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Terpolymerizations of CO_2, Propylene Oxide, and Various Epoxides Using a Cobalt(III) Complex of Salen-Type Ligand Tethered by Four Quaternary Ammonium Salts

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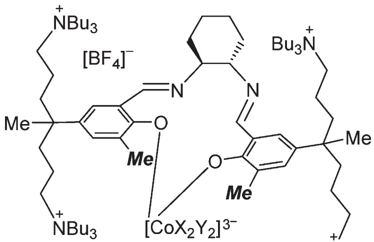
ABSTRACT: Terpolymerizations of CO_2/propylene oxide (PO)/cyclohexene oxide (CHO), CO_2/PO/1-hexene oxide (HO), and CO_2/PO/1-butene oxide (BO) were carried out without the formation of cyclic carbonates and ether linkages with a cobalt(III) complex of a Salen-type ligand tethered by four quaternary ammonium salts (**1**). The activities were excellent, in the range of (0.62−1.6) × 10^6 g/mol-Co (TOF, 4400−14 000 h^{-1}). In all three of terpolymerizations, the data for the PO mole fractions in the feed (f_{PO}) and the polymers (F_{PO}) fit the Fineman−Ross plot well to determine the monomer reactivity ratios. The linear dependencies of the T_g's of the polymers on the mole fractions of the third monomers (F_{CHO}, F_{HO}, and F_{BO}) were observed with the relationships of "T_g (°C) = 81 × F_{CHO} + 40", "T_g (°C) = −62 × F_{HO} + 38", and "T_g (°C) = −27 × F_{BO} + 38", respectively. The decomposition temperature of the resin increased when the third monomer was employed. The GPC data indicated that the polymer chains grew in an immortal passion from four 2,4-dinitrophenolates as well as the two 2,4-dinitrophenols in **1**. High molecular weights (M_n) above 200 000 were attainable because of the high activities.

Introduction

Recently, a highly active catalyst was found for the CO_2/propylene oxide (PO) copolymerization,[1] while trying to develop a catalyst on the concept of binding two components or two metal centers.[2] The binding situated both components in close proximity regardless of the low catalyst concentration or high polymerization temperature to achieve a high turnover number (TON) as well as a high molecular weight. The highly active catalyst was a cobalt(III) complex prepared from a Salen-type ligand tethered by four quaternary ammonium salts. Later, we elucidated that the cobalt(III) complex adopted an unusual binding mode, where imine nitrogens on the Salen-type ligand did not coordinate but, instead, the counteranions of the tethered quaternary ammonium coordinated to cobalt (**1**).[3] Complex **1** showed a high TON up to 16 000 and a high turnover frequency (TOF) of 16 000 h^{-1} that produced a strictly alternating copolymer with a high molecular weight (M_n) of up to 300 000 and a high selectivity (> 99%). Another advantage of **1** was that the catalyst was efficiently removed after polymerization from a polymer solution through filtration over a short pad of silica gel. The collected catalyst on the silica surface could then be recovered and reused. Catalyst residue removal is crucial for the copolymerization not only because the catalyst residue colors the resin but also because the residue is toxic and causes a severe thermal degradation during processing.[4] Catalyst **1** can be prepared on a large scale.[5] All of these merits may allow for a continuous commercial process. These performances were a significant improvement not only over the initial Zn-based heterogeneous catalysts[6] but also over other types of homogeneous catalysts.[7] The best catalytic activities for the Zn-based heterogeneous catalytic system were reported to be in the range of 350 g polymer per g of zinc, which corresponded to a TON of 220.[8] The best TON achieved with the binary system of [(Salen)Co(III) complexes]/(onium salt or base), where the two components were not bound, was below 1000.[9]



X = 2,4-dinitrophenolate
Y = [X...H...X]
1

The CO_2/PO copolymer is attractive due to its favorable properties. While most of polymers used in daily life are derived from petroleum, this copolymer, which consists of alternating CO_2 and PO subunits, is composed of 44 wt % CO_2. Recently, a preparation route for PO was reported from a renewable resource, glycerol.[10] The copolymer burns gently in air without emitting toxic materials and adheres strongly to a cellulosic substrate. The barrier property for O_2 and water is also good as a film. On the other hand, some disadvantages hamper wide application. The copolymer has a glass transition temperature (T_g) of ∼40 °C, which limits its versatile utility. A higher T_g than 40 °C is required to allow its use as structural materials and a lower T_g than room temperature may be beneficial to applying it to a soft film. It starts to decompose at the relatively low temperature of ∼180 °C, which deters blending with other polymers that are normally processable above 200 °C. In this work, terpolymerizations of CO_2, PO, and various epoxides such as cyclohexene oxide (CHO), 1-hexene oxide (HO), or 1-butene

