Syntheses, properties and applications of CO_2-based functional polymers

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SUMMARY

Carbon dioxide (CO_2) is an abundant, inexpensive, nontoxic, and renewable C1 resource in organic synthesis. Converting CO_2 into high-value-added fuels or materials has attracted broad interests. Using CO_2 to construct polymeric materials is also highly desirable because from which carbonate, ester groups, etc. with many unique properties could be generated. In this review, we summarize current advances in the synthesis, property and application of CO_2-based functional polymers. On the basis of the introduction of CO_2/epoxide, CO_2/olefin, CO_2/alkyne, CO_2/isocyanide, and CO_2/frustrated Lewis pair (FLP) polymerizations, diverse properties and versatile properties of CO_2-based polymers, such as superior thermal properties, aggregation-induced emission (AIE), amphipathy and degradation are summarized. Future focuses in CO_2-based functional polymers are also discussed.

INTRODUCTION

Carbon dioxide (CO_2) is a common gas in the atmosphere and one of the important feedstock for the "photosynthesis" of green plants. It plays a vital role in maintaining the carbon-oxygen balance in the atmosphere. In recent years, frequent human production and living activities have led to the massive use of fossil fuels, and the concentration of CO_2 in the atmosphere is increasing at an unprecedented rate. According to statistics, the concentration of CO_2 in the atmosphere has increased from about 280 ppm (volume fraction, the same below) before industrialization to about 410 ppm in 2021. Based on this growth rate, it is anticipated to reach 540~970 ppm by 2100, which greatly exceeds the changes caused by natural environment and other factors in the past 650 000 years.[1]

The continuous increase of CO_2 caused much more problems of climate change. To tackle climate change, the Paris Agreement was passed at the Climate Conference in 2015, and a series of detailed plans for all countries to jointly tackle global climate change after 2020 were formulated. Recently, the "double carbon" strategy was formulated and implemented in China, aiming at reducing CO_2 emissions. From another point of view, CO_2 is regarded as a cheap, abundant, nontoxic, and sustainable C1 feedstock in the field of organic synthesis.[2] Thus, the conversion of CO_2 has attracted wide attention not only for generating high-value-added fuels or materials but also for reducing CO_2 emission to some extent.

CO_2 is a non-polar molecule with a delocalized π bond containing three centers and four electrons, showing excellent thermodynamic stability and kinetic inertness.[2] To realize CO_2 conversion, two issues need to addressed in general. One is activating CO_2 via suitable catalysts (Figure 1). There are several catalytic systems being developed for CO_2 activation, including organic base,[3] tungstate,[4] *N*-heterocyclic carbine (NHC),[5] *N*-heterocyclic olefin (NHO),[6] frustrated Lewis pair (FLP),[7] and transition metal,[8] etc. All of them could form complexes with CO_2, facilitating its subsequent conversion. The other is using high-energy substrates to react with CO_2 (Figure 1). The substrates are usually chosen as epoxides, alkenes, alkynes etc., which are activated by organo- or metal-based catalysts (Ag, Cu, Co, Pd, *etc*.) to generate low-energy products, such as organic carbonates and esters.[2] For example, the epoxides and propargylic alcohols are activated by organo- or metal-based catalysts, which could readily react with CO_2 towards cyclic carbonates.[9] The terminal alkynes activated by Ag(I) or Cu(I) catalysts could react with CO_2 via the carboxylation towards alkynoates.[2] Butadiene could be activated by Pd(0) catalyst and react with CO_2 towards a six-membered ring lactones.[10]

CO_2-based polyols with high mass percentage of CO_2 produced by the polymerization of CO_2 and epoxides are regarded as low-cost products instead of traditional polyols for the synthesis of polyurethane (PU). Life cycle assessment indicates that the CO_2-based polyols with 20 wt% CO_2 could reduce greenhouse gas emissions by 11-19% and save fossil resource by 13-16%.[11,12] In addition, PU from CO_2-based polyols show improved hydrolysis/oxidation resistance.[13,14] Thus, many works about CO_2-based polyols towards polyurethane have been done in the past few decades and these polyols have been well industrialized.[15]

Inspired by these mass-produced CO_2-based polyols, many new CO_2-based functional polymers are emerged in recent years. This review focuses on CO_2-based functional polymers developed in the last few years. The CO_2-based polycarbonates and their copolymers have superior thermal properties, which could be used as foams, adhesives, engineering plastics, etc. The CO_2-based amphiphilic polymers were designed, synthesized and applied in the areas of bioimaging, therapy, lithium ion battery, etc. The CO_2-based polymers with aggregation-induced emission (AIE) features were also reported for chemosensor, photopattern, and light emitting diode (LED) applications. Last but not least, some CO_2-based degradable polymers could be regarded as chemically recyclable materials, nanocatalysts, dynamic gels and so on

(Figure 2). To make the review clear, we summarize the progresses of CO_2-based functional polymers by the co-monomer categories. Their synthetic routes, versatile properties, and diverse applications are introduced in detail. Since the development of catalysts, and the polymerization mechanisms have been summarized in previous excellent reviews, we will not discuss them here.[9,10,16-20]

EPOXIDE-BASED POLYMERS

The polymerization of CO_2 and epoxides is the first reported CO_2-based example, and the general reaction formulas are shown in Figure 3A and 3B. In 1969, Inoue *et al.* found that the use of a mixed system of diethyl zinc and water can catalyze the polymerization of propylene oxide (PO) and CO_2 to generate poly(propylene carbonate) (PPC).[21] This seminal discovery opened up a new research field in polymer chemistry. However, this polymerization suffers from the selectivity problems, such as product selectivity (polycarbonte or cyclic carbonate), structural selectivity (ether or carbonate in polymer chain), regio- and stereo-selectivity. In the past 50 years, various transition metal catalysts have been developed to control the selectivity of CO_2/epoxide polymerization.[17-20,22] Moreover, the residue of metallic species in the polymers is another problem for their applications. Recently, bifunctional organoboron catalysts were emerged as a kind of metal-free catalysts with unprecedented efficiency, which could solve the metal residues in the produced polymers.[23]

CO_2-based polycarbonates with superior thermal properties

PPC has low glass transition temperature (T_g = 37 ^{o}C), which limits its use in many areas.[16] To improve the thermal properties of CO_2-based polycarbonates, many research groups from all over the world have made a lot of efforts. The rigidity of polymer backbone could be realized via the incorporation of aryl or cycloaliphatic groups, which makes segmental mobility become bad and therefore increase the T_g. For example, Darensbourg *et al.* used the binary and bifunctional (salen)Co(III) catalysts for the copolymerization of indene oxide (IO) and CO_2 to produce the corresponding poly(indene carbonate) (PIC) with an increased T_g (up to 138 ^oC).[24] In this work, aromatic groups were first incorporated in the backbone of CO_2-based polycarbonates. Lu *et al.* used the chiral biphenol-linked dinuclear Co(III) complexes to catalyze the polymerization of 1,4-dihydronaphthalene oxide (CDO) and CO_2, and poly(1,4-dihydronaphthalene carbonate) (PCDC) with >98% enantioselectivity and high molecular weight (up to 40700 g/mol) were obtained. PCDC exhibited a very high T_g (up to 150 ^oC).[25,26] Except for petroleum-based polycarbonates (PIC and PCDC), the biorenewable poly(limonene-8,9-oxide carbonate) (PLOC), which was generated from limonene dioxide (LDO) and CO_2, also possesses a high T_g (up to 135 ^oC). Further modification of pendent alkene groups of PLOC through CO_2 insertion could further increase the T_g to 180 ^oC.[27,28]

