FULL PAPERS

Carbonylative Polymerization of Oxetanes Initiated by Acetyl Cobalt Complexes

Yessi Permana, Koji Nakano, Makoto Yamashita, Daisuke Watanabe, and Kyoko Nozaki*[a]

Abstract: Four acetyl cobalt complexes, [AcCo(CO)$_3$P(p-tolyl)$_3$] (**1**; p-tolyl=4-Me-C$_6$H$_4$), [AcCo(CO)$_3$P(OPh)$_3$] (**2**), [AcCo(CO)$_3$P(NMe$_2$)$_3$] (**3**), and [AcCo(CO)$_2$(dppp)] (**4**; dppp=1,3-bis(diphenylphosphanyl)propane), were synthesized, characterized, and examined as catalysts for the unprecedented carbonylative polymerization of oxetanes. Copolymers containing ester (4-hydroxyalkanoate) and/or ether units were obtained with complexes **1** and **2**, but not with complexes **3** and **4** either in the presence or absence of additional phosphorus ligands. The ester unit/ether unit ratio varied in the range 21:79–63:37, and the highest ester/ether ratio of 63:37 was achieved by using complex **1** in the presence of a further 5 equivalents of P(OPh)$_3$. Although direct carbonylative polymerization is possible, preformation and ring opening of the γ-lactone is also suggested as an alternative pathway.

Keywords: carbonylation · cobalt · lactones · oxetanes · ring-opening polymerization

Introduction

Aliphatic polyesters have gained growing interest owing to their biodegradability.[1] The production of such polymers in nature relies on bacterial processing.[2] On the other hand, synthetic methods toward aliphatic polyesters have attracted considerable interest. One of the most common synthetic methods is ring-opening polymerization of lactones such as β-lactones, δ-lactones, or ε-lactones, which contain a four-, six-, or seven-membered ring, respectively [Eq. (1)].[3–5] In sharp contrast, however, γ-lactones, which contain a five-membered ring, have not yet been successfully utilized as monomers in ring-opening polymerization under practical conditions [Eq. (2)],[6–9] except for a few examples of copolymerizations with methyl methacrylate,[7] δ-valerolactone,[10] and ε-caprolactone.[8,11,12] These examples are limited to incorporation of the unsubstituted γ-lactone of 2–43%; the

highest incorporation was achieved by the copolymerization of γ-butyrolactone and ε-caprolactone, in a 98:1 ratio, initiated by aluminum isopropoxide trimer ([Al(OiPr)$_3$]) to give only 6% conversion of γ-butyrolactone.[11] The low polymerizability of γ-lactone is explained by the thermodynamic stability of its five-membered-ring structure;[13] that is, after nucleophilic ring opening of the γ-lactone by a growing anionic chain end, rapid "back-biting" immediately takes place to regenerate the original γ-lactone. However, by use of harsh reaction conditions, homopolymerization was reported to occur. For example, poly(γ-butyrolactones) with molecular weights (M_n) of 30 000–35 000 g mol^{-1} could be prepared under ultrahigh pressures of 1.2–2.0 GPa at 100–160 °C.[3a, 14]
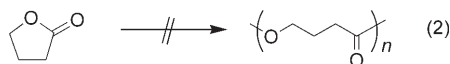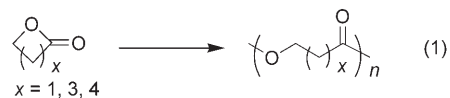
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$$x = 1, 3, 4 \qquad (1)$$

$$(2)$$

As another approach to polyesters, carbonylative polymerization of oxirane, a three-membered cyclic ether, is known to provide an equivalent of poly(β-lactone) [Eq. (3)]. Furukawa et al. reported the first example of the copolymer-

ization of oxirane with carbon monoxide (CO) by using AlEt$_3$/Co(acac)$_3$ (acac=acetylacetonate) and AliBu$_3$/H$_2$O/Co(acac)$_3$.[15]

$$\triangle\!\!\!O + CO \longrightarrow \left(O \diagdown \diagup \diagdown \underset{O}{\diagup}\right)_n \quad (3)$$
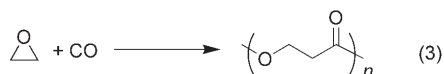
Recently, Rieger and co-workers reported that [Co$_2$(CO)$_8$]/3-hydroxypyridine is an active catalyst for the alternating copolymerization of propylene oxide with CO.[16] Several other catalyst systems have also been reported,[17–22] including an acyl cobalt complex, [AcCo(CO)$_3$P(o-tolyl)$_3$] (o-tolyl=2-Me-C$_6$H$_4$).[21,23,24]

As the ring opening of γ-lactones under mild and industrially practical conditions is apparently impossible for the incorporation of the 4-hydroxyalkanoate unit into a polymer, the carbonylative polymerization of oxetane, a four-membered cyclic ether, should provide the only efficient synthetic strategy [Eq. (4)]. Herein, we report the first example of carbonylative polymerization of oxetane, which allowed us to incorporate the 4-hydroxyalkanoate unit into a polymer chain. Acetyl cobalt complexes **1–4** (Scheme 1) were examined as catalysts in the absence and presence of free phosphorus ligands. The product contains ester and ether units because simple ring-opening enchainment without carbonylation also occurred as well as the targeted carbonylative enchainment. The highest incorporation of the ester unit, up to 63 %, was achieved by complex **1** in the presence of free P-(OPh)$_3$ ligand for the carbonylative polymerization of 3-methoxymethyl-3-methyloxetane (**5a**), which was easily prepared from a commercially available oxetane.
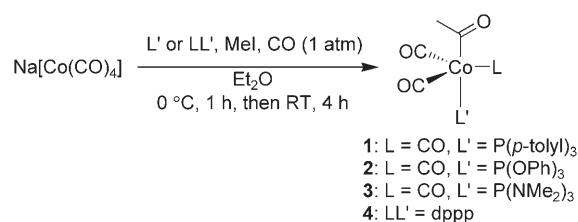
$$\underset{O}{\square} + CO \longrightarrow \left(O \diagdown \diagup \diagdown \underset{O}{\diagup}\right)_n \quad (4)$$
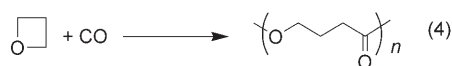
Results and Discussion

Synthesis and Characterization of Catalysts

The acetyl cobalt complexes [AcCo(CO)$_3$L] and [AcCo(CO)$_2$L$_2$] (L=phosphorus ligand) **1–4** were synthesized as potential catalysts for the oxetane/CO copolymerization (Scheme 1). According to the literature, treatment of

Abstract in Indonesian: Metoda sintesa baru bagi poliester rantai lurus yang ramah lingkungan ditemukan melalui polimerisasi oksetan dan gas karbon monoksida menggunakan katalis logam kobal **1** dan **2**. Penggunaan katalis kobal **1** yang ditambahkan ligan P(OPh)$_3$ sebanyak lima ekivalen mampu menghasilkan polimer dengan unit ester sampai dengan 63 %.

$$Na[Co(CO)_4] \xrightarrow[\substack{Et_2O \\ 0\ °C,\ 1\ h,\ then\ RT,\ 4\ h}]{L'\ or\ LL',\ MeI,\ CO\ (1\ atm)} \begin{array}{c} \overset{O}{\|} \\ OC_{\cdots}\ Co\!-\!L \\ OC^{\diagup}\ |\ \\ L' \end{array}$$

1: L = CO, L' = P(p-tolyl)$_3$
2: L = CO, L' = P(OPh)$_3$
3: L = CO, L' = P(NMe$_2$)$_3$
4: LL' = dppp

Scheme 1. Synthesis of acetyl cobalt complexes **1–4**. dppp=1,3-bis(diphenylphosphanyl)propane.

