Ring-Opening Copolymerization of Cyclohexene Oxide and Cyclic Anhydrides Catalyzed by Bimetallic Scorpionate Zinc Catalysts

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Abstract: The catalytic activity and high selectivity reported by bimetallic heteroscorpionate acetate zinc complexes in ring-opening copolymerization (ROCOP) reactions involving CO2 as substrate encouraged us to expand their use as catalysts for ROCOP of cyclohexene oxide (CHO) and cyclic anhydrides. Among the catalysts tested for the ROCOP of CHO and phthalic anhydride at different reaction conditions, the most active catalytic system was the combination of complex 3 with bis(triphenylphosphine)iminium as cocatalyst in toluene at 80 °C. Once the optimal catalytic system was determined, the scope in terms of other cyclic anhydrides was broadened. The catalytic system was capable of copolymerizing selectively and efficiently CHO with phthalic, maleic, succinic and naphthalic anhydrides to afford the corresponding polyester materials. The polyesters obtained were characterized by spectroscopic, spectrometric, and calorimetric techniques. Finally, the reaction mechanism of the catalytic system was proposed based on stoichiometric reactions.

Keywords: ring-opening copolymerization; epoxides; cyclic anhydrides; polymers; zinc complexes

1. Introduction

Commercial polyester materials are currently produced by polycondensation reactions between diols and diacids at high reaction temperature and prolonged reaction times to afford high-molecular weight polyesters [1,2]. In recent years, a broad range of biodegradable polyesters have been obtained via ring-opening polymerization (ROP) of cyclic esters (Scheme 1a) as a more sustainable alternative to traditional polyester materials [3–10]. In fact, polycaprolactone and polylactide have already been used for several applications [11–14]. However, the microstructure and properties of the resulting polymers are restricted by the limited number of commercially available cyclic esters. In this regard, the ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides (Scheme 1b) has emerged in recent years as alternative to the ROP of cyclic esters to prepare a larger number of polyester materials with a broader range of microstructures, properties and applications [15].

The ROCOP reaction of epoxides and cyclic anhydrides requires the use of a catalyst system, which is usually comprised by a combination of a metal complex and a nucleophile source [15]. A wide range of metal complexes, including chromium [16–20], magnesium [21–23],...
The ROCOP reaction of epoxides and cyclic anhydrides requires the use of a catalyst such as tetrabutylammonium salts (TBAX), bis-(triphenylphosphine)iminium salts (PFN-X) or 4-dimethylaminopyridine (DMAP) to increase the efficiency and selectivity of the metal complex [15]. In this context, zinc acetate complexes have displayed excellent catalytic activity and selectivity for the ROCOP reaction of epoxides and cyclic anhydrides. Coates et al. developed a very efficient β-diminate zinc acetate complex for the ROCOP of different epoxides and bi- or tricyclic anhydrides to afford the corresponding polymers with high molecular weights and narrow polydispersities [48]. Williams et al. obtained several homo- and heterobimetallic zinc complexes with outstanding catalytic activity and selectivity towards the synthesis of well-controlled polyester materials [21,44,45]. These bimetallic catalysts can activate both monomers facilitating the nucleophilic attack of the alkoxide or carboxylate group of one zinc atom to the activated monomer on the second zinc center. Moreover, these complexes have also catalyzed the synthesis of a broad range of multiblock polymeric materials by ROCOP of epoxides, anhydrides, carbon dioxide or lactones [49,50]. Zinc amido-oxazolinate complexes [43,46] have also been tested as catalysts for the ROCOP of epoxides and cyclic anhydrides, obtaining TOF values up to 4000 h⁻¹ [43]. It was observed that there is a relationship between catalytic activity and epoxide substrates used due to the effect of the electronic and steric properties of the epoxides in the chain propagation step [46]. Schiff-base zinc complexes in combination with a range of cocatalysts have been investigated as catalyst systems for the bulk and solution ROCOP of cyclohexene oxide (CHO) and maleic anhydride (MA) to produce polymeric materials [42]. The results showed alternating poly(cyclohexene maleate) when the process was carried out in toluene using a combination of zinc complex and DMAP as a cocatalyst.

