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Epoxide Polymerization and Copolymerization with Carbon Dioxide Using Diethylaluminum Chloride-25,27-Dimethoxy-26,28-dihydroxy-*p-tert*-butyl-Calix[4]arene System as a New Homogeneous Catalyst

W. Kuran[a]; T. Listos[a]; M. Abramczyk[a]; A. Dawidek[a]

[a] Division of Polymer Synthesis & Processing Chemistry Department, Warsaw University of Technology, Warsaw, Poland

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EPOXIDE POLYMERIZATION AND COPOLYMERIZATION WITH CARBON DIOXIDE USING DIETHYLALUMINUM CHLORIDE—25,27-DIMETHOXY-26,28-DIHYDROXY-*p*-*tert*-BUTYL-CALIX[4]ARENE SYSTEM AS A NEW HOMOGENEOUS CATALYST

Witold Kuran,[*] **Tomasz Listos, Marek Abramczyk, and Andrzej Dawidek**
Division of Polymer Synthesis & Processing
Chemistry Department
Warsaw University of Technology
3, Noakowskiego Street
00-664 Warsaw, Poland

ABSTRACT

Previously unknown substituted chelate phenolatoaluminum chloride, (25,27-dimethoxy-*p*-*tert*-butylcalix[4]arene-26,28-diolato) aluminum chloride, was derived from the reaction of diethyl-aluminum chloride and 25,27-dimethoxy-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene at reactants 1:1 mole ratio. It was applied successfully for the polymerization of propylene oxide and cyclo-hexene oxide, and their copolymerization with carbon dioxide, leading to respective oligomers and co-oligomers. The catalyst structure and the structure of the obtained low-molecular-weight polymers and copolymers were studied using NMR spectroscopy. Poly(propylene oxide) obtained in the presence of the studied cata-lyst appeared to contain isotactic diads predominantly, whereas the obtained poly(cyclohexene oxide) did not exhibit any significantly prevailing sequences of either isotactic nor syndiotactic diads. The polymerization mechanism has been proposed and discussed in view of the obtained results.

INTRODUCTION

In the course of our investigations of epoxide polymerization and copolym-erization with carbon dioxide, we applied metal alkyl-polyhydric phenol homogeneous systems [1-5], as well as metal alkyl-γ-alumina heterogeneous systems [6] as catalysts. A significantly high effectiveness of these systems has been observed when using combinations of diethylzinc or triethylaluminum and trihydric phenol like pyrogallol [1, 2]. A high molecular weight of resulting polymers was characteristic of the above processes. The structure of active sites and the mech-anism of the epoxide polymerization and copolymerization with carbon dioxide involving such sites has been proposed and previously discussed [1-6]. It should be noted that the above catalysts form multinuclear species and the epoxide ring-opening consists in the monomer coordination with more electrophilic metal atom, followed by the nucleophilic attack, carried out by the adjacent metal atom, onto the coordinating monomer molecule [4-6]:

X = Ar, R, C(O)OR;   Y = Et, OX
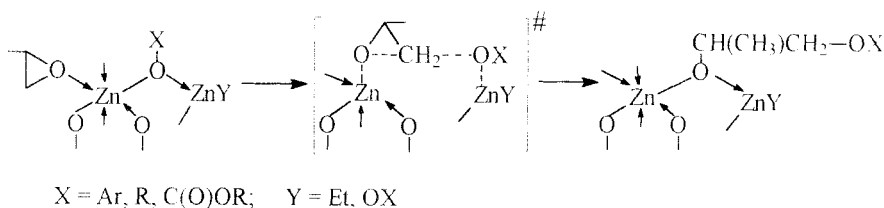
In order to check whether polyhydric phenols can form with organo-metallics catalysts containing mononuclear species which might be active in epoxide polymerization and copolymerization with carbon dioxide, 25,26,27,28-tetra-hy-droxy-*p-tert*-butylcalix[4]arene (caH$_4$) and 25,27-dimethoxy-26,28-dihydroxy-*p-tert*-butylcalix[4]arene (dmcaH$_2$) for reactions with metal alkyl like triethyl-alum-inum were used previously [7]. Products of these reactions appeared to promote propylene oxide polymerization and its copolymerization with carbon dioxide affording respective low-molecular-weight polymers. However, obtained catalysts were not isolated nor characterized.