Na[Co(CO)$_4$] with MeI and P(p-tolyl)$_3$ (p-tolyl=4-Me-C$_6$H$_4$) under CO atmosphere provided phosphine complex **1**.[25,26] We also prepared phosphite complex **2**, phosphorus triamide complex **3**, and bidentate phosphine complex **4** by a process similar to that for **1**. All the complexes **1–4** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as FTIR spectroscopy and elemental analysis.

The electronic nature of the cobalt center is reflected by the carbonyl absorptions of **1–4** (Table 1). The frequencies

Table 1. IR data of acetyl cobalt complexes **1–4** (KBr).

Complex	P ligand	$\tilde{v}_{CO}$ [cm^{-1}]	$\tilde{v}_{CO}$ for Ac [cm^{-1}]
1	P(p-tolyl)$_3$	1973 (s), 1958 (s)	1663 (m)
2	P(OPh)$_3$	1990 (s), 1971 (s)	1676 (m)
3	P(NMe$_2$)$_3$	1969 (s), 1944 (s)	1655 (m)
4	dppp	1967 (m), 1911 (s)	1628 (s)

of the stretching vibrations of the carbonyl ligands and the C=O bond in the acetyl ligand decrease in the order **2** > **1** > **3** > **4**, and correspondingly the degree of electron back donation from the cobalt center to the carbonyl groups increases in the order **2** < **1** < **3** < **4**. In other words, the electron-donating ability of apical phosphorus ligands increases in the order P(OPh)$_3$ < P(p-tolyl)$_3$ < P(NMe$_2$)$_3$ < dppp. These trends match that previously reported for [RC(=O)Co(CO)$_3$L] (L=phosphorus ligand).[23e,27–29]

Complexes **1**, **2**, and **4** were further characterized by single-crystal X-ray analysis (Figure 1 and Table 2).[30] The complexes adopt a trigonal-bipyramidal conformation with three CO ligands at the equatorial sites and an acetyl and a phosphorus ligand at the apical sites, except for complex **4**, in which the chelating phosphine coordinates at both apical and equatorial sites.

The Co−P bond lengths are 2.2489(7) (**1**), 2.1782(7) (**2**), and 2.2182(10); 2.2257(11) Å (**4**). The shorter Co−P bond of complex **2** is well-related to the electron-withdrawing character of P(OPh)$_3$: stronger back donation from the Co center to the phosphorus atom results in the shorter Co−P bond.[31] This electron-withdrawing character of P(OPh)$_3$ decreases electron density on the cobalt center to cause the Co−C(acetyl) bond to lengthen (2.039(3) Å) in complex **2** relative to that in phosphine complexes **1** (2.0077(8) Å) and **4** (1.985(3) Å).
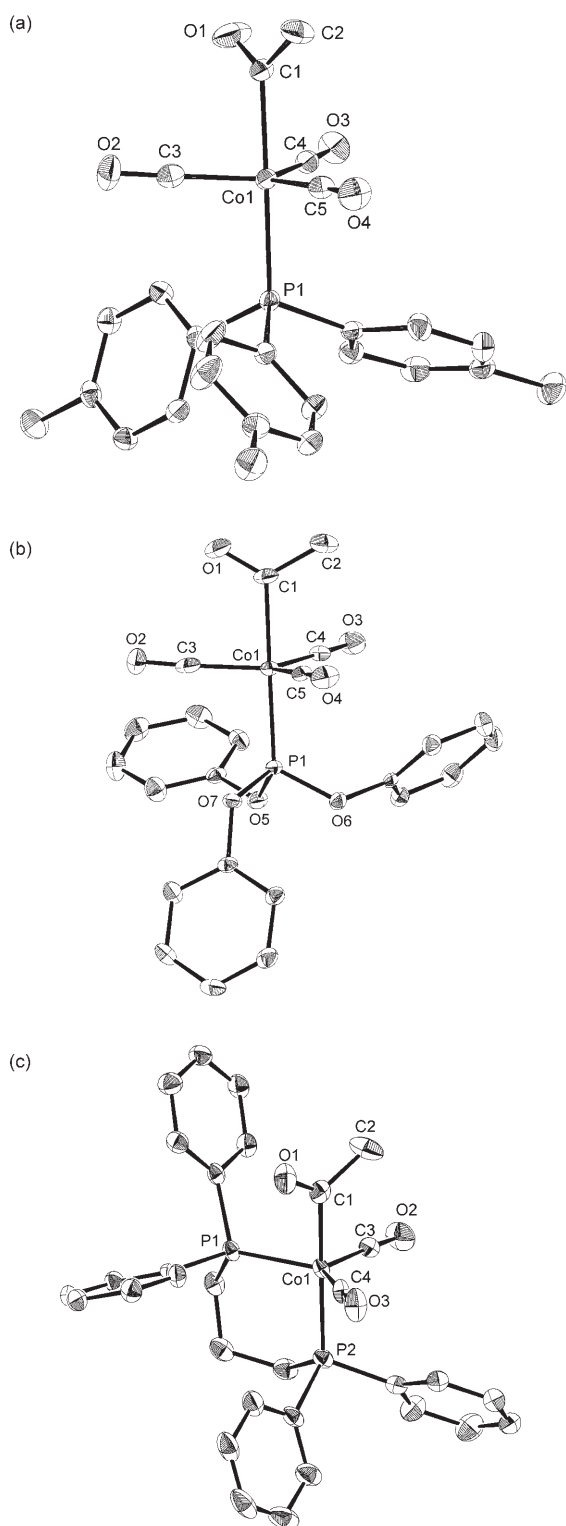
(a)

(b)

(c)

Figure 1. ORTEP drawings of a) **1**, b) **2**, and c) **4** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) in **1**: Co−C1 2.0077(18), average Co−CO 1.7849(19), Co−P 2.2489(7), C1−O1 1.204(2), average C=O 1.144(2). Selected bond lengths (Å) in **2**: Co−C1 2.039(3), average Co−CO 1.793(3), Co−P 2.1782(7), C1−O1 1.215(3), average C=O 1.140(3). Selected bond lengths (Å) in **4**: Co−C1 1.985(3), average Co−CO 1.759(3), average Co−P 2.22195(105), C1−O1 1.206(4), average C=O 1.148 (4).

Table 2. Crystallographic data and structure-refinement details for complexes **1**, **2**, and **4**.