**Scheme 1.** Synthesis of polyester materials via (a) ROP of cyclic esters; (b) ROCOP of epoxides and cyclic anhydrides.

Scorpionate aluminum and zinc complexes have been developed as efficient catalysts for the ROCOP of carbon dioxide and epoxides to afford polycarbonates and the terpolymerization reaction of epoxides, cyclic anhydrides and carbon dioxide [3,36,51–53]. The zinc-based complexes displayed good catalytic activity and selectivity for the synthesis of medium molecular weight poly(cyclohexene carbonate) (PCHC) with narrow molecular weight distributions in the absence of a nucleophile as a cocatalyst [52,53]. The use of helical aluminum catalysts for the ROCOP of a range of epoxides and cyclic anhydrides or CHO and CO₂ afforded the synthesis of polyester and polyether-polycarbonate materials respectively [36,51]. Furthermore, we have recently reported a new family of acetate zinc complexes as catalysts for the ROCOP of CHO with CO₂ to afford polycarbonates or the terpolymerization of CHO, CO₂ and phthalic anhydride (PA) to produce polyester-polycarbonate materials [53]. Encouraged by the catalytic activity and selectivity displayed...
by these complexes in ROCOP reactions involving CO₂, in this work, we have studied
the use of these friendly zinc complexes as catalysts for the ROCOP of CHO and cyclic
anhydrides with the aim of extend the substrate scope for these complexes in the synthesis
of polymeric materials. In addition, a mechanistic proposal has been presented for this
catalytic process.

2. Materials and Methods

All manipulations were performed under nitrogen, using standard Schlenk techniques.
Microanalyses were carried out with a Perkin–Elmer 2400 CHN analyzer (PerkinElmer, Inc.,
Waltham, MA, USA). ¹H and ¹³C NMR spectra were recorded on a Bruker Ascend TM-500
spectrometer (Bruker, Billerica, MA, USA) and referenced to the residual deuterated solvent.
Gel permeation chromatography (GPC) measurements were performed on a Shimadzu
LC-20A instrument (Shimadzu Corporation, Kyoto, Japan) equipped with a TSK-GEL
G3000H column and a refractive index detector (RID-20A). The GPC column was eluted
with THF at 25 °C at 1 mL·min⁻¹ and was calibrated using eight monodisperse polystyrene
standards in the range 580–48,300 Da. TGA analysis was performed on a TA instrument
TGA-Q50 (TA Instruments Inc., New Castle, DE, USA). 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 DSC-Q20 (TA Instruments Inc., New Castle, DE, USA).
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. The MALDI-ToF spectra were acquired using
a Bruker Autoflex II TOF/TOF spectrometer (Bruker, Billerica, MA, USA) using dithranol
(1,8,9-trihydroxyanthracene) as matrix material and NaOAc as additive. Commercially
available chemicals (Alfa Aesar, Ward Hill, MA, US, Sigma-Aldrich, Munich, Germany and
Fluka, Buchs, Switzerland) were used as received.

2.1. Materials and Reagents

Toluene was predried over sodium wire and distilled under nitrogen from sodium.
Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by
several freeze-thaw cycles. The synthesis of ligand precursors and zinc complexes was
conducted as previously reported [53–55]. Cyclohexene oxide (Sigma-Aldrich, Munich,
Germany) was pre-dried over calcium hydride, distilled under vacuum and stored under
nitrogen in a glove box. Phthalic, maleic and succinic anhydride (Sigma-Aldrich) were
sublimed three times and naphthalic anhydride was recrystallized in chloroform and
stored under nitrogen in a glove box. All other reagents were purchased from common
commercial sources and used as received.

