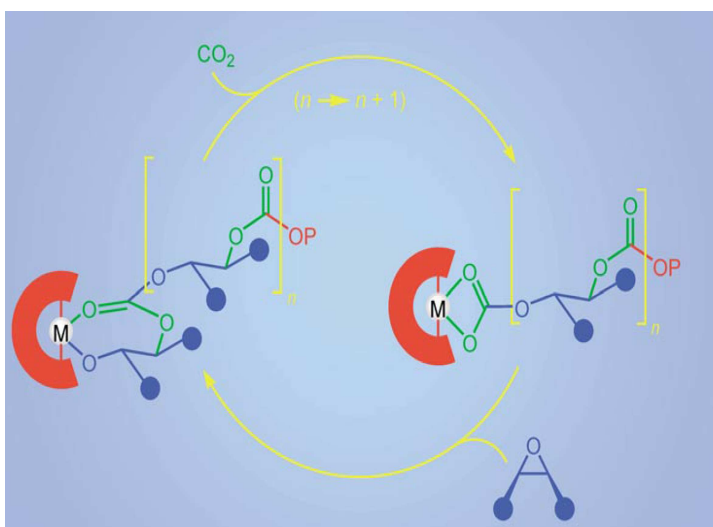


Making Plastics from Carbon Dioxide: Copolymerization of Epoxides and CO₂



Contents:

I Global warming

II Utilization of CO₂

III Copolymerization of epoxides and CO₂

a Background of copolymerization of epoxides and CO₂

b First example of copolymerization of epoxides and CO₂

c Salen metal complexes as catalysts

1 Cr salen complex

2 Co salen complex

d Zinc catalysts

1 Coates's β -diiminate zinc catalysts

2 Asymmetric copolymerization using zinc catalysts

IV Outlook

Review:

1 Chem. Rev. **2001**, *101*, 953.

2 Angew. Chem. Int. Ed. **2004**, *43*, 6618.

3 Chem. Rev. **2007**, *107*, 2388.

I Global warming!

Fig 1 sea-level rise caused by global warming

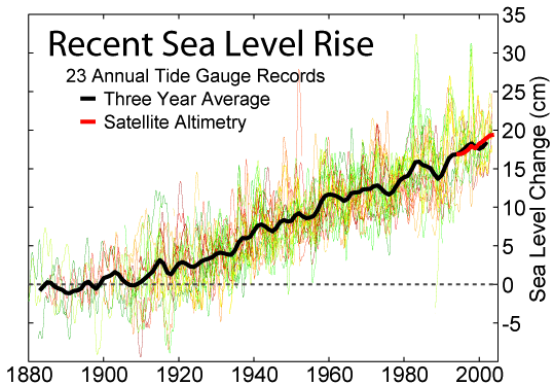
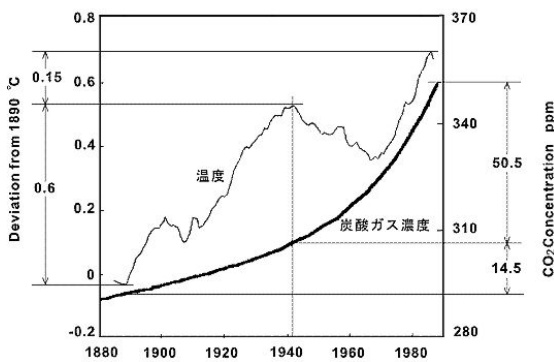


Fig 2: Desertification



Fig 3 The major reason of global warming



On the other hand, since petroleum resources are predicted to be exhausted within the next century at the current rate of consumption, there is a growing effort to develop new chemical processes using biorenewable resources. CO₂ is an abundant, inexpensive, and nontoxic biorenewable resource. CO₂ might be an attractive raw material!

II Utilization of CO₂

a Situation in Japan: 1997 Kyoto Protocol; 2008 TOYAKO Summit Conference.

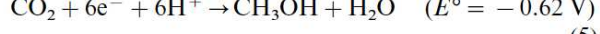
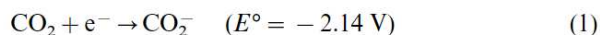
Fig 4 Immobilization of CO₂ in Japan

b Reduction of CO₂

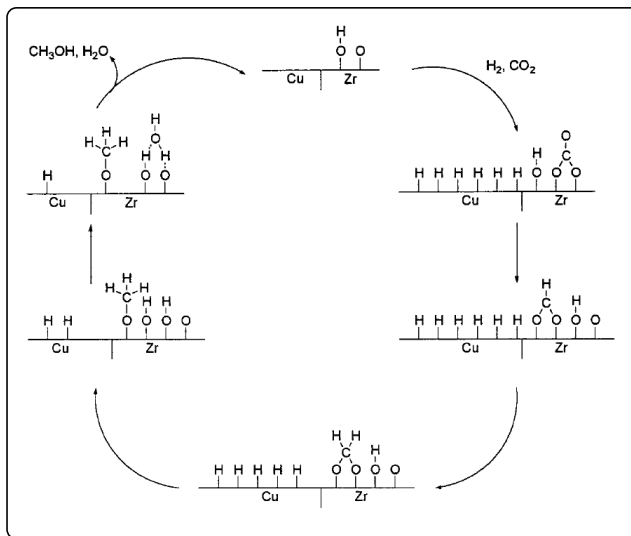
Methods:

Electrochemical reduction;
Metal-catalyzed hydrogenation;
Photochemical reduction and so on

Scheme 1 Example of electrochemical reduction:



Scheme 2 Example of metal catalyzed: Cu/ZrO₂ heterogeneous catalytic hydrogenation of CO₂ to methanol

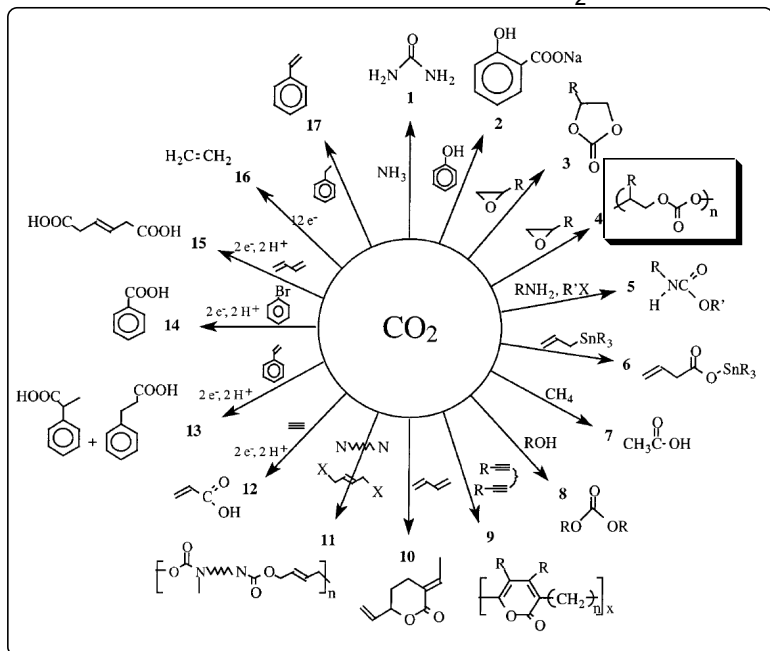


Example of chemical transformation of CO₂:

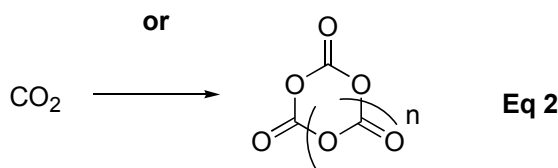
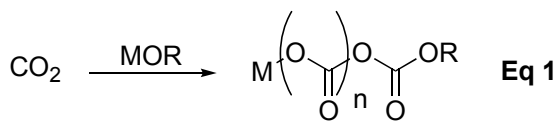
Mori miwako group, *JACS* 2002, 124, 10008.

c Chemical transformation of CO₂

Scheme 3 Chemical transformations of CO₂



One of the most efficient way to immobilize CO₂ is polymerization of CO₂

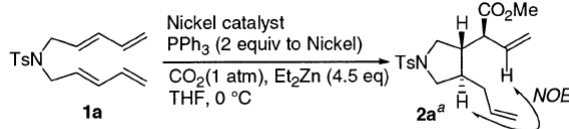


So far it is very difficult!

