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Homogeneous Catalyst Design for the Synthesis of Aliphatic Polycarbonates and Polyesters

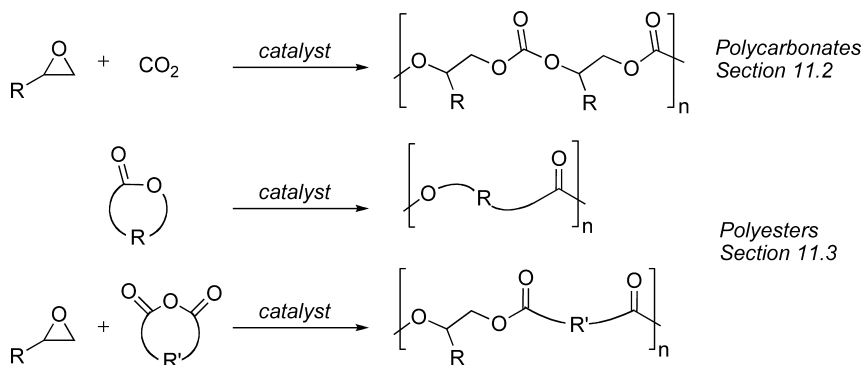
Geoffrey W. Coates and Ryan C. Jeske

11.1

Introduction

Synthetic polymers are more important now than at any other time in history. Although polymeric materials are indispensable in a diverse array of applications, ranging from commodity packaging and structural materials to technologically complex biomedical and electronic devices, their synthesis and proper disposal pose important environmental challenges. Two ways to achieve new polymers with reduced environmental impact are (1) the development of synthetic procedures that reduce energy consumption, the use of non-renewable resources (fossil fuels) or the generation of chemical waste; and (2) the synthesis of polymers that are easily recycled and/or biodegraded [1]. At the present time, fossil fuels are the predominant source of carbon for raw materials used in the chemical industry, with synthetic plastics accounting for approximately 7% of worldwide oil and gas consumption [2]. Because these resources have an uncertain future [3], there is significant interest in finding new routes from biorenewable resources to important chemicals, especially polymers. In addition, the current worldwide production of plastics is approximately 150 million tons per year [2]. Since 30 million tons of this material end up in landfills or are incinerated in the USA alone, there is growing interest in biodegradable and recyclable polymers. Biodegradable materials are especially valuable in applications where unwanted dispersal in the environment leads to disastrous ecological problems. One example of note is the North Pacific Subtropical Gyre, an area of ocean the size of Texas between California and Hawaii, where 6 billion pounds of floating plastic have accumulated over the last half-century [4]. The Technology Vision 2020 Report sponsored by the American Chemical Society proposed that the development of sustainable routes to polymeric materials will be a major challenge for the US chemical industry in the 21st century [5], and a 2005 workshop by the National Research Council of the National Academies [6] concluded that the development of environmentally benign materials should be a major goal of future research.

It is therefore timely to summarize some recent progress in the development of biodegradable polymers, especially those from renewable resources. The focus of this chapter is the development and application of homogeneous catalysts for the synthesis of biodegradable, aliphatic polycarbonates and polyesters (Scheme 11.1). Due to limitations of space, this review will not be comprehensive and will focus on select examples of homogeneous catalysts for the synthesis of aliphatic polyesters and polycarbonates, with emphasis on catalysts that exhibit high activities, control of polymer stereochemistry, composition and/or molecular weight, especially those that are used for the polymerization of commodity monomers.



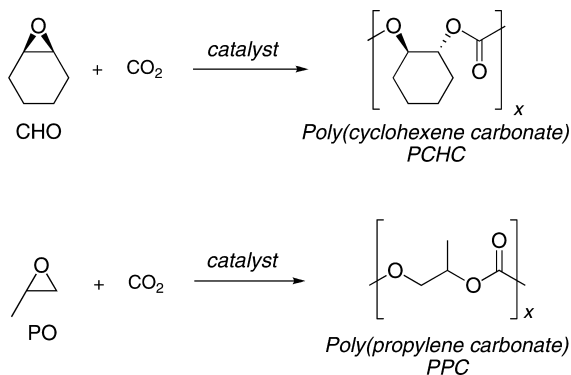
Scheme 11.1 Overview of the focus of this chapter: homogeneous catalysts for the synthesis of aliphatic polyesters and polycarbonates.

11.2

Synthesis of Aliphatic Polycarbonates from Epoxides and Carbon Dioxide

Since petroleum resources are predicted to be exhausted within the next century at the current rate of consumption [7], there is a growing effort to develop new chemical processes using biorenewable resources [8]. One such resource of particular interest is CO_2 , a non-toxic, non-flammable, naturally abundant C_1 feedstock [9]. The reaction of CO_2 with metal complexes has been extensively studied, revealing potential pathways for catalytic reactions. However, the thermodynamic stability of CO_2 has hampered its utility as a reagent for chemical synthesis; in fact, its high stability makes it an ideal medium for many chemical processes [10]. To overcome this limitation, reactions employing CO_2 with highly reactive reagents have been explored. In particular, the catalytic coupling of CO_2 with heterocycles has received a considerable amount of attention over the past 35 years [11, 12]. A majority of these publications involve the reaction of CO_2 with epoxides to generate polycarbonates (Scheme 11.2).

The high cost ($\sim \$100 \text{ lb}^{-1}$) of aliphatic polycarbonates is one of the main barriers to their widespread use as bulk polymeric materials. More economically viable processes and the synthesis of new types of improved aliphatic polycarbonates would



Scheme 11.2 Alternating copolymerization of cyclohexene oxide (CHO) and propylene oxide (PO) with CO₂.

clearly increase the number of applications for these polymers, and also lower their cost. A significant contributor to the cost of these materials is the low activity of the industrial zinc–dicarboxylic acid catalysts used to copolymerize epoxides and CO₂. As a result, a significant amount of recent research has been focused on the discovery and development of new catalysts for this process.

There are many parallels between the development of alkene polymerization catalysts and those for CO₂–epoxide polymerization. In each field, the catalysts initially discovered were heterogeneous in nature; subsequent work was focused on the empirical optimization to provide higher activity and selectivity for the polymerizations. Eventually, discrete, homogeneous metal complexes were explored in academic laboratories as a way to probe reaction mechanisms. By gaining a detailed understanding of the polymerizations at the molecular level, it was hoped that the lessons learned could then be applied to the design of improved catalytic systems. In some cases, these new homogeneous catalysts have significant advantages over their heterogeneous counterparts.

Heterogeneous catalysts are the workhorse of many industrial processes. Although they have many processing advantages over their soluble counterparts, heterogeneous catalysts often contain multiple active sites that result in polymers with broad polydispersity indices (PDIs) and composition distributions. In many cases, only a small percentage of the metal sites are active and residual catalyst remains in the polymeric product. As a result of these drawbacks, a significant amount of research has been directed towards the development of well-defined, single-site homogeneous catalysts. Homogeneous catalysts are typically of the form L_nMR, where L_n is a set of permanently bound ligands, M is a metal center and R is an efficient initiation group. These homogeneous catalysts are discrete species, rendering them amenable to precise modification and detailed mechanistic studies. Most of the major advances in metal-catalyzed polymerization, including stereoselective and living alkene polymerization, lactide and lactone polymerization, alkene metathesis and alkene–CO copolymerization, are the result of progress in homogeneous catalyst design. Homogeneous catalysts are being used to develop unique polymer architectures that lead to new,

industrially relevant materials, although it should be noted that most industrial polymerization catalysts are still of the heterogeneous variety.

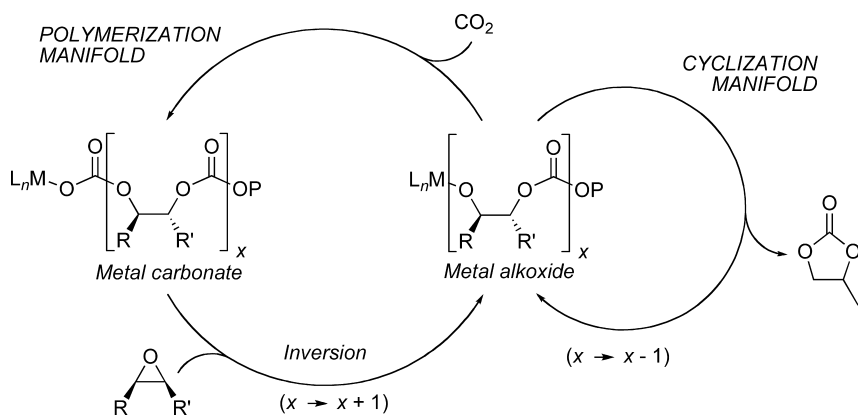
The purpose of this section is to give a thorough account of the CO₂-epoxide polymerization literature, with strong emphasis on single-site homogeneous catalysts and their mechanisms of operation. This section is largely based on a review written in part by one of the authors in 2004 [11], and is updated with select papers referencing the original article. The review is organized according to the active metal center of the catalyst and, although polymerization is the focus, the production of cyclic carbonates will be discussed when appropriate.

11.2.1

Background

In 1969, Inoue and co-workers made the remarkable discovery that a mixture of ZnEt₂ and H₂O was active for catalyzing the alternating copolymerization of propylene oxide (PO) and CO₂, marking the advent of epoxide-CO₂ coupling chemistry [13]. Following their discoveries, Kuran and co-workers developed a copolymerization system using ZnEt₂ and trihydric phenols, including pyrogallol and 4-bromopyrogallol, that produced poly(propylene carbonate) (PPC) with turnover frequencies (TOFs) up to 0.3 h⁻¹ at 35 °C and 60 atm CO₂ [14]. In an effort to develop more active catalysts, Hattori and co-workers synthesized a heterogeneous catalyst from Zn(OH)₂ and glutaric acid. Under 30 atm CO₂ and at 60 °C, the Zn(OH)₂-glutaric acid mixture yielded PPC with a TOF of 1.1 h⁻¹ ($M_n = 12\,000\text{ g mol}^{-1}$) [15].

While the discoveries of ZnEt₂-R(OH)_x and Zn(OH)₂-glutaric acid catalysts for epoxide-CO₂ coupling marked salient scientific findings, the active species responsible for polymer and cyclic formation remain unknown. Nevertheless, epoxide-CO₂ copolymerization is generally accepted to proceed via a coordination-insertion mechanism (Scheme 11.3).



Scheme 11.3 The basic mechanism of epoxide-CO₂ copolymerization and the formation of cyclic carbonates (L_n = ligand set; M = metal; P = polymer chain).