2.2. General Procedure for the ROCOP of CHO with Cyclic Anhydrides

In the glovebox, zinc complex (50.09 µmol), cocatalyst (0.01 mmol) and cyclic anhydride
(5.09 mmol) were placed into a 10 mL Schlenk equipped with a small stir bar.
Toluene (2 mL) and cyclohexene oxide (5.09 mmol) were added to the reaction mixture.
Then, the Schlenk was taken out of the glovebox and placed in a preheated oil bath under
a nitrogen atmosphere at the desired temperature. The conversion of cyclic anhydride into
the corresponding polyester was monitored by NMR. Once the polyester was obtained, the
viscous mixture was dissolved in the minimum amount of dichloromethane, precipitated
with an excess of methanol to remove the unreacted reactants, catalyst, and co-catalyst and
finally, was filtered off and dried to afford a white solid.

3. Results

Dinuclear zinc complexes 1–3 (Figure 1) were synthesized in excellent yields as previ-
ously reported [53]. These complexes showed high stability in solution and in solid-state
in the presence of air for months. As previously commented, these complexes displayed
good catalytic activity for the synthesis of polycarbonates from the reaction of cyclohexene
oxide with carbon dioxide and for the preparation of terpolymers [53].
In order to extend the scope of application of these compounds in catalysis, further studies for ROCOP reactions were carried out. First, we explored the use of these complexes for the preparation of poly(\(\text{PA-alt-CHO}\)) (6) via ROCOP of phthalic anhydride (4) and cyclohexene oxide (5) (Scheme 2) and the results are shown in Table 1. Conversion and selectivity towards 6 were determined by \(^1\)H NMR spectroscopy of the crude reaction mixture.

\[ \text{PA, 4} + \text{CHO, 5} \xrightarrow{1-3 (0-1 \text{ mol\%}), \text{Cocatalyst}(0-2 \text{ mol\%})} 80^\circ\text{C}, \text{toluene, 16 h} \quad \text{poly(\(\text{PA-alt-CHO}\)), 6} + \text{poly(CHO), 7} \]

\(\text{Scheme 2. Synthesis of poly(\(\text{PA-alt-CHO}\)) (6) catalyzed by complexes 1–3.}\)

Initially, the ROCOP reaction of 4 and 5 was investigated using 1 mol.% of complexes 1–3 at 80 °C for 16 h under solvent-free conditions (Table 1, entries 1–3). Under these reaction conditions, complexes 1–3 displayed good catalytic activity but low selectivity towards the synthesis of 6 probably due to the low solubility of the anhydride into the epoxide. Thus, in order to improve the solubility of PA into CHO, the concentration of CHO in the reaction mixture was increased. Unfortunately, 79–82% of polyether was obtained under these conditions (Table 1, entries 4–6). Importantly, bimetallic zinc complexes 1–3 required the addition of PA into the reaction mixture to catalyze the ROP of CHO (Table 1, entries 7–9).

The addition of toluene as a solvent resulted in an increase of the selectivity towards the formation of 6, although the catalytic activity decreased (Table 1, entries 10–12). Complex 3 displayed the highest catalytic activity and therefore complex 3 was selected to optimize the catalytic system. Entries 12 and 13 of Table 1 show that a more coordinative solvent such as THF caused a decrease in the catalytic activity of the system. On the other hand, lower conversion was achieved when using nondistilled CHO (Table 1, entry 14). As it was expected, the addition of an external nucleophile such as of 4-dimethylaminopyridine (DMAP) not only increased the selectivity but also the catalytic activity of complex 3 (Table 1, entries 15 and 16) [3,38].

In order to continue with the optimization of the catalytic system for the synthesis of 6, the addition of a range of nucleophiles was investigated using 1 mol.% of complex 3 and 2 mol.% of the corresponding cocatalyst in toluene at 80 °C for 16 h. The results are shown in Table 2. Tetraethylammonium chloride (TBAC), bromide (TBAB) and iodide (TBAI) were initially screened as cocatalyst obtaining conversions in the range of 66 to 88% with excellent selectivities towards 6 (93–97%) (Table 2, entries 1–3). Then, bis(triphenylphosphine)iminium chloride (PPNCl), azide (PPNCl3) and 2,4-dinitrophenolate (PPNCl2) were studied as cocatalysts (Table 2, entries 4–6) obtaining excellent conversions and selectivities towards 6. In addition, when the reaction time was decreased to 8 h (Table 2, entries 8 and 9), higher conversion was obtained when using PPNCl as a cocatalyst (Table 2, entry 8). Finally, a control experiment using 2 mol.% of PPNCl...
in the absence of complex 3 (Table 2, entry 10) confirmed that both catalyst components are needed to achieve excellent conversion and selectivity.