Today let me introduce copolymerization of epoxides and CO₂ to you.

Novel Catalytic CO₂ Incorporation Reaction: Nickel-Catalyzed Regio- and Stereoselective Ring-Closing Carboxylation of Bis-1,3-dienes

Scheme 4 Ni-catalyzed ring-closing carboxylation

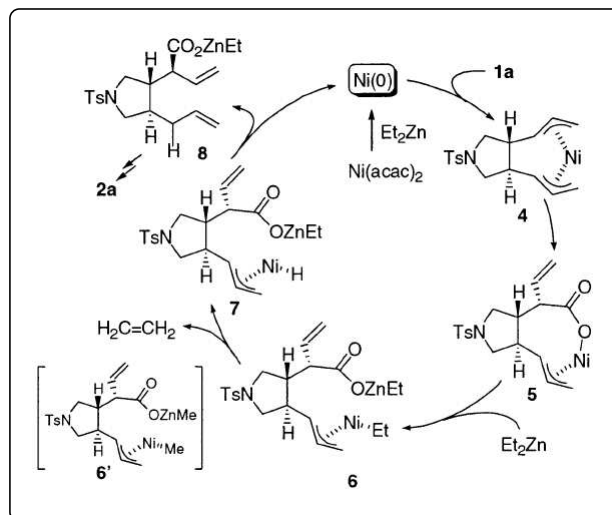


catalyst (mol %) time (h) yield (%)

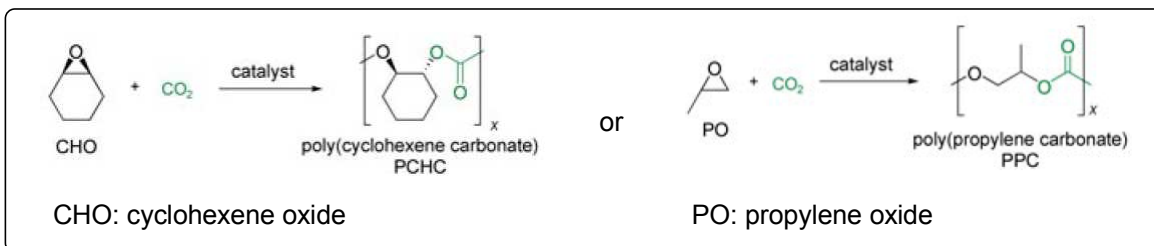
Ni(cod) ₂ (20)	3.5	75
Ni(acac) ₂ (5)	24	72

^a The product was isolated and characterized after treatment with diazomethane.

Scheme 5 Possible reaction mechanism

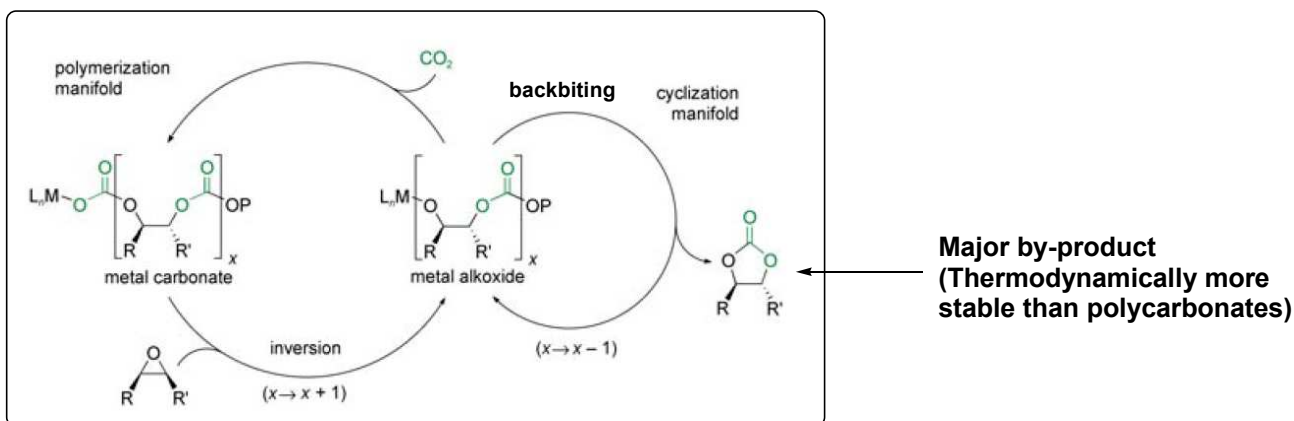


III Copolymerization of epoxides and CO₂

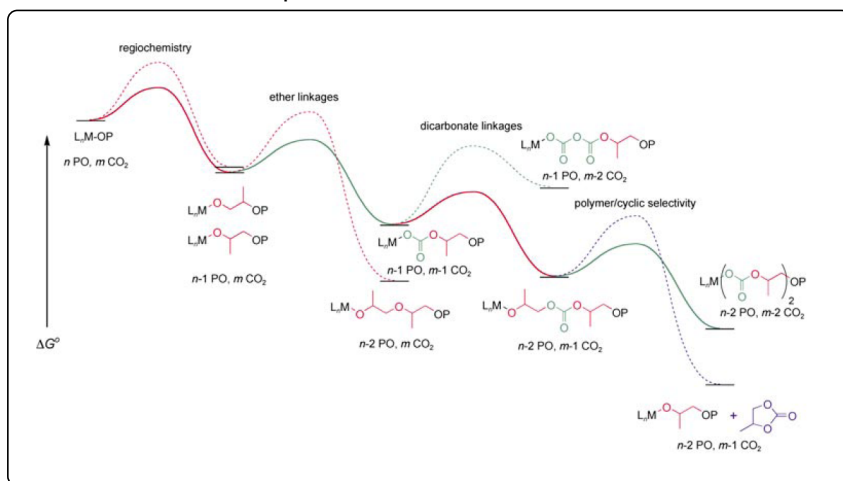


a Background of copolymerization of epoxides and CO₂

Scheme 6 The basic mechanism of epoxide and CO₂ copolymerization and the formation of cyclic carbonates

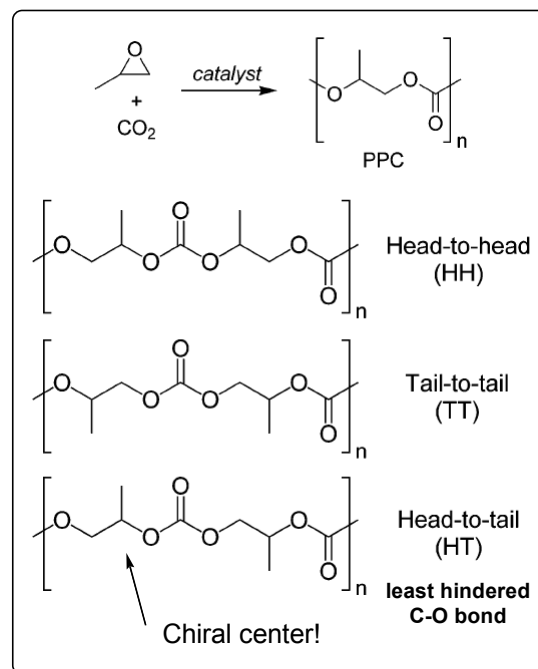


Scheme 7 Qualitative, ideal free-energy profile depicting alternating copolymerization of propylene oxide and CO₂, as well as potential side-reactions.



low temperature is better!

