

Synthesis, Catalysing and Application of Functional Carbon Dioxide-based Polymers

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Abstract. CO₂ has the characteristics of low chemical activity and dynamic stability, and it is difficult to activate. Despite of these difficulties, it has attracted increasing attention to make the most of CO₂, which is a potentially renewable resource. CO₂-based polymers have superior functions and a wide range of uses. the rational utilization of CO₂ can not only alleviate the environmental problems caused by emissions, but also be a vital measure of human energy utilization. Meanwhile, in view of the low chemical activity of carbon dioxide, to achieve the synthesis of CO₂-based polymer, the study of catalyst is essential. This paper mainly summarizes the research progress of CO₂-based biodegradable plastics and application of different catalysts in the process of synthesis, including using porous hyper crosslinked polymer supported ionic liquids to catalyze the synthesis of CO₂-based biodegradable plastic, which has the most promising development prospect. But realizing the industrialization of the synthesis of biodegradable plastics from carbon dioxide is still in dilemma. In addition, the article also introduces a kind of CO₂-based hyperbranched poly prodrug molecule, while the future development prospects of other CO₂-based polymers may apply in the biomedical field are also prospected. If CO₂-based polymers applied in biomedicine area can be realized, it will be a major milestone in the history of human health study.

Keywords: CO₂-based degradable polymers, catalyst, application in biochemical.

1. Introduction

With the development of technology and industry, global CO₂ emissions are gradually increasing. By 2020, the global annual carbon emissions have exceeded 30 billion tons each year, while relevant data shows that the growth rate of global carbon dioxide emissions is slowing down. However, it is still difficult to achieve negative growth in CO₂ emissions due to weak climate and energy policies. Thus, effective ways of converting CO₂ into value-added products is desired to achieve alleviation of CO₂ emission. From one aspect, make full and reasonable use of carbon dioxide to synthesize various substances can reduce the consumption of raw materials in the original synthesis method of certain substances to improve the utilization structure of resources. Moreover, synthesizing functional polymers through CO₂ can effectively reduce the released greenhouse gases, which is of great significance for environmental protection.

The utilization of functional CO₂-based polymers has been widely focused on. Aliphatic polycarbonate prepared from CO₂ and epoxy compounds has excellent degradability and is used as biodegradable plastics, of which the relevant research and techniques have become mature. Based on previous studies, some researchers synthesized a new CO₂-based super branch polymer that will be mentioned in the fourth part of this paper. Through their discovery, the applications of functional CO₂-based polymers extend to the field of biological medicine. The carbon fixation by polymerization not only reduces the greenhouse gases, but also decreases the environmental damage to some traditional non-degradable materials. Therefore, it is of great significance to explore the development and the perspective trend of functional CO₂-based polymers.

2. Research status of functional CO₂-based polymers

The so-called carbon dioxide-based polymer is the high polymer that combines carbon dioxide and other monomers by catalysis process, which is often applied in different fields and plays a variety of functions because of its tremendous performance. This article primarily discusses biodegradable plastics which belong to functional carbon dioxide-based polymers. Carbon dioxide-based biodegradable plastics are also called carbon dioxide polymers or carbon dioxide copolymers, mainly containing polycarbonate and other substances.

According to the review of Qian, data displays that approximately 31%~50% proportion of biodegradable plastics made from carbon dioxide is composed of CO₂ [1]. Therefore, a way for the captured CO₂ to be effectively used is provided, where CO₂ replaces the traditional plastic raw materials to produce biodegradable plastics, decreasing the consumption of non-renewable fossil fuels. CO₂-based polymer degradable plastics have similar properties to conventional plastics that can be reused multiple times. What is different is that the discarded CO₂-based polymer degradable plastics can also be decomposed by microorganisms in nature, unlike the traditional ones that need a long time to degrade, which can reduce the accumulation of plastic waste in nature, avoiding the "white pollution" effectively. Apart from that, even when these substances are burned, only water and carbon dioxide are released, which may not produce an additional toxic gas that can pollute the atmosphere.

