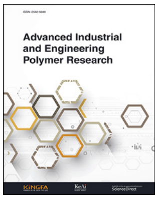
Advanced Industrial and Engineering Polymer Research 2 (2019) 143–160

Contents lists available at ScienceDirect

Advanced Industrial and Engineering Polymer Research

journal homepage: http://www.keaipublishing.com/aiepr



CO_2 derived biodegradable polycarbonates: Synthesis, modification and applications

Shuxian Ye, Shuanjin Wang, Limiao Lin, Min Xiao[**], Yuezhong Meng[*]

The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials and Engineering, Sun Yat-sen University, Guangzhou, 510275, PR China

ARTICLE INFO

Article history:
Received 22 August 2019
Received in revised form
24 September 2019
Accepted 30 September 2019

Keywords:
Carbon dioxide
Poly(propylene carbonate)
Biodegradable plastic
Copolymerization
CO_2-based polymer

ABSTRACT

Fixation carbon dioxide into polymer is a feasible proposal to construct high value-added biodegradable plastic. These polymers are environmentally friendly and energy-saving owing to that the raw material is waste gas and finally they decompose back into CO_2. This review mainly focuses on our group work of recent advancements on CO_2-based copolymers, especially for poly (propylene carbonate) (PPC). We also extensively introduce the improvements on thermal and mechanical performances of PPC by physical and chemical modifications. Meanwhile, their practical application is further discussed in detail as well to replace the conventionally non-biodegradable plastics. The commercial PPC has already been found an enormous application prospect in versatile packaging industry.

1. Introduction

Carbon dioxide (CO_2) is regarded as one of the main environmental pollutants causing the greenhouse effect [1]. Greenhouse effect or the climate warming reflecting in the world has already been 1 °C higher than preindustrial times, which urges people to reduce CO_2 emission year by year and ideally by 2050, achieve zero net CO_2 emission globally [2]. *Global Energy & CO_2 Status Report 2017* reveals that global energy-related CO_2 emission rose by 1.4% and reached a historic high of 32.5 Gt (Fig. 1), equivalent to consume 14.0 Gt oil [3]. Undoubtedly, such large CO_2 emission goes beyond the balance of natural photosynthesis, microorganisms, plants and algae utilizing CO_2 as the most important C1 source for the synthesis of organics. CO_2, a non-toxic, abundant, cheap and easily obtained carbon source, arouses great interest among the scientists all over the world to decrease massive CO_2 in the atmosphere. On the one hand, development of clean energy may reduce CO_2 emission sharply even reach zero net CO_2 emission so that eases the greenhouse effect. On the other hand, capture of CO_2 is an effective way to convert the greenhouse gas into many fine chemicals and commodities, although the chemical utilization of CO_2 is less than 1% since CO_2 as reactant for a chemical reaction [4].

From the standpoint of economy and ecology, it's highly desirable to utilize CO_2 instead of disposing it. One of the cost-effective utilization approaches is to employ CO_2 to produce a series of polymers with biodegradable and tailored properties. Nowadays, polyolefin plastic wastes have brought about dreadful consequences, called "white-pollution", which results from the random discard and landfill of the packaging materials, agricultural mulch films, food wrappers and so on. Polyolefins just can be degraded extremely slow by the presence of oxygen and UV rays [5]. This urgent project has forced scientists to develop biodegradable materials, which can be degraded by microorganisms buried in the ground under suitable condition. In fact, development of biodegradable polymers encounters difficulties in replacing the polyolefin plastics because of the costly raw materials. Therefore, utilization of CO_2, an excellent feedstock, finds expression in synthesizing cheap, sustainable and biodegradable polycarbonates. For example, direct copolymerization of CO_2 with different epoxides such as ethylene oxide (EO), propylene oxide (PO), cyclohexene oxide (CHO) or isobutylene oxide (BO) to construct aliphatic polycarbonates and poly (carbonate-ether)s.

As we all know, CO_2 is a symmetrical linear nonpolar molecule containing two orthogonal π orbital bonds. Thus, it is chemically stable and hard to be activated. In order to make copolymerization smoothly, high active catalysts have been applied to activate the

---

[*] Corresponding author. Fax: +86 20 84114113.

[**] Corresponding author.

E-mail addresses: stsxm@mail.sysu.edu.cn (M. Xiao), mengyzh@mail.sysu.edu.cn (Y. Meng).

https://doi.org/10.1016/j.aiepr.2019.09.004

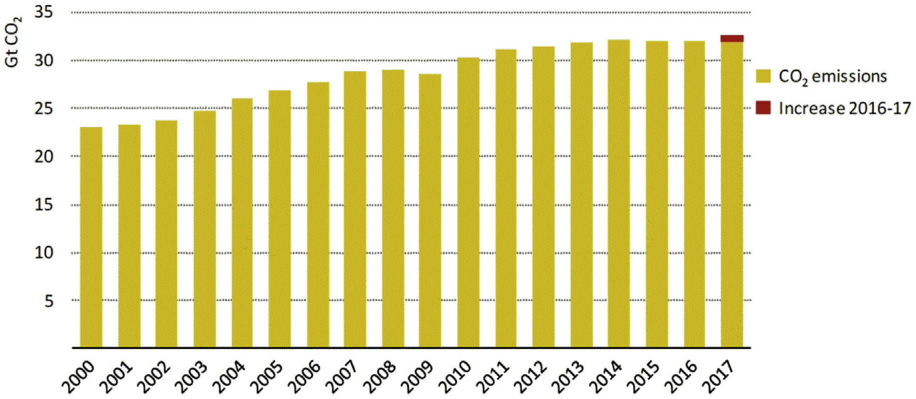


Fig. 1. Global energy-related CO_2 emissions, 2000–2017 [3].

inherently inactive CO_2. In 1969, Inoue and co-workers creatively copolymerized CO_2 with PO catalyzed by diethyl zinc/water complex, preparing poly (propylene carbonate) (PPC) with 88% carbonate content but a low yield of 4.2 g of polymer/g catalyst [6,7]. After that, there is a boom in exploring related catalysts for the copolymerization of CO_2 and epoxides, focusing on the high catalytic activities and the well-defined structures for mechanism investigations [8–12]. Ree et al. copolymerized CO_2 and PO with zinc glutarate (ZnGA) under optimized conditions and achieved a high yield of about 64 g polymer/g catalyst. Our group have successfully synthesized zinc carboxylate catalysts for the preparation of PPC and then fixed ZnGA into a matrix to form supported catalyst with a high yield of 160.4 g polymer/g catalyst [13,14]. It is worth mentioning that zinc dicarboxylates (e.g. ZnGA) have exhibited the most catalytic efficiency among the simple catalytic systems for constructing aliphatic polycarbonate from CO_2 and PO reported so far. In general, the mechanism of the alternating copolymerization catalyzed by zinc-based systems, has been proposed to propagate via monomer insertion into the growing polymer chain end with a coordinated anionic nature.

Owing to the ester bonds on its backbone, PPC has been demonstrated to be a biodegradable polymer. In this regard, researchers show great interest in constructing PPC with tailored properties. Our group have reported that the as-made alternating structure PPC with ZnGA as catalyst possesses high molecular weight and good biodegradability in both soil burial and buffer solution immersion tests [15]. Moreover, the alternating PPCs exhibit superior thermal and mechanical properties with much higher glass transition and decomposition temperatures than those of conventional PPCs containing ether bonds. As a result, the melt process can be applied to PPC's processing like commercial polyethylene. It is widely accepted that to a great extent, the properties of amorphous polymers depend on the molecular weight, especially in processability and mechanical properties. Particular technics are applied to understand the correlation of the molecular weight, thermal properties, mechanical properties and rheological behavior of synthesized PPC due to the potentially massive applications in packaging film, injection and foamed materials. To further enhance some properties of PPC, modification is an effective method, such as copolymerization, blending, crosslinking and fabrication of block copolymer.

Fig. 2. PPC production base in Tianguan Group.

The fixation of waste CO_2 into PPC is a remarkable achievement due to a low carbon footprint towards polymeric materials. CO_2 takes a shortcut into CO_2-based fully degradable plastics with potential and wide applications. PPC finds its applications in barrier materials, foaming materials, electrolyte and so on. Industrialization of PPC is the base of practical application of PPC-related products. Significantly, in 2006, the industrial scale PPC production was launched in Tian-Guan Enterprise (Group) Co. Ltd, Henan, China at a scale of 5000 t/annum (t/a) (Fig. 2). Working together with the researchers in Tianguan Group, modified technological and apparatus have been developed [16–19]. With a rapid growth, the production scale has reached 25,000 t/a in 2012. Tian-Guan company produces 550 kt/a ethanol using corn by alcoholic fermentation process each year. However, this process simultaneously yields almost equal amount of by-product of waste CO_2. In this case, the recycling of CO_2 is an impendency issue in order to prevent the massive carbon dioxide into atmosphere to cause worse environmental pollutant. Therefore, the company utilizes CO_2 as a starting reactant and copolymerizes it with propylene oxide to produce biodegradable PPC. The whole process eventually achieves the zero pollution without waste discharge. The technology was transferred from our group at Sun Yat-sen University, Guangzhou, China. The PPC copolymer contains more than 43 wt.% carbon dioxide, *i.e.*, we have the ability to convert the industrial waste into a high value-added biodegradable plastic.

Biodegradable PPC is an attractive material with various applications. Our group have put in enormous efforts on not only the improvement of catalytic reactivity, but also the development of PPC-based products. Previously, we have reviewed the synthesis, performance and modification of PPC [20]. More recently, CO_2-based plastics were depicted systematically [21]. This review aims to give an overview of our group's work on producing PPC, summarizing the advances in catalyst systems, polymer synthesis via binary copolymerization and ternary polymerization, as well as modifications and applications of PPC.

2. Development of catalyst

Applicable catalyst plays a vital role in commercial process of PPC. In the accepted mechanism for the coupling reaction of CO_2 and epoxide, epoxide firstly coordinate with a metal center with subsequent CO_2 insertion to a metal alkoxide alternatively. Epoxide needs to be activated via coordination to the active site of metal before insertion into metal-oxygen bond, but CO_2 doesn't need to be activated by catalyst. In this process, side reactions such as copolymerization of epoxide and backbiting of metal alkoxide into a neighboring carbonate bond are unavoidable, resulting in polyether and cyclic carbonate respectively. Our group have exploited different heterogeneous/homogeneous Zn catalyst, the most successful one of which is zinc glutarate catalyst [22–24].

2.1. Heterogeneous metal containing catalyst

Up to now, zinc dicarboxylates, especially ZnGA, are considered to be the most commercial suitable catalysts for production of PPC with reasonably high molecular weights. Table 1 summarizes the six types of heterogeneous catalyst we reported. By controlling the purity of raw materials and mixing way, we have synthesized high-purity crystalline ZnGA catalyst using zinc oxide as reactant. In the synthesis of PPC, PO acts as both monomer and solvent in the load of ZnGA with a high yield, which make PPC a good application in industrial. We successfully prepared zinc dicarboxylate by ultrasonic methodology with high reaction speed and conversion rate [13]. Compared with mechanical stirring, the ZnGA catalyst prepared by ultrasonic presents high crystallinity and perfectness in small-sized crystallites [22]. It is believed that the morphological structure of ZnGA has a strong effect on catalytic reactivity. ZnGA was synthesized by magnetic stirring and subsequently fragmented by ultrasonic to gain 0.2–0.3 μm particles. Using this catalyst, the highest yield of PPC (160 g polymer/g catalyst) can be obtained [23]. We have also prepared alternating PPC with high molecular weight employing supported zinc glutarate (s-ZnGA) as catalysts, which can enlarge surface area of ZnGA and expose more active cites on the catalyst surface. ZnGA supported on silicon dioxide (ZnGA–SiO_2) exhibits a high catalytic yield of (359 g polymer/g Zn) [25]. When dispersing ZnGA on the surface of acid-treated montmorillonite (MMT), we synthesized ZnGA–MMT catalyst with a smaller crystal size but same crystalline structure as compared with that of pure ZnGA. The as-made catalyst gives PPC a high yield (115 g polymer/g ZnGA) [26]. Moreover, ZnGA catalyst, supported on a perfluorinated compound containing 7–12 carbons (ZnGA-PFC), achieves a very high yield (126 g polymer/g catalyst). The resulting copolymer exhibits high glass transition temperature (T_g) (46.46 °C) and decomposition temperature (255.8 °C) [14].

Zinc glutarate has proved to be the most effective catalysts to produce aliphatic polycarbonate with considerably high molecular weight. However, the high cost of preparing ZnGA from zinc oxide and glutaric acid limits its practicable application in the production of PPC. In comparison with ZnGA, inexpensive zinc adipate (ZnAA) has been reported to exhibit relatively potentially catalytic activity for the copolymerization of CO_2 and PO (7–19 g polymer/g catalyst) [27]. In this regard, improving the catalytic activity of ZnAA is much meaningful for commercial utilization of CO_2. We synthesized zinc adipate with high catalytic activity from zinc oxide and adipic acid via mechanical and magnetic stirring routes with a high degree of crystallinity and crystal quality [28]. By optimizing the reaction conditions, high molecular weight alternating PPC can be afforded in a relatively high yield (110.3 g polymer/g catalyst) [29]. It is noteworthy that the catalytic performance of ZnAA is much lower than that of ZnGA. Composite catalysts also show greatly improved catalytically efficiency than conventional ZnGA catalyst. In this catalytic system, synergistic effect between main catalyst and co-catalyst enhances the catalytic efficiency. We prepared a composition catalyst, zinc dicarboxylate as main catalyst and tertiary amine as co-catalyst, via mixing and aging process to make the tertiary amine complexation with zinc dicarboxylate (Scheme 1) [30–32]. In this catalyst system, coordination capacity of active center is enhanced, which increases the catalytic efficiency and shorten the reaction time from 40 h to 24 h with good selectivity. The yield using ZnGA/4,4′methylenebis (N,N-dimethylaniline) (ZnGA/DMAPM) composite as catalyst is up to 373 polymer/g zinc [30]. Moreover, product shows improved performances. In zinc adipate/tertiary amine catalytic system, high selectivity PPC with a considerable yield (>280 g polymer/g zinc) and high molecular weight ($M_n > 250$ kg·mol^{-1}) was afforded because the steric hindrance limited the backbiting reaction of the zinc alkoxide species as illustrated in Scheme 2 [32]. Besides ZnAA, zinc pimelate (ZnPA) was developed to accelerate the copolymerization rate of CO_2 and PO by magnetic stirring method [33]. However, the as-made catalyst just has a modest catalytically efficiency (95 g polymer/g catalyst).

