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The Cobalt Porphyrin−Lewis Base System: A Highly Selective Catalyst for Alternating Copolymerization of CO_2 and Epoxide under Mild Conditions

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ABSTRACT: The use of a cobalt porphyrin ((TPP)CoCl, **1**) in combination with dimethylaminopyridine (DMAP) for the alternating copolymerization of CO_2 and epoxide is described. The (TPP)CoCl (**1**)−DMAP system quantitatively produced the alternating copolymer from CO_2 and cyclohexene oxide (CHO) under optimized conditions (50 atm, 80 °C). This calatyst system also worked satisfactorily for the alternating copolymerization of CO_2 and a terminal epoxide, e.g., propylene oxide (PO), without formation of cyclic carbonate to give the polycarbonate. The alternating copolymerization of CO_2 and epoxide (CHO, PO) was achieved under very mild conditions, such as at ambient temperature and under CO_2 at 1 atm, by using the **1**−DMAP catalyst system.

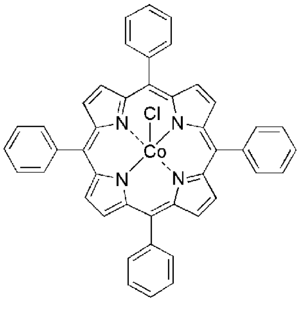
Introduction

Polymer synthesis using CO_2 as a monomer is of interest because the polymer is expected to carry ester groups in its main chain and to exhibit remarkable properties.[1] The first example of copolymerization of CO_2 and epoxide was realized by using the Et_2Zn-H_2O catalyst.[2] Since this discovery was reported by Inoue, Koinuma, and Tsuruta in 1969,[2] many catalysts for this copolymerization were developed based on organic and inorganic zinc compounds in combination with protic compounds.[3] From the 90s onward, zinc complexes with well-defined structures, such as zinc bis(phenoxide) with bulky substituents,[4] zinc bis(salicylaldiminate),[5] zinc bis(β-diiminate),[6] and zinc prolinolate complex,[7] have been reported to exhibit high catalytic activity for the copolymerization of CO_2 and epoxide.

We have made efforts to develop efficient catalysts for the alternating copolymerization based on metalloporphyrins and metal Schiff base complexes, because these complexes are suited to control molecular weights and their distribution of the produced polycarbonates as well as to regulate selective formation of the alternating copolymer. Recent successful examples are manganese porphyrin,[8] zinc (*N*-methylporphyrin),[9] aluminum salophen,[10] and dinuclear zinc Schiff base complex.[11]

In the course of this study, our attention was paid to chlorocobalt porphyrin ((TPP)CoCl; **1**). See Chart 1 for structure of (TPP)CoCl (**1**). The cobalt−axial group bond in cobalt porphyrin is known to have a covalent-bond character as exemplified by a fact that the Co−C bond in organocobalt porphyrin is resistant to hydrolysis, and cobalt is a highly oxophilic metal.[12] Therefore, when the cobalt porphyrin is applied to the catalyst for the alternating copolymerization, CO_2 incorporation into a copolymer is expected to take place easily and precisely, since elimination of CO_2 from the propagating end of the growing polymer, which may lead to polyether formation, should be difficult to occur. In close relation to our expectation, two important catalytic systems for the CO_2−epoxide coupling were found in the literature. One is the alternating copolymerization of CO_2 and epoxide mediated by cobalt Schiff base complexes,[13−16] and the other is the cyclic carbonate synthesis from CO_2 and epoxide catalyzed by cobalt porphyrin.[17,18] However, to the best of our knowledge, no research for cobalt porphyrin-assisted alternating copolymerization of CO_2 and epoxide has been reported so far.

