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Co-Ni Cyanide Bi-Metal Catalysts: Copolymerization of Carbon Dioxide with Propylene Oxide and Chain Transfer Agents

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Abstract: Synthesis of copolymers from carbon dioxide (CO₂) and epoxides is an important research direction as such processes utilize the abundant greenhouse gas and deliver useful products. Specifically, cooligomers of CO₂ and propylene oxide (PO) with a non-alternating structure can be used for polyurethane preparation. They are synthesized by employing Zn-Co cyanide catalysts. The application of alternative metal cyanide complexes is interesting from scientific and practical points of view. The purpose of this work was to study the copolymerization of CO₂ and PO in the presence of Co-Ni cyanide catalysts and chain transfer agents (CTAs) in order to obtain low molecular weight products. Three Co-Ni catalysts with different contents of complexing agents were synthesized, characterized by several analytical methods and applied for this reaction. The complex without complexing agents was chosen for detailed investigation. 1,6-Hexanediol proved to be a more preferred CTA than poly(propylene glycol) and adipic acid. An oligo(ethercarbonate) (M_n = 2560, PDI = 2.5, CO₂ = 20 mol.%) capped with OH groups was synthesized with relatively high productivity (1320 g_{PO+CO2}/g_{cat} in 24 h) and characterized by matrix-assisted laser desorption/ionization (MALDI) MS and NMR methods. The main chain transfer routes during the cooligomerization were suggested on the basis of the research results.

Keywords: metal cyanide catalyst; cobalt; nickel; carbon dioxide; propylene oxide; copolymerization; chain transfer agent; oligo(ethercarbonate); polyurethanes

1. Introduction

 CO_2 utilization for the production of chemicals attracts a lot of attention because it can decrease the use of fossil-based starting materials [1]. One way of utilizing CO_2 is incorporating it into copolymers with epoxides [2–11]. A lot of efforts were given to the synthesis of the alternating copolymers (structure 1 in Scheme 1) of CO_2 with propylene oxide (PO) because PO is a cheap and industrially relevant epoxide. However, these materials have glass transition temperature around 40 °C which makes them inconvenient for usage. On the other hand, the inclusion of ether linkages resulting in poly(ethercarbonate)s (structure 2 in Scheme 1) decreases the glass transition temperature. One of the options to use CO_2/PO copolymerization products is the preparation of low molecular weight materials and their incorporation into polyurethanes (PU) [12–23]. The application of non-alternating CO_2/PO cooligomers is especially attractive because, in some cases, they may substitute poly(propylene glycol)s (PPGs) thereby decreasing the consumption of fossil derived PO [1,22]. Oligo(ethercarbonate)s



(structure 4 in Scheme 1) can be efficiently produced by CO₂/PO cooligomerization in the presence of Zn-Co metal cyanide catalysts and chain transfer agents (CTAs) [22–34]. Usually, polyols or polycarboxylic acids (structure 5 in Scheme 1) are employed to control molecular weight of the final products. The advantages of these catalysts are relatively high activity, low content of unsaturated chain ends, the absence of product coloration and regioregularity of PO units in the polymer chains. However, the catalytic materials are prone to give considerable amounts of propylene carbonate (PC) as a by-product (structure 3 in Scheme 1). Depending on particular Zn-Co complex and reaction conditions used, its amount can vary from several percent to dozens of percent. As these catalysts are used for industrial production of PPGs and oligo(ethercarbonate)s and have been thoroughly studied for PO polymerization and CO_2/PO co(poly)oligomerization, the issues related to intellectual property may also arise when the application of the catalysts is necessary.



Scheme 1. Different products of PO/CO₂ copolymerization.

Other metal cyanide complexes were also applied to copolymerize PO and CO₂: Zn-Cr [35,36], Zn-Fe [36–41], Zn-Ni-Fe, Zn-Ni-Co [42], Zn-Mo, Zn-Mn, Zn-Cd [36], Zn-Ni [36,43,44], Co-Ni [43,45]. Co-Ni catalyst obtained by dehydration of $Co(H_2O)_2[M(CN)_4]$ 4H₂O seemed to us to be attractive as it copolymerized CO₂ and PO with relatively high productivity and produced no PC [45]. Additionally, it was shown that performance of a Co-Ni complex prepared in the presence of complexing agents competed with that of a Zn-Co catalyst when these materials were used to catalyze PO oligomerization in the presence of PPG [46]. As there is no data on target preparation of CO₂/PO cooligomers in the presence Co-Ni cyanide complexes and CTAs, we explored this process to estimate their reactivity and the composition of the final products. It was found that a Co-Ni complex without complexing agents can efficiently catalyze CO₂/PO cooligomerization in combination with 1,6-hexanediol (HD) to give an oligo(ethercarbonate) capped mainly with secondary OH groups. Most of OH ends of HD participated in the chain transfer processes.

2. Results and Discussion

2.1. Catalyst Characterization

Three Co-Ni complexes were prepared during this work: Co-Ni(0), Co-Ni(t), Co-Ni(P). The first complex was synthesized following the procedure described in [45]. The difference is that the precipitated solid was washed two times with deionized (DI) water. Co-Ni(t) and Co-Ni(P) were prepared in general accordance with the method published in [46]. However, when the latter was followed exactly as it was described, the product was heterogeneous in color. This happened because it seems to have heterogeneous distribution of poly(tetrahydrofuran) (poly(THF)) over the material. For this reason, the published method was modified; that is washings with H₂O/tBuOH,

poly(THF)/tBuOH and with pure tBuOH as well as additional centrifugations were done (see Section 3.2). Data on catalyst characterizations are presented in Table 1.

