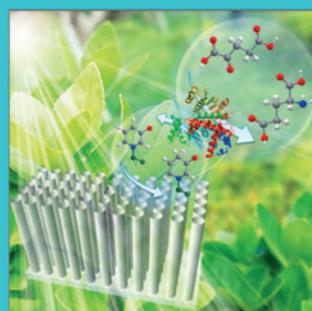
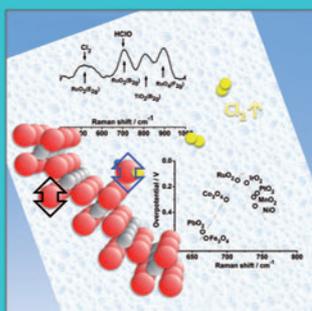
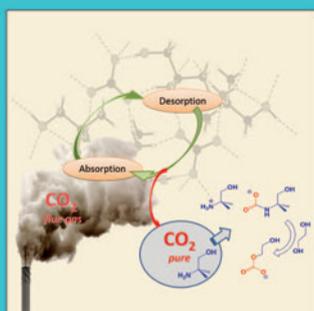
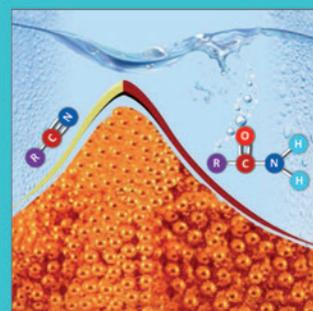
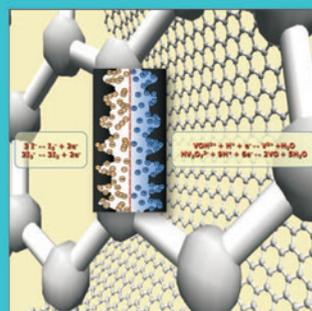
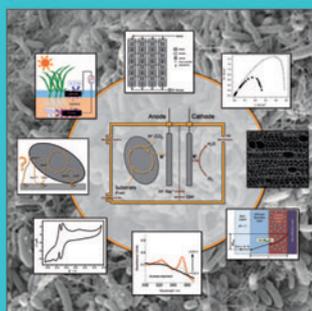
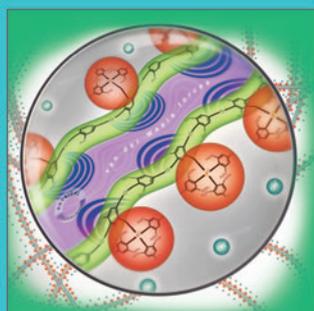
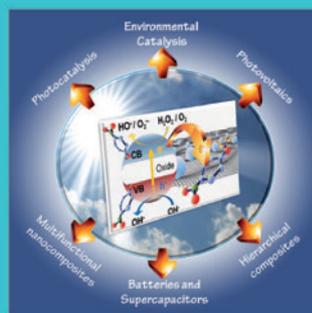
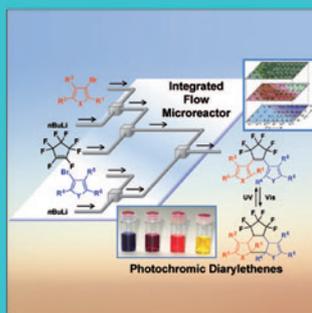
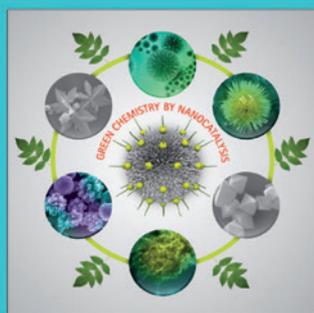


CHEMISTRY & SUSTAINABILITY

CHEM SUS CHEM

ENERGY & MATERIALS



Reprint

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY-VCH

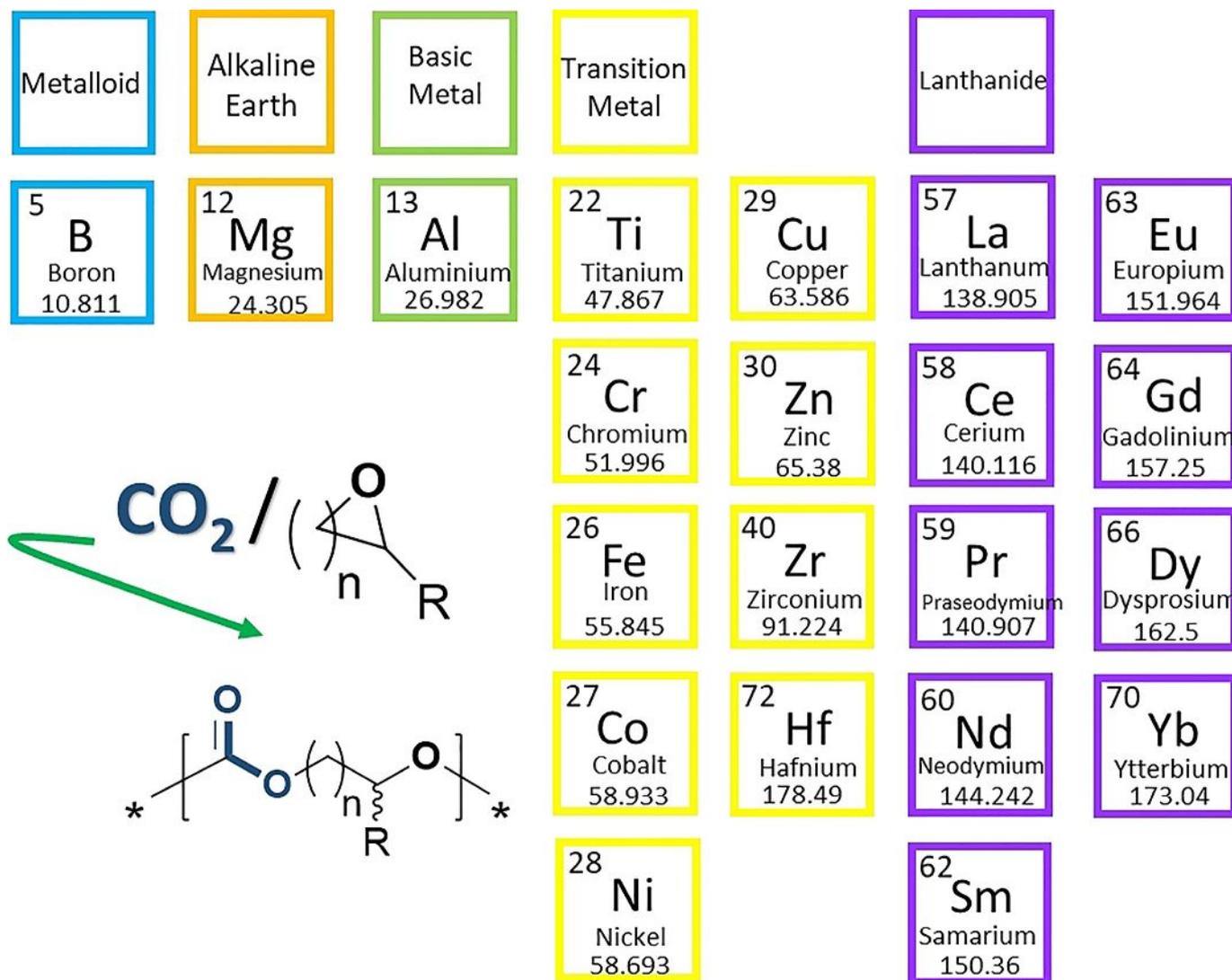
www.chemsuschem.org

A Journal of



Update and Challenges in Carbon Dioxide-Based Polycarbonate Synthesis

Jin Huang,^[a, b] Joshua C. Worch,^[b] Andrew P. Dove,^{*, [b]} and Olivier Coulembier^{*, [a]}



The utilization of carbon dioxide as a comonomer to produce polycarbonates has attracted a great deal of attention from both industrial and academic communities because it promises to replace petroleum-derived plastics and supports a sustainable environment. Significant progress in the copolymerization of cyclic ethers (e.g., epoxide, oxetane) and carbon dioxide has

been made in recent decades, owing to the rapid development of catalysts. In this Review, the focus is to summarize and discuss recent advances in the development of homogeneous catalysts, including metal- and organo-based complexes, as well as the preparation of carbon dioxide-based block copolymer and functional polycarbonates.

1. Introduction

Over the past century, plastics have revolutionized the industrial sector by allowing for the replacement of natural building blocks, such as metal, wood, and stone, with cheaper, more durable, and adaptable synthetic materials.^[1] Although the continued development of the plastics industry has revolutionized many sectors, including automotive, healthcare, electronics, and packaging, the environmental stress of producing and disposing of such materials is acutely apparent.^[2] Currently, the majority of consumer plastics are manufactured from petroleum-derived sources, and the abuse of such fossil fuels is accelerating carbon dioxide (CO₂) emissions, leading to a warmer, more unstable, global environment.^[3] As such, there is a substantial incentive to diversify the plastics industry by producing materials with lower environmental impact. Currently, polyesters, such as poly(lactic acid) (PLA) or poly(butylene succinate) (PBS), account for a substantial proportion of the global production capacity of biodegradable plastics.^[4] However, polycarbonates, which can be prepared by using CO₂ as a comonomer, have been noted for their biodegradability and diverse properties and thus could become an increasingly useful sustainable plastic.^[5]

Compared with highly reactive carbon monoxide (CO), both the fully oxidized state and centrosymmetric structure of CO₂ render it relatively inert. However, the presence of the two electronegative oxygen atoms confers a somewhat electrophilic behavior to the carbon atom, which makes it susceptible to undergo nucleophilic attack.^[6] From a purely chemical perspective, CO₂ is a sustainable, biorenewable, nontoxic, and nonflammable C₁ feedstock that could be valorized in a variety of chemicals. These include small molecules, such as carboxylic acids, cyclic carbonates, and methanol, or longer hydrocarbon chains (C₅–C₁₁),^[7] as well as polymeric structures. Hence, efforts have been directed towards CO₂ homopolymerization to pro-

duce poly(CO₂).^[8] Although direct polymerization is possible, requiring formidably high temperature and pressure (4 × 10⁴ MPa, 1800 K),^[9] the process is entropically disfavored, converting ineluctably poly(CO₂) into CO₂ gas under normal temperature conditions and lower pressure. For these reasons, the use of CO₂ as a comonomer remains the only practical approach to incorporating CO₂ into polymer structures.

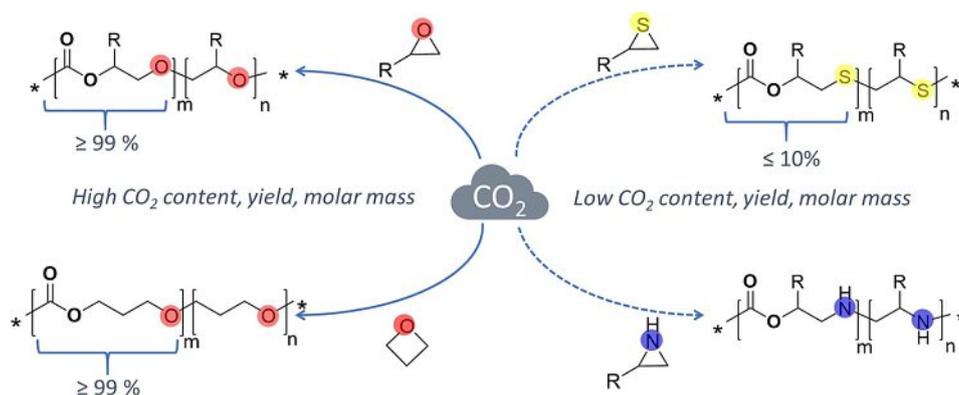
To prepare CO₂-based copolymers, two techniques have been developed. The first consists of preparing a CO₂-based monomer followed by a polymerization process ("monomer to polymer" technique, M to P), and the second entails a direct "chain-up" process of CO₂ with other comonomers. The M to P technique provides a wide range of polymer precursors,^[10] and offers the advantage of using sublimed dry ice as a CO₂ resource. In contrast, byproducts and uneconomical purification processes are generally involved in this time-consuming approach.^[10c] As far as the CO₂ chain-up technique is concerned, polycondensation and ring-opening copolymerization (ROcP) have been used and reported. The polycondensation methodology allows various products to be prepared through the copolymerization of CO₂ with corresponding substrates, such as diols,^[11] diamines, and dihalides.^[11,12] However, uncontrollable polymerization presents some drawbacks and these, along with the concomitant byproducts, plague the development of such a method for potential industrial applications.

The ROcP of CO₂ with heterocycles presents a desirable route to access polycarbonates,^[13] since only a few small-molecule byproducts are produced in a controlled manner. Typically, three- or four-membered heterocyclic molecules, which feature high ring strain, such as epoxide (EP), oxetane, episulfide (ES), or aziridine (AD), are suitable comonomers in CO₂-based ROcP. The driving force of the process is then entirely based on cleavage of the C–X (X = N, O, S) bond, which depends on the nature of the heterocyclic molecule ring-strain energy (*E_r*). Relative to the other comonomers, ES possesses the lowest *E_r* value (≈ 17.7 kcal mol⁻¹),^[14] which considerably reduces its reactivity with CO₂.^[15] However, EP (*E_r* = 27.2 kcal mol⁻¹),^[16] oxetane (*E_r* = 24.8 kcal mol⁻¹),^[17] and AD comonomers (*E_r* = 26–27 kcal mol⁻¹)^[18] are sufficiently reactive to theoretically expect a chain-up process with CO₂ (Scheme 1). Despite the high ring strain of ADs, the main drawback of CO₂/AD copolymerization, along with the issue of the CO₂-catalyzed homopolymerization of AD,^[19] is the formation of nonproductive carbamic acid species. This results in an uncontrollable copolymerization, with the appearance of cyclic side products and some branched copolymer structures.^[20] Hence, the copolymerization of CO₂ with EP and oxetane to form aliphatic polycarbonates represents the best and most common route to prepare polymers, due to

[a] Dr. J. Huang, Prof. Dr. O. Coulembier
Laboratory of Polymeric and Composite Materials (LPCM)
Center of Innovation and Research in Materials and Polymers (CIRMAP)
University of Mons, Place du Parc 23
7000, Mons (Belgium)
E-mail: Olivier.Coulembier@umons.ac.be

[b] Dr. J. Huang, Dr. J. C. Worch, Prof. Dr. A. P. Dove
School of Chemistry, University of Birmingham
Edgbaston, Birmingham, B15 2TT (UK)
E-mail: A.Dove@bham.ac.uk

 The ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/cssc.201902719>.



