Mechanistic Aspects of the Metal Catalyzed Alternating Copolymerization of Epoxides and Carbon Monoxide

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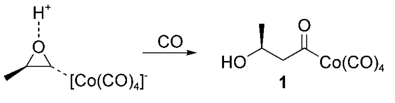
Abstract: The cobalt-catalyzed alternating copolymerization of epoxides and CO is a novel, direct approach to aliphatic polyesters, such as poly(hydroxybutyrate) (PHB). This reaction was found to be catalyzed by Ph_3Si-$[Co(CO)_4]$ (**4**) and pyridine affording in a first step the stable mono-insertion product Ph_3Si-O-CH(CH_3)-CH_2-CO-$Co(CO)_4$ (**5**). However, a profound mechanistic understanding, especially of the role of pyridine as the key component for the polymerization reaction was missing. ATR-IR online monitoring under catalytic conditions and DFT calculations were used to show that an acylpyridinium cation is formed by cleavage of the cobalt–acyl bond of **5** in the presence of pyridine. The Lewis acid thus generated activates the next incoming epoxide monomer for ring opening through $[Co(CO)_4]^-$. The catalytic cycle is completed by a subsequent CO insertion in the new cobalt–alkyl bond. The calculations are used to explore the energetic hypersurface of the polymerization reaction and are complemented by extended experimental investigations that also support the mechanistic hypotheses.

Keywords: carbonylation · density functional calculations · epoxides · polymerization

Introduction

Heck reported as early as 1963 on the ring opening of epoxides by tetracarbonylhydridocobalt(I),[1] to give a stable acyl cobalttetracarbonyl compound (**1**, Scheme 1) in the presence of carbon monoxide. However, no evidence for consecutive multiple ring opening/CO insertion sequences was provided in these pioneering studies. The catalytic ring expansion of epoxides is, as well, established in literature.[2]



Scheme 1. Ring opening of propylene oxide by $H[Co(CO)_4]$.

These earlier results encouraged us to focus our work on the synthesis of poly(hydroxybutyrate) (PHB) from the cheap and easy available industrial chemicals propylene oxide (PO) and CO. This class of biopolyester materials is of high interest due to its properties that can resemble those of isotactic polypropylene.[3] Our initial forays into that field surprisingly revealed that besides the ring opening of β-butyrolactone, there is a direct alternating copolymerization reaction of propylene oxide and CO to give PHB.[4–6]

This direct copolymerization reaction, which combines a Lewis acid (LA) induced epoxide ring opening process with a metal centered CO insertion, was initiated from **2** (Scheme 2),[7] simply by adding pyridine. However, a detailed mechanistic understanding, including the identification of the catalytically important intermediates, was lacking.

The reactions are usually carried out by using [Lewis acid]$^+$$[Co(CO)_4]^-$-type compounds. This basic group of carbonylation catalysts can generate β-butyrolactone, a reaction recently intensively investigated by Coates and Alper,[8] as well as polyester. We have previously reported in experimental and theoretical studies on the control of the product distribution by choice of the proper Lewis acid.[7,9] The intermediate species LA-O-CH(CH_3)-CH_2-CO-$Co(CO)_4$ (**2**), that

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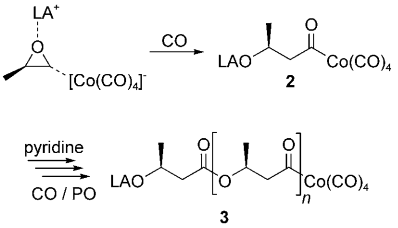
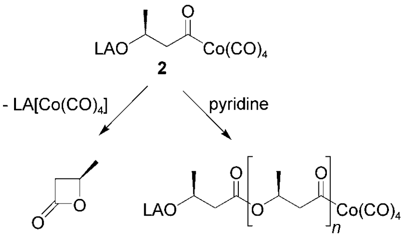


Scheme 2. Direct alternating copolymerization of propylene oxide and CO.

is formed after the first ring opening/CO insertion sequence can undergo the two different reaction pathways, depicted in Scheme 3. Labile LA–O interactions, resulting from weak Lewis acids (e.g. LA: $BF_3{\cdot}OEt_2$, $AlMe_3$) allow a backbiting process and produce lactones. More stable LA–O bonds, emerging from strong LA fragments (e.g. LA: Ph_3Si^+), however, afford a polymerization reaction in the presence of pyridine donors; the LA moiety remains bonded to the chain end. We report herein on a combination of experimental and theoretical techniques to elucidate the mechanism of this direct, pyridine induced alternating copolymerization reaction.