Controlling the stereoregularity of CO_2-based polycarbonates could also improve their thermal properties. Many excellent works have been done by Lu, Coates, Nozaki *et al.* in this aspect.[25,26,29-32] Lu *et al.* developed the chiral dinuclear (salen)Co(III) catalysts to achieve high enantioselectivity (90–98% ee) and precise molecular weight control for cyclohexene oxide (CHO) and CO_2 polymerization under mild reaction conditions. Thus, a series of highly enantio-pure alicyclic polycarbonates were obtained. (*R*,*R*)- and (*S*,*S*)-configured isotactic polycarbonates could form crystalline stereocomplexes, resulting in a significant improvement in their thermal properties. For example, the equal amounts of (*S*,*S*)- and (*R*,*R*)-PCDC mixed together could generate a crystalline stereocomplex with a very high melting temperature (T_m up to 373 ^oC).[25] Coates *et al.* also reported the chiral ZnBDI catalysts, which were used to synthesize highly isotactic poly(cyclohexene carbonate) (PCHC) (M_n = 11 kDa, >99% ee) with high T_m values (up to 267 ^oC).[31]

As aforementioned, traditional PPC has poor thermal properties. However, Nozaki *et al.* prepared a stereo-gradient PPC, which has a higher decomposition temperature (T_d = 273 ^oC) than that of stereo-irregular one (T_d ~ 240 ^oC).[32] Zhang, Lu, Lee, Darensbourg *et al.* also reported multi-block copolymers with improved thermal performance generated from multi-component polymerizations.[33-38] Lee *et al.* reported a three-component polymerization of CO_2, PO, and various epoxides such as CHO, 1-hexene oxide (HO), or 1-butene oxide (BO) in the presence of (salen)Co(III) catalysts tethered by four quaternary ammonium salts. The initial decomposition temperatures of resultant terpolymers are increased above 200 ^oC.[33] Lu *et al.* used enantio-pure biphenyl-linked dinuclear Co(III) complexes to catalyze three-component polymerization of CO_2, CHO, and β-butyrolactone (BBL). The ratio of carbonate and ester units in the resultant polymers could be controlled by changing CHO and BBL feed ratio, or altering CO_2 pressure, which could affect the relative rate between BBL ring-opening polymerization and CO_2/CHO copolymerization. The produced terpolymers show optically active with a mixed T_g and a high T_m with values higher than 200 °C.[34] They also reported a binary catalyst system consisting of SalcyCo(III)OTs (Salcy = N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-diamino-cyclohexane; OTs = *p*-toluenesulfonate) and 7-methyl-1,5,7-triazabicyclo [4.4.0]dec-5-ene (MTBD) to synthesize statistical terpolymers with a single T_g via a one-pot three-component polymerization of *β*-propiolactone (BPL), epoxides, and CO_2. This is the first example of a statistical carbonate and ester terpolymer in which the two components are distributed in the polymeric backbone based on probability.[35] Williams *et al.* synthesized a series of poly(cyclohexene carbonate-*b*-decalactone-*b*-cyclohexene carbonate) [PCHC-PDL-PCHC] by using a highly active organometallic hetero-dinuclear Zn(II)/Mg(II) catalyst.[39] The new Zn(II)/Mg(II) organometallic catalyst could avoid the use of cocatalyst and achieve high selectivity of the reaction in a very low monomer concentration. It is also highly switchable between CO_2 and epoxide ring-opening copolymerization (ROCOP) and lactone ring opening polymerization (ROP) cycles, furnishing a one-pot route toward precise poly(ester-b-carbonates). They also obtained CO_2-based copolymers with high molecular weights (up to 40000 g/mol) and multiple composition ratio. When the content of PCHC is 50%, the resultant copolymer is a toughened plastic with a high modulus (up to 238 MPa) and a breaking elongation of 900%, far exceeding the existing CO_2-based polycarbonate (less than 2%). When the PCHC content decreased to 28%, the obtained copolymer is an elastomer, because the mechanical properties show typical rubbery polymer behavior. Interestingly, when the PCHC content further reduced to 20%, the obtained copolymer could be used as adhesives. Williams *et al.* also performed a three-component polymerization of CO_2 and commercial bio-based monomers of limonene oxide (from waste citrus fruit peel), and ε-decalactone (from triglycerides) towards ABA triblock polymers. The terpolymers show 20 time increase in elongation at break, retain good tensile strength and are 20 time tougher than poly(limonene carbonate) (PLC). They show a processing temperature window of higher than 140 ℃ and could produce optically transparent toughened plastic films.[40] Recently, Williams *et al.* also reported a trinuclear dizinc-(II)sodium(I) catalyst without additives or cocatalysts. It is easily switched between three different catalytic cycles (ROP of CHO, ROCOP of CO_2 and CHO, and ROCOP of CHO and phthalic anhydride), thus allowing precise control of CO_2 incorporation within polyesters and polyethers.[41] Furthermore, they used the highly active and selective catalyst, Mg(II)Co(II), for the three-component polymerization of tricyclic anhydride, CHO and CO_2 toward precise triblock (ABA), pentablock (BABAB) and heptablock (ABABABA) polymers (where A = poly(cyclohexylene oxide-alt-tricyclic anhydride), PE; B = poly(cyclohexene carbonate), PCHC). They also carried out a four-component polymerization of anhydride, CO_2, CHO and ε-caprolactone toward a CBABC pentablock copolymer (A = PE, B = PCHC, C = poly(caprolactone), PCL).[42]

CO_2-based amphiphilic polycarbonates

Besides improving thermal performance, CO_2-based polymerization could also produce amphiphilic polycarbonates with versatile properties for biological imaging, therapy, and lithium ion battery applications. Generally, several steps were needed to prepare amphiphilic polycarbonates (Figure 4A). First, the copolymerization of PO and CO_2 was allowed to react for sufficient time to ensure complete conversion of PO before another functional epoxy monomer was added. Subsequently, after careful release of CO_2, the second epoxy monomer was added into the reactor followed by recharging with CO_2. The block copolymers were thus synthesized by a "one pot, two step" strategy by sequentially adding different monomers. Then, the deprotection of *tert*-butyl ester or thiol-ene click reaction was carried out for the introduction of carboxyl groups to the side chains of block copolymer, thus furnishing the amphiphilic polycarbonates. Because of the biocompatibility of these amphiphilic polycarbonates, the conjugates of them and some drugs (paclitaxel and platinum) or contrast medium (gadolinium) could be applied for biological imaging and therapy.

Grinstaff *et al.* reported the paclitaxel (PTX)-poly(1,2-glycerol carbonate) (PGC) conjugates with high and controlled drug loadings (up to 74 wt%).[43] They evaluated the efficacy of PGC–PTX NPs as a single dose in murine models of peritoneal mesothelioma (Figure 4B). Mice received an intraperitoneal (IP) injection of either rhodamine (Figure 4B, I) or PGC–PTX-Rho NPs (Figure 4B, II) in saline three weeks after IP tumor inoculation. Three days after injection, animals were euthanized, and the peritoneum was assessed under ambient and ultraviolet (UV) light. The results indicated that PGC–PTX-Rho NPs preferentially localized to IP tumors. Subsequent *in vivo* studies showed that a single dose of PGC-PTX NPs could achieve comparable curative effect to seven weekly doses of standard PTX, which holds potential to become an ideal replacement for current chemotherapeutic drugs. Lu *et al.* prepared the gadolinium (Gd^{3+})-polycarbonate conjugates and applied in tumor imaging.[44] Much higher magnetic resonance imaging (MRI) signal could be obtained in tumor regions than a simple chelated Gd^{3+} complex because of the enhanced permeability and retention effect of cancer cells. In addition, these conjugates could be cleared from the body in a short time due to their biodegradability property. Darensbourg *et al.* also reported the water-soluble platinum-polycarbonate conjugates with platinum loading of 21.3-29.5 wt%, which may serve as platinum drug delivery carriers.[45]