Table 1. Synthesis of poly(PA-alt-CHO) 6 catalyzed by complexes 1–3.

| Entry | [Cat]:[CHO]:[PA] | Catalyst | Solvent | Conversion (%)
|-------|-----------------|----------|---------|----------------|
| 1     | 1:100:100       | 1        | -       | 70 22 78      |
| 2     | 1:100:100       | 2        | -       | 75 20 80      |
| 3     | 1:100:100       | 3        | -       | 76 28 72      |
| 4     | 1:200:100       | 1        | -       | 75 20 80      |
| 5     | 1:200:100       | 2        | -       | 77 18 82      |
| 6     | 1:200:100       | 3        | -       | 78 21 79      |
| 7     | 1:100:0         | 1        | -       | 0 - -         |
| 8     | 1:100:0         | 2        | -       | 0 - -         |
| 9     | 1:100:0         | 3        | -       | 0 - -         |
| 10    | 1:100:100       | 1        | Toluene | 42 42 58      |
| 11    | 1:100:100       | 2        | Toluene | 42 43 58      |
| 12    | 1:100:100       | 3        | Toluene | 50 43 57      |
| 13    | 1:100:100       | 3        | THF     | 35 46 54      |
| 14    | 1:100:100       | 3        | Toluene | 35 45 55      |
| 15    | 1:100:100       | 3        | Toluene | 57 90 10      |
| 16    | 1:100:100       | 3        | Toluene | 90 95 5       |

Reactions were carried out at 80 °C for 16 h using 1 mol.% of complexes 1–3 as catalysts. Conversion relative to PA was determined by 1H NMR spectroscopy. Nondistilled CHO was used. 1 mol.% of 4-dimethylaminopyridine was used as cocatalyst. 2 mol.% of 4-dimethylaminopyridine was used as cocatalyst.

Table 2. Influence of the cocatalyst in the optimization of the catalytic system for the synthesis of poly(PA-alt-CHO) (6).

| Entry | [3]:[Cocat]:[CHO]:[PA] | Cocatalyst | Conversion (%) | Polyester, 6 (%) | Polyether, 7 (%) |
|-------|-------------------------|------------|---------------|------------------|------------------|
| 1     | 1:2:100:100             | TBAC       | 84            | 97               | 3                |
| 2     | 1:2:100:100             | TBAB       | 88            | 93               | 7                |
| 3     | 1:2:100:100             | TBAI       | 66            | 97               | 3                |
| 4     | 1:2:100:100             | PPNCI      | 96            | 97               | 3                |
| 5     | 1:2:100:100             | PPNN\textsubscript{3} | 66         | 95               | 5                |
| 6     | 1:2:100:100             | PPNDNP     | 95            | 96               | 4                |
| 7     | 1:2:100:100             | DMAP       | 90            | 95               | 5                |
| 8     | 1:2:100:100             | PPNCI      | 60            | 94               | 6                |
| 9     | 1:2:100:100             | PPNDNP     | 45            | 93               | 7                |
| 10    | 0:2:100:100             | PPNCI      | 40            | 96               | 4                |

Reactions were carried out in toluene (2 mL) at 80 °C for 16 h using complex 3 and a cocatalyst. Conversion relative to PA was determined by 1H NMR spectroscopy. Reaction was carried out for 8 h. Complex 3 was not added.

