Copolymerization

Highly Active, Binary Catalyst Systems for the Alternating Copolymerization of CO_2 and Epoxides under Mild Conditions**

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Chemical fixation of CO_2 is of great interest with respect to the development of truly environmentally benign processes, as there are many possibilities for CO_2 to be used as a safe and cheap C_1 feedstock in organic synthesis.[1] One of the most promising reactions in this area is the alternating copolymerization of CO_2 and epoxides to polycarbonates,[2] which was first reported by Inoue et al.[3] These polycarbonates not only exhibit interesting material properties, but also have the additional environmental advantages resulting from their biodegradability.[4] In recent decades, numerous catalyst systems have been developed for this transformation.[5] Although the advances have been significant, high catalyst loading, elevated CO_2 pressure, and long reaction time are usually prerequisites for obtaining appreciable amounts of polymer, which are often not perfectly alternating and exhibit broad molecular-weight distributions. Recently, several efficient catalyst systems for the copolymerization of CO_2 and alicyclic epoxides such as cyclohexene oxide have been reported to offer significant advantages over traditional

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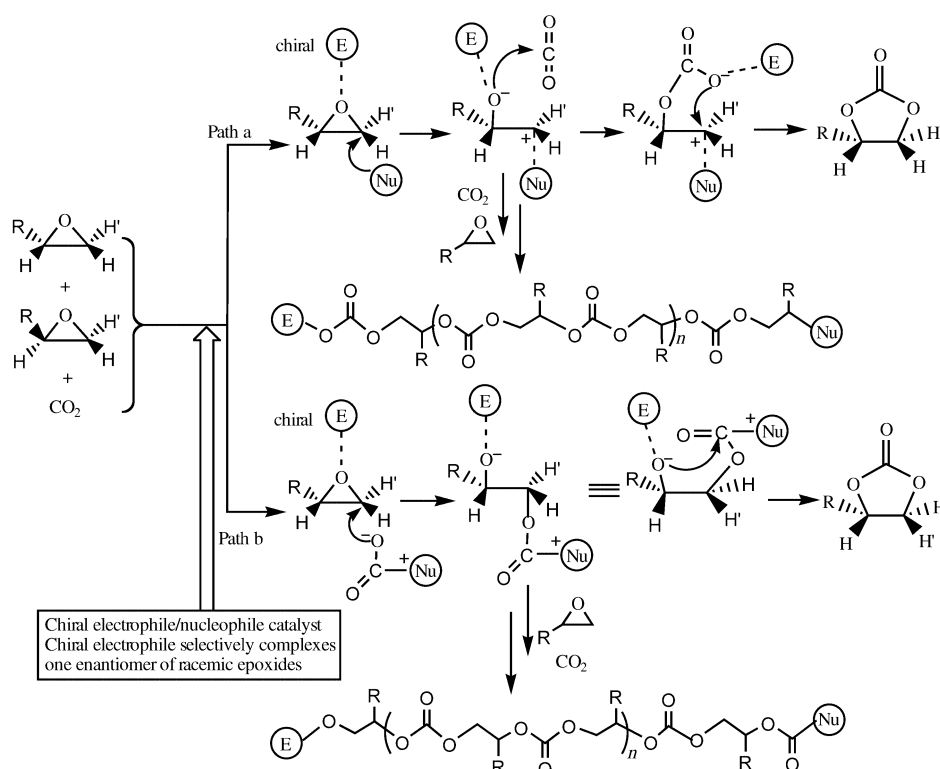E-mail: lxb-1999@163.com

heterogeneous catalysts.[6–12] Unfortunately, these catalysts do not readily polymerize CO_2 and aliphatic epoxides such as propylene oxide (PO). Recently, Coates and co-workers[13] reported the first highly active zinc β-diiminate catalysts bearing electron-withdrawing groups for the synthesis of poly(propylene carbonate) (PPC) with carbonate linkages up to 99%, but along with the formation of cyclic propylene carbonate (PC; 7–25%). A simple decrease in temperature and increase in CO_2 pressure suppressed the formation of PC and increased the selectivity for PPC. A similar effect was reported by Darensbourg and co-workers, who used chiral salen chromium chloride, alone or in conjunction with *N*-methylimidazole as a catalyst, for this reaction.[14] Herein, we report the use of a highly active binary catalyst system, which consists of a chiral cobalt complex [(salcy)Co^{III}X] and a quaternary ammonium salt (*n*Bu₄NY) for completely alternating copolymerization of CO_2 and aliphatic epoxides under extremely mild conditions.

