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Copolymerization of Epoxides with Carbon Dioxide Catalyzed by Iron–Corrole Complexes: Synthesis of a Crystalline Copolymer

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Supporting Information

ABSTRACT: Iron–corrole complexes were found to copolymerize epoxides with CO_2. The first iron-catalyzed propylene oxide/CO_2 copolymerization has been accomplished. Moreover, the glycidyl phenyl ether (GPE)/CO_2 copolymerization with this catalyst provided a crystalline material as a result of the isotactic poly(GPE) moiety.

Iron is one of the most ideal metals as catalysts for chemical transformations since it is abundant on the earth, cost-effective, and environmentally benign.[1] Indeed, iron catalysts have been widely used to date as Lewis acid and oxidation catalysts. Recently, in terms of sustainable chemistry, iron catalysts have emerged as promising alternatives to more expensive catalysts in modern metal-catalyzed reactions such as cross-coupling reactions and hydrogenations catalyzed by platinum-group metals.[2]

Carbon dioxide is also abundant on the earth and is an attractive carbon source for materials synthesis.[3] The alternating copolymerization of epoxides with CO_2, which was first reported by Inoue and co-workers in 1960s,[4] has been considered as one of the most promising processes.[5] Previously reported active catalysts have typically been based on zinc,[6] aluminum,[7] chromium,[8] cobalt,[9] and M(IV) (M = Ti, Ge).[10] Iron-containing complexes have also been reported as active catalysts, but the examples are still limited.[11] Recently, a dinuclear iron complex[12] and a mononuclear iron complex[13] were shown to catalyze epoxide/CO_2 copolymerization, but the reported examples are still limited to cyclohexene oxide (CHO). To the best of our knowledge, no example of an iron catalyst that mediates the copolymerization of CO_2 with other epoxides has ever been reported.

The polycarbonates prepared by epoxide/CO_2 copolymerization are known to be amorphous, except for perfectly stereocontrolled poly(CHO-*alt*-CO_2) and poly(epichlorohydrin-*alt*-CO_2), which exhibited crystallinity.[14] Here we present iron complexes with a corrole ligand as the first examples of iron complexes applicable to not only CHO/CO_2 but also propylene oxide (PO)/CO_2 copolymerization. Furthermore, the copolymerization was applied to glycidyl phenyl ether (GPE), which provided highly crystalline copolymers. Among the obtained copolymers, the PO/CO_2 and GPE/CO_2 copolymers consisted of both carbonate and ether linkages, while the CHO/CO_2 copolymers were rich in carbonate linkage.

Iron–corrole complexes **1–3** used in this work are shown in Figure 1.[15] In complexes **1** and **2**, the iron center in the formal +4 oxidation state is ligated by a trianionic, tetradentate corrole ligand and a monoanionic axial ligand.[16] Such a structure is identical to that of the metal(IV) complexes that we previously applied to the PO/CO_2 copolymerization.[10] In addition to complexes **1** and **2**, iron(III)–corrole complex **3** without any monoanionic axial ligand was also investigated as a catalyst for the copolymerization.[17]

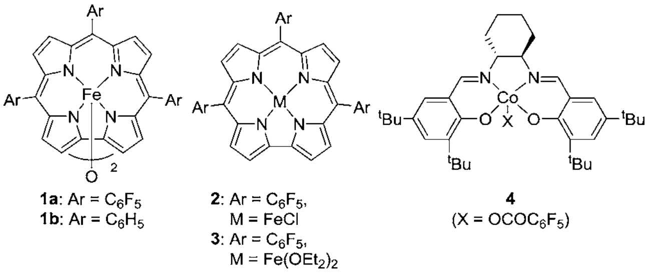

Figure 1. Structures of iron–corrole complexes **1–3** and reference Co complex **4** used in this work.

