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Aluminum bisphenoxides: Promising challengers for a catalyzed copolymerization of cyclohexene oxide with CO_2

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Abstract

Reacting triethyl aluminum and diethyl aluminum chloride with the chelating bisphenol ligands mdtbpH2 and mmcpH2 [mmcpH2: 2,2′-methylenebis(4-methyl-6-(1-methyl-cyclohexyl)phenol); mdtbpH2: 2,2′-methylenebis(4,6-di-*tert*-butyl-phenol)] afforded monomeric and dimeric aluminum bisphenoxides with reactive Al–Cl and Al–C_2H_5 moieties. We present here the X-ray structure determination of some of the isolated compounds as well as the preliminary catalytic tests in copolymerization reactions with cyclohexene oxide and carbon dioxide.

Keywords: Aluminum bisphenoxides; Cyclohexene oxide; Aliphatic polycarbonate; IR spectroscopy; NMR spectroscopy; GPC; Carbon dioxide; Co-catalyst

1. Introduction

Polycarbonates find an ever increasing use as engineering thermoplastics. With characteristics such as a high ductility, a very good transparency, a high heat and impact resistance as well as a high biocompatibility, polycarbonates are considered as specialty polymers and are used in technological applications in many different fields [1]. The usual industrial ways of synthesizing polycarbonates involve the reaction between alcohols and reactive C_1-synthons such as phosgene or carbon monoxide [2,3]. The problems encountered in the industry by the use of such toxic reagents could be overcome by the use of CO_2 as a C_1-building block. One more incentive is that the so-obtained aliphatic polycarbonates actually display promising characteristics such as a low toxicity and a good biodegradability making them interesting precursors for new materials and a useful complement to the usual polycarbonates [4,5]. Owing to the high thermodynamic stability of carbon dioxide, the use of catalysts and/or more reactive substrates is necessary. Many CO_2-based catalytic systems for a copolymerisation of CO_2 with epoxides (cyclohexene oxide and propylene oxide) have already been reported [6–8]. These well documented studies and reviews indicate that especially coordination compounds based on zinc, chromium and, at a lesser extent, aluminum are promising candidates for new highly active catalytic systems dealing with the copolymerisation of epoxides with carbon dioxide. Transition metal- and main group alkoxides are promising candidates for new catalytic systems involving an activation of CO_2 [9–11]. A catalytic copolymerization of epoxides and CO_2 would require two complementary coordination sites at the active center: an acidic site allowing the epoxide to coordinate (metallic core) and a nucleophilic site (oxygen of an alkoxide ligand) able to attack either the carbon atom of the CO_2 molecule or the α-carbon atom of the epoxide and promote the insertion of a new monomer into the reactive metal–oxygen bond thus increasing the already-formed polycarbonate chain. Generally, the presence of ligands other than alkoxide such e.g. chlorine or alkyl groups yields to a induction period before a copolymerisation reaction actually starts due to a lower reactivity of the metal–halide, respectively metal–carbon, bonds relative to an epoxide insertion and the formation of the resulting reactive alkoxide. Although aluminum alkoxides have been already studied in the copolymerisation of epoxides (e.g. propylene oxide) and CO_2 as early as in the 80s by the research group of Inoue [6], only a couple of studies dealing with new aluminum-based catalytic systems have been reported by Beckman [12], Ree [13] and Darensbourg [14] in the last decade. We focused on the cheap and easy-to-handle aluminum tri-isopropoxide which was widely used as a catalyst in the Meerwein–Ponndorf–Verley reduction and in ring opening polymerizations of cyclic anhydrides, ε-caprolactone [15] and

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lactides [16]. First series of experiments with cyclohexene oxide and CO_2 showed that this Lewis acid is highly active in the copolymerisation of cyclohexene oxide (CHO) with carbon dioxide [17]. On the basis of ^{27}Al NMR spectra and according to literature data, we demonstrated that the high reactivity of the catalyst is due to a rearrangement of the stable tetrameric aluminum isopropoxide at ca. 80 °C to a more reactive oligomer and, during the copolymerisation, to a further fragmentation into reactive monomeric species. In order to gain more information on the active species involved in the catalysis and to have a better control on the formation of the copolymer chains, a "simplification" of the catalytic system was necessary. The use of chelating alkoxo ligands can elegantly provide a structurally well-defined aluminum catalyst for a copolymerization of epoxides with CO_2. This approach was recently used by the research groups of Gibson [18] and Darensbourg [14] by using aluminum-based salen derivative in the stereoselective polymerization of lactides and the copolymerization of cyclohexene oxide with CO_2 respectively (salen: *N*,*N*′-bis-(salicylidene)-1,2-ethylenediimine). Bulky 2,2′-methylene-bisphenols constitute a versatile and easy-to-handle toolbox for the coordination chemist. The synthesis on a large scale (above 50 g) of these chelating ligands from formaldehyde and the corresponding bulky phenols is relatively easy and allows the rapid development of a ligand library (Scheme 1) [19,20].

Aluminum 2,2′-methylene-bisphenoxides have been already extensively studied by the groups of Okuda [21], Lin [22] and Chisholm [23] in ring opening polymerization (ROP) of lactones, in Diels–Alder coupling reactions, in the Meerwein–Ponndorf–Verley reduction and recently in the ROP of epoxides.

By employing triethyl aluminum and diethyl aluminum chloride with the chelating bisphenol ligands mdtbpH2 and mmcpH2 [mmcpH2: 2,2′-methylenebis(4-methyl-6-(1-methylcyclohexyl)phenol); mdtbpH2: 2,2′-methylenebis(4,6-di-*tert*-butyl-phenol)], we performed the synthesis of different complexes displaying different molecular complexities (monomer and dimer) and different reactive bonds relative to an epoxide insertion (Al–Cl and Al–C). We present here the X-ray structure determination of some of the isolated compounds as well as the preliminary catalytic tests in copolymerisation reactions with CHO and carbon dioxide.

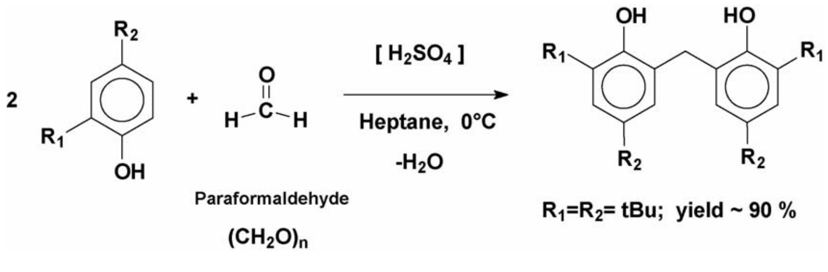
2. Results and discussion

When the selected ethyl aluminum starting compounds ($ClAlEt_2$ and $AlEt_3$) were reacted with ca. 1 molar equiv. of the bulky chelating bisphenols $mdtbpH_2$ and $mmcpH_2$ in hexane or THF at 0 °C, a vigorous evolution of ethane was observed. A small excess (5–10% molar) of the ethyl aluminum derivatives generally affords higher yields of aluminum bisphenoxides. The reaction mixture was allowed to warm up to room temperature (3–5 h) and the different aluminum bisphenoxides were obtained in high yields as colorless crystals after several days staying at −25 °C. The use of a coordinating solvent like THF yields as expected tetra-coordinated monomeric species, and inhibits the formation of dimeric species as observed when *n*-hexane was used as a solvent (Scheme 2).

