Synthesis of Mononuclear Magnesium Bis(alkoxide) Complex and Its Reactivity in Ring-Opening Copolymerization of Cyclic Anhydrides with Epoxides

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Abstract

Synthesis of a new mononuclear magnesium complex in bulky bis(alkoxide) ligand environment and its reactivity in ring-opening polymerization (ROP) and ring-opening copolymerization (ROCOP) are reported. Reaction of n-butyl-sec-butylmagnesium with two equivalents of HOR (HOR = di-tert-butylphenylmethanol, HOC^{t}Bu$_2$Ph) formed Mg(OR)$_2$(THF)$_2$. The reaction proceeded via Mg(OR)(sec-Bu)(THF)$_2$ intermediate that was independently synthesized by treating n-butyl-sec-butylmagnesium with one equivalent of HOR. Mg(OR)$_2$(THF)$_2$ led to active albeit not well-controlled ROP of *rac*-lactide. In contrast, well-behaved ROCOP of epoxides with cyclic anhydrides was observed, including efficient and altenating copolymerization of phtalic anhydride with cyclohexene oxide as well as rare copolymerization of phtalic anhydride with limonene oxide and terpolymerization of phtalic anhydride with both cyclohexene oxide and limonene oxide. In addition, novel copolymerization of dihydrocoumarin with limonene oxide is described.

Introduction

There is a significant current interest in polyesters as biodegradable and renewable alternatives to polyolefins.[1, 2] The conventional step-growth synthesis of polyesters via condensation of diacids with diols generally requires harsh reaction conditions (high temperatures) to allow a significant degree of monomers conversion, which often results in the lack of control over polymer properties.[3] While ROP of cyclic esters – a chain-growth polymerization – enables better control of polymer properties and also uses renewable precursors, it can afford only limited number of different polymer architectures due to the limited amount of possible precursors.[4-6]

In the last decade, the ring-opening copolymerization (ROCOP) of cyclic anhydrides with epoxides is emerging as a promising alternative route for the synthesis of polyesters.[7, 8] Compared to ROP, ROCOP provides access to more structurally diverse polyesters, due to the availability of large libraries for both monomers. For both synthetic processes, catalysts based on coordination compounds of benign metals such as group 2 and 12 metals offer significant advantages since it is not necessary to remove the catalyst residues that eventually contaminate the resulting material.[9-12] Magnesium complexes, because of their low cost and toxicity as well as the high abundance of the chemical element, are attractive from both an economic and environmental point of view. Either homoleptic alkoxide/alkyl complexes[13] or heteroleptic complexes[14-21] in which the metal centre is stabilized by multidentate ancillary ligands have been reported as efficient catalysts for the ROP of cyclic esters. Otherwise, the examples of magnesium catalysts that exibit catalytic behavior toward the ROCOP of epoxides and anhydrides are extremely rare. Homoleptic alkoxide magnesium complexes such as polymeric magnesium ethoxide ($Mg(OEt)_2$)[22] and mononuclear magnesium 2,6-di-tert-butyl-4-methylphenoxide ($Mg(BHT)_2(THF)_2$)[23] were shown to be active in the copolymerization of maleic anhydride and propylene oxide. Recently, Williams reported the first example of a well-defined heteroleptic bimetallic magnesium complex that demonstrated ROCOP of phthalic anhydride and cyclohexene oxide;[24] it was also active in copolymerizations of epoxides with anhydrides and CO_2.[25] Subsequently, heterobimetallic complexes of magnesium and zinc, with improved performances in comparison to the related homometallic species, were reported by the same author.[26] Herein we describe a new well-defined monomeric magnesium complex supported by bulky bis(alkoxide) ligand environment, $Mg(OR)_2(THF)_2$ (OR = OC^tBu_2Ph), that exhibits active ROCOP of various anhydride/epoxide mixtures, in addition to active ROP of lactide. The sustainable and non-toxic nature of the complex (containing a non-toxic metal and easily synthesizable ligand) contribute to its biocompatiblity, and constitute an attractive feature of the newly reported catalytic system.

Results and Discussion

Complex synthesis and structure

We have previously demonstrated that the bulky alkoxide ligand [OC^{t}Bu$_2$Ph] (OR hereafter) enables formation of well-defined mononuclear complexes M(OR)$_2$(THF)$_2$ with middle and late 3d transition metals (M = Mn-Co) in M(II) oxidation states.[27-34] As Mg(II) features similar ionic radius to Mn(II) and Fe(II), the formation of a similar complex was hypothesized. Treatment of n-butyl-sec-butylmagnesium (0.7 M solution in hexane) with two equivalents of HOR forms cleanly the desired Mg(OR)$_2$(THF)$_2$ complex **1** (**Figure 1**). The reaction proceeds via Mg(OR)(sec-Bu)(THF)$_2$ intermediate (**2**), that can be isolated in high yield from the reaction of n-butyl-sec-butylmagnesium with one equivalent of HOR. The selectivity of the protonolysis of n-butyl vs. sec-butyl likely originates in the steric difference between the two alkyl groups. The intermediate nature of **2** in the synthesis of **1** is further demonstrated by the reaction of **2** with HOR, which forms **1** in 95% isolated yield.