At present, with the CO₂ involved in the synthesis of carbon dioxide-based biodegradable plastic research, the attention of increasing people is being aroused to start research in this area. Several synthetic methods have been discovered, including synthesizing biodegradable plastics polycarbonate with CO₂, which has the most mature development. With the development of synthesis technology, polymerization of CO₂ with another raw material to produce the new-type carbon dioxide-based biodegradable plastics.

2.1. Polycarbonate

Polycarbonate (PC), which has relatively mature production technology, also called Makrolon, can be divided into aromatic polycarbonate and aliphatic polycarbonate according to the structure of the ester group, of which the aliphatic polycarbonate (APC) belongs to the carbon dioxide-based polymers. Polycarbonate would turn into a transparent glass when cooling down after being melted. Its excellent optical and mechanical properties, coupled with its biodegradability, enable polycarbonate to become a focus of the plastics production industry. Nevertheless, the mechanical properties of aliphatic polycarbonate are worse than those of aromatic polycarbonate, which leads to some limitations in the application of APC in engineering plastics. At present, only aromatic polycarbonate has been industrially produced, which means that the synthesis of APC from CO₂ is only at the research stage, so finding ways to tackle this problem is particularly important for the utilization of CO₂ in biodegradable plastics production.

Aliphatic polycarbonate was first discovered by Inoue in 1969, which was synthesized by coupling reaction of CO₂ and propylene oxide (PO) with catalyst Zn [2, 3]. This substance is also called propylene polycarbonate (PPC), which is a kind of aliphatic polycarbonate. Inoue's method is the main way of synthesis of aliphatic polycarbonate. The reaction equation is shown in Fig. 1. PPC can not only be biodegraded but also undergo thermal degradation. The reaction equation is shown in Fig. 2. However, there is no specific answer to the specific changes during thermal degradation [4].

Due to the limitations and high production cost of the above synthesis method polymerizing propylene oxide and CO₂, some researchers have begun to develop a new synthesis path using CO₂ and other substances to produce polycarbonate. Researchers from the University of Bath in the UK have developed a new technology for preparing polycarbonate, of which the synthetic way is to use sugar and CO₂ as the raw materials [5]. The polycarbonate synthesized by this method can completely replace the traditional one synthesized by bisphenol A which is toxic. This synthesis method can be completed at low pressure and room temperature, which improves the safety of experiment and

production while reducing the production cost by using relatively cheap sugar and CO₂ as raw materials.

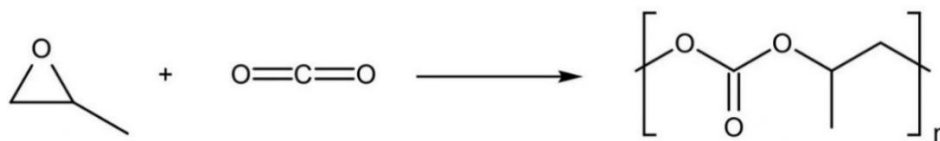


Figure 1. Co-polymerization of CO₂ and propylene oxide to PPC.

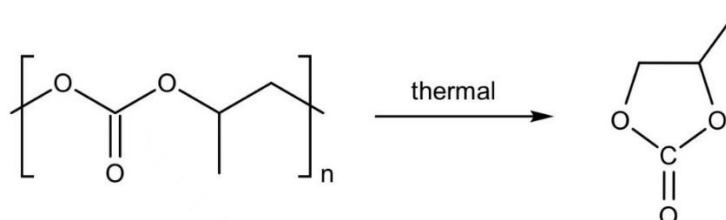


Figure 2. The main thermal degradation of PPC.

