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Ring-Opening Co-polymerization of Epoxides with Cyclic Anhydrides promoted by Bimetallic and Monometallic Phenoxy-Imine Aluminum complexes.

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Abstract: Two dinuclear aluminum alkyl complexes bearing salen ligand with alkyl backbone of different length between the nitrogen atoms (1,3-propylene (**1**) and 1,5-pentylene (**2**)) and the related hemi-salen aluminum complex (**3**) were tested as catalysts in the ring-opening copolymerization of cyclohexene oxide (CHO) and limonene oxide (LO) with succinic anhydride (SA) and phthalic anhydride (PA). The effects of different reaction conditions (cocatalyst and reaction solvent) on the productivity and selectivity of the reactions were evaluated. The comparison of the catalytic behavior of the dinuclear complexes bearing the aluminum reactive centers at different distances as well as of their mononuclear counterpart suggested that the copolymerization follows a monometallic pathway differently from what observed in the homopolymerization of CHO.

Introduction

Aliphatic polyesters are emerging as an important class of materials alternatives to petroleum-based polymers.[1] They are biodegradable and often biocompatible and, for these properties, they find application both as commodities for packaging materials[2] and in niche markets, for the production of biomedical devices.[3]

Different synthetic approaches can be used to produce polyesters.[4] The most traditional one is the polycondensation of diols with diacids; however, this method requires high temperatures to remove the byproducts for achieving high molecular weight polymers with significant consequences on the energy costs and on the control of polymerization process. Alternatively, these polymers can be produced by the ring-opening polymerization (ROP) of the related cyclic esters.[5] Although this synthetic method allows to use mild reaction conditions for the production of high molecular weight polymers even with sophisticated microstructures,[6] its usefulness is limited by the restricted availability of structurally different monomers.

A more versatile way for producing polyesters with variable architectures is the alternating ring-opening co-polymerization (ROCOP) of epoxides and cyclic anhydrides.[7] This synthetic approach is very promising thanks to the wide availability of relatively cheap monomers[1b, 8] but it suffers from the restricted availability of catalytic systems able to produce high molecular weight polymers with rigorously alternate microstructures.

The first remarkable example of catalyst able to promote this reaction was the 2-cyano-β-diketiminato zinc complex reported by Coates and co-workers in 2007.[9] After this discovery, few successful single catalysts active in the ROCOP of epoxides and anhydride have been reported.[7a] The most significant examples include complexes of trivalent metals such as Cr (III), Co (III), Mn (III) or Al (III) with tetradentate dianionic ligands such as porphirinate,[10] salen,[11] salan[12], and of type OSSO[13] or ONSO.[14]

More recently, bimetallic chromium and aluminum complexes showed improved performances in comparison to the related monometallic derivatives, [12],[15] suggesting the hypothesis of a bimetallic mechanism for the ROCOP of epoxide/anhydride, as already suggested for the homopolymerization of epoxides[16] and the epoxide/CO_2 copolymerization.[17] In this context, noteworthy examples are the homo- and hetero- bimetallic complexes of magnesium and zinc reported by Williams. These showed high selectivity towards polyester formation without any addition of nucleophilic cocatalysts.[18] Other contributes are the bimetallic complexes of nickel, cobalt and zinc reported by Ko.[19]

Recently, we used traditional salen ligands, with alkyl backbone of different length between the nitrogen atoms, as coordinative environments for the synthesis of bimetallic aluminum complexes as catalysts for the ROP of racemic lactide (*rac*-LA) and cyclohexene oxide (CHO). In the ROP of *rac*-LA, we demonstrated that, when the architecture of the ligand forces the two coordinative pockets in proximal positions, higher activity and stereoselectivity are achieved, thanks to the cooperation between the two metal centers. [20]

More interestingly, the bimetallic species bearing aluminum centers spatially adjacent is the only one active in the homopolymerization of cyclohexene oxide, thus confirming the hypothesis of a bimetallic mechanism.[20]

On the base of these results, and considering that intramolecular bimetallic synergistic effects were recently invoked in the ROCOP of epoxides with anhydrides,[12] we decided to explore the behavior of the bimetallic and monometallic phenoxy-imine aluminum complexes in the copolymerization of cyclohexene oxide (CHO) and limonene oxide (LO) with succinic (SA) and phthalic (PA) anhydrides. The effects of the use of different cocatalysts and reaction conditions were also evaluated.