Table 1. Results of catalyst characterizations obtained by energy-dispersive X-ray spectroscopy (EDX) and nitrogen adsorption–desorption.

Catalyst	Co Source	Complexing Agents	Co/Ni (EDX)	BET, m ² /g
Co-Ni(t)	CoCl ₂	tBuOH, poly(THF)	1.32	33.3
Co-Ni(P)	CoCl ₂	tBuOH, poly(THF)	1.01	19.6
Co-Ni(0)	CoSO ₄	-	1.01	23.3

The higher surface area and Co/Ni ratio were obtained for Co-Ni(t). The lowest surface area was for Co-Ni(P), synthesized with the intention to introduce more poly(THF) compared to Co-Ni(t). Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for the three catalysts are shown in Figures 1 and 2. Co-Ni(0) started to decompose at temperatures greater than 400 °C. Before that, it lost about 0.3 wt.%, which should be associated with the removal of water molecules, with approximately 0.1 wt.% (from ≈70 °C to ≈140 °C) accounting for water molecules interacting with the metal centers [47]. The rest of the water (0.2 wt.%) might be related to the exposure of the material to the atmosphere during the sample preparation. The other two Co-Ni materials had several regions of weight loss. Co-Ni(t) released volatiles with relatively low dm/dT values at temperatures up to about 225 °C when the weight loss was 0.9 wt.%. This most likely happened due to the detaching of tBuOH and H₂O molecules. Then there was weight loss "acceleration" up to about 275 °C. After this temperature, dm/dT showed declining behavior until about 430 °C (a total weight loss of 3.8 wt.%) when the Co-Ni structure started to decompose. In the case of Co-Ni(P), the stage after 225 °C (a total weight loss of 0.6 wt.%) was followed by another raise of dm/dT and the sample weight decreased by 13.0% when a temperature of 400 °C was reached. Such behavior of Co-Ni(P) during its decomposition might be related to the presence of coordinated and non-coordinated poly(THF) molecules. As can be seen from the TG and DTG graphs, there are also differences in decomposition behavior for the three catalysts at temperatures higher than 400 °C. These phenomena imply different organization of Co-Ni cyanide structures in these materials.



Figure 1. Thermogravimetry (TG) curves for the Co-Ni complexes used in this work and for poly(tetrahydrofuran) (poly(THF)).



Figure 2. Derivative thermogravimetry (DTG) curves for the Co-Ni complexes used in this work and for poly(THF).

Morphology of the Co-Ni complexes was characterized by SEM (Figure 3). Co-Ni(0) had the smallest particle size and seem to have narrower particle distribution compared to the other complexes. In the case of Co-Ni(P), the catalyst particles have a high degree of agglomeration due to the presence of excess poly(THF).





(a)

Figure 3. Cont.



Figure 3. SEM images of: (a) Co-Ni(0); (b) Co-Ni(t); (c) Co-Ni(P).

The powder X-ray diffraction (XRD) patterns of the complexes show two major broad peaks of relatively low intensity (Figure 4). The peaks at $2\theta = 19.4^{\circ}$ are asymmetric and those at $2\theta = 25.2^{\circ}$ result from the overlap of at least two peaks. Scatter from an amorphous phase is seen for Co-Ni(t) and Co-Ni(P). This can be related to the presence of complexing agents in the materials. The crystal phases should have nano structures because the corresponding peaks are broad. The presence of similar broad peaks means these products have the same main crystalline phases. Co-Ni(t) and Co-Ni(P) have additional crystalline phases (peaks at 16° and 28.4° , respectively).



Figure 4. XRD patterns of the Co-Ni complexes used in this work.

2.2. CO₂/PO Copolymerization

The Co-Ni materials were tested as catalysts for PO/CO₂ conversion in the presence of PPG-425 (Table 2). The initial intention was to try the catalyst described in [46] to catalyze CO₂/PO copolymerization as it competed with a Zn-Co complex in performance when catalyzing PO homooligomerization. As mentioned, it was necessary to add washings to the previously published catalyst synthesis method. This modified procedure afforded Co-Ni(t). It contained less complex agents and performed worse in PO homooligomerization when compared with the data from [46]. Therefore, more poly(THF) was used during the catalyst synthesis in order to obtain a material with a higher proportion of complexing agents. Accordingly, Co-Ni(P) was synthesized. This complex turned out to be inactive though. The other two materials had quite similar performance (Table 2).

Attempts to increase the surface area of Co-Ni(0) were made by using the ball-milling method. Indeed, the surface area could be increased up to $50 \text{ m}^2/\text{g}$ when the following conditions were applied: steel container, ZrO_2 balls, 140/1 ball-to-powder ratio, 400 rpm, 60 min. The obtained material was inactive in the copolymerization process. The catalyst activity was lost even when a short treatment time was used: steel container, ZrO_2 balls, 140/1 ball-to-powder ratio, 500 rpm, 10 min. The reasons for this phenomenon were not studied.