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Table 1. CO_2, PO, and CHO Terpolymerization Results[a]

entry	f_{CHO}[b]	F_{CHO}[c]	A[d]	TOF[e] (h^{-1})	selectivity[f]	M_n[g] ($\times 10^{-3}$)	M_w/M_n	T_g (°C)	T_{50}/T_5[h] (°C)
1	0.20	0.12	1.1	9700	>99	174	1.21	52	236/211
2	0.30	0.19	1.1	9200	>99	166	1.19	56	243/218
3	0.40	0.26	1.1	8900	>99	171	1.17	59	252/226
4	0.50	0.33	0.84	6500	>99	134	1.20	65	258/237
5	0.60	0.43	0.90	6800	>99	149	1.16	74	254/227
6	0.70	0.52	0.77	5700	>99	124	1.17	83	263/246
7	0.80	0.64	0.66	4700	>99	110	1.18	96	260/242
8[i]	0.80	0.64	1.4	5000	>99	210	1.17	95	257/234
9[j,k]	0.80	0.62	1.1	7900	>99	144	1.21	93	253/230
10[k]	1.00	1.00	0.73	5100	>99	92	1.23	115	265/239

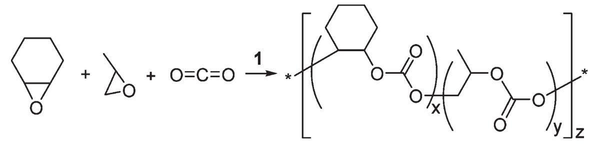
[a] Polymerization conditions: PO + CHO (200 mmol), {[PO] + [CHO]}/[Cat.] = 100 000 (**1**, 5.0 mg), CO_2 pressure of 20 bar, temperature of 70−75 °C, reaction time of 60 min. [b] Mole fraction of cyclohexene oxide in the feed. [c] Mole fraction of cyclohexene oxide in the polymer. [d] Activity in units of 10^6 g/mol-Co. [e] Turnover frequency of PO + CHO. [f] Selectivity of polycarbonate over cyclic carbonate in units of % as determined using ^{1}H NMR spectroscopy of the crude product. [g] Determined on GPC using a polystyrene standard. [h] The temperature at 50% and 5% weight loss, respectively, on the TGA curve of the polymer. [i] Reaction time of 120 min. [j] CO_2 pressure of 30 bar. [k] Induction times were observed (60 min for entry 9; 260 min for entry 10).

oxide (BO) are reported using the highly active catalyst **1**. The terpolymers may provide a solution to the disadvantages of the CO_2/PO copolymer.

Results and Discussion

CO_2, PO, and Cyclohexene Oxide (CHO) Terpolymerizations. Catalyst **1** efficiently terpolymerized CO_2, PO, and CHO with various feed ratios of PO and CHO (eq 1 and Table 1). The activities of (0.66−1.1) × 10^6 g/mol-Co were attained from running the polymerization for 1.0 h and were significantly higher than those achieved previously in the same terpolymerization using the binary system of (Salen)Co(III) complex and quaternary ammonium salt (0.061 × 10^6 g/mol-Co through 4 h running), $[Zn(O\text{-}2,6\text{-}F_2C_6H_3)_2]_2$ (4.2 g polymer/(g-Zn h), and a ternary system of $Y(CCl_3CO_2)_3/ZnEt_2$/glycerine (5−10 kg/mol-Zn).[11] These activities were comparable to those attained in polyolefin production catalyzed using an efficient homogeneous CGC-type catalyst ((0.5−5) × 10^6 g/mol-Ti through running for several minutes).[12] The turnover frequency (TOF) decreased as the mole ratio of CHO feed increased, implying that CHO was less active than PO, and indeed, the TOF (5100 h^{-1}, entry 10) attained for the CO_2/CHO copolymerization was about 1/3 of the TOF for the CO_2/PO copolymerization (15 000 h^{-1}). However, the activity was increased from 0.66 × 10^6 g/mol-Co (TON, 4700) to 1.4 × 10^6 g/mol-Co (TON, 10 000) by doubling the polymerization time (entry 7 versus 8). Therefore, the catalyst was not deactivated during the polymerization. The polymerization rate (TOF) was also increased from 4700 to 7900 h^{-1} by increasing the CO_2 pressure from 20 to 30 bar (entry 7 versus 9).

Cyclic carbonate side products were not observed if the polymerization solution was filtered over a silica pad immediately after venting CO_2. All of the colored catalyst was collected on the silica pad furnishing a colorless polymer, and the collected catalyst could be recovered and reused using a previously reported method.[1] Cyclic carbonates formed if the polymerization solution was not filtered directly after CO_2 venting. No signals were observed at 3−4 ppm in the ^{1}H NMR spectra of the polymers (Figure 1), which indicated strictly alternating placement of CO_2 after PO or CHO with no ether linkages.