The mechanism includes several prevailing principles:

1. *Mechanism.* The alternating copolymerization of epoxides and CO₂ is a two-step process; the insertion of CO₂ into a metal alkoxide is followed by insertion of epoxide into a metal carbonate. Hence most catalysts (polymerization initiators) are metal alkoxide or metal carboxylate species that are similar to the putative catalytic intermediates.
2. *Regiochemistry.* In the copolymerization of CO₂ and aliphatic epoxides (propylene oxide, etc.), epoxide ring opening is typically favored at the least-hindered C–O bond, although cleavage is normally observed at both C–O bonds, giving regioirregular polymers.
3. *Stereochemistry.* In the copolymerization of CO₂ and alicyclic epoxides, such as cyclohexene oxide (CHO), C–O bond cleavage typically occurs with inversion of configuration at the site of attack (S_N2-type mechanism) to give the *trans* ring-opened product. In general, tactic polycarbonates are not formed by chain-end control mechanisms, presumably due to the distance between the stereogenic center of the chain end and the active metal center. There are examples of stereocontrol by site-control mechanisms using chiral metal catalysts (see below).
4. *Polymer–cyclic selectivity.* Cyclics are a common by-product of the copolymerization of CO₂ and aliphatic epoxides. Many systems produce predominantly cyclics, which are thermodynamically more stable than polycarbonates. The percentage of polymer typically increases at lower reaction temperatures. Systems can be tuned to favor cyclics or polymer formation, depending on the catalyst, additives, CO₂ pressure, epoxide concentration and temperature. Cyclic formation results from degradation of the growing polycarbonate chain by depolymerization or backbiting. In most cases, cyclic carbonate is thought to form via backbiting of a metal-alkoxide into an adjacent carbonate linkage (Scheme 11.3).
5. *Ether and dicarbonate linkages.* The presence of ether linkages due to consecutive epoxide enchainment can be observed in some aliphatic polycarbonates. Most systems can be tuned to favor CO₂ incorporation by catalyst selection, CO₂ pressure, epoxide concentration and polymerization temperature. The enthalpically disfavored consecutive insertion of two molecules of CO₂ to give dicarbonate linkages has not been reported.

These prevailing principles are depicted in a qualitative free energy profile for the copolymerization of epoxides and CO₂ in Figure 11.1.

As observed in early studies, only a few metals have been found to be active for the coupling of epoxides and CO₂, including Al, Cr, Co, Mg, Mn, Li, Zn, Cu and Cd. Studies have shown large differences in catalytic efficacy resulting from the organic frameworks surrounding these metals, especially in the case of zinc. Accordingly, subsequent studies have largely been focused on the empirical modification of ligands to generate improved catalysts. This section will focus on complexes of three metals for epoxide–CO₂ copolymerization: chromium, cobalt and zinc.

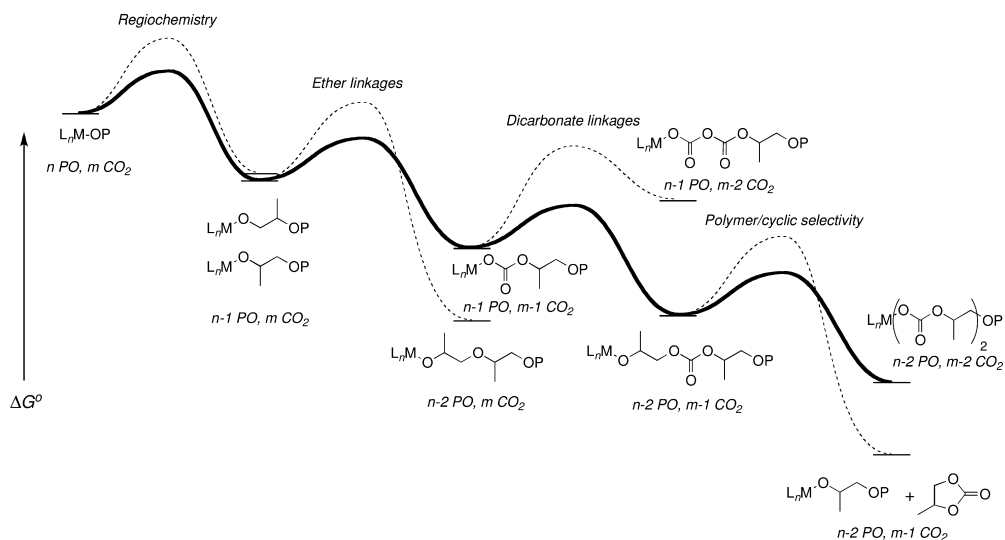
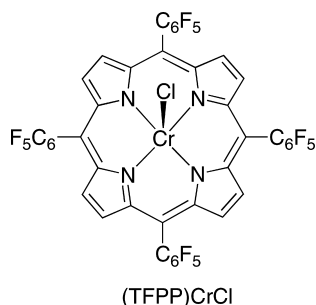


Figure 11.1 Qualitative, ideal free-energy profile depicting alternating copolymerization of epoxides and CO_2 , and also potential side-reactions.

11.2.2

Chromium Catalysts

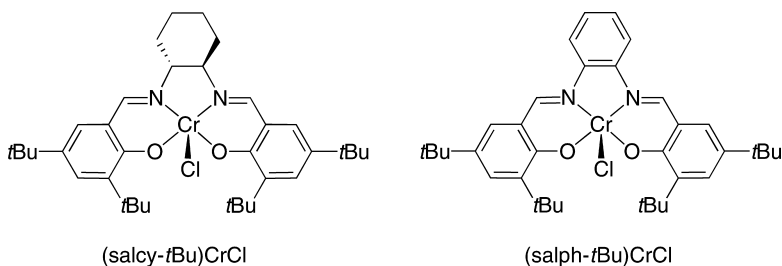
Following a lead by Kruper and Dellar [16], who reported that chromium porphyrins catalyzed the synthesis of cyclic carbonates from epoxides and CO_2 , Holmes and co-workers developed (TFPP)CrCl (Scheme 11.4), which showed activities of up to 173 h^{-1} for the alternating copolymerization of CHO and CO_2 at 225 atm CO_2 (supercritical CO_2) and 95°C [17]. The copolymerization only yielded polycarbonate when (TFPP)CrCl was combined with a co-catalyst such as DMAP. The fluorinated aromatic moieties improved catalyst solubility in supercritical CO_2 and consequently increased the yields of PCHC. Similar to aluminum porphyrin catalysts for epoxide- CO_2 copolymerization, these chromium analogs yielded



Scheme 11.4 A chromium-porphyrin complex for epoxide and CO_2 copolymerization.

polycarbonates with narrow PDIs ($M_w/M_n = 1.08–1.50$) and low molecular weights ($M_n = 1500–9400 \text{ g mol}^{-1}$). Furthermore, the resultant PCHC contained high percentages of carbonate linkages (97%). More recently, polymer-supported chromium porphyrins have been found to be active for PCHC production [18].

Darensbourg and Yarbrough reported that the air-stable complex (salcy-*t*Bu)CrCl (Scheme 11.5) was an effective catalyst for the alternating copolymerization of CHO and CO_2 [19]. At 80°C and 60 atm CO_2 , (salcy-*t*Bu)CrCl converted CHO to PCHC with a moderate TOF of 10.4 h^{-1} . Analysis of the polycarbonate showed nearly 100% carbonate linkages, a M_n of 8900 g mol^{-1} and an M_w/M_n of 1.2. Based on the turnover number (TON) and lack of cyclic by-product, the PCHC should exhibit a theoretical molecular weight of approximately $35\,000 \text{ g mol}^{-1}$. Like the chromium porphyrin systems, activities increased upon addition of *N*-methylimidazole (MeIm), such that 5 equiv. MeIm tripled the copolymerization rates to 32.2 h^{-1} . Although the complex (salcy-*t*Bu)CrCl is chiral, the resultant polymer was completely atactic, as determined by ^{13}C NMR spectroscopy. Additionally, (salcy-*t*Bu)CrCl catalyzed the coupling of PO and CO_2 to PC and PPC, although activities were not specified. At 80°C , cyclic PC is the predominant product, but as the temperature is reduced to 40°C , PPC production becomes a competitive pathway. Finally, silylated aliphatic epoxides, such as 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and CO_2 can also be copolymerized by salen-chromium complexes and MeIm co-catalyst [20].



Scheme 11.5 Chromium–salen complexes for epoxide and CO_2 copolymerization.

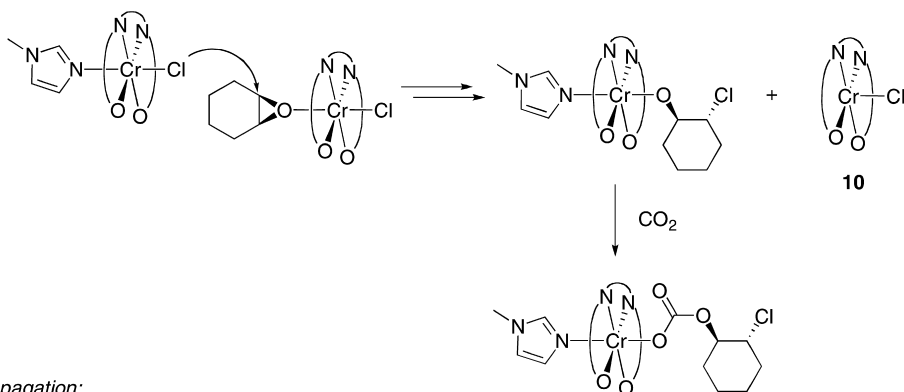
Subsequent work detailed the intricate energetics of polymer versus cyclic formation using (salcy-*t*Bu)CrCl [23]. In CHO– CO_2 coupling, the activation energies (E_a) for CHC and PCHC were 31.8 and $11.2 \text{ kcal mol}^{-1}$, respectively, which illustrate higher activation barriers for cyclic formation. The activation barriers for PC and PPC in PO– CO_2 coupling were determined to be 24.0 and $16.2 \text{ kcal mol}^{-1}$, respectively. The significantly larger E_a for CHC versus PCHC is consistent with the exclusive formation of PCHC, whereas the slightly larger E_a for PC versus PPC is consistent with the formation of PC during PO– CO_2 copolymerization. A detailed study on the nature of the co-catalyst on catalytic behavior has also been performed [21].