Co-Ni(0) complex is easy to prepare, therefore it was chosen for further studies regarding the possibility to control product molecular weight by the introduction of different CTAs (Table 3). Copolymerization in neat PO at 90 °C resulted in a high molecular weight product with a broad distribution (run 4). After two hours of reaction, temperature inside the autoclave increased to 97 °C

and returned back to 90 °C only at the end of the process. The high value of PDI and the spontaneous temperature raise could result from the high viscosity of the reaction mixture as well as exothermicity of the process rendering it to be out of control to some extent. The reaction in the presence of PPG-425 had a lower rate and molecular weight decreased (run 5). The presence of ten times higher amount of CTA induced a drop of activity and the length of polymer chains as well as reduction of the proportion of carbonate units in the whole product mixture (run 6). It should be noted that in this case the conversion of the CTA to poly(ethercarbonate) was far from complete because the peak of PPG-425 was found in the gel permeation chromatography (GPC) trace of the reaction product. Surprisingly, it turned out that the carbonate content in the newly formed polymer segments was higher than the content at the lower PPG/cat ratio.

Table 2. Results of CO₂/PO conversion in the presence of synthesized Co-Ni complexes.

Run ¹	Catalyst	Prod. ² , g/g	w(PC) ² , wt.%	ν(POCO ₂) ² , mol.%	M _n , g/mol	PDI ²	conv(PO) ² , %
1	Co-Ni(t)	269	0.1	30	51,650	6.6	17
2	Co-Ni(0)	233	0.0	30	48,300	6.8	14
3	Co-Ni(P)	inactive					

¹ Reaction conditions: PO/cat = 1330 g/g (cat is the abbreviation for catalyst), poly(propylene glycol) (PPG)-425/cat = 0.024 mol/g, 90 °C, 3 h, copolymerization method I, initial pressure 2.0 MPa (r.t.), reaction pressure 4.3 MPa. ² Prod., w(PC), ν (POCO₂), PDI, conv(PO) are productivity (the total mass of products formed divided by the catalyst mass), the mass fraction of propylene carbonate (PC) in the product mixture (PC and polymer), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the polymer chains (see Supplementary Materials), polydispersity index and PO conversion, respectively.

Table 3. Results of CO₂/PO copolymerization in the presence of PPG-425 or adipic acid (AdipA).

Run ¹	СТА	CTA/cat, mol/g	Time, h	Prod. ² , g/g	w(PC) ² , wt.%	ν(POCO ₂) ² , mol.%	ν(POCO ₂) * ² , mol.%	M _n , g/mol	PDI ²	Conv(PO) ² , %
4	no	0	3	376	0	33	33	543,910	58.1	23
5	PPG-425	0.024	3	233	0	30	31	48,300	6.8	14
6	PPG-425	0.24	3	44	0.5	12	48	28,960	3.7	2
7	AdipA	0.024	3	176	0.2	36	37	25,490	6.1	10
8	AdipA	0.24	3	11	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
9	PPG-425	0.24	24	377	0.6	22	30	28,950	4.8	23
10 ³	PPG-425	0.24	24	407	19.5	19	27	26,170 (1,844,790)	2.6 (1.2)	27
$11 \ ^{4}$	PPG-425	0.24	24	traces	n.d.	-	-	n.d.	n.d.	n.d.

¹ Reaction conditions: Co-Ni(0), PO/cat = 1330 g/g, 90 °C, initial pressure 2.0 MPa (r.t.), reaction pressure 4.3 MPa, polymerization method I was used for runs 4–8 and method II was used for the other experiments. ² Prod., w(PC), v(POCO₂), v(POCO₂) *, PDI, conv(PO) are productivity (the total mass of products formed divided by the catalyst mass), the mass fraction of PC in the product mixture (PC and polymer), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the polymer chains (see Supplementary Materials), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the newly formed polymer segments, polydispersity index and PO conversion, respectively. ³ Bis(triphenylphosphoranylidene)ammonium chloride (PPNCI) was added into the system, PPNCI/Co = 1. ⁴ 4-(Dimethylamino)pyridine (DMAP) was added into the system, DMAP/Co = 1. Traces of the products resulted (PPG and PC). CTA: chain transfer agent.

As dicarboxylic acids served as efficient CTAs for Zn-Co catalysts [24,31–33], adipic acid (AdipA) was used because it is an inexpensive, easily available and industrially important acid (runs 7, 8). It follows from the obtained data that, compared to PPG-425, AdipA is more efficient in decreasing molecular weight of the product and a somewhat higher carbonate unit content was obtained at a low load of this CTA (run 7 vs. run 5). However, at the higher CTA/cat ratio, the catalyst productivity was much lower and AdipA was not used further in the investigation.

Prolonging the reaction time to 24 h considerably increased catalyst productivity when using PPG-425 (run 9). Attempts were made to improve CO_2 incorporation into the polymer chains by introduction of a cocatalyst: PPNCl (bis(triphenylphosphoranylidene)ammonium chloride), DMAP (4-(dimethylamino)pyridine). We speculated that the high degree of PO homopolymerization could be decreased by weakening polymer chain coordination to active catalytic centers and that Lewis bases could be useful in the implementation of this idea. Indeed, when PPNCl was used, more CO_2

reacted (run 10). However, this increment was related to a higher fraction of PC in the product and the polymer had a somewhat lower carbonate unit fraction compared to the run without PPNCl. It is interesting that when PPNCl was used, a bimodal molecular weight distribution (MWD) was found for the resulting polymer. The introduction of a stronger Lewis base, DMAP, suppressed catalytic activity and only PC and PPG resulted (run 11).

