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The Cobalt-Catalyzed Alternating Copolymerization of Epoxides and Carbon Monoxide: A Novel Approach to Polyesters

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The catalytic synthesis of polyolefins,[1] polyketones,[2] and polycarbonates[3] through insertion reactions of small, technically available, cheap monomers is of both fundamental and industrial importance. A comparable process leading to aliphatic polyesters is, to our knowledge, not yet described. We report here on the cobalt-catalyzed alternating copolymerization of propene oxide and carbon monoxide,[4] affording atactic and isotactic polyhydroxybutyrates (PHB, Scheme 1). This unprecedented metal-catalyzed process gives access to one of the most important exponents of biodegradable polymers.

The carbonylation of epoxide to yield lactone—a precursor for polyester—has an example.[5] In 1993 Drent and co-workers patented a mixture of dicobaltoctacarbonyl $Co_2(CO)_8$ and 3-hydroxypyridine as catalyst for the carbonylation of epoxides, resulting primarily in the formation of β-lactones. We decided to use this as the starting point for our investigations. However, in contrast it was found using the same catalytic mixture that polyester and not lactone is the major product. The polymers are regioregular and even isotactic when using enantiomerically pure propene oxide (Table 1). To clarify the discrepancy in observations, the reaction of propene oxide and CO with the catalytic mixture was studied by means of online ATR-IR monitoring.[6] The concentration dependence of lactone and polyester products as a function of time can be taken from Figure 1. To a first approximation the lactone concentration develops linearly with time and remains the minor product. The rate of formation of the major product, polyhydroxybutyrate (PHB), is independent of the presence of lactone and steadily increases during the entire reaction time of about 17 h. This fits well with the concentration of propene oxide, which decreases over the same time until it is fully consumed. An analysis by ^1H NMR spectroscopy revealed in addition that the amount of β-butyrolactone is not larger than 15% of the propene oxide consumed at any time. Repeating the reaction under the same conditions without epoxide but with butyrolactone as monomer yields no polyester (Figure 2, A). The polyester formation starts spontaneously after addition of epoxide to this reaction mixture (B)[7] and proceeds (C) until all epoxide is converted into polyester. The lactone concentration does not decrease but grows marginally during the process. This indicates that the polyester is directly produced from propene oxide and CO and that the lactone is a side product and not an intermediate leading to PHB.

The following experiment affirms the latter conclusion. Polymerization reactions using enantiomerically pure S-(−)PO or R-(+)-PO gave exclusively isotactic PHBs (Table 1, entry 4). We isolated the same isotactic material by repeating this reaction in the presence of racemic β-butyrolactone. This observation cannot be explained by a lactone intermediate which should lead to a lesser tactic polymer but is fully consistent with a direct regiospecific alternating copolymerization of epoxide and carbon monoxide. A possible mechanism pertaining the formation of regio- and stereoregular polyhydroxybutyrates is based on a sequence of a ring-opening of the epoxide and a CO insertion at a tetracarbonyl cobaltate species.

Scheme 1. Regiospecific Copolymerization of Propene Oxide with Carbon Monoxide

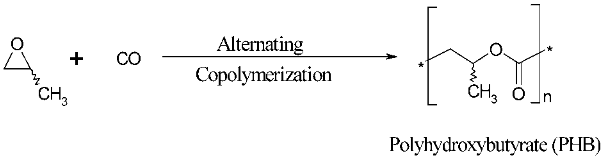

Table 1. Copolymerizations of Epoxides with Carbon Monoxide[a]

entry	monomer	convers. of epoxide [%][b]	yield polyester [g][c]	M_w [g/mol]/D
1	EO/5 mL	80	2.8[g]	7400/1.6
2	EO/20 mL[e]	25	7.4	5100/1.7
	EO/20 mL[f]	30	8.8	10500/1.8
3	rac-PO/2 mL	>90	1.8 (atactic)[d]	3800/2.0
4	S(−)-PO/2 mL	>90	1.4 (isotactic)[d]	4200/1.3
5	S(−)-PO 2 mL/rac-BL 0.5 mL	>90	1.2 (isotactic)[d]	4100/1.4

[a] Diglyme (10 mL), $Co_2(CO)_8$ 109 mg, 3-hydroxypyridine 61 mg, 4 h. (1), 18 h (3−5); CO 60 bar, 75 °C. [b] Conversion dertermined by ^1H NMR of the reaction mixture. [c] Yield after precipitation in methanol (1, 2, 4, 5) or hexane/diethyl ether (3). [d] Tacticity determined by ^1H- and ^{13}C NMR.[8] [e] Diglyme 80 mL, 3-hydroxypyridine 760 mg, $Co_2(CO)_8$ 684 mg, CO 60 bar, 80 °C, 1 h. [f] As in [e] and dimethoxypropane 1.1 g. [g] Melting point of polyester is 62 °C determined by DSC.

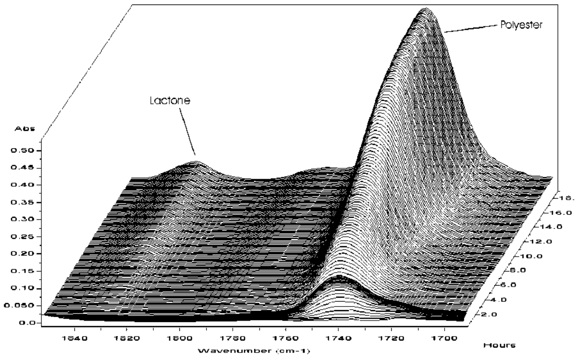

Figure 1. Stack-plot IR-online monitoring of propene oxide carbonylation reaction (catalyst: $Co_2(CO)_8$/3-hydroxypyridine).

