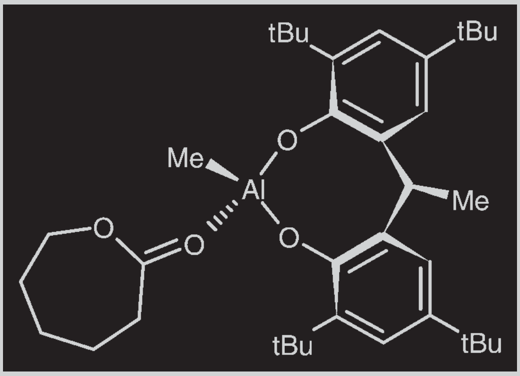
Summary: The isolation and structural characterization of a methylaluminium(bisphenoxide)-ε-caprolactone complex is reported. While the three-coordinate methylaluminium complex was found not to catalyze the polymerization of ε-caprolactone, its oxygenation led to the formation of an aluminium methoxide compound, which appeared to be a very good initiator. The relative propensity of the Al–X bonds for monomer insertion in the initial step of polymerization is also discussed.



Structure of the methylaluminium(bisphenoxide)-ε-caprolactone complex reported here.

Towards the Nature of Active Sites in Polymerization of Cyclic Esters Initiated by Aluminium Alkoxides: First Structurally Authenticated Aluminium-ε-Caprolactone Complex

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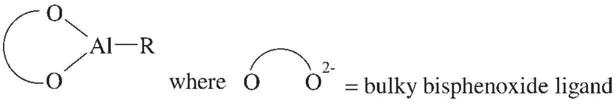
Introduction

In principle, the ring-opening polymerization of cyclic esters is thought to occur by a coordination-insertion pathway mechanism, whereby the metal center serves to activate the carbonyl group toward attack by the metal-bound alkoxide initiator, and initiation proceeds by insertion of a monomer unit into the metal-alkoxide bond with cleavage of the acyl-oxygen bond of the monomer.[1] In recent years, aluminium alkoxides have been employed extensively as efficient initiators for the controlled polymerization of lactones,[2,3] and the most widely encountered mechanistic models involve the three-coordinate metal center as the active species, while higher-coordinate centers are frequently cited as dormant species.[2a] The Lewis acidity of these species has been believed to be a crucial parameter that dictates the catalytic properties of such systems, however, no structural information is available for the Lewis acid-base adducts formed between the aluminium center and ε-caprolactone (ε-CL). In addition, for various alkylaluminium alkoxides, including alkylaluminium derivatives of bulky bisphenols, **I** (see below), it has been suggested that the initiation of polymerization may occur at both the Al–C and the Al–O bond.[4] Moreover, recently we demonstrated univocally that the terminal aluminium-aryloxide linkage in the cationic species is able to initiate the polymerization of ε-CL.[5]



I

As a part of our study on the activation of heterocyclic monomers by the group 13 Lewis acids,[5,6] we describe here the first structurally characterized aluminium-ε-CL complex that was isolated from the reaction of methylaluminium(bisphenoxide) [MeAl(bisphenoxide)] with ε-CL. In addition, we show that the latter complex is inactive as an initiator for ε-CL polymerization but forms an efficient catalytic system upon addition of dry air.

Experimental Part

General Remarks

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere before use. ε-CL was purified by distillation over calcium hydride and stored under N_2. $AlMe_3$ and 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP–H_2) were purchased from Aldrich and used without further purification. MeAl(EDBP) was prepared according to the published procedure.[7] ^1H NMR spectra were recorded on a Varian Mercury 400 spectrometer with chemical shifts given in ppm according to the C_6D_6 chemical shift. Gel permeation chromatography (GPC) analyses versus polystyrene standards were carried out, and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) analyses were performed on a Kratos Kompact MALDI 4 V5.2.1 spectrometer.

Preparation of MeAl(EDBP)(ε-CL) (2)

MeAl(EDBP) (0.9 g, 1.88 mmol) (**1**) and CH_2Cl_2 (10 mL) were placed in a Schlenk vessel and then ε-caprolactone (0.22 mL, 2.04 mmol) was added at ambient temperature. The stirred solution was heated to 40 °C for 15 min. After being cooled, the product was isolated as a white solid after removal of the dichloromethane under vacuum. The product was later crystallized from a dichloromethane/hexane solution. Yield: 1.184 (90%).