When PPG-425 was replaced with HD, much higher productivity and a lower M_n value were obtained compared to the run with PPG-425 (Table 4, run 12 vs. Table 3, run 9). Further increasing HD/cat synthesized the product with M_n around 2000 (run 13). The MWD was quite broad though. We also tried to initiate cooligomerization in the absence of CO₂ (run 14). However, the obtained product layered upon standing. One layer consisted mainly of a PO homooligomer and another one was composed of a CO₂/PO cooligomer. Runs carried out at higher temperatures afforded higher productivities and the products had higher molecular weights and lower PDI values (runs 15, 16). Finally, at the twice higher HD/cat ratio, an oligomer with relatively narrow PDI was synthesized (run 17). T_g were measured for the products obtained in runs 15–17. As follows from Table 4, the values were far below 0 °C.

The oligo(ethercarbonate) obtained in run 17 (OECHD) was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) and different NMR techniques in order to reveal HD incorporation into the oligomer chains and the nature of oligomer end groups.

Table 4. Results of CO ₂ /PO c	copolymerization in the	presence of 1,6-hexanediol	(HD).
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Run ¹	CTA/cat, mol/g	Т, °С	Prod. ² , g/g	w(PC) ² , wt.%	ν(POCO ₂) ² , mol.%	ν(POCO ₂) * ² , % mol	M _n , g/mol	PDI ²	Conv(PO) ² , %	T _g , [°] C
12	0.24	90	1116	1.1	35	37	8360	9.2	66	n.d.
13	0.47	90	700	3.7	36	40	1970	6.0	41	n.d.
14^{3}	0.47	90	1172	3.4	33	35	n.d.	n.d.	70	n.d.
15^{4}	0.47	105	1163	3.9	31	33	3740	4.4	71	-43.4
16^{4}	0.47	120	1642	3.6	23	24	4620	2.8	100	-47.4
17^{4}	0.94	120	1528	6.5	25	26	2560	2.5	95	-48.6

¹ Reaction conditions: Co-Ni(0), PO/cat = 1330 g/g, 24 h, initial pressure 2.0 MPa (r.t.), reaction pressure 4.3 MPa, polymerization method II. ² Prod., w(PC), ν (POCO₂), ν (POCO₂)*, PDI, conv(PO) are productivity (the total mass of products formed divided by the catalyst mass), the mass fraction of PC in the product mixture (PC and polymer), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the polymer chains (see Supplementary Materials), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the newly formed polymer segments, polydispersity index and PO conversion, respectively. ³ Heating of the autoclave was started without CO₂. The gaseous monomer was introduced after 14 min. ⁴ Initial pressure was 1.4 MPa in order to keep reaction pressure equal to 4.3 MPa.

2.3. MALDI-TOF MS Analysis of the Oligo(Ethercarbonate) Synthesized in the Presence of HD

Firstly, a sample preparation method described in [26] was employed (see Section 3.4). Accordingly, 2,5-dihydroxybenzoic acid (DHBA) matrix and acetonitrile/water (1/2) solvent were used. It turned out, however, that it gives a relatively high intensity of unsaturated (allyl or propenyl) terminated chains, not well resolved peaks and poor spectrum quality for a high molecular weight region (e.g., m/z > 1300). When a sample preparation procedure involving the use of trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) matrix and THF solvent [48] was applied, the signals of the unsaturated chains diminished greatly, and the resolution improved. Spectra in the presence of sodium trifluoroacetate and without it gave similar results. However, peaks had higher intensity in the latter case. The MALDI-TOF MS spectrum of the OECHD (Figure 5) is quite complex due to the non-alternating product structure and close positions of isotopic distributions.



Figure 5. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS spectrum of OECHD in the range m/z = 700-2100.

The hydroxyl terminated species incorporating HD units $HO-(CH_2)_6-O-(C_3H_6O)_x(CO_2)_yHNa$ dominate in the MALDI-TOF MS spectrum. The position of the peaks corresponding to the monoisotopic species in the spectrum can be described by the equation:

$$58.04 \cdot x + 43.99 \cdot y + 118.1 + 22.99 = m_{MI}/z,$$
(1)

where x is the number of PO units; y is the number of CO₂ units; 58.04, 43.99, 118.1 and 22.99 are the monoisotopic masses of PO, CO₂, HD and Na, respectively; m_{MI} is the monoisotopic mass corresponding to the peak in the spectrum; z = 1 (the charge of species).

As an example, Figure 6 shows the isotopic distributions with monoisotopic masses (m/z_{MI}) 925.57, 939.62 and 953.67. The first distribution was assigned to HO- $(CH_2)_6$ -O- $(C_3H_6O)_{12}(CO_2)_2$ HNa (in theory, $m/z_{MI} = 925.57$). Another possibility was CH₂CHCH₂O(C_3H_6O)₁₂(CO₂)₃HK. In this case, the monoisotopic mass had to be equal to 925.48 though. Additionally, a peak corresponding to CH₂CHCH₂O(C_3H_6O)₁₂(CO₂)₃HNa with m/z = 909.6 was not found in the spectrum. The group of signals with $m/z_{MI} = 939.62$ corresponds to HO- $(CH_2)_6$ -O- $(C_3H_6O)_{13}(CO_2)$ HNa. The peaks with $m/z_{MI} = 953.67$ represent HO- $(CH_2)_6$ -O- $(C_3H_6O)_{14}$ HNa that is a product of PO homopolymerization. Small signals with $m_{MI}/z = 955.50$ correspond to HO- $(CH_2)_6$ -O- $(C_3H_6O)_{11}(CO_2)_4$ HNa.