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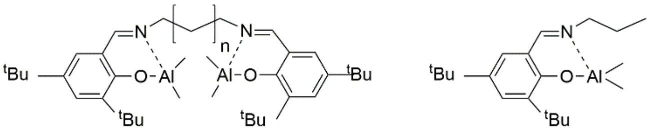
Finally, a comparison of the catalytic behavior of the bimetallic phenoxy-imine aluminum complexes and of the related monometallic complex was performed to verify the hypothesis of bimetallic mechanism.

Results and Discussion

Copolymerization of cyclohexene oxide with anhydrides.

The bimetallic aluminum-alkyl complexes **1** and **2** were obtained, in quantitative yields, by direct reaction between the salen proligands and two equivalents of $AlMe_3$. Similarly, complex **3** was produced by reaction of the phenoxy-imine proligand with a single equivalent of $AlMe_3$ (Scheme 1).[20-21]

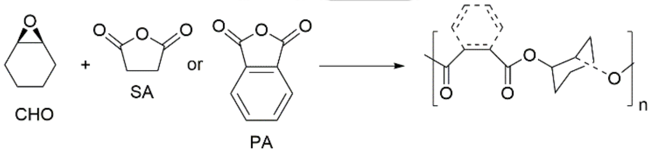


1 n = 1
2 n = 3

3

Scheme 1. Bimetallic aluminum complexes **1** and **2** and the phenoxy-imine complex **3**.

Initially, we investigated the copolymerization of succinic anhydride (SA) and cyclohexene oxide (CHO) employing the bimetallic aluminum complex **1** (scheme 2) under different reaction conditions. The polymers produced were characterized by ^1H NMR, GPC and MALDI-ToF-MS analyses. Selected data are reported in Table 1. The composition of the obtained polymers was estimated by ^1H NMR analysis, by comparing the integrals of the signals of epoxide/anhydride sequences with those of sequential enchainment of epoxides. Generally, the NMR spectra performed in $CDCl_3$ do not allow a good estimation because of the overlapping of the polyether signals with the signals of chain end groups of the polyesters. Williams solved this problem performing these analyses in deuterated DMSO.[18c] Alternatively, we observed that the use of a high resolution ^1H NMR analysis allowed a faultless separation of the resonances enabling the precise determination of the ratio of the two sequences. Thus, the microstructural analyses of all polymers were performed in $CDCl_3$ by using a 600 MHz spectrometer.



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

The copolymerization reactions CHO/SA were initially performed at 110 °C in the absence of solvent, with an epoxide:anhydride:catalyst ratio of 250:250:1. Under these conditions, complex **1** was a very active catalyst; the almost quantitative conversion of CHO was achieved after less than 1 hour (entry 1, Table 1). The polymer obtained was a poly(ester-ether), with 54% of ester functionalities.

In toluene solution, the activity was significantly lower as a consequence of the reduced concentration of the monomer (entry 2, Table 1). At the same time, a discrete increment of the selectivity was observed (63% of ester linkages), as a consequence of the reduced rate of the CHO homopolymerization in toluene solution, as previously reported.[20]

According to recent published data concerning the ROCOP of epoxides and cyclic anhydrides promoted by porphyrinato and salophen chromium catalysts,[22] and as frequently reported in the reaction between epoxides and CO_2,[23] the presence of a nucleophilic cocatalyst has benefical effects on the catalytic activity and selectivity. In fact, the addition of one equivalent of DMAP (4-(N,N dimethylamino)pyridine) clearly improved the anhydride incorporation and therefore the ester content (up to 94%) of the obtained polymer (entry 3, Table1). When the amount of cocatalyst was doubled, the activity did not change significantly, while a certain increment of selectivity was observed and the percentage of esters linkages reached 97% (entry 4, Table 1, see figure 1). Performing the reaction in toluene solution and in the presence of two equivalents of DMAP (entry 5, Table1), the copolymerization proceeded in an exclusive alternating fashion with an ester content linkages > 99%. Increasing the amount of DMAP up to 8 equivalents, the selectivity of the process was preserved with a significant increase of the activity (entry 6, Table1).