Scheme 3. Two different reaction pathways from the intermediate LA-O-$CH(CH_3)$-CH_2-CO-$Co(CO)_4$.

Results and Discussion

Our initial investigations started from mixtures of $[Co_2(CO)_8]$ and 3-hydroxypyridine, originally investigated by Drent et al.[10] Due to the complex reaction pattern,[11] we have introduced $Ph_3Si[Co(CO)_4]$ (**4**, Figure 1) as a well-defined species. This stable catalyst precursor is easily prepared from commercially available Ph_3SiH and $[Co_2(CO)_8]$.[12] Online ATR-IR spectroscopy was used to monitor all carbonylation reactions in the autoclave under polymerization conditions (T_p = 75 °C; p_{CO} = 60 bar) and indicates the rapid and quantitative formation of the stable acyl compound Ph_3Si-O-$CH(CH_3)$-CH_2-CO-$Co(CO)_4$ (**5**) from **4** in the presence of CO and propylene oxide. Complex **5** remains stable in this reaction mixture under CO pressure over hours. No indication of any further PO/CO insertion reactions can be observed, in accord with Heck's early studies.

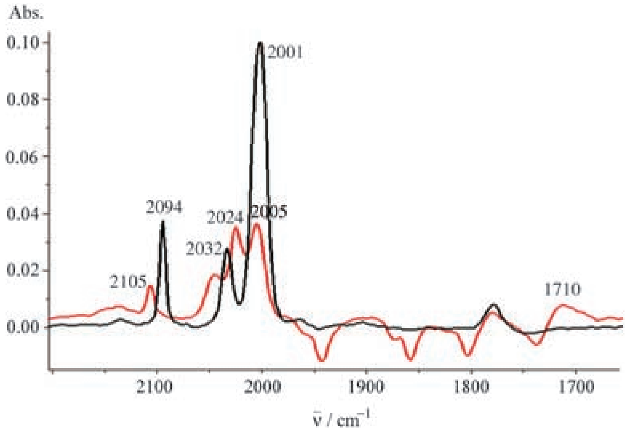


Figure 1. Conversion of the catalyst (**4**, black: $Ph_3Si[Co(CO)_4]$) to the cobalt-acyl species (**5**, red: Ph_3Si-O-$CH(CH_3)$-CH_2-CO-$Co(CO)_4$).

The addition of pyridine to this system[13] (containing a toluene solution of **5**, PO and CO) induces the spontaneous formation of poly(hydroxybutyrate) (Table 1, entry 1). This is indicated by a growing absorption at 1744 cm^{-1} in the IR spectrum, which starts to appear immediately upon pyridine addition (Figure 2a).[14] From Figure 2b it becomes clear that the polymer formation is accompanied by a reduction of the concentration of complex **5** and the formation of free cobaltate anions (1889 cm^{-1}). Already 5 min after the addition of pyridine, a steady state acyl concentration is reached (blue and red curves) and polyester formation starts (blue).[15] The presence of a Ph_3Si-O end group was later detected by ^1H NMR analysis of the isolated polyester product.[16]

Table 1. Polymerization conditions.

Entry	Catalyst (equiv)	Additive (equiv)	Equiv PO	*T* [°C]/*t* [h]/*p* [bar]	PHB
1	$Ph_3Si[Co(CO)_4]$ (1)	pyridine (1)	150	75/20/60	yes
2	$Ph_3Si[Co(CO)_4]$ (1)	DMAP (1)	150	75/20/60	(yes)
3	$Ph_3Si[Co(CO)_4]$ (1)	lutidine (1)	150	75/20/60	–
4	$Ph_3Si[Co(CO)_4]$ (1)	4-*tert*-butyl-py (1)	150	75/20/60	yes
5	$Ph_3Si[Co(CO)_4]$ (1)	4-MeO-py (1)	150	75/20/60	yes
6	$PPN[Co(CO)_4]$ (1)	–	120	75/24/60	–
7	$PPN[Co(CO)_4]$ (1)	**9** (1)	150	75/20/60	yes