Complex	1	2	4
Formula	$C_{26}H_{24}CoO_4P$	$C_{23}H_{18}CoO_7P$	$C_{31}H_{29}CoO_3P_2$
M_r	490.35	496.27	570.41
T [K]	120(2)	120(2)	103(2)
λ [Å]	0.71070	0.71070	0.71070
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
a [Å]	10.308(3)	9.5979(4)	10.307(3)
b [Å]	12.531(3)	11.0455(7)	21.188(7)
c [Å]	18.354(5)	20.8127(13)	12.555(4)
α [°]	90.0000(11)	90	90.0000(13)
β [°]	96.2539(13)	90	90.0876(13)
γ [°]	90.0000(11)	90	90.0000(13)
V [Å³]	2356.7(11)	2206.4(2)	2741.9(16)
Z	4	4	4
D_{calcd} [g cm⁻³]	1.382	1.494	1.382
μ [mm⁻¹]	0.826	0.893	0.773
$F(000)$	1016	1016	1184
Crystal size [mm³]	0.55×0.45×0.25	0.75×0.50×0.45	0.50×0.40×0.07
2θ range [°]	3.15–25.00	3.43–25.00	3.20–25.00
No. of reflections collected	22214	14070	8758
No. of independent reflections	4104	3869	4529
R_{int}	0.0183	0.0222	0.0292
No. of parameters	293	290	335
GOF on F^2	1.090	1.214	1.083
$R1$, $wR2$ ($I>2\sigma(I)$)	0.0286, 0.0728	0.0216, 0.0589	0.0433, 0.0826
$R1$, $wR2$ (all data)	0.0299, 0.0737	0.0228, 0.0783	0.0533, 0.0873

Reactions of Oxetanes 5a–e with CO by Using Complexes 1–4

With complexes **1–4** in hand, we investigated the copolymerization of oxetane **5a** with CO. Oxetane **5a** was readily prepared from commercially available 3-hydroxymethyl-3-methyloxetane.[32] Copolymers containing both ester and ether units were obtained with complexes **1** and **2**, but no reaction proceeded with complexes **3** or **4** (Table 3). The reaction of **5a** with CO by using complex **1** (5a/Co=200) under 8.0 MPa of CO at 100°C for 12 h gave a copolymer with an activity of 300 g (mol Co)⁻¹ h⁻¹, an ester/ether ratio of 27:73, and an M_n value of 4900 g mol⁻¹ (polydispersity index, PDI=1.5) (Table 3, entry 1). The catalytic activity and the ester/ether ratio increased from 100 to 140°C (Table 3, entries 1–3), whereas the high reaction temperature of 160°C (Table 3, entry 4) decreased the formation of the ester unit. Thus, copolymerization at 140°C gave the highest incorporation of the 4-hydroxyalkanoate unit (47%) in the polymer (Table 3, entry 3) in this series. The molecular weights of the copolymers obtained decreased with increasing reaction temperature in spite of an increase in copolymer yields, most probably due to chain transfer (Table 3, entries 1–4). When compared at the same temperature, phosphite complex **2** exhibited higher catalytic activity and produced a higher-molecular-weight copolymer than complex **1**, but it provided the copolymer with a lower ester-unit content (compare Table 3, entries 1–3 with entries 6–8). The temperature dependency of the catalytic activity, ester/ether ratio,

Table 3. Copolymerization of oxetanes and CO initiated by complexes **1–4** and **6**.

5a: R = CH$_2$OMe, R' = Me   **5d**: R = CH$_2$OnBu, R' = Me
5b: R = R' = H
5c: R = CH$_2$OEt, R' = Me   **5e**: R = R' = Me

Entry	Oxetane	Complex	L' ([equiv])	T [°C]	Yield [%]	Activity [g(mol of Co)$^{-1}$ h^{-1}]	x/y[a]	M_n[b] [g mol^{-1}] (PDI)
1	**5a**	1	–	100	12	300	27:73	4900 (1.5)
2	**5a**	1	–	120	48	1000	32:68	4400 (1.6)
3	**5a**	1	–	140	54	1200	47:53	3900 (1.7)
4	**5a**	1	–	160	69	1500	44:56	3400 (2.1)
5	**5a**	2	–	80	72	1400	8:92	7800 (2.1)
6	**5a**	2	–	100	80	1600	16:84	6500 (2.3)
7	**5a**	2	–	120	81	1600	21:79	5300 (2.5)
8	**5a**	2	–	140	60	1300	34:66	5000 (2.4)
9	**5a**	3	–	140	no reaction			
10	**5a**	4	–	140	no reaction			
11	**5b**	1	–	140	5	50	28:72	oligomeric[c]
12	**5c**	1	–	140	6	140	60:40	2900 (2.4)
13	**5d**	1	–	140	11	420	43:57	oligomeric[c]
14	**5e**	1	–	140	trace copolymer[d]			
15	**5a**	1	P(p-tolyl)$_3$ (1 equiv)	140	12	260	60:40	2800 (1.2)
16	**5a**	1	P(p-tolyl)$_3$ (5)	140	no reaction			
17	**5a**	1	P(OPh)$_3$ (1)	140	19	420	59:41	3300 (1.3)
18	**5a**	1	P(OPh)$_3$ (5)	140	19	430	63:37	3000 (1.1)
19	**5a**	2	P(p-tolyl)$_3$ (1)	140	8	220	22:78	oligomeric[c]
20	**5a**	2	P(OPh)$_3$ (1)	140	30	660	59:41	3200 (1.5)
21	**5a**	2	P(OPh)$_3$ (5)	140	trace copolymer[d]			
22	**5a**	6[e]	–	140	37	810	29:71	3900 (1.9)

[a] Production ratio was estimated by ^{1}H NMR spectroscopy. [b] Determined by gel-permeation chromatography with a polystyrene standard. [c] $M_n \leq 1700$ g mol^{-1}. [d] Conversion < 4%. [e] Complex **6** is [BnCOCo(CO)$_4$].[23b]

and molecular weight observed with **2** was similar to that with **1** (Table 3, entries 5–8). The highest molecular weight of 7800 g mol^{-1} was obtained with **2** at 80 °C (Table 3, entry 5).

The reaction of unsubstituted oxetane **5b** with CO by using **1** gave an oligomeric product with an ester/ether ratio of 28:72 (Table 3, entry 11). Copolymerization of ethyl ether **5c** with CO by using the same catalyst provided a copolymer with 60% ester units, which is higher than the copolymer derived from **5a** under the same reaction conditions, and an M_n value of 2900 g mol^{-1} (compare Table 3, entry 12 with entry 3). Copolymerization with **5d**, which has a longer alkyl chain on the alkoxy group, initiated by the same catalyst provided only an oligomeric product with an unexpectedly low proportion of ester units (Table 3, entry 13). Copolymerization of dimethyl-substituted oxetane **5e** gave only trace amounts of the copolymer (Table 3, entry 14). However, although the **5c**-derived copolymer contained more ester units, the yield was considerably lower (6%).

Structural Analysis of the Copolymers

The product copolymers were characterized by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. The ^{1}H NMR spectrum of the copolymer obtained in Table 3, entry 3 is shown in Figure 2a. The peaks at 0.8–1.0 ppm were identified as due to protons of the methyl side chains directly attached to the quaternary carbon atoms. Compared with the ^{1}H NMR spectrum of the homopolymer of poly-**5a** (see below; Figure 2b), the peaks at 0.8–1.0 ppm show a complex pattern, which implies the existence of neighboring ester and ether units. This is also supported by MALDI-TOF MS analysis of the copolymers obtained: multiple signals were detected for the polymer obtained in Table 3, entry 3, which correspond to a variety of combinations of x and y in Table 3.[33] On the other hand, the existence of both polyether and polyester blocks was proven by the following studies. Hydrolysis of poly-(**5a**/*co*-CO) with concentrated HCl at 85 °C for 40 h in dioxane provided poly-**5a** (22%), oligo-**5a** (31%), γ-lactone **7a**, and its demethylated product **7a′** (12% for **7a** + **7a′**) after separation by GPC (Scheme 2).[33]

The existence of high-molecular-weight poly-**5a** after separation suggests that the polymeric material obtained in Table 3 contained a certain amount of poly-**5a** from the beginning. Lactone **7a** was most probably derived from the back-biting degradation of the polyester unit, that is, poly-(**5a**/*alt*-CO), under hydrolysis. Oligo-**5a** was probably derived from a polymer containing both ether and ester linkages.