Pursuant to our own efforts toward the development of highly efficient catalysts for coupling CO_2 with epoxides under mild conditions,[15] we became interested in the possibility of developing catalyst systems for the direct synthesis of optically active cyclic carbonates from racemic epoxides, which are inexpensive or easily accessible from inexpensive commercial starting materials. Based on the fact that chiral [(salcy)Co^{III}] complexes (Jacobsen catalyst) were shown to be highly efficient and enantioselective catalysts for the hydrolytic kinetic resolution of terminal epoxides,[16] we recently designed a bifunctional nucleophile–electrophile catalyst system consisting of chiral [(salcy)Co^{III}] complexes and quaternary ammonium salts for the direct synthesis of optically active cyclic carbonates from racemic epoxides.[17] In this system, the chiral [(salcy)Co^{III}] complex was proposed to serve as an electrophile for selectively complexing one enantiomer of the racemic epoxides, and the anion of the quaternary ammonium salt serves as a nucleophile. The regioselective attack of a nucleophile or activated CO_2 at the coordinated epoxide on the less substituted carbon atom leads to enantioselective ring opening of the epoxide with subsequent formation of the chiral cyclic carbonates through intermolecular cyclic elimination (Scheme 1). We were delighted to find that the solvent-free reaction of racemic PO (0.2 mol) with CO_2 in the presence of [(salcy)-Co^{III}(O₂CCCl₃)] (**1b**; 0.05 mol%) as a chiral electrophile in conjunction with *n*Bu₄NBr (0.05 mol%) as nucleophile proceeded within 3 h at room temperature and 2.0 MPa pressure to afford a mixture of unconverted PO and PC with moderate enantioselectivity (Table 1, entry 2), along with a small quantity of PPC. To our surprise, the resulting PPC shows >99% carbonate linkage in the ^{1}H NMR spectrum. Further investigation showed that simple changes in the axial group X of chiral [(salcy)Co^{III}X] and the anion Y of *n*Bu₄NY drastically affect the PPC/PC selectivity (Table 1, entries 1–8). It seems that the use of a cobalt complex with an electron-withdrawing axial group X and a quaternary ammonium salt, whose anion exhibits poor leaving ability, increases the selectivity for PPC. For example, in the presence of *n*Bu₄NBr cocatalyst, a change in the axial group X of chiral [(salcy)Co^{III}X] from acetate to dinitrophenol resulted in an increase in the selectivity of PPC

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Scheme 1. A bifunctional nucleophile–electrophile catalyst system for the direct synthesis of enantiomerically pure cyclic carbonates or linear polycarbonates from racemic epoxides and CO_2.

from 3 to 78%. On the other hand, with complex **1d** as catalyst, a change in the anion of cocatalyst nBu$_4$NY from Br$^-$ to Cl$^-$ or CH$_3$COO$^-$ resulted in an increase in the selectivity for PPC from 78 to 99%. The results may be explained in terms of greater advantages for producing linear polycarbonates by successive insertion of CO_2/epoxide towards the M–O bond as compared with the formation of cyclic carbonates by intermolecular cyclic elimination (Scheme 1) in the catalyst systems that consist of a strong electrophile in conjunction with a nucleophile with poor leaving ability. Notably, these binary catalyst systems based on chiral [{(1R,2R)-(tBu)$_2$sal-cy}CoX] complexes all preferentially consume (S)-PO over (R)-PO with $K_{rel} = 2.8$–3.5. Notably, these cobalt complexes or quaternary ammonium salts by themselves show no (or only very low) catalytic activity under the conditions employed. Interestingly, the binary catalyst systems are inactive for the homopolymerization of PO over 1 day.

A significant drawback in the use of CO_2 as a reagent in organic synthesis is the potential danger associated with operating at high temperatures and pressures. Prior to the present work, Coates et al. reported the first discrete cobalt complexes alone as catalysts for the copolymerization of CO_2 and PO, but these complexes are inactive at low CO_2 pressures.[18] We were gratified to discover that the binary catalyst system can operate very efficiently at low temperatures and with CO_2 at atmospheric pressure. The highest activity occurs at 1.0–2.0 MPa and is maintained at 50% of the optimum TOF at only 0.2 MPa. An increase in the pressure beyond the optimal range results in a dramatic decrease in activity. Interestingly, the variation of CO_2

pressure does not lead to an observable decrease in selectivity for PPC formation. In contrast, in the presence of [(bdi)-ZnOAc] catalyst (bdi = β-diiminate),[13] an increase in the pressure of CO_2 is beneficial for suppressing PC formation and effectively increases the selectivity for polymer while moderately decreasing the catalyst activity for PPC formation. Surprisingly, a change in the reaction temperature from 25 to 40°C, only significantly affects the activity of the catalyst, rather than the selectivity for PPC formation (Table 1, entry 16).

All the isolated polymers have narrow molecular-weight distributions, consistent with controlled polymerization; however, the M_n values are not close to the expected values, which indicates the existence of chain transfer during the reaction. The ^{1}H NMR spectra of all PPCs produced show >99% carbonate linkages, and the ^{13}C NMR spectra show that these polymers have an unprecedented head-to-tail content of >95% (Figure 1). Such a microstructure is consistent with a highly stereoselective ring opening of PO, and is in contrast to polymers prepared in the presence of zinc glutarate[19] (~60% head-to-tail linkages) and [(bdi)ZnOAc] (~54% head-to-tail linkages). Also, the catalyst system was found to be applicable to other aliphatic epoxides, providing the corresponding polycarbonates with >99% carbonate linkages (Table 1, entries 17 and 18).

