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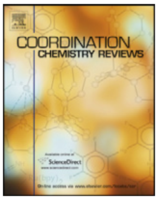

Review

Recent advances in CO_2/epoxide copolymerization—New strategies and cooperative mechanisms

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ABSTRACT

The catalytic copolymerization of CO_2 with epoxides has been known for over 40 years. Even though many heterogeneous and homogeneous catalyst systems have been developed, catalyst activity and selectivity still remain too low for large scale industrial application.

Recent investigations have identified new copolymerization pathways with strong evidence for cooperative (bifunctional) mechanisms. At high dilutions, traditional discrete mononuclear single-site catalyst systems generally show a loss in activity. This effect can be overcome with the help of recently developed dinuclear and binary linked systems that involve cooperative mechanisms and thus permit high catalyst efficiency.

Abbreviations: BDI, β-diiminate; CHC, cyclohexene carbonate; CHO, cyclohexene oxide; DMAP, 4-(dimethylamino)pyridine; DNP, 2,4-dinitrophenolate; *N*-MeIm, *N*-methylimidazole; OAc, acetate; PC, propylene carbonate; PCHC, poly(cyclohexene carbonate); PO, propylene oxide; PPC, poly(propylene carbonate); PPNCl, *bis*(triphenylphosphine)iminium chloride; TOF, turn-over frequency; TON, turn-over number; tpp, tetraphenylporphyrin, porphyrin; ZnAA, zinc adipate; ZnGA, zinc glutarate; ZnPA, zinc pimelate; ZnSA, zinc succinate.

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Bimetallic
Cooperative
Bifunctional

This review gives an overview on the most recent advances in CO_2/epoxide copolymerization, new mechanistic studies and strategies for future catalyst developments.

1. Introduction

1.1. CO_2 activation into new products

Crude oil remains the most important chemical feedstock of our times. The importance of fossil fuel resources for mankind becomes clear when its broad areas of usage are fully considered. The utilization of crude oil ranges from energy carrier (fuel) to a suppliant for carbon-containing molecules used in chemical synthesis and as building blocks for polymeric materials. At current rates of consumption, worldwide crude oil reserves are rapidly depleting, thus emphasizing the importance of alternative, renewable carbon-based sources for raw materials [1–4].

One possible source is CO_2, which is released in many combustion processes and is (alongside methane) considered as a main contributor to the so-called Greenhouse Effect [5–8]. Current global CO_2 emissions are estimated to exceed 31 billion t/year [9]. One long considered strategy to reduce atmospheric CO_2 content is CCS (carbon capture and storage), which is assumed to considerably diminish the CO_2 concentration *via* storage [10–12]. Intense research activities in this area indicate promising results in the near future, however the thought of retaining huge CO_2 reservoirs is not very appealing. As global warming is thought to principally result from excessive combustion of fossil fuels, emphasis should be placed upon restricting CO_2 emissions rather than processing excess CO_2 after its generation. Independent of such environmental considerations, the chemical utilization of excess CO_2 is an important topic.

A significantly more meaningful strategy is the utilization of abundant, non-toxic and non-flammable CO_2 as a C1-feedstock for chemical reactions [13–18], however the thermodynamic stability of CO_2 has thus far precluded its usage as a widespread chemical reagent. Methods to overcome the high energy barriers are based upon reduction, oxidative coupling with unsaturated compounds on low valent metal complexes and increasing the electrophilicity of the carbonyl carbon [19,20]. Specifically, the reaction of CO_2 with highly reactive substrates, such as epoxides, affords valuable materials which can be produced on industrially relevant scales [21–25].

The use of CO_2 as a chemical feedstock will never be able to compensate emission-based CO_2, however this strategy potentially provides access to high-value products from a non-toxic, renewable and low-cost resource. Current examples of the industrial utilization of CO_2 include the large-scale production of urea, salicyclic acid and several carbonate-based materials (Scheme 1). A further large-scale industrial application of CO_2 potentially lies in the production of the biodegradable thermoplastics poly(propylene carbonate) (PPC, Scheme 2A) and poly(cyclohexene carbonate) (PCHC, Scheme 2B).

The usage of CO_2 in this manner could substitute the environmentally malign industrial synthesis involving polycondensation of *trans*-diols (*e.g. Bis*phenol-A) with highly toxic phosgene by utilizing the energy rich three-membered, highly ring-strained oxiranes to react with CO_2.

The outstanding properties of polycarbonates such as strength, lightness, durability, biodegradability, heat resistance, easy processability, high transparency and good electrical insulation render these materials of high industrial importance with applications in the automotive, electronics, optical media, glazing and sheeting industries as well as across the medical and healthcare sectors.

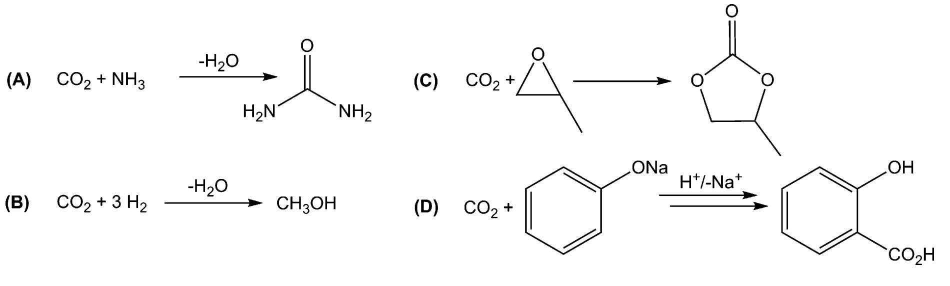
1.2. First steps in copolymerization of CO_2 and epoxides

The complete historical development of this area has been comprehensively reviewed by others and the interested reader is directed to these publications [24–31]. The copolymerization of CO_2 with epoxides has been known since 1969 when Inoue et al. combined $ZnEt_2$, water, CO_2 and PO to yield a small quantity of polymeric material [32,33]. The subsequent investigations in this area were frequently frustrated by low catalytic activities and the formation of undesired by-products such as cyclic carbonates and/or high degrees of ether linkages in the polymer chains. Furthermore, many systems that show polymer formation with the CHO/CO_2 system, only yield cyclic carbonate or show no conversion at all with PO/CO_2 as monomers.

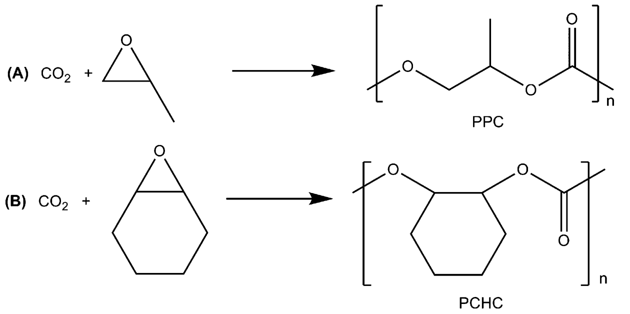
Shortly after the initial discovery from Inoue et al. the effect of dihydric molecules (*e.g.* resorcinol [34], dicarboxylic acids [35] and primary amines [36]) in combination with $ZnEt_2$ was studied on the copolymerization of CO_2 and PO. In 1976–1977 Kuran et al. developed new catalyst systems with trihydric phenols such as pyrogallol and 4-bromopyrogallol [37,38]. The first catalytic observations (PO/CO_2) with these systems suggested that monoprotic molecules such as alcohols and secondary amines exclusively yield cyclic propylene carbonate (PC) whereas di- and tri-protic species yield PPC [38–42]. In order to overcome the low activities generally encountered, Soga et al. synthesized the first well-defined heterogeneous catalyst system from a $Zn(OH)_2$/glutaric acid mixture for the copolymerization of CO_2 and PO [40].

The first homogeneous single-site catalyst was developed by Inoue et al. in 1986, comprising a tetraphenylporphyrin ligand (tpp) with an aluminum metal center (Fig. 1A) [43].

In 1995 a series of discrete zinc phenoxide derivatives as catalysts were synthesized by Darensbourg et al. These catalysts demonstrated moderate activities for PO/CO_2 copolymerization



Scheme 1. Utilization of CO_2 as a C1-feedstock for chemical reactions: (A) synthesis of urea (146×10^6 t/a); (B) methanol (6×10^6 t/a); (C) cyclic carbonate (0.040×10^6 t/a), (D) salicylic acid (0.060×10^6 t/a) [13,17,18].



Scheme 2. Alternating copolymerization of propylene oxide (PO) (A) and cyclohexene oxide (CHO) (B) with CO_2.

with approximately 10% polyether content even under high CO_2 pressures (55 bar) (Fig. 1B) [44–46]. With modification of the substituents on the phenoxide ligands, catalytic activities varied only slightly.

The first breakthrough which lead to a more systematic catalyst design was the exploration of β-diiminate zinc catalysts (BDI) in CHO/CO_2 copolymerization by Coates et al. [47,48], where minor variations in the electronic and steric character of the BDI ligand framework showed dramatic changes in catalytic activity (Fig. 1C). Moreover the BDI catalysts could be tailored to achieve high activities in PO/CO_2 copolymerizations [49]. To date, salen-type systems (Fig. 1D) have received the most attention for CO_2/epoxide copolymerization [27]. All of the above-detailed complex categories will be reviewed in the following sections.

2. Catalyst systems for CO_2/epoxide copolymerization

The development of active CO_2/epoxide copolymerization catalysts resembles in many aspects the early advances in alkene polymerization with the first active catalyst systems being heterogeneous in nature. Although the composition of these heterogeneous catalysts is often ambiguous and the active sites poorly defined, they are nonetheless employed industrially for the production of polycarbonates. Indeed, the majority of commercial PPC is produced with the use of the heterogeneous zinc glutarate system (Section 2.2.1). In this system, the Zn–Zn distances are typically between 4.6 and 4.8 Å and the variation of these values in homologous catalyst structures is probably reflected in lower activities. This indicates that the spatial distance between two metal centers is crucial for significant copolymerization activity and that the directed design of homogeneous systems containing a defined metal–metal distance would raise observed activity levels.

Whilst there remains an industrial reliance on heterogeneous systems, homogeneous catalysts are still subject to intense study, not least because their soluble nature permits *in situ* examination of the polymerization mechanisms. It is for this reason that homogeneous catalysts remain the subject of intense research activity. The determination of their solution state behavior facilitates the design of improved catalysts with enhanced efficiency. These topics form the scope of this review which comprises four main sections.

The first part gives an overview of the copolymerization pathways that are encountered in CO_2/epoxide copolymerization.

The second part provides a resume about the well-investigated but, from a mechanistic point of view, poorly understood zinc-dicarboxylates and concludes with mechanistic considerations.

The third part focuses on traditional homogeneous catalysts and the progress made to date with these systems. The main ligand families covered are porphyrins, phenoxides, β-diiminates and salens, which are covered in their respective sections. Several of these studies imply that multi-site catalysts or binary systems are required to deliver alternating copolymers from CO_2 and epoxides.

In the final part of this review, the most recent advances and new strategies to circumvent the problems that have been uncovered with the traditional catalyst systems are outlined. Here the focus lies on the development of new dinuclear and binary linked catalyst systems that are able to initiate a cooperative mechanism in CO_2/epoxide copolymerizations. Furthermore the strategy of immobilizing homogeneous systems on substrates is reviewed. For a convenient comparison of the different catalytic systems, the productivity is given as turn-over-number (TON) in mol/mol and the activity as turn-over-frequency (TOF) in TON h^{-1}. In cases where it is relevant, the selectivity towards copolymerization and the corresponding quality of the produced polymer is given.

2.1. Mechanistic aspects of CO_2/epoxide copolymerization

2.1.1. Copolymerization mechanism

Despite intense research activities in the area of CO_2/epoxide copolymerization, a profound understanding of the underlying mechanisms is still lacking and thus, this field is under continual investigation and review. Homogeneous catalysts of the form L_nMX generally contain only one specific active-site, which can easily be tailored by modifying either the ligand framework (L_n), the catalytically active metal center (M) or the initiating group (X). The mechanistic aspects of the initiation step of L_nMX complexes is currently a highly active field of research, with a number of different mechanisms being proposed. The possible mechanism pathways are described with a model salen-complex (Scheme 3).

Reaction pathway A involves two metal complexes and an intermolecular interaction of two active sites (Scheme 3A). In a theoretical study conducted by us, we predicted chain growth to take place *via* attack of a metal-bound alkyl carbonate on a metal-coordinated epoxide [50]. Such a bimolecular process has also been observed by Jacobsen et al. for the asymmetric ring-opening of epoxides [51–53]. Other investigations have indicated a bimetallic initiation, followed by a monometallic propagation step [54–57]. The bimetallic pathway generally is thought to occur in the absence of cocatalysts at low epoxide/catalyst loadings and is rate-dependent on the Lewis acidity of the metal center as well as the

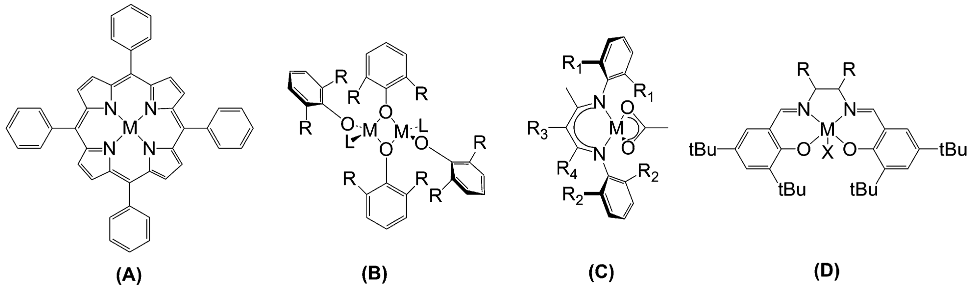
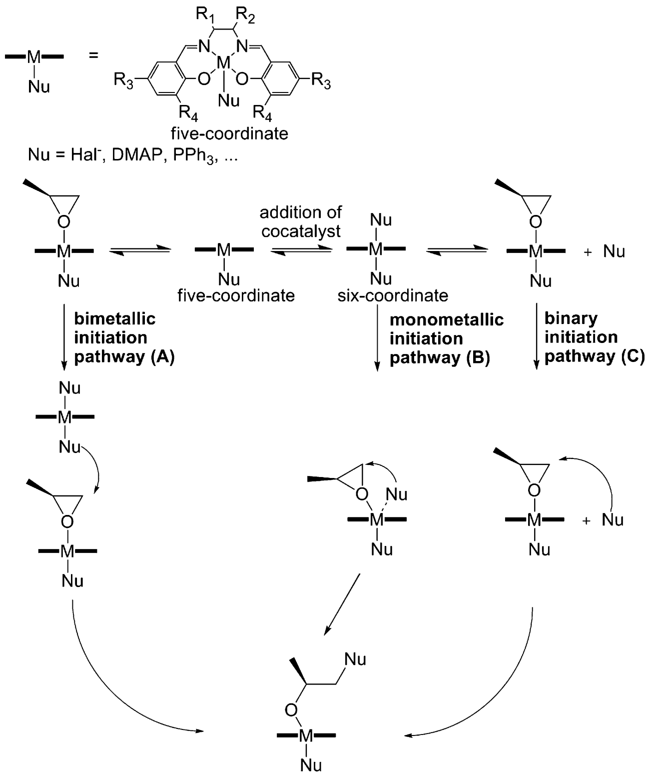


Fig. 1. Representative homogeneous single-site catalysts for epoxide/CO_2 copolymerization (A: porphyrin system, B: phenoxides system, C: β-diiminate system, D: salen system).