High-Pressure IR Studies of Complexes 1 and 2 under CO Pressure

To elucidate the different catalytic performances of phosphine complex **1** and phosphite complex **2**, their behavior under CO pressure was investigated.[23d,e]

Upon exposure to CO pressure of 7.0 MPa at 100 °C, no clear replacement of the P(p-tolyl)$_3$ ligand by CO in complex **1** (0.03 M in THF) was observed even after 3 h
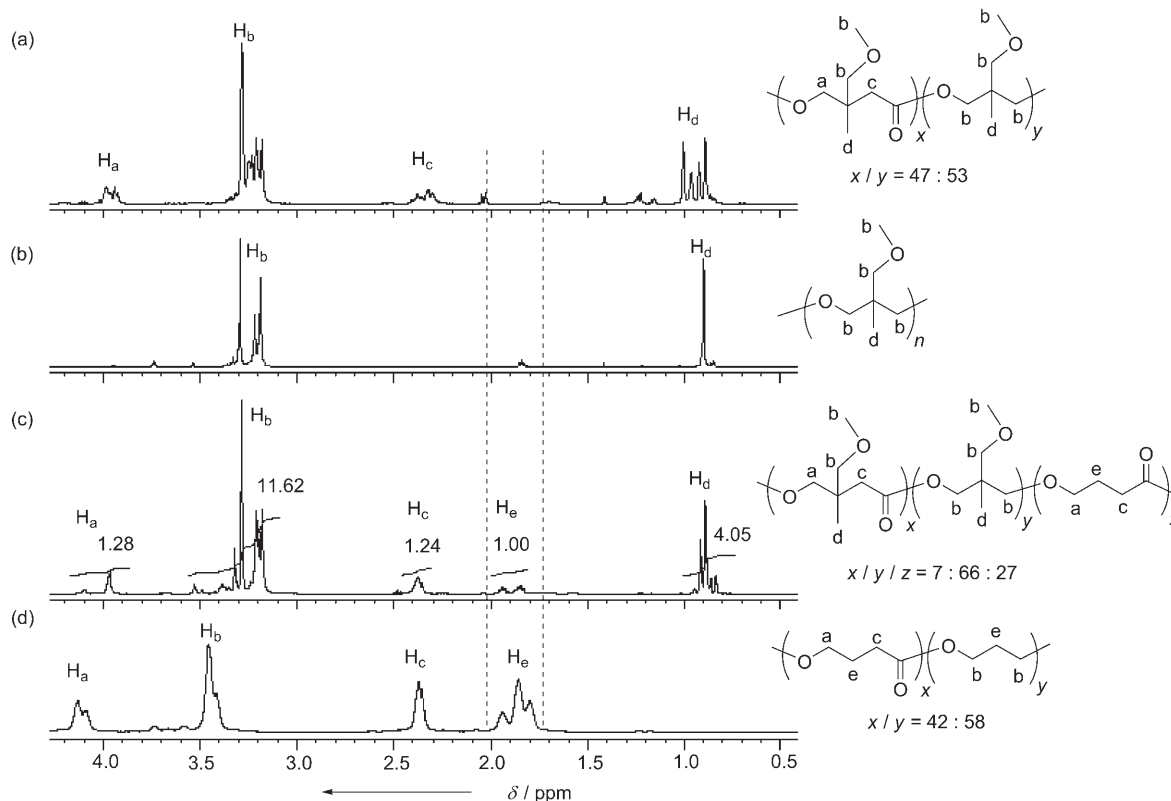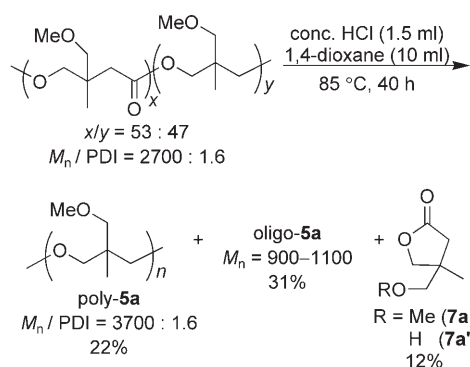
Figure 2. ¹H NMR spectra of a) copolymer obtained from copolymerization of oxetane **5a** with CO, b) poly-**5a**, c) terpolymer from polymerization of oxetane **5a** with CO in the presence of **7b**, and d) copolymer from oxetane **5b** with CO.

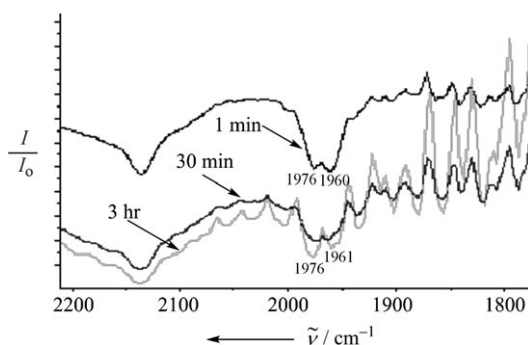Scheme 2. Hydrolysis of poly-(**5a**/co-CO) with concentrated HCl.

(Figure 3). On the contrary, the exposure of complex **2** (0.06 M in THF) to 7.0 MPa of CO at 100 °C resulted in immediate conversion into [AcCo(CO)$_4$]. Within 5 min, the initial carbonyl stretching vibrations disappeared, and new absorptions appeared at 2003 and 2023 cm^{-1}, which accorded with the reported values for [AcCo(CO)$_4$] (Figure 4).[23d,e] Notably, the reaction of **2** to give [AcCo(CO)$_4$] is a reversible process. When the pressure of CO was released to ambient pressure, we detected the absorptions due to **2** again. This easier replacement of P(OPh)$_3$ by CO relative to P(p-tolyl)$_3$ may be explained as follows: the thermodynamic stabilities of complex **2** and [AcCo(CO)$_4$] are similar, whereas

Figure 3. IR spectra of **1** in THF after CO exposure at 7.0 MPa at 100 °C.
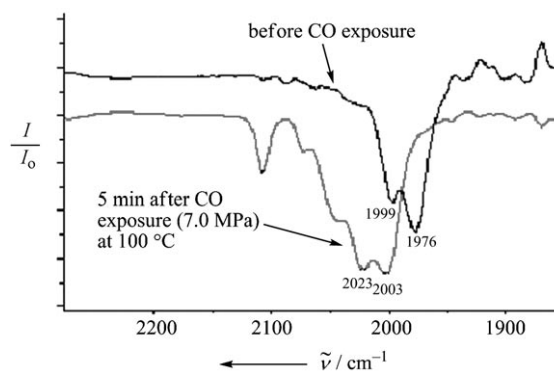
Figure 4. IR spectra of **2** before and after CO exposure in THF.

complex **1** is much more stable than either **2** or [AcCo(CO)$_4$] through electron donation of the phosphine ligand. A similar relationship between lability and the electron-donating ability of phosphorus ligands was also reported by Jia et al.[23]