Rieger and co-workers found that the slightly modified complex (salph-*t*Bu)CrCl and DMAP co-catalyst rapidly copolymerized PO and CO_2 (TOFs approaching 226 h^{-1}) at 75°C and only 13 atm CO_2 [22]. Analysis of the PPC revealed molecular weights up to $16\,700 \text{ g mol}^{-1}$ (lower than predicted assuming the lack of chain transfer reactions), PDIs as low as 1.36 and carbonate linkages as high as 98%. The

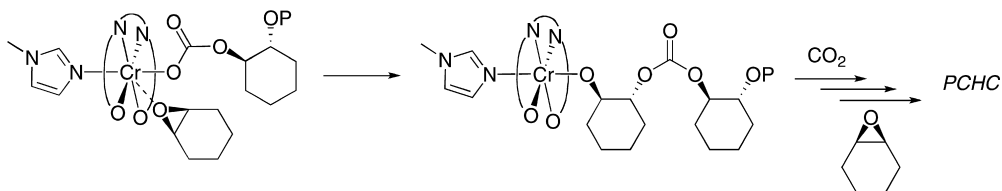
DMAP-to-(salph-*t*Bu)CrCl ratio drastically affected the ratio of products in the coupling process. Without DMAP, no conversion to PC or PPC was observed. Interestingly, co-catalyst was not essential for copolymerization using (salcy-*t*Bu)CrCl. At 0.5 equiv. DMAP, the maximum ratio of PPC to PC formation ($154 : 34 \text{ h}^{-1}$) was observed. Higher DMAP-to-(salph-*t*Bu)CrCl ratios decreased the proportion of PPC to PC until only PC was observed. For example, when 2 equiv. DMAP were added, only PC was observed with a TOF of 602 h^{-1} .

The proposed CO_2 -epoxide copolymerization mechanisms using seemingly similar catalysts, (salcy-*t*Bu)CrCl-MeIm and (salph-*t*Bu)CrCl-DMAP, differ considerably. At the current time, there is a lack of agreement regarding the mode of operation of these catalysts. Darensbourg *et al.* offered a dual CHO- CO_2 copolymerization mechanism for the (salcy-*t*Bu)CrCl-MeIm system, where initiation occurs by a bimetallic process and propagation operates via monometallic enchainment of epoxide [23]. Initiation is accelerated by MeIm, which aids in chloride attack on a CHO monomer bound to a second salen-chromium complex (Scheme 11.6). Subsequent CO_2 insertion into the newly generated chromium alkoxide generates a chromium carbonate. Because rate studies showed a first-order dependence on both CHO and catalyst, chain propagation was proposed to occur by a concerted epoxide ring opening that proceeds through a four-membered transition state.

Initiation:

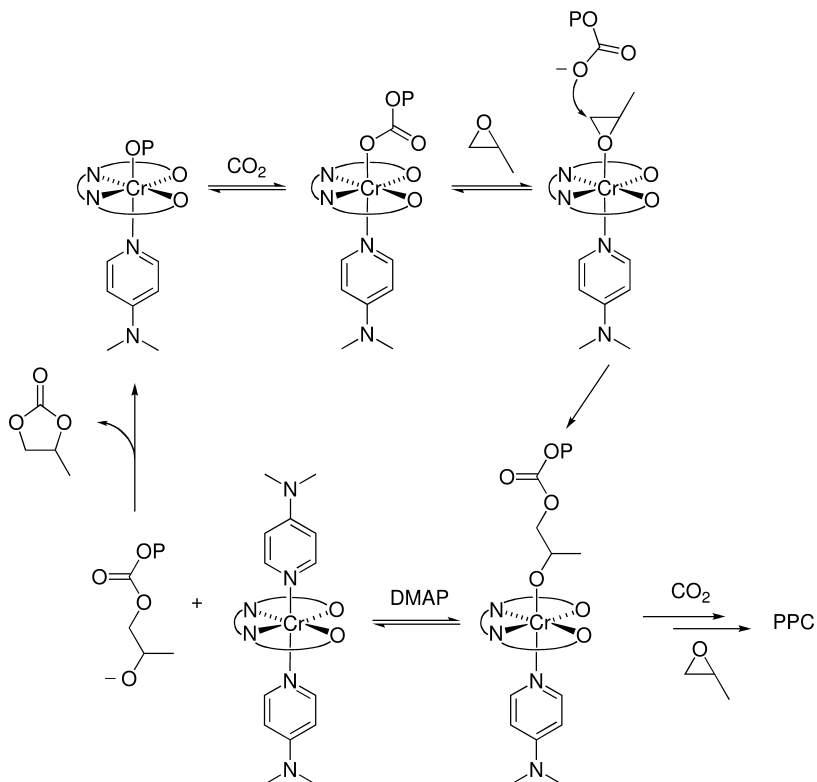


Propagation:



Scheme 11.6 Proposed CO_2 -CHO copolymerization mechanism using (salcy-*t*Bu)CrCl-MeIm (P = polymer chain).

Alternatively, in PO–CO₂ copolymerization using (salph-*t*Bu)CrCl–DMAP, Rieger and co-workers proposed that DMAP coordinates strongly to Cr and facilitates dissociation of the polymer chain alcoholate and carbonate (Scheme 11.7) [22]. Under sufficient pressures of CO₂, the dissociated carbonate attacks PO-bound (salph-*t*Bu)CrCl–DMAP in a monometallic fashion. Subsequent CO₂ insertion into the newly formed chromium alkoxide propagates the polycarbonate chain. The anionic nature of the chain-end promotes degradative backbiting to cyclic propylene carbonate. Therefore, increased amounts of DMAP enhance cyclic formation and eventually exterminate copolymer formation.



Scheme 11.7 Proposed PO–CO₂ copolymerization mechanism for (salph-*t*Bu)CrCl–DMAP catalyst system.

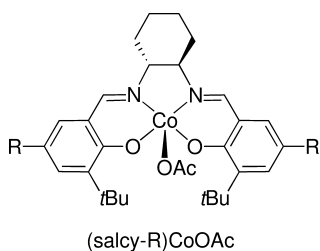
Owing to similar catalysts and coupling processes, it is unlikely that all of the epoxide ring-opening steps discussed above are occurring simultaneously. Furthermore, no mechanism has accounted for the retention of stereochemistry as reported by Kruper and Dellar or the low polymer molecular weights that are indicative of chain transfer or the formation of macrocycles. All studies do agree that CO₂ reacts with a metal alkoxide and cyclic formation occurs through backbiting of a metal alkoxide into an adjacent carbonate linkage. Detailed mechanistic studies must be

performed to delineate the various intermediates and epoxide ring-opening steps involved in these highly active salen-type chromium catalysts.

11.2.3

Cobalt Catalysts for Epoxide–CO₂ Copolymerization

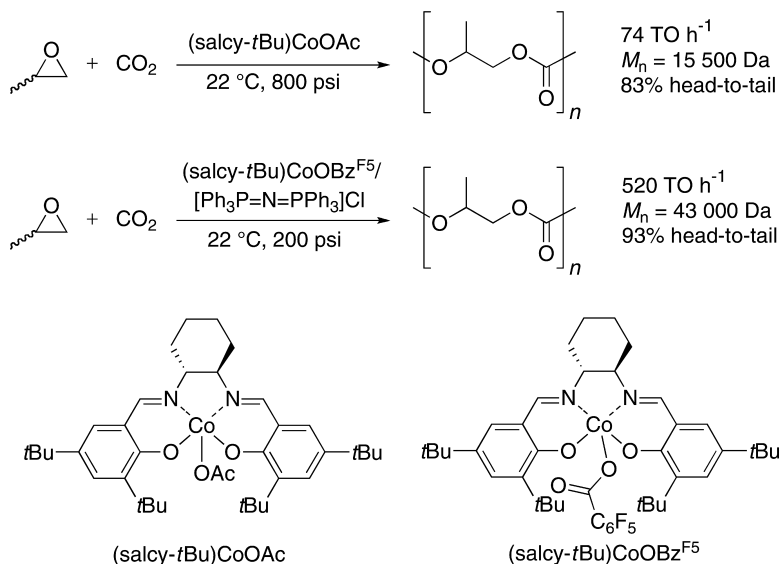
In 1979, Co(OAc)₂ was reported to copolymerize PO and CO₂ with an extremely low TOF (0.06 h⁻¹) [24]. Since that report, few examples of cobalt-catalyzed coupling of epoxides and CO₂ have been reported. He and co-workers reported the synthesis of ethylene carbonate using (salen)Co–co-catalyst mixtures [25]. More recently, Coates and co-workers found that (salcy)CoOAc complexes (Scheme 11.8) exhibited moderate activities (up to 81 h⁻¹ with R = Br) for the copolymerization of PO and CO₂ [26]. At 25 °C and 55 atm CO₂, (salcy-Br)CoOAc catalyzed the copolymerization to yield PPC with no observable cyclic by-products, 95% carbonate linkages, an *M*_n of 15 300 g mol⁻¹ and a PDI of 1.22. Pressures of 55 atm were essential for polymerization activity as lower pressures (40 atm) significantly hindered the copolymerization. In contrast to the related salen chromium catalysts, no heterocyclic additives were necessary to effect the copolymerization. In addition, all (salcy-R)CoOAc showed unprecedented selectivities for PPC formation (>99% PPC versus PC). (*S*)-PO–CO₂ copolymerization using enantiomerically-pure (salcy-*t*Bu)CoOAc yielded isotactic (*S*)-PPC (TOF = 71 h⁻¹; >99% PPC:PC; 99% carbonate linkages; *M*_n = 6900 g mol⁻¹; *M*_w/*M*_n = 1.58) with the highest reported level of head-to-tail linkages (93%). Finally, complex (salcy-*t*Bu)CoOAc exhibited a modest level of selectivity (*k*_{rel} = 2.8) in the kinetic resolution of PO.



Scheme 11.8 Cobalt–salen complexes (R = Br, H, *t*Bu) for epoxide and CO₂ copolymerization.