Scheme 8 Regiochemistry of PPC



Other key point of this reaction:

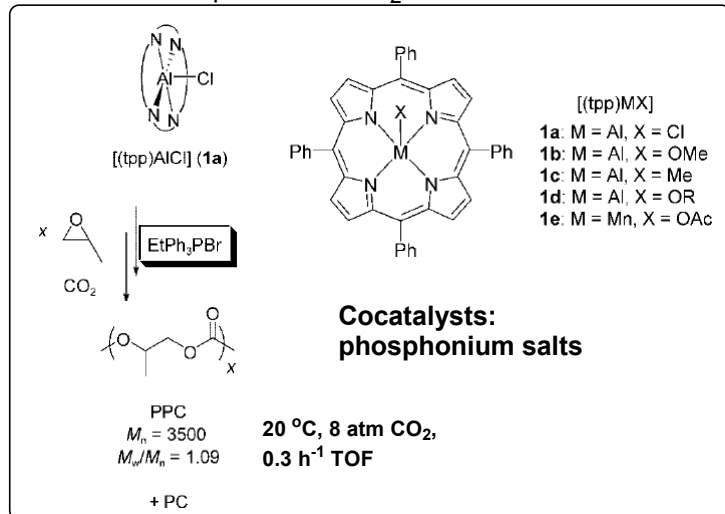
- 1 TOF
- 2 Pressure(CO₂)
- 3 temperature
- 4 M_n
- 5 M_w/M_n

b First example: Inoue group (aluminum catalysts)

Makromol. Chem. **1978**, *179*, 1377.

Macromolecules **1982**, *15*, 682.

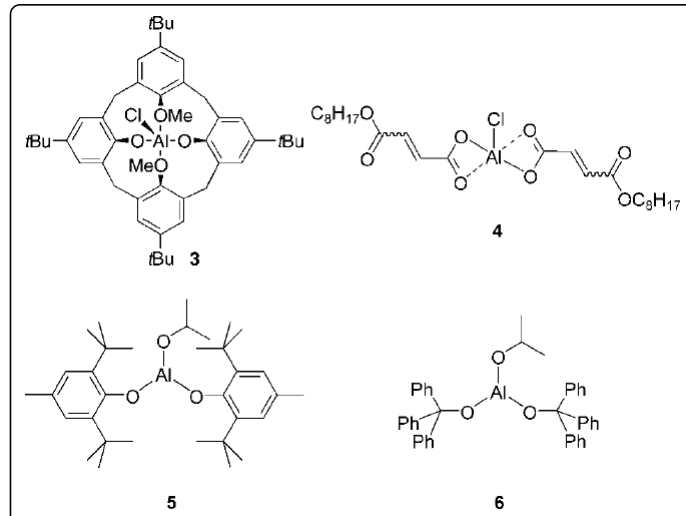
Scheme 9 Aluminum porphyrins for copolymerization of epoxide and CO₂



Scheme 10 Other aluminum catalysts:

3: Aluminum calix-4-arene (Kuran, 1998)

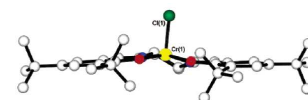
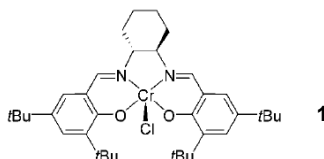
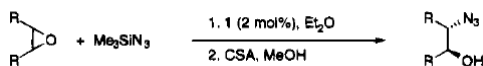
4,5,6: Aluminum alkoxides complex (Beckman, 1999, 2000)



C Salen metal complex:

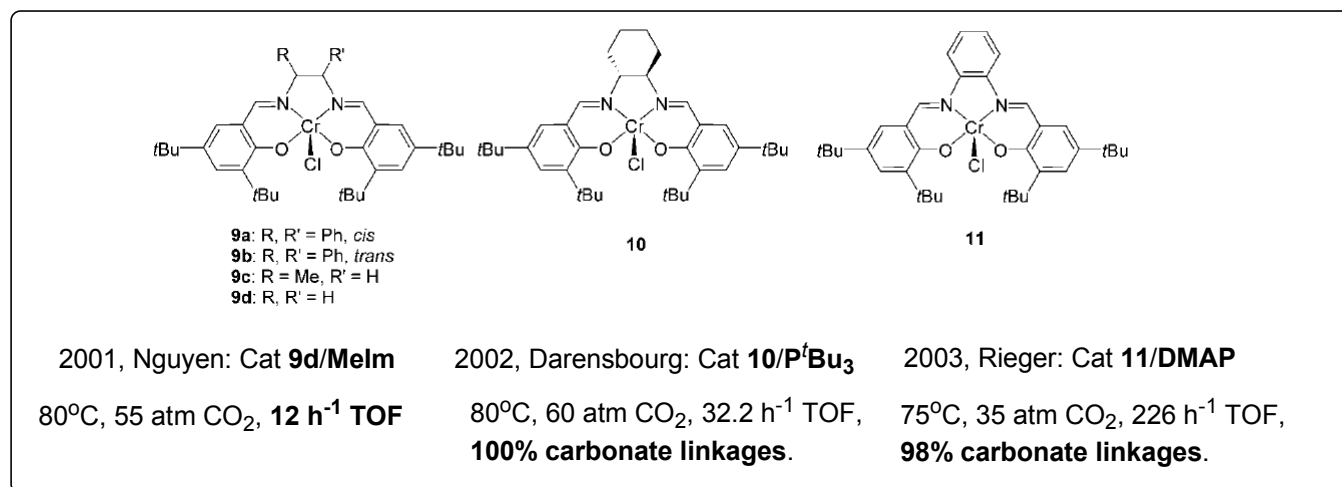
1 Cr Salen complex

i Jacobsen group: *JACS* **1995**, *117*, 5897.

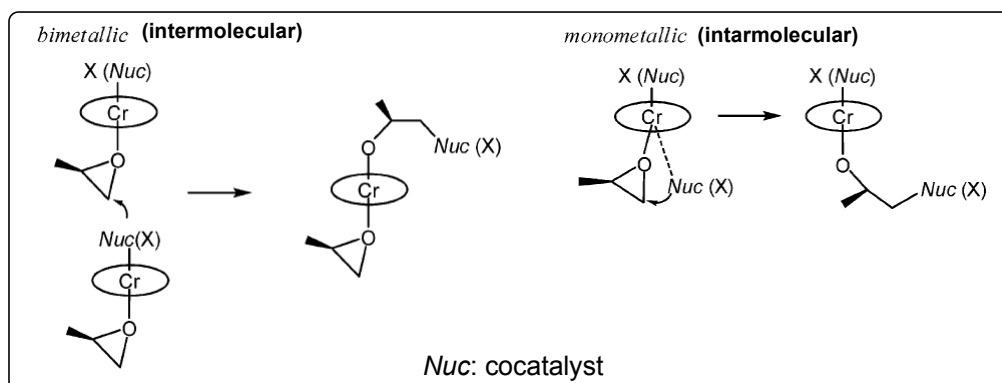


First example of copolymerization of Salen complex: Jacobsen *PCTInt. Appl.* WO00/09463, 2000.