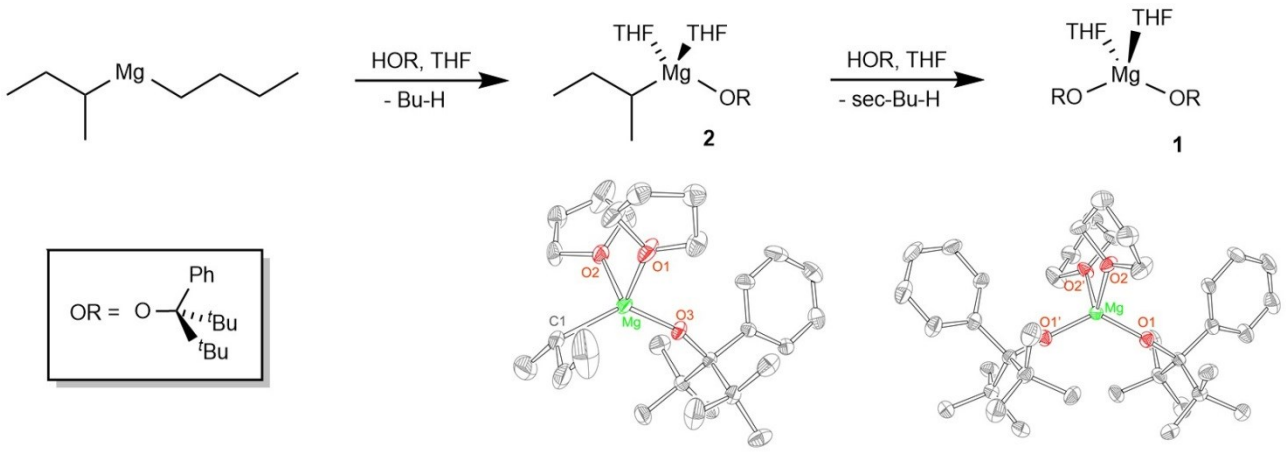


Figure 1. Syntheses and structures of complexes **1** and **2**. Selected bond distances (Å) and angles (º) for **1**: Mg O1 1.828(2), Mg O2 2.048(2), O1 Mg O1' 126.8(1), O2 Mg1 O2' 91.04(1). Selected bond distances (Å) and angles (º) for **2**: Mg O1 2.053(1), Mg O2 2.959(1), Mg O3 1.834(1), Mg C1 2.123(7), O3 Mg C1 131.6(2), O2 Mg O1 88.51(5).

Complex **1**, as well as the intermediate **2**, was characterized by proton and carbon NMR spectroscopy, X-ray crystallography, and elemental analysis. Proton NMR spectrum of complex **1** demonstrates five aromatic signals for the ligand phenyl group, consistent with its restricted rotation (see ESI). In contrast, four tert-butyl groups give rise to one singlet, suggesting effective C_{2v} symmetry in solution. The spectrum of **2** contains four resonances attributable to the *sec*-butyl group (Mg-C*H*(Me)(Et) at 0.19 ppm), in addition to the resonances attributable to one OR ligand

and two THF ligands. Solid-state structures of **1** and **2** are also given in Figure 1; selected bond distances and angles are provided in the Figure caption. X-ray crystallography reveals mononuclear structure for both **1** and **2**. Both complexes exhibit distorted tetrahedral geometry, with narrow THF-Mg-THF angles (91 º (1) and 89 º (2), and broader RO-Mg-OR/RO-Mg-C angles (127 º (1) and 131 º). Complex **1** exhibits crystallographic C_2 symmetry; the C_2-symmetric structure of **1** is isomorphous with previously reported structures of other $M(OR)_2(THF)_2$ complexes (M = Mn, Fe, Co),[28, 30] all crystallizing in *F*dd2 space group. We note that **1** is a rare example of a mononuclear magnesium bis(alkoxide) complex;[13, 35] several comparable bis(aryloxide) complexes were also reported.[36-42] We also note that related mono(aryloxide)mono(alkyl) magnesium complexes [Mg(OAr)(R)] had been previously reported by Carpentier and coworkers (Ar = 2,6-^{t}Bu$_2$-4-MeC_6H_2, R = hexyl),[43] Henderson and coworkers (Ar = 2,6-^{t}Bu$_2C_6H_3$, R = n-Bu),[38] Kuhn, Laufer and coworkers (Ar = 2,4,6-^{t}Bu$_3C_6H_2$, R = n-Bu),[44] and Nifant'ev and coworkers (Ar = 2,6-^{t}Bu$_2$-4-MeC_6H_2, R = n-Bu).[45] Most complexes exhibited dimeric structures $Mg_2(\mu_2\text{-OAr})_2R_2$; Nifant'ev and coworkers also described structurally similar monomeric complex Mg(O-2,6-^{t}Bu$_2$-4-MeC_6H_2)(n-Bu)$(THF)_2$.[45] Mg(O-2,6-^{t}Bu$_2$-4-MeC_6H_2)(n-Bu)$(THF)_2$ exhibited close structural parameters to **2**, with slightly wider THF-Mg-THF angle (99 º vs. 89 º in **2**).

LA polymerization

To test the reactivity of **1** in the ring-opening polymerization of cyclic esters, we conducted ROP studies using *rac*-lactide precursor. Polymerization runs were carried out using 10 μmol of the catalyst using different ratios of lactide:catalyst precursor (100:1, 200:1, 300:1) in dichloromenthane and toluene (see ESI for details). Monomer conversion was monitored by ^{1}H NMR spectroscopy. The catalyst exhibited moderate polymerization activity; the reaction was slightly faster in dichloromethane compared with toluene. For example, approximately 30% consumption of LA was observed in dichloromethane after 30 minutes, and in toluene after 1 hour, when 200 equivalents of the monomer were used. However, the polymerization does not appear to be well-controlled, giving relatively large molecular weight distribution (Đ= 1.79 ÷ 4.89), and lower than expected M_n values (Table S1). Moreover, in most of the cases, with the increase of the conversion molecular weights decrease, while the dispersity values increase, thus suggesting that transesterification reactions do occur during the polymerization reactions. To prevent possible catalyst aggregation and enable better polymerization control, we have attempted polymerization in a coordinating solvent, THF (Table S1). The activity in THF was relatively high (very similar to DCM), and some decrease in the PDI values was obtained. Cui, Chen and coworkers have

demonstrated that the addition of relatively non-bulky alcohols (as initiators) to $Mg(n\text{-}Bu)_2$ resulted in a more controlled behavior.[13] Lactide polymerization with **1** in the presence of one equivalent or ten equivalents of added $PhCH_2OH$ has resulted in a significantly higher activity, and significantly lower PDI values, consistent with the previous reports. Finally, we have also compared the reactivity of **2** with the reactivity of **1** (see Table S3). While the overall polymerization reactivity of **2** is similar to **1**, it appears less reactive, exhibiting somewhat lower monomer conversion.

