Schiff-Base Aluminum Complexes as Bifunctional Catalysts for the Selective Ring-Opening Co-Polymerization of Cyclohexene Oxide and Succinic Anhydride

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Abstract: The ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides is emerging as a powerful method for the synthesis of polyesters with innovative structures and properties. In this work, a series of dialkyl-aluminum complexes stabilized by Schiff-base ligands with different functional side arms (pyridine, amine, or phosphine) and different substituents on the phenoxy moieties have been synthetized and tested as catalysts in the ROCOP of cyclohexene oxide (CHO) and succinic anhydride (SA). The selectivity of the catalysts in the ROCOP was significatively depending on the nature of the pendant arm and/ or of the substituents of the ligand framework. The complexes designed to have a dynamic coordination sphere in which the side arms simulate the role of a neutral cocatalyst favored the desired selectivity, giving poly(CHO-alt-SA) with narrow dispersity and negligible ether linkage. NMR investigations and DFT calculations rationalized the observed behavior.

Introduction

The development of sustainable materials is one of the key strategies adopted by the current society to contrast the plastic pollution,[1] these include utilizing sustainable monomers and the development of polymers that can be chemically recycled/degraded.[2]

Among these materials, aliphatic polyesters represent the most promising class. They are generally produced by either polycondensation of diacids and diols or by Ring-Opening Polymerization (ROP) of cyclic esters.

In the last years, alternating Ring Opening Co-Polymerization (ROCOP) between epoxides and cyclic anhydrides is emerging as a powerful and versatile synthetic method to produce polyesters with a larger array of structures thanks to the combination of two distinct building blocks.[3]

Notable examples of catalysts active in the ROCOP include complexes of magnesium,[4] zinc,[5] chromium,[6] cobalt,[6a, 7] and aluminum,[8] with salen or phenoxide based ligands.[9] In most cases, these complexes guarantee the selectivity of the polymerization process only in the presence of a cocatalyst, that can be a neutral (substituted pyridine or phosphine) or ionic nucleophilic species (onium salt).

The examples of catalysts that are selective without any addition of cocatalyst are rare. The first example was the BDI-Zn catalyst reported by Coates.[5a] Subsequently, Williams described a series of homo- and heterobimetallic complexes of magnesium and zinc showing high activity and selectivity in the ROCOP of cyclohexene oxide and phthalic anhydride.[5c] In 2016 Lu reported the first asymmetric copolymerization of *meso*-epoxides by enantiopure bimetallic salen–Al complexes containing a binaphthol-linked ligand.[10] More recently, Chen and Pang reported a trinuclear salen–Al complex that, thanks to the intramolecular interaction between the three subunits, showed high activity for the ROCOP reactions in the absence of any cocatalyst. [11]

Interestingly, all the described complexes are, or are supposed to be, multimetallic species.

The first mechanistic studies concerning the role of the ionic cocatalyst during the propagation steps of ROCOP catalytic process revealed the epoxide ring-opening by a cocatalyst-associated carboxylate specie as the rate-limiting step.[12]

On the base of these results, the development of bifunctional catalytic systems in which the Lewis acid and nucleophilic centres are covalently tethered revealed a promising strategy.

Although examples of bifunctional catalysts have been diffusely reported for the reaction between epoxide and carbon dioxide,[13] for epoxides and anhydride copolymerizations they are definitively rare.

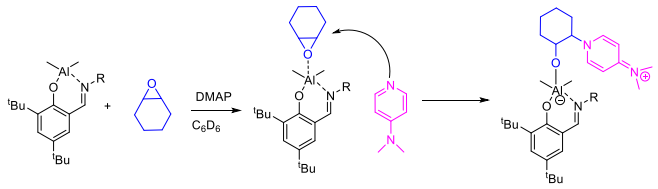
Lee and co-workers reported cobalt-salen complexes with attached quaternary ammonium groups as selective bifunctional catalysts for the copolymerization of propylene oxide and phthalic anhydride. [14] Analogously, Coates reported a bifunctional catalyst for the ROCOP of propylene oxide (PO) and carbic anhydride (CPMA) in which the salen complex and an aminocyclopropenium cocatalyst are covalently tethered.[15]

Kleij and co-workers recently described aminotriphenolate cobalt complexes containing two cis ligating dimethylaminopyridine (DMAP) units.[16] The reversible coordination of one of these ligands provided a coordinative unsaturated Co(III) aminotriphenolate complex and one free DMAP, as a sort of "intrinsic bicomponent system". This showed a moderate activity for the copolymerization of cyclohexene oxide and phthalic anhydride.