Additionally, polyethylene carbonate (PEC) also belongs to aliphatic polycarbonate, which is obtained by the copolymerization of CO₂ and ethylene oxide (EO). Cyclic carbonate is also possible to be produced in this process. The reaction process is shown in Fig. 3. Zhou et al. applied Co-Zn DMC catalyst to catalyse the copolymerization of CO₂ and EO. They then studied the influence of different experimental conditions on the reaction results and found that temperature was an important factor affecting the content of carbonate bonds in PEC, which means the temperature, either too high or too low, would cause side reactions [6]. Although PEC shows biodegradability, the application of PEC as a biodegradable plastic is not as popular as PPC. The main research related to the use of EO as the third monomer to improve the performance of CO₂-based copolymers [7, 8].

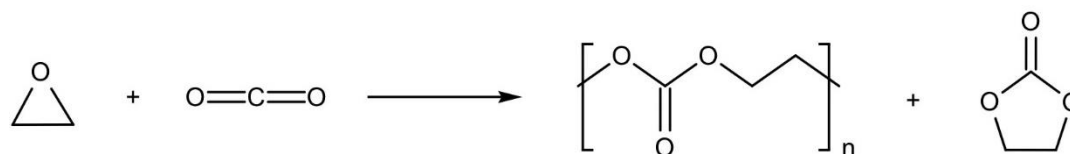


Figure 3. Co-polymerization of CO₂ and EO to PEC.

Apart from the PPC and PEC mentioned above, of which the glass-transition temperature is low, to some extent, the temperature resistance is poor. Another kind of aliphatic polycarbonate called Poly cyclohexene carbonate (PCHC) has better performance. As shown in Fig. 4, PCHC is formed by the polymerization of CO₂ and cyclohexane oxide (CHO). At present, the synthesis process of PCHC in the laboratory is mainly carried out in the high-pressure reaction kettle. CHO and catalyst should be added to the reaction kettle first before adding carbon dioxide. The reaction needs to be controlled under a certain temperature and pressure [9]. Cyclic carbonate may also occur in the reaction products. Ye et al. reported a CO₂-CHO copolymerization catalysed by an active anion polymerization system of lithium metal salts and alkyl aluminium [10]. They coordinated the polymerization activities of the two monomers to make the rates of the two copolymerization tend to be the same and obtained a polycarbonate compound with high selectivity and carbonate content [10]. They also found that the catalytic system composed of lithium metal salts and tri-isobutyl aluminium can effectively catalyse anionic copolymerization of CHO and CO₂ to prepare polycarbonate with high carbonate selectivity [10]. PCHC is the material most likely to develop into a new generation of CO₂-based biodegradable plastics.

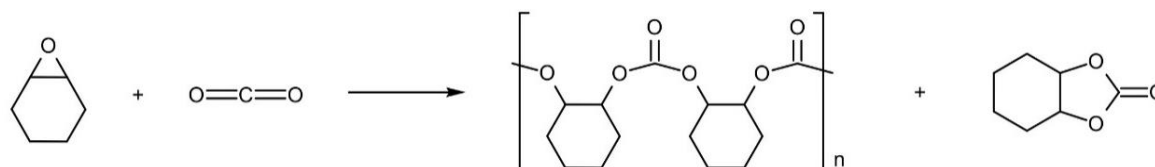


Figure 4. Co-polymerization of CO₂ and CHO to PCHC.

2.2. Another CO₂-based biodegradable plastic

In addition to polycarbonate, which is widely attracted by researchers, there is another substance that belongs to CO₂-based biodegradable plastics. Considering the deficits in the industrious application, some researchers have reported other biodegradable plastics, which are equally superior to polycarbonate. For example, researchers from Cornell University in the United States of America discovered another carbon dioxide-based biodegradable plastic called polycarbonate limonene (PLC), which was debuted with CO₂ and renewable resources [11, 12]. Using these ingredients, they synthesis PLC, a new polymer, which is a copolymer of carbon dioxide and R-epoxy-limonene (LO) monomer. PLC shows a series of similar characteristics compared with polystyrene (PS), which is a common type of plastic as well as good biodegradability.