Figure 7 presents a higher molecular weight region of the spectrum. Peaks for HO-(CH₂)₆-O-(C₃H₆O)₂₄(CO₂)₂HNa at $m_{MI}/z = 1622.06$ and others separated from it by about m/z = 1.00, share this spectrum area with peaks corresponding to HO-(CH₂)₆-O-(C₃H₆O)₂₁(CO₂)₆HNa (1623.89, 1624.89, 1625.89, 1626.90 and 1627.90). The peaks at 1621.95 and 1622.96 correspond, most probably, to allyl (or propenyl) terminated polymer chains, e.g., CH₂CHCH₂O(C₃H₆O)₂₁(CO₂)₆HNa.



Figure 6. Expansion of the MALDI-TOF MS spectrum in the range m/z = 924-959.



Figure 7. Expansion of the MALDI-TOF MS spectrum showing a region with m/z = 1620-1630.

It should be underlined that as the molecular weight increases, the relative intensity of peaks corresponding to PO homooligomers decreases compared to peaks corresponding to CO₂-containing species. An example to support this statement is shown in Figure 8. The peaks at 1592.12, 1593.13 and 1594.13 (HO-(CH₂)₆-O-(C₃H₆O)₂₅HNa) have a much lower total intensity than that of the peaks at 1593.95, 1594.96, 1595.96, 1596.96 and 1597.97 (HO-(CH₂)₆-O-(C₃H₆O)₂₂(CO₂)₄HNa). The signals corresponding to CO₂-rich chains HO-(CH₂)₆-O-(C₃H₆O)₁₉(CO₂)₈HNa (m/z = 1595.78, 1596.79, 1597.79) can also be seen in Figure 8.



Figure 8. Expansion of the MALDI-TOF MS spectrum showing a region for m/z = 1591.5-1598.5.

2.4. NMR Analysis of the Oligo(Ethercarbonate) Synthesized in the Presence of HD

To analyze OECHD, ¹H, ¹³C, COSY, HSQC and HMBC spectra were used (Figure 9, Figure 10 and Figures S1–S8 in Supplementary Materials) for definite signal assignments. ¹H and ¹³C NMR spectra are presented in Figures 9 and 10. The ¹³C spectrum acquired with the addition of Cr(acac)₃ into the system (see Section 3.4), can be used for quantitative analysis. That is poly(ethercarbonates) with ν (POCO₂) up to at least 25% mol. can be quantitatively characterized by ¹³C NMR spectroscopy according to the method described here. It can be concluded that HD participated in the chain transfer processes and was incorporated into polymer chains. According to calculations, 96% of HD reacted during the cooligomerization. The inset in Figure 10 shows that there are signals for carbons belonging to unreacted HD ends. However, these constitute only about 1.4% from the ends which participated in the chain transfer. That is, after one OH group of HD reacted, another one also participated in the cutting of some polymer chain. After the chain transfer by HD, the resulting alkoxide reacts with PO or CO₂ to give an ether or carbonate linkage, respectively.

Secondary OH groups were identified in the spectra and are much more abundant compared to unreacted HD groups. The polymer chains observed by MALDI MS contain HD fragments and, according to the ¹H NMR spectrum, the ratio of the number of secondary hydroxyls to the number of HD units is 1.86. That is, there are other chain ends: terminal units derived from PO with primary OH groups and/or terminal units with secondary hydroxyls preceded by carbonate linkages. It is not surprising that most of the chain ends are secondary OH groups because PO homopolymerization in the presence of CoNi(CN)₄ afforded a regioregular product in the absence of a CTA [45]. The relative amount of chain ends containing double bonds is low (for the formation of unsaturated chain ends in PO polymerization see [49–51] and references therein). Small peaks at 5.25, 5.29 and 5.9 ppm were found when ¹H NMR spectrum was obtained at a high number of scans. When these signals correspond not to some impurity but to double bonds, the peaks at 5.9 represent CH groups. The ratio of the number of such protons to H_s is about 1.3/1000, that is, if unsaturated chains are present, their amount is very low.

On the basis of the analyses carried out, we can outline chain transfer processes and the role of HD for the studied catalyst (Scheme 2).







Figure 10. ¹³C NMR spectrum of OECHD.

Main chain transfer reactions



Scheme 2. Chain transfer reactions during CO_2/PO cooligomerization in the presence of Co-Ni(0) and HD. Chain transfer should also occur with the participation of metal-carbonate ends resulting in OC(O)OH groups which after decarboxylation afford OH end groups. The representation of CO_2 units in the cooligomer chains should be understood as showing a non-alternating cooligomer structure only.

