

## Tetracoordinate aluminum complexes bearing phenoxy-based ligands as catalysts for epoxides/anhydrides copolymerization: some mechanistic insights.

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A series of dimethyl aluminum complexes of the type [E,O]AlMe<sub>2</sub> stabilized by phenoxy-imine, phenoxy-thioether and phenoxy-amine ligands have been tested as catalysts for the ring-opening copolymerization of epoxides and anhydrides. All complexes revealed to be active in the copolymerization of cyclohexene oxide with succinic anhydride showing activities higher than pentacoordinate salen aluminum complexes. Interestingly, these complexes revealed to be active in the copolymerization of limonene oxide with phthalic anhydride. A moderate influence of the ligand structure on the efficiency and selectivity of the catalyst was also observed. Some mechanistic insights have been gained by NMR studies allowing to identify a zwitterionic species formed in the initiating step of the polymerization reaction.

### Introduction

Polyesters represent an important class of polymers that are emerging as an attractive alternative to the petroleum derived plastics.<sup>1-3</sup> Generally, they are produced by either polycondensation of diacids and diols or by ring-opening polymerization (ROP) of cyclic esters.<sup>4</sup> The latter method allows a strict control over the polymer microstructure, but it lacks adequate affinity toward functionalized or aromatic substrates that may limit the properties of the final material.<sup>5,6</sup>

An alternative synthetic method is the alternating ring opening co-polymerization (ROCOP) of epoxides and anhydrides promoted by metal complexes<sup>7,8</sup> or organocatalysts.<sup>9-14</sup> This method revealed to be very promising and versatile, it was used in tandem approaches<sup>15,16</sup> and for the preparation of multiblockpolyesters by switchable catalysis.<sup>17-19</sup>

Further advantage is the availability of large libraries of monomers, some of those are currently available from renewable resources.<sup>2,3,20</sup>

Limonene oxide (LO), for example, is an interesting example of bio-based non-food resource; it is derived mainly from the (R)-limonene isomer, produced by more than 300 plants, and it is traditionally used as a flavor agent, in the fragrance industry, and as a green solvent.<sup>21</sup> As substrate, it is used for reaction with CO<sub>2</sub> for the production of cyclic carbonates or polycarbonates.<sup>22-25</sup> The use of limonene oxide (LO) as monomer is desirable, since the presence of an alkenyl group leads to functional polymers of interest for many applications such as reactive substrates, coating resins, electronic and biomedical materials. Regarding the copolymerization with

anhydrides, only few examples have been reported in the literature.<sup>15,26-28</sup>

The weak side of this catalysis is the scarce availability of efficient initiators able to control the monomer selectivity and to produce high molecular weight polymers.

The first example of catalyst able to produce high molecular weight polyesters with a perfectly alternate structure was the 2-cyano- $\beta$ -diketiminato zinc complex reported by Coates in 2007.<sup>29,30</sup>

After this discovery, some metal complexes have been identified as active initiators for this kind of polymerization; most of them borrowed from the CO<sub>2</sub>/epoxides polymerization catalysis.<sup>31-34</sup> The most significant examples are complexes of trivalent metals, such as Cr(III),<sup>35-40</sup> Co(III),<sup>41-43</sup> Al(III)<sup>36,44,45</sup> and Fe(III),<sup>46,47</sup> and of bivalent metals, such as Zn<sup>48,49</sup> and Mg,<sup>50,51</sup> supported by multidentate ancillary ligands, such as porphyrinate,<sup>35,52-54</sup> salen,<sup>55-58</sup> salan,<sup>59</sup> salalen<sup>60,29,56</sup> and aminotriphenolate ligands.<sup>27,47</sup> Some of these complexes showed interesting results in terms of chemo-<sup>19,61</sup> and stereo-selectivity.<sup>62-64</sup>

In this context, we reported bimetallic aluminum complexes supported by salen ligands with high activity for the ROCOP of cyclohexene oxide and limonene oxide with succinic and phthalic anhydrides.<sup>65,66</sup> Although the experimental evidences supported the hypothesis of a monometallic mechanism in which no cooperation between metal centers was involved, they resulted more active than related penta-coordinate aluminum complexes.<sup>58</sup>

On the base of these results, we decided to investigate the catalytic behavior in the copolymerization of epoxides with cyclic anhydrides of different tetracoordinate aluminum complexes supported by bidentate monoanionic ligands of phenoxide type such as phenoxy-imine, phenoxy-amine and phenoxy-thioether ligands. Although these complexes have been diffusely investigated in the ROP of cyclic esters,<sup>67-72</sup> no study has been reported regarding the copolymerization of epoxides with anhydrides.

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Electronic Supplementary Information (ESI) available: detailed experimental procedures and NMR spectra of complexes.

In this work, the effects of the structure of the ancillary ligand on the performance of dimethyl aluminum complexes in terms of activity and selectivity as well as some aspects concerning the structure of the active species and the role of the cocatalyst are discussed.

## Results and discussion

### Copolymerization of cyclohexene oxide with anhydrides: effects of catalyst structure on catalytic behavior.

To study the effects of the steric and electronic environment of the metal center on the catalytic performance, a phenoxy-imine ligand platform, with variable R-imino substituents, was chosen (scheme 1).