Recently, we observed that tetra-coordinate monometallic aluminum complexes supported by bidentate monoanionic phenoxy-imine ligands promote the ring opening co-polymerization of epoxides with anhydrides in a perfectly alternate manner in the presence of a neutral co-catalyst such

as DMAP.[17] NMR studies revealed a clear role of DMAP in the initiation step in which a zwitterionic species is formed by opening of an epoxide unit coordinated to the metal center by the nucleophilic attack of DMAP (scheme 1). Since the selectivity is observed only when DMAP is added as cocatalyst, it is evident that the species has a determinant role also in the propagation steps of the reactions. With the aim to develop bifunctional catalysts and to clarify the role of DMAP during the propagation steps, we selected Schiff base ligands bearing a neutral pendant donor arm which was envisaged might simulate the role of a neutral cocatalyst.

Herein, the effect of the structure of the ancillary ligand and of the additional pendant arm on the performance of {ON}$AlMe_2$ complexes in terms of activity, as well as selectivity, is discussed.



Scheme 1. Zwitterionic species formed by opening of a coordinated epoxide unit by DMAP.

Results and Discussion

Synthesis and characterization of dimethyl aluminum complexes

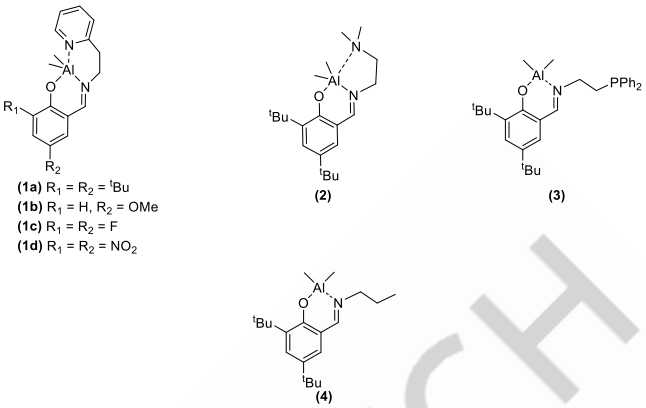
With the aim to design bifunctional catalysts, a series of potentially tridentate salicylaldimine ligands, each bearing a pendant N, or P donor arm attached to the imine nitrogen atom, were synthetized (Scheme 2).[18]

The first objective was to explore the effect of the presence of a pyridine-type pendant arm on a phenoxy-imine[19] ligand platform, in terms of denticity of the chelating ligand. Different substituents were introduced on the *ortho*-and/or *para*-positions of the phenoxide ring to modulate the steric and electronic properties of the ligand (complexes **1a-d,** scheme 2).

Subsequently, the nature of the additional donor was modified introducing an amine or phosphine pendant arm (complexes **2** and **3,** scheme 2). For comparison, the simple Schiff base aluminum complex, lacking the third donor, was synthetized (complex **4**, scheme 2).

All the pro-ligands were obtained, in almost quantitative yields, by condensation between the corresponding salicylaldehyde and amine reagents, at reflux in ethanol for several hours, as previously reported in literature.[20]

The related [N,O-D] aluminum dialkyl complexes were synthesized by reacting the respective pro-ligand with one equivalent of the aluminum precursor.[21] After mixing of the reagents for two hours at room temperature, the resonances of the ligands in the ^{1}H NMR spectra appeared shifted respect to those of the free species and the signal relative to the -OH proton disappeared. The obtained complexes were fully characterized by multinuclear NMR spectroscopy, including 2D experiments ^{1}H-^{1}H COSY and NOESY (see Supporting Information).



Scheme 2. Phenoxy-based aluminum complexes **1**-**4** explored in this work.