2.5. Comparison of the Performance of Co-Ni(0) with the Published Data

Comparison of the performance of Co-Ni(0) with that of other catalysts is presented in Table 5. Results published for Zn-Co complexes vary depending on catalyst preparation method and reaction conditions used. It can be concluded that Zn-Co catalysts are generally more efficient than Co-Ni(0) (e.g., Table 5, entry 3). Catalysts based on other combinations of metals were mostly applied without the introduction of CTAs into the copolymerization process. It seems they were employed with the intention to get copolymers with high ν (POCO₂). Therefore, direct comparison is difficult here. It can be generally concluded that published catalysts not based on Zn-Co metal combination afforded relatively low productivities. The productivities were often calculated per gram of metal used, therefore they will have much lower values when expressed per gram of catalyst. They should be even lower in the presence of CTAs as it is a common phenomenon for PO/CO₂ copolymerization. Despite the comparison difficulties, we can highlight that Co-Ni(0) showed relatively high productivity and low PC proportion in the product. The cooligomer chains are capped with OH groups. This is a very important factor when oligomers are used for PU preparation.

Catalyst	°C ℃	P, MPa	Time, h	PO/Cat, g/g	Prod. ¹ , g/g _{cat}	СТА	ν(POCO ₂) ¹ , mol.%	w(PC) ¹ , wt.%	M _n , g/mol	PDI ¹	Ref.
Co-Ni	120	4.3	24	1330	1528	HD	25	6.5	2560	2.5	-
Zn-Co	60	4.0	24	1037	1300	PPG-350	50.5	4.8	3800	1.3	[26]
Zn-Co	80	4	5	1660	2440	sebacic acid	45.2	8.2	2500	1.35	[33]
Zn-Fe	60	3.8	40	138	774 g/g _{Zn}	-	91	n.a.	98	1.9	[37]
Zn-Cr	70	4	24	83	n.a.	-	82.5	n.a.	68,600	1.68	[35]
Zn-Fe	60	4	40	n.a.	85	-	64.7	n.a.	2200	2.44	[38]
Zn-Ni	130	5.0	20	553	483	-	52	9.1	21,660	3.2	[44]
Zn-Ni	130	5.0	10	4610	483	PPG-400	32	9.1	$M_w = 35,390$	n.a.	[36]
Zn-Fe	55	n.a.	40	138	916 g/g _{Zn}	-	92	n.a.	83,200	1.87	[41]
Zn-Fe	60	3	24	49.8	4.4 g/g _{Zn}	-	48.3	n.a.	3354	1.01	[40]
Zn-Ni-Co	100	3	40	415	2480 g/g _{Zn}	-	43.6	n.a.	10,000	4.3	[42]
Zn-Ni	60	4	24	83	259 g/g _{Zn}	-	83.5	n.a.	10,344	1.45	[43]
Co-Ni	60	4	24	83	$183 g/g_{Co}$	-	73.7	n.a.	8478	1.44	[43]

Table 5. Comparison of the performance of Co-Ni(0) with the performance of other metal cyanide catalysts.

¹ Prod., v(POCO₂), w(PC), PDI are productivity (the total mass of products formed divided by the catalyst mass), the molar fraction of -CH₂-CH(CH₃)-OC(O)O- units in the polymer chains, the mass fraction of PC in the product mixture (PC and polymer) and polydispersity index, respectively. n.a.: the data are not available.

3. Materials and Methods

3.1. Materials

K₂Ni(CN)₄·H₂O (Strem, Newburyport, MA, USA), CoCl₂·6H₂O (99.1%, ACS, Alfa Aesar, Haverhill, MA, USA), CoSO₄·7H₂O (99.9%, J&K, Shanghai, China), poly(THF) (Sigma Aldrich, Saint Louis, MO, USA, M_n = 2000) and tBuOH (≥99.5%, ACS, Aladdin, Shanghai, China) were used without any purification. PO (99.5%, J&K, Shanghai, China) was deoxygenated by bubbling nitrogen through it (320 mL) over 2 h. The epoxide monomer was dried by stirring it with CaH₂ for 3 days and distilled under a nitrogen atmosphere. CO₂ had 99.999% purity. The following reagents were dried by heating under high vacuum: 1,6-hexanediol (Sigma Aldrich, 99%, 35 g, 55 °C for 27 h), PPG-425 (Sigma Aldrich, 30 mL, 90 °C for 10 h), adipic acid (Aladdin, ≥99.5%, 100 °C for 18 h), PPNCl (Sigma Aldrich, 97%, 5 g, 65 °C for 10 h). DMAP (Sigma Aldrich, ≥99%) was sublimed and dried with the aid of P₂O₅ for several days.

3.2. Catalyst Synthesis

The synthesis procedures for the Co-Ni complexes are outlined in Scheme 3.

Co-Ni(0): The catalyst was obtained in general accordance with a published procedure [45]. Two solutions were prepared. Solution 1: $K_2Ni(CN)_4$ (1.60 g, 6.64 mmol), 27 mL of deionized (DI) water. Solution 2: $CoSO_4 \cdot 7H_2O$ (1.87 g, 6.64 mmol), 27 mL of DI water. Solution 2 was added over solution 1 via a dropping funnel for about 3 min and mechanically stirred at 30 °C. Solution 2 was added to mechanically stirred solution 1 (30 °C) via a dropping funnel during about 3 min. Then, 29 mL of DI water was added to this suspension. The resulting mixture was stirred at 30 °C for 1 h. Subsequently, the suspension was vacuum filtered through a 0.2 µm paper filter. The obtained solid was dispersed in 70 mL of DI water, stirred for 15 min and filtered in the same manner as before. This washing and filtration were repeated one more time. The complex was dried in a Schlenk flask using a high vacuum line for 5 h. Its color changed from pink to purple. Afterwards, it was grinded with a mortar and pestle and dried at 60 °C on a high vacuum line for 12 h.