Amphiphilic polycarbonates were also made into polymeric electrolyte materials for lithium-ion battery applications. Aliphatic polycarbonates have low T_g values and contain a large fraction of polar carbonyl groups, which are favorable for ion transport and offer a high solvation power towards numerous salts, respectively. Notably, they are more stable and safer than conventional liquid electrolytes.[46] Thus, various CO_2-based polycarbonates have been fabricated into both solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs). SPEs include a blend of one or more polymers wherein a lithium salt is dispersed. Grinstaff *et al.* reported a SPE which contains poly(*n*-butylglycidyl ether carbonate) and 65 wt% LiTFSI (lithium bis(trifluoromethane sulphonyl) imide). It showed enhanced ionic conductivities in the order of 10^{-5} S cm^{-1} at 25 ℃ and 10^{-3} S cm^{-1} at 120 ℃, which are comparable with the typical ionic conductivities for liquid electrolyte lithium-ion batteries.[47] Tominaga *et al.* found that the addition of TiO_2 nanoparticles to a poly(ethylene carbonate) electrolyte with LiFSI salt could increase the lithium transference number and ionic conductivity upon addition of only 1 wt% TiO_2.[48] Tominaga *et al.* also increased the ether linkages in the polymer backbone to make aliphatic polycarbonates have a lower T_g, which furnished a poly(ethylene carbonate/ethylene oxide)/LiFSI electrolyte with an increased ionic conductivity in the order of 10^{-4} S cm^{-1} at 60 ℃ and an increased lithium transference number of 0.66.[49] Besides SPEs, CO_2-based polycarbonates have also been studied as components of GPEs. A three-component polymerization of CO_2, propylene oxide, and maleic anhydride could readily produce poly(propylene carbonate maleate) (PPCMA), which are easily crosslinked with dicumyl peroxide (DCP) as radical initiator. Then, the materials could be fabricated as a GPE for lithium-ion battery. The ionic conductivity of the PPCMA GPE with 1.2 wt% of DCP reaches the maximum value of 8.43×10^{3} S cm^{-1} at room temperature and 1.42×10^{-2} S cm^{-1} at 50 ^{o}C, which are only slightly lower than that of commercial fully liquid electrolyte batteries.[50] Wu *et al.* introduced PPC into gel polymer electrolytes based on poly(vinylidene fluoride) (PVdF).[51] PVdF/PPC electrolytes exhibited higher ionic conductivity than that of pure PVdF electrolytes, because the presence of amorphous PPC could reduce the crystallinity of PVdF. Meng *et al.* reported single-ion-conducting polyelectrolytes via a multi-component polymerization of PO, allyl glycidyl ether (AGE), and CO_2.[52] The grafting of 3-mercaptopropionic acid (MPA) to the pendant alkene groups via thiol-ene click reaction and subsequently lithiation afforded a poly(lithium carboxylate) with 41.0 mol% lithium content. This polyelectrolyte exhibited a high Li transference number of 0.86 and a high ionic conductivity of 1.61×10^{-4} S/cm at 80 ^{o}C (Figure 4C).

CO_2-based polycarbonates for 3D scaffolds

PPC is a kind of biodegradable aliphatic polyesters, synthesized via the polymerization of CO_2 and PO. They also have good biocompatibility, noncytotoxicity, and noninflammatory properties. Therefore, PCC and PCC-X composites are very suitable for native tissue regeneration because they can mimic the natural morphology of the extracellular matrix (ECM) that surrounds cells.[53] Srinivasan *et al.* prepared ultrathin fibers of PPC via optimization of process parameters in electrospinning process. The obtained electrospun fibers of PPC were found to exhibit good thermal stability and tensile strength and support the adhesion of mouse NIH 3T3 fibroblasts. Thus, the polymers showed great potential to be used as a 3D scaffold for tissue engineering.[54] Peng *et al.* prepared parallel-aligned PPC microfibers with a fiber diameter of 1.48 ± 0.42 μm by electrospinning and modified by oxygen plasma treatment. Because chitosan is a cationic polysaccharide with good biodegradability, cell adhesion, and biocompatibility, they then introduced chitosan nanofibers into the PPC fiber mats by freeze drying. They found that Young's modulus experienced a 26% improvement after the introduction of chitosan nanofibers.[55]

Gelatin is another natural polymer which can be blend with PPC to prepare scaffold by electrospinning process. Peng *et al.* carried out cell-culture experiments and found that the PPC/gelatin scaffolds had favorable interactions with fibroblast cells. They also found that the addition of HAc in the PPC solution did not negatively influence the growth and proliferation of cells. Thus, these PPC/gelatin scaffolds have great potential in vascular scaffolds, bone tissue, and nerve tissue engineering.[56] Fu *et al.*

synthesized biodegradable PPC foams with controlled morphology via the saturation of a PPC/graphene oxide (GO) nanocomposite using supercritical carbon dioxide (scCO_2) technology. Then the 3D tissue engineering scaffold was prepared by supercritical drying process. The cytotoxicity test and cell culture tests revealed that the PPC/GO foams were biocompatible and noncytotoxic.[57] Dehghani *et al.* reported a melt blended PPC/starch composites for biomedical applications. The long-term biodegradation behavior of PPC-starch composites showed that they were well-tolerated *in vivo* as the inflammation of foreign body diminished within 2-4 weeks post-implantation. The PPC/starch (50/50 wt%) composites also have enhanced mechanical properties, showing a 170-fold increase in the compression strength compared with neat PPC. This property could extend the PPC/starch composites applications from soft tissue regeneration to hard musculoskeletal tissue repair.[58,59] In their further works, a new and efficient blending method for generating the polymer-ceramic composites utilizing PPC, starch, plasticizer agents, and bioglass was reported.[60] The increased mechanical strength and reduced wettability of the composites are desirable properties for biomedical applications. They were made into screws which were further tested in subcutaneous and bone implantation models. The results showed that these composites were well tolerated in mice for up to 6 months and with a faster degradation rate than polylactic acid (PLA) and a greater capacity for bone ingrowth.

CO_2-based recyclable polycarbonates via ring-closure depolymerization mechanism

The research on chemically recyclable polymers has become a very hot topic nowadays. They represented a kind of novel polymers, which could be depolymerized under specific conditions back to their monomers. This strategy is hopeful to address the end-of-life issue of synthetic polymers.[61,62]

Darensbourg *et al.* systematically investigated the depolymerization of various CO_2-based polycarbonates for the first time.[63,64] Generally, only cyclic carbonates could be formed from CO_2-based polycarbonates through backbiting mechanisms, because the free energy barriers of the depolymerization of polycarbonates to their corresponding epoxy monomers (12.7-17.4 kcal mol^{-1}) were always higher than the process to generate cyclic carbonates (10.7-14.6 kcal mol^{-1}).[63] However, the depolymerization of poly(cyclopentene carbonate) shows a different tendency. Darensbourg *et al.* found that both cyclopentene oxides and cyclopentene carbonates could be formed during the depolymerization of a hydroxyl-terminated poly(cyclopentene carbonate) in toluene in the presence of sodium bis(trimethylsilyl)amide. Because CO_2 is a product of the depolymerization, the depolymerization rates and the ratio of degradation products could be significantly controlled via changing the pressure of added CO_2. When the depolymerization of poly(cyclopentene carbonate) was carried out in the presence of high pressure of added CO_2, the rate of the reaction was greatly inhibited and the only product was cyclopentene carbonate. On the contrary, performing the depolymerization at reduced pressure led to faster degradation and enhanced cyclopentene oxide production.[64]

In 2017, Lu *et al.* reported a novel degradable polycarbonate, which was synthesized by the polymerization of 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine (BEP), and CO_2 at 60 ^{o}C. Upon heating the resultant polycarbonate at 100 ^{o}C, it rapidly depolymerized into the starting epoxy monomers in a quantitative yield (Figure 5A). This polymerization-depolymerization loop could be repeated several times without any change in the structures of the monomer and polymer.[65] They also found that if the catalyst was removed, the polycarbonate was stable at 200 ^{o}C and the depolymerization toward the epoxy monomer could only happen at a much higher temperature of 260 ^{o}C. Coincidentally, Sablong *et al.* also reported that a bio-based poly(limonene carbonate) could be depolymerized to the corresponding limonene oxide monomer in a quantitative yield in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Figure 5B).[66]

Five-membered cyclic carbonate (5CC)-based polymers for foams, adhesives, coatings and 3D printing

Five-membered cyclic carbonates (5CCs), generally derived from CO_2 and epoxides, are a kind of important chemical products. They could react with amines, so the bis-5CCs could be regarded as the monomers for the polymerization with diamines to yield polyhydroxyurethanes (PHUs) (Figure 3C).[67,68] Notably, this is an isocyanate-free route to polyurethanes. PHUs have many hydroxyl groups in the side chains, which are absent in classical polyurethanes, which greatly enrich their properties.