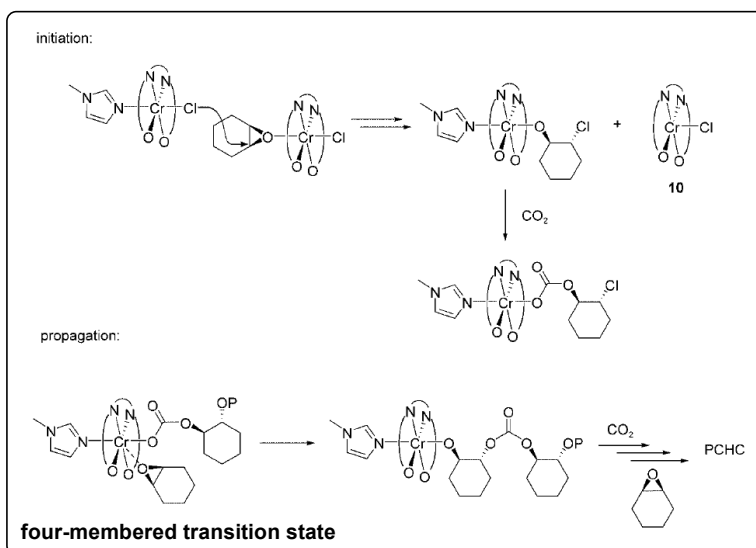
ii Other groups developed the salen complex system with cocatalysts:



iii Proposed mechanism with cocatalyst in the initiation step:



iv Intermolecular bimetallic pathway:

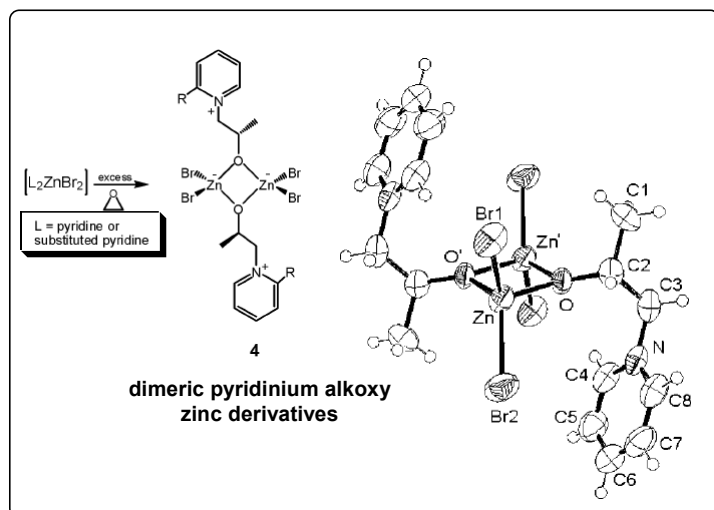


v Intarmolecular monometallic pathway:

Darensbourg; Chem. Rev. 2007, 107, 2388.

Scheme 11: X-ray structure of intermediate 4

Kim group; Angew. Chem. Int. Ed. 2000, 39, 4096.



Scheme 12: The case in Cr-salen/DMAP system

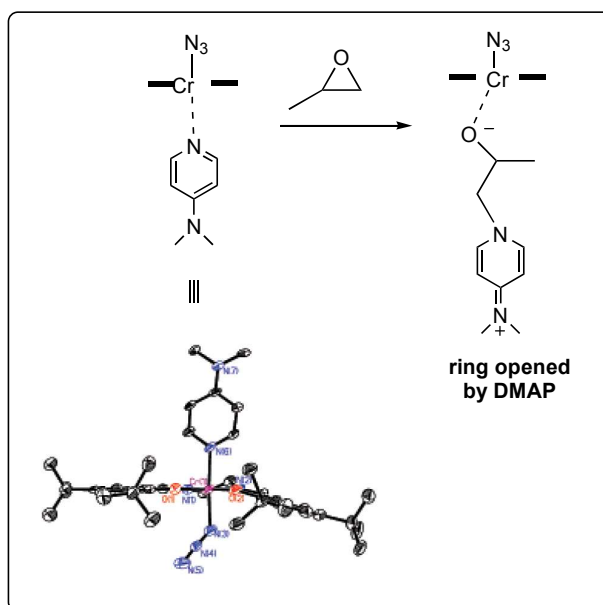
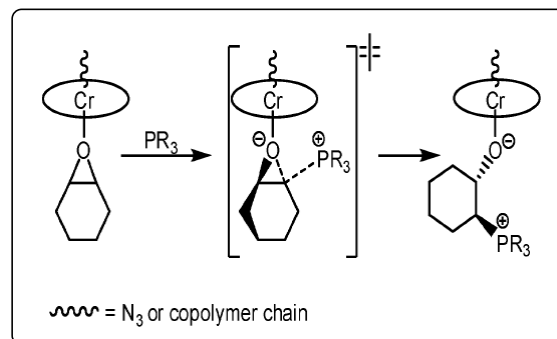


Table 1 Effect of various phosphines on the rate of copolymerization of cyclohexene oxide and CO₂ catalyzed by Cr Salen complex:

phosphine	cone angle (deg)	TON ^b	TOF ^c
P[C(CH ₃) ₃] ₃	182	1277	638
P(2,4,6-tri-CH ₃ OC ₆ H ₂) ₃	185	1417	354
P(C ₆ H ₁₁) ₃	170	1318	329
P(<i>p</i> -CH ₃ OC ₆ H ₄) ₃	145	1293	323
P(<i>o</i> -CH ₃ OC ₆ H ₄) ₃	153	1170	292
P(<i>p</i> -CH ₃ C ₆ H ₄) ₃	145	1301	325

Sterical phosphines are effective cocatalysts

Scheme 13 Activation of phosphines by formation of phosphonium zwitterions



vi Cocatalyst as a turning tools:

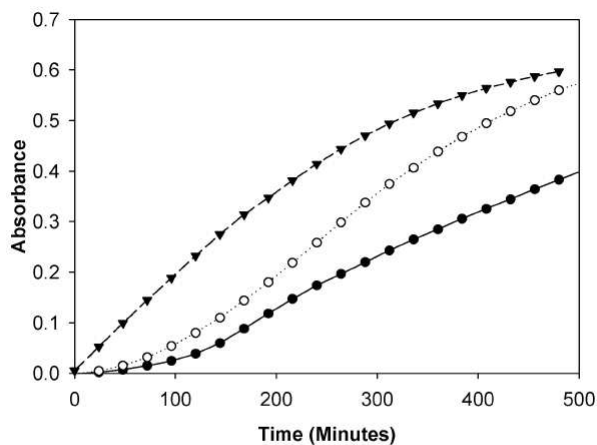
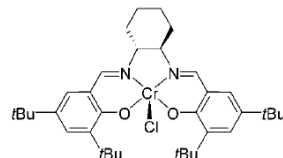
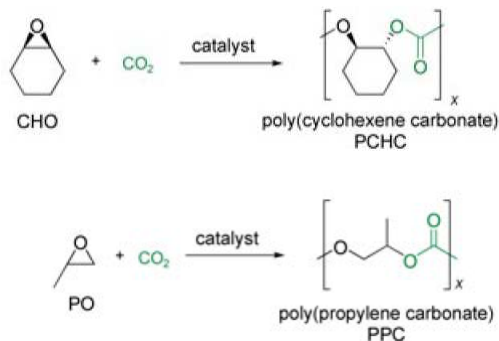


