Making Plastics from Carbon Dioxide: Copolymerization of Epoxides and CO₂

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III Copolymerization of epoxides and CO₂
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      1  Cr salen complex
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   d Zinc catalysts
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IV  Outlook

Review:

2008/3/12, Z. Chen (D1)
I Global warming!

Fig 1 sea-level rise caused by global warming

![Recent Sea Level Rise](image)

23 Annual Tide Gauge Records
- Three Year Average
- Satellite Altimetry

1880 1900 1920 1940 1960 1980 2000

Fig 2: Desertification

![Desertification](image)

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 3 The major reason of global warning

![The major reason of global warning](image)

Let's concentrate on immobilization of CO₂ by chemical methods!
b Reduction of CO$_2$

**Methods:**
- Electrochemical reduction;
- Metal-catalyzed hydrogenation;
- Photochemical reduction and so on

**Scheme 1** Example of electrochemical reduction:

\[
\begin{align*}
\text{CO}_2 + e^- &\rightarrow \text{CO} (E^0 = -2.14 \text{ V}) \\
\text{CO}_2 + 2e^- + 2\text{H}^+ &\rightarrow \text{HCOOH} (E^0 = -0.85 \text{ V}) \\
\text{CO}_2 + 2e^- + 2\text{H}^+ &\rightarrow \text{CO} + \text{H}_2\text{O} (E^0 = -0.76 \text{ V}) \\
\text{CO}_2 + 4e^- + 4\text{H}^+ &\rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O} (E^0 = -0.72 \text{ V}) \\
\text{CO}_2 + 6e^- + 6\text{H}^+ &\rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} (E^0 = -0.62 \text{ V}) \\
\text{CO}_2 + 8e^- + 8\text{H}^+ &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} (E^0 = -0.48 \text{ V})
\end{align*}
\]

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c Chemical transformation of CO$_2$

**Scheme 3** Chemical transformations of CO$_2$

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**Scheme 2** Example of metal catalyzed:
Cu/ZrO$_2$ heterogeneous catalytic hydrogenation of CO$_2$ to methanol

**Scheme 4** Ni-catalyzed ring-closing carboxylation of Bis-1,3-dienes

**Scheme 5** Possible reaction mechanism

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One of the most efficient way to immobilize CO$_2$ is polymerization of CO$_2$

**Eq 1**

\[
\text{CO}_2 \xrightarrow{\text{MOR}} \text{M(\text{O})\text{O\text{OR}}} \quad \text{Eq 1}
\]

**Eq 2**

\[
\text{CO}_2 \xrightarrow{} \text{O\text{O\text{OR}}} \quad \text{Eq 2}
\]

So far it is very difficult! Today let me introduce copolymerization of epoxides and CO$_2$ to you.
III Copolymerization of epoxides and CO$_2$

CHO: cyclohexene oxide
PO: propylene oxide

a Background of copolymerization of epoxides and CO$_2$

**Scheme 6** The basic mechanism of epoxide and CO$_2$ copolymerization and the formation of cyclic carbonates.

**Scheme 7** Qualitative, ideal free-energy profile depicting alternating copolymerization of propylene oxide and CO$_2$, as well as potential side-reactions.

**Scheme 8** Regiochemistry of PPC

Other key point of this reaction:
1 TOF
2 Pressure(CO$_2$)
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 CO$_2$

C Cocatalysts: phosphonium salts

$\begin{align*}
\text{CPC} \\
M_4 = 3500 \\
M_r/M_n = 1.09
\end{align*}$

20 °C, 8 atm CO$_2$
0.3 h$^{-1}$ TOF

C Salen metal complex:
1 Cr Salen complex


ii Other groups developed the salen complex system with cocatalysts:

2001, Nguyen: Cat 9d/Melm
80°C, 55 atm CO$_2$, 12 h$^{-1}$ TOF

2002, Daresbourg: Cat 10/P$^3$Bu$_3$
80°C, 60 atm CO$_2$, 32.2 h$^{-1}$ TOF, 100% carbonate linkages.

2003, Rieger: Cat 11/DMAP
75°C, 35 atm CO$_2$, 226 h$^{-1}$ TOF, 98% carbonate linkages.

iii Proposed mechanism with cocatalyst in the initiation step:

$\text{Nuc}: \text{cocatalyst}$
iv Intermolecular bimetallic pathway:

![Diagram of bimetallic pathway with equations and structures]

v Intermolecular monometallic pathway:

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

**Scheme 11**: X-ray structure of intermediate 4

![Diagram of intermediate 4 with structure and bond angles]

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

![Diagram of Cr-salen/DMAP system with structures and bond angles]

**Scheme 13**: Activation of phosphines by formation of phosphonium zwitterion

![Diagram of phosphonium zwitterion formation with structures and bond angles]

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

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Cone angle (deg)</th>
<th>TONb</th>
<th>TOFc</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[(CH₂)₃]₁</td>
<td>182</td>
<td>1277</td>
<td>638</td>
</tr>
<tr>
<td>P(2,4,6-tri-CH₃OC₆H₄)</td>
<td>185</td>
<td>1417</td>
<td>354</td>
</tr>
<tr>
<td>P(C₆H₅H₃)</td>
<td>170</td>
<td>1318</td>
<td>329</td>
</tr>
<tr>
<td>P(p-CH₃OC₆H₄)</td>
<td>145</td>
<td>1293</td>
<td>323</td>
</tr>
<tr>
<td>P(o-CH₃OC₆H₄)</td>
<td>145</td>
<td>1170</td>
<td>292</td>
</tr>
<tr>
<td>P(p-CH₃C₆H₄)</td>
<td>145</td>
<td>1301</td>
<td>325</td>
</tr>
</tbody>
</table>