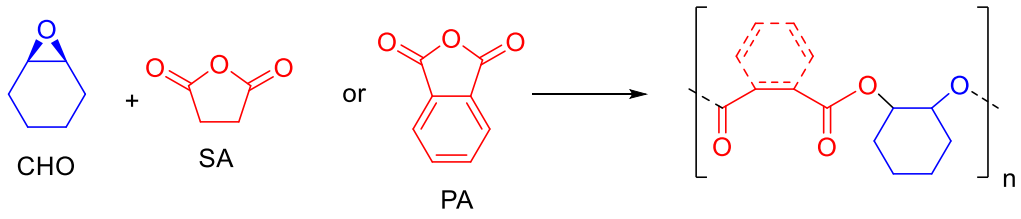
In order to observe the end groups of the polymer chains, a polymerization experiment was carried out in the presence of 25 equivalents of the monomer. The sample was analyzed by ^{1}H NMR (see ESI) which showed the presence of $HOCH(CH_3)CO$- and -$CH(CH_3)COOH$ terminal groups as prevailing chain end groups.[46] The $HOCH(CH_3)CO$- groups can be generated during the termination reaction by the hydrolysis of the metal-growing chain bond while the formation of the carboxylic acid end groups can be attributable both to the hydrolysis of the magnesium-alkoxide bond by reaction with adventitous molecules of water and to chain transfer reactions occurring during the polymerization reaction in which water molecules act as the chain transfer agent.

^{1}H NMR analysis of the methine region of the homonuclear decoupled protonic spectra of the polymer samples obtained from *rac*-lactide showed the formation of atactic polymers (see ESI), as predictable by considering the non chiral nature of the catalyst.

Overall, LA polymerization activity exhibited by $Mg(OR)_2(THF)_2$ appears similar to the LA polymerization activity exhibited by a related $Mg(OCPh_3)_2(THF)_2$ complex, reported by Cui, Chen, and coworkers.[13] Following these experiments, we turned to investigate ROCOP.

Copolymerization of CHO with cylic anhydrides

Initially, we explored the copolymerization of cyclohexene oxide (CHO) with phthalic (PA) and succinic anhydride (SA) using the magnesium complex **1** under different reaction conditions (Scheme 1). The polymers produced were characterized by ^{1}H NMR, GPC and MALDI-ToF-MS analyses. Selected data are reported in Table 1. The composition of the obtained polymers was estimated by ^{1}H NMR analysis, by comparing the integrals of the signals of epoxide/anhydride sequences with those of sequential enchainment of epoxides.



Scheme 1. Synthesis of polyesters from cyclohexene oxide (CHO) and succinic (SA) or phthalic anhydride (PA).

Table 1 . Ring Opening co-Polymerization promoted by $Mg(OR)_2(THF)_2$[a].

Entry	Anhydride (equiv)	CHO (equiv)	Cocat (equiv)	Time (h)	T (°C)	[b]conv. (%)	[c]Ester (%)	[d]M_n (KDa)	Đ
1	PA (100)	100	BnOH(1)	96	110	61	>99	3.5	1.20
2	PA (100)	800	BnOH(1)	24	110	>99	>99	5.9	1.33
3 [e]	PA (100)	800	BnOH(1)	5	110	76	25	1.8	1.21
4	PA (250)	250	PPNCl (1)	24	110	83	92	13.9	1.21
5	PA (250)	250	PPNCl (1)	24	80	16	97	4.1	1.16
6	SA(250)	250	PPNCl (1)	24	80	68	93	1.7	1.24
7	SA (100)	800	BnOH(1)	24	110	19	>99	4.6	1.22

[a]Reaction conditions: Mg = $1.0 \cdot 10^{-5}$ mol; solvent = 1 mL of toluene. [b]Conversion of anhydride determined by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) of reaction mixture. [c]Determined by integrating the normalized resonances for ester linkages (4.80–5.26 ppm) and ether linkages (3.22–3.64 ppm). [d] Experimental M_n and $Đ$ values were determined by GPC analysis in THF using polystyrene standards. [e] Solvent free.

The ring-opening copolymerization of phthalic anhydride and cyclohexene oxide using the magnesium complex **1** as a catalyst in the presence of benzyl alcohol (BnOH) was investigated (entry 1, Table 1). Initially, an epoxide : anhydride: catalyst ratio of 100:100:1, with the concentration of both monomers at 1.0 M in toluene solution was used. Under these reaction conditions, the catalytic activity was relatively low, comparable with that obtained with the bimetallic magnesium catalyst reported by Williams for which 19 equiv. of PA were converted in 22 h at 100 °C producing a polyester with about 20% of ether junctions.[26] Surprisingly, the poly(1,2-cyclohexylene-1,2-phthalate) obtained by **1** showed a perfectly alternating structure, with a percentage of ether linkages lower than of 0.3% (see Figure 2). A significant increase of the

catalytic activity was registered when the copolymerization was performed in the presence of an excess of cyclohexene oxide (entry 2, Table 1), in agreement with the well-documented first-order dependence of ROCOP with respect to the epoxide monomer.[47] However, even under these reaction conditions, the selectivity was preserved. In contrast, when the polymerization was performed in the absence of solvent, the percentage of ester linkages decreased dramatically (entry 3, Table 1).