PHUs could be used as foams generated via physically blown, chemically blown or self-blown. A commercial hydrofluorocarbon (Solkane) was used as physical blowing agent to fabricate PHU foams with densities lower than 0.22 kg m^{-3}. The PHU were prepared by the polymerization of diamine and tris-5CC at 80 ^{o}C for 14 h, followed by heating at 100 ^{o}C for 4 h to obtain full conversion of the carbonate groups.[69] ScCO$_2$ was also used for foam preparation. A thermoplastic PHU was impregnated with scCO$_2$ at 100-300 bar, followed by cooling, depressurization and heating above 80 ^{o}C to produce foams.[70] Poly(methylhydrogenosiloxane) (MH 15) was used as a chemical blowing agent for the formation of PHU foams in the presence of a thiourea. MH 15 reacted concurrently with the diamines to release hydrogen gas, which is used for the formation of foams.[71,72] Self-blown could happen via the polymerization of cadaverine and sorbitan biscarbonate. The bubbles were attributed to a side-reaction in which cyclization of the obtained nucleophilic primary hydroxy groups yielded an isosorbide structure and CO$_2$.[73] Self-blown PHU foams could also be generated by exploiting chemo- and regio-selective additions of amines and thiols to 5CCs. Decarboxylation is a key process for generation of the blowing agent (CO$_2$).[74]

PHUs could be used as excellent adhesives, due to the abundance of hydrogen bonding moieties in the PHU chains.[75] PHU adhesives could be divided into the following types of solvent-free, hot-melt, PHU−epoxy hybrid, PHU−siloxane hybrid, and PHU−inorganics hybrid adhesives, etc. Caillol *et al.* first reported the solvent-free adhesive properties of isocyanate-free PHUs.[76] They showed excellent adhesive properties on glass substrates. The experimental results showed that the shear force to peel the PHUs from glass was higher than that to break the glass owing to the hydrogen bonding interaction between Si-O groups of glass and hydroxyl groups of the hydroxyurethane moieties. Tryznowski *et al.* reported hot-melt PHU adhesives for wood joints. The thermoplastic PHU was heated at elevated temperature, followed by cooling to solidify the adhesive, giving a high adhesion values up to 3.19 MPa.[77] Lambeth *et al.* fabricated PHU-epoxy hybrid adhesives. The epoxy and hydroxyurethane moieties operated in synergy to create high performance adhesives with a maximum lap-shear adhesion value of 27 MPa that is ~1.7 or ~1.3 higher than pure epoxy or PHU formulations, respectively.[78] Sardon et al. reported monocomponent non-isocyanate polyurethanes adhesives, which were synthesized by adding (3-aminopropyl)triethoxysilane to a PHU prepolymer based on five-membered cyclic carbonates and Priamine 1074. Interestingly, the curing process could be proceeded under ambient conditions through a sol–gel process.[79] Detrembleur *et al.* found that the PHUs containing 5 wt% ZnO nanofiller displayed a lap-shear strength of 16.3 ± 1.4 MPa, which is 145 % higher than that of corresponding polymer without nanofiller.[80]

Besides foams and adhesives, PHUs are also widely used as coatings. Lower viscosity is required for the coating, because they need to form a homogeneous thin film on large 2D or 3D substrates. PHU based coatings could be the solvent-free, solvent-based, water-borne, radiation-curable, and PHU−X hybrid ones. The solvent-free PHU coatings have high viscosity which limits their applications, so solvent-based or water-borne coatings are preferred. Kathalewar *et al.* investigated the structure-properties relationship of various solvent-based PHU coatings made from bis(cyclic carbonate)s and diamines, *i.e.* hexamethylene (HMDA) or isophorone diamine (IPDA). They found that the abrasion resistance increased with enhancing the content of HMDA. The PHU coatings show better adhesive strength, comparable mechanical properties, and improved chemical resistance compared with those of epoxy analogues owing to the presence of the hydroxyl groups in the polymers which increase the coating and substrate and the interchain interactions by hydrogen bonding.[81] Water-borne PHU coatings are more environmentally friendly, avoiding the use of organic solvents, but they are harder to prepare due to their poor dispersion in water. Some new strategies have emerged to synthesize water-borne PHU coatings in the past few years. For examples, Wu *et al.* synthesized a series of carboxylic acid-functional poly(cyclic carbonate)s by the reaction of dianhydrides with glycerol carbonates. Then water dispersible precursors were furnished upon neutralization with 2-dimethylaminoethanol or trimethylamine. The following thermal curing process with aliphatic diamines at 90−120 °C provided PHU coatings on glass and tin substrates. The resultant coatings displayed high gloss and excellent chemical resistance.[82] Fan *et al.* first prepared PHUs oligomers (M_n up to ~5000 g/mol), post-modification of them readily produced polyelectrolytes. After curing from room temperature to 120 ^oC, the PHUs coatings, constructed by mixing aqueous solution of polyelectrolytes was mixed with a water emulsion and suspension of epoxy hardeners and depositing on glass or Al substrates, with high pencil hardness (up to 4 H), adhesive force (up to grade 1) were obtained.[83] Besides thermal curing, PHU coating could be cured by ultraviolet or visible light. Zhu *et al.* reported that the light activated cross-linking process of methacrylic-functional oligo(ester-urethane)s with

2,2-dimethoxy-2-phenylacetophenone occurred on tin plates at room temperature. Then the PHU coatings with good to excellent adhesion were obtained.[84] Soucek *et al.* also designed a PHU coating via mixing UV curable α,ω-acrylated polyesters with reactive bismethacrylate urethane, showing very high hardness.[85]

Hybrid PHU coatings were widely studied to meet various special performance, such as abrasion resistance, anticorrosion, flame retardancy, or antimicrobial/bacterial/fungal properties. The typical examples are given below. Zhou *et al.* reported the anti-corrosion coatings which were prepared by the amine-terminated PHU, tetraethyl orthosilicate (TEOS), and BPA-based epoxy. The anti-corrosion performance of these hybrid coatings was evaluated by electrochemical impedance spectroscopy and salt spray. The resistance of coated steel surfaces to corrosion following immersion in saline medium for 55 days was highest at a TEOS content of 5 wt%.[86] Gharibi *et al.* reported the anti-microbial coatings obtained through sol-gel hydrolysis and condensation reaction of soybean oil derived reactants. The presence of quaternary ammonium salt moieties with hydrophobic fatty ester residue at a proper concentration in coatings formulations led to excellent anti-bacterial activity against Gram-positive and Gram-negative bacteria as well as a fungal strain.[87] Farid *et al.* used sunflower oil and CO_2 to prepare PHU coatings. They found that the incorporation of $ZrO_2@SiO_2$ NPs showed significant improvement for the PHU coatings in the thermal stability and flame retardancy characters.[88] Some other hybrid PHUs have also been prepared by combining $Al(OH)_3$, multiwalled carbon nanotubes (MWCNTs), ZnO, polyhedral oligomeric silsesquioxane materials

(POSS), etc.[75]

PHUs were also used in 3D printing. Schimpf *et al.* reported semicrystalline PHUs thermoplastics which were synthesized by melt-phase polyaddition of the difunctional cyclic carbonates and 1,12-diaminododecane. They were further employed in extrusion-based additive manufacturing by means of fused deposition modeling or fused filament fabrication. Hydroxyl groups presented in PHUs imply strong hydrogen bonding, which is beneficial with respect to the 3D printing technique.[89]