2.2. Homogeneous metal containing catalyst

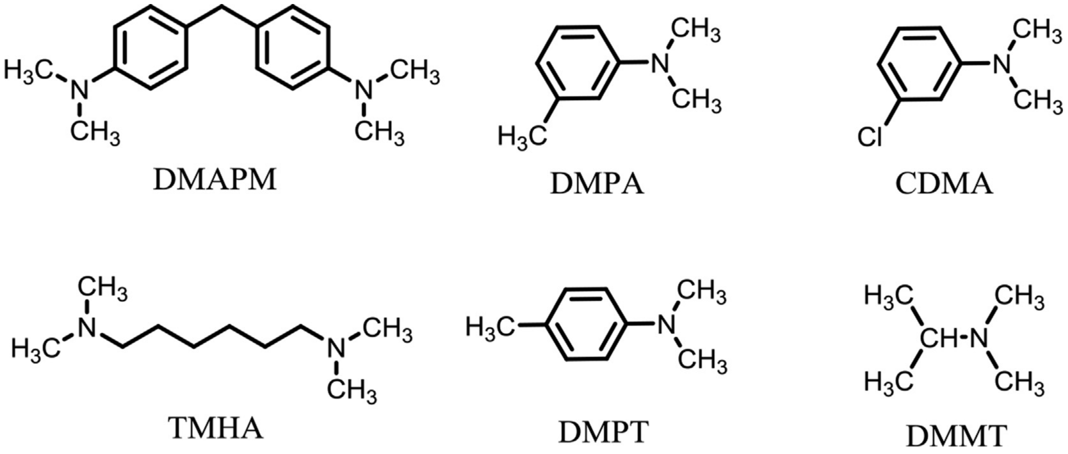
Compared with heterogeneous zinc complexes, homogeneous zinc catalysts have higher dispersal, selectivity and conversion; moreover, the well-defined formation and soluble single active-site crystal of them are favorable to study the reaction mechanism of the copolymerization of CO_2 and epoxides. In the preparation of PPC, zinc-hydroxy acids complexes were synthesized by hydrothermal process with good selectivity and high catalytic efficiency (115 g polymer/g Zn) [34]. Zinc phenol hydroxyl complex catalysts achieved catalytic activity above 85 g polymer/g Zn [35]. We also synthesized a polymer-supported zinc catalyst, zinc metallophthalocyanine-containing poly (arylene ether sulfone) (ZM-PAE) by reacting phthalocyanine group-containing poly (arylene ether sulfone)s with zinc glutarate, which possesses an activity of 30 g polymer/g catalyst (196 g polymer/g zinc) [36]. On the

Table 1
Heterogeneous catalysts for production of PPC[a].

No.	Catalyst	CO_2/MPa	Yield/(g polymer/g catalyst).	Productivity/(g polymer/g Zn)	M_n/(kg·mol^{-1})	Ref.
1	ZnGA	5.2	160	480	26.3	[23]
2	ZnGA–SiO_2	5.2	–	359	–	[25]
3	ZnGA–MMT	5.2	–	344	14.5	[26]
4	ZnGA-PFC	5.0	126	–	56.1	[14]
5	ZnGA/DMAPM^b	5.0	–	373	26.4	[30]
6	ZnAA	5.2	110	354	53.4	[29]
7	ZnAA/DMAPM^c	5.0	–	285	25.9	[32]
8	ZnPA	5.2	95	325	39.1	[33]

Copolymerization conditions: 60 °C, 40 h; ^{b}80 °C, 24 h; ^{c}90 °C, 32 h.

[a] All resultant PPC is the insoluble fraction in methanol.



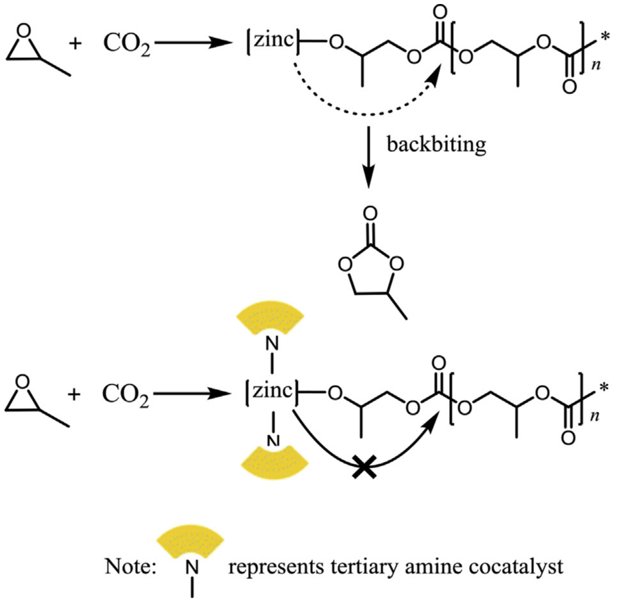
Scheme 1. Tertiary amine compounds as co-catalysts for copolymerization of CO_2 and PO [30–32].

whole, the homogeneous zinc catalysts applied in producing PPC display the inferior catalytic performance in comparison with heterogeneous zinc catalysts.

Interestingly, homogeneous zinc catalysts exhibit high catalytic efficiency in CO_2/CHO system. In the copolymerization of CO_2 and CHO, we developed a range of salicylaldiminato-zinc and tri-zinc complexes including various Schiff base ligands with tailored reactivity (Scheme 3) [24]. The catalytic efficiency has achieved 359 g polymer/g Zn in a suitable reaction condition. Furthermore, it's proved that the steric size and electronic density around the Zn metal centers have a violent influence on the catalytic performance of zinc complexes. Meaningfully, the tri-zinc complexes catalyzed polymerization mechanism was investigated (Scheme 4) [37].

2.3. Metal-free catalyst

Although metal catalysts are extremely mature both in the industry and in academia, they inevitably suffer from complicated synthesis, high cost or environmental issues. Hopefully, organic catalysts are developed to be a realistic alternative to metal-based catalysts for ring-opening polymerization of cyclic esters or lactones to biodegradable polyesters. Hydrogen bonding-based catalyst systems are demonstrated as the effective and tunable ones for several common cyclic monomers by adjusting the acidity/alkalinity of Lewis acid/Lewis base [38]. Recently, our group firstly realized the synthesis of high-molecular-weight poly (γ-butyrolactone) from nonstrained γ-butyrolactone using economical ureas/alkoxides at elevated reaction temperature [39]. Lately, the sustainable polyester synthesis was achieved by applying (thio) ureas/organic bases catalyst system to copolymerization of epoxides and cyclic anhydrides with high reactivity [40]. The turnover frequency (TOF, *ca.* 456 h^{-1}) in the ring-opening alternating copolymerization of CHO and PA is the highest reported one, even comparable to metal-based catalysts [41–43]. In addition, phosphazene base is also the rising catalyst for the preparation of aliphatic polyesters under mild condition (60 °C) [44,45]. However, both hydrogen bonding-based catalysts and phosphazene bases are lacking in the ability of directly copolymerization of epoxides and CO_2. It's challengeable to directly synthesize polycarbonates from CO_2 and epoxides using metal-free catalysts until Feng's group make a significant breakthrough in the anionic copolymerization of epoxides and CO_2 with triethyl borane (TEB) as activator (Scheme 5) [46]. Whereafter, theoretical mechanistic investigation into the role of TEB using DFT calculations indicated that only 2 equivalent of TEB to the initiator in experiment was suitable [47]. More recently, they prepared well-defined PPC diols and polyols with controllable molecular weights and polycarbonate contents utilizing multi-functional carboxylate salts as initiators [48]. This creative use of TEB in PPC synthesis has inspired the explorations on alternating polymerization of epoxides and carbonyl sulfide [49] or anhydrides [50], self-polymerization of PO [51] and so on. In a word, there is a bright future in developing metal-free catalyst system for alternating polymerization of epoxides and CO_2.

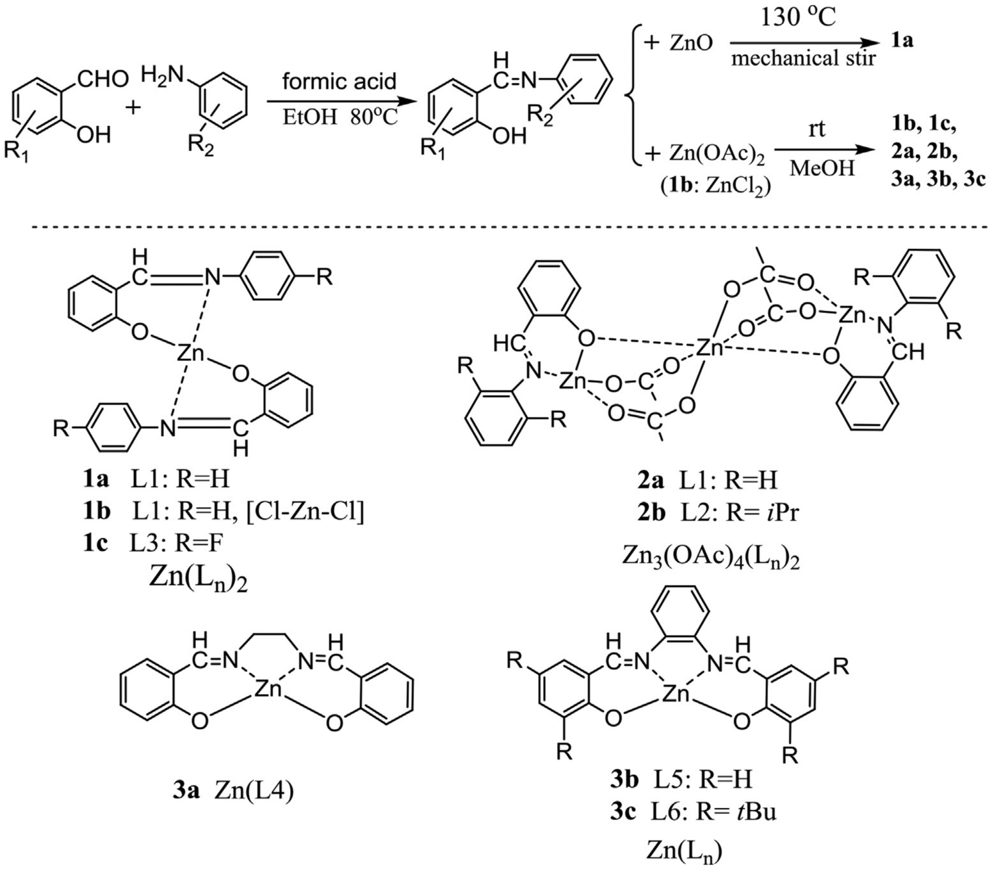


Scheme 2. Mechanism of cyclic carbonate suppression in the presence of the tertiary amine cocatalyst [32].

3. CO_2-based polymer

3.1. Biodegradable PPC

It's important to suppress ether linkages, improve selectivity and stereoselectivity of CO_2 -based polycarbonates. Meanwhile, mechanical property, thermal stability, and processability are vital in practical applications. We have conducted lots of work on the construction of PPC not only in the preparation of catalyst as mentioned before but also in changing the reaction condition.



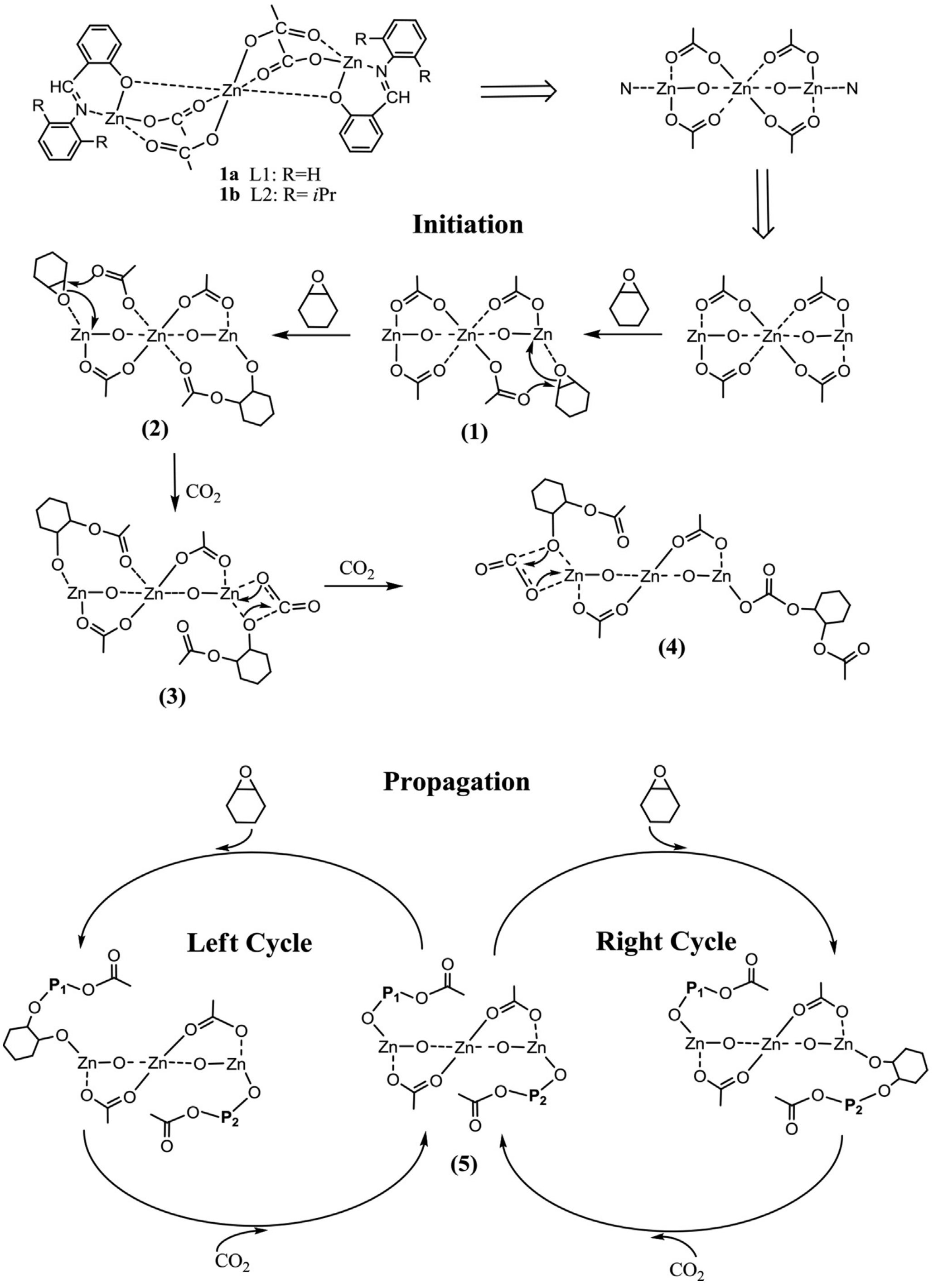
Scheme 3. Synthesis of Schiff base zinc and tri-zinc complexes [24].

Amorphous PPC exhibits a range of glass transition temperature of 30–46 °C, high toughness with a yield strength around 30 MPa, which is stronger than that of polyethylene (22 MPa) and regular grade polypropylene (27 MPa) [20]. The thermal stabilities and mechanical properties of PPC are inferior to the industrially produced polycarbonate. It is hoped that the yield, molecular weight, by-product control, and properties of PPC can be improved by optimizing the reaction condition.

Undoubtedly, the molecular weight plays a vital role in the performances of PPC. We have synthesized high molecular weight PPC using s-ZnGA catalyst with high thermal stability [14], and found that the reaction time of 40 h, temperature of 60 °C and pressure of 5.2 MPa were the optimized reaction conditions [52]. In the synthesis of PPC, homopolymer polyether and cyclic carbonate (Scheme 6) are two kinds of by-products greatly impacting the molecular weights and performances of PPC. Besides the side reactions, impurities containing active hydrogen including water, ethanol, and propanal may not be neglected in the production of PPC [53,54]. Propanal increases the catalytic activity while water and ethanol show a crosscurrent. These impurities have an unfavorable effect on the molecular weights, broaden the molecular weight distributions and increase the ether bond content of PPC.