The effect of the catalyst loading on the catalytic activity, selectivity and molecular weight of the resulting copolymers was investigated (Table 3). When the catalyst loading was increased to 2 mol.% (Table 3, entry 1), quantitative conversion and 97% selectivity towards 6 were achieved. On the other hand, lower conversions and good selectivities were obtained when the catalyst loading was decreased (Table 3, entries 3–4). As can be seen in Table 3, low molecular weights ($M_n = 2.46–3.67$ kg/mol) and narrow polydispersity values (1.39–1.58) were obtained. Moreover, the reduction of the catalyst loading resulted in a slight increase in the molecular weight of the polyesters obtained (Table 3, entries 1–4).
Table 3. Effect of the catalyst loading on the activity of the catalytic system for the synthesis of poly(PA-alt-CHO) (6) 1.

| Entry | [3]:[PPNCl]:[CHO]:[PA] | Conversion (%) 2 | Polyester, 6 (%) 2 | M_n exp (kg·mol⁻¹)(PDI) 3 |
|-------|-------------------------|------------------|-------------------|--------------------------|
| 1     | 1:2:50:50               | 100              | 97                | 2.46 (1.58)              |
| 2     | 1:2:100:100             | 96               | 97                | 2.87 (1.49)              |
| 3     | 1:2:150:150             | 76               | 95                | 3.29 (1.45)              |
| 4     | 1:2:200:200             | 70               | 91                | 3.67 (1.39)              |

1 Reactions were carried out in toluene (2 mL) at 80 °C for 16 h using complex 3 and PPNCl. 2 Conversion relative to PA determined by 1H NMR spectroscopy. 3 Determined by GPC.

Having determined the optimal reaction conditions, the use of several cyclic anhydrides was examined for the ROCOP process using CHO as epoxide substrate (Scheme 3) and the results are listed in Table 4. When succinic or maleic anhydride were used as the cyclic anhydride substrate, the ROCOP proceeded smoothly and excellent conversions and selectivities were obtained, affording the corresponding low to medium molecular weight polyester materials with narrow polydispersities (Table 4, entries 1–4). However, the use of naphthalic anhydride as monomer for the ROCOP with CHO was challenging (Table 4, entries 5–7). When the reaction was carried out in toluene at 80 °C, only 55% conversion of NA into poly(NA-alt-CHO) (13) was obtained (Table 4, entry 5). Therefore, the ROCOP of CHO and NA was studied using CHO as solvent. As can be seen in Table 4 (entries 6 and 7), higher conversions were achieved under these reaction conditions. Furthermore, all polyesters displayed low to medium molecular weights which were influenced by the solvent used in the process.

Scheme 3. ROCOP of CHO and different cyclic anhydrides catalyzed by complex 3 and PPNCl.

Table 4. Synthesis of polyesters 11–13 catalyzed by complex 3 and PPNCl 1.

| Entry | [3]:[PPNCl]:[CHO]:[CA] | CA     | Conversion (%) 2 | Polyester, 6 (%) 2 | M_n exp (kg·mol⁻¹)(PDI) 3 |
|-------|-------------------------|--------|------------------|-------------------|--------------------------|
| 1     | 1:2:100:100             | SA     | 100              | 97                | 2.95 (1.43)              |
| 2     | 1:2:200:200             | SA     | 99               | 99                | 4.03 (1.34)              |
| 3     | 1:2:100:100             | MA     | 100              | 89                | 2.40 (1.51)              |
| 4     | 1:2:200:200             | MA     | 100              | 90                | 3.52 (1.39)              |
| 5     | 1:2:100:100             | NA     | 55               | 96                | 2.07 (1.48)              |
| 6 4   | 1:2:100:100             | NA     | 100              | 96                | 2.92 (1.45)              |
| 7 4   | 1:2:200:200             | NA     | 98               | 98                | 3.89 (1.37)              |

1 Reactions were carried out in toluene (2 mL) at 80 °C for 16 h using complex 3 and PPNCl. 2 Conversion relative to the cyclic anhydride determined by 1H NMR spectroscopy. 3 Determined by GPC. 4 Reactions were carried out using CHO (2 mL) as solvent.
All polymers were characterized by NMR and IR spectroscopy (Figure 2 and Figures S1–S12 in the SI), gel permeation chromatography (GPC) (Figure S13 in the SI) and MALDI-ToF mass spectroscopy (Figure 3 and Figure S14 in the SI). The NMR spectra of copolymers 6,11–13 are in good agreement with those previously reported [32,36] and confirmed the formation of the corresponding alternating copolyester (Figure 2). On the other hand, the IR spectra of copolymers clearly showed the presence of a strong band in the range 1710–1729 cm⁻¹ corresponding to the ν(C=O) stretching vibration of the ester group, which is shifted to lower wavenumbers compared with that of the corresponding cyclic anhydride starting materials (1736–1777 cm⁻¹).