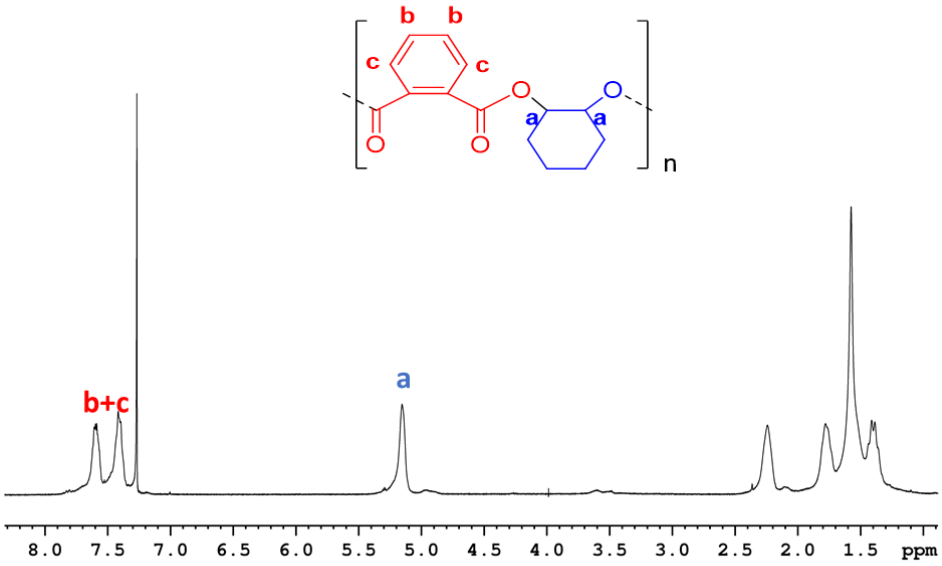


Figure 2. ^{1}H NMR (400 MHz, C_6D_6 298 K) of PA/CHO copolymer obtained in entry 1 of Table 1.

Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) was used in order to confirm the chain end-group fidelity. For samples obtained in the presence of benzyl alcohol, two major distributions were observed attributable to a full polymeric repeat unit or a half polymeric repeat unit (i.e., one extra epoxide incorporated on the chain end), as expected from an alternating copolymerization system. The end-groups for both major distributions were calculated to correspond to BnOH initiation (Figure 3). A third family of signals of lower intensity was observed for polymer chains having as chain end groups the alkoxy fragment originally coordinated to the magnesium center.

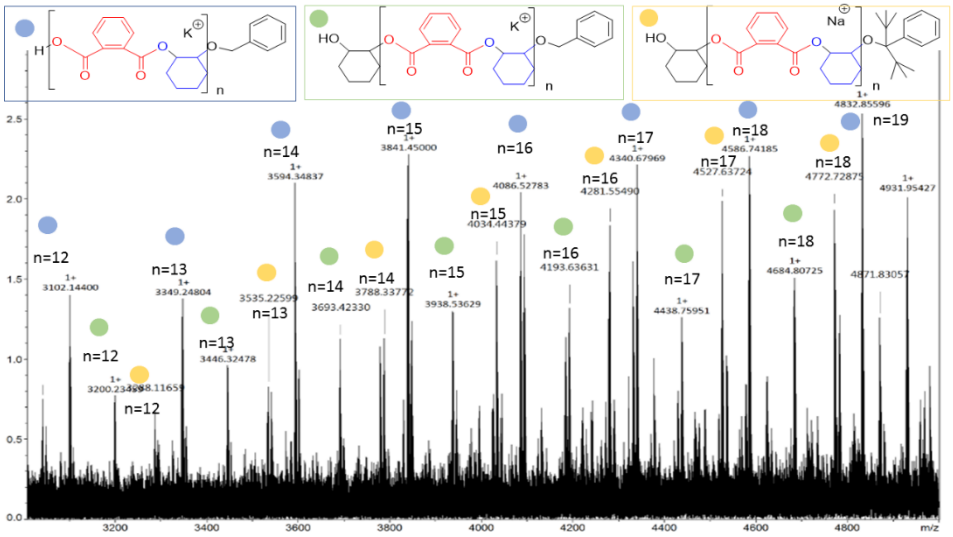


Figure 3. MALDI-ToF-MS spectrum of PA/CHO copolymer synthesized by **1** (entry 1 MT9, Table 1).

To gain additional insight about the initiation steps, a polymerization experiment in the absence of alcohol, under the same reaction conditions described by entry 1, was performed. After 96 h, a conversion of 46% of PA was achieved, showing an activity lower than that obtained in the presence of BnOH. The NMR analysis of the polymer revealed the production of copolymer with a perfectly alternating structure and a percentage of polyether sequences lower than 1 %. As for the chain-end group analysis, OH end-capped chains were the prevailing product while the percentage of polymeric chains with OR ligand as the chain-end group was less than 5% (see Figure S13). A reasonable hypothesis about the initiation step is that the first opening of the epoxide was mainly performed by the nucleophilic species that are present in the polymerization medium (such as alcohol or as traces of water) while the insertion on the metal-ligand bond is only a sporadic phenomenon.

According to several reports, various metal catalysts exhibit remarkably higher activity and selectivity when used in combination with a cocatalyst that is neutral nucleophilic species such as 4-(dimethylamino)pyridine (DMAP) or onium salts such as bis(triphenylphosphine)iminium chloride (PPNCl).[48] Thus, the copolymerization reactions of CHO/PA were subsequently performed by using complex **1** in combination with one equivalent of PPNCl. As expected, the presence of the onium salt had beneficial effects on the catalytic activity: at 100 °C, after 24 hours, the magnesium catalyst **1** was able to convert about 207 equivalents of both monomers (entry 4, Table 1). Surprisingly, the catalytic system formed by **1** and PPNCl revealed to be less selective, producing a polymer containing a moderate percentage of ether linkages. A lower activity was observed when

the reaction was performed at lower temperature (entry 5, Table 1) with a moderate benefit on the selectivity.