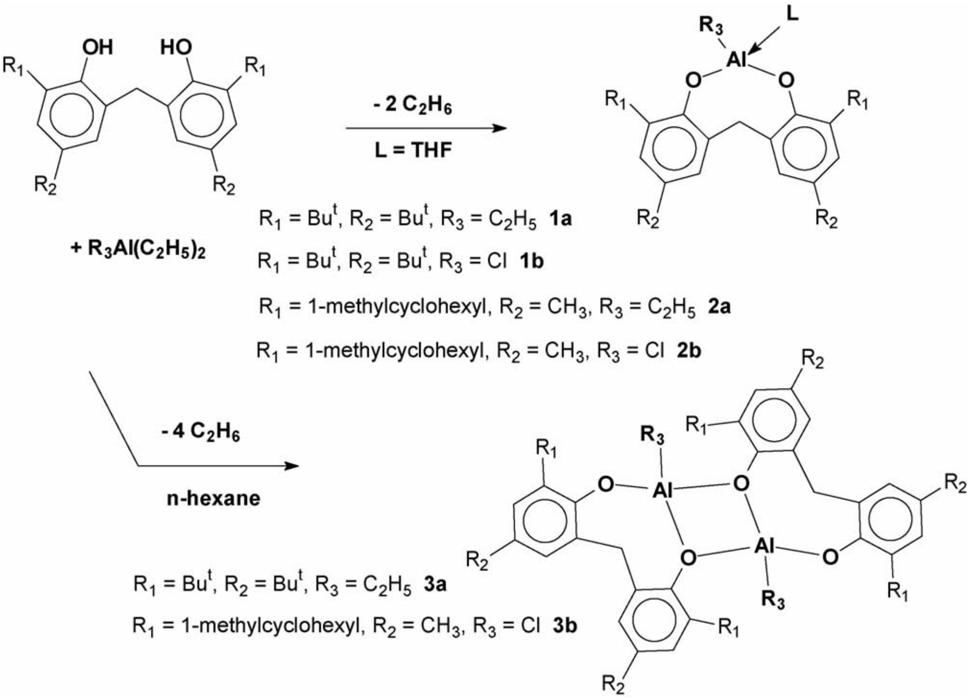
2.1. Spectroscopic characterization of the aluminum bisphenoxides *1–3*

Based on the ^{1}H NMR spectra of the monomeric compounds **1a–b** and **2a–b**, the substituents on one of the phenyl rings of the bisphenoxide ligand are chemically equivalent to the corresponding substituents on the other ring. These observations suggest that there is a plane of symmetry passing through the bridging methylene carbon and the aluminum atom. In comparison, in the dimeric compounds **3a** and **3b** each of the substituents on the two phenyl rings exhibit a unique resonance, suggesting that the two halves of the 2,2′-methylenebisphenols are not equivalent at room temperature in solution. This was corroborated by ^{13}C NMR spectroscopy in the case of **3a** where two distinct sets of signals attributed to two non-equivalent bisphenoxides can be observed. Owing to the similar structural features found in **3a** and **3b**, we expected a similar behavior for compound **3b**. Unfortunately the spectrum recorded for the bisphenoxo aluminum chloride, **3b**, displayed a poorer resolution than the spectrum of **3a** as well as only one set of resonances for the bisphenoxide ligand. Whether this fact is due to a lower solubility of **3b** in benzene or to be attributed to other phenomena is not clear and will be the subject of further studies.

The two hydrogens of the bridging methylene (C7) in the monomeric compounds **1a–b** and **2a–b** are observed to be magnetically non-equivalent with two different sets of chemical shifts between 3.31 and 3.42 ppm for the hydrogens exo and between 3.80 and 3.97 ppm for the hydrogens endo ($^2J_{HH}$ ranging from 13.60 to 14.25 Hz, Table 1). The chemical shifts obtained for the hydrogen endo and exo are comparable to the ones reported for other aluminum bisphenoxides bearing steric demanding groups [21–23]. The evaluation of the endo–exo character (endo: pointing towards the Al atom; exo: not pointing towards Al) for the non-equivalent hydrogens of the



Scheme 1. General synthesis and structure of substituted 2,2′-methylene bisphenoxides.



Scheme 2. Structures and nomenclature of the different bisphenoxides used in this study.

methylene bridge was based on 2D-NOESY experiments. The hydrogens of the bridging methylene are also, as expected, non-equivalent in the dimeric compounds; however it is interesting to note that for the dimeric compounds **3a** and **3b**, the ^{1}H chemical shifts of the C-7 exo protons are observed at 3.48 and 3.55 ppm, respectively ($^2J_{HH}$: 13.64 and 13.72 Hz) and the C-7 endo protons at 4.39 and 4.40 ppm. The signals are about 0.1 (exo) and 0.6 ppm (endo) downfield than the monomeric compounds. The reason for this feature probably results from the bridging character of oxygen O(1) of the bisphenoxide ligands and a deshielding of the ring current of the phenyl ring in the bisphenoxide backbone. This leads also to a deshielding of the methylene bridges, the endo hydrogen being more strongly deshielded due to the proximity of the aluminum atom. This can be further verified by the crystal structure studies of **3a** and **3b** (vide infra). The aluminum bound ethyl groups in monomeric **1a** and **2a** occurred as quadruplets and triplets in the ^{1}H spectra at ca. 0.1 and 1.0 ppm, respectively. In comparison, the Al-bound ethyl groups in compound **3a** seem to display different geometries according to the chemical shift recorded: 0.11, 0.15 for the methylene and 0.51, 0.65 ppm for the methyl fragment. Interestingly two broad, averaged signals corresponding to methylene and methyl groups belonging to Al–Et fragments were found in the ^{13}C spectrum at 7.4 and 21.6 ppm, respectively.

2.2. Molecular structure determinations of **1a**, **2a**, **3a** and **3b**

Suitable crystals for structure determination of **1**–**3a** and **3b** were obtained by slowly cooling a hot toluene solution. The thermal ellipsoid plots of the monomeric and dimeric bisphenoxides are provided in Figs. 1 and 2, respectively. Experimental data for the crystal structures of monomeric and dimeric compounds are listed in Table 2. Selected bond lengths and bond angles of **1a**–**2a** and **3a**–**3b** are summarized in Table 3.

The structures of **1a** and **2a** show monomeric features and the geometry around Al is slightly distorted from the ideal tetrahedral geometry with the bond distances Al–O(1):1.7217(18) and 1.713(2), Al–O(2):1.7156(18) and

Table 1
Comparison of different ^{1}H chemical shifts for the free ligands and the monomeric and dimeric aluminum bisphenoxides

	$AlCH_2CH_3$	$AlCH_2CH_3$	C(7) (H_{EXO})	C(7) (H_{ENDO})	$J_{H–H}$ (Hz)
$mdtbpH_2$	–	–	3.93		–
$mmcpH_2$	–	–	3.81		–
1a	0.08	1.07	3.39	3.88	13.70
1b	–	–	3.39	3.97	13.72
2a	0.05	1.04	3.31	3.83	13.60
2b	–	–	3.42	3.80	14.25
3a	0.11, 0.15	0.51, 0.65	3.48	4.39	13.64
3b	–	–	3.55	4.40	13.72

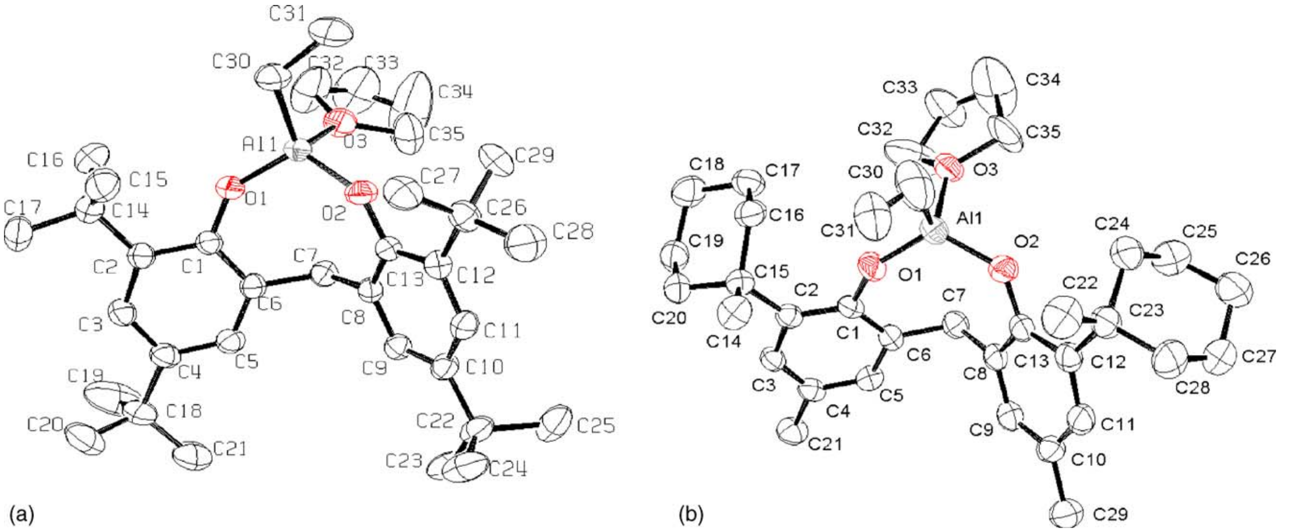


Fig. 1. ORTEP drawings (50% probability) of the monomeric compounds (**1a**) [(THF)Al(C_2H_5)(mdtbp)].1.6 THF and (**2a**) [(THF)Al(C_2H_5)(mmcp)] (solvent molecules present in the cell omitted for sake of clarity).

