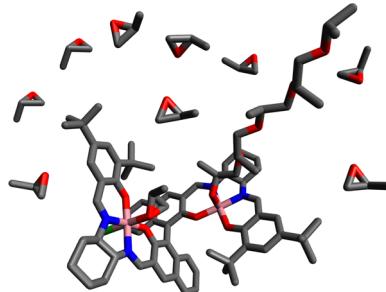


## Stereoselective Epoxide Polymerization and Copolymerization

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### 1. INTRODUCTION

#### 1.1. Background

In 1929, Staudinger and co-workers<sup>1</sup> predicted a correlation between the physical properties of a polymer and its main-chain stereochemistry. Not until 1947, however, was the first synthetic stereoregular polymer reported. Amid considerable controversy, Schildknecht and co-workers<sup>2</sup> attributed the semicrystalline properties of a poly(isobutyl vinyl ether) to the ordered stereochemistry, or tacticity, of its polymer backbone. In the 1950s, research in the field of stereoregular polymerization gained tremendous momentum when academic and industrial laboratories discovered heterogeneous titanium catalysts for synthesis of semicrystalline isotactic polypropylene.<sup>3</sup> Since these initial discoveries, synthesis of polymers of defined stereochemistry has been actively pursued in both industrial and academic laboratories.<sup>4</sup>

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In 1949,<sup>5</sup> Baggett and Pruitt<sup>6</sup> of Dow Chemical discovered that iron(III) chloride reacted with propylene oxide to form poly(propylene oxide), which could be divided into amorphous and semicrystalline materials using solvent fractionation. These results were first reported in U.S. patents issued in 1955. Soon thereafter, Natta<sup>7</sup> and Price<sup>8</sup> provided evidence that the semicrystalline material was isotactic poly(propylene oxide) in which the main-chain methyl substituents were of the same relative configuration. This finding marked the first discovery of stereoselectivity in a catalyst for epoxide polymerization. Notably, the first synthesis of isotactic poly(propylene oxide) actually precedes that of isotactic polypropylene.

Several parallels may be drawn between isotactic polypropylene and isotactic poly(propylene oxide). Both polymers were discovered around the same time and initially prepared from poorly defined heterogeneous catalyst mixtures. Since their discovery, well-defined homogeneous catalysts have been developed, and the study of these systems has led to a better understanding of polymerization mechanisms.<sup>4,9</sup> Isotactic polypropylene (melting temperature,  $T_m = 165\text{--}170\ ^\circ\text{C}$ )<sup>10</sup> and isotactic poly(propylene oxide) ( $T_m = 67\ ^\circ\text{C}$ )<sup>11</sup> are both semicrystalline polymers, in sharp contrast to their amorphous, atactic analogs. Despite their many historical similarities, the two polymers have taken divergent commercial paths. Large-scale production of isotactic polypropylene began in 1957, and it is now one of the most important industrial polymers. By contrast, isotactic poly(propylene oxide) is not currently produced on a commercial scale. This difference may be attributed to the much slower progress of catalyst development in epoxide polymerization. In recent years, however, significant advances have been made in stereocontrolled epoxide polymerization by well-defined catalysts that allow for the extraordinarily fast production of poly(propylene oxide) and with high levels of isotacticity. In addition, these advances have opened up the field of stereoselective copolymerization of epoxides with  $\text{CO}_2$ .

## 1.2. Scope

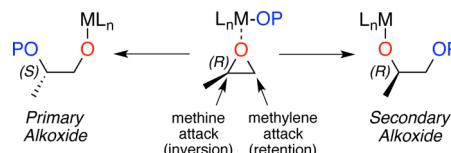
Many of the important contributors to the field of stereoselective epoxide polymerization have written accounts of their research,<sup>12</sup> but a complete and up-to-date review of the entire field does not exist. This comprehensive review covers a wide range of the stereoselective epoxide polymerization and copolymerization literature, with an emphasis on well-defined catalysts.<sup>13</sup> Discussion of strategies for controlling the relative configuration of main-chain stereogenic centers of epoxide polymers is included. Because the emphasis is on stereochemical control of polymerization by the catalyst or initiator, polymerization of enantiopure epoxides is generally not covered, although such systems are mentioned occasionally for comparison when they are used to prepare isotactic samples.

## 2. BASIC CONCEPTS IN STEREOSELECTIVE EPOXIDE POLYMERIZATION

There are three predominant classes of epoxide polymerization mechanisms: (1) cationic, (2) anionic, and (3) metal-mediated. In general, cationic epoxide polymerizations afford little control of stereochemistry. Anionic and metal-mediated polymerizations are related, as their active species are typically of the form  $\text{L}_n\text{M}-\text{OR}$  ( $\text{L}_n$  is an optional ancillary ligand set, and OR is an alkoxide). The epoxide is enchainable after attack by the alkoxide group, and the newly enchainable epoxide is inserted

between the oxygen atom of the chain end and the metal center (Scheme 1).

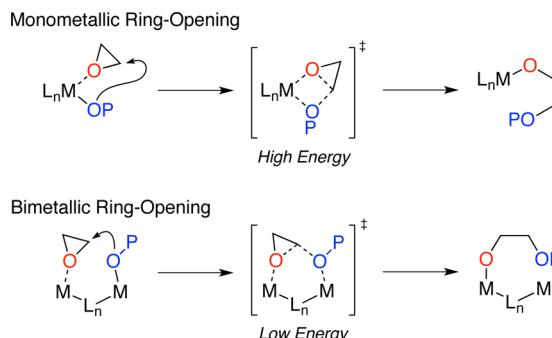
**Scheme 1. Regio- and Stereochemistry of  $\text{S}_{\text{N}}2$ -Type Epoxide Ring Opening<sup>a</sup>**



<sup>a</sup>OP = polymer chain.

The nature of the metal determines the ionic nature of the M–O bond. In general, group I and II metal alkoxides are considered anionic initiators, whereas other metal (transition, lanthanide, and main group) alkoxides are more covalent in nature. Many early examples of metal-based catalysts for epoxide polymerization consisted of multimetallic aggregates, and therefore, multimetallic transition states for epoxide enchainment are commonly proposed. Worth mentioning, however, is that there is little early experimental evidence for such proposals despite compelling circumstantial support.<sup>14</sup> As for potential mechanisms for mono- and bimetallic ring opening of epoxides, the bimetallic transition state appears much less strained and likely lower in energy than that of monometallic ring opening, supporting the early bimetallic proposals (Scheme 2). The preference for a bimetallic

**Scheme 2. Potential Mechanisms and Transition States for Mono- and Bimetallic Ring Opening of Epoxides**



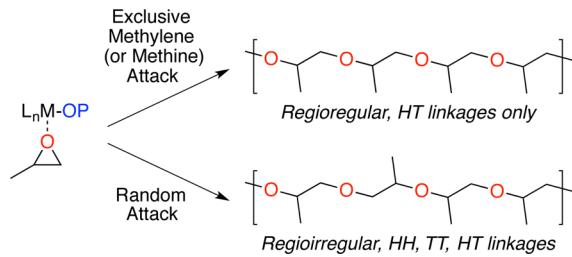
mechanism is confirmed by the most recent advances in stereoselective epoxide polymerization in which a discrete bimetallic catalyst synthesizes highly isotactic poly(propylene oxide) with a high turnover frequency (TOF; *vide infra*). Jacobsen et al.<sup>15</sup> have conclusively shown that the asymmetric ring opening of epoxides catalyzed by chiral salicylaldimine complexes proceeds through a bimetallic mechanism.

## 2.1. Regiochemistry

Both the ancillary ligands surrounding the active metal center and the growing polymer chain influence the regiochemistry and stereochemistry of epoxide polymerization.<sup>16</sup> When the epoxide is monosubstituted (e.g., propylene oxide), enchainment can occur in two ways: (1) attack at the methylene to give a secondary metal alkoxide, or (2) attack at the methine with inversion to give a primary metal alkoxide (Scheme 1). The polymer is regioregular when only one process dominates; it is regiorandom when both processes occur (Scheme 3). In regioregular poly(propylene oxide), every repeat unit is

oriented the same way, giving exclusive head-to-tail (HT) linkages. When regioerrors occur, head-to-head (HH) and tail-to-tail (TT) linkages are present. High levels of regioirregularity generally result in amorphous polymers, regardless of the stereocenters present. Therefore, these polymers must be regioregular before the stereoselectivity of the catalyst can be considered.

**Scheme 3. Regioregular and Regioirregular Poly(propylene oxide) Showing Head-to-Tail (HT), Head-to-Head (HH), and Tail-to-Tail (TT) Linkages**



The regiochemistry of a polymer, such as poly(propylene oxide), can be readily determined using  $^{13}\text{C}$  NMR spectroscopy.<sup>17</sup> In general, discrete metal-based catalysts polymerize monosubstituted epoxides to give substantially regioregular polyethers.

## 2.2. Chain-End and Enantiomeric-Site Control of Stereochemistry

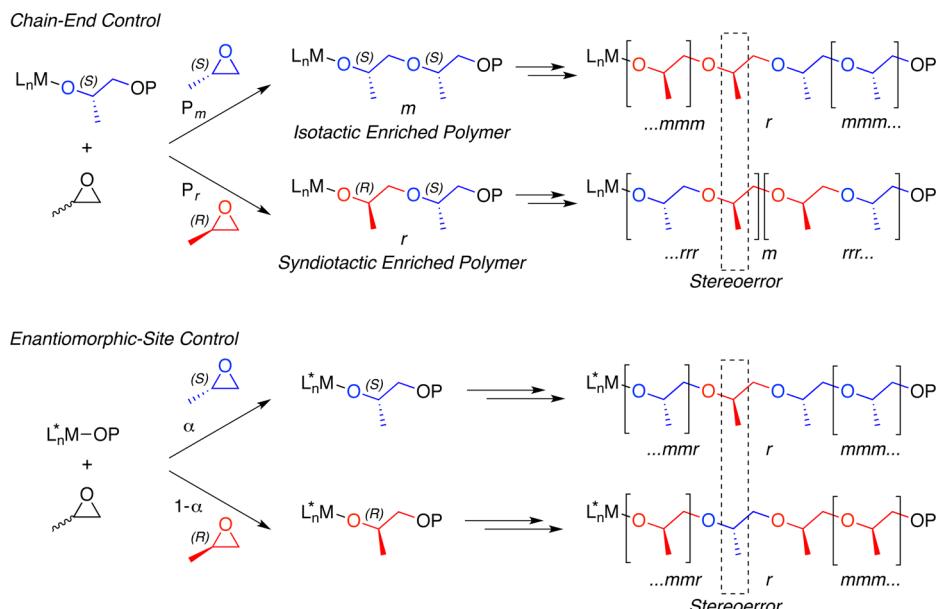
Assuming the production of regioregular polyether, stereocontrol in epoxide polymerization can take place in two ways. In a chain-growth polymerization reaction, the end of the polymer chain remains at the active metal center during monomer enchainment. Thus, the stereogenic center from the last enchained monomer unit influences the stereochemistry of monomer enchainment. If this influence is significant, the mode of stereochemical regulation is referred to as polymer chain-end control.<sup>18</sup> If the active site is chiral due to the ligand set ( $\text{L}_n^*$ )

and overrides the influence of the polymer chain end, the mechanism of stereochemical regulation is called enantiomeric-site control (Scheme 4).<sup>18</sup> In the former mechanism, a stereochemical error is propagated, but in the latter, a correction occurs because the ligands direct the stereochemical events. In the case of stereocontrol in epoxide polymerizations, almost all reported systems are regulated by enantiomeric-site control.

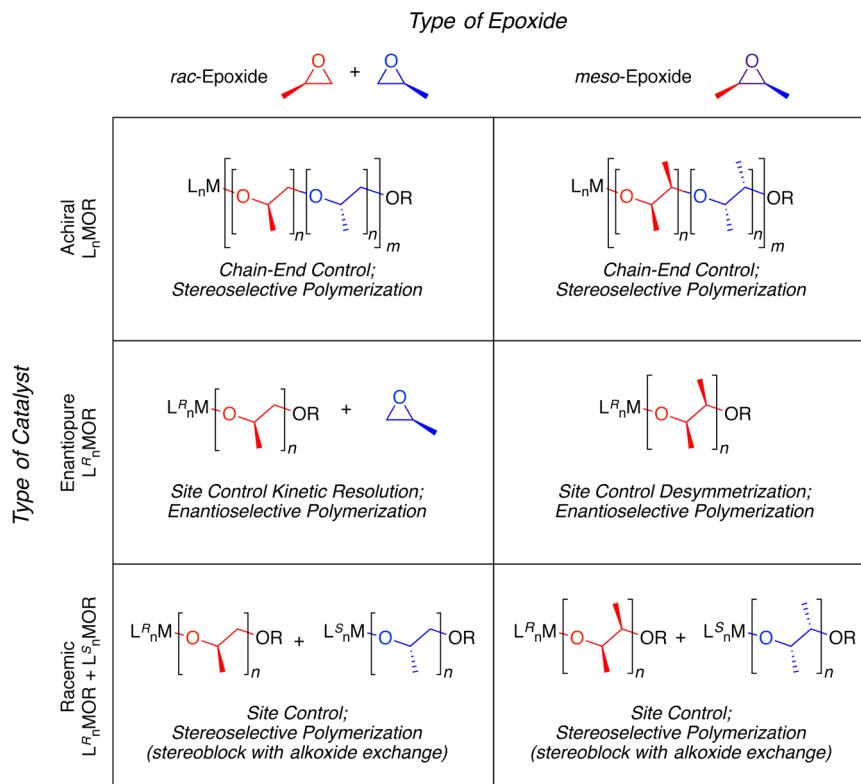
Scheme 4 introduces the parameters used to describe the stereoselectivity of the monomer enchainment process. For chain-end control, the parameters  $P_m$  and  $P_r$  refer to the probability of meso and racemic placements ( $P_m + P_r = 1$ ), respectively. The Bovey formalism is a convenient way to describe polymer tacticity, with a lower case  $m$  for meso and a lower case  $r$  for racemic relationships between adjacent stereogenic centers.<sup>19</sup> A  $P_m$  value equal to unity indicates isotacticity; a  $P_r$  value equal to unity signifies syndiotacticity. For site control mechanisms, the parameter  $\alpha$  represents the probability of selecting one enantiomer of the monomer for enchainment. When  $\alpha$  is 1 or 0, an isotactic polymer forms; an  $\alpha$  of 0.5 results in an atactic polymer.

Since stereoselective epoxide catalysts predominantly lead to isotactic polymers, Figure 1 shows the six basic classifications of isoselective epoxide polymerization according to the type of monomer (racemic or meso) and type of catalyst (achiral, enantiopure, or racemic). Achiral catalysts can induce isoselectivity in the polymerization of both meso and racemic epoxides via chain-end control mechanisms, but periodic defects are propagated, leading to synthesis of isotactic polymers with stereoblock structures. Enantiopure catalysts can stereoselectively resolve racemic monomers, producing isotactic polymers enriched in one enantiomer of the monomer and leaving behind monomer enriched in the other enantiomer. The quantitative measure of stereocontrol in such a system is given by the parameter  $k_{\text{rel}}$ , which is the ratio of the rate constant for polymerization of the faster reacting enantiomer to that of the slower reacting enantiomer of the monomer

**Scheme 4. Chain-End and Enantiomeric-Site Mechanisms of Stereocontrol<sup>a</sup>**



<sup>a</sup> $\text{L}_n^*$  is a chiral ligand set.