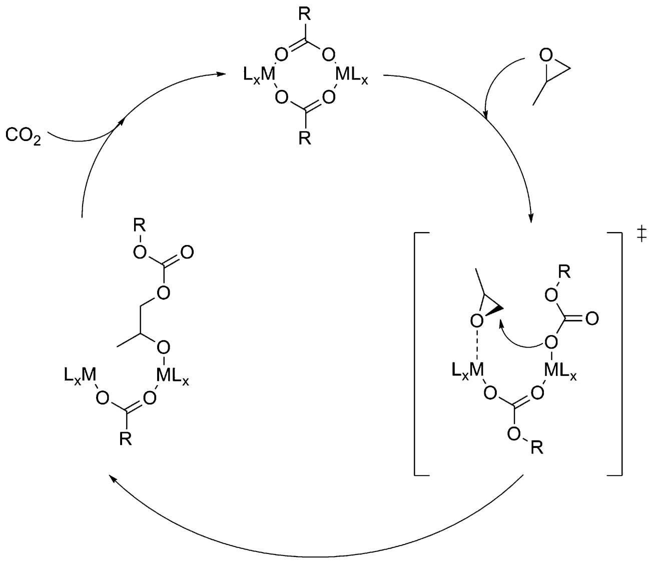
Scheme 3. Initiation mechanisms for a generalized salen-complex: bimetallic pathway (A), monometallic pathway (B), binary pathway (C).

nucleophilicity of the axial ligand X and therefore upon the type of the catalytic system. For example, mechanistic studies conducted by Chisholm et al. with metal–porphyrin systems strongly indicate that the initiation step is monometallic [58].

Reaction pathway B involves an intramolecular attack of the nucleophile on the pre-coordinated epoxide, which formally is comparable with an associative ligand exchange mechanism (Scheme 3B). In the monometallic pathway, a nucleophile (Nu) ring-opens the epoxide at the least hindered C–O bond (even though some regio-irregularity is always observed). As both X and Nu can serve as initiator groups, they are both generally integrated into the polymer chain as end groups. Such a mechanism is, however, rather unlikely as the corresponding transition state in commonly applied metal complexes is thermodynamically disfavored.

Reaction pathway C involves the interaction of a binary catalyst/cocatalyst system, where the added nucleophile adopts the role of attacking the pre-coordinated epoxide (Scheme 3C). The abundance of investigations on such binary systems have shown that the addition of a nucleophilic cocatalyst can significantly improve the activity and selectivity even at low CO_2 pressures and/or elevated temperatures depending on the nature of the added nucleophile [30,59–76].

A catalytic cycle for the bimetallic formation of polycarbonate is presented in Scheme 4. As shown by Coates et al. the rate determining step is the incorporation of the epoxide [77]. The key step in the catalytic cycle is the ring-opening of the epoxide as a result of the nucleophilic attack by a carbonate end-group. However the carbonate group is a very weak nucleophile, such that the epoxide must be pre-coordinated and pre-activated by a Lewis acid, which may be another metal center or cocatalyst. Following the ring-opening of the epoxide, CO_2 is inserted into the metal–alkoxy bond. These iterative insertions are repeated in further catalytic cycles thus leading to the formation of the copolymer.



Scheme 4. Bimetallic catalytic mechanism for CO_2/PO copolymerization.

Homogeneous systems were considered to follow a cooperative (bimetallic or binary) pathway in many early publications [22,24,39,78–81]. This explains the loss in activity at higher dilutions, which are often observed with such systems. The above-shown mechanistic considerations lead to the conclusion that two interacting species need to be in spatial proximity to achieve high catalytic activity. Therefore new strategies in CO_2/epoxide copolymerization increasingly focus on dinuclear and binary linked systems (Sections 2.4.1 and 2.4.2).

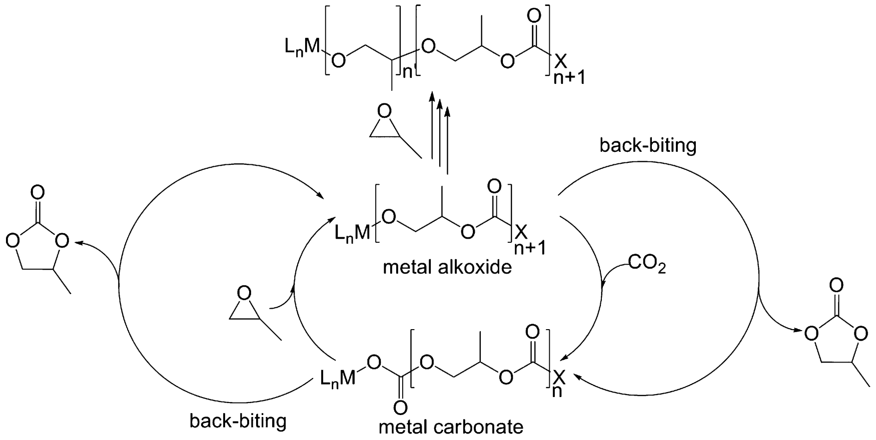
2.1.2. *Factors influencing copolymerization*

Beside self-evident parameters as temperature, pressure and catalyst/cocatalyst concentration, several other factors must be taken into consideration in the copolymerization of CO_2 and epoxides:

2.1.2.1. Viscosity and dilution problems. A major drawback which limits polymer yields is the viscosity of polymerization mixtures at higher monomer conversions. During the copolymerization process, the viscosity of the reaction medium increases with polymer formation and diffusion of the monomer to the active catalyst site is therefore impeded. Higher solvent contents can facilitate monomer diffusion; however activities have a propensity to drop at high catalyst dilutions, principally due to an overall decrease of monomer concentration and due to the spatial separation of two potentially interacting species. The combination of two metal centers or linkage of two binary components into one ligand framework can counter this effect (Sections 2.4.1 and 2.4.2).

2.1.2.2. Side reactions. Side reactions typically occur when epoxides are consecutively inserted into the growing polymer chain or through the production of cyclic carbonate *via* a back-biting pathway (Scheme 5). The consecutive insertion of two CO_2 molecules has never been observed as this is strongly disfavored from a thermodynamic perspective [26].

One advantage of two adjacent interacting species in cooperative catalysis is the constant contact of the polymer chain to an active metal center during the reaction. Therefore the so-called back-biting reaction is suppressed and depolymerization is minimized. This back-biting can occur from an anionic carbonate group or an anionic alkoxide chain end (Scheme 6) [50].



Scheme 5. Side product: polyether formation through consecutive PO insertions, formation of cyclic carbonate through chain back-biting.

Factors enhancing the back-biting and therefore cyclic carbonate content include higher temperatures and cocatalysts that help dissociate the growing polymer chain from the metal center.

2.1.2.3. Chain transfer. Any traces of water, alcohol or acid in the polymerization medium can initiate a chain transfer, which results in lower molecular weights than theoretically calculated [82–84]. The minor contribution of a consecutive back-biting mechanism and the release of the by-product cyclic carbonate has been previously discussed [84]. However, the protonated chain-end is considered to be insufficiently nucleophilic for the back-biting event to take place [82]. Although the copolymerization reagents are generally dried, molecular weights and PDI usually differ from those expected, an effect which has to be accounted for in this field of chemistry.

2.2. Heterogeneous catalysts systems

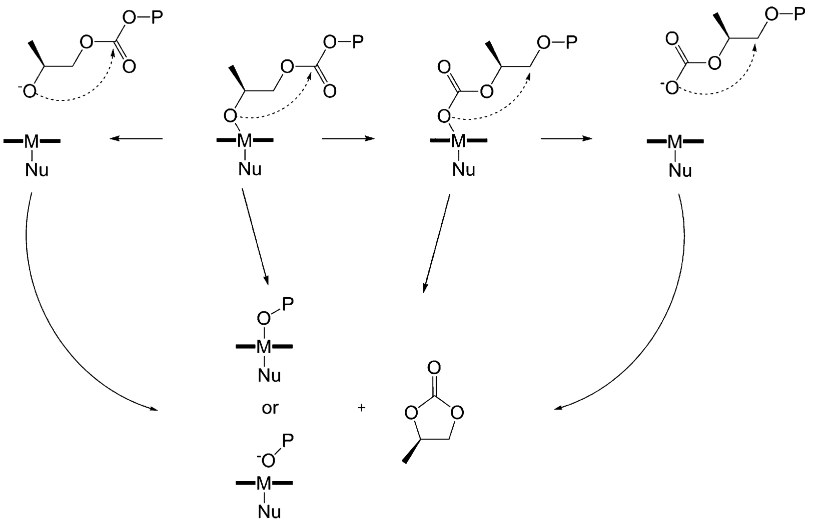
2.2.1. Zinc dicarboxylates

Even though huge steps in homogeneous catalysis have been made over the last years, the traditional heterogeneous zinc-dicarboxylate systems remain industrially relevant as they are easy to prepare and handle, non-toxic and economically viable. An excellent set of reviews on this topic has been published [26–28,85]. This review therefore summarizes the most recent observations for heterogeneous systems with particular emphasis upon polymerization mechanisms on heterogeneous surfaces and directions for future catalyst development.

Despite the numerous advantages of the heterogeneous zinc carboxylate system, the exact nature of the catalytically active species is still unknown, which renders systematic modifications of the system difficult.

The zinc glutarate (ZnGA) system, comprising Zn and glutaric acid, has been subject to the most intensive studies. There are several ways to prepare ZnGA, namely by the introduction of different Zn sources (*e.g.* ZnO, $Zn(OH)_2$, $Zn(OAc)_2$, $Zn(NO_3)_2$, $Zn(ClO_4)_2$, $ZnEt_2$) and carboxylate sources (*e.g.* glutaric acid, anhydride, methyl ester, glutaronitrile) [35,40,86–88]. Although the same product structure is found for all synthetic strategies (X-ray powder diffraction studies) [86–89], activities can vary considerably. The standard procedure combining zinc oxide and glutaric acid affords ZnGA with the highest activity [87].

The molecular structure of ZnGA has only recently been elucidated [90,91] and consists of a unique structure type with four carboxyl groups coordinating one Zn center with the glutarate ligands in either a bent or an extended conformation (Fig. 2). This particular conformation leads to the formation of two metallacycles A and B that introduce a porosity which is not conducive for monomer diffusion [86]. These investigations showed that overall activity is restricted to the outer surface of the ZnGA-particles.



Scheme 6. Chain back-biting mechanism [50].

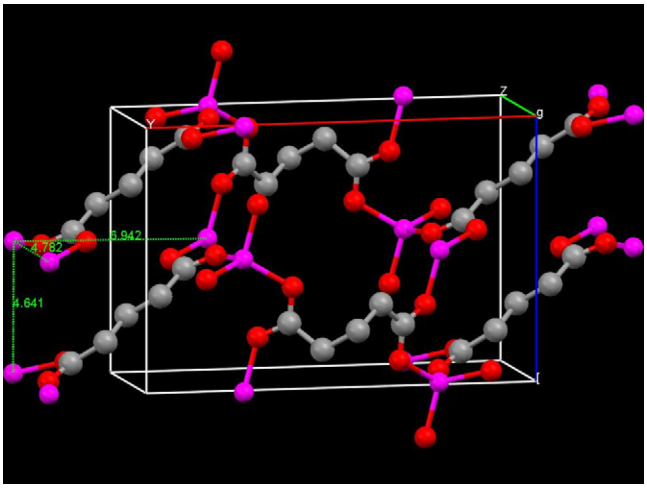


Fig. 2. Crystal structure of ZnGA; view along *b*-axis including the material porosity [90,91].

Strategies to increase the activity were therefore focused on increasing the ZnGA surface area [89,92] by one of four methods:

- variation of stirring procedure: magnetic or mechanic;
- post-modification: ball-milling or ultrasonic preparation;
- introduction of additives: substrates with high surface area;
- addition of growth controllers: block copolymers or monoacids.

Each of these strategies has been tested in the literature and shown to enhance activity, although the desired high activities that have been realized for several homogeneous catalysts have not been achieved with ZnGA to date. Indeed, Coates et al. categorized catalyst systems by their catalytic activity (low TOF < 5 h^{-1}, moderate TOF between 5 and 200 h^{-1}, high TOF > 200 h^{-1}; all values given in mol epoxide converted/mol catalyst × time interval) and heterogeneous catalysts still remain in the lower region of this scale [26].

A supported ZnGA on montmorillonite was obtained by a solution procedure and showed a slightly increased activity (TOF = 5.51 h^{-1}) compared to more standard procedures (TOF ≈ 3.00 h^{-1}) [93]. Introduction of templates, such as amphiphilic block copolymers, during the synthesis of ZnGA can slightly increase the activity, presumably due to the inhibition of agglomeration (before: TON = 64 g/g, TOF = 3.06 h^{-1}; after: TON = 83 g/g, TOF = 3.97 h^{-1}) [86,94]. The different stirring methods (magnetic, mechanical) and particularly the ultrasonic preparation of ZnGA considerably increase the efficiency, thus yielding the highest activity achieved for a zinc carboxylate system [89,95]. Regeneration of zinc carboxylate catalysts after complete polymerization gave less product than the freshly synthesized catalyst [96]. The influence of traces of water, ethanol, remaining residues of unreacted glutaric acid or other proton donors as chain transfer agents upon catalytic activity has already been suggested [84].

With regards to the surface constitution of the carboxylate catalysts, the active species is still unidentified. MALDI–TOF mass spectrometric studies have shown that the copolymer is terminated by an OH group, thereby indicating that Zn–OH groups are the active initiating species in the ZnGA system (Fig. 3) [84,97]. In an early study, Inoue et al. combined diethyl zinc and glutaric acid to yield a ZnGA with very low activity [35], presumably due to the presence of ethyl groups at Zn (which are known to react sluggishly with epoxide and CO_2) [38,47,98]. However, post-activation of the surface-situated Zn-ethyl species with SO_2 leads to ethyl-sulfinato groups and a considerable increase in activity, achieving activities approaching the best known for ZnGA to date (Fig. 3) [99].

Another aspect often and ambivalently discussed is the crystallinity of the resulting Zn-containing materials, as it seems that amorphous catalysts are less active than their highly crystalline counterparts [86–89,92,100,101]. However, the crystallinity of the catalyst prepared from $ZnEt_2$ is less than that of a catalyst prepared by the standard procedure with ZnO [86], but a higher surface area and potentially better initiator groups on the surface are probably responsible for the higher activity.

Other investigations have introduced various dicarboxylic acids, derivatives of zinc glutarate and mixtures of di- or mono-acids with variable success [86,92,102]. In particular the substitution of glutaric acid by derivatives with other functionalities in the hydrocarbon chain (*e.g.* 2-ketoglutaric acid, 3,3-dimethylglutaric acid, diglycolic acid) afforded materials with no appreciable activity, presumably due to different solid-state constitutions and asso-

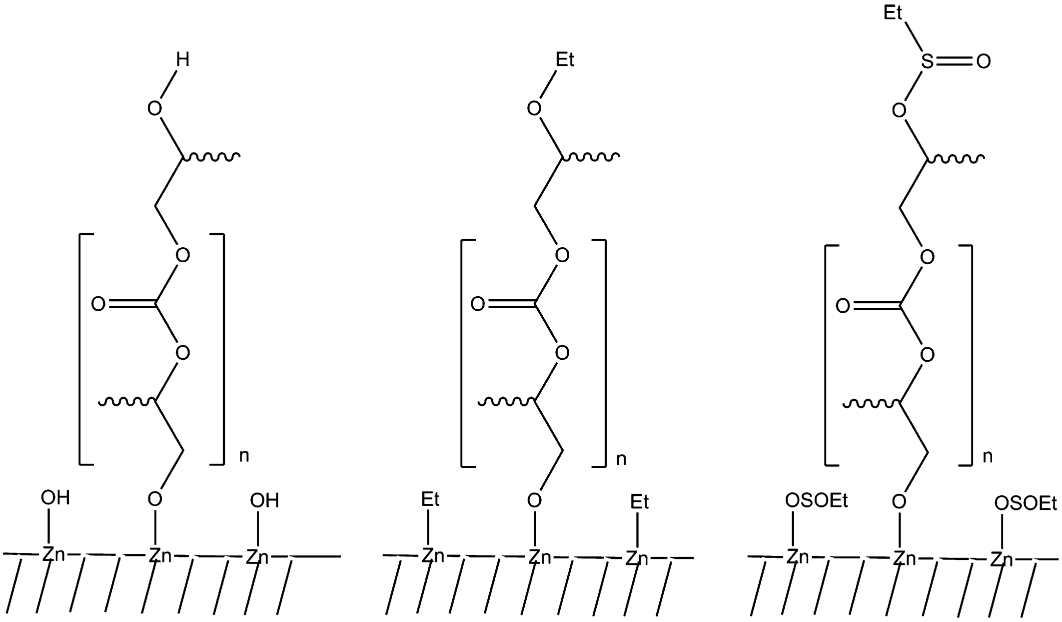


Fig. 3. Initiator groups ZnOH, $ZnEt_2$ and $Zn(SO_2Et)$ on the surface of heterogeneous zinc-dicarboxylates and associated polymer end groups.