Chart 1. Structure of (TPP)CoCl (1)



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In the present paper, we wish to report that the (TPP)CoCl (**1**)−dimethylaminopyridine (DMAP) system is a novel catalyst system for the highly selective alternating copolymerization of CO_2 and epoxide under very mild conditions (Scheme 1).[19]

Results and Discussion

Alternating Copolymerization of CO_2 and Cyclohexene Oxide (CHO) by Using the Cobalt Porphyrin((TPP)CoCl; 1)−Cocatalyst Systems. The copolymerization of CO_2 and cyclohexene oxide (CHO) was first attempted at 80 °C under 50 atm of CO_2 with cobalt porphyrin ((TPP)CoCl; **1**) alone as the catalyst at an initial mole ratio ($[CHO]_0/[\mathbf{1}]_0$) of 500 in CH_2Cl_2. However, the alternating copolymer was not produced. The product was a polymer rich in ether linkages (carbonate linkages = 4%; Table 1, run 1).

The combined use of metalloporphyrins or metal Schiff base complexes witha cocatalyst, such as Lewis basic amine or phosphine or quaternary onium salt, was often found to result

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Scheme 1. Alternating Copolymerization of CO_2 and Epoxide by the (TPP)CoCl (1)−DMAP System

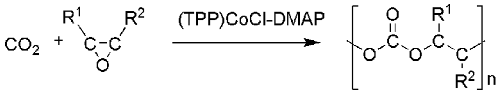


Table 1. Copolymerization of CO_2 and CHO by the (TPP)CoCl (1)−Cocatalyst System

		product				
				polymer		
run[a]	cocatalyst	yield (%)[b]	selectivity[c]	carbonate linkages (%)[d]	M_n[e]	M_w/M_n[e]
1	none	48	100:0	4	5 400	4.15
2	DMAP	>99	100:0	>99	14 500	1.13
3	Py	87	100:0	>99	19 300	1.33
4	PyCHO	16	100:0	>99	2 900	1.24
5	MeIm	80	100:0	>99	14 300	1.73
6	Ph_3P	36	−[f]	0	12 500	3.44
7	Et_4NOAc	20	−[f]	0	6 800	2.90
8	Et_3N	0	−[f]			

[a] $[\mathbf{1}]_0 = 0.05$ mmol, $[CHO]_0/[cocatalyst]_0/[\mathbf{1}]_0 = 500/0.5/1$, solvent = CH_2Cl_2 (3.5 mL), time = 24 h. [b] Yield (%) = isolated product (g)/{[CO_2 (44 g/mol) + CHO (98 g/mol)]25 (mmol)} × 100. [c] Yield ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture. [d] Estimated from the ^1H NMR spectrum of the reaction mixture. [e] Estimated by GPC on the basis of polystyrene standards. [f] No absorption due to polycarbonate or cyclic carbonate was found in the IR spectrum of the reaction mixture.

in improving the polymerization rate and/or the content of carbonate linkages of the copolymer. Thereat, the copolymerization of CO_2 and CHO was carried out with (TPP)CoCl (**1**) in the presence of *N*,*N*-dimethylaminopyridine (DMAP) (0.5 equiv to **1**). The **1**−DMAP system gave the alternating copolymer in 99%, without production of cyclic carbonate (carbonate linkages >99%, $M_n = 14\,500$ [$M_{calcd} = 71\,000$], $M_w/M_n = 1.13$; Table 1, run 2). The M_n value of the obtained copolymer increased linearly with the CHO conversion, retaining a narrow, but bimodal, distribution, although the M_n was much lower than the theoretical value (Figure 1). The details of the difference between observed and calculated values of the copolymer molecular weights and a bimodal distribution of the observed molecular weight were described in the following section.

A living nature of the alternating copolymerization of CO_2 and CHO by the **1**−DMAP system was demonstrated through a two-stage reaction ($[CHO_{first\ feed}]_0/[CHO_{second\ feed}]_0/[\mathbf{1}]_0 = 500/500/1$). When CHO was added to the reaction system after CHO of the first feed was almost consumed (the first stage; 6 h, conversion >95%), the copolymerization resumed to attain complete consumption of the second-feed CHO (the second stage; 6 h, conversion >95%). A clear increase in molecular weight of the obtained alternating copolymer from 13 200 ($M_w/M_n = 1.15$) to 27 800 ($M_w/M_n = 1.24$) with retaining a narrow polydispersity (Figure 2).