Although it was originally thought that ammonium salt co-catalysts limited the (*R,R*)-(salcy)CoX-catalyzed reaction of PO–CO₂ to the production of PC [27], PPC was recently achieved through the careful choice of the complex and co-catalyst [28]. Specifically, (salcy-*t*Bu)CoOAr (OAr = 4-nitrophenoxy, 2,4-dinitrophenoxy or 2,4,6-trinitrophenoxy) derivatives with [*n*Bu₄N]Y (Y = Cl, OAc) co-catalysts were described by Lu and Wang to afford PPC with impressively enhanced rates and selectivity [28]. Coates and co-workers have also furthered catalyst optimization, which also led to the use of organic salt co-catalysts (Scheme 11.9) [29]. Specifically, (salcy-*t*Bu)CoOBzF₅ (OBzF₅ = pentafluorobenzoate), in combination with [Ph₃P=N=PPh₃]Cl ([PPN]Cl), was found to produce a highly active catalyst for the living, alternating copolymerization of PO and CO₂, yielding PPC with no detectable by-products. The PPC generated using these catalyst systems is highly regioregular and has up to 99%

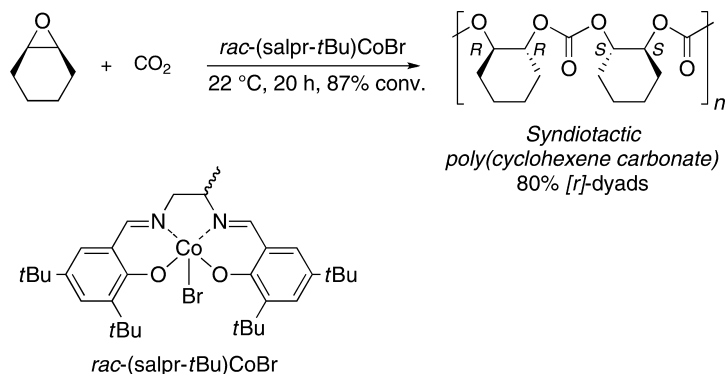
carbonate linkages with a narrow molecular weight distribution (MWD). In the case of [PPN]Cl with (*R,R*)-(salcy)CoOBzF₅, an unprecedented catalytic activity of 520 turnovers per hour was achieved for the copolymerization of *rac*-PO and CO₂, yielding iso-enriched PPC with 93% head-to-tail connectivity.



Scheme 11.9 Propylene oxide and CO₂ copolymerization by cobalt–salen complexes.

Two recent studies have extended the co-catalyzed cobalt–salen system by cleverly designing systems with covalent linkages between the metal complex and co-catalyst [30]. These systems claim higher conversions to polymer without undesirable backbiting reactions, and also higher thermal stability of the catalysts.

Coates and co-workers recently reported the first syndiospecific copolymerization of cyclohexene oxide and CO₂ (Scheme 11.10) [31]. Using the complex (*rac*-salpr-*t*Bu),



Scheme 11.10 Syndiospecific cyclohexene oxide and CO₂ copolymerization by a cobalt–salen complex.

CoBr, poly(cyclohexene carbonate) was formed with 80% $[r]$ -centered tetrads, as determined by ^{13}C NMR spectroscopy. The carbonyl and methylene regions were best simulated using Bernoullian statistical methods, supporting a chain-end stereochemical control mechanism.

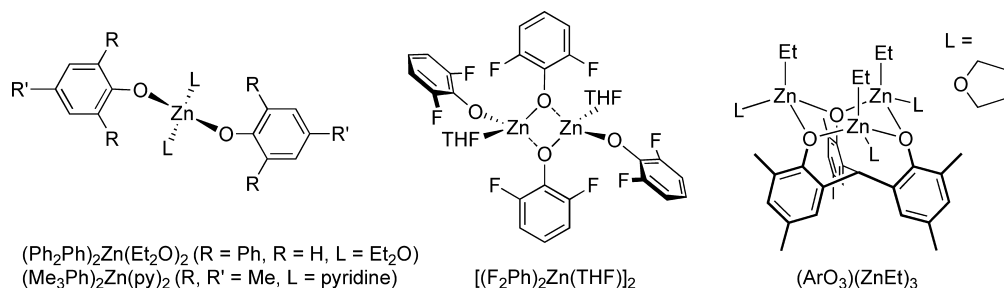
11.2.4

Zinc Catalysts for Epoxide–CO₂ Copolymerization

A variety of metal-based catalysts have shown activity for the coupling of epoxides and CO₂; however, few have exhibited the success associated with zinc-based complexes. Therefore, the majority of the work reported in this field has been performed using complexes with zinc as the active metal center. These catalysts have undergone a renaissance over the past 10 years, shifting the focus from heterogeneous mixtures to discrete and single-site catalysts which exhibit unprecedented reaction rates and selectivities.

11.2.4.1 Zinc Phenoxides for Epoxide–CO₂ Copolymerization

Heterogeneous systems are often marred by poor reproducibility and the production of non-uniform polymers, caused by the presence of many different types of active sites that produce polymers with different activities and selectivities. To address these issues, Darensbourg and Holtcamp reported in 1995 the first discrete zinc complexes for the alternating copolymerization of epoxides and CO₂ (Scheme 11.11) [32]. This discovery marked an important step in the development of catalysts for the copolymerization of CO₂ and epoxides. The compound (Ph₂Ph)₂Zn(Et₂O)₂, which was synthesized from 2,6-diphenylphenol and Zn[N(SiMe₃)₂]₂, crystallized as a bis[(2,6-diphenyl)phenoxy]zinc complex containing two diethyl ether solvent molecules coordinated to a tetrahedral zinc center. Under 55 atm CO₂ and at 80 °C, PCHC (91% carbonate linkages; $M_n = 38\,000\text{ g mol}^{-1}$; $M_w/M_n = 4.5$) was produced with a TOF of 2.4 h⁻¹. Additionally, (Ph₂Ph)₂Zn(Et₂O)₂ catalyzed the random terpolymerization of CHO, PO and CO₂, yielding polycarbonate with approximately 20% propylene carbonate linkages, 70% cyclohexene carbonate linkages and 10% ether linkages. Approximately the same ratios of PO and CHO incorporation were observed regardless of the feedstock composition.



Scheme 11.11 Zinc phenoxide compounds for alternating epoxide–CO₂ copolymerization.

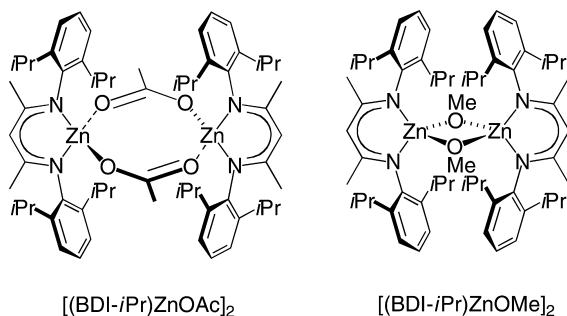
Subsequent work investigated the steric influences of *N*-aryl substituents, including compounds such as $(\text{Me}_2\text{Ph})_2\text{Zn}(\text{py})_2$, on CHO–CO₂ copolymerization (Scheme 11.11) [33]. Complex $(\text{Me}_2\text{Ph})_2\text{Zn}(\text{py})_2$ displayed the highest activities (TOF = 9.6 h⁻¹), thus illustrating that bulky *ortho* substituents were not essential for high copolymerization rates. Electronic perturbations of the *N*-aryl *ortho* substituents revealed that electron-withdrawing groups resulted in higher activities for CHO–CO₂ copolymerization: F > Cl > Br [34]. Addition of 2,6-dihalophenols to $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ gave four-coordinate, dimeric zinc phenoxides with bound THF solvent molecules. The compound $[(\text{F}_2\text{Ph})_2\text{Zn}(\text{THF})]_2$ demonstrated a moderate TOF of 7.6 h⁻¹. Analysis of the PCHC revealed PDIs of over 42, molecular weights of 42 000 g mol⁻¹, a *T*_g of 115 °C and >99% carbonate linkages [35]. In general, zinc bisphenoxide compounds catalyzed PO–CO₂ copolymerization at 40 °C and PO–CO₂ cyclization at 80 °C in unspecified yields. Finally, zinc bisphenoxide catalysts were active for CHO homopolymerization, CHO–CO₂ copolymerization and CHO–PO–CO₂ terpolymerization, but did not readily react with bulky alicyclic epoxides such as α -pinene and *exo*-2,3-epoxynorbornane.

In a related study, Dinger and Scott reported that zinc phenoxide cluster compounds showed activity for the alternating copolymerization of CHO and CO₂ [36]. A variety of solvent-dependent tri-, tetra-, penta- and hexanuclear compounds were synthesized from tris(3,5-dialkyl-2-hydroxyphenyl)methanes and ZnEt₂. For example, $(\text{ArO}_3)(\text{ZnEt})_3$ (Scheme 11.11) catalyzed the copolymerization of CHO and CO₂ to give PCHC with 81% carbonate linkages and a TOF of 1.3 h⁻¹.

Although the discrete catalysts above represent an important advance in catalyst design, the active species for the copolymerization remain unclear. Regarding these phenoxide–zinc complexes, one or more ligands are likely to act as polymerization initiators and thus become the chain-end of the growing polymer chain.

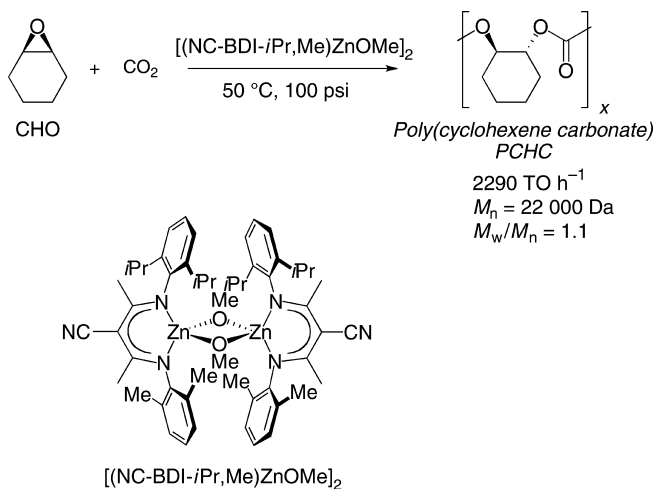
11.2.4.2 Single-site β -Diiminate Zinc Catalysts for Epoxide–CO₂ Coupling

Coates and co-workers discovered a highly active, living epoxide–CO₂ copolymerization system using bulky β -diiminate (BDI) zinc catalysts at low pressures (7 atm CO₂) and temperatures (50 °C) (Scheme 11.12) [37].



Scheme 11.12 β -Diiminate (BDI) zinc catalysts for epoxide–CO₂ copolymerization.