We also studied the thermal stability and thermal decomposition mechanism of PPC for a better understanding and thus to provide a direction to design a more thermally stable polymer for practical application. Table 2 and Table 3 list the thermal and mechanical properties of PPC with different relative molecular mass [20,55]. The thermal decomposition analysis of alternating PPC have been conducted by combination of thermogravimetric analysis/infrared spectroscopy (TG/IR) and pyrolysis-gas chromatograph/mass spectrometry (Py-GC/MS) techniques [56]. The result shows that the catalyst has little effect on the decomposing mechanism, but can accelerate the depolymerization rate by slightly reducing the activation energy. In addition, chain scission occurs at relatively lower temperature and unzipping reaction needs high temperature because of the high activation energy to form cyclic propylene carbonate and 1,2-propanediol. PPC can be melt extruded like commercial polyolefins in a temperature range from 150 to 170 °C [57]. Calculated by Ozawa method, the thermal decomposition activation energies of different molecule-weight PPCs ($M_n = 42{,}000$–$86{,}000$ g/mol) are in the range of 105–118 kJ/mol [58]. Moreover, both high molecular weight PPC, i.e. with a low hydroxyl end group content, and the end-capping PPC show higher thermally stability due to the rate of chain unzipping from terminal hydroxy group is hindered.

In the molten state, PPC exhibits pseudoplastic flow behavior via rheological measurement and the rheological behavior depending on the molecular weight [55]. The increased shear rate decreases the flow activation energy of PPCs. The essential work of fracture (EWF) analysis is a widely acceptable method for the fracture characterization. After EWF analysis, the PPC ($M_n \approx 30{,}000$ g/mol) completely recovered from plastic deformation 8 days later, indicating that the initial entanglement network structure preserved after unloading without significant change [59]. With the increasing molecular weight of PPC, there's an increase in the fracture toughness, thermal decomposition temperature and T_g [60]. Remarkably, the specific essential fracture work ($w_e = 12.6\ \mathrm{kJ \cdot m^{-2}}$) of the high molecular weight PPC ($M_n = 141{,}000$ g/mol) is close to poly (vinyl chloride) ($w_e = 12$–$14\ \mathrm{kJ \cdot m^{-2}}$). Degradation behaviors of PPCs exhibit good biodegradability according to both soil burial and buffer solution immersion tests [15].



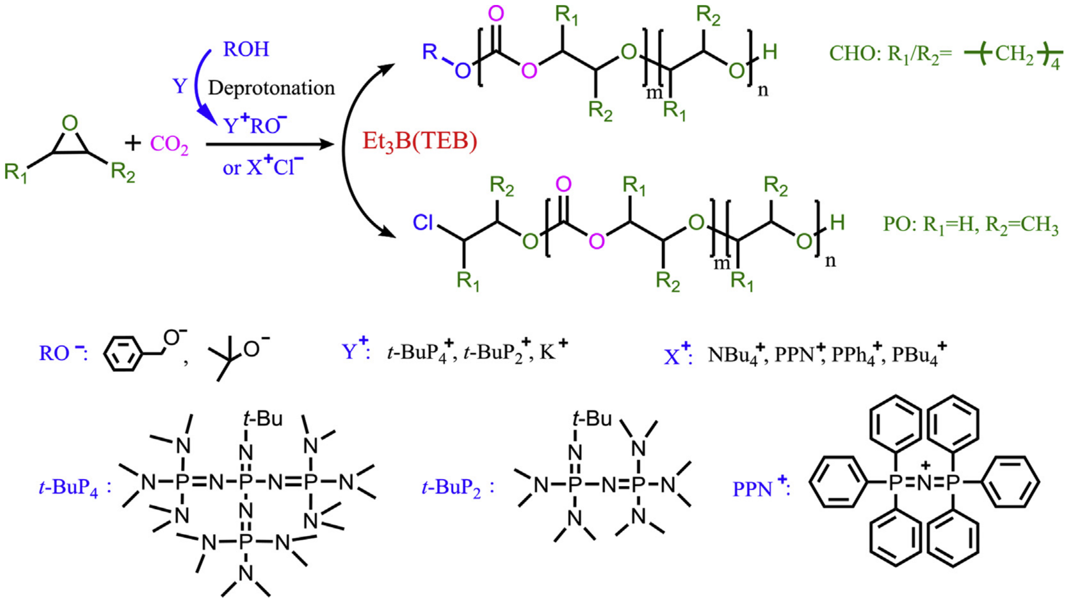
Scheme 4. Proposed mechanism for the copolymerization of CO_2 and CHO catalyzed by tri-zinc complexes [37].

3.2. Third monomer into PPC

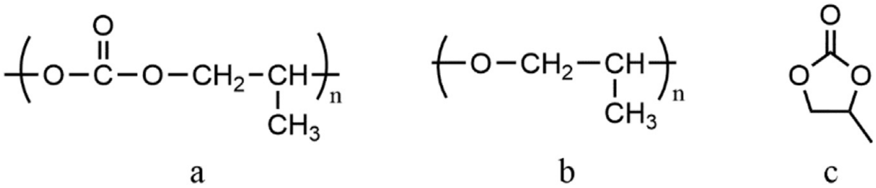
Production of PPC is the most effective way to convert CO_2 into a high value-added biodegradable plastic. However, the amorphous polymer possesses poor thermal stability and low mechanical strength with a relatively low T_g (<50 °C), which results in practical limitations. To broaden PPC's scope of application, one effective way is to introduce bulky or rigid structure, or crystalline segment into the backbone of PPC to reach desirable properties. For example, introducing a third monomer including cyclic epoxides, cyclic esters, anhydrides and acrylates into the backbone of PPC via ring-opening copolymerization is a practicable method to adjust the T_g or T_m of terpolymers. However, it's still a challenge to regulate the composition and structure of the resulting copolymers due to the different reactivity of PO and the third monomer. To expand the application of PPC, terpolymerization of CO_2 and other two monomers have also been developed. The main third monomers into PPC are displayed in Scheme 7. Table 4 summarizes the thermal and mechanical performance of the main CO_2-based terpolymers.

3.2.1. Epoxide

The amorphous poly (cyclohexene carbonate) (PCHC) from CO_2 and cyclohexene oxide (CHO) possesses a high T_g of 120 °C because of rigid cyclohexyl groups on the backbone. Hence, the introduction



Scheme 5. Anionic copolymerization of epoxides and CO_2 with TEB as activator [46].



Scheme 6. Structures of (a) PPC, (b) polyether and (c) cyclic carbonate

Table 2
Thermal properties of PPC as a function of molecular weight [55].

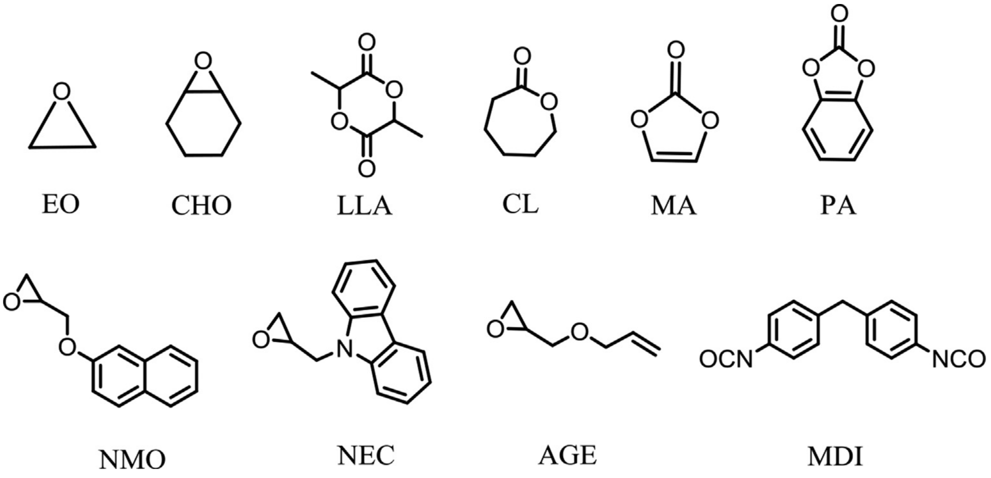
No.	M_n/(kg·mol^{-1})	T_g/°C	$T_{5\%}$/°C	T_{max}/°C
1	26.9	26.7	239.0	258.1
2	36.6	36.0	233.0	256.1
3	56.0	38.2	256.0	271.0
4	62.5	40.8	256.6	271.6
5	89.0	41.0	251.0	276.4
6	114.0	42.1	258.0	279.5
7	144.6	46.5	255.8	275.8

$T_{5\%}$: 5% weight loss temperature; T_{max}: maximum weight loss temperature.

of cyclohexene carbonate (CHC) units into PPC can reduce flexibility of chain and strengthen interchain interaction, leading to an improvement on mechanical property of PPC. We synthesized poly (l,2-propylene carbonate-*co*-1,2-cyclohexylene) (PPCHC) from CHO, PO and CO_2 with supported multi-component zinc dicarboxylate catalyst with improved T_g and tensile strength [61–63]. The as-made ultra-high molecular weight polymers exhibited a 5% weight loss temperature ($T_{5\%}$) of 267.7 °C and high tensile strength of 35.42 MPa [61]. Moreover, we studied the thermal degradation kinetics of PPCHC by thermogravimetric analysis [64]. Using Ozawa method, the calculated degradation activation energies are lower than that of PPC, indicating that the thermal degradation of PPCHC starts more easily because it overcomes a lower energy barrier to decompose. The polymerization mechanism of PO and CO_2 is anion coordination polymerization, which is a kind of “active polymerization”. Under appropriate conditions, the anion on the chain end can remain reactive even when the monomer is completely consumed. Once rejoining the monomer into the system, chain propagation continues, making the relative molecular mass continuously increases. We employ this strategy on incorporating a third monomer to construct block copolymer by one-pot method [65]. The thermal and mechanical performances of the block copolymers lie between those of PPC and PCHC. PPC-*b*-PCHCs, prepared via a one-pot procedure with multi-component zinc catalyst

Table 3
Static mechanical properties of PPCs with varying molecular weight (23 °C) [20].

No.	M_n/(kg·mol^{-1})	Tensile strength/MPa	Young modulus/MPa	Elongation/%
1	26.9	11.65 ± 1.07	405.5 ± 78.4	583.9 ± 91.9
2	36.2	17.49 ± 1.95	709.6 ± 88.9	604.3 ± 131
3	45.0	23.90 ± 3.07	1050 ± 98.6	533.4 ± 48.8
4	50.2	33.09 ± 2.31	1209 ± 114	519.9 ± 132
5	71.8	32.86 ± 1.08	1341 ± 69.0	337.1 ± 5.29
6	88.8	37.43 ± 2.96	1532 ± 473	14.80 ± 5.65
7	98.7	34.70 ± 2.86	1739 ± 119	14.54 ± 3.92
8	114.2	40.20 ± 2.44	1755 ± 219	21.51 ± 10.5



Scheme 7. Third monomers introduced into PPC.

Table 4
Thermal and mechanical properties of terpolymer CO_2, PO and a third monomer.

Polymer	Third monomer feed content[a]/%	M_nx10^{-4}/(g·mol^{-1})	T_g/°C	$T_{5\%}$/°C	T_{max}/°C	Tensile strength/MPa	Elongation/%	Ref.
PPCHC	5.0	19.8	41	257	291	34.2	2.8	[61]
PPC-*b*-PCHC	11.1	27.4	40/67/112	256	297/342	36.8	8.9	[66]
PPEC	14.4	4.8	14	266	–	–	–	[70]
PPCNE	4.3	7.4	42	265	–	34.9	6.1	[71]
PPCNM	4.4	6.7	40	250	–	35.9	302.3	[72]
PPCMA	4.8	6.3	37	234	252	–	–	[75]
PPCPA	4.8	6.4	39	249	252	36.2	387.3	[78]
PPCCL	5.0	6.7	39	188	244/323	–	–	[80]
PPC-*b*-PLA	6.0	11.8	49	247	284	38.2	92.4	[84]
PPCMDI	1.4	40.4	40	242	277	38.3	12.7	[86]

[a] The molar fraction of the loaded third monomer with respect to the total moles of PO and the third monomer.

(Zn2G), exhibit three glass transition temperatures at 40 °C, 66 °C and 115 °C, a thermal decomposition temperature up to about 300 °C and a tensile strength of 40 MPa [66]. The improved performances of PPC-*b*-PCHC meet demands in hot processing and serving as plastics at room temperature. Furthermore, we employed dynamic mechanical analysis (DMA), nanoindentation and nanoscratch test to characterize the micromechanical properties of PPC-*b*-PCHCs [67].

In order to improve the degradation property of PPC, ethylene oxide (EO) was added in CO_2 and PO copolymerization system [68–70]. When the content of EO increases, the T_g of the resultant polymer shows a downward trend below that of PPC due to the more flexible segments without pendent methyl groups on the backbone. Incorporation of bulky pendants into PPC is a considerable way to enhanced its thermal stability and mechanical property. We employed N-(2,3-epoxylpropyl)carbazole (NEC) and [(2-naphthyloxy)methyl]oxirane (NMO) as a third monomer to copolymerize with CO_2 and PO and the resultant terpolymers were named PPCNE and PPCNM respectively [71,72]. These terpolymers exhibit significantly increased thermal decomposition temperature of 34–40 °C higher than that of pure PPC. Terpolymer of allyl glycidyl ether (AGE), CO_2 and PO with double bond on the side chain can be modified with polyethylene glycol via thiol-ene click reaction to produce grafted amphiphilic polymer [73]. This environmentally friendly polymer can be used as nanometer carrier for controlled drug release due to its self-assembled behavior into nanoparticles in water.

3.2.2. Anhydride

Anhydrides, another kind of abundantly available monomers, are used to construct biodegradable aliphatic polyesters. Terpolymers from CO_2, epoxides and anhydrides are biodegradable polymers with tailorable degradation rate as well as thermal and mechanical performances. In the chain propagation of polymer, anhydride and CO_2 play the same role, meaning competitively insertion into the active end. We synthesized terpolymers of CO_2, epoxides and anhydrides using supported zinc dicarboxylate as catalyst [74]. These terpolymers contain double bonds or rigid benzene ring on their main chain, which is able to improve the thermal and mechanical performances of materials. Poly (propylene carbonate maleate) (PPCMA) was prepared from CO_2, PO and maleic anhydride (MA) catalyzed by s-ZnGA with a modest yield of 72.5 g polymer/g catalyst [75]. Introduction of ester unit (lower than 15%) and double bonds into the backbone of terpolymer, PPCMA exhibits enhanced degradability and thermally stability with a decomposition temperature of 263 °C. Moreover, at elevated temperatures, PPCMAs are easily crosslinked using dicumyl peroxide (DCP) as crosslinking agent, which leads to significant improvements in the thermal and mechanical properties in comparison with their uncrosslinked counterparts [76]. Crosslinked PPCMA shows the highest T_g of 42.9 °C and tensile strength of 45.59 MPa with 0.8 wt.% DCP content and a decomposition temperature of 300 °C with 0.6 wt.% DCP content. Apart from crosslinking, ethylenic double bonds on PPCMAs can also easily be subjected to sulfonation to amphiphilic sulfonated PPCMAs as polymer surfactants. PPCMAs were fabricated with an ester content higher than 30% using ZnAA as catalyst and then sulfonated by adding sodium hydrogen sulphite into unsaturated double bonds of the polyester unit (Scheme 8) [77]. The results reveal that the sulfonated biodegradable terpolymer adsorb at the air/water interface with the surface tension of 47.5 mN·m^{-1}.