3. Catalysts for the polymerization of carbon dioxide

One of the most widely currently used methods for synthesizing CO₂-based biodegradable plastics is the polymerization of CO₂ and epoxypropane. Either way of polymerization, the catalysts are essential. There are many kinds of catalysts used for the polymerization of CO₂, such as ternary rare-earth catalyst, ionic liquid catalyst, porous organic polymer catalyst, etc.

3.1. Ternary rare-earth catalyst

In past studies, the polymerization of CO₂-based polymers depended on metal catalysts for synthetic degradable plastics, while some of the catalysts are toxic, such as tin-containing catalysts, which cannot apply to food and medicine. In order to tackle this problem, researchers focused on substitutions, and the rare earth met the demand and standard. It is well-known that China holds the most abundant resources of rare earth, and it has been widely used in the realm of the polymerization of carbon dioxide with epoxypropane taking advantage of yttrium, molybdenum, and other mixed metallic reagents. In 1991, Shen coined polymerization with rare earth ternary catalyst to catalyze. Since then, researchers have found that polycarbonate obtained from rare earth ternary catalysts presents a high molecular weight, narrow distribution range, high thermal stability, and high content of polycarbonate chain [13, 14]. Based on previous studies, Meng et al. added tetramethylammonium fluoride (TMAF) to the rare earth ternary catalytic system in 2016 [15]. This transfer agent has a stronger electron-attracting effect to catalyze the alternating copolymerization of carbon dioxide and epoxypropane, further improving the catalytic activity, shortening the induction period of the catalyst, and accelerating the reaction rate.

The rare earth ternary catalyst has relatively high catalytic activity, low toxicity, and clean residues, which is superior to conventional metal catalysts. But it remains difficult in convoluted exploitation and preparation with its instability, no storability, and high costs, to some extent.

3.2. Ionic liquid catalyst

Recently, a novel environment-friendly medium called ionic liquid has been discovered, which presents high structural designability, good chemical stability, and high catalytic activity [16]. Traditional metal and metal complex catalysts are inferior to ionic liquid catalysts' performance. The traditional one requires strict and harsh reaction conditions, which have poor stability, and low catalytic activity, while ionic liquids can adapt to a variety of reaction conditions, targeted to be applied to the synthesis of substances with different demands. Ionic liquid catalyst can not only act as the reaction solvent but also presents the catalytic effect without additional cocatalyst when the reaction of CO₂ and epoxypropane is carried out to synthesize polycarbonate [17].

Ionic liquid catalysts can be divided into homogeneous ionic liquid catalysts and multi-phase ionic liquid catalysts; the former shows higher activity and can be divided into traditional ionic liquid and functional ionic liquid. According to the report, groups with lower positive charge density are more nucleophilic, which compounds better with epoxides and leads them to open-loop on account of the positive charge density inversely proportioned to the catalytic activity [16]. The catalytic activity of

cations in traditional ionic liquids was the highest in imidazole salts, followed by quaternary ammonium salts and the lowest in pyridine salts. In 2014, Meng studied whether carboxyl shifts affect the catalytic activity of cyclic carbonate synthesis by ionic liquids [16, 18]. He found that pyridine bromide liquids containing inter-carboxyl groups had the highest activity, while pyridine bromide liquids with ortho-carboxyl groups had reduced activity due to hydrogen bonding. Fig. 5 illustrates the catalytic mechanism of a quaternary ammonium ionic liquid catalyst. Functionalized ionic liquids present higher catalytic activity, which bonds cations or anions of ordinary ionic liquids with functional groups accompanying specific functions. Take the hydroxylation of ionic liquids as an example. Zhang's research group theoretically calculated the polymerization of CO₂ and epoxypropane catalysed by 2-hydroxyethyl-triethyl ammonium bromide by the density functional theory (DFT) method in 2015 [16, 19]. They found that the open-loop reaction is the decisive step in the process. The electrostatic attraction has a synergistic effect with the hydrogen bond brought by hydroxylation, which can increase the stability of the intermediate transition state material and make it react quickly. In Fig. 6, the most favorable route found by Zhang for the fixation of CO₂ with PO catalyzed by HETEAB (i) (route 4), HEMIMB (ii) (route 8), Et₄NBr (iii) (route 7) [C₂mim] Br (iv) (route 9) and route 6 is shown [19].

