Alternating Copolymerization of Epoxides and Anhydrides Catalyzed by Aluminum Complexes

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ABSTRACT: The optimization of an organoaluminum catalytic system for the copolymerization of epoxides and anhydrides is presented. For this purpose, the influence of different variables in the process, such as catalysts, cocatalyst, solvent, or substrates, has been analyzed. Kinetic studies, a proposal for the catalytic mechanism, and full characterization of the copolymers obtained are also discussed. Finally, a new copolymer, poly(limonene succinate), obtained by the optimized catalytic system is reported.

INTRODUCTION

Biodegradable polymeric materials derived from renewable and bioderived resources are a potential alternative to petroleum-based plastics.1−5 Amongst them, biodegradable polyesters such as polylactide (PLA) and polycaprolactone (PCL) have already found many applications.6−10 These polymers are often obtained by ring-opening polymerization (ROP) of cyclic esters catalyzed by organometallic complexes11−21 and organocatalysts.22−28 However, the design of new biodegradable polyester architectures with improved properties by ROP is seriously restricted by the limited number of commercially available cyclic esters. The development of other catalytic processes for the preparation of a broader range of biodegradable polyesters is necessary.

A promising alternative is the ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides. This methodology could expand the scope of biodegradable polyesters because of the large number of epoxides and cyclic anhydrides commercially available (Scheme 1).29−31 The main drawbacks of this process are still the low molecular weight of the obtained polymers and the modest selectivity of the catalysts tested. In the search of better catalysts for the development of biodegradable architectures, systems based on zinc,32−36 cobalt,37−39 chromium,40−43 and aluminum44−47 have been thoroughly studied. Amongst them, aluminum complexes are the most attractive because of its Earth’s crust abundance.

In this matter, our research group has significantly contributed to the development of novel aluminum complexes as catalysts for a considerable range of catalytic processes (Chart 1).48−57 A family of aluminum catalysts supported by heteroscorpionate ligands were developed for the ROP of cyclic esters55,56,58 (Chart 1a). On the other hand, neutral bi-54 (Chart 1b,c) and bifunctional48,50 (Chart 1d,e) aluminum complexes have been reported as catalysts for the formation of cyclic carbonates from epoxides and carbon dioxide.

Recently, novel scorpionate aluminum complexes have been reported as versatile catalysts for the ROP of cyclic esters and ROCOP of cyclohexene oxide (CHO) and phthalic anhydride (PA) (Scheme 2).49 The most active catalyst allowed us to obtain poly(cyclohexene phthalate) with an excellent selectiv...
ity. Therefore, on the basis of these results, in this work, we expand our studies on the use of aluminum complexes as catalysts for the ROCOP of a wider range of epoxides and cyclic anhydrides including bioderived limonene oxide (LO) in order to prepare a broader range of polyester materials including poly(limonene succinate) which has not been previously reported. Moreover, NMR experiments and a kinetic study have been carried out in order to better understand the catalytic process.

■ RESULTS AND DISCUSSION

ROCOP of Epoxides and Cyclic Anhydrides. Mono- and bimetallic alkyl aluminum complexes 1–4 (Chart 2) were prepared in excellent yields as previously reported\(^5^7\) and tested as catalysts for the ROCOP of CHO and succinic anhydride (SA) using 1 mol % of aluminum loading at 80 °C in toluene as a solvent (Scheme 3), and the results are shown in Table 1.