**Figure 1.** Classification of stereocontrol according to type of epoxide and catalyst ( $L^R_n$  and  $L^S_n$  are chiral ligand sets that give R- and S-preferring catalysts, respectively).

assuming that the reaction is first order in monomer. This ratio can be extracted from plots of monomer enantiomeric excess (ee) versus conversion ( $C$ ) of monomer or polymer ee versus  $C$  of monomer (eq 1).<sup>20</sup>

$$k_{\text{rel}} = \frac{k_{\text{fast}}}{k_{\text{slow}}} = \frac{\alpha}{(1-\alpha)} = \frac{\ln[(1-C)(1-\text{ee}_{\text{epoxide}})]}{\ln[(1-C)(1+\text{ee}_{\text{epoxide}})]} \\ = \frac{\ln[1-C(1+\text{ee}_{\text{polymer}})]}{\ln[1-C(1-\text{ee}_{\text{polymer}})]} \quad (1)$$

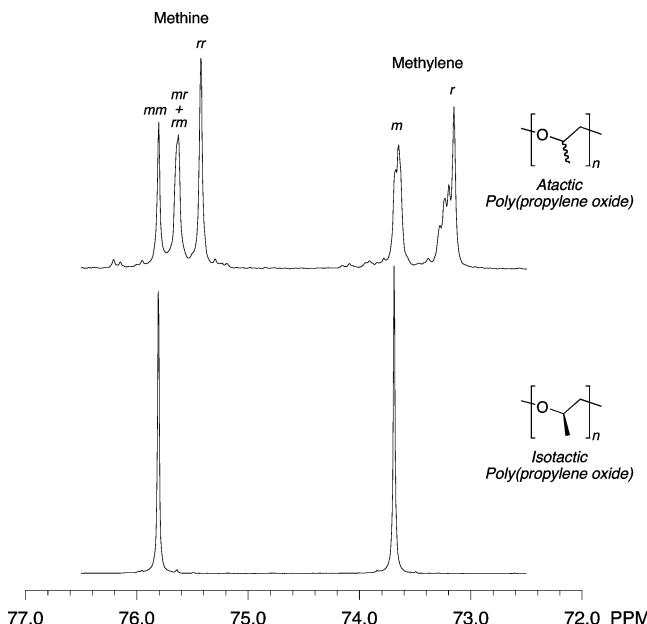
Desymmetrization of *meso*-epoxides by enantiopure catalysts results in isotactic polymers. Racemic catalysts can produce isotactic polymer chains via stereoselective polymerization of racemic epoxides in which each enantiomer of the catalyst enchains its preferred enantiomer of the monomer. In addition, racemic catalysts can stereoselectively polymerize *meso*-epoxides to give enantiomeric isotactic polymers.

### 2.3. Analysis of Polymer Stereochemistry

Several techniques, including solvent fractionation, X-ray diffraction, IR spectroscopy, differential scanning calorimetry (DSC), and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, are commonly used to determine the type of tacticity and degree of stereoregularity of a polymer sample. Because polymer thermal properties ( $T_m$  and glass transition temperature,  $T_g$ ) depend on many factors besides tacticity (such as molecular weight, regiodefects, and sample history), they can be used only to reveal general information about polymer stereochemistry. Notably, many early systems were reported before widespread use of DSC and analyzed using traditional melting point analysis. Thus, slight differences in  $T_m$  may result. In enantiomerically enriched polymers, optical rotation can be used to determine absolute configurations as well as the degrees

of enantiomeric purity when an enantiopure reference polymer is available for comparison.

The most useful method for determining polymer tacticity and quantifying stereochemical purity is NMR spectroscopy.<sup>19,21</sup> In many cases the chemical shifts for the various polymer nuclei are sensitive to adjacent stereogenic centers, resulting in fine structures that provide quantitative information about polymer microstructure once the shift identities are assigned. For example, the methyl, methylene, and methine regions of a high-resolution  $^{13}\text{C}$  NMR spectrum of atactic poly(propylene oxide) contain several peaks, each of which represents a different stereosequence (Figure 2). Because the position of each peak in the spectrum has been assigned,<sup>17a,b,22</sup> a routine  $^{13}\text{C}$  NMR spectroscopic experiment can reveal both the tacticity and the degree of stereo- and regioregularity of a poly(propylene oxide) sample. The ratio of the peaks can also be used to determine the mechanism of stereocontrol because the spectrum can be simulated using the statistical models presented above (Scheme 4). Scheme 4 also shows that isospecific chain-end control mechanisms produce polymers with isolated *r*-diad (and corresponding *mr* and *rm* triad) errors, whereas enantiomeric-site control mechanisms produce polymers with isolated *rr*-triad errors. Similar analyses can also be applied to polycarbonates, often by examining the carbonate peak in the  $^{13}\text{C}$  NMR spectrum. Unfortunately, because many of the early studies reviewed herein were performed before widespread use of NMR spectroscopy, quantification of the level of stereochemical control is often absent in the older literature.



**Figure 2.** Methine and methylene regions of the  $^{13}\text{C}$  NMR spectra of atactic and isotactic poly(propylene oxide).

### 3. STEREOSELECTIVE EPOXIDE HOMOPOLYMERIZATION

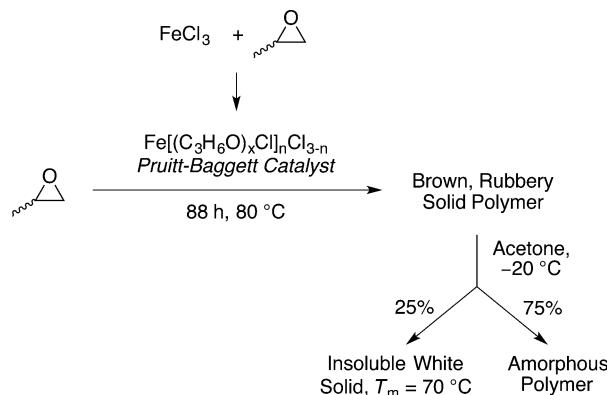
The vast majority of papers reporting stereoselective epoxide polymerization focus on isoselective propylene oxide polymerization. We therefore chose to organize this review based on the metal of the active center of the catalyst. The most commonly used metals for stereoselective epoxide polymerization are iron, aluminum, zinc, and cobalt, and research using these metals forms the foundation of this section of the review. Other metals have been used, however, and are covered as well. Although the focus of this review is stereoselective polymerization of meso and racemic epoxides by well-defined catalysts, select examples of heterogeneous catalysts or polymerization of enantiomerically pure epoxides are presented to provide historical perspective or illustrate characterization data or physical properties.

#### 3.1. Iron-Based Catalysts for Stereoselective Epoxide Homopolymerization

In 1949, Dow Chemical Co. scientists Malcolm Pruitt and Joseph Baggett discovered iron(III) halide catalysts for stereoselective polymerization of propylene oxide.<sup>5a</sup> Since the initial patent reports of this discovery in 1955,<sup>6</sup> a significant amount of work has been performed to clarify the nature of the active species as well as to apply these catalysts to a wider range of stereoselective epoxide polymerizations.

**3.1.1.  $\text{FeCl}_3$ -Based Catalysts.** Pruitt and Baggett<sup>6</sup> reported that a catalyst for propylene oxide polymerization could be formed by reacting  $\text{FeCl}_3$  with 0.5–3.0 equiv of propylene oxide in diethyl ether. The brown residue was used to polymerize propylene oxide over 88 h at 80 °C to yield a rubbery brown solid in 94% yield (Scheme 5). The solid was dissolved in hot acetone, and on cooling to –20 °C, one-fourth of the material crystallized as a fluffy white solid with a  $T_m$  of 70 °C. After solvent removal, the remaining material was identified as an amorphous polymer. Semicrystalline polyethers have also been formed from styrene oxide, epichlorohydrin, 1,2-epoxybutane, and *cis*- and *trans*-2,3-epoxybutanes using this

**Scheme 5. Polymerization of Propylene Oxide Using the Pruitt–Baggett Catalyst**

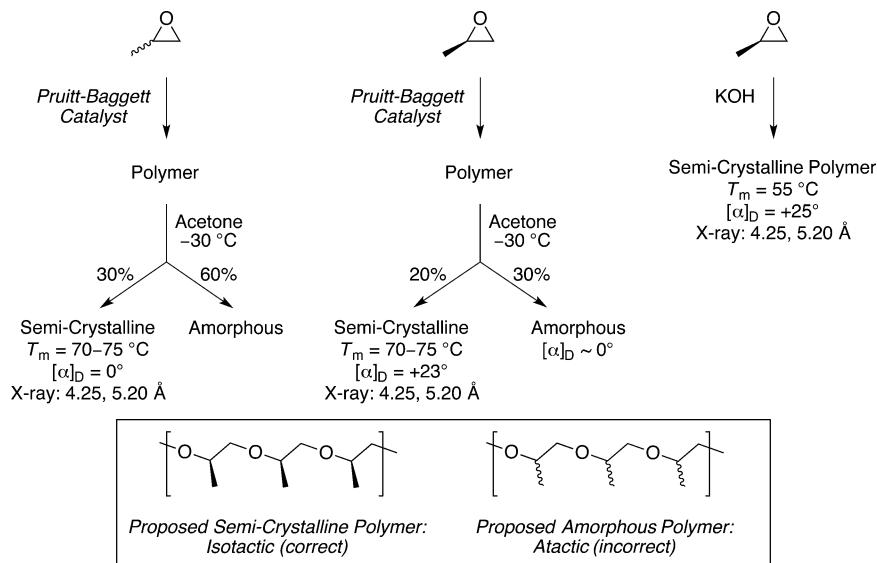


system.<sup>6b,c,23</sup> Catalysts with higher activity and isoselectivity can be formed via careful hydrolysis of the Pruitt–Baggett catalyst.<sup>24</sup> Ferric alkoxides,<sup>25</sup> hydrates ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), and basic acetates also catalyze epoxide homopolymerization.<sup>6b,26</sup>

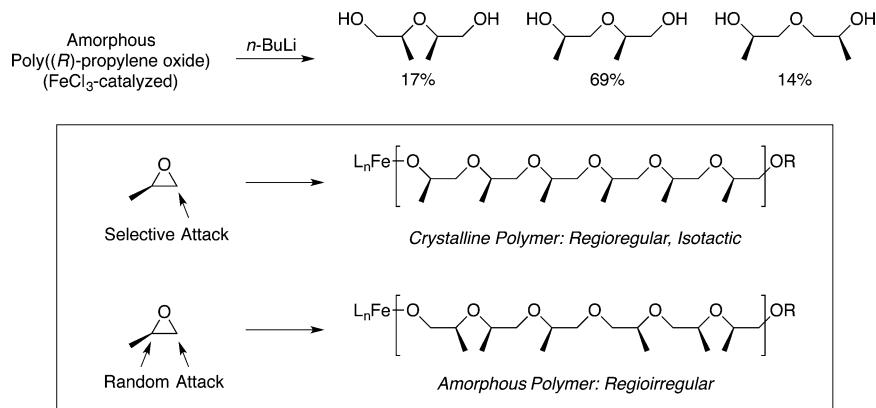
The ability to synthesize semicrystalline polymers from racemic propylene oxide raised many significant questions about the mechanism of polymerization and the structures of the catalyst and polymer. Currently, only the structure of the polymer has been generally agreed on. In 1956, Price and co-workers<sup>8</sup> reported the polymerization of enantiopure *R*-propylene oxide using the Pruitt–Baggett catalyst. The polymer formed was separated into two fractions: (1) an amorphous, virtually optically inactive material, and (2) a semicrystalline, optically active material with the same specific optical rotation as that of polymer made using KOH (which produces isotactic polymer when enantiopure epoxide is used). X-ray diffraction data for this polymer matched that of the semicrystalline material originally reported by Pruitt and Baggett. On the basis of these data, the structure of the semicrystalline polymers was proposed to be isotactic; the polymer from *rac*-propylene oxide was a racemic mixture of isotactic polymer chains, whereas that from the enantiopure propylene oxide was an isotactic polymer chain of a single enantiomer (Scheme 6). Natta nearly simultaneously proposed the same isotactic polymer structure. Although the amorphous material was proposed to be atactic poly(propylene oxide) in which the Lewis acidic iron centers caused racemization via a carbocationic intermediate, this supposition was later shown to be incorrect. An important concept resulting from Price's work was the postulate that at least two types of active sites are present in the Pruitt–Baggett catalyst. These sites independently produce amorphous and isotactic polymer.

Price and co-workers<sup>27</sup> degraded the amorphous fraction of poly(propylene oxide) prepared using *R*-propylene oxide and the Pruitt–Baggett catalyst with *n*-butyllithium or ozone followed by lithium aluminum hydride. Dimeric glycols were then separated from the resultant mixture of degradation products, and their structures and stereochemistries were determined using gas chromatography assuming random cleavage of the polymer chain. Instead of finding only HT placements of the methyl groups, they discovered that 17% of the dimers exhibited HH structures with primarily meso stereochemistry (Scheme 7). On the basis of these results, they postulated that the main mode of ring opening was attack on the methylene carbon and that structural irregularities (HH and TT units) were caused by periodic attack at the methine carbon

Scheme 6. Proposed Structures of Semicrystalline and Amorphous Poly(propylene oxide)s



Scheme 7. Determination of the Structure of Amorphous Poly(propylene oxide)



with inversion of stereochemistry. Detailed fractionation and  $^{13}\text{C}$  NMR studies by Ugur and Alyuruk $^{15\text{c}}$  and Powell $^{26}$  confirmed the presence of these regiodefects and showed that the  $T_m$  of the polymer decreased as the number of defects increased. In addition, polymers with regiodefects also had lower molecular weights than those without, suggesting a link between these features. $^{17\text{c}}$

Many variants of the Pruitt–Baggett catalyst have been explored. Notably, Furukawa and co-workers $^{28}$  added (*R*)-bornyl ethyl ether during partial hydrolysis of the catalyst in an attempt to generate a chiral catalyst for the kinetic resolution of *rac*-propylene oxide. A ratio of iron to water to (*R*)-bornyl ethyl ether of 1:1.5:0.5 achieved slight asymmetric induction ( $k_{\text{rel}} = 1.7$ ) for preferential polymerization of (*S*)-propylene oxide.

The mechanism of polymerization and structures of the active species of the Pruitt–Baggett-type catalysts remain unknown, although a variety of mechanisms have been proposed. Borkovec $^{29}$  reported the ring opening of ethylene oxide by  $\text{FeCl}_3$  to give chlorine-terminated polyethylene glycols on hydrolysis, suggesting that one or more chlorines on the iron centers in the active catalysts are converted to alkoxides. Similar results have been observed for propylene oxide. $^{30\text{a}}$  In addition, the amorphous polymer contains aldehyde and alkene end groups, consistent with propagating species of the form

$\text{L}_n\text{Fe}-\text{OP}$  (where P = polymer chain) and E2 elimination processes involving propylene oxide and  $\text{L}_n\text{Fe}-\text{OP}$  species. It is therefore generally accepted that iron alkoxides are the active species for polymerization. However, the nature of the active site and the detailed mechanism of enchainment are still under debate. Corey $^{31}$  proposed a monomeric active species in which the stereogenic centers of the polymer chain control tacticity. Price $^{8\text{b},27\text{a}}$  proposed a bimetallic active site, whereas Osgan $^{26}$  proposed a trinuclear complex and Gurgiolo $^5$  a polymeric chain of multimetallic active sites. In the absence of powder or single-crystal X-ray diffraction data, the active species will likely remain unknown. A better understanding of the active site of the Pruitt–Baggett catalyst would be useful for developing well-defined and selective catalysts for stereoselective epoxide polymerizations.

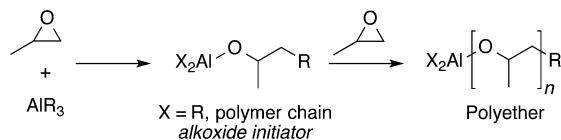
### 3.2. Aluminum-Based Catalysts for Stereoselective Epoxide Homopolymerization

After the discovery of Pruitt–Baggett iron-based systems, a wide variety of metal complexes were screened for epoxide homopolymerization. Compared to most metal systems, aluminum-based catalyst systems exhibited relatively high activities and high yields of isotactic polyether. As a result, aluminum-based catalyst systems compose a large part of the

early examples of metal-mediated stereoselective epoxide polymerization literature.

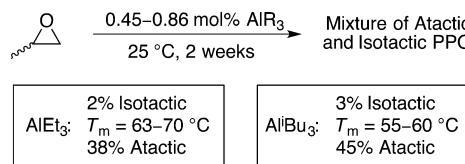
**3.2.1.  $\text{AlX}_3/\text{H}_2\text{O}$ -Based Catalysts.** The first reported aluminum catalysts for polymerization of epoxides were simple aluminum precursors such as  $\text{AlCl}_3$ <sup>30</sup> and  $\text{AlR}_3$  ( $\text{R} = \text{Me, Et, } \text{iBu}$ ).<sup>12a,h,30,32</sup> During a screening of metal chloride initiators, Colclough and co-workers<sup>30</sup> reported that  $\text{AlCl}_3$  is active for polymerization of propylene oxide. The isolated polymer products, however, were largely or completely amorphous. Noting the success of  $\text{Al(O}^{\text{i}}\text{Pr})_3$  systems for polymerization of propylene oxide,<sup>33</sup> Price<sup>32a</sup> proposed that simple  $\text{AlR}_3$  complexes could be used as initiators because the reaction of an aluminum alkyl with an epoxide monomer generates a metal alkoxide that could in turn initiate polymerization (Scheme 8).