Complex **1a** has been reported here for the first time. The solid-state structure of an analogous complex bearing a methylene pyridine-type pendant arm was described as weakly coordinated.[22] The structure of complex **1a** in solution was studied by ^{1}H-^{1}H NOESY at room temperature in C_6D_6. A NOESY correlation between protons of the pendant arm and the protons of methyl groups at the aluminum centre suggested that, under these conditions, the ligand behaves as a tridentate ligand, binding to aluminum via the oxygen, the imine- and the pyridine- nitrogen atoms (Figure S7). The same coordination was observed for complex **1b**. The ^{1}H-^{1}H NOESY spectra, recorded at higher temperature (50 °C), showed the loss of the coordination of pyridine for both complexes.

For complexes **1c** and **1d,** the ^{1}H-^{1}H NOESY spectra performed in C_6D_6 at room temperature and at 50 °C, revealed a stronger coordination of the pyridine pendants at the more Lewis acidic metal centres most likely due to the presence of electron withdrawing substituents (Figure S9).

The crystal structure of **2**, previously reported in the literature,[23] showed that the ligand pendant arm donor is bound to aluminum in the solid state. The ^{1}H-^{1}H NOESY spectrum, performed at room temperature in C_6D_6 solution, confirmed the coordination of the additional amine to the Al centre. The same coordination was preserved also at higher temperature (50°C) and in the presence of one equivalent of cyclohexene oxide (CHO); this is expected because of the higher Lewis basicity of the sp^3 amine nitrogen in comparison to the sp^2 imine nitrogen of pyridine.

As for an analogous of complex **3**, the softer phosphine donor is reported non bounding in the solid state.[24] The ^{31}P NMR spectrum of complex **3** showed a unique singlet at -19 ppm, the same value of the free ligand, thus demonstrating that, even in solution, the phosphine atom is not coordinated to the aluminum.

These observations put in evidence the ability of the ancillary ligands to create a dynamic coordination sphere that supports the metal centre offering a denticity that is depending on its Lewis acidity.

The strength of coordination bond of the pendant nucleophilic arm to Al was investigated by molecular modeling studies. The free energy gap between the minimum energy structures of the complexes with a decoordinated pendant arm and their corresponding coordinated species (DG = $G_{decoordinated}$ –

$G_{coordinated}$) are reported in Figure 1. As for pyridine-type complexes (**1a-d**) decoordination free energies are negative, when phenoxy-imine moiety is substituted with electron-donating groups (**1a-b**), and positive with electron-withdrawing groups (**1c-d**). These results agree with NMR data that indicate a decoordination of the pendant arm over 50°C only for **1a** and **1b**. As for amine-type complex (**2**), the coordination of the pendant arm is favored (decoordination DG = +1.7 kcal/mol), as also observed in the crystal structure. On the contrary, with a phosphine pendant arm the minimum energy structure with a coordinated arm was impossible to locate, indicating that the coordination is largely unfavored, as suggested by NMR studies. By matching experimental and theoretical investigations, the lability of the pendant arm can be summarized with the following trend **3 > 1a > 1b > 1c > 2 > 1d**.

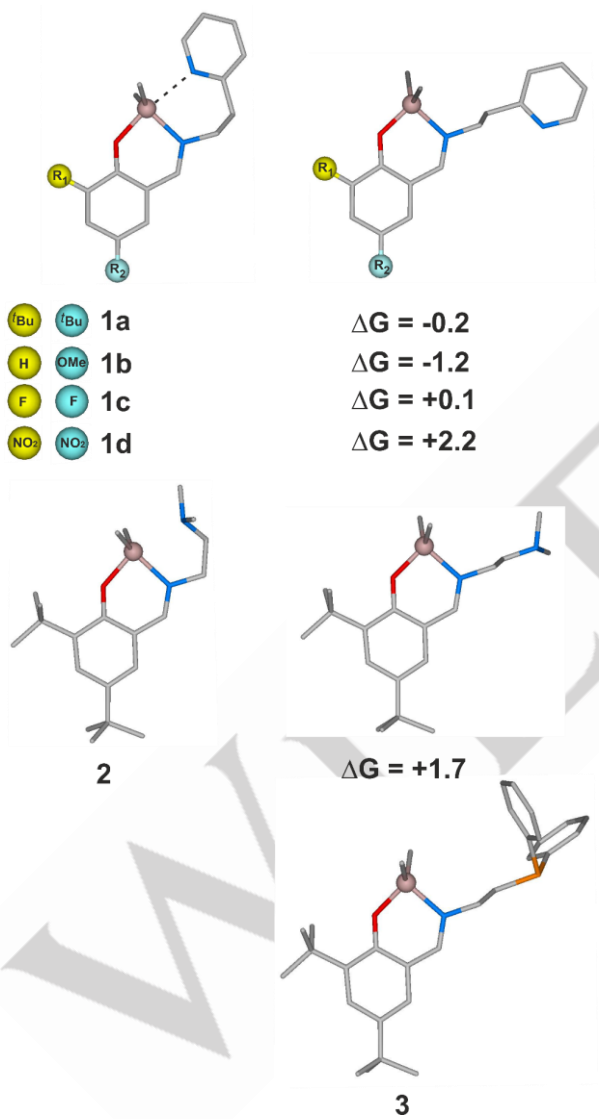
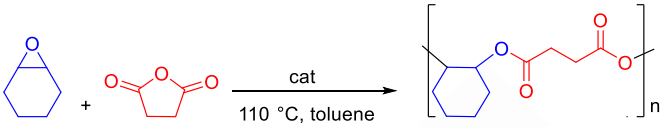