5CC-based polymers for luminescent materials

In the past few years, many types of non-conjugated luminescent polymers (NCLPs) obtained from non-luminescent monomers have sprung up and gradually become a new class of materials with specific structures and emission mechanisms.[90] Zhang *et al.* reported a siloxane containing CO_2-based PHU, which exhibited strong fluorescence in solid state with high photostability, broad absorption and emission, and excitation-dependent characteristics, while the low mass hydroxyurethane with carbamate and hydroxyl groups showed almost no luminescence.[91] This result indicates that the polymerization can greatly enhance the carbonyl interactions, further enhancing the fluorescence intensity of PHU. When the hydroxyl group in the side chain of PHU was mostly protected, the fluorescence intensity decreased significantly, indicating that hydrogen bonding is very important to shorten the distances between carbonyl groups and induce n–π* transitions between oxygen atoms and carbonyl groups. After figuring out the mechanism of luminescence, they applied these unorthodox luminescent polymers in many areas.[92-96] For example, they fabricated a pure white LED via solely using the fluorescein-centered polymer phosphores excited by a blue LED chip.[92] They also synthesized carbonized polymer dots (CPDs) from CO_2 (Figure 6). The prepared CPDs showed quantum yields of 11.3 % in the solid state, which could be appropriately applied as light-emitting diode (LED) convertors to produce multicolor LEDs by varying the chip type and CPD content, providing a new pathway toward low-cost and high-performance multicolor LEDs.[93] They also evaluated the biocompatibility of a fluorescent PHU that could be applied in selective iron detection with a detection limit of 4.56 μM. They also applied PHU in methylthiazolyldiphenyl-tetrazolium, cytokine release, and hemolysis assays. The results showed that the PHU has much lower cytotoxicity and immunotoxicity than the traditional isocyanate PU, and a good blood compatibility with less than 5% hemolysis rate.[96] Therefore, the PHU showed great potential to be prospectively applied as medical materials. Moreover, Thomas *et al.* reported that non-isocyanate polyurethane nanocapsules could provide a site-specific delivery vehicle and improve the therapeutic efficacy of a drug or be used to produce organelle-specific imaging studies.[97]

OLEFINS-BASED POLYMERS

Olefins as the large-scale industrial chemical products have been converted into high-performance polymeric materials, such as polyethylene and polypropylene. The polymerization of the olefins with CO_2 in an alternating fashion is regarded as the most popular route toward CO_2-sourced polyesters, which possess both high performance and degradability. In 2006, Miller *et al*. studied the thermodynamics and kinetics of the polymerization of CO_2 and the olefins. Computational studies predicted that a perfect alternating ethylene/CO_2 polymerization is endothermic by 9.4 kcal mol^{-1}. Kinetically, the high activation energy for CO_2 insertion within the growing chain competes with the facile homo-polymerization of ethylene. Thus, the ethylene/CO_2 polymerization is difficult to achieve.[98]

Compared with ethylene, butadiene has relatively higher reactivity. In 1978, Musco *et al.* found that CO_2 can react with butadiene in bulk or in benzene to produce six-membered ring lactone of 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVL), which has rich chemical reactivity.[99] However, EVL monomer for free radical polymerization was still an unsolved problem until 2014, when Nozaki *et al.* obtained the polymers with high molecular weights via the free radical polymerization of it (Figure 7A).[100] When the traditional azobisisobutyronitrile (AIBN) initiated the polymerization, the yields and molecular weights of the products were both very low. However, when 1,1'-azobis(cyanocyclohexane) with a longer half-life was used as an initiator, the yields and molecular weights of the products improved significantly. The authors also explored the influence of the solvent and Lewis acid on the polymerization, and it is found that when zinc chloride was used as Lewis acid and ethylene carbonate as the solvent, the yield can be increased to 59%, and the number-average molecular weight (M_n) of the resultant polymer could increase to 62000. Moreover, the "one-pot, two-step" tandem polymerization could be performed without separation and purification, realizing the indirect polymerization of CO_2 and butadiene. In addition, through the introduction of the third component of isoprene or

1,3-pentadiene, the authors also realized a three-component polymerization. Through the differential scanning calorimetry (DSC) characterization, the authors found that the prepared CO_2-based polymer has T_g as high as 192 ^{o}C, holding great potential in applications as engineering plastics. Lin *et al.* found that the polymerization of EVL can be realized upon simply heating in the presence of O_2 without any additive and solvent.[101] The polymers with M_n values up to 239000 and quantitative monomer conversions were obtained in 24 h. The resultant polymers can be easily functionalized using thiol-ene click reaction by taking advantage of the abundant C=C bonds in the polymer chains. Ni *et al.* reported a highly reactive trivinyl monomer derived from CO_2 and butadiene, *i.e.* methyl-2-ethylidene-5-hydroxyhept-6-enoate methacrylate (MEDMA), which was synthesized via ring cleavage of EVL and subsequent esterification with methacryloyl chloride. Chemoselective reversible addition-fragmentation chain transfer (RAFT) polymerization of MEDMA catalyzed by 2-cyanoprop-2-yl-dithiobenzoate (CPDB) was achieved and well-defined polymers were obtained under optimized conditions (Figure 7B).[102] Functional groups like amino and carboxyl groups could be introduced to the resultant polymers through thiol-ene click reaction. The NH_2-modified polymers could self-assemble into micelles and showed topology-dependent self-assembly behaviors. Jian *et al.* also reported almost the same CO_2-based trivinyl monomer and performed its polymerization with ethylene in the presence of palladium complex (Figure 7C). Notable, this polymerization is chemoselective (reactive acrylate and allyl ester, inert 1,2-disubstituted acrylate), regioselective (five-membered γ-butyrolactone and six-membered δ-valerolactone) and stereoselective (different diastereomers in five-membered γ-butyrolactone).[103] The resultant polyethylenes have noncyclic and cyclic ester units and readily modified pendant double bonds, providing a possibility to access various functional polymeric materials. Other monomers containing both vinyl and epoxy groups could also be used to generate CO_2-based polymers via the free radical polymerization, which could be applied as chemosensors.[104,105]

TRIPLE-BOND MONOMER-BASED POLYMERS

Triple-bond monomers include alkyne, cyanide, and isocyanide, etc. Compared with vinyl monomers, triple-bond monomers possess much more abundant chemical properties.[106] Tremendous organic reactions based on CO_2 and triple-bond compounds have been reported,[2] but only few polymerizations were explored. Lu *et al.* achieved indirect polymerization of CO_2 and 2-butyne via α-methylene-β-butyrolactone ($M_\beta BL$) intermediate. $M_\beta BL$ was synthesized via four-step reactions. Subsequent ring-opening polymerization of $M_\beta BL$ by achiral Salen aluminum complexes afforded syndiotactic enriched polyesters with controllable molecular weights and narrow polydispersity (Figure 8A).[107] They then investigated thermal properties of the resultant polyesters. The syndiotactic-enriched polyesters show high melting points (T_m, up to 109.2 ^oC) when the syndiotacticity is 0.79. Thermogravimetric analysis (TGA) revealed the onset degradation temperature (T_d) was 276 ^oC and the relative derivative thermogravimetry (DTG) curve showed the maximum degradation temperature was 295 ^oC for the isotactic polyesters, indicative of its high thermal stability. The wide-angle X-ray diffraction (WAXD) profiles indicated that the resultant polyesters were semicrystalline. Lu *et al.* further polymerized $M_{\beta}BL$ with different lactones, and diblock polyesters consisting of semicrystalline and amorphous segments were yielded. Moreover, the vinylidene groups in the resultant copolymers facilitated the post-modification through radical-initiated crosslinking reactions and thiol-ene click reaction, producing functionalized and cross-linking polymers with enhanced thermal property.[108] Lu *et al.* also used NaI as the initiator to prepare crystalline circular polymers.[109]

Besides the indirect polymerization of CO_2 and alkynes, Qin and Tang *et al.* developed a series of new multi-component polymerizations based on CO_2 and triple-bond monomers toward various functional polymers in recent years.[110-118] In 2018, they reported a facile and efficient three-component polymerization of CO_2, diynes, and alkyl dihalides under mild reaction conditions (Figure 8B).[111] After screening various catalysts, Ag_2WO_4 was proved to be the best one for this polymerization because of the excellent coordination of silver ions with ethynyl groups and the high charge density of the $[WO_4]^{2-}$ to activate CO_2 by forming the $[WO4]^{2-}/CO_2$ adducts. Under optimized conditions, *i.e.* in *N*,*N*-dimethylacetamide (DMAc) at 80 °C under CO_2 (balloon) for 12 h in the presence of Ag_2WO_4 and Cs_2CO_3, soluble and thermally stable poly(alkynoate)s with high weight-average molecular weights (M_w up to 31400) were obtained in high yields (up to 95%). A triphenylamine (TPA)-containing ethynyl-terminated telechelic polymer could also be produced and used as the macromonomer to prepare poly(alkynoate)s with higher molecular weights by either continually adding alkyl dihalides into the reaction solution or mixing the isolated telechelic polymers with alkyl dihalide and catalytic system under a CO_2 atmosphere.