The MALDI-ToF spectrum of polymer obtained by **1**/PPNCl (Figure 4) showed clearly patterns for polymer chains with a significantly higher CHO than PA content, coherently with that observed from ^{1}H NMR analysis. Two families of distributions were detected corresponding to ligand or OH end-capped chains (designed by circles and triangles, respectively). Neither linear polymer chains with Cl end groups nor cyclic polymers were detected. This could mean that the initiation reactions in the ROCOP of CHO with PA are performed by different groups depending on the nature of the cocatalyst: when BnOH was used, the first nucleophilic attack was performed preferentially by the exogeneous alcohol. In the presence of PPNCl, the nucleophilic attack was performed by the traces of water or by the alkoxide ligand OR originally coordinated to magnesium. Therefore, in contrast to the other catalytic systems, the chlorine atom of PPNCl was not an efficient initiating group.

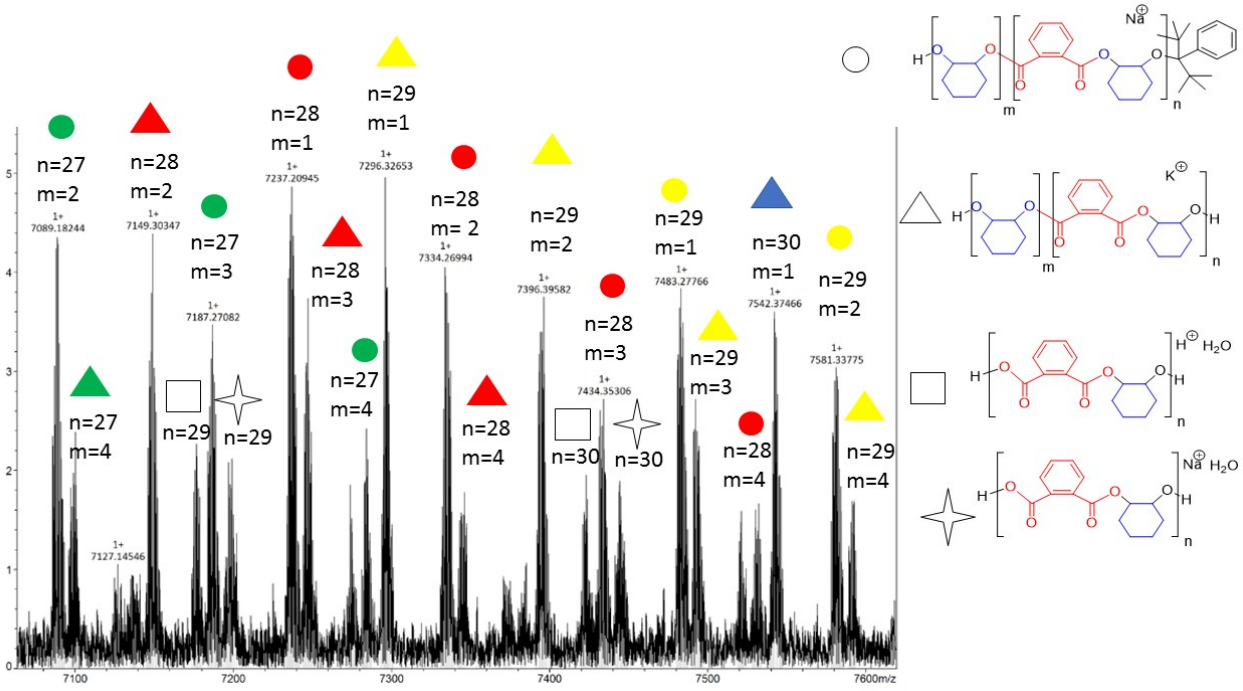


Figure 4. MALDI-ToF-MS spectrum of PA/CHO copolymer synthesized by **1**/PPNCl (entry 5, Table 1).

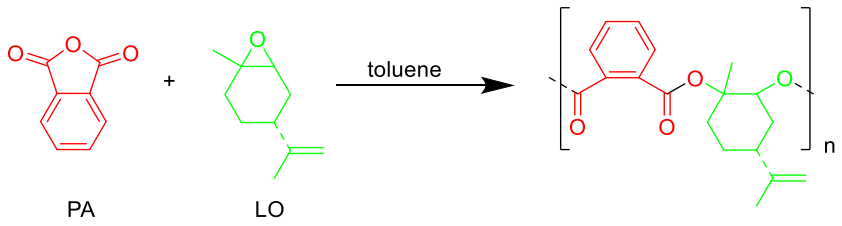
Subsequently, the reactivity of complex **1** was extended to the copolymerization of cyclohexene oxide with succinic anhydride (SA). Under the same reaction conditions explored for

PA, complex **1** showed an analogous behavior: the polymerization was selective only when BnOH was used as activator (entry 6 vs entry 7, Table 1).

The GPC analysis of all obtained polymers displayed distributions with moderately narrow dispersities (Đ<1.33). The number average molecular weight values (M_n) measured by GPC (without any calibration correction) were always lower than the theoretical ones expected for a living system. This could be a consequence of the presence of protic impurities present within monomers that can act as chain transfer agents

Copolymerization of phthalic anhydride with limonene oxide

Considering the structural analogy between CHO and LO (limonene oxide), we decided next to explore the reactivity of the commercial LO, a mixture of *cis* and *trans* R isomers, derived mainly from the R-limonene isomer present in orange oils (Scheme 2).[49] As a monomer, it has been used in the copolymerization with CO_2[50-53] and, less frequently, with cyclic anhydrides.[54-60] Complex **1**, activated by PPNCl, showed a good activity in toluene solution (entry 1, Table 2). The catalyst did not show any preference toward one of the two isomers of limonene oxide. A similar activity was achieved by using benzyl alcohol as activator (entry 2, Table 2).



