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Switchable, chiral aluminium catalysts for ring opening polymerisations†

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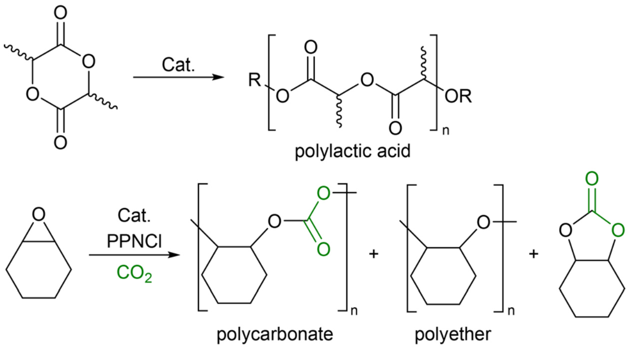
A switchable, solvent-free catalytic system was developed in which Al methyl aminebis(phenolate) catalysts selectively initiate the formation of a polyether from cyclohexene oxide under CO_2 atmosphere or the ring opening copolymerisation (ROCoP) of cyclohexene oxide and CO_2 through the addition of a PPNCl (bis(triphenylphosphine)iminium chloride) cocatalyst to form poly(cyclohexene carbonate).

Recent research has focused on the concept of switchable catalysis, defined in a recent themed collection of Royal Society of Chemistry papers as 'multiple, catalytically active species with different reactivity generated from a single precursor in the presence of external stimuli'.[1–4] By switching the activity of the catalyst, a novel polymer forms, including gradient co-polymers and periodic co-block polymers.[5] This approach works well with existing reactions such as ring opening polymerisation (ROP) and CO_2 co-polymerisations where the polymers are derived from sustainable materials but lack some of the favourable properties found with the more well established oil-derived polymers.[6] Thus, utilising a switchable catalyst, functional materials can be produced whilst also harnessing sustainable resources to aid the advancement of renewable materials and the circular economy.[7–9] Two classes of polymers which have gained significant interest are polyesters produced from cyclic esters, such as polylactic acid (PLA),[10–15] and polycarbonates using CO_2 as a co-monomer (Scheme 1).[16,17]

The incorporation of CO_2 into the alternating polymer chain with an epoxide is a method of utilising this environmentally deleterious gas, partially replacing carbon in the polymer backbone with a plentiful and freely available C_1 source.[18,19] While there are many catalysts capable of polymerising one or the other, there are relatively few reported to copolymerising both. Even more scarce are examples where the selectivity of the polymerisation can be influenced by the addition of an external compound.[1–4] Within a wide range of catalysts that have been used in the ROP of lactide,[20–23] Al complexes have been targeted as low cost, low toxicity, high abundance alternatives to the use of transition metal catalysts, with several groups investigating their activity for ROP.[24–26] Although the coordination of amine bis(phenolate) (ABP) ligands to Al has been reported, the effect of an ester-functionalised ligand has not.[27–30] Al complexes are also active towards the polymerisation of epoxides and the ROCoP of CO_2 and epoxides.[31–34] In this paper, we describe the synthesis (Scheme 2) and application of Al-ABP complexes in the polymerisation of *rac*-lactide, and the switchable ROP/ROCoP catalytic system of CHO (cyclohexene oxide) and CO_2.

The proligands[35,36] L^1H_2–L^4H_2 were reacted with trimethyl aluminium at 90 °C in toluene and, following purification, the corresponding Al complexes were produced in good yields (Scheme 2). Analysis of the ^1H NMR spectrum of **1** revealed the absence of the phenolic O–H resonances as well as the pres-



Scheme 1 Polylactic acid derived from lactide and the products derived from the reaction of CO_2/cyclohexene oxide.