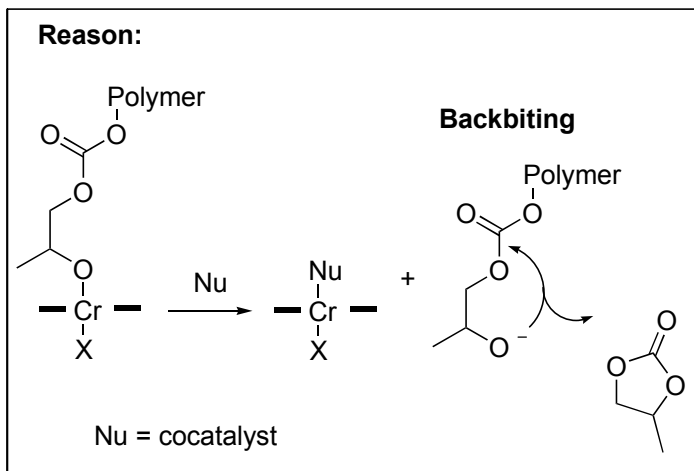
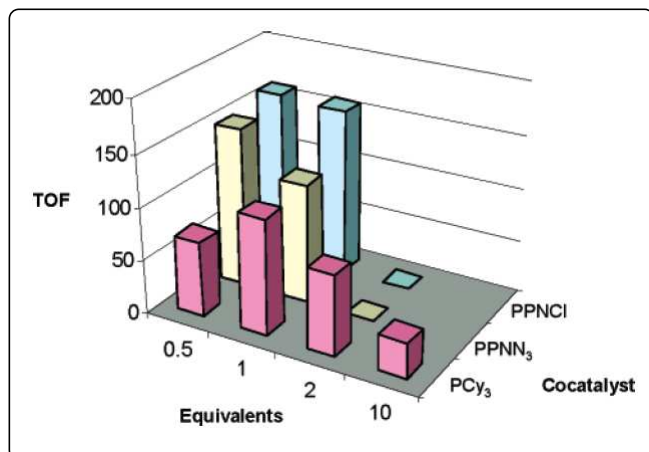
Figure 22. Comparison of in situ infrared profiles of copolymer production from CO₂ and cyclohexene oxide utilizing catalyst 1 and the three classes of cocatalysts: PPN⁺Cl⁻ (▼), PCy₃ (○), and *N*-MeIm (●).

Table 2 Catalytic activity in the presence of PPNX cocatalyst.

X	TOF ^b
N ₃	608
Cl	494
Br	420
I	360
OAc	350
HCO ₃	280

^a The carbonate content of all copolymers isolated was greater than 99%. ^b Mol of epoxide consumed/mol of catalyst h.

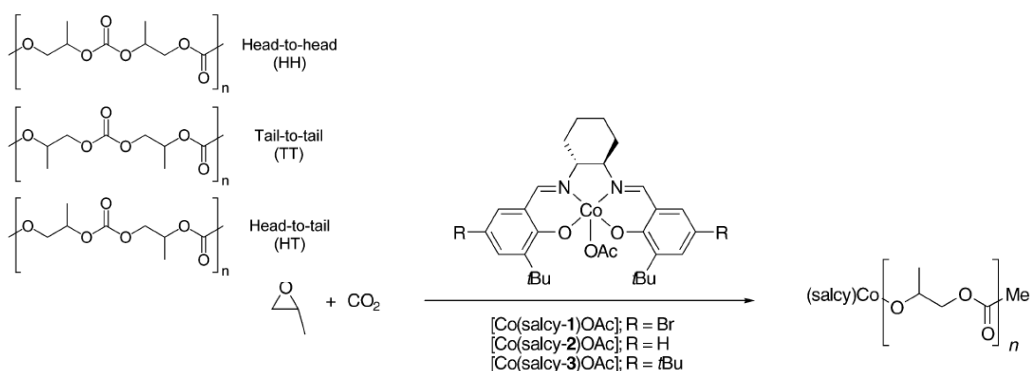
Fig 4: Cocatalyst loading



2 Co (III) Salen complex:

Competition of data in carbonate linkages, TOF, pressure, temperature and so on.

i 2003: Coates group (Co Salen complex only), *Angew. Chem. Int. Ed.* 2003, 42, 5484.

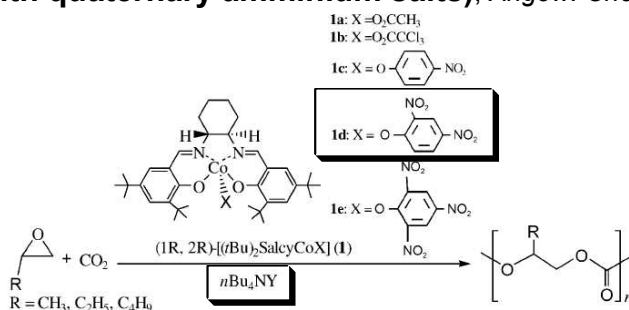


*** 1mPa = 145 psi**

Entry	Catalyst	Epoxide	[PO]:[Cat]	Pressure [psi]	Temp [°C]	Time [h]	TOF ^[b] [h ⁻¹]	Selectivity (% PPC) ^[c]	Carbonate Linkages [%] ^[c]	\bar{M}_n ^[d] [g mol ⁻¹]	PDI (\bar{M}_w/\bar{M}_n)
1	[Co(salcy-1)OAc]	rac-PO	500	800	25	3	81	>99	95	15 300	1.22
2	[Co(salcy-1)OAc]	rac-PO	500	600	25	3	19	>99	94	3100	2.60
3	[Co(salcy-1)OAc]	rac-PO	500	800	40	3	17	>99	90	5600	1.21
4	[Co(salcy-1)OAc]	rac-PO	500	800	30	3	69	>99	94	12 200	1.26
5	[Co(salcy-1)OAc]	rac-PO	500	800	20	3	42	>99	95	8000	1.44
6	[Co(salcy-1)OAc]	rac-PO	500	800	15	3	31	>99	95	7600	1.51
7	[Co(salcy-1)OAc]	rac-PO	200	800	25	3	51	>99	95	8200	1.25
8	[Co(salcy-1)OAc]	rac-PO	2000	800	25	8	38	>99	95	21 700	1.41
9	[Co(salcy-2)OAc]	rac-PO	200	800	25	3	51	>99	96	6600	1.21
10	[Co(salcy-2)OAc]	rac-PO	500	800	25	3	66	>99	96	9000	1.31
11	[Co(salcy-3)OAc]	rac-PO	200	800	25	3	42	>99	99	5700	1.28
12	[Co(salcy-3)OAc]	rac-PO	500	800	25	3	59	>99	99	8100	1.57
13	[Co(salcy-3)OAc]	(S)-PO	500	800	25	3	71	>99	99	6900	1.58
14 ^[e]	[Zn(BDI)OAc]	rac-PO	2000	300	25	2	184	87	99	35 900	1.11
15 ^[f]	[Cr(salph)Cl]	rac-PO	1500	490	75	4	160	71	98	16 700	1.38

[a] All of the polymerizations were carried out in 3.5 mL of neat propylene oxide (PO). [b] Turnover frequency of PO to PPC. [c] Determined by using ¹H NMR spectroscopy. [d] Determined by gel permeation chromatography in tetrahydrofuran at 40°C, calibrated with polystyrene standards. [e] Reference [14]. [f] Reference [16].

ii 2004: Lu group (with quaternary ammonium salts), *Angew. Chem. Int. Ed.* 2004, 43, 3574.



Entry	1	Y	Epoxide	t [h]	P [MPa]	TOF ^[b] [h ⁻¹]	Selectivity ^[c] [% PPC]	Carbonate linkages [%] ^[d]	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	23 500	1.29	3.2
4	d	Cl	PO	3	2.0	257	99	>99	30 400	1.36	3.4
5	d	I	PO	3	2.0	272	69	>99	22 100	1.34	2.8
6	d	OAc	PO	3	2.0	167	99	>99	18 200	1.23	3.1
7	c	Cl	PO	3	2.0	185	96	>99	21 000	1.48	2.9
8	e	Cl	PO	3	2.0	248	99	>99	27 500	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]	— ^[f]
11	d	Cl	PO	3	0.2	130	98	>99	18 200	1.29	3.2
12	d	Cl	PO	3	0.4	190	99	>99	28 300	1.31	3.5
13	d	Cl	PO	3	1.0	243	99	>99	29 900	1.41	3.3
14	d	Cl	PO	3	4.0	219	99	>99	28 700	1.42	3.3
15	d	Cl	PO	3	6.0	173	99	>99	25 500	1.33	3.4
16 ^[g]	d	Cl	PO	3	4.0	371	99	>99	24 000	1.37	2.8
17	d	Cl	1,2-BuO ^[h]	6	2.0	61	99	>99	11 600	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 ¹H 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.

iii 2006: Nozaki group (with a piperidinium end-capping arm)

Angew. Chem. Int. Ed. **2006**, *45*, 7274.