Thanks to the robustness and function group tolerance of the polymerization, functional groups, such as the tetraphenylethylene (TPE), silole, and tetraphenylpyrazine (TPP) moieties featuring aggregation-induced emission (AIE) characteristics could be facilely incorporated into the polymer chains. AIE, conceptually coined by Tang *et al.* in 2001, refers to a unique phenomenon that a kind of luminogens are non- or weakly emissive when molecularly dissolved but induced to emit intensely upon aggregation.[119-121] The photophysical properties studies of resultant poly(alkynoate)s revealed that they also showed typical AIE feature. Notably, the absolute fluorescence quantum yields of the AIE-active poly(alkynoate)s are up to 61%, which is much higher than that of reported AIE polymers.[122-124]

Based on above-mentioned works, Qin and Tang *et al.* developed a facile and efficient one-pot, two-step, four-component tandem polymerization of CO_2, diynes, alkyl dihalides, and primary/secondary amines (Figure 8C).[112] Regioregular and tunable stereoregular poly(aminoacrylate)s were generated in high yields. Interestingly, the reaction with primary or secondary amines could result in distinctly different stereoregularity of resultant poly(aminoacrylate)s. Using primary amines as monomers could generate polymers with 100% *Z*-isomeric units, whereas the secondary amines furnished polymers with over 95% *E*-isomeric units. They further use versatile monomer combination such as "$A_2+B_2+CO_2+C_1$", "$A_2+B_1+CO_2+C_2$", and "$A_1+B_2+CO_2+C_2$" to produce polymers with tunable structures and properties, where, A, B, and C represent alkyne, bromoalkyl, and amino monomers, respectively. Similar with above work, TPE could be incorporated into the polymer skeletons to generate poly(aminoacrylate) with AIE features. Thanks to its electronic-rich properties and excellent fluorescent behaviors in the aggregate state, the AIE-active poly(aminoacrylate) could be used as a chemosensor for explosive detection. The nanoaggregates of the poly(aminoacrylate) in THF/water mixtures were regarded as the probe with the commercially available picric acid (PA) as a model explosive. With gradual addition of PA into the nanoaggregates of the poly(aminoacrylate), the PL intensity of this AIE probe progressively decreased. The quenching constant was deduced from the Stern-Volmer plots to be 1.45×10^4 L/mol in the PA concentration range of 0-140 μmol/L and the limit of detection (LOD) was thus calculated to be 5.5×10^{-6} mol/L.

Besides linear polymers, developing CO_2-based hyperbranched polymers is of great significance because they could not only increase the incorporation content of CO_2 into polymers, but also generate advanced architectures and unique properties. Qin and Tang *et al.* designed and synthesized tri/tetrayne monomers for the polymerization with CO_2 and alkyl dihalides toward hyperbranched poly(alkynoate)s (*hb*-PAs).[113,114] The resultant *hb*-PAs possess two types of ethynyl groups in their branched chains and on their peripheries, which show different reactivities, thus, they could undergo site-selective, three-step functionalizations with nearly 100% conversion in each step. In the first step, the alkynoate groups could react with primary amines via a catalyst-free amino-yne click reaction to selectively convert them into aminoacrylate groups, while the terminal ethynyl groups remain intact. In the second step, the terminal ethynyl groups of *hb*-PAs could be easily converted to reactive alkynoate groups by the post-reaction of CO_2 and alkyl halides under the same reaction conditions as the polymerization. In the third step, the newly formed alkynoate groups on the peripheries of *hb*-PAs could further react with secondary amines under the catalyst-free conditions. Thus, sequence-controlled poly(aminoacrylate)s were successfully obtained via the site-selective three-step functionalizations of *hb*-PAs.

CO_2-based *hb*-PAs could serve as the platform polymers for diverse functionalizations. Qin and Tang *et al.* synthesized an amphiphilic polymer *hb*-P**1** from CO_2, triyne, alkyl dihalide, hydrophobic 1-butyl iodide, and hydrophilic, bromo-terminated poly(ethylene glycol) (mPEG-Br) via a one-pot, three-step, five-component tandem polymerization. Then, DOX, which contains an aliphatic amino group, was chosen as an anti-cancer drug to react with *hb*-P**1** toward polyprodrug amphiphile *hb*-P**2-1**. Benzylamine was also reacted with *hb*-P**1** to produce *hb*-P**2-2** under the same conditions for comparison (Figure 9A). Both *hb*-P**2-1** and *hb*-P**2-2** could self-assemble in aqueous solutions and form nanoparticles (NPs) with diameters of 98 and 84 nm, respectively (Figure 9B-9D). Through the analysis of UV-vis spectrophotometry, it was concluded that *hb*-P**2-1** NPs possess high drug loading content (44.3 wt%). The amphiphilic polymer *hb*-P**2** contained bulky enamine groups that were acid sensitive and could be converted to amino and aldehyde/ketone groups under weak acidic conditions. The *in vitro* release of DOX from *hb*-P**2-1** NPs in phosphate buffered saline (PBS) indeed confirmed that DOX could slowly release about 78% at a pH value of 5.0 after dialysis for 150 h, which was very similar to lysosomal environment of the tumor cells. They then studied the *in vitro* cellular uptake and imaging of *hb*-P**2-1** and *hb*-P**2-2** NPs using confocal laser scanning microscopy (CLSM) and confirmed good specificity of both *hb*-P**2-1** and *hb*-P**2-2** NPs toward lysosomes. The *in vitro* cytotoxicity was then investigated. The *hb*-P**2-2** NPs as the control were almost nontoxic to HeLa cells at concentrations up to 100 μg mL^{-1}, while *hb*-P**2-1** NPs demonstrated dose-dependent cytotoxicity to HeLa cells. The IC_{50} value of 0.096 μg mL^{-1} was superior to that of free DOX (0.128 μg mL^{-1}). Moreover, they also introduced a commercial dye, Coumarin 343 (C343), to the triphenylamine (TPA) moiety-containing hb-PAs to construct artificial light-harvesting system with high energy transfer efficiency (up to 92%). Through the introduction of pyrene moiety to *hb*-PAs, white light-emitting polymers were also prepared with high absolute fluorescence quantum yield (up to 10.6%) and CIE chromaticity coordinates of (0.31, 0.32).

CO_2-based poly(alkynoate)s are an emerging kind of unsaturated polyester, which contains both ester and ethnynyl groups in the main chains. Qin and Tang *et al.* found that CO_2-based poly(alkynoate)s could be degraded with benzamidine via the addition-heterocyclization-cleavage reactions toward diols and high-value-added *N*-heterocyclic compounds.[115] This degradation is temperature-dependent. The pyrimidone derivative **1** were obtained at 110 ℃ (Figure 10A, path A) while imidazolone derivative **2** were obtained at 60 ℃ (Figure 10A, path B) or at room temperature upon addition of the Bu_3P catalyst (Figure 10A, path C). Since the degraded products possess the AIE feature and could be continuously precipitated during the degradation, the degradation process of the poly(alkynoate)s could be visualized under UV light with a thin-film of poly(alkynoate)s slowly immersed into the toluene solution containing benzamidine and Bu_3P at room temperature (Figure 10B). Kinetics investigations via *in situ* Fourier transform infrared (FT-IR) spectroscopy suggested that the molar ratio of benzamidine had almost no effect on the degradation rate at 110 ℃, but it exerted significant influence at 60 ℃ during the degradation. When Bu_3P was used as the catalyst, the degradation was greatly promoted. It only took 5 min for complete degradation at 110 ^{o}C with Bu_3P. They also employed density functional theory (DFT) to analyze the mechanism of different degradation paths. The path B was observed with lower energy barrier (40.6 kcal/mol) than that of path A (44.0 kcal/mol), but with a more unstable product than that of path A, which indicated that only path B could occur under low temperature. Meanwhile, path A is favored at high temperature with a more stable product.

