

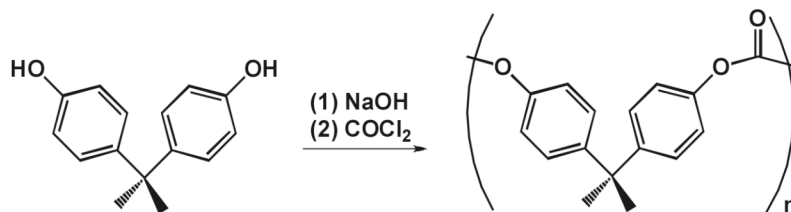
# The Copolymerization of CO<sub>2</sub> and Epoxides by Salen-Derived Complexes: A Mechanistic Investigation

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Literature Seminar

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Polycarbonates are widely used as biodegradable plastics and plasticizers. They are transparent, heat-resistant, strong, and electrically insulating.<sup>1</sup> The polycarbonate most widely used in commercial applications is bisphenol A polycarbonate, which is marketed as LEXAN, CALIBRE, MAKROLON, and PANLITE. Typically polycarbonates are used when cheaper polyolefins do not perform well. Bisphenol A polycarbonate costs ~\$1.30/lb whereas most polyolefins are ~\$0.70/lb.<sup>2</sup> Industrially, bisphenol A polycarbonate is made by deprotonation of bisphenol A, followed by copolymerization with phosgene (Scheme 1). There is much current interest in the metal-catalyzed copolymerization of CO<sub>2</sub> and epoxides which has the ability to produce polycarbonates with narrow molecular weight distributions in a green chemistry process.

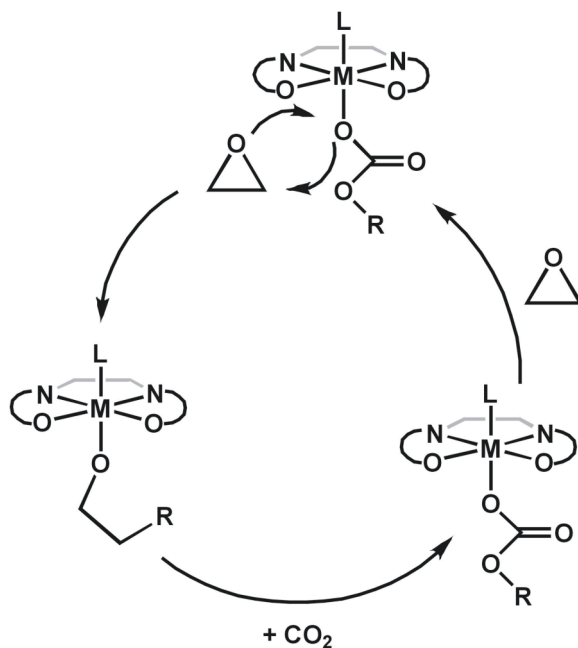


**Scheme 1.** Industrial synthesis of bisphenol A polycarbonate.

In 1969, Inoue discovered that ZnEt<sub>2</sub> and H<sub>2</sub>O (1:1) in benzene react to form an unknown ethyl zinc oxide that was capable of copolymerizing CO<sub>2</sub> and a variety of epoxides with low turnover frequency.<sup>4</sup> This initial discovery encouraged new research toward the copolymerization of CO<sub>2</sub> and epoxides, mostly with Zn catalysts.<sup>5</sup> These heterogeneous reactions exhibited low turnover frequencies (TOF) and broad polydispersity indices (PDI). In 1978, Inoue synthesized the first single-site catalyst, Al(tpp)Cl (tpp = tetraphenylporphyrin).<sup>6</sup> In 1995, Jacobsen discovered that his Cr(salen)Cl catalysts were able to effect the asymmetric ring-opening of epoxides.<sup>7</sup> Subsequent studies showed that this Cr(salen)Cl was active for the copolymerization of epoxides and CO<sub>2</sub>.<sup>8</sup> The copolymerization of CO<sub>2</sub> and epoxides is currently studied with zinc alkoxide complexes, as well as salen-derived cobalt and chromium complexes. This seminar has been focused on salen-derived chromium and cobalt complexes as much mechanistic work has been published on the topic.