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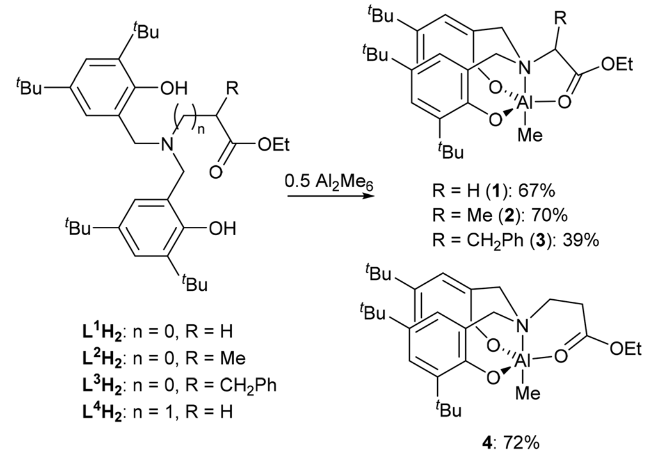


Scheme 2 Synthesis of ABP Al–Me complexes.

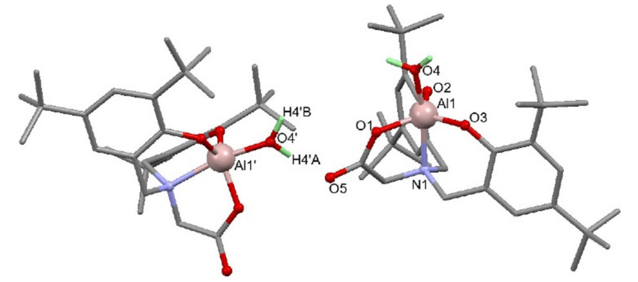
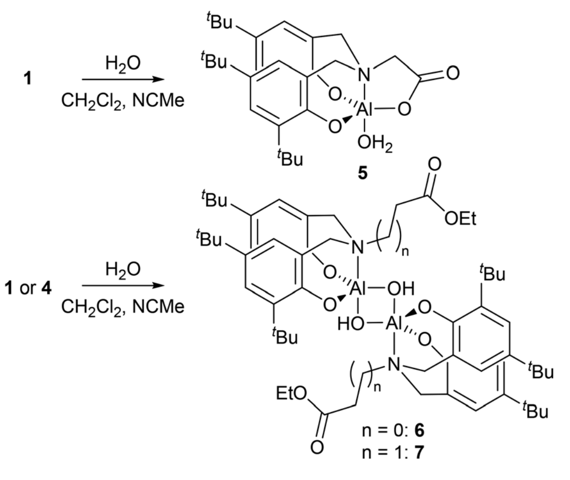


Fig. 1 Molecular structure of **5**. Disorder and hydrogen atoms (excluding atoms bonded to oxygen) omitted for clarity. Selected bond lengths for (Å): Al1–O1 1.822(6), Al1–O2 1.750(5), Al1–O3 1.767(5), Al1–O4 1.869 (5), Al1–N1 2.100(5), O1–C1 1.289(11), C1–O5 1.227(10). Selected bond angles (°): O1–Al1–O2 120.1(3), O1–Al1–O3 118.4(3), O1–Al1–O4 87.6 (3), O1–Al1–N1 82.1(2).

ence of doublets in the region of the spectra associated with the protons of the *N*-methylene bridge, indicating that the atoms had become diastereotopic, which along with a singlet at −0.36 ppm for the Al–Me group confirms the coordination of the ligand to the metal centre.[35,36] Similar observations were made in the ^{1}H NMR spectra of **2–4**. In each case, the proposed products were found to be consistent with the data obtained from high resolution mass spectrometry (HRMS).

Attempts to grow crystals of **1–4** that were suitable for SCXRD studies proved unsuccessful when using rigorously dry solvents. Previously we have found that adventitious capture of water from bench solvents can result in the formation of oxo-bridged aggregates,[36–38] thus crystallisations of **1** and **4** from 'wet' solvents revealed either monometallic (**5**) or bimetallic complexes (Scheme 3, **6** and **7**).