Co-Ni(t): The procedure written in [46] was followed with the exception that washings were added in order to obtain a final product with homogeneous composition. Three solutions were prepared. Solution 1: $K_2Ni(CN)_4$ (2.10 g, 8.72 mmol), 35 mL of deionized water. Solution 2: CoCl₂ (11.32 g, 87.2 mmol), tBuOH (13.5 g), DI water (87 mL). Solution 3: poly(THF) (3.49 g), tBuOH (13.5 g), DI water (0.9 mL). Solution 2 was added to solution 1 upon vigorous mechanical stirring for 60 min at 50 °C. After that, solution 3 was added dropwise via a dropping funnel to the resulting suspension for 8 min. After the addition was finished, the mixture was stirred for 3 min, centrifuged for 10 min at

6000 rpm and the liquid part was decanted. The obtained solid was reslurried in tBuOH (22.5 g) and DI water (29 mL) and stirred for 30 min. Poly(THF) (3.49 g) in tBuOH (13.2 g) was added and stirred for 3 min. The mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The obtained solid was reslurried in tBuOH (44.2 g) and DI water (19 mL) and stirred for 30 min. A total of 2.3 g of tBuOH was additionally used to transfer the remainder from the flask to centrifugation vials. The mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was reslurried in tBuOH (58.1 g) and stirred for 30 min. A total of 6.2 g of tBuOH was additionally used to transfer the remainder for 30 min. A total of 6.2 g of tBuOH was additionally used to transfer the flask to centrifugation vials. Then this mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was reslurried in tBuOH (58.1 g) and stirred for 30 min. A total of 6.2 g of tBuOH was additionally used to transfer the remainder from the flask to centrifugation vials. Then this mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was decanted for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was dried on a high vacuum Schlenk line for 5 h at 60 °C. During this period, the color of the substance changed from pink to purple. Afterwards, the complex was grinded with mortar and pestle. It turned

out that the last operation was not very necessary because, in contrast to Co-Ni(0), it was a crumbly



Scheme 3. The outline of synthesis procedures for Co-Ni complexes used in this work.

Co-Ni(P): The synthesis procedure was adapted in order to incorporate a higher amount of poly(THF) into the final product compared to Co-Ni(t). Three solutions were prepared. Solution 1: $K_2Ni(CN)_4$ (1.60 g, 6.64 mmol), 27 mL of deionized (DI) water. Solution 2: CoCl₂ (8.62 g, 66.4 mmol), t-BuOH (10.3 g), DI water (66 mL). Solution 3: poly(THF) (7.97 g), t-BuOH (15.4 g), DI water (1.0 mL). Solution 2 was added to solution 1 upon vigorous mechanical stirring for 60 min at 50 °C and the suspension was stirred for an additional 20 min. After that, solution 3 was added dropwise via a dropping funnel to the resulting suspension over 10 min. When the addition was finished, the mixture was stirred for 3 min, centrifuged for 10 min at 6000 rpm and for 5 min at 8000 rpm and the

liquid part was decanted. The obtained solid was reslurried in tBuOH (20.2 g) and DI water (11 mL) and stirred for 30 min. Poly(THF) (7.97 g) in tBuOH (15.4 g) was added and the suspension was stirred for 3 min. The mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted. A total of 3.9 g of tBuOH was used to transfer the remainder from the vials to a flask for washing. The obtained solid was reslurried in tBuOH (28.7 g) and stirred for 30 min. Poly(THF) (3.98 g) in tBuOH (7.72 g) was added and the mixture was stirred for 6 min. Then 3.9 g of tBuOH were additionally used to transfer the remainder from the liquid part was decanted. The resulting solid was reslurried in tBuOH (27.1 g) and stirred for 30 min. A total of 3.9 g of tBuOH was additionally used to transfer the remainder from the flask to centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was reslurried in tBuOH (27.1 g) and stirred for 30 min. A total of 3.9 g of tBuOH was additionally used to transfer the remainder from the flask to centrifuged for 10 min at 6000 rpm and the liquid part was decanted. The resulting solid was reslurried in tBuOH (27.1 g) and stirred for 30 min. A total of 3.9 g of tBuOH was additionally used to transfer the remainder from the flask to centrifugation vials. This mixture was centrifuged for 10 min at 6000 rpm and the liquid part was decanted in a high vacuum Schlenk line for 15 h at 60 °C. During this period, the color of the substance changed from pink to purple.