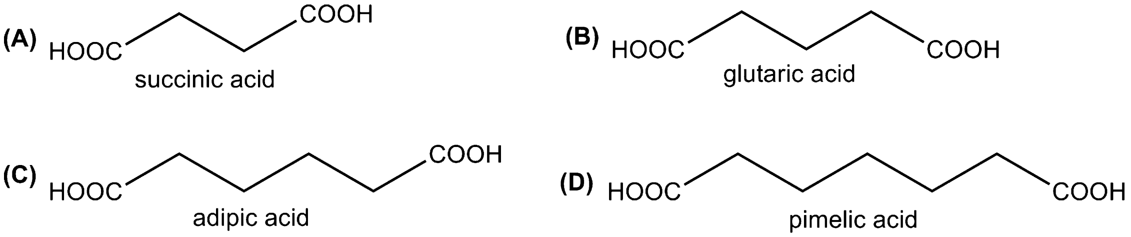


Fig. 4. Various dicarboxylic acids used in the synthesis of heterogeneous catalyst systems.

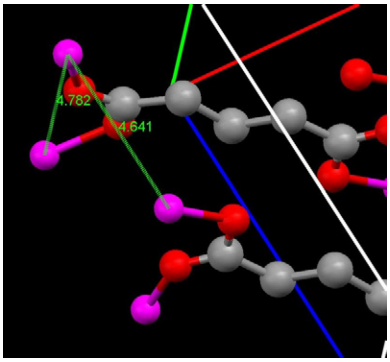


Fig. 5. Representative metal distances in zinc glutarate (Zn–Zn distance = 4.6–4.8 Å).

ciated variations of the local environment around the Zn center [86,99,103].

Further attempts to form active heterogeneous Zn-containing systems were based on the exchange of glutaric acid for its higher or lower homologues. It was long thought that the zinc carboxylate system with glutaric acid (GA, C_5) was the only system with a considerably high activity for copolymerization, whereas other variants such as succinic acid (SA, C_4), adipic acid (AA, C_6) or pimelic acid (PA, C_7) were presumed to be inactive (Fig. 4). However, recent reports have demonstrated that ZnAA [104,105] (TOF = 5.65 h^{-1}) and ZnPA [101] (TOF = 5.20 h^{-1}) show similar activities to ZnGA when appropriately treated. Adipic acid is of particular interest as this is a large-scale industrial product.

Interestingly the same trend of activity for analogous structures of ZnGA is observed when the functionalization route with $ZnEt_2$, followed by SO_2 activation, is employed. Almost no activity is observed for ZnSA (TOF = 0.07 h^{-1}), whereas the activity slightly decreases in the order of ZnGA (TOF = 6.17 h^{-1}) > ZnAA (TOF = 5.18 h^{-1}) > ZnPA (TOF = 4.50 h^{-1}) [99].

These results indicate that the activity of heterogeneous zinc dicarboxylate systems of this type is dependent on a defined spatial structure which is influenced by the dicarboxylic acid used. Of these systems, only the solid state structures of ZnGA and ZnSA [106,107] have been reported so far. In the structure of ZnSA, the necessary Zn–Zn distance is only found on one of the main *hkl*-indiced plains, whereas for ZnGA, the corresponding distance of 4.6–4.8 Å is found on each main *hkl* plain (Fig. 5). From the molecular structures of ZnSA and ZnGA, it can be concluded that at least two zinc centers in spatial proximity need to be present for copolymerization activity.

The optimal Zn–Zn distance for CO_2/epoxide copolymerization is assumed to lie between 3 and 5 Å, as can also be deduced from investigations with homogeneous systems (see following sections). These results strongly indicate that for heterogeneous systems a very specific metal–metal distance is required for high copolymerization activities. However the activities with such systems are restricted due to a restrained surface and diffusion limitations. Therefore, new strategies have to focus on homogeneous systems that comprise two metal centers or a cooperative binary linked ligand system.

2.3. *Traditional homogeneous catalyst systems*

2.3.1. *Porphyrin systems*

Shortly after the first tetraphenylporphyrin ligand (tpp) with an aluminum metal center was developed, trials with the addition of cocatalysts were reported (Fig. 6). Porphyrin (tpp)AlCl catalysts, in conjunction with quaternary organic salts or triphenylphosphine, are active at ambient temperature and relatively high catalyst loadings with low TOFs. Following these results, Kruper and Dellar investigated the activity of (tpp)CrX (X = Cl, Br, OAc) complexes (in addition to 4–10 equivalents of nitrogen donors such as *N*-methylimidazole (*N*-MeIm) or (4-dimethylamino)pyridine (DMAP)) which predominantly yield copolymer with the CHO/CO_2 system, but only cyclic carbonate with PO/CO_2 [108–110]. The DMAP cocatalyst fulfils two roles; firstly the amine labilizes the metal–X bond and secondly it promotes insertion of CO_2 into the metal–OR bond [58].

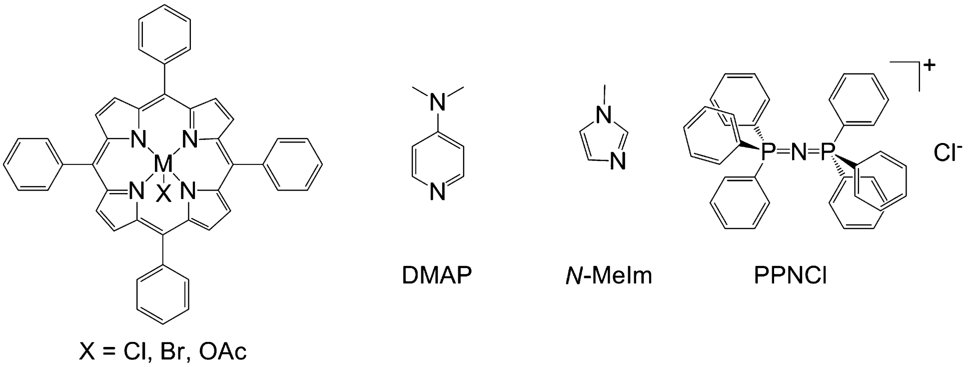


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Fig. 6. Representative structure of the porphyrin system and commonly used cocatalysts.

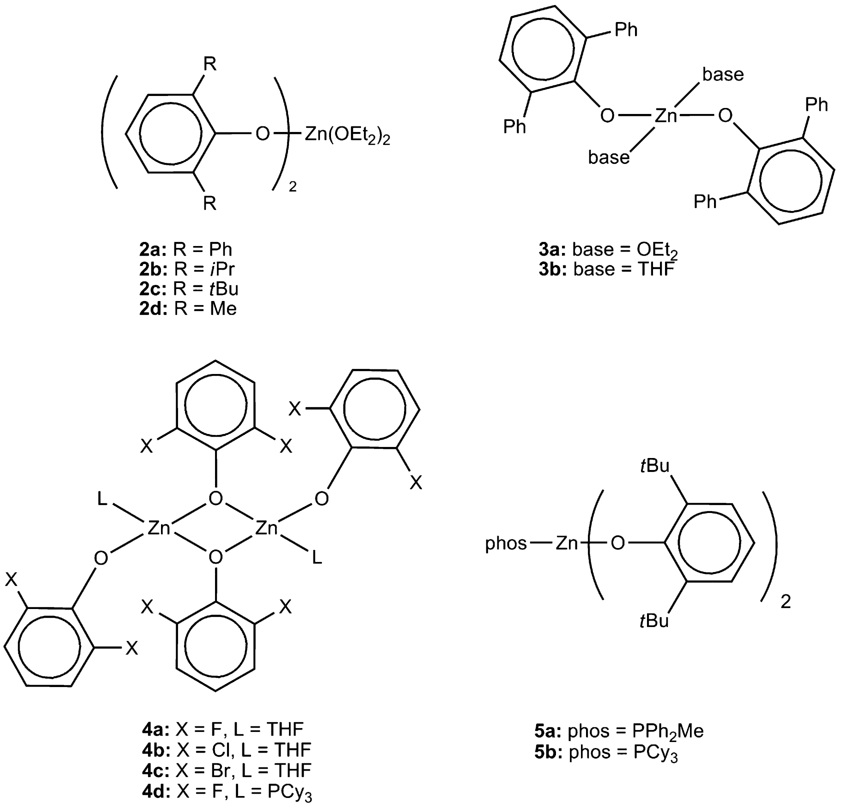


Fig. 7. Active phenoxide systems for CO_2/epoxide copolymerizations [44–46,117,118].

Whilst cobalt–porphyrin systems have been traditionally overlooked in favor of other metal-containing systems, Wang and co-workers have shown through a series of experiments that the (tpp)CoCl/cocatalyst system is indeed active in the PO/CO_2 copolymerization. Furthermore they demonstrated that the efficiency of this binary system decreases with the exchange of cocatalyst in the order $PPNCl > Bu_4NCl > Et_4NBr \sim Bu_4NBr \gg Bu_4NI$ [111]. This study directly challenged the assumption that Co-porphyrins demonstrate low activity (as a result of the reduced Lewis acidity of the cobalt center in these complexes) [112]. Also (tpp)CoCl complexes, in association with DMAP [113] and phenyltrimethylammonium tribromide [114] are efficient systems for the catalytic coupling of CO_2 and PO, affording cyclic carbonate. Without cocatalyst, the effect of the substituent X in (tpp)CoX on the catalytic activity decreases in the order $Cl \sim Br > I \gg OAc$ (with the (tpp)CoOAc system being completely inactive for PPC formation).

These new developments with porphyrin systems give a strong indication for a favorable cooperative mechanism in CO_2/epoxide copolymerization which is highly dependent on the catalyst and cocatalyst combination used.

2.3.2. Phenoxide systems

The discovery in 1986 of the first soluble and therefore well-characterized aryl-oxide zinc complex initiated the development of a new family of complexes [115] which have been demonstrated to be active catalysts for epoxide/CO_2 copolymerizations.

Numerous investigations have shown that the activity of these complexes is linked to the substitution pattern of the aryl ligand framework and the “base” ligand present at the metal center. The exchange of Zn for other metals (*e.g.* Cd) [116] demonstrated a loss in activity. However, Zn-containing systems have demonstrated the highest activities.

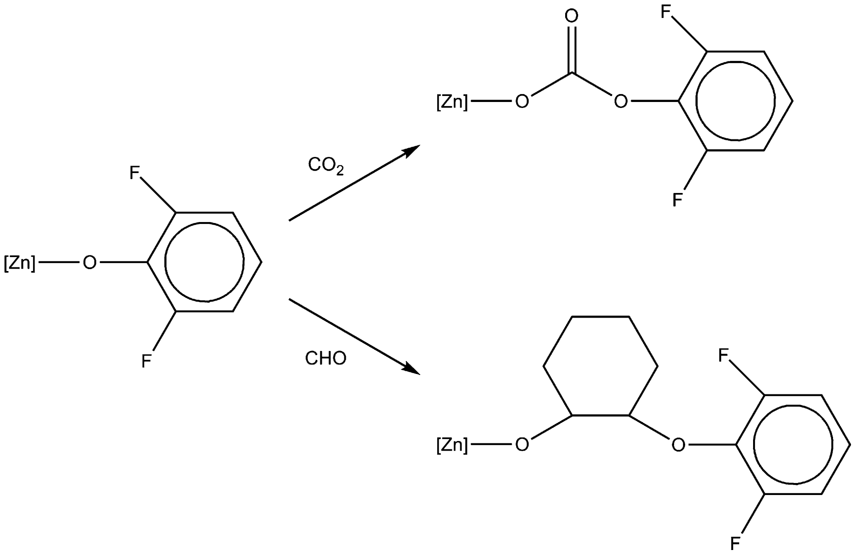
The effect of ligand substitution on CHO/CO_2 copolymerization was demonstrated with monomeric Zn complexes bearing different substituents (R) in the *ortho*-position of the aryl rings (**2a**–**d**, Fig. 7). For early investigations on phenoxides, no TOF values were given and therefore values in this section are reported in g polymer/g Zn. The R group significantly affects the catalyst efficiency, where the yield increases with decreasing substituent size (477 g/g (*i*Pr), 602 g/g (Ph), 677 g/g (*t*Bu), 1441 g/g (Me)) [45].

Dimeric phenoxide complexes of the type **3** (Fig. 7) have shown activities around 88 g/g in CHO/CO_2 copolymerizations, whereas no copolymer formation was observed for the PO/CO_2 system. However, complex **3a** is an active system for the terpolymerization of CHO, PO and CO_2 with moderate incorporation of PO (*ca.* 20%) [44].

The introduction of halides in the *ortho*-position of the aryl rings increases the activity of the correspondent catalyst in the order $Br < Cl < F$ (Fig. 7, **4a**–**c**) [46,117]. The authors attribute this trend to a decrease in electron density at the metal center, which reflects the increased electronegativity of the substituted halide, thereby increasing the binding ability of the metal center to the epoxide. This emphasizes that epoxide activation is generally more important than CO_2 insertion in complexes of this nature.

Analysis of the polymer with ^{19}F NMR spectroscopy demonstrated the presence of different F-containing environments in the polymer. This indicates that the initiation mechanism occurs *via* nucleophilic addition of the zinc-bound phenoxide to the first monomer (Scheme 7) [117].

Replacement of the labile Et_2O and THF bases by phosphorus donors in Zn-phenolate complexes of the type **3** and **4a**–**c** has a pronounced impact on the complex activities, as phosphines can irreversibly bind to the active metal site (**4d**) [117]. However the introduction of phosphine donors such as PPh_2Me (**5a**) and PCy_3 (**5b**) in monometallic Zn phenolate complexes increases the percentage of polymeric carbonate linkages without loss of catalytic



Scheme 7. Initiation step in fluoro-phenolate Zn complexes [117].

activity. This demonstrates that two adjacent coordination sites are needed for consecutive epoxide insertions [118].

Mechanistic investigations with Zn-phenoxide complexes of this type have long been frustrated due to the lack of a spectroscopic probe suitable for Zn systems. It is for this reason that early mechanistic studies focused on Cd complexes as these analogous compounds are active for epoxide/CO_2 copolymerizations (albeit with lower activities than their respective Zn complexes) and adopt similar geometries to the analogous Zn complexes (Fig. 8) [117,118].

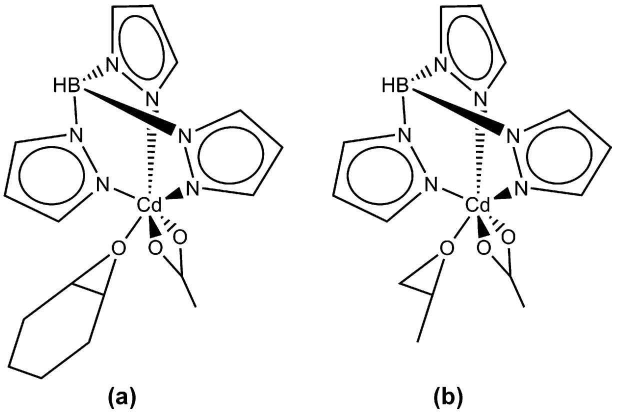
^{113}Cd NMR spectroscopic investigations with L_nCd(THF)(acetate) demonstrated that the labile THF ligands in these systems can be easily replaced by a CHO (**6a**) or PO (**6b**) molecule [119]. In both cases the epoxide was weakly bound to the Cd-center and solution-state equilibrium studies permitted the determination of the thermodynamic parameters for epoxide insertion. The complexes with coordinated PO and CHO were both crystallographically characterized and therefore represent the first isolated intermediates in the initiation step of CO_2/CHO and CO_2/PO copolymerizations with metal carboxylate complexes [120].