Phthalic anhydride (PA), containing rigid benzene ring, was also introduced to react with CO_2 and PO to obtain poly (propylene carbonate phthalic anhydride) (PPCPA) [78]. The thermal and mechanical performances of PPCPA are drastically improved due to the existence of benzene ring. However, introducing excessive PA into PPC causes an increase of polyether content and thus, T_g and tensile strength of PPCPA decrease. Evaluated by Fineman-Ross methodology, the reactivity ratios of CO_2 is much higher than that of PA, resulting in a random sequence of carbonate and ester segments in the terpolymer [79]. The result indicates that under relatively lower CO_2 pressures, incorporating a small amount of PA can inhibit the formation of polyether.

3.2.3. Lactone and lactide

Catalyzed by ZnGA, we synthesized aliphatic poly (carbonate-ester)(PPCCL) with long CL rich sequence via terpolymerization of CL, PO and CO_2 [80]. The existence of comonomer CL results in a semi-crystalline terpolymers with significantly improved thermal/mechanical properties and excellent melt processability. Thermal degradation mechanism analysis of PPCCLs by means of the combination of TG/FTIR and Py-GC/MS indicates that at low temperature, unzipping reaction is a dominant pathway via backbiting of ester and carbonate bond to form caprolactone and cyclic propylene carbonate respectively. As for at relatively high temperature, chain scission dominates including main intramolecular transesterification reaction and random fracture (Scheme 9) [81]. Plant-derived poly (ʟ-lactide) (PLLA), produced from renewable starch, is semi-crystalline polymer. Alternatively, terpolymerization of CO_2, PO and LA to get the copolymer poly (ʟ -lactide-co-propylene carbonate) (PLAPC) is an another way to tailor PPC's properties. The nonisothermal crystallization behavior and kinetics of PLAPC uncovers that both the existent catalyst and increased polycarbonate (PC) content can hinder the macromolecular segments from crystallizing due to an increase of energy barrier [82]. Furthermore, thermal degradation of PLAPC was measured by TG/FTIR and Py-GC/MS [83]. With an increase of PC content, maximum decomposition temperature decreases and the activation energy of degradation increases. Backbiting ester interchange reaction is the dominant decomposition behavior of PLAPC while accompanying with intramolecular transesterification and chain scission at relative higher pyrolysis temperature, which is similar to the pyrolysis mechanism of PPCCL [81]. Besides random copolymers of PLAPC, we reported copolymerization of CO_2 with PO and LLA with long LLA rich sequence (PPC-*b*-PLA) as well [84]. The synthesized terpolymers are a kind of semicrystalline polymer in which the crystalline PLA segment function as strong noncovalent crosslinking domains.

3.2.4. Isocyanate

It is known that crosslinking is an effective method to greatly increase the molecular weight, which has a significant impact on the performances of polymer. Adding a small amount of diisocyanate into CO_2/PO copolymerization system can obtain micro-crosslinking PPC with enhanced thermal and mechanical properties, in which diisocyanate acts as both crosslinking agent and chain extender [85]. We introduced 4,4′-diphenylmethane diisocyanate (MDI) as a third monomer to improve mechanical property and thermal stability of PPC owing to the ultra-high molecular weight (Scheme 10) [86]. In consideration of controlling the gel content in a proper range to maintain the thermoplastic property of PPC, the MDI feed amount is better to be smaller than 1.5 wt.% based on PO content.

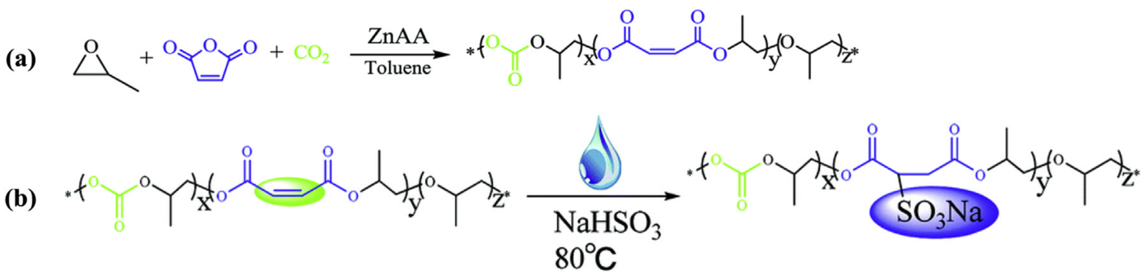
3.2.5. Others

Besides introducing a third monomer into PPC, terpolymer from CO_2 and other monomers arouses our interest to develop various type of CO_2-based polymer. Semi-crystalline terpolymers from CO_2, CHO, and CL were synthesized through one-step synthesis with tri-zinc complexes as catalyst [87]. The result indicates that in this reaction, CL has a higher reactivity than CHO and increases the catalytic efficiency. We also investigated the kinetics of this reaction detailedly [37]. The resultant copolymer, poly (caprolactone-*co*-cyclohexene carbonate) (p (CL-*co*-CHC)) turned out to be semi-crystalline. As we all known, the crystallization behavior of crystalline polymer is a fundamental problem in polymer physics, since the biodegradation, mechanical property and heat resistance depend on their crystallinity and crystallization morphology strongly. We studied the crystallization behavior of p (CL-*co*-CHC) [88], finding that poly (cyclohexene carbonate)(PCHC) segments act as a nucleating agent and restrict the transport of PCL segments.

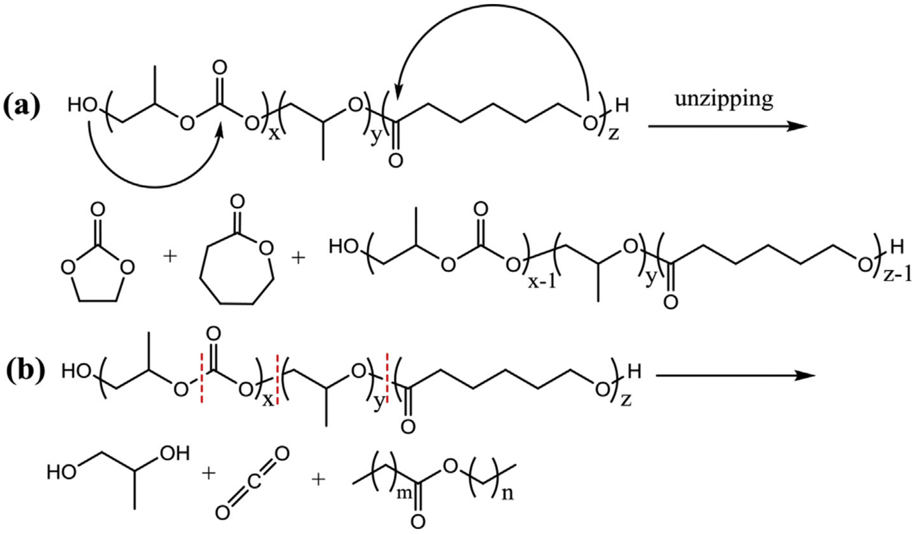
3.3. Block/alternating copolymer

For block copolymers, their thermal and mechanical properties can be adjusted simply by changing the content of different components. PPC-based block copolymers attract our attention by endowing products with great biodegradability. High-molecular-weight PPC is useless in the synthesis of block copolymers for limited active end groups. In contrast, low-molecular-weight PPC terminated with reactive groups shows great advantages in building PPC-based block copolymers. In this case, PPC macrodiols ($M_n \approx 3000$ Da) with a high carbonate content (>85%) were properly synthesized via alcoholysis high-molecular-weight PPC by 1,4-butanediol (BDO) in bulk [89,90]. Inspired by the effective alcoholysis, we tried to produce amino-capped PPC oligomers by ammonolysis in the presence of diamines. To our disappointment, carbonate bonds are so vulnerable to be attacked by amino groups that no end-amino groups exist in oligomers.

PPC macrodiol find its application in polyurethane industry combining poly (propylene glycol), 4,4′-diphenylmethane diisocyanate and BDO [89]. In addition, we firstly synthesized biodegradable poly (propylene carbonate)-multiblock-poly (butylene



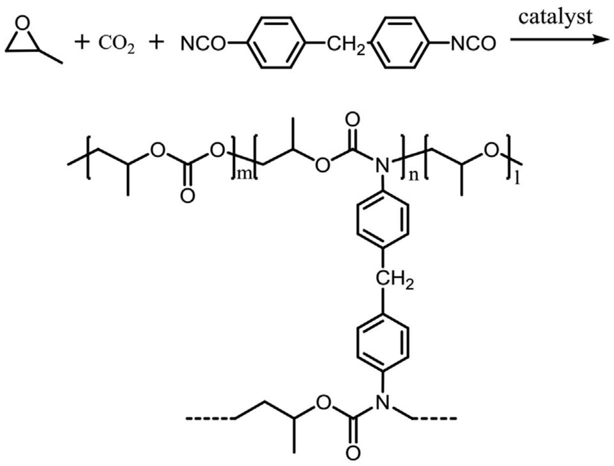
Scheme 8. (a) Terpolymerization of CO_2, PO and MA catalyzed by ZnAA; (b) Sulfonation of PPCMA using sodium hydrogen sulfite [77].



Scheme 9. Possible decomposition pathway of PPCCL (a) Unzipping of PPCCL backbone and (b) main chain scission [81].

succinate) (PPC-*mb*-PBS) from dihydroxy-terminated PPC (PPC—OH) and dicarboxy-terminated PBS (PBS—COOH) via a coupling reaction (Scheme 11) [91]. The products show good processability, improved mechanical strength, and low brittle-toughness transition temperature. Subsequently, the multiblock topology structure of PPC-*mb*-PBS was simulated by molecular dynamics, discovering that the simulated results are in very good agreement with the experimented one [92].

Besides the direct fixation of CO_2 into polycarbonate, incorporating CO_2 into urethane group arouses our great interest. Different from the aforementioned PPC-*mb*-PBS, in this work, we tactfully introduced CO_2 into monomer rather than polymer chain by reacting CO_2, methanol and diamine over CeO_2 catalysts in one pot to prepare dimethyl hexane-1,6-diyldicarbamate [93]. Shortly afterwards, various CO_2-source dicarbamates and diamide diols were applied to construct alternating poly (urethane-*co*-amide)s (PUAs) (Scheme 12) [94]. These high-performance PUAs are able to match conventional long chain polyamides. This work provides an indirect conversion of CO_2 into useful polymers, and another work about utilizing CO_2-source dicarbamates to synthesize poly (urethane-*co*-ester) is going on.



Scheme 10. Copolymerization of CO_2, PO in the presence of MDI [86].

4. Modification and application of PPC

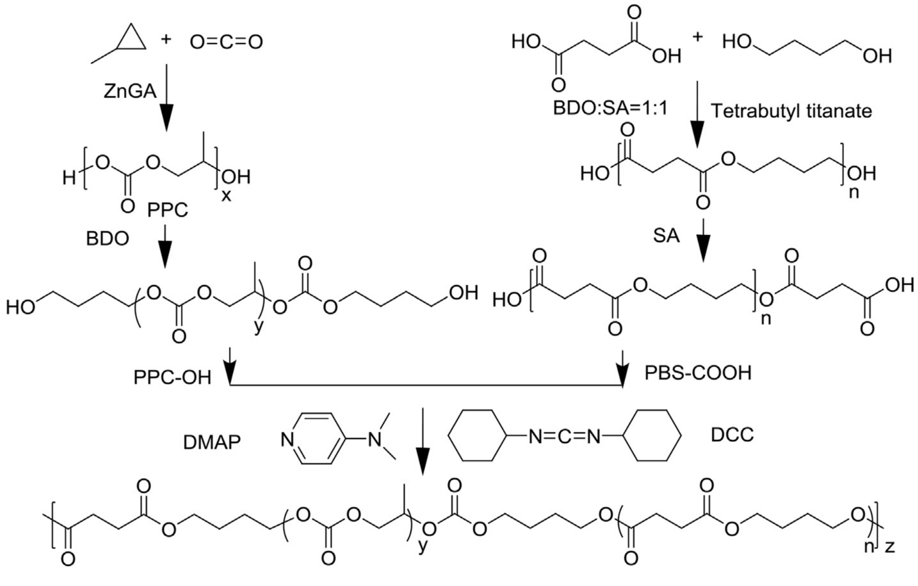
Biodegradable, high-value and CO_2-based PPC is an amorphous polymer with low T_g and high viscosity at high temperature, thus exhibiting poor mechanical properties. Therefore, proper modifications should be applied to widen PPC's application area, of which the copolymerization is the most convenient approach. Besides copolymerization modification, our group have also made effects in blending modification of PPC. Recently, PPC's performances and applications were reviewed by Mekonnen [95]. The industrial packaging application was introduced in that review. Here, PPC blending are mainly divided into following four categories, (1) blending with natural degradable polymers, (2) blending with synthetic biodegradable polymers, (3) blending with non-degradable polymers, (4) blending with inorganic fillers. After modifications, PPC finds its applications in barrier materials, foam materials and polymer electrolytes.

4.1. Modification

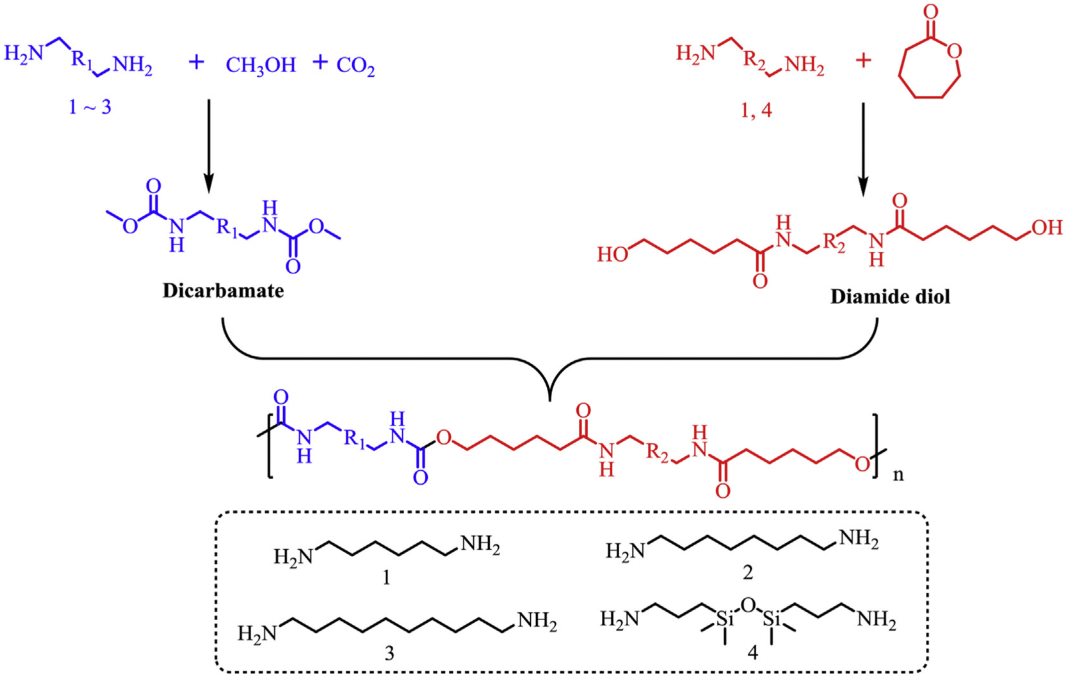
4.1.1. Blending with natural degradable polymers

Starch is abundant, renewable, degradable and inexpensive, so it has been widely used as a component in biodegradable composites, which reduces the production cost of PPC composites. When incorporating unmodified cornstarch (CS) into PPC by simply melt compounding [96–98], the hydrogen bonds between starch and PPC improved tensile strength, stiffness and thermal stability. However, the weak interfacial compatibility leads to obvious gaps and voids between starch particles and PPC matrix, which results in a brittle PPC/starch composite. To enhance interfacial adhesion, the simple modifications of CS such as grafted by poly (methyl acrylate) (PMA) [99], acetylation [100,101] and wrapped with poly (vinyl alcohol) (PVA) [102] can work effectively. As a result, the composites with modified CS show an improvement in thermal stability and greater elongation because of the enhanced interfacial effect.