Effect of Additional Ligands and Consideration of Active Species

As ligand dissociation seems to be critical under the polymerization reaction conditions, we carried out the **5a**/CO copolymerization in the presence of additional phosphorus ligands. Addition of 1.0 equivalent of either free P(*p*-tolyl)$_3$ or P(OPh)$_3$ ligand in the copolymerization of oxetane **5a** and CO initiated by phosphine complex **1** increased the proportion of ester units to 60%; however, the catalytic activity and molecular weight were sacrificed (Table 3, entries 15 and 17). Although a large excess of P(OPh)$_3$, up to 5.0 equivalents in the above copolymerization, resulted in slightly more ester units (Table 3, entry 18), an equivalent excess of P(*p*-tolyl)$_3$ deactivated the reaction (Table 3, entry 16). Complex **2** showed a similar phenomenon only in the addition of free P(OPh)$_3$ in a 1:1 ratio to the catalyst (Table 3, entry 20). A lower proportion of ester units was obtained when 1.0 equivalent of P(*p*-tolyl)$_3$ (Table 3, entry 19) was added, and only trace amounts of the copolymer was produced when up to 5.0 equivalents of the phosphite was added (Table 3, entry 21). In the absence of any ligand, that is, in the reaction initiated by [BnCOCo(CO)$_4$] (**6**), a copolymer with an ester/ether ratio of 29:71 and an M_n value of 3900 g mol^{-1} (PDI = 1.9) was obtained in 37% yield (Table 3, entry 22). The above observations may be summarized as follows. The stronger electron donor P(*p*-tolyl)$_3$ increases the ester content relative to the weaker donor (thus, weaker binder) P(OPh)$_3$ (Table 3, entries 3 and 8). Addition of extra amounts of a phosphorus ligand seemed to increase the ester content (Table 3, entries 15, 17, 18, and 20), although there were some exceptions (Table 3, entry 19). A large excess of a free phosphorus ligand retarded the reaction (Table 3, entries 16 and 21). This was probably the result of an equilibrium shift from a tetracarbonyl cobaltate species to a phosphorus-ligated cobaltate.[34] In other words, the more Lewis acidic ligand-free cobalt species tend to give a higher ether content, whereas the less acidic cobalt species, achieved by the coordination of a phosphorus ligand, is less active for the homopolymerization of **5a**. As a result, copolymers with a higher ester content were obtained in the presence of an appropriate amount of phosphorus ligands.

## Possibility of Direct or Indirect Pathway in Carbonylative Polymerization of Oxetanes

To obtain more information about the mechanism of the cobalt-catalyzed carbonylative polymerization of oxetanes, the possibility of indirect carbonylative polymerization, which involves formation of γ-lactone **7a** as an intermediate

followed by its subsequent ring-opening polymerization together with a ring-opening polymerization of the oxetane **5a** (Scheme 3), should also be taken into account.[35–37]
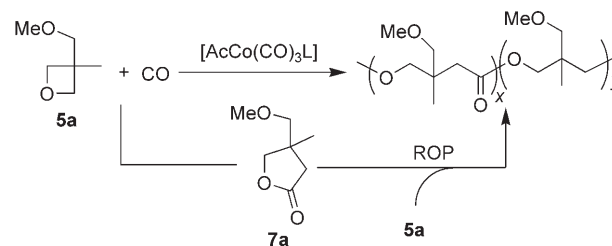
Scheme 3. Plausible pathways in oxetane/CO copolymerization. ROP = ring-opening polymerization.

Thus, we first heated a mixture of γ-butyrolactone **7b** with complex **1** or **2** at 140 °C for 12 h, which resulted in recovery of **7b** either in the presence or absence of CO (8.0 MPa). No reaction proceeded when lactone **7b** was treated in the presence of complex **1** and oxetane **5a**. On the other hand, the reaction of **7b** in the presence of **1**, CO (8.0 MPa), and oxetane **5a** at 140 °C gave a terpolymer containing the ester unit derived from **7b** (Scheme 4).


39% yield, $x / y / z$ = 7 : 66 : 27
M_n / PDI = 3200 : 2.0
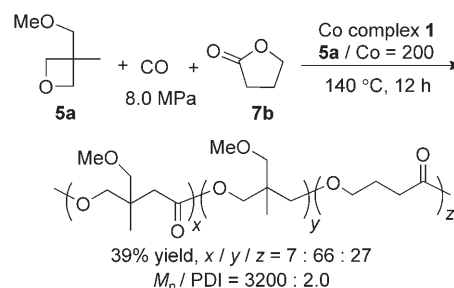
Scheme 4. Copolymerization of oxetane **5a** and CO in the presence of γ-lactone **7b**.

Incorporation of **7b** was confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the terpolymer obtained (Figure 2c) is compared with that of the **5a**/CO copolymer (Figure 2a). In Figure 2c, there are broad peaks at 1.7–1.9 ppm, which were not observed in Figure 2a. By comparing the spectrum in Figure 2c with that of a copolymer obtained from unsubstituted oxetane **5b** and CO (Figure 2d),[38] the broad peaks at 1.7–1.9 ppm were assigned to the methylene protons H$_e$ in the ester unit derived from **7b**. The ratio of ester to ether units from **5a** to the ester unit from **7b**, that is, $x/y/z$ in Scheme 4, is 7:66:27, which corresponds to the total ester/ether ratio of 34:66. Thus, the incorporation of γ-butyrolactone **7b** indicates that the occurrence of an indirect pathway exists. On the other hand, the direct pathway is still possible. Notably, there was a significant decrease in the total ester/ether ratio from 47:53 in the copolymerization without **7b** (Table 3, entry 3) to 34:66 with **7b** (Scheme 4). The fact that the presence of **7b** inhibited the

incorporation of ester units in the **5a**/CO copolymerization seems to contradict the indirect pathway.

In sharp contrast to the observations with substituted oxetane **5a**, the opposite trend was observed with unsubstituted oxetane **5b**. The copolymerization of **5b** with CO provided the corresponding copolymer with an ester/ether ratio of 7:93 when the reaction was carried out at 100 °C for 20 h under CO pressure of 6.0 MPa in the presence of **1** (0.36 mol%). Notably, in this case, γ-lactone **7b** was obtained in 16% yield along with the desired copolymer and the remaining **5b** (21%).[39] Furthermore, the ester content increased when the copolymerization was carried out in the presence of an equimolar amount of **7b** (Scheme 5). Hence, the indirect pathway may be more probable for the reaction of **5b**.
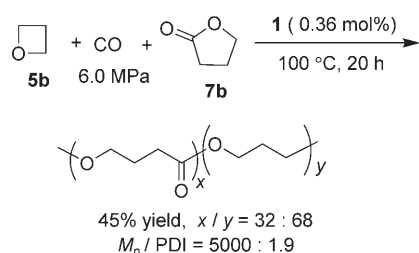
Scheme 5. Copolymerization of oxetane **5b** and CO in the presence of γ-lactone **7b**.

Conclusions

We have successfully achieved the first example of copolymerization of oxetane and CO initiated by acetyl cobalt complexes. The copolymerization afforded polymers containing ester and ether units. The phosphorus ligands ligated to the cobalt center were observed to control the ratio of ester to ether units, the catalytic activity, and the molecular weight of the copolymer. The reaction with phosphite complex **2**, in which P(OPh)$_3$ was instantaneously substituted by CO under the copolymerization conditions, provided a copolymer with higher molecular weight, whereas the reaction with P(p-tolyl)$_3$ complex **1** gave a copolymer with higher ester-unit content. In the presence of a free phosphorus ligand, a copolymer with 63% ester content was produced. The possible mechanism of indirect carbonylative polymerization via a γ-lactone intermediate was suggested.

Experimental Section

General

All operations involving air- and/or moisture-sensitive compounds were carried out with standard Schlenk techniques under argon atmosphere purified by passing through a hot column packed with a BASF R3-11 catalyst, except where CO was used as indicated. NMR spectra were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H, 202 MHz for ^{31}P, and 125 MHz for ^{13}C). Infrared spectra were recorded on a Shimadzu FTIR 8400 spectrometer or ASI ReactIR1000™ spectrometer with a SiComp™ probe for high-pressure conditions. The number-average molecular weight and polydispersity index of the copolymer were determined by gel-permeation chromatography (GPC) by using a GL Sciences instrument equipped with two columns (Shodex KF-804L) and THF as an eluent at 40 °C at 1 mL min^{-1} relative to polystyrene standards. X-ray data were collected on a RIGAKU MERCURY CCD diffractometer. Elemental analysis was performed at the Microanalytical Laboratory of the Department of Chemistry, the Graduate School of Science, the University of Tokyo. Na[Co(CO)$_4$][40] and oxetanes **5a**, **5c**, and **5d**[32] were synthesized according to literature procedures.