Catalytic activities of other cobalt porphyrins, such as bromocobalt porphyrin−pyridine complex ((TPP)CoBr···Py) and (TPP)Co^{II}, were examined under the identical conditions. (TPP)CoBr···Py was comparable to the **1**−DMAP system, where the alternating copolymerization of CO_2 and CHO by (TPP)CoBr···Py produced the polycarbonate although the yield was lower (yield = 61%, carbonate linkages >99%, $M_n = 16\,000$, $M_w/M_n = 1.21$). As contrasted to the trivalent cobalt complex, **1**, the bivalent complex, (TPP)Co, was inactive for the copolymerization to result in the complete recovery of unreacted monomers.

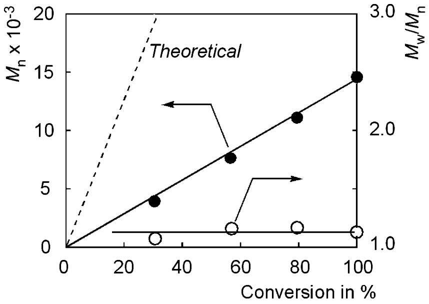


Figure 1. Alternating copolymerization of CO_2 and CHO by the (TPP)-CoCl (**1**)−DMAP system (for the reaction conditions, see Table 1, run 2): relationship between the conversion of CHO and M_n (M_w/M_n) of the copolymer.

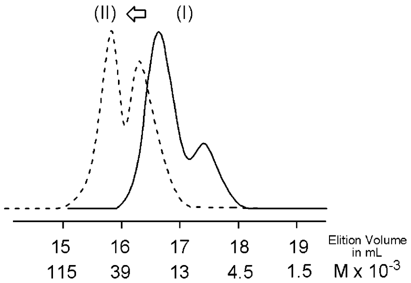


Figure 2. Two-stage alternating copolymerization of CO_2 and CHO by the (TPP)CoCl (**1**)−DMAP system: GPC profiles of the copolymers formed in the first stage (conversion >95%, $M_n = 13\,200$, $M_w/M_n = 1.15$; **I**) and in the second stage (conversion >95%, $M_n = 27\,800$, $M_w/M_n = 1.24$; **II**).

To tune the catalyst activity, the influence of cocatalyst on copolymerization was investigated. When DMAP was replaced by pyridine (Py) or pyridine aldehyde (PyCHO), the catalyst systems gave the alternating copolymers in 87% and 16%, respectively (carbonate linkages >99% in both cases; Table 1, runs 3 and 4). Introduction of electron-releasing substituents on the pyridine ring increased the yield of copolymer (Table 1, runs 2−4). The alternating copolymer was also obtained with 1-methylimidazole (MeIm) (yield = 80%, carbonate linkages >99%; Table 1, run 5). In each case using triphenylphosphine (Ph_3P) or tetraethylammonium acetate (Et_4NOAc) as the cocatalyst, the homopolymer of CHO was the only product (Table 1, runs 6 and 7). Triethylamine (Et_3N) disturbed any reaction of CO_2 and CHO (Table 1, run 8).

The mole ratio of DMAP to **1** ($[DMAP]_0/[\mathbf{1}]_0$) was very important for the selective and fast production of the polycarbonate. The catalyst system composed of **1** and an equimolar amount of DMAP afforded the alternating copolymer in quantitative yield (carbonate linkages >99%, $M_n = 18\,000$, $M_w/M_n = 1.23$; Table 2, run 3). The use of a larger amount of DMAP ($[DMAP]_0/[\mathbf{1}]_0 = 2, 10$) increased in the formation of cyclic carbonate (polycarbonate/cyclic carbonate = 95/5 and 50/50; Table 2, runs 2 and 1). On the contrary, when the mole ratio of DMAP to **1** was decreased to 0.1, the carbonate unit content of the produced copolymer decreased to 20% (Table 2, run 5). As already mentioned above, in the absence of DMAP, the obtained copolymer was rich in ether linkages (carbonate linkages = 4%, Table 2, run 6).[20]

In order to realize the alternating copolymerization of CO_2 and CHO under mild conditions, the copolymerization was tried at a lower temperature, such as 40 °C or 25 °C. The copolymerization was somewhat retarded but gave the alternating copolymer (carbonate linkages >99%; 40 °C, yield = 54%; 25 °C, yield = 11%; Table 3, runs 2 and 3).