(1)

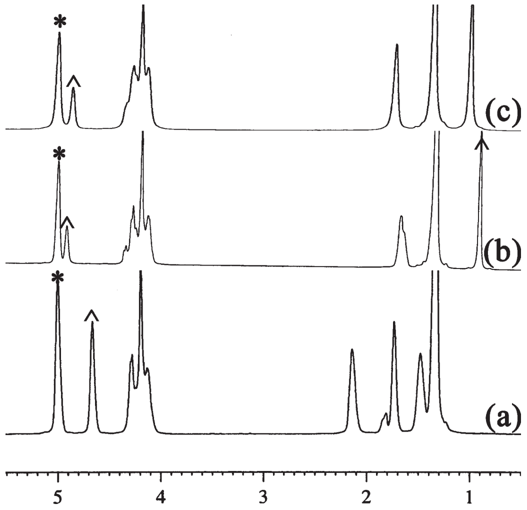


Figure 1. ^{1}H NMR spectra of the terpolymers of CO_2/PO/CHO (a), CO_2/PO/HO (b), and CO_2/PO/BO (c) (entry 3 for Tables 1−3; "*" signals from PO; "∧" signals from CHO, HO, or BO).

The PO mole fraction in the polymers (F_{PO}) was calculated from the integration values of the well resolved [PO]-MeC(*H*)O signal and [CHO]−C*H*O signals in the ^{1}H NMR spectra (Figure 1). The terpolymerization was treated as a copolymerization of the PO−CO_2 and CHO−CO_2 units because ether linkages were not observed. The data for the PO mole fractions in the feed (f_{PO}) and the polymers (F_{PO}) fit the Fineman−Ross plot well (R^2 = 0.99, Figure 2), and the monomer reactivity ratios r_{PO} (k_{11}/k_{12}) and r_{CHO} (k_{22}/k_{21}) were 1.7 and 0.37, respectively (Chart). The $r_{PO} \times r_{CHO}$ value was 0.63, indicating some deviation from the ideal copolymerization, for which the $r_{PO} \times r_{CHO}$ value is 1.0 ($k_{11}/k_{12} = k_{21}/k_{22}$ in Chart). These monomer reactivity ratio values indicated that consequent placement of the two CHO−CO_2 units was somewhat unfavorable, which was in agreement with lowered activity with increasing CHO mole fraction in the feed (f_{CHO}).

The glass transition temperatures (T_g's) linearly increased with increasing CHO mole fraction in the polymers (F_{CHO}). The linear equation "$T_g(°C) = 81 \times F_{CHO} + 40$" was derived from the fit (Figure 3). This equation corresponded well to the T_g's of the CO_2/PO copolymer (40 °C) as well as the CO_2/CHO copolymer (115 °C). The decomposition temperature increased with increasing F_{CHO} even though the relationship was not as strict as the relationship between T_g and F_{CHO}.

The molecular weights (M_n) of the polymers obtained under the same conditions (entries 1−7) were linearly dependent on the activities measured with units of g-polymer/mol-Co, which supported living or immortal polymerization. The number of polymer chains per cobalt was

Table 2. CO_2, PO, and HO Terpolymerization Results^a

entry	f_{HO}^{b}	F_{HO}^{c}	A^{d}	TOF^e (h^{-1})	selectivity^f	M_n^{g} ($\times 10^{-3}$)	M_w/M_n	T_g (°C)	T_{50}/T_5^{h} (°C)
1	0.20	0.11	0.98	8600	>99	150	1.27	32	230/201
2	0.30	0.17	1.1	9100	>99	145	1.15	29	239/212
3	0.40	0.24	0.91	6700	>99	114	1.18	24	233/220
4	0.50	0.32	1.0	7700	>99	120	1.13	19	237/212
5	0.60	0.43	0.75	5700	>99	66	1.23	11	254/227
6	0.70	0.53	0.72	5200	>99	64	1.14	5	250/221
7	0.80	0.65	0.62	4400	>99	51	1.17	−2	241/220
8^i	0.80	0.65	1.6	5600	>99	198	1.20	−2	238/214
9^j	0.80	0.64	1.1	7800	>99	101	1.11	−2	249/219
10	1.00	1.00	0.70	4900	>99	102	1.23	−15	253/225

^{a} Polymerization conditions: PO + HO (200 mmol), {[PO] + [HO]}/[Cat.] = 100 000 (**1**, 5.0 mg), CO_2 pressure of 20 bar, temperature of 70−75 °C, reaction time of 60 min. ^{b} Mole fraction of 1-hexene oxide in the feed. ^{c} Mole fraction of 1-hexene oxide in the polymer. ^{d} Activity in units of 10^6 g/mol-Co. ^{e} Turnover frequency of PO + HO. ^{f} Selectivity of polycarbonate over cyclic carbonates in units of % as determined using ^{1}H NMR spectroscopy of the crude product. ^{g} Determined on GPC using a polystyrene standard. ^{h} The temperature at 50% and 5% weight loss, respectively, on the TGA curve of the polymer. ^{i} Reaction time of 120 min. ^{j} CO_2 pressure of 30 bar.