By the combination of experimental Zn studies and their related Cd systems, it has been determined that both mono- and bimetallic Zn-phenoxides have the potential to produce high molecular weight PCHC. Unfortunately, copolymerizations with PO and CO_2 remain challenging and progress with these systems been frustrated by low activities and a propensity for chain back-biting to form PC. However successful terpolymerizations of PO/CHO/CO_2 have demonstrated that Zn-phenoxides have great potential in this area to produce novel mixed polycarbonate materials.

2.3.3. *β-Diiminate systems (BDI)*

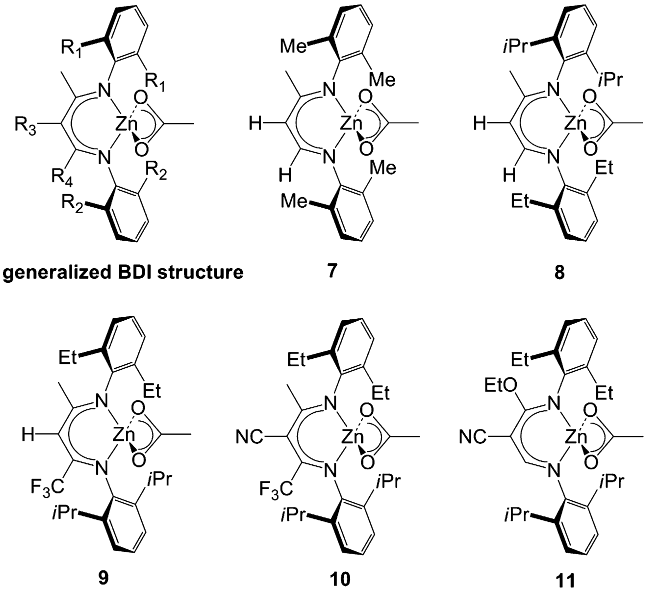
2.3.3.1. Influence of ligand framework. β-Diiminate ligands have recently gained considerable attention in the areas of coordination chemistry as well as in CO_2/epoxide chemistry [121]. The sterically demanding environment of BDI ligands inhibits *bis*-ligation of the complexed metals, allowing the BDI metal system to retain free coordination sites crucial for any catalytic process. The structure of the BDI ligand framework lends itself towards variation of both steric and electronic properties. This versatility is a helpful tool in understanding the underlying mechanisms of CO_2/epoxide copolymerization

Over the years, a broad range of BDI catalysts have been developed (Fig. 9). These generally incorporate a Zn metal cen-



(a) **(b)**

Fig. 8. Cd model complexes for epoxide insertions [119].



generalized BDI structure **7** **8**

9 **10** **11**

Fig. 9. Generalized β-diiminate (BDI) ligand framework and representative catalysts for epoxide/CO_2 copolymerization.

ter and demonstrate copolymerization activities at relatively low pressures (7 bar CO_2) and moderate temperatures (<50 °C) [47–49,77,122–125]. The majority of these catalysts are only active for CHO/CO_2 copolymerization but adjustment of the reaction conditions can significantly modify the selectivity towards PO, with a reduced temperature generally increasing the polymeric carbonate over cyclic carbonate ratio [49,97,126].

Minor modifications of the *N*-aryl ligands (R_1, R_2) significantly influence the catalytic activity. Methyl-substituted BDI ligands are inactive (**7**, TOF = 0 h^{-1}), whereas the incorporation of ethyl and isopropyl substituents at the *N*-aryl ring enhance the activity towards CHO/CO_2 copolymerization (**8**, TOF = 729 h^{-1}) [77,122,127]. Symmetrical ligands, where R_1 and R_2 are either Et or *i*Pr are inactive for both PC and PPC formation [49]. The introduction of an unsymmetrical ligand framework and electron-withdrawing groups on the diimine backbone (*e.g.* R_3 or R_4 = CN, CF_3) considerably enhance the activity, especially towards PO (**9**, TOF = 424 h^{-1}) [48,49,127,128]. Nevertheless, it should be mentioned that the incorporation of more electron-withdrawing groups results in inactivity of the catalyst, presumably due to the high Lewis acidity of the metal center which results in a very strong, irreversible Zn-epoxide bond (**10**). Other modifications of the backbone, such as utilization of the aminoamidoacrylate **11** and amidoimidomalonate pattern only slightly modulate the catalytic efficiency (**11**, TOF = 158 h^{-1}) [126,128,129].

2.3.3.2. Bimetallic considerations. Most reports only consider dimeric BDI species as being the active complex for CO_2/epoxide copolymerization. In the dimeric state the two metal centers are held in close proximity to each other by bridging anionic ligands, thus permitting facile interaction to form the respective polycarbonate. Molecular structure investigations have shown that, in the solid state, most β-diiminate complexes are dimeric. However, in solution a monomer–dimer equilibrium exists, being highly dependent on temperature as well as on catalyst concentration and steric properties of the ligand [47,77,122,125,128]. Dilution of the system by addition of monomer or an inert solvent shifts the position of equilibrium to the monomeric side, resulting in a reduced catalyst activity. At very low catalyst concentration, the equilibrium is completely shifted to the monomeric side and almost no catalytic activity is observed [130,131]. However at high catalyst concentrations, the epoxide conversion is limited due to resulting viscosity problems [66,130,131].

The possibility of some contribution from a monometallic mechanism with these catalysts cannot be discounted. Zn-BDI derivatives comprising sterically encumbering initiators, such as O*t*Bu or $OSiPh_3$, retain their monomeric form in both the solid and solution state. The monomeric complex **12** however is effective (but exhibits lower activities than the dimeric complexes) for the copolymerization of CHO and CO_2 (Fig. 10) [132,133]. In such monomeric catalyst species, the initial ring-opening step involving the bulky alkoxide initiators presumably proceeds *via* a monometallic transition state.

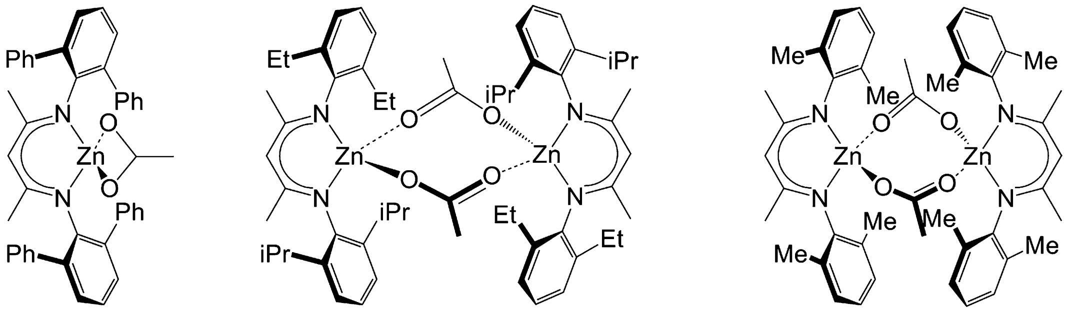
In other catalytic systems, the metal–metal distances differ from complex to complex but are generally found in the range of 3–5 Å [49,77,128]. For dimeric BDI complexes the distance between the two metal centers is flexible and the system is able to adjust the metal–metal distance necessary for copolymerization.

The metal–metal distance as well as the monomer–dimer equilibrium can be controlled by the *ortho*-substituents of the *N*-aryl ring, with more sterically congested complexes having increased zinc-zinc separations in the solid state (Fig. 10). Furthermore, the aggregatory state in solution shows a monomer–dimer equilibrium which is strongly influenced by the *N*-aryl substituents. Finally the nature of the bridging ligand influences the monomer–dimer equilibrium.

The introduction of bulky groups on the *N*-aryl substituents in BDI frameworks (Ph, 4-*t*Bu-Ph) affords predominantly monomeric complexes in solution which consequently exhibit lower activities than their dimeric counterparts. Asymmetrically substituted complexes with moderately bulky *i*Pr- and Et groups **13** exist in a loosely bound dimeric form and are effective catalysts for alternating CO_2/CHO copolymerization. Exchange of the *i*Pr substituent for a less bulky Me group on the *N*-aryl ring leads to more tightly bound dimers **14** which are completely unreactive for copolymerization [77,122]. Studies imply that the monomer/dimer equilibrium can be shifted by temperature with the dimeric complex being present at lower temperatures [77,134]. Kinetic studies with different BDI complexes show that the copolymerization follows a zero-order in CO_2, a first-order in epoxide and a 1.0–1.8 order dependence in total metal [77]. Therefore, variations in ligand sterics and electronics, alongside polymerization temperature, play a major role in discriminating one catalytic pathway over other alternatives.

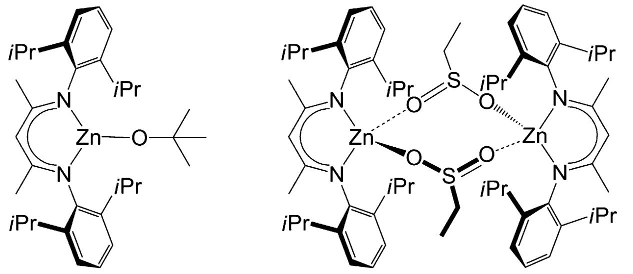
2.3.3.3. Influence of initiating group. The activity of the catalytic system can be modified and examined by the introduction of initiating groups. For instance, acetate serves as an initiating group which mimics CO_2. Mechanistic studies have revealed that the epoxide is attacked by the metal–acetate bond in the initial step of the copolymerization [77]. Complexes with alkoxide groups [122] and ethylsulfinato groups [98] as initiators exhibit comparable or slightly enhanced activities, respectively (Fig. 11, **16**).

In general the order of catalytic activity of BDI-Zn complexes of the general formula L_nZnX with different initiation groups decreases with X = SO_2Et > O*i*Pr > OMe > OAc, where the order of reactivity is the opposite of the order of the leaving ability of the initiation groups [98,135]. The bimodal distribution in GPC elugrams leads to the assumption that, for the ethylsulfinato complexes,



12 **13** **14**

Fig. 10. Monomeric complex **12** incapable of dimerization (generally considered as unreactive), loosely bound dimeric complex **13** (highly reactive), tightly bound dimeric complex **14** (unreactive) [77,122,132,133].



15 **16**

Fig. 11. BDI complex with bulky *i*Pr groups: monomeric **15** and ethylsulfinato-bridged dimeric form **16** [98,122].

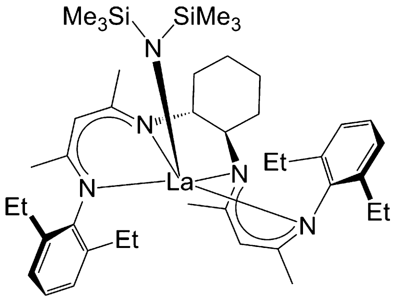


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Fig. 12. Lanthanoid-based BDI complex [137,138].

a monomer–dimer equilibrium is also present in which the two species possess different activities/polymerization rates, thus leading to different molecular weights in the obtained polymer [98].

2.3.3.4. Influence of metal center. The Lewis acidity of the metal center and its steric and electronic environment is of major importance for the activity of a complex. The introduction of Cu and Mg into BDI frameworks affords inactive systems for CO_2/epoxide copolymerization [133,136]. By contrast, rare earth metal complexes (Ln = La, Y) show some activity (Fig. 12, **17**, TOF = 12.7 h^{-1}) which is rather low in comparison to the most active zinc- and chromium-based catalyst systems [137,138].

Molecular structure and solubility studies suggest that only the monomeric species is present in these complexes in the solid state as well as in solution and therefore a monometallic mechanism is prevalent. However, blind tests with the precursors $Y[N(SiMe_3)_2]_3$ (TOF = 8.9 h^{-1}) and $La[N(SiMe_3)_2]_3$ (TOF = 0.86 h^{-1}) show that these complexes are also active for copolymerization reactions. These experiments show that to date the most successful BDI systems are still Zn-based.

The observations with various BDI system over recent years strongly imply a bimetallic mechanism in CO_2/epoxide copolymerization. The system is strongly influenced by modifications in the ligand framework, the initiator group, the bridging ligand and the incorporated metal center. New strategies therefore have focused on the development of dinuclear BDI and BDI-like structures (Section 2.4.1).

2.3.4. Salen systems

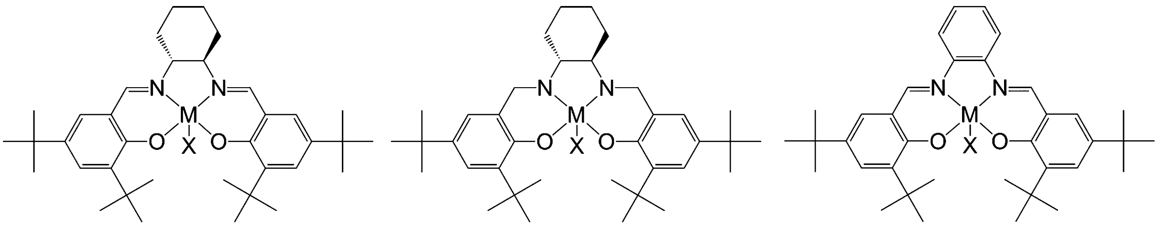
The salen system represents the most investigated homogeneous system for CO_2/epoxide copolymerization and considerable developments have been made with this system. An excellent and extensive review on (salen)MX catalyst systems has been provided by Darensbourg in 2007 [27]. This section of our review focuses on the newest developments and advances in the field of (salen)MX catalysts and only repeats data reported previously if necessary for a more in-depth understanding.

Although the first generation of salen catalysts demonstrated lower activities than representative BDI-Zn [49] (TOF = 160 h^{-1}, PPC = 71%) catalysts (*vide supra*), they introduced several advantages such as high polymer selectivity as well as excellent regioselectivity. Moreover, the copolymerization with salen complexes typically proceeds under mild temperatures and pressures.

Initial investigations focused on Cr as the incorporated metal center, but recently the (salen)CoX complex system has garnered more attention (Fig. 13, **18a**) [54,55,60,61,64,67,139]. The first cobalt catalyst **18a** with M = Co and X = OAc was reported by Coates et al. in 2003 and produced PPC with 99% carbonate content with TOFs around 70 h^{-1} [67]. In addition to exchange of the metal center, simple changes to the axial group X of (salen)MX complexes drastically affect the PPC/PC selectivity, which emphasizes the potential effect of cocatalyst addition (*e.g.* PPNCl, DMAP, *N*-MeIm, Fig. 6) [54,60,61]. For example, addition of substoichiometric PPNCl amounts to complex **18a** with M = Co and X = pentafluorobenzoate increases the activity up to TOFs of 620 h^{-1} [54]. From GPC analyses, it was concluded in this study that one copolymer chain is produced from one complex, whereas upon addition of cocatalyst, two copolymer chains are formed per metal center.

In general, the ideal ionic cocatalyst for high activities and selectivities consists of a bulky cation, which decreases in the order $[PPN]^+ > [nHept_4N]^+ > [nBu_4N]^+ > [nEt_4N]^+$ and an anion with poor leaving group ability, where $Cl^- > Br^- > I^- > ClO_4^-$ [61]. For neutral cocatalysts, bulky Lewis bases (*e.g.* DMAP) are preferred over their less sterically hindered counterparts (*e.g.* *N*-MeIm), as such bases render the catalyst system completely inactive due to their tight bonding to the metal center, which hinders effective epoxide binding and activation.

Studies conducted by us have shown that traditional (salphen)-Cr(III) complexes **18c** only gave activity in combination with DMAP, whereas reactions in the absence of cocatalyst showed no activity, producing neither PPC nor PC [73]. At higher cocatalyst concentrations however, the polymer chain end is in a coordination equilibrium with the cocatalyst and is detached from the metal center, which promotes depolymerization through back-biting [70]. This effect is attributed to a reduced activation barrier, which facilitates backbiting. Therefore no more than one or two equivalents of ionic cocatalysts should be added during copolymerization if a high polymer content is desired in the end-product.