Thanks to the fast Bu_3P-catalyzed degradation of CO_2-based poly(alkynoate)s at room temperature with a fluorescence color change, the degradation was proved to occur on the polymer thin films, which could be introduced into microcontact printing (μCP) to generate fluorescence patterns in micro-scale. The *N*-heterocyclic compounds **1** and **2** obtained from CO_2-based poly(alkynoate)s possess unique AIE features and could be applied in diverse areas. The antibacterial property investigation of pyrimidine derivative **1** showed that the growth of gram-positive bacterium

Staphylococcus aureus could be effectively inhibited with nearly 90% inhibition ratio. The imidazolone derivative **2** could be used for the detection of Au(III) ions, showing very high specificity and sensitivity. The quenching constant was deduced to be 218670 M^{-1} from the Stern-Volmer plot of the relative PL intensity (I_0/I) *versus* the concentration of Au^{3+} ($[Au^{3+}]$) and the LOD was thus calculated to be 6.5×10^{-7} M. Moreover, compound **2** could also selectively extract Au^{3+} under practical conditions in the presence of a high concentration of interference metal ions. The extraction capacity of degraded product **2** is 475 mg $\cdot Au^{3+}$/g, which is higher than traditional materials. The imidazolone derivative **2** was also easily protonated with fluorescence color and intensity change. Thus, it could serve as a chemosensor for sensitive and selective detection of ammonia and biogenic amines generated through the food spoilage process.

Besides the CO_2-based poly(alkynoate)s, Qin and Tang *et al.* developed $Pd(OAc)_2/LiO^tBu$-catalyzed one-pot, three-component polymerization of CO_2, bis(propargylic alcohol)s, and aryl dihalides under atmospheric pressure (Figure 8D).[116] It's a new and direct way to generate 5CC-based polymers with high M_w (up to 42500) in high yield (up to 96%) from CO_2. The DFT calculation and *in situ* FT-IR spectroscopy study indicated that there is synergistic reaction effect among CO_2, bis(propargylic alcohol)s, and aryl dihalides. Amines were introduced for the post-modification of resultant 5CC-based polymers via a catalyst-free regioselective ring-opening reaction. Thanks to the robustness and universality of this polymerization, the TPE unit could be facilely introduced into the polymer skeletons to generate AIE-active 5CC-based polymers. Optically active monomers could be used to synthesize chiral polymers. The circular dichroism (CD) spectra revealed that the polymers inherited the chiral properties from the monomers. Multi-functionalized propargylic alcohol monomers could also be designed and synthesized for the polymerization with CO_2 to construct hyperbranched 5CC-based polymers. An insoluble porous polymer was obtained with a Brunauer-Emmett-Teller (BET) surface area of 172 $m^2 g^{-1}$.

Bis(propargylic alcohol)s were also used to react with CO_2 toward bis-5CC monomers for further polymerization by Detrembleur *et al.* (Figure 8E).[125,126] They found these new bis-5CC monomers could react easily with the nucleophiles through a regioselective ring opening reaction. Using bis(primary amine)s as the comonomers could generate poly(β-hydroxy-2-oxazolidone)s via sequential ring opening and closing reactions, whereas the bis(secondary amine)s as the comonomers furnished poly(β-oxo-urethane)s with the regioselective ring opening reaction.[125] Subsequently, Detrembleur *et al.* found dithiols could also be used as the comonomers for the polymerization with the bis-5CC monomer. The poly(thioether-co-cyclic carbonate)s could be obtained when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) served as the catalyst. When they carried out the polymerizations in the presence of DBU along with the fluorinated alcohol 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (FA), the poly(monothiocarbonate)s were generated.[126] Moreover, they found that these unsaturated poly(oxazolidone)s present high T_g (90 ~ 130 ^{o}C) and T_d values (> 360 ^{o}C), showing great potential for applications under the conditions with high temperatures.[127,128] These novel CO_2-based polymers were also optimized as solid electrolytes for room temperature operating lithium batteries. The electrochemical performance of conventional poly(ethylene oxide) (PEO)-SPEs has been greatly improved by using these polymers.[129,130]

Compared with terminal alkyne monomers, internal alkyne monomers showed less reactivity with CO_2. Recently, Qin and Tang *el al.* successfully achieved the polymerization of CO_2 and internal alkyne monomers in the presence of CuI/7-methyl-1,5,7- triazabicyclo[4.4.0]dec-5-ene (MTBD) catalytic system (Figure 8F).[117] This one-pot MCTP that combines three sequential carboxylation-cyclization-esterification reactions could be facilely performed in DMAc under atmospheric pressure. The poly(β-alkoxyacrylate)s with good thermal stability, high decomposition temperatures, and high char yields were obtained in high yields (up to 96%). The products showed the polymerization-induced emission (PIE) effect, and the non-luminescent monomers could be directly converted into AIE-active poly(β-alkoxyacrylate)s through the polymerization. Meanwhile, Tsuda *et al.* also reported a polymerization of CO_2 and internal alkyne monomers toward poly(2-pyrones) (Figure 8G).[131] This polymerization was catalyzed by nickel(0) complexes in THF and MeCN mixed solvent. To prevent intramolecular cyclization reaction, the R^9 group in the diynes should be aromatic or aliphatic ones with more than 5 carbon atoms. Under the same conditions, CO_2 could also react with cyclodiyne monomer to generate ladder poly(2-pyrone) (Figure 8G). The resultant poly(2-pyrone) has excellent heat resistance, and the thermal decomposition temperature under nitrogen atmosphere is as high as 420 °C.

Isocyanide monomer is another kind of significant triple-bond monomers, which could also be used to generate novel CO_2-based polymers. Dong *et al.* developed a catalyst-free one-pot three-component polymerization of diisocyanides, ester activated alkynes, and CO_2, and spiropolymers with 1,6-dioxospiro[4,4]nonane-3,8-diene as the spirostructural unit in the main chains were yielded (Figure 8H).[132] The resultant spiropolymers showed excellent solubility and high thermal stability. Qin and Tang *et al.* also reported an efficient three-component polymerization of CO_2, diisocyanides, and bis(2-iodoaniline)s toward soluble and thermally stable poly(benzoyleneurea)s (Figure 8I).[118] The resultant polymers could self-assemble into spheres with sizes of 200-1000 nm owing to the hydrogen bonding interactions of the amide groups in main chains. Moreover, the TPE-containing polymers with AIE features could not only be used to visualize the self-assembly processes, but also act as fluorescent probes to selectively and sensitively detect Au(III) ions.

OTHER MONOMER-BASED POLYMERS

Besides aforementioned monomers of epoxides, olefins, alkynes and isocyanides, other monomers such as frustrated Lewis pair (FLP)-based monomers were also used to polymerize with CO_2, breaking the restrictions of known CO_2-based polymerizations.

FLP is a pair of bulky Lewis acid and base. Due to the large steric hindrance, classical Lewis adducts could not be formed, which have special reactivity. Stephan *et al.* have proved that FLPs can tightly bind CO_2 and form CO_2-bridged compounds.[7,133,134] Yan *et al.* designed and synthesized a self-complementary FLP monomer M**1**, in which one side is bulky triarylborane as the Lewis acidic group and the other is triarylphosphine as the Lewis basic moiety (Figure 11A). The spontaneous and catalyst-free polymerization of FLP monomer M**1** and CO_2 could be successfully carried out at ambient temperature (20 °C) and under low CO_2 pressure conditions (1.0 atm). A well-defined CO_2/FLP-based polymer with a high molecular weight (~50000) and a quantitative conversion (~95%) was obtained.[135] Interestingly, this CO_2/FLP-based polymer could be regarded as a new kind of chemically recyclable polymers. The depolymerization of them could happen at 70 °C, from which the original FLP monomer was gradually obtained. After undergoing five monomer-polymer-monomer cycles, the monomer conversions to reconstruct the polymer could still attain ~80%.