**Scheme 3. ROCOP of CHO and SA Catalyzed by Aluminum Complexes 1–4**

\[
\begin{align*}
\text{CHO} + \text{SA} & \xrightarrow{\text{catalyst}} \text{Poly(cyclohexene succinate)} \\
\text{(1–4) (0.1 mol %)} & \text{Cocatalyst (0.5–5 mol %)} \\
\text{Toluene, 16h, 80°C} & \\
\end{align*}
\]

**Table 1. ROCOP of CHO and SA Catalyzed by 1–4**

| entry | cat. | cocat. | conv. (%)<sup>b</sup> | polyester (%)<sup>b</sup> |
|-------|------|--------|------------------------|--------------------------|
| 1     | 1    |        | 71                     | 50                       |
| 2     | 2    |        | 74                     | 43                       |
| 3     | 3    |        | 81                     | 52                       |
| 4     | 4    |        | 83                     | 50                       |
| 5     | 1    | TBAB<sup>c</sup> | 93                     | 85                       |
| 6     | 2    | TBAB<sup>c</sup> | 93                     | 88                       |
| 7     | 3    | TBAB<sup>c</sup> | 93                     | 81                       |
| 8     | 4    | TBAB<sup>c</sup> | 100                    | 91                       |
| 9     | TBAB<sup>c</sup> |          | 25                     | 89                       |

<sup>a</sup>Reactions were carried out at 80 °C in toluene for 16 h using 1 mol % of aluminum complexes 1 and 2 or 0.5 mol % of aluminum complexes 3 and 4. <sup>b</sup>Determined by NMR. <sup>c</sup>0.5 mol % of TBAB.

First, we investigated the ROCOP process in the absence of a cocatalyst (Table 1, entries 1–4), and the results showed that good conversions with low selectivities were obtained. Because previous reports confirmed that adding a nucleophile source as a cocatalyst increased the copolymerization selectivities, the effect of adding tetrabutylammonium bromide (TBAB) as a cocatalyst was studied, showing that selectivities could be improved up to 91% toward the synthesis of the polyester (Table 1, entries 5–8). Entries 1–8 evidenced that bimetallic complexes 3–4 were more active for the ROCOP of CHO and SA than the monometallic counterparts 1–2. On the other hand, the catalytic activities of ethyl derivatives 2 and 4 are slightly higher than the methyl complexes 1 and 3 which have been previously observed for scorpionate aluminum complexes. Finally, a reaction control using TBAB as a catalyst showed that the cocatalyst by itself could catalyze the reaction but less efficiently. NMR studies confirmed that the presence of TBAB is crucial in order to increase the selectivity toward the synthesis of polyester (Figure 1). A stoichiometric mixture of complex 4 and CHO in the absence of TBAB showed that 47% of CHO is converted into polyether at the beginning of the reaction at room temperature (Figure 1a). However, when a stoichiometric amount of TBAB is added into the reaction mixture, no polyether was observed even after 4 h of reaction at 80 °C (Figure 1b).

To optimize the catalytic system comprising complex 4, the influence of the cocatalyst for the ROCOP of CHO and SA was studied in the first instance (Figure 2 and Supporting Information). In general, the tetrabutylammonium salts displayed slightly higher catalytic activity than their corresponding bis(triphenylphosphine)iminium ones (PPNX), and TBAB showed to be the optimal cocatalyst for the catalytic system in terms of activity and selectivity. Changing the bromide counterion to a dinitrophenolate (DNP) counterion for PPNX cocatalysts gave rise to an increase in activity and selectivity. N-Methylimidazole (NMI) and dimethylaminopyr-
idine (DMAP) were also investigated obtaining a good selectivity but a lower catalytic activity than that obtained when using TBAB as a cocatalyst. The higher catalytic activity when using a bromide counterion could be due to the good balance between nucleophilicity and steric hindrance to ring open the epoxide.

Because the best catalyst system for the ROCOP of CHO and SA is the combination of complex 4 and TBAB, we investigated the solvent effect on the catalytic process (Table 2). We first studied the reaction in the absence of a solvent to maximize the sustainability of the process but complete conversion of the starting materials into the polyester was not achieved because of solidification of the reaction mixture and the selectivity toward the formation of polyester decreased down to 18% (Table 2, entry 1). The catalytic system acted efficiently in a range of different solvents, but the different polarities of the solvents did not significantly impact on the selectivity of the process (Table 2, entries 2–5).