In addition to starch, natural plant-based lignocellulosic fibers are usually adapted to PPC composites [103]. *Hildegardia populifolia* is able to increase stiffness and tensile strength of the composites along with a lower elongation at break [104]. Wood flour, characterized by good mechanical properties with low density, were blended with PPC by melt mixing to enhance the thermotolerance and tensile strength of PPC [105].



Scheme 11. Schematic diagram of synthesis of PBS-*mb*-PPC by coupling reaction [91].



Scheme 12. Schematic illustration of the synthesis of poly (amide-*co*-urethane) copolymers from CO_2-based dicarbamates [94].

4.1.2. Blending with synthetic biodegradable polymers

Poly (butylene succinate) (PBS), a crystalline polymer, is known as a synthetic biodegradable aliphatic polyester with excellent thermal stability and superior mechanical properties. PPC blended with PBS exhibits good ductility, great interfacial adhesion and improved thermal stability, providing composites with wide applications [106]. To perfect the compatibility between PPC and PBS, we used triphenylmethane tri-isocyanate (TTI) as reactive coupling agent to combine with the terminated hydroxyl groups of PPC and PBS, resulting in PPC/PBS blends with good comprehensive properties [107,108]. A uniaxial orientation film from PPC/PBS (70/30), owned an orientation degree of 0.247, can be readily prepared by a calendaring process.

Introducing polylactide (PLA) into PPC matrix is capable of overcoming the shortcomings such as terrible flowability and processability of filler reinforced systems. Our group discovered that PLA played a vital role in the improvement on tensile strength and thermal stability except elongation at break of PPC [109]. These composites display two phases with indistinct interface. In order to enhance the interfacial interactions between PPC and PLA, 2,4-toluene diisocyanate (TDI) was applied as compatibilizer to react with hydroxy group of the two components [110]. The tensile strength of the compatible composites is drastically elevated from 23 MPa to 44.7 MPa. 4,4-methylene diphenyl diisocyanate (MDI) is used to make a better compatibility as well. We calendered the blends into films with obvious orientation only in machine direction (MD) [111]. With an increasing degree of orientation from

0.058 to 0.102, the tensile strength in MD reaches 48.6 MPa from 38.8 MPa.

PVA, a biodegradable vinyl polymer, was blended with PPC by solution casting, displaying a higher T_g, strength and modulus than PPC matrix [112,113].

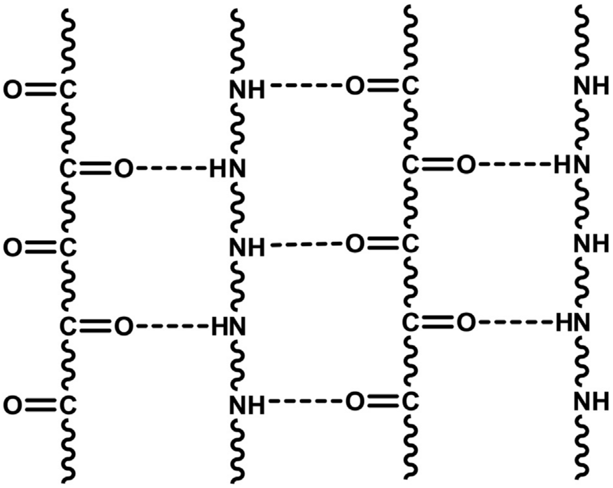
4.1.3. Blending with synthetic non-biodegradable polymers

To extend application of PPC, we blended nondegradable poly (ethylene-co-vinyl alcohol) (EVOH) with PPC matrix. EVOH is a semi-crystalline and hydrophilic polymer with good physical properties, high oil resistance, superior gas barrier properties and high processability, vastly used in packing materials [114]. The strong intermolecular interactions between PPC's carbonyl groups and EVOH's hydroxyl groups played an important role in the good compatibility of the blends [115]. Moreover, when increasing EVOH content, the thermal stability and tensile strength of blends were enhanced. All PPC/EVOH blends had a two-phase microstructure and the weight loss rate is faster than that of neat PPC because of the water adsorption of EVOH [116,117]. However, the relatively high-priced EVOH will raise the cost of PPC so that practical applications are unavoidably limited. It is worth mentioning that PVA has similar structure to EVOH, but it has so close melting point and decomposition temperature that it is difficult to process by melting. Wisely, introducing PVA to replace partial EVOH to prepare PPC/PVA/EVOH blends can lower the price of the blends [118]. Multi-component modification is also applied in PPC resin for reducing the production cost and for a better property [119]. We prepared the PPC/EVOH/Starch/$CaCO_3$ composites for the purpose of improving the comprehensive performances and reducing the cost of PPC based composites [120]. The composites behave enhanced thermal stability and meanwhile the aggregation behavior of $CaCO_3$ particles and starch particles reduce the tensile strength.

Actually, toughening PPC is rarely achieved due to relatively weak chemical interactions between different components. Thermoplastic polyurethane (TPU) elastomer, a liner polymer containing soft segments and hard segments, has similarly chemical structure to PPC, which is believed to have better miscibility with PPC. Hydrogen bonds (Scheme 13) between the urethane moiety of TPU and the carbonyl groups in PPC increased the interaction of polymeric chains, and thus toughness and thermal stability were improved [121]. Next, PPC/(PVA-TPU) ternary blends were successfully prepared by melting compounding method with TPU as a polymeric plasticizer [122,123]. The mechanical properties of as-prepared films are enhanced intensely at low temperature. What's more, polyvinyl formal was melt blended with PPC to increase the Vicat softening temperature [124]. Polystyrene (PS) was also studied in the blending of PPC to reduce the application cost of the composites [125].

4.1.4. Blending with inorganic fillers

Natural mineral fillers attract our attention owing to their low price, dimensional stability and recyclability [126]. $CaCO_3$ particles reinforced PPC possessed enhanced tensile strength, stiffness, and ductility because of great bonding between particles and matrix [127]. $CaCO_3$ have price advantage and their hydrophilic behavior increases the water adsorption, thereby accelerating the biodegradation of PPC. Polymer/layered silicate nanocomposites attract much interest because low filler loading improves physical and thermal properties exceptionally. Organo-vermiculite lower (OVMT), the 2:1 layered silicate, had been intercalated by cetyltrimethyl ammonium bromide, and then direct melt intercalation of PPC to form PPC/VMT nanocomposites (Fig. 3). The nanocomposites exhibit a lower weight loss temperature and inferior mechanical properties on account of the amine compounds generated from the intercalating agent at high temperature, which accelerates the thermal hydrolysis of PPC [128]. Conversely, organo-modified montmorillonite (OMMT) blended with PPC by direct melt intercalation and formed intercalation-exfoliated PPC/OMMT nanocomposites with increased thermal decomposition temperature, storage modulus and Young's modulus in comparison with pure PPC [129]. Layered double hydroxides (LDHs) are host-guest materials with strong interlayer electrostatic interactions, hydrophilic property and small gallery space. We constructed PPC/MgAl layered double hydroxide (PPC/MgAl-LDH) nanocomposites by solution intercalation of PPC into MgAl-LDH interlayers, achieving superior thermal and mechanical properties over PPC matrix [130].



Scheme 13. Schematic illustration of hydrogen bonding between PPC and TPU [121].

Rodlike fillers are adopted to improve the mechanical and thermal properties PPC resin. Glass fiber (GF), is cheap and widely used for making composites for its high strength and high modulus. GF reinforced PPC composites lower the cost of the production and improves the thermal properties with applicably comprehensive properties [131]. Moreover, introduction of attapulgite (AT) into PPC matrix by solution blending is a feasible way to improve the thermal stability of aliphatic polycarbonate [132]. We also creatively introduced halloysite nanotube (HNT) to toughen PPC without particle reunion [133]. On this basis, TDI was used as compatibilizer to further improve the performances of PPC/HNT blends [134]. These blends have a better interfacial contact between the two components than pure PPC/HNT compositions.

4.1.5. Crosslinking

Crosslinking modification is an effective method to improve mechanical property, solvent resistance and thermal stability of polymer. Crosslinked polymer has increased melt viscosity, which provides a possible approach to foaming. We dissolved PPC in chloroform and then added peroxyl compounds as crosslinking agent and multifunctional monomer containing multi-olefinic bond as co-crosslinking agent, to synthesize crosslinked PPC by static heating method [135]. The resultant product possessed enhanced mechanical strength and a gel content of 50–74%.

4.2. Application

4.2.1. Barrier material

Polymers are commonly used inexpensive, lightweight and flexible packaging materials. For example, EVOH, PVA and poly (vinylidene chloride) (PVDC) exhibit outstanding high barrier property. PPC chains have a closer molecular chains arrangement, and thus bring about a higher molecular bulk density (~1.3 g·cm^{-3})

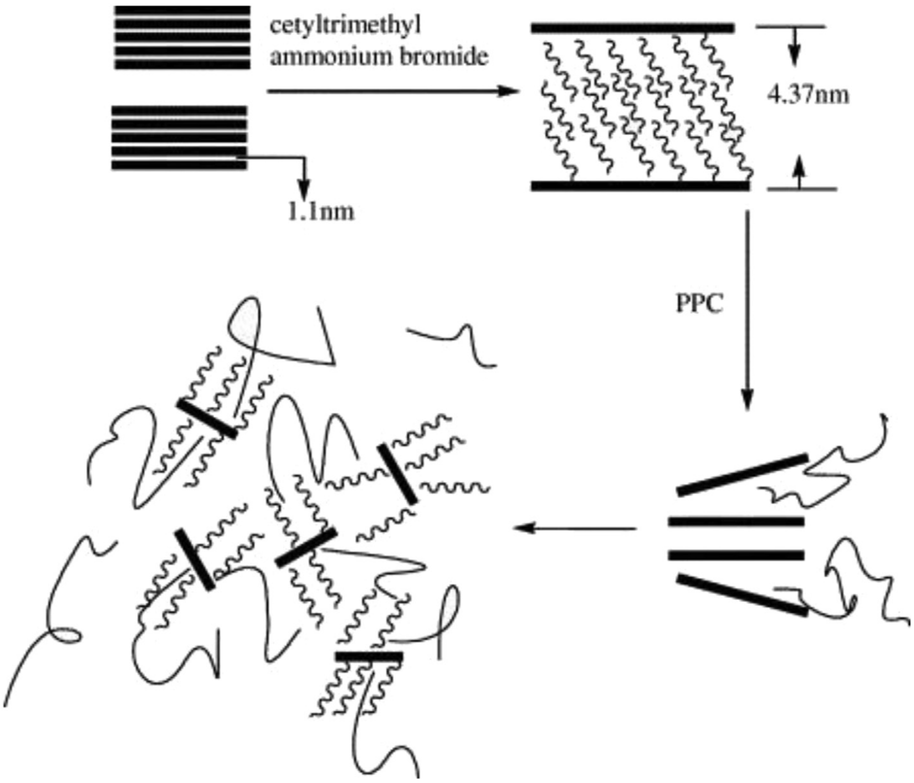


Fig. 3. Representation of the intercalation process of OVMT within PPC matrix [128].

and smaller free volume. As a result, pure PPC is capable of blocking some gases to go through, which shows an oxygen permeability coefficient (OP) of 2.25 $cm^3 \cdot mm \cdot m^{-2} \cdot day^{-1}$ (23 °C, 0% relative humidity) and water vapor permeability coefficient (WVP) of 1.05 $g \cdot mm \cdot m^{-2} \cdot day^{-1}$ (23 °C, 85% relative humidity) respectively [136,137]. However, small volume molecules can still permeate PPC because the free volume exists between molecular chains. In this sense, high barrier property may achieve by adding another component as filler into the neat PPC to make free volume smaller. Different PPC based composite films present diverse OP and WVP. We intercalated water-soluble polymer into organic-modified layered silicate in solution, and then melt blended with PPC to obtain a high barrier nanocomposite plastic film with good resistance to moisture and gas [138]. When combining plasticizer with the nanocomposite, the as-made film can act as a substitute to EVOH in manufacture high barrier packaging products [139]. We firstly reported PPC/aluminum flake (PPC/ALF) composite films as packaging materials [136]. ALF, a high aspect ratio platelet-type material, results in tortuous diffusion pathways within PPC. PPC/5%ALF displays the enhanced oxygen and water vapor barrier properties at 23 °C (OP, 0.73 $cm^3 \cdot mm \cdot m^{-2} \cdot day^{-1}$ under dry condition; WVP, 0.79 $g \cdot mm \cdot m^{-2} \cdot day^{-1}$ under 85% relative humidity). After that, organic-modified layered double hydroxide (OLDH) were used to prepare PPC/OLDH nanocomposite film by a melt-blending method [137]. PPC/2%OLDH film exhibits lower WVP and OP in comparison with pure PPC, reduced by 54% and 17% respectively. Meanwhile, its tensile strength is increased by 83% with little decrease of elongation at break. Table 5 lists the barrier property of PPC composite films.

4.2.2. Plasticizer

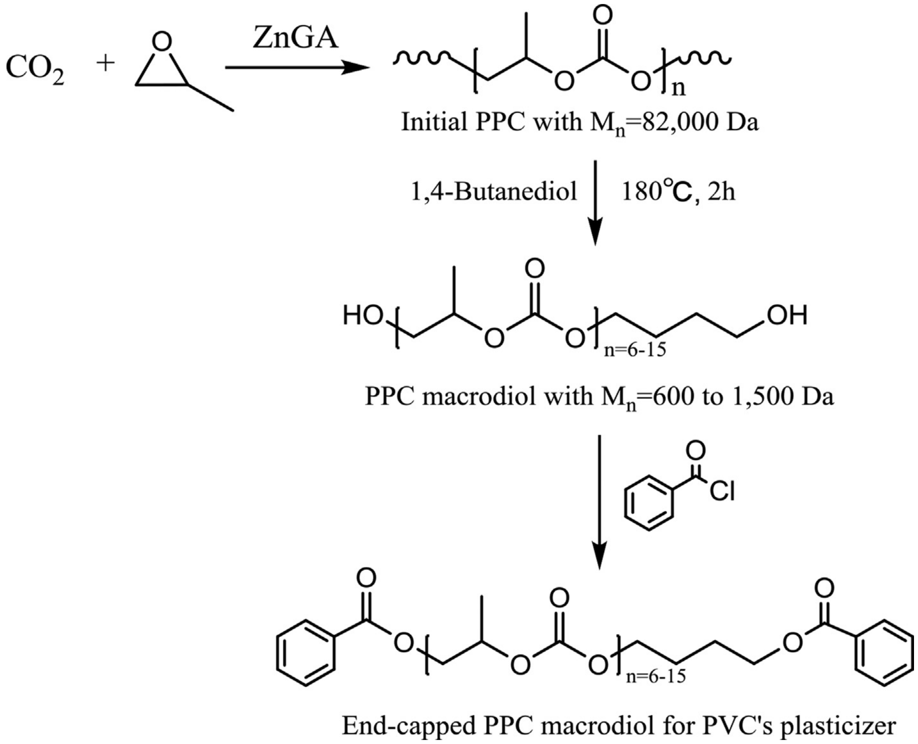
Plasticizer is a polymer additive widely used in industry. When adding it in the plastic processing, the plastic will be flexible and easy to be processed. Poly (vinyl chloride) (PVC) is the third general plastics. In PVC's commercial production, we developed an environmentally friendly, nontoxic, sustainable and biodegradable plasticizer from PPC [140]. PPC macrodiols ($M_n = 600–1500$ Da) were synthesized via alcoholysis of high-molecular-weight PPC [89], and then reacted with benzoyl chloride (BC) to gain aromatic esters end-capped macrodiols (Scheme 14). This plasticizer shows good compatibility with PVC, which can be explained by the strong interaction between carbonate groups and polar C—Cl bonds of PVC. Moreover, the PPC macrodiol demonstrated a dramatically low migration rate due to the relatively high molecular weight of PPC.