Scheme 14 Catalyst design to suppress the production of cyclic carbonate

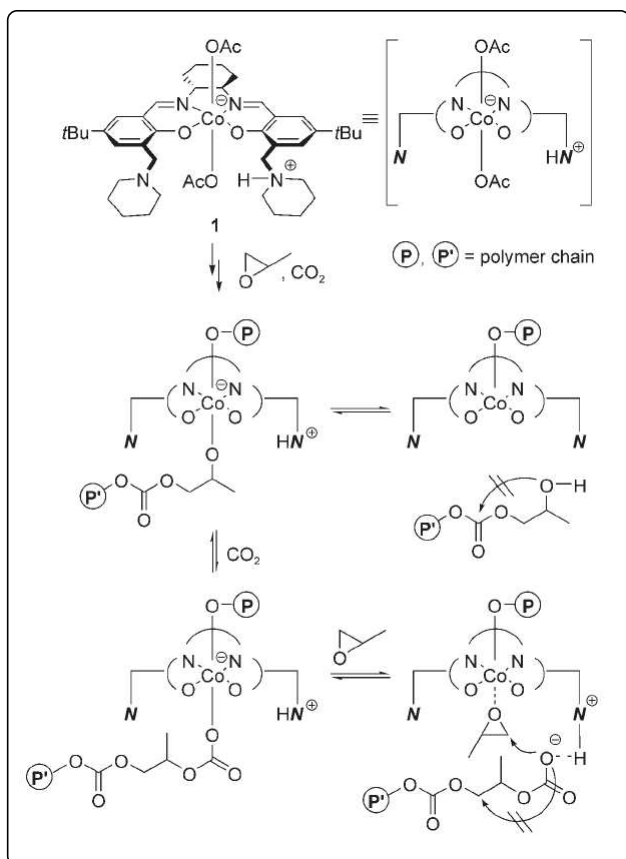
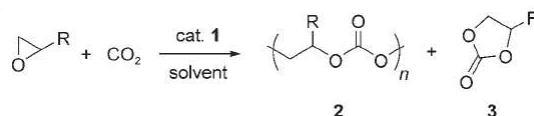


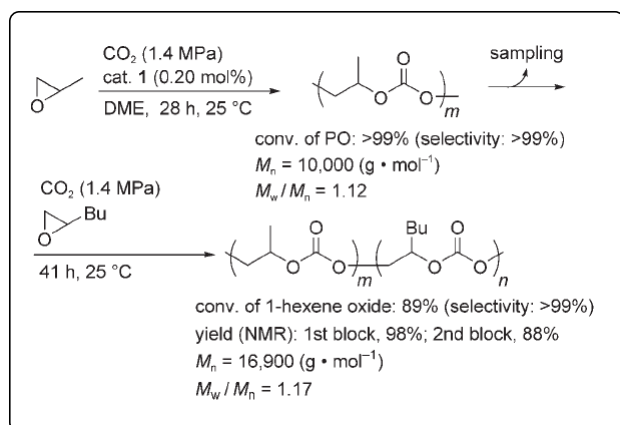
Table 3: Copolymerization of epoxides with CO_2 catalyzed by cobalt complex **1**



Entry	R	Solvent	t [h]	Yield of 2+3 [%] ^[b]	2/3 ^[b]	M_n [g mol ⁻¹] ^[d]	M_w/M_n ^[c]
1	Me	—	3	38	99:1	12 600	1.13
2	Me	—	12	77	99:1	23 900	1.14
3	Me	—	116	79	96:4	83 700	1.28
4	Me	—	1	34	90:10	7100	1.22
5	Me	DME	6	53	99:1	13 200	1.10
6	Me	DME	48	>99	97:3	26 500	1.10
7 ^[d]	Me	DME	20	95	95:5	5100	1.06
8	Et	DME	48	89	97:3	31 000	1.12
9	Bu	DME	48	89	98:2	34 300	1.14

[a] Reaction conditions: epoxide (14.3 mmol in entries 1, 2, and 4–9; 47.2 mmol in entry 3), **1** (epoxide/**1** = 2000 in entries 1, 2, and 4; 6500 in entry 3; 1000 in entries 5–9), CO_2 (initial pressure: 1.4 MPa), DME (1.0 mL in entries 5–9), at 25 °C (entries 1–3 and 5–9) or 60 °C (entry 4).
 [b] Determined on the basis of ^1H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] Determined by size-exclusion chromatography analysis using a polystyrene standard. [d] Methanol (20 equivalents based on **1**) was added.

Scheme 15: Synthesis of a block terpolymer



d Zinc catalysts:

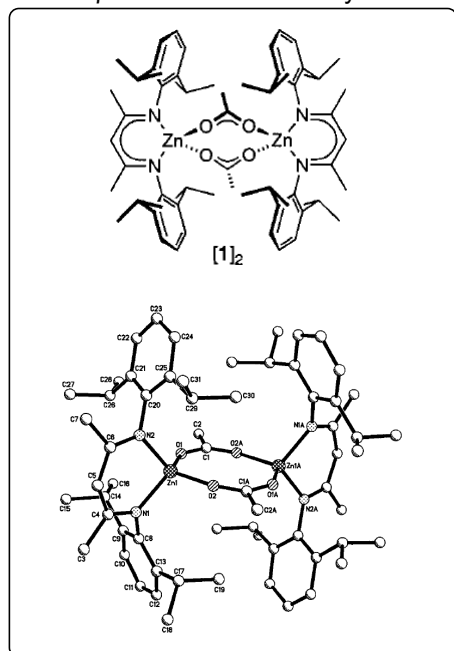
1 Coates' s β -diiminate zinc catalysts

i High-activity Zn(II)-based catalysts for the copolymerization of CO_2 and cyclohexene oxide.

JACS 1998, 120, 11018.

JACS 2001, 123, 8738.

Scheme 16 X-ray crystal structure of the dimer of β -diiminate zinc catalyst **1**