1.720(2), Al–O(3):1.8850(19) and 1.870(2), and Al–C(30) 1.950(3) and 1.955(4), respectively. These distances are all compatible with the bond lengths reported for four-coordinated aluminum phenoxides containing steric bulky substituents [21–23]. The largest angles around the tetrahedrally coordinated aluminum center involve the eight-membered ring of the bisphenoxides with 115.8° for **1a** and 117.1° for **2a**. The Al–O(3) bond distances associated with the coordinated THF bond are notably longer than the Al–O bisphenoxide distances as might be expected for dative bonds and slightly longer than the Al–O bridging distances found in the dimers (Table 3).

The structures of **3a** and **3b** show a dimeric feature containing an Al_2O_2-rhombus core bridging through one oxygen atom (O1) of the bisphenoxide ligands, and the geometry around Al is distorted from tetrahedral as shown in Fig. 2a and b.

In both dimers, the bridging oxygen atom-aluminum atom distances are roughly equivalent for the two Al centers with Al–O(1) distance of 1.862(3) Å for **3a** and 1.844(2) Å for **3b** and with Al–O(1)′ distances of 1.874(3) Å for **3a** and 1.845(2) Å for **3b**. The Al–O bond distances for the terminal-bound phenoxide moieties are Al–O(2) 1.700(2) Å for **3a** and 1.674(2) Å for **3b**, respectively. The recorded distances and angles are well within the normal range previously reported for dimeric aluminum bisphenoxides [22].

3. Catalytic screening of the aluminum bisphenoxides in the copolymerisation of cyclohexene oxide (CHO) with carbon dioxide

First catalytic screening tests showed that these aluminum compounds are able to catalyze a copolymerization of CHO with CO_2. The different tests were performed with a substrate-to-catalyst molar ratio of 1000:1 and a CO_2 to substrate molar ratio of ca. 2:1, the copolymerization results are summarized in Table 4. The tests were performed above 80 °C and 90 bar CO_2;

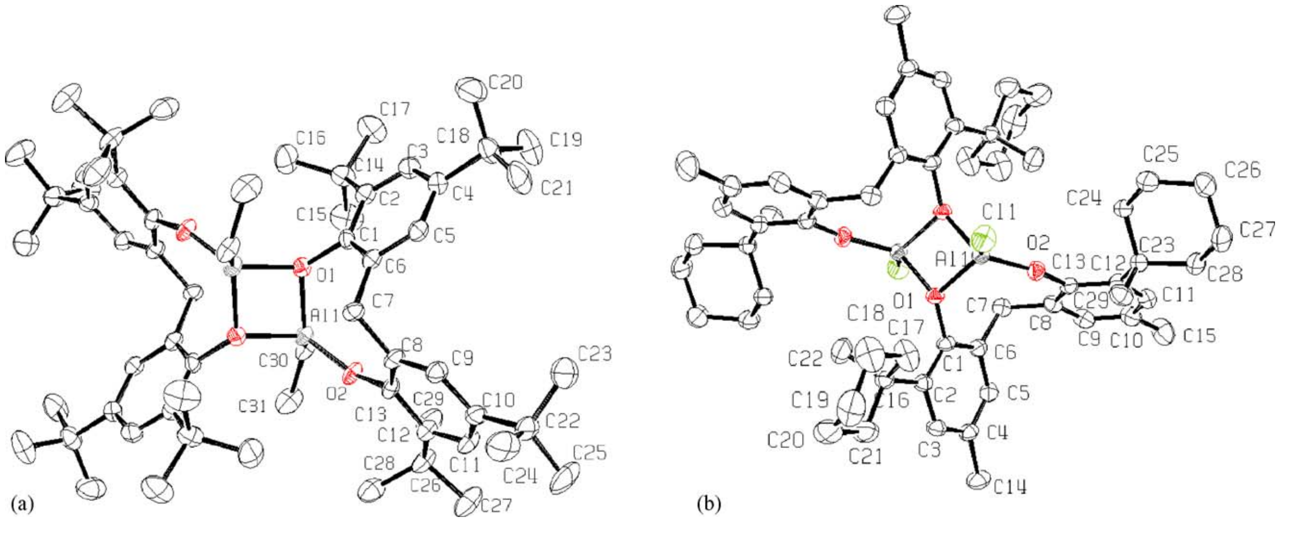


Fig. 2. ORTEP drawings (50% probability) of the dimeric compounds (**3a**) $[Al(C_2H_5)(mdtbp)]_2$ and (**3b**) $[Al(Cl)(mmcp)]_2$.

Table 2
Experimental data for the crystal structures of monomeric (**1a** and **2a**) and dimeric (**3a** and **3b**) aluminum bisphenoxides compounds

	1a [(THF)Al(C_2H_5)(mdtbp)]. 1.6 THF	**2a** [(THF)Al(C_2H_5)(mmcp)]	**3a** [Al(C_2H_5)(mdtbp)]$_z$	**3b** [Al(Cl)(mmcp)]$_2$
Crystal data				
Empirical formula	$C_{35}H_{55}AlO_3$. 1.6 THF	$C_{35}H_{51}AlO_3$	$C_{38}H_{55}AlO_2$	$C_{36}H_{46}AlClO_2$
Molecular mass	666.14	546.74	570.80	573.16
Crystal color	Colorless	Colorless	Colorless	Colorless
Crystal size (mm)	1.0 × 0.9 × 0.7	0.25 × 0.05 × 0.05	0.3 × 0.35 × 0.1	0.3 × 0.3 × 0.1
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*2(1)/*c* (No. 14)	*P*2(1)/*c* (No. 14)	*P*-1 (No. 2)	*P*2(1)/*c* (No. 14)
a (Å)	13.5017(13)	10.5142(9)	10.0281(12)	10.0047(8)
b (Å)	19.2244(18)	15.6338(13)	12.3366(15)	10.6334(9)
c (Å)	17.2289(17)	19.4057(16)	14.2885(17)	30.108(3)
α (°)	90	90	89.875(2)	90
β (°)	107.8710(10)	96.7870(10)	88.721(2)	92.0840(10)
γ (°)	90	90	87.225(2)	90
V (Å^3)	4256.2(7)	3167.5(5)	1765.2(4)	3200.8(5)
Z	4	4	2	4
D calc. (g cm^{-3})	1.040	1.146	1.074	1.189
μ (mm^{-1})	0.084	0.096	0.087	0.177
F (0 0 0)	1464	1192	624	1232
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	200(2)	200(2)
θ-range (°)	1.58–28.34	1.68–28.34	1.43–28.31	1.35–28.36
Index ranges	$-18 \le h \le 17$	$-14 \le h \le 13$	$-13 \le h \le 13$	$-13 \le h \le 13$
	$-24 \le k \le 25$	$-20 \le k \le 20$	$-16 \le k \le 14$	$-14 \le k \le 14$
	$-22 \le l \le 22$	$-25 \le l \le 25$	$-17 \le l \le 19$	$-39 \le l \le 40$
Solution and refinement				
Number of reflections measured	49354	38034	13359	38502
Number of independent reflections	10385	7760	8283	7965
GOF	1.042	1.011	0.945	1.034
R [I. 2θ(I)]	0.0842	0.0682	0.0805	0.0735
$wR2$[I.2θ(I)]	0.2401	0.1911	0.1802	0.1924
Largest e-max, e-min (eÅ^{-3})	0.961 and −0.464	0.654 and −0.364	0.532 and −0.317	0.916 and −0.648

Table 3
Comparison of selected bond distances (Å) and bond angles (°) for **1a**, **2a**, **3a** and **3b**