Sterical phosphines are effective cocatalysts

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74x11
vi Cocatalyst as a turning tools:

\[
\begin{align*}
\text{CHO} + \text{CO}_2 & \xrightarrow{\text{catalyst}} \text{poly(cyclohexene carbonate)} \\
\text{PO} + \text{CO}_2 & \xrightarrow{\text{catalyst}} \text{poly(propylene carbonate)}
\end{align*}
\]

**Table 2** Catalytic activity in the presence of PPNX cocatalyst.

<table>
<thead>
<tr>
<th>X</th>
<th>TOF (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>608</td>
</tr>
<tr>
<td>Cl</td>
<td>494</td>
</tr>
<tr>
<td>Br</td>
<td>420</td>
</tr>
<tr>
<td>I</td>
<td>360</td>
</tr>
<tr>
<td>OAc</td>
<td>350</td>
</tr>
<tr>
<td>HCO(_3)</td>
<td>280</td>
</tr>
</tbody>
</table>

\(^{a}\) 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.

Scheme 14 Catalyst design to suppress the production of cyclic carbonate

Table 3: Copolymerization of epoxides with CO$_2$ catalyzed by cobalt complex 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Solvent</th>
<th>t [h]</th>
<th>Yield of 2 + 3 [%]$^a$</th>
<th>2/3$^b$</th>
<th>$M_n$ [g mol$^{-1}$]$^c$</th>
<th>$M_w/M_n$$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>=</td>
<td>3</td>
<td>38</td>
<td>99:1</td>
<td>12 600</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>=</td>
<td>12</td>
<td>77</td>
<td>99:1</td>
<td>23 900</td>
<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>=</td>
<td>116</td>
<td>79</td>
<td>96:4</td>
<td>83 700</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>=</td>
<td>1</td>
<td>34</td>
<td>90:10</td>
<td>71 000</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>DME</td>
<td>6</td>
<td>53</td>
<td>99:1</td>
<td>13 000</td>
<td>1.10</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>DME</td>
<td>48$^d$</td>
<td>&gt;99</td>
<td>97:3</td>
<td>26 500</td>
<td>1.10</td>
</tr>
<tr>
<td>7$^d$</td>
<td>Me</td>
<td>DME</td>
<td>20</td>
<td>95</td>
<td>95:5</td>
<td>51 000</td>
<td>1.06</td>
</tr>
<tr>
<td>8</td>
<td>Et</td>
<td>DME</td>
<td>48$^d$</td>
<td>89</td>
<td>97:3</td>
<td>31 000</td>
<td>1.12</td>
</tr>
<tr>
<td>9</td>
<td>Bu</td>
<td>DME</td>
<td>48$^d$</td>
<td>89</td>
<td>98:2</td>
<td>34 300</td>
<td>1.14</td>
</tr>
</tbody>
</table>

[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 $^1$H 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 CO₂ and cyclohexene oxide.

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 CO₂ and cyclohexene oxide

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

$^a$ 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-Ph₂C₆H₄O)₂Zn(Et₂O)₂ (3). $^e$ Data from ref 13 for HO₂CH=CHC=CH₂C₆H₄F₁₉ZnO (4).

ii Proposed copolymerization mechanism using β-diiminate zinc catalyst:

Scheme 18 Insertion reaction of CO₂

Scheme 19 Insertion reaction of CHO
Scheme 20 Proposed copolymerization mechanism and epoxide ring-opening transition state:

![Scheme 20](image)

Scheme 21 Unsymmetrical, electron-deficient β-di-zinc complex for the copolymerization of propylene oxide and CO₂

Scheme 22 Alternating copolymerization of limonene oxide and carbon CO₂

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

Scheme 24 Synthesis of alkene cross-linking polycarbonate nanoparticles

**Table 1**

<table>
<thead>
<tr>
<th>entry</th>
<th>time (h)</th>
<th>Mₖ (g/mol)</th>
<th>Mₛ/Mₖ</th>
<th>% vinyls cross-linked</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>54 100</td>
<td>1.20</td>
<td>0</td>
<td>114</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>45 700</td>
<td>1.14</td>
<td>42</td>
<td>157</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>39 500</td>
<td>1.26</td>
<td>59</td>
<td>167</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>33 000</td>
<td>1.19</td>
<td>70</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>31 500</td>
<td>1.19</td>
<td>76</td>
<td>194</td>
</tr>
</tbody>
</table>

* All reactions were run with 2 mol % of Ru catalyst at 22 °C with 1.0 mg polymer/mL toluene. * Determined by GPC in THF at 40 °C versus polystyrene standards. * Determined by ¹H NMR spectroscopy. * 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-CO\(_2\) copolymerization


Scheme 25 Synthesis of complex 2a and its structure

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

Scheme 26 Asymmetric alternating copolymerization of CHO and CO\(_2\)

Scheme 27 Proposed structure of copolymerization

Each signal = 142.2n (repeating unit) + 252.3 (1a) + 1.0 (H) + 23.0 (Na\(^+\) ion)


Scheme 28 Proposed mechanism

IV Outlook:
Remained task:
1 Completely controlled asymmetric CHO-CO\(_2\) copolymerization
2 Polymerization of CO\(_2\)

Metal Salen complex
(Efficient catalysts for copolymerization of epoxides and CO\(_2\))

Bimetallic Schiff base complex

How about?