**Scheme 8. Polyether Synthesis Using Aluminum Alkyl Complexes**



Price<sup>32a</sup> conducted propylene oxide polymerizations with both  $\text{AlEt}_3$  and  $\text{Al}^{\text{i}}\text{Bu}_3$  for 2 weeks at room temperature or 80 °C. In most cases, conversions between 40% and 56% were achieved in which ~5% of the isolated polymer was acetone-insoluble isotactic material (Scheme 9). Even though aluminum alkyls were active for polymerization of propylene oxide, they exhibited very low activities and produced only small amounts of semicrystalline poly(propylene oxide) (PPO).

**Scheme 9. Conversion and Selectivity for  $\text{AlR}_3$ -Initiated Propylene Oxide Polymerization**



Vandenberg<sup>12h</sup> investigated the reaction of epichlorohydrin with  $\text{Al}^{\text{i}}\text{Bu}_3$ . Polymer was formed, but later experiments revealed that activity was due to water contamination in the monomer. Vandenberg<sup>12a,32b-d</sup> then synthesized  $\text{AlR}_3/\text{H}_2\text{O}$  mixtures, which were very effective catalysts for propylene oxide polymerization. In addition to producing acetone-insoluble isotactic poly(propylene oxide), Vandenberg reported the synthesis of acetone insoluble polyethers from monomers such as *o*-chlorophenyl glycidyl ether, *p*-chlorophenyl glycidyl ether, butadiene monoxide, styrene oxide, hexyl glycidyl ether, allyl glycidyl ether, epibromohydrin,<sup>32c,d</sup> 1,4-dichloro-2,3-epoxybutane,<sup>34</sup> trimethylsilyl glycidyl ether,<sup>12h</sup> *cis*-1,4-trimethylsiloxy-2,3-epoxybutane, and 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane.<sup>35</sup> Of particular interest are the polymers formed from the last three epoxides because hydrolysis of these polymers leads to polyethers with hydroxyl functionalities, providing elastomeric, water-soluble materials.<sup>12h,35,36</sup>

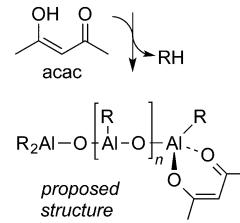
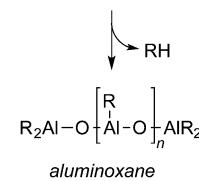
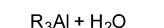
More recently, Barron and Lenz<sup>37</sup> revisited  $\text{Al}^{\text{i}}\text{Bu}_3/\text{H}_2\text{O}$  catalyst systems. While trying to reproduce early work with the  $\text{Al}^{\text{i}}\text{Bu}_3/\text{H}_2\text{O}$  system (in solution or in bulk), they did not

observe an appreciable amount of semicrystalline polymer, isolating only rubbery amorphous material. However, slow addition of 2 equiv of propylene oxide to a solution of the preformed  $\text{Al}^{\text{i}}\text{Bu}_3/\text{H}_2\text{O}$  complex at -78 °C resulted in a solid adduct. This isolable catalyst mixture had activity similar to that of previous systems and produced ~30 wt % isotactic polymer, with an isotactic diad content greater than 90%. This result improved on previously reported systems that produced polymer with isotactic diad contents of 60–70%. The authors attributed this increased stereoregularity in their system to the absence of residual  $\text{Al}^{\text{i}}\text{Bu}_3$ , which was removed during isolation of the  $\text{Al}^{\text{i}}\text{Bu}_3/\text{H}_2\text{O}$ /propylene oxide adduct.

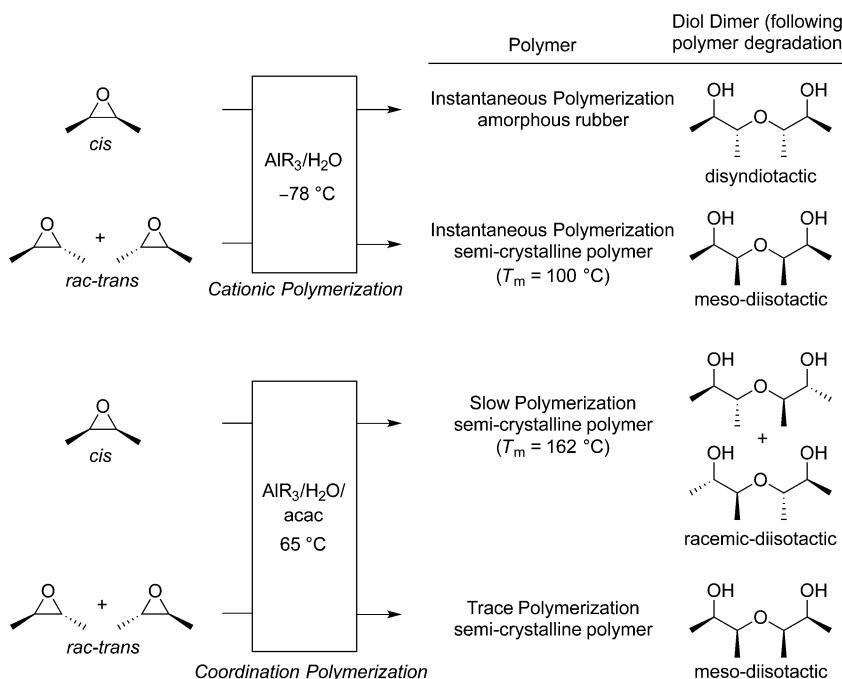
A multicomponent calixarene-neodymium complex activated with 6–16 equiv of  $\text{Al}^{\text{i}}\text{Bu}_3/\text{H}_2\text{O}$  ( $\text{Al:H}_2\text{O} = 2:1$ ) formed poly(propylene oxide) containing 58–71% isotactic polymer as determined by solvent fractionation. The reaction was run for 1–2 days at 70 °C.<sup>38</sup> The nature and degree of influence of the neodymium complex on the aluminum alkyl/water catalyst has not been determined.

**3.2.2. Aluminum–Acetylacetone Complexes.** Most proposed mechanisms of epoxide polymerization feature coordination of the epoxide to the metal center before monomer enchainment occurs. To examine the effect of blocking these epoxide coordination sites, Vandenberg<sup>12b,32b-d</sup> added chelating agents such as acetylacetone (acac) to the  $\text{AlR}_3/\text{H}_2\text{O}$  catalyst mixtures. Rather than slowing the polymerization rate as expected, these additives increased it, resulting in a new class of active catalysts. Although the exact structures of these presumably oligomeric catalysts are unknown, several features have been determined, including the presence of an oxygen atom that bridges two aluminum atoms, the presence of alkyl groups on the aluminum atoms, and chelation of the acac ligand to some of the aluminum atoms (Scheme 10).<sup>12a</sup>

**Scheme 10. Synthesis of  $\text{AlR}_3/\text{H}_2\text{O}/\text{Acetylacetone}$  Polymerization Catalysts ( $n > 0$ )**



Varying the molar composition of the  $\text{AlR}_3/\text{H}_2\text{O}/\text{acac}$  system yields catalysts that polymerize epoxides to high molecular weight polyethers in high conversions. Although the acetone-insoluble, isotactic polymer fraction varies with the catalyst system and epoxide used, it is in general approximately 30% of the isolated total polymer mass.<sup>32c,d</sup> To elucidate the polymerization mechanism that results from this catalyst system, Vandenberg used both the  $\text{AlR}_3/\text{H}_2\text{O}$  and the  $\text{AlR}_3/\text{H}_2\text{O}/\text{acac}$  catalyst systems to polymerize *cis*- and *trans*-2,3-epoxybutane. Information obtained from the resulting polymers

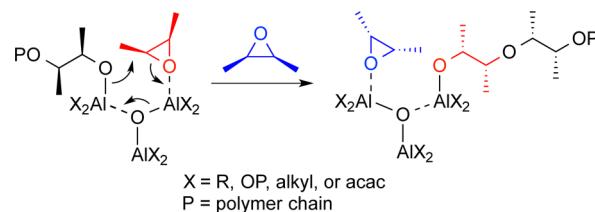
Scheme 11. Stereoselectivity of the Polymerization of *cis*- and *trans*-2,3-Epoxybutane Using  $\text{AlR}_3/\text{H}_2\text{O}$  Catalysts

and their diol decomposition products allowed the mechanistic inferences summarized in Scheme 11.<sup>12a,h,39</sup>

The  $\text{AlR}_3/\text{H}_2\text{O}$  catalyst systems rapidly polymerize *cis*- and *trans*-2,3-epoxybutane at  $-78^\circ\text{C}$ , consistent with a cationic enchainment mechanism. *cis*-2,3-Epoxybutane produces an amorphous rubber polymer, whereas *trans*-2,3-epoxybutane produces a semicrystalline polymer with a  $T_m$  of  $100^\circ\text{C}$ . By contrast, even at  $65^\circ\text{C}$ , the  $\text{AlR}_3/\text{H}_2\text{O}/\text{acac}$  catalyst system results in only trace polymerization of *trans*-2,3-epoxybutane and slow polymerization of *cis*-2,3-epoxybutane to give a semicrystalline polymer with a  $T_m$  of  $162^\circ\text{C}$ . Vandenberg attributes this slower polymerization to a coordination–insertion mechanism. The extremely slow polymerization of *trans*-2,3-epoxybutane is attributed to its larger steric bulk compared with that of *cis*-2,3-epoxybutane, hindering coordination of the epoxide to the metal center.

Degradation of the above polyethers obtained from the  $\text{AlR}_3/\text{H}_2\text{O}$  and  $\text{AlR}_3/\text{H}_2\text{O}/\text{acac}$  catalyst systems to diol dimers allowed determination of the stereochemistry of the monomer to units in the polymer chain.<sup>39c</sup> The diol products from all four polymers showed that one stereocenter from each epoxide was inverted during the ring-opening step of polymerization. *cis*-2,3-Epoxybutane (with exclusively *RS* stereocenters) produced diols with *RR* and *SS* stereocenters, whereas *trans*-2,3-epoxybutane (with *RR* and *SS* stereocenters) produced diols with only *RS* stereocenters. This observation suggests that an inversion of configuration occurs at the site of attack for both the cationic and the coordination–insertion mechanisms.

To explain the geometry of the backside attack observed in the coordination–insertion mechanism, Vandenberg<sup>12h</sup> proposed the bimetallic transition-state structure shown in Scheme 12. In this structure, one aluminum center activates an epoxide while an adjacent aluminum center binds a polymer alkoxide, providing a favorable geometry for ring opening of the activated epoxide. Although little experimental evidence exists for bimetallic processes in the aluminum catalyst systems studied

Scheme 12. Proposed Bimetallic Enchainment of Epoxides Using (acac) $\text{Al}$  Complexes<sup>12h</sup>

by Vandenberg, more recent catalyst systems have been shown to have bimetallic epoxide ring-opening mechanisms.<sup>14,40</sup>

Catalyst systems combining various alkyl aluminum species and acac with rare earth elements have been shown to produce poly(propylene oxide) that can be solvent fractionated to yield isotactic poly(propylene oxide).<sup>41</sup> Owing to the high molar loadings of aluminum relative to rare earth metals (4:1 to 50:1) used in these catalyst systems, the role of the rare earth metals is unclear.

**3.2.3. Aluminum Alkoxide Catalysts.** Aluminum alkoxides have also been examined for polymerization of epoxides. These complexes would appear to be better initiating systems owing to their structural similarity to the propagating species, but few accounts of their use have been reported. Price<sup>33</sup> first showed that  $\text{Al}(\text{O}^{\text{i}}\text{Pr})_3$  initiated polymerization of propylene oxide but with extremely low activity. After 2 days at  $80^\circ\text{C}$ , a total of 13% conversion was achieved (11% atactic and 2% isotactic).

**3.2.4. Aluminum Alkoxides with Zinc Cocatalysts.** Addition of  $\text{ZnCl}_2$  as a cocatalyst to  $\text{Al}(\text{O}^{\text{i}}\text{Pr})_3$  greatly increases the activity and selectivity for isotactic poly(propylene oxide). In contrast to the 2% conversion to isotactic poly(propylene oxide) observed in the absence of  $\text{ZnCl}_2$ ,<sup>33</sup> conversion as high as 16% (27% of the mass of isolated polymer) is possible when a ratio of 95:5  $\text{Al}(\text{O}^{\text{i}}\text{Pr})_3:\text{ZnCl}_2$  is used. Although higher activities can be achieved by increasing the amount of zinc

present, such increases compromise the fraction of isotactic poly(propylene oxide).

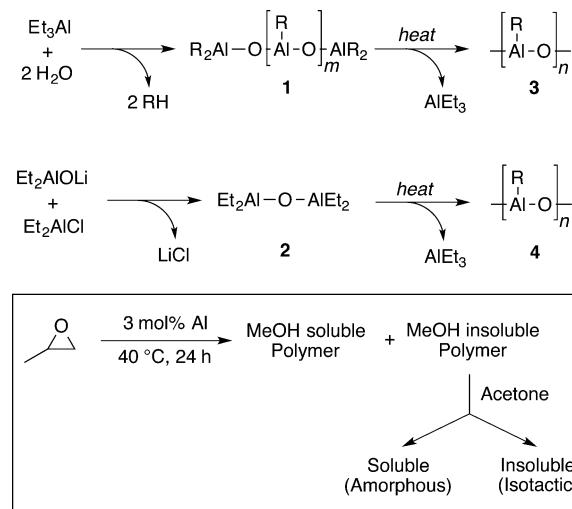
Preliminary work investigating the microstructure of poly(propylene oxide) synthesized using aluminum- and aluminum/zinc-based catalysts was accomplished using polymer degradation studies.<sup>27a</sup> Jedlinski<sup>42</sup> used <sup>13</sup>C NMR spectroscopy to examine the microstructure of poly(propylene oxide) obtained from Al(O*i*Pr)<sub>3</sub> and Al(O*i*Pr)<sub>3</sub>/ZnCl<sub>2</sub> systems and to investigate modes of epoxide ring opening. The <sup>13</sup>C NMR spectrum of poly(propylene oxide) synthesized using Al(O*i*Pr)<sub>3</sub> displayed a significant number of regioerrors.<sup>43</sup> By contrast, poly(propylene oxide) synthesized using Al(O*i*Pr)<sub>3</sub>/ZnCl<sub>2</sub> had a <sup>13</sup>C NMR spectrum consistent with that of a regioregular (HT only) polymer. Furthermore, fractionation with acetone showed the soluble portion to be regioregular and mostly atactic material, whereas <sup>13</sup>C NMR analysis of the insoluble portion was consistent with highly isotactic poly(propylene oxide).

Al(O*i*Pr)<sub>3</sub>/ZnCl<sub>2</sub> was also active for polymerization of phenylglycidyl ether.<sup>44</sup> Varying the aluminum precursors (Al(O*i*Pr)<sub>3</sub>, AlEt<sub>3</sub>) and use of the ZnCl<sub>2</sub> cocatalyst yielded poly(phenyl glycidyl ether) of varying composition (2–33% isotactic) and *T<sub>m</sub>* (180–210 °C). Ronda and co-workers<sup>45</sup> optimized the Al(O*i*Pr)<sub>3</sub>/ZnCl<sub>2</sub> system for polymerization of additional glycidyl ethers to afford highly stereo- and regioregular isotactic polyethers. Other mechanistic investigations of the Al/Zn systems have examined the initiation step of the Al(O*i*Pr)<sub>3</sub>/ZnEt<sub>2</sub> catalyst using model epoxides.<sup>46</sup> Both *p*-chlorophenylglycidyl ether and phenylglycidyl ether have been polymerized using <sup>14</sup>C-labeled Al(O*i*Pr)<sub>3</sub>, and the end groups of the resulting polymers have been examined.<sup>47</sup> Interestingly, no more than 50% of the resulting polymer chains are terminated by isopropoxide; those remaining are terminated with ethyl groups. Furthermore, no correlation occurs between the end group and the microstructure of the polymer chains.