In complex **1**, the coordinated ligand shows a simple n-propyl on the imine nitrogen.<sup>66</sup> For complexes **2a-e**, the ligands have a phenyl substituent on the imine nitrogen with different substituents on the aromatic ring.

Subsequently, the neutral imine donor was substituted with a less Lewis basic amine or a softer thioether donor (complexes **3** and **4**).

The ligands were synthesized according to published procedures.<sup>67-69, 73</sup> All the related aluminum-alkyl complexes were obtained, in quantitative yields, by direct reaction between the opportune pro-ligand with one equivalent of AlMe<sub>3</sub> (Scheme 1). The identity of all complexes was established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see SI).

Initially, we tested the dialkylaluminum complexes in the copolymerization of succinic anhydride (SA) and cyclohexene oxide (CHO) (scheme 2), that are benchmark monomers in this catalysis.

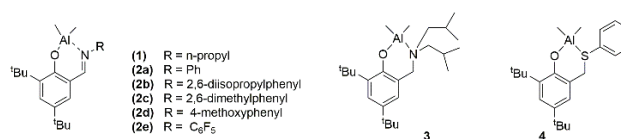
The polymers produced were characterized by <sup>1</sup>H NMR, GPC and MALDI-ToF-MS analyses. The copolymer composition was estimated by <sup>1</sup>H NMR analysis performed in CDCl<sub>3</sub> by using a 600 MHz spectrometer, by comparing the integrals of the signals of epoxide/anhydride sequences with those of epoxide homosequences.<sup>74</sup>

Initially, the CHO/SA copolymerizations were performed at 110 °C in the absence of solvent, with an [epoxide]:[anhydride]:[catalyst] ratio of 125:125:1, and in the presence of one equivalent of 4-(N,N dimethylamino)pyridine (DMAP) as cocatalyst. Selected data are reported in Table 1.

Under the explored reaction conditions, all complexes were active producing poly(ester-ether)s.

Although the differences in the catalytic behaviors are minor, some trends can be discussed.

Complexes **2a-e**, with phenyl groups on the imine donors, showed activities higher than that of complex **1** (entries 2-6, Table 1) preserving a good selectivity (>73%). However, in the presence of electron-withdrawing fluorine atoms (complex **2e**), the catalytic activity was slightly lower (compare entry 6 with entries 2-5 of Table 1). For complexes **3** and **4**, in which an amine or a thioether neutral donor were introduced, a decrease of both activity and selectivity was observed (entries 7-8, Table 1).



Scheme 1. Structures of the aluminium complexes .

Subsequently, the same set of polymerizations was performed in toluene solution (Table 2). As expected, the activities were significantly lower, because of the reduced concentration of the monomers.<sup>75</sup> For the phenoxy-imine catalysts the trend of activity in the bulk polymerizations was substantially confirmed except for catalyst **1**, for which an unsuspected high activity was observed.

In terms of selectivity, a discrete increment was observed for all catalysts. However, a weak steric effect was evident: the presence of substituents on the *ortho* positions of the phenyl group slightly compromised the selectivity (entries 3 and 4 of Table 2). As already observed in bulk, complexes **3** and **4** were somewhat less efficient.

The best performing catalysts, **2a** and **2d**, were chosen to optimize the reaction conditions. With a reduced catalyst loading and by increasing the amount of DMAP up to 2 equivalents, a significant increase of the activity was observed (entries 9 and 10, Table 2). The turn over frequencies, (TOF) evaluated for complexes **2a** and **2d** after 50 min, were 102 and 105 h<sup>-1</sup>, respectively. These activities are higher than those reported for all the previously investigated monometallic salen aluminum complexes for which the TOF are ranging from 15 h<sup>-1</sup> to 50 h<sup>-1</sup>, depending on the structure of the ligand-diimine backbone.<sup>76</sup> The less steric encumbrance of tetracoordinate Al complexes could be responsible of their higher activity.

The MALDI-ToF-MS spectrum of the polymer obtained by entry 10 of Table 2 showed two distinct distributions, both corresponding to DMAP end-capped chains consisting in sequences of [CHO+SA] repeating units, coherently with perfectly alternating



Scheme 2. Synthesis of polyesters from succinic anhydride (SA) and cyclohexene oxide (CHO).

**Table 1.** Ring Opening Co-polymerizations of CHO with SA by **1-4** in the absence of solvent<sup>a</sup>

Entry	Cat	<sup>b</sup> Conv SA (%)	<sup>b</sup> Ester (%)	<sup>c</sup> TOF (h <sup>-1</sup> )	<sup>d</sup> Mn <sub>GPC</sub> (KDa)	<sup>d</sup> Đ
1	<b>1</b>	44	89	66	2.43	1.18
2	<b>2a</b>	69	97	104	1.85	1.19
3	<b>2b</b>	64	80	96	1.62	1.23
4	<b>2c</b>	60	73	90	1.86	1.23
5	<b>2d</b>	66	87	99	1.42	1.17
6	<b>2e</b>	54	88	80	1.43	1.15
7	<b>3</b>	40	73	60	1.88	1.23
8	<b>4</b>	43	42	65	1.45	1.16