Table 2. Copolymerization of CO_2 and CHO by the (TPP)CoCl (1)−DMAP System

		product				
				polymer		
run[a]	$[DMAP]_0/[\mathbf{1}]_0$	yield (%)[b]	selectivity[c]	carbonate linkages (%)[d]	M_n[e]	M_w/M_n[e]
1	10	53	50:50	>99	1 500	1.66
2	2	64	95:5	>99	6 800	1.72
3	1	>99	100:0	>99	18 000	1.23
4[g]	0.5	>99	100:0	>99	14 500	1.13
5	0.1	19	100:0	20	6 100	3.30
6[h]	0	48	−[f]	0	5 400	4.15

[a] $[\mathbf{1}]_0 = 0.05$ mmol, $[CHO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.5/1$, solvent = CH_2Cl_2 (3.5 mL), time = 24 h. [b] Yield (%) = isolated product (g)/{[CO_2 (44 g/mol) + CHO (98 g/mol)]25 (mmol)} × 100. [c] Yield ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture. [d] Estimated from the ^{1}H NMR spectrum of the reaction mixture. [e] Estimated by GPC on the basis of polystyrene standards. [f] No absorption due to polycarbonate or cyclic carbonate was found in the IR spectrum of the reaction mixture. [g] The same data set as run 2 in Table 1. [h] The same data set as run 1 in Table 1.

Table 3. Copolymerization of CO_2 and CHO by the (TPP)CoCl (1)−DMAP System

			product				
	reaction conditions		polymer				
run[a]	temp (°C)	pressure (atm)	yield (%)[b]	selectivity[c]	carbonate linkages (%)[d]	M_n[e]	M_w/M_n[e]
1[f]	80	50	>99	100:0	>99	14 500	1.13
2	40	50	54	100:0	>99	9 400	1.10
3	25	50	11	100:0	>99	5 000	1.08
4[g]	25	1	15	100:0	>99	1 500	1.11

[a] $[\mathbf{1}]_0 = 0.05$ mmol, $[CHO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.5/1$, solvent = CH_2Cl_2 (3.5 mL), time = 24 h. [b] Yield (%) = isolated product (g)/{[CO_2 (44 g/mol) + CHO (98 g/mol)]25 (mmol)} × 100. [c] Yield ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture. [d] Estimated from the ^{1}H NMR spectrum of the reaction mixture. [e] Estimated by GPC on the basis of polystyrene standards. [f] The same data set as run 2 in Table 1. [g] Without solvent.

The interaction between **1** and DMAP was examined by UV−visible absorption spectral measurement of **1** in the presence of DMAP in CH_2Cl_2 ($[\mathbf{1}]_0 = 1 \times 10^{-5}$ mmol/L) at various DMAP-to-**1** mole ratios ($[DMAP]_0/[\mathbf{1}]_0 = 0-10$). The spectra showed that the absorption maximum at 424 nm decreased with increasing DMAP, while a new absorption band at 440 nm appeared and increased in its intensity (Figure 3). This result indicated the coordination of DMAP to **1** as an axial ligand to form a hexacoordinated complex (Scheme 2).

Molecular Weights of the Alternating Copolymer. As already mentioned above, The M_n of the alternating copolymer (14 500) produced by the copolymerization of CO_2 and CHO by the **1**−DMAP system in CH_2Cl_2 at 80 °C under 50 atm CO_2 ($[CHO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.5/1$, yield >99%; Table 1, run 2) was much lower than the theoretical value (71 000) on the assumption that all the molecules of **1** participated in initiation and propagation. In this case, the GPC chromatogram showed a bimodal molecular weight distribution of the produced copolymer (Figure 4). Each of the two copolymers corresponding to two peaks in the chromatogram had a very narrower molecular weight distribution ($M_w/M_n = 1.07$ and 1.06; Figure 4, broken curves). The M_n of the higher-molecular-weight copolymer (19 000) was twice as large as that of the lower-molecular-weight copolymer (9000).