**3.2.5. Well-Defined Aluminoxane Catalysts.** The success of AlR<sub>3</sub>/H<sub>2</sub>O systems prompted the study of analogous well-defined aluminoxane catalyst systems such as R<sub>2</sub>Al—O—[Al(R)O]<sub>m</sub>—AlR<sub>2</sub> (*m* = 0,1) for propylene oxide. Araki<sup>48</sup> studied several homogeneous organoaluminum compounds and the aluminoxanes resulting from their pyrolysis (Scheme 13). The catalyst **1** (*m* ~ 10) was compared to the well-defined catalyst **2**, each with the same Al:H<sub>2</sub>O ratio of 2:1.<sup>48b</sup> Under the same polymerization conditions, **1** was less active than **2**, reaching 70% and 90% conversion, respectively, but the isolated isotactic material was similar in each. Furthermore, aluminoxanes **3** and **4** exhibited similar activities and selectivities. Because the polymer isolated from each catalyst system had a similar composition, the authors suggested that despite different starting organoaluminum species, similar active species are generated during polymerization, although their exact natures are unknown.

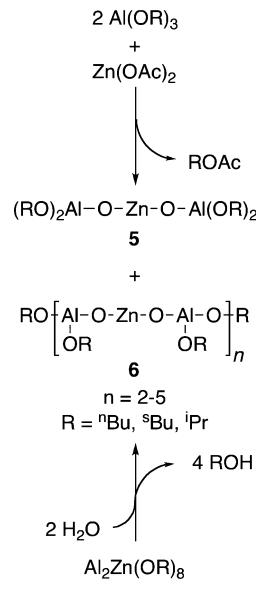
**3.2.6. Catalysts with Al—O—M—O—Al Frameworks.** Because some theories suggest the necessity of a polynuclear active site and a benefit in adding zinc to the aluminum-based polymerization systems, well-defined polynuclear complexes have been screened for polymerization activity. Osgan<sup>49</sup> described the synthesis of Al—O—Zn—O—Al complexes (Scheme 14) and their use in the polymerization of epoxides. The first reported synthesis of this class of complexes was based on an ester elimination route,<sup>49a</sup> giving mixtures of trinuclear **5** and oligomeric **6**, although an improved synthetic route through hydrolysis of Al/Zn clusters later provided **5** in

**Scheme 13. Aluminoxane Catalysts for Propylene Oxide Polymerization**



**Scheme 14. Synthesis of  $\mu$ -Oxometal Complexes**

*Ester Elimination Route*



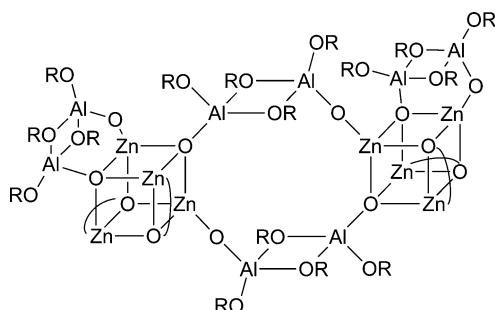
*Hydrolysis Route*

much higher yield.<sup>49d</sup> These well-defined initiators had activities comparable to those of catalysts synthesized via the ester elimination route.

Complex **5** is particularly active for polymerization of propylene oxide, with polymerizations reaching 50% conversion in 5 min at 50 °C in 1 M solutions with 0.1 mol % zinc.<sup>50</sup> Similar to results with the aforementioned Al/Zn/H<sub>2</sub>O mixtures, a portion of the isolated polyether (from 4–80%, but generally 50% of the total mass of the isolated polymer) was partially isotactic (*T<sub>m</sub>* = 60 °C).<sup>49a,b,50,51</sup>

Teyssie and co-workers<sup>51</sup> conducted detailed <sup>1</sup>H, <sup>13</sup>C, and <sup>27</sup>Al NMR studies to characterize the catalyst structure and deduce the origins of high molecular weight isotactic and low molecular weight atactic polymer fractions obtained using catalyst **5** (R = <sup>n</sup>Bu). From these studies, they determined that complex **5** exists as a complex mixture of globular, rigid

aggregates exhibiting extremely slow alkoxide exchange in hydrocarbon solution, even at elevated temperatures. The average number of units of **5** in each cluster is estimated to be 8, as shown in Figure 3. Finally, they proposed that the low



**Figure 3.** Depiction of a proposed  $[(RO)_4Al_2O_2Zn]_8$  aggregate ( $(RO)_4Al_2O$  linkages are truncated for clarity).

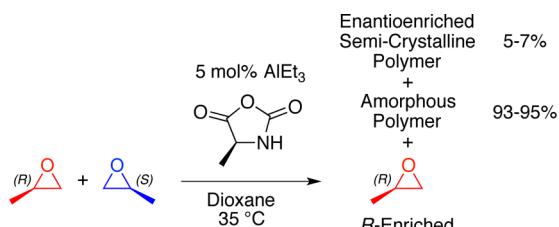
molecular weight polyether was produced on the outermost, fringe aluminum centers at which rapid alkoxide exchange occurs (each aluminum produces multiple chains), whereas the high molecular weight isotactic material was produced on a few (<5%) of the aluminum centers toward the middle of the cluster.

Complex **6** is also active for other epoxides, producing insoluble polymer fractions from 1-butene oxide, epichlorohydrin, allyl glycidyl ether, phenyl glycidyl ether, and styrene oxide.<sup>49b</sup> Although the semicrystalline fractions produced from each epoxide have not been studied in detail, the properties of the material synthesized from phenyl glycidyl ether matches those described by Price.<sup>44</sup>

The true structures of aluminum and zinc homo- and heterometallic systems are still being debated, but significant evidence points to the in situ association of the metal centers to form complex aggregates with multiple active sites. Owing to the similar polymer composition from the disparate array of starting materials, it is reasonable to presume that each system generates very similar active species and that the nature of the precatalysts does not necessarily influence the polymerization but rather affects the in situ generation of the catalytically active sites.

**3.2.7. Chiral Alkoxides and Amides.** Given that aluminum alkoxides initiate polymerization of propylene oxide, researchers hypothesized that enantiopure, chiral ligands could facilitate stereoselective polymerization of epoxides to generate optically active polymers while kinetically resolving racemic monomers. Initial efforts by Tsuruta and co-workers<sup>52</sup> demonstrated the kinetic resolution of propylene oxide with modest selectivity using an *N*-carboxy-L-(+)-alanine anhydride/AlEt<sub>3</sub> system (Scheme 15). Both the polymer and the unreacted

**Scheme 15. Polymerization of Propylene Oxide with AlEt<sub>3</sub>/N-Carboxy-L-(+)-Alanine Anhydride**

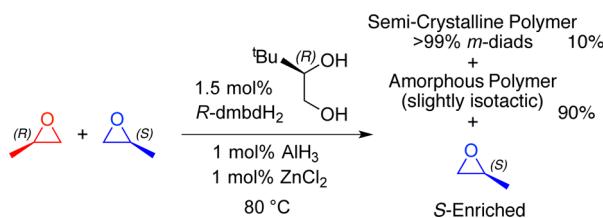


monomer were enantioenriched. The residual monomer was slightly enriched in the *R* enantiomer, whereas the polymer was slightly enriched in the *S* enantiomer. As expected, the optical activity of the monomer increased with increasing conversion, corresponding to a  $k_{\text{rel}}$  of ~1.2.

Jedlinski<sup>53</sup> used tris[(1*R*,2*S*,5*R*)-menthyloxide]aluminum initiators with a ZnCl<sub>2</sub> cocatalyst. Although up to 10 wt % of the isolated polymer was isotactic, the unreacted epoxide was optically inactive, evidence that stereoselectivity was absent despite the use of the chiral ligand.

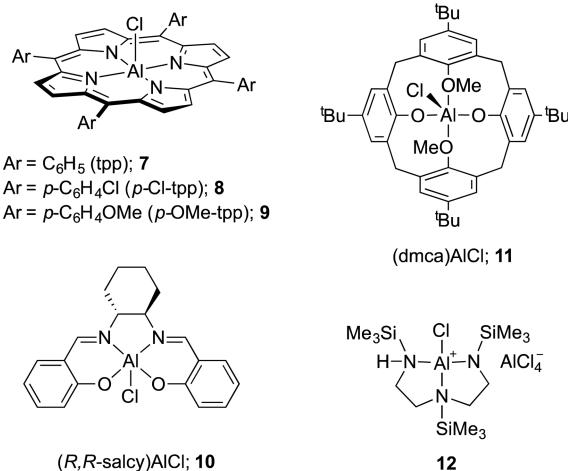
Haubenstock and co-workers<sup>54</sup> synthesized a chiral aluminum alkoxide complex for polymerization of propylene oxide. The complex was formed by addition of AlH<sub>3</sub> to 1.5 equiv of (*R*)-(−)-3,3-dimethyl-1,2-butanediol (*R*-dmbdH<sub>2</sub>). The aluminum alkoxide complex was only slightly active for propylene oxide polymerization, requiring 3 weeks to reach 85% conversion and showing no enantiomeric enrichment of the residual propylene oxide. Addition of ZnCl<sub>2</sub> to the complex at an aluminum:zinc ratio of 1:1 resulted in a more active polymerization system (Scheme 16) in which the residual

**Scheme 16. Polymerization of Propylene Oxide with a [(*R*-dmbd)<sub>1.5</sub>Al]<sub>n</sub>/ZnCl<sub>2</sub> Catalyst**



propylene oxide displayed increasing optical rotation as the conversion to polymer increased. On the basis of the optical activity of the unreacted propylene oxide,  $k_{\text{rel}}$  was determined to be 1.05, and on fractionation of the total polymer, 10% of the total mass was found to be an acetone-insoluble, isotactic polymer with greater than 99% *m*-diads. The remaining acetone-soluble polymer was atactic.<sup>54</sup> Given the low  $k_{\text{rel}}$  observed and the highly isotactic (though limited in quantity) polymer produced, it is unclear whether the kinetic resolution of the monomer is caused by the preferential polymerization of one enantiomer of propylene oxide to semicrystalline polymer or by other side reactions. Although slight enantioenrichment of monomer occurs, this system does not significantly improve the yield of isotactic poly(propylene oxide) compared with that of similar systems.<sup>33,46,53</sup>

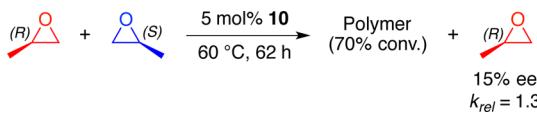
**3.2.8. Aluminum–Porphyrin Complexes.** Takeda and Inoue<sup>55</sup> reported that 5,10,15,20-tetraphenylporphyrin aluminum chloride (**7**, Figure 4) is active for polymerization of propylene oxide with a TOF of 400 h<sup>−1</sup>; the polymer is highly regioregular and moderately stereoregular with 69% *m*-diads.<sup>55</sup> The selectivity of the catalyst system corresponds to a polymer chain-end control mechanism. Later work by Aida and Inoue<sup>56</sup> confirmed that **7** shows living polymerization behavior for propylene oxide, although the reported activity of the complex was much lower than that in their initial report, requiring 6 days to reach 100% conversion. Related complexes **8** and **9** were also reported to be active for propylene oxide polymerization. A detailed <sup>13</sup>C NMR study by Le Borgne and co-workers<sup>17b</sup> confirmed the microstructure of the polymer proposed by Inoue.



**Figure 4.** Well-defined complexes for polymerization of epoxides (dmca = dimethylcalixarene; salcy = N,N'-bis-(2-hydroxybenzylidene)-(1R,2R)-cyclohexane-1,2-diamine; tpp = 5,10,15,20-tetraphenylporphyrin).

**3.2.9. Aluminum–Schiff Base Complexes.** Le Borgne and co-workers<sup>57</sup> used the well-defined *N,N'*-bis(2-hydroxybenzylidene)-(1R,2R)-1,2-cyclohexanediamine (salcy) aluminum chloride complex (**10**) to oligomerize propylene oxide (Figure 4). At a catalyst loading of 5%, **10** oligomerized propylene oxide to 70% conversion in 62 h (TOF = 0.2 h<sup>-1</sup>) with a *k*<sub>rel</sub> of 1.3, slightly higher than that of previously reported systems.<sup>52</sup> The unreacted monomer showed an optical rotation of +1.85°, corresponding to an ee of 15% (Scheme 17). The

#### Scheme 17. Kinetic Resolution of Propylene Oxide Using 10



oligomers were reported to display both chloro and secondary hydroxyl end groups, suggesting that each aluminum center was responsible for growth of a single oligomer chain.<sup>57b</sup>

**3.2.10. Aluminum–Calixarene Complexes.** A dimethylcalixarene-based aluminum chloride complex (**11**) was synthesized by Kuran and co-workers<sup>58</sup> to polymerize propylene oxide (Figure 4). Although the complex had low activity (TOF = 0.06 h<sup>-1</sup>), it produced a regioregular polymer with an *m*-diad content of 74%.

**3.2.11. Other Well-Defined Aluminum Systems.** Bertrand and co-workers<sup>59</sup> synthesized complexes of *N,N,N'*-tris(trimethylsilyl)diethylenetriamine aluminum chloride (**12**) that were slightly active for propylene oxide polymerization. Catalyst **12** (Figure 4) produced regioregular low molecular weight polymer with 60% *m*-diads and 50% *mm*-triads.

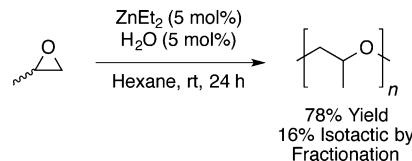
#### 3.3. Zinc-Based Catalysts for Stereoselective Epoxide Homopolymerization

The finding that addition of zinc salts as cocatalysts could enhance the activity of aluminum epoxide polymerization catalysts<sup>33,54</sup> has prompted interest in designing new zinc catalyst systems for stereoregular epoxide polymerization.

**3.3.1. Alkyl Zinc/H<sub>2</sub>O Catalysts.** In 1959, Furukawa and co-workers<sup>60</sup> discovered that diethylzinc reacted with propylene oxide when activated with water, oxygen, or alcohol to form

high molecular weight poly(propylene oxide). This result was surprising, as these protic cocatalysts are well known to decompose diethylzinc. Thus, Zn–O–Zn moieties were proposed to be the active species owing to their structural similarity to aluminum catalysts.<sup>32b</sup> The isotactic fraction of poly(propylene oxide) isolated from these systems exhibited high crystallinity and matched the semicrystalline poly(propylene oxide) obtained by Price (Scheme 18).<sup>8b</sup>

**Scheme 18. Semicrystalline Poly(propylene oxide) Obtained with ZnEt<sub>2</sub>/H<sub>2</sub>O**



Hurst and co-workers<sup>61</sup> explored the versatility of the ZnEt<sub>2</sub>/H<sub>2</sub>O catalyst by polymerizing a variety of epoxides and investigated the effect of the epoxide substituent on the crystallinity of the resultant polymer through polymerizations of *tert*-butyl ethylene oxide and styrene oxide. Poly(*tert*-butyl ethylene oxide) (semicrystalline fraction yield = 51%, *T<sub>m</sub>* = 149 °C) with high steric bulk on the side chains was obtained with crystallinity similar to that of poly(propylene oxide), whereas poly(styrene oxide) (semicrystalline part yield 26%, *T<sub>m</sub>* = 152–162 °C) had a low percentage of crystallinity.

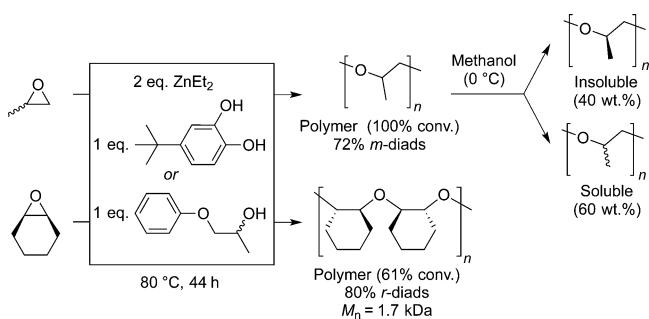
In 1985, Rabagliati and co-workers<sup>62</sup> reported a ZnPh<sub>2</sub>/H<sub>2</sub>O system for polymerization of propylene oxide that demonstrated the strong influence of the Zn:H<sub>2</sub>O ratio on the regioregularity of the polymer. An equimolar Zn:H<sub>2</sub>O ratio yielded a highly regioregular polymer, whereas lower Zn:H<sub>2</sub>O ratios produced regioerrors. The authors suggested that these results are due to a coordination–insertion mechanism at high Zn:H<sub>2</sub>O ratios, whereas a competitive cationic/coordination–insertion mechanism occurs at lower ratios.