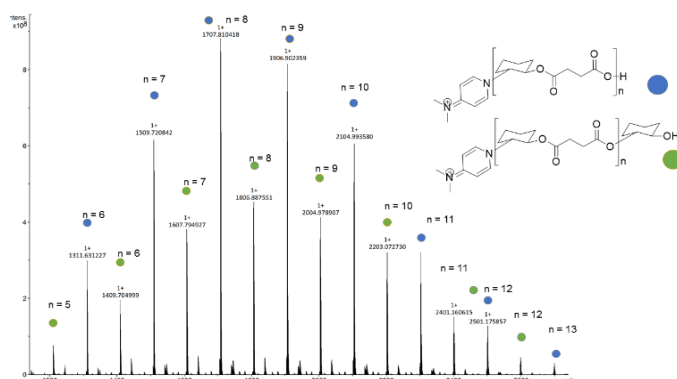
<sup>a</sup>Reaction conditions: cat = 2.0 · 10<sup>-5</sup> mol, [SA]:[CHO]:[Al]:[DMAP] = 125:125:1:1, T = 110 °C, time = 50 min. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Calculated from SA conversion. <sup>d</sup>Molecular weight data M<sub>n, GPC</sub> (KDa) and Đ were determined by GPC, in THF vs polystyrene standards. structure containing more than 99% of ester linkages (Figure 1).<sup>77</sup>

For all the polymers, the GPC analysis displayed monomodal distributions with moderately narrow dispersities (Đ ≤ 1.50), indicating a controlled behavior of the ROCOP reaction. However, the number average molecular weight (M<sub>n</sub>) values measured by GPC (without any calibration correction) were always lower than the theoretical expected values for a living system. This has been observed as a consequence of the presence of protic impurities that can act as chain transfer agents (CTAs).<sup>78</sup>

**Table 2.** Ring Opening co-Polymerization of CHO with SA by **1-4** in toluene solution.<sup>a</sup>

Entry	Cat	<sup>b</sup> Conv SA (%)	<sup>b</sup> Ester (%)	<sup>c</sup> TOF (h <sup>-1</sup> )	<sup>d</sup> Mn <sub>GPC</sub> (KDa)	<sup>d</sup> Đ
1	<b>1</b>	94	>99	42	1.57	1.17
2	<b>2a</b>	91	>99	37	1.91	1.20
3	<b>2b</b>	87	94	36	1.81	1.22
4	<b>2c</b>	87	95	30	1.82	1.26
5	<b>2d</b>	100	>99	41	1.85	1.23
6	<b>2e</b>	62	>99	31	3.75	1.12
7	<b>3</b>	85	90	27	1.97	1.27
8	<b>4</b>	86	87	33	1.52	1.15
9 <sup>e</sup>	<b>2a</b>	91	>99	102	3.85	1.20
10 <sup>e</sup>	<b>2d</b>	91	>99	105	4.09	1.24
11 <sup>f</sup>	<b>2b*</b>	83	93		2.57	1.23
12 <sup>f</sup>	<b>1**</b>	80	>99		2.31	1.30

<sup>a</sup>Reaction conditions: cat = 2.0 · 10<sup>-5</sup> mol, [SA]:[CHO]:[Al]:[DMAP] = 125:125:1:1, T = 110 °C, toluene 1 mL, time = 5 h. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Calculated from SA conversion after 50 min. <sup>d</sup>Molecular weight data M<sub>n, GPC</sub> (KDa) and Đ were determined by GPC, in THF vs polystyrene standards. <sup>e</sup>[Al] = 1 · 10<sup>-5</sup> mol [SA]:[CHO]:[Al]:[DMAP] = 250:250:1:2; time 3h.



**Figure 1.** MALDI-ToF-MS spectrum of SA-CHO copolymer synthesized in entry 10 of Table 2.

### Copolymerization of limonene oxide with phthalic anhydride.

Copolymerizations of limonene oxide (LO) with phthalic anhydride (PA) (scheme 3) were performed in toluene solution by using the commercially available monomer: the mixture of *cis* and *trans* R-limonene oxide (Table 3). In toluene solution, **1** converted nearly 90% of the monomers after 8 hours (entry 1, Table 3).

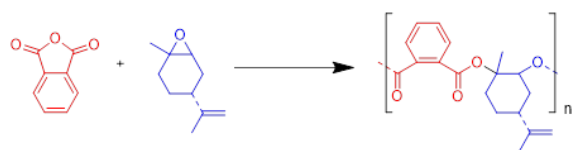
The reactivity scale was like that observed for CHO/SA copolymerization, where the phenoxy-imine complexes showed activities higher than phenoxy-amine or phenoxy-thioether complexes (entries 1-5, Table 3).

The <sup>1</sup>H NMR analysis of all the obtained copolymers showed the absence of ether linkages, thus perfectly alternated copolymers were obtained, as expected for the bulky nature of LO. The microstructure elucidated by the <sup>13</sup>C NMR analysis showed an atactic polymer, coherently with the achiral structure of the catalysts.

As already observed in the ROCOP of CHO/SA, the molecular weights of the obtained polymers were systematically lower than the theoretical values for a living catalyst system, although the dispersities were very narrow (Đ ≤ 1.10).