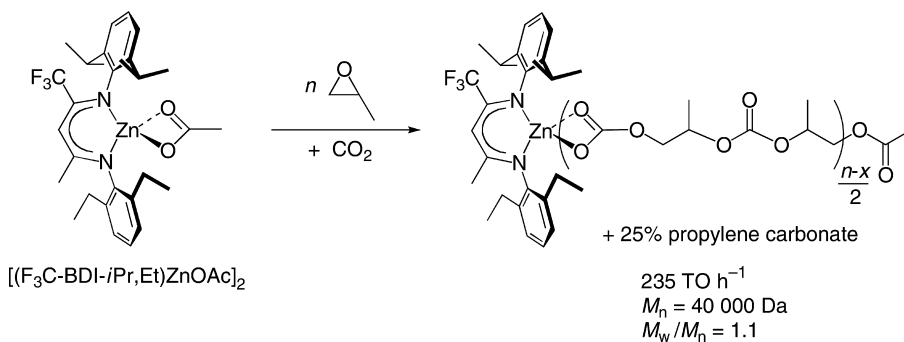
Several key design features, including initiating groups, sterics and electronics drastically altered the efficacy of the catalysts. To model the growing polycarbonate chain, zinc acetate $[(\text{BDI-}i\text{Pr})\text{ZnOAc}]_2$ and methoxide $[(\text{BDI-}i\text{Pr})\text{ZnOMe}]_2$ complexes were synthesized as mimics for zinc carbonates and zinc alkoxides (Scheme 11.12). BDI zinc acetate, methoxide, isopropoxide and bis(trimethylsilyl)amido complexes were all active for the alternating copolymerization of CHO and CO_2 . The combination of the unsymmetrical ligand geometries and the electron withdrawing cyano substituent yielded the most active catalysts reported to date [38]. At 50°C and in only 10 min, $[(\text{NC-BDI-}i\text{Pr,Me})\text{ZnOMe}]_2$ catalyzed the copolymerization of 1000 equiv. CHO at 7 atm CO_2 to give high-MW polymers ($M_n \approx 22\,000\text{ g mol}^{-1}$), narrow PDIs ($M_w/M_n = 1.1$) and an extremely high TOF of 2290 h^{-1} (Scheme 11.13).



Scheme 11.13 A highly active β -diiminato (BDI) zinc catalyst for cyclohexene oxide– CO_2 copolymerization.

In an attempt to isolate monomeric β -diiminato complexes, Chisholm and co-workers investigated bulky initiators including *t*BuOH and Ph_3SiOH [39]. As expected, the monomeric compounds $(\text{BDI-}i\text{Pr})\text{Zn}(\text{THF})\text{OSiPh}_3$ and $(\text{BDI-}i\text{Pr})\text{ZnOtBu}$ were active for CHO– CO_2 alternating copolymerization. Unexpectedly, their $(\text{BDI}i\text{Pr})\text{ZnNiPr}_2$, an analog of Coates and co-workers' compound $(\text{BDI-}i\text{Pr})\text{ZnN}(\text{SiMe}_3)_2$, was not active for the copolymerization, although it readily reacted with CO_2 to generate $(\text{BDI-}i\text{Pr})\text{ZnOC}(=\text{O})\text{NiPr}_2$. Rieger and co-workers have shown that an ethyl sulfinate is a viable initiator for the copolymerization [40]. The compound $[(\text{BDI-}i\text{Pr})\text{ZnOS}(=\text{O})\text{Et}]_2$ was synthesized by bubbling SO_2 through a $(\text{BDI})\text{ZnEt}$ solution and was also active for CHO– CO_2 copolymerization. Catalytic activities were comparable to that of $[(\text{BDI-}i\text{Pr})\text{ZnOAc}]_2$, due to similar active species. As a result of bimodal GPC traces, monomeric and dimeric BDI zinc species were believed to be active, although no mechanistic studies were conducted. Oligomeric BDI ligands have been made from 4,4'-methylenedianiline and 2,4-pentanedione. These zinc complexes have shown modest activity for CHO– CO_2 copolymerization ($\text{TOF} = 11.3\text{ h}^{-1}$) [41].

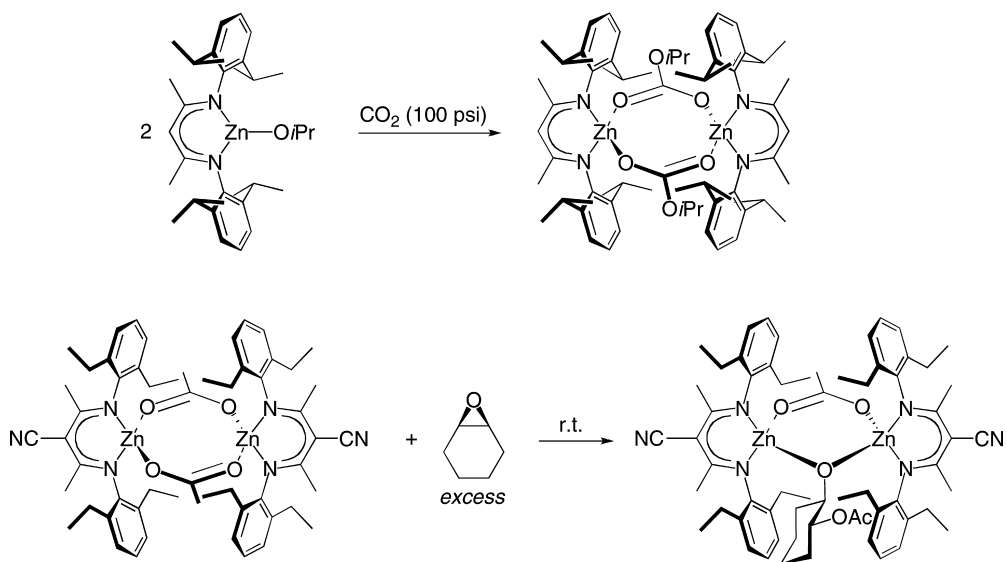
Subtle electronic and steric perturbations to (BDI)ZnOR (R = alkyl or acyl) complexes resulted in dramatic enhancements of activity for CHO–CO₂ copolymerization. During the course of these studies, catalysts for PO–CO₂ coupling were also discovered by Coates and co-workers [42]. Further modifications of the ligand architecture generated the most potent catalyst reported at that time for PO–CO₂ copolymerization, [(F₃C-BDI-*i*Pr,Et)ZnOAc]₂ (Scheme 11.14). The complex copolymerized PO and CO₂ at 25 °C and 7 atm CO₂ to give PPC (>99% carbonate linkages; $M_n = 36\,700\text{ g mol}^{-1}$; $M_w/M_n = 1.13$) with a TOF of 235 h^{-1} . However, the selectivity for polymer was only 75%. Increasing the CO₂ pressure to 35 atm favored polymer formation with a selectivity of 93%, while only moderately attenuating the catalytic activity (TOF = 138 h^{-1}).



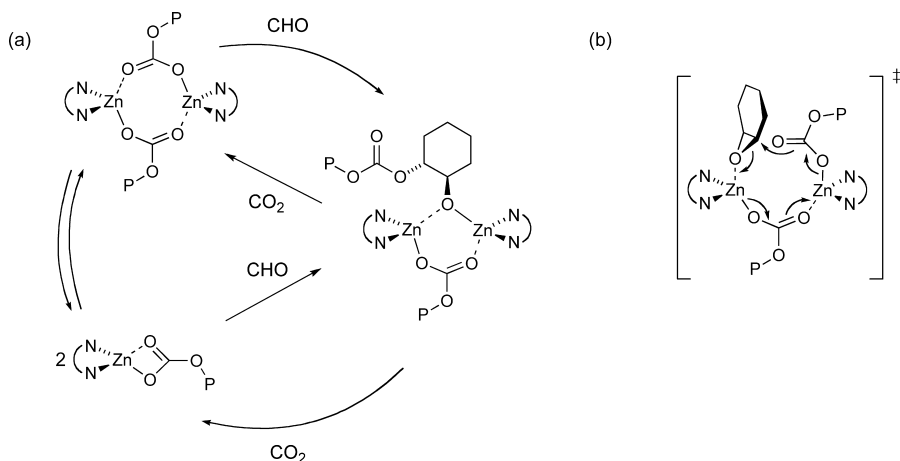
Scheme 11.14 A highly active β-diiminato (BDI) zinc catalyst for propylene oxide–CO₂ copolymerization.

More recently, Coates and co-workers performed mechanistic studies on the (BDI)ZnOR-catalyzed copolymerization of CHO and CO₂ [43]. Stoichiometric reactions of the copolymerization initiation steps showed that zinc alkoxides insert CO₂, whereas zinc acetates react with CHO. For example, (BDI)ZnOiPr complexes were found to react with CO₂ and (BDI)ZnOAc complexes were found to react with cyclohexene oxide (Scheme 11.15). The resultant compounds were characterized by single-crystal X-ray analysis and served as model compounds for presumed intermediates in the copolymerization. Due to the expeditious reaction of CO₂ with (BDI-*i*Pr)ZnOiPr, CHO insertion was predicted to be the rate-determining step. To monitor propagation, rate studies were performed on (BDI)ZnOAc complexes using *in situ* FTIR spectroscopy. The rate studies revealed a zeroth-order dependence in CO₂ and a first-order dependence in CHO. Hence insertion of CHO into a zinc carbonate was indeed the rate-determining step.

The copolymerization of CHO (1.98 M in toluene) in 20 atm CO₂ at 50 °C using sterically unhindered, dimeric complexes resulted in an order in [(BDI)ZnOR], where R = alkyl, acyl or polymer chain, of ~1. However, under the same conditions, an order in [(BDI)ZnOR] approaching 2 was determined for bulky complexes. On the basis of [(BDI)ZnOR] solution studies (R = alkyl or acyl), stoichiometric insertion reactions and rate studies, a bimetallic mechanism was proposed (Scheme 11.16). Sterically encumbered BDI zinc complexes ring open CHO in a bimetallic transition state with a



Scheme 11.15 Insertion reaction of (BDI)ZnOR complexes with CO_2 and CHO.