4.2.3. Polymer electrolyte

PPC possesses amorphous nature, low T_g, and biodegradability. When applied to polymer electrolytes, it can promote salt dissociation and increase ion transport via segment mobility. Moreover, similar to the industrialized organic ethylene carbonate (EC) solvents, PPC shows good interfacial contact with commonly used electrodes. Crosslinked terpolymer of CO_2, PO and unsaturated cyclic anhydride was used as polymer electrolyte membrane after activated by liquid electrolyte solution with high mechanical properties, good thermal properties and ionic conductivity [141,142]. CO_2-based multifunctional polycarbonate finds its application in not only gel electrolyte but also all-solid-state electrolyte. We synthesized poly (ethylene oxide) (PEO)/PPC electrolyte by solution-casting [143]. PPC decreased the crystallinity of PEO, and consequently, an increase of ionic conductivity occurs, up to 6.83×10^{-5} $S \cdot cm^{-1}$ at room temperature with 50% PPC content. What's more, the PEO/50% PPC polymer electrolyte possessed good electrochemical stability up to 4.5 V. When introducing nano-TiO_2 as filler into PPC/PEO polymer matrixes, the crystallinity of PEO decreases and thus enhances the lithium ion transference number and the ionic conductivity of the composite polymer electrolytes [144]. The result reveals that PEO/PPC/3%TiO_2 composite polymer

Table 5
OTR, OP, WVTR, and WVP of the PPC composite films.

Sample	Thickness (μm)	OTR ($cm^3 \cdot m^{-2} \cdot day^{-1}$)	OP ($cm^3 \cdot mm \cdot m^{-2} \cdot day^{-1}$)	WVTR ($g \cdot m^{-2} \cdot day^{-1}$)	WVP ($g \cdot mm \cdot m^{-2} \cdot day^{-1}$)	Ref.
PPC	485 ± 5	4.60 ± 0.001	2.25 ± 0.004	2.16 ± 0.05	1.0 5 ± 0.02	[136]
PPC/5%ALF	563 ± 5	1.30 ± 0.001	0.73 ± 0.006	1.41 ± 0.05	0.79 ± 0.03	[136]
PPC/2%OLDH	505 ± 5	2.06 ± 0.001	1.04 ± 0.006	2.04 ± 0.05	1.03 ± 0.03	[137]



Scheme 14. Synthesis route of end-capped PPC macrodiol as PVC's plasticizer [140].

electrolyte shows good interfacial stability with the lithium electrode, recording the maximum ionic conductivity of $1.4 \times 10^{-5}\ S \cdot cm^{-1}$ at room temperature, $8 \times 10^{-5}\ S \cdot cm^{-1}$ at 80 °C and the electrochemical stability window of 4.5 V vs Li^+/Li. More recently, poly (propylene carbonate allyl glycidyl ether) (PPCAGE) was functionalized via thiol–ene click reaction, followed by lithiation, to construct a single-ion-conducting polymer electrolyte (Fig. 4) [145]. This all-solid-state electrolyte exhibits highest ionic conductivity of 1.61×10^{-4} S/cm at 80 °C, high lithium ion transference number of 0.86, and electrochemical stability window of 4.3 V vs Li^+/Li. This method for fabrication of all-solid-stat electrolyte have been patented [146].

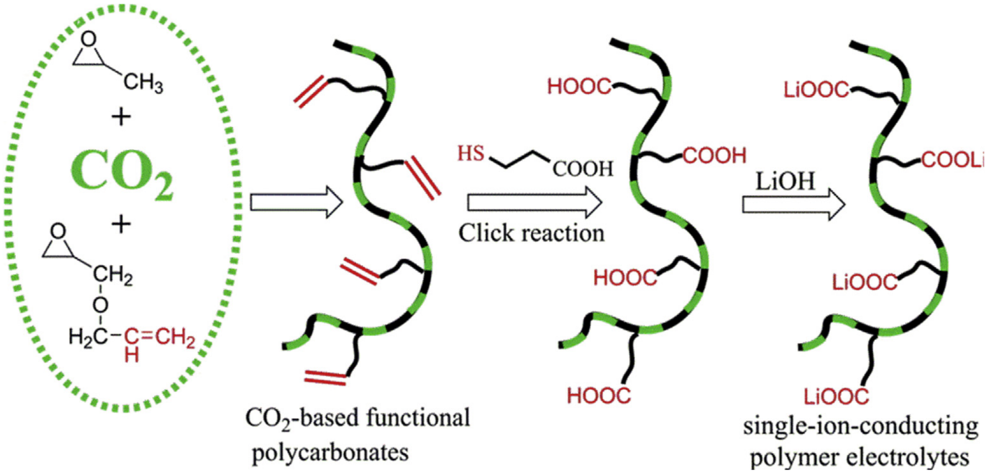


Fig. 4. Fabrication of PPCAGE-based single-ion-conducting polymer electrolyte [145].

4.2.4. Other applications

Completely biodegradable pressure-sensitive adhesive was synthesized by combination of PPC, tackifier, accelerant, intensity regulator, lubricant, filler and mixed solvent [147]. Fully biodegradable plastic films and stone paper were also developed [148,149]. We invented PPC coating solution with various concentration to increase the hydrolysis resistance of the aliphatic biodegradable polyester products by coating it on the surface of them [150].

5. Conclusions

PPC occupies an important position among the general plastics by virtue of its biodegradability and unparallel CO_2 utilization. Industrialization of PPC in Tianguan Group is a mature technology derived from our group and it's hopeful to expand the scale of PPC production. There is a bright prospect of CO_2-based materials. We have paid intensive efforts on the preparation and evaluation of heterogeneous zinc dicarboxylate catalyst system, in which zinc glutarate exhibits the best catalytic performance, although its catalytic mechanism needs deeply understood. Further exploration is required to the improvement of catalytic performance as well. In future studies, developing a high-efficiency and nontoxic metal catalytic system is inevitable, expecting that the resultant polymer has trance amounts of residual catalyst or the catalyst can be easily removed from the matrix. Or better yet, the minimal residual content of catalyst displays a favorable influence on the product like in-situ reinforcement. Moreover, non-metal catalyst may be developed in the synthesis of CO_2-based aliphatic polycarbonate.

Recently, copolymerization of CO_2 and PO is the most convenient approach for maximum utilization of the waste gas. However, a low T_g and amorphous morphology of PPC can't satisfy common demand even on the general plastics. Introducing a third monomer is able to adjust PPC' performances by evaluating T_g, endowing crystallinity and enhancing biodegradability. In addition, the reinforcement of PPC's thermal and mechanical is delightfully achieved by blending modification as well. Various fillers are employed to tailor PPC's performances and as a result, the scope of application expands to a large extent. Extensive application including barrier material, foam material and polymer electrolyte have been well developed. Broad application prospect acts as an impetus to make PPC composite materials blossom.

In summary, PPC is the best developed CO_2-based aliphatic polycarbonate and possesses a preponderant application in biomedicine. Besides polycarbonate, we exploit a method for indirect utilization of CO_2 by fixing it into a monomer and then reacting with another monomer to synthesize polymer. In future, our group will pay more attention to explore the promising pathway to develop CO_2-based polymers, for example, poly (ester-*co*-carbonate)s.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (Grant No. 51673131), the Special-funded Program on National Key Scientific Instruments and Equipment Development of China (Grant No. 2012YQ230043) and the Fundamental Research Funds for the Central Universities (171gjc37) for financial support of this work.

References

[1] K. Kacholia, R.A. Reck, Comparison of global climate change simulations for 2 × CO_2 -induced warming, Clim. Change 35 (1997) 53–69.
[2] D. Normile, Key Climate Panel, Citing Impending Crisis, Urges Crash Effort to Reduce Emissions, 2018-10-08. https://www.sciencemag.org/news/2018/10/key-climate-panel-citing-impending-crisis-urges-crash-effort-reduce-emissions.
[3] Global Energy & CO_2 Status Report 2017, 2018-03. https://www.iea.org/geco/.
[4] M. Aresta, A. Dibenedetto, Utilisation of CO_2 as a chemical feedstock: opportunities and challenges, Dalton Trans. 28 (2007) 2975.
[5] A.C. Albertsson, C. Barenstedt, S. Karlsson, T. Lindberg, Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene, Polymer 36 (1995) 3075–3083.
[6] S. Inoue, H. Koinuma, T. Tsuruta, Copolymerization of carbon dioxide and epoxide, J. Polym. Sci., Part B. 7 (1969) 287–292.
[7] S. Inoue, H. Koinuma, T. Tsuruta, Copolymerization of carbon dioxide and epoxide with organometallic compounds, Makromol. Chem. 130 (1969) 210–220.
[8] B. Li, G. Wu, W. Ren, Y. Wang, D. Rao, X. Lu, Asymmetric, regio- and stereo-selective alternating copolymerization of CO_2 and propylene oxide catalyzed by chiral chromium salan complexes, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 6102–6113.
[9] C.E. Anderson, S.I. Vagin, W. Xia, H. Jin, B. Rieger, Cobaltoporphyrin-catalyzed CO_2/epoxide copolymerization: selectivity control by molecular design, Macromolecules 45 (2012) 6840–6849.
[10] T. Ohkawara, K. Suzuki, K. Nakano, S. Mori, K. Nozaki, Facile estimation of catalytic activity and selectivities in copolymerization of propylene oxide with carbon dioxide mediated by metal complexes with planar tetradentate ligand, J. Am. Chem. Soc. 136 (2014) 10728–10735.
[11] X. Li, R. Duan, X. Pang, B. Gao, X. Wang, X. Chen, Rigid linked dinuclear salph-Co(III) catalyst for carbon dioxide/epoxides copolymerization, Appl. Catal., B 182 (2016) 580–586.
[12] W. Wu, X. Sheng, Y. Qin, L. Qiao, Y. Miao, X. Wang, F. Wang, Bifunctional aluminum porphyrin complex: soil tolerant catalyst for copolymerization of CO_2 and propylene oxide, J. Polym. Sci., Part A: Polym. Chem. 52 (2014) 2346–2355.
[13] Y. Meng, S. Wang, L. Du, H. Zhang, Preparation of Zn Dicarboxylate Catalyst, CN1302694A, 2001.
[14] Q. Zhu, Y. Meng, S. Tjong, X. Zhao, Y. Chen, Thermally stable and high molecular weight poly(propylene carbonate)s from carbon dioxide and propylene oxide, Polym. Int. 51 (2002) 1079–1085.
[15] L. Du, Y. Meng, S. Wang, S. Tjong, Synthesis and degradation behavior of poly(propylene carbonate) derived from carbon dioxide and propylene oxide, J. Appl. Polym. Sci. 92 (2004) 1840–1846.
[16] L. Gan, F. Du, Y. Meng, M. Xiao, X. Li, Z. Wang, S. Wang, Q. Zhu, Aid-free Devolatilization Apparatus for Aliphatic Polycarbonate, CN2903062Y, 2007.
[17] L. Gan, F. Du, Y. Meng, M. Xiao, X. Li, Z. Wang, S. Wang, Q. Zhu, Additive-free Devolatilization Process and Apparatus for Production of Aliphatic Polycarbonate Resin, CN101003620A, 2007.
[18] Y. Meng, L. Gan, F. Du, X. Qi, M. Xiao, S. Wang, Q. Zhu, J. Xu, Method and Apparatus for Preparation of Aliphatic Polycarbonate, CN101003619A, 2007.
[19] Y. Meng, L. Gan, F. Du, X. Qi, M. Xiao, S. Wang, Q. Zhu, J. Xu, Apparatus for Preparing Aliphatic Polycarbonate from Carbon Dioxide and Epoxides, CN201010619Y, 2008.
[20] Y. Meng, J. Wu, M. Xiao, S. Wang, H. He, D. Han, Progress and application of biodegradable plastic derived from copolymerization of carbon dioxide with epoxides, Petrochem. Technol. 39 (2010) 241–248.
[21] Y. Xu, L. Lin, M. Xiao, S. Wang, A.T. Smith, L. Sun, Y. Meng, Synthesis and properties of CO_2 -based plastics: environmentally-friendly, energy-saving and biomedical polymeric materials, Prog. Polym. Sci. 80 (2018) 163–182.
[22] S. Wang, L. Du, X. Zhao, Y. Meng, S. Tjong, Synthesis and characterization of alternating copolymer from carbon dioxide and propylene oxide, J. Appl. Polym. Sci. 85 (2002) 2327–2334.
[23] Y. Meng, L. Du, S. Tiong, Q. Zhu, A.S. Hay, Effects of the structure and morphology of zinc glutarate on the fixation of carbon dioxide into polymer, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 3579–3591.
[24] Y. Xu, M. Xiao, S. Wang, M. Pan, Y. Meng, Activities comparison of Schiff base zinc and tri-zinc complexes for alternating copolymerization of CO_2 and epoxides, Polym. Chem. 5 (2014) 3838–3846.
[25] Y. Meng, Q. Zhu, S. Zhang, X. Liu, L. Du, Supported Catalyst of Zinc Binary Carboxylate and its Production Process, CN1377732A, 2002.
[26] J. Wang, Q. Zhu, X. Lu, Y. Meng, ZnGA–MMT catalyzed the copolymerization of carbon dioxide with propylene oxide, Eur. Polym. J. 41 (2005) 1108–1114.
[27] S.A. Motika, T.L. Pickering, A. Rokicki, B.K. Stein, Catalyst for the Copolymerization of Epoxides with CO_2, US5026676A, 1991.
[28] F. Du, J. Wang, M. Xiao, S. Wang, Y. Meng, Preparation and characterization of zinc adipate and its catalytic activity for the copolymerization between CO_2 and propylene oxide, Res. J. Chem. Environ. 13 (2009) 69–77.
[29] J. Wang, D. Shu, M. Xiao, Y. Meng, Copolymerization of carbon dioxide and propylene oxide using zinc adipate as catalyst, J. Appl. Polym. Sci. 99 (2006) 200–206.