**3.3.2. Zinc Alkoxide Catalysts.** Furukawa and co-workers<sup>60</sup> reported the use of methanol and ethanol as protic additives to diethylzinc-based catalyst systems. They found that the resulting polyethers are isolated in lower yields and show crystallinity lower than that of polyethers synthesized from the ZnEt<sub>2</sub>/H<sub>2</sub>O catalyst systems. In 1994, Kuran<sup>63</sup> used ZnEt<sub>2</sub>/polyhydric phenol, phenol, and 1-phenoxy-2-propanol catalyst systems to polymerize propylene oxide and cyclohexene oxide (Scheme 19). Although the poly(propylene oxide) formed from these catalyst systems contained 72% isotactic *m*-diads, the poly(cyclohexene oxide) showed 80% syndiotactic *r*-diads.

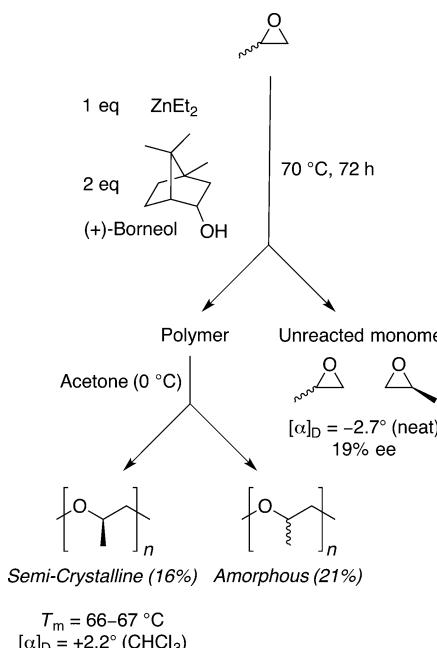
**3.3.3. Chiral Zinc Alkoxide Catalysts.** Inoue and co-workers<sup>64</sup> were the first to report that enantiopure alcohols such as (+)-borneol and (-)-menthol were effective additives for stereoselective polymerization of epoxides with diethylzinc (Scheme 20). For example, *rac*-propylene oxide was polymerized with ZnEt<sub>2</sub>/(+)-borneol (1:2) in toluene at 70 °C to give optically active poly(propylene oxide), for which the specific rotation in chloroform was +2.2°. Furthermore, the unreacted monomer was optically active ([ $\alpha$ ]<sub>D</sub> = -2.7°),<sup>64c</sup> indicating that consumption of (*R*)-propylene oxide was greater than that of (*S*)-propylene oxide. In related chemistry, styrene oxide has been polymerized with a diethylzinc/ $\alpha$ -pinene oxide catalyst system to give isotactic, regioregular polymer.<sup>65</sup>

Sepulchre and co-workers<sup>66</sup> polymerized cyclohexene oxide using diethylzinc modified with water and achiral and chiral

**Scheme 19. Polymerization of Epoxides with  $ZnEt_2$ /1-Phenoxy-2-propanol/4-*tert*-Butylcatechol**



**Scheme 20. Preparation of Enantioenriched Poly(propylene oxide) from *rac*-Propylene Oxide Using  $ZnEt_2$ / $(+)$ -Borneol**

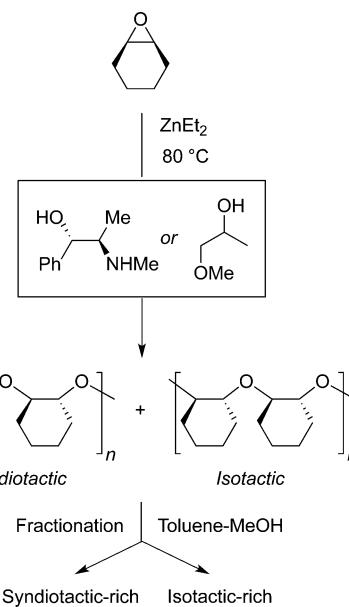


alcohols. They found that using catalyst systems consisting of either  $ZnEt_2$ /1-methoxy-2-propanol or  $ZnEt_2$ /(1*S*,2*R*)-ephedrine give mixtures of isotactic and syndiotactic poly(cyclohexene oxide), which can be separated through solvent fractionation. They proposed that simultaneous production of isotactic and syndiotactic polymer chains was the result of a mixture of different types of bimetallic active sites (Scheme 21).<sup>12a</sup>

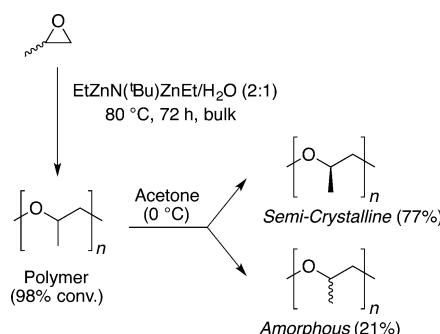
**3.3.4. Catalysts with  $ZnN(R)Zn$  Frameworks.** The  $ZnR_2/H_2O$  and  $ZnR_2/R'OH$  systems discussed herein are heterogeneous in common organic solvents; well-defined homogeneous catalysts have been sought to further elucidate the polymerization mechanism and improve catalyst activity and stereoselectivity. Araki and Oguni<sup>48a,67</sup> initially reported the syntheses of soluble  $Et_2AlOAlEt_2$  and  $EtZnN(^{t}Bu)ZnEt$  complexes that were activated for propylene oxide polymerization in the presence of a small amount of water. The reactions produced 77% semicrystalline isotactic polymer (Scheme 22).

**3.3.5. Zinc Alkoxide Clusters.** Tsuru and co-workers<sup>68</sup> synthesized and investigated the polymerization activity of semicrystalline zinc clusters. Complexes  $[Zn(OMe)_2 \cdot (EtZn-OMe)_6]$  (**13**),  $[Zn(OCH_2CH_2OMe)_2 \cdot (EtZn-OCH_2CH_2OMe)_6]$  (**14**), and  $[\{CH_3OCH_2CH(Me)\}_2 \cdot (EtZn-OCH_2CH_2OMe)_6]$  (**15**) were formed via addition of the corresponding alkoxyalcohols to  $ZnEt_2$  at 5 °C followed by heating at 50–80 °C and cooling to 5 °C. The molecular structure of each zinc structure was determined through X-ray crystallography (Figures 5 and 6).<sup>68a,d,e</sup>

**Scheme 21. Preparation of a Mixture of Isotactic and Syndiotactic Poly(cyclohexene oxide)**

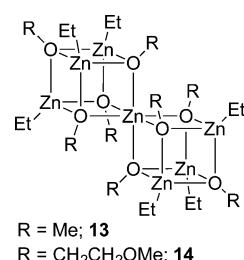


**Scheme 22. Stereospecific Polymerization of Propylene Oxide with  $EtZnN(^{t}Bu)ZnEt/H_2O$**



$OZnOCH(Me)CH_2OCH_3\}_2 \cdot \{EtZnOCH(Me)CH_2OCH_3\}_2$  (**15**) were formed via addition of the corresponding alkoxyalcohols to  $ZnEt_2$  at 5 °C followed by heating at 50–80 °C and cooling to 5 °C. The molecular structure of each zinc structure was determined through X-ray crystallography (Figures 5 and 6).<sup>68a,d,e</sup>

Scheme 23 shows the activity of each zinc cluster for propylene oxide polymerization. Although **13** and **14** are isostructural, they have different polymerization activities; **13** reaches 91% conversion in 216 h, whereas **14** reaches only 22% conversion in 240 h. The tacticity of the polymers produced by both zinc clusters is similar, however, with 63% *m*-diads for **13**



**Figure 5. Structures of complexes **13** and **14**.**

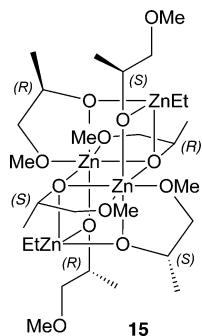
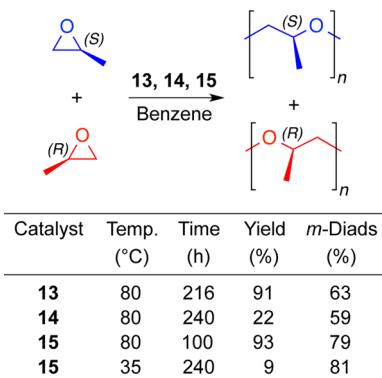


Figure 6. Structure of complex 15.

**Scheme 23. Polymerization of Propylene Oxide with Zinc Alkoxide Cluster Catalysts**


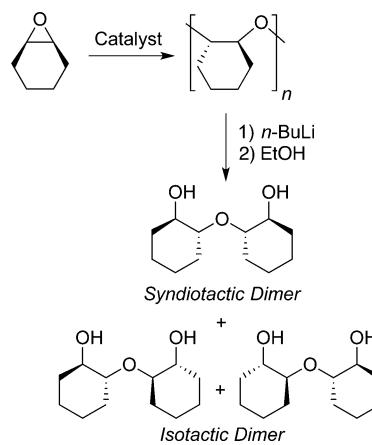
and 59% *m*-diads for **14**. Complex **15** is more active and more stereoselective for propylene oxide polymerization, reaching 93% conversion in 100 h and producing a polymer with 79% *m*-diads. The molecular structure of **15** is significantly different from those of **13** and **14**, containing six methoxy isopropyl groups in a chairlike structure. The methoxy groups exist in three different coordination environments: they can be noncoordinated, endo coordinated, or exo coordinated. Studies using deuterated catalysts have shown that the noncoordinating methoxyisopropyl groups initiate polymerization, while the coordinated methoxyisopropyl groups provide the chiral structure during polymerization.<sup>68g</sup>

Of these zinc clusters, only **15** is active for cyclohexene oxide polymerization (Scheme 24).<sup>69</sup> By examining the decomposition products from the polymer, Tsuruta and co-workers determined that the poly(cyclohexene oxide) formed was predominantly syndiotactic.

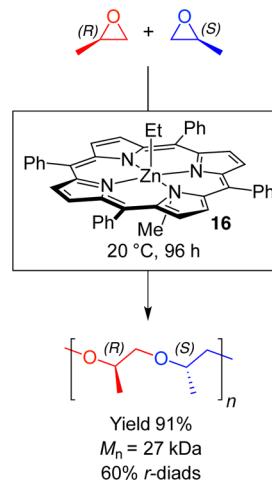
**3.3.6. Zinc Porphyrin-Based Catalysts.** Inoue and co-workers<sup>55</sup> reported the polymerization of propylene oxide at 20 °C with a zinc porphyrin catalyst ( $\text{Et}_2\text{Zn}/\text{N-methyl-5,10,15,20-tetraphenylporphyrin}$ , **16**). Unlike other zinc-based catalyst systems, which produce either atactic or semi-isotactic poly(propylene oxide), **16** produces poly(propylene oxide) with 60% syndiotactic *r*-diads.

**3.4. Alkali and Alkali Earth Metal-Based Catalysts (Potassium, Magnesium, Calcium) for Stereoselective Epoxide Homopolymerization**

Price<sup>70</sup> reported that potassium *tert*-butoxide slowly polymerizes *p*-methoxyphenyl glycidyl ether, *p*-tolyl glycidyl ether, phenyl glycidyl ether, *p*-chlorophenyl glycidyl ether, and 2,6-xyllyl glycidyl ether. Polymers from the first three monomers exhibit semicrystalline fractions; the amount of semicrystalline

**Scheme 24. Syndiospecific Polymerization of Cyclohexene Oxide with **15****


Catalyst	Syndiotactic Dimer (%)	Isotactic Dimer (%)
$\text{ZnEt}_2$	66	34
$(\text{EtZnOMe})_4$	66	34
<b>15</b>	81	19

**Scheme 25. Syndiotactic Poly(propylene oxide) Prepared with **16****


material decreases in the order *p*-MeO > *p*-Me > H. Poly(*tert*-butylethylene oxide) prepared with potassium *tert*-butoxide gives partially semicrystalline material that was initially proposed to be syndiotactic.<sup>71</sup> Price<sup>27d,e,70,72</sup> later showed that the material gives near equal amounts of erythro and threo HT dimers on degradation.

Osgan and Price<sup>33</sup> found that magnesium(II) methoxide and chloride polymerize propylene oxide in low yield over 10 days to give a polymer that consists of 10–20% isotactic material. By contrast, Colclough<sup>30</sup> reported that magnesium(II) chloride is inactive for propylene oxide polymerization. Vandenberg<sup>32b</sup> reported that magnesium alkyl compounds are active for the partially stereoselective polymerization of 1-alkene oxides, epichlorohydrin, styrene oxide, and glycidyl ethers, but no details have been provided. Tsuruta<sup>73</sup> studied the mechanism of propylene oxide polymerization by  $\text{MgEt}_2$  and found that near racemic monomer results in completely amorphous polymer.

Krylov and Livshits<sup>74</sup> reported the kinetic resolution polymerization of *rac*-propylene oxide using magnesium (+)-tartrate. After 13 months at ambient temperature, 0.2 g of catalyst and 4.3 g of monomer gave 0.4 g of polymer with a specific optical rotation of  $-9.2^\circ$  (versus  $-25 \pm 5^\circ$  for enantiopure isotactic polymer).

### 3.5. Titanium-Based Catalysts for Stereoselective Epoxide Homopolymerization

Osgan and Price<sup>33</sup> reported that  $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4/\text{ZnCl}_2$  catalyzes the polymerization of propylene oxide to give 7% isotactic material. Colclough<sup>30</sup> concurrently reported that  $\text{TiCl}_4$  produces some semicrystalline poly(propylene oxide) when a small amount of water is added, although few details were provided.

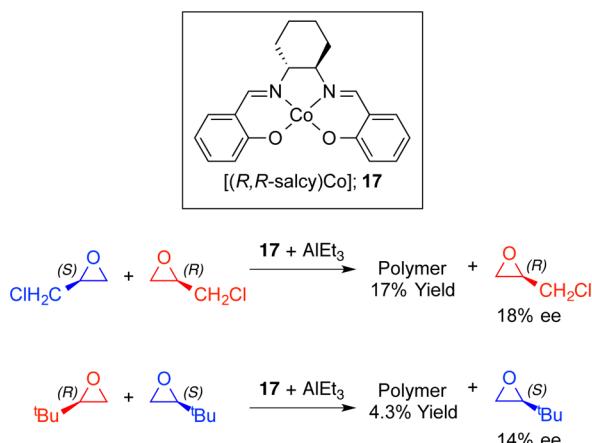
### 3.6. Manganese-Based Catalyst for Stereoselective Epoxide Homopolymerization

Strohmeier and Hartmann<sup>75</sup> polymerized propylene oxide using ultraviolet-irradiated  $\text{Mn}_2(\text{CO})_{10}$ . The resultant material could be fractionated to yield up to 39% semicrystalline, isotactic polymer with a  $T_m$  of 63 °C.

### 3.7. Cobalt-Based Catalysts for Stereoselective Epoxide Homopolymerization

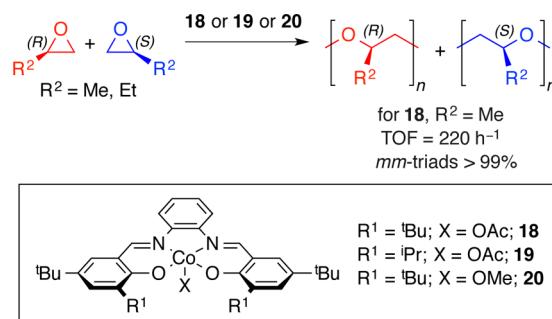
Tsuruta<sup>76</sup> used enantiopure (*salcy*)Co (17) complexes activated with  $\text{AlEt}_3$  for epoxide polymerization (Scheme 26). No enantioselectivity was observed for *rac*-propylene oxide, but a low  $k_{\text{rel}}$  of approximately 1.5 was observed for *tert*-butyl ethylene oxide and epichlorohydrin.