Yan *et al.* also designed and synthesized two olefins-based monomers with bulky substituent groups, 4-styryl-di(pentafluorophenyl)borane and 4-styryl-dimesitylphosphine, as the FLP acceptor and donor, respectively. RAFT polymerization was carried out to furnish two diblock polymers P**2** and P**3** consisting of the complementary FLP blocks and polystyrene block (Figure 11B).[136] Mixing equimolar amounts of P**2** and P**3** in toluene showed no significant reaction. When CO_2 gas was passed through the mixture, a rapid binding reaction occurred with the solution altering from transparent to semiopaque. P**2**/CO_2/P**3** adduct was confirmed via NMR spectra. It could return back to P**2**, P**3** and CO_2 upon heating up to 60 °C. This process could be repeated at least three cycles. Through transmission electron microscope (TEM) observation, P**2**/CO_2/P**3** adduct could form typical core-corona micelles with a mean size of 40 nm. Interestingly, these micelles with highly activated CO_2 species could be used as recyclable nanocatalysts for C1 catalytic conversion. A model translation of amines and CO_2 to their formamides was investigated. Aliphatic secondary amines, such as diethyl amine, morpholine, and piperidine, can be quantitatively converted to their formamides with a turnover number (TON) over 12000 at room temperature within only 3 h. The nanocatalysts have excellent recyclable and reusable performance, and their catalytic activity could retain over 80% after 8 cycles.

Moreover, Yan *et al.* subsequently synthesized a new FLP-based polymer P**4** via RAFT polymerization of styrene, 4-styryl-di(pentafluorophenyl)borane and 4-styryl-dimesitylphosphine, in which both frustrated Lewis acidic and basic monomers, triarylborane and triarylphosphine, were as the side chains of one polymer backbone (Figure 11B).[137] The hydrodynamic radius of P**4** in diluted chloroform solution was reduced after binding CO_2 due to the folding process. When the temperature exceeded 60 ^{o}C, the polymer chains unfolded due to the dissociation of CO_2. If CO_2 was added again, a refolding process of P**4** was accessible. The thermally-unfolded and CO_2-folded cycle could be sustained even over 10 rounds. This CO_2-folded single-chain nanoparticles could be used as recyclable carboxylase mimics for CO_2 conversion. CO_2 could insert on the saturated C(sp^3)-H bond and unsaturated C(sp^2 and sp)-H bonds to generate a series of carboxyl products.

They also designed and synthesized multi-functionalized FLP-based monomers M**2** and M**3** to binding CO_2 for the formation of a dynamic cross-linked network (Figure 11C).[138] This dynamic gel could attain a tensile strength of 3.4 MPa and 410% elongation at break, showing satisfactory mechanical properties. Thus, its self-healing ability was examined. The cutting surfaces were swept by CO_2 for 1 min (excess of gas) and then put together immediately without pressing. A 98% recovery of the original fracture stress (tensile strength) only took 2 h, indicating the rapid and efficient self-healing ability. Besides M**2** and M**3** with soft linkers, novel multi-functionalized FLP-based monomers M**4** and M**5** with the rigid linker of 1,3,5-triazine were also constructed by the authors (Figure 11D).[139] They could interconnect with CO_2 gas in 2D direction, forming planar networks and further self-curving into energetically favorable vesicles with an average diameter of 300 ± 40 nm through dynamic assembly regulation.

CONCLUSIONS AND REMARKS

This review highlighted recent advances in the synthesis, property and application of CO_2-based functional polymers. In the synthesis aspect, besides widely studied CO_2/epoxide polymerization toward poly(carbonate)s, other new CO_2-based polymerizations, such as CO_2/olefins, CO_2/alkyne, CO_2/isocyanide, and CO_2/FLP polymerizations, have sprung up, further providing various novel CO_2-based polymers. In the property and application aspects, CO_2-based polymers could not only possess superior thermal properties, serving as foams, adhesives and engineering plastics, etc., but also own amphiphilic property for biological imaging, therapy and lithium ion battery. The CO_2-based luminescent polymers with AIE features emerged in the past few years, which could be applied in diverse areas, such as chemosensor, fluorescence pattern, and LED. The chemically recyclable CO_2-based polymers also attract more attention for sustainable development.

According to aforementioned works, the following aspects may be the future research focus: (1) more types of monomers need to be developed for the polymerization with CO_2 to obtain new CO_2-based polymers with novel structures and higher CO_2 content; (2) cheap and readily available catalysts need to be explored to make the polymerization conditions be milder, more efficient, and environmentally friendly; (3) unique properties and applications of CO_2-based polymers compared with other non-CO_2-sourced polymers need to be carried forward.

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AUTHOR CONTRIBUTIONS

B.S., A.J.Q., and B.Z.T conceived the review. B.S. contributed to data collecting and analyzing and manuscript writing. A.J.Q. and B.Z.T contributed to project design, manuscript revision, and financial support.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Figure Titles and Legends

Figure 1. General strategies for efficient CO_2 conversion

Figure 2. The properties and applications of CO_2-based functional polymers

Figure 3. The synthetic routes toward CO_2 and epoxide-based polymers

Figure 4. CO_2-based amphiphilic polycarbonates (A) General strategy for constructing amphiphilic polycarbonates for the biological imaging, therapy and lithium ion battery. (B) *In vivo* peritoneal distribution and efficacy of PGC–PTX NPs as a single dose. Three weeks after IP tumor inoculation, mice received either (I) rhodamine or (II) PGC–PTX-Rho NPs at equivalent rhodamine doses. Three days after injection, the peritoneum was assessed under ambient (left) and UV light (right). The largest IP tumors are circled in yellow in each image. PGC–PTX-Rho NPs are visualized primarily in areas of tumor under UV light. Reprinted with permission from Grinstaff *et al.* (2017).[43] Copyright 2017 Royal Society of Chemistry. (C) Temperature dependence of ionic conductivity of poly(lithium carboxylate) with 41.0, 24.0, and 13.4 mol% lithium containing moieties, respectively. Reprinted with permission from Meng *et al.* (2016).[52] Copyright 2016 American Chemical Society.

Figure 5. The polymerization-depolymerization process between the recyclable polycarbonates and the epoxide/CO_2 monomers in the presence of different catalyst systems

Figure 6. Schematic representation of the formation of CPDs and their application in multicolor LEDs Reprinted with permission from Zhang *et al.* (2021).[93] Copyright 2021 Royal Society of Chemistry.

Figure 7. The synthetic routes toward CO_2 and olefins-based polymers

Figure 8. The synthetic routes toward CO_2 and triple-bond monomer-based polymers

Figure 9. CO_2-based hyperbranched polymers (A) The synthetic routes toward hyperbranched polyprodrug amphiphiles, (B) the schematic illustration of amphiphilic polymers *hb*-P**2-1** and *hb*-P**2-2**, (C, D) hydrodynamic diameter distribution of *hb*-P**2-1** and *hb*-P**2-2** in water (Inset: transmission electron microscope (TEM) image determined for the aqueous dispersion of *hb*-P**2-1** and *hb*-P**2-2**). Scale bar = 200 nm. Reprinted with permission from Qin *et al.* (2020).[113] Copyright 2020 Wiley Online Library.

Figure 10. The degradation of CO_2-based poly(alkynoate)s (A) Product-selective degradation of poly(alkynoate)s toward diols and *N*-heterocyclic compounds, (B) photographs of the film of poly(alkynoate)s before and after degradation. Reprinted with permission from Qin *et al.* (2021).[115] Copyright 2021 Chinese Chemical Society.

Figure 11. CO_2/FLP-based polymers (A) Schematic representation of reversible polymerization of CO_2/FLP-based chemically recyclable polymers, (B) FLP-based block polymers and CO_2 for the formation of recyclable nanocatalysts for CO_2 catalytic conversion, (C) CO_2/FLP-based dynamic crosslinked network with unprecedented gas-regulated viscoelastic, mechanical, and self-healing performance, (D) CO_2/FLP-based 2D polymerization to fabricate a CO_2-bridged vesicular system. Reprinted with permission from Yan *et al.*[135-139] Copyright 2019 American Chemical Society and 2018-2020 Wiley Online Library.