^1H NMR (400 MHz, 25 °C, C_6D_6) $\delta = 0.04$ (s, 3H, Al*Me*), 1.41, 1.64 (s, 36H, $Ar^t\mathit{Bu}$), 0.70 (m, 6H, $C(O)CH_2(\mathit{CH}_2)_3CH_2O$), 1.76 (d, 3H, $–CH\mathit{CH}_3$, J_{HH} 7.2 Hz), 1.67 (br s, 2H, $C(O)\mathit{CH}_2(CH_2)_3CH_2O$), 3.03 (br s, 2H, $C(O)CH_2(CH_2)_3\mathit{CH}_2O$), 5.26 (q, 1H, $\mathit{CH}CH_3$, J_{HH} 7.2 Hz), 7.35, 7.69 (d, 4H, H_{aryl}, J_{HH} 2.7 Hz).

IR (CH_2Cl_2): 1 640 cm^{-1} (C=O).

$(C_{37}H_{57}AlO_4)_n$ $(592.85)_n$: Calcd. C 74.96, H 9.69, Al 4.55; Found C 75.45, H 10.32, Al 4.24.

Polymerization Conditions

Polymerization reactions were carried out in a stainless steel reactor under a nitrogen atmosphere in a dichloromethane solution. The polymer was dissolved in CH_2Cl_2 (50 mL) and hydrolyzed with 5% HCl (20 mL). The organic phase was separated, washed with water (3 × 75 mL), dried over sodium sulfate, and was filtered. The resulting solution was concentrated and the polymer precipitated by the addition of methanol. The polycaprolactone sample was dried under vacuum and submitted for GPC and MALDI-TOF analysis.

MeAl(EDBP)/ε-CL System

$[MeAl(EDBP)]_2$ (0.25 g, 0.52 mmol) was dissolved in CH_2Cl_2 (20 mL) and ε-caprolactone (3.00 g, 26.11 mmol) was added. The reaction was performed at 40 and 80 °C and stopped after 72 h. No polymerization of ε-CL to afford polycaprolactone was observed. Similar results were obtained for the ε-CL/MeAl(EDBP)(ε-CL) system under analogous conditions.

MeAl(EDBP)/ε-CL/O_2 System

In a typical run, to the solution of $[MeAl(EDBP)]_2$ (0.25 g, 0.52 mmol) in CH_2Cl_2 (20 mL), ε-caprolactone (3.00 g, 26.11 mmol) was added at ambient temperature (ε-CL/Al ratio was 50:1). A balloon containing dry air was connected to the system for 15 min and then the polymerization was performed at 40 °C for 12 h. We note that the $[MeAl(EDBP)]_2$/ε-CL/O_2 system shows some induction period during which polymerization of ε-CL is observed. The MALDI-TOF analyses revealed an end group of 32 Da. ^1H NMR ($CDCl_3$) data for the polycaprolactone chain: $\delta = 1.36$ (m, 2H, $–CH_2–$), 1.62 (m, 4H, $–CH_2–$), 2.28 (t, 2H, $C(O)CH_2–$), 4.03 (t, 2H, $O–CH_2–$),3.5 (s, end groups OCH_3), 4.0 (br s, $CH_2\mathit{OH}$).