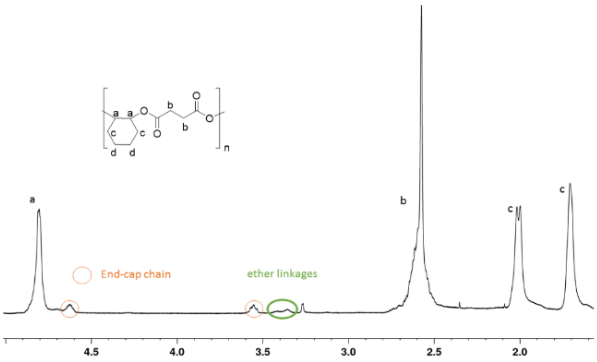


Figure 1. ^1H NMR spectrum (600 MHz, $CDCl_3$) of the SA/CHO copolymer obtained in entry 4 of Table 1.

Complex **1** showed very high activities, much higher than those reported for all the previous investigated monometallic penta-coordinate salen aluminum complexes.[24] In terms of turnover frequencies (TOF calculated on catalyst concentration), complex **1** showed TOF up to 250 h^{-1} and 72 h^{-1}, in bulk and in solution, respectively (entries 3 and 6 of Table 1). Under the same reaction conditions, the monometallic penta-coordinate salen aluminum complexes showed activities in the ranges 25 h^{-1}<TOF < 100 h^{-1} and 15 h^{-1}<TOF < 50 h^{-1}, for reactions performed in bulk and in solution respectively, depending on the structure of the ligand-diimine backbone.[24]

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Table 1. Ring Opening co-Polymerization of CHO withanhydrides promoted by **1**[a]

Entry	Cocat (equiv)	Anhydride	Conditions	Time (min)	[b]CHO conv. (%)	[b]ester (%)	[c]M_{nGPC} ($\times 10^3$)	[c]PDI
1	-	SA	bulk	50	94	54	5.51	1.56
2	-	SA	toluene	300	100	63	5.34	1.43
3	DMAP (1)	SA	bulk	50	84	94	1.78	1.18
4	DMAP (2)	SA	bulk	50	79	97	1.98	1.16
5	DMAP (2)	SA	toluene	240	84	>99	1.81	1.19
6	DMAP (8)	SA	toluene	180	87	>99	1.45	1.19
7	DMAP (2)	MA	toluene	300	66	45	0.75	2.20
8	DMAP (2)	PA	toluene	240	85	98	3.56	1.06

[a] Reaction conditions: **1** = 1.10-5 mol; [**1**]/[CHO]/[anhydride] = 1:250:250; T= 110 °C; 1 mL of toluene. [b]Determined by 1H NMR spectroscopy of crude reaction mixture. [c] MnGPC and PDI were determined by GPC, in THF vs polystyrene standards.

The GPC analysis of all obtained polymers displayed always monomodal distributions with narrow polydispersity indexes (<1.23) for polymers obtained in the presence of cocatalyst, indicating a controlled behaviour of the ROCOP reaction. The number average molecular weight values (M_n) measured by GPC (without any calibration correction) were coherent with the values calculated by evaluation of chain end groups performed by NMR, and they were always lower than the theoretical ones expected for a living system.

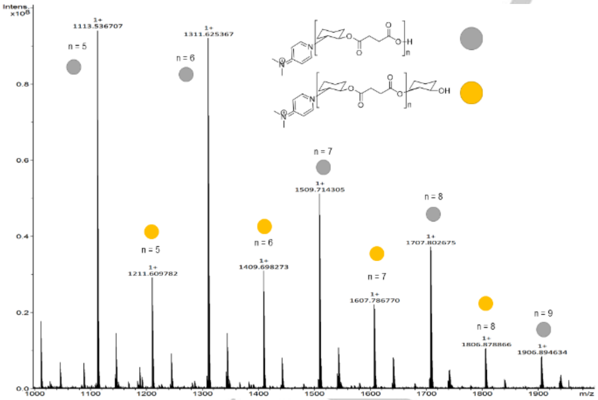

Figure 2. MALDI-ToF-MS spectrum of SA-CHO copolymer synthesized in entry 6 of Table 1

Many authors observed this discrepancy and they often attributed this to the presence of protic impurity traces, such as diacid resulting from hydrolyzed anhydride and/or trace of water, that can act as chain transfer agents (CTAs).[25] On the other hand, this means that the activity of the catalytic system is not compromised by the presence of protic species in the polymerization medium.