Figure 1. Minimum energy structures of complexes 1a-d, 2 and 3. Free energies decoordination of the pendant arm are reported in kcal/mol.

Effect of the substituents

Complexes **1–4** were tested as catalysts in the copolymerization of cyclohexene oxide (CHO) with succinic anhydride (SA) to investigate their activity and selectivity towards polyester formation (Scheme 3). All obtained polymers have been characterized by ^{1}H NMR (600 MHz) spectroscopy, GPC and MALDI-TOF-MS analyses.



Scheme 3. Phenoxy-based aluminum complexes **1**-**4** explored in this work.

The polymerizations were performed at 110 °C, with an [epoxide]:[anhydride]:[catalyst] ratio of 250:250:1. Selected polymerization data are reported in Table 1.

Initially, the catalytic behavior of complex **1a** was compared with that of the previously reported bicomponent system formed by complex **4** and one equivalent of DMAP.[17]

In the absence of solvent, the two catalytic systems, **1a** and **4**/DMAP, showed comparable activity. The turnover frequencies (TOF), calculated on SA conversion, were 67 h^{-1} and 80 h^{-1} (entries 1 and 2 of Table 1), respectively. A lower selectivity was observed for the complex **1a** that produced a poly(ester-co-ether) with 53% of ester functionalities .

Subsequently, the polymerizations were conducted in toluene solution (entries 3-5 of Table 1).

Under these conditions, the achieved activities were significantly lower, especially in the case of complex **1a** for which the complete conversion of both the monomers was achieved only after 24 hours (time not optimized). The lower activity observed for complex **1a** could be a consequence of scarce efficiency in the initiation steps; when 1 equv of DMAP was added, the activity of complex **1a** drastically enhanced (entry 6), being thus quite similar to the catalytic system **4**/DMAP.

Interestingly, complex **1a** resulted able to produce a rigorously alternate polyester in the absence of a hexogen cocatalyst, demonstrating that it can act as an efficient bifunctional catalyst (entries 3 and 4 of Table 1). The MALDI–ToF MS spectrum of the polymer obtained by **1a** (entry 3, Table 1, Figure 2) confirmed this hypothesis. It showed the presence of two major distinct distributions, both corresponding to linear polymer chains consisting in sequences of [CHO+SA] repeating units, coherently with a perfectly alternating structure. [25]

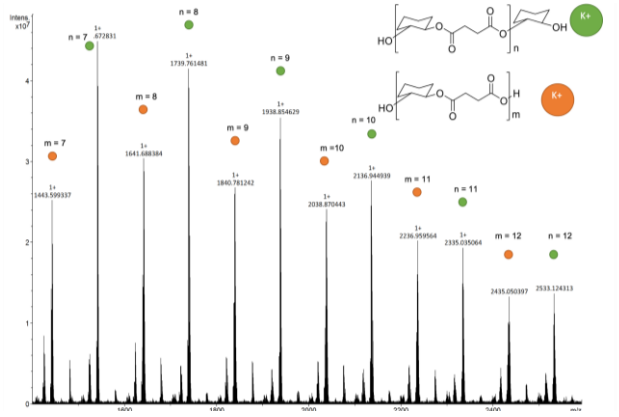


Figure 2 MALDI-ToF-MS spectrum of SA-CHO copolymer synthesized in entry 3 of Table 1