A mechanistic proposal for the occurrence of multiple, alternating PO/CO insertions starts with the cleavage of the cobalt–acyl bond in **5** by pyridine to give an acylium cation and tetracarbonyl cobaltate (**6**, Scheme 4).[17–20] Interaction of the Lewis-acidic acylium cation with PO (**7**) activates the

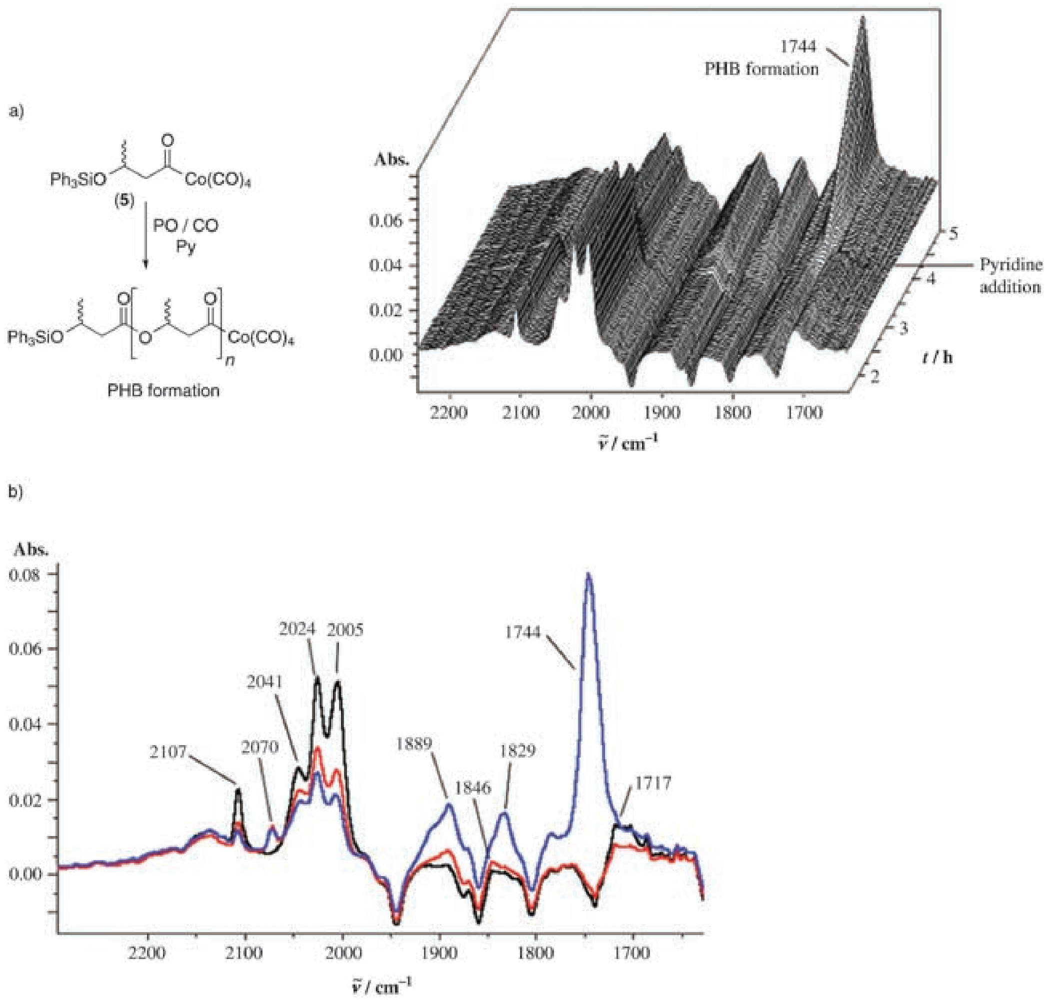
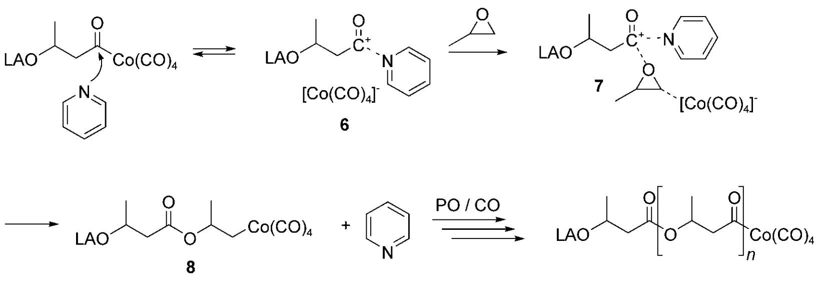