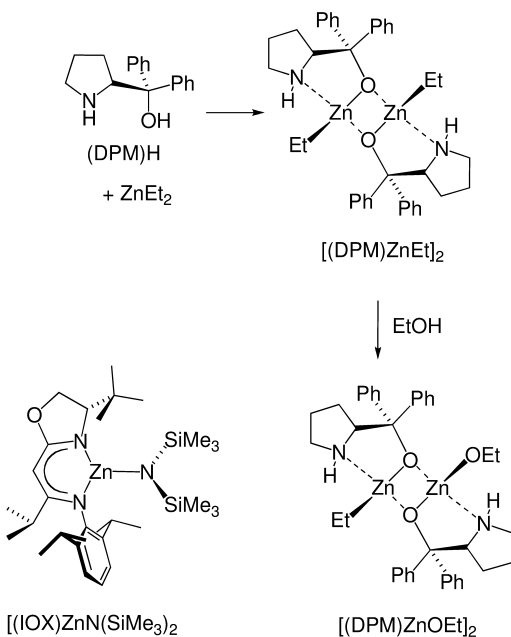
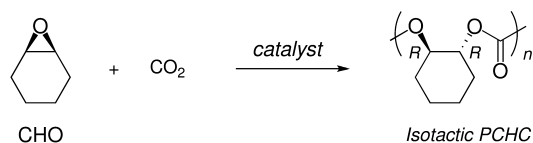
Scheme 11.16 Proposed (a) copolymerization mechanism and (b) epoxide ring-opening transition state using BDI zinc complexes (CHO = cyclohexene oxide; P = polymer chain).

predominantly monomeric ground state. Conversely, sterically unhindered BDI zinc complexes insert CHO in a bimetallic transition state with a completely dimeric ground state. A clever application of this finding was reported by Lee *et al.*, who synthesized bimetallic zinc species in order to take advantage of the bimetallic

transition state for epoxide enchainment [44]. The resulting compounds exhibited excellent TONs at very low catalyst loadings and produced high molecular weight polymers ($>200\,000\text{ g mol}^{-1}$).

11.2.4.3 Zinc Catalysts for Asymmetric CHO–CO₂ Copolymerization

There is significant interest in controlling the absolute stereochemistry of ring opening in epoxide–CO₂ copolymerization for several reasons. First, microstructure directly affects polymer properties [45]. Second, the kinetic resolution of racemic epoxides or desymmetrization of *meso*-epoxides by copolymerization is a potential route to valuable chiral building blocks. CHO, a *meso* molecule, is an ideal substrate for desymmetrization using chiral catalysts. In 1999, Nozaki *et al.* reported that a 1 : 1 mixture of ZnEt₂ and (*S*)- α,α -diphenylpyrrolidine-2-ylmethanol (DPM)H was active for stereoselective CHO–CO₂ copolymerization at 40 °C and 30 atm CO₂ (Scheme 11.17) [46]. The polycarbonate contained 100% carbonate linkages, an M_n of 8400 g mol⁻¹ and a PDI of 2.2. Hydrolysis of PCHC with base produced the corresponding *trans*-cyclohexane-1,2-diol with 73% enantiomeric excess. ¹³C NMR



Scheme 11.17 Chiral zinc catalysts for the asymmetric, alternating copolymerization of CHO and CO₂.

spectroscopic studies of model polycarbonate oligomers afforded spectral assignments for isotactic dyads (153.7 ppm) and syndiotactic dyads (153.3–153.1 ppm) [47]. Finally, ring opening proceeded by complete inversion of configuration (S_N2 mechanism), hence no *cis*-cyclohexane-1,2-diol was observed.

In a more recent study, Nozaki and co-workers isolated presumed intermediates in the asymmetric alternating copolymerization [48]. Reaction of $ZnEt_2$ and (*S*)- α,α -diphenylpyrrolidine-2-ylmethanol yielded dimeric $[(DPM)ZnEt]_2$, which was structurally characterized by X-ray diffraction studies (Scheme 11.17). At 40 °C and 30 atm CO_2 , $[(DPM)ZnEt]_2$ catalyzed the formation of isotactic PCHC ($M_n = 11\,800\text{ g mol}^{-1}$; $M_w/M_n = 15.7$; TOF = 0.6 h^{-1}) with a slightly lower enantiomeric excess (*ee*) of 49%. When the copolymerization was attempted with $[(DPM)ZnOEt]_2$ and 0.2–1.0 equiv. EtOH, enantioselectivities increased up to 80% *ee* and better control of molecular weights and PDIs resulted. The compound $[(DPM)ZnOEt]_2$ was proposed to be the active initiating species. End-group analysis by MALDI-TOF mass spectrometry revealed that in the absence of EtOH, signals assignable to the amino alcohol-initiated polymerization were identified. However, as EtOH addition was increased from 0.2 to 1.0 equiv., signals corresponding to the amino alcohol-derived polycarbonate disappeared as peaks for the EtOH-initiated PCHC emerged. This was further confirmed by end-group analysis using 1H NMR spectroscopy. Finally, mechanistic studies suggested that the dimeric form of the catalyst is, in fact, the active species.

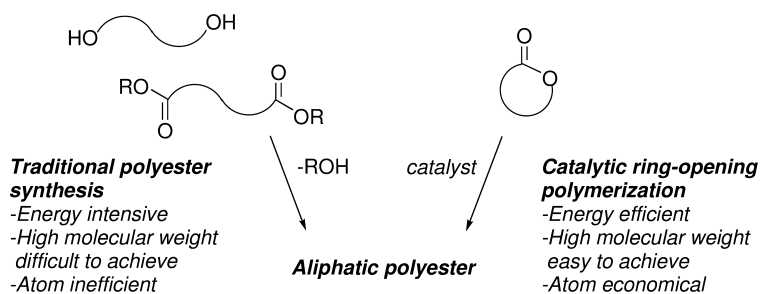
In 2000, Coates and co-workers developed C_1 -symmetric imine–oxazoline (IOX) ligated zinc bis(trimethylsilyl)amido compounds for the stereoselective, alternating copolymerization of CHO and CO_2 (Scheme 11.17) [49]. Through multiple electronic and steric manipulations, the compound $(IOX)ZnN(SiMe_3)_2$ was found to exhibit the highest enantioselectivity (*RR:SS* ratio = 86 : 14; 72% *ee*). The resultant PCHC possessed 100% carbonate linkages, an M_n of $14\,700\text{ g mol}^{-1}$, a PDI of 1.35 and a T_g and T_m of 120 and 220 °C, respectively. Furthermore, stereocontrol was also achieved in the alternating copolymerization of cyclopentene oxide (CPO) and CO_2 , producing poly(cyclopentene carbonate) with an *RR:SS* ratio of 88 : 12 (76% *ee*). As revealed by ^{13}C NMR spectroscopy, the experimental carbonyl tetrad concentrations matched the predicted tetrad concentrations for an enantiomeric-site control mechanism. The contributions described above represent an important step forward in the production of well-defined, tactic polycarbonates.

11.3

Synthesis of Aliphatic Polyesters

Aliphatic polyesters constitute an important class of polymers due to their biodegradability [50, 51] and biocompatibility [51, 52], which allows their use in drug delivery systems [51], artificial tissues [52] and commodity materials [53]. As only 6% of plastics in the USA are currently recycled [54], the production of economically competitive biodegradable polymers has recently become of great interest to the scientific community [53a, 55]. Although the polycondensation of a diol and a diacid is the

most common method for aliphatic polyester synthesis, the coordination–insertion method, which employs a well-defined single-site catalyst to effect the ring-opening polymerization (ROP) of cyclic esters, has become increasingly important over the past few decades [50–56]. One reason for this growing attention is that condensation polymerization is energy intensive, requiring high temperature and removal of the alcohol or water by-product to achieve high molecular weight (M_n) polymers; also, very precise stoichiometry between the diacid and diol is required to achieve a high M_n [51, 57]. Conversely, ROP by the coordination insertion mechanism is much more energy efficient; this technique typically uses mild reaction conditions and avoids the formation of small-molecule by-products (Scheme 11.18).



Scheme 11.18 Comparison of methods for aliphatic polyester synthesis.

Many extensive reviews have recently been published on the subject of the ROP of cyclic esters [50b,c, 51, 56]. We will avoid duplicating these and focus our discussion on the ROP of lactide (LA) with high stereocontrol, butyrolactone (BL), ϵ -caprolactone (CL) and its derivatives and the copolymerization of epoxides and cyclic anhydrides. We will refrain from discussing catalysts not bearing ancillary ligands $[M(OR)_x]$, which are among the most common catalysts for the ROP of cyclic esters, and instead refer the reader to the aforementioned reviews for discussion of these compounds. Instead, we will focus on the use of biorenewable starting materials and also discuss some examples of ROP using organocatalysts, of interest in applications requiring ultra-pure (metal-free) materials. Although this topic has recently been reviewed [58], we feel that it deserves mention here as well.

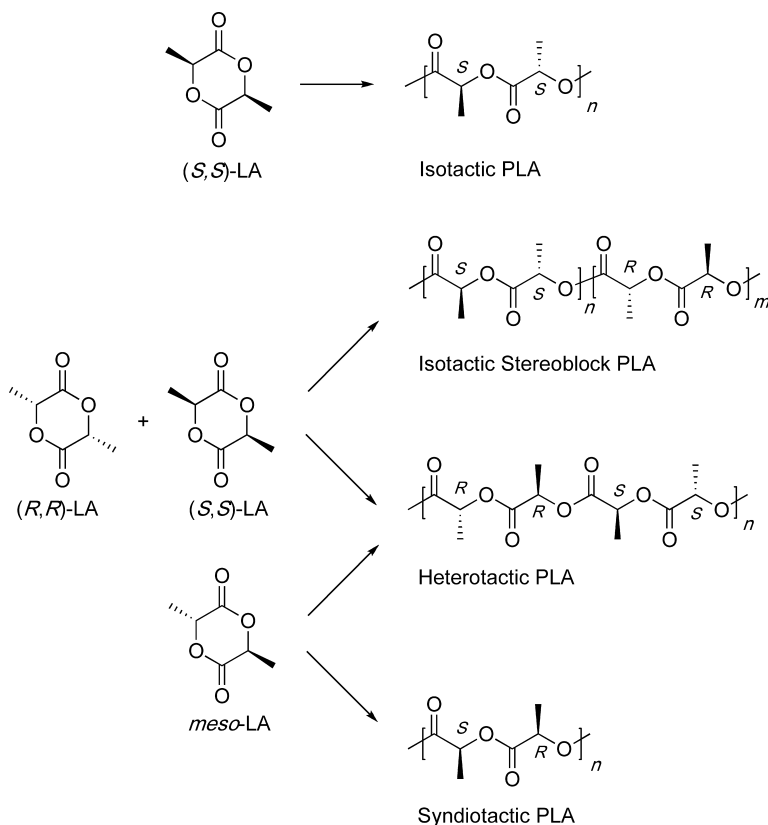
11.3.1

Synthesis of Poly(lactic Acid)

11.3.1.1 Background

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester synthesized from lactide, a biorenewable monomer derived from corn. One of the most common and useful polyesters [50b,c, 56], PLA is used in a wide range of applications, including food packaging and textiles, and has been commercialized by many companies such as

Cargill and Teijin under the trade name Natureworks [53a, 59]. As the LA dimer contains two stereocenters, there are a number of different PLA stereoarchitectures available (Scheme 11.19) and each possesses different physical properties. A great deal of research has been focused on stereochemical control in PLA synthesis; we will provide a summary of these efforts here.