Scheme 1. General characteristics of the copolymerization of CO₂ with ring-strained heterocyclic monomers.

the high reactivity and chemical tunability of the oxygen heterocycles (Scheme 1).^[21]

Only a few oxetane/CO₂ coupling studies have been reported;^[22] this is likely to be due to the relatively higher cost and lower inherent reactivity of oxetanes compared with that of oxiranes.^[23] Consequently, CO₂/EP copolymerizations have been

studied extensively, not only for the superior ring-opening activity of EPs, but also for the more economical synthesis of EPs based on petroleum^[24] and/or biological starting materials.^[25]

Two recent reviews have highlighted some metal catalysts used for CO₂-derived polycarbonate synthesis; the first focuses on functional polycarbonates^[26] and the second excludes magnesium, copper, and metal-centered catalysts.^[27] Herein, we focus on progress realized in the preparation of cyclic carbonate synthons and aliphatic polycarbonate preparation from CO₂/EP copolymerization. Furthermore, it is considered comprehensive for all metal-based processes and includes the rapidly developing field of organocatalytic approaches. Currently, the field is still considered young, since the first example of copolymerization dates back to 1969,^[28] and the early work of Baba et al. on oxetane/CO₂ copolymerization was only reported in 1984.^[29] Today, the field is rapidly expanding, with primary developments encompassing polycarbonate syntheses under increasingly mild (and more economical) conditions, which should place these materials at the forefront of the next generation of plastics.

Olivier Coulembier graduated from the University of Mons-Hainaut in 2005 and moved to Stanford University and the IBM Almaden Research Center to undertake periods of postdoctoral research under the supervision of Prof. Robert M. Waymouth and Dr. James L. Hedrick. He is currently a research associate of the Belgian F.N.R.S. in the Laboratory of Polymeric and Composite Materials (LPCM) at the University of Mons. His research focuses on the (non-)organometallic ring-opening polymerization of cyclic monomers and the valorization of carbon dioxide by the use of organic catalysts.



Andrew P. Dove is Professor of Chemistry at the University of Birmingham, UK. He obtained his Ph.D. under the supervision of Prof. Vernon Gibson from Imperial College London in 2003 before postdoctoral study at both Stanford University and IBM, under the supervision of Prof. Robert Waymouth and Dr. James Hedrick. He returned to the UK as a RCUK Fellow at the University of Warwick in 2005 before being promoted to Assistant (2006), Associate (2009), and Full Professor (2014). He moved to Birmingham in 2018. He was awarded the Macro Group UK Young Researcher Medal in 2009, the RSC Gibson-Fawcett Award in 2014, the Biomacromolecules/Macromolecules Young Researcher Award in 2016, and the RSC Norman Heatley Award in 2018.



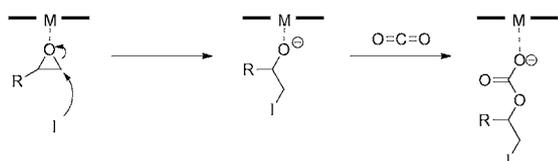
2. Metallo-Organic Catalysts

To improve the properties of materials and lower the associated costs of their production, catalyst development has become a primary focus in the synthesis of aliphatic polycarbonates from CO₂ synthons. Metal-based catalysts have garnered the most attention because they often display superior catalytic activities, remain active under mild conditions, and are easily tunable. Specifically, metals are particularly attractive as catalysts due to their versatile oxidation states and bonding modes (e.g., variability of coordination number and the ability to form both σ and π bonds).^[30] Moreover, such catalysts can be easily tuned to modulate activity and/or selectivity by ligand substitution, through which the electron density at the metal center and overall coordination sphere can be altered. As such, both main-group and transition-metal catalysts have been extensively developed for CO₂-based polymer synthesis. Before reviewing the updates of metal-based catalysts, we provide an overview of the mechanism and kinetics of polycarbonate synthesis.

2.1. Mechanism and kinetics of copolymerization

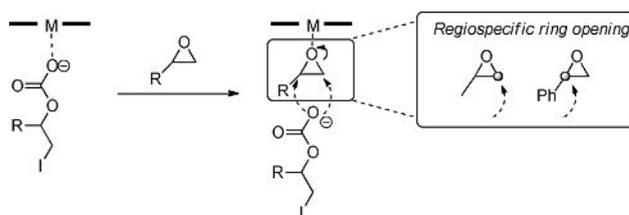
2.1.1. General mechanism

The mechanistic aspects of metal-catalyzed CO₂/EP copolymerization were first investigated by Tsuruta and co-workers by using diethylzinc (ZnEt₂) as a catalyst; the oxygen-metal (O-M) species (alkoxide) was found to be of prime importance in initiating copolymerization.^[28] Briefly, direct copolymerization of CO₂/EP is initiated by a ring-opened EP (alkoxide) that can subsequently attack CO₂, resulting in the formation of carbonate species (Scheme 2).



Scheme 2. The initiation of CO₂/EP copolymerization.

Ring opening of the EP may proceed through different pathways, depending on the nature of the terminal group, that is, the relative electron-donating or -withdrawing effects of dangling functional groups present on the three-membered cyclic monomer. For example, the electron-donating methyl group present on propylene oxide (PO) will favor the EP being opened by methylene (–CH₂–O–) bond cleavage. Electron-withdrawing groups, such as the aromatic phenyl of styrene oxide (SO), on the other hand, will prompt methine (–PhCH–O–) bond cleavage (Scheme 3).^[32] It is crucial to note that such cleavages may occur simultaneously during a polymerization process, leading to the production of regioirregular architectures.^[33]



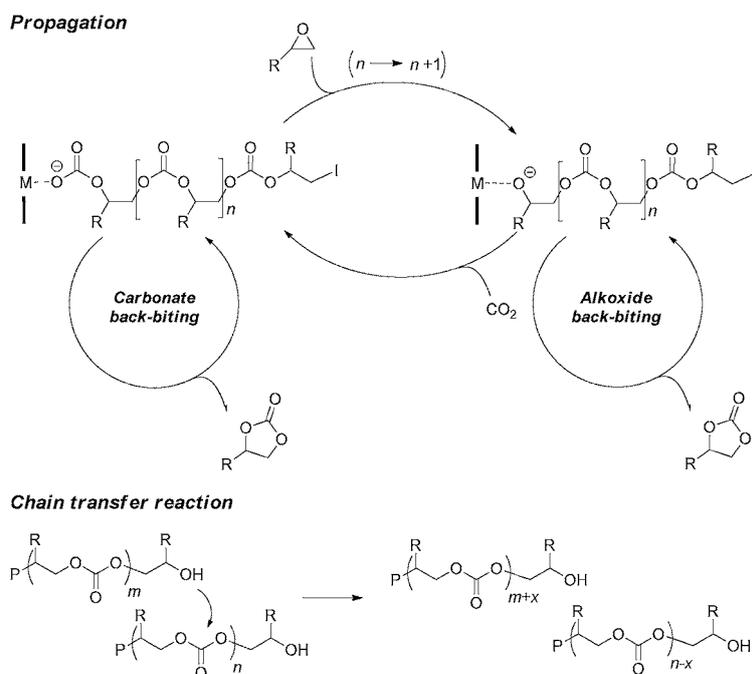
Scheme 3. Regiofavored C–O bond cleavage of EP with different substituents.

Idealized copolymerization to form polycarbonates involves cycling between two species (alkoxide and carbonate) from the alternative insertion of EP and CO₂, whereas undesirable cyclic byproducts or ether domains can be formed and chain-transfer reactions may also occur (Scheme 4).

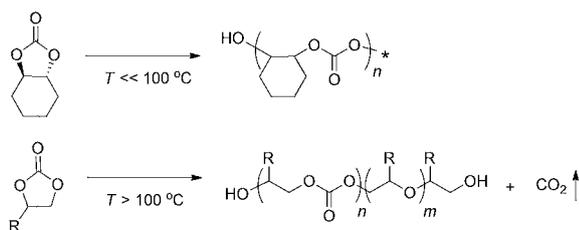
Common byproducts in such copolymerizations are five-membered cyclic carbonates (5CCs), which are often produced by back-biting reactions from the activated polymer chain (Scheme 4).^[34] The formation of 5CCs can be detrimental because they are thermodynamically stable (apart from *trans*-cyclohexane carbonate (*trans*-CHC) species with a large dihedral angle (29.7°; –O-CH-CH-O-),^[35] leading to high ring strain.^[36] However, 5CCs favor entropically driven polymerization at high temperatures (> 100 °C), resulting in poly(carbonate-co-ether) with the concomitant release of CO₂ (Scheme 5).^[37]

2.1.2. Kinetic perspective

Organometallic-based systems generally yield small amounts of 5CCs because the activation energy barrier of polymerization (E_p) is lower than that of cycle formation (E_c) (96.8 vs.



Scheme 4. The idealized propagation pathway of CO₂/EP copolymerization.



Scheme 5. Temperature-dependent ring-opening polymerization (ROP) pathways of 5CCs.

137.5 kJ mol⁻¹ for E_p vs. E_d .^[21b] The coupling of CO₂/EP is a first-order process related to the catalyst and EP concentration, but has zero-order dependence with respect to the CO₂ pressure.^[38] However, in the dinuclear catalytic system reported by Rieger,^[38b] CO₂ pressure dramatically affects the kinetic behavior of copolymerization. For low-pressure conditions (0.5–2.5 MPa), CO₂ insertion is rate limiting because the reaction displays first-order dependence on CO₂ pressure, and zero-order dependence on EP, assuming constant catalyst concentration. From 2.5 to 4 MPa, the reaction becomes zero order with respect to CO₂ and first-order relative to the EP. Conversely, under high-pressure conditions (≥ 5 MPa), the ring opening of the EP monomer becomes the rate-limiting step.^[38b]

2.2. Main-group-metal catalysts

Main-group metals, such as magnesium, aluminum, and zinc, are attractive alternatives to transition-metal-based systems due to their low toxicity and relatively high abundance. Recently, several main-group-based homogeneous catalysts that display sufficient activity for CO₂/EP copolymerization have been developed.

2.2.1. Magnesium catalysts

Kember and Williams developed a sophisticated bimetallic complex with macrocyclic ancillary ligands (**Mg-I**; Figure 1) that displayed a high activity for cyclohexane oxide (CHO) and CO₂ copolymerization to yield poly(cyclohexane carbonate) (PCHC).^[39] Up to 750 h⁻¹ TOF was observed, which was 20 times greater than that of previous Mg-based catalysts^[40] at 0.01 mol % **Mg-I** catalyst loading (1.2 MPa CO₂ at 100 °C) and without the production of the cyclohexane carbonate (CHC) byproduct. The decreased Lewis acidity and electropositive nature of magnesium contributed to a strong metal–carbonate bond, which enhanced the rate of chain propagation compared with that of cyclic byproduct formation. Notably, the high carbonate content in the resulting polymer (>99%), and near-quantitative yields, are even observed in the presence of excess exogenous water. Considering that many organometallic systems (e.g., cobalt–salen complexes) are deactivated in the presence of water,^[41] this result is particularly important for industrial-scale applications, in which air- and moisture-free processes can be difficult and costly.

Recently, a commercially available dialkylmagnesium species (**Mg-II**; Figure 1) effectively catalyzed isoselective CHO/CO₂ copolymerization (up to 82% isotacticity); this is the first reported use of an achiral catalyst to synthesize a stereocontrolled polycarbonate.^[42] The TOF was modest, at 0.1 MPa (6 h⁻¹), and could be increased approximately tenfold (TOF = 62 h⁻¹ at 1 MPa CO₂), but at the expense of diminished stereocontrol.

2.2.2. Aluminum catalysts

After a triethylaluminum-catalyzed CO₂/EP copolymerization protocol was reported,^[43] numerous Al-based catalysts featuring various ligands (such as porphyrin,^[44] salophen,^[45] salen,^[46] and dihydroxy-*p*-*tert*-butylcalix[4]arene (DMCA)) were explored for polycarbonate synthesis.^[47] Porphyrin ligands are ubiquitous in metal complexes for CO₂ copolymerization because of their well-defined coordination modes and promoted reactivity at the axial bond on the metal center, which is perpendicular to the porphyrin plane. Bifunctional porphyrin–Al complexes (**Al-I**; Figure 1) have successfully yielded polycarbonates by incorporating CO₂.^[48] After the installation of electron-donating substituents on the porphyrin ligand to modulate the Lewis acidity at the aluminum center, high-molecular-weight polymers were isolated with decreased cyclic byproducts compared with ligands bearing electron-withdrawing groups. Before this example, aluminum–porphyrin systems had yielded only low-molecular-weight polymers ($M_n = 4.5$ kg mol⁻¹).^[44] Contrastingly, in another study, aluminum complexes bearing porphyrin ligands substituted with electron-withdrawing fragments were more active and afforded polycarbonates with high molecular weights ($M_n = 33.5$ kg mol⁻¹, $D_M = 1.05$).^[49] Sugimoto and co-workers investigated a series of aluminum chiral catalysts for the enantioselective copolymerization of CO₂ and CHO.^[50] Aluminum–salen complexes (**Al-II**; Figure 1), activated with tetraethyl acetate (Et₄NOAc), afforded highly alternating copolymers, but with low molecular weights ($M_n = 1.9$ –6.8 kg mol⁻¹, $D_M = 1.14$ –1.22) and modest enantiomeric excess (*ee*) values of up to 23%. Under similar reaction conditions, the selectivity of the reaction was increased by using Al– β -ketoiminate complexes (**Al-III**; Figure 1) paired with a Lewis base (*N,N*-dimethyl-4-aminopyridine) cocatalyst (49% *ee*). The enantioselectivity was further improved to 80% *ee* by introducing bisamine Lewis base cocatalysts; however, high-molecular-weight polymers still remain elusive. More recently, a structurally simple triisobutylaluminum (TiBA; **Al-IV**; Figure 1) catalyst, coupled with lithium ions as the initiating species, catalyzed the synthesis of alternating polycarbonates in a controlled manner with moderate molecular weights ($M_n = 19.6$ kg mol⁻¹, $D_M = 1.10$).^[51] Another aluminum-centered catalyst, featuring aminophenolate ligands (**Al-V**; Figure 1), produced moderate-molecular-weight copolymers from CHO and CO₂ ($M_n = 29$ kg mol⁻¹, $D_M = 3.16$), but only 54% carbonate content was observed in the isolated materials.^[52] This nonalternating structure, that is, enhanced ether content, is likely the result of the off-target coordination between the aluminum metal center and heteroatoms of the ligand that serve to inhibit the insertion of a carbonate anion.