The MALDI-ToF-MS spectrum of the LO/PA copolymer obtained by **1** (entry 1, Table 3) showed two distinct series of peaks. Each series exhibited a *m/z* interval of 300 between the consecutive peaks, corresponding to a [LO + PA] repeating unit, in agreement with a perfectly alternating structure of the obtained copolymer (Figure 2).

The thermal analysis showed glass transition temperatures lower than 43°C because of the low molecular weights achieved.



**Scheme 3.** Synthesis of polyesters from phthalic anhydride (PA) and limonene oxide (LO).

**Table 3.** Ring Opening co-Polymerizations of LO with PA promoted by aluminum complexes **1-4**.

<sup>a</sup> Entry	Cat	Time (h)	<sup>b</sup> PA conv. (%)	<sup>c</sup> $M_{nGPC}$ (KDa)	<sup>d</sup> $\bar{D}$	T <sub>g</sub> (°C)
1	<b>1</b>	8	89	2.75	1.07	35.6
2	<b>2a</b>	8	72	2.23	1.07	27.3
3	<b>2b</b>	8	69	2.75	1.10	42.9
4	<b>2c</b>	8	76	3.20	1.08	39.5
5	<b>2d</b>	8	78	2.34	1.09	32.8
6	<b>3</b>	17	80	2.62	1.10	40.7
7	<b>4</b>	17	87	2.53	1.10	30.2

<sup>a</sup>Reaction conditions: cat = 2.0·10<sup>-5</sup> mol, [PA]:[LO]:[cat]:[DMAP] = 125:125:1:1, T = 110 °C, toluene 1 mL. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy of crude reaction mixture. <sup>c</sup>Molecular weight data  $M_{nGPC}$  (g/mol) and  $\bar{D}$  were determined by GPC, in THF vs polystyrene standards.

## Study of the reaction mechanism.

### a. Identification of the reaction intermediates

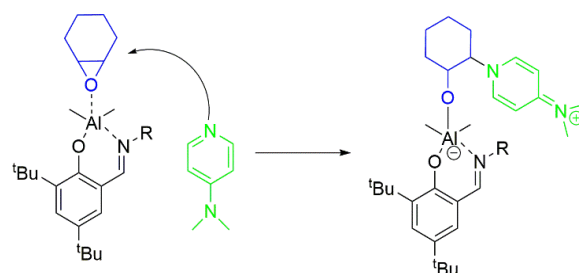
Recently, detailed mechanistic studies regarding the epoxide/anhydride copolymerization promoted by a catalytic system formed by (salph)AlCl and [PPN]Cl have been reported by Tolman and Coates.<sup>79</sup> The authors suggested a mechanism involving two catalytic cycles wherein the alternating copolymerization proceeds via anionic 6-coordinate intermediates formed by combinations of (salph)AlX and [PPN]X (X = alkoxide or carboxylate).

Although these elegant studies clearly elucidate several mechanistic aspects of the copolymerization process, they are tailored for a specific catalytic system.

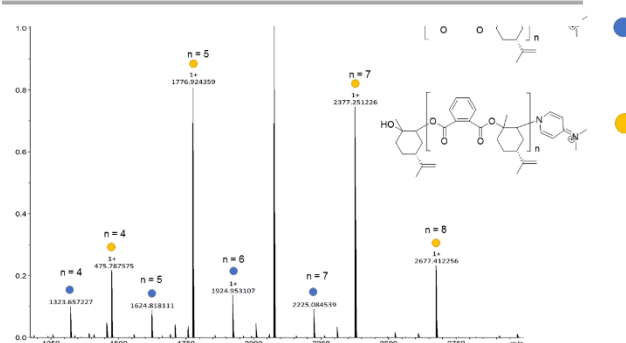
For phenoxy-imine aluminum complexes, characterized by a lower coordination number and activated by a neutral cocatalyst, a different mechanism could be involved.

To have more insights about the structure of the intermediates involved in the polymerization process promoted by phenoxy-imine aluminum complexes, different experiments were performed and monitored by NMR analysis.

Initially, complex **2b** (0.05 M in 0.5 mL of C<sub>6</sub>D<sub>6</sub>) was mixed with 1 equivalent of CHO. No reaction was observed after 1 hour at room temperature and neither upon heating the reaction mixture at 70 °C for 5 h. This was coherent with the results previously reported for complex **1** that was not able to promote the polymerization of cyclohexene oxide.<sup>65</sup>



**Scheme 4.** Formation of zwitterionic species in the initiation steps



**Figure 2** MALDI-ToF-MS spectrum of PA/LO copolymer synthesized by **1** (entry 1, Table 3).

Then, a new experiment was performed by adding one equivalent of DMAP into the solution of **2b** and CHO. After one hour at room temperature the spectrum of the mixture revealed to be a simple overlap of the spectra of the starting compounds suggesting the absence of interaction of CHO and DMAP with the metal center.

The formation of a new species (**2b\***) was observed only after heating the sample at 70 °C for 12 hours.