Table 1. Ring Opening Co-Polymerization of CHO with SA promoted by complexes 1a-d and 5.[a]

Table 1 Ring Opening Co-Polymerization of CHO with SA promoted by complexes **1a, 1b, 1c, 1d** and **4**.[a]

Entry	Cat	^{i}PrOH (eq)	t (h)	^{c}Conv SA (%)	^{c}Ester (%)	$^{d}M_{nGPC}$ (KDa)	$^{d}Đ$
1[b]	**1a**	-	2	54	53	2.7	1.44
2[b]	**4/DMAP**	-	1	32	88	1.3	1.37
3	**1a**	-	4	21	>99	2.1	1.33
4	**1a**	-	24	100	>99	3.2	1.44
5	**4/DMAP**	-	1	25	>99	1.6	1.47
6	**1a/DMAP**	-	1	24	>99	2.3	1.35
7	**1a**	2	5	40	>99	2.3	1.47
8	**1b**	2	5	50	>99	2.6	1.30
9	**1c**	2	5	57	80	1.2	1.50
10	**1d**	2	4	47	47	1.3	1.31
11	**1c**	2	24	94	74	2.1	1.98

[a]Reaction conditions: [Al] = 10^{-5} mol, [SA]:[CHO]:[Al] = 250:250:1, T = 110 °C, toluene 1 mL. [b] Solvent free reactions [c]Determined by ^{1}H NMR spectroscopy. [d]Molecular weight data M_{nGPC} (g/mol^{-1}) and Đ were determined by GPC, in THF vs polystyrene standards.

Both series describe α,ω-hydroxy-terminated chains, probably produced by nucleophilic attack of water or cyclohexane diol present in traces, in the polymerization medium.

Neither methyl groups as chain end groups or polymer series initiated by the side arm of the ligand precursor were detected.[26] This observation suggests that the metal acts as Lewis acid centre that coordinates the monomer (CHO) and actives it for the nucleophilic attack by adventitious water molecules present as impurity in the monomers.

To improve the efficiency of the initiating step, the polymerization reaction was performed in the presence of two equivalents of isopropanol as initiator. As expected, entry 7 showed a slightly increased activity (compare of entry 7 vs entry 3, Table 1; TOFs: 20 h^{-1} *vs.* 13 h^{-1}), while the selectivity of the catalytic system was preserved.

The MALDI–ToF MS spectrum of the polymer obtained by **1a/** ^{i}PrOH (entry 7, Table 1) revealed that the polymer chains were end-capped by one isopropyl ester –OCH(CH$_3$)$_2$ and a hydroxyl -OH group highlighting the involvement of the alcohol in the initiation step (Figure 3). Thus, considering the beneficial presence of the alcohol as initiator, the latter reaction conditions were chosen to investigate the activity and selectivity of catalyst when varying the Lewis acidity of the metal centre by introduction of electron-donating (complex **1b**) or electron-withdrawing (complexes **1c-d**) substituents in the *ortho* and/or *para* positions of the aromatic ring of the ligand.

A comparison among pyridine-type complexes **1a-d**, showed that, while the activity was substantially the same, a significant difference was observed in terms of selectivity. For all complexes full conversions can be obtained after 24 h (see for example entry 11 of Table 1.

Introducing a methoxy substituent, a strong electron-donating group, on the *para* position of the aryl ring, a perfect selectivity was achieved (entry 8 , Table 1).

Differently, in the presence of electron-withdrawing substituents a significant loss of selectivity was observed (entries 9 and 10, Table 1), and the percentage of ester linkages decreased up to 47% in the case of complex **1d** with nitro substituents.

All the obtained polymers displayed monomodal distributions of the molecular weights with moderately narrow polydispersities (Đ < 1.5).

As often observed for the polyesters produced with this route, the number average molecular weight (M_n) (values measured by GPC without any calibration correction) were always lower than the theoretical expected ones for a living system. This is imputable to the presence of protic impurity traces that can act as chain transfer agents.