Syntheses

1: A solution of Na[Co(CO)$_4$] (0.59 g, 3.1 mmol) in diethyl ether (30 mL) was cooled to 0 °C. Neat P(p-tolyl)$_3$ (0.97 g, 3.2 mmol) was added under argon atmosphere, and the mixture was stirred under CO atmosphere (1 atm) for about 5 min before addition of MeI in excess (0.25 mL, 4.0 mmol). Stirring was continued for 1 h at 0 °C and for a subsequent 4 h at room temperature. The solution was filtered under argon atmosphere, and the filtrate was quickly added to rigorously stirred hexane to give a purified precipitate of **1** (1.03 g, 2.1 mmol, 69%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from diethyl ether/hexane at 4 °C. IR (KBr): $\tilde{v}$ = 2043 (w), 1973 (s), 1958 (s), 1663 cm^{-1} (m; C=O); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ = 2.39 (s, 9 H), 2.75 (s, 3 H), 7.20–7.32 ppm (m, 12 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 21.5, 50.1 (d, $^3J_{P,C}$ = 22.5 Hz), 129.5 (d, $J_{P,C}$ = 11.3 Hz), 130.4 (d, $J_{P,C}$ = 46 Hz), 133.0 (d, $J_{P,C}$ = 11.3 Hz), 141.1, 199.3 (d, $^2J_{P,C}$ = 20 Hz), 240.1 ppm (d, $^2J_{P,C}$ = 35 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 48.1 ppm (s); elemental analysis: calcd (%) for C$_{26}$H$_{24}$CoO$_4$P: C 63.68, H 4.94; found: C 63.42, H, 5.13.

2: The preparation was carried out by using Na[Co(CO)$_4$] (0.80 g, 4.1 mmol), P(OPh)$_3$ (1.2 mL, 4.6 mmol), and MeI (0.30 mL, 4.8 mmol) in a manner similar to that for **1**, except for the treatment after the reaction. After a total of 5 h of stirring, diethyl ether was removed under reduced pressure at ambient temperature. The pressure was maintained at about 50 kPa to avoid decarbonylation from an acetyl ligand. The mixture was extracted with toluene and filtered under argon atmosphere. The filtrate was concentrated under reduced pressure, and recrystallization from hexane at −30 °C gave **2** as colorless crystals (1.49 g, 3.0 mmol, 73%). Single crystals suitable for X-ray crystallography were obtained from diethyl ether/hexane at 4 °C. IR (KBr): $\tilde{v}$ = 2064 (w), 1990 (s), 1971 (s), 1676 cm^{-1} (m; C=O); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ = 2.50 (s, 3 H), 7.25 (br s, 9 H), 7.39 ppm (br s, 6 H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ = 50.8 (d, $^3J_{P,C}$ = 43.8 Hz), 123.5, 127.9, 132.0, 152.5, 199.1, 235.3 ppm (d, $^2J_{P,C}$ = 60 Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ = 161.2 ppm (s); elemental analysis: calcd (%) for C$_{23}$H$_{18}$CoO$_7$P: C 55.67, H 3.67; found: C 55.74, H 3.56.

3: Complex **3** was synthesized in a similar manner to complex **1** by using Na[Co(CO)$_4$] (0.94 g, 4.9 mmol), P(NMe$_2$)$_3$ (1.0 mL, 5.5 mmol), and MeI (0.40 mL, 6.4 mmol) to give **3** (1.07 g, 3.1 mmol, 63%) as a greenish powder. IR (KBr): $\tilde{v}$ = 2039 (w), 1969 (s), 1944 (s), 1655 cm^{-1} (m; C=O); ^{1}H NMR (CDCl$_3$, 25 °C): δ = 2.58 (s, 18 H), 2.71 ppm (s, 3 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 37.8 (d, $^2J_{P,C}$ = 6.3 Hz), 49.9 (d, $^3J_{P,C}$ = 31.3 Hz), 199.7 (br s), 244.4 ppm (d, $^2J_{P,C}$ = 45 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 43.9 ppm (s); elemental analysis: calcd (%) for C$_{11}$H$_{21}$CoN$_3$O$_4$P: C 37.83, H 6.06, N 12.03; found: C 37.56, H 6.01, N 11.82.

4: Complex **4** was synthesized in a manner similar to complexes **1** and **3** by using Na[Co(CO)$_4$] (0.10 g, 0.52 mmol), dppp (0.28 g, 0.68 mmol), and MeI (0.10 mL, 1.56 mmol) to give **4** (0.21 g, 0.37 mmol, 72%) as a yellow powder. Single crystals suitable for X-ray crystallography were obtained from acetone/hexane at −30 °C. IR (KBr): $\tilde{v}$ = 1967 (m), 1911 (s), 1628 cm^{-1} (s); ^{1}H NMR (CDCl$_3$, −60 °C): δ = 1.71 (br, 2 H, PCH$_2$CH$_2$CH$_2$P), 2.04–2.74 (br, 7 H, COCH$_3$, PCH$_2$CH$_2$CH$_2$P), 6.50–8.15 ppm (br, ArH); ^{13}C{^{1}H} NMR (CDCl$_3$, −60 °C): δ = 18.7 (br, PCH$_2$CH$_2$CH$_2$P), 28.3 (br, PCH$_2$CH$_2$CH$_2$P), 30.0 (br, PCH$_2$CH$_2$CH$_2$P), 50.9 (br, CoCOCH$_3$), 128.3 (s, Ar), 129.6 (d, $J_{P,C}$ = 40 Hz, Ar), 130.6 (s, Ar), 132.0 (s, Ar), 136.2 (br, Ar), 203.2 (br s, CoCO), 252.7 ppm (br, CoCOCH$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, −60 °C): δ = 19.2 (d, $J_{P,P}$ = 61 Hz), 36.4 ppm (d, $J_{P,P}$ = 57 Hz); elemental analysis: calcd (%) for C$_{31}$H$_{29}$CoO$_3$P$_2$: C 65.27, H 5.12; found: C 64.99, H 5.22.

X-ray Crystallography

In each case, a suitable crystal was mounted with mineral oil onto a glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Measurements were made to $2\theta_{max} = 55°$. Structures were solved by direct methods with SIR-97[41] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[42]). Intensities were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by using AFIX instructions.

Copolymerization

Typical procedure for copolymerization of **5** with CO: Complex **1** (25 mg, 5.0×10^{-2} mmol) was placed in a 20-mL Schlenk tube and dried in vacuo. Oxetane **5a** (1.2 mL, 10 mmol) was placed in another Schlenk tube and degassed by three freeze–pump–thaw cycles. The oxetane was introduced into the catalyst-containing Schlenk tube, and the solution was then transferred to a 50-mL autoclave. After CO was introduced at pressure (8.0 MPa), the mixture was stirred at 140°C for 12 h. The reaction mixture was cooled to ambient temperature, and the CO pressure was slowly released. The reaction was quenched with aqueous HCl (0.1 M, 1 mL), and the mixture was dissolved in THF. The volatile materials were evaporated under vacuum, and the residue was weighed to determine the activity of the catalyst. The residue was dissolved in chloroform and washed with 0.1 M aqueous HCl. The organic layer was dried over Na_2SO_4 and concentrated. A small portion of the resulting residue was analyzed by size-exclusion chromatography and ¹H NMR spectroscopy to determine the component of the reaction product. The ester/ether ratio was calculated by the integration of the ¹H NMR peaks at around 4.0 ppm ($H_a =$ signals for methylene group next to acyloxy group) and 3.5–3.2 ppm ($H_b =$ signals for methylene and methyl groups next to ether oxygen atom).