The <sup>1</sup>H NMR spectrum of **2b\*** (see figure 3) show all signals related to the phenoxy-imine moiety and two singlets (at -0.40 and -0.85 ppm) relative to diastereotopic methyl groups bound to aluminum. Moreover, new resonances corresponding to methyls of a reacted DMAP unit (j) and to protons of an opened CHO monomer unit (g and g') were detected (see Figure 3 and S11). These attributions were confirmed by COSY spectrum (see Figure S12)

A DOSY NMR experiment (see Figure 4) of **2b\*** showed that the signals of the aluminum complex, the opened CHO unit and the DMAP fragment lay at the same diffusion coefficient, and therefore belonged to the same structure.

All these data suggest the formation of a zwitterionic species produced by attack of the DMAP to the CHO unit coordinated at the metal center (scheme 4).

An analogue zwitterionic species **2a\*** was obtained by the reaction of complex **2a** with one equivalent of CHO and DMAP (see Figure S 13).

A diverse behavior was observed with complex **1**.<sup>80</sup> After heating of the reaction mixture **1**/CHO/ DMAP for 24 h at 70 °C, the formation almost quantitative of a new species (**1\***) was observed in which neither CHO and DMAP are involved.

The structure of **1\*** was not completely elucidated but the NMR data (see figures S15 and S16) suggest the formation of a

multinuclear species obtained by a partial hydrolysis of the aluminum-methyl bonds of complex **1** by the adventitious traces of water present or occurring into the sample.<sup>81</sup>

alkyl bonds of the species **1** by water that, progressively, could contaminate the sample.

To confirm the structure of the species **1\*\***, and to have more

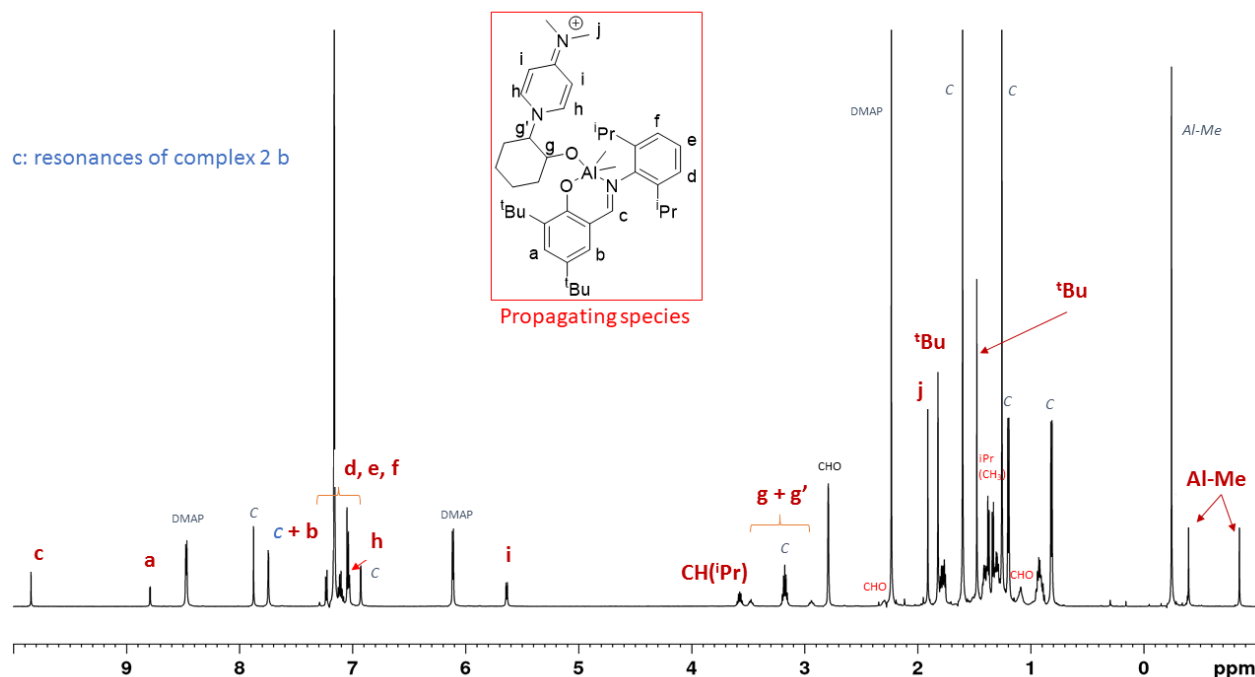


Figure 3. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub> 298 K) of the species **2b\***

After additional 6 hours at 70 °C, the <sup>1</sup>H NMR spectrum revealed the formation of a new species **1\*\*** (Figure S17 of SI) and, after prolonged reaction time (5 days at 70 °C), the quantitative conversion of species **1\*** into species **1\*\*** was obtained.

The structure of species **1\*\*** was established by <sup>1</sup>H-<sup>1</sup>H COSY, and <sup>1</sup>H-<sup>13</sup>C HSQC (Figures 5 and S18, S19 of SI).