Figure 2. a) ATR-IR stack-plot. PHB formation (1744 cm^{-1}) starts immediately after pyridine addition to a solution of **5** in toluene and PO under CO pressure (60 bar). b) black: Acyl–cobalttetracarbonyl complex (2107, 2041, 2024, 2005, 1717 cm^{-1}); red: 5 min after pyridine addition; blue: 20 min after pyridine addition (PHB (1744 cm^{-1}), $[Co_2(CO)_8]$ (2070, 1846 cm^{-1}), $[Co(CO)_4]^-$ anion (1889 cm^{-1}), β-butyrolactone (1829 cm^{-1})).

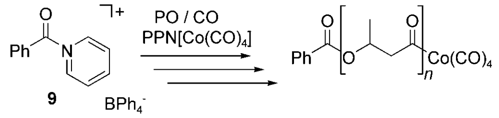
epoxide, so that ring opening can occur by nucleophilic attack of $[Co(CO)_4]^-$ (**6** → **7**).[21] This sequence affords an ester group and a new cobalt–alkyl σ bond (**8**), which subsequently inserts CO thus completing the first catalytic cycle.[22]

In order to probe the feasibility of such a process, we synthesized the easily accessible acyl-pyridinium salt **9** (Scheme 5).[23] This stable compound shows no reactivity toward PO and CO. Also PPN$[Co(CO)_4]$[24] alone does not react with PO and CO (Table 1, entry 6). However, if **9** is added to PO and PPN$[Co(CO)_4]$ dissolved in toluene under carbon monoxide pressure, the immediate formation of PHB (1744 cm^{-1}) is observed (Table 1, entry 7). The identical characteristic absorptions of the acyl-cobalttetracarbonyl species (2107, 2049, 2028, 2005 cm^{-1}), $[Co(CO)_4]^-$ and PHB as in the case of pyridine addition (Figure 2) appear in the ATR-IR spectrum, indicating the occurrence of the same chemistry.

This crucial role of the nitrogen base prompted us to use differently substituted pyridines such as 4-dimethylamine- (DMAP), 2,6-dimethyl- (lutidine), 4-methoxy- and 4-*tert*-bu-



Scheme 4. Proposed mechanism for the epoxide insertion into a cobaltcarbonyl–acyl bond by pyridine mediation.



Scheme 5. Initiation of PO/CO copolymerization by an acyl-pyridinium salt in the presence of PPN[Co(CO)$_4$].

tylpyridine to learn more about electronic and steric effects (Table 1, entries 2–5). The application of DMAP, which is a much stronger nucleophile than pyridine, was expected to accelerate the cleavage of the acyl–cobalttetracarbonyl bond. However, the resulting acyl-pyridinium cation should be much better stabilized by DMAP, thus retarding the activation of the next epoxide monomer. 4-Methoxy- and 4-*tert*-butylpyridine, both showing a donor capacity in between pyridine and DMAP, were additionally used.

Indeed, the characteristic absorptions of the acyl species disappeared immediately when one equivalent of DMAP was added and at the same time the strong absorption of a [Co(CO)$_4$]$^-$ anion (1889 cm^{-1}) appeared (Figure 3, black → red (0.5 equiv DMAP) → blue (1 equiv DMAP)). Most importantly, the acyl-pyridinium intermediate could now be detected for the first time in the ATR-IR spectrum (1721 cm^{-1}), resulting, however, in a very slow PHB formation (not depicted in Figure 3).