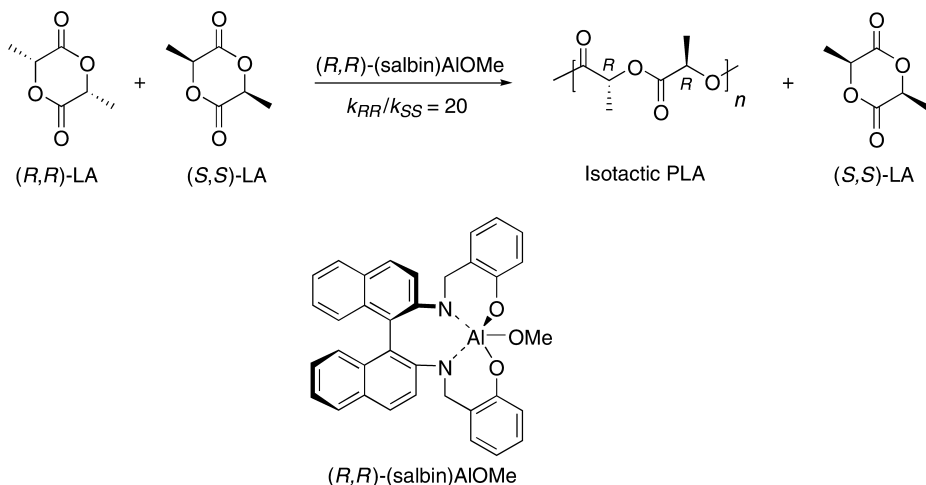


Scheme 11.19 Tacticities of poly(lactic acid) (PLA) and synthetic routes to their formation (LA = lactide).

11.3.1.2 Aluminum Catalysts for the Synthesis of PLA

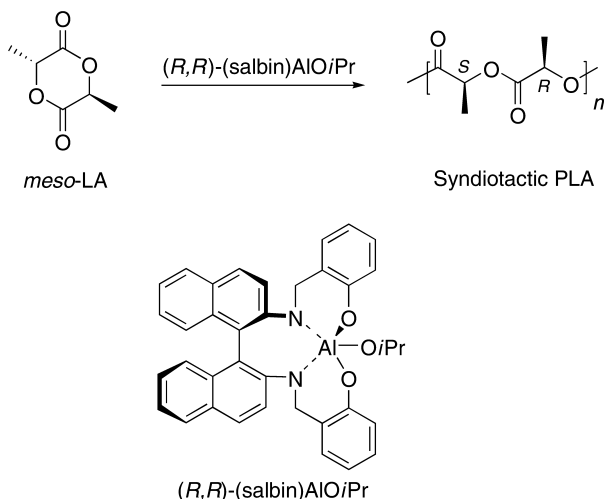
In 1996, Spassky *et al.* reported the kinetic resolution polymerization of *rac*-LA in which the chiral aluminum alkoxide complex (*R,R*)-(salbin)AlOMe showed a preference for (*R,R*)-LA over the *S,S*-enantiomer by a factor of 20 (Scheme 11.20) [60]. This reaction produced predominantly isotactic PLA when the polymerization was run to less than 50% conversion. However, it only slowly approached 100% conversion because of the inactivity of the *S,S*-enantiomer. When polymerizations of *rac*-lactide were allowed to proceed to full conversion, a stereoblock copolymer resulted with a

small amount of tapering. This catalyst system exhibited excellent molecular weight control and the polymers produced possessed narrow PDIs.



Scheme 11.20 Kinetic resolution ring-opening polymerization of *rac*-LA using (*R,R*)-(salbin)AlOMe.

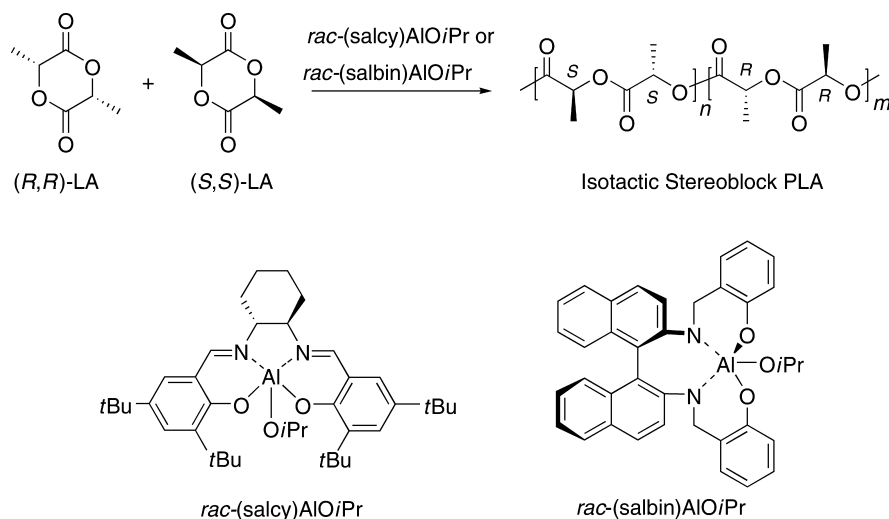
Ovitt and Coates reported the synthesis of syndiotactic PLA from *meso*-LA using (*R,R*)-(salbin)AlO*i*Pr (Scheme 11.21) [61a]. PLA with an M_n of 12 000 g mol^{-1} and a PDI of 1.05 was produced in 14 h at 70 °C. Notably, this PLA was highly syndiotactic, with an enantiotopic selectivity of 96%. The ROP of *meso*-LA by *rac*-(salbin)AlO*i*Pr in toluene at 70 °C produced heterotactic PLA after 40 h, with an M_n of 13 600 g mol^{-1} and a PDI of 1.07. Control experiments were used to show that the formation of heterotactic PLA was a result of polymer exchange between (*R,R*)-(salbin)AlO*i*Pr and



Scheme 11.21 Syndiospecific ring-opening polymerization of *meso*-LA using (*R,R*)-(salbin)AlO*i*Pr.

(*S,S*)-(salbin)AlO*i*Pr. Interestingly, stereoblock PLA could also be produced in a living fashion through the ROP of *rac*-LA using *rac*-(salbin)AlO*i*Pr for initiation [62]. This result further supported the proposed polymer exchange mechanism, in which sequences of the preferred LA enantiomer are formed by each enantiomer of (salbin)AlO*i*Pr, followed by chain exchange, which resulted in a stereoblock formation possessing –RRRRRRSSSSSS– sequences in the polymer chain.

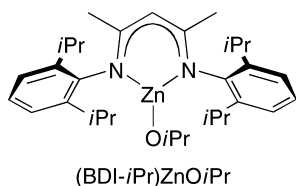
Feijen and co-workers employed the aluminum alkoxide complex *rac*-(salcy)AlO*i*Pr in their synthesis of isotactic stereoblock PLA from *rac*-LA (Scheme 11.22) [63]. Also, it was discovered that at higher temperatures (130 °C instead of 70 °C), PLA could be polymerized without the use of solvent. Under these harsher conditions, they produced isotactic PLA with a higher M_n (24 000 g mol⁻¹), while retaining the narrow PDI associated with well-controlled, living polymerizations. In addition, the groups of Chen, Nomura and Gibson have all made recent seminal contributions in this area [64].



Scheme 11.22 Isospecific ring-opening polymerization of *rac*-LA using racemic, chiral aluminum alkoxides to produce isotactic stereoblock PLA.

11.3.1.3 Zinc Catalysts for the Synthesis of PLA

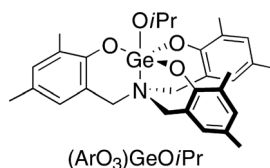
Coates and co-workers have reported that the β -diimine zinc compound (BDI-*i*Pr)ZnO*i*Pr is an effective catalyst for the stereoselective ROP of LA (Scheme 11.23) [65]. Highly heterotactic PLA (M_n 38 000 g mol⁻¹, PDI 1.10) was produced via chain-end control from 200 equiv. of *rac*-LA in 20 min at 20 °C. A heterotactic linkage probability of 94% was achieved by performing the polymerization at 0 °C for 2 h. Using (BDI-*i*Pr)ZnO*i*Pr, *meso*-LA was polymerized to afford syndiotactic PLA through the same chain-end control mechanism. Although it is not able to produce isotactic PLA from *rac*-LA like the chiral aluminum catalysts (Scheme 11.22), (BDI-*i*Pr)ZnO*i*Pr exhibited much higher activity while maintaining excellent molecular weight control.



Scheme 11.23 β -Diiminato zinc alkoxide (BDI-*i*Pr)ZnOiPr used for the synthesis of heterotactic and syndiotactic PLA.

11.3.1.4 Germanium Catalysts for the Synthesis of PLA

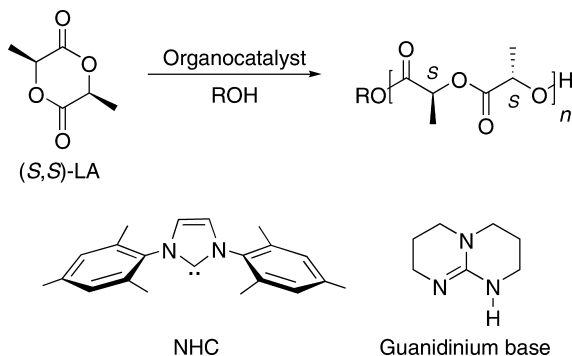
The first germanium catalyst for the ROP of LA was reported by Davidson and co-workers [66]. They used a mixed germanium alkoxide-aryloxide [(ArO₃)GeOiPr, Scheme 11.24] to produce predominantly heterotactic PLA from the ROP of *rac*-LA in the absence of solvent. Molecular weights as high as 52 000 g mol⁻¹ were obtained, with a PDI of 1.19. This was the first example of heterotactic PLA synthesis under solvent-free conditions.



Scheme 11.24 Germanium catalyst (ArO₃)GeOiPr for the synthesis of heterotactic PLA.

