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New Catalytic Systems for Fixation of Carbon Dioxide into Valuable Poly(Alkylene Carbonates)

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Abstract

Fixation of carbon dioxide into valuable products is a promising method to mitigate the issues of global warming and decrease the consumption of fossil-fuel carbon sources. Poly alkylene carbonates (PACs) are environmentally friendly and low-cost polymers that are synthesized from copolymerization of carbon dioxide and epoxides. PACs are contemplated as an alternative to commercially available non-degradable polymers in the market for a broad range of applications. However, a burden for the synthesis of this group of polymers is the chemical activation of thermodynamically stable CO_2. It is, therefore, imperative to develop a catalyst with high efficiency to overcome this hurdle. In this chapter, we describe the development and recent advances in the catalytic systems that have been designed to activate CO_2 for copolymerization with epoxides. In particular, we will focus on the industrial trends presented in the patents for conversion of CO_2 into PACs.

Keywords: Carbon Dioxide Fixation, Epoxides, Polycarbonates, Catalysts

1. Introduction

Carbon dioxide is one of the main greenhouse gases that contributes to global warming [1]. One of the approaches to tackle this issue is to fix CO_2 as a raw material into valuable polymers [2]. The polymer industry is an emerging market that mostly relies on petrochemical products derived from fossil-fuel feedstocks. However, CO_2 is a cheap, renewable, non-toxic and the most abundant carbon source. The consumption of CO_2 as a reactant for the synthesis of carbon-based products is a key step to cut down the reliance on the fossil fuels.

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Alternative copolymerization of CO_2 with epoxides, such as propylene oxide (PO) and cyclohexene oxide (CHO), results in the formation of biodegradable PACs. As the physical properties of PACs are comparable to conventional polymers, they can be used for a broad range of applications such as packaging, agricultural and biomedical industries [3]. One of the obstacles in the synthesis of PACs is the design of an efficient catalyst that can reduce the activation energy of thermodynamically stable CO_2 for such polymerization reaction [4]. In addition to activity, it is pivotal to design a selective catalyst that reduces the yield of by-products during the PAC copolymerization reactions [5]. Other factors that are contemplated in developing a catalyst are cost and toxicity.

Since 1696 that poly(propylene carbonate) (PPC) was synthesized, many efforts have been attempted to design catalysts [6]. These catalysts are mainly classified into two categories: (1) homogeneous and (2) heterogeneous. This classification is based on their solubility in the reaction media; therefore, the homogenous catalysts are those that are in the same phase as reactants and heterogeneous are those that are in another phase. Regardless of large number of research in this area, only a few of conventional metal-based heterogeneous catalysts have been used for the commercial PACs synthesis that possess acceptable activity and selectivity for large-scale production [3]. However, physical properties of this type of catalysts affect their selectivity and activity remarkably. For example, particle size, crystallinity, microstructure and morphology are key factors that show impact on the activity of a catalyst and the yield of the final product [7–9]. Many bench-scale studies have been conducted to promote the catalyst activity for the synthesis of PACs, and particularly poly(propylene carbonate) [3, 10]. In this chapter, we provide an insight about these types of catalysts. Prior to a discussion about catalyst, the main advantages of PACs are described. Then various catalysts that are available for their synthesis are introduced, followed by discussion about strategies that have been undertaken to promote the activity of these catalysts and finally, an overview of patents filed for the synthesis of PACs are briefly reviewed.

2. Copolymerization of CO_2 and epoxides

Direct copolymerization of CO_2 and epoxides such as ethylene oxide, propylene oxide, isobutylene oxide, cycloheptene oxide, cyclopentene oxide and cyclohexene oxide results in the formation of PACs, which is a typical example of fixation of CO_2 in polymers [11]. PACs have excellent physical properties, including low density, transparency, durability, colourability and processability, and also they exhibited decent electrical insulation properties [12]. Accordingly, these types of polymers have a broad range of applications in electronics, optical media and have been used for the preparation of sheets, automotive productions, medical devices and healthcare products [10]. Furthermore, they are commercially used as a binder, plasticizer and raw material for polyurethane synthesis [3]. However, the most important feature of PACs that has attracted attention in recent years, as a potent alternative for conventional polymers, is their biodegradability. PACs degrade into water and CO_2 when exposed to moisture and enzymes or non-sterilized soil such as landfills [3]. PACs can be considered as an alternative to non-degradable polymers to address the growing concerns about the

disposal of plastics in municipal waste, shortage of allocated spaces for landfills and consumer pressure for sustainable products. The list of some companies that use PACs in commercial scale for different purposes is presented in Table 1. PPC is used in combination with acrylonitrile butadiene styrene (ABS) to make a scratch resistance plastic by Bayer MaterialScience [13]. Furthermore, poly(propylene carbonate) and poly(hydroxybutyrate) are blended with other polymeric materials or mixed with inorganic solids to form the alternative plastic to acrylonitrile butadiene styrene by Baden Aniline and Soda Factory (BASF) –a chemical company [14]. Cardia Bioplastics (CO$_2$ Starch Pty Ltd) has developed a method to manufacture commercially PPC/starch blends [15], and they currently manufacture huge amount of degradable plastic bags globally from this blend.