The copolymerization of PO with CO_2 ([PO]/**1** = 4000 ([PO]/Fe = 2000), P_{CO_2} = 2.0 MPa) was carried out at 60 °C for 1 h using complex **1a** in the presence of $[Ph_3P{=}N{=}PPh_3]Cl$ ([PPN]Cl) as an additive (0.5 equiv relative to Fe; Table 1, entry 1). The copolymer was obtained with high catalytic activity [turnover frequency (TOF) = 1004 (mol of PO incorporated into the copolymer)·(mol of Fe)$^{-1}$·h^{-1}] without the concomitant production of propylene carbonate (PC). On the basis of ^{1}H NMR analysis, the obtained copolymer was poly(PC-*co*-PO), in which the amount of carbonate linkages was rather minor (17%) because of consecutive insertion of PO without CO_2 incorporation. ^{13}C NMR analysis suggested that carbonate linkages were distributed over the polymer chain in a random manner rather than existing as a block. The catalytic performance was susceptible to the **1a**/[PPN]Cl molar ratio. The copolymerization did not proceed in the absence of [PPN]Cl (entry 2). Increasing the amount of [PPN]Cl resulted in a

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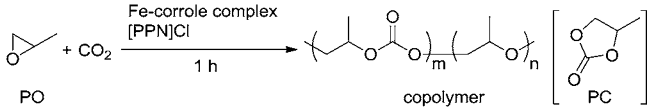
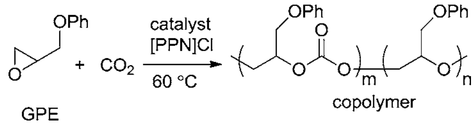
Table 1. Copolymerization of Propylene Oxide with Carbon Dioxide Using Fe−Corrole Complexes 1−3[a]



entry	Fe complex	equiv of [PPN]Cl[b]	P_{CO_2} (MPa)	T (°C)	yield of copolymer + PC (%)[c]	copolymer/PC[c]	TOF for copolymer[d]	carbonate-linkage content (%)[c]	M_n (g·mol^{-1})[e]	M_w/M_n[e]
1	**1a**	0.50	2.0	60	51	>99/<1	1004	17	29000	1.26
2		0	2.0	60	0.1	>99/<1	2	–	–	–
3		0.76	2.0	60	26	>99/<1	525	21	18000	1.20
4		1.0	2.0	60	3	34/66	19	62	–	–
5[f]		0.50	2.0	40	7	>99/<1	74	23	8000	1.11
6		0.50	2.0	80	65	>99/<1	1314	11	51000	1.32
7		0.50	0.50	60	59	>99/<1	1158	6	38000	1.38
8		0.50	5.0	60	11	>99/<1	229	29	5700	1.17
9[g]		0.50	2.0	60	8	>99/<1	197	24	12000	1.15
10	**2**	0.50	2.0	60	35	>99/<1	701	18	30000	1.21
11	**3**	0.50	2.0	60	60	>99/<1	1209	19	39000	1.18

[a] Conditions: PO (1.0 mL, 14.3 mmol) and Fe complex [(7.0−7.2) × 10^{-3} mmol of Fe] in a 50 mL autoclave for 1 h. [b] Relative to Fe. [c] Determined by ^{1}H NMR analysis of the crude product using phenanthrene as an internal standard. [d] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)$^{-1}$·h^{-1}. [e] Determined by size-exclusion chromatography (SEC) using a polystyrene (PS) standard. [f] 2 h. [g] PO (2.5 mL, 35.8 mmol), 2 h.

Table 2. Copolymerization of Glycidyl Phenyl Ether with Carbon Dioxide Using Fe−Corrole Complex 1a[a]



entry	cat.	P_{CO_2} (MPa)	time (h)	conv. of GPE (%)	copolymer yield (g)	copolymer TOF[d,e]	carbonate-linkage content (%)[d]	m/r[f]	M_n (kg·mol^{-1})[g]	M_w/M_n[g]	$T_g/T_c/T_m$ (°C)[h]	T_{d5} (°C)[i]
1	**1a**	2.0	1	20	0.174[d]	401	9	–[j]	–[j]	–[j]	–[j]	–[j]
2	**1a**	2.0	49	>99	1.06	41	11	74/26	13.7	7.01	13/92/183	344
3	**1a**	5.0	95	>99	1.05	21	22	79/21	5.1	14.4	11/79/180	317
4	**1a**	0	24	>99	1.06	83	none	67/33	15.4	8.7	9/99/186	394
5[b]	**4**	2.0	24	59	0.57	26	95	–[k]	13.0	1.2	46/–[l]/–[l]	210
6[c]	**1a**	2.0	116	>99	1.07	17	10	>99/<1	2.8	41	15/88/172	347