MALDI-ToF analysis supported the formation of alternating poly(PA-alt-CHO) without the presence of polyether chains (Figure 3). The MALDI-ToF spectrum showed three major distributions of poly(PA-alt-CHO) end-capped with a carboxylic acid end-group and a hydroxyl, a cyclohexanol or a carboxylic acid end-groups with sodium or potassium as counterion. Even though the chloride initiates the copolymerization, no chloride end-group was shown due to the resulting acyl chloride was unstable and quickly hydrolyzed to the corresponding carboxylic acid during the work-up procedure.

Inductively coupled plasma–mass spectrometry (ICP–MS) was used to determine the metal content of the polyester synthesized in Table 3, entry 2. The Zn content of the polymer was determined to be 1.700 mg·g⁻¹ by ICP–MS, confirming that most of the catalyst was removed in the purification process. However, this result showed that it is impossible to entirely remove the metal traces from the polymer when using a homogeneous catalyst.

The thermal properties of the resulting polyesters were investigated by differential scanning calorimetry (DSC) (Figures S16, S18, S20 and S22 in the SI). As can be seen in Figure 4, the glass transition temperature ($T_g$) of the copolymers is highly dependent on the substrate used. Thus, poly(SA-alt-CHO) and poly(MA-alt-CHO) displayed lower $T_g$ values than the polyesters in which an aromatic anhydride was used. Moreover, poly(NA-alt-CHO) showed the highest $T_g$ value because of the stiffness of the polyester. TGA analysis of polyesters 6,11–13 showed that all polyesters decompose around 300 °C (Figures S15, S17, S19 and S21 in the SI).
Then, several stoichiometric reactions were carried out in order to gain insight into the reaction mechanism for the ROCOP of CHO and PA catalyzed by the catalytic system comprised by complex 3 and PPNCl (Figure 5). Addition of two equivalents of PPNCl to a
solution of complex 3 in CDCl₃ resulted in minor changes in the NMR spectrum of complex 3 (Figure 5b). When 4 was added to the catalytic system, no changes in the NMR spectrum were observed after 24 h of reaction at 80 °C (Figure 5c). On the contrary, new signals showed up at around 8.5 ppm when PA was added to the catalytic system, suggesting that the first step of the copolymerization corresponds with the ring-opening of the cyclic anhydride (Figure 5d).

![Diagram](image)

**Figure 5.** (a) ¹H NMR spectrum of compound 3 in CDCl₃. (b) ¹H NMR spectrum of compound 3 + PPNCl in CDCl₃. (c) ¹H NMR spectrum of compound 3 + PPNCl + cyclohexene oxide 4 at 80 °C and t = 24 h in CDCl₃. (d) ¹H NMR spectrum of compound 3 + PPNCl + phthalic anhydride 5 at 80 °C and t = 24 h in CDCl₃.

The reaction of one equivalent of 4 and 5 with one equivalent of complex 3 and 2 equivalents of PPNCl at 80 °C was also monitored by ¹H NMR (Figure 6). It is worth noting that even at room temperature phthalic anhydride was activated by the catalytic system, and the chloride anion provided by PPNCl was able to ring-open the activated anhydride as it is supported by the appearance of new resonance signals at 8.3 ppm. When the reaction temperature was increased up to 80 °C, the signal at 8.30 ppm increased its intensity, ascertaining the fact that the first step of the copolymerization is the ring-opening of the cyclic anhydride. On the other hand, no changes in the signal of CHO were observed within 16 h. After that, most of the cyclic anhydride was ring-opened and a new signal at 4.98 ppm showed up which corresponds to the ester moiety (Figure 6).
Figure 6. Reaction one equivalent of cyclohexene oxide 4 and phthalic anhydride 5 with one equivalent of complex 3 and two equivalents of PPNCl in CDCl3, (a) at room temperature; (b) at 80 °C after 0 h; (c) at 80 °C after 16 h.