The versatility of the optimized catalyst system was studied toward the synthesis of a range of polyesters derived from the combination of CHO and SA, PA, and maleic (MA) anhydrides (Chart 3). Moreover, the synthesis of biobased polyesters derived from LO and SA, PA, and MA was also investigated (Chart 3).

Table 3 collects the efficiency of the catalytic system toward the different substrates. Good selectivities toward the synthesis of the corresponding polyester were obtained in all cases. The experimental molecular weights obtained for the polymers are lower than the theoretical values probably because of the presence of transesterification reactions or chain transfer reactions. These results might be justified by the presence of traces of water or diacid from the hydrolysis of the corresponding cyclic anhydride. It is worth noting that under the same reaction conditions, when CHO was used as the substrate, the conversions were higher (Table 3, entries 1–3) than those obtained for LO (Table 3, entries 7–9). These results showed that the trisubstituted epoxide LO was a much more challenging substrate for this reaction than a disubstituted one. The effect of decreasing the [monomers]/
The resulting polymers were analyzed by MALDI-ToF MS in order to determine the end group. When a combination of complex 4 and TBAB was used as a catalyst system, the MALDI-ToF spectrum showed multiple end-group series of peaks with an m/z interval of 198 mass units, indicating a controlled alternating microstructure (Figure 4a).

The major series (blue diamond) is in good agreement with a polymer chain with two hydroxyl end groups in the polyester, and the second major series containing hydroxyl- and carboxylic acid end groups (red diamond) was observed, indicating the existence of chain transfer agents during the copolymerization. When DMAP was used as a cocatalyst, the MALDI-ToF spectrum showed one end-group series of peaks which corresponds to perfectly alternating poly-(cyclohexene succinate) chains with DMAP and an hydroxyl group as chain ends (Figure 4b).

Figure 3. 1H NMR spectrum (CDCl3, 25 °C) of poly(cyclohexene succinate) obtained in Table 3, entry 1.

Table 3. GPC Data for Selected Copolymers

| entry | epoxy/anhydride | conv. (%) | polyester (%) | M_\text{num} | PDI |
|-------|-----------------|-----------|--------------|-------------|-----|
| 1     | CHO/SA          | 100       | 91           | 1656        | 1.34 |
| 2     | CHO/MA          | 97        | 62           | 2109        | 1.25 |
| 3     | CHO/PA          | 100       | 95           | 3572        | 1.11 |
| 4     | CHO/PA^d        | 100       | 98           | 2088        | 1.09 |
| 5     | CHO/PA^f         | 100       | 95           | 2533        | 1.21 |
| 6     | CHO/PA'         | 100       | 94           | 3114        | 1.16 |
| 7     | LO/SA           | 47        | 92           | 1194        | 1.50 |
| 8     | LO/MA           | 50        | 88           | 1536        | 1.49 |
| 9     | LO/PA           | 59        | 93           | 2856        | 1.36 |

^dReactions were carried out at 80 °C in toluene for 16 h using [epoxide]/[anhydride]/[TBAB] = 200:200:1:1. Determined by GPC. ^f Determined by NMR.

Analysis of the MALDI-ToF spectrum of the novel poly(limonene succinate) revealed the existence of three series with an interval between the consecutive peaks of 252 (Figure 5). These series correspond to chains with two hydroxy—limonene end groups (blue diamond) and chains with hydroxyl and carboxylic acid groups (red diamond). The presence of water or limonene-1,2-diol in the reaction mixture could explain this observation.

**Thermal Properties of Copolymers.** The thermal properties of the obtained polyesters were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (see the Supporting Information). The glass-transition temperatures (T_g’s) of the polyesters prepared using the optimized catalytic system were determined by DSC, and the results are listed in Table 4.

As expected, in all cases, the T_g values for polymers derived from CHO (Table 4, entries 1–3) were higher than those obtained when using LO (Table 4, entries 4–6). Similarly, when varying the cyclic anhydride, the T_g increased on the order PA > MA > SA. These results suggest an increase of the T_g values with the rigidity of the monomer. TGA revealed that all polymers are stable in the range of temperatures from 10 to 200 °C except for LO/MA for which the range of temperatures was from 10 to 125 °C (see the Supporting Information).