Scheme 2. Synthesis of polyesters from limonene oxide (LO) and phthalic anhydride (PA).

Table 2 . Ring Opening co-Polymerization of LO promoted by $Mg(OR)_2(THF)_2$.

[a]Entry	PA (equiv)	CHO (equiv)	LO (equiv)	Time (h)	[b]PA conv. (%)	M_n (KDa)	Đ
1	250	-	250	48	79	12.5	1.20
2 [c]	100	-	800	24	45	7.3	1.16
3	200	100	150	72	61	9.2	1.21

[a]Reaction conditions: [PA]: [LO]: [Mg]: [PPNCl]: = 250:250:1:1 and Mg = $1.0 \cdot 10^{-5}$ mol; Solvent = 1 mL of toluene. T=80 °C [b]Determined by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) of crude reaction. [c] BnOH was used as cocatalyst instead of PPNCl.

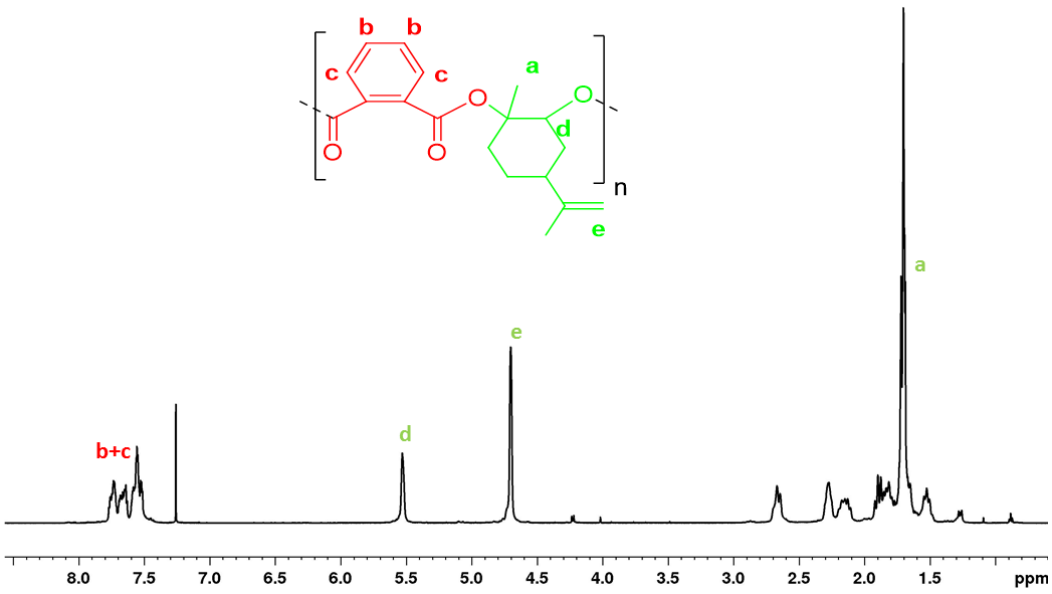


Figure 5. ^{1}H NMR (400 MHz, $CDCl_3$ 298 K) of PA/LO copolymer obtained in entry 1 of Table 2.

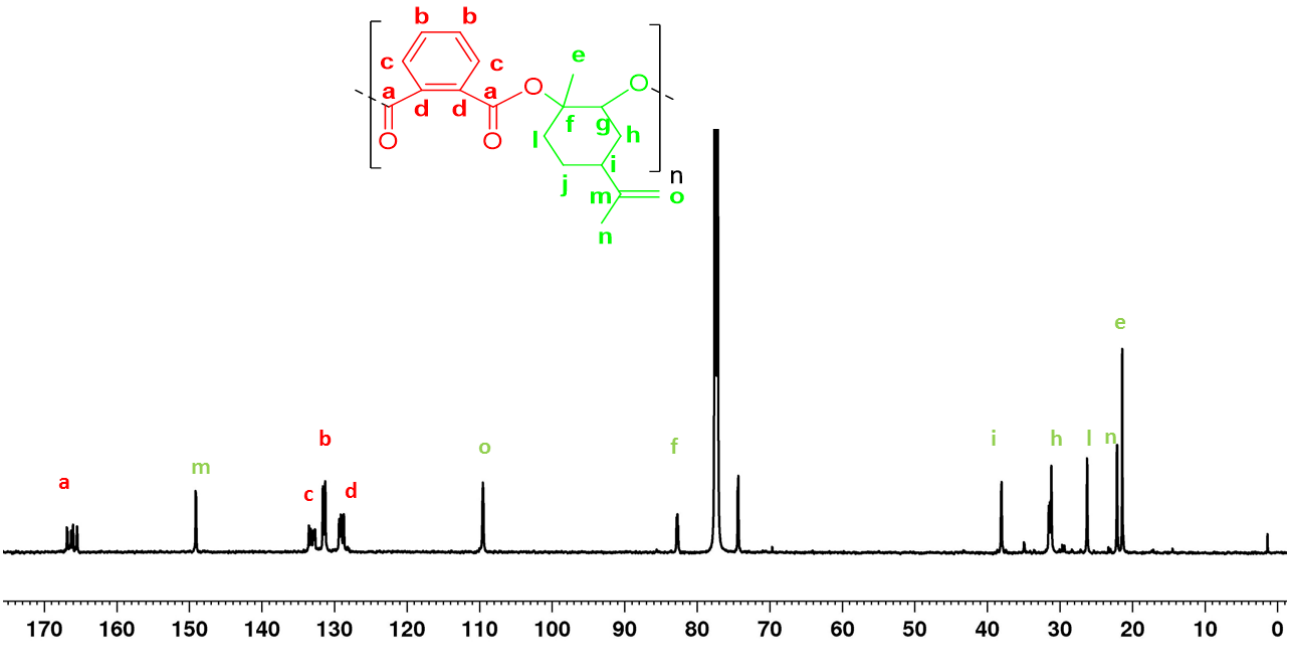


Figure 6. ^{13}C NMR (100 MHz, $CDCl_3$ 298 K) of PA/LO copolymer obtained in entry 1 of Table 2.