In this paper, we deal with the synthesis and characterization of a new homogeneous catalyst based on alkylmetal chloride like diethylaluminum chloride (Et$_2$AlCl) and polyhydric phenol like dmcaH$_2$ which appeared to be (25,26-dimeth-oxy-*p-tert*-butylcalix[4]arene-26,28-diolato)aluminum chloride [(dmca)AlCl]. Results obtained from propylene oxide and cyclohexene oxide polymerization and copolymerization with carbon dioxide in the presence of this catalyst are reported. Preliminary results concerning the (dmca)AlCl synthesis and characterization as

well as its use for the propylene oxide polymerization and copolymerization with CO_2 were already announced [8].

EXPERIMENTAL

Materials

Propylene oxide (1,2-epoxypropane) (PO) (from Fluka AG) was dried on CaH_2 and distilled under normal pressure. Cyclohexene oxide (1,2-epoxy-cyclohexane) (CHO) (from Aldrich) was purified by distillation under reduced pressure. Commercial-grade CO_2 was used without further purification.

Diethylaluminum chloride (Et_2AlCl) (from Aldrich) was distilled in a nitrogen atmosphere under reduced pressure.

25,26,27,28-Tetrahydroxy-*p-tert*-butylcalix[4]arene (caH_4) was prepared from *p-tert*-butylphenol and formaldehyde (38 wt% solution in water) [9]. 25,27-Dimethoxy-26,28-dihydroxy-*p-tert*-butylcalix[4]arene ($dmcaH_2$) was synthesized from caH_4 and methyl *p*-toluenesulfonate [9].

Benzene, toluene and tetrahydrofuran (from Aldrich) were dried and purified by distillation according to common procedure. All the materials were stored under deoxygenated and dried nitrogen.

Catalyst Preparation

The catalyst was prepared immediately before use. A solution of Et_2AlCl in toluene was slowly added to a stirred suspension of $dmcaH_2$ in toluene at room temperature. After the addition was completed, stirring was continued until the calixarene suspension disappeared and the required amount of ethane evolved.

The catalyst was characterized by elemental analysis (Perkin Elmer 240 microanalyzer), ^{1}H- and ^{27}Al-NMR spectroscopy ($CDCl_3$ or C_6D_6 were used as solvents) (Varian VXR 300 MHz spectrometer) and molecular weight determination (under nitrogen in benzene solution, at concentration of ca. 4 wt%) using a standard freezing point depression apparatus.

Polymerization Procedure

Reactions were carried out in glass ampoules sealed by a screw with a gasket on coupling or in stainless steel autoclaves of 60 mL capacity as it was described previously [4, 5].

In order to remove catalyst residues from the obtained polymerization products, samples were further purified by column chromatography on silica gel (Kieselgel 0.040-0.063), eluent: hexane/ethyl acetate (vol. ratio 9:1).

Polymerization products were characterized using elemental analysis, IR spectroscopy (Specord 80-Carl Zeiss Jena), ^{1}H- and ^{13}C-NMR spectroscopy (recorded in $CDCl_3$ solution) (Varian VXR 300 MHz spectrometer), and viscosity measurements (Ubbelohde viscometer, in benzene). Molecular weight measurements of the oligomers were carried out using vapour osmometer (Hewlett Packard 302B, in chloroform) or by gel-permeation chromatography (GPC) in tetrahydrofuran (Shimadzu C-R4a Chromatopac apparatus).

Cyclic carbonates were determined from IR spectra ($v_{C=O}$ = 1800 cm^{-1} and $v_{C=O}$ = 1805 cm^{-1} for propylene carbonate and cyclohexene carbonate, respectively).

RESULTS AND DISCUSSION

Catalyst

DmcaH$_2$ was reacted with Et$_2$AlCl at the 1:1 reactant mole ratio in toluene medium at room temperature. The product formed in this reaction, (25,27-dimethoxy-p-tert-butylcalix[4]arene-26,28-diolato)aluminum chloride, (dmca)AlCl, was isolated from the solution and analyzed by elemental analysis, ^{1}H- and ^{27}Al-NMR spectroscopy and molecular weight determination.

Cryoscopic measurements on (dmca)AlCl showed that it formed monomeric species in benzene solution at freezing temperature. The molecular weight of (dmca)AlCl for:

$C_{46}H_{58}O_4AlCl$ formula: Calc.   736.5 g/mol

Found   719.4 g/mol

$M_{found}/M_{calc.}$ = 0.98.

Elemental analysis:

$C_{46}H_{58}O_4AlCl$ (736.5):   Calc.   C 74.9   H 7.9   Cl 4.8

Found - C 72.2   H 7.9   Cl 4.9.