SCXRD studies of **5** revealed a monometallic complex featuring a carboxylate donor, loss of the Al–Me group and binding of water to the 5-coordinate trigonal bipyramidal Al (Fig. 1). This demonstrates the fate of complex **1** in non-dry reaction and polymerisation conditions.



Scheme 3 Reactions of **1** and **4** with water.

With fewer equivalents of water, single crystal X-ray diffraction (SCXRD) experiments revealed hydrolysis of only the Al–Me group in **1** and **4** to give bimetallic Al complexes featuring bridging hydroxide groups and uncoordinated ester functionalities (Fig. 2 for **6**, see ESI for **7**†)

Complexes **1–4** were investigated for their ability to initiate the ROP of *rac*-lactide (catalyst loading = 200 : 1 with *rac*-lactide in dry toluene) at 130 °C over 24 hours (Table 1). All complexes showed good activity reaching >90% conversion after 24 hours.

Reactions run in the presence/absence of benzyl alcohol proceeded at a similar rate, showing that the Me group does not need to be exchanged for an alkoxide first.[27,29] The tacticity of the PLA chains produced was investigated and it was found that complex **2** has an isotactic bias with P_{i} = 0.61 and 0.60 (Table 1, entries 3 and 4). The other complexes did not show any significant enhancement in the stereoselectivity of the enchainment, suggesting the addition of the chiral methyl group influenced the tacticity of the polymer formed. All com-

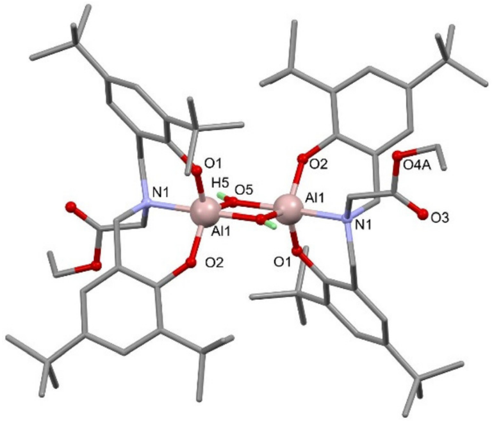


Fig. 2 Molecular structure of **6** with hydrogen atoms, except OH, and second position of disordered ester group omitted for clarity. Selected bond lengths (Å): Al1–O1 1.743(2), Al1–O2 1.760(2), Al1–O5 1.792(2), Al1 O5′ 1.879(2), Al1 N1 2.097(2), O3 C32 1.195(3), O4A C32 1.369(4). Selected bond angles (°): N1–Al1–O1 90.5(1), N1–Al1–O2 90.5(1), N1–Al1–O5 93.9(1), N1 Al1 O5′ 172.1(1), Al1–O5–Al1′ 101.9 (1).

Table 1 Solution state polymerisation data for complexes **1–4**

Entry	Cat.	Conversion[b] (%)	P_i[c]	$M_{n(calc)}$[d] (g mol^{-1})	$M_{n(obs)}$[e] (g mol^{-1})	Đ[e]
1	**1**	90	0.57	26 000	24 800	1.06
2[a]	**1**	96	0.56	13 800	4866	1.08
3	**2**	90	0.60	27 200	25 500	1.20
4[a]	**2**	86	0.61	13 900	8000	1.05
5	**3**	94	0.56	27 200	26 100	1.04
6[a]	**3**	96	0.55	13 900	6900	1.10
7	**4**	94	0.50	25 800	17 300	1.04
8[a]	**4**	97	0.53	12 400	5744	1.08

Conditions [Al] : 200[LA], [Al] = 0.01 M, 1 mL of toluene, 130 °C, time = 24 h. [a] [M] : 2[BnOH]. [b] Calculated from ^{1}H NMR spectrum, analysis of the integration of the lactide and poly(lactic acid) resonances in the methylene region. [c] Determined using homonuclear decoupled ^{1}H NMR spectroscopy. [d] Calculated as $M_{n(calc)}$ = ([LA]/[M]) × conversion × M_{wLA} or $M_{n(calc)}$ = ([LA]/[M]/[BnOH]) × conversion × M_{wLA} for reactions initiating with BnOH. [e] Determined from GPC trace at 30 °C in THF, using polystyrene standards.