Name of Company	Country	Application	Website
Life Cycle Products	England	Plastic bag and waste management products	www.lifecycleproducts.co.uk
Nature Works Packaging	Australia	Shopping bag	www.natureworkspackaging.com
Drogaria Araujo	Brazil	Biohybrid™ bags	www.araujo.com.br
AZOmaterials	England	Organic binders for nanoparticles	www.azom.com
Novomer	USA	Polyurethane hot-melt adhesive	www.novomer.com
Mengxi High-tech Group	China	Medical dressings, biodegradable packaging	www.mengxigroup.com
Jiangsu Jinlong-CAS Chemical Co., Ltd	China	Biodegradable packaging	www.zkjlchem.com
TaiZhou BangFeng Plastic Co., Ltd	China	Disposable biodegradable dishes	www.cn-bf.net
Cardia Bioplastics™	Australia	Shopping bag	www.cardiabioplastics.com

Table 1. List of Some Companies That Use PACs in Commercial Scale

PACs can be used for biomedical applications as an alternative to current biodegradable polymers such as poly(lactic acid) (PLA). For example, enzymatic degradation of PPC leads to producing benign products that include only water and CO$_2$, which does not cause any inflammation in biological environment. However, PLA degrades by hydrolysis and generates lactic acid, reduces the pH in surrounding tissue leads to inflammation. In addition, studies by Zhong et al. in 2012 and Yang et al. in 2013 demonstrated the potential of using PPC for producing scaffolds for tissue engineering application [16–18].

PACs are superior polymers for the agricultural purposes. For example, they can be used for the production of plastic films for agricultural mulches as an alternative to non-degradable polyethylene. It is therefore eradicating the risk of accumulation of plastic residues in agricultural spots, the high cost of collecting mulches after the harvesting season and contamination

with soil and dirt. PACs can also be used for designing biodegradable packaging products as they are transparent and have minimal permeability to oxygen and water [19].

It is pivotal to determine the presence of any impurities that may have an adverse effect on physical properties and also the toxicity of a product fabricated from a polymer for food and biomedical applications. For instance, in processing PACs, the type of epoxide, by-product, catalyst and any other impurities may have an impact on their properties [20]. In an ideal copolymerization, CO_2 and epoxide molecules form carbonate linkage. However, in reality, two molecules of epoxide may also bond and produce undesirable products. The presence of ether linkage has adverse effects on properties such as mechanical strength, thermal transition, thermal decomposition temperatures and molecular weight [21]. Therefore, the design of an active catalyst plays a critical role in promoting selectivity for the synthesis of favourable copolymer and reducing the rate of reaction of undesirable products.

3. PACs synthesis

The first discovery of PACs synthesis goes back to 1969 when Inoue et al. used a mixture of diethyl zinc ($ZnEt_2$) and water as a catalyst to conduct the copolymerization of CO_2 and propylene oxide and form PPC [22]. Shortly after that, the same group successfully used triethylaluminium as another organometallic catalyst for the synthesis of PPC [6]. However, the yield of the copolymerization reaction in the presence of these catalysts was low due to the formation of side products and presence of ether linkages on the polymer backbone. To address the issue of low catalyst activity, other hydrogen donor compounds rather than water have been used in combination with $ZnEt_2$ [23, 24]. It was found that donor compounds with two or three active hydrogen sites formed multi-site catalytic systems with higher activity and selectivity compared with mono-site components. Therefore, the reaction was conducted towards alternative copolymerization of CO_2 and PO, and the amount of undesirable cyclic propylene carbonate (cPC) reduced. Furthermore, a series of metal salts of acetic acid were used to catalyze the copolymerization of carbon dioxide and PO [25, 26]. Besides, a combination of zinc hydroxide with dicarboxylic acids was used to enhance the yield of desirable polymer product; among all, catalyst system derived from zinc, hydroxide and glutaric acid showed the superior activity [27].

One common mechanism proposed for the copolymerization of CO_2 and epoxides is coordination–insertion mechanism catalyzed via metal compounds with Lewis acid and Lewis base active sites [10, 28]. In the coordination step, the epoxide molecule is coordinated by the metallic centre of a catalyst (Lewis acid active site) and then attacked by nucleophile site (Lewis base site) and undergone ring opening to form metal-bound alkoxide [10]. The nucleophilic attack can take place by either the nucleophile active site on the metal catalyst (bifunctional homogenous catalysts) or a separate compound (binary catalysts) and resulted to activation of alkoxide [20]. CO_2 molecule then inserted into the metal-oxygen bond and initiated the reaction by forming metal carbonate. Up to this stage, all the steps were associated with the activity of the catalyst; however, the pathway of the reaction after this step relies on the