Table 3. CO_2, PO, and BO Terpolymerization Results^a

entry	f_{BO}^{b}	F_{BO}^{c}	A^{d}	TOF^e (h^{-1})	selectivity^f	M_n^{g} ($\times 10^{-3}$)	M_w/M_n	T_g (°C)	T_{50}/T_5^{h} (°C)
1	0.20	0.16	1.0	9500	>99	160	1.20	33	227/210
2	0.30	0.22	0.84	7800	>99	134	1.23	31	216/202
3	0.40	0.30	1.1	10000	>99	150	1.27	31	233/210
4	0.50	0.38	1.1	9900	>99	164	1.24	29	235/213
5	0.60	0.49	1.1	9900	>99	154	1.24	27	232/210
6	0.70	0.59	1.1	9700	>99	160	1.20	23	229/209
7	0.80	0.71	0.97	8500	>99	145	1.20	19	225/206
8^i	0.80	0.71	1.4	6100	>99	200	1.21	18	220/202
9^j	0.80	0.71	1.6	14000	>99	264	1.19	20	220/199
10	1.00	1.00	1.2	10300	>99	180	1.15	9	241/211

^{a} Polymerization conditions: PO + BO (200 mmol), {[PO] + [BO]}/[Cat.] = 100 000 (**1**, 5.0 mg), CO_2 pressure of 20 bar, temperature of 70−75 °C, reaction time of 60 min. ^{b} Mole fraction of 1-butene oxide in the feed. ^{c} Mole fraction of 1-butene oxide in the polymer. ^{d} Activity in units of 10^6 g/mol-Co. ^{e} Turnover frequency of PO + BO. ^{f} Selectivity of polycarbonate over cyclic carbonates in units of % as determined using ^{1}H NMR spectroscopy of the crude product. ^{g} Determined on GPC using a polystyrene standard. ^{h} The temperature at 50% and 5% weight loss, respectively, on the TGA curve of the polymer. ^{i} Reaction time of 120 min. ^{j} CO_2 pressure of 30 bar.

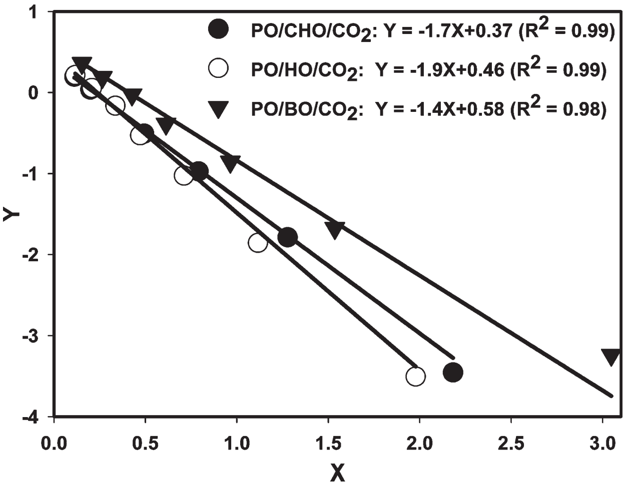
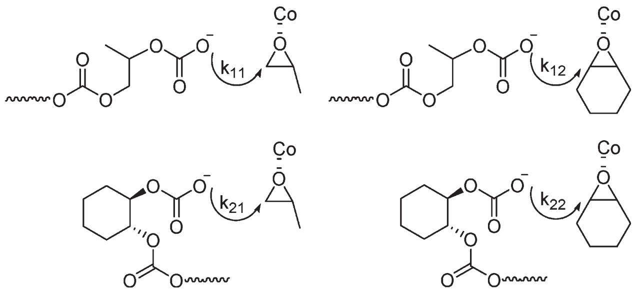


Figure 2. Fineman−Ross plots ($Y = \{f_{PO}/(1-f_{PO})\}\{(1-2F_{PO})/F_{PO}\}$; $X = \{f_{PO}^2/(1-f_{PO})^2\}\{(1-F_{PO})/F_{PO}\}$).

calculated by dividing the calculated molecular weight, which was obtained using the equation "($F_{CHO} \times 142 + F_{PO} \times 102$) × TON", by the GPC-measured molecular weight (M_n). The numbers of polymer chains per cobalt for entries 1−7 were in the range of 5.6−6.1. Considering some deviation of the actual molecular weight from the GPC-measured one because of the PS standards used, the data agreed quite well with the fact that the polymer chains grew from all four dinitrophenolates and two dinitrophenols in **1**. The data also indicated that chain transfer reactions were negligible during the polymerization. Increasing the TON value from 4700 to 10 000 by increasing the reaction time from 1 to 2 h resulted in an increased molecular weight (M_n) from 110 000 to 210 000 (entry 7 versus 8), which further supporting the living character in this polymerization. The

Chart 1. Kinetic Parameters in the CO_2/PO/CHO Terpolymerization



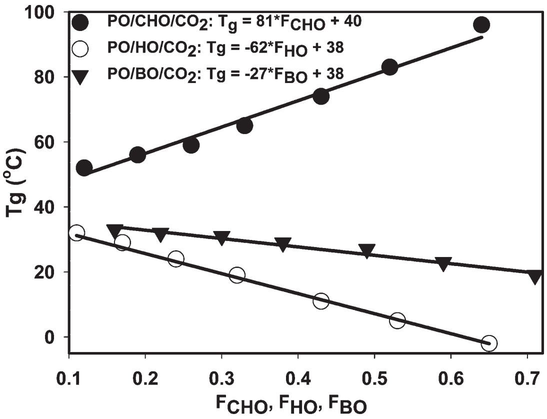


Figure 3. Relationships between the T_g's and the mole fractions of CHO, HO, and BO in the terpolymers.