**Kinetic Studies on the Synthesis of Poly(cyclohexene phthalate) Catalyzed by Complex 4 and TBAB.** In order to gain insight into the polymerization process catalyzed by complex 4 and TBAB, a kinetic study for the synthesis of poly(cyclohexene phthalate) was performed in toluene at 80 °C. Samples were taken from the polymerization reaction every hour and analyzed by NMR to determine the conversion of the starting materials into the corresponding polyester and the selectivity of the process. Experiments carried out under these reaction conditions showed a good fit to first-order kinetics.

First, the order with respect to the concentration of complex 4 was investigated by carrying out reactions using [4] = 0.1–0.75 mol % whilst keeping constant [TBAB] = 0.5 mol %. Similarly, the order with respect to the concentration of TBAB was determined by carrying out reactions using [TBAB] = 0.25–1.0 mol % whilst keeping constant [4] = 0.25 mol %. The plots log([4]) versus log([k_1avg]) and log([TBAB]) versus log([k_1avg]) showed a good fit to a straight line with slopes of 0.84 and 1.12, respectively (Figures 6 and 7), suggesting that the reactions are first order with respect to the concentration of complex 4 and TBAB. This was confirmed by plotting [4] versus k_1avg and [TBAB] versus k_1avg, which also fitted to a straight line (Figures 8 and 9).

Finally, a plausible mechanism for the ROCOP catalyzed by a combination of complex 4 and TBAB is proposed in Scheme 4. A first step is expected for the activation of CHO by one aluminum center of complex 4 to give rise to the intermediate 4a followed by nucleophilic attack of the cocatalyst to form an alkoxide derivative 4b. This alkoxide intermediate might ring open an activated monomer of PA by the second aluminum center to yield a carboxylate species 4c which can undergo successive alternating ring-opening reactions of epoxides and anhydrides to form the desired polyester materials.

**CONCLUSIONS**

The identification of catalytic systems capable of promoting ROCOP of epoxides and cyclic anhydrides in a controlled manner is a field needed to be developed. Even though this
catalytic reaction could give rise to a plethora of new biodegradable macrostructures, there are still drawbacks to be overcome, such as the low molecular weight of the obtained polymers or the modest selectivity of the catalysts. To improve efficiency in selectivity for the ROCOP, in this work, we present an optimized catalytic system based on organo-aluminum entities. The catalytic system comprising complex 4 as a catalyst, TBAB as a cocatalyst, toluene as a solvent, CHO and PA or SA as substrates, and a temperature of 80 °C can carry out the reactions to give rise to copolymers CHO/PA and CHO/SA with 100% of conversion and up to 90% of selectivity. Although the molecular weights of the copolymers obtained are low ranging from 1200 to 3600 g/mol, those copolymers could be used for a range of applications such as coatings and resins.31

The kinetics of the reaction are first order with respect to the concentration of complex 4 and TBAB. It is worth noting that amongst the copolymers obtained, the poly(limonene succinate) is reported for the first time. Finally, a mechanism for the catalytic reaction is also proposed along the article.

■ EXPERIMENTAL PART

General Procedures and Techniques. All manipulations of air- and water-sensitive compounds were carried out under dry nitrogen using Braun Labmaster glovebox or standard Schlenk line techniques. NMR spectra were recorded on Bruker Ascend TM-500/400 spectrometers and referenced to the residual deuterated solvent. TGA of the products was performed on a TGA instrument (model TGA-Q50). The heating rate for the sample was 10 °C/min, and the nitrogen flow rate was 60 mL/min. DSC curves were obtained under N2 atmosphere on a TA Instrument (model DSC-Q20). Samples were weighed into aluminum crucibles with 5 mg of sample and subjected to two heating cycles at a heating rate of 10 °C/
min. GPC measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a TSK-GEL G3000H column and an ELSD-LTII light scattering detector or/and a RID-20A differential refractive index detector. The GPC column was eluted with tetrahydrofuran (THF) at 50°C at a flow rate of 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–48 300 Da.