All the spectral data were coherent with a rigid multinuclear structure (dimeric or tetrameric) of the type (L-AIO)<sub>n</sub> (n = 2 or 4) in which the aluminum centers are bound via oxygen atom bridges. Once more the CHO and DMAP units appeared as free species, not coordinated at the metal center. This species was reasonably formed by the exhaustive hydrolysis of aluminum-

information about the times required for its formation, **1\*\*** was purposely synthesized by adding the opportune amount of deuterated water to a benzene solution of complex **1**.

Initially, by adding sub-stoichiometric amounts of D<sub>2</sub>O to a solution of complex **1** in deuterated benzene, the species **1\*** was obtained. After the addition of global two equivalents of D<sub>2</sub>O, within 10 min at 70°C, **1\*** was quantitatively converted into the species **1\*\*** (Figure 5 and Figure S20 of SI). This confirmed the nature of the species **1\*\*** and that the hydrolysis of the aluminum-alkyl bonds is fast, in fact it was complete after heating at 70°C for only 10 min.

The structure proposed for **1\*\*** was also addressed through DOSY NMR spectroscopy and mass spectrometry (ESI). Both experiments (see Figure S21 and S22 of SI) support the

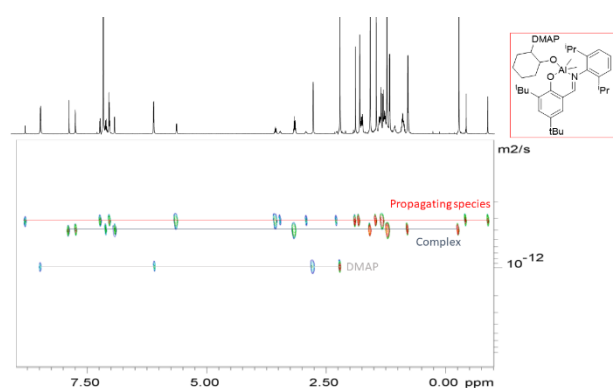


Figure 4. DOSY NMR (600 MHz, C<sub>6</sub>D<sub>6</sub> 298 K) of **2b\***

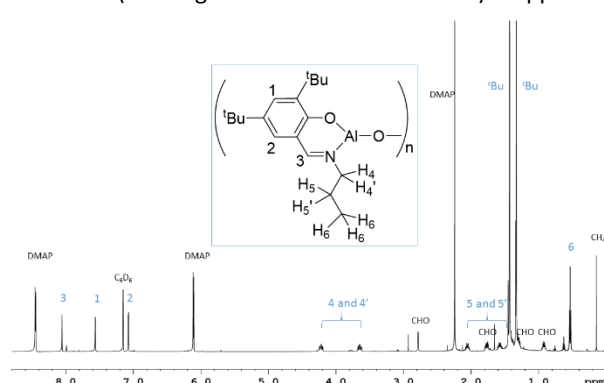


Figure 5. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub> 298 K) of the species **1\*\***

hypothesis that **1\*\*** was a discrete tetrameric species of the type(L-AlO)<sub>4</sub>

the experiments reported in Table 2, **2b\*** revealed a similar behavior (compare entries 11 and 3, Table 2). These observations suggest that **2b\*** is an intermediate of the

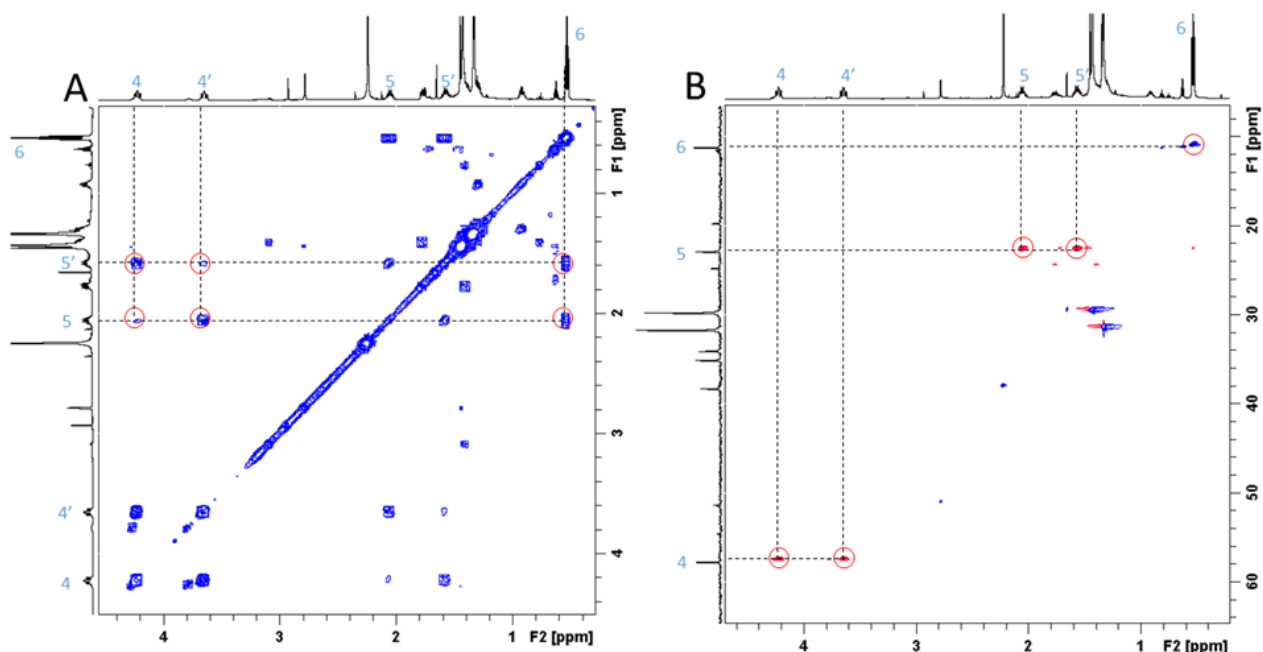


Figure 6 A) A section of the <sup>1</sup>H COSY NMR spectrum of **1\*\***) and B) a section of HSQC NMR spectrum of **1\*\*** (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)