**Scheme 26. Kinetic Resolution of *tert*-Butyl Ethylene Oxide and Epichlorohydrin Using 17**



In 2005, Coates and co-workers<sup>11</sup> reported the first catalyst capable of polymerizing *rac*-propylene oxide to exclusively regioregular *rac*-isotactic poly(propylene oxide). This achiral catalyst, 18 (Scheme 27), produces polymer with greater than 99% *mm*-triads and high molecular weight (greater than 52 kDa). Racemic 1-butene oxide was also polymerized by 18. The resultant poly(butene oxide) is highly regioregular and isotactic with an *mm*-triad content greater than 99%, but its activity is lower than that observed for propylene oxide. The more sterically hindered monomer *rac*-1-hexene oxide yields only ~3% poly(hexene oxide), however, even with an extended reaction time. The polymerizations are highly sensitive to the reaction conditions, exhibiting activity in neat epoxide, diethyl ether, and toluene but not in tetrahydrofuran or methylene chloride. Polymerization activity is also sensitive to temperature, with decreased catalyst activity at temperatures higher or

**Scheme 27. Isoselective Polymerization of Epoxides Using 18–20**



lower than 0 °C. The polyether produced by 18 shows very high tacticity, and stereoerrors are undetectable by NMR spectroscopy. For this reason it is impossible to determine whether the stereocontrol is a result of chain-end or enantiomeric-site control, frustrating attempts to determine the source of stereocontrol in the polymerization system.

A later report<sup>77</sup> described the investigation of substituent and initiator (X) variations to 18 to elucidate the mechanisms of polymerization and stereocontrol. When the *o*-phenolate groups are changed from *tert*-butyl to isopropyl (19), the activity and stereoselectivity for the polymerization of propylene oxide are reduced; the stereoerrors present in the resultant polyether are characteristic of an enantiomeric-site control mechanism. Other small variations to the structure of 18, including the initiator, diamine, and *p*-phenolate substituent, lead to catalysts of widely varying activity. For example, replacing the *p*-*tert*-butyl group with either a smaller methyl group or a larger [ $\text{C}(\text{CH}_3)_2\text{CH}_2\text{Bu}$ ] alkyl substituent results in complete loss of catalytic activity. Likewise, variation of the axial initiator (X) has a strong effect on activity, which is unexpected because X becomes a polymer end group and is presumably far from the metal center for most of the polymerization. Furthermore, the activity of 18 also varies depending on crystallization conditions. Taken collectively, these observations and others suggest that undissolved 18 initiates polymerization.

In support of this argument, when the acetate group of 18 is changed to a methoxide group 20 produces a slower but still highly isoselective catalyst that is also crystalline, allowing for determination of its solid state structure. This structure (Figure 7) reveals that each metal center of 20 is coordinated to a methanol molecule that is hydrogen bound to another methanol molecule, which is also hydrogen bound to the methoxide of the next molecule of 20. This arrangement results in an infinite coordination polymer with neighboring 20 molecules related through pseudo- $C_2$  symmetry, creating a chiral environment for homopolymerization of propylene oxide where adjacent stacks exhibit mirror image symmetry. The cobalt centers in each stack are separated by 7.13 Å. The displacement of a cobalt-coordinated methanol by a propylene oxide molecule is proposed to result in a favorable geometry for ring opening of the epoxide by the adjacent methoxide. This yields a growing alkoxide chain and an empty cobalt coordination site for the next propylene oxide molecule to be incorporated into the polymer.

The bimetallic nature of this mechanism is consistent with previously proposed epoxide polymerization mechanisms. Blum and co-workers<sup>77</sup> used *in operando* bright field microscopy to study the polymerization of epoxides on the surface of 18 and

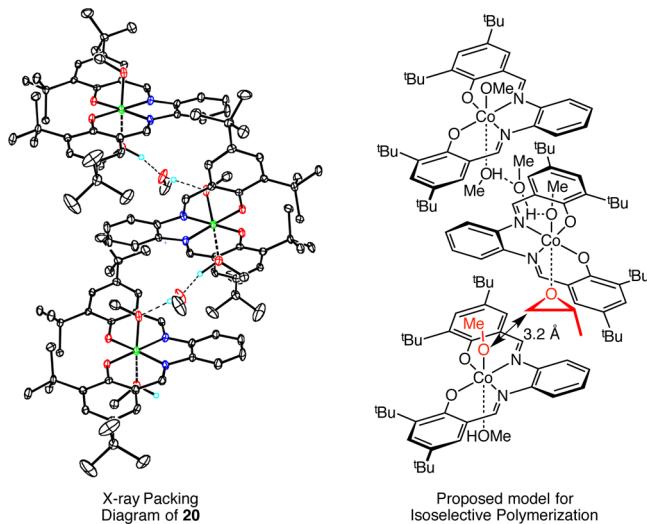


Figure 7. X-ray crystal structure of 20.

20. To prevent dissolution of the crystals in propylene oxide, they used gaseous ethylene oxide as a model substrate. The studies revealed that loci of polymerization are present on the crystal surfaces rather than as a homogeneous covering of the surface. These results are consistent with the proposed solid state mechanism of polymerization.

In 2008, Coates and co-workers<sup>78</sup> reported the homogeneous, bimetallic catalyst 21, which is active for polymerization of a variety of monosubstituted, terminal epoxides when combined with an ionic cocatalyst salt such as bis(triphenylphosphine)iminium acetate, [PPN][OAc] (Figure 8).

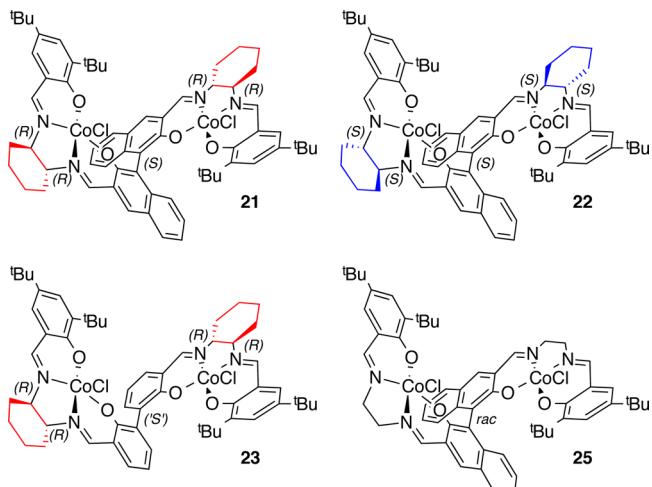


Figure 8. Bimetallic catalysts for epoxide polymerizations.

and Scheme 28). The bimetallic catalyst was designed to mimic the solid state structure of 20, with two metal centers positioned in a geometry favorable for epoxide polymerization. This catalyst/cocatalyst combination kinetically resolves racemic epoxides into valuable enantiopure epoxides and isotactic polyethers with high  $k_{\text{rel}}$  values (greater than 200 for many epoxides), high *mm*-triad content (greater than 98% for many epoxides), and high TOFs (up to 30 000 h<sup>-1</sup>).<sup>79</sup> The catalyst polymerizes numerous monosubstituted epoxides, including alkyl, aryl, unsaturated, and fluorinated epoxides as well as glycidyl ethers. The resultant polymers are highly

isotactic, and the unreacted enantiomer can be recovered from the reaction mixture. Complex *rac*-21 is the first catalyst capable of isoselectively polymerizing a large variety of epoxides to isotactic polyethers.

Synthesis of the diastereomer of 21, 22,<sup>80</sup> demonstrates that the stereoselectivity of these bimetallic catalyst motifs is determined by the stereochemistry of the binaphthol linker. Complex 22 selects for the same propylene oxide enantiomer as 21, although 22 is less active and slightly less selective than 21. Switching from a chiral binaphthol linker to an achiral biphenol linker<sup>79</sup> results in a complex in which the stereochemistry of the diamines determines the preferred linker conformation. Crystal structures of the tetrapyridine-adducted cobalt complex with (1*R*,2*R*)-1,2-diaminocyclohexane, 23·py<sub>4</sub>,<sup>79</sup> and the aluminum chloride complex with (1*S*,2*S*)-1,2-diaminocyclohexane, 24,<sup>81</sup> reveal that in the solid state, (1*R*,2*R*)-1,2-diaminocyclohexane results in a complex with pseudo-*S* stereochemistry at the biphenol, whereas (1*S*,2*S*)-1,2-diaminocyclohexane gives a complex with pseudo-*R* stereochemistry at the biphenol. Complex 23 is effective for enantioselective polymerization of propylene oxide, selecting the same enantiomer that 21 does with a  $k_{\text{rel}}$  of 32 and a TOF of 490 h<sup>-1</sup>.<sup>79</sup>

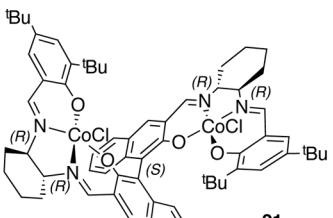
Complex *rac*-21 is desirable because it shows exceptional activity and isoselectivity for polymerization of a variety of terminal epoxides. However, it requires that both enantiomers of 21 be independently synthesized and combined in equimolar amounts due to formation of inseparable diastereomers when a one-pot synthesis of the ligand for *rac*-21 is attempted. Because the chirality of the diamines has little effect on this class of catalysts, achiral ethylene diamine can be used to synthesize *rac*-25 to avoid the problem of diastereomer formation.<sup>80</sup> Complex *rac*-25 is active for polymerization of propylene oxide when combined with [PPN][OAc] but produces poly(propylene oxide) with an *mm*-triad content of only 67%. Switching the cocatalyst from [PPN][OAc] to [PPN][OPiv] (OPiv = pivalate,  $\text{^tBuCO}_2^-$ ) increases both the activity and the isoselectivity of *rac*-25, resulting in poly(propylene oxide) with an *mm*-triad content of 97%. As observed for 21, *rac*-25 is active for polymerization of a range of monosubstituted epoxides with various functional groups (Scheme 29).

Because the cocatalyst salt plays a significant role in the kinetics and stereoselectivity of the polymerization, optimization studies were performed for both the anionic and the cationic parts of the cocatalyst.<sup>82</sup> The combination of base-stable, phosphazinium cations and sterically bulky pivalate anions gives the highest stereoselectivities and activities, with a  $k_{\text{rel}}$  of greater than 300 for many epoxides. A mechanistic study<sup>79</sup> of 21 using density functional theory calculations found that the most energetically favorable initiation and propagation pathways involved the carboxylate anions from the cocatalyst binding as exo ligands.

### 3.8. Main Group Metal-Based Catalysts (Boron and Tin) for Stereoselective Epoxide Homopolymerization

Colclough<sup>30</sup> reported that  $\text{BCl}_3$  and  $\text{SnCl}_4$  produce some semicrystalline poly(propylene oxide) when a small amount of water is added, but few details are provided. Schütz and co-workers<sup>83</sup> found that tin phosphate coordination polymers can be used as catalysts for polymerization of propylene oxide, producing polymers with up to 88% isotactic *m*-diads and no allyl end groups. They proposed a bimetallic mechanism involving adjacent tin metal centers in the coordination polymer chain. Vandenberg<sup>12a</sup> found that  $\text{BF}_3$  etherate is a

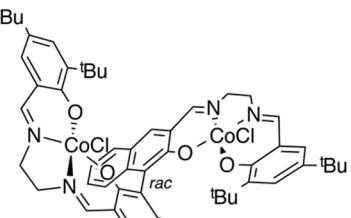
Scheme 28. Epoxide Polymerization with 21/[PPN][OAc]



**21**

$(R)$ -epoxide + $(S)$ -epoxide	$[PPN][OAc]$	$(R)$ -epoxide + $\left[ \begin{array}{c} (S) \\   \\ R-O-C(R)- \\   \\ O \\ \backslash \\ R \end{array} \right]_n$					
epoxide	TOF (min <sup>-1</sup> )	$M_n$ (kDa)	$k_{rel}$	epoxide	TOF (min <sup>-1</sup> )	$M_n$ (kDa)	$k_{rel}$
$O$	91	26	>300	$O$	760	140	>70
$O$	16	61	>300	$O$	960	130	>70
$O$	6	77	>100	$O$	14	79	>20
$O$	10	8	>50	$O$	21	46	>300
$O$	14	33	>50	$O$	11	50	>70
$O$	130	110	>100		190	20	>300
$O$	230	69	>80				

Scheme 29. Epoxide Polymerization with 25/[PPN][OPiv]



**25**

$(R)$ -epoxide + $(S)$ -epoxide	$[PPN][OPiv]$	$\left[ \begin{array}{c} O \\   \\ R \\   \\ O \end{array} \right]_n + \left[ \begin{array}{c} O \\   \\ (S) \\   \\ R \\   \\ O \end{array} \right]_n$					
epoxide	TOF (min <sup>-1</sup> )	$M_n$ (kDa)	<i>mm</i> -triads (%)	epoxide	TOF (min <sup>-1</sup> )	$M_n$ (kDa)	<i>mm</i> -triads (%)
$O$	440	107	97	$O$	20	59	≥97
$O$	480	163	97	$O$	3600	278	≥97
$O$	14	85	≥97	$O$	180	135	92

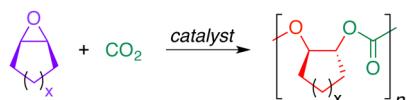
viable catalyst for *cis*- and *trans*-2-butene oxide polymerization at  $-78\text{ }^\circ\text{C}$ ; the *cis* monomer gave amorphous polymer, whereas the *trans* monomer provided highly semicrystalline polymer ( $T_m = 94\text{ }^\circ\text{C}$ ). Degradation of the polymers revealed *rac*- and *meso*-2,3-butane diols, respectively, consistent with inversion of one stereocenter during polymerization.

#### 4. STEREOSELECTIVE EPOXIDE COPOLYMERIZATION WITH CARBON DIOXIDE

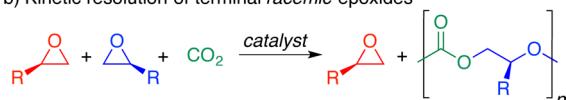
Because petroleum and natural gas are nonrenewable resources, research in industry and academia has been directed toward developing new materials derived from renewable resources.  $\text{CO}_2$  is appealing because it is nontoxic, nonflammable, and abundant. Although  $\text{CO}_2$  is challenging to use due to its high thermodynamic stability, Inoue<sup>84</sup> demonstrated in 1969 that it

can be catalytically copolymerized with epoxides to give polycarbonates. Others have since reported metal-based catalysts that produce atactic polycarbonates.<sup>85</sup> Unfortunately, these materials have limited applications because of poor physical properties.<sup>86</sup> A promising approach to improving their thermal and mechanical properties is to introduce stereoregularity into the polymer chain.<sup>87</sup> In this section of the review, we cover examples of epoxide/CO<sub>2</sub> copolymerization catalysts that either desymmetrize *meso*-epoxides (Figure 9a) or kinetically resolve terminal *rac*-epoxides (Figure 9b).

a) Desymmetrization of *meso*-epoxides



b) Kinetic resolution of terminal *rac*-epoxides

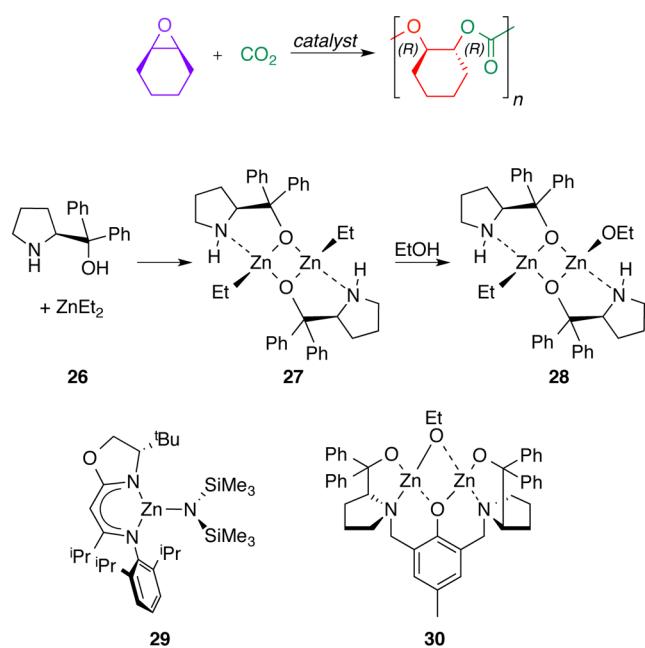


**Figure 9.** Stereoselective polymerizations with (a) *meso*-epoxides and (b) terminal *rac*-epoxides.

#### 4.1. Zinc-Based Catalysts for Stereoselective Copolymerization of Epoxides and CO<sub>2</sub>

Early examples of the enantioselective copolymerization of epoxides and CO<sub>2</sub> used chiral zinc-based catalysts (Scheme 30).