Materials and Reagents. The synthesis of aluminum complexes was performed as previously reported.58,61,62 Solvents were predried over a sodium wire (toluene, n-hexane, THF) and distilled under nitrogen from sodium (toluene, THF) or sodium–potassium alloy (n-hexane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze thaw cycles. CHO and LO (Sigma-Aldrich) were predried over calcium hydride, distilled under vacuum, and stored under nitrogen in a glovebox. PA (Sigma-Aldrich) was kept in a glovebox and used as received. SA and MA (Sigma-Aldrich) were sublimed three times and stored under nitrogen in the glovebox. All other reagents were

| entry | copolymer | $M_n,\text{exp}$ | $T_g$ (°C)$^c$ |
|-------|-----------|-----------------|----------------|
| 1     | CHO/SA    | 1656            | 44             |
| 2     | CHO/MA    | 2109            | 84             |
| 3     | CHO/PA    | 3572            | 103            |
| 4     | LO/SA     | 1194            | 26             |
| 5     | LO/MA     | 1536            | 27             |
| 6     | LO/PA     | 2856            | 50             |

$^a$Reactions were carried out at 80°C in toluene for 16 h using 0.5 mol % of aluminum complex 4 and 0.5 mol % of TBAB. $^b$Determined by GPC. $^c$Determined during the second heating cycle.

Figure 5. MALDI-ToF spectrum of poly(limonene succinate) obtained using a combination of complex 4 and TBAB.

Figure 6. Plot of log($k_{\text{obs}}$) vs log[4] for the ROCOP of CHO and PA.

Figure 7. Plot of log($k_{\text{obs}}$) vs log[TBAB] for the ROCOP of CHO and PA.

Figure 8. Plot of $k_{\text{obs}}$ vs [4] for the ROCOP of CHO and PA.
Representative Copolymerization Procedure. In the glovebox, complex 4 (20 \(\mu\)mol), cocatalyst (20 \(\mu\)mol), and a cyclic anhydride (4 mmol) were placed into a 10 mL Schlenk equipped with a small stir bar. Toluene (2 mL) was added, and the reaction mixture was stirred. Then, the epoxide (4 mmol) was added and the reaction mixture was placed in a preheated oil bath at the desired temperature. After the appropriate time, a small aliquot was taken from the reaction mixture for NMR analysis to determine the monomer conversion and process selectivity. The viscous mixture was then dissolved in a minimum amount of dichloromethane or toluene and precipitated into an excess of MeOH or pentane. The polymer was then dried and collected as a white or light-yellow solid typically in 80−85% yield.

Representative Kinetic Procedure. In the glovebox, complex 4 (2−15 mM), TBAB (5−20 mM), and PA (4 mmol) were placed in a 10 mL vial equipped with a small stir bar. Toluene (2 mL) was added, followed by the addition of CHO (4 mmol). The vials were placed in a preheated multireactor at the desired temperature. Small aliquots were taken for NMR analysis to determine monomer conversions and reaction selectivities at the desired times.
Abbreviations

- PLA: poly(lactic acid); PCL: poly(caprolactone); ROP: ring-opening polymerization; ROCOP: ring-opening copolymerization; CHO: cyclohexene oxide; L0: limonene oxide; SA: succinic anhydride; PA: phthalic anhydride; MA: maleic anhydride; TBAB: tetrabutylammonium bromide; PPNX: bis-(triphosphophosphin)iminium salts; DNP: dinitrophenolate counterion; NMI: N-methylimidazole; DMAP: dimethylaminoimidazole; GPC: gel permeation chromatography; MALDI-ToF: matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; DSC: differential scanning calorimetry; TGA: thermogravimetric analysis.

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