selectivity of the catalyst. In fact, selectivity is a function of the type of alkoxide. Commonly, the metal carbonate goes towards its ring closure and forms propylene carbonate or propagates by multiple coordination and insertion of CO_2 and produces polycarbonate chain [29]. If the second pathway is followed by the alternative coordination–insertion mechanism, the resulted polycarbonate has 100% carbonate linkage in its structure; however, some catalysts can also homopolymerize epoxides and form ether linkages on the backbone of polymer [10]. The schematic of suggested coordination–insertion mechanism for the copolymerization of epoxides and CO_2 is demonstrated in Figure 1.
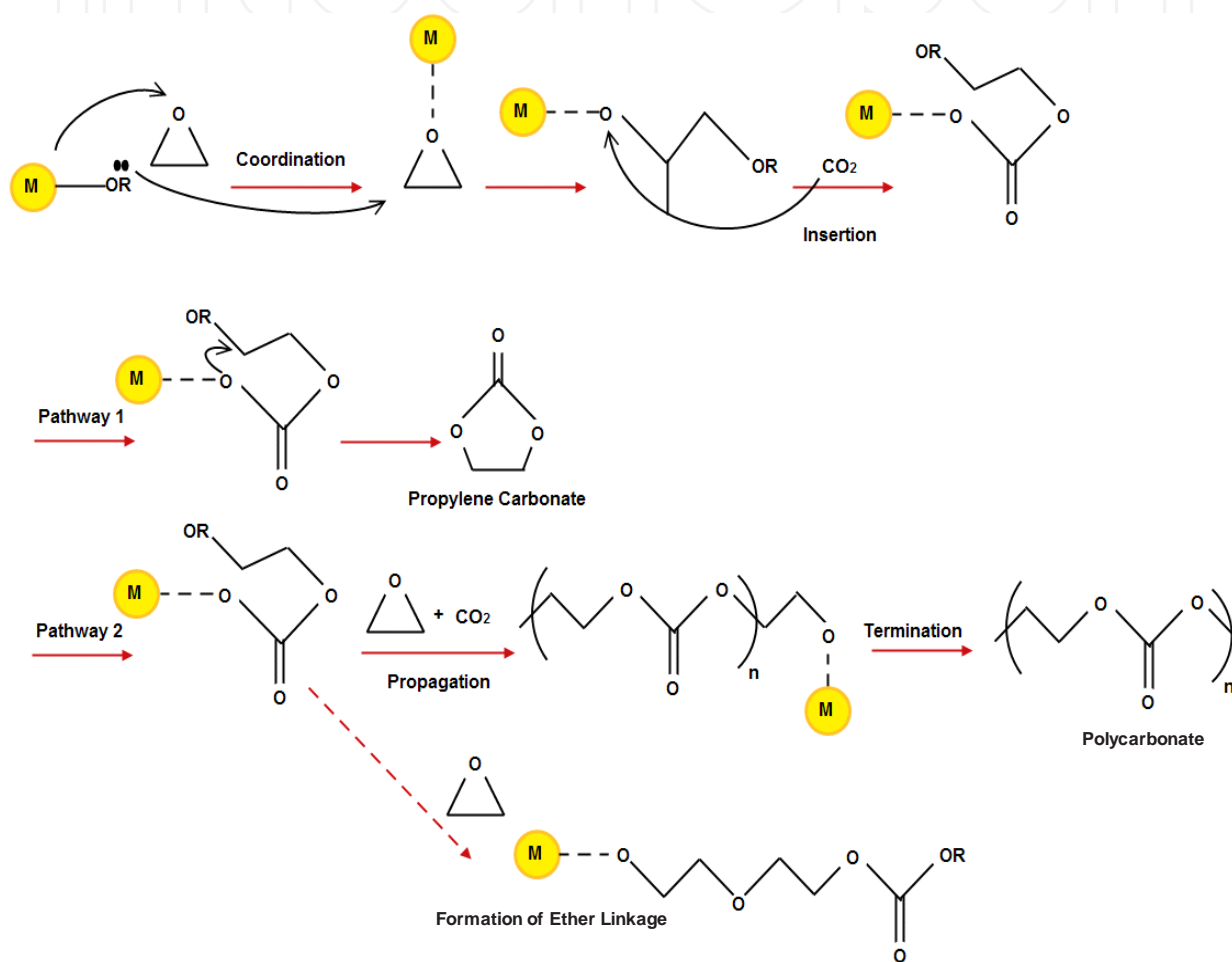
Figure 1. Coordination–insertion mechanism suggested for the copolymerization of epoxides with CO_2

4. Catalytic systems for CO_2/epoxide polymerization

Since 1696 when PPC was first synthesized, many efforts were carried out to develop both homogeneous and heterogeneous catalysts with high selectivity [30]. In the following section, various types of homogeneous and heterogeneous catalysts that have been used for the reaction between CO_2 and epoxides are described.

4.1. Homogenous catalysts

Triphenyl phosphate (TPP) compounds with a metal atom in the centre were the first group of homogeneous catalyst reported for copolymerization of CO_2 and epoxides [31, 32]. TPP compounds showed high activity; however, this catalysts were not very efficient, and the yield of PACs was very low even after more than one weak reaction. Nitrogen donors compounds such as N-methylimidazole and (4-dimethylamino)pyridine (DMAP) were added to TPP compounds to enhance the yield of reaction. However, this catalyst system could only be used for the copolymerization of COH and CO_2. For the other epoxides, only cyclic alkylene carbonates were produced [33, 34].

Chen et al. investigated the effect of metal type located in the centre of TPP compounds on the activation of propylene oxide. It was found that the type of metal influenced the acidity strength of catalysts and, therefore, the strength of epoxide metal bond and the yield of copolymer synthesis [35]. Among three types of metal used in this study, chromium-based catalyst exhibited higher selectivity compared to Al and Co towards the formation of PPC from the reaction between PO and CO_2.