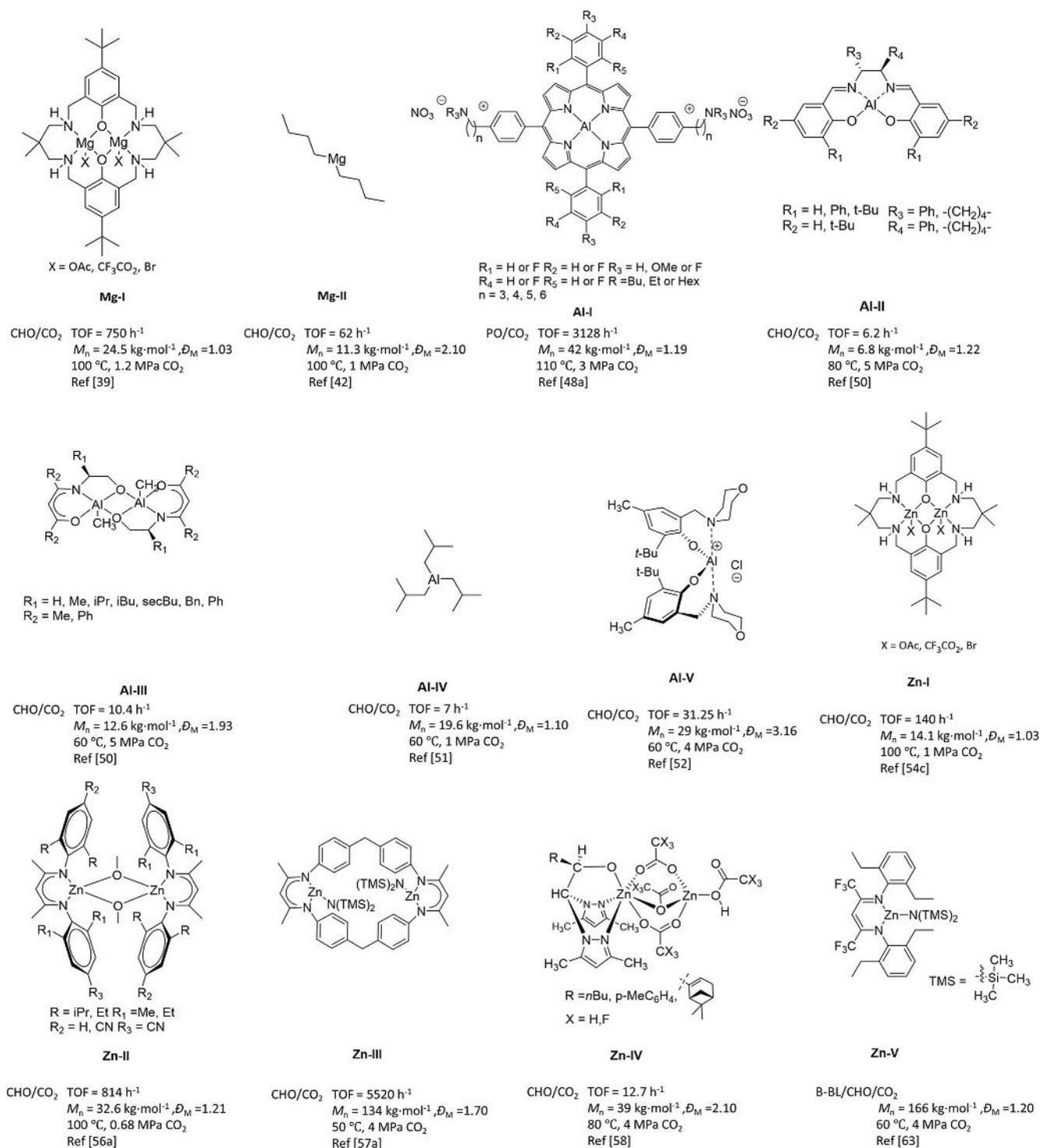


Figure 1. Representative Mg-, Al-, and Zn-based catalysts for CO₂/EP copolymerization. TOF = turnover frequency, β-BL = β-butyrolactone.

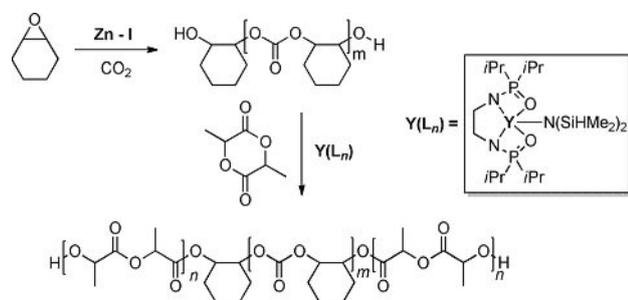
2.2.3. Zinc catalysts

Although zinc shares characteristics of both main-group and transition metals, the element is better defined as a main-group metal due to similarities with magnesium, such as similar atomic size and preferred oxidation states.^[53] Because zinc-based catalysts (diethyl zinc/H₂O) were first screened for CO₂/EP copolymerization in 1969, interest in catalyst development

has accelerated due to the large relative abundance of the metal.^[28] A dinuclear zinc structure bearing a macrocyclic ancillary ligand (**Zn-I**; Figure 1) has demonstrated remarkable activity in CO₂/CHO copolymerization at only 0.1 MPa CO₂.^[54] Continuing work, with a heterodinuclear (Mg and Zn) system, presents the advantage of being cocatalyst-free, and displays a higher activity relative to that with a homo-dinuclear center.^[55] The asymmetric β-diketimate-based zinc catalyst (**Zn-II**;

Figure 1) also displayed good activity in CO₂/CHO copolymerization (TOF = 814 h⁻¹) under a modest CO₂ pressure (≈ 1 MPa).^[56] More recently, Rieger and co-workers developed β-diiminato-containing Zn complexes (**Zn-III**; Figure 1) that were very active in the copolymerization of CO₂ with various EPs, including CHO, PO, SO, limonene oxide (LO), octene oxide (OO), and epichlorohydrin (ECl).^[38b,57] High catalytic activity (TOF = 5520 h⁻¹) was observed at only moderate pressure (4 MPa CO₂); this is a particularly promising result for potential industrial translation. A reported novel dizinc catalyst bearing heteroscorpionate ligands (**Zn-IV**; Figure 1) yielded CO₂/CHO polycarbonates with high molecular weight ($M_n = 39 \text{ kg mol}^{-1}$) at 4 MPa CO₂ in just 48 h.^[58]

Although CO₂/CHO copolymerization is often used as a benchmark in academic investigations, the polycarbonates produced from this reaction are not likely to replace commodity plastics because of their inferior thermal and mechanical properties (such as lower T_g , heat deflection, and strength).^[5b,59] However, the introduction of a third comonomer to produce terpolymeric architectures provides access to materials with a broader range of thermal and mechanical properties that are positioned to compete with the portfolio of modern thermoplastics (polypropylene or polyethylene, for instance). Consequently, interest in terpolymeric structures is increasing and Zn-based catalysts have shown particular utility within this area. By combining **Zn-I** complexes in the presence of an yttrium initiator, a novel triblock copolymer (poly(lactide)-*b*-PCHC-*b*-poly(lactide); Scheme 6) was successfully prepared that featured two distinct glass transition temperatures ($T_g = 60$ and 80°C).^[60]



Scheme 6. Copolymerization of CHO and subsequent block copolymerization with lactide.

In a similar study, poly(ϵ -caprolactone)-*b*-PCHC-*b*-poly(ϵ -caprolactone) was prepared in a one-pot process by combining CHO, CO₂, and ϵ -caprolactone (CL) in the presence of **Zn-I**.^[61] Rieger et al. reported the **Zn-III**-catalyzed synthesis of a flexible triblock polymer, PCHC-*b*-poly(dimethylsiloxane)-*b*-PCHC, by using poly(dimethylsiloxane) as a chain-transfer agent to overcome the inherent brittleness of PCHC.^[62]

Usually, triblock CO₂-based polycarbonate synthesis requires a multistep manipulation and poly(diols) as a macroinitiator. This process is both time-consuming and results in a fixed sequence of the resultant microstructure, which limits access to more diverse materials and potential corresponding applica-

tions. As such, producing block copolymers through a simple transformation is promising for the industrial-scale utilization of CO₂. Thanks to recent advances in catalyst development, simple tuning of the CO₂ pressure to control the sequence of copolymers has become a reality. Moreover, the **Zn-V** complexes have been applied to the synthesis of sequence-controlled terpolymers for which CO₂ pressure was leveraged as a chemoselective agent in a one-pot synthesis.^[63] If subjecting the mixture to low pressure (0.3 MPa CO₂), a statistical terpolymer ($M_n = 69 \text{ kg mol}^{-1}$, $D_M = 1.60$) is obtained from β -BL, CO₂, and CHO. By using the same monomer combination, a block terpolymer (poly(β -BL)-*b*-poly(CHC); $M_n = 146 \text{ kg mol}^{-1}$, $D_M = 1.20$) was isolated by simply increasing the CO₂ pressure (4 MPa) in the reaction vessel.

Williams and co-workers leveraged **Zn-I** and similar dinuclear catalysts to afford control over polycarbonate microstructures with a mixed monomer feedstock, in which the monomer reactivity was dependent upon the nature of the polymer chain end (Zn–O bond).^[64] Similarly, these authors reported a series of sequence-controlled copolymers from a four-component monomer mixture composed of CL, CHO, phthalic anhydride (PA), and CO₂. Various copolymeric architectures were obtained through a one-pot methodology because the mechanism could switch between distinct catalytic cycles to effect the microstructure of the growing polymer chain (Figure 2).^[64c] Some of the unique structures included semi- and fully aliphatic polyesters, poly(ester-*b*-ester), polycarbonates, and poly(ester-*b*-carbonate). The ability to rationally tune the polymer microstructure from monomer mixtures is a significant advancement and is particularly applicable for industrial applications because it allows access to numerous architectures in a straightforward and potentially more economical manner.

2.3. Transition-metal catalysts

Transition-metal catalysis continues to be the cornerstone of many synthetic advances in chemistry because of the high versatility imparted by predictable oxidation-state switching and facile structural tuning enabled by ligand development and substitution.^[65] Furthermore, transition-metal complexes are generally more resistant to oxidative and/or hydrolytic degradation, which can plague many main-group catalyst complexes. However, the glaring weakness is that the natural abundance of some transition metals is extremely low, which makes them quite expensive and hampers their sustainability.^[66] Nevertheless, efforts to improve the recyclability of such catalysts and/or increase catalytic efficiencies should lessen raw material requirements if used in synthetic applications.

2.3.1. Cobalt catalysts

Organometallic cobalt complexes are known to be particularly effective at catalyzing CO₂ copolymerization because cobalt has high Lewis acidity and can adopt a variety of oxidation states.^[41a] Some of the most studied complexes feature tetradentate salen ligands^[41c,67] and tetraazamacrocyclic-porphyrin^[49,68] with Co^{III} metal centers.

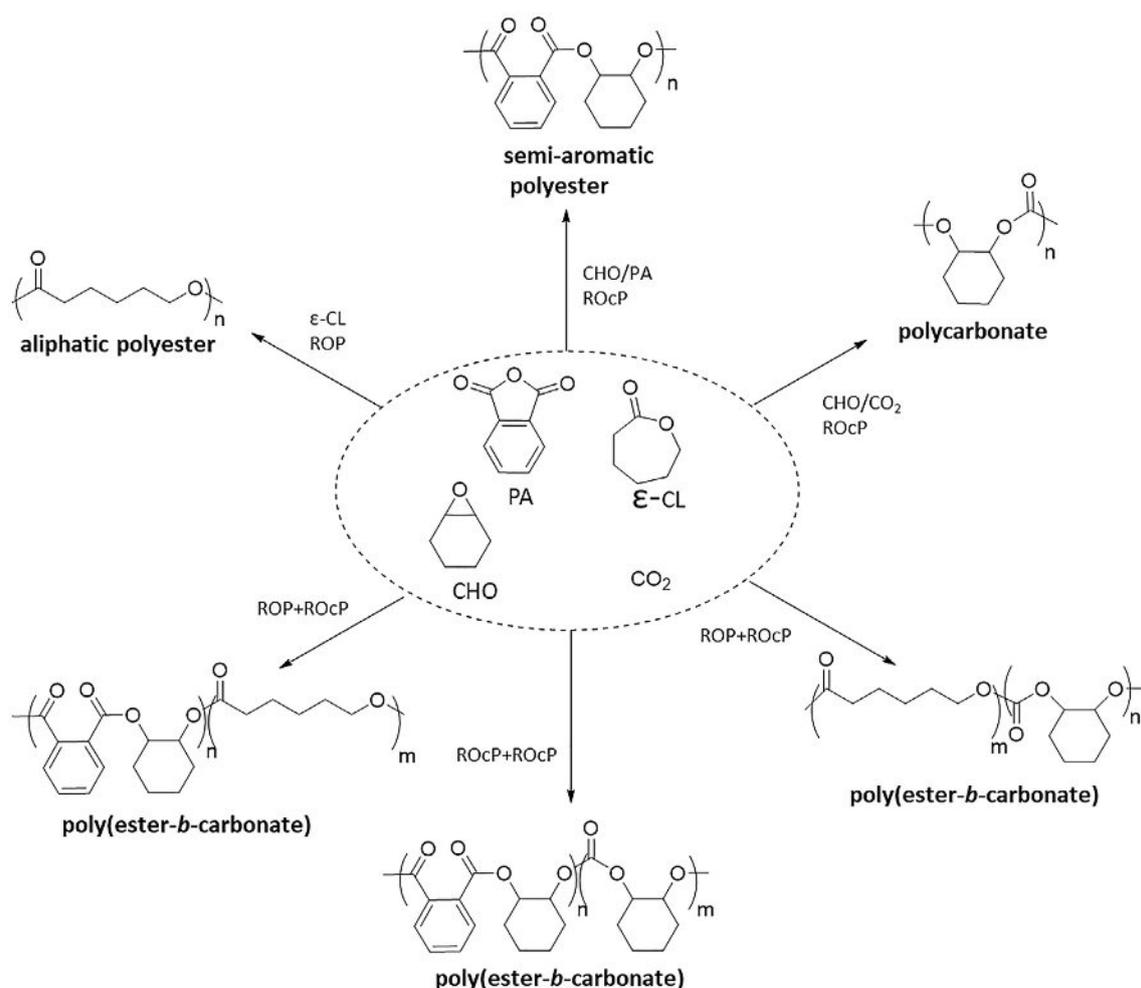


Figure 2. A range of polymer products with different microstructures produced through the chemoselective catalysis of a four-component monomer mixture.^[64c]

Lu et al. first reported the preparation of moderate-molecular-weight ($M_n = 25.9 \text{ kg mol}^{-1}$, $D_M = 1.07$) alternating CO₂/ECL copolymers by using Co^{III}-based catalysts (**Co-I** and **Co-II**; Figure 3).^[69] ECL is a notoriously challenging monomer for copolymerization because chloride elimination is a significant competing reaction near ambient temperature (25 °C), which contributes to the formation of cyclic carbonate species. Consequently, in the study in question, the activity of the cobalt species was critical in the polymerization reaction proceeding below ambient temperatures (0 °C).