In summary, chiral [(salcy)Co^{III}X] in conjunction with a quaternary ammonium salt is a highly efficient catalyst for the copolymerization of CO_2 with epoxides under extremely mild temperatures and pressures to afford the corresponding completely alternating copolymers with >95% head-to-tail

Table 1: CO_2/Epoxides copolymerization results.[a]

1a: X =O_2CCH_3
1b: X =O_2CCCl_3
1c: X = O—⟨ ⟩—NO_2
1d: X = O—⟨ ⟩ (NO_2, NO_2)
1e: X = O—⟨ ⟩ (NO_2, NO_2, NO_2)

(1R, 2R)-[(tBu)$_2$SalcyCoX] (1)
nBu$_4$NY

R = CH$_3$, C$_2$H$_5$, C$_4$H$_9$

Entry	1	Y	Epoxide	t [h]	P [MPa]	TOF[b] [h^{-1}]	Selectivity[c] [% PPC]	Carbonate linkages [%][c]	M_n[d] [g mol^{-1}]	PDI(M_w/M_n)	K_{rel}[e]
1	a	Br	PO	3	2.0	228	3	>99	—[f]	—[f]	3.9
2	b	Br	PO	3	2.0	264	6	>99	—[f]	—[f]	4.7
3	d	Br	PO	3	2.0	289	78	>99	23500	1.29	3.2
4	d	Cl	PO	3	2.0	257	99	>99	30400	1.36	3.4
5	d	I	PO	3	2.0	272	69	>99	22100	1.34	2.8
6	d	OAc	PO	3	2.0	167	99	>99	18200	1.23	3.1
7	c	Cl	PO	3	2.0	185	96	>99	21000	1.48	2.9
8	e	Cl	PO	3	2.0	248	99	>99	27500	1.43	3.0
9	d	–	PO	24	2.0	2	95	>99	—[f]	—[f]	—[f]
10	–	Cl	PO	24	2.0	<1	0		—[f]	—[f]	—[f]
11	d	Cl	PO	3	0.2	130	98	>99	18200	1.29	3.2
12	d	Cl	PO	3	0.4	190	99	>99	28300	1.31	3.5
13	d	Cl	PO	3	1.0	243	99	>99	29900	1.41	3.3
14	d	Cl	PO	3	4.0	219	99	>99	28700	1.42	3.3
15	d	Cl	PO	3	6.0	173	99	>99	25500	1.33	3.4
16[g]	d	Cl	PO	3	4.0	371	99	>99	24000	1.37	2.8
17	d	Cl	1,2-BuO[h]	6	2.0	61	99	>99	11600	1.26	—[f]
18[g]	d	Cl	1,2-HO[i]	8	2.0	48	98	>99	7300	1.11	—[f]

[a] The reaction was carried out with neat epoxide (14 mL, 200 mmol; catalyst/co-catalyst/epoxide = 1:1:2000) at 25 °C, unless otherwise noted. [b] Turnover frequency of epoxide to products (polycarbonate and cyclic carbonate). [c] Determined by using ^{1}H NMR spectroscopy. [d] Determined by means of gel permeation chromatography in THF at 35 °C, calibrated with polystyrene standards. [e] $K_{rel} = \ln[1-c(1+ee)]/\ln[1-c(1-ee)]$; c = conversion, ee = enantiomeric excess of unconverted epoxide. [f] Not applicable. [g] 40 °C. [h] 1,2-Butene oxide. [i] 1,2-hexene oxide.
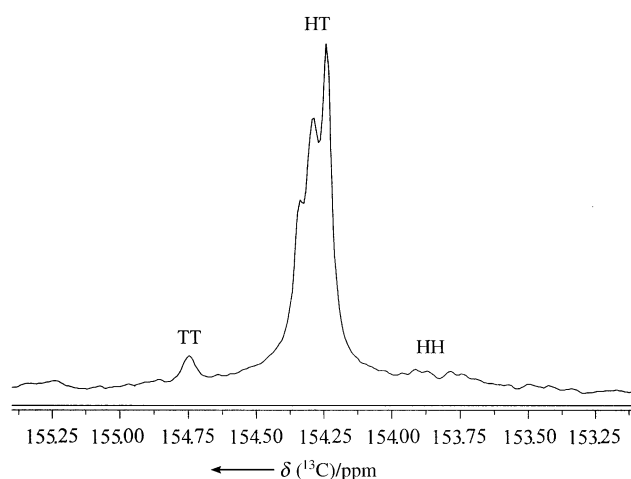

Figure 1. The carbonyl region of the ^{13}C NMR spectrum of a representative sample of poly(propylene carbonate) (PPC).

linkages. To our knowledge, these binary catalyst systems exhibit the highest reported activities for PO/CO_2 copolymerization. Furthermore, they offer unprecedented opportunities for controlling the regio- and stereochemistry of copolymerization. Further studies are focused on elucidating the catalytic mechanism and developing new bifunctional nucleophile–electrophile catalyst systems that exhibit higher regio- and stereoselectivity for epoxide ring opening in CO_2/epoxide copolymerization.

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