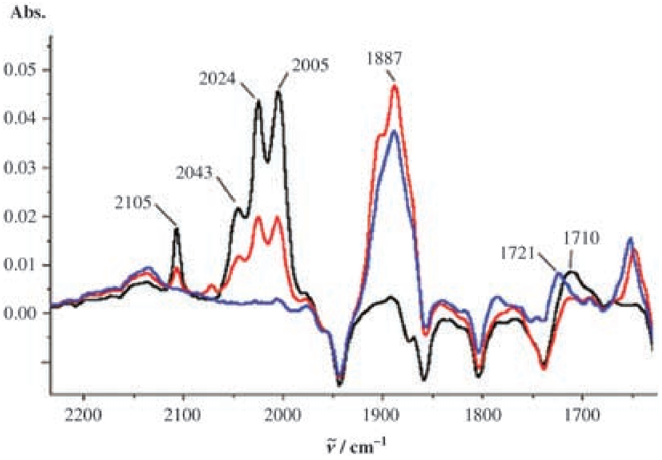


Figure 3. ATR-IR spectra: DMAP addition to a Ph$_3$Si-O-CH(CH$_3$)-CH$_2$-CO-Co(CO)$_4$ solution in toluene. Black: Acyl–cobalttetracarbonyl complex (2105, 2043, 2024, 2005, 1710 cm^{-1}); red: 5 min after 0.5 equiv DMAP addition; blue: after additional 0.5 equiv DMAP addition, [Co$_2$(CO)$_8$] (2070, 1846 cm^{-1}), [Co(CO)$_4$]$^-$ anion (1887 cm^{-1}), acyl-pyridinium salt (1721 cm^{-1}).

Theoretical calculations of the characteristic vibrational frequencies support our findings. Experimentally, the CO vibration of the anion is found around 1889 cm^{-1} (Figure 3, 1887 cm^{-1}).[25] The calculated values are about 50 cm^{-1} lower in frequency (Table 2, column 1, 3 % error). This difference is used as calibration error. The acylium C=O vibration was calculated at 1774 cm^{-1} (Table 2, column 2) application of the calibration error yielded a corrected value of 1724 cm^{-1} while the actual measurement was found at 1721 cm^{-1}.

Table 2. Calculated vibrational frequencies for [Co(CO)$_4$]$^-$ anion and a complex of [Co(CO)$_4$]$^-$ with an acyl-pyridinium species (product side of Figure 4; details see Theoretical Methods).

[Co(CO)$_4$]$^-$ vibrations [cm^{-1}]	[Co(CO)$_4$]$^-$ + acyl-pyridinium vibrations [cm^{-1}]	Description
–	1774.35	acylium C=O
1931.43	1938.46	CO valence
1932.02	1953.23	CO valence
1932.07	1991.37	CO valence
2018.57	2042.83	CO valence

The less nucleophilic 4-methoxy- and 4-*tert*-butylpyridines both gave a higher rate of PHB-formation with an optimum for the methoxy substituted species. The situation changed completely in case of lutidine, which did not lead to PHB, not even after 20 h of reaction time. No cleavage of the acyl-cobalttetracarbonyl bond occurred (no acyl-lutidinium species was detected), presumably due to the high steric demand of the two ortho methyl substituents.

Density functional theory was used to investigate the central steps of the proposed mechanism. Details of the methodology are given below (Theoretical Methods). Based on the mechanism of lactone formation from epoxides and CO, as described in ref. [9] a Lewis acid is required to activate the epoxide prior to the nucleophilic attack. Therefore, an acyl-pyridinium species was proposed to be a good candidate for the Lewis acid able to activate PO. And indeed, a favorable ring-opening reaction is found in a model system (ethylene oxide, growing chain terminated by OH) in the presence of an acyl-pyridinium species (Figure 4). In the transition state the backside attack of the Co nucleophile on the epoxide ring is clearly visible: The Co–carbon distance is determined to be 309 pm and the distance between the epoxide oxygen and the acylium carbon is 189 pm, in a linear arrangement of the three particles, that is a prerequisite for successful ring opening. The bond between the pyri-