The copolymerization of IO and CO₂ can be conducted under mild reaction conditions with **Co-II** and **Co-III** (Figure 3).^[70] To obtain high-molecular-weight polymers, the reaction was performed at 0 °C with a low catalyst loading (0.1 mol%) because cyclic carbonate formation is thermodynamically favored. Although a low catalyst loading (0.1 mol%) led to correspondingly longer induction periods for the binary catalyst system, the resulting polycarbonate was still isolated with reasonable properties ($M_n = 9.7 \text{ kg mol}^{-1}$, $D_M = 1.09$, $T_g = 138 \text{ °C}$). With **Co-III** and **Co-IV**, the monomer scope was expanded to include BO (poly(*trans*-2-butene carbonate), $M_n =$

13.9 kg mol^{-1} , $D_M = 1.05$, 24 h)^[71] and CPO (poly(cyclopentane carbonate), $M_n = 23.5 \text{ kg mol}^{-1}$, $D_M = 1.06$, 5 h).^[72]

Although polycarbonates with saturated backbones are not very amenable to postpolymerization modifications, the introduction of unsaturated units (e.g., alkenes)^[73] affords a polymer that can be functionalized through thiol-based click chemistry (Scheme 7).^[74] The cobalt-catalyzed copolymerization of CHDO and CO₂ affords high-molecular-weight poly(cyclohexadiene carbonate) ($M_n = 35.9 \text{ kg mol}^{-1}$), which possesses robust thermal properties ($T_g = 123 \text{ °C}$) that are slightly higher than those of the saturated analogue ($T_g = 116 \text{ °C}$). The replacement of cobalt in the **Co-IV** scaffold with other metals, such as zinc or magnesium, has also been investigated, but the cobalt catalyst displayed superior performance (TOF = 65 h⁻¹), and thus led to a polymer with higher molecular weight and lower dispersity ($M_n = 12.9 \text{ kg mol}^{-1}$, $D_M = 1.18$).^[75] Regiochemical considerations have also been investigated in the CHDO/CO₂ system by examining the effect of the alkene in the monomer unit (1,3-CHDO vs. 1,4-CHDO).^[76] Copolymerization conducted with 1,3-CHDO displayed increased reaction kinetics and yielded 40.8% selectivity of polymer formation and 100% conversion for 1,3-

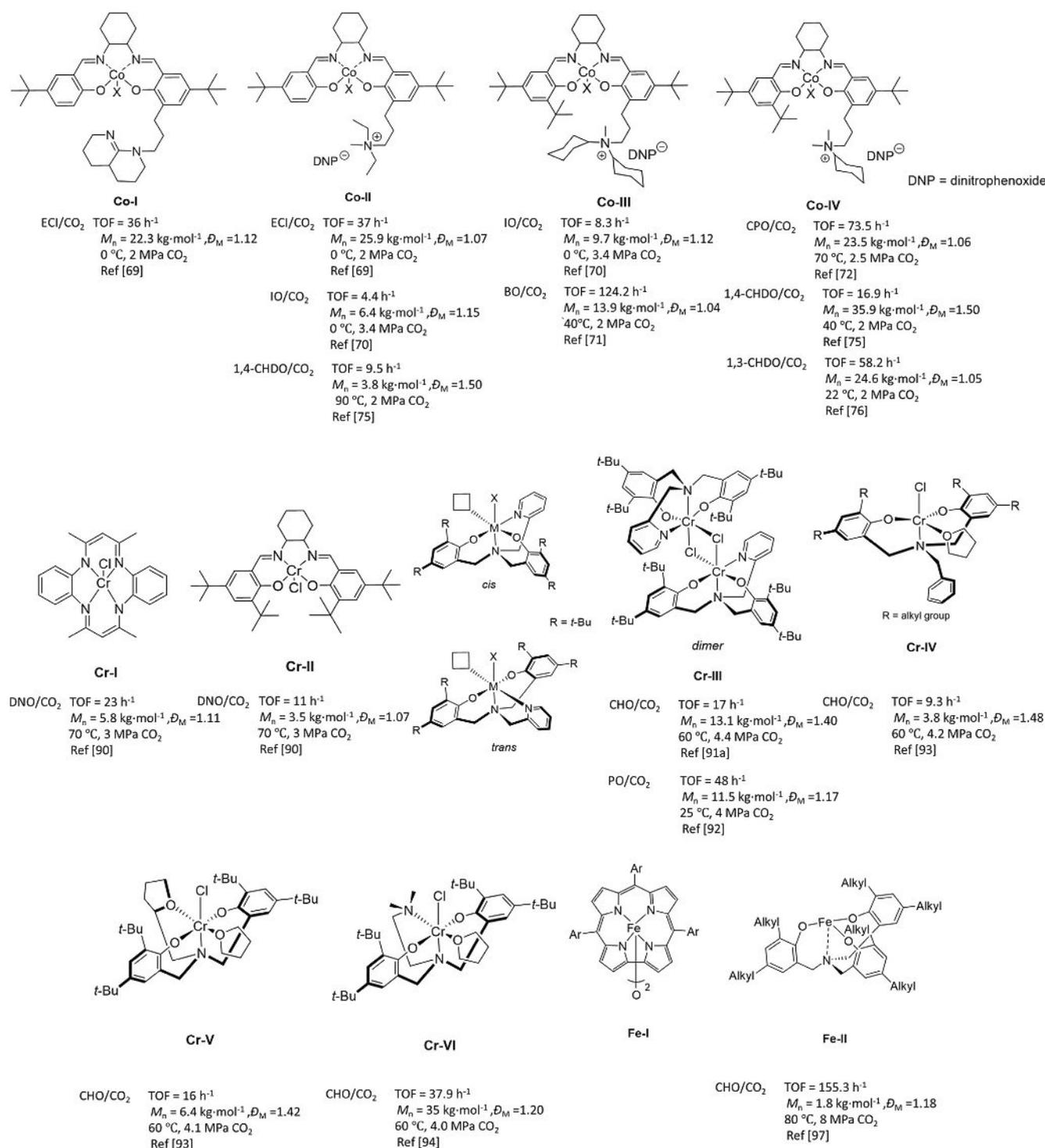
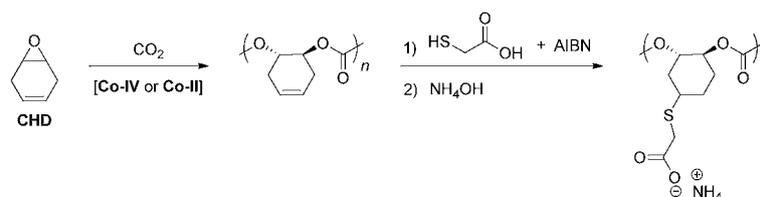


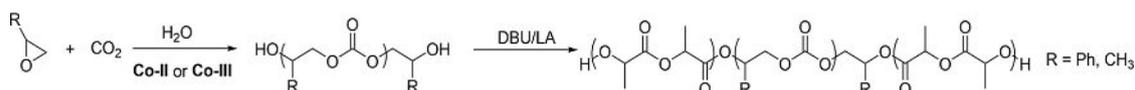
Figure 3. Representative Co, Cr, and Fe-based catalysts for CO₂/EP copolymerization. IO = indene oxide, BO = butene oxide, CPO = cyclopentane oxide, CHDO = cyclohexadiene oxide, DNO = 1,4-dihydronaphthalene oxide.

CHDO, whereas inferior catalytic activity was observed for 1,4-CHDO/CO₂ (36.6% selectivity of polymer formation with 57% conversion for 1,4-CHDO), although poly(1,3-cyclohexadiene carbonate) featured a slightly lower *T*_g (104–108 °C) than that of poly(1,4-cyclohexadiene carbonate) (*T*_g = 123 °C).

Similarly to the zinc-catalyzed synthesis of poly(lactide)-*b*-poly(carbonate)-*b*-poly(lactide) materials,^[60] Co^{III} catalysts have also found utility in the preparation of triblock CO₂-based polymeric structures (Scheme 8). In selected studies, both PO^[77] and SO^[78] were copolymerized with CO₂ to form ABA-type block copolymers with a degradable carbonate-containing



Scheme 7. Representative functional polycarbonate synthesis with cobalt-salen complexes and subsequent postpolymerization functionalization. AIBN = azobisisobutyronitrile.



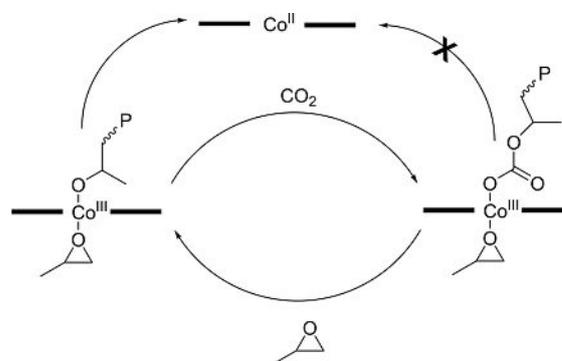
Scheme 8. One-pot synthesis of poly(carbonate-*b*-ester) from CO₂/EP/lactide terpolymerization. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, LA = lactide.

block. Building upon this concept, more structurally complex comonomers, such as allyl glycidyl ether^[79] or cyclic phosphates,^[80] were also successfully copolymerized with CO₂ in the polycarbonate block. These studies highlight a promising route to incorporate CO₂ into more functional materials. Moreover, the advantages imbued by simple, one-pot synthesis and increasing monomer diversity should make this method attractive to industry.

Although mononuclear Co^{III}-salen complexes have been widely used for CO₂/EP copolymerization, dinuclear systems also demonstrate high activity, yet operate through a mechanism distinct to that of single-site cobalt complexes. In one study, a dinuclear cobalt catalyst with a macrocyclic ancillary ligand yielded a copolymer from CO₂/CHO under mild conditions (0.1 MPa CO₂).^[81] Dissimilar to the alternating insertion of CO₂ and alkoxide in single-site systems, Williams and co-workers proposed a different catalytic cycle for dinuclear catalysts, in which ligated EP on one metal center attacked the neighboring cobalt that was ligated to the carbonate polymer chain end. Additionally, dinuclear Co^{III}-salen species have also been used for stereospecific CO₂/EP copolymerization to yield stereocomplexed polycarbonates^[82] or crystalline-gradient terpolymers.^[83]

As a consequence of their facile synthesis and ease of handling, porphyrin ligands have also been widely investigated in cobalt complexes for CO₂ copolymerization. Rieger and co-workers demonstrated the facile tuning of catalytic activity in single-site metal cobaltoporphyrin complexes, in which electron-withdrawing substituents on the periphery of the porphyrin led to only cyclic carbonate formation, whereas substitution with electron-donating groups (e.g., alkoxy group) on the catalyst yielded high-molecular-weight CO₂/PO copolymers ($M_n = 46.5 \text{ kg mol}^{-1}$, $D_M = 1.20$) at only 30 °C. Following studies involving single-site cobalt-porphyrin complexes, dinuclear complexes were synthesized and examined in CO₂ copolymerization.^[84] In contrast to dinuclear cobalt-salen species, unfortunately, no rate enhancement or increase in polymer selectivity formation was observed if bis-*para*-tethered dinuclear complexes were employed for CO₂/PO copolymerization; this sug-

gested that polymer growth occurred from just a single metal center. For catalysts featuring a bis-*ortho*-tethered porphyrin, polymerization was even more sluggish (which was likely to be due to steric constraints) and the cyclic carbonate was the predominant reaction product. As suggested by the results of UV/Vis and NMR spectroscopy experiments, it is likely that Co^{III}-alkoxide species can hydrolyze to form an inactive Co^{II} species.^[84,85] Nevertheless, polymer formation is still possible if CO₂ insertion occurs and forms the more stable cobalt-carbonate complex (Scheme 9), but this is not as pronounced as that in Co^{III}-salen complexes.^[35]



Scheme 9. The possible propagation route and deactivation pathways for Co^{III}-catalyzed CO₂/PO polymerization (P represents the growing polymer chain).^[86]

2.3.2. Chromium catalysts

Chromium-salen complexes generally perform markedly worse than their cobalt analogues, and thus, often lead to lower amounts of polymer formation due to diminished catalytic activities.^[70–73,87] Likewise, this observation is also apparent for thioligated chromium catalysts.^[88] It has been hypothesized that the inferior nature of chromium species is a consequence of the larger spherical volume of six-coordinate chromium (relative to Co), which promotes back-biting along the polymer chain.^[89] To overcome this issue, a chromium catalyst featuring

a less sterically hindered salen-type ligand (**Cr-I**) was investigated in the copolymerization of DNO and CO₂ (Figure 3).^[90] The planar geometry of the azaannulene ligand opened up the coordination sphere around the metal center and allowed polymerization to proceed to 63% conversion, with only 11% cyclic carbonate formation (TOF = 23 h⁻¹). However, a chromium complex bearing the classic salen ligand (*tert*-butyl substituents; **Cr-II**) resulted in poor conversion (32%) and larger amounts of cyclic carbonate byproduct (39%) with a modest TOF (11 h⁻¹).

Kozak et al. developed a series of Cr^{III}-aminobis(phenolato) (ABP) catalysts (**Cr-III**; Figure 3) for CO₂/CHO copolymerization to yield moderate-molecular-weight polycarbonate ($M_n = 13.1 \text{ kg mol}^{-1}$, $D_M = 1.40$) in just 24 h at a low catalyst loading (0.2 mol% Cr and 0.1 mol% cocatalyst).^[91] Both *trans* and *cis* geometries feature an accessible, vacant coordination site that allows an ionic species to coordinate with the metal center. Although the chloride-bridged dimer was isolated and confirmed by X-ray diffraction, it is likely that the monometallic five-coordinate complex that is ligated by ionic cocatalysts (e.g., azide, chloride) is involved in the catalytic cycle because the combination of the cocatalyst and Cr^{III} dimer affords a heterogeneous mixture in neat CHO. The **Cr-III** complex with cocatalysts is also active in the copolymerization of CO₂ with PO, with decent activity (TOF = 48 h⁻¹) at a mild temperature (25 °C).^[92]

In a follow-up study in 2014, two similar chromium complexes featuring either tri- or tetradentate ligands were synthesized by replacing the pyridyl arm of **Cr-III** with either a non-coordinating benzyl moiety (**Cr-IV**; Figure 3) or a tetrahydrofuran group of modest donicity (**Cr-V**; Figure 3).^[93] Overall, the tridentate complex resulted in lower molecular weight polymers ($M_n = 3.8 \text{ kg mol}^{-1}$, $D_M = 1.48$); this was likely to be due to catalyst instability, whereas the tetradentate ligand led to better results ($M_n = 6.4 \text{ kg mol}^{-1}$, $D_M = 1.42$). Notably, the **Cr-V** complex still performed worse than that of **Cr-III**; this is likely to be due to the weaker donating ability of the ethereal oxygen in the tethering group, and thus, highlights the critical importance of ligand tuning. A recent report from Kozak and co-workers described a new complex in which the tetrahydrofuran moiety in **Cr-IV** was replaced with the more strongly donating amino group (**Cr-VI**; Figure 3), which led to an improvement of CO₂/CHO copolymerization; so providing a controlled, high-molecular-weight polycarbonate ($M_n = 35 \text{ kg mol}^{-1}$, $D_M = 1.12$).^[94]

Chromium-porphyrin complexes have also been screened in the synthesis of CO₂-based polycarbonates.^[68f,95] Compared with main-group-containing Al-porphyrin counterparts,^[48b] the catalytic activity of chromium complexes is less dependent on CO₂ pressure, since CO₂ insertion is more favorable due to the high oxidation state (III) of chromium in the organometallic complex (3 MPa CO₂ for Al-porphyrin vs. 0.1 MPa for CO₂ Cr-porphyrin).^[68f] Furthermore, porphyrin-containing chromium catalysts generally display better kinetics (TOF = 150 h⁻¹) than those of structurally similar aluminum (TOF = 73 h⁻¹) or cobalt (TOF = 140 h⁻¹) analogues. This is probably due to the higher polarity, and thus reactivity, of the M–O bond in the chromium catalysts.^[68d]

2.3.3. Iron catalysts

Because iron is one of the most earth-abundant metals, there are considerable financial and environmental motivations to develop catalytic systems with comparable activity to that of robust transition-metal-based catalysts. Nozaki et al. reported the copolymerization of various EPs with CO₂, such as PO, CHO, and glycidyl phenyl ether (GPE), by using Fe–corrole catalysts (**Fe-I**; Figure 3).^[96] However, the incorporation of CO₂ was minimal (9%) at 60 °C (2 MPa CO₂, 1 h), affording primarily a polyether. Another Fe-based catalyst (**Fe-II**; Figure 3) displayed switchable polymerization behavior (selectivity for cyclic vs. linear topology).^[97] By increasing the ratio of cocatalyst (tetrabutylammonium halide, Bu₄NX; X = Cl, Br, or I), the cyclic polymer was isolated because the nucleophile rapidly replaced the M–OCO₂ adduct to inhibit propagation. In contrast, a low catalyst loading of both Fe complexes and corresponding halide (**Fe-II**/Bu₄NCl = 1:1, 0.5 mol%) promoted the formation of a linear structure, even if supercritical CO₂ (8 MPa) was employed as the reaction medium at 85 °C for 3 h.