Test of incorporation of **7b**: Double the molar equivalent of unsubstituted γ-butyrolactone **7b** (1.5 mL, 19 mmol) was introduced into a 50-mL autoclave containing a mixture of complex **1** (24 mg, 5.0×10^{-2} mmol) and oxetane **5a** (1.2 mL, 9.5 mmol), as treated in the procedure for the copolymerization of **5a** and CO. After CO was introduced at pressure (8.0 MPa), the mixture was stirred at 140°C for 12 h. The reaction mixture was cooled to 0°C to avoid any loss of **7b**, and the CO pressure was slowly released. Naphthalene (1.0 mmol, 128 mg), used as an internal standard, was introduced into the mixture, followed by a rinse of CDCl₃. ¹H NMR spectroscopic and GC analyses were performed to determine the remaining **7b** after the reaction. It was observed by both techniques that 19% of **7b** was consumed in the polymerization. After the analyses, the mixture was dissolved in chloroform and washed with aqueous HCl (0.1 M). The organic layer was dried over Na_2SO_4 and concentrated in vacuo at 50°C to give the terpolymer (1.11 g). The $x/y/z$ ratio was calculated to be 7:66:27 by integration of the ¹H NMR peaks at around 4.0 (H_a), 3.5–3.2 (H_b), and 1.9–1.7 ppm ($H_e =$ central methylene group of ester unit from **7b**). The yields were determined to be 23% for **5a** and 16% for **7b**. No reaction proceeded in the absence of either CO or oxetane.

Copolymerization of **5b** with CO in the presence of **7b**: Oxetane **5b** (1.0 mL, 15.4 mmol) and γ-butyrolactone **7b** (1.2 mL, 15.4 mmol) were introduced into a 20-mL Schlenk tube containing complex **1** (27 mg, 5.6×10^{-2} mmol). The mixture was degassed by three freeze–pump–thaw cycles. After CO was introduced at pressure (6.0 MPa), the mixture was stirred at 100°C for 20 h. Naphthalene (1.0 mmol, 128 mg), used as an internal standard, was introduced into the mixture of crude product, followed by a rinse of CDCl₃. ¹H NMR spectroscopic analysis was performed to determine the remaining **7b** after the reaction. It was observed that 27% of **7b** was consumed in the polymerization. After the analysis, the mixture was dissolved in chloroform and washed with aqueous HCl (0.1 M). The organic layer was dried over Na_2SO_4 and concentrated in vacuo at 50°C for 2 h to give the copolymer (0.92 g). The x/y ratio was calculated to be 32:68 by integration of the ¹H NMR peaks at 4.2–4.0 (H_a) and 2.0–1.7 ppm (H_e). The yield of the copolymer was determined to be 45%.

Hydrolysis of Poly-(5a/co-CO) with Concentrated HCl

Poly-(**5a**/*co*-CO) (242 mg), obtained from the copolymerization of **5a** and CO initiated by **1**, was dissolved in 1,4-dioxane (10 mL), followed by addition of concentrated HCl (1.5 mL). The solution was stirred for 40 h at 85°C. After the reaction, the mixture was diluted with water and washed over CHCl₃ followed by drying in vacuo. The organic mixture was recovered quantitatively. The mixture was separated by GPC (CHCl₃ as an eluent) and characterized by ¹H NMR spectroscopy to give poly-**5a** (22%), oligo-**5a** (31%), γ-lactone **7a**, and its demethylated product **7a′** (12% for **7a+7a′**).

Acknowledgements

[1] For recent reviews, see: a) C. K. Williams, *Chem. Soc. Rev.* **2007**, *36*, 1573–1580; b) M. Vert, *Biomacromolecules* **2005**, *6*, 538–546; c) Y. Zheng, E. K. Yanful, A. S. Bassi, *Crit. Rev. Biotechnol.* **2005**, *25*, 243–250.

[2] For recent reports on the biological processing of aliphatic polyesters, see: a) D. P. Martin, S. F. Williams, *Biochem. Eng. J.* **2003**, *16*, 97–105; b) R. Carlson, F. Srienc, *J. Biotechnol.* **2006**, *124*, 561–573; c) C. C. Chien, C. C. Chen, M. H. Choi, S. S. Kung, Y. H. Wei, *J. Biotechnol.* **2007**, *132*, 259–263; d) L. L. Madison, G. W. Huisman, *Microbiol. Mol. Biol. Rev.* **1999**, *63*, 21–53.

[3] For recent reviews, see: a) A. C. Albertsson, I. K. Varma, *Adv. Polym. Sci.* **2002**, *157*, 1–40; b) O. Coulembier, P. Degéea, J. L. Hedrick, P. Dubois, *Prog. Polym. Sci.* **2006**, *31*, 723–747.

[4] For recent reports, see: a) M. Möller, R. Kånge, J. L. Hedrick, *J. Polym. Sci. Part A* **2000**, *38*, 2067–2074; b) L. R. Rieth, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 15239–15248; c) F. A. Jaipuri, B. D. Bower, N. L. Pohl, *Tetrahedron: Asymmetry* **2003**, *14*, 3249–3252; d) K. M. Schreck, M. A. Hillmyer, *Tetrahedron* **2004**, *60*, 7177–7185; e) B. C. Wilson, C. W. Jones, *Macromolecules* **2004**, *37*, 9709–9714; f) F. Majoumo-Mbea, E. Smolensky, P. Lönnecke, D. Shpasser, M. S. Eisen, E. Hey-Hawkins, *J. Mol. Catal. A* **2005**, *240*, 91–98; g) A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel, J.-F. Carpentier, *Angew. Chem.* **2006**, *118*, 2848–2850; *Angew. Chem. Int. Ed.* **2006**, *45*, 2782–2784; h) B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth, J. L. Hedrick, *Macromolecules* **2006**, *39*, 8574–8583; i) W. Jeong, J. L. Hedrick, R. M. Waymouth, *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.

[5] For recent reports on the ring-opening polymerization of lactides, see: a) B. J. O'Keefe, M. A. Hillmyer, W. B. Tolman, *J. Chem. Soc. Dalton Trans.* **2001**, 2215–2224; b) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; c) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326; d) Z. Zhong, P. J. Dijkstra, J. Feijen, *Angew. Chem.* **2002**, *114*, 4692–4695; *Angew. Chem. Int. Ed.* **2002**, *41*, 4510–4513; e) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, Jr., M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2003**, *125*, 11350–11359; f) P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689; g) D. Bourissou, B. Martin-Vaca, A. Dumitrescu, M. Graullier, F. Lacombe, *Macromolecules* **2005**, *38*, 9993–9998; h) H. Y. Chen, H. Y. Tang, C. C. Lin, *Macromolecules* **2006**, *39*, 3745–3752; i) L. M. Hodgson, A. J. P. White, C. K. Williams, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 6646–6651; j) N. Nomura, R. Ishii, Y. Yamamoto, T. Kondo, *Chem. Eur. J.* **2007**, *13*, 4433–4451; k) D. A. Culkin, W. Jeong, S. Csihony, E. D. Gomez,

N. P. Balsara, J. L. Hedrick, R. M. Waymouth, *Angew. Chem.* **2007**, *119*, 2681–2684; *Angew. Chem. Int. Ed.* **2007**, *46*, 2627–2630.