	1a	2a	3a	3b
Al–O1	1.7217(18)	1.713(2)	1.862(3)	1.844(2)
Al–O1′	–	–	1.874(3)	1.845(2)
Al–O2	1.7156(18)	1.720(2)	1.700(2)	1.674(2)
Al–O3	1.8850(19)	1.870(2)	–	–
Al–C7	3.228	3.261	3.326; 3.544	3.293; 3.625;
Al–Al#	–	–	2.870(2)	2.8218(17)
Al–Cl	–	–	–	2.0898(12)
Al–C30	1.950(3)	1.955(4)	1.938(4)	–
Cl–Al–O1			–	121.47(8)
Cl–Al–O2	–	–	–	106.68(8)
O1–Al–O2	115.76(9)	117.08(11)	112.62(12)	112.59(10)
O1–Al–O3	105.22(9)	103.17(11)	–	–
O2–Al–O3	100.50(9)	101.11(12)	–	–
C30–Al–O1	112.33(11)	112.77(16)	121.69(15)	–
C30–Al–O2	114.92(11)	115.83(17)	108.02(15)	–
C30–Al–O3	106.36(11)	104.21(19)	–	–
O1#–Al–O2	–	–	118.26(12)	125.43(11)
O1#–Al–O1	–	–	79.61(12)	80.20(9)
C30–Al–O1#	–	–	114.90(15)	–
Cl–Al–O1#	–	–	–	109.84(7)

such temperature- and pressure domains are usually necessary to get a CO_2-enriched epoxide phase and guarantee the experimental conditions for a co-polymerization with negligible amounts of the by-product cyclic carbonate [24]. Both monomeric aluminum bisphenoxides displaying aluminum–chlorine (**1b**–**2b**) or aluminum–carbon (**1a**–**2a**) bonds initiated the co-polymerizations which likely lead to growing (Al–OR$_{polymer}$) chains with terminal C–Cl bonds, respectively C–C_2H_5 moieties. Generally, the catalytic activity is better than the activity reported for monodentate aluminum alkoxides [12]. The dimeric bisphenoxide complexes **3a** and **3b** are bridged in the solid state and in apolar, non-coordinating media. The bridges are cleaved upon addition of a donor ligand like, e.g. THF or CHO and the active species of the catalysis are then comparable to the species obtained with monomeric bisphenoxides **1a**–**b** and **2a**–**b**. The formation of the actual active catalytic species, an aluminum-alkoxide (Al–O$_{epoxide}$–T, where T stands for chlorine or ethyl, see Scheme 1) resulting from the first insertion of an epoxide molecule into the Al–Cl or Al–C bond implies a latency time before a copolymerisation reaction actually starts. In this preliminary study we could not notice a markedly different reactivity between Al–Cl or Al–C bonds.

The activation and insertion of carbon dioxide into an epoxidic C–O bond with formation of a carbonate is easily

Table 4
Copolymerization of cyclohexene oxide and carbon dioxide (catalyst to substrate molar ratio: 1:1000, reaction time 18 h)

Catalyst	Polymer yield (%)	CO_3 content (%)[a]	M_n (g/mol)[b]	M_w/M_n	TON[c]	P (bar)[d]	T (°C)[d]
1a	39.3	6.8	16156	1.58	468	90	117
1b	51.7	17.4	9951	1.85	719	82	99
2a	55.5	20.5	7068	1.85	668	105	87
2b	64.0	21.4	8332	2.30	855	86	93
3a	51.7	16.9	5647	2.65	359	88	95
3b	63.1	17.0	4884	2.33	478	75	95
[*N*,*N*′-Bis(3-nitro, 5-*tert*-butylsalicylidene)ethylenediimine] aluminum chloride[e]	–	74	25400[f]	–	194[d]	34	80
$ClAl(O–Cy)_2$[g]	–	12; 7.3	4531[h]	2.6	–	80	60
$(C_8H_{17}OCOCH{=}CHOCO)AlCl(O–Cy)$[g]	–	11,7; 7.9	3274[h]	4.1	–	80	62

[a] Evaluated via ^1H NMR.
[b] Evaluated via gel permeation chromatography.
[c] Mol of epoxide consumed per mol of catalyst.
[d] After 8 h reaction time.
[e] Ref. [14].
[f] Calculated.
[g] Ref. [12], Al/CHO: 1/100.
[h] After 24 h reaction time.

assessed via IR spectroscopy which moreover allows us to distinguish between polycarbonate ($\nu_{C=O}$ at 1740 cm^{-1}) and the different monomeric cyclic carbonates (*trans*-cyclohexyl carbonate at 1823 cm^{-1} or *cis*-cyclohexyl carbonate at 1806 cm^{-1} [25]). In our case the IR-spectra of the reaction mixture show, under the chosen experimental conditions, no formation of cyclic carbonate. ^{13}C NMR spectroscopy of the final products confirmed the CO_2 incorporation into the polymer and allowed an estimation of the tacticity of the copolymer. With cyclohexene oxide being a *meso* compound, its controlled opening can yield either isotactic or syndiotactic polymers. Based on the formation of pure poly(cyclohexene carbonate), the research groups of Nozaki [26] and Coates [27] proposed a new interpretation of the ^{13}C NMR spectra of poly(cyclohexene carbonates) and could precisely attributed the different ^{13}C-signals to different carbonate fragments' geometries and so easily access the tacticity of a given copolymer: the ^{13}C NMR signal for the carbonate carbons of isotactic fragments is observed at 153.7 ppm whereas the signals for carbonate carbons of syndiotactic fragments are observed at higher field between 153.3 and 153.1 ppm. In our case, the isolated polyether-carbonates display one signal at ca. 155 ppm in benzene-d_6 (resp. 154 ppm in chloroform-d_1) in the carbonate region of the spectrum (Fig. 3). This broad signal results most likely from the superposition of different carbonate signals coming from isolated carbonate fragments displaying different tacticities separated by pure polyether regions as it can be expected for a statistical copolymer (Scheme 3).

The quantification of the CO_2 insertion in the final copolymers (i.e. the ether- to carbonate-linkage ratio) can be readily performed via ^1H NMR spectroscopy and directly taken from the integration ratio between methine protons of the polycarbonates units (4.7 ppm) and the polyether units (3.4 ppm); the rest of the aliphatic backbone produces broad signals in the range of 1.2–2.2 ppm. The isolated copolymers generally contain more ether linkages than carbonate linkages (approx. in a 3:1 ratio i.e. 21% carbonate in the copolymer, in the best case) due to the generally higher Lewis acidity of aluminum phenoxides compared to comparable monodendate bulky zinc phenoxides [28]. The aluminum-based catalytic systems used in such copolymerisation reactions habitually have to cope with a selectivity problem due to the more favorable ring opening polymerization of the epoxide (Scheme 3).

In order to optimize the catalytic system toward a pure copolymerisation, we ran a couple of experiments at higher CO_2-pressure (up to 130 bar) without significant improvement of the CO_2-incoporation into the copolymer. Poor solubility of these aluminum bisphenoxide catalysts in a CO_2-rich phase or in supercritical CO_2 might be the cause for this lack of reactivity and has to be assessed more in detail.

Surprisingly mdtbp-based compounds **1a** and **1b** displayed a significantly different reactivity compared to the mmcp-based monomeric bisphenoxides **2a** and **2b**, both of which showed a similar reactivity towards a copolymerisation (CO_3 content of ca. 20% and M_n between 7000 and 8000 g/mol). The reason why **1a** favors the formation of polyethers (carbonate content of ca. 7% and M_n around 15,000 g/mol) whereas **1b** yields the usually obtained poly(ether-carbonate) remains unclear. This low CO_2-insertion into the copolymer despite a similar steric demand and electron donating abilities of the tertiobutyl and 1-Me-cyclohexyl substituents is under further study.

The molecular weights of the isolated copolymers (M_n and M_w) and the related polydispersities, were obtained via gel permeation chromatography (see Section 5 for more details). The average molecular weights of the isolated copolymers are reasonably high, ranging from ca. 7000 to 16,000 g/mol for the monomeric compounds and around 5000 g/mol for the dimeric catalysts. The molecular weight distributions are generally quite broad, ranging from 1.85 to 2.65, which suggest that the