2.3.4. Nickel catalysts

Ko and co-workers largely pioneered nickel-catalyzed CO₂/EP copolymerization.^[98] The imine-chelated complex (**Ni-I**; Figure 4), in particular, proved remarkably active (in the absence of a cocatalyst) in the ROCp of CO₂/CHO (turnover number (TON) = 2484, TOF = 38.7 h⁻¹, $M_n = 47.7 \text{ kg mol}^{-1}$, $D_M = 1.19$).^[98a] By modifying the bonding environment of the nitrogen atoms (imine to amine), the resulting nickel catalyst (**Ni-II**; Figure 4) displayed increased stability and efficiency (TON > 4000) under similar reaction conditions.^[98b] The same catalyst (**Ni-II**) also performed well if the alkene-containing monomer VCHO was used; thus showing the potential to create a functional polycarbonate. Following this study, the acetate bridge in **Ni-I** was substituted with a trifluoroacetate linker (**Ni-III**; Figure 4) and higher efficiency was observed (TON = 1728, TOF = 432 h⁻¹).^[98c] Other Ni-based catalysts modified with Schiff base ligands (**Ni-IV**; Figure 4)^[98d] or carbene ligands (**Ni-V**; Figure 4)^[98e] have also displayed some catalytic activity in CHO/CO₂ copolymerization (**Ni-IV**, TON = 840; and **Ni-V**, TON = 280), but these metrics are relatively low compared with those of salen-type Ni complexes (see **Ni-I**, **Ni-II**, and **Ni-III**).

2.3.5. Titanium, zirconium, and hafnium catalysts

Group IV transition-metal complexes (Ti, Zr, and Hf) have only recently been explored in CO₂-based copolymerization reactions, but they have proven to be remarkably effective thus far. The first instance of tetravalent Group IV catalyzed copolymerization of CO₂/PO was reported in 2011.^[99] N-Heterocyclic carbenes (NHCs) bear a lone electron pair that can serve as a ligand, in which the ease of dissociation from the metal center, in part, determines the reactivity of the metal center.^[100] Such dissociation can be overcome by the introduction of anionic tether moieties to the NHC.^[101] Titanium catalysts bearing a bis-anionic NHC pincer ligand (**Ti-I** or **Ti-II**; Figure 5) were in-

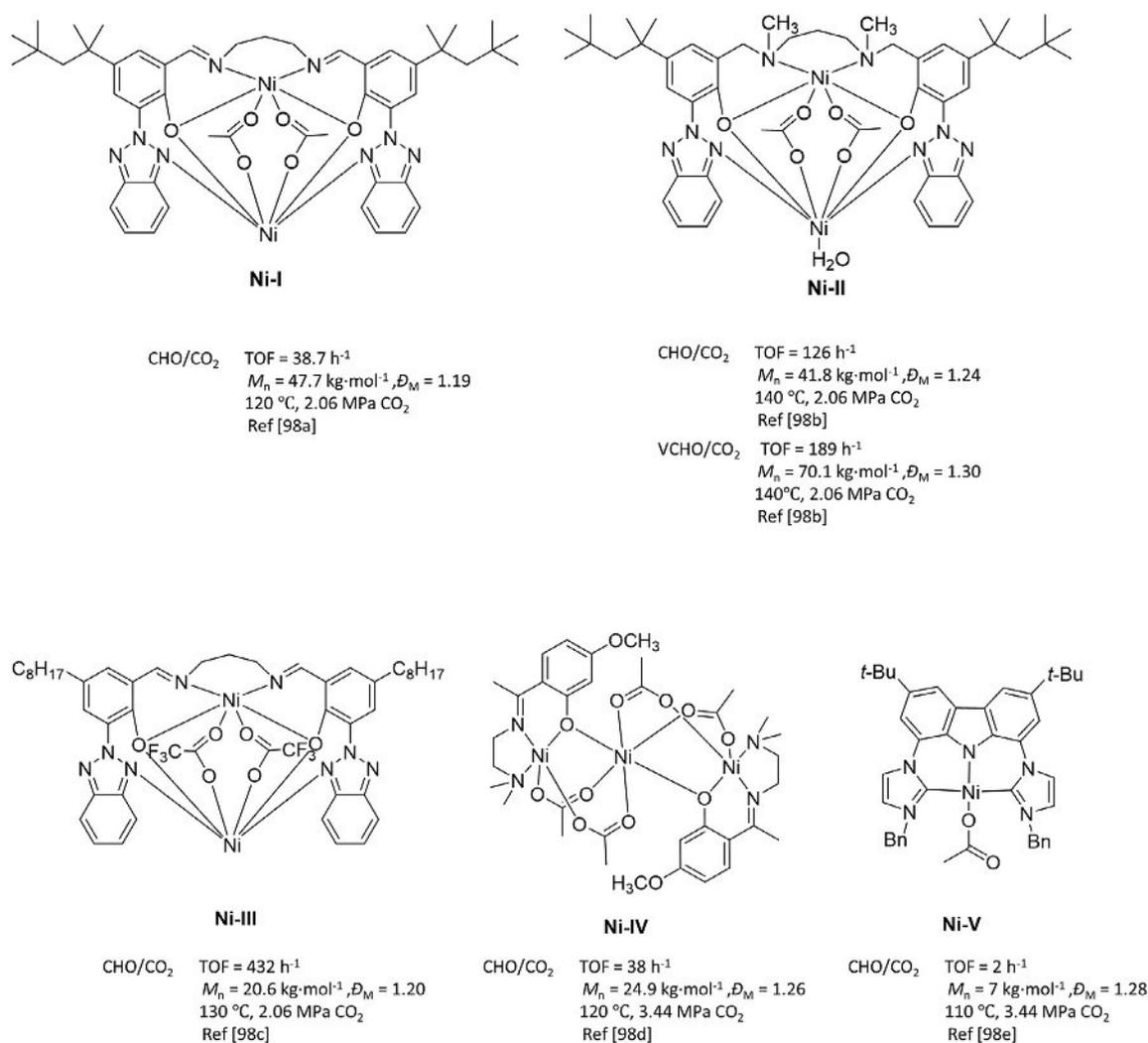


Figure 4. Representative Ni-based complexes for CO₂/EP copolymerization. VCHO = 4-vinyl-1,2-cyclohexane oxide, Bn = benzyl.

investigated in CO₂-based copolymerizations, and in the absence of an activating halide cocatalyst only the polyether was observed.^[102]

Le Roux^[102a] postulated that a six-coordinate titanium complex served as a crucial intermediate species in the mechanism of polycarbonate formation after undergoing anion exchange (Cl or *O**i*Pr from the cocatalyst) because the addition of neutral cocatalysts, such as 4-dimethylaminopyridine (DMAP), did not promote polycarbonate formation (Scheme 10).

The catalytic system was further improved by substituting the halide cocatalyst for larger anions, including OBn, OAc, N₃, and tri-*tert*-butyl silicate oxide (OSi(*O**t*Bu)₃); Scheme 11).^[103] In the presence of relatively bulky organic salts, such as bis(triphenylphosphine)iminium chloride or azide (PPNCl or PPNN₃, respectively), the copolymerization of CHO and CO₂ was active under extremely low CO₂ pressure (0.05 MPa) to afford a polycarbonate (M_n = 7.7 kg mol⁻¹, D_M = 1.54) within 15 min. However, the overall conversion remained low (< 35%), even after a prolonged reaction time.

The scope of salen-based catalysts was expanded by introducing titanium as the active metal center (**Ti-III**; Figure 5).^[104]

However, if applied in CO₂/CHO copolymerization, only modest-molecular-weight polycarbonate was isolated (M_n up to 6.3 kg mol⁻¹) at 4 MPa CO₂ and 60 °C after 20 h. Moreover, the coordinatively saturated Ti-salen complex (**Ti-IV**; Figure 5) only afforded cyclic carbonate, even in the presence of the large PPNCl cocatalyst. This confirmed the conclusion of Le Roux and co-workers, who also implicated this nucleophilic exchange from cocatalysts as a crucial step before chain propagation.^[102a] They also observed that employing a dianionic ligand (**Ti-V**; Figure 5) increased the catalytic activity (TOF = 577 h⁻¹ for 1 h), relative to that of a catalyst bearing a trianionic ligand (**Ti-III**; TOF = 41 h⁻¹ for 8 h).^[105]

A heterodinuclear Ti/Zn catalyst was recently synthesized and screened in CO₂/EP copolymerizations; however, only low-molecular-weight polycarbonates were produced (M_n = 2 kg mol⁻¹, D_M = 1.35).^[106] It is possible that this poor activity is due to the minimally active polymer chain exchange between the Ti and Zn centers, similar to the dinuclear mechanism proposed for dinuclear zinc catalysts.^[106] Nevertheless, other complexes that feature half-salen ligands paired with Ti, Ti–Ti, or Zr–Zr metal centers (**Ti-VI**, **Ti-VII**, or **Zr-I**; Figure 5) have exhib-

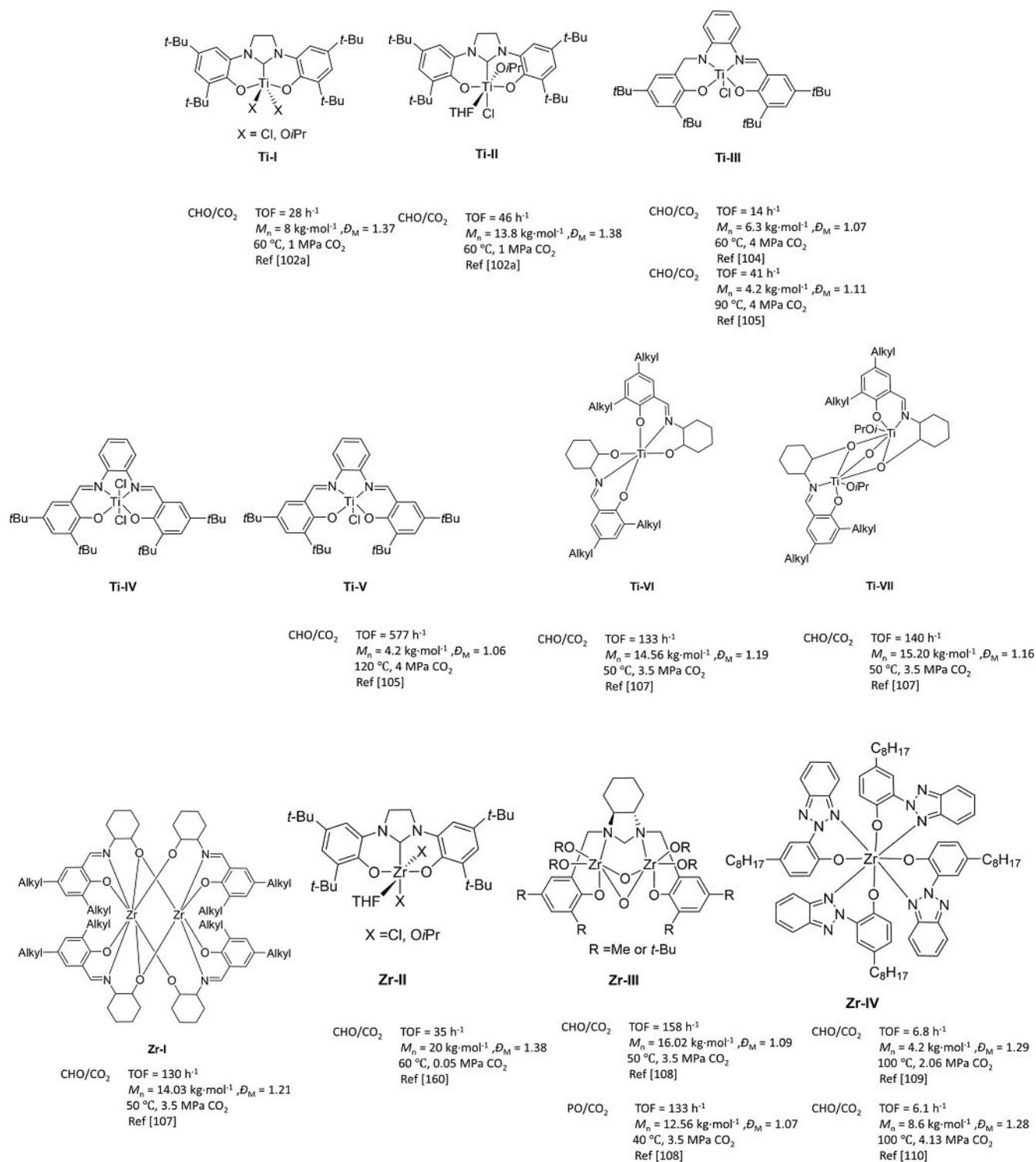
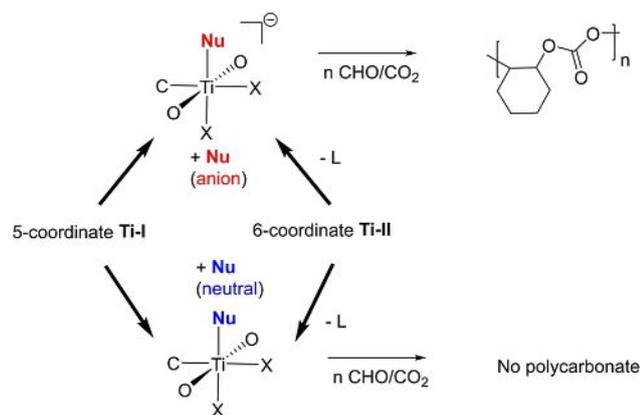