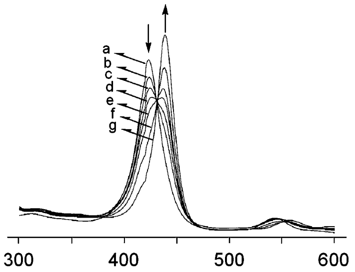


Figure 3. UV−vis spectra of (TPP)CoCl (**1**) in the presence of DMAP in CH_2Cl_2 ($[(TPP)CoCl]_0 = 1 \times 10^{-5}$ mmol/L) at various DMAP-to-**1** mole ratios; $[DMAP]_0/[\mathbf{1}]_0$ = (a) 0, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.7, and (g) 1.

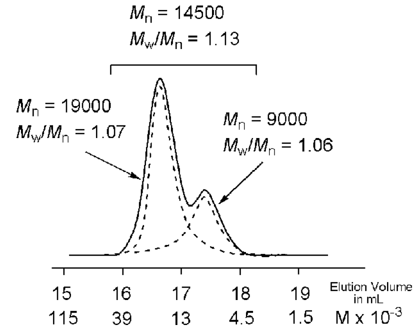
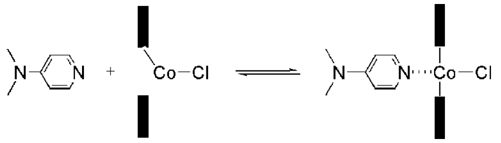


Figure 4. Alternating copolymerization of CO_2 and CHO by the (TPP)-CoCl (**1**)−DMAP system (for the reaction conditions, see Table 1, run 2): GPC profile of the copolymer ($M_n = 14\,500$, $M_w/M_n = 1.13$).

Scheme 2. Interaction between (TPP)CoCl (1) and DMAP in Solution



The MALDI-TOF mass spectrum of a co-oligomer ($[CHO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.5/1$, 50 atm, 80 °C, 20 min, conversion = 6%, $M_n = 1600$, $M_w/M_n = 1.15$) showed that the co-oligomer was composed of a copolymer carrying two OH groups at both terminals and a copolymer that had terminal Cl and OH groups. The introduction of OH groups into both ends was due to an “immortal polymerization” probably caused by concomitant water, as previously reported for the copolymerizations catalyzed by the aluminum Schiff base complex−ammonium salt system[10] and the cobalt salen complex having a piperidinium side arm.[16]

Before the copolymerization of CO_2 and CHO with the **1**−DMAP system ($[CHO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.5/1$, 80 °C, 50 atm, 6 h), the autoclave reactor containing **1** in the solid state was heated at 120 °C for 6 h in vacuo in order to remove the concomitant water. The copolymerization thus started and gave the alternating copolymer quantitatively (carbonate linkages >99%), but the obtained copolymer still showed a bimodal GPC elution pattern. The M_n of the obtained copolymer (29 600) was higher than that of the copolymer from the copolymerization without subjecting it to the prior heating process (14 500). The amount of the residual water, estimated from the observed M_n with considering the initinal CHO-to-**1** ratio, was equimolecular to **1**.[21] This estimation indicated that one molecule of water per one molecule of **1** survived the drying procedure by virtue of the possible strong coordination of water to the cental cobalt ion. In this connection, a networking structure of Co−O−H···Cl−Co hydrogen bonding was observed in the X-ray crystal structure analysis for a hexacoordinated aquochlorocobalt porphyrin, (TPP)CoCl(H_2O).[22]

Table 4. Copolymerization of CO_2 and PO by the (TPP)CoCl (1)−DMAP System

	reaction conditions			product				
						polymer		
run^a	temp (°C)	pressure (atm)	time (h)	yield (%)^b	selectivity^c	carbonate linkages (%)^d	M_n^{e}	M_w/M_n^{e}
1	80	50	24	>99	40:60	>99	8 800	1.32
2	40	50	24	53	95:5	98	9 000	1.23
3	25	50	24	40	99:1	97	7 000	1.16
4	40	50	48	95	95:5	99	14 900	1.18
5^f	25	1	24	25	95:5	98	1 600	1.22

[a] $[\mathbf{1}]_0 = 0.05$ mmol, $[PO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.75/1$, solvent = CH_2Cl_2 (3.5 mL), time = 24 h. [b] Yield (%) = isolated product (g)/{[CO_2 (44 g/mol) + PO (58 g/mol)]25 (mmol)} × 100. [c] Yield ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture. [d] Estimated from the ^1H NMR spectrum of the reaction mixture. [e] Estimated by GPC on the basis of polystyrene standards. [f] $[\mathbf{1}]_0 = 0.05$ mmol, $[PO]_0/[\text{cocatalyst}]_0/[\mathbf{1}]_0 = 500/0.75/1$, without solvent.