^{1}H-NMR spectral data for the (dmca)AlCl catalyst confirmed its chemical composition (Table 1). The different value of the chemical shift of methyl protons, ArOC$\underline{H}_3$, in (dmca)AlCl with respect to dmcaH$_2$ testifies for the complexing of the aluminum atoms with methoxy groups. One signal at δ = 56.2 ppm in ^{27}Al-NMR spectrum, can be attributed to penta-coordinate aluminum atom.

The obtained results can confirm the course of the reaction in the dmcaH$_2$ - Et$_2$AlCl system as in Equation 1 and the proposed structure of (dmca)AlCl involv-

TABLE 1. ^{1}H-NMR Spectral Data (in ppm) for dmcaH$_2$ and (dmca)AlCl[a]

Group	dmcaH$_2$	(dmca)AlCl
H$_{Ar}$	7.1-6.8 (multiplet)	7.3-6.8 (multiplet)
-Ar-CH$_2$-Ar-	4.2, 3.3 (8H, 2 doublets)	4.2, 3.3 (8H, 2 doublets)
Ar-OH	7.3 (2H, singlet)	—
Ar-OCH$_3$	3.8 (6H, singlet)	4.0 (6H, singlet)
Ar-C(CH$_3$)$_3$	1.3, 0.9 (36H, 2 singlets)	1.5, 0.7 (36H, 2 singlets)

[a]For dmcaH$_2$ and (dmca)AlCl preparation and analyses see Experimental part; solvent $= C_6D_6$; Ar, C_6H_2; dmcaH$_2$, 25,27-dimethoxy-26,28-dihydroxy-p-$tert$-butylcalix[4]arene; (dmca)AlCl, (25,27-dimethoxy-p-$tert$-butylcalix[4]arene-26,28-diolato)aluminum chloride.

ing penta-coordinate Al atom with Cl nucleophilic substituent:

$$+AlEt_2Cl \atop -2\ EtH \qquad (1)$$
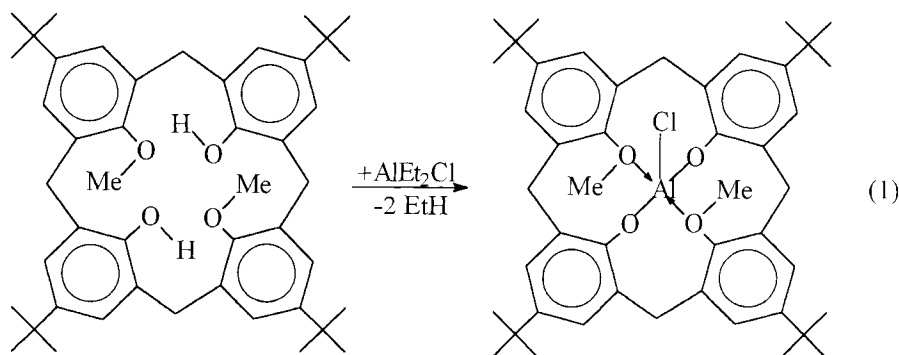
Considering the above results, it can be expected that the AlO$_4$ moiety of the (dmca)AlCl catalyst forms a rigid structure like distorted trigonal bipyramid [10].

Polymerization

Conditions and results of epoxide polymerizations in the presence of the new (dmca)AlCl catalyst are listed in Table 2.

The (dmca)AlCl catalyst appeared to give low-molecular-weight poly(propylene oxide) (PPO) and poly(cyclohexene oxide) (PCHO), containing the chlorine moiety as chain end-group, in yields of ca. 20-78 wt%. The molecular weights of

TABLE 2. Propylene Oxide (PO) and Cyclohexene Oxide (CHO) Polymerization
in the Presence of (dmca)AlCl as Catalyst[a]

Run	Reaction conditions			Oligoethers	
	Monomer	temp. C	time h	yield mol%	M_n
	PO	35	500	40	780[b]
1					690[c]
2	PO	35	168	20	1960[d]
3	PO	70	168	20	4160[d]
4	CHO	35	264	78	1260[e,f]
5	CHO	70	264	65	1150[g]

[a]Polymerization conditions: amount of the epoxide: PO = 100 mmol (5.8g);
CHO = 50 mmol (4.9g); solvent = toluene; for Run 1: 16 mL, for Runs 2-5: 10
mL; amount of the catalyst = 2 mmol; (dmca)AlCl, (25,27-dimethoxy-*p-tert*-
butylcalix[4]arene-26,28-diolato)aluminum chloride.