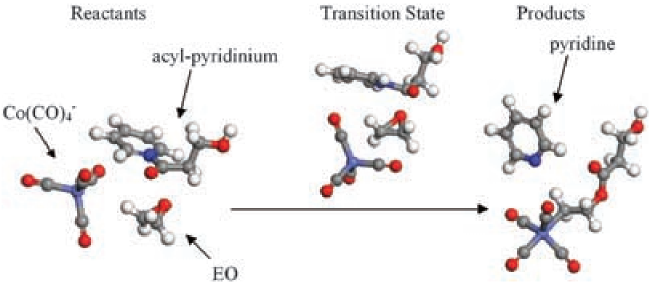


Figure 4. Epoxide ring opening. Acyl-pyridinium species functions as Lewis acid. Ethylene oxide (EO) is used as model epoxide. Activation energy: 59 kJ mol^{-1}; reaction energy yield: -180 kJ mol^{-1}. Energies calculated at the B-P86/TZVP//B-P86/SV(P) level of theory.

dinium nitrogen and the acyl carbon on the reactant side is 149 pm, which widens to 166 pm in the transition state; this indicates the activating interaction with the epoxide molecule. On the side of the products the new bonds have been formed (Co–C 121, O–C 146 pm) while the N–C bond (425 pm) is broken. Importantly, pyridine has dissociated from the ring-opened species (Figure 4, products), emphasizing its role as co-catalyst.

Subsequently, CO insertion in the newly formed cobalt–alkyl bond occurs, as already discussed in literature.[9] At this stage, for many systems, lactone formation is the next step in the catalytic cycle. However, in the presence of a base/nucleophile such as pyridine, the situation is different and polymer is produced. In order to obtain a productive catalytic cycle for polymerization, pyridine attacks the cobalt–acyl bond affording a new acyl-pyridinium fragment (Figure 5). The activation energy for this process is 44 kJ mol^{-1} and the reaction energy +23 kJ mol^{-1}, showing the endothermic nature of this particular sequence. However, the energy yield of the epoxide ring-opening step (−180 kJ mol^{-1}!) clearly drives the overall polymerization cycle.

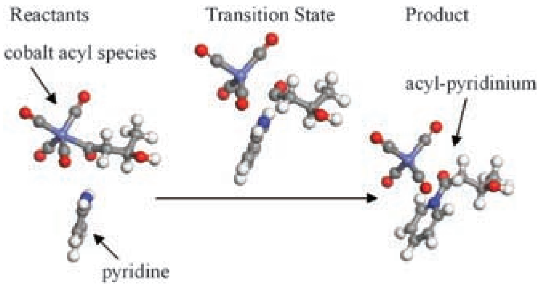


Figure 5. Formation of acyl–pyridinium species. Activation energy: 44 kJ mol^{-1}; reaction energy yield: +23 kJ mol^{-1}. Energies calculated at the B-P86/TZVP//B-P86/SV(P) level of theory. The transition state displays a "side-on" attack of the pyridine nitrogen on the Co–acyl bond (transition state: Co–C: 260, N–C: 186 pm). On the product side the new bond of the acylium carbon atom to pyridine has been formed and the bond to cobalt is broken (Co–C: 294, N–C: 173 pm).

The role of pyridine therefore, is to generate the acyl-pyridinium species, which acts as an intermediate Lewis acid at the growing end of the polymer chain. In the presence of other (permanent) Lewis acids, lactone formation would be the main route.[9] A second, important factor for the suppression of the lactone formation cycle is a stable chain end of the growing polymer chain (Ph_3Si-O-).[7]

Conclusion

The direct alternating copolymerization of epoxides and CO is a new, direct route to aliphatic polyesters. The polymerization mechanism combines a CO insertion with an epoxide ring-opening reaction. Online ATR-IR-experiments identify the role of pyridine to act in the cleavage of the cobalt–acyl bond affording acyl-pyridinium cations that perform as Lewis Acids in the ring opening of the epoxide monomer. These key intermediates could be monitored in case of DMAP and helped to support the mechanistic proposal. Theoretical calculations showed a suitable low energy mechanistic pathway on the energy hypersurface, which does not suffer from low energy yields but explains the experimentally observed low reaction rates by relatively high energy barriers. It is part of the current research activities to find theoretically and experimentally more feasible routes for this three-particle problem.

Experimental Section

Polymerization reactions were conducted in a 250 mL Büchi reactor equipped with a ReactIR SiComp probe (Mettler Toledo) for in-situ ATR-IR measurements under high pressure conditions.