18a **18b** **18c**

Fig. 13. Representative (salen)MX (**18a**), (salan)MX (**18b**) and (salphen)MX (**18c**) complex.

The cocatalyst can also give both a positive and a negative effect on the overall rate of copolymerization [74]. The initiation time is generally lengthened due to competitive insertion with epoxide at the metal-site *trans* to the nucleophile, which leads to an induction period. This effect is much more pronounced for (salen)MX-systems **18a** than for the corresponding saturated (salan)MX-systems **18b** [59]. Meanwhile propagation is enhanced considerably and as a result, accelerated overall activities can be observed [59,73,74,76]. The combination of (salan)MX-complexes in conjunction with (neutral) cocatalysts efficiently enhances the catalytic activity as well as the regio- and stereo-selectivity of the alternating copolymerization of CO_2 and PO [59,76]. This effect is attributed to the sp^3-hybridized amino donors in the salan ligand, and the resulting reduced Lewis acidity of the metal center and the facilitated reversible epoxide/cocatalyst binding. It was also proposed that the salan-ligand system is conformationally much more flexible than its rigid and planar salen counterpart. Therefore a penta-coordinate complex is formed, in which one vacant coordination site can be found in an equatorial or an axial position of the coordination octahedra [59]. The reduced nucleophilicity of the metal center and the coordinative flexibility could both facilitate dissociation and re-association of the cocatalyst and the growing polymer chain, thereby increasing back-biting, but simultaneously considerably enhancing the activity [50,59,76].

During copolymerization, the Lewis base coordinates to the (salen)MX metal center in the axial position (*trans* to the propagating species) forming the resulting complex (salen)M-XNu, which results in an improved electronic environment for propagation. The (salen)M-X can also be ligated by corresponding epoxides or coordinating solvents such as THF [53,140]. The competitive equilibrium between (salen)MX-epoxide and (salen)MX-Nu is shifted depending on the catalyst/cocatalyst/epoxide ratio and can have profound effects on the PPC/PC (respectively PCHC/CHC) ratio and overall activity, with an excess of cocatalyst generally leading to reduced activity and higher PC (respectively CHC) content [30,57,65,70,73]. In the presence of very strongly coordinating nucleophiles, the ligation process is irreversible and subsequent exchange by epoxide is precluded.

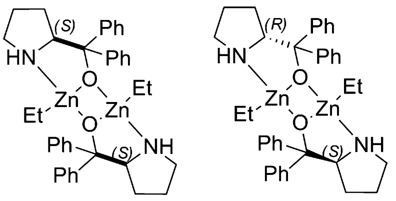
These conclusions, in addition to the observations from related homogeneous systems, have recently lead to reports of binary linked salen systems which are reviewed later in this article (Section 2.4.2).

2.4. New strategies with homogeneous catalyst systems

2.4.1. Dinuclear BDI catalysts and similar systems

As indicated in the previously discussed BDI catalysts, a bimetallic mechanism is needed for enhanced activities in CO_2/epoxide copolymerizations. It is for this reason that dinuclear BDI and BDI-like systems have been developed over the last years.

In 1999 Nozaki et al. used diethyl zinc and a chiral amino alcohol (*S*)-diphenyl(pyrrolidin-2-yl)methanol (Scheme 8) for the copolymerizations of cyclohexene, cyclopentene and *cis*-butene oxide with CO_2, respectively [141]. The copolymerizations with cyclohexene oxide were carried out under 30 bar CO_2 using equimolar ratios of diethyl zinc to amino alcohol. The resulting copolymers were the first alternating polycarbonates with isotactic units up to 70%.



19 20

Fig. 14. Dinuclear homo- and hetero-chiral zinc complexes [142].

The hydrolysis of the copolymers with aqueous NaOH leads to the corresponding diols. In the case of CHO the *meso*-cyclohexane diol was not obtained, which clearly confirmed S_N2-type ring opening of the epoxide. The *trans*-cyclohexane diol yielded an enantiomeric excess of up to 70% (*R*,*R*)-cyclohexane diol.

In a further study in 2003, Nozaki and co-workers crystallized the desired complex **19** from the synthesis of diethyl zinc and (*S*)-diphenyl(pyrroridin-2-yl)methanol (Fig. 14) [142]. The obtained catalyst adopts a dimeric structure with the two zinc centers adopting a distorted tetrahedral geometry. The zinc-zinc distance in this catalyst was determined to be 3.00 Å.

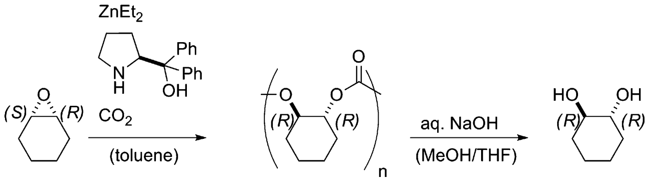
The copolymerization reaction of CHO and CO_2 was performed in toluene at 40 °C and yields perfectly alternating polycarbonate. However the isotactic ratio never exceeded 50% and was therefore lower than in the previous report. The MALDI–TOF mass spectrum showed a series of peaks, which could be attributed to copolymers initiated by the amino alcohol ligand. Therefore presumably the enantiomerically pure ligand dissociates from the active metal site and the chiral information around the zinc center is lost. To overcome this problem, ethanol was added to the reaction mixture, which lead to the formation of new Zn-OR moieties. These new Zn-alkoxide groups could initiate the copolymerization, whereas ethyl groups were unable to initiate the reaction.

The MALDI–TOF mass spectrum of these polymers showed a series of peaks with an ethoxy-end group and an increased isotactic ratio in the polymer of 75%. Several different alcohols were tested in the *in situ* initiation for the copolymerization, with a higher nucleophilicity of the alkoxide species leading to better copolymerization results.

Nozaki and co-workers used the *R*- and *S*-enantiomer of the ligands to form a hetero-chiral complex (Fig. 14, **20**) [143]. This catalyst is less active than those previously reported, however the complex indicated an asymmetric amplification, which is the first reported for the copolymerization process. However no TOF values were given for this kind of catalyst.

In 2003 Coates et al. introduced a new type of ligand for dinuclear structures [125]. The β-oxo-δ-diimine (BODDI) ligands can be coordinated with diethyl zinc to form a dinuclear complex. The reaction of these complexes with acetic acid affords zinc acetate systems (Fig. 15, **21**) which are potentially active in the copolymerization of CO_2, but corresponding experiments have not been reported to the best of our knowledge.

In 2005 Ding and co-workers used Trost's intramolecular dinuclear zinc complex for the copolymerization of CHO and CO_2



Scheme 8. Chiral amino alcohol complex [141].

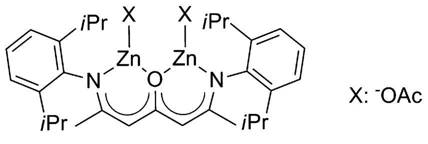


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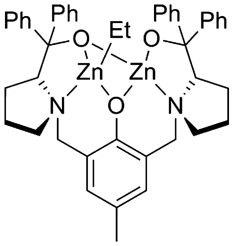
Fig. 15. Dinuclear BODDI catalyst [125].



22

Fig. 16. Dinuclear Trost complex [144].

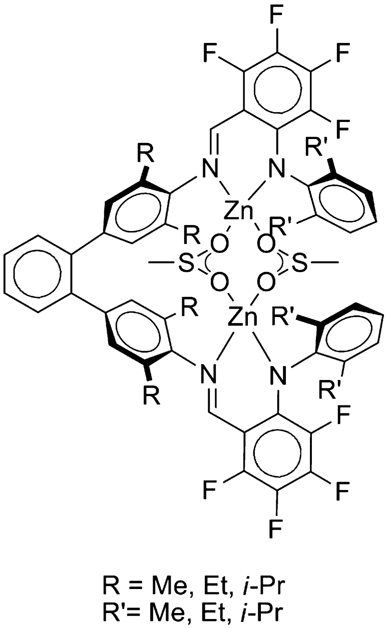
(Fig. 16, **22**) [144]. The catalyst was prepared *in situ* by complexation of the ligand with $ZnEt_2$ and the copolymerization reaction carried out under 30 bar CO_2 in toluene at 80 °C and a catalyst/CHO loading of 1:500. The TOFs at these conditions were around 140 h^{-1} and the conversion and selectivity for poly(cyclohexene carbonate) up to 99%.

The dinuclear Zn catalysts **22** were also highly active in diluted solutions and retained their selectivity even under very low CO_2 pressures (*i.e.* 1 bar), even though the activities decreased to 3 h^{-1}. The analogous Mg complex was also active in CHO/CO_2 copolymerization [145].

By substitution of the prolinol framework, varied ligand structures were tested in copolymerization reactions. Electron donating groups lead to a decrease in epoxide conversion, however the introduction of electron withdrawing groups promoted consecutive epoxide insertions, yielding a polymer with a high degree of polyether linkages.

In 2005 Lee et al. reacted the anilido-aldimine ligands with dimethyl zinc and subsequently with SO_2 to generate “closed” and “open” dinuclear zinc complexes (Fig. 17, **23** and **24**) [130]. A combination of NMR spectroscopic studies at varying temperatures and X-ray crystallographic analysis demonstrated the dinuclear nature of these catalysts, with zinc-zinc distances of 4.88 Å and 4.69 Å for the “open” and “closed” structure, respectively. The distances are in the same range as the previously reported β-diketiminato ethyl sulfinato zinc complexes (4.98 Å) [98].

These dinuclear catalysts are highly active for the copolymerization of CHO and CO_2 even under highly diluted conditions (catalyst/CHO = 1:17 000) and showed TOFs of up to 200 h^{-1} with molecular weights of up to 280 000 g/mol and a carbonate content around 90%. The copolymerization activity is very sensitive to the nature of the *ortho*-substituents of the aromatic moiety and the “open” catalyst is active, whereas the “closed” is completely inactive. The difference in efficiency is probably due to better access to the metal centers in the “open” structure.

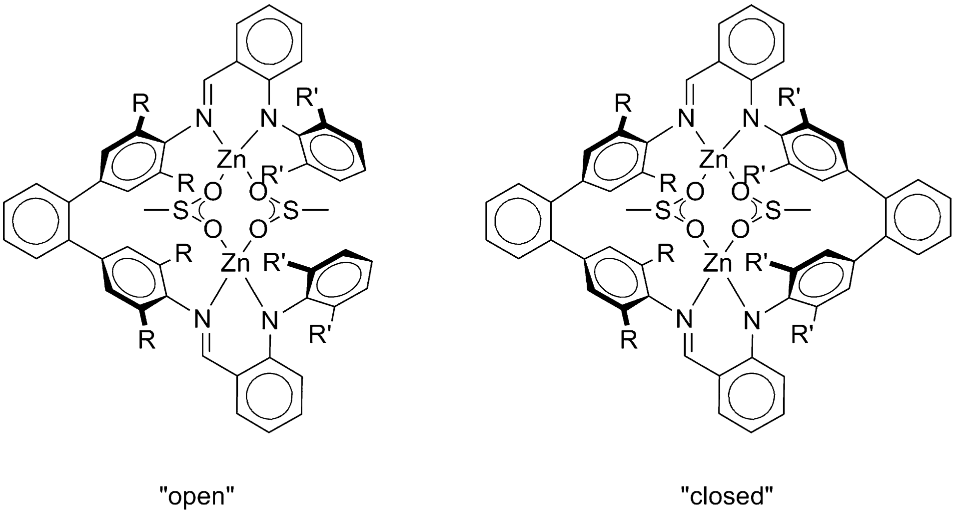


25

Fig. 18. Fluorinated dinuclear zinc complex [146].

In 2006 Lee et al. prepared fluorinated anilido-aldimine ligands, which through complexation with dimethyl zinc afforded dinuclear complexes [146]. Reaction of these complexes with SO_2 converts the complexes into active catalysts for the copolymerization of CHO and CO_2 (Fig. 18, **25**).

The Zn–Zn separation of compound **25** is slightly smaller (about 4.82 Å), compared to the non-fluorinated complex **23**.



"open"
23

"closed"
24

R = Me, Et, *i*Pr
R'= Me, Et, *i*Pr

Fig. 17. “Open” and “closed” dinuclear zinc complexes [130].

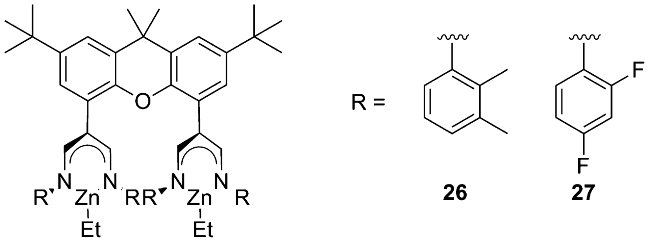


Fig. 19. Dinuclear xanthdim complexes [147].

Again, copolymerization reactions can be carried out, with the highest TOF of 2860 h^{-1} being obtained at high dilutions (catalyst/CHO = 1:50 000). The electron-withdrawing fluorine groups presumably influence the Lewis acidity of the metal center, thereby increasing its CO_2/epoxide binding strength. At the same time the system is less sensitive to chain transfer agents, due the reduced basicity of the ligand nitrogen donors. As a drawback, the percentage of carbonate linkages is lower for the fluorinated than for the non-fluorinated system, which is attributed to the increased reaction speed and the lowered selectivity.

Limberg, Hultzsch and co-workers reported in 2007 xanthdim ligands which afforded dinuclear zinc complexes after complexation with diethyl zinc (Fig. 19, **26** and **27**) [147]. Zn–Zn distances of 4.92 Å and 5.60 Å were reported for the fluorinated and non-fluorinated complexes, respectively. The ligand structure allows the parallel orientation of two metal centers, in comparison to the above-mentioned dinuclear structures in which they are generally orientated face to face.

The reaction of the zinc ethyl moieties in the dinuclear xanthdim complexes with SO_2 was unsuccessful due to the formation of oligomeric or polymeric coordination species. However the complexes comprising zinc ethyl groups were tested successfully in the copolymerization of CHO and CO_2. In traditional mononuclear BDI complexes the ethyl groups are not able to bridge two monomers to form an active dimer. However this unfavorable dimerization with ethyl groups can be overcome by activation with SO_2, which affords an active dimeric system with bridging ethylsulfinato-groups [98]. However, for complexes **26** and **27** the dinuclear nature implies an activity even with non-activated ZnEt moieties.

The non-fluorinated catalysts lead to poly(cyclohexene carbonate) with a relatively low content of carbonate linkages (50%). This problem could be overcome by dilution of the reaction mixture with toluene which increases the content of the carbonate groups (up to 91%) with a low TOF of 9 h^{-1}. The fluorinated complex mainly affords polyether formation (8% carbonate linkages), the reason for this being the higher Lewis acidity of the metal center and therefore the accelerated ring opening of the epoxide [147]. The experiments show that these dinuclear xanthdim catalysts with parallel BDI-type ligands are only moderately active, which is attributed to overcrowding of the reaction pocket [147].

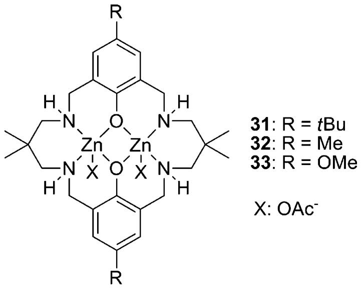


Fig. 21. Dinuclear Robson-type complexes [149,150].

Harder and co-workers used bridged β-diiminato ligands for the preparation of dinuclear zinc and calcium complexes (Fig. 20) [148]. The zinc complexes were all characterized by X-ray crystal diffraction, with the Zn–Zn distances for the 1,4-phenylene, 1,3-phenylene and 2,6-pyridylene complexes being 8.17 Å, 6.10 Å and 3.79 Å, respectively.