**Scheme 30.** Zinc-Based Catalysts for Stereoselective Copolymerization of Cyclohexene Oxide and CO<sub>2</sub>



catalyst	T <sub>rxn</sub> (°C)	M <sub>n</sub> (kDa)	PDI	% ee	ref.
26	40	8.4	2.2	73	88
27	40	11.8	15.7	49	91
28	40	7.7	1.63	80	91
29	20	14.7	1.35	72	90
30 <sup>a</sup>	60	44	1.82	18	93

<sup>a</sup> Catalyst 30 gives predominantly S,S pCHC.

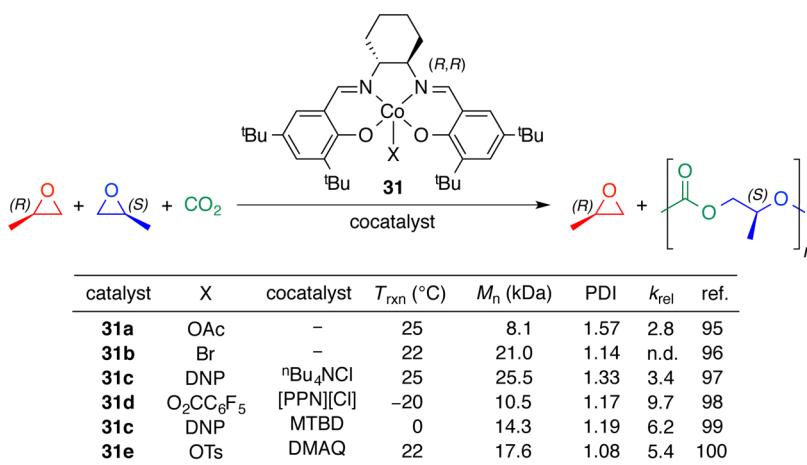
In 1999, Nozaki and co-workers<sup>88</sup> reported that a 1:1 mixture of (*S*)- $\alpha,\alpha$ -diphenylpyrrolidine-2-yl-methanol and ZnEt<sub>2</sub> (**26**) copolymerizes cyclohexene oxide with CO<sub>2</sub> at 40 °C and 440 psi CO<sub>2</sub> to give poly(cyclohexene carbonate). The polymer is perfectly alternating with an M<sub>n</sub> of 8.4 kDa and a PDI of 2.2. Hydrolysis with base yields the corresponding *trans*-cyclohexane-1,2-diol with 73% ee. The authors subsequently studied the carbonyl region of the <sup>13</sup>C NMR spectra of model poly(cyclohexene carbonate) oligomers to assign isotactic (153.7 ppm) and syndiotactic (153.3–153.1 ppm) diads,<sup>89</sup> which agree with those proposed by Coates and co-workers.<sup>90</sup> No *cis*-diol is observed on polymer degradation, which indicates that the reaction proceeds through an S<sub>N</sub>2-type mechanism.

Nozaki and co-workers<sup>91</sup> also prepared well-defined precatalysts for this copolymerization. Crystals of dimeric complex **27** suitable for X-ray analysis were obtained from the 1:1 reaction of (*S*)- $\alpha,\alpha$ -diphenylpyrrolidine-2-yl-methanol and ZnEt<sub>2</sub>. Under the same conditions used above (40 °C and 440 psi CO<sub>2</sub>), **27** gives iso-enriched poly(cyclohexene carbonate) (M<sub>n</sub> = 11.8 kDa, PDI = 15.7, TOF = 0.6 h<sup>-1</sup>) with an ee of 49%, which is lower than that observed using *in situ* catalyst **26**. The authors found that ee increases when ethanol is added to polymerizations catalyzed by **27**. The highest ee achieved with **27** (80%) is realized when it is pretreated with 0.5 equiv of ethanol and subsequently reprecipitated with tetrahydrofuran/hexane. The authors proposed that the product of this reaction is **28**, although they were unable to isolate crystals suitable for X-ray analysis. They proposed that the high enantioselectivity of *in situ* catalyst **26** is due to an impurity (e.g., EtZnOEt) in the ZnEt<sub>2</sub> used to make the catalyst. End-group analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry as well as <sup>1</sup>H NMR spectroscopy revealed that polymerization is initiated by the aminoalcohol when **27** is used. However, as ethanol is added, the proportion of aminoalcohol-terminated poly(cyclohexene carbonate) decreases as the proportion of ethanol-terminated poly(cyclohexene carbonate) grows. Furthermore, the authors observed a nonlinear relationship between the enantiopurity of the ligand and the ee of the hydrolyzed polycarbonate, which suggests a bimetallic mechanism.<sup>92</sup>

In 2000, Coates and co-workers<sup>90a</sup> reported C<sub>1</sub>-symmetric imine-oxazoline-ligated zinc bis(trimethylsilyl)amido complexes that are effective in the stereoselective copolymerization of cyclohexene oxide/CO<sub>2</sub>. After optimization of the electronic and steric properties of the ligand, compound **29** was found to exhibit the highest enantioselectivity (72% ee). The resulting poly(cyclohexene carbonate) is perfectly alternating and has an M<sub>n</sub> of 14.7 kDa, a PDI of 1.35, and T<sub>g</sub> and T<sub>m</sub> of 120 and 220 °C, respectively. Furthermore, **29** catalyzes the copolymerization of cyclopentene oxide and CO<sub>2</sub> to produce poly(cyclopentene carbonate) (PCPC) with 76% ee. As revealed by <sup>13</sup>C NMR spectroscopy, the experimental carbonyl tetrad distributions for PCPC match those predicted for an enantiomeric-site control mechanism. Related compounds have recently been shown to give PCHC with up to 94% ee.<sup>90b</sup>

In 2005, Ding and co-workers<sup>93</sup> reported the use of the dinuclear zinc complex **30** for asymmetric copolymerization of cyclohexene oxide and CO<sub>2</sub>. Complex **30**, originally introduced by Trost<sup>94</sup> in 2000 as a catalyst for enantioselective aldol condensations, is generated *in situ* (5 mol %), and copolymerization is performed at 60 °C for 24 h under 440 psi CO<sub>2</sub>. The catalyst gives perfectly alternating poly(cyclohexene carbonate) in quantitative yield with an M<sub>n</sub> of

**Scheme 31.** Effect of Initiator and Cocatalyst on the Stereoselectivity of Complexes **31a–e** in *rac*-Propylene Oxide/CO<sub>2</sub> Copolymerization<sup>a</sup>



<sup>a</sup>n.d. = not determined, DNP = 2,4-dinitrophenoxide, PPN = bis(triphenylphosphine)iminium, MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, DMAQ = *N,N*-dimethylaminoquinoline.

44 kDa and a PDI of 1.82; however, the ee of the diol derived from the hydrolyzed polymer is only 18%.

#### 4.2. Cobalt-Based Catalysts for Stereoselective Copolymerization of Epoxides and Carbon Dioxide

Recently, (salen)Co(III)-based (salen = *N,N'*-bis(salicylidene)-1,2-diaminoalkane) catalysts have been found to be highly effective for enantioselective copolymerization of epoxides and CO<sub>2</sub>. Lu and Daresbourg<sup>85g</sup> reviewed cobalt-based catalysts for making cyclic carbonates and polycarbonates, and Kleij and co-workers<sup>85h</sup> recently reviewed selected examples of stereoselective cobalt catalysts for making polycarbonates. We focus herein on examples of enantioselective catalysts for polymerization of epoxides and CO<sub>2</sub>. Because there are many examples of both the kinetic resolution of terminal *rac*-epoxides and the desymmetrization of *meso*-epoxides, they are discussed separately.

**4.2.1. Kinetic Resolution of *rac*-Epoxides.** Coates and co-workers<sup>95</sup> were the first to report the use of (salen)Co(III)-based catalysts for copolymerization of propylene oxide and CO<sub>2</sub>. Although these catalysts require high CO<sub>2</sub> pressure (800 psi), they selectively produce polycarbonate over cyclic carbonate. The resulting polymers are highly regioregular and highly alternating. With *rac*-propylene oxide, catalyst **31a** (Scheme 31) exhibits a *k<sub>rel</sub>* of 2.8 and preferentially consumes (*S*)-propylene oxide. Because the same enantiomer of propylene oxide is consumed preferentially with approximately the same *k<sub>rel</sub>* as that observed by Jacobsen and co-workers<sup>40</sup> for the cobalt-catalyzed asymmetric ring opening of aliphatic epoxides with benzoic acid, a similar mechanism is proposed for this polymerization.

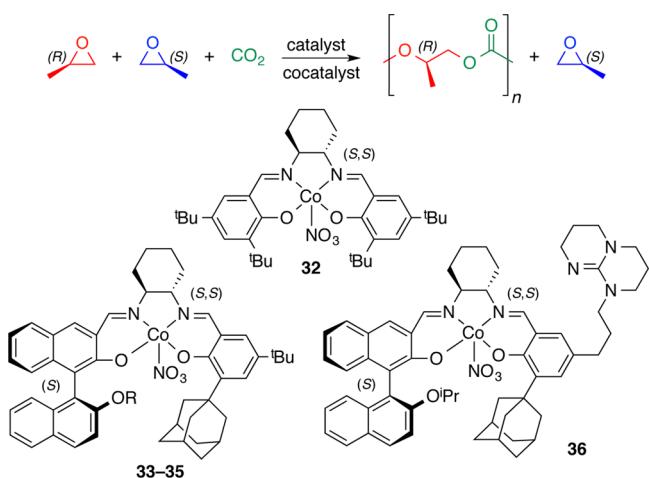
Subsequent research has demonstrated that both the enantiopture of the catalyst and the presence of a cocatalyst dramatically impact the activity and stereoselectivity of (salen)Co(III) complexes (Scheme 31). Coates and co-workers<sup>96</sup> reported in 2005 that polymerization of *rac*-propylene oxide/CO<sub>2</sub> with **31b** in the absence of cocatalyst gives essentially atactic polycarbonate at high CO<sub>2</sub> pressure, consistent with earlier results obtained with **31a**. However, when *rac*-**31b** is used instead, syndioenriched poly(propylene carbonate) is observed by <sup>13</sup>C NMR spectroscopy—the first report of this polymer architecture. Others later found that the

combination of nucleophilic cocatalysts and enantiopure (salen)Co(III) complexes gives iso-enriched poly(propylene carbonate) and allows for this copolymerization to proceed under low CO<sub>2</sub> pressure. Lu and co-workers<sup>97</sup> found that using <sup>n</sup>Bu<sub>4</sub>NCl with **31c** gives iso-enriched poly(propylene carbonate) with a *k<sub>rel</sub>* of 3.5 at 25 °C. Coates and co-workers<sup>96,98</sup> subsequently found that the combination of [PPN][Cl] with **31d** also yields iso-enriched poly(propylene carbonate) with a *k<sub>rel</sub>* up to 9.7 at −20 °C. In addition to onium salts, neutral amine cocatalysts can enhance enantioselectivity. Lu and co-workers<sup>99</sup> found that using 7-methyl-1,5,7-triazabicyclo[4.4.0]-dec-5-ene (MTBD) with **31c** improves the *k<sub>rel</sub>* to 6.2 at 0 °C, and Paddock and Nguyen<sup>100</sup> were able to achieve a *k<sub>rel</sub>* up to 5.4 using *N,N*-dimethylaminoquinoline (DMAQ) with **31e** at room temperature.

Lu and co-workers<sup>101</sup> prepared asymmetric (salen)Co(III) complexes containing a chiral 1,1'-bi-2-naphthol (BINOL) unit on one side and a 3-adamantyl substituent on the other (Scheme 32). Higher enantioselectivity is observed relative to enantiopure symmetrical (salen)Co(III) complexes. At 25 °C and 145 psi CO<sub>2</sub>, **32** (the enantiomer of **31** with a nitrate initiator) with PPNCl exhibited a *k<sub>rel</sub>* of 4.6. By comparison, multichiral **33** with [PPN][Cl] gives a *k<sub>rel</sub>* of 9.8 under the same conditions. The bulk of the BINOL unit significantly impacts the enantioselectivity of the catalyst. *k<sub>rel</sub>* increases to 10.6 and 12.4 under the same conditions with bulkier BINOL units (**34** and **35**, respectively). *k<sub>rel</sub>* of **35**/[PPN][Cl] improves to 23.7 by decreasing the temperature to −25 °C. The highest *k<sub>rel</sub>* in this polymerization to date (24.3) is achieved at −20 °C with a similar catalyst that has a pendant triazabicyclododecene (TBD) cocatalyst (**36**).<sup>102</sup>

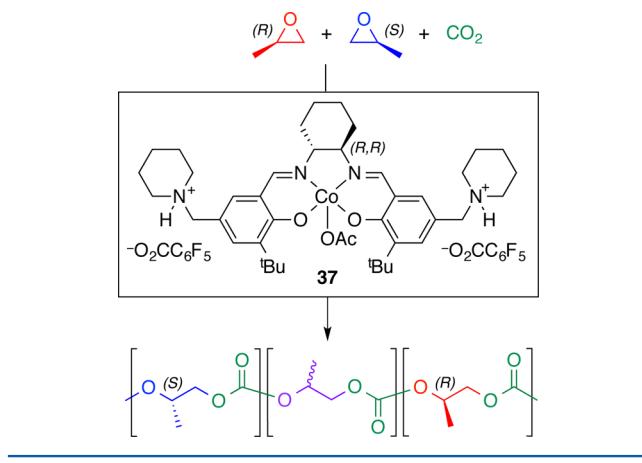
In 2011, Nozaki and co-workers<sup>103</sup> reported a (salen)Co(III) catalyst with covalently attached piperidiniums (**37**) that produces stereogradient poly(propylene carbonate) (Scheme 33). This catalyst design is similar to one that they reported in 2006.<sup>104</sup> The covalently attached piperidiniums give **37** several advantages over alkyl-substituted (salen)Co(III) complexes. The catalyst is active without a nucleophilic cocatalyst, and it gives perfectly alternating poly(propylene carbonate) without concomitant formation of propylene carbonate. Furthermore, this catalyst reaches full conversion of propylene oxide when

**Scheme 32.** Highly Enantioselective Catalysts for Kinetic Resolution of Propylene Oxide with CO<sub>2</sub>



catalyst	R	cocatalyst	T <sub>rxn</sub> (°C)	M <sub>n</sub> (kDa)	PDI	k <sub>rel</sub>	ref.
32	-	PPNCI	25	28.0	1.16	4.6	101
33	Me	PPNCI	25	29.9	1.13	9.8	101
34	nBu	PPNCI	25	29.0	1.12	10.6	101
35	iPr	PPNCI	25	28.7	1.13	12.4	101
35	iPr	PPNCI	-25	6.5	1.18	23.7	101
36	-	-	-20	20.4	1.15	24.3	102

**Scheme 33.** Synthesis of Stereogradient Poly(propylene carbonate) Using 37 with Covalently Attached Piperidinium Substituents

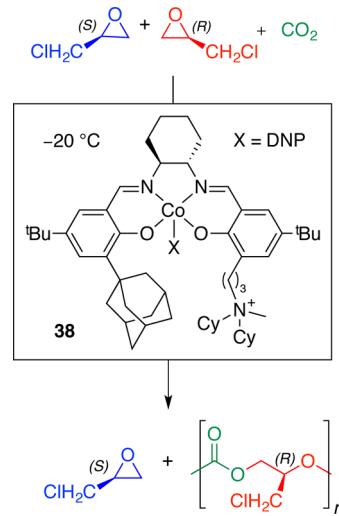


the polymerization is performed in solvent. Due to the enantioselectivity of 37 ( $k_{\text{rel}} = 3.5$ ), (S)-propylene oxide is consumed first, yielding stereogradient poly(propylene carbonate). This polymer exhibits an unusually high thermal decomposition temperature that is greater than that of isotactic poly(propylene carbonate) (281 versus 245 °C).