The ^{1}H NMR analysis of the obtained copolymer (Figure 5) confirmed the absence of ether linkages, as expected because of the bulky nature of LO. The microstructure of the LO/PA

copolymer, elucidated by the ^{13}C NMR analysis (Figure 6), showed an atactic polymer, coherently with the achiral structure of the catalyst.

Next, the catalytic activity of complex **1** in the terpolymerization of phthalic anhydride with both epoxides, CHO and LO, was tested (entry 3, Table 2). The reaction was performed under the same reaction conditions used for the related copolymerizations and monitored by ^{1}H NMR. Aliquots of the reaction mixture were taken at different times to evaluate the conversions of all the monomers. After 24 hours a conversion of about 30% of CHO was achieved while no conversion of LO was observed. The intensity of resonances of the anhydride within the polymer was consistent with the intensity of resonances of the CHO reacted. After 48 hours, conversions of 60% of CHO, 18% of LO and 40% of PA were achieved (18 LO and 40 PA). After additional 24 hours, an almost complete conversion of CHO was achieved (95%) while the conversions of LO and PA were 44% and 61%, respectively. During terpolymerization, the rate of incorporation of cyclohexene oxide was faster compared with that of limonene oxide. Thus, the CHO incorporation was preferred although a gradual consumption of LO was observed, as evident by evaluating the conversions of the two epoxides versus time. These data supported the hypothesis of gradient microstructure for the terpolymer in which a gradual change in epoxide composition from CHO predominantly to predominantly LO. The ^{1}H NMR spectrum of the crude polymer accounted for a terpolymer containing a 1:1.4 ratio of LO and CHO (Figure 7).

GPC analysis of the obtained polymer revealed a bimodal molecular weight distribution. To clarify if the obtained sample was a mechanical mixture of the two copolymers or a true terpolymer a DOSY experiment was performed (Figure 8). The DOSY experiment showed that the signals of all the monomeric units lay at the same diffusion coefficient, and therefore belonged to the same polymeric chains, thus confirming the formation of a terpolymer.

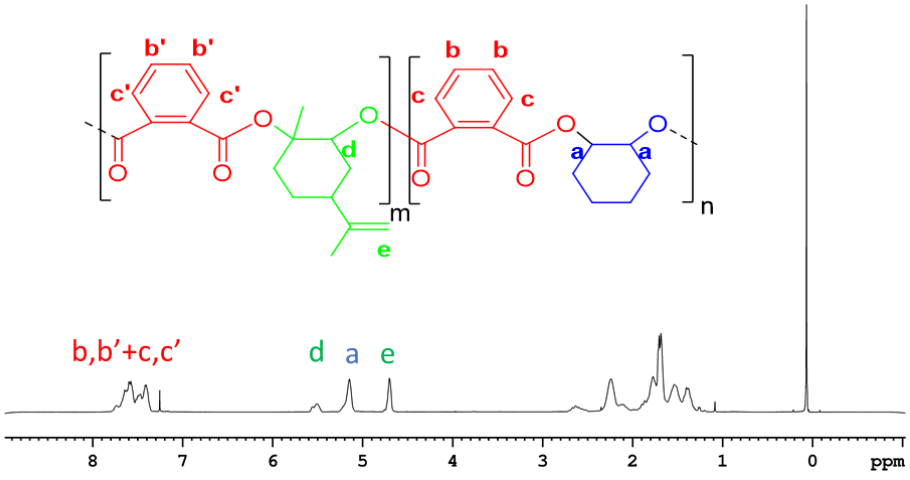


Figure 7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of PA/CHO-PA/LO copolymer obtained in run 2 of Table 2.

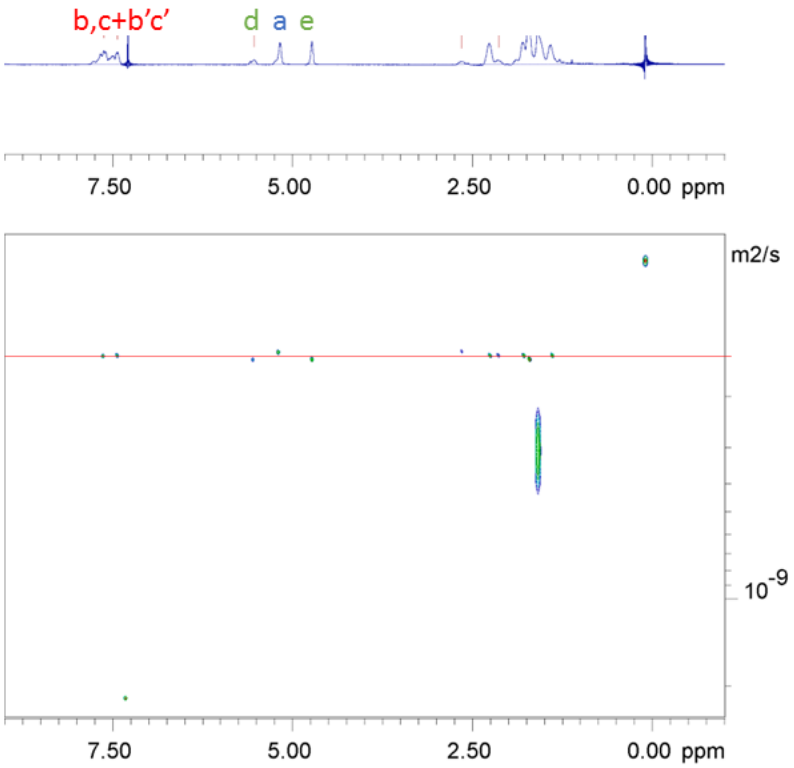
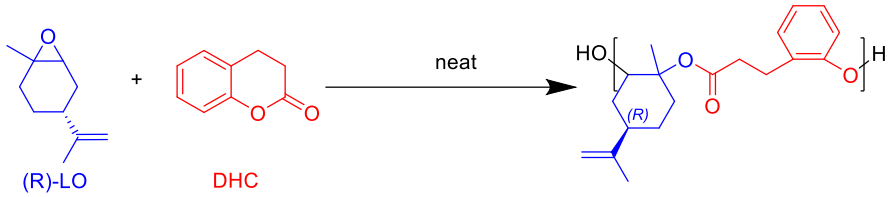