In a metal complex catalyst, the metal acts as Lewis acid to attack the epoxide and after that the nucleophile part of the catalyst opens the epoxide ring. The nucleophile part of the catalyst can be either a ligand attached to the metal complex or a co-catalyst. In the former group, the nucleophile ligand can often be a salen, a porphyrin, a phthalocyanine or an amido macrocycle [30]. The nature of metal in the catalyst is critical in its activity and selectivity and also the quality of the resulted polymer. Indeed, the strength of epoxide metal bond can determine the pathway of reaction. When this bond is too weak, the reaction proceeds towards formation of ether linkages and backbiting while the high strength of the bond may lead to closure of the ring and formation of cyclic carbonates [36].

After TPP compounds, great number of metal complex catalytic systems such as phenoxide [37–39] and β-diiminate (BDI) [29, 40] were investigated in terms of their activity for copolymerization of CO_2 and epoxides that are discussed in this section.

4.1.1. Phenoxide complexes

Phenoxide compounds include an aryl ligand that plays the role of nucleophile site of a catalyst [41]. It was found that the activity of a catalyst is dramatically higher when the phenoxide compounds contain zinc atom as a metal centre [42]. It was found that this group of metal complexes are only able to activate and catalyze CHO to react with CO_2 and are not efficient in activation of other epoxides such as PO [37, 43, 44].

4.1.2. β-diiminate complexes

BDI is a family of complexes that include an aryl or acyl ligand with the molecular formula of L_nMOR (R: alkyl, acyl) [40]. BDIs have broad applications in inorganic as well as organic and polymer synthesis, especially in the polymerization of lactides [45]. In the case of copolymerization of epoxides and CO_2, BDIs have been used in a large number of studies. The results

demonstrated that both the nature of metal centre and the aryl ligand have significant effect on the activity and selectivity of the catalyst [29, 40, 46]. For example, only zinc metal showed remarkable efficiency and selectivity towards the copolymerization of propylene oxide and carbon dioxide [47, 48].

4.1.3. Metal salen complexes

Salens are a class of organic compounds including 1,6-bis(2-hydroxyphenyl)-2,5-diaza-hexa-1,5-diene ligand that are broadly used in the synthetic chemistry [49]. Metal salen complexes were first used for the ring opening copolymerization of epoxides in 1995 [50]. This family of catalysts has several advantages over other complexes for the copolymerization of epoxides and CO_2. They are highly selective towards the synthesis of polycarbonates in the mild reaction condition (ambient temperature) [51]. Metal salen catalysts can be categorized according to the type of metal in the centre.

Chromium-based salen complexes ((salen)CrCl) were efficient in the copolymerization of epoxides and CO_2 [52]. Two years after the first discovery, Jacobsen et al. successfully synthesized PCHC with 100% carbonate linkage using chiral salen chromium chloride catalyst [53]. The chromium-based salen complexes, however, showed low activity in the copolymerization of CO_2 and PO due to the negligible differences between the activation energy of PO and PPC compared to cyclohexene carbonate (CHC) versus poly(cyclohexene carbonate) (PCHC) [54]. Therefore, the selectivity of the catalyst is a critical factor for the copolymerization of PO and CO_2. The addition of co-catalyst was found to be an efficient approach to tackle this issue. In 2003, Rieger et al. attempted to add co-catalyst 4-(N,N-dimethylamino)pyridine (DMAP) to chromium salen and were able to successfully synthesize PPC with 98% carbonate linkage and minimal PC side product [55]. They proposed that strong coordination of DMAP to chromium promoted the propagation of polymer chain and formation of carbonate linkages. The type of initiator was another factor that had an impact on the selectivity of chromium salen catalysts for the synthesis of PPC. It was found that changing the initiator from phosphines to azide in combination with $Cr(salen)N_3$ catalyst significantly stimulated the reaction pathway towards the formation of PPC rather than cyclic propylene carbonate [56].

The metal centre has a pivotal role in catalyst activity and selectivity of the metal salen complexes. The first cobalt salen complexes (Co(salen)AOc) was introduced in 2003 for the copolymerization of PO and CO_2, which resulted in producing PPC with 99% carbonate linkage [57]. In addition, it was found that similar to the chromium salen catalysts, the addition of co-catalyst to the cobalt salen complexes has an impact on their activity and selectivity. For instance, the addition of sub-stoichiometric amount of bis(triphenylphosphine)iminium (PPN) as co-catalyst to a cobalt salen increased the yield of PPC synthesis to 36% with 99% carbonate linkage [58]. However, any further effect on yield enhancement led to the formation of cyclic propylene compounds due to backbiting degradation of the polymer chain. To accomplish high activity of a catalyst without losing the selectivity, Nakano et al. designed a cobalt salen complex with piperidinyl and piperidinium arms [59]. This modification resulted in producing 99% PPC with 97% conversion yield. Basically in this reaction, the side arms played the role of in situ co-catalysts. This approach was a breakthrough in the copolymerization of CO_2 and

epoxides as it reduced the catalyst loading significantly. Similarly, a cobalt complex containing two tertiary amine cations on pendant arms was designed and showed high activity and above 90% conversion yield for very low catalyst loadings such as 1:50,000 (catalyst/ PO) [60].