The MALDI-ToF-MS spectrum of the crude product obtained by catalyst **1** in bulk without the addition of cocatalyst (entry 1, Table 1), showed two major distributions (see figure S1 of supporting information) having a lightly higher CHO than SA content, coherently with the NMR evaluation. One series corresponds to linear polymer chains with a methyl and an hydroxyl end group while the other series describes α,ω-hydroxy-terminated chains, probably originated by nucleophilic attack of the methyl group of the catalyst and of water present in traces, respectively. Cyclic products are also observed, because of intramolecular transesterification side reactions occurring during the polymerization.

The MALDI-ToF-MS spectra of the polymers obtained in the presence of DMAP as the cocatalyst (entry 6, Table 1) showed two distinct distributions, both corresponding to linear polymer chains consisting in sequences of [CHO+SA] repeating units, coherently with perfectly alternating structures containing more than 99% of ester linkages (Figure 2). Cyclic products were not detected. End group determination revealed exclusively DMAP end-capped chains. [26]

Subsequently, we screened different anhydrides under the same conditions optimized for CHO/SA copolymerization.

Since polyesters with backbones containing aromatic or semi-aromatic repeating units, thanks to their good physical properties are materials of remarkable interest that cannot be obtained by ROP,[11c] we extended our studies to the phthalic (PA) (see entry 7 of Table 1). For the CHO/PA copolymerization the activity was identical to that obtained with SA, although a not perfect selectivity was observed (entry 8 of Table 1).

The copolymerization of CHO with maleic anhydride (MA) showed low conversion and poor selectivity (see entry 7 of Table 1).

As already discussed, the molecular weights of the obtained polymers were lower than the expected ones.

Effect of the Cocatalyst and of the solvent

The preliminary tests of copolymerization of CHO with the phthalic anhydride revealed that this is a very reactive monomer although the polymerization reaction was not perfectly selective. Considering that the nucleophilic cocatalysts were also found to play an important role during the epoxide/anhydride copolymerization, not only in terms of activity but also of selectivity,[24] we decided to investigate the effect of different cocatalysts on the ring-opening copolymerization of CHO with phthalic anhydride.

Herein we have studied and compared the effect of different types of nucleophilic cocatalysts, including several ammonium salts and the (bis(triphenylphosphine)iminium) salt. Because of the scarce solubility of ionic cocatalysts in toluene, the copolymerizations were performed in CH_2Cl_2 at 50 °C. The main results are given in Table 2.

Table 2. Copolymerization of CHO-PA in CH_2Cl_2 catalyzed by **1** with Different Cocatalysts.[a]

Entry	Cocat (equiv)	[b]CHO conv (%)	[b]Ester (%)	[c]M_{nGPC} (×10^3)	[c]PDI
1	DMAP (2)	20	71	1.76	1.09
2	DMAP (8)	40	97	2.88	1.16
3	PPNCl (2)	21	89	1.67	1.22
4	PPNCl (4)	25	95	4.49	1.14
5	PPNCl (8)	61	>99	2.45	1.40
6	TBABr (2)	30	90	2.88	1.12
7	TBABr (4)	35	>99	3.00	1.17
8	TBABr (8)	46	>99	2.89	1.17
9	TBACl (2)	21	81	1.99	1.08
10	TBAI (2)	16	76	1.68	1.07
11	PPh_3 (2)	16	76	1.63	1.08

[a] All reactions were carried out with 10 μmol of **1** at 50 °C, in 1 mL of dichloromethane, [**1**]/[CHO]/[anhydride] = 1:250:250. [b] Determined by ^1H NMR after 20 h. [c] Experimental M_n and PDI values were determined by GPC analysis in THF using polystyrene standards.

In the experiments in which two equivalents of cocatalyst were used, no remarkable differences in terms of activity were observed and, in all cases, the conversions achieved were around 20%, after 20 hours (entries 1, 3, 10 and 11 of Table 2). Noteworthy, significant effects were instead observed on the selectivity of the catalytic process. In methylene dichloride, DMAP revealed to be less selective than in toluene solution (entry 1, Table 2). Although even the reaction temperature was changed, the observed decrease in the percentage of ester linkages is attributable to the nature of the solvent rather than the different temperature. In fact, previous studies performed by Coates[11b] and Duchateau[24] showed that the hydrocarbon solvents have beneficial effects on the selectivity of the catalytic process.