These studies put in evidence a different behavior of complex **1** in comparison to complexes **2a** and **2b**. In fact, in the presence of one equivalent of both monomer and cocatalyst, **2a** and **2b** produced zwitterionic species derived from the attack of DMAP at the coordinate CHO unit. Otherwise, complex **1** was not able to promote the direct formation of an analogue intermediate, but it evolved into a multinuclear species by side hydrolysis reactions.

This aspect was rationalized by analysis of the structure of complex **1** in benzene solution by DOSY experiments. These showed a dimeric structure of complex **1** in the concentrations used, probably as consequence of the reduced steric encumbrance offered by the ancillary ligand. It is reasonable that in the dimeric structure the coordination of the monomer at the metal center could be failed.

This could explain the different behavior of complex **1** in the CHO/SA copolymerization performed in solution and in bulk.

Possibly, when the reaction is performed in bulk, the high concentration of catalyst favors the formation of bimetallic species with a consequent reduction of the catalytic activity.

#### b. Tests of reactivity of the intermediates.

To test the role of the identified intermediates in the polymerization process, **2b\*** was used as catalyst in the ROCOP of CHO/SA. Under the same reaction conditions described for

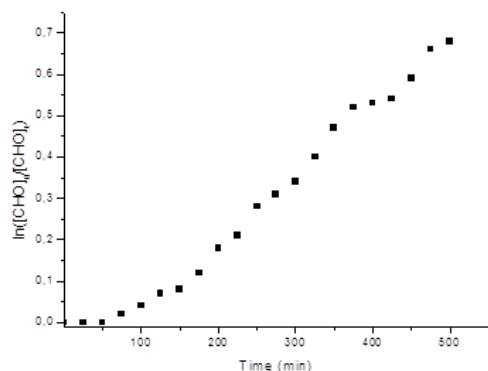
polymerization process formed in the initiation step in which the aluminum center of the complex acts as a Lewis acid coordinating an epoxide unit that is subsequently attacked by the cocatalyst.

Subsequently, these studies were extended to **1\*\*** species. Although the monomers used in these experiments were purified by conventional techniques, they could contain protic impurities, due to their high hydrophilicity. Thus, it is reasonable to believe that species **1\*\*** could be formed also in the polymerization medium. On the other hand, bimetallic aluminum species of the type (salen)Al μ-oxo dimers<sup>82, 83</sup> were described by different authors as efficient catalysts for asymmetric Michael additions<sup>84</sup> and for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides.<sup>85</sup> Thus, we decided to investigate the catalytic relevance of species **1\*\*** in the copolymerization of CHO with succinic anhydride.

Firstly, an equivalent of succinic anhydride was added into the solution containing species **1\*\***, the unreacted CHO and DMAP, the resulting mixture was heated at 80 °C for 1 hour. After this time, no variation of the structure of species **1\*\*** was detected (Figure S17 of SI). Reasonably, the low concentration of both the monomers was not suitable for the formation of an active species because of the high stability of the multinuclear species **1\*\***.

Consistently with this rationale, after the addition of five equivalents of SA and of CHO, the <sup>1</sup>H NMR analysis showed a distinctive evolution of the species **1\*\***, consisting with the disappearing of the rigid multinuclear structure and of the free

DMAP, and the progressive consumption of both monomers. This new species did not change during all the polymerization process and showed a structure coherent with a phenoxy-imine aluminum complex bearing a growing chain (Figure S18 of SI). Kinetics studies of such polymerization process (figure 7) showed the existence of an induction period (about 50 minutes), possibly a consequence of the initial inertia of the multinuclear species **1\*\*** that slowly converted to the putative propagating species.



**Figure 7** Plot of  $\ln([CHO]_0/[CHO]_t)$  vs time. (The linear fit depicting a reaction order of unity with respect to monomer concentration is reported in Figure S19 of the SI).

After this time, the polymerization rate was first-order dependent on the CHO concentration (with a  $k_{app} = 1.66 \cdot 10^{-3} \text{ min}^{-1}$  and  $R^2 = 0.990$ ) as previously observed by different authors (figure S25 of SI)

Kinetics studies were repeated under reaction conditions analogous to those described in table 2 for the copolymerization experiments: at  $100^\circ\text{C}$  and in deuterated toluene solution. In this case no induction period was detected, and the polymerization rate was first-order dependent on the CHO concentration (figure 8). Thus, the inertia of the species **1\*\*** can be easily overcome operating under the polymerization reactions, i.e. in the presence of high concentration of the monomers and at high temperature.