Many research activities have focused on the area of homogeneous catalysts for CO_2–epoxide copolymerization due to the design flexibility and high activity. However, none of them has been used in large scale due to complicated synthesis process and low selectivity for PACs copolymerization. On the other hand, heterogeneous catalysts are generally non-toxic and economically viable due to the simpler synthesis process and easier handling. In the next section, the heterogeneous catalysts that are designed for the synthesis of PACs are described.

4.2. Heterogeneous catalysts

4.2.1. Organometallic compounds

The organometallic compounds for the copolymerization of CO_2 and epoxides are designed from the combination of a hydrogen donor compound and a metal-based complex to activate CO_2 and open the ring of the epoxide. The commonly used hydrogen donors are water, primary amines, dihydric phenols, trihydric phenols, aromatic dicarboxylic acids and aromatic hydroxycarboxylic acids [61]. Several efficient organometallic catalysts with well-defined structures have been developed for the copolymerization of carbon dioxide and epoxide. However, the activity of the catalyst derived from zinc hydroxide and glutaric acid was superior compared to other compounds [27]. Ree et al. copolymerized PO and CO_2 using zinc glutarate (ZnGA) obtained from various zinc sources. As a result, zinc glutaric derived from zinc oxide and glutaric acid yielded the highest catalyst activity of 64 g /g of catalyst [62]. Discovery of the catalyst activity of zinc glutarate for copolymerization of CO_2 and epoxides was a breakthrough in the field especially after 1995 when Darensbourg et al. substituted organic solvents, as the reaction media, by supercritical fluid [63]. This makes the copolymerization process more environmentally friendly and economically viable.

4.2.2. Double-Metal Cyanide (DMC) complexes

DMCs are another group of heterogeneous catalyst that are efficiently used for the homopolymers of epoxides. The first DMCs that showed average activity for copolymerization of PO and CO_2 to produce PPC were $Zn_3[Fe(CN)_6]_2$ and $Zn_3[Co(CN)_6]_2$, a double-metal cyanide compound based on Zn and Fe or Co [64–66]. The activity of zinc–cobalt–DMC catalyst was comparable with zinc glutarate [3, 21]. However, it was found that the system suffered from low selectivity at low temperatures and poor activity at high temperatures [67]. In addition to these catalysts, Darensbourg et al. and Robertson et al. attempted to modify the catalyst structure by increasing the crystallinity of DMC-based catalyst [68, 69]. It was also found that the low molecular weight polyols could act as an initiator to activate DMCs and promote the copolymerization reaction [70].

4.2.3. Rare earth metal catalysts

In the very first attempts, rare earth metal complexes such as $Y(P_2O_4)_3$–Al(i-Bu)$_3$–glycerine were used for the copolymerization of PO and CO_2 and formation of high molecular weight PPC. However, the structure of the resulted copolymer consisted of up to 90% of ether linkages [71]. In the next discoveries, rare earth metal catalysts showed an increase in selectivity and reduction in synthesis time for copolymerization of CO_2 with epoxides [72–74]. Yttrium carboxylate in combination with $ZnEt_2$ significantly improved carbonate linkage percentage on the PPC and PCHC backbone [75]. A ternary catalytic system of rare earth complex, diethyl zinc and glycerine resulted in an extremely high molecular weight PPC [76]. Likewise, PO was successfully copolymerized with CO_2 and formed PPC by using $Y(CCl_3COO)_3$, $ZnEt_2$ and glycerine ternary system [76]. Rare earth metal catalytic systems, in general, can be used to adjust the microstructure of the polymer chain. For instance, head-to-tail linkage and molecular weight distribution of PPC was successfully adjusted by using yttrium carboxylate as a catalyst.

Comparing all heterogeneous catalytic systems created so far, conventional zinc glutarate is the only catalyst that has been used commercially for alternative copolymerization of CO_2 and PO. Zinc glutarate exhibits high activity and favourable selectivity [62, 77]. It is cheap, non-toxic and easy to synthesize and can be used for manufacturing relatively high molecular weight PPC with superior carbonate linkage percentage [5]. However, its activity is still one or two order of magnitude lower than the common catalysts used for synthesis of conventional polyolefins [78]. Therefore, enhancement of the catalytic activity of ZnGA was the topic of several studies [7–9].

4.2.4. Catalyst activity of zinc glutarate

Particle size, crystallinity, microstructure and morphology are the key factors that have impacts on activity and yield of the final product. These characteristics can be tuned by changing the source of zinc and glutarate, their particle size, purity, synthesis method and processing condition.

Ree et al. studied the effect of various zinc sources on the activity of ZnGA catalyst [62]. Their results showed that the highest activity of ZnGA was achieved when zinc was derived from zinc oxide. Zinc glutarate from various sources of glutarate was synthesized in another study carried out by Ree et al. [7]. Results of catalyst activity demonstrated that the yield of PPC was significant when zinc oxide and glutaric acid were used for the synthesis of ZnGA. The effect of zinc and glutarate source and synthesis media on the microstructure of ZnGA was also investigated in a study carried out by Kim et al. [8]. This study demonstrated that the highest activity was acquired when ZnGA was synthesized in toluene media due to achieving low surface area and perfect crystallinity.