[30] Y. Meng, L. Tang, M. Xiao, S. Wang, D. Han, Composite Catalyst Used for Preparing CO_2-propylene Oxide Copolymer, its Preparation Method and Application, CN102702501A, 2012.

[31] Y. Meng, L. Tang, M. Xiao, S. Wang, D. Han, Composite Zinc Dicarboxylate Catalyst and its Preparation Method and Application, CN102952264A, 2013.

[32] L. Tang, M. Xiao, Y. Xu, S. Wang, Y. Meng, Zinc adipate/tertiary amine catalytic system: efficient synthesis of high molecular weight poly(propylene carbonate), J. Polym. Res. 20 (2013) 190.

[33] Q. Zhu, Y. Meng, S. Tjong, Y. Zhang, W. Wan, Catalytic synthesis and characterization of an alternating copolymer from carbon dioxide and propylene oxide using zinc pimelate, Polym. Int. 52 (2003) 799–804.

[34] X. Li, Y. Meng, M. Xiao, S. Wang, D. Han, S. Quan, Zn-hydroxy Acid Complex Catalyst for Copolymerization between CO_2 and Propylene Oxide, CN101759849A, 2010.

[35] X. Li, Y. Meng, S. Quan, Zinc Phenol Hydroxyl Complex Catalysts and the Preparation Methods and Applications, CN102936334A, 2013.

[36] Y. Meng, W. Wan, M. Xiao, A.S. Hay, Synthesis of metallophthalocyanine end-capped polymers and their catalytic activity for the copolymerization of CO_2 and propylene oxide, Green Chem. 6 (2004) 249–253.

[37] Y. Xu, L. Lin, C. He, J. Qin, Z. Li, S. Wang, M. Xiao, Y. Meng, Kinetic and mechanistic investigation for the copolymerization of CO_2 and cyclohexene oxide catalyzed by trizinc complexes, Polym. Chem. 8 (2017) 3632–3640.

[38] C. Thomas, B. Bibal, Hydrogen-bonding organocatalysts for ring-opening polymerization, Green Chem. 16 (2014) 1687–1699.

[39] L. Lin, D. Han, J. Qin, S. Wang, M. Xiao, L. Sun, Y. Meng, Nonstrained γ-butyrolactone to high-molecular-weight poly(γ-butyrolactone): facile bulk polymerization using economical ureas/alkoxides, Macromolecules 51 (2018) 9317–9322.

[40] L. Lin, J. Liang, Y. Xu, S. Wang, M. Xiao, L. Sun, Y. Meng, Fully alternating sustainable polyesters from epoxides and cyclic anhydrides: economical and metal-free dual catalysis, Green Chem. 21 (2019) 2469–2477.

[41] E.H. Nejad, C.G.W.V. Melis, T.J. Vermeer, C.E. Koning, R. Duchateau, Alternating ring-opening polymerization of cyclohexene oxide and anhydrides: effect of catalyst, cocatalyst, and anhydride structure, Macromolecules 45 (2012) 1770–1776.

[42] D.J. Darensbourg, R.R. Poland, C. Escobedo, Kinetic studies of the alternating copolymerization of cyclic acid anhydrides and epoxides, and the terpolymerization of cyclic acid anhydrides, epoxides, and CO_2 catalyzed by (salen) CrIIICl, Macromolecules 45 (2012) 2242–2248.

[43] M. Hatazawa, R. Takahashi, J. Deng, H. Houjou, K. Nozaki, Cationic Co–salphen complexes bisligated by DMAP as catalysts for the copolymerization of cyclohexene oxide with phthalic anhydride or carbon dioxide, Macromolecules 50 (2017).

[44] S. Liu, C. Ren, N. Zhao, Y. Shen, Z. Li, Phosphazene bases as organocatalysts for ring-opening polymerization of cyclic esters, Macromol. Rapid Commun. 39 (2018) 1800485.

[45] H. Li, J. Zhao, G. Zhang, Self-buffering organocatalysis tailoring alternating polyester, ACS Macro Lett. 6 (2017) 1094–1098.

[46] D. Zhang, S.K. Boopathi, N. Hadjichristidis, Y. Gnanou, X. Feng, Metal-free alternating copolymerization of CO_2 with epoxides: fulfilling “green” synthesis and activity, J. Am. Chem. Soc. 138 (2016) 11117–11120.

[47] D. Zhang, X. Feng, Y. Gnanou, K. Huang, Theoretical mechanistic investigation into metal-free alternating copolymerization of CO_2 and epoxides: the key role of triethylborane, Macromolecules 51 (2018) 5600–5607.

[48] N.G. Patil, S.K. Boopathi, P. Alagi, N. Hadjichristidis, Y. Gnanou, X. Feng, Carboxylate salts as ideal initiators for the metal-free copolymerization of CO_2 with epoxides: synthesis of well-defined polycarbonates diols and polyols, Macromolecules 52 (2019) 2431–2438.

[49] J. Yang, H. Wu, Y. Li, X. Zhang, D.J. Darensbourg, Perfectly alternating and regioselective copolymerization of carbonyl sulfide and epoxides by metal-free Lewis pairs, Angew. Chem. Int. Ed. 56 (2017) 5774–5779.

[50] L. Hu, C. Zhang, H. Wu, J. Yang, B. Liu, H. Duan, X. Zhang, Highly active organic Lewis pairs for the copolymerization of epoxides with cyclic anhydrides: metal-free access to well-defined aliphatic polyesters, Macromolecules 51 (2018) 3126–3134.

[51] C. Zhang, H. Duan, L. Hu, C. Zhang, X. Zhang, Metal-free route to precise synthesis of poly (propylene oxide) and its blocks with high activity, ChemSusChem 11 (2018) 4209–4213.

[52] H. He, P. Song, J. Wu, M. Xiao, S. Wang, Y. Meng, Effects of reaction time and pressure on the copolymerization of carbon dioxide and propylene oxide using supported zinc glutarate catalyst, Acta Polym. Sin. (2010) 1148–1151.

[53] L. Gao, M. Xiao, S. Wang, F. Du, Y. Meng, Copolymerization of carbon dioxide and propylene oxide with zinc glutarate as catalyst in the presence of compounds containing active hydrogen, J. Appl. Polym. Sci. 104 (2007) 15–20.

[54] L. Gao, M. Xiao, S. Wang, F. Du, Y. Meng, Effect of water, ethanol and propanal on the copolymerization of carbon dioxide and propylene oxide, Polym. Mater. Sci. Eng. 23 (2007) 32–35.

[55] X. Li, Y. Meng, G. Chen, R.K.Y. Li, Thermal properties and rheological behavior of biodegradable aliphatic polycarbonate derived from carbon dioxide and propylene oxide, J. Appl. Polym. Sci. 94 (2004) 711–716.

[56] X. Li, Y. Meng, Q. Zhu, S. Tjong, Thermal decomposition characteristics of poly (propylene carbonate) using TG/IR and Py-GC/MS techniques, Polym. Degrad. Stab. 81 (2003) 157–165.

[57] X. Li, Y. Meng, Q. Zhu, Y. Xu, S. Tjong, Melt processable and biodegradable aliphatic polycarbonate derived from carbon dioxide and propylene oxide, J. Appl. Polym. Sci. 89 (2003) 3301–3308.

[58] X. Lu, Q. Zhu, Y. Meng, Kinetic analysis of thermal decomposition of poly(-propylene carbonate), Polym. Degrad. Stab. 89 (2005) 282–288.

[59] K. Fung, H. Zhao, J. Wang, Y. Meng, S. Tjong, R.K.Y. Li, Essential work of fracture (EWF) analysis for compression molded alternating poly (propylene carbonate), Polym. Eng. Sci. 44 (2004) 580–587.

[60] X. Wang, R.K.Y. Li, Y. Cao, Y. Meng, Essential work of fracture analysis of poly(propylene carbonate) with varying molecular weight, Polym. Test. 24 (2005) 699–703.

[61] J. Wu, M. Xiao, H. He, S. Wang, D. Han, Y. Meng, Synthesis and characterization of high molecular weight poly(1,2-propylene carbonate-co-1,2-cyclohexylene carbonate) using zinc complex catalyst, Chin. J. Polym. Sci. 29 (2011) 552–559.

[62] Y. Meng, Y. Zou, S. Wang, M. Xiao, F. Du, H. Zhang, Poly (methylethylene Carbonate)-Poly (cyclohexylene Carbonate) Copolymer and its Preparation Method, CN1786045A, 2006.

[63] Y. Zou, Y. Meng, Synthesis and characterization of terpolymer poly (propylene cyclohexene carbonate)s, Acta Chim. Sin. 64 (2006) 2111–2114.

[64] Q. Liu, Y. Zou, Y. Bei, G. Qi, Y. Meng, Mechanic properties and thermal degradation kinetics of terpolymer poly (propylene cyclohexene carbonate)s, Mater. Lett. 62 (2008) 3294–3296.

[65] Y. Meng, S. Chen, S. Wang, M. Xiao, J. Wu, D. Han, F. Du, L. Gan, J. Wu, S. Wu, Methyl Ethylene Carbonate Block Copolymer and its Preparation Method, CN101906208A, 2010.

[66] S. Chen, M. Xiao, S. Wang, D. Han, Y. Meng, Novel ternary block copolymerization of carbon dioxide with cyclohexene oxide and propylene oxide using zinc complex catalyst, J. Polym. Res. 19 (2012) 9800.

[67] S. Chen, M. Xiao, S. Wang, D. Han, Y. Meng, Mechanical properties of block poly(propylene carbonate-cyclohexyl carbonate) investigated by nano-indentation and DMA methodologies, J. Appl. Polym. Sci. (2012) 1979–1986.

[68] Y. Meng, Y. Zou, H. Zhang, Poly(methyl)ethylene-ethylene Carbonic Acid Esters and its Preparation, CN1831029A, 2006.

[69] Y. Zou, M. Xiao, X. Li, S. Wang, Y. Meng, Biodegradability enhanced terpolymer of propylene oxide and ethylene oxide with carbon dioxide using zinc glutarate as catalyst, Polym. Polym. Compos. 15 (2007) 53–58.

[70] Y. Zou, S. Wang, M. Xiao, Y. Meng, Synthesis and characterization of terpolymer polycarbonates from propylene oxide and ethylene oxide with carbonate dioxide, Polym. Mater. Sci. Eng. 23 (2007) 120–123.

[71] L. Gao, F. Du, M. Xiao, S. Wang, Y. Meng, Thermally stable aliphatic polycarbonate containing bulky carbazole pendants, J. Appl. Polym. Sci. 108 (2008) 3626–3631.

[72] L. Gao, M. Xiao, S. Wang, Y. Meng, Thermally stable poly(propylene carbonate) synthesized by copolymerizing with bulky naphthalene containing monomer, J. Appl. Polym. Sci. 108 (2008) 1037–1043.

[73] M. Xiao, W. Luo, Y. Meng, S. Wang, D. Han, Y. Xu, J. Lu, Method for Preparing Aliphatic Polycarbonate-G-Polyethylene Glycol Amphiphilic Graft Polymer, CN108623813A, 2018.

[74] Y. Meng, P. Song, F. Du, X. Li, S. Wang, M. Xiao, L. Gan, G. Liu, J. Qiao, Preparation of Crosslinked Propylene Oxide, Cyclic Anhydride and Carbon Dioxide Copolymers, CN101104681A, 2008.

[75] P. Song, M. Xiao, F. Du, S. Wang, L. Gan, G. Liu, Y. Meng, Synthesis and properties of aliphatic polycarbonates derived from carbon dioxide, propylene oxide and maleic anhydride, J. Appl. Polym. Sci. 109 (2008) 4121–4129.

[76] P. Song, S. Wang, M. Xiao, F. Du, L. Gan, G. Liu, Y. Meng, Cross-linkable and thermally stable aliphatic polycarbonates derived from CO_2, propylene oxide and maleic anhydride, J. Polym. Res. 16 (2008) 91–97.

[77] Y. Liu, K. Deng, S. Wang, M. Xiao, D. Han, Y. Meng, A novel biodegradable polymeric surfactant synthesized from carbon dioxide, maleic anhydride and propylene epoxide, Polym. Chem. 6 (2015) 2076–2083.

[78] P. Song, M. Xiao, S. Wang, F. Du, Y. Meng, Synthesis and properties of terpolymers derived from carbon dioxide, propylene oxide and phthalic anhydride, Polym. Mater. Sci. Eng. 25 (2009) 1–4.

[79] Y. Liu, M. Xiao, S. Wang, L. Xia, D. Hang, G. Cui, Y. Meng, Mechanism studies of terpolymerization of phthalic anhydride, propylene epoxide, and carbon dioxide catalyzed by ZnGA, RSC Adv. 4 (2014) 9503–9508.

[80] W. Luo, M. Xiao, S. Wang, D. Han, Y. Meng, Gradient terpolymers with long ε-caprolactone rich sequence derived from propylene oxide, CO_2, and ε-caprolactone catalyzed by zinc glutarate, Eur. Polym. J. 84 (2016) 245–255.

[81] W. Luo, M. Xiao, S. Wang, S. Ren, Y. Meng, Thermal degradation behavior of Copoly(propylene carbonate ε-caprolactone) investigated using TG/FTIR and Py-GC/MS methodologies, Polym. Test. 58 (2017) 13–20.

[82] G. Huang, Y. Zou, W. Luo, M. Xiao, D. Han, S. Wang, Y. Meng, Nonisothermal crystallization behavior and kinetics of poly(l-lactide-co-propylene carbonate), J. Therm. Anal. Calorim. 121 (2015) 877–883.

[83] G. Huang, Y. Zou, M. Xiao, S. Wang, W. Luo, D. Han, Y. Meng, Thermal degradation of poly(lactide-co-propylene carbonate) measured by TG/FTIR and Py-GC/MS, Polym. Degrad. Stab. 117 (2015) 16–21.

[84] L. Tang, W. Luo, M. Xiao, S. Wang, Y. Meng, One-pot synthesis of terpolymers with longl-lactide rich sequence derived from propylene oxide, CO_2, and l-lactide catalyzed by zinc adipate, J. Polym. Sci., Part A: Polym. Chem. 53 (2015) 1734–1741.

[85] Y. Meng, J. Wu, Q. Wang, M. Xiao, H. He, D. Han, Preparation of Poly(urethane Propylene Carbonate) from Carbon Dioxide, Propylene Oxide, and Isocyanates, CN101597376A, 2009.

[86] J. Wu, M. Xiao, H. He, S. Wang, D. Han, Y. Meng, Copolymerization of propylene oxide and carbon dioxide in the presence of diphenylmethane diisoyanate, J. Polym. Res. 18 (2011) 1479–1486.

[87] Y. Xu, S. Wang, L. Lin, M. Xiao, Y. Meng, Semi-crystalline terpolymers with varying chain sequence structures derived from CO$_2$, cyclohexene oxide and ε-caprolactone: one-step synthesis catalyzed by tri-zinc complexes, Polym. Chem. 6 (2015) 1533–1540.

[88] L. Lin, Y. Xu, J. Qin, S. Wang, M. Xiao, Y. Meng, Correlation between crystallization behavior and mechanical properties of biodegradable poly(-caprolactone-*co*-cyclohexene carbonate), Polym. Plast. Technol. 57 (2017) 1530–1541.

[89] W. Luo, J. Qin, M. Xiao, D. Han, S. Wang, Y. Meng, Synthesis of aliphatic carbonate macrodiols and their application as sustainable feedstock for polyurethane, ACS Omega 2 (2017) 3205–3213.