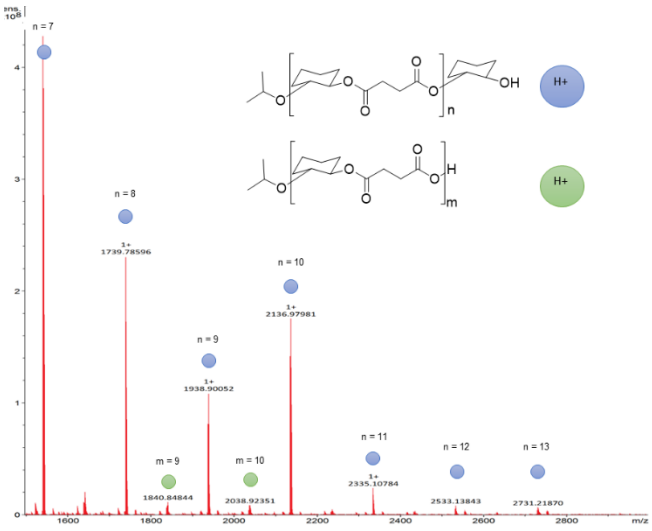


Figure 3. MALDI-TOF spectrum of polyester CHO/SA obtained by **1a** in the presence of ^{i}PrOH (entry 7, Table 1).

Effect of the additional pendant arm.

To further study the effect of the additional neutral donor in the pendant arm, it was changed from a pyridine to a tertiary amine or a phosphine.

As already discussed for the effect of the substituents on the phenoxide ring, also in this case the activity was substantially independent by the nature of the neutral donor (compare SA conversions of entries of table 2) while for both catalysts (2 and 3) a weak loss of selectivity was observed.

In light of collected data, the complete selectivity in the ROCOP of CHO/SA was limited to complexes **1a** and **1b** bearing a pyridine pendant arm and electron donating substituents on the phenoxide ring.

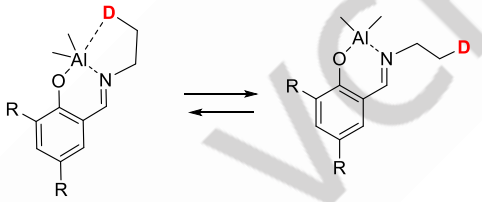
According to the pendant arm lability scale (**3 > 1a > 1b > 1c > 2 > 1d**) as well as to NMR data, **1a** and **1b** pendant arm seem to exhibit a dynamic coordination to the metal (Scheme 4), while other complexes would generally be blocked in a decoordinated intermediate (**3**) or in a coordinated intermediate (**1c-d** and **2**).

Table 2. Ring Opening Co-Polymerization of CHO with SA promoted by complexes **1a, 2** and **3**.[a]

Entry	Cat	t (h)	Conv SA[b] (%)	Ester[c] (%)	[d]M_{nGPC} (KDa)	Đ[d]
1	**1a**	5	40	>99	2.3	1.47
2	**2**	4	51	90	3.2	1.73
3	**3**	4	51	94	3.4	1.37

[a]Reaction conditions: [Al] = 10^{-5} mol, [SA]:[CHO]:[Al]:[^{i}PrOH] = 250:250:1:2, T = 110 °C, toluene 1 mL. [b]Determined by ^{1}H NMR spectroscopy. [c]Calculated from CHO conversion. [d]Molecular weight data M_{nGPC} (g/mol^{-1}) and Đ were determined by GPC, in THF *vs* polystyrene standards.

The co-catalyst has usually a role both in the initiation and in the propagation step of the polymerization process. In the initiation reactions, it promotes the nucleophilic attack to the first monomer unit activated by coordination at the metal centre. During the propagation, its coordination to the metal can modulate the acidity of the reactive centre influencing the energy profiles of the both the propagation reaction and the competing reactions. As for the co-catalyst free polymerizations investigated in this work, the apto flexible ancillary ligand can emerge as valuable assistant in several reaction steps. To explore the role of the pendant arm during the initiation and propagation, NMR studies were conducted.