The cocatalysts PPNCl and TBABr resulted to be the most selective, producing polymers with about 90 % of ester linkages (entries 3 and 6 of Table 2). Among the ammonium salts, TBAX (X = Cl, Br, I), the highest selectivity was obtained by the bromide salt (entries 6, 9 and 10 of Table 2). Among the two chloride salts PPNCl and TBACl, the first one resulted more selective (entries 3 and 9 of Table 2), reasonably the nucleophilicity of the anion chloride is influenced by the nature of the associated cation since, in methylene chloride solution, the ions exist in the form of ion pairs linked electrostatically.

By using 4 equivalents of the cocatalyst TBABr a perfect selectivity of the reaction was obtained (entry 7 of Table 2). To achieve the same results with PPNCl, eight equivalents were necessary (entries 5 and 8 of Table 2), while with the same molar amount of DMAP, lower selectivity was still achieved (entry 2 of Table 2). Poor activity and selectivity were obtained when PPh_3 is used as cocatalyst (entry 11 of Table 2).

These results suggest that the selection of the optimal cocatalyst depend on the polarity of the reaction medium. Thus, ionic cocatalysts are more efficient in polar solvents, while neutral ones are the best choice when less polar solvents are used. To confirm this hypothesis, we tested the cocatalysts that revealed to be the most efficient in methylene chloride, TBABr and PPNCl, also in toluene. Performing the same reactions in toluene, the activities and selectivities of TBABr and PPNCl diminished drastically, reasonably because of the low solubility of these species. A significant reduction of the selectivity was also evident (entries 1 and 2 of Table 3).

Table 3. Copolymerization CHO-PA in toluene solution catalyzed by **1** with different cocatalysts.[a]

Entry	Cocat	[b]CHO conv (%)	[b]Ester (%)	[c]M_{nGPC} (×10^3)	[c]PDI
1	TBABr	30	76	2.05	1.09
2	PPNCl	54	64	2.34	1.09
3	PPh_3	42	76	2.13	1.08
4[d]	TBABr	91	91	3.38	1.11
5[d]	PPNCl	91	75	4.27	1.15
6[d]	DMAP	81	98	4.33	1.10

[a] All reactions were carried out with 10 μmol of **1** at 110°C, in 1 mL of toluene, [**1**]/[cocatalyst]/[CHO]/[PA] = 1:2:250:250. [b] Determined by ^1H NMR after 5 h. [c] Experimental M_n and PDI values were determined by GPC analysis in THF using polystyrene standards. [d] Catalyst dissolved in 0.1 mL of CH_2Cl_2.

The neutral cocatalyst PPh_3 resulted a poor cocatalyst also in toluene solution. To avoid spurious effects due to the different solubility of cocatalysts, we performed additional polymerizations

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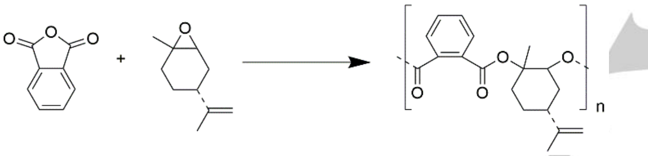
by dissolving preventively the cocatalysts in the minimum amount of CH_2Cl_2 and adding the resulting solution in the reaction medium (toluene). Not surprisingly, the obtained results confirmed that, in toluene solution, ionic cocatalysts were less selective than the neutral DMAP (entries 4-6 of Table 3).

Copolymerization of limonene oxide with anhydrides.

Limonene oxide (LO) is a biorenewable-based resource derived from the (R)-limonene, a naturally occurring terpene that is available in large amount in the peel of many citrus fruits. As non-food resource, it represents a great opportunity for sustainable catalysis. As monomer, it is used for copolymerization with CO_2[27] and with anhydrides.[28] Additionally, bearing a vinyl pendant group as extra functionality, it offers the opportunity of post-polymerization modifications to functional polymers.33,[29] Considering the structural analogies between CHO and LO, we decided to explore the reactivity of the commercially available monomer: the mixture of *cis* and *trans* R limonene oxide in the ROCOP with phthalic anhydride (scheme 3). Complex **1**, activated by DMAP, showed a very high activity in bulk allowing an almost quantitative conversion of the monomers in two hours (entry 1, Table 4). As expected, in toluene solution, the activity of **1**/DMAP decreased drastically because of dilution effects, as already observed for the CHO copolymerization (entry 3, Table 4).