Recently, enantiopure (salen)Co(III)-based catalysts have been applied to the kinetic resolution of terminal epoxides other than propylene oxide. Lu and co-workers<sup>102</sup> found that 37/[PPN][Cl] resolves 1,2-butene oxide and 1,2-hexene oxide at 0 °C with  $k_{\text{rel}}$  values of 9.8 and 6.7, respectively. In addition, the kinetic resolution of phenyl glycidyl ether using a similar catalyst was reported with a  $k_{\text{rel}}$  of 3.1.<sup>103</sup> Lu and Darenbourg<sup>104</sup> used 35/[PPN][DNP] for the kinetic resolution of styrene oxide with a  $k_{\text{rel}}$  of 3.3. Lu and Darenbourg<sup>105</sup> also recently investigated the kinetic resolution of epichlorohydrin with a (salen)Co(III) complex bearing a

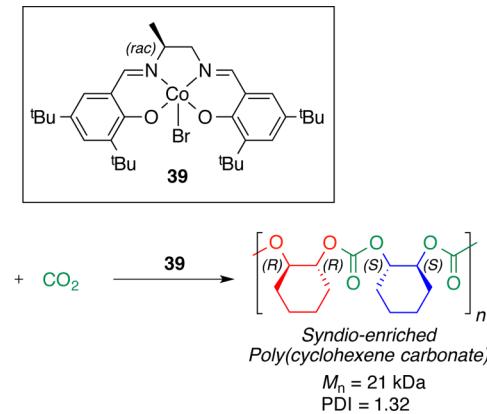
covalently tethered bulky ammonium salt (38), which exhibits a  $k_{\text{rel}}$  of 8.9 at -20 °C (Scheme 34).

**Scheme 34.** Kinetic Resolution of Racemic Epichlorohydrin with CO<sub>2</sub> Using 38<sup>107</sup>



**4.2.2. Desymmetrization of meso-Epoxides.** Coates and co-workers<sup>108</sup> reported the first syndioselective copolymerization of cyclohexene oxide and CO<sub>2</sub> using (salen)Co(III) catalysts in 2006. The highest level of syndioselectivity is observed when *rac*-39 is used at 22 °C and 800 psi CO<sub>2</sub>. The resulting polymer has an  $M_n$  of 21.0 kDa and a PDI of 1.32 with 81% *r*-centered tetrads (Scheme 35) and greater than 96%

**Scheme 35.** Copolymerization of Cyclohexene Oxide with CO<sub>2</sub> and 39 To Give Syndioenriched Poly(cyclohexene carbonate)<sup>108</sup>



carbonate linkage selectivity. Enantiomerically pure, racemic, and achiral (salen)Co(III) catalysts all produce syndioenriched poly(cyclohexene carbonate), suggesting that syndioselectivity is due to a chain-end control mechanism. The effects of catalyst structure and reaction conditions on selectivity and catalytic activity were also investigated. Greater steric bulk around the metal center and low CO<sub>2</sub> pressure decrease syndioselectivity and activity. Addition of [PPN][Cl] as a cocatalyst increases catalytic activity but decreases syndioselectivity.

In contrast to the above results, Coates and co-workers<sup>108</sup> found that 40 (Figure 10) with bulky cumyl substituents gives iso-enriched poly(cyclohexene carbonate) (65% *m*-centered

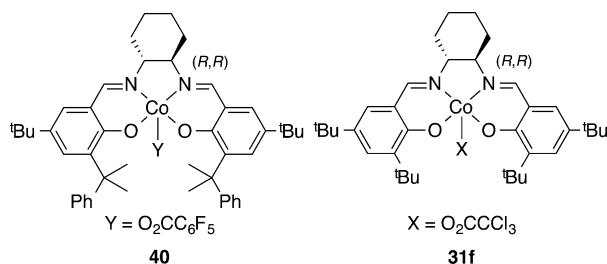
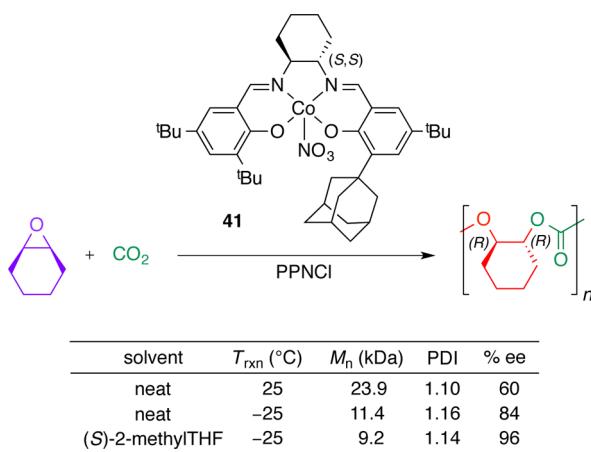


Figure 10. Structures of complexes 40 and 31f.

tetrad) at low  $\text{CO}_2$  pressure. Lu and co-workers<sup>109</sup> independently reported the isoselectivity of related cobalt complexes. At 25 °C and 220 psi  $\text{CO}_2$ , 31f (Figure 10) with [PPN][Cl] gives poly(cyclohexene carbonate) with an ee of 38%. This catalyst is less selective, with an ee of 28%, but more active when the temperature and pressure are increased to 80 °C and 360 psi  $\text{CO}_2$ , respectively. Efforts to improve the stereoselectivity by changing the diamine backbone were unsuccessful.

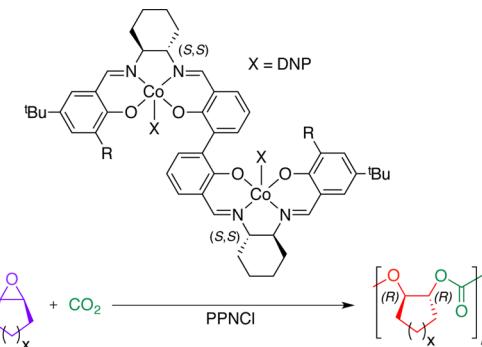
In 2012, Lu and co-workers<sup>110</sup> reported a series of  $C_1$ -symmetric catalysts that are highly stereoselective for copolymerization of cyclohexene oxide with  $\text{CO}_2$  (Scheme 36). Improved enantioselectivity is achieved by increasing the

Scheme 36. Highly Stereoselective Copolymerization of Cyclohexene Oxide with  $\text{CO}_2$  Using 41<sup>110</sup>

steric bulk of the ortho substituent on one side of the ligand from a *tert*-butyl group (38% ee, 32) to an adamantyl group (60% ee, 41). Higher selectivity with 41 is observed (84% ee) when the polymerization is performed at -25 °C. The highest selectivity (96% ee) is achieved by performing the polymerization with 41 at -25 °C in a 1:3 mixture of cyclohexene oxide and (S)-2-methyltetrahydrofuran, which the authors propose acts as a chiral induction agent. This polymer has an  $M_n$  of 9.2 kDa, a PDI of 1.14, and a  $T_m$  of 216 °C. The authors also tested multichiral catalyst 36 with [PPN][Cl], which is highly enantioselective in the kinetic resolution of propylene oxide in polycarbonate synthesis (vide supra). At room temperature, this catalyst gives an ee of 84%; lowering the temperature to 0 °C improves the ee to 90%. The enantioselectivity of 36 is not improved in the presence of (S)-2-methyltetrahydrofuran.

Although 41 is highly selective at low temperature, its catalytic activity is modest (TOF less than 3 h<sup>-1</sup> at -25 °C), and the molecular weight of the resulting polymers is low. Lu

and co-workers<sup>81</sup> addressed these issues with bimetallic catalysts in which two (salen)Co(III) moieties are attached through a biphenol linker (42–44, Scheme 37). These catalysts

Scheme 37. Bimetallic Cobalt-Based Complexes for Desymmetrization of Cyclohexene Oxide and Cyclopentene Oxide<sup>81</sup>

catalyst	R	monomer	solvent	$T_{\text{rxn}}$ (°C)	$M_n$ (kDa)	PDI	% ee
42	'Bu	CPO (x = 1)	neat	25	35.0	1.28	81
43	Me	CPO (x = 1)	toluene	25	107.9	1.36	>99
44	H	CHO (x = 2)	neat	25	18.9	1.23	81
44	H	CHO (x = 2)	toluene	0	35.6	1.35	98

exhibit improved catalytic activity and produce higher molecular weight polymer with both cyclopentene oxide and cyclohexene oxide while maintaining high enantioselectivity. The improved activity and selectivity observed in bimetallic (salen)-based catalysts has precedence. Jacobsen and co-workers observed similar improvements in the asymmetric ring opening of cyclopentene oxide with bimetallic (salen)CrCl complexes.<sup>111</sup> Also, Coates and co-workers<sup>13b,78b,79,80,82</sup> found that 21, which contains two (salen)Co(III) moieties attached with a binaphthol linker, is exceptionally active and enantioselective in the homopolymerization of terminal epoxides (vide supra).

Lu and co-workers<sup>81</sup> investigated cyclopentene oxide/ $\text{CO}_2$  copolymerization using 21/[PPN][DNP]; modest enantioselectivity (ee = 25%) and activity (TOF < 10 h<sup>-1</sup>) were observed at 25 °C in neat epoxide. By contrast, the biphenol-bridged analogue 42 exhibits an increased ee of 81% and improved activity (TOF = 191 h<sup>-1</sup>) under the same conditions while producing polymer with a molecular weight of 35 kDa (Scheme 37). Unexpectedly, reducing the steric bulk of the ortho substituents from *tert*-butyl groups to methyl groups (43) improves the ee to over 99% while maintaining a TOF greater than 100 h<sup>-1</sup> at 25 °C. Isotactic poly(cyclopentene carbonate) with molecular weight up to 107.9 kDa is obtained when the polymerization is performed in toluene, which allows the polymerization to reach full conversion of epoxide. A similar catalyst with protons in the ortho positions (44) can copolymerize cyclohexene oxide and  $\text{CO}_2$  with [PPN][DNP] in neat epoxide at 25 °C with a high TOF of 1409 h<sup>-1</sup> to give poly(cyclohexene oxide) with an ee of 81% and a molecular weight of 18.9 kDa. The stereoselectivity of 44 in polymerizing cyclohexene oxide with  $\text{CO}_2$  is greatly improved (ee = 98%) when the polymerization is performed in toluene at 0 °C, although the TOF is reduced to 42 h<sup>-1</sup> under these conditions.

### 4.3. Other Metal-Based Catalysts for Stereoselective Copolymerization of Epoxides and CO<sub>2</sub>

Sugimoto and co-workers<sup>112</sup> reported in 2012 a series of aluminum-based catalysts that form iso-enriched poly(cyclohexene carbonate). The most enantioselective catalyst from this study is a dimeric  $\beta$ -ketoiminate Al complex that gives an ee of 74%. However, the resulting polymer has a low  $M_n$  (7.3 kDa) and low carbonate linkage selectivity (86%).

There are few examples of chromium-based catalysts that exhibit enantioselectivity in the copolymerization of epoxides and CO<sub>2</sub> (Figure 11). The earliest report was in a patent in

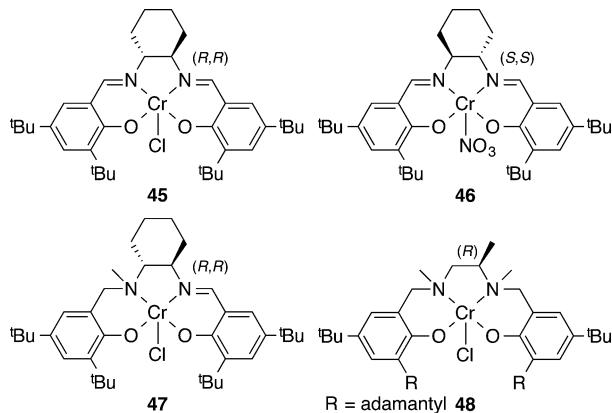


Figure 11. Structures of complexes 45–48.

2000 by Jacobsen and co-workers<sup>113</sup> in which 1-hexene oxide is copolymerized with CO<sub>2</sub> using (R,R)-(salen)CrCl (45) with a  $k_{rel}$  of 2.8. In 2007 Lu and co-workers<sup>114</sup> copolymerized cyclohexene oxide and CO<sub>2</sub> using (S,S)-(salen)CrNO<sub>3</sub> (46) with strong N-heterocyclic bases to give iso-enriched poly(cyclohexene carbonate) (ee = 14.5%). Terpolymerizations of cyclohexene oxide and (R)-propylene oxide with CO<sub>2</sub> were performed, and it was found that the ee (based on the 1,2-cyclohexane diol obtained from degradation in base) increased when [(R)-propylene oxide]/[cyclohexene oxide] was increased. They attribute this result to the influence of chain-end control. In 2009, Nozaki and co-workers<sup>115</sup> reported that an enantiopure (salalen)CrCl (47) catalyst with [PPN][Cl] copolymerizes cyclohexene oxide and CO<sub>2</sub> with an ee of 11%. The salalen ligand is an asymmetric salen ligand framework in which one of the imines is reduced. Finally, Lu and co-workers<sup>116</sup> found in 2007 that an enantiopure (salan)CrNO<sub>3</sub> catalyst (48) with "Bu<sub>4</sub>NO<sub>3</sub> exhibits a  $k_{rel}$  of 7.1 at room temperature for copolymerization of *rac*-propylene oxide and CO<sub>2</sub>.

## 5. CONCLUSIONS AND OUTLOOK

Stereoselective polymerization and copolymerization of epoxides to stereoregular polymers is a field with a venerable history that has undergone a recent resurgence of activity. While the original field focused on heterogeneous catalyst mixtures that were mainly used for the isoselective homopolymerization of propylene oxide, current research has expanded to well-defined homogeneous catalysts that enantioselectively polymerize epoxides to isotactic polyethers or polycarbonates. While these polymers have not yet found significant commercial success, it is hoped that further catalyst development will lead to polymers with attractive properties and applications. Potential applications include semicrystalline polyurethane

midblock segments and biodegradable semicrystalline thin films. Stereoselective copolymerization of epoxides with cyclic anhydrides to yield stereoregular polyesters will also be a likely target of future research. While stereoregular epoxide polymers may never reach the lofty heights of their near simultaneously discovered polyolefin brethren, their biocompatibility (for many polyethers) and biodegradability (for many aliphatic polycarbonates and polyesters) make them attractive polymers to meet the demands of the 21st century.

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### Notes

The authors declare no competing financial interest.

### Biography



Ian Childers (second from right) was born in Latrobe, PA, in 1987. He received his B.S. degree in Chemistry from Washington and Lee University in 2010, where he performed research under the guidance of Erich Uffelman. He is currently a Ph.D. student at Cornell University in the group of Geoff Coates, where his research interests include bimetallic catalysis and epoxide polymerization.

Julie Longo (left) was born in Atlanta, GA. She attended Emory University and received her B.S. degree in Chemistry in 2011. She entered the Ph.D. program at Cornell University in 2011 and joined the lab of Geoff Coates, where she is currently a National Science Foundation Graduate Research Fellow. Her research interests include developing biodegradable polymers from cyclic anhydrides and epoxides.

Nathan Van Zee (second from left) grew up in Lake Worth, FL, and graduated from the Harriet L. Wilkes Honor College of Florida Atlantic University in 2010 with a B.A. degree in Liberal Arts with a concentration in chemistry. He is currently a Ph.D. student at Cornell University in the group of Geoff Coates, where he is an NSF IGERT Fellow. His research interests include catalysis and polyester synthesis.

Anne LaPointe (middle) grew up in Sunnyvale, CA, and received her B.S. degree in Chemistry from Stanford University in 1990 and Ph.D. degree in Inorganic Chemistry from the Massachusetts Institute of Technology in 1994 with Professor Richard R. Schrock. She then moved to the University of North Carolina at Chapel Hill, where she was a NSF Postdoctoral Fellow in Professor Maurice S. Brookhart's group. In 1997 she returned to California and joined Symyx Technologies as a member of the catalysis group. She has been at Cornell University since 2010, where she is Director of the Catalyst Discovery and Development Laboratory. Her research interests include catalysis, high-throughput experimentation, synthetic inorganic and organometallic chemistry, and polymer chemistry.

Geoff Coates (right) was born in 1966 in Evansville, IN. He received his B.A. degree in Chemistry from Wabash College in 1989 working with Roy G. Miller and Ph.D. degree in Organic Chemistry from Stanford University in 1994 with Robert M. Waymouth. After being an NSF Postdoctoral Fellow with Robert Grubbs at the California Institute of Technology, he joined the faculty at Cornell University in 1997 and was appointed to the first Tisch University Professorship in 2008. Research in the Coates group focuses on development of single-site catalysts for small molecule and polymer synthesis as well as preparation and characterization of well-defined polymer architectures.

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