General polymerization procedure: The autoclave was charged with toluene (40 mL) under argon and cooled to 5 °C. After addition of Ph_3Si-[$Co(CO)_4$] (900 mg, 2.1 mmol) under argon the system was sealed and pressurized with CO (20 bar). Subsequently, PO (22 mL, 0.31 mol) was added to the autoclave through a high-pressure burette with CO (40 bar). The quantitative formation of an acyl-cobalttetracarbonyl species was detected by online ATR-IR spectroscopy over 10–20 minutes. Heating of the system first to 50 °C and then to 75 °C did not change the IR spectrum in the carbonyl area. Finally, a solution of pyridine (2.1 mmol) in toluene (10 mL) (analogous: DMAP, lutidine, 4-methoxy- and 4-*tert*-butylpyridine) was added to the reaction mixture through the high-pressure burette with 50–60 bar of CO. During this process the CO pressure increases step-wise in the autoclave. However, the polymerization reaction was induced by pyridine addition and the pressure was kept constant (60 bar) from there on during the entire polymerization time. The copolymerization reactions were carried out at 75 °C for 20 h. Subsequently, the reactor was cooled to 10 °C and vented. Polymer products were isolated by pouring the solutions into pentane (400–600 mL). The isolated oily products were washed several times with pentane, dried in vacuum at 50–60 °C and analyzed further.

PPN[$Co(CO)_4$]—Carbonylation test: The autoclave was charged with diglyme (60 mL) under argon and was brought to 25 °C. PPN[$Co(CO)_4$] (3.47 mmol) together with propylene oxide (30 mL) were introduced. The carbonylation test was carried out at 75 °C for 24 h after pressurizing the reactor with CO (60 bar). For termination the autoclave was cooled (10 °C) and gases were vented off. NMR spectroscopy of the resulting solutions complement the ATR-IR analysis. Carbonylation was not observed (no lactone or polyester was found by ATR-IR or NMR analysis).

Polymerization procedure with the acyl-pyridinium compound 9: The autoclave was charged with toluene (50 mL) and PO (12 mL) at 25 °C. After the addition of the acyl-pyridinium salt $[Ph\text{-}CO\text{-}Py]^+[BPh_4]^-$ (2.1 mmol) the autoclave was sealed and pressurized with 20 bar of CO. Subsequently, a solution of PPN[$Co(CO)_4$] (2.1 mmol) in PO (10 mL) was added to the autoclave through a high-pressure burette with CO (40 bar). The temperature was brought to 75 °C and the autoclave was pressurized with CO (60 bar). The polymerization was carried out for 20 h. Then, the reactor was cooled (10 °C) and the remaining gases were vented off. Polymer products were isolated by pouring the solution into pentane (400–600 mL). The isolated oily products were washed several times with pentane, dried in vacuum at 50–60 °C and analyzed further.

Theoretical methods: The overall copolymerization reaction involving CO and epoxides was conceptually split into several steps. For each of the steps the corresponding reaction mechanism was investigated by locating the transition state (TS) and the associated reactants and products. The nature of all transition states was verified (only one negative eigenvalue of the hessian). Reactants and products were identified by inducing small distortions in the TS structure along the eigenvector associated with the negative eigenvalue. Distortions with positive and negative amplitude lead to reactants and products after subsequent geometry optimization. All calculations were performed with the quantum-chemistry package TURBOMOLE.[26] DFT methodology was used at the B-P86/SV(P)[27] level of theory to locate all stationary points. Single-point energy calculations were carried out using the TZVP[28] basis set. Energies are given without zero-point energy correction. Geometries were optimized on an 20 processor Pentium II Linux cluster and an 64 CPU IBM SP3. Calculation of hessians (vibrational spectra) was achieved with a modified version of TURBOMOLE's NumForce utility. The numerical calculation of second derivatives requires $6N$ (N = number of atoms) energy and gradient calculations, which can be efficiently distributed and carried out in parallel on a network of workstations. This calculation is achieved using TURBO-SERVER an in-house development of BASF polymer research, harnessing the power of ordinary NT desktop PCs to carry out quantum chemical calculations "at night".[29] The effect of solvent was not taken into account.

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