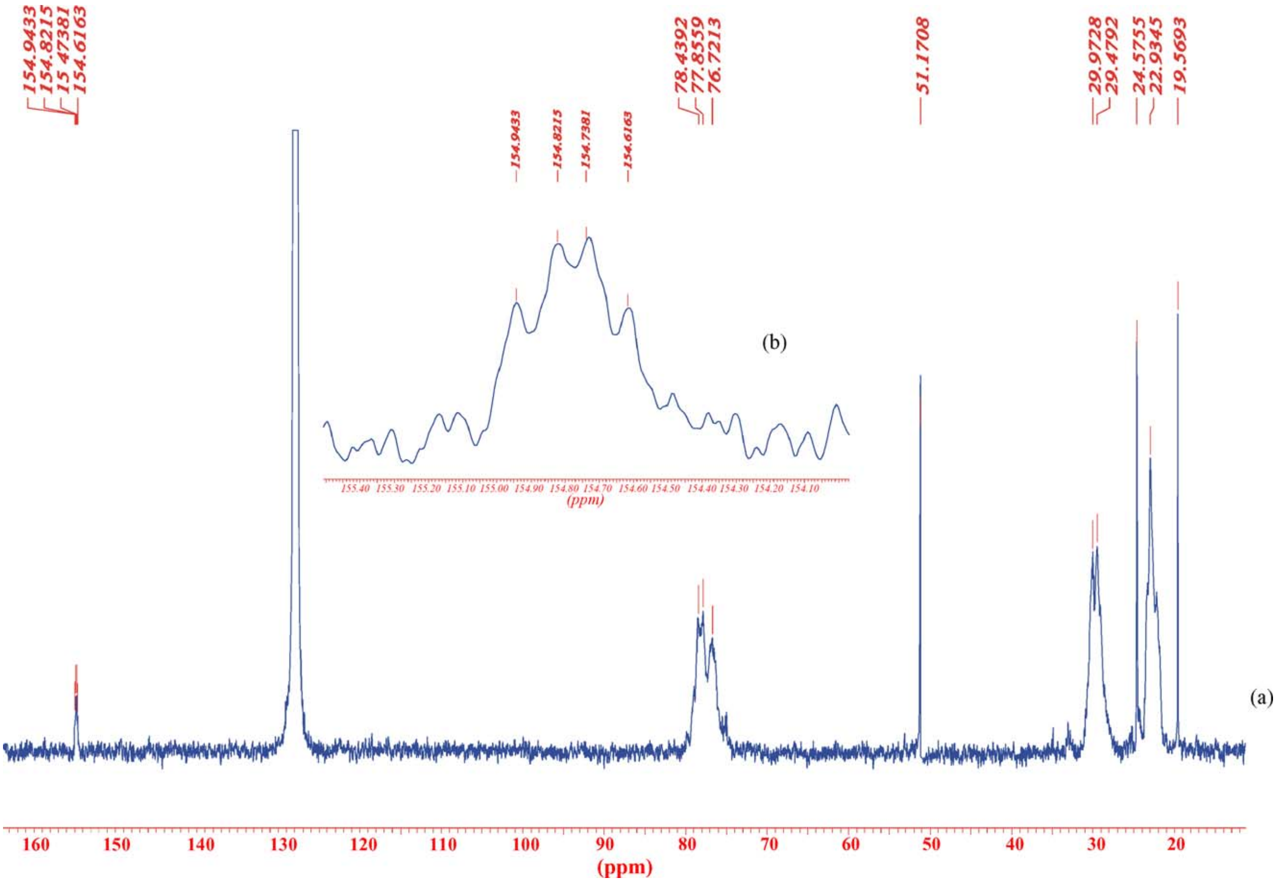
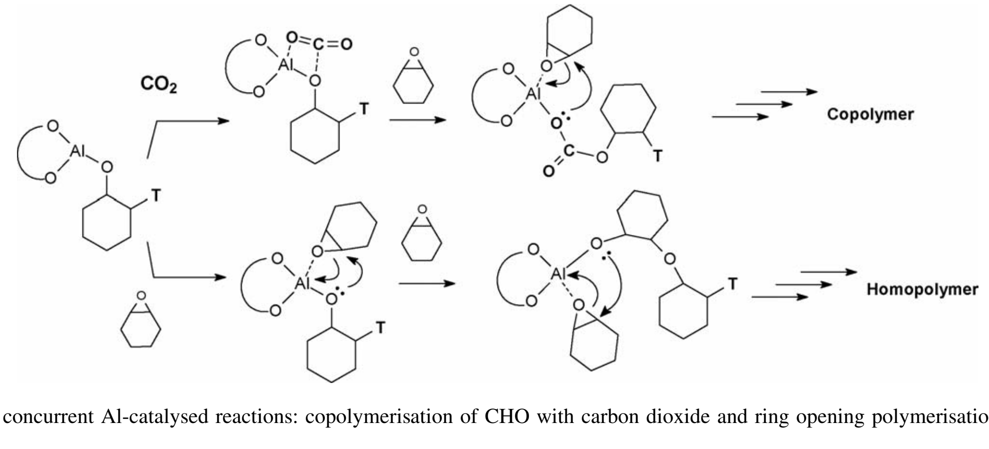


Fig. 3. (a) ^{13}C NMR-spectrum (solution, benzene-d_6) of a poly(ether-carbonate) obtained from the copolymerisation of CHO with CO_2. The three sharp signals at 51.17, 24,57 and 19.57 ppm result from remaining cyclohexene oxide (b) enlargement of the carbonate region of the ^{13}C-spectrum.

''single-site character'' of the catalysis involving the aluminum bisphenoxides is not as high as anticipated. Although only one polymer chain can grow on the active aluminum center, secondary reactions leading to a termination or a transfer of the polymer chain instead of its elongation seem to be responsible for the lack of selectivity of the system. This is probably due to the environment at the aluminum atom found in these bidendate bisphenoxides: despite the use of steric demanding substituents there is still enough space around the active center to allow a binuclear side-reaction involving another aluminum-bisphenoxide species to take place. In comparison, the literature known bulky tetradendate salen derivatives of group 13 [14,23] all display a distorted square pyramidal geometry typical of salen complexes [7], with a significantly narrower docking site for the epoxide or CO_2 molecule. The presence of steric demanding groups in these compounds, without the help of a supplementary co-catalyst, hinders a potential binuclear side-reaction.

Considering the numerous studies on different catalytic systems involving the use of electron-donating Lewis bases as co-catalysts to improve the CO_2-incorporation into the



Scheme 3. Two concurrent Al-catalysed reactions: copolymerisation of CHO with carbon dioxide and ring opening polymerisation of the epoxide.

copolymer [6,7], it was interesting to assess the influence of some co-catalysts together with one representative aluminum bisphenoxide, compound **1b**, on the course of the copolymerisation. These co-catalysts were neutral Lewis bases like 1-methyl-imidazole and triphenyl phosphine or ionic ammonium derivatives like tetraethylammonium *p*-toluenesulfonate, tetrabutylammonium bromide and bis(triphenyl phosphoranylidene) ammonium chloride. The purpose of using a Lewis base is both: (i) to facilitate the formation of the first active alkoxo-species by labilizing the aluminum-nucleophile bond in the catalyst (Al–C or Al–Cl) and (ii) to promote the elongation of the copolymer chain via an insertion of a monomer into the active $A–O_{polymer}$ bond. The experiments involving phosphine or amine as co-catalysts proved to be unsuccessful, producing no polycarbonates and only traces of cyclic carbonate. The ammonium salts delivered only small amounts of cyclic carbonate. Interestingly the reaction carried out with bis(triphenyl phosphoranylidene) ammonium chloride as a co-catalyst produced significantly more cyclic carbonate than the other ammonium salts and no copolymers (up to 50% yield, via ^1H NMR). Altogether the reactivity of the ammonium salts follows the trend $[Et_4N\ MeC_6H_4SO_3] < [n\text{-}Bu_4NBr] \ll [PPNCl]$. Such a low cooperation between catalyst and co-catalyst is most probably due to the tetrahedral coordination geometries around the aluminum atom. Considering the aluminum salen derivatives recently reported by Darensbourg and Billodeaux [14] which display a good catalytic activity and allow a further fine tuning by using a co-catalyst, it can be seen that the typical square pyramidal geometry found in these salen complexes plays a predominant role. This constrained geometry allows a co-catalyst to coordinate in *trans* position of either the starting nucleophile (Cl or Et) or the growing polymer chain and thus to efficiently activate the Al-nucleophile bond. Such a favorable interaction cannot be found in the tetrahedral coordination geometry of the aluminum bisphenoxides.

4. Conclusion

In conclusion, we have synthesized several tetracoordinated aluminum bisphenoxides with two different steric demanding substituents, 1-Me-cyclohexyl and *tert*-butyl, and structurally characterized four new compounds via X-ray diffraction. We could furthermore demonstrate that these compounds showed interesting catalytic activities in the copolymerisation of cyclohexene oxide with CO_2. These aluminum complexes were also tested in conjunction with a series of anionic and neutral co-catalysts to optimize the copolymerization of cyclohexene oxide with CO_2. Our preliminary studies have shown that the use of co-catalysts, in opposition to literature known systems, does not improve the CO_2-incorporation into the polymer and that, in one specific case, the monomeric *cis*-cyclohexylene carbonate is produced in significant quantities. Despite displaying a general lower activity in the copolymerization of carbon dioxide with CHO than the salen-based aluminum systems, these aluminum bisphenoxides through the versatility of the 2-2′-bisphenoxide “tool-kit” are noteworthy candidates for new copolymerization catalysts. More work is actually in progress to optimize the ligand system and the resulting aluminum alkoxides as well as to spectroscopically characterize the nature of some intermediates involved in the catalysis.