Alternating Copolymerization of CO_2 and Propylene Oxide (PO) by Using the 1−DMAP System. It is often the case that the metal complex catalysts which are developed for the alternating copolymeriation of CO_2 and CHO cannot generate the polycarbonate from CO_2 and terminal epoxide such as propylene oxide (PO).[3] In such cases, the main products are cyclic carbonate and/or no reaction occurs between CO_2 and PO. The cyclic carbonate formation is a subsidiary side reaction during the alternating copolymerization of CO_2 and PO and tends to take place at higher temperature. The **1**−DMAP system is expected to conduct the alternating copolymerization of CO_2 and PO to afford the polycarbonate, because the catalyst system selectively produced the alternating copolymer from CO_2 and CHO even at a lower temperature around the room temperature, as described in the former section.

By use of the **1**−DMAP system, the copolymerization of CO_2 and PO ($[PO]_0/[DMAP]_0/[\mathbf{1}]_0 = 500/0.75/1$) selectively gave the alternating copolymer in CH_2Cl_2 at 25 °C in 24 h (carbonate linkages = 97%, polycarbonate/cyclic carbonate = 99/1, M_n = 7000, M_w/M_n = 1.16; Table 4, run 3), although the reaction proceeded rather slowly (40% yield). Also at 40 °C, the copolymeriation proceeded more rapidly to attain 53% polymer yield in the same reaction time, without lowering the selectivity (carbonate linkages = 98%, polycarbonate/cyclic carbonate = 95/5, M_n = 9000, M_w/M_n = 1.23; Table 4, run 2). When the copolymerization was conducted at an elevated temperature, such as 80 °C, a significant amount of cyclic carbonate (polycarbonate/cyclic carbonate = 40/60) was generated under otherwise similar conditions (Table 4, run 1).

The high selectivity of polycarbonate over cyclic carbonate at 40 °C was maintained after a longer reaction time to attain quantitative formation of the alternating copolymer. The alternating copolymeriation of CO_2 and PO by using the **1**−DMAP system was carried out at 40 °C for 48 h and afforded the alternating copolymer almost quantitatively (polycarbonate/cyclic carbonate = 95/5, carbonate linkages = 99%, M_n = 14 900, M_w/M_n = 1.18, Table 4, run 4). The ^{13}C NMR spectrum of the obtained copolymer (Table 4, run 4) in the carbonyl region showed that the poly(propylene carbonate) had a high content of head-to-tail connectivity (>95%) and an atactic stereoregularity.

Alternating Copolymerization of CO_2 and Epoxide by Using the 1−DMAP System Under 1 atm CO_2. A topic of current interest is the development of catalysts that realize the alternating copolymerization of CO_2 and epoxide under mild conditions (at room temperature, under low-pressure CO_2) from the viewpoints of resource, energy, and environmental problems. Very recently, we reported the first example of the alternating copolymerization of 1 atm CO_2 and CHO with (TPP)MnOAc.[8] Following our finding, synthesis of the alternating copolymer from CO_2 (1−5 atm) and CHO by using intramolecular dinuclear zinc[23] or magnesium complexes[24] was reported by Ding et al., and the alternating copolymerization of 1 atm CO_2 and PO was documented by Lu et al. by using the cobalt Schiff base complex−ammonium salt system.[14b]

Even under CO_2 at 1 atm, the **1**−DMAP system gave the alternating copolymer of CO_2 and CHO with the retaining of a high content of carbonate linkages (yield = 15%, carbonate linkages = 99%, M_n = 1500, M_w/M_n = 1.11; Table 3, run 4). While (TPP)MnOAc, which is an excellent catalyst for CO_2−CHO alternating copolymerization, did not work for the CO_2−PO copolymerization,[8] the **1**−DMAP system was very effective for not only the CO_2−CHO copolymerization but also the CO_2−PO copolymerization. The CO_2−PO copolymerization by the **1**−DMAP system proceeded alternatingly to form polycarbonate under 1 atm CO_2 (yield = 25%, carbonate linkages = 98%, M_n = 1600, M_w/M_n = 1.22; Table 4, run 5).