11.3.1.5 Metal-free Catalysts for the Synthesis of PLA

Hedrick and co-workers reported the use of an *N*-heterocyclic carbene (NHC, Scheme 11.25) as an organocatalyst for the ROP of cyclic esters through a monomer activation pathway in which the nucleophilic NHC ring opens the cyclic ester and activates it towards attack by the alcohol initiator or the propagating alcoholic polymer chain end [67]. This novel method is of great environmental interest as typical ROPs



Scheme 11.25 Ring-opening polymerization of LA using organocatalysts.

require the removal of the residual catalyst (metal) from the polymer during purification. With an organocatalyst, metal removal is unnecessary and this eliminates the need for expensive purification steps and large volumes of solvent waste. In 2 h, the authors were able to polymerize 120 equiv. of (*S,S*)-LA using benzyl alcohol as the initiator, with a PDI of 1.12.

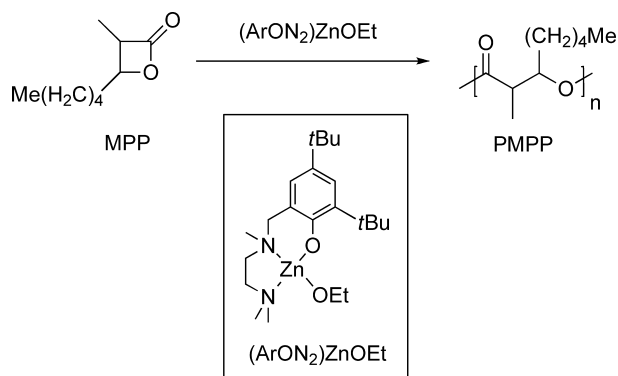
Recently, Waymouth and co-workers reported the ROP of LA in which they used a commercially available guanidinium base (Scheme 11.25) with 4-pyrenebutanol as an initiator for the ROP of (*S,S*)-LA [68]. This organocatalyst system exhibited activity that is faster than with many metal catalysts as it polymerized 500 equiv. of LA in 1 min at 20 °C to afford an M_n of 63 000 g mol⁻¹ and a PDI of 1.11. They proposed a bifunctional nucleophilic mechanism in which a nitrogen atom on the guanidine base ring opens the cyclic ester while the adjacent nitrogen atom, through a hydrogen bond, activates the alcohol initiator or polymer chain end for nucleophilic attack at the nearby *N*-acyl bond. They hypothesized that this process is responsible for the exceptionally high LA ROP activities that were observed.

11.3.2

Synthesis of Poly(hydroxyalkanoate)s

Poly(hydroxyalkanoate)s (PHAs) are naturally occurring biodegradable and biocompatible polymers that are produced by bacteria and other organisms [50a,d, 52]. Because of the high cost of PHA synthesis via bacterial fermentation, a number of synthetic efforts have been developed for the synthesis of these aliphatic polyesters. We will present just a brief overview of PHA synthesis as a more extensive review has already been published [50b].

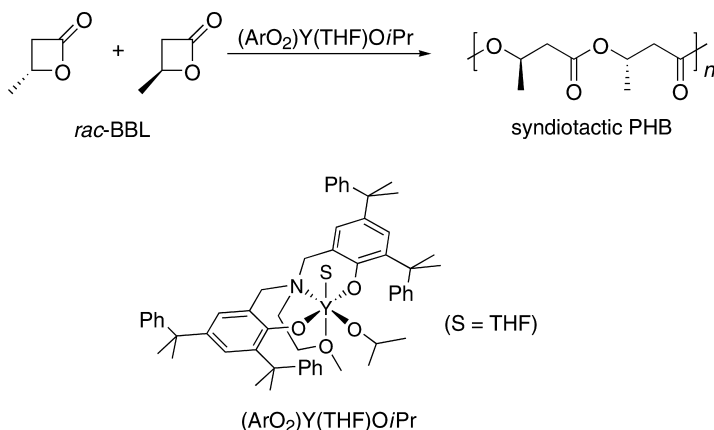
Schreck and Hillmyer have reported a synthesis of poly(α -methyl- β -pentyl- β -propiolactone) [69] (PMPP) from the corresponding lactone using a zinc complex (Scheme 11.26), previously shown to be highly active for the ROP of LA [70]. However, the ROP of MPP proceeded significantly more slowly than that of LA. This reaction required 75 h to achieve 89% conversion and an M_n of 40 000. Lactone MPP is readily synthesized from propionic acid and hexanal, two compounds that can be produced



Scheme 11.26 Polymerization of (α -methyl- β -pentyl- β -propiolactone) using a zinc alkoxide.

from biorenewable resources. PMPP was targeted as a biodegradable, biorenewable alternative to polyethylene that is blended with PLA in order to increase the mechanical toughness of PLA.

Poly(3-hydroxybutyrate) (PHB), one of the most common PHAs, can be synthesized to give isotactic polyester through the use of optically pure (*R*)- or (*S*)- β -butyrolactone (BBL); however, syndiotactic PHB has been an elusive target. Notably, in a recent study, Carpentier and co-workers employed an yttrium isopropoxide complex $(\text{ArO}_2)\text{Y}(\text{THF})\text{OiPr}$ (Scheme 11.27) to generate highly syndiotactic PHB in 1 min from *rac*-BBL [71]. The polymer contained 90% syndiotactic linkages and possessed an M_n of 23 000 g mol^{-1} and a PDI of 1.15. A decrease in temperature from 20 to -20°C resulted in an increase in syndiotacticity to 94%.



Scheme 11.27 Synthesis of syndiotactic PHB using yttrium catalyst $(\text{ArO}_2)\text{Y}(\text{THF})\text{OiPr}$.

Another report of high activity in the polymerization of BBL comes from Coates and co-workers [72]. They used a β -diiminate zinc catalyst, $(\text{BDI-}i\text{Pr})\text{ZnOiPr}$, to effect the ROP of *rac*-BBL in 5 min at 70°C to produce PHB with an M_n of 25 000 and a PDI of 1.14. At a monomer : initiator ratio of 2000 : 1, M_n values as high as 144 000 g mol^{-1} were achieved. Also, isotactic PHB was generated using optically pure (*R*)-BBL in the feed, although complete conversion was not realized as the highly crystalline polymer precipitated out of benzene solution at 67% conversion. It was also shown that the catalyst system is active for the ROP of β -valerolactone (BVL).

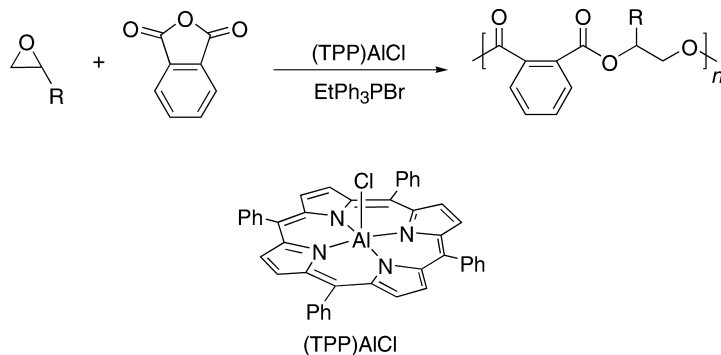
N-Heterocyclic carbenes (NHCs, Scheme 11.25) have also been shown by Hedrick and co-workers to effect the ROP of BBL [67]. They were able to polymerize 44 equiv. of BBL relative to pyrenebutanol initiator to afford PHB with a PDI of 1.15.

11.3.3

ROP of Other Cyclic Esters

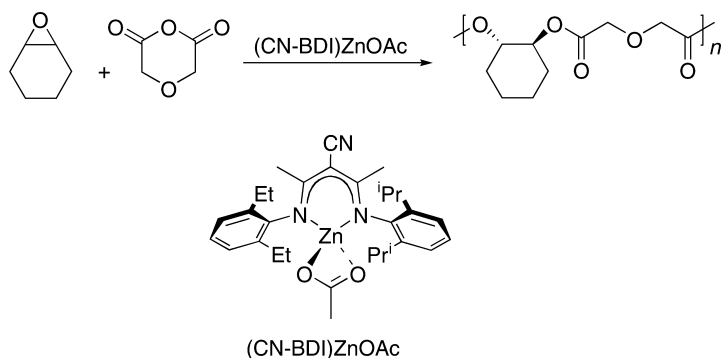
In addition to LA and BBL, ϵ -caprolactone (CL) and similar lactones are suitable monomers for the synthesis of biodegradable aliphatic polyesters via well-defined

anhydride, including propylene oxide and cyclohexene oxide (Scheme 11.29). With a chloride initiator, polymers with M_n values up to 4000 g mol^{-1} were synthesized, while PDIs were as low as 1.08. The system was shown to be living by the addition of more epoxide to the growing poly(alkylene phthalate), which caused a noticeable increase in M_n while retaining the narrow PDI. However, one drawback to this system is the long reaction times required: 4–16 days were necessary to achieve full conversion of 25 equiv. of each monomer.



Scheme 11.29 Copolymerization of epoxides and maleic anhydride using (TPP)AlCl–EtPh₃PBr.

Recently, Coates and co-workers reported a more efficient method for the synthesis of aliphatic polyesters from epoxides and cyclic anhydrides using a β -diiminate (BDI) zinc complex, (CN-BDI)ZnOAc [76], which has been developed for use in ROP reactions over the past decade. This complex was active for a number of combinations of epoxides and cyclic anhydrides, including cyclohexene oxide and diglycolic anhydride (Scheme 11.30). M_n values in excess of $50\,000 \text{ g mol}^{-1}$ and PDIs as low as 1.11 were obtained. This system is noteworthy in that most ROPs can be performed in a matter of hours, instead of days, and can attain high molecular weight polymers while retaining low PDIs.



Scheme 11.30 Alternating copolymerization of epoxides and cyclic anhydrides using (CN-BDI)ZnOAc.

11.3.5

Summary

Interest in aliphatic polyesters has increased considerably over the past few decades, due in large part to their biodegradable properties and the biorenewable origin of many of the monomers. These materials have found many uses in today's society, from drug delivery systems, degradable tissue scaffolds and sutures, to commodity plastics and textiles. Although the cost of aliphatic polyesters has decreased, they are still more expensive than polyalkenes. With continuing research and an increasing public knowledge of, and interest in, this area, the cost of aliphatic polyesters is expected to become more competitive with polyalkenes. This development should be instrumental in lessening the environmental impact of our heavy dependence on non-biodegradable and non-biorenewable plastics.

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