11 h, and a signal at 6.22 ppm appeared as a consequence of the insertion of the monomer at the Al–O bond (Figure 10).

When the asymmetrical catalyst **2a** is reacted with CHO in an equimolecular ratio, the peaks at 6.18 and 6.47 ppm, corresponding to double-bond protons, are shifted to 6.18 and 5.85 ppm. Two new peaks appear at 3.79 and 4.82 ppm, assigned to the CH ether proton and the ester proton, respectively, from cyclohexene oxide (Figure 11). We suppose that cyclohexene oxide is inserted into both the Al–O ether bond and the Al–O ester one; thus, each aluminum catalyst should initiate two polymeric chains. This assumption is in good agreement with the obtained molecular weights of these polymers (Table 5).

By comparison, when the asymmetric zinc catalyst **1c** is reacted with CHO, the ^1H NMR spectra show that the signals at 5.97 and 6.20 ppm, assigned to the CH double-bond protons, remain unchanged after 7 days. The peak at 3.65 ppm attributed to the CH ether proton increases as the signal at 3.04 ppm (CH cyclic ether proton from the monomer) decreases, suggesting the insertion of CHO into the Zn–O ether bond (Figure 12). The reaction is very slow at 15 °C, because after 20 days there is still some monomer unreacted.

The structure of the obtained polymers can be determined from the methine proton resonance in the ^1H NMR spectra. The polymers show a predominantly atactic structure, similar to that found by Malhotra and Blanchard[42] for a polycyclohexene oxide synthesized cationically. The ^1H NMR spectra of two samples of poly(cyclohexene oxide) synthesized with the asymmetric zinc catalyst **1c** (CP-8, Table 3) and the aluminum homologue **2a** (CP-100, Table 5) are presented in Figure 13.

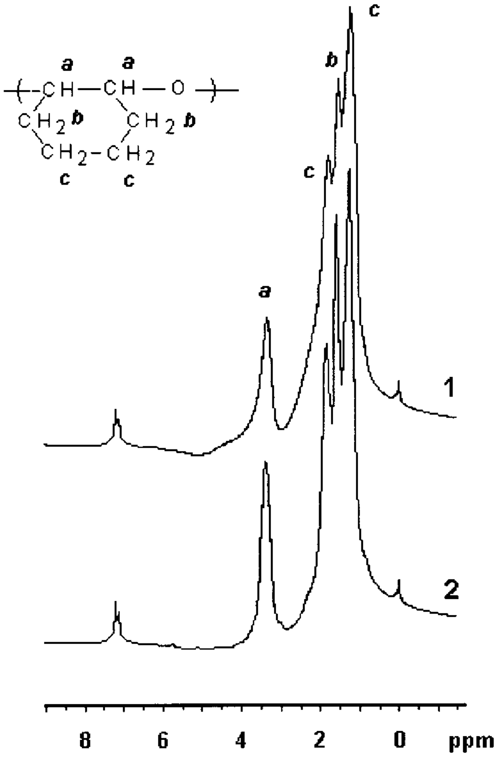


Figure 13. ^1H NMR spectra for poly(cyclohexene oxide) synthesized with asymmetrical zinc catalyst (1) and aluminum homologue (2).

Copolymerization of CO_2 and CHO. The results for the polymerization of cyclohexene oxide in carbon dioxide using zinc catalysts are presented in Table 6.

As we expected from the NMR study of the catalyst–monomer mixture, the activities of the zinc catalysts are generally low. From the table we observed that yields, expressed as g of polymer/g of Zn, are influenced not only by the initial CO_2/CHO ratios but also by the temperature. Thus, at the same monomer and catalyst concentrations and comparable molar ratios CO_2/CHO (SP-2 vs SP-5) the yield increases strongly when reaction temperature is increased. Molecular weights decrease when catalyst concentration increases, as was expected. The molecular weight distribution is large, and the products are a mixture of methanol-soluble and methanol-insoluble fractions. When $[CO_2]/[CHO]$ increases, a decrease of polydispersity index was observed. The methanol-soluble fraction is predominantly polyether, and the insoluble fraction has a predominantly polycarbonate structure. For example, the ether/carbonate units ratio, determined from ^{1}H NMR integrals of the peaks at 3.74 and 4.67 ppm, is 2.48/1.0 for the soluble fraction, yet only 0.37/1.0 for the insoluble one (polymer obtained in run SP-2).

Not suprisingly, in the copolymerization of cyclohexene oxide and carbon dioxide using aluminum catalysts, the yields are much higher than when the zinc homologues were used (Table 7). The most reactive catalyst in homopolymerization (**2a**) gave the lowest yield in copolymerization with carbon dioxide. The highest yield was obtained with the aluminum alkoxide catalyst, but the extent of incorporation of carbon dioxide was low. The copolymers obtained with asymmetric (**2a**) and alkoxy (**2b**) aluminum catalysts exhibit a bimodal molecular weight distribution, suggesting that difference in reactivity exists not only between Al−O ether and ester bonds but also between Al−O ether and carbonate ones. The reactivity of Al−O bond is close to those of carbonate one. Thus, a good yield and a carbonate/ether ratio of 1/3.6 was obtained with the double ester substituted aluminum catalyst. As we saw above, these species have a high degree of symmetry and are partly hexacoordinated. Rearrangements in coordination probably take place involving both CHO and carbon dioxide and thus are favorable to a higher carbonate content in the polymeric chain.

Conclusions

By studying analogous zinc and aluminum catalysts, we found that aluminum derivatives are more active in both homopolymerization and copolymerization of cyclohexene oxide and carbon dioxide. The study by ^{1}H NMR spectroscopy of the reaction between catalysts and CHO showed that the insertion of monomer occurs into the Me−O ether bond for zinc catalysts and into both ether and ester bonds for aluminum analogues. From ^{27}Al NMR spectra, it was observed that aluminum catalysts exist as penta- and hexacoordinated species but after reaction with monomer become predominantly pentacoordinated. During initiation the equilibrium between five and six hypercoordinated species is shifted toward lower coordination. The nature of the catalysts and their symmetry influence the yield in the copolymerization of CHO and CO_2 and the amount of carbon dioxide inserted into polymeric chain. Using aluminum catalysts, the obtained turnovers in the copolymerization of CHO and CO_2 ranged between 149.85 and 340.4 g of polymer/g of metal, which means 41.2−93.6% yield.

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