N-Donors, such as pyridine compounds, are known to cleave the Co−Co bond in carbonyl clusters leading to the formation of the $Co(CO)_4^-$ anion.[9] Accordingly, this species was detected as a major carbonyl product (1889 cm^{-1}, Figure 3) after treatment of $Co_2(CO)_8$ with 3-hydroxypyridine in diglyme/propene oxide.

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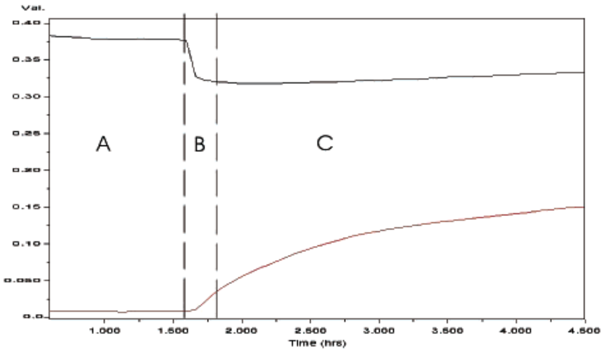


Figure 2. Profile of polyester (red) and lactone (black) from IR-online monitoring of reaction mixture with lactone added from the beginning and propene oxide added after 1.5 h (catalyst: $Co_2(CO)_8$/3-hydroxypyridine).

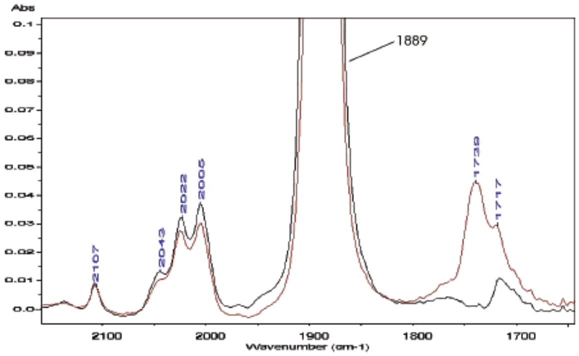
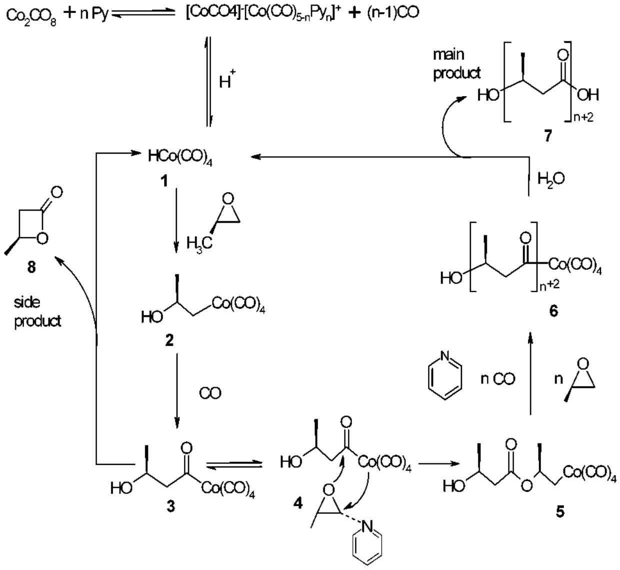


Figure 3. IR spectrum of the carbonyl region in copolymerizing propene oxide/CO (catalyst: $Co_2(CO)_8$/3-hydroxypyridine). Spectrum after 5 min (black) and after 20 min (red).

Scheme 2. Proposed Reaction Mechanism



Heck and others showed that $HCo(CO)_4$, which results in our case most probably from protonation of $Co(CO)_4^-$ by the acidic OH group of 3-hydroxypyridine, reacts smoothly with epoxides even at low temperatures to give compound **2** (Scheme 2).[10] This reactive species undergoes a facile carbonylation in the presence of carbon monoxide to form the acyl complex **3** (2107, 2042, 2024, 2006, 1717 cm^{-1}, Figure 3). Heck found in his pioneering study no evidence for further multiple ring-opening and insertion reactions of epoxides; rather, it was reported that **3** affords methyl 3-hydroxybutyrate[10a] after treatment with methanol. We could observe using the ATR-IR method, that in situ generated complex **1**[10b] reacts with excess propene oxide under CO atmosphere to yield an acyl complex. Its structure is—following the study by Heck—assigned to complex **3**. If now a simple base such as pyridine (3-hydroxypyridine is here not a prerequisite) is added to the reaction mixture, the immediate formation of polyhydroxybutyrate, indicated by a growing absorption around 1740 cm^{-1}, is observed. It follows that pyridine is essential for the formation of the polyester; its exact role, though, remains unclear at the moment. It may assist in the electrophilic attack of the cobalt-bonded acyl carbon atom on the epoxide (**4** → **5**, Scheme 2).[11] In addition, it seems likely that in such a mixture, a pyridine-induced back-biting reaction in compound **3** (e.g., by deprotonating the −OH group, Scheme 2) is responsible for the observed slow formation of β-butyrolactone (**8**) in a side reaction. Further investigations on the mechanism are under way.

The molecular weights (GPC) of the isolated polymers are relatively low, probably due to a chain termination reaction by water (Scheme 2, 6 → 7). MALDI-TOF and NMR measurements on our PHBs enforced this consideration by the presence of hydroxylic and olefinic next to carboxylic end groups (**7**). The water may result from a pyridine-assisted dehydration of the chain end to give an olefin terminus.[12] Thus, polymerization reactions in the presence of water scavenger resulted in a higher-molecular weight polymer (Table 1, entry 2). Our current efforts are directed toward the development of a highly active catalyst for the preparation of higher-molecular weight polyester.

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Supporting Information Available: MALDI data of a PHB polyester (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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