*X-Ray Structure Determination of **2***

Single crystals of **2**, suitable for X-ray diffraction studies, were placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) in an inert atmosphere. The data were collected on a Nonius Kappa-CCD diffractometer at 150(2) K. Crystal data for **2**, $C_{36}H_{57}O_4Al_1 \cdot 1/2C_6H_{14}$: $M = 623.26$, crystal dimensions $0.50 \times 0.40 \times 0.20$ mm^3, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.1820(3)$ Å, $b = 12.0630(4)$ Å, $c = 22.5940(8)$ Å, $\beta = 106.8070(10)°$, $V = 3\,961.1(2)$ $Å^3$, $Z = 4$, $F(000) = 1\,428$, $D_c = 1.111$ $g \cdot m^{-3}$, $\mu(\text{Mo K}\alpha) = 4.19$ mm^{-1}, $\theta_{max} = 20.81°$, 4 139 unique reflections which were used in all calculations. The structure was solved by direct methods using the SHELXS-97 program,[8] and was refined by full matrix least-squares on F^2 using the program SHELXL-97.[9] Hydrogen atoms were included in idealized positions and refined isotropically. Refinement converged at $R_1 = 0.0944$, $wR_2 = 0.1433$ for all data and 419 parameters ($R_1 = 0.0595$, $wR_2 = 0.1227$ for 3 084 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal to 1.109. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = 0.438/−0.330 $e \cdot Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 227290. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The reaction of $[MeAl(EDBP)]_2$ (**1**)[7] [where EDBP = 2,2′-ethylidenobis(4,6-di-*tert*-butylphenolate)] with 1 equivalent of ε-CL in CH_2Cl_2 allows for the isolation of the Lewis acid-base adduct MeAl(EDBP)(ε-CL) (**2**) which has been characterized by ^1H NMR and IR spectroscopy.

Complex **2** is indefinitely stable as a solid and in solution under an inert atmosphere, showing no further reaction of the coordinated ε-CL at ambient or even elevated temperature. The ^{1}H NMR spectra show no complexity and a single resonance pattern is observed at room temperature. However, the IR data are especially noteworthy as they revealed important structural information relevant to the understanding of polymerization catalysis. The IR spectrum of **2** in CH_2Cl_2 solution shows only one band for the carbonyl group stretching frequency at 1 640 cm^{-1}. The observed decrease in the carbonyl stretching frequency in comparison to that in free ε-CL (1 728 cm^{-1}) by 88 cm^{-1} is consistent with the strong coordination of the carbonyl group to the metal center. The paucity of structural data for the metal-lactone complexes[a] prompted us to investigate the X-ray structure of the unique adduct **2**.

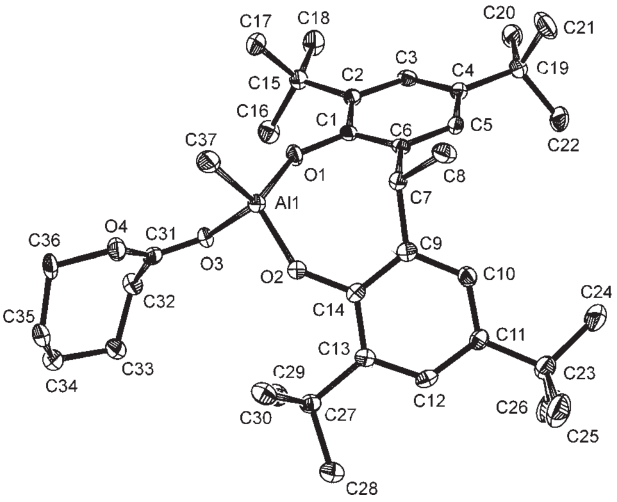


Figure 1. Molecular structure of **2** with 30% thermal ellipsoids; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Al(1)–O(1) 1.719(3), Al(1)–O(2) 1.721(3), Al(1)–O(3) 1.876(3), Al(1)–C(37) 1.933(4), C(31)–O(3) 1.246(6), C(31)–O(4) 1.305(5).

The molecular structure of **2** is shown in Figure 1. Compound **2** is monomeric with no unusual intermolecular contacts. The metal center is four coordinate and its coordination-sphere geometry can be described as a distorted tetrahedral. The lactone molecule is coordinated by the carbonyl oxygen atom with the aluminium being in the nodal plane of the C=O bond, and the complex adopts a *syn* conformation. The Al–O$_{ester}$ bond distance in **2** (1.876(3) Å) is essentially very similar to that observed in the related MeAl(EDBP)(THF) complex [1.864(6) Å].[7] The Al–O bond lengths associated with the dianionic EDBP ligand in **2** (the average value of 1.720 Å) are within the ranges expected for four-coordinate adducts of alkyl(bisaryloxide)aluminium species with Lewis bases.[11]