[6] M. Hayakawa, M. Mitani, T. Yamada, T. Mukaiyama, *Macromol. Chem. Phys.* **1997**, *198*, 1305–1317.

[7] R. Solaro, G. Cantoni, E. Chiellini, *Eur. Polym. J.* **1997**, *33*, 205–211.

[8] M. Nishiura, Z. Hou, T. Koizumi, T. Imamoto, Y. Wakatsuki, *Macromolecules* **1999**, *32*, 8245–8251.

[9] G. Odian, *Principles of Polymerization*, *4th ed.*, Wiley Interscience, New York, **2004**, p. 581.

[10] J. Kadokawa, Y. Iwasaki, H. Tagaya, *Green Chem.* **2002**, *4*, 14–16.

[11] A. Duda, S. Penczek, *Macromol. Chem. Phys.* **1996**, *197*, 1273–1283.

[12] S. Agarwal, X. Xie, *Macromolecules* **2003**, *36*, 3545–3549.

[13] W. Saiyasombat, R. Molloy, T. M. Nicholson, A. F. Johnson, I. M. Ward, S. Poshyachinda, *Polymer* **1998**, *39*, 5581–5585.

[14] a) A. Ohishi, Y. Taguchi, K. Fujita, Y. Ikeda, T. Masuda (Agency of Industrial Sciences and Technology, Japan), JP 3026216, B1 20000371, **2000**; b) A. Ohishi, Y. Taguchi, K. Fujita (National Institute of Advanced Industrial Science and Technology, Japan), JP 2003252968, A2 20030910, **2003**.

[15] J. Furukawa, Y. Iseda, T. Saegusa, H. Fujii, *Makromol. Chem.* **1965**, *89*, 263–268.

[16] M. Allmendinger, R. Eberhardt, G. A. Luinstra, B. Rieger, *J. Am. Chem. Soc.* **2002**, *124*, 5646–5647.

[17] D. Takeuchi, Y. Sakaguchi, K. Osakada, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 4530–4537.

[18] M. Allmendinger, R. Eberhardt, G. A. Luinstra, B. Rieger, *Macromol. Chem. Phys.* **2003**, *204*, 564–569.

[19] K. Nakano, K. Fumitaka, K. Nozaki, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 4666–4670.

[20] J. T. Lee, H. Alper, *Macromolecules* **2004**, *37*, 2417–2421.

[21] G. Liu, L. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 14716–14717.

[22] M. Allmendinger, F. Molnar, M. Zintl, G. A. Luinstra, P. P. Pflugl, B. Rieger, *Chem. Eur. J.* **2005**, *11*, 5327–5332.

[23] Acetyl cobalt initiated copolymerization of aziridine with CO was also reported; see: a) L. Jia, E. Ding, W. R. Anderson, *Chem. Commun.* **2001**, 1436–1437; b) L. Jia, H. Sun, J. T. Shay, A. M. Allgeiger, S. D. Hanton, *J. Am. Chem. Soc.* **2002**, *124*, 7282–7283; c) J. Zhao, E. Ding, A. M. Allgeiger, L. Jia, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 376–385; d) D. J. Darensbourg, A. L. Phelps, N. L. Gall, L. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 13808–13815; e) H. Xu, N. L. Gall, L. Jia, W. W. Brennessel, B. E. Kucera, *J. Organomet. Chem.* **2005**, *690*, 5150–5158.

[24] For a recent review on carbonylative polymerization of oxiranes, see: T. L. Church, Y. D. Y. L. Getzler, C. M. Byrne, G. W. Coates, *Chem. Commun.* **2007**, 657–674.

[25] Phosphine complex **1** was reported by Cowley and co-workers, but neither its structural analysis nor its catalytic application has been reported; see: S. A. Llewellyn, M. L. H. Green, A. R. Cowley, *J. Organomet. Chem.* **2005**, *690*, 2358–2364.

[26] X-ray structures of [AcCo(CO)$_3$PPh$_3$] and [AcCo(CO)$_3$P(*o*-tolyl)$_3$] were reported by Jia and co-workers;[23d] the acyl cobalt complex [ClCH$_2$C(=O)Co(CO)$_3$PPh$_3$] was also synthesized and characterized; see: V. Galamb, G. Pályi, R. Boese, G. Schmid, *Organometallics* **1987**, *6*, 861–867.

[27] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.

[28] J. S. Haasz, F. Haasz, V. Galamb, A. Benedetti, C. Zucchi, G. Pályi, *J. Organomet. Chem.* **1991**, *419*, 205–217.

[29] C. H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573–1578.

[30] CCDC-663061 (**1**), -663062 (**2**), and -663063 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

[31] The smaller cone angle of P(OPh)$_3$ might be an alternative reason for the shorter Co−P bond.[23e]

[32] A. J. McAlees, R. McCrindle, A. R. Woon-Fat, *Inorg. Chem.* **1976**, *15*, 1065–1074.

[33] See Supporting Information.

[34] Examples of substitution reactions of sodium tetracarbonylcobaltate(−I): F. Ungvary, A. Wojcicki, *J. Am. Chem. Soc.* **1987**, *109*, 6848–6849.

[35] Carbonylative ring expansion of oxetanes: a) M. D. Wang, S. Calet, H. Alper, *J. Org. Chem.* **1989**, *54*, 20–21; b) Y. D. Y. L. Getzler, V. Kundnani, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 6842–6843.

[36] An example of ring-opening polymerization of oxetanes: S. Kanoh, A. Takeuchi, K. Fukuda, C. Chinwanitcharoen, M. Motoi, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 4570–4579.

[37] For examples of carbonylative ring expansion of oxiranes, see: a) E. Drent, E. Kragtwijk (Shell Internationale Research Maatschappij, B. V., The Netherlands), Eur. Pat. Appl. EP 577206, **1994** [*Chem. Abstr.* **1994**, *120*, 191517 c]; b) J. T. Lee, P. J. Thomas, H. Alper, *J. Org. Chem.* **2001**, *66*, 5424–5426; c) Y. D. Y. L. Getzler, V. Mahadevan, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1174–1175; d) V. Mahadevan, Y. D. Y. L. Getzler, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2905–2908; *Angew. Chem. Int. Ed.* **2002**, *41*, 2781–2784; e) Y. D. Y. L. Getzler, V. Mahadevan, E. B. Lobkovsky, G. W. Coates, *Pure Appl. Chem.* **2004**, *76*, 557–564; f) J. A. R. Schmidt, V. Mahadevan, Y. D. Y. L. Getzler, G. W. Coates, *Org. Lett.* **2004**, *6*, 373–376; g) J. A. R. Schmidt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2005**, *127*, 11426–11435; h) J. W. Kramer, E. B. Lobkovsky, G. W. Coates, *Org. Lett.* **2006**, *8*, 3709–3712; i) T. L. Church, Y. D. Y. L. Getzler, G. W. Coates, *J. Am. Chem. Soc.* **2006**, *128*, 10125–10133.

[38] In this case, the copolymerization of trimethylene oxide and CO was carried out by using a catalyst system of [Co$_2$(CO)$_8$]/BnBr/ phenanthroline additive[20] to give 50% yield of the copolymer with an ester content of 42% (see Supporting Information); the employment of this catalyst system for the copolymerization of oxetane **5a** and CO under similar reaction conditions gave a copolymer with a lower ester content (30%).

[39] See Supporting Information.

[40] W. F. Edgell, J. Lyford IV, *Inorg. Chem.* **1970**, *9*, 1932–1933.

[41] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[42] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**.