5. Experimental

All manipulations were carried out under a dry argon atmosphere. Commercially available triethyl aluminum, diethyl aluminum chloride (Aldrich) and 2,2′-methylene-bis(4-methyl-2-(1-methylcyclohexyl)phenol) were reagent grade and used without further purification. 2,2′-Methylene-bis(4,6-di-*t*-butylphenol) was synthesized according to the literature from 2,4-di-*t*-butyl phenol and paraformaldehyde with sulfuric acid as catalyst [20]. Cyclohexene oxide (Aldrich) was distilled under vacuum over CaH_2. CH_2Cl_2, THF, *n*-hexane and MeOH were dried by standard methods [29] and stored under argon. Carbon dioxide (Messer Griesheim, purity 99.9990%) was used without further purification. NMR deuteriated solvents (Chemotrade) were degassed, dried over Molecular sieves Linde 4 Å and stored under argon.

5.1. Analyses

The NMR spectra of the catalysts and copolymer solutions in benzene-d_6, chloroform-d_1 or toluene-d_8 were recorded with a Varian Inova 400 spectrometer (^1H 399.81 MHz, ^{13}C: 100.54 MHz). TMS was used as internal standard (^{13}C, ^1H) with different deuteriated solvents. The chemical shifts δ (in ppm) are given relative to the residual signal of the solvent. Infrared spectra (KBr pellets and thin films between KBr plates) were recorded on a BIORAD 175C FT-IR spectrometer in the range of 4000–400 cm^{-1}. Molecular weights and MWD of the polymers were measured using a Merck gel permeation chromatograph (Lichograph Gradient pump L-6200 with thermostat, LaChrom RI detector L-7490), equipped with a pre-column and two different columns (PSS SDV 5 m 1000 and 100 Å). THF was used as eluent, and calibration was performed using polystyrene standards. The X-ray analyses were performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10–20 s per frame, thus collecting a full sphere of data using an ω-scan technique with $\Delta\omega$ ranging from 0.3° to 0.45°. The data were corrected for Lorentz and polarisation effects. An experimental absorption corrections has been performed [30]. The structures were solved with direct methods and refined against F2 [31].

For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used [32]. Crystallographic data of the structures have been deposited at the Cambridge Crystallographic Database Centre, supplementary publications Nos. CCDC 289825–289828. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033, email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

5.2. Synthesis and characterisation

5.2.1. General procedure for the synthesis of the aluminum complexes

To an ice-cold solution (ice bath, 0–4 °C) of the ligand in an anhydrous solvent (THF in the case of monomers and hexane for the dimers), a solution (0–4 °C) of the aluminum starting compound ($\mathrm{Et_3Al}$ or $\mathrm{Et_2AlCl}$) in the similar solvent was slowly added. The mixture was stirred for 4 h, allowed to warm up to RT and then dried in vacuo. The solid was washed twice with a small amount of the solvent used, concentrated and stored several days at −25 °C to yield colorless crystals.

*5.2.1.1. (Tetrahydrofuran)-ethyl-{2,2′-methylenebis(4,6-di-t-butylphenato)}aluminium(III) (**1a**).* 2,2′-Methylenebis(4,6-di-*t*-butylphenol) (2.81 g, 6.64 mmol) in 100 cm^3 of anhydrous THF and a 2.0 M solution of $\mathrm{Et_3Al}$ (8.627 mmol) in THF. Yield of isolated crystals: 3.02 g, 83%.

IR (nujol, cm^{-3}): 2932 (s), 2860 (s), 1457 (s), 1362 (s), 1293 (s), 1240 (m), 1001 (m), 920 (m), 856 (s), 770 (m), 668 (m), 650 (m), 599 (m); ^{1}H NMR: δ (ppm) = 0.08 (q, 2 H, $\mathrm{AlC\mathit{H}_2CH_3}$), 1.07 (t, 3 H, $\mathrm{AlCH_2C\mathit{H}_3}$), 1.22 (s, 18 H, $\mathrm{C_6{-}C(C\mathit{H}_3)_3}$), 1.31 (s, 18 H, $\mathrm{C_4{-}C(C\mathit{H}_3)_3}$), 2.01 ($\mathrm{O(CH_2C\mathit{H}_2{-})}$ in THF), 3.39 (d, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 13.55 Hz, $\mathrm{H_{EXO}}$), 3.88 (d, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 13.70 Hz, $\mathrm{H_{ENDO}}$), 4.18 ($\mathrm{O(C\mathit{H}_2CH_2{-})}$ in THF), 7.05 (s, 2 H, $\mathrm{C_3{-}H}$), 7.20 (s, 2 H, $\mathrm{C_5{-}H}$); ^{13}C NMR: δ (ppm) = 1.1 ($\mathrm{Al\mathit{C}H_2CH_3}$), 8.8 ($\mathrm{AlCH_2\mathit{C}H_3}$), 25.5 ($\mathrm{O(CH_2\mathit{C}H_2{-})}$ in THF), 30.0 ($\mathrm{C_6{-}C(\mathit{C}H_3)_3}$), 31.8 ($\mathrm{C_4{-}C(\mathit{C}H_3)_3}$), 33.2 ($\mathrm{{-}\mathit{C}H_2{-}}$), 34.2 ($\mathrm{C_6{-}\mathit{C}(CH_3)_3}$), 35.3 ($\mathrm{C_4{-}\mathit{C}(CH_3)_3}$), 70.13 ($\mathrm{O(\mathit{C}H_2CH_2{-})}$), 122.0 ($\mathrm{\mathit{C}_3{-}H}$), 125.1 ($\mathrm{\mathit{C}_5{-}H}$), 129.9 ($\mathrm{\mathit{C}_2{-}CH_2{-}bridge}$), 137.4 ($\mathrm{\mathit{C}_6{-}C(CH_3)_3}$), 139.9 ($\mathrm{\mathit{C}_4{-}C(CH_3)_3}$), 152.9 ($\mathrm{\mathit{C}_1{-}O{-}Al}$); Anal. Calcd for $\mathrm{C_{35}H_{55}O_3Al}$: C, 76.31; H, 10.07; Found: C, 76.26; H, 10.27.

*5.2.1.2. (Tetrahydrofuran)-chloro-{2,2′-methylenebis(4,6-di-t-butylphenato)}aluminum (III) (**1b**).* **1b** was already described in the literature, chemical shifts found in NMR spectroscopy (^{1}H, ^{13}C), IR data and elementary analysis agree with the data reported by Lin [22b]. 2,2′-Methylenebis(4,6-di-*t*-butylphenol) (3.55 g, 8.37 mmol) in 100 cm^3 of anhydrous THF reacted with a 2.0 M solution of $\mathrm{Et_2AlCl}$ (8.79 mmol) Yield of isolated crystals: 3.68 g, 78.9%.

*5.2.1.3. (Tetrahydrofuran)-ethyl-{2,2′-methylenebis(4-methyl-2-(1-methylcyclohexyl) phenato)} aluminium (III) (**2a**).* 2,2′-Methylenebis(4-methyl-2-(1-methylcyclohexyl)phenol) (0.981 g; 2.34 mmol) in 50 cm^3 of anhydrous THF reacted with a solution of $\mathrm{Et_3Al}$ (0.294 g, 2.57 mmol) in THF. Yield of isolated crystals: 1.01 g, 79%.

IR (nujol, cm^{-3}): 2940 (s), 2850 (s), 1459 (s), 1376 (m), 1286 (s), 1173 (m), 1039 (m), 1001 (s), (m), 855 (s), 651 (s); ^{1}H NMR: δ (ppm) = 0.05 (q, 2 H, $\mathrm{AlC\mathit{H}_2CH_3}$), 1.04 (t, 3 H, $\mathrm{AlCH_2C\mathit{H}_3}$), 1.28 (s, 6 H, $\mathrm{{-}C\mathit{H}_3}$ in Cy), 1.42 (b, 4 H, $\mathrm{O(CH_2C\mathit{H}_2{-}}$ of THF), 1.64 (br, ax. H in Cy), 1.88 (br, eq. H in Cy), 2.17 (s, 6 H, $\mathrm{C_4{-}C\mathit{H}_3}$), 3.31 (s, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, J = 13.60 Hz $\mathrm{H_{EXO}}$), 3.83 (s, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, J = 13.60 Hz, $\mathrm{H_{ENDO}}$), 4.1 (b, 4 H, $\mathrm{O(C\mathit{H}_2CH_2{-}}$ of THF)), 6.82 (d, 2 H, $\mathrm{C_5{-}\mathit{H}}$), 6.97 (d, 2 H, $\mathrm{C_3{-}\mathit{H}}$). ^{13}C NMR: δ (ppm) = 7.6 ($\mathrm{Al\mathit{C}H_2CH_3}$), 16.6 ($\mathrm{AlCH_2\mathit{C}H_3}$), 19.9 ($\mathrm{C_4{-}\mathit{C}H_3}$), 21.8, 21.9, 23.9, 24.5 (carbons 3, 4, 5 and Me in Cy, THF partly overlapping); 25.8 ($\mathrm{O(CH_2\mathit{C}H_2{-})}$), 32.4 ($\mathrm{C_2{-}\mathit{C}H_2{-}}$), 35.6, 36.1 (carbons 2 and 6 in Cy), 69.5 ($\mathrm{O(\mathit{C}H_2CH_2{-})}$), 125.4 ($\mathrm{\mathit{C}_5{-}H}$); 127.6 ($\mathrm{\mathit{C}_3{-}H}$); 128.0 ($\mathrm{\mathit{C}_4{-}CH_3}$); 129.6 ($\mathrm{\mathit{C}_2{-}CH_2{-}}$); 136.5 ($\mathrm{\mathit{C}_6}$); 152.1 ($\mathrm{\mathit{C}_1{-}O{-}Al}$). Anal. Calcd for $\mathrm{C_{35}H_{51}O_3Al}$: C, 78.88; H, 9.40. Found: C, 78.92; H, 9.32.