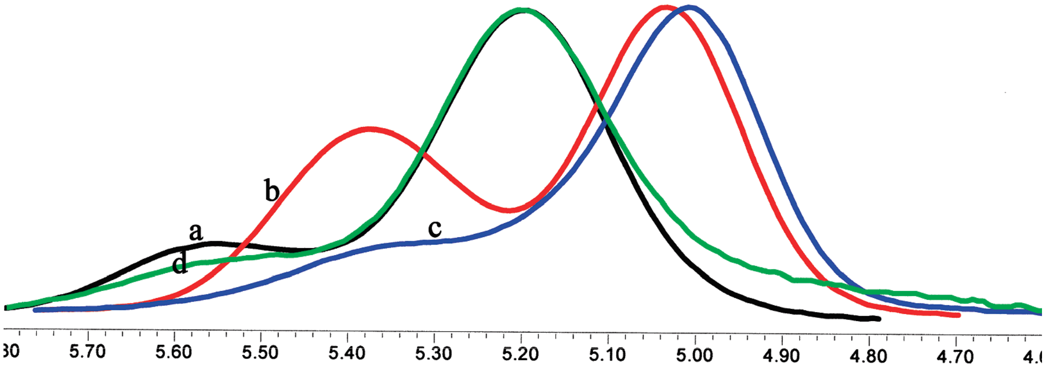
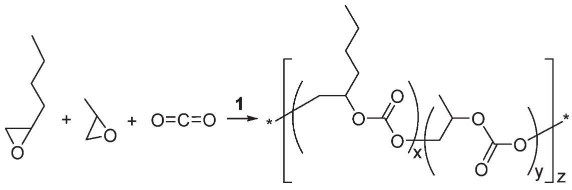


Figure 4. GPC curves: (a) entry 3 in Table 1; (b) entry 9 in Table 1; (c) entry 3 in Table 2; (d) entry 3 in Table 3.

drift of monomer mole ratio in this terpolymerization pot was not so significant that the F_{CHO} was not altered by increasing the TON value from 4700 to 10 000. At the end of polymerization, the CHO mole fraction in the feed (f_{CHO}) became 0.81 and 0.82 for entries 7 and 8, respectively.

Although the M_w/M_n value was not large (~1.2), bimodal distributions of the molecular weight were observed in the GPC curves of these terpolymers (Figure 4). Similar bimodal distributions were also observed in the CO_2/PO copolymerizations carried out using **1** as well as other similar type Salen-cobalt(III) complexes tethered quaternary or tertiary ammonium salt units.[13,1,2c] The peak molecular weight on the high molecular weight portion was always twice that of the lower molecular weight portion. Nozaki attributed the high molecular weight portion to the polymer chains grown from water.[13] A bimodal distribution was observed because the polymer chains derived from the water grew biaxially while those derived from DNP anion or DNP-H grew uniaxially. In the GPC traces of most of the polymers (entries 1−8), the high molecular weight portions grown from water were small compared to the low molecular weight portions grown from DNP's, indicating a small amount of chain transfer reaction with water (Figure 4). In the GPC trace of the polymer obtained at high pressure of CO_2 (entry 9, curve b in Figure 4), the high molecular weight portion grown from water was significant. The number of polymer chains per cobalt was higher (7.0) than those calculated for other polymers (5.8 ± 0.3) with a small amount of the high molecular weight portion. In this polymerization at high CO_2 pressure, some induction time (60 min) was observed. Increasing CO_2 pressure was accompanied by influx of more water into reaction system, which results in some induction time as well as an increase in the high molecular weight portion in the GPC curve because of the failure to completely remove water in the CO_2 gas. In the CO_2/CHO copolymerization (entry 10), an induction time (260 min) was also observed along with a significant amount of the high molecular weight portion in the GPC curve. The number of polymer chains per cobalt was 8.1, indicating some chain transfer reactions with water.

CO_2, PO, and 1-Hexene Oxide (HO) Terpolymerization. Catalyst **1** also efficiently terpolymerized CO_2, PO, and 1-hexene oxide (HO) with various feed ratios of PO and HO (eq 2 and Table 2). The TOF decreased with increasing HO mole fraction in the feed (f_{HO}) and was slightly lower than the TOF observed in the CO_2/PO/CHO terpolymerization at the same feed ratio (4400−9100 h^{-1}). The activities were in the range of (0.62−1.1) × 10^6 g/mol-Co after running the polymerization for 1.0 h. The TON could be increased from 4400 to 11 000 without sacrificing TOF by doubling the polymerization time (entry 7 versus 8). The TOF could be also increased from 4400 to 7800 h^{-1} by increasing the CO_2 pressure from 20 to 30 bar (entry 7 versus 9). Cyclic carbonate side products and ether-linkages were not observed in the polymer backbones.