Scheme 17 Synthesis of β -diiminate zinc catalyst

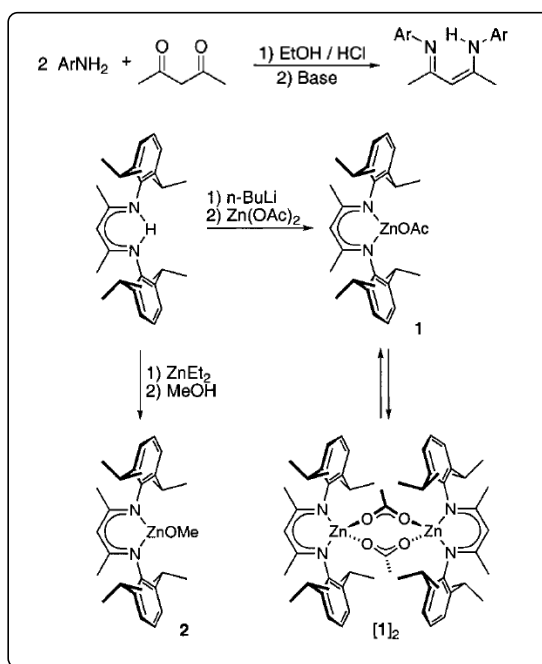


Table 4 Results of copolymerization of CO_2 and cyclohexene oxide

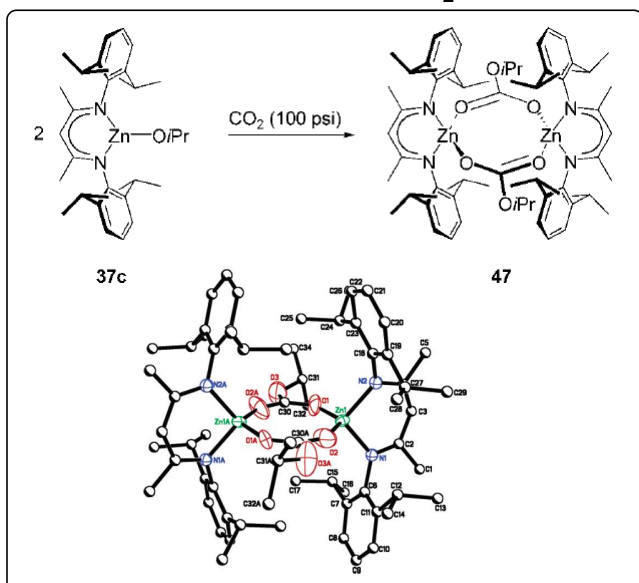
catalyst	temp (°C)	pressure (psig)	reaction length (h)	% carbonate linkages	M_n ($\times 10^{-3}$) (GPC)	M_w/M_n (GPC)	TON ^b	TOF ^c (h^{-1})
1	20	100	2	95	21.3	1.07	270	135
1	50	100	2	96	31.0	1.11	494	247
1	80	100	2	95	25.7	1.17	412	206
2	50	100	2	95	19.1	1.07	449	224
3^d	80	800	69	91	38.0	4.5	173	2.5
4^e	100	2000	24	93	17.0	6.4	216	9.0

^a All of the reactions were performed in neat CHO. ^b Moles of CHO consumed per mole of zinc. ^c Moles of CHO consumed per mole of zinc per hour. ^d Data from ref 12 for $(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{Zn}(\text{Et}_2\text{O})_2$ (**3**). ^e Data from ref 13 for $\text{HO}_2\text{CCH}=\text{CHCO}_2(\text{CH}_2)_2\text{C}_6\text{F}_{13}/\text{ZnO}$ (**4**).

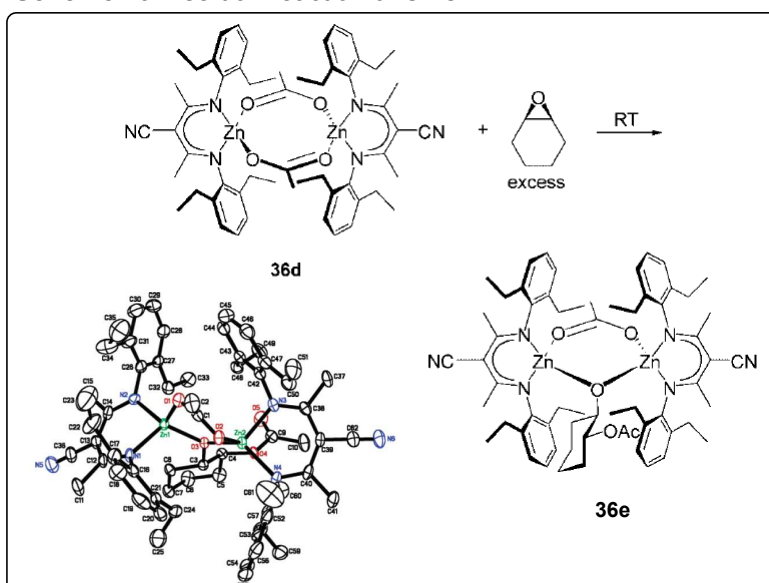
ii Proposed copolymerization mechanism using β -diiminate zinc catalyst:

JACS 2003, 125, 11911.

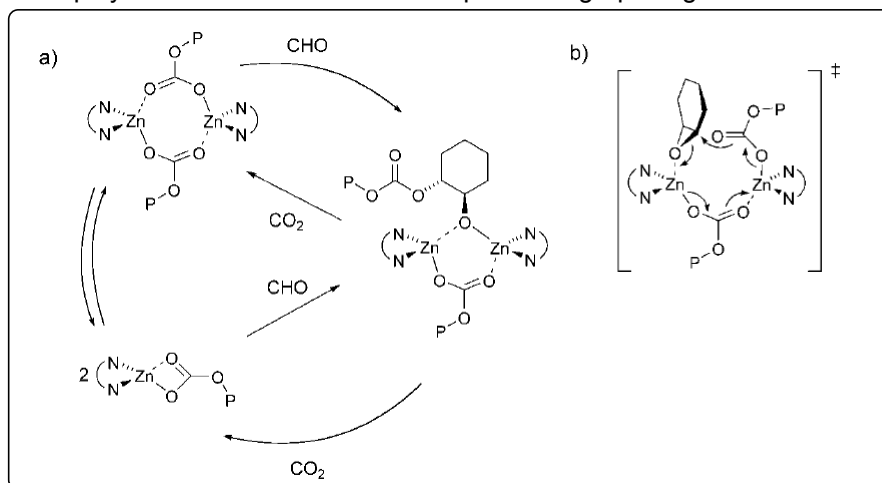
Scheme 18 Insertion reaction of CO_2



Scheme 19 Insertion reaction of CHO

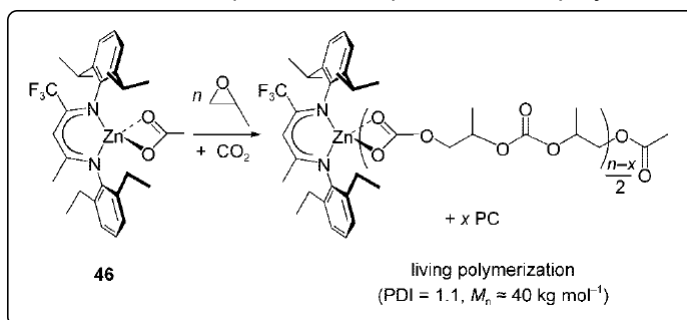


Scheme 20 Proposed copolymerization mechanism and epoxide ring-opening transition state:



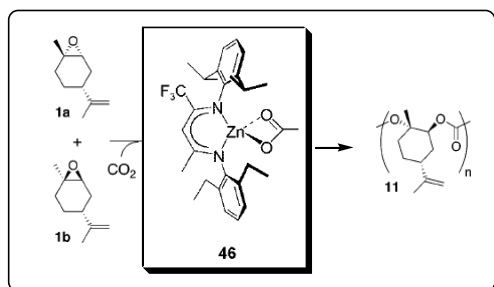
Scheme 21 Unsymmetrical, electron-deficient β -di-zinc complex for the copolymerization of **propylene oxide** and CO_2

JACS 2002, 124, 14284.

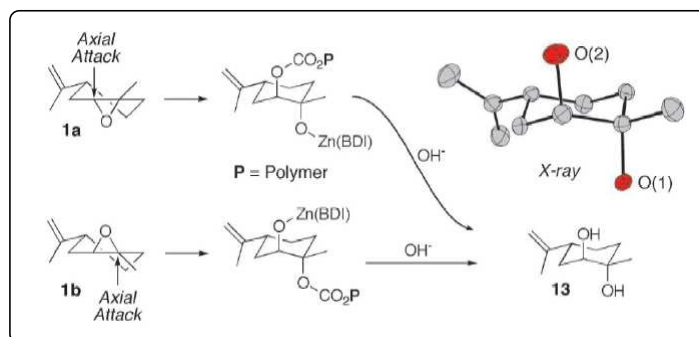


Scheme 22 Alternating copolymerization of **limonene oxide** and carbon CO_2

JACS 2004, 126, 11404.