[90] Y. Meng, W. Luo, S. Wang, M. Xiao, D. Han, Preparation of Aliphatic Polycarbonate Diols, CN105694020A, 2016.

[91] J. Qin, L. Lin, S. Wang, S. Ye, W. Luo, M. Xiao, D. Han, Y. Meng, Multiblock copolymers of PPC with oligomeric PBS: with low brittle–toughness transition temperature, RSC Adv. 8 (2018) 14722–14731.

[92] J. Qin, W. Luo, M. Li, P. Chen, S. Wang, S. Ren, D. Han, M. Xiao, Y. Meng, A novel multiblock copolymer of CO$_2$-based PPC-mb-PBS: from simulation to experiment, ACS Sustain. Chem. Eng. 5 (2017) 5922–5930.

[93] K.A. Alferov, Z. Fu, S. Ye, D. Han, S. Wang, M. Xiao, Y. Meng, One-pot synthesis of dimethyl hexane-1,6-diyldicarbamate from CO$_2$, methanol, and diamine over CeO$_2$ catalysts: a route to an isocyanate-free feedstock for polyurethanes, ACS Sustain. Chem. Eng. 7 (2019) 10708–10715.

[94] J.Q.J.J.X. Qin, S.X. Ye, S.J. Wang, M. Xiao, Y.J. Tao, G.X. Jie, Y.Z. Meng, High performance poly(urethane-co-amide) from CO$_2$-based dicarbamate: an alternative to long chain polyamide, RSC Adv. (2019), https://doi.org/10.1039/C9RA04646A.

[95] R. Muthuraj, T. Mekonnen, Carbon dioxide–derived poly(propylene carbonate) as a matrix for composites and nanocomposites: performances and applications, Macromol. Mater. Eng. 303 (2018) 1800366.

[96] X. Ge, X. Li, Q. Zhu, L. Li, Y. Meng, Preparation and properties of biodegradable poly(propylene carbonate)/starch composites, Polym. Eng. Sci. 44 (2004) 2134–2140.

[97] X. Lu, F. Du, X. Ge, M. Xiao, Y. Meng, Biodegradability and thermal stability of poly(propylene carbonate)/starch composites, J. Biomed. Mater. Res. A. 77 (2006) 653–658.

[98] Y. Meng, X. Ge, X. Li, Degradable Poly(methylethylene Carbonate)-Starch Composite Material, CN1528811A, 2004.

[99] X. Ge, Y. Xu, Y. Meng, R.K.Y. Li, Thermal and mechanical properties of biodegradable composites of poly(propylene carbonate) and starch–poly(methyl acrylate) graft copolymer, Compos. Sci. Technol. 65 (2005) 2219–2225.

[100] S. Zeng, S. Wang, M. Xiao, D. Han, Y. Meng, Preparation and properties of biodegradable blend containing poly (propylene carbonate) and starch acetate with different degrees of substitution, Carbohydr. Polym. 86 (2011) 1260–1265.

[101] Y. Meng, S. Zeng, M. Xiao, S. Wang, D. Han, F. Du, F. Wang, Fully Degradable Polymethyl Ethylene Carbonate-Starch Acetate Blend and its Preparation, CN102020838A, 2011.

[102] F. Du, Y. Meng, L. Gan, X. Li, S. Wang, X. Qi, M. Xiao, J. Qiao, X. Li, Producing Multi-Component Completely Biodegradable Polymer Composite, CN101293994A, 2008.

[103] Y. Meng, X. Li, Q. Zhu, S. Wang, M. Xiao, Natural Plant Fiber-Reinforced Fully Degradable Polymer Composite Material and its Preparation, CN1422899A, 2003.

[104] X. Li, Y. Meng, S. Wang, A.V. Rajulu, S. Tjong, Completely biodegradable composites of poly(propylene carbonate) and short, lignocellulose fiber Hildegardia populifolia, J. Polym. Sci., Polym. Phys. 42 (2004) 666–675.

[105] X. Ge, Q. Zhu, Y. Meng, Fabrication and characterization of biodegradable poly(propylene carbonate)/wood flour composites, J. Appl. Polym. Sci. 99 (2006) 782–787.

[106] M. Pang, J. Qiao, J. Jiao, S. Wang, M. Xiao, Y. Meng, Miscibility and properties of completely biodegradable blends of poly(propylene carbonate) and poly(butylene succinate), J. Appl. Polym. Sci. 107 (2008) 2854–2860.

[107] G. Chen, Y. Wang, S. Wang, M. Xiao, Y. Meng, Orientation microstructure and properties of poly(propylene carbonate)/poly(butylene succinate) blend films, J. Appl. Polym. Sci. 128 (2013) 390–399.

[108] G. Chen, B. Li, J. Zhao, L. Gan, S. Wang, M. Xiao, Y. Meng, Preparation and properties of compatible poly (propylene carbonate)/poly(butylene succinate) blends, Polym. Mater. Sci. Eng. 29 (2013) 148–151.

[109] W. Chen, M. Xiao, S. Wang, L. Wen, Y. Meng, Preparation and properties of biodegradable blends of poly(propylene carbonate) and poly(lactic acid), Polym. Mater. Sci. Eng. 26 (2010) 142–145.

[110] Q. Zhao, M. Xiao, S. Wang, J. Ruan, Y. Meng, Preparation and properties of poly(propylene carbonate)/poly(lactic acid) blend with diisocyanate as compatibilizer in melt process, Polym. Mater. Sci. Eng. 27 (2011) 152–155.

[111] G. Chen, J. Zhao, B. Li, L. Gan, S. Wang, M. Xiao, Y. Meng, Preparation and properties of poly(propylene carbonate)/poly(lactic acid) blend films, Polym. Mater. Sci. Eng. 29 (2013) 128–131.

[112] Y. Meng, Y. Cao, M. Xiao, Q. Zhu, X. Wang, Preparation of Fully Biodegradable Poly(propylene Carbonate)-Poly(vinyl Alcohol) Composite via Solution Blending, CN1687234A, 2005.

[113] Y. Cao, F. Du, X. Wang, Y. Meng, New biodegradable blends from aliphatic polycarbonate and poly(vinyl alcohol), Polym. Polym. Compos. 14 (2006) 577–584.

[114] J.M. Lagarón, E. Giménez, R. Gavara, J.J. Saura, Study of the influence of water sorption in pure components and binary blends of high barrier ethylene–vinyl alcohol copolymer and amorphous polyamide and nylon-containing ionomer, Polymer 42 (2001) 9531–9540.

[115] J. Jiao, S. Wang, M. Xiao, Y. Xu, Y. Meng, Processability, property, and morphology of biodegradable blends of poly(propylene carbonate) and poly(ethylene-co-vinyl alcohol), Polym. Eng. Sci. 47 (2007) 174–180.

[116] X. Wang, F. Du, J. Jiao, Y. Meng, R.K. Li, Preparation and properties of biodegradable polymeric blends from poly(propylene carbonate) and poly(ethylene-co-vinyl alcohol), J. Biomed. Mater. Res. B Appl. Biomater. 83 (2007) 373–379.

[117] Y. Meng, X. Wang, Q. Zhu, M. Xiao, J. Jiao, M. Cao, L. Guan, Preparation of Degradable Poly(propylene Carbonate)-Ethylene-Vinyl Alcohol Copolymer Composite, CN1775857A, 2006.

[118] X. Chen, S. Wang, M. Xiao, D. Han, Y. Meng, Miscibility, properties and morphology of biodegradable blends of UHMW-PPC/PVA/EVOH, J. Polym. Res. 18 (2010) 715–720.

[119] Y. Meng, J. Qiao, F. Du, S. Wang, M. Xiao, J. Jiao, Degradable Polymethylethylene Carbonate Resin Composition with Net Zero Carbon Dioxide Release, CN100999602A, 2007.

[120] J. Qiao, F. Du, M. Pang, M. Xiao, S. Wang, Y. Meng, Fabrication and properties of degradable PPC/EVOH/starch/CaCO$_3$ composites, J. Wuhan Univ. Technol.-Materials Sci. Ed. 23 (2008) 362–366.

[121] D. Han, G. Chen, M. Xiao, S. Wang, S. Chen, X. Peng, Y. Meng, Biodegradable and toughened composite of poly(propylene carbonate)/thermoplastic polyurethane (PPC/TPU): effect of hydrogen bonding, Int. J. Mol. Sci. 19 (2018) 2032.

[122] Y. Zhao, G. Chen, M. Xiao, S. Wang, Y. Meng, Biodegradable PPC/(PVA-TPU) ternary blend blown films with enhanced mechanical properties, J. Polym. Res. 23 (2016) 80.

[123] Y. Meng, Y. Zhao, S. Wang, M. Xiao, F. Du, G. Zhu, L. Gan, D. Han, J. Wu, Polypropylene Carbonate Composition with Good Film-Forming Performance, Dimensional Stability, Tensile Strength, CN104371296A, 2015.

[124] Y. Meng, Z. Guo, M. Xiao, S. Wang, D. Han, F. Du, L. Gan, Biodegradable Polymethylethylene Carbonate Composite and its Preparation Method, CN102786788A, 2012.

[125] M. Pang, X. Ge, J. Jiao, L. Guan, J. Qiao, S. Wang, Y. Meng, Preparation and properties of poly(propylene carbonate)/polystyrene composites, Polym. Mater. Sci. Eng. 23 (2007) 155–158.

[126] Y. Meng, X. Li, S. Wang, Q. Zhu, M. Xiao, Degradable Polymer/natural Mineral Filler Composite Material and its Preparation, CN1422898A, 2003.

[127] X. Li, S. Tjong, Y. Meng, Q. Zhu, Fabrication and properties of poly(propylene carbonate)/calcium carbonate composites, J. Polym. Sci., Polym. Phys. 41 (2003) 1806–1813.

[128] J. Xu, R.K.Y. Li, Y. Xu, L. Li, Y. Meng, Preparation of poly(propylene carbonate)/organo-vermiculite nanocomposites via direct melt intercalation, Eur. Polym. J. 41 (2005) 881–888.

[129] J. Xu, R.K.Y. Li, Y. Meng, Y. Mai, Biodegradable poly(propylene carbonate)/montmorillonite nanocomposites prepared by direct melt intercalation, Mater. Res. Bull. 41 (2006) 244–252.

[130] L. Du, B. Qu, Y. Meng, Q. Zhu, Structural characterization and thermal and mechanical properties of poly(propylene carbonate)/MgAl-LDH exfoliation nanocomposite via solution intercalation, Compos. Sci. Technol. 66 (2006) 913–918.

[131] W. Chen, M. Pang, M. Xiao, S. Wang, L. Wen, Y. Meng, Mechanical, thermal, and morphological properties of glass fiber-reinforced biodegradable poly(propylene carbonate) composites, J. Reinf. Plast. Compos. 29 (2009) 1545–1550.

[132] P. Song, Y. Wang, R. Wang, W. Sun, Z. Lei, X. Liu, Y. Meng, Preparation and thermal stability of poly (propylene carbonate)/organo-attapulgite nanocomposites, N. Chem. Mater. 40 (2012) 49–51.

[133] W. Chen, M. Xiao, S. Wang, L. Wen, Y. Meng, Preparation and properties of poly(propylene carbonate)/halloysite nanotubes composites, Polym. Mater. Sci. Eng. 26 (2010) 142–145.

[134] L. Chen, S. Wang, M. Xiao, Y. Meng, Preparation of poly(propylene carbonate)/halloysite nanotube composite with diisocyanate as compatilizer, Polym. Mater. Sci. Eng. 27 (2011) 157–159, 164.

[135] Y. Meng, Y. Cao, M. Xiao, Q. Zhu, X. Wang, H. Zhang, Preparation of Cross-linked Poly(propylene Carbonate), CN1696197A, 2005.

[136] L. Zhai, G. Li, Y. Xu, M. Xiao, S. Wang, Y. Meng, Poly(propylene carbonate)/aluminum flake composite films with enhanced gas barrier properties, J. Appl. Polym. Sci. (2014) 41663.

[137] G. Li, W. Luo, M. Xiao, S. Wang, Y. Meng, Biodegradable poly(propylene carbonate)/layered double hydroxide composite films with enhanced gas barrier and mechanical properties, Chin. J. Polym. Sci. 34 (2016) 13–22.

[138] Y. Meng, G. Li, J. Zheng, M. Xiao, S. Wang, D. Han, Biodegradable High-Barrier Plastic Film Material and Manufacture Method, CN104194022A, 2014.

[139] Y. Meng, D. Yang, F. Du, M. Xiao, X. Zhang, S. Wang, G. Zhu, L. Zhai, D. Han, L. Gan, High-barrier Polypropylene Carbonate Composite Film Packaging Material and Preparation Method Thereof, CN103804879A, 2014.

[140] W. Li, J. Qin, S. Wang, D. Han, M. Xiao, Y. Meng, Macrodiols derived from CO_2-based polycarbonate as an environmentally friendly and sustainable PVC plasticizer: effect of hydrogen-bond formation, ACS Sustain. Chem. Eng. 6 (2018) 8476−8484.

[141] Y. Meng, X. Yu, S. Wang, M. Xiao, P. Song, Q. Zhao, G. Liu, Crosslinked Poly(methylethylene Carbonate) Electrolyte Films and the Manufacturing Methods Therefor, CN101200554A, 2008.

[142] X. Yu, M. Xiao, S. Wang, D. Han, Y. Meng, Fabrication and properties of crosslinked poly(propylene carbonate maleate) gel polymer electrolyte for lithium-ion battery, J. Appl. Polym. Sci. (2010) 2078−2083.

[143] X. Yu, M. Xiao, S. Wang, Q. Zhao, Y. Meng, Fabrication and characterization of PEO/PPC polymer electrolyte for lithium-ion battery, J. Appl. Polym. Sci. 115 (2010) 2718−2722.

[144] X. Yu, M. Xiao, S. Wang, Y. Meng, Fabrication and properties of PPC/PEO/TiO2 composite polymer electrolyte for lithium-ion battery, Res. J. Chem. Environ. 15 (2011) 5−12.

[145] K. Deng, S. Wang, S. Ren, D. Han, M. Xiao, Y. Meng, A novel single-ion-conducting polymer electrolyte derived from CO_2-based multifunctional polycarbonate, ACS Appl. Mater. Interfaces 8 (2016) 33642−33648.

[146] M. Xiao, K. Deng, Y. Meng, S. Wang, D. Han, S. Ren, X. Huang, A Kind of Taking Carbon Dioxide-Based Polycarbonate as Main Chain for Lithium Single Ion Conduction Solid State Polymer Electrolyte and its Preparation Method, CN106410270A, 2017.

[147] Y. Meng, F. Du, S. Wang, Y. Chen, M. Xiao, D. Han, Method for Preparing Completely Biodegradable Pressure-Sensitive Adhesive, CN101412897A, 2009.

[148] F. Du, X. Chen, Y. Meng, S. Wang, M. Xiao, L. Gan, J. Wu, Fully Biodegradable Plastic Films and Production Process Thereof, CN101851406A, 2010.

[149] Y. Meng, G. Xu, M. Xiao, F. Du, S. Wang, D. Han, Biodegradable Stone Paper, CN104693710A, 2015.

[150] Y. Chen, Y. Liu, X. Fang, Y. Meng, Method for Improving Hydrolysis Resistance of Biodegradable Polyester Resin, CN102875829A, 2013.