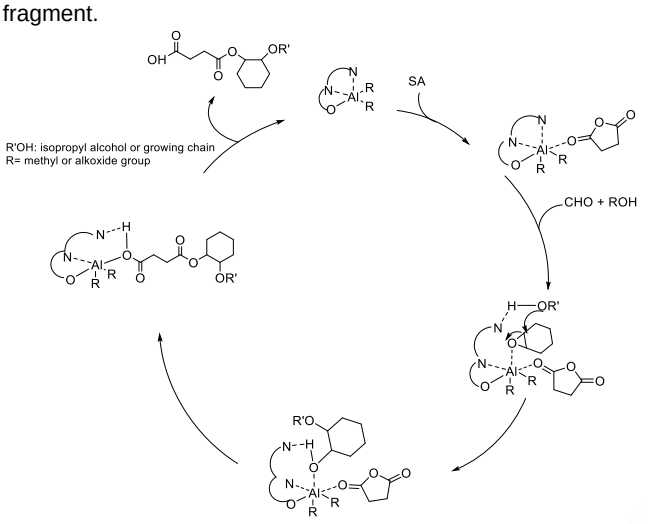


Scheme 4. Flexibility of the pendant arm

NMR mechanistic studies

According to experimental data, alcohol, when involved, participates to the initiation steps. To clarify its role, alcoholysis experiments of complex **1a** were monitored by ^{1}H NMR spectroscopy. The alcoholysis of complex **1a** (15 µmol) was performed with two equivalents of ^{i}PrOH in deuterated toluene at 50 °C. Surprisingly, the exhaustive substitution of methyl groups of complex **1a** with the isopropoxide groups occurred only after 24 hours, extraordinary slowly in comparison to polymerization times.[27] The same results were obtained with complex **1b**. This suggests that, reasonably, the alcohol behaves as an initiator. Subsequently, one equivalent of complex **1b** was mixed with 1 equivalent of CHO at room temperature. ^{1}H DOSY (Figure S13) and ^{1}H-^{1}H NOESY experiments showed the non-coordinated state of the CHO. No coordination or reactivity was observed after heating one day at 70 °C. After the addition of 1 equivalents of SA, the ^{1}H-^{1}H NOESY experiment registered at 50 °C (to solubilize SA) showed the coordination of SA to the Al centre. A strong correlation among the methyl groups of the metal complex with the anhydride was observed. New interactions between SA and CHO were also visible, suggesting that SA coordination promoted the subsequent coordination of CHO and initiation of the polymerization. SA is required in the initiation step for the following polymerization to proceed. Based on the above results, a reaction mechanism has been proposed for complexes **1a** and **1b** (Scheme 5) in which the initial coordination of the anhydride at the metal centre induces the dissociation of the pendant arm thus freeing a coordination site for the incoming epoxide. At this point the initiation reaction occurs by nucleophilic attack of the alcohol to the coordinated epoxide favored by the assistance of the labile pendant arm in

activating the hydroxyl group via H bonding. The following reaction is the nucleophilic attack of the alkoxide group to the coordinated anhydride. After that, the polymer chain propagation could proceed by coordination of a subsequent couple of monomers and the alternating enchainment between the Lewis acid-activated epoxide or anhydride and the Lewis base-mediated activation of the growing chain by the pyridine fragment.



Scheme 5. Proposed mechanism for copolymerization of CHO and SA with aluminum complexes **1a** and **1b**.

Conclusion

In this paper we report new aluminum complexes bearing phenoxy-imine ligands having an additional neutral donor behave as bifunctional catalysts in the ring opening polymerization of cyclohexene oxide and succinic anhydride producing perfectly alternate poly(CHO-alt-SA) in the absence of any cocatalyst. The selectivity of the process seems to be depending on the coordinative fluxionality of the pendant donor. The denticity of the ancillary ligand can be controlled by the introduction of substituent groups which modulate the Lewis acidity of the metal centre and/or by an opportune choice of the additional neutral donor. The aluminum complexes having electron donating groups in which the pendant arm is reversibly coordinate at the metal centre (**1a-b**) are the most selective catalysts producing polyesters with perfectly alternate structures. Differently, in complexes with electron withdrawing substituents (**1c-d**), or stronger nucleophilic arm (**2**), the pendant donor would be stably coordinated and polyesters with polyether sequences in the chain are preferably formed. A slight decrease of selectivity is observed when the pendent arm is permanently de-coordinated, as well (complex **3**).The selectivity of these innovative bifunctional systems is tuned by modifying the nature of substituents and the structure of the ancillary ligands has proven successful. The approach described herein appears promising and the next step will be to optimize further the structure of the ligand and to change the nature of the metal centre.