Again, the proposed bimetallic mechanism is an important aspect of such dinuclear zinc catalysts. Dinuclear *para*-$(ZnEt)_2$ **28** and *meta*-$(ZnEt)_2$ **29** complexes initiate CHO/CO_2 copolymerization without SO_2 activation, a trend which has already been reported for the previously mentioned xanthdim catalysts **26** and **27**.

The activity is considerably higher for the *meta*-$(ZnEt)_2$ complex **29** (TOF = 129 h^{-1}) than for the *para*-$(ZnEt)_2$ complex **28** (TOF = 36 h^{-1}), presumably because the zinc-zinc distance in the *meta*-substituted ligand is much more suitable for the copolymerization. This illustrates the importance of a controlled metal–metal distance in these catalyst systems. Activation with SO_2 increases the activity of *meta*-$(ZnSO_2Et)_2$ (TOF = 181 h^{-1}) and a three-fold dilution raises the activity even further (TOF = 262 h^{-1}) delivering polymer with a molecular weight of up to 100 000 g/mol and 99% carbonate linkages.

Complex **30**, which comprises a pyridine fragment in the center of the ligand framework is inactive, presumably due to the presence of the heterocyclic *N*-atom. This alters the complex conformation or coordinates to the Zn atoms thereby reducing their Lewis acidity, thus inhibiting CHO coordination and subsequent ring-opening.

In 2009 Williams et al. reported a dinuclear zinc catalyst with a reduced Robson-type ligand structure for the copolymerization of CHO and CO_2 (Fig. 21, **31**) [149], with an acetate group initiator at the zinc centers and the Zn–Zn distance being around 3.11 Å [150].

Copolymerization reactions can be carried out with **31** at pressures as low as 1 bar CO_2, with activities and TOFs up to 25 h^{-1} and a high copolymer to cyclic carbonate ratio (TOF = 140 h^{-1} at 10 bar CO_2). Room temperature NMR spectra of this complex showed broad resonances, whilst in higher temperature measurements, the peaks coalesce to observable resonances. This behavior indicates a fluxional complex structure in the solution state.

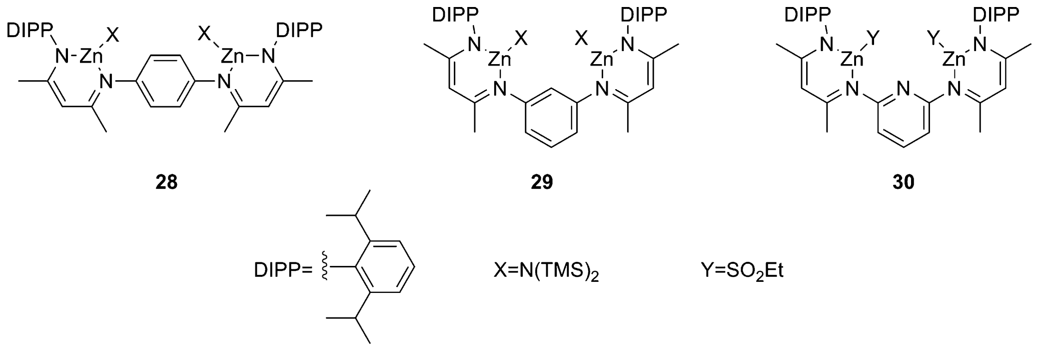


Fig. 20. Bridged dinuclear Zn-BDI complexes [148].

In further work, Williams and co-workers altered the substituents in the *para*-position of the phenolic moieties (Fig. 21, **31**–**33**) [150]. Introduction of a methyl **32** or methoxy group **33** in the *para*-position of the aryl backbone of the ligand moderately decreases activity in the copolymerization of CHO and CO_2 (**32**: TOF = 8.3 h^{-1}, **33**: TOF = 6 h^{-1}). This effect is associated with the lower Lewis acidity of the metal center and a decreased binding and activation of epoxide and CO_2.

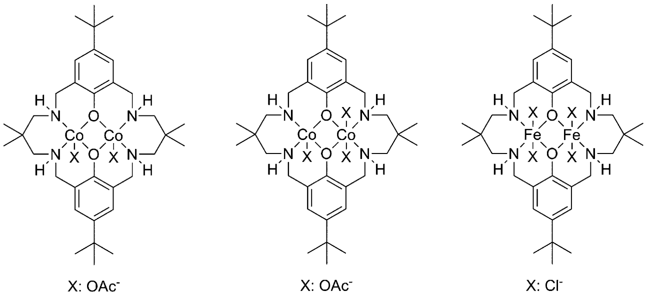
In 2010 Williams et al. used the same ligand structure for the synthesis of dinuclear cobalt and iron complexes for the copolymerization of CHO and CO_2 (Fig. 22, **34a**–**c**) [151]. Complexes comprising cobalt acetate centers were selected for these studies in order to compare the complexes with the previously reported zinc catalysts. Complexation was achieved by reaction of the ligand with cobalt(II) acetate which affords the desired Co(II) compound **34a** with a TOF of 410 h^{-1} at 1 bar CO_2. The subsequent aerial oxidation leads to a mixed valency Co(II)/Co(III) complex **34b** with a slightly increased TOF of 480 h^{-1} at this pressure and a TOF of 1700 h^{-1} at 10 bar.

The Co-Co distances in **34a** and **34b** are close to 3 Å. Copolymerizations of CHO and CO_2 under 1 bar CO_2 pressure and at 80 °C demonstrate activities of an order of magnitude greater than those of the zinc analogues (TOF up to 172 h^{-1}). Additionally the selectivity of the cobalt catalysts (1% cyclic carbonate) for the polymer formation is higher than that of the zinc complexes (4% cyclic carbonate). The activity of these complexes at low pressures is attributed to the coordinative flexibility of the ligand system. Furthermore, the two closely linked metal centers facilitate a bidentate carboxylate binding mode, thus lowering the energy barrier for CO_2 insertion. The higher activity of the cobalt catalysts is attributed to the enhanced nucleophilicity of the metal-bound carbonate group and thus better incorporation of the epoxide.

Recently, Williams et al. reported two iron(III) centers in this ligand framework and the corresponding copolymerization data (Fig. 22, **34c**) [152]. This system was able to produce copolymer with CHO/CO_2 and demonstrated a TOF of 107 h^{-1} at 80 °C, 10 bar and a [Fe]/[CHO] ratio of 1000. The system did not yield copolymer with PO, but introduction of one equivalent of PPNCl per Fe-center allowed the conversion of PO into cyclic propylene carbonate with TOFs around 25 h^{-1}.

Independently, we recently reported a mononuclear Fe-system that shows similar behavior towards PO and produces cyclic propylene carbonate in relatively high yields (Fig. 23, **35**) [153]. Preliminary experiments also indicate the copolymer formation with CHO/CO_2 and a strong dependence on the cocatalyst system. These studies show for the first time that CO_2/epoxides can be copolymerized into polycarbonates *via* iron-complexes. In the near future, this could allow an ecological as well as economical favorable alternative to the preferentially used toxic metals cobalt and chromium.

These reports all indicate that future work should focus on dinuclear ligand structures or binary linked systems as presented in the next section, especially when factors such as high dilutions and temperatures are considered.



34a **34b** **34c**

Fig. 22. Dinuclear Robson-type complex with Co- and Fe-centers [151,152].

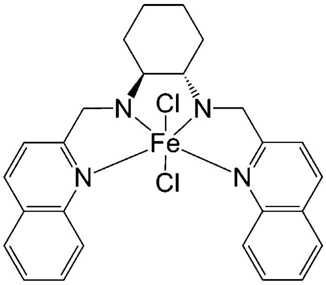


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Fig. 23. Mononuclear tetraamine-iron complex [153].

2.4.2. Binary linked salen systems

In order to increase the activity of the previously investigated salen complexes, different aspects have been addressed. As discussed previously (*vide supra*), a binary or a dinuclear catalytic system is presumably needed for CO_2/epoxide copolymerization with high activities. At the same time higher catalyst dilutions are needed to overcome diffusion limitations and enhance TON, and therefore TOF values. At such high dilutions, all associative processes are disfavored by the mass action law. The probability of formation of an active species by interaction of two catalyst molecules or a catalyst and a cocatalyst molecule is therefore decreased and activities tend to drop.

In order to overcome the low activities typically observed at low catalyst concentrations, new strategies are centered on tethering the cocatalyst to the same ligand framework. In this way, even at high dilutions, the interacting species remain in close proximity and these systems therefore retain their activity.

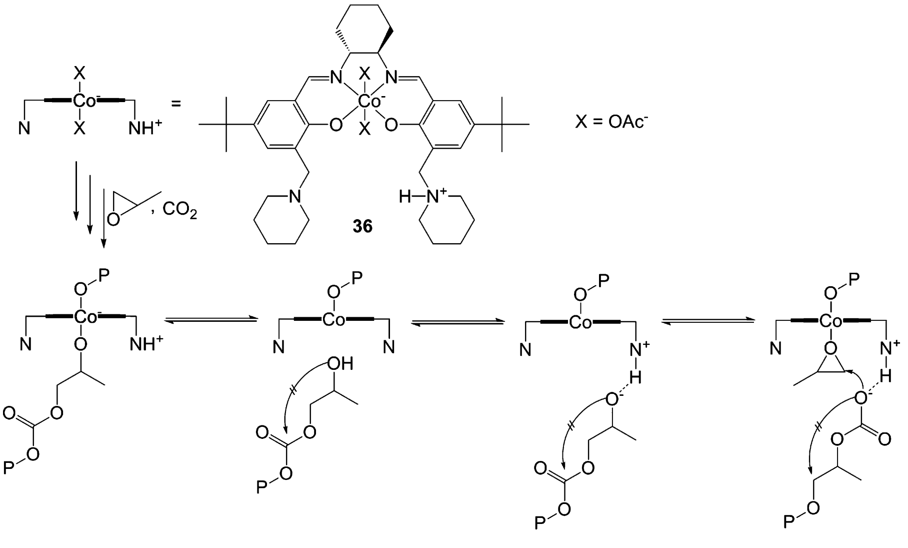
Nozaki et al. synthesized a piperidinium end-capped (salen)Co(III) complex which copolymerizes PO and CO_2 without the generation of cyclic propylene carbonate (PC) with a TOF of 254 h^{-1} (Scheme 9) [82].

The high polymer selectivity observed with **36** is presumably achieved due to the piperidinium arm, which inhibits the formation of cyclic carbonate by protonation of the anionic propagating species when it dissociates from the metal center.

This protonation leads to a reduced nucleophilicity of the chain-end and hinders chain back-biting, a process leading to cyclic carbonate formation. Therefore the [epoxide]/[catalyst] ratio can be raised to 6500 and the polymerization temperature can be increased to 60 °C, whereupon activities reach TOF = 600 h^{-1} and a high PPC/PC ratio is retained. Complete epoxide conversion could be achieved by addition of solvents such as DME (1,2-dimethoxyethane), toluene or dichloromethane. In this way, the polymerization mixtures become less viscous and diffusion of the monomers to the active site is retained. Another advantage of this system is that following complete monomer consumption, another monomer feedstock (*e.g.* 1-hexene oxide) can be added resulting in the formation of block terpolymers.

A similar strategy has been employed in related salen-type systems. A quaternary ammonium cation has been anchored on the salen ligand framework **39** resulting in higher activities, higher PPC/PC content and the possibility of terpolymerizing CHO, PO and CO_2 (Fig. 24) [154–157].

In contrast to the piperidinium-anchored catalyst **36** reported above, inhibition of back-biting occurs due to higher coulombic interactions of the growing chain with the catalyst molecule **39** as a whole. Therefore the polymer is considered to not diffuse to any great distance from the active metal site in complex **39**. Additionally the nucleophilicity of the anionic chain end is decreased



Scheme 9. Piperidinium end-capped (salen)Co(III) [82].

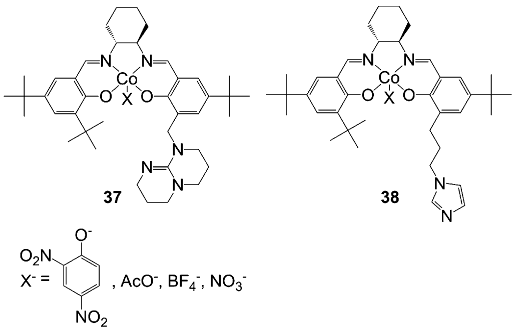


Fig. 24. Representative (salen)Co(III) complexes with tethered sterically hindered organic bases and quaternary ammonium salts [154–157].

through interaction with the positively charged groups. In this way the activity of the quaternary ammonium salt anchored (salen)CoX complex remains high (**37**, X = OAc, TOF = 7100 h^{-1}; **38**, X = NO_3, TOF = 7 h^{-1}; **39**, X = 2,4-dinitrophenoxy: TOF = 3500 h^{-1}) even at high [monomer]/[catalyst] ratios of >25 000 and high temperatures >80 °C. The copolymers produced have a molecular weight of around 50 000–100 000 g/mol and narrow PDI's around 1.3. At such conditions the traditional binary systems comprising (salen)CoX and PPNCl produce only cyclic carbonate or are completely inactive.

A considerable improvement to these anchored motifs was made by Lee et al., who included four (or more) quaternary ammonium groups attached to the salen framework (Fig. 25, **40**–**42**) [158–160].

This anchoring strategy gives rise to a catalyst which is able to be recovered after copolymerization whilst retaining its activity. At the same time, the catalyst residues can be removed from the produced polymer in a simple manner. In contrast to other salen systems, such binary linked complexes are strongly influenced by the nature of the *ortho*-substituent in the salicylaldimine moiety. The highest TOFs were achieved with a methyl substituted salen **42** and four anchored ammonium salt units; 25% PO conversion was observed in 15 min at [PO]/[cat] ratio of 25 000 which corresponds to TOF = 26 000 h^{-1}, a PPC/PC selectivity of greater than 99% and a carbonate content above 99% [158]. The TON and TOF could be considerably improved by increasing the reaction time at higher PO/catalyst loadings of up to 100 000 (TOF = 22 000 h^{-1}, TON = 22 000). At such high TONs, the copolymer produced has a molecular weight of 285 000 g/mol (PPC/PC selectivity 96%) and the cobalt level in the isolated polymer reaches 26 ppm and can even be lowered by separating the residual cobalt complex by filtration of the polymerization mixture through a short pad of silica gel. The salen complex can be recovered and reactivated with 2,4-dinitrophenol and exhibits a comparable catalytic performance.

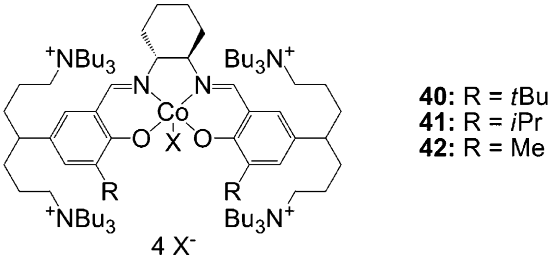
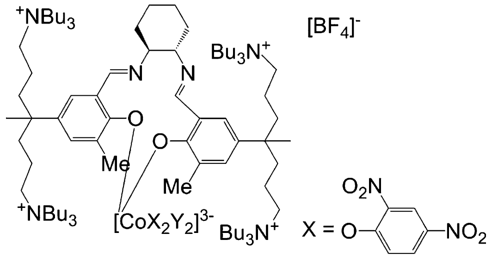


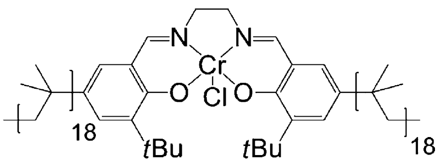
Fig. 25. Salen with four anchored ammonium salt units [158–160].