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

Table 4. Ring Opening co-Polymerization of LO with PA promoted by **1** and **3**.[a]

Entry	Cat	[c]LO conv (%)	Time (h)	[d]M_{nGPC} ($\times 10^3$)	[d] PDI	Tg (°C)
1	**1**	72	2	3.75	1.15	52.9
2	**3**	91	2	4.36	1.15	83.7
3 [b]	**1**	56	5	2.30	1.10	-
4 [b]	**3**	63	5	2.42	1.16	12.3

[a] Reaction conditions: [LO]:[PA]:[cat]:[DMAP] = 250:250:1:2; T= 130 °C, [b] 1 mL of toluene. [c] Determined by ^1H NMR spectroscopy. [d] M_{nGPC} (g/ mol^{-1}) and PDI were determined by GPC, in THF vs polystyrene standards.

Interestingly, the bimetallic aluminum complex **1** showed higher activities in comparison to the related monometallic penta-coordinate salen aluminum complex, for which less than 30% of monomer was converted and no isolable polymer was obtained. The ^1H NMR analysis of the copolymers obtained showed, in all cases, the absence of ether linkages, thus perfectly alternated copolymers were obtained, as expected because of the bulky nature of LO. The microstructure elucidated by the ^{13}C NMR analysis showed atactic polymers, coherently with the achiral structure of the catalyst (see Figure S6 of ESI).

As already observed in the ROCOP of CHO/SA, the molecular weights of obtained polymers were systematically lower than the theoretical values for a living catalyst system, as a consequence of the protic impurities present in the polymerization medium. However, complex **1** was able to exert good control on the polymerization. The evolution of molecular weights of the polyesters plotted against the PA conversion (Figure 3 and Table S1 of the ESI) displayed a linear correlation while the molecular weight distributions remained narrow (PDI < 1.22).

The MALDI-ToF-MS spectrum of the crude product obtained by **1**/DMAP (entry 1 of Table 4) showed two distinct series of peaks. Each series exhibited an m/z interval of 300 between the consecutive peaks, corresponding to a [LO + PA] repeating unit, confirming a perfectly alternating structure of the obtained copolymer. The two distributions correspond to DMAP end-capped chains, hydroxyl functionalized, consisting of n PA and (n + 1) LO units and n [PA+ LO] units, respectively (Figure 4).

Mechanism and Kinetics.

We observed that bimetallic complex **1** showed a catalytic activity higher than that achieved with the penta-coordinate monometallic aluminum complexes bearing analogous ligands.[24] To verify the role of a possible cooperation between aluminum centers, we compared the catalytic behaviour of complex **1** with those of complexes **2** and **3.**

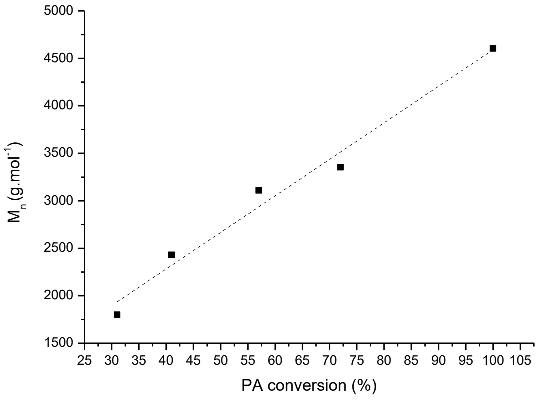


Figure 3. Linear dependence of M_n *vs* conversion of PA for ROCOP catalysed by complex **1** (R = 0.974). Polymerization conditions: [**1**]:[DMAP]:[PA]:[LO]=1:2:250:250, T = 130°C.

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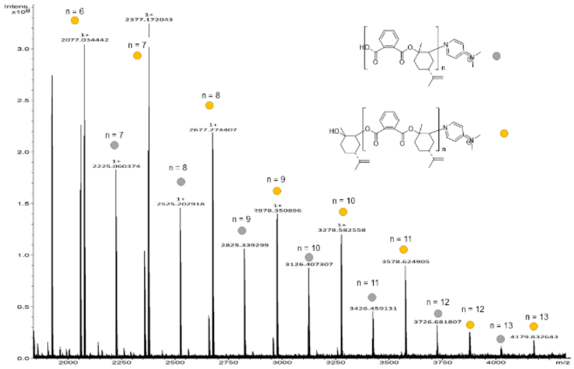


Figure 4. MALDI-ToF spectrum of LO/PA copolymer obtained by **1**/DMAP (entry 3 of Table 4)

In complex **2,** the presence of a long alkyl bridge (five methylene groups) between the imine functionalities precludes the interaction between the reactive centers. Complex **3** is the related monometallic species, whose structure reproduces the coordinative environment of each aluminum center of the dinuclear complexes **1** and **2**.