Particle size and purity of reactants are other parameters that have effect on the activity of ZnGA [9]. It was shown that highly pure ZnO with large particle size resulted in ZnGA with the superior crystallinity and large particle size. In addition, in a bench-scale study, it was shown that when magnetic stirring was used rather than other methods of mixing, the degree

of crystallinity of ZnGA was promoted and resulted in achieving higher yield and larger molecular weight PPC. In yet another study, Pluronic PE6400 was used as an amphiphilic template to increase the degree of crystallinity and enhance the surface area of ZnGA [79]. It is important to note that in this study a mixture of ethanol/water was used as a solvent for the synthesis of ZnGA, and they achieved 83 g PPC/g activity for ZnGA. The yield of PPC production was increased nearly 20% when this catalyst was used for the copolymerization reaction.

Reducing the particle size of crystalline particles of ZnGA is another strategy that has been carried out to increase the catalyst activity [9]. Ball milling method can be used to reduce the particle size; however, it is important to optimize the processing time as long-hour milling might reduce the degree of crystallinity. It was also attempted to increase the surface area to elevate the ZnGA catalyst activity. As an example, PPC with the yield of 115.2 g PPC/g catalyst was obtained when high surface montmorillonite (MMT) was used for ZnGA support [80].

Optimization of the reaction condition was the subject of several studies with the aim of increasing the yield of polymerization. High yield of 126 g PPC/g catalyst was reported for a zinc glutarate supported on a perfluorinated compound with PO/catalyst ratio of 200 ml/g under mechanical stirring [81]. An optimum PO/catalyst ratio of 312 ml/g resulted in PPC yield of 160 g PPC/g catalyst for ZnGA prepared using ultrasonic stirring method [9]. Duan et al. in 2010 investigated the effect of pressure on the yield of copolymerization, product composition, molecular structure and thermal stability of PPC [82]. The results showed a significant enhancement in catalyst selectivity towards the formation of PPC and reduction of by-products. Dehghani research group established a green method to synthesis ZnGA in super-critical CO_2 and eliminated usage of the organic solvent [2]. This study demonstrated that the crystallinity of catalyst produced in this solvent-free process was a function of processing parameters such as temperature and pressure. In addition, the yield of PPC copolymerization was significantly improved when catalyst processed by this technique was compared to ZnGA that was synthesized in toluene.

4.3. New advances in the copolymerization of CO_2 and epoxides

To enhance the catalytic activity and selectivity towards the copolymerization of CO_2 and epoxides, several measures have been taken such as bimetallic catalyst systems, non-metallic catalysts, ionic liquids (ILs), and supported catalysts.

4.3.1. Bimetallic catalyst systems

The idea behind the bimetallic pathway for the copolymerization of carbon dioxide and epoxides is to conduct the ring opening of epoxide and activation of carbon dioxide at the same time. In fact, one of the metal centres is in charge of the coordination and activation of the epoxide and the other metal centre associates with coordination and activation of CO_2 [28]. It was found that the bimetallic pathway involved a second-order dependence on the metal concentration, whereas the monometallic pathway associated with a first order kinetic [30]. For instance, a double zinc centre complex showed high activity and selectivity in the conver-

sion of cyclohexene oxide and CO_2 to PCHC at very low CO_2 pressure [83]. Particularly, the bimetallic pathway showed remarkable improvement in the catalyst activity of the salen catalysts. In addition, a piperidinium end-capped (salen) Co(III) complex copolymerized PO and CO_2 without the generation of cyclic propylene carbonate [59].

4.3.2. Non-metallic catalysts and ionic liquids

An ionic liquid is a salt in which the ions are poorly coordinated. Accordingly, these solvents are liquid at the temperatures below 100°C, or even at room temperature. ILs are broadly used as reaction media, co-catalyst and catalyst for the chemical reactions. In the case of the reaction of epoxides and CO_2, several researchers have focused on the application of ILs. The mechanism of the reaction involved ring opening of the epoxide through a nucleophilic attack by the anion followed by insertion of carbon dioxide and ring closure [28]. Indeed, the absence of metallic centre as Lewis acid resulted in the selectivity of reaction towards the formation of cyclic carbonate compounds [30]. 1-n-butyl-3-methylimidazolium tetrafluoroborate successfully activated CO_2 and propylene oxide for the synthesis of propylene carbonate [84]. Under high-pressure condition, 100% conversion of propylene oxide was achieved by using 1-octyl-3-methylimidazolium tetrafluoroborate as catalyst [85]. However, the reaction was only selective towards the formation of cPC, and no polymer was achieved.

4.3.3. Supported catalytic systems

In these systems, the active catalyst should be anchored to the supporting material through a strong covalent bond in order to avoid possible leaching during the reaction. In fact, the immobilization of a catalyst on the solid support enables its rapid recovery and recycling. However, in some cases, immobilization shows adverse effect on catalyst activity due to limiting the diffusion of the reactants and intermediate compounds into and from the active sites of the catalyst [30]. Mesoporous materials with high surface area such as MCM-41 or SBA-15 have been used as supports to tackle this hurdle [28]. The zn β-diiminate catalyst was supported on controlled pore glass, and mesoporous SBA-15. This catalyst showed significant activity in the alternating copolymerization of CHO and CO_2. However, the resulted copolymer contains higher ether linkages than their corresponding non-supported catalysts due to the starvation of the active sites, particularly in the last stages of the reaction [86].