Figure 5. Representative Ti- and Zr-based catalysts for CO₂/EP copolymerization.

ited great activity and control (e.g., yielding poly(CHC) with $M_n = 15.2 \text{ kg mol}^{-1}$ and 84% carbonate content) for a wide substrate scope (including LA, ϵ -CL, CHO, PO, and SO).^[107]

Le Roux and co-workers recently reported Zr–NHC complexes (**Zr-II**; Figure 5) for the synthesis of poly(CHC).^[108] Unlike the sluggish performance of the Ti–NHC/DMAP catalytic

system, the Zr–NHC/DMAP mixture was more active, potentially due to the larger coordination sphere of zirconium, within which both anion and neutral coligands could be accommodated to form a stable six-coordinate species. A Zr–salen catalyst (**Zr-III**; Figure 5) was also active in different polymerization pathways, including the ROP of LA, ϵ -CL, and EP, or the ROCp



Scheme 10. The proposed mechanism of Ti-catalyzed CO₂/CHO copolymerization.

of CO₂/EP, through which moderate-molecular-weight polycarbonates ($M_n = 16.02 \text{ kg mol}^{-1}$, $D_M = 1.09$) were obtained under relatively mild reaction conditions (50 °C, 3.5 MPa CO₂).^[109]

The benzotriazole phenolate (bis-BZH) chelating species was used to form various Group IV (Ti, Zr, Hf) complexes possessing ethereal bridges.^[110] The catalysts were assessed for activity in both ROP of LA and ROCp of CO₂/CHO, and Zr–bis-BZH complexes displayed decent performance (TOF = 6.8 h⁻¹) for CO₂-based polycarbonate synthesis compared with that of Hf analogues (TOF = 3 h⁻¹). Tetrabenzotriazole phenolate (BZH) Group IV complexes were also investigated in CO₂/CHO copolymerization; the Zr catalyst (**Zr-IV**) again outperformed that of Group IV analogues to afford a controlled ($D_M = 1.28$) polycarbonate with moderate molecular weight (**Zr-IV** $M_n = 8.6 \text{ kg mol}^{-1}$, 93% carbonate content vs. Hf–BZH $M_n = 4 \text{ kg mol}^{-1}$ 76% carbonate content vs. Ti–BZH, $M_n = 0 \text{ kg mol}^{-1}$). The order of reactivity for the complexes follows $Zr \approx Hf > Ti$; this can possibly be explained by the larger atomic radii of Zr and Hf, which may open up the coordination sphere relative to that of the smaller Ti metal center.^[111]

2.3.6. Lanthanide catalysts

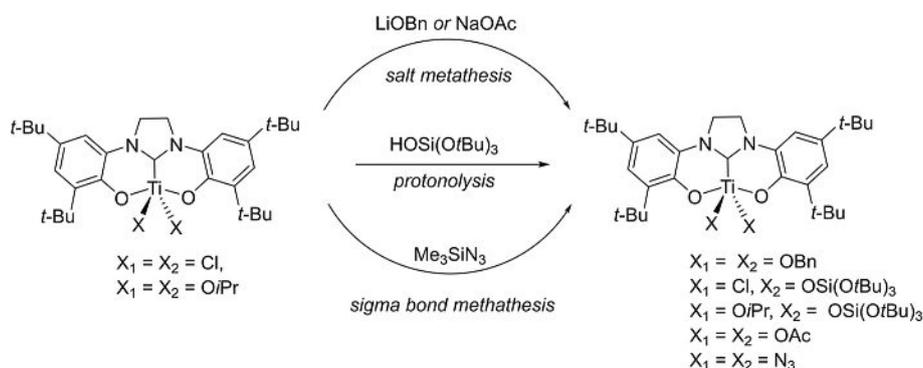
Compared with the large number of investigations involving transition-metal complexes, lanthanide catalysts have been

largely ignored. Nevertheless, some lanthanide complexes can possess superior air stability, relative to that of transition-metal species, and this should provide a great advantage in CO₂ copolymerization processes. Dysprosium Schiff base complexes (**Dy-I**; Figure 6) were observed to be robust catalysts for CO₂/CHO copolymerization (TON = 1620), yielding moderate-molecular-weight polycarbonate (up to $M_n = 22 \text{ kg mol}^{-1}$) under optimized conditions (3.44 MPa CO₂, 100 °C). However, in this case, the dispersities of the polymers ($D_M = 2.02\text{--}5.69$) were quite high, which indicated significant termination or chain-transfer processes.^[112]

Inspired by the salen dinuclear complexes from the group of Williams,^[55] mixed heterometallic structures, featuring a lanthanide (Ln) and main-group metal (Zn) connected through a macrocyclic tri(salen) ligand (**La-I**; Figure 6), were found to possess the unique property of rapid inter-/intramolecular acetate ligand exchange.^[113] After careful screening of several lanthanide metals, the Ce/Zn complex exhibited superior catalytic performance (TOF = 370 h⁻¹). Telomerization of CO₂/CHO copolymerization was successful by adjusting the amount of acetate counterion, resulting in a polymer with “controllable” molecular weight. The heterometallic (Nd/Zn) complex (**Nd-I**; Figure 6) afforded extremely high molecular weight polycarbonates ($M_n = 295 \text{ kg mol}^{-1}$, $D_M = 1.65$) in just 12 h under mild conditions (25 °C, 0.7 MPa CO₂).^[114] Moreover, the polymer molecular weight was found to be extremely sensitive to the reaction temperature, for example, $M_n \approx 50 \text{ kg mol}^{-1}$ at 70 °C, and this inverse relationship continued at higher temperatures. It was surmised that, at elevated temperatures, the catalyst could also degrade the polymer backbone because there was an equilibrium between propagation and depolymerization, which favored the latter as the temperature increased. A ytterbium–salen complex (**Yb-I**; Figure 6) paired with halide cocatalysts was found to be quite active for CO₂/CHO copolymerization; optimized conditions gave a polycarbonate with $M_n = 11.4 \text{ kg mol}^{-1}$ at 2 MPa CO₂ and 70 °C.^[115] Other lanthanides (Sc, Y) were also examined in the same organometallic framework, but they displayed diminished activity.

2.3.7. Copper catalysts

Although Cu organometallic complexes have been widely studied in both small-molecule and polymerization catalysis



Scheme 11. Synthetic route to Ti-based catalysts with various anions.

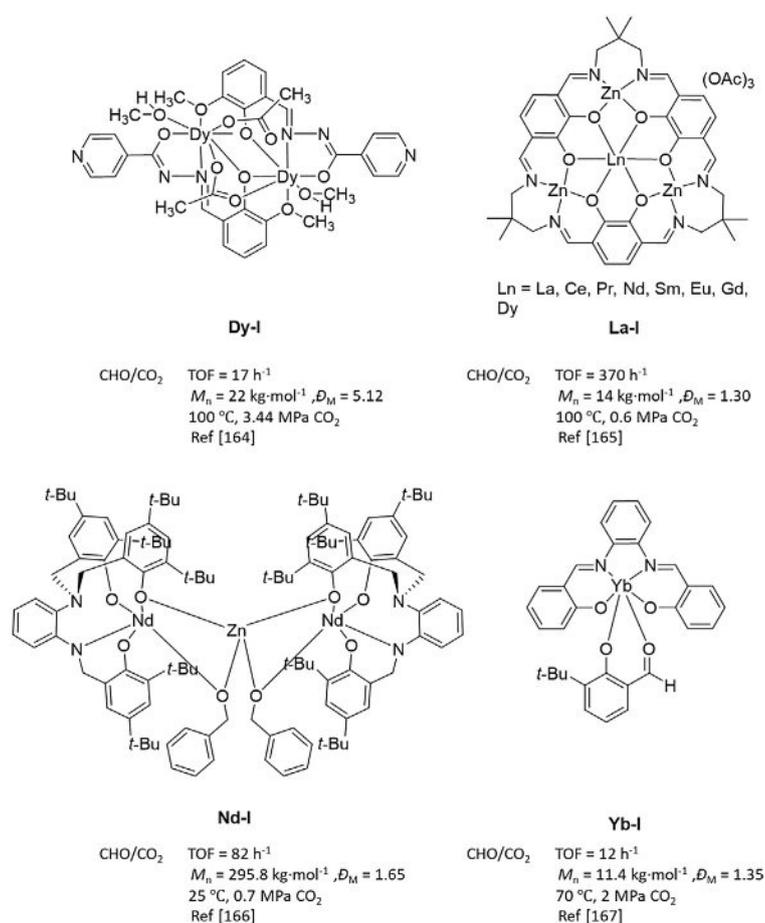


Figure 6. Representative lanthanide-based catalysts for CO_2/EP copolymerization.

(for example, controlled radical polymerization), they are relatively unexplored as CO_2/EP copolymerization catalysts. In fact, there is only one such study, as reported by Ko and co-workers (**Cu-I**; Figure 7), which demonstrated unremarkable activity (TOF = $11.5\text{--}18.8 \text{ h}^{-1}$).^[116]

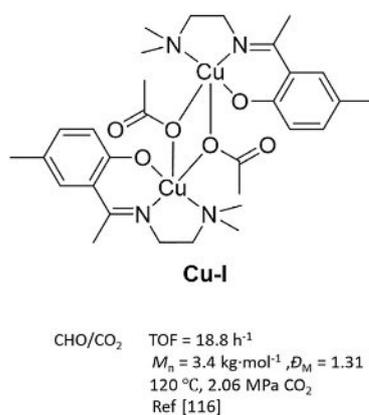


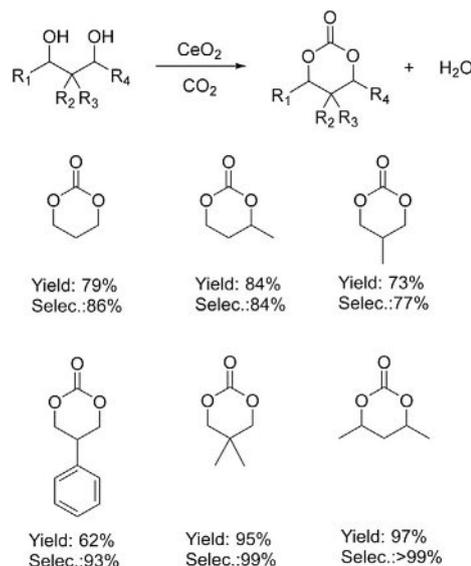
Figure 7. Representative Cu-based catalyst for CO_2/EP copolymerization.

2.4. Novel cyclic carbonate monomers derived from CO_2

Although direct incorporation of CO_2 into macromolecular architectures through copolymerization strategies represents a convenient path to more sustainable polymers, an alternative method for incorporating CO_2 into polymers is to use it as a reagent in the synthesis of cyclic carbonate monomers from naturally derived alcohols. Initially, 5CCs were investigated as precursors to polycarbonates; however, ring opening is unfavorable without the elimination of CO_2 . As such, attention has turned to six-membered cyclic carbonates (6CC) that can undergo controlled ROP by using either metal catalysts or organocatalysts.^[117] This strategy does not simply increase the valorization of CO_2 , but broadens the functional group scope of the resulting polycarbonates, and thus, potentially leads to new materials with interesting thermal and/or mechanical properties.

One of the most common established routes to 6CCs is cerium(IV) oxide (CeO_2)-catalyzed coupling of CO_2 and various diols (Scheme 12).^[10a,b]

After the groups of Baba^[29,118] and Darensbourg^[119] pioneered the trimethylene carbonate (TMC) synthesis by using oxetane and CO_2 , the group of Kleij developed an aluminum-catalyzed coupling reaction between a heterocyclic oxide and CO_2 (**Al-VI**; Figure 8).^[22b] The reaction method is particularly effective for the synthesis of functional 5CCs and TMC. However, the analogous coupling reaction for producing a 6CC from CO_2 and 3,3-dimethyloxetane is not very selective (54%) and is low yielding for 6CC product formation (26% yield), presumably due to steric inhibition from the adjacent methyl groups.



Scheme 12. a) Synthesis of 6CCs from the corresponding diol substrates. b) The library of 6CCs synthesized from CO_2 and various diols.^[10a] Selec. = selectivity.

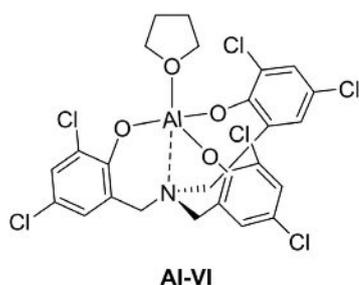
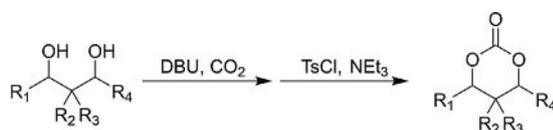


Figure 8. Representative Al catalyst for 6CC synthesis.

3. Organocatalysts

In an effort to address environmental concerns, including impacts on health, high cost, and the inherent oxygen and moisture lability of metal-based catalysts, metal-free methods for CO₂-based polycarbonate synthesis have been developed contemporaneously. Although organocatalysts present essential green chemistry benefits, they have traditionally lagged behind their metal counterparts, in terms of stability and activity. Nevertheless, the development of robust organocatalysts for polycarbonate synthesis remains a priority. Organocatalysts have been successfully employed to activate CO₂ for the synthesis of cyclic carbonate monomers, such as 5CCs,^[120] but these monomers are not particularly suitable for ring-opening protocols. Furthermore, efforts aimed at incorporating CO₂ into copolymeric structures, while suppressing the formation of 5CC products, have traditionally yielded predominantly cyclic byproducts instead (Scheme 3). As previously mentioned, the synthesis of 6CCs (from CO₂ and oxetane substrates, as mentioned in Section 2.4) is an alternative approach to the use of CO₂ in polycarbonate synthesis. However, the dramatic difference in acidity between EP and oxetane has made organocatalyzed approaches more challenging.^[23c,d] Nevertheless, Buchard and co-workers reported the first instance of 6CCs synthesized from the corresponding diols and CO₂ at very low pressure (0.1 MPa CO₂) (Scheme 13) with DBU in 2015.^[121] This system was recently applied to give seven- and eight-membered cyclic carbonates.^[10c]



Scheme 13. Organocatalytic synthesis of 6CCs from CO₂ and diol substrates.

The DBU-catalyzed mechanism was hypothesized to begin with single CO₂ insertion into one alcohol to form the carbonate after deprotonation. Following this, intramolecular attack from the second alcohol completes the cyclization process to form the corresponding 6CC. Interestingly, the cyclization step is ineffective without the addition of tosyl chloride to form a good leaving group, and DFT studies have corroborated the high energy barrier in the cyclization step.^[121] After the suc-

cessful synthesis of 6CCs, numerous other green CO₂-based copolymers from renewable feed stocks were explored. Other compounds, such as mannopyranose,^[122] thymidine,^[123] 2-deoxy-D-ribose,^[124] and glycoside^[125] derivatives, were coupled directly with CO₂ by using organobases to afford cyclic monomers that were polymerized to form novel polycarbonates with promising biomaterial applications.