Table 2 ROP of CHO

Entry	Cat.	Conv.[a] (%)	% CO_3[b]	TON/TOF[c] (h^{-1})	M_w/M_n[d] (g mol^{-1})	Đ[d]
1	**1**	23	4	135/34	25 542/17 231	1.48
2	**2**	14	4	82/3	32 624/21 149	1.54
3	**4**	56	5	329/14	31 395/22 253	1.41

Results of polymerisations carried out in neat cyclohexene oxide (2 mL), 20 bar CO_2 in absence of initiator (no PPNCl), ratio 3.5 [Al] : 2000 [CHO], [cat.] : [monomer]. Conditions 75 °C, 24 hours. [a] Calculated from ^{1}H NMR spectrum. [b] % CO_3 includes cyclic carbonate and poly carbonate. [c] Calculated as conversion × (monomer/cat ratio)/time, or TON/time. [d] Determined from GPC trace at 30 °C in THF, using polystyrene standards. GPC using refractive index detector.

plexes showed excellent control over the molecular weight of the polymer chains, with most dispersity values lower than 1.10 and chain lengths close to their calculated values for M_n. Polymerisation in the melt also delivered excellent control (see ESI†).

Complexes **1**, **2** and **4** were investigated for their activity as catalysts in the ROCoP of CHO and CO_2 using a standard set of reaction conditions (24 hours, 75 °C, 20 bar CO_2) and a catalyst loading of 3.5 : 2000 units of monomer. Initial reactions resulted in formation of poly(cyclohexene oxide) with almost no incorporation of CO_2 (Table 2).

Even under a relatively high-pressure of CO_2 (20 bar) only trace formation of carbonate was observed (as cyclohexene carbonate). **4** was the most active catalyst with a 56% conversion of polyether observed (Table 3, entry 3). Polyethers with high molecular weight have been synthesised with reasonable Đ values of 1.4 to 1.5 for all the Al-ABP complexes. The M_w values are similar to polymers synthesised in the literature by an aluminium β-ketoamino complex (M_n 1240 g mol^{-1} to 2500 g mol^{-1}) and in line with a zinc complex [Zn(C_6F_5)$_2$(toluene)] which generated M_n values in a range of 14 600 g mol^{-1} to 39 100 g mol^{-1}.[39,40] Plommer and co-workers also found that without an initiator aluminium complexes led to the production of polyether with molecular weights around 180 kg mol^{-1} (in one minute with a 53% yield) to 500 kg mol^{-1} (1 h with a 13% yield), both demonstrating narrow polydispersity (obtained using a multi-light scattering detector).[32]

Interestingly, utilising a [1] : [1] ratio of catalyst (**1**, **2** or **4**) to PPNCl cocatalyst under an atmosphere of CO_2 resulted in significantly increased rates of CO_2 incorporation with poly(cyclohexene carbonate) becoming the major product (Scheme 1 and Table 3), as deduced from analysis of the ^{1}H NMR spectra of the polymers. This demonstrates the potential for a switchable catalytic system in which the Al-ABP complexes can polymerise CHO to a polyether but with the addition of PPNCl, switch to forming a polycarbonate.