*5.2.1.4. (Tetrahydrofuran)-chloro-{2,2′-methylenebis(4-methyl-2-(1-methylcyclohexyl) phenato)} aluminium(III) (**2b**).* 2,2′-Methylenebis(4-methyl-2-(1-methylcyclohexyl)-phenol) (0.724 g, 1.72 mmol) in 50 cm^3 of anhydrous THF reacted with a solution of $\mathrm{Et_2AlCl}$ (0.270 g, 2.24 mmol) in 2 cm^3 of THF. Yield of isolated crystals: 0.79 g, 83%.

IR (nujol, cm^{-3}): 2930 (s), 2857 (s), 1458 (s), 1372 (m), 1301 (m), 1291 (s), 1176 (sm), 999 (sm), 931 (m), 854 (m), 672 (sm); ^{1}H NMR: δ (ppm) = 1.21 (s, 6 H, $\mathrm{{-}C\mathit{H}_3}$ in Cy), 1.42 (b, 4 H, $\mathrm{O(C\mathit{H}_2CH_2{-}}$ of THF)); 1.55–1.67 (br, ax. H in Cy), 1.99 (br, eq. H in Cy), 2.19 (s, 6 H, $\mathrm{C_4{-}C\mathit{H}_3}$), 3.42 (d, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 14.25 Hz, $\mathrm{H_{EXO}}$), 3.80 (d, 1 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 14.25 Hz, $\mathrm{H_{ENDO}}$), 4.07 (b, 4 H, $\mathrm{O(CH_2C\mathit{H}_2{-}}$ of THF)), 6.84 (d, 2 H, $\mathrm{C_5{-}\mathit{H}}$), 6.974 (d, 2 H, $\mathrm{C_3{-}\mathit{H}}$); ^{13}C NMR: δ (ppm) = 21.8 ($\mathrm{C_4{-}\mathit{C}H_3}$); 21.9, 22.0 (carbons 3 and 5 in Cy); 24.4 (Me in 1-Me–Cy), 25.6 ($\mathrm{O(CH_2\mathit{C}H_2{-})_2}$); 25.9 (carbons 4 in Cy); 31.6 (carbons 1 in Cy); 32.2 ($\mathrm{C_2{-}\mathit{C}H_2{-}}$); 36.7, 37.2 (carbons 2 and 6 in Cy); 66.1 ($\mathrm{O(\mathit{C}H_2CH_2{-})_2}$); 125.9 ($\mathrm{\mathit{C}_4{-}CH_3}$); 127.6 ($\mathrm{\mathit{C}_4{-}CH_3}$); 128.6 ($\mathrm{\mathit{C}_3{-}H}$); 129.0 ($\mathrm{\mathit{C}_2{-}CH_2{-}}$); 136.5 ($\mathrm{\mathit{C}_6}$); 150.7 ($\mathrm{C_{1,1'}{-}O{-}Al}$); Anal. Calcd for $\mathrm{C_{33}H_{46}O_3AlCl}$: C,71.65; H, 6.32. Found: C, 71.84; H, 6.40.

*5.2.1.5. Bis[ethyl-{2,2′-methylenebis(4,6-di-t-butylphenato)}aluminium(III)] (**3a**).* 2,2′-Methylenebis(4,6-di-*t*-butylphenol 2.583 g, 6.10 mmol) in 40 cm^3 of anhydrous hexane was reacted with a solution of $\mathrm{Et_3Al}$ (0.834 g, 7.31 mmol) in hexane. Yield of isolated crystals: 2.47 g, 85 %.

IR (nujol, cm^{-1}): 2926 (s), 2853 (s), 1462 (s), 1379 (m), 1310 (m), 1293 (m), 1279 (m), 240 (m), 1163 (m), 1099 (m), 938 (m), 880 (m), 821 (m), 774 (m), 742 (m), 660 (m), 632 (m); ^{1}H NMR: δ (ppm) = 0.11 and 0.15 (m, 2 H, $\mathrm{AlC\mathit{H}_2CH_3}$), 0.51 and 0.65 (t, 3 H, $\mathrm{AlCH_2C\mathit{H}_3}$, J = 8.0 Hz), 1.24, 1.28 (s, 2× 18 H, $\mathrm{C_{6,6'}{-}C(C\mathit{H}_3)_3}$), 1.32, 1.38 (s, 2× 18 H, $\mathrm{_{4,4'}{-}C(C\mathit{H}_3)_3}$), 3.48 (d, 2 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 13.64 Hz, $\mathrm{H_{EXO}}$), 4.39 (d, 2 H, $\mathrm{{-}C\mathit{H}_2{-}}$, $J_{\mathrm{H-H}}$ = 13.64 Hz, $\mathrm{H_{ENDO}}$), 7.19 (s, 4 H, $\mathrm{C_{3,3'}{-}\mathit{H}}$), 7.05 (s, 4 H, $\mathrm{C_{5,5'}{-}\mathit{H}}$); ^{13}C NMR: δ (ppm) = 7.4 ($\mathrm{Al\mathit{C}H_2CH_3}$), 21.6 ($\mathrm{AlCH_2\mathit{C}H_3}$), 30.2 ($\mathrm{C_6{-}C(\mathit{C}H_3)_3}$), 31.4 ($\mathrm{C_{6'}{-}C(\mathit{C}H_3)_3}$), 31.8 ($\mathrm{C_4{-}C(\mathit{C}H_3)_3}$), 32.1 ($\mathrm{C_{4'}{-}C(\mathit{C}H_3)_3}$), 34.2 ($\mathrm{C_6{-}\mathit{C}(CH_3)_3}$), 34.5 ($\mathrm{C_{6'}{-}\mathit{C}(CH_3)_3}$), 35.0 ($\mathrm{C_4{-}\mathit{C}(CH_3)_3}$), 35.5 ($\mathrm{C_{4'}{-}\mathit{C}(CH_3)_3}$), 36.1 ($\mathrm{{-}CH_2{-}}$), 123.7 ($\mathrm{\mathit{C}_3{-}H}$), 124.1 ($\mathrm{\mathit{C}_{3'}{-}H}$), 126.5 ($\mathrm{\mathit{C}_5{-}H}$), 130.4 ($\mathrm{\mathit{C}_{5'}{-}H}$), 133.1 ($\mathrm{\mathit{C}_{2,2'}}$), 140.2 ($\mathrm{\mathit{C}_6}$, $\mathrm{{-}C(CH_3)_3}$), 140.8 ($\mathrm{\mathit{C}_{6'}{-}C(CH_3)_3}$), 144.7 ($\mathrm{\mathit{C}_4{-}C(CH_3)_3}$), 147.4 ($\mathrm{\mathit{C}_{4'}{-}C(CH_3)_3}$), 151.2 ($\mathrm{\mathit{C}_{1,1'}{-}O{-}Al}$); Anal. Calcd for $\mathrm{[C_{31}H_{47}O_2Al]_2}$: C, 77.78; H, 9.90: Found: C, 75.26; H, 10.15.

*5.2.1.6. Bis[chloro-{2,2′-methylenebis(4-methyl-2-(1-methylcyclohexyl)phenato)}aluminium(III)] (**3b**).* The synthesis of **3b** was described elsewhere without X-ray characterization; the chemical shifts found in NMR spectroscopy (^{1}H, ^{13}C), the IR and elementary analysis data agree with these reported by Braune [33]. 2,2′-Methylenebis(4-methyl-2-(1-methylcyclohexyl)phenol) (0.70 g, 1.67 mmol) in 40 cm^3 of *n*-hexane was reacted with a solution of Et_2AlCl (0.26 g, 2.71 mmol) in 4 cm^3 of *n*-hexane, yield of pale yellow crystals: 0.63 g, 78.3%.