In 2016, the first metal-free CO₂-based polycarbonate synthesis was achieved by activating an EP with a strong Lewis acid (triethyl borane) in the presence of organic cation species, such as ammonium halides.^[126] The Lewis acid was crucial to lowering the activation barrier of EP ring opening to compete with the back-biting of carbonate species. Both PO and CHO were copolymerized with CO₂, to obtain polycarbonates ($M_n = 43 \text{ kg mol}^{-1}$, $D_M = 1.10$) with a high carbonate content (99%). More recently, triarylboranes were reported in a metal-free protocol, through which the selectivity between cyclic carbonate/polycarbonate reaction products could be controlled, according to the relative Lewis acidity of the borane species.^[127] An organocatalyzed approach, featuring a binary system composed of 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene and tetrabutylammonium iodide, was also effective for CO₂ copolymerization with trimethylene oxide (TMO), which was a traditionally challenging monomer.^[22a] An oligocarbonate ($M_n = 2 \text{ kg mol}^{-1}$) was obtained after 24 h under 10 MPa CO₂ and 130 °C; this demonstrates one of the only instances of organocatalyzed CO₂/TMO copolymerization.

4. Summary and Outlook

The copolymerization of CO₂/EP offers an efficient approach to sustainable polycarbonates and has accordingly attracted a great deal of attention in recent decades. Industrial-scale processes have been applied for these copolymerizations, as a result of better catalysts, enabling the process to become more economically viable. In turn, this could facilitate the production of a diverse array of polycarbonates with tunable thermomechanical properties under increasingly mild conditions. Nevertheless, the current portfolio of nondegradable plastics remains comparatively inexpensive, but environmental concerns associated with their irresponsible use are drastically increasing. Therefore, it is imperative to continue the development of more sustainable polymers (those from renewable sources and/or possessing biodegradability) and lower the cost of such materials. As it stands, renewable plastics from bio-based monomers and CO₂ are poised to compete with petroleum-derived products. For example, poly(limonene carbonate)^[128] and 2,5-furandicarboxylic acid (FDCA; a monomer from biomass waste/CO₂)^[31] have led to various methodologies of CO₂ utilization and shown great promise as robust plastics for the future.

The issue of replacing petroleum commodity plastics remains a great challenge for the chemistry community, but producing polycarbonates from CO₂, and sustainable polymers, in general, are still nascent and further improvements will certainly be gained from more efficient catalysts. Although few studies on the preparation of CO₂-based polycarbonate address the

application of heterogeneous catalysts, homogeneous catalytic approaches with organo-(metallic) catalysts to convert and valorize CO₂ as a comonomer continue to thrive. Organocatalyzed methods could provide a breakthrough and further drive the production price down, while offering an even greener approach. Although both metal- and organic-based catalysts present several respective advantages and viable options for CO₂-based polymer synthesis, overcoming sensitivity to contamination (e.g., oxygen, moisture), and the use of air as a CO₂ resource, could allow CO₂-based fabrication to be carried out on a global industrial scale.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide · homogeneous catalysis · polycarbonates · ring-opening polymerization · synthetic methods

- [1] A. L. Andradý, M. A. Neal, *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 1977–1984.
- [2] B. C. Gibb, *Nat. Chem.* **2019**, *11*, 394–395.
- [3] T. J. Crowley, R. A. Berner, *Science* **2001**, *292*, 870–872.
- [4] T. P. Haider, C. Völker, J. Kramm, K. Landfester, F. R. Wurm, *Angew. Chem. Int. Ed.* **2019**, *58*, 50–62; *Angew. Chem.* **2019**, *131*, 50–63.
- [5] a) M. Taherimehr, P. P. Pescarmona, *J. Appl. Polym. Sci.* **2014**, *131*, 41141; b) G. A. Luinstra, E. Borchardt in *Synthetic Biodegradable Polymers* (Eds.: B. Rieger, A. Künkel, G. W. Coates, R. Reichardt, E. Dinjus, T. A. Zevaco), Springer, Berlin, **2012**, pp. 29–48.
- [6] T. Janes, Y. Yang, D. Song, *Chem. Commun.* **2017**, *53*, 11390–11398.
- [7] a) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933; b) J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, *Nat. Commun.* **2017**, *8*, 15174.
- [8] a) S. Ghosh, A. Barron, *C. J. Carbon Res.* **2016**, *2*, 2010005; b) X. Yong, J. S. Tse, C. S. Yoo, *J. Phys. Chem. C* **2017**, *121*, 115–122.
- [9] V. Iota, C. S. Yoo, H. Cynn, *Science* **1999**, *283*, 1510.
- [10] a) M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4*, 1893–1896; b) M. Tamura, H. Wakasugi, K.-i. Shimizu, A. Satsuma, *Chem. Eur. J.* **2011**, *17*, 11428–11431; c) T. M. McGuire, E. M. López-Vidal, G. L. Gregory, A. Buchard, *J. CO₂ Util.* **2018**, *27*, 283–288.
- [11] M. Tamura, K. Ito, M. Honda, Y. Nakagawa, H. Sugimoto, K. Tomishige, *Sci. Rep.* **2016**, *6*, 24038.
- [12] a) Z. Chen, N. Hadjichristidis, X. Feng, Y. Gnanou, *Macromolecules* **2017**, *50*, 2320–2328; b) Z. Chen, N. Hadjichristidis, X. Feng, Y. Gnanou, *Polym. Chem.* **2016**, *7*, 4944–4952.
- [13] E. J. Beckman, *Science* **1999**, *283*, 946.
- [14] W. Ando, N. Choi, N. Tokitoh in *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 173–240.
- [15] I. Palard, M. Schappacher, B. Belloncle, A. Soum, S. M. Guillaume, *Chem. Eur. J.* **2007**, *13*, 1511–1521.
- [16] I. Erden in *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 97–144.
- [17] R. J. Linderman in *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 721–753.
- [18] W. H. Pearson, B. W. Lian, S. C. Bergmeier in *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 1–60.
- [19] G. D. Jones, A. Langsjoen, S. M. M. C. Neumann, J. Zomlefer, *J. Org. Chem.* **1944**, *09*, 125–147.
- [20] a) O. Ihata, Y. Kayaki, T. Ikariya, *Macromolecules* **2005**, *38*, 6429–6434; b) K. Soga, S. Hosoda, S. Ikeda, *Macromol. Chem. Phys.* **1974**, *175*, 3309–3313; c) W. Kuran, A. Rokicki, D. Romanowska, *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 2003–2011.
- [21] a) Y. Tanaka, *J. Macromol. Sci. Part A* **1967**, *1*, 1059–1068; b) G. Trott, P. K. Saini, C. K. Williams, *Philos. Trans. R. Soc. London Ser. A* **2016**, *374*, 20150085.
- [22] a) M. Alves, B. Grignard, A. Boyaval, R. Méreau, J. De Winter, P. Gerbaux, C. Detrembleur, T. Tassaing, C. Jérôme, *ChemSusChem* **2017**, *10*, 1128–1138; b) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, *135*, 1228–1231.
- [23] a) H. K. Eigenmann, D. M. Golden, S. W. Benson, *J. Phys. Chem.* **1973**, *77*, 1687–1691; b) B. Ringnér, S. Sunner, H. Watanabe, *Acta Chem. Scand.* **1971**, *25*, 141–146; c) S. Aoshima, T. Fujisawa, E. Kobayashi, *J. Polym. Sci. Part A* **1994**, *32*, 1719–1728; d) J. A. Burkhard, G. Wuitschik, M. Rogers-Evans, K. Müller, E. M. Carreira, *Angew. Chem. Int. Ed.* **2010**, *49*, 9052–9067; *Angew. Chem.* **2010**, *122*, 9236–9251; e) J. A. Bull, R. A. Croft, O. A. Davis, R. Doran, K. F. Morgan, *Chem. Rev.* **2016**, *116*, 12150–12233.
- [24] W. M. H. Sachtler, C. Backx, R. A. Van Santen, *Catal. Rev.* **1981**, *23*, 127–149.
- [25] J. Marco-Contelles, M. T. Molina, S. Anjum, *Chem. Rev.* **2004**, *104*, 2857–2900.
- [26] Y. Wang, D. J. Darensbourg, *Coord. Chem. Rev.* **2018**, *372*, 85–100.
- [27] C. M. Kozak, K. Ambrose, T. S. Anderson, *Coord. Chem. Rev.* **2018**, *376*, 565–587.
- [28] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Part B* **1969**, *7*, 287–292.
- [29] A. Baba, H. Meishou, H. Matsuda, *Macromol. Rapid Commun.* **1984**, *5*, 665–668.
- [30] C. Masters, *Homogeneous Transition Metal Catalysis: A Gentle Art*, Chapman & Hall, London, **1981**.
- [31] a) G. R. Dick, A. D. Frankhouser, A. Banerjee, M. W. Kanan, *Green Chem.* **2017**, *19*, 2966–2972; b) A. Banerjee, G. R. Dick, T. Yoshino, M. W. Kanan, *Nature* **2016**, *531*, 215.
- [32] W.-M. Ren, T.-J. Yue, X. Zhang, G.-G. Gu, Y. Liu, X.-B. Lu, *Macromolecules* **2017**, *50*, 7062–7069.
- [33] M. H. Chisholm, D. Navarro-Llobet, Z. Zhou, *Macromolecules* **2002**, *35*, 6494–6504.
- [34] a) D. J. Darensbourg, S.-H. Wei, *Macromolecules* **2012**, *45*, 5916–5922; b) D. J. Darensbourg, S.-H. Wei, A. D. Yeung, W. C. Ellis, *Macromolecules* **2013**, *46*, 5850–5855; c) D. J. Darensbourg, A. D. Yeung, S.-H. Wei, *Green Chem.* **2013**, *15*, 1578–1583.
- [35] D. J. Darensbourg, S. J. Wilson, *Green Chem.* **2012**, *14*, 2665–2671.
- [36] a) K. Tezuka, K. Komatsu, O. Haba, *Polym. J.* **2013**, *45*, 1183; b) W. Guerin, A. K. Diallo, E. Kirilov, M. Helou, M. Slawinski, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Macromolecules* **2014**, *47*, 4230–4235; c) S. E. Felder, M. J. Redding, A. Noel, S. M. Grayson, K. L. Wooley, *Macromolecules* **2018**, *51*, 1787–1797.
- [37] a) L. Vogdanis, B. Martens, H. Uchtmann, F. Hensel, W. Heitz, *Macromol. Chem. Phys.* **1990**, *191*, 465–472; b) J.-C. Lee, M. H. Litt, *Macromolecules* **2000**, *33*, 1618–1627.
- [38] a) D. J. Darensbourg, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342; b) M. W. Lehenmeier, S. Kissling, P. T. Altenbuchner, C. Bruckmeier, P. Deglmann, A.-K. Brym, B. Rieger, *Angew. Chem. Int. Ed.* **2013**, *52*, 9821–9826; *Angew. Chem.* **2013**, *125*, 10004–10009; c) F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen, C. K. Williams, *J. Am. Chem. Soc.* **2011**, *133*, 17395–17405.
- [39] M. R. Kember, C. K. Williams, *J. Am. Chem. Soc.* **2012**, *134*, 15676–15679.
- [40] Y. Xiao, Z. Wang, K. Ding, *Macromolecules* **2006**, *39*, 128–137.
- [41] a) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462–1484; b) S. J. Na, S. S. A. Cyriac, B. E. Kim, J. Yoo, Y. K. Kang, S. J. Han, C. Lee, B. Y. Lee, *Inorg. Chem.* **2009**, *48*, 10455–10465; c) X.-B. Lu, L. Shi, Y.-M. Wang, R. Zhang, Y.-J. Zhang, X.-J. Peng, Z.-C. Zhang, B. Li, *J. Am. Chem. Soc.* **2006**, *128*, 1664–1674.
- [42] S. Ghosh, D. Pahovnik, U. Kragl, E. Mejía, *Macromolecules* **2018**, *51*, 846–852.
- [43] H. Koinuma, H. Hirai, *Macromol. Chem. Phys.* **1977**, *178*, 1283–1294.
- [44] T. Aida, M. Ishikawa, S. Inoue, *Macromolecules* **1986**, *19*, 8–13.
- [45] H. Sugimoto, H. Ohtsuka, S. Inoue, *J. Polym. Sci. Part A* **2005**, *43*, 4172–4186.
- [46] D. J. Darensbourg, D. R. Billodeaux, *Inorg. Chem.* **2005**, *44*, 1433–1442.