(2)

In the ^{1}H NMR spectra of the CO_2/PO/HO terpolymers, the [PO]-MeC(H)O and [HO]-CH_2CHO signals were not well resolved (Figure 1). Therefore, the HO mole fractions in the polymer (F_{HO}) could not be accurately calculated from these two signals. However, the HO mole fraction (F_{HO}) was calculated using the integration values in the ^{1}H NMR spectra because the [HO]-CH_3 signal was well isolated from other signals at 0.9 ppm. The data for the PO mole fractions in the feed (f_{PO}) and the polymers (F_{PO}) fit the Fineman−Ross plot well (R^2 = 0.99, Figure 2). The monomer reactivity ratios, r_{PO} and r_{HO}, were 1.9 and 0.46, respectively. The $r_{PO} \times r_{HO}$ value was 0.87, which was close to the value (1.0) for ideal copolymerization. These monomer reactivity ratios indicated that consequent placement of the two HO−CO_2 units was not as unfavorable as the two CHO−CO_2 units in the CO_2/PO/CHO terpolymerization. Even though the consequent placement of the two HO−CO_2 units was allowed, the activity unreasonably decreased with increasing HO feed.

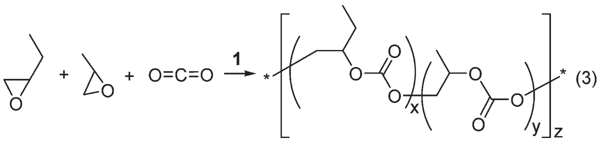
The glass transition temperatures (T_g's) linearly decreased with increasing HO mole fractions in the polymers (F_{HO}). The linear equation "T_g (°C) = $-62 \times F_{HO} + 38$" was derived from the fit (Figure 2). This equation corresponded well to the T_g of the CO_2/PO copolymer (40 °C) but deviated somewhat from the T_g of CO_2/HO copolymer (−15 °C, entry 10). This study demonstrated that the T_g of the CO_2/PO copolymer could be modulated in the range of 0−100 °C using the third monomer of HO or CHO. The decomposition temperatures of the terpolymers were also higher than the CO_2/PO copolymer (226 and 196 °C at 50% and 5% weight loss, respectively, on the TGA curve) and slightly lower than the CO_2/PO/CHO terpolymers at similar compositions.

In the GPC curves of the CO_2/PO/HO terpolymers, a bimodal distribution of molecular weights was observed even though the M_w/M_n values were low, in the range of 1.14−1.27 (curve c in Figure 4). The molecular weights (M_n) were lower, in the range of 51 000−150 000, because of the lower activities compared to the CO_2/PO/CHO terpolymerizations. Increasing the activity (TON) through

Figure 5. Obtained viscous polymerization solution and the isolated resin (entry 8 in Table 1).

increasing the reaction time resulted in an increased molecular weight up to 198 000 (entry 8). The number of polymer chains per cobalt was calculated by dividing the calculated molecular weight obtained by the equation "(F_{HO} × 144 + F_{PO} × 102) × TON" by the GPC-measured molecular weight (M_n). The values of 6.1−6.6 for the number of chains were acceptable at a low HO feed (entries 1−3), but the values that were obtained at a high HO feed were high (8.2 for entry 4; 10 for entries 5 and 6; 11 for entry 7). These high numbers indicated that there some chain transfer reactions occurred for the high HO feed. However, the high molecular portion did not increase from the chain transfer with water in the GPC curves. Almost the same high molecular weight portions were observed in the GPC curves for entries 1−7. 1-Hexene oxide was sold as contaminated with ~3% acetic acid. Some chain transfer reaction with the residual acetic acid probably occurred, resulting in the high number of polymer chains per cobalt as well as the lowered activity at the high HO feed. Stirring 1-hexene oxide over CaH_2 for a long time (> 10 days) was necessarily required to achieve the polymerization activities in Table 2.

CO_2, PO, and 1-Butene Oxide (BO) Terpolymerization. Catalyst **1** efficiently terpolymerized CO_2, PO, and 1-butene oxide (HO) with various feed ratios of PO and BO (eq 3 and Table 3). The activity was unaltered by variations of the feed ratio ((0.84−1.1) × 10^6 g/mol-Co; TOF, 7800−10 000 h^{-1}). The activity (TON) was increased by increasing either the reaction time or CO_2 pressure (entry 7 versus 8 or 9). The activity at 30 bar was 1.6 × 10^6g/mol-Co (TON, 14 000), which was almost the upper limit. An almost unstirrable viscous polymerization solution was obtained at this condition (Figure 5). A decrease of TOF from 8500 to 6100 h^{-1} by lengthening the reaction time from 1 to 2 h (entries 7 and 8) may be attributed to some diffusion problem at the latter stage of polymerization by forming a very thick viscous solution.