Recoverable aluminium salen catalysts bonded to poly(ethylene glycol bismethacrylate) and polystyrene exhibited comparable catalyst activity in the copolymerization of CO_2 and epoxides [87]. Chromium salen catalysts anchored on the aminopropylsilyl-modified silica in combination with an IL were used to catalyze the reaction of the styrene oxide and CO_2 [88]. The resulted catalysts exhibited 100% conversion yield; however, they were only selective towards the formation of cyclic carbonates.

Metal salen complexes were also immobilized on the surface of supporting material to facilitate their recovery after synthesis. For instance, zinc β-diiminate complex is immobilized on the surface of mesoporous silica (SBA-15), and this catalyst was used for the copolymerization of CHO and CO_2. However, ether linkage also occurred in the presence of this catalyst. In another

study, chromium salen catalyst, immobilized on the surface of silicates, was used for the copolymerization of styrene oxide and CO_2 with nearly 50% activity and 80% selectivity [88]. In yet another example, aluminium salen catalyst, bonded on the surface of the polystyrene, was used for the copolymerization of CO_2 and styrene oxide [87]. In addition to the potential of being recovered, the supported aluminium salen catalyst exhibited similar activity to the unsupported aluminium salen compounds.

5. Industrial activities and commercial advances

A list of patents filed for the copolymerization of CO_2 and epoxide is shown in Table 2. Since 1969, most patents filed for the copolymerization of CO_2 and epoxides focused on developing heterogeneous catalysts, particularly zinc-based catalysts. The first catalyst, diethyl zinc, was developed by Inoue et al. in 1973 [89]. This patent that was sponsored by Nippon Oil Seal Industry Company demonstrated that the presence of co-catalyst significantly increased the yield of the copolymerization of ethylene oxide and CO_2 nearly threefold. The co-catalyst includes a hydrogen donor-based compound that was added to an organometallic compound, formed from metals that belonged to group II or group III [90].

A process for preparing soluble zinc catalysts by the reaction of zinc compounds with either a dicarboxylic acid anhydride or an alcohol or a monoester of a dicarboxylic acid was reported and filed in 1987 [91]. This catalyst system that was soluble in most of solvents was useful for the copolymerization of epoxides and carbon dioxide to form polycarbonates. In 1989 and 1990, two patents, both sponsored by Japanese companies such as Mitsui Petrochemical Industries, were filed for the development of several catalysts containing zinc oxide that reacted with an organic dicarboxylic acid such as glutaric acid or adipic acid [92, 93]. These patents introduced zinc glutarate from the source of zinc oxide and glutaric acid as the most efficient catalyst for the copolymerization of propylene oxide and carbon dioxide.

In 1998, dicarboxylic acids were used to successfully synthesize co-, ter-, and block-polymers from epoxides and carbon dioxide. This study that was sponsored by Buna Sow Leuna Olefinverbund GmbH consisted of two dicarboxylic acids, which could be aliphatic, aromatic or a mixture of the two, in combination with a divalent inorganic zinc salt [94]. In 2003 and 2004, new patents were filed to investigate catalyst efficiency of a range of zinc complexes synthesized from different dicarboxylic acids (chosen from pentane diol, hexane diol, 1,5-dibromopentane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,6-dibromohexane, glutaronitrile, adiponitrile, glutarimide, adipamide, glutaralaldehyde and adipaldehyde) precursor and zinc precursor (chosen from zinc acetate dihydrate, zinc hydroxide, zinc nitrate hexahydrate, zinc perchlorate hexahydrate, zinc oxide and zinc sulphate) [95, 96]. Among them, the complex synthesized of zinc perchlorate hexahydrate and glutaronitrile showed the highest yield of 67% over a period of 30-h reaction for copolymerization of PO and carbon dioxide.

As mentioned before, zinc carboxylates, particularly zinc glutarate, are the only group of catalysts that could be effective in the commercial and large-scale synthesis of polycarbonates. However, the activity of this group of catalysts is still remarkably lower than the conventional

catalysts used for the synthesis of polyolefins. Consequently, many research and development activities are still focusing on novel catalysts for the synthesis of polycarbonates. For this purpose, most patents in the last decade focused on designing bimetallic or metal cyanide compounds to increase both yield and selectivity for the synthesis of polycarbonates [97]. For example, highly selective and active cobalt containing cyanide catalysts for producing poly(alkylene carbonates) from alkylene oxide and carbon dioxide was documented in 2005 [98]. However, the final product has still 10% cyclic carbonate by-product. In 2009, bimetallic complex of Zn(H), Co(II), Mn(II), Mg(II), Fe(II), Cr(III)-X or Fe(III)-X was reported for copolymerization of carbon dioxide and cyclohexene oxide or propylene oxide [99]. Following these developments in 2012, a catalyst was invented from the reaction of one double-metal cyanide compound, one organic complexing agent and one primary alcohol having 6–24 carbon atoms (sponsored by Henkel Ag & Co.). The compound was effective in catalyzing both homopolymerizations of epoxides or copolymerization of epoxides with carbon dioxide [100]. In the same year, a process for the synthesis of a polycarbonate from carbon dioxide and epoxides using a bimetallic catalyst system and a chain transfer agent was reported [101]. This invention that was sponsored by Imperial Innovations Limited exhibited that bimetallic complexes were successful in improvement of both activity and selectivity of PACs synthesis and accomplished above 90% yield of copolymerization with 99% carbonate linkage.