Conclusion

The (TPP)CoCl (**1**)−DMAP system is a novel catalyst system for the alternating copolymerization of CO_2 and epoxide (CHO and PO). Although cyclic carbonate formation is a common side reaction in the copolymerization of CO_2 and PO, the copolymerization by the **1**−DMAP system selectively produced the alternating copolymer without production of the cyclic carbonate. This catalyst system achieved the alternating copolymerization under mild condition, that is, under 1 atm CO_2 and at room temperature.

Experimental Section

Materials. CH_2Cl_2 was washed successively with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and brine, dried over $CaCl_2$, and distilled over CaH_2 under nitrogen. Toluene and THF were distilled over sodium benzeophenone ketyl in a nitrogen atmosphere. DMF was distilled over CaH_2 under reduced pressure.

Commercial CO_2 was used without purification. 1,2-Epoxypropane (PO) was refluxed over a mixture of KOH and CaH_2 and distilled under nitrogen. 1,2-Epoxycyclohexene (CHO) was distilled over KOH and CaH_2 under reduced pressure.

5,10,15,20-Tetraphenylporphyrin ($TPPH_2$) was synthesized from pyrrole (0.4 mol, 28 mL) and benzaldehyde (0.4 mmol, 40 mL) in propionic acid (2 L) under reflux for 0.5 h. The crude product, which precipitated overnight at room temperature, was collected and recrystallized from $CHCl_3$/MeOH (1/2 v/v) to give $TPPH_2$ as purple crystals (8.6 g, 9.6%).[25]

Pyridine, 4-formylpyridine (PyCHO), and 1-methylimidazole (MeIm) were distilled over CaH_2 under nitrogen. *N*,*N*-Dimethylaminopyridine (DMAP) and triphenylphosphine (PPh_3) were recrystallized from toluene. Commercial Et_4NOAc was dried at 120 °C in vacuo for 6 h.

Synthesis of Cobalt Complex. Synthesis of Cobalt(II) Tetraphenylporphyrin ((TPP)Co).[26] $TPPH_2$ (3.25 mmol, 2.0 g) was refluxed for 1 h in acetic acid (2 L) with an excess of cobalt(II) chloride hexahydrate (16.8 mmol, 4.0 g) and sodium acetate (48.6 mmol, 4.0 g). The crystalline product was washed, respectively, with water, aqueous sodium bicarbonate, water, and methanol and then was dried in vacuo to give a red solid of (TPP)Co (1.98 g, 91%). UV−vis absorption spectrum (methanol), λ_{max}/nm: 410, 528.

Synthesis of Chlorocobalt Tetraphenylporphyrin ((TPP)CoCl).[27] After the suspension of (TPP)Co (1.49 mmol, 1.0 g) in methanol (1 L) containing concentrated hydrochloric acid (10 mL) was stirred at room temperature in a flask open to the air for several hours, the reaction mixture became a clear solution. The solution was filtered and concentrated under reduced pressure. The separated crystalline precipitates were collected by filtration and recrystallized from chloroform−hexane (0.99 g, 94%). Found: C, 73.94; H, 4.17; N, 7.85%. Calcd. for $C_{44}H_{28}N_4CoCl$: C, 74.74; H, 3.99; N, 7.92%. UV−vis absorption spectrum (methanol), λ_{max}/nm ($\epsilon/10^3$): 312(20.4), 426(284), 541(17.3).