(3)

The BO mole fractions in the polymers (F_{BO}) were calculated from the integration values of the [PO]-MeC(*H*)O and [BO]-CH_2C*H*O signals because they are well resolved in the ^{1}H NMR spectra of CO_2/PO/BO terpolymers recorded on a 600 MHz instrument (Figure 1). The data for the PO mole fractions in the feed (f_{PO}) and the polymers (F_{PO}) fit the Fineman−Ross plot well (R^2 = 0.98, Figure 2). The monomer reactivity ratios, r_{PO} and r_{BO}, were 1.4 and 0.58, respectively. The $r_{PO} \times r_{BO}$ value was 0.81, which was close to the value (1.0) for ideal copolymerization. The glass transition temperatures (T_g) linearly decreased with increasing BO mole fraction in the polymers (F_{HO}), but the slope was not so steep as the CO_2/PO/HO terpolymers (Figure 2). The linear equation "T_g (°C) = −27 × F_{BO} + 38" was derived from the fit. This equation corresponded well with the T_g's of the CO_2/PO copolymer (40 °C) and the CO_2/BO copolymer (9 °C, entry 10). The decomposition temperatures of the terpolymers were slightly higher than the CO_2/PO copolymer (226 and 196 °C at 50% and 5% weight loss, respectively, on the TGA curve). The molecular weights (M_n) increased linearly with increasing activities, which supported living or immortal polymerization, and a high molecular weight (M_n) up to 264 000 was achieved at a high activity of 1.6 × 10^6 g/mol-Co (TON, 14 000). The number of polymer chains per cobalt was calculated by dividing the calculated molecular weight, which was obtained by the equation "(F_{BO} × 116 + F_{PO} × 102) × TON", by the GPC-measured molecular weight (M_n) and was in the range of 6.0−6.9, which was consistent with the chain-growing from all four DNP anions as well as the two DNP-H's in **1**. A bimodal distribution of molecular weight was also observed with a small amount of the high molecular weight portion (curve d in Figure 4), indicating small amount of chain transfer reactions with water.

Summary. Terpolymerizations of CO_2/propylene oxide (PO)/cyclohexene oxide (CHO), CO_2/PO/1-hexene oxide (HO), and CO_2/PO/1-butene oxide (BO) were realized with catalyst **1** without the formation of cyclic carbonates or ether linkages. The activities in the range of (0.66−1.6) × 10^6 g/mol-Co (TOF, 4400−14 000 h^{-1}) were excellent and comparable to the activities attained in polyolefin production. The activity (TON) was increased by increasing either the reaction time or the CO_2 pressure, and full conversion to a very viscous thick polymerization solution occurred within 2 h (Figure 5). In all of the three terpolymerizations, the data for the PO mole fractions in the feed (f_{PO}) and the polymers (F_{PO}) fit the Fineman−Ross plot well, which was useful in determining the monomer reactivity ratios (r_{PO} = 1.7, r_{CHO} = 0.37 for CO_2/PO/CHO terpolymerization; r_{PO} = 1.9, r_{HO} = 0.46 for CO_2/PO/HO terpolymerization; r_{PO} = 1.4, r_{BO} = 0.58 for CO_2/PO/BO terpolymerization). The linear dependencies of the T_g's of the polymers on the mole fraction of the third monomers (F_{CHO}, F_{HO}, and F_{BO}) were observed with relationships of "T_g (°C) = 81 × F_{CHO} + 40", "T_g (°C) = −62 × F_{HO} + 38", and "T_g (°C) = −27 × F_{BO} + 38", respectively. These results demonstrated that the T_g of CO_2/PO copolymer could be modulated in the range of 0−100 °C using a third monomer of CHO, HO, or BO. The decomposition temperature of the resin was also increased using a third monomer. The GPC data indicated that the polymer chains grew in an immortal passion from four DNP's as well as two DNP-H's in **1**, and a high molecular weight (M_n) above 200 000 was achieved from high TON's. We failed in incorporating the third epoxide such as styrene oxide, isobutylene oxide, or glycidyl ether at the polymerization condition of [epoxide]/[**1**] = 100 000. The failure may be attributed to a failure in scrubbing the impurities the third monomer contains. The commercial grade of the third monomer contains ~30 000 ppm level of impurities.