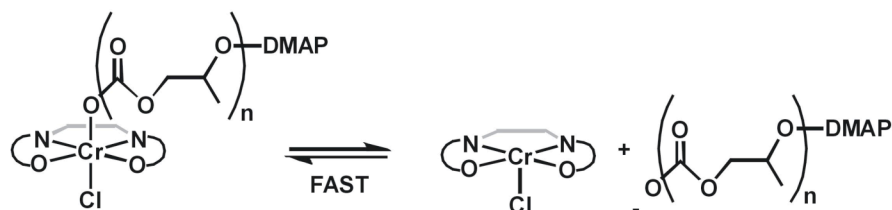
The generic mechanism of the copolymerization of CO<sub>2</sub> with epoxides catalyzed by Cr(salen)Cl is outlined in Scheme 2. A common unwanted product in the copolymerization of CO<sub>2</sub> with epoxides is the thermodynamically favored cyclic carbonate species.<sup>9</sup> For each reaction the conditions must be optimized to avoid the formation of such cyclic species. Most studies are performed with cyclohexene oxide (CHO), wherein the copolymerization produces only a small amount of cyclic product. In 2003, Darensbourg showed with elegant kinetic studies that the activation barriers for the formation of cyclic propylene carbonate (PC) was only

30 kJ/mol higher than that of polypropylene carbonate (PPC). Following this study it was apparent that the copolymerization of propylene oxide with CO<sub>2</sub> would be highly temperature dependent.<sup>9</sup> Later it was shown that increasing the CO<sub>2</sub> pressure for the reaction led to a substantial reduction of cyclic species formed and consequently increased TOFs. Unexpectedly, they discovered that different cocatalysts could substantially increase the TOF up to 1200 mol epoxide consumed/ mol catalyst · hr, which was the most active chromium catalyst reported at the time.<sup>10</sup>



**Scheme 2.** Catalytic cycle of the copolymerization of CO<sub>2</sub> and epoxides.

The catalytic cycle drawn in Scheme 2 is a living catalyst, in that the growing polymer chain does not dissociate from the metal. In 2005, Reiger suggested in a theoretical paper that catalysis could be occurring as an immortal catalyst, meaning the polymer chain was quickly dissociating and reassociating with the metal center (Scheme 3). It was previously known that Al(salen)X catalysts produced cyclic carbonate exclusive. Reiger's calculations showed that among chromium, iron, and aluminum salen complexes, aluminum complexes most easily dissociated the growing polymer. This DFT work was the first to suggest that formation of cyclic species occurred after dissociation of the polymer chain.<sup>11,12</sup> It was then hypothesized that any immortal character in catalysis would be detrimental to polymer growth as the free polymer chain could easily decompose into cyclic species.



**Scheme 3.** Depiction of immortal catalysis with a Cr(salen)Cl species.

To study this hypothesis, new catalysts have been designed to minimize immortal behavior. In 2007, Lee showed that a Co(salen)X species bearing tethered ammonium groups discouraged the anionic polymer from dissociating. Although some chain-transfer events do occur, their catalyst achieves TOFs of  $3300 \text{ h}^{-1}$ , does not produce cyclic carbonates, and requires much lower catalyst loadings (0.004 mol%).<sup>13</sup>

Future challenges in this field remain to better understand the mechanism of polycarbonate formation. The field has diverged into both chromium and cobalt salen complexes, of which the most recent work is being done with cobalt salen complexes as they show some preference for stereochemical control of the resulting polymer. As catalysts perform better, new challenges in this field will be that of creating block polymers and utilizing renewable resources for polycarbonates.

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