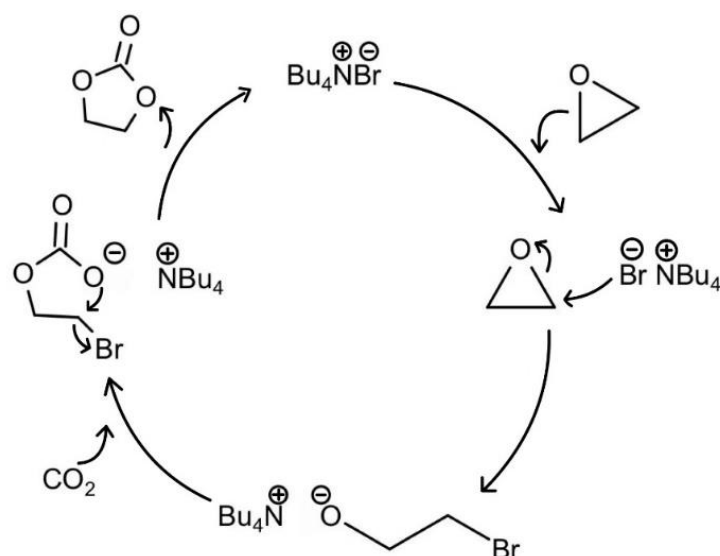


Figure 5. Possible mechanism of addition reaction of CO₂ with epoxy compound catalysed by Bu₄NBr.

However, the above homogeneous ionic liquid usually needs to be separated by high-temperature distillation, which will bring large energy consumption and high production cost. In contrast, the multi-phase ionic liquid catalyst is easier to separate and can be reused by loading the ionic liquid onto recyclable carriers [16]. It can be divided into the inorganic supported ionic liquid catalyst, the organic polymer-supported ionic liquid catalyst, and the polymer-supported ionic liquid catalyst. Apart from that, the latest report indicated that some researchers used covalent bonding to immobilize ionic liquids in the framework and pores of porous hyper crosslinked polymers, which became the porous hyper crosslinked polymer-supported Ionic liquids (HCP-ILs) [17]. It has become an attentive focus in the realm of catalysing the polymerization of CO₂ and epoxypropane because of its diverse synthetic methods, wide source of raw materials and highly tunability of functional group and active site.