All complexes were used as catalysts in the ROCOP of CHO/SA, in the same molar concentration. The reactions were performed in the toluene solution and in the presence of two equivalents of DMAP.

Complexes **1** and **3** showed the same activity (CHO conversion of 26 and 28 % after 50 mins, respectively), suggesting that for the bimetallic complex **1** a single aluminum center is involved in the catalytic process and that no cooperation takes place between the metal centers, although chain transfer phenomena between the two aluminum atoms are plausible. Reasonably, the simultaneous growth of two chains on complex **1** is precluded because of the excessive steric encumbrance, as previously observed for the same complex in the ROP of LA.[20] Coherently, a doubled activity (CHO conversion = 53% after 50 min) was achieved with complex **2.** In this case, the longer distance between the aluminum atoms allows the growth of two polymeric chains, one for each metal center.

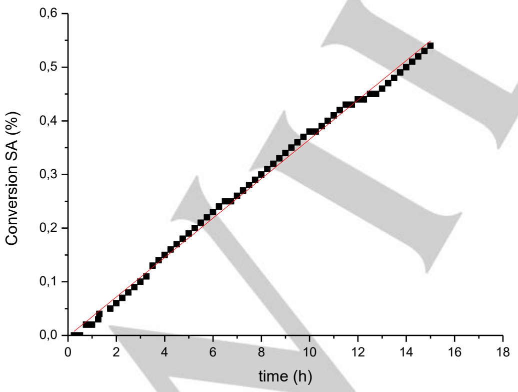
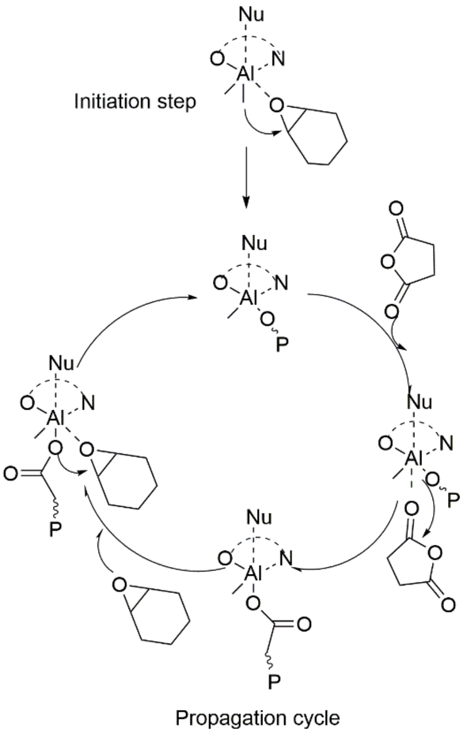


Figure 5. Linear dependence of the SA conversion vs time**.** R^2 = 0.9959.

Analogous results were obtained by complexes **1** and **3** in the LO/PA copolymerization, both in bulk and in solution (entries 2 and 4, Table 4). These observations suggest that no cooperation between the adjacent aluminum centers is operative in the ROCOP promoted by these systems, thus the activity is depending only by the concentration of the active aluminum centers present in the reaction medium and not by their proximity.

To have more insight in the copolymerization mechanism promoted by complex **1,** we studied the kinetics of the reaction and in particular the relationship between succinic anhydride conversion and reaction time (Figure. 5). The ^{1}H NMR data showed a linear dependence of the % SA conversion vs. time signifying a zero order dependence of the rate on SA concentration. Thus, the rate of polymerization is not depending on the concentration of succinic anhydride, suggesting that the rate-determining step of the copolymerization is the insertion of the epoxide on the carboxylate intermediate to regenerate the metal alkoxide intermediate, as already reported by other authors.[11a, 18c, 30]

These observations suggest the reaction mechanism described in scheme 4.



Scheme 4. Mechanism for epoxide/anhydride copolymerization promoted by phenoxy-imine aluminum complexes.