- [47] W. Kuran, T. Listos, M. Abramczyk, A. Dawidek, *J. Macromol. Sci. Part A* **1998**, *35*, 427–437.
- [48] a) W. Wu, X. Sheng, Y. Qin, L. Qiao, Y. Miao, X. Wang, F. Wang, *J. Polym. Sci. Part A* **2014**, *52*, 2346–2355; b) X. Sheng, W. Wu, Y. Qin, X. Wang, F. Wang, *Polym. Chem.* **2015**, *6*, 4719–4724.
- [49] C. Chatterjee, M. H. Chisholm, *Inorg. Chem.* **2011**, *50*, 4481–4492.
- [50] K. Nishioka, H. Goto, H. Sugimoto, *Macromolecules* **2012**, *45*, 8172–8192.
- [51] D. Zhang, H. Zhang, N. Hadjichristidis, Y. Gnanou, X. Feng, *Macromolecules* **2016**, *49*, 2484–2492.
- [52] N. Ikpo, S. M. Barbon, M. W. Drover, L. N. Dawe, F. M. Kerton, *Organometallics* **2012**, *31*, 8145–8158.
- [53] C. W. Bock, A. K. Katz, G. D. Markham, J. P. Glusker, *J. Am. Chem. Soc.* **1999**, *121*, 7360–7372.
- [54] a) P. K. Saini, C. Romain, C. K. Williams, *Chem. Commun.* **2014**, *50*, 4164–4167; b) N. Yi, J. Unruangsri, J. Shaw, C. K. Williams, *Faraday Discuss.* **2015**, *183*, 67–82; c) M. R. Kember, P. D. Knight, P. T. R. Reung, C. K. Williams, *Angew. Chem. Int. Ed.* **2009**, *48*, 931–933; *Angew. Chem.* **2009**, *121*, 949–951; d) A. M. Chapman, C. Keyworth, M. R. Kember, A. J. J. Lennox, C. K. Williams, *ACS Catal.* **2015**, *5*, 1581–1588; e) A. Thevenon, J. A. Garden, A. J. P. White, C. K. Williams, *Inorg. Chem.* **2015**, *54*, 11906–11915.
- [55] J. A. Garden, P. K. Saini, C. K. Williams, *J. Am. Chem. Soc.* **2015**, *137*, 15078–15081.
- [56] a) N. M. Rajendran, A. Haleel, N. D. Reddy, *Organometallics* **2014**, *33*, 217–224; b) M. Kröger, C. Folli, O. Walter, M. Döring, *Adv. Synth. Catal.* **2006**, *348*, 1908–1918.
- [57] a) S. Kissling, P. T. Altenbuchner, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, U. B. Seemann, B. Rieger, *Chem. Eur. J.* **2015**, *21*, 8148–8157; b) M. Reiter, S. Vagin, A. Kronast, C. Jandl, B. Rieger, *Chem. Sci.* **2017**, *8*, 1876–1882.
- [58] J. Martínez, J. A. Castro-Osma, A. Lara-Sánchez, A. Otero, J. Fernández-Baeza, J. Tejada, L. F. Sánchez-Barba, A. Rodríguez-Diéguez, *Polym. Chem.* **2016**, *7*, 6475–6484.
- [59] G. P. Wu, S. D. Jiang, X. B. Lu, W. M. Ren, S. K. Yan, *Chin. J. Polym. Sci.* **2012**, *30*, 487–492.
- [60] M. R. Kember, J. Copley, A. Buchard, C. K. Williams, *Polym. Chem.* **2012**, *3*, 1196–1201.
- [61] S. Paul, C. Romain, J. Shaw, C. K. Williams, *Macromolecules* **2015**, *48*, 6047–6056.
- [62] M. Reiter, A. Kronast, S. Kissling, B. Rieger, *ACS Macro Lett.* **2016**, *5*, 419–423.
- [63] S. Kernbichl, M. Reiter, F. Adams, S. Vagin, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 6787–6790.
- [64] a) P. K. Saini, G. Fiorani, R. T. Mathers, C. K. Williams, *Chem. Eur. J.* **2017**, *23*, 4260–4265; b) C. Romain, C. K. Williams, *Angew. Chem. Int. Ed.* **2014**, *53*, 1607–1610; *Angew. Chem.* **2014**, *126*, 1633–1636; c) C. Romain, Y. Zhu, P. Dingwall, S. Paul, H. S. Rzepa, A. Buchard, C. K. Williams, *J. Am. Chem. Soc.* **2016**, *138*, 4120–4131.
- [65] F. P. Pruchnik, S. A. Duraj, *Organometallic Chemistry of the Transition Elements*, Springer, Boston, MA, **1990**.
- [66] Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2016**, *55*, 5352–5353; *Angew. Chem.* **2016**, *128*, 5438–5439.
- [67] a) W.-M. Ren, Z.-W. Liu, Y.-Q. Wen, R. Zhang, X.-B. Lu, *J. Am. Chem. Soc.* **2009**, *131*, 11509–11518; b) E. K. Noh, S. J. Na, S. S. S.-W. Kim, B. Y. Lee, *J. Am. Chem. Soc.* **2007**, *129*, 8082–8083; c) C. T. Cohen, T. Chu, G. W. Coates, *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878; d) O. M. Chukanova, G. P. J. K. Belov, *Kinet. Catal.* **2016**, *57*, 821–825; e) B. Liu, X. Zhao, H. Guo, Y. Gao, M. Yang, X. Wang, *Polymer* **2009**, *50*, 5071–5075; f) H. Li, Y. Niu, *Polym. J.* **2011**, *43*, 121.
- [68] a) H. Sugimoto, S. Inoue, *Pure Appl. Chem.* **2006**, *78*, 1823–1834; b) X. Jiang, F. Gou, H. Jing, *J. Catal.* **2014**, *313*, 159–167; c) H. Sugimoto, K. Kuroda, *Macromolecules* **2008**, *41*, 312–317; d) C. Chatterjee, M. H. Chisholm, A. El-Khaldy, R. D. McIntosh, J. T. Miller, T. Wu, *Inorg. Chem.* **2013**, *52*, 4547–4553; e) C. E. Anderson, S. I. Vagin, W. Xia, H. Jin, B. Rieger, *Macromolecules* **2012**, *45*, 6840–6849; f) C. Chatterjee, M. H. Chisholm, *Inorg. Chem.* **2012**, *51*, 12041–12052.
- [69] G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, T.-Q. Xu, D. J. Darensbourg, *J. Am. Chem. Soc.* **2011**, *133*, 15191–15199.
- [70] D. J. Darensbourg, S. J. Wilson, *Macromolecules* **2013**, *46*, 5929–5934.
- [71] D. J. Darensbourg, W.-C. Chung, *Macromolecules* **2014**, *47*, 4943–4948.
- [72] D. J. Darensbourg, W.-C. Chung, S. J. Wilson, *ACS Catal.* **2013**, *3*, 3050–3057.
- [73] D. J. Darensbourg, W.-C. Chung, C. J. Arp, F.-T. Tsai, S. J. Kyran, *Macromolecules* **2014**, *47*, 7347–7353.
- [74] P. Derboven, D. R. D'hooge, M. M. Stamenovic, P. Espeel, G. B. Marin, F. E. Du Prez, M.-F. Reyniers, *Macromolecules* **2013**, *46*, 1732–1742.
- [75] M. Winkler, C. Romain, M. A. R. Meier, C. K. Williams, *Green Chem.* **2015**, *17*, 300–306.
- [76] D. J. Darensbourg, W.-C. Chung, A. D. Yeung, M. Luna, *Macromolecules* **2015**, *48*, 1679–1687.
- [77] Y. Liu, W.-M. Ren, G.-P. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 10602–10606; *Angew. Chem.* **2013**, *125*, 10796–10800.
- [78] G.-P. Wu, D. J. Darensbourg, X.-B. Lu, *J. Am. Chem. Soc.* **2012**, *134*, 17739–17745.
- [79] Y. Wang, J. Fan, D. J. Darensbourg, *Angew. Chem. Int. Ed.* **2015**, *54*, 10206–10210; *Angew. Chem.* **2015**, *127*, 10344–10348.
- [80] G.-P. Wu, D. J. Darensbourg, *Macromolecules* **2016**, *49*, 807–814.
- [81] M. R. Kember, F. Jutz, A. Buchard, A. J. P. White, C. K. Williams, *Chem. Sci.* **2012**, *3*, 1245–1255.
- [82] Y. Liu, W.-M. Ren, W.-P. Zhang, R.-R. Zhao, X.-B. Lu, *Nat. Commun.* **2015**, *6*, 8594.
- [83] Y. Liu, W.-M. Ren, K.-K. He, X.-B. Lu, *Nat. Commun.* **2014**, *5*, 5687.
- [84] C. E. Anderson, S. I. Vagin, M. Hammann, L. Zimmermann, B. Rieger, *ChemCatChem* **2013**, *5*, 3269–3280.
- [85] W. Xia, S. I. Vagin, B. Rieger, *Chem. Eur. J.* **2014**, *20*, 15499–15504.
- [86] W. Xia, K. A. Salmeia, S. I. Vagin, B. Rieger, *Chem. Eur. J.* **2015**, *21*, 4384–4390.
- [87] a) K. A. Salmeia, S. Vagin, C. E. Anderson, B. Rieger, *Macromolecules* **2012**, *45*, 8604–8613; b) D. J. Darensbourg, R. R. Poland, C. Escobedo, *Macromolecules* **2012**, *45*, 2242–2248.
- [88] a) B. Han, L. Zhang, S. J. Kyran, B. Liu, Z. Duan, D. J. Darensbourg, *J. Polym. Sci. Part A* **2016**, *54*, 1938–1944; b) G. Si, L. Zhang, B. Han, H. Zhang, X. Li, B. Liu, *RSC Adv.* **2016**, *6*, 22821–22826.
- [89] R. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.
- [90] D. J. Darensbourg, S. J. Kyran, *ACS Catal.* **2015**, *5*, 5421–5430.
- [91] a) K. Devaine-Pressing, C. M. Kozak, *ChemSusChem* **2017**, *10*, 1266–1273; b) R. K. Dean, L. N. Dawe, C. M. Kozak, *Inorg. Chem.* **2012**, *51*, 9095–9103.
- [92] R. K. Dean, K. Devaine-Pressing, L. N. Dawe, C. M. Kozak, *Dalton Trans.* **2013**, *42*, 9233–9244.
- [93] H. Chen, L. N. Dawe, C. M. Kozak, *Catal. Sci. Technol.* **2014**, *4*, 1547–1555.
- [94] K. Ni, C. M. Kozak, *Inorg. Chem.* **2018**, *57*, 3097–3106.
- [95] N. D. Harrold, Y. Li, M. H. Chisholm, *Macromolecules* **2013**, *46*, 692–698.
- [96] K. Nakano, K. Kobayashi, T. Ohkawara, H. Imoto, K. Nozaki, *J. Am. Chem. Soc.* **2013**, *135*, 8456–8459.
- [97] M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij, P. P. Pescarmona, *Green Chem.* **2013**, *15*, 3083–3090.
- [98] a) C.-H. Li, H.-J. Chuang, C.-Y. Li, B.-T. Ko, C.-H. Lin, *Polym. Chem.* **2014**, *5*, 4875–4878; b) P.-M. Lin, C.-H. Chang, H.-J. Chuang, C.-T. Liu, B.-T. Ko, C.-C. Lin, *ChemCatChem* **2016**, *8*, 984–991; c) L.-S. Huang, C.-Y. Tsai, H.-J. Chuang, B.-T. Ko, *Inorg. Chem.* **2017**, *56*, 6141–6151; d) C.-Y. Tsai, F.-Y. Cheng, K.-Y. Lu, J.-T. Wu, B.-H. Huang, W.-A. Chen, C.-C. Lin, B.-T. Ko, *Inorg. Chem.* **2016**, *55*, 7843–7851; e) T.-Y. Lee, Y.-J. Lin, Y.-Z. Chang, L.-S. Huang, B.-T. Ko, J.-H. Huang, *Organometallics* **2017**, *36*, 291–297.
- [99] K. Nakano, K. Kobayashi, K. Nozaki, *J. Am. Chem. Soc.* **2011**, *133*, 10720–10723.
- [100] E. Peris, *Chem. Rev.* **2018**, *118*, 9988–10031.
- [101] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705–2733.
- [102] a) C. C. Quadri, E. Le Roux, *Dalton Trans.* **2014**, *43*, 4242–4246; b) J. Hessevik, R. Lalrempuia, H. Nsiri, K. W. Törnroos, V. R. Jensen, E. Le Roux, *Dalton Trans.* **2016**, *45*, 14734–14744.
- [103] C. C. Quadri, R. Lalrempuia, J. Hessevik, K. W. Törnroos, E. Le Roux, *Organometallics* **2017**, *36*, 4477–4489.
- [104] Y. Wang, Y. Qin, X. Wang, F. Wang, *Catal. Sci. Technol.* **2014**, *4*, 3964–3972.
- [105] Y. Wang, Y. Qin, X. Wang, F. Wang, *ACS Catal.* **2015**, *5*, 393–396.
- [106] J. A. Garden, A. J. P. White, C. K. Williams, *Dalton Trans.* **2017**, *46*, 2532–2541.

- [107] M. Mandal, U. Monkowius, D. Chakraborty, *New J. Chem.* **2016**, *40*, 9824–9839.
- [108] R. Lalrempuia, F. Breivik, K. W. Törnroos, E. Le Roux, *Dalton Trans.* **2017**, *46*, 8065–8076.
- [109] M. Mandal, D. Chakraborty, V. Ramkumar, *RSC Adv.* **2015**, *5*, 28536–28553.
- [110] C.-K. Su, H.-J. Chuang, C.-Y. Li, C.-Y. Yu, B.-T. Ko, J.-D. Chen, M.-J. Chen, *Organometallics* **2014**, *33*, 7091–7100.
- [111] H.-J. Chuang, B.-T. Ko, *Dalton Trans.* **2015**, *44*, 598–607.
- [112] C.-H. Ho, H.-J. Chuang, P.-H. Lin, B.-T. Ko, *J. Polym. Sci. Part A* **2017**, *55*, 321–328.
- [113] H. Nagae, R. Aoki, S.-n. Akutagawa, J. Kleemann, R. Tagawa, T. Schindler, G. Choi, T. P. Spaniol, H. Tsurugi, J. Okuda, K. Mashima, *Angew. Chem. Int. Ed.* **2018**, *57*, 2492–2496; *Angew. Chem.* **2018**, *130*, 2518–2522.
- [114] J. Qin, B. Xu, Y. Zhang, D. Yuan, Y. Yao, *Green Chem.* **2016**, *18*, 4270–4275.
- [115] A. Decortes, R. M. Haak, C. Martín, M. M. Belmonte, E. Martín, J. BenetBuchholz, A. W. Kleij, *Macromolecules* **2015**, *48*, 8197–8207.
- [116] C.-Y. Tsai, B.-H. Huang, M.-W. Hsiao, C.-C. Lin, B.-T. Ko, *Inorg. Chem.* **2014**, *53*, 5109–5116.
- [117] a) S. Tempelaar, L. Mespouille, O. Coulembier, P. Dubois, A. P. Dove, *Chem. Soc. Rev.* **2013**, *42*, 1312–1336; b) L. Mespouille, O. Coulembier, M. Kawalec, A. P. Dove, P. Dubois, *Prog. Polym. Sci.* **2014**, *39*, 1144–1164.
- [118] A. Baba, H. Kashiwagi, H. Matsuda, *Organometallics* **1987**, *6*, 137–140.
- [119] D. J. Darensbourg, A. Horn, Jr., A. I. Moncada, *Green Chem.* **2010**, *12*, 1376–1379.
- [120] F. D. Bobbink, W. Gruszka, M. Hulla, S. Das, P. J. Dyson, *Chem. Commun.* **2016**, *52*, 10787–10790.
- [121] G. L. Gregory, M. Ulmann, A. Buchard, *RSC Adv.* **2015**, *5*, 39404–39408.
- [122] G. L. Gregory, L. M. Jenisch, B. Charles, G. Kociok-Köhn, A. Buchard, *Macromolecules* **2016**, *49*, 7165–7169.
- [123] G. L. Gregory, E. M. Hierons, G. Kociok-Köhn, R. I. Sharma, A. Buchard, *Polym. Chem.* **2017**, *8*, 1714–1721.
- [124] G. L. Gregory, G. Kociok-Köhn, A. Buchard, *Polym. Chem.* **2017**, *8*, 2093–2104.
- [125] D. Pati, X. Feng, N. Hadjichristidis, Y. Gnanou, *J. CO₂ Util.* **2018**, *24*, 564–571.
- [126] D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou, X. Feng, *J. Am. Chem. Soc.* **2016**, *138*, 11117–11120.
- [127] K. A. Andrea, F. M. Kerton, *ACS Catal.* **2019**, *9*, 1799–1809.
- [128] a) F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis, G. W. Coates, *Angew. Chem. Int. Ed.* **2015**, *54*, 1215–1218; *Angew. Chem.* **2015**, *127*, 1231–1234; b) F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro, R. Ciriminna, *ACS Omega* **2018**, *3*, 4884–4890; c) O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger, A. Greiner, *Green Chem.* **2016**, *18*, 760–770.

Manuscript received: October 3, 2019

Accepted manuscript online: November 25, 2019

Version of record online: January 9, 2020