The ^{1}H NMR spectra of the crude reaction mixture indicated that the polycarbonate polymer was formed as the major product. Further inspection of the NMR spectra shows only trace quantities of the *trans*-CHC isomer and there was no

Table 3 ROCoP of CHO and CO_2

Entry	Cat.	T [°C]	Bar	Conv.[a] (%)	% CO_3[b]	TON/TOF[c] (h^{-1})	M_w/M_n (g mol^{-1})	Đ
1	**1**	75	5	27	95	158/7	2819/2036	1.38
2	**1**	75	20	51	94	300/13	2538/1986	1.27
3	**2**	75	5	32	96	188/8	2641/2152	1.22
4	**2**	75	20	41	94	241/10	3161/2455	1.29
5	**4**	75	5	33	96	194/8	3627/2857	1.27
6	**4**	75	20	56	97	329/14	4658/3757	1.24
7	**1**	100	20	47	97	276/12	4286/3037	1.4
8	**1**	75	20	51	94	300/13	2538/1986	1.27
9	**1**	75	20	37	66	—/—	3688/2870	1.22
10	**1**	60	20	38	95	224/9	3076/2320	1.33
13	**2**	75	20	41	94	241/10	3161/2455	1.29
14	**2**	60	20	29	95	171/7	1902/1509	1.26
15	**4**	75	20	56	97	329/14	4658/3757	1.24
16	**4**	60	20	56	95	329/14	2074/1986	1.20

Results of polymerisations carried out in neat cyclohexene oxide (2 mL) with PPNCl, ratio 3.5[Al] : 3.5[PPNCl] : 2000[CHO], [cat.] : [initiator] : [monomer]. Conditions 75 °C. [a] Calculated from ^{1}H NMR spectrum. [b] % CO_3 includes cyclic carbonate and poly carbonate. [c] Calculated as conversion × (monomer/cat ratio)/time, or TON/time.

observable signal for *cis*-CHC. This was confirmed with further HSQC experiments were performed on an 800 MHz spectrometer (see ESI†).

At CO_2 pressures of 20 bar, conversions to the copolymer were good with very high incorporation of CO_2, resulting in almost complete formation of carbonate junctions 94% to 97% for all three catalysts (Table 3 entries 2, 4 and 6) in preference to polyether. Reducing the pressure of CO_2 to 5 bar resulted in lower conversion to polymers but these polymers retained their high incorporation of CO_2 (Table 3, entries 1, 3 and 5). Increasing the pressure from 5 to 20 bar increased the M_w of the polymers marginally for complexes **2** and **4**, however, complex **1** showed a decrease in the M_w of the polymer with the increase of pressure. Complex **4** was the most active catalyst for this reaction, and **4** displayed the same efficiency at the lower temperature 60 °C as the reaction carried out at 75 °C.

There is a clear viscosity limit for this solvent free reaction as conversion did not extend beyond 60%. The addition of 2.2 mL of toluene did not lead to an increase in conversion, however, an increase in the molecular weights was observed alongside a decrease in CO_2 incorporation (see ESI, Table S4†). Presumably, the addition of solvent assists with the diffusion of the monomer through the sample, however, the choice of solvent is important as donor solvents such as THF can coordinate to the catalyst and inhibit polymerisation.[41] The M_w and M_n values reported here are similar to those found for other related aluminium complexes.[31,42] Combined with cocatalysts (such as tetrabutylammonium bromide, TBAB) some aluminium complexes have proven extremely active achieving M_n values of 14.5 kg mol^{-1}.[43] Work with aluminium porphyrin complexes has also been successful without the need for a cocatalyst, generating M_n values of 96 kg mol^{-1}.[44] With complex **4**, the rate of reaction reaches a plateau after 15 hours (see ESI, Table S3†). The conversion of CHO remained roughly constant at *ca.* 55% over the time period of 15 hours to 48 hours. Again, we anticipate this is viscosity limited due to the decrease in mobility of polymer solutions.

Conclusions

Four novel Al ABP complexes featuring pendent ester arms were synthesised. Complexes **1–4** were active for the ROP of *rac*-lactide both in the solution phase and melt conditions with low dispersities (<1.10). A switchable catalytic system for the ROCOP of CO_2 and cyclohexene oxide was demonstrated by the addition or absence of PPNCl with the aluminium bis(phenolate) complexes. Polycarbonates were successfully synthesised at low pressures of 5 bar CO_2 and at temperatures down to 60 °C using PPNCl.

Conflicts of interest

There are no conflicts to declare.

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