3.3. Copolymerization Procedure

Copolymerization reactions were carried out in a stainless steel 100 mL autoclave equipped with a magnetic stir bar and a temperature sensor measuring the temperature of the reaction mixture. Two methods were used to implement the process. In method I, the autoclave dried by pumping at 80 °C for 1 h was opened, a catalyst (25-28 mg) was placed inside, the autoclave was sealed and then pumped again for 30 min at room temperature (r.t.) and for 2 h at 60 °C. Then the reactor was filled with nitrogen and allowed to cool to room temperature. After pumping the autoclave for 10 min at room temperature, PO and CTA were introduced using the pressure difference from the flask connected to the autoclave. In method II, the empty reactor was pumped for 1 h at 70 °C, filled with nitrogen, cooled to room temperature and transferred to a glove box. The catalyst, PO and CTA were charged into the autoclave inside the glove box under a nitrogen atmosphere. CO₂ was introduced to reach an initial pressure at r.t. After CO₂ pressure stabilization, heating of the autoclave started to reach the desired process temperature. The moment the temperature of the reaction mixture reached 40 °C was considered the copolymerization starting point. When the desired temperature was reached, CO_2 was added to set the pressure to 4.3 MPa. After the reaction time was over, the autoclave was cooled in an ice bath, CO_2 was slowly released, $CHCl_3$ was added inside and the mixture was thoroughly stirred to guarantee its homogeneity. A small amount of the resulting mixture was taken for ¹H NMR analysis. Volatiles were removed with the aid of a rotary evaporator and by pumping on a Schlenk line to determine product mass. Polymers were purified by dissolution in toluene and washing the solution with 10% ammonia in DI water and several times with DI water. The previously described drying procedure was repeated to obtain solvent-free products.

3.4. Characterization of Polymers and Catalysts

NMR spectra were recorded with a Bruker DRX-500 MHz NMR spectrometer. $CDCl_3$ was used as a solvent. A relaxation delay of 5 s was set for ¹H NMR data acquisition. To record a ¹³C NMR spectrum which can be integrated, an inverse gated decoupling pulse sequence was applied. In this case, a relaxation delay of 10 s, 4000 scans and 14 wt.% sample concentration were employed. Then 0.23 wt.% of Cr(acac)₃ was introduced to decrease T₁ relaxation time in this experiment [52].

Molecular weights were measured with a Waters GPC system calibrated with polystyrene standards (PDI = 1.02). Chloroform served as eluent (1 mL/min, 40 $^{\circ}$ C).

Glass-transition temperatures (Tg) were measured by a differential scanning calorimeter (DSC, Netzsch Model 204, (Netzsch, Shanghai, China) as an inflection point on a DSC curve. A heating/cooling rate of 10 °C/min was applied. The samples were heated to 130 °C then cooled by liquid nitrogen to -120 °C. The Tg values were registered during the subsequent heating.

MALDI-TOF MS analysis was performed using a Bruker ultrafleXtreme spectrometer (Bruker, Guangzhou, China). DHBA or DCTB was the matrix. In the latter case, the analysis was done with

sodium trifluoroacetate as an ionizing agent and without it. The methods of sample preparation described in [26,48] were followed.

Powder XRD spectra were recorded on a RIGAKU D-MAX 2200 VPC diffractometer (Rigaku Corporation, Tokyo, Japan) operated at 40 kV and 26 mA using Cu-K α radiation (λ = 1.5406 Å) and a scan speed of 5°/min.

Nitrogen adsorption–desorption measurements were implemented on a Micromeritics ASAP 2460 analyzer at –196 °C after degassing samples under vacuum at 120 °C. Brunauer–Emmett–Teller (BET) equation was used to calculate the total surface area.

TG traces were registered on a PerkinElmer Pyris Diamond TG/DTA instrument (PerkinElmer Inc., Waltham, MA, USA) with a heating rate of 10 K/min under a nitrogen atmosphere.

SEM images were obtained with a thermal field emission scanning electron microscope (FE-SEM, Quanta 400F, FEI, Hillsboro, OR, USA). An EDX system was used to determine the Co/Ni ratio in the synthesized materials.

4. Conclusions

Three Co-Ni complexes with different contents of complexing agents were prepared and characterized by several methods. CO_2/PO copolymerization catalyzed by the Co-Ni material containing no complexing agents was studied in the presence of different CTAs. HD containing primary OH groups is a more preferable CTA than PPG-425 containing secondary OH groups as it affords higher catalyst productivity. Adipic acid proved to be inefficient when oligomer production is desired. Low molecular weight cooligomers were obtained and the one with the lowest PDI was characterized by different methods. The obtained cooligomer is capped with OH groups. The content of unsaturated end groups is low (<0.15% with respect to OH end groups). HD efficiently incorporates into the polymer chains as most of its OH groups participate in chain-transfer reactions. The obtained oligomer (POCO₂ = 25 mol.%, M_n = 2560, PDI = 2.5) can be synthesized with relatively high productivity (1320 g_{PO+CO2}/g_{cat} calculated to represent PO and CO₂ converted to the cooligomer) with almost full PO conversion in 24 h (PO/cat = 1330 g/g).

As the potential of Co-Ni cyanide catalysts for CO_2 /epoxide copolymerization has not been well studied yet, we believe there is a lot of space for further improvement by tuning the catalyst structure, introduction of additives into the process and optimization of reaction conditions. Although a serious problem of intense product coloration caused by catalyst residues exists in this case. Therefore, the practical application of the catalysts requires very high productivity to be achieved and an efficient purification method to be developed.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/8/632/s1, Figure S1: ¹³C NMR spectra of OECHD in the region from 65 to 78 ppm, Figure S2: ¹³C NMR spectra of OECHD in the region from 13 to 45 ppm, Figure S3: COSY spectrum of OECHD, Figure S4: A fragment of an HSQC spectrum of OECHD, Figure S5: A fragment of an HSQC spectrum of OECHD, Figure S6: Selective HMBC spectrum of OECHD, Figure S7: A fragment of an HMBC spectrum of OECHD, Figure S8: A fragment of an HMBC spectrum of OECHD, F

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