IR (nujol, cm^{-1}): 2926 (s), 2855 (s), 1486 (s), 1377 (m), 1302 (m), 1261 (m), 1190 (m), 1139 (m), 1097 (m), 982 (sm), 936 (m), 788 (m), 655 (m), 555 (m). ^1H NMR: δ (ppm) = 1.11, 1.19 (s, 2× 6 H, $–CH_3$ in Cy); 1.35 (br, ax. H in Cy); 1.69 (br, eq. H in Cy); 2.18, 2.26 (s, 2× 6 H, $C_{4,4'}–CH_3$), 3.55 (d, 2 H, $–CH_2–$, $J_{H–H}$ = 13.72 Hz, H_{EXO}); 4.40 (d, 2 H, $–CH_2–$, $J_{H–H}$ = 13.72 Hz, H_{ENDO}); 6.92, 6.94 (d, 4 H, $C_{5,5'}–H$), 6.99, 7.02 (d, 4 H, $C_{3,3'}–H$); ^{13}C NMR: δ (ppm) = 21.6 ($C_4–CH_3$); 23.6 (broad signal, carbons 3, 5 in Cy); 25.5 (Me in 1-Me–Cy); 26.6 (carbons 4 in Cy); 35.3 ($C_2–CH_2–$); 37.2, 37.8, 37.6 (carbons 2, 6, 1 in Cy); 127.3 ($C_{4,4'}–CH_3$); 127.8 ($C_{5,5'}–H$); 129.5 ($C_{3,3'}–H$); 129.8 ($C_2–CH_2–$); 137.1 (C_6); 149.0 (C_1–O–Al); Anal. Calcd for $C_{58}H_{76}O_4Al_2Cl_2$: C, 72.41; H, 7.96. Found: C, 72.49; H, 7.79.

5.2.2. *General procedure for autoclave experiments*

We developed a kind of ‘‘multi-reactor’’ system involving four high pressure reactors equipped with magnetically coupled stirring systems and electrical heating mantles (Magnetic stirrer + aluminum block + thermoelement). Temperature and pressure were monitored via a digital multimeter (HP 34970A) connected to a personal computer.

The copolymerization was typically conducted in 70 mL stainless steel (SS316) autoclaves equipped with standard Swagelock fittings and a separate loop made of stainless steel tubing which can be operated independently of the main reactor body. Because of the general moisture sensitivity of metal alkoxides and in order to get reproducible results, the reactors were heated at 100 °C and purged with argon prior to use. Cyclohexene oxide (20 mL) was transferred into the autoclave, the reactor was then pressurized with CO_2 (60 bar) for a few minutes under stirring and afterwards weighed, the procedure was repeated until the desired CHO/CO_2 molar fraction was reached (ca. 20 g CO_2). Owing to the high Lewis acidity of the aluminum bisphenoxides and their ability to also catalyze a homopolymerization of the epoxide, the catalyst was first dissolved under argon into ca. 1 mL of an unreactive solvent (toluene or CH_2Cl_2) and introduced into the separate loop. After establishing the communication with the epoxide/CO_2 mixture in the autoclave, the solution was allowed to diffuse into the reaction mixture through gravity. This procedure though time-consuming was necessary to get reproducible results and clearly evaluate the reactivity of the catalyst in pure copolymerization reactions. After the reaction time the autoclaves were cooled down to RT (water bath) and the carbon dioxide slowly (!) vented, under stirring, in a fume hood. The poly(ether-carbonates) are obtained as white foamy solids or syrupy liquids which can be easily dissolved in CH_2Cl_2. After opening the remaining solid/syrupy solution was dissolved in dichloromethane and the aluminum catalyst was then hydrolyzed with 10% HCl aqueous solution (50–100 mL) and separated from the unreacted cyclohexene oxide and copolymers via a separating funnel. The organic extract were washed two times with saturated $NaHCO_3$ and dried with $MgSO_4$. The short-chain copolymers were then separated from the long-chain ones via repeated dissolving in CH_2Cl_2 and consecutive precipitation in methanol. The long chain copolymers are eventually dried under vacuum at ca. 60 °C.

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References

[1] W. Kuran, Polymeric Material Encyclopedia, vol. 9, CRC Press, 1996.

[2] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 681.

[3] M.A. Pacheco, C.L. Marshall, Energy Fuels 11 (1997) 2.

[4] M. Acemoglu, Int. J. Pharm. 277 (2004) 133.

[5] X.H. Öi, Y.Z. Meng, G.Q. Chen, R.K.Y. Li, J. Appl. Polym. Sci. 94 (2004) 711.

[6] R. Sugimoto, S. Inoue, J. Polym. Sci.: Part A: Polym. Chem. 42 (2004) 5561.

[7] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Bilodeaux, Acc. Chem. Res. 37 (2004) 836.

[8] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618.

[9] M. Aresta, A. Dibenedetto, C. Pastore, Inorg. Chem. 42 (2003) 3256.

[10] V.C. Arunasalam, I. Baxter, J.A. Darr, S.R. Drake, M.B. Hursthouse, K.M. Abdul Malik, D.M.P. Mingos, Polyhedron 17 (1998) 641.

[11] D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, Organometallics 19 (2000) 4563.

[12] T. Sarbu, E.J. Beckman, Macromolecules 32 (1999) 6904.

[13] J.H. Jung, M. Ree, T. Chang, J. Polym. Sci.: Part A: Polym. Chem. 37 (1999) 3329.

[14] D.J. Darensbourg, D.R. Billodeaux, Inorg. Chem. 44 (2005) 1433.

[15] A. Kowalski, A. Duda, S. Penczek, Macromolecules 31 (1998) 2114.

[16] D. Tian, P. Dubois, R. Jerome, Macromolecules 30 (1997) 2575.

[17] T.A. Zevaco, A. Janssen, J. Sypien, E. Dinjus, Green Chem. 7 (2005) 659.

[18] P. Hormnirun, E.L. Marshall, V.C. Gibson, A.J.P. White, D. Williams, J. Am. Chem. Soc. 126 (2004) 2688.

[19] Y. Ohba, K. Ito, H. Maeda, H. Ebara, S. Tabaki, T. Nagasawa, Bull. Chem. Soc. Jpn. 71 (1998) 2393.

[20] P.A. Odorisio, S.D. Pastor, J.D. Spivack, R.K. Rodebaugh, D. Bini, Phosphorus Sulfur 19 (1984) 285.

[21] (a) I. Taden, H.-C. Kang, W. Massa, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. 3 (2000) 441;
(b) W. Braune, J. Okuda, Angew. Chem. Int. Ed. 42 (2003) 64.

[22] (a) Y.-C. Liu, B.-T. Ko, C.-C. Lin, Macromolecules 34 (2001) 6196;
(b) C.-H. Lin, L.-F. Yan, F.-C. Wang, Y.-L. Sun, C.-C. Lin, J. Organomet. Chem. 587 (1999) 151.

[23] M.H. Chisholm, D. Navarro-Llobet, W.J. Simonsick, Macromolecules 34 (2001) 8851.

[24] M.S. Super, R.M. Enick, E.J. Beckman, J. Chem. Eng. Data 42 (1997) 664.

[25] D.J. Darensbourg, J.L. Rodgers, R.M. Mackiewicz, A.L. Phelps, Catal. Today 98 (2004) 485.

[26] (a) K. Nozaki, K. Nakano, T. Hiyama, J. Am. Chem. Soc. 121 (1999) 11008;
(b) K. Nakano, K. Nozaki, T. Hiyama, Macromolecules 34 (2001) 6325.

[27] M. Cheng, N.A. Darling, E.B. Lobkovsky, G.W. Coates, Chem. Commun. 20 (2000) 2007.

[28] D.J. Darensbourg, M.W. Holtcamp, Macromolecules 28 (1995) 7577.

[29] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, 1988.

[30] SADABS, Siemens Area Detector Absorption Correction Programme, Siemens, 1997.

[31] (a) G.M. Sheldrick, SHELX-97, Universität Göttingen, 1997;
(b) L. Zsolnai, G. Huttner, XPMA, Universität Heidelberg, 1994
(c) L.J. Farrugia, ORTEP III for Windows (1.0.3.), J. Appl. Cryst. 30 (1997) 565.

[32] F.H. Allen, O. Kennard, Chem. Des. Automat. News 8 (1993) 31.

[33] W. Braune, Ph.D. Thesis, 2003. Johannes Gutenberg University, Mainz, Germany.