The authors propose that in this type of catalyst, the imino-nitrogens do not coordinate to the metal center, instead the counter anions of the quaternary ammonium cations ligate the cobalt (in this case 2,4-dinitrophenolate, DNP) (Fig. 26) [160]. As a result, the tetradendate coordination of regular salen systems shifts into an unusual bidentate coordination mode, which is presumably responsible for the high activity (Fig. 25, **43** and **44**). Introduction of bulkier aryl substituents such as *t*Bu (**40**) or *i*Pr (**41**) prevent bidentate coordination in favor of tetradentate coordination. As a result the activities drop, thus emphasizing the importance of a bidentate binding mode for this catalyst system. The tethered cationic side arms hold the anionic chain ends in the coordination sphere of the metal center, thus allowing rapid and efficient copolymerization. The growth of the polymer chains commences from the DNP initiator in the catalysts and hence most polymer chains contain



43: (Y = X)
44: (Y = X...H...X)

Fig. 26. Unusual binding mode of binary linked salen complexes [160].



45

Fig. 27. Polyisobutylene supported salen Cr(III) complex [161].

a DNP end group. However a bimodal distribution is found in GPC elugrams, a certain amount being initiated by DNP, the rest showing initiation *via* hydroxyl groups that result from chain-transfer reactions with water. However as DNPs are highly explosive in the dry state, new catalysts with inexpensive anions (*e.g.* 4-nitrophenolate, 2,4-dichlorophenolate) that replace the hazardous DNP have been investigated [160].

Another strategy to separate the catalyst after copolymerization has been investigated by Darensbourg et al. The salen derivative **45** contains two polyisobutylated (PIB) phenol groups and is phase-selectively soluble in the heptane phase of a heptane/DMF or similar mixtures (Fig. 27) [161].

Complex **45** could be completely separated from the polymer by extraction after copolymerization at 80 °C, 35 bar CO_2. The same initial rates of polymerization were observed as for Cr(salen) complexes without PIB-anchors. Recycling of the catalyst however lead to a 20–30% reduction in polymerization activity, presumably due to acidolysis of the Cr(III) center from the PIB-salen complex.

The addition of cocatalysts to traditional salen complexes can considerably influence the efficiency of the system. Through tethering of cocatalyst functionalities to the salen ligand framework, the activity and selectivity towards polymerization can therefore be increased by a factor of several orders of magnitude in comparison to earlier systems indicating a potentially successful direction for future catalyst development.

2.4.3. Dinuclear salen systems

Jacobsen et al. suggested that the activity of catalytic CO_2/epoxide copolymerization can be increased by utilization of flexibly linked dinuclear species and prepared bifunctional salen complexes [51,162]. Other early experiments reported a combined gas-phase and solution-phase study of mono- and dinuclear (salen)Cr^{III} complexes, which suggested the important role of dinuclear species in the homopolymerization of epoxides [163].

In 2010, Nozaki et al. further investigated this system and synthesized a series of complexes with different spacer lengths (Fig. 28, **46**–**49**) [164]. Copolymerization experiments under 53 bar and at 22 °C in 2 h with a [PO]/[Co] ratio of 1000 indicated the optimal spacer length to be $n = 4$ (**48,** TOF = 180 h^{-1}), in comparison to $n = 10$ (**46**, TOF = 150 h^{-1}), $n = 7$ (**47**, TOF = 130 h^{-1}) and $n = 3$ (**49**, TOF = 140 h^{-1}). The racemic mixture of the mononuclear catalyst **50** shows a comparable activity at such copolymerization conditions (TOF = 100 h^{-1}). The optimal distance between two metal centers not only accelerates the alternating copolymerization, but also the homopolymerization of PO, which results in a somewhat lower content of carbonate linkages in the resulting polymer.

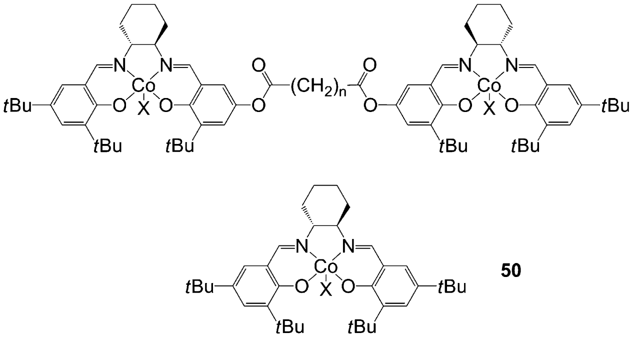
The main characteristic of the dinuclear cobalt complex however was the retention of catalytic activity even under low concentrations [PO]/[Co] = 3000 (*e.g.* for **48**, TOF = 150 h^{-1}), whereas the efficiency of the mononuclear complex **50** decreases (TOF = 20 h^{-1}) under such conditions. Addition of 0.5 equivalent PPNCl cocatalyst further increased the activity of the dinuclear system (**48**, TOF = 1280 h^{-1}), as well as that of the mononuclear system (**50**, TOF = 1180 h^{-1}). This indicates, as previously discussed that in presence of cocatalysts a binary mechanism is operating, which is independent of the dinuclearity of the system. Therefore activity and selectivity can easily improved by controlling the amount and nature of added cocatalyst.

In 2010, a similar study was independently conducted by us. A new synthetic route allowed the preparation of dinuclear salphen(Cr) complexes with different linker lengths (Fig. 29, **51** and **52**) [165]. Even though such systems generally show a slightly lower activity than mononuclear salen systems, the same trend upon dilution is observed. Complex **51** with a spacer length of $n = 6$ shows a TOF of up to 49 h^{-1} under copolymerization conditions of 40 bar and 60 °C, with a [PO]/[Cr] ratio of 2000. At a [PO]/[Cr] ratio of 20 000, the TOF even increases to 82 h^{-1}. In contrast, the activity of the mononuclear complex **53** drops from TOF = 67 h^{-1} to TOF = 7 h^{-1} upon dilution.

These investigations strongly indicate the copolymerization of CO_2 and epoxides to proceed *via* a bimetallic mechanism.

2.4.4. Immobilized salen and BDI systems

Immobilization of catalysts on a surface provides an effective means to recover and regenerate the catalyst after copolymerization. Immobilization of Zn-BDI catalysts for the copolymerization of epoxides and CO_2 onto silica materials (mesoporous SBA-15

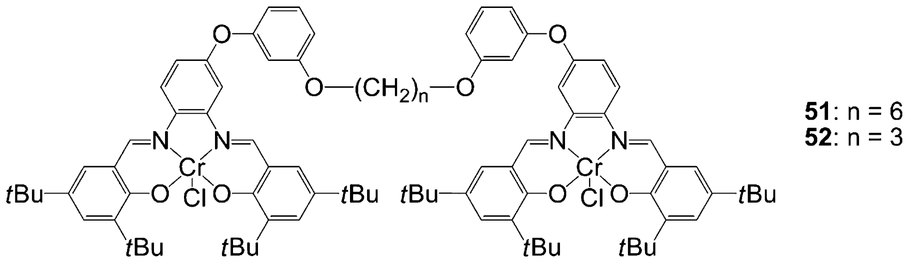


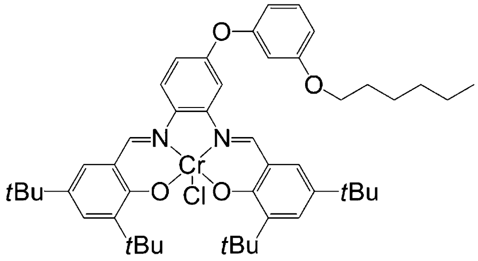
46: n = 10
47: n = 7
48: n = 4
49: n = 3

X = $OC(=O)C_6F_5$

50

Fig. 28. Mono- and dinuclear salen(Co) complexes [164].





53

Fig. 29. Mono- and dinuclear salphen(Cr) complexes [165].

and controlled-pore glass (CPG)) (Fig. 30, **54**) gave moderate polymerization activities in comparison with their homogeneous analogues, presumably as a result of pore diffusion effects [166]. Recovery and potential regeneration of the catalyst were not reported.

García et al. described recyclable salen(Cr)Cl and salen(Al)X derivatives which were covalently anchored to a silicon polymer-support *via* a linker (Fig. 31, **55** and **56**) but only exhibited activity towards cyclic carbonate production from styrene oxide [52,167,168].

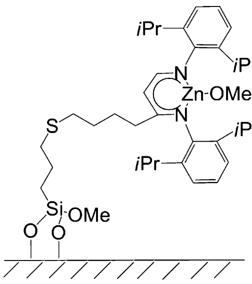


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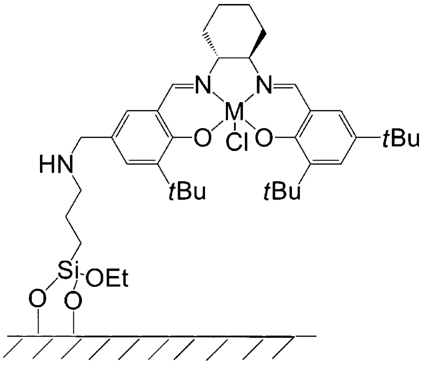
Fig. 30. Immobilized BDI complexes [166].



55: M = Cr
56: M = Al

Fig. 31. Silica supported Cr- and Al-salen complexes [52,167,168].

3. Summary and outlook

From the data covered in this review, it is apparent that huge progress has been made in CO_2/epoxide copolymerization catalysis. After 40 years of intense research, clear ligand/complex families have been developed, mechanistic insights have been gained and significant advances in activity and selectivity have been made.

Investigations with traditional phenoxide and BDI catalysts have indicated that a bimetallic mechanism is probable in CO_2/epoxide copolymerization. The same mechanism has also been proposed for the long known but poorly understood heterogeneous zinc-dicarboxylate systems. Unfortunately an intrinsic activity limit is hindering further development of these systems.

The development of dinuclear BDI complexes indicates that the introduction of two metal species into a single ligand framework can considerably increase yield and selectivity towards copolymerization. The main advantage of such BDI systems is their high activity and the commonly used Zn metal as the active center, which renders these catalysts suitable for industrial usage. Unfortunately, to date most of these systems only demonstrate activity for CHO/CO_2 copolymerizations with only cyclic carbonate being produced in PO/CO_2 processes.

The addition of cocatalysts to traditional porphyrin and salen complexes can considerably influence the efficiency of these systems. Through careful modification of the long established salen ligands, anchored binary catalytic systems have been developed that are able to increase the activity towards polymerization by a factor of several orders of magnitude in comparison to earlier systems.

Immobilization of salen and BDI systems affords materials with lower activities for copolymerization, but make a separation of the catalyst from the product achievable.

All of these results imply that through the development of dinuclear and binary anchored catalyst systems, high catalytic activities can be achieved for epoxide/CO_2 copolymerizations even at high dilutions and temperatures. However, most of these systems still are incapable of copolymerizing propylene oxide with CO_2. Moreover, many of the systems comprise a toxic metal center and a high degree of metal content in the final polymer, which disfavors their industrial application. Furthermore, a rather lengthy synthesis route towards the ligand framework renders most of the complexes unsuitable for industrial purposes. Therefore future research activity will have to focus on the development of systems with easily accessible complexes that comprise non-toxic metals, which additionally can be completely separated from the polymer.

In conclusion, the advances that have been made in the research field of CO_2/epoxide copolymerization catalysis over recent years are very promising and allow us to look forward to a new class of polymeric materials which are accessible on an industrial scale in the near future.