Synthesis of Bromocobalt Tetraphenylporphyrin−Pyridine Complex ((TPP)CoBr···Py).[26] The reaction of (TPP)Co (0.07 mmol, 59 mg) with HBr (48% in water, 0.75 mL) in pyridine (15 mL) was conducted at 30 °C overnight. The solvent was removed under reduced pressure from the reaction mixture. The residue was dissolved in $CHCl_3$, washed with water, and recrystallized from $CHCl_3$−hexane to give the bromocobaltporphyrin−pyridine complex in 72% yield (42 mg). Found: C, 71.06; H, 4.07; N, 8.55%. Calcd. for $C_{49}H_{33}N_5CoBr$: C, 70.85; H, 4.00; N, 8.43%. UV−vis absorption spectrum (CH_2Cl_2), λ_{max}/nm: 338, 435, 553.

Copolymerization of CO_2 and Epoxide. A typical procedure for the copolymerization of CO_2 and CHO by (TPP)CoCl was as follows: A stainless steel autoclave (150 mL) containing (TPP)CoCl (0.05 mmol) and DMAP (0.025 mmol), dried in vacuo, was purged with nitrogen. A prescribed amount of CHO (25 mmol) and CH_2Cl_2 (3.5 mL) was added with a hypodermic syringe. The copolymerization was started by the pressurization of the solution by CO_2 up to 50 atm (52 kg/cm^2, 735 psi). The mixture was stirred for 24 h at 80 °C.

The autoclave was cooled, and excess CO_2 was discharged, to this was added methanol to stop the polymerization. A small portion of the products was subjected to ^{1}H NMR and IR analyses for determining the polymer structure and to gel permeation chromatography (GPC) for estimating the average molecular weights.

Measurement. ^{1}H NMR measurements were performed with $CDCl_3$ as a solvent at 30 °C on a Bruker DPX-400 spectrometer, with respect to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. IR spectra were recorded with a Horiba FT-210 spectrometer.

GPC was performed at 40 °C on a Tosoh model HLC-8020 high-speed liquid chromatograph equipped with a differential refractometer detector with THF as an eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained with standard polystyrenes (TSK standard polystyrene from Tosoh Co.); the weight-average molecular weights (M_w's) by light scattering [weight-average molecular weight/number-average molecular weight (M_w/M_n) by GPC] were 1.09×10^6 (1.08), 3.72×10^4 (1.02), 1.71×10^4 (1.01), 5.87×10^3 (1.08).

MALDI-TOF MS analyses were performed on a PerSpective Biosystems Voyager mass spectrometer equipped with a 337-nm nitrogen laser (pulse width, 3 ns). All experiments were carried out at an accelerating potential of 20 kV in the linear mode under a pressure of 6.75×10^{-8} mmHg. Ions below $m/z = 600.00$ or 1000.00 were removed with pulse deflection. In general, mass spectra from 50 laser shots were accumulated to produce a final spectrum. Adrenocorticotropic hormone (ACTH) fragment 18-39 (molecular weight = 2465), angiotensin II (molecular weight = 1046), and bradykinin fragment 1-7 (molecular weight = 757) were used as internal standards to calibrate the mass scale. Sample solutions were composed of the copolymer (10^{-3} M), dithranol as a matrix (10^{-3} M) in THF, and sodium trifluoroacetate as a cationizing agent (10^{-3} M) in H_2O.

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(19) A preliminary part of this study was reported in the reference 3g.

(20) In relation to the polyether formation in the absence of DMPA, it was of much interest to note that the homopolymerization of CHO did not occur when the **1**−DMPA system ($[\mathrm{DMAP}]_0/[\mathbf{1}]_0 = 0.5$) was used as a catalyst in CH_2Cl_2 at 80 °C ($[\mathrm{CHO}]_0/[\mathbf{1}]_0 = 500$), while the homopolymer was readily produced by **1** alone (yield = 92 %, M_n = 18 000, $M_w/M_n = 2.58$).

(21) Other efforts to remove water were unsuccessful. For example, the copolymerization of CO_2 and CHO in the presence of a dying agent, such as molecular sieves 4Å and $MgSO_4$, under otherwise the same

conditions afforded a copolymer abounding in ether linkages. Use of **1** after the Dean−Stark distillation of a benzene solution of **1** gave essentially the same result that was observed for the direct drying process by heating **1** in the solid state under reduced pressure.
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