[a] Conditions: GPE (1.1 mL, 7.4 mmol) and **1a** (1.8 × 10^{-3} mmol) in a 50 mL autoclave at 60 °C. [b] Conditions: GPE (1.1 mL, 7.4 mmol) and complex **4** (3.7 × 10^{-3} mmol) in a 50 mL autoclave at 15 °C. [c] (*S*)-GPE was used. [d] Determined by ^{1}H NMR analysis of the crude product using phenanthrene as an internal standard. [e] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)$^{-1}$·h^{-1}. [f] Meso/racemo ratio in the ether diad, as determined by ^{13}C NMR analysis. [g] Determined by SEC using a PS standard. [h] Glass transition temperature/crystallization temperature (cooling process)/melting temperature as determined by DSC. [i] Decomposition temperature of 5% weight loss. [j] Not determined because of difficulty in separating the monomer from the copolymer. [k] Not determined because of the low content of ether linkages. [l] Not observed.

higher content of carbonate linkages (up to 62%). However, it diminished the catalytic activity and the copolymer selectivity, giving a large amount of PC (entries 3 and 4). The polymerization temperature and CO_2 pressure also affected the catalytic performance: increasing the polymerization temperature resulted in lower carbonate-linkage content and higher catalytic activity (entries 1, 5, and 6), while higher CO_2 pressure gave higher carbonate-linkage content and lower catalytic activity (entries 1, 7, and 8).

Other iron−corrole complexes also copolymerized PO with CO_2. Monomeric complex **2** with chloride as a monoanionic axial ligand demonstrated slightly lower catalytic activity than complex **1a** to give the copolymer enriched with ether linkages (entry 10). Complex **3** without any monoanionic axial ligand also copolymerized PO with CO_2, exhibiting a high catalytic activity comparable to that of complex **1a** (entry 11). These complexes exhibited dependences on the reaction conditions similar to those of complex **1a** [see the Supporting Information (SI)]. In contrast, iron(III) complexes with 5,10,15,20-tetraarylporphyrin ligands (aryl = C_6F_5, Ph) gave only cyclic carbonate. Accordingly, the combination of iron with a corrole ligand was crucial for the copolymerization.

The copolymerization of CHO with CO_2 was also successfully accomplished using the iron−corrole complexes under the standard conditions for PO/CO_2 copolymerization (CHO/Fe/[PPN]Cl = 2000/1.0/0.50, P_{CO_2} = 2.0 MPa; see the SI). Complexes **1a**, **1b**, **2**, and **3** all gave the copolymer selectively without any concomitant production of cyclic cyclohexene carbonate (CHC). The resulting copolymers possessed high carbonate-linkage content (>90%). The highest catalytic activity (TOF = 109 h^{-1}) detected with **3** in 3 h was higher than that of the previously reported dinuclear iron(III) complex (highest TOF = 54 h^{-1}).[18] The ^{13}C NMR spectrum showed that the resulting copolymer was almost atactic.[19]

Finally, we focused on GPE as a comonomer. The copolymerization of CO_2 with glycidyl ethers has been less developed than those with PO and CHO, although it was shown in the early studies that glycidyl ethers can be used as a comonomer in the copolymerization. Recently, several glycidyl ethers, such as allyl-, phenyl-, and methoxyethyl-substituted ones, have been copolymerized with CO_2 to produce functional polycarbonates.[20] Here we report the formation of a crystalline GPE/CO_2 copolymer with an ether-rich structure. Representative results are summarized in Table 2. Cyclic carbonate was not detected in any entries. Under the same conditions as entry 1 of Table 1 for PO/CO_2, a GPE/CO_2 copolymer with both carbonate and ether linkages in the main chain was obtained (carbonate/ether = 9/91; Table 2, entry 1). The TOF of 401 h^{-1} was much lower than that for PO (1004 h^{-1}). When the reaction time was increased to 49 h^{-1}, GPE was completely consumed, affording a copolymer with a carbonate-linkage content of 11% (entry 2). Elevating the CO_2 pressure to 5.0 MPa gave a copolymer with a higher carbonate-linkage content of 22% (entry 3).