[b]Molecular weight calculated from the Cl content of 4.61 wt% (presence of
the chlorine moiety as chain end-group).

[c]Molecular weight distribution determined from GPC: $M_w/M_n = 1.36$.

[d]Molecular weight determined from viscosity measurements (Ubbelohde
viscometer, in benzene at 35(C).

[e]Molecular weight calculated from the Cl content of 2.81 wt% (presence of
the chlorine moiety as chain end-group).

[f]Molecular weight distribution determined from GPC: $M_w/M_n = 1.51$ (for
fraction of $M_n = 11570$ and $M_w = 17530$).

[g]Molecular weight determined from vapour osmometer measurements (in
CHCl$_3$ solution).

these oligomeric products are in the 780 to 4770 range. It is to be noted that the
value of the molecular weight distribution of oligo(propylene oxide) - M_w/M_n =
1.36 (Table 2, Run 1). and oligo(cyclohexene oxide) - $M_w/M_n = 1.51$ (Table 2, Run
4) was rather low. ^{1}H-NMR spectra of PO and CHO oligomers exhibit similar
chemical shifts to those described previously in the literature [4, 11] and contain
characteristic signals which can be attributed to protons: $\delta = 1.04$-1.17 [-CH(C$\underline{H}_3$)-

], 3.36-3.86 [-OC$\underline{H}$(CH$_3$)-, -OCH(CH$_3$)C$\underline{H}_2$-, -CH(CH$_3$)O$\underline{H}$ and -C$\underline{H}_2$Cl] ppm for PPO (Table 2, Run 2) and δ = 1.1-1.4 [-C$\underline{H}_2$-C$\underline{H}_2$-], 1.5-2.1 [-OCHC$\underline{H}_2$-], 3.3-3.6 [-OC$\underline{H}$- , -CHO$\underline{H}$ and C$\underline{H}$Cl] ppm for PCHO (Table 2, Runs 4, 5).

The ^{13}C-NMR spectrum of the oligo(propylene oxide) obtained with the (dmca)AlCl catalyst (Table 2, Run 2) exhibits three main split signals corresponding to $\underline{C}$H$_3$, $\underline{C}$H$_2$, and $\underline{C}$H carbons appearing around δ = 17.3, 73.2 and 75.3 ppm, respectively. The intensity of the observed signals allows to conclude that the oligoether contains only regular head-to-tail linkages of PO units. Two signals at 73.2 ppm are characteristic for isotactic and syndiotactic diads (mole fraction of isotactic diads is equal to ca. 74 mol%) and three signals around δ = 75.3 are attributable to isotactic, heterotactic and syndiotactic triads.

A detailed ^{13}C-NMR spectral analysis of the propylene oligoethers obtained with (dmca)AlCl as catalyst shows the presence of three signals located around: δ = 47.3 (which can be assigned to carbon in -$\underline{C}$H$_2$Cl group), and 65.9 and 67.3 (characteristic to terminal carbon in -$\underline{C}$H(CH$_3$)OH group) ppm, respectively. It appears therefore that the initiation reaction occurs due to the incorporation of PO into the Al-Cl bond yielding oligo(propylene oxide) (Equation 2).

$$(dmca)Al\text{---}Cl \ + \ \underset{O}{\overset{CH_3}{HC\text{---}CH_2}} \longrightarrow (dmca)Al\text{---}O\text{--}\underset{\overset{|}{CH_3}}{CH}\text{---}CH_2\text{---}Cl$$

$$\underset{\xrightarrow{\hspace{2cm}}}{n \ \underset{O}{\overset{CH_3}{HC\text{---}CH_2}}} \ (dmca)Al\text{---}O\text{---}\underset{\overset{|}{CH_3}}{CH}\left(\!CH_2\text{---}O\text{---}\underset{\overset{|}{CH_3}}{CH}\!\right)_n\!\!CH_2\text{---}Cl \ \xrightarrow{hydrolysis}$$