Experimental Section

General considerations: All the operations of synthesis and handling of air-sensitive chemicals were performed in an inert atmosphere, using Schlenk techniques and/or a glove-box in nitrogen atmosphere. The used glassware was dried in an oven at 120 ° C and subsequently subjected to vacuum-nitrogen cycles. The solvents used were suitably dried. Deuterated solvents were purchased from Sigma–Aldrich and dried over activated 3-Å molecular sieves prior to use. All the reagents used for the synthesis of the complexes and the lactide were purchased from Sigma Aldrich. The NMR spectra were recorded with BRUKER ADVANCE instruments operating at 600, 400 and 300 MHz for ^{1}H. Molecular masses (M_n and M_w) and their dispersities (M_w / M_n) were measured by gel permeation chromatography (GPC), using THF as the eluent (1.0 mL min^{-1}) and narrow polystyrene standards were used as the reference. MALDI mass spectra were recorded using a Bruker solariX XR Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were prepared at the concentration of 1.0 mg mL-1 in THF, while the matrix (DCTB) was mixed at a concentration of 10.0 mg mL^{-1}.

Synthesis of complexes

To a stirred solution containing 100 mg (1.3 mmol) of AlMe3 (97 % wt) in dry benzene (2 mL) was added dropwise a solution of the appropriate pro-ligand (1.3 mmol) in dry benzene (2 mL). The reaction mixture was stirred for 2 hours at room temperature. The solvent was then removed under vacuum, to yield a yellow solid. The resulting solid was washed with dry hexane and dried in vacuo. For complex (1c), dry THF was used for the complex synthesis because of the poor solubility of the appropriate pro-ligand in benzene. All complexes were obtained with yields higher than 85%.

Copolymerization reactions

The copolymerization reactions were conducted at 110 °C either in 1 mL of toluene or under neat conditions. For experiments involving solvent, succinic anhydride was introduced into a reactor vessel equipped with magnetic stirring under a nitrogen atmosphere. Subsequently, a solution containing the chosen catalyst and cyclohexene oxide (and cocatalyst in select cases) in 1 mL of toluene was added to the same vessel. Isopropanol was included as an initiator in certain experiments. For experiments conducted without solvent, the procedure is the same but cyclohexene oxide and the catalyst were added to the vessel containing anhydride without being dissolved in toluene.

At the end of the reaction, dichloromethane was introduced in the vessel and the product was dried under vacuum.

Supporting Information

Experimental details about the synthesis of the ligands and complexes, NMR spectra and computational details are reported in the SI data.

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Keywords: Schiff bases, polyesters, Ring opening polymerization, epoxide, anhydride

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[25] The minor population are related the same sequences with Na+ ions

[26] For the polymer produced in entry 6, in the presence of DMAP, end-group determination revealed exclusively DMAP end-capped chains (see ESI). However, other initiation groups cannot be excluded since the polymer chains initiated by DMAP are intrinsically charged and can then overwrite the originally uncharged chains in the MALDI-TOF MS spectra.

[27] the 1H NMR spectra revealed multiple products and no one species could be isolated and fully characterized, even increasing the amount of alcohol and the reaction time up to more than one day. In particular, methyl groups bound to the aluminum center were still observed after 4h at 100 °C. Consequently, the {OND}Al-(OiPr)2 complex cannot be formed in the reaction medium before the beginning of the polymerization since at 4h a usual 20% of conversion of both monomers is observed.

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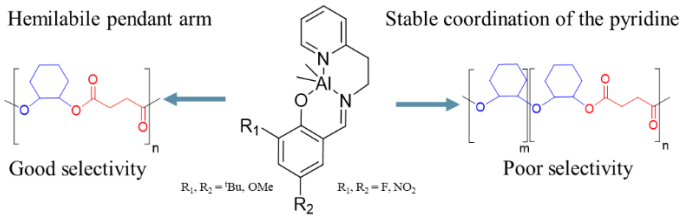

Simple bifunctional aluminum catalysts for the ring opening polymerization of cyclohexene oxide and succinic anhydride are described. Their selectivity in promoting an alternated copolymerization of the two monomers is depending on the hemilabile behavior of the nitrogen neutral donor of the pyridine pendant arm: the introduction of electron donating substituents on the phenoxy rings of the ancillary ligand promotes a complete selectivity.