A plausible mechanism for the ROCOP of CHO and PA catalyzed by the catalytic system comprised by complex 3 and PPNCl is proposed in Scheme 4. Firstly, the epoxide and cyclic anhydride may coordinate to the two zinc centers to form intermediate 3a. Then, the chloride anion could attack at the activated cyclic anhydride to generate the metal carboxylate specie 3b which can therefore ring-open the activated molecule of CHO by the second zinc center to give rise to the alkoxide specie 3c, which could in turn experiment consecutive ring-opening reactions of cyclic anhydrides and epoxides to afford the corresponding polyester. Even though this proposal could be the main mechanism, an initiation step by an acetate group to result in polymers with an acetate end-group cannot be ruled out.

Scheme 4. Proposed mechanism for the ROCOP of CHO and PA catalyzed by complex 3 and PPNCl.
4. Conclusions

Bimetallic acetate zinc catalysts 1–3 were investigated as catalysts for the ROCOP of cyclohexene oxide and phthalic anhydride to obtain the corresponding poly(PA-alt-CHO). To optimize the copolymerization process, the effect of the solvent, temperature, type of cocatalyst, catalyst/cocatalyst ratio, and catalyst loading were studied. The combination of 1 mol.% of complex 3 and 2 mol.% of PPNCI at 80 °C for 16 h using toluene as solvent resulted to be an efficient catalyst system for ROCOP of CHO and PA with conversion and selectivity values up to 100% and 97%, respectively. This catalyst system also catalyzed ROCOP of CHO with succinic, maleic and naphthalic anhydrides to give rise to several polymer materials with low to medium molecular weight and narrow polydispersities. Stoichiometric reactions suggested that the first step of the copolymerization process is the ring-opening of the cyclic anhydride by the chloride counterion. Further catalyst development is ongoing in our research group to increase the catalytic activity and productivity of bimetallic zinc complexes as catalysts for ring-opening copolymerization processes.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/103390/polym13101651/s1, Figure S1. $^1$H NMR spectrum of poly(PA-alt-CHO) (6), Figure S2. $^{13}$C($^1$H) NMR spectrum of poly(PA-alt-CHO) (6), Figure S3. IR spectra of: poly(PA-alt-CHO) (6), PA (4), Figure S4. $^1$H NMR spectrum of poly(SA-alt-CHO) (11), Figure S5. $^{13}$C($^1$H) NMR spectrum of poly(SA-alt-CHO) (11), Figure S6. IR spectra of: (a) poly(SA-alt-CHO) (11), (b) SA (8), Figure S7. $^1$H NMR spectrum of poly(MA-alt-CHO) (12), Figure S8. $^{13}$C($^1$H) NMR spectrum of poly(MA-alt-CHO) (12), Figure S9. $^{13}$C($^1$H) NMR spectrum of poly(MA-alt-CHO) (12), Figure S10. $^1$H NMR spectrum of poly(NA-alt-CHO) (13), Figure S11. $^{13}$C($^1$H) NMR spectrum of poly(NA-alt-CHO) (13), Figure S12. IR spectra of: (a) poly(NA-alt-CHO) (13), (b) NA (10), Figure S13. GPC profile of poly(PA-alt-CHO) (6), Figure S14. MALDI-ToF spectrum of poly(PA-alt-CHO) (6), Figure S15. TGA analysis of poly(PA-alt-CHO) (6), Figure S16. DSC analysis of poly(PA-alt-CHO) (6), Figure S17. TGA analysis of poly(SA-alt-CHO) (11), Figure S18. DSC analysis of poly(SA-alt-CHO) (11), Figure S19. TGA analysis of poly(MA-alt-CHO) (12), Figure S20. DSC analysis of poly(MA-alt-CHO) (12), Figure S21. TGA analysis of poly(NA-alt-CHO) (13), Figure S22. DSC analysis of poly(NA-alt-CHO) (13).

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