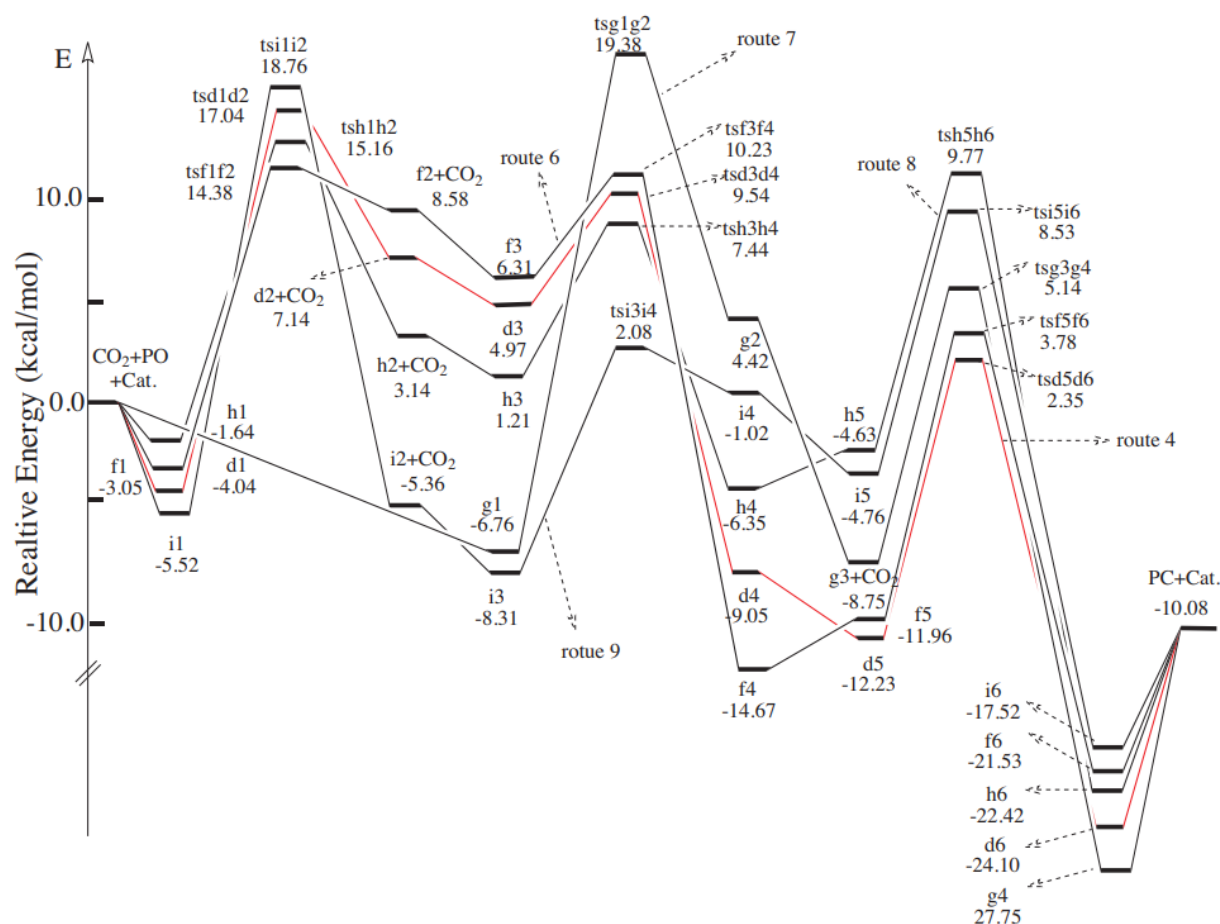


Figure 6. The most favorable route for the fixation of CO₂ with PO catalyzed by HETEAB (i) (route 4), HEMIMB (ii) (route 8), Et₄NBr (iii) (route 7) [C₂mim] Br (iv) (route 9) and route 6 [19].

3.3. Porous organic polymer catalyst

Porous organic polymers are amorphous porous materials formed by the irreversible polymerization of organic groups or some organic fragments. According to the formation mode and structure of these organic materials, they mainly can be divided into the polymer of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), hyper-crosslinked polymers (HCPs), porous aromatic frameworks (PAFs), covalent triazine based frameworks (CTFs) and porous polymer networks (PPNs) [20]. POPs have chemical adjustability, high selectivity for CO₂ adsorption, and a large adsorption capacity for CO₂. The high flexibility of POPs structure design maximizes specific surface area and has higher catalytic efficiency than other catalysts. POPs can be guided and purposefully introduced into the functional groups according to the various activation modes of CO₂ required for reactions to be more suitable for different reactions. Therefore, POPs catalysts can be divided into POPs catalysts containing one active component and POPs catalysts containing two active components. Some of these are the porous hyper crosslinked polymer-supported ionic liquids (HCP-ILs) mentioned above in section 3.2.