As last verification, **1\*\*** was tested as catalyst in the ROCOP of CHO/SA under the usual same reaction conditions described for the experiments reported in Table 2 showing a similar behavior (compare entries 12 and 1, Table 2). The MALDI-ToF analysis of the obtained polymer showed structure already discussed (figure S26 of SI)

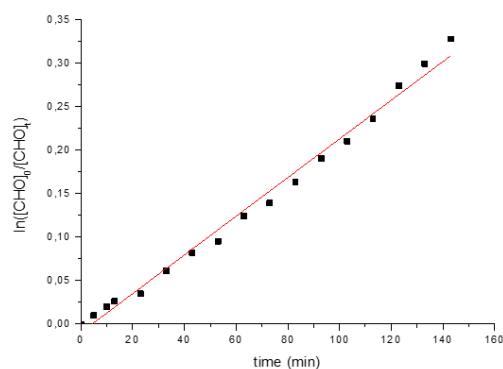
In summary, these studies suggest that for phenoxy-imine aluminum complexes the metal center acts simply as Lewis acid coordinating an epoxide unit. This undergoes a nucleophilic attack by the cocatalyst producing a zwitterionic species that is an intermediate of the polymerization process.

In the case of complex **1**, the dimeric structure favored in concentrate solutions, prevents the coordination of the monomer thus new multimetallic species are produced by hydrolysis side reactions of the aluminum-methyl bonds due to the presence of water within monomers and/or the co-catalyst.

However, under the reaction conditions used for the ROCOP, also these species evolve toward the formation of a propagating species bearing a growing chain with a DMAP end unit.

## Experimental

**Materials and methods.** All manipulations of air- and/or water-



**Figure 8** Plot of  $\ln([CHO]_0/[CHO]_t)$  vs time describes a reaction order of unity with respect to monomer concentration,  $k_{app} = 2.22 \cdot 10^{-3} \text{ min}^{-1}$  ( $R^2 = 0.990$ ).

sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glovebox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at  $120^\circ\text{C}$  overnight and exposed three times to vacuum–nitrogen cycles.

Benzene, hexane and toluene (Sigma-Aldrich) were distilled under nitrogen over sodium benzophenone. The aluminum precursor  $\text{AlMe}_3$  was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. Cyclohexene oxide and limonene oxide were purchased from Sigma-Aldrich and distilled over  $\text{CaH}_2$ . All other chemicals were commercially available and used as received unless otherwise stated.

NMR spectra were recorded on Bruker Avance 250, 300, 400 and 600 MHz spectrometers at 298 K, unless otherwise stated. Chemical shifts ( $\delta$ ) are expressed as parts per million and coupling constants (J) in hertz.  $^1\text{H}$  NMR spectra are referenced using the residual solvent peak at  $\delta = 7.16$  for  $\text{C}_6\text{D}_6$  and  $\delta = 7.27$  for  $\text{CDCl}_3$ .  $^{13}\text{C}$  NMR spectra are referenced using the residual solvent peak at  $\delta = 128.06$  for  $\text{C}_6\text{D}_6$  and  $\delta = 77.23$  for  $\text{CDCl}_3$ . The measurement of diffusion has been carried out by observing the attenuation of the NMR signals during a pulsed field gradient experiment using the double stimulated echo pulse sequence.<sup>86, 87</sup> In particular, 2D DOSY PGSE NMR spectra were performed on a Bruker Avance 600 spectrometer at 298 K without spinning.

Mass spectra were acquired using a Bruker solarix XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T

refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were ionized in positive ion mode using the MALDI ion source.

Glass transition temperature (T<sub>g</sub>) of the polymers were measured by differential scanning calorimetry (DSC) using a DSC 2920 apparatus manufactured by TA Instruments under a nitrogen flux of 50 mL min<sup>-1</sup> with a heating and cooling rate of 10 °C min<sup>-1</sup> in the range -10 to 200 °C. All calorimetric data were reported for the second heating cycle.

## Conclusions

The ring-opening copolymerization of succinic anhydride and cyclohexene oxide in the presence of differently substituted phenoxy-based aluminum complexes, in combination with equimolar amounts of DMAP as co-catalyst, was studied. All complexes showed activities higher than those reached with traditional salen aluminum complexes. Good activities were achieved also in the copolymerization of limonene oxide with phthalic anhydride.

A study of the effects of the structure of the ancillary ligands on the activity and the selectivity of complexes revealed that higher activities are obtained with phenoxy-imine complexes especially when electron-donating substituents are attached to the phenoxy-moiety. For phenoxy-amine or phenoxy ether complexes lower activity and selectivity are achieved.

A clear role of DMAP in the initiation step emerged by the NMR studies of the active species as well as by the MALDI ToF analysis of the obtained polymers showing that the first event of the polymerization process is the opening of an epoxide unit coordinated at the metal center by the nucleophilic attack of DMAP. The resulting zwitterionic species in which the aluminium center is pentacoordinate was identified as a plausible intermediate of the polymerization reaction.

## Conflicts of interest

There are no conflicts to declare

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