The products thus obtained were further characterized by differential scanning calorimetry (DSC) and ^{13}C NMR analysis. The data for Table 2, entry 3 are shown in Figure 2 as a representative example. It is notable that the copolymers obtained in entries 2 and 3 were crystalline materials, as melting temperatures (T_m) were detected at around 180 °C by DSC. Crystallization temperatures were also detected. It is likely that the high crystallinity of the copolymers originated from the iso-enriched polyether moieties. From the ^{13}C NMR spectra, the obtained copolymers were suggested to contain iso-enriched polyether linkages on the basis of the peaks at δ 68.79 (meso) and 68.63 (racemo) [meso/racemo (m/r) = 74/26 for entry 2 and 79/21 for entry 3]. The meso selectivity was similar to that in the control experiment in the absence of CO_2, that is, homopolymerization of GPE catalyzed by **1a** (m/r = 67/33, T_m = 186 °C; entry 4).[21]

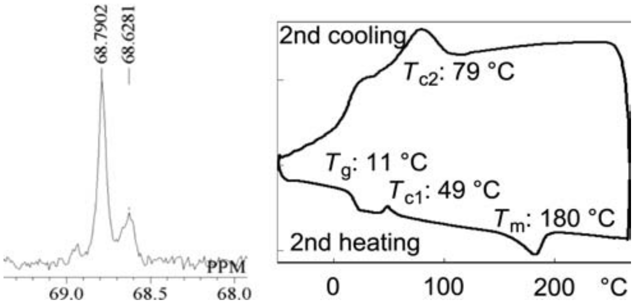


Figure 2. (left) Methylene region of the ^{13}C NMR spectrum and (right) DSC curve of the copolymer from Table 2, entry 3.

In contrast, a GPE/CO_2 copolymer with a high carbonate-linkage content of 95% was obtained using cobalt catalyst **4** (entry 5). The copolymer was amorphus, and neither T_c nor T_m was detected. Thus, the unique crystallinity attained with **1a** in the GPE/CO_2 copolymerization may be summarized as resulting from (i) the high content of ether linkages in the copolymer and (ii) the high meso selectivity in the polyether diad. The GPE/CO_2 copolymer obtained using enantiomerically pure GPE showed a slightly lower melting temperature (172 °C) in spite of its perfect stereoregularity (m/r > 99/1) (entry 6). This trend is similar to that observed for homopolymers of GPE: the melting temperature of a GPE homopolymer from racemic GPE (190 °C) was higher than that from enantiomerically pure GPE (176 °C).[21a]

The iron−corrole complexes in combination with [PPN]Cl were also applicable to homopolymerization of PO (see the SI). In particular, iron(III) complex **3** demonstrated high activity (TOF of up to 685 h^{-1}), providing a polymer with M_n = 95 kg·mol^{-1} and M_w/M_n = 1.22 in 2 h at 25 °C. The ^{13}C NMR spectrum showed that the obtained poly(PO) possessed a regioregular and slightly iso-enriched structure (see the SI).[22]

In conclusion, iron−corrole complexes were found to copolymerize epoxides with CO_2, providing the first example of iron-catalyzed PO/CO_2 and GPE/CO_2 copolymerization. In particular, the GPE/CO_2 copolymers were found to be crystalline materials because of the existence of isotactic poly(GPE) units.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental procedures for the preparation of Fe−corrole complexes and the polymerizations; results of PO/CO_2 and CHO/CO_2 copolymerizations and PO homopolymerization; and NMR spectra, DSC curves, and TGA thermograms of the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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