The model compounds **1** and **2** were further investigated for their catalytic activities in the polymerization of ε-CL. Under rigorously anaerobic conditions, both compounds were found to be inactive for the polymerization, even at elevated temperatures up to 80 °C. This result is striking as it is often anticipated that the more electrophilic initiators will polymerize cyclic esters faster.[2a] In the case of compound **2**, there is a strong activation of the monomer (vide supra) and both the Al–O and Al–C bonds are present into which the insertion of ε-CL may potentially occur, however, the ring-opening polymerization in this system does not proceed. Nevertheless, when **1** or **2** were used as initiators in the presence of dioxygen, the polymerization was readily observed and led to the formation of polycaprolactone (PCL) after several hours in very high yield (~99%). It is reasonable that the observed induction period involved the oxygenation of the Al–C bond to give the aluminium alkoxide compound, $[Al(\mu\text{-OMe})(EDBP)]_2$, which is then the real initiator. The MALDI-TOF spectrum of the obtained PCL (Figure 2) revealed the monomodal molecular weight distribution ($\overline{M}_w/\overline{M}_n$, 1.07).[b]

The mass difference was 114 in each case and the presence of an end group of 32 Da, corresponding to an OMe group, was found. The presence of the OMe end group confirms the formation of the aluminium methoxide species in the reaction between O_2 and **1** or **2**.[c] This finding fully agrees with the well-documented catalytic activity of aluminium alkoxides supported by bulky biphenoxide ligands in the polymerization of ε-CL.[3,4,7] In regard to the latter catalytic system, the model studies by Lin et al. revealed the formation of a five-coordinate adduct between dimeric $[Al(\mu\text{-OCH}_2Ph)(MMPEP)]_2$ [where MMPEP-H_2 = 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)-phenol)] and benzyl aldehyde,[3e] which suggest that higher coordinate aluminium centers are likely to be involved in the initiation step of cyclic esters polymerization.

Conclusion

This work provides the synthesis and structural characterization of the first example of aluminium-ε-CL complex,

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[a] We note that the structurally characterised metal-ε-caprolactone complexes are very rare, and a search of the Cambridge Crystallographic Database reveals only data for rare earth metal complexes with ε-caprolactone, see ref.[10]

[b] The narrow molecular weight distribution was confirmed by GPC, $\overline{M}_w/\overline{M}_n = 1.06$. The GPC analysis revealed only one peak of $\overline{M}_n$ and $\overline{M}_w$ equal to 6 453.83 and 6 811.77 Da, respectively. It is also important to note that while both GPC and MALDI-TOF revealed almost the same polydispersity value, the average molecular weight was much lower, probably because longer chains remained in matrix.

[c] We have studied indepedently the latter reaction and confirmed univocally the formation of **3**, however, this complex reaction deserves a more detailed discussion and will be reported in a full paper elsewhere. The interaction of dioxygen with metal alkyls is of continued interest to us, see for example ref.[12]

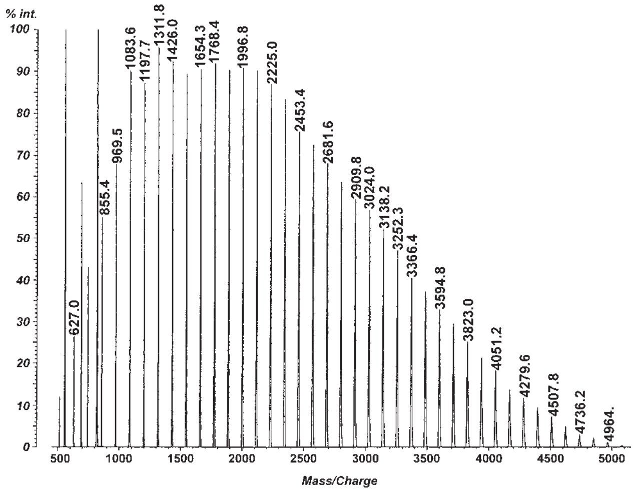

Figure 2. MALDI–TOF spectrum of PCL obtained with the MeAl(EDBP)/ε-CL/O_2 system as the initiator.

MeAl(bisphenoxide)(ε-CL). The lack of initiation efficiency in the polymerization of ε-CL by this adduct demonstrates that the strong coordination of ε-CL to the Lewis acid center is not the decisive factor determining the initiation step of polymerization. Although three-coordinate aluminium compounds are very often discussed in the literature as active species, our results lend strong evidence that higher coordinate aluminium centers are active sites in the polymerization of cyclic esters. Further studies concerning the nature of active species in the ring-opening polymerization of heterocyclic monomers are in progress.

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