References

[1] H. Danner, R. Braun, Chem. Soc. Rev. 28 (1999) 395.
[2] T.U. Gerngross, S.C. Slater, Sci. Am. 283 (2000) 37.
[3] R.A. Gross, B. Kalra, Science 297 (2002) 803.
[4] M. Okada, Prog. Polym. Sci. 27 (2001) 87.
[5] B.D. Santer, K.E. Taylor, T.M.L. Wigley, T.C. Johns, P.D. Jones, D.J. Karoly, J.F.B. Mitchell, A.H. Oort, J.E. Penner, V. Ramaswamy, M.D. Schwarzkopf, R.J. Stouffer, S. Tett, Nature 382 (1996) 39.
[6] W.S. Broecker, Science 278 (1997) 1582.
[7] G.A. Meehl, W.M. Washington, Nature 382 (1996) 56.
[8] K. Kacholia, R.A. Reck, Climatic Change 35 (1997) 53.
[9] Department of Energy (US), International Energy Agency Report, 0484, 2009.
[10] Wissenschaftlicher Beirat der Bundesregierung Globale Umweltveränderungen, Sequestrierung von CO_2: Technologien, Potenziale, Kosten und Umweltauswirkungen, 2003.
[11] J. Paul, C.-M. Pradier, Carbon Dioxide Chemistry: Environmental Issues, R. Soc. Chem., 1994.
[12] W. Keim, A. Behr, G. Schmitt, Principles of Industrial Chemistry. Industrial Products and Processes, Sale und Sauerlander, Frankfurt, 1986.
[13] B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Chem. Rev. 110 (2010) 4554.
[14] H. Arakawa, et al., Chem. Rev. 101 (2001) 953.
[15] A.I. Cooper, J. Mater. Chem. 10 (2000) 207.
[16] C. Bolm, O. Beckmann, O.A.G. Dabard (Eds.), Angew. Chem. Int. Ed. 38 (1999) 907.
[17] R. Dittmeyer, W. Keim, G. Kreysa, A. Oberholz, Winnacker-Küchler: Chemische Technik 4 (2005).
[18] T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312.
[19] C. Bruckmeier, M.W. Lehenmeier, R. Reichardt, S. Vagin, B. Rieger, Organometallics 29 (2010) 2199.
[20] T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
[21] M.S. Super, E.J. Beckman, Trends Polym. Sci. 5 (1997) 236.
[22] S. Inoue, CHEMTECH 6 (1976) 588.
[23] E.J. Beckman, Science 283 (1999) 946.
[24] W. Kuran, Prog. Polym. Sci. 23 (1998) 919.
[25] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.
[26] G.W. Coates, D.R. Moore, Angew. Chem. 43 (2004) 6618.
[27] D.J. Darensbourg, Chem. Rev. 107 (2007) 2388.
[28] H. Sugimoto, S. Inoue, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 5561.
[29] M.R. Kember, A. Buchard, C.K. Williams, Chem. Commun., 2010, in press, doi:10.1039/c1030cc02207a.
[30] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Billodeaux, Acc. Chem. Res. 37 (2004) 836.
[31] K. Nozaki, Pure Appl. Chem. 76 (2004) 541.
[32] S. Inoue, H. Koinuma, T. Tsuruta, Makromol. Chem. 130 (1969) 210.
[33] M. Kobayashi, S. Inoue, T. Tsuruta, Macromolecules 4 (1971) 658.
[34] M. Kobayashi, Y.-L. Tang, T. Tsuruta, S. Inoue, Makromol. Chem. 169 (1973) 69.
[35] M. Kobayashi, S. Inoue, T. Tsuruta (Eds.), J. Polym. Sci. Polym. Chem. Ed. 11 (1973) 2383.
[36] S. Inoue, M. Kobayashi, H. Koinuma, T. Tsuruta, Makromol. Chem. 155 (1972) 61.
[37] W. Kuran, S. Pasynkiewicz, J. Skupinska, Macromol. Chem. Phys. 177 (1976) 1283.
[38] W. Kuran, S. Pasynkiewicz, J. Skupinska, Makromol. Chem. 178 (1977) 2149.
[39] W. Kuran, T. Listos, Macromol. Chem. Phys. 195 (1994) 977.
[40] K. Soga, E. Imai, I. Hattori, Polym. J. 13 (1981) 407.
[41] W. Kuran, S. Pasynkiewicz, J. Skupinska, A. Rokicki, Makromol. Chem. 177 (1976) 11.
[42] A. Rokicki, W. Kuran, Makromol. Chem. 180 (1979) 2153.
[43] T. Aida, M. Ishikawa, S. Inoue, Macromolecules 19 (1986) 8.
[44] D.J. Darensbourg, M.W. Holtcamp, Macromolecules 28 (1995) 7577.
[45] D.J. Darensbourg, M.W. Holtcamp, G.E. Struck, M.S. Zimmer, S.A. Niezgoda, P. Rainey, J.B. Robertson, J.D. Draper, J.H. Reibenspies, J. Am. Chem. Soc. 121 (1999) 107.
[46] C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman, D.J. Darensbourg, Polymer 42 (2001) 3995.
[47] M. Cheng, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 120 (1998) 11018.
[48] D.R. Moore, M. Cheng, E.B. Lobkovsky, G.W. Coates (Eds.), Angew. Chem. Int. Ed. 41 (2002) 2599.
[49] S.D. Allen, D.R. Moore, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 14284.
[50] G.A. Luinstra, G.R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, Chem. Eur. J. 11 (2005) 6298.
[51] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421.
[52] L.P.C. Nielsen, C.P. Stevenson, D.G. Blackmond, E.N. Jacobsen, J. Am. Chem. Soc. 126 (2004) 1360.
[53] K.B. Hansen, J.L. Leighton, E.N. Jacobsen, J. Am. Chem. Soc. 118 (1996) 10924.
[54] C.T. Cohen, T. Chu, G.W. Coates, J. Am. Chem. Soc. 127 (2005) 10869.
[55] D.J. Darensbourg, J.C. Yarbrough, J. Am. Chem. Soc. 124 (2002) 6335.
[56] D.J. Darensbourg, J.C. Yarbrough, C. Ortiz, C.C. Fang, J. Am. Chem. Soc. 125 (2003) 7586.
[57] D.J. Darensbourg, J.L. Rodgers, R.M. Mackiewicz, A.L. Phelps, Catal. Today 98 (2004) 485.
[58] M.H. Chisholm, Z. Zhou, J. Am. Chem. Soc. 126 (2004) 11030.
[59] D.-Y. Rao, B. Li, R. Zhang, H. Wang, X.-B. Lu, Inorg. Chem. 48 (2009) 2830.
[60] X.-B. Lu, Y. Wang (Eds.), Angew. Chem. Int. Ed. 43 (2004) 3574.
[61] 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. 128 (2006) 1664.
[62] L. Shi, X.-B. Lu, R. Zhang, X.-J. Peng, C.-Q. Zhang, J.-F. Li, X.-M. Peng, Macromolecules 39 (2006) 5679.
[63] C.T. Cohen, G.W. Coates, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 5182.
[64] R.L. Paddock, S.T. Nguyen, Macromolecules 38 (2005) 6251.
[65] Y. Niu, W. Zhang, X. Pang, X. Chen, X. Zhuang, X. Jing, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 5050.
[66] C.T. Cohen, C.M. Thomas, K.L. Peretti, E.B. Lobkovsky, G.W. Coates, Dalton Trans. (2005) 237.
[67] Z.Q. Qin, C.M. Thomas, S. Lee, G.W. Coates (Eds.), Angew. Chem. Int. Ed. 42 (2003) 5484.
[68] H. Sugimoto, K. Kuroda, Macromolecules 41 (2008) 312.
[69] L. Guo, C. Wang, W. Zhao, H. Li, W. Sun, Z. Shen, Dalton Trans. (2009) 5406.
[70] D.J. Darensbourg, P. Bottarelli, J.R. Andreatta, Macromolecules 40 (2007) 7727.
[71] D.J. Darensbourg, A.L. Phelps, Inorg. Chem. 44 (2005) 4622.
[72] D.J. Darensbourg, R.M. Mackiewicz, J. Am. Chem. Soc. 127 (2005) 14026.
[73] R. Eberhardt, M. Allmendinger, B. Rieger, Macromol. Rapid Commun. 24 (2003) 194.
[74] D.J. Darensbourg, R.M. Mackiewicz, J.L. Rodgers, C.C. Fang, D.R. Billodeaux, J.H. Reibenspies, Inorg. Chem. 43 (2004) 6024.
[75] D.J. Darensbourg, R.M. Mackiewicz, J.L. Rodgers, A.L. Phelps, Inorg. Chem. 43 (2004) 1831.
[76] B. Li, G.-P. Wu, W.-M. Ren, Y.-M. Wang, D.-Y. Rao, X.-B. Lu, J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 6102.
[77] D.R. Moore, M. Cheng, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 125 (2003) 11911.
[78] Y. Hino, Y. Yoshida, S. Inoue, Polym. J. 16 (1984) 159.
[79] T. Tsuruta, Makromol. Chem. 6 (1986) 23.
[80] W. Kuran, Appl. Organomet. Chem. 5 (1991) 191.
[81] W. Kuran, T. Listos, Pol. J. Chem. 68 (1994) 1071.
[82] K. Nakano, T. Kamada, K. Nozaki (Eds.), Angew. Chem. Int. Ed. 45 (2006) 7274.
[83] H. Sugimoto, H. Ohtsuka, S. Inoue, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 4172.
[84] L.J. Gao, M. Xiao, S.J. Wang, F.G. Du, Y.Z. Meng, J. Appl. Polym. Sci. 104 (2007) 15.
[85] G.A. Luinstra, Polym. Rev. 48 (2008) 192.
[86] M. Ree, Y. Hwang, J.-S. Kim, H. Kim, G. Kim, H. Kim, Catal. Today 115 (2006) 134.
[87] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, J. Polym. Sci. Part A 37 (1999) 1863.
[88] J.-S. Kim, M. Ree, T.J. Shin, O.H. Han, S.J. Cho, Y.-T. Hwang, J.Y. Bae, J.M. Lee, R. Ryoo, H. Kim, J. Catal. 218 (2003) 209.
[89] Y.Z. Meng, L.C. Du, S.C. Tiong, Q. Zhu, A.S. Hay, J. Polym. Sci. Part A 40 (2002) 3579.
[90] Y.Q. Zheng, J.L. Lin, H.L. Zhang, Z. Kristallogr. New Cryst. Struct. 215 (2000) 535.
[91] J.-S. Kim, H. Kim, M. Ree, Chem. Mater. 16 (2004) 2981.
[92] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, Kor. Polym. J. 7 (1999) 333.
[93] J.T. Wang, Q. Zhu, X.L. Lu, Y.Z. Meng, Eur. Polym. J. 41 (2005) 1108.
[94] J.-S. Kim, H. Kim, J. Yoon, K. Heo, M. Ree, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 4079.
[95] S.J. Wang, L.C. Du, X.S. Zhao, Y.Z. Meng, S.C. Tjong, J. Appl. Polym. Sci. 85 (2002) 2327.
[96] W.E. Caroll, S.A. Motika, US Patent 4,960,862 (1990).
[97] M.H. Chisholm, D. Navarro-Llobet, Z. Zhou, Macromolecules 35 (2002) 6494.
[98] R. Eberhardt, M. Allmendinger, G.A. Luinstra, B. Rieger, Organometallics 22 (2003) 211.
[99] R. Eberhardt, M. Allmendinger, M. Zintl, C. Troll, G.A. Luinstra, B. Rieger, Macromol. Chem. Phys. 205 (2004) 42.
[100] J.S. Kim, M. Ree, S.W. Lee, W. Oh, S. Baek, B. Lee, T.J. Shin, K.J. Kim, B. Kim, J. Luning, J. Catal. 218 (2003) 386.
[101] Q. Zhu, Y.Z. Meng, S.C. Tjong, Y.M. Zhang, W. Wan, Polym. Int. 52 (2003) 799.
[102] S. Inoue, T. Takada, H. Tatsu, Makromol. Chem. Rapid Commun. 1 (1980) 775.
[103] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, Y.T. Hwang, T. Chang, Polym. Eng. Sci. 40 (2000) 1542.
[104] J.T. Wang, D. Shu, M. Xiao, Y.Z. Meng, J. Appl. Polym. Sci. 99 (2006) 200.
[105] A.M. Sakharov, V.V. Il'in, V.V. Rusak, Z.N. Nysenko, S.A. Klimov (Eds.), Russ. Chem. Bull. Int. Ed. 51 (2002) 1451.
[106] T.A. Bowden, H.L. Milton, A.M.Z. Slawin, P. Lightfoot, Dalton Trans. (2003) 936.
[107] J. Pan, G. Zhang, Y. Zheng, J. Lin, W. Xu, J. Cryst. Growth 308 (2007) 89.
[108] W.J. Kruper, D.V. Dellar, J. Org. Chem. 60 (1995) 725.
[109] T. Aida, S. Inoue, J. Am. Chem. Soc. 107 (1985) 1358.
[110] F. Kojima, T. Aida, S. Inoue, J. Am. Chem. Soc. 108 (1986) 391.

[111] Y. Qin, X. Wang, S. Zhang, X. Zhao, F. Wang, J. Polym. Sci. Part A 46 (2008) 5959.
[112] P. Chen, M.H. Chisholm, J.C. Gallucci, X. Zhang, Z. Zhou, Inorg. Chem. 44 (2005) 2588.
[113] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 45 (2004) 2023.
[114] L. Jin, H. Jing, T. Chang, X. Bu, L. Wang, Z. Liu, J. Mol. Catal. A 261 (2007) 262.
[115] R.L. Geerts, J.C. Huffman, K.G. Caulton, Inorg. Chem. 25 (1986) 1803.
[116] D.J. Darensbourg, S.A. Niezgoda, J.D. Draper, J.H. Reibenspies, J. Am. Chem. Soc. 120 (1998) 4690.
[117] D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, J.H. Reibenspies, J. Am. Chem. Soc. 122 (2000) 12487.
[118] D.J. Darensbourg, M.S. Zimmer, P. Rainey, D.L. Larkins, Inorg. Chem. 39 (2000) 1578.
[119] D.J. Darensbourg, M.W. Holtcamp, B. Khandelwal, K.K. Klausmeyer, J.H. Reibenspies, J. Am. Chem. Soc. 117 (1995) 538.
[120] D.J. Darensbourg, S.A. Niezgoda, M.W. Holtcamp, J.D. Draper, J.H. Reibenspies, Inorg. Chem. 36 (1997) 2426.
[121] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
[122] M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 8738.
[123] M. Cheng, N.A. Darling, E.B. Lobkovsky, G.W. Coates, Chem. Commun. (2000) 2007.
[124] G.W. Coates, M. Cheng, US Pat. Appl., US 6,133,402 (2000).
[125] S.D. Allen, D.R. Moore, E.B. Lobkovsky, G.W. Coates, J. Organomet. Chem. 683 (2003) 137.
[126] M. Kroeger, M. Doering, Catal. Today 115 (2006) 146.
[127] C.M. Byrne, S.D. Allen, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 126 (2004) 11404.
[128] M. Kroeger, C. Folli, O. Walter, M. Doering, Adv. Synth. Catal. 347 (2005) 1325.
[129] M. Kroeger, C. Folli, O. Walter, M. Doering, J. Organomet. Chem. 691 (2006) 3397.
[130] B.Y. Lee, H.Y. Kwon, S.Y. Lee, S.J. Na, S. Han, H. Yun, H. Lee, Y.-W. Park, J. Am. Chem. Soc. 127 (2005) 3031.
[131] W.J. van Meerendonk, R. Duchateau, C.E. Koning, G.-J.M. Gruter, Macromol. Rapid Commun. 25 (2004) 382.
[132] M.H. Chisholm, J.C. Huffman, K. Phomphrai, J. Chem. Soc. Dalton Trans. (2001) 222.
[133] M.H. Chisholm, J. Gallucci, K. Phomphrai, Inorg. Chem. 41 (2002) 2785.
[134] L.R. Rieth, D.R. Moore, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 15239.
[135] B. Liu, C. Tian, L. Zhang, W. Yan, W. Zhang, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 6243.
[136] M. Walther, K. Wermann, M. Lutsche, W. Gnther, H. Grls, E. Anders, J. Org. Chem. 71 (2006) 1399.
[137] D.V. Vitanova, F. Hampel, K.C. Hultzsch, J. Organomet. Chem. 690 (2005) 5182.
[138] B.B. Lazarov, F. Hampel, K.C. Hultzsch, Z. Anorg. Allg. Chem. 633 (2007) 2367.
[139] B. Liu, X. Zhao, H. Guo, Y. Gao, M. Yang, X. Wang, Polymer 50 (2009) 5071.
[140] D.J. Darensbourg, R.M. Mackiewicz, D.R. Billodeaux, Organometallics 24 (2005) 144.
[141] K. Nozaki, K. Nakano, T. Hiyama, J. Am. Chem. Soc. 121 (1999) 11008.
[142] K. Nakano, K. Nozaki, T. Hiyama, J. Am. Chem. Soc. 125 (2003) 5501.
[143] K. Nakano, T. Hiyama, K. Nozaki, Chem. Commun. (2005) 1871.
[144] Y. Xiao, Z. Wang, K. Ding, Chem. Eur. J. (2005) 3668.
[145] Y. Xiao, Z. Wang, K. Ding, Macromolecules 39 (2006) 128.
[146] T. Bok, H. Yun, B.Y. Lee, Inorg. Chem. 45 (2006) 4228.
[147] M.F. Pilz, C. Limberg, B.B. Lazarov, K.C. Hultzsch, B. Ziemer, Organometallics 26 (2007) 3668.
[148] D. Piesik, S. Range, S. Harder, Organometallics 27 (2008) 6178.
[149] M.R. Kember, P.D. Knight, P.T. Reung, C.K. Williams, Angew. Chem. 121 (2009) 949.
[150] M.R. Kember, A.J.P. White, C.K. Williams, Inorg. Chem. 48 (2009) 9535.
[151] M.R. Kember, A.J.P. White, C.K. Williams, Macromolecules 43 (2010) 2291.
[152] A. Buchard, M.R. Kember, K. Sandeman, C.K. Williams, Chem. Commun. 46 (2010), doi:10.1039/c1030cc02205e, in press.
[153] J.E. Dengler, M.W. Lehenmeier, S. Klaus, C.E. Anderson, E. Herdtweck, B. Rieger, Eur. J. Inorg. Chem. (2010), doi:10.1002/ejic.201000861, in press.
[154] W.M. Ren, Z.W. Liu, Y.Q. Wen, R. Zhang, X.B. Lu, J. Am. Chem. Soc. 131 (2009) 11509.
[155] W.M. Ren, X. Zhang, Y. Liu, J.F. Li, H. Wang, X.B. Lu, Macromolecules 43 (2010) 1396.
[156] E.K. Noh, S.J. Na, S. Sujith, S.W. Kim, B.Y. Lee, J. Am. Chem. Soc. 129 (2007) 8082.
[157] J.E. Seong, S.J. Na, A. Cyriac, B.W. Kim, B.Y. Lee, Macromolecules 43 (2010) 903.
[158] S. Sujith, J.K. Min, J.E. Seong, S.J. Na, B.Y. Lee (Eds.), Angew. Chem. Int. Ed. 47 (2008) 7306.
[159] J. Na Sung, S. Sujith, A. Cyriac, E. Kim Bo, J. Yoo, K. Kang Youn, J. Han Su, C. Lee, Y. Lee Bun, Inorg. Chem. 48 (2009) 10455.
[160] J. Yoo, S.J. Na, H.C. Park, A. Cyriac, B.Y. Lee, Dalton Trans. 39 (2010) 2622.
[161] C. Hongfa, J. Tian, J. Andreatta, D.J. Darensbourg, D.E. Bergbreiter, Chem. Commun. (2008) 975.
[162] R.G. Konsler, J. Karl, E.N. Jacobsen, J. Am. Chem. Soc. 120 (1998) 10780.
[163] E. Schön, X. Zhang, Z. Zhou, M.H. Chisholm, P. Chen, Inorg. Chem. 43 (2004) 7278.
[164] K. Nakano, S. Hashimotoa, K. Nozaki, Chem. Sci. 1 (2010) 369.
[165] S.I. Vagin, R. Reichardt, S. Klaus, B. Rieger, J. Am. Chem. Soc. 132 (2010) 14367.
[166] K. Yu, C.W. Jones, Organometallics 22 (2003) 2571.
[167] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, J. Garcia, J. Catal. 228 (2004) 254.
[168] M. Alvaro, C. Baleizao, E. Carbonell, M.E. Ghoul, H. García, B. Gigante, Tetrahedron 61 (2005) 12131.