Figure 8. ^{2}D DOSY NMR (600 MHz, $CDCl_3$, RT) of poly[(cyclohexene phthalate)-block-(poly[(limonene phthalate)].

Copolymerization of limonene oxide with dihydrocoumarin

Finally, aiming to develop novel functional polymers, we tested the reactivity of complex **1** in the copolymerization of LO with dihydrocoumarin, an aromatic 6-member lactone that cannot be homopolymerized by ROP because of the low ring strain. The copolymer of LO with dihydrocoumarin is an attractive material: since both monomers are derived from renewable resources, this product represents an example of totally biorenewable polyester.



Scheme 3. Synthesis of polyesters from limonene oxide (LO) and dihydrocoumarin (DHC).

Because of the low reactivity of both monomers, the reaction was performed at high temperature (100 °C) for seven days. After this time, a solid product was obtained after precipitation in wet hexane. The polymer was analyzed by NMR spectroscopy and MALDI ToF. The ^{1}H NMR analysis of the reaction mixture demonstrated a polymeric chain with an alternating sequence of the two monomers. The alternating structure was confirmed by the MALDI-ToF-MS spectrum (Figure S12 in ESI). No stereoselectivity for the incorporation of a specific stereoisomer of limonene oxide was observed. The opening of the epoxide was not regioselective as demonstrated by the presence of two different signals for the methine proton of the limonene portion (protons 1 and 2 of Figure 9, see also Figure S11 in ESI). This was further confirmed by the presence of two signals for the corresponding methine carbons. A complete assignment of the resonances of the ^{13}C spectrum was also performed (Figure S12 in ESI). The thermal stability of the oligomeric sample of DHC/LO (as determined through thermogravimetric analysis [TGA]) showed a complete degradation obtained at temperature higher than 270 °C (see Figure S14).

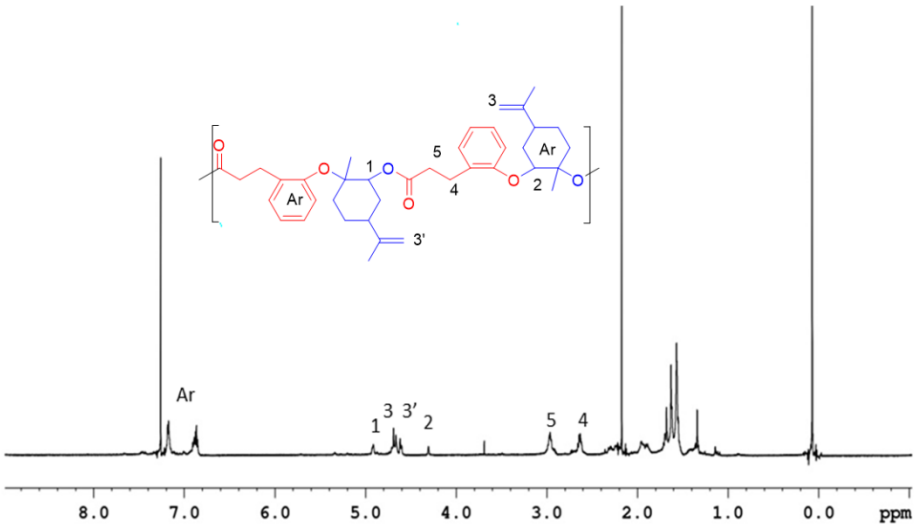


Figure 9. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of DHC/LO copolymer.

Summary and conclusions

We have reported synthesis, ROP, and ROCOP with a new well-defined mononuclear magnesium complex $Mg(OR)_2(THF)_2$ (OR = OC^tBu_2Ph). The complex led to active albeit not well controlled ROP of lactide precursor; utilization of coordinating solvent (THF) or benzyl alcohol as a co-catalyst leads to somewhat better control of polymerization. In contrast, well-behaved ROCOP was obtained with a variety of different monomers. While the use of PPNCl as nucleophilic initiator leads to an efficient copolymerization CHO with PA or SA, the structure of the resulting copolymers was found to be only moderately alternating, demonstrating small amount of ether linkages. In contrast, the use of BnOH as an initiator forms perfectly alternating copolymer of PA with CHO. More challenging biorenewable monomer, LO, was also co-polymerized with PA. The combination of PA with both CHO and LO leads to the formation of terpolymer, whose integrity was confirmed by DOSY. Finally, the combination of two biorenewable precursors, LO and dihydrocumarin, formed a fully biorenewable novel copolymer. No stereoselectivity was observed in all the above reactions, likely due to the achiral nature of the catalyst. Our future plans include investigation of additional monomers, as well as the design of chiral metal pre-catalysts, which could lead to the stereospecific enchainment of monomers in the copolymer structure.

Electronic supplementary information (ESI) available: general experimental data, synthetic and polymerization procedures, crystal and refinement data, NMR and MS spectra. CCDC 1961128-1961129.

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