$$HO\text{---}\underset{\overset{|}{CH_3}}{CH}\left(\!CH_2\text{---}O\text{---}\underset{\overset{|}{CH_3}}{CH}\!\right)_n\!\!CH_2\text{---}Cl \qquad\qquad (2)$$
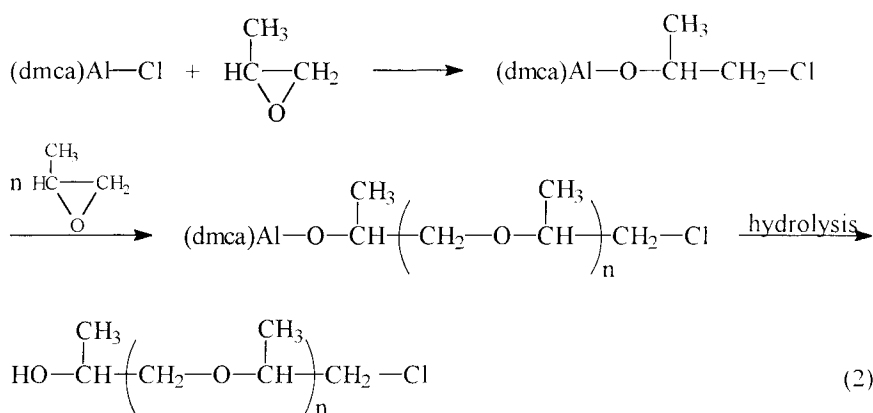
The ^{1}H-NMR spectra of the poly(cyclohexene oxide)s (Table 2, Runs 4, 5) of the methine region exhibit three signals with chemical shifts at (δ = 3.3, 3.4 and 3.5 ppm which can be attributed to heterotactic, syndiotactic and isotactic triads; in amounts of 37, 33 and 30 mol%, respectively.

The (dmca)AlCl catalyst was found to promote the epoxide-carbon dioxide reactions leading to the low-molecular-weight copolymers and cyclic carbonates (Table 3). Low-molecular-weight copolymers appeared to be respective oligo(alkylene ether-carbonate)s of the carbonate unit contents in the range 13-18 mol%. It

TABLE 3. Reaction of Propylene Oxide (PO) and Cyclohexene Oxide (CHO) with Carbon Dioxide in the Presence of (dmca)AlCl as Catalyst[a]

| Run | Reaction conditions | | | Oligo(alkylene ether-carbonate)s | | | Cyclic carbonate |
	Comonomers (mole ratio)	temp. C	time h	yield[b] mol%	CO_2[c] mol%	M_n	yield[b] in mol-%
1	PO/CO_2 (1:2.5)	35	168	38	13	5620[d]	14
2	PO/CO_2 (1:2.5)	70	168	31	17	930[e]	12
3	CHO/CO_2 (1:5)	35	264	26	18	1930[f]	4
4	CHO/CO_2 (1:5)	70	264	36	17		7

[a]Copolymerization conditions: amount of the comonomer: PO = 100 mmol (5.8g); CHO = 50 mmol (4.9g); CO_2 = 250 mmol (11g); partial pressure of CO_2 = ca. 60 atm (610^6 Pa); solvent = toluene (10 mL); amount of catalyst = 2 mmol; (dmca)AlCl, (25,27-dimethoxy-p-tert-butylcalix[4]arene-26,28-diolato)aluminum chloride.

[b]With respect to the epoxide.

[c]Amount of CO_2 (oxycarbonyl-groups content) in oligo(alkylene ether-carbonate).

[d]Molecular weight determined from viscosity measurements (Ubbelohde viscometer, in benzene).

[e]Molecular weight calculated from Cl content of 3.81 wt% (presence of the chlorine moiety as chain end-group).
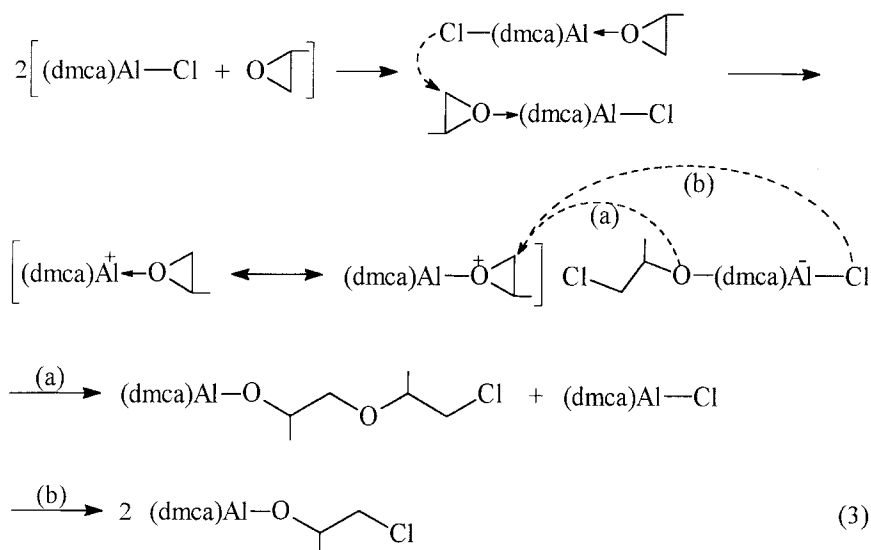
[f]Molecular weight calculated from Cl content of 1.84 wt% (presence of the chlorine moiety as chain end-group).