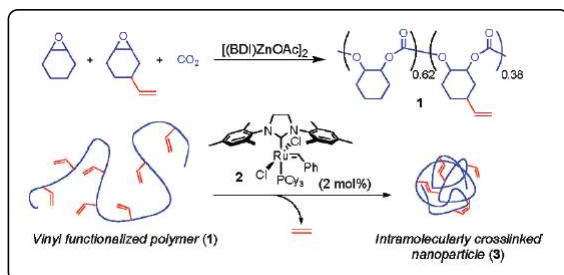
Scheme 23 Ring opening of **1a** and **1b** during copolymerization and hydrolytic cleavage to give diaxial diol **13**



iii Formation of nanoparticles by intramolecular cross-linking: following the reaction progress of single polymer chains

JACS 2007, 129, 11350.

Scheme 24 Synthesis of alkene cross-linked polycarbonate nanoparticles



entry	time (h)	M_n^b (g/mol)	M_w/M_n^b	% vinyls cross-linked ^c	T_g^d (°C)
1	0	54 100	1.20	0	114
2	0.25	45 700	1.34	42	157
3	0.50	39 500	1.26	59	167
4	2.0	33 000	1.19	70	185
5	4.0	31 500	1.19	76	194

^a All reactions were run with 2 mol % of Ru catalyst at 22 °C with 1.0 mg polymer/mL toluene. ^b Determined by GPC in THF at 40 °C versus polystyrene standards. ^c Determined by ¹H NMR spectroscopy. ^d Determined by differential scanning calorimetry (second heat).

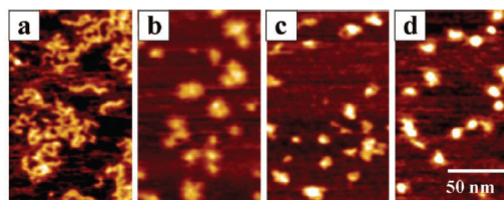
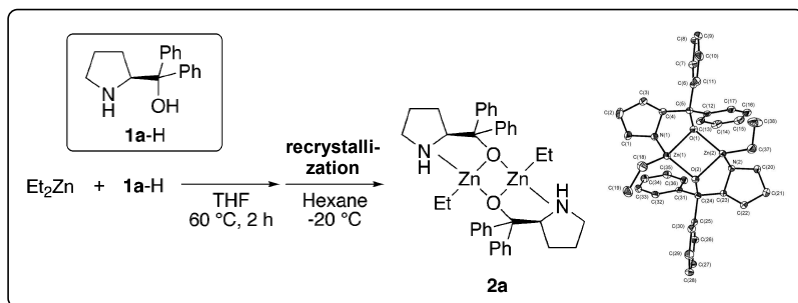


Figure 1. AFM height images for the nanoparticles in Table 1: (a) entry 1, (b) entry 2, (c) entry 3, (d) entry 5. (e) The plot presents the square of

2 Zinc catalysts for asymmetric CHO-CO₂ copolymerization

i Nozaki Group: *JACS* 1998, 121, 11008.

Scheme 25 Synthesis of complex 2a and its structure



Scheme 26 Asymmetric alternating copolymerization of CHO and CO₂

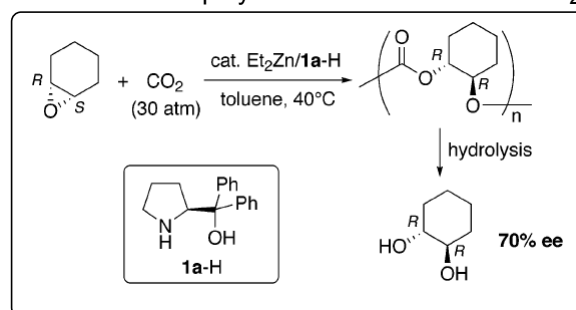
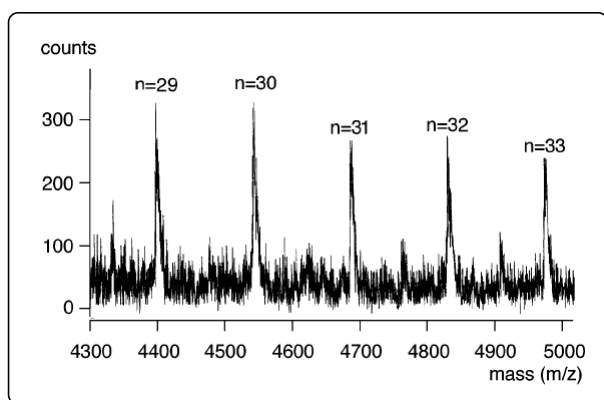
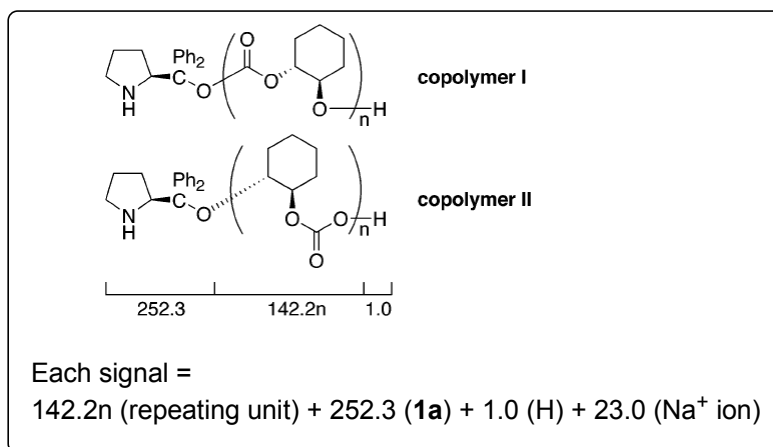


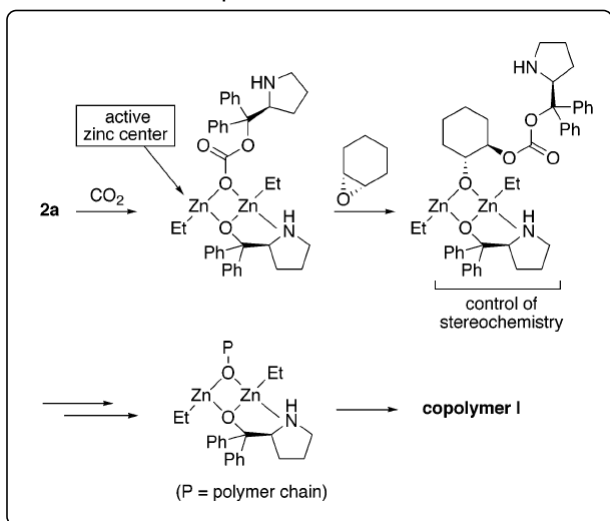
Fig 5 MALDI-TOF mass spectrum to determine the end group



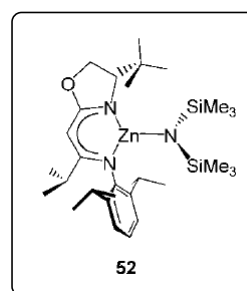
Scheme 27 Proposed structure of copolymerization



Scheme 28 Proposed mechanism



ii Coates group: *Chem. Commun.* 2000, 2007.



IV Outlook:

Remained task:

- 1 Completely controlled asymmetric CHO-CO₂ copolymerization
- 2 Polymerization of CO₂