There are also metal complex-based POPs catalysts, and we take the metal porphyrin catalyst as an example here. The first time to use the material for catalytic copolymerization of carbon dioxide and propylene oxide was in 1978, reported by Inoue and other scientists, which illustrated that the metal porphyrin catalyst is made by the reaction of metal tetraphenyl porphyrin derivatives with organic salts and triphenyl complexes [13, 21]. This kind of catalyst is superior to carbon dioxide cycloaddition, which catches many researchers' attention. And they gain a series of catalysts by designing and changing the structure of the metal porphyrin complex monomer, which is not static. In 2018, the Ding research group prepared a dual-function porous ionic liquid polymer, Mg-por/pho POP [22]. It can achieve efficient reaction under mild conditions, which constructs imidazole ionic

liquid and metal porphyrin in a polymer framework. In the same year, another research group, Yang, made it possible to adhere to the surface of carbon nanotubes after polymerization, which increased the surface reaction area, showing its superior catalytic activity and stability. This ionic liquid polymer catalyst is ZnTPy-BIM4/CNTs.

Although some properties of the POPs catalyst are better than those of similar catalysts, it still has the development space to reach an ideal state if it makes up for the troubles of complex production and high costs in reality.

4. Application and prospect of functional CO₂-based polymers

As more attention is put on the utmost utilization of CO₂, functional CO₂-based polymers are widely concerned, especially the biodegradable plastic polycarbonate synthesized by CO₂, accounting for its sustainable and eco-friendly features that lead to many relevant studies. From the exploitation till now, it has mainly been used as packaging materials and environmental protection materials daily, such as plastic film used for planting vegetables in agriculture, etc. The application fields and specific uses of CO₂-based biodegradable plastics have been listed in Table 1.

In addition to CO₂-based biodegradable plastics used in medical devices like infusion tubes, the application in biomedical also was reported by Zhang, that Qin and his team synthesised a hyperbranched polyalkenoate ester (hb-Pas) with CO₂, multifunctional alkynes, and dehalogenases under atmospheric pressure, which has the properties of high molecular weight and branching degree [23-26]. It can be used as a platform polymer for chemical post-modification to derive a variety of functions and applications. The hyperbranched polyalkenoate ester synthesised from CO₂ was covalently linked with doxorubicin, an anticancer drug containing a single amino group, and modified with hydrophilic polyethylene glycol in the periphery, to obtain the amphiphilic hyperbranched poly prodrug molecule with high drug loading. This poly prodrug molecule slowly releases Adriamycin in the slightly acidic environment of cancer cell lysosomes, achieving better efficacy than Adriamycin alone in inhibiting cancer cells [23]. This discovery exploited the field of functional CO₂-based polymers, which made the development instead of confining in the boundary of biodegradation plastic, but gradually carried out the application in the biomedicine realm and obtained more fruits beneficial to human health.

Table 1. The application fields and specific uses of CO₂-based biodegradable plastics.

Application Fields		Main Uses
Low Percentage Recovery in Nature	Cushioning packaging materials for transport	Foam sheet materials, profiles
	Civil building materials	Profiles for intermountain and sea civil engineering maintenance, water absorption
	Agricultural plastics	Plastic film, seedling container, plastic film
	Field goods	Golf tees, sea and mountaineering disposables
Conductive Composting Fields	Food packaging material	Food packaging bag, tableware, tray, etc.
	Sanitary products	Physiological hygiene products, disposable diapers, etc.
	Daily groceries	Shrink film, garbage bags, light shopping bags, cosmetics containers, etc.
Medical Materials Fields	The medicinal materials	Human suitability medical materials, disposable medical appliances
	Packaging	Large container of infusion equipment, drug packaging

5. Conclusion

To sum up, the research on functional carbon dioxide polymers has been maturing, and discoveries have been made in the synthesis methods, the raw materials and catalysts used in the synthesis process. In addition to CO₂-based biodegradable plastics that reduce the environmental pollution from traditional plastics, there are also new applications of hyperbranched polymers synthesized from CO₂-based monomers in the field of biomedicine, which enables the applications of functional carbon dioxide polymers to continue to expand. As a new material with cheap CO₂ as raw material, if the overall production cost and other problems can be solved so that a larger scale of production can be achieved, the application of functional CO₂-based polymers will also be more considerable in the future.

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