should be emphasized that the chlorine-containing chain terminal was present in the obtained copolymers which was confirmed by elemental analysis, and ^{13}C-NMR spectra, like in the case of respective homopolymers.

IR spectroscopic studies on the obtained copolymers revealed the presence of propylene or cyclohexene carbonate linkages ($v_{C=O}$ = 1745 cm^{-1} or $v_{C=O}$ = 1750 cm^{-1}, respectively) in their chains.

The stereochemistry of epoxide ring-opening in the cyclohexene oxide-carbon dioxide copolymerization with (dmca)AlCl catalyst was elucidated by applying the alkaline hydrolysis of obtained oligo(cyclohexene ether-carbonate) (Table 3, Run 3) and determinig the structure of resulting cyclohexanediol isomers, *trans*-1,2-cyclohexanediol and *cis*-1,2-cyclohexanediol. The *trans*-diol was found to be present in a post-hydrolyzed mixture in a ca. sevenfold excess with respect to the *cis*-diol which testified for the predominant *threo*-enchainment of monomeric units in the copolymer chain. Therefore, considering that cyclohexene oxide is a *cis*-epoxide, an inversion of the configuration at the carbon atom of the cleft epoxide C-O bond in the course of the copolymerization is proved.

The results of the studies of the epoxide polymerization with the (dmca)AlCl catalyst, especially the inversion of the configuration at the carbon atom of the cleft epoxide C-O bond, indicate that the reaction consists in a simultaneous participation of two molecules of the catalyst according to the tentative scheme presented in Equation 3.

$$2\left[(dmca)Al\text{—}Cl + O\triangleleft \right] \longrightarrow$$

$$(dmca)\overset{+}{Al}\text{—}O\triangleleft \longleftrightarrow (dmca)Al\text{—}\overset{+}{O}\triangleleft$$

$$\xrightarrow{(a)} (dmca)Al\text{—}O \diagup \diagdown O \diagup \diagdown Cl + (dmca)Al\text{—}Cl$$

$$\xrightarrow{(b)} 2\ (dmca)Al\text{—}O \diagup \diagdown Cl \tag{3}$$

It is important to note that according to the proposed mechanism, the rearward attack of the nucleophilic substituent onto the coordinating monomer is carried out by the hexa-coordinate aluminum species. We should emphasize that the backside nucleophilic attack, proved by the inversion of the configuration of the carbon atom of the cleft epoxide C-O bond during polymerization, is possible only in the bimolecular reaction according to Equation 3, but cannot take place in a monomeric complex of the catalyst with the monomer (in the latter case no inversion of the configuration would be observed). It is worth noting that equil-

ibrium reactions, may explain narrow molecular weight distributions of polyethers resulting from epoxide polymerizations in the presence of the (dmca)AlCl catalyst.

CONCLUSION

The reaction between $AlEt_2Cl$ and 25,27-dimethoxy-26,28-dihydroxy-*p-tert*-butylcalix[4]arene gives quantitavely (dmca)AlCl as a product. It appeared to be homogeneous and to form monomeric mononuclear aluminum species.

This new homogeneous catalyst appeared to promote the epoxide polymerization and copolymerization with carbon dioxide. Such polymerization and copolymerization seem to afford a new route for the synthesis of oligomeric polyethers and poly(ether-carbonate)s with functional end groups.

The obtained results suggest that the initiation step consists in the incorporation of aluminum-coordinated monomers into the Al-Cl bond. The polymerization of the racemic propylene oxide seems to be controlled sterically by chain-end stereocontrol mechanism and proceeds with a relatively high degree of stereo-selection yielding isotactic PPO predominantly. On the contrary, the polym-erization of cyclohexene oxide, which is an achiral monomer, is barely controlled stereo-chemically; i.e. it is not stereospecific and yields nearly atactic PCHO.

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