Experimental Section

General Remarks. CO_2 gas (99.999% purity) was dried through storage in a column of molecular sieves 3A at a pressure of 30 bar. Propylene oxide (PO), cyclohexene oxide (CHO), 1-hexene oxide (HO), and 1-butene oxide (BO) were dried by stirring them over CaH_2 and then were vacuum-transferred to reservoirs. The ^1H NMR (600 MHz) spectra were recorded on a Bruker, Advance 600. The gel permeation chromatograms (GPC) were obtained at room temperature in $CHCl_3$ using a Waters Millennium apparatus with polystyrene standards. The T_g data were determined from a second heating at a heating rate of 10 °C/min with DSC (differential scanning calorimetry, Thermal Analysis Q10). The cobalt(III) complex **1** was prepared through the reported method.[3,5]

A Typical Terpolymerization. A bomb reactor was assembled inside a glovebox after catalyst **1** (5.0 mg, 2.0 μmol), PO, and CHO (total amount of PO + CHO, 200 mmol) were charged. The CO_2 gas was pressurized to 15 bar, and then the reactor was immersed in an 80 °C oil bath. The pressure increased with increasing solution temperature, reaching ~20 bar at ~50 min. The temperature inside the bomb reactor was monitored using a thermocouple. After ~50 min, the solution temperature reached ~70 °C. When the pressure reached its maximum under a closed system, it remained steady for some time. We could read a starting of pressure drop indicating initiation of the polymerization. The polymerization was performed for 1 h after the initiation, and a 3−4 bar pressure drop was observed after 1 h polymerization. The reactor was cooled to room temperature through immersion in an ice bath. After CO_2 gas was released, the reactor was opened, and an aliquot was taken and dissolved in $CDCl_3$. The ^1H NMR analysis of the solution was used to calculate the selectivity and carbonate linkage. The viscous solution was diluted with 20 mL of methylene chloride and filtered over a short pad of silica gel to give a colorless solution. Any volatiles were removed using a rotary evaporator to give a white residue. The polymer lump was removed from the flask and then broken manually into pieces. The polymer pieces were placed in a hood overnight to evaporate some residual epoxides and then were completely dried in an oven at ~150 °C for 30 min. The yield was 2.8 g for entry 8 in Table 1. Figure 5 shows the obtained viscous polymerization solution along with the isolated resin for entry 8 in Table 1.

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References and Notes

(1) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 7306.

(2) (a) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 931. (b) Ren, W.-M.; Liu, Z.-W.; Wen, Y.-Q.; Zhang, R.; Lu, X.-B. *J. Am. Chem. Soc.* **2009**, *131*, 11509. (c) Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082. (d) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc.* **2005**, *127*, 3031. (e) Bok, T.; Yun, H.; Lee, B. Y. *Inorg. Chem.* **2006**, *45*, 4228. (f) Xiao, Y.; Wang, Z.; Ding, K. *Chem.—Eur. J.* **2005**, *11*, 3668. (g) Piesik, D. F.-J.; Range, S.; Harder, S. *Organometallics* **2008**, *27*, 6178.

(3) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. *Inorg. Chem.* **2009**, *48*, ASAP (DOI: 10.1021/ic901584u).

(4) (a) Liu, B.; Chen, L.; Zhang, M.; Yu, A. *Macromol. Rapid Commun.* **2002**, *23*, 881. (b) Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975.

(5) Min, J.; Seong, J. E.; Na, S. J.; Cyriac, A.; Lee, B. Y. *Bull. Korean Chem. Soc.* **2009**, *30*, 745.

(6) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B* **1969**, *7*, 287. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210.

(7) (a) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. (b) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388. (c) Sugimoto, H.; Kuroda, K. *Macromolecules* **2008**, *41*, 312. (d) Guo, L.; Wang, C.; Zhao, W.; Li, H.; Sun, W.; Shen, Z. *Dalton Trans.* **2009**, 5406. (e) Cui, D.; Nishiura, M.; Tardif, O.; Hou, Z. *Organometallics* **2008**, *27*, 2428.

(8) (a) Luinstra, G. A. *Polym. Rev.* **2008**, *48*, 192. (b) Ree, M.; Hwang, Y.- T.; Kim, H.; Kim, G.; Kim, H. *Catal. Today* **2006**, *115*, 134.

(9) (a) Lu, X.-B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574. (b) Lu, X.-B.; Shi, L.; Wang, Y.-M.; Zhang, R.; Zhang, Y.-J.; Peng, X.-J.; Zhang, Z.-C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664. (c) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237. (d) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869. (e) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251.

(10) Yu, Z.; Xu, L.; Wei, Y.; Wang, Y.; He, Y.; Xia, Q.; Zhang, X.; Liu, Z. *Chem. Commun.* **2009**, 3934.

(11) (a) Shi, L.; Lu, X.-B.; Zhang, R.; Peng, X.-J.; Zhang, C.-Q.; Li, J.-F.; Peng, X.-M. *Macromolecules* **2006**, *39*, 5679. (b) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487. (c) Quan, Z.; Min, J.; Zhou, Q.; Xie, D.; Liu, J.; Wang, X.; Zhao, X.; Wang, F. *Macromol. Symp.* **2003**, *195*, 281.

(12) Wu, C. J.; Lee, S. H.; Yun, H.; Lee, B. Y. *Organometallics* **2007**, *27*, 6685. (b) Wu, C. J.; Lee, S. H.; Yu, S. T.; Na, S. J.; Yun, H.; Lee, B. Y. *Organometallics* **2008**, *27*, 3907. (c) Na, S. J.; Wu, C. J.; Yoo, J.; Kim, B. E.; Lee, B. Y. *Macromolecules* **2008**, *42*, 4055.

(13) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274.