Patent Number	Catalyst	Epoxide	Activity (g/g catalyst)	Reference
US 3585168	Diethyl zinc and water [a]	Propylene oxide Ethylene oxide Styrene oxide Isobutylene oxide		[89]
US 4783445	Soluble zinc-based catalysts as a result of the reaction of zinc compounds (zinc oxide and zinc acetate) and dicarboxylic acids (maleic anhydride and monomethyle adipate) [a]	Ethylene oxide Propylene oxide Cyclohexene oxide		[91]
US 4943677	Zinc polycarboxylate catalyst (from zinc oxide and glutaric acid) in present of a hydrogen donor compound such as phenol and benzoic acid (acidity range 3-20 pKa) [a]	Propylene oxide		[102]
US 4981948	zinc containing solid catalyst by contacting zinc oxide with an organic dicarboxylic acid (oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, 1,5-pentane dicarboxylic acid, 1,6-hexane dicarboxylic acid, 1,8-octane	Propylene oxide	60.7 (max)	[92]

Patent Number	Catalyst	Epoxide	Activity (g/g catalyst)	Reference
	dicarboxylic acid and 1,10-decane dicarboxylic acid) and aromatic dicarboxylic acids (phthalic acid, isophthalic acid, terephthalic acid, 1,2-naphthalene dicarboxylic acid, 1,3-naphthalene dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid, 1,6-naphthalene dicarboxylic acid, 1,7-naphthalene dicarboxylic acid, 1,8-naphthalene dicarboxylic acid, 2,3-naphthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid and 2,7-naphthalene dicarboxylic acid) [a]			
US 5026676	Zinc carboxylate catalyst by reaction of zinc compounds (zinc oxide, $Zn(OH)_2$, $Zn(CO_3)_2$ and $Zn(OAc)_2$) with a dicarboxylic acid (glutaric acid or adipic acid) [a]	Propylene oxide	26 (max)	[93]
WO 2003029325	Zinc glutarate and zinc-cobalt based double metal cyanide catalyst [a]	Propylene oxide Ethylene oxide		[97]
WO 2004000912	Catalysts from the oxidizing of a dicarboxylic acid precursor (chosen from pentanediol, hexanediol, 1,5-dibromopentane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,6-dibromohexane, glutaronitrile, adiponitrile, glutarimide, adipaimide, glutaraldehyde and adipaldehyde) and a zinc precursor (chosen from zinc acetate dihydrate, zinc hydroxide, zinc nitrate hexahydrate, zinc perchlorate hexahydrate, zinc oxide and zinc sulphate) [a]	Propylene oxide		[95]
US 20060089252	Cobalt salen catalyst [b]	Propylene oxide		[98]
WO 2009130470	Bimetallic complex of Zn(II), Co(II), Mn(II), Mg(II), Fe(II), Cr(III)-X or Fe(III)-X[b]	Cyclohexene oxide Propylene oxide		[99]
WO 2012136658	Double-metal cyanide compound [b]	Propylene oxide		[100]

Patent Number	Catalyst	Epoxide	Activity (g/g catalyst)	Reference
WO 2013034750	Bimetallic catalyst with metal centre from (Mg(II), Zn(II), Ca(II), Ge(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, A1(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-(X)$_2$ or Ti(IV)-(X)$_2$) [b]	Cyclohexene oxide		[101]

[a] Heterogeneous catalysts, [b] Homogeneous catalysts

Table 2. List of the Filed Patents in the Field of CO$_2$ and Epoxide Copolymerization

6. Conclusions

This review demonstrated the significant advances that have been accomplished for developing active catalysts for the copolymerization of carbon dioxide and epoxides in the last four decades. In fact, a broad range of catalysts have been designed and examined with high activity and selectivity for the synthesis of biodegradable poly(alkylene carbonates). In addition, the mechanistic aspects of CO$_2$ cycloaddition to epoxides have been recognized and reported. Regardless of the structure of the catalyst and some slight differences, the overall mechanism proposed for the copolymerization of CO$_2$ and epoxides is coordination–insertion mechanism catalyzed via metal compounds with Lewis acid and Lewis base active sites.

Homogeneous catalysts for CO$_2$–epoxide copolymerization were proposed such as phenoxide, β-diiminate and metal salen complexes. The two former groups only showed activity for copolymerization of CHO and CO$_2$. In addition, salen catalysts exhibited activity and selectivity for a broader range of epoxides copolymerized by CO$_2$. However, none of these homogenous catalysts was used in commercial scale due to complicated synthesis process and low selectivity. Among several heterogeneous catalysts designed, organometallic complexes, particularly zinc glutarate, are the most effective catalysts because of both high activity and selectivity, low cost, non-toxicity and simple manufacturing process. In the last decade, attempts have been undertaken to design bimetallic catalysts to enhance activity towards copolymerization of CO$_2$ with epoxides. However, these studies are still in their infancy and have not yet used in the commercial scale.

In summary, the biodegradable polycarbonates are promising polymers that are produced from bonding CO$_2$ with epoxides that are partially renewable with huge market value for production of broad range of products such as food packaging materials, healthcare devices and agricultural mulches. Developing an efficient catalyst that reduces the cost and minimizes the catalyst consumption and by-product is still attractive as an alternative to non-degradable polymers in many applications to remedy the global issue of plastic wastes in landfills.

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