Initiation step proceeds by ring opening of the epoxide by an initiation group that can be the labile group bound to the metal catalyst or the nucleophilic cocatalyst. The resulting metal alkoxide intermediate reacts with the anhydride to produce a metal carboxylate intermediate. The propagation steps consist in iterative and alternate insertions of the two monomers. Since the rate determining step is the insertion of the epoxide on the carboxylate intermediate, the presence of a Lewis base/ nucleophilic cocatalyst has a very significant role, since coordinating to the central metal ion can modulate the acidity of the reactive center and improve the lability of the carboxylate intermediate. We speculate that the lower coordination number of these complexes in which the reactive aluminum center is tetra-coordinate in comparison to the traditional penta-coordinate complexes allows the simultaneous coordination of the nucleophilic cocatalyst and of the incoming epoxide monomer at the same aluminum center. Thus, the attack of the carboxylate growing chain on the coordinated epoxide can occur in an intramolecular way increasing the reaction rate**.**

Thus, two different mechanisms are operative for these catalysts in the homopolymerization of CHO and in the co-polymerization of CHO with SA, respectively. For the homopolymerization of CHO a bimetallic coordination-insertion mechanism was proposed in which one of the Lewis acidic metal centers binds the incoming monomer and activates it for the nucleophilic attack by the growing polymer chain bound to the proximal aluminum atom Otherwise, in the copolymerization reaction a monometallic pathway is more plausible.

Conclusions

Bimetallic phenoxy-imine aluminum complexes are effective catalysts in ring opening copolymerization of cyclohexene oxide with succinic and phthalic anhydrides. ^{1}H NMR analysis and the MALDI-ToF-MS spectra of obtained copolymers show completely alternating microstructures. The good control of the polymerization processes was also confirmed by the narrow polydispersity indexes of the molecular weights and by their linear relationship toward the conversion of the monomer. Analogous results were obtained in the ROCOP of the less reactive limonene oxide with the phthalic anhydride.

The effects of different cocatalysts and reaction solvents were also investigated, revealing that non-ionic cocatalysts, such as DMAP, are more selective in apolar media while ionic cocatalysts are more efficient in polar solvents such as methylene chloride. The higher activity showed for these complexes in comparison to the related penta-coordinate aluminum complexes suggests that lower coordination of the reactive aluminum centers could have a role in promoting the reaction rate since they permit the simultaneous coordination of the nucleophilic cocatalyst and the incoming epoxide monomer. The comparison of the catalytic behavior of the dinuclear complexes bearing the aluminum reactive centers at different distances as well as of their mononuclear counterpart suggests that the copolymerization follows a monometallic pathway, differently from what observed in the homopolymerization of CHO.

Experimental Section

Synthetic procedures Generals.

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glove-box or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

Materials and methods.

Reagents and Solvents. Benzene, hexane and toluene (Sigma Aldrich) were distilled under nitrogen over sodium benzophenone. CH_2Cl_2 was distilled over CaH_2. The aluminum precursor $AlMe_3$ was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. CHO and LO were purchased from Aldrich and distilled over CaH_2. All other chemicals were commercially available and used as received unless otherwise stated. The synthesis and characterization of complexes **1-3** are described in the ESI.

NMR analysis. The NMR spectra were recorded on Bruker Advance 250, 300, 400 and 600 MHz spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at $\delta = 7.16$ for C_6D_6 and $\delta = 7.27$ for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at $\delta = 128.06$ for C_6D_6 and $\delta = 77.23$ for $CDCl_3$.

Thermal analysis. Glass transition temperature (Tg) 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−1 with a heating and cooling rate of 10 °C min−1 in the range −10 to 200 °C. All calorimetric data were reported for the second heating cycle.

MALDI-ToF-MS Analysis. 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. More details are described in The ESI.

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Keywords: NO ligands• Polymerization• Catalysis • Anhydrides• Schiff bases

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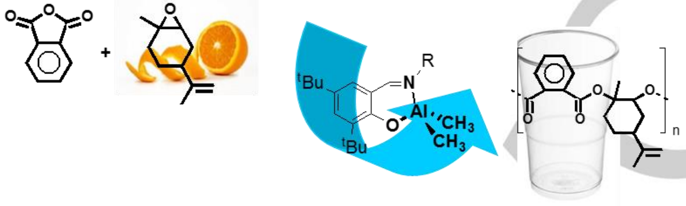
FULL PAPER

Bimetallic and monometallic phenoxy-imine aluminum complexes are very active catalysts in the ring-opening copolymerization of cyclohexene oxide and limonene oxide with anhydrides producing perfectly alternated polyesters.



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Ring-Opening Co-polymerization of Epoxides with Cyclic Anhydrides promoted by Bimetallic and Monometallic Phenoxy-Imine Aluminum complexes.