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Review

CO_2-Based Block Copolymers: Present and Future Designs

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The utilization of carbon dioxide (CO_2) as a monomer for copolymerization with three-membered cyclic ethers, also known as oxiranes or epoxides, has received much renewed interest due to the need for degradable polymeric materials derived from renewable resources. Since the early discovery of the catalytic coupling of CO_2 and oxiranes to afford polycarbonates, the area has progressed significantly over the 50 succeeding years. Herein, we describe the currently well-established catalyzed copolymerization process of oxiranes and carbon dioxide utilizing homogeneous metal catalysts. Pertinent to the commercial success of this process is the presence of rapid and reversible chain-transfer reactions that occur in the presence of protic impurities or additives leading to the formation of macropolyols. The focus of this review is to summarize the various synthetic strategies for the production of designer block copolymers for various applications in material science and biomedicine.

Highlights

Polycarbonates derived in part from carbon dioxide are provided by the completely alternating incorporation of epoxide and CO_2 molecules into a growing polymer chain. This process is an alternative to the step-growth, environmentally unfavorable pathway involving diols and phosgene.

A major challenge in synthesizing block polymers is the ability to chemoselectively control the incorporation of monomers from the polymerization of a mixed monomer feedstock. This ability to direct the polymer sequences of course determines the polymer structure and thermal/mechanical properties.

Through current advances that have been developed for the synthesis of well-defined CO_2-based block copolymers, it is possible to overcome some of the weaknesses of polycarbonates derived from both aliphatic and alicyclic epoxides (e.g., low glass transition temperature and brittleness).

Mechanistic Aspects of CO_2/Epoxide Copolymerization Reactions

The atom-economic synthesis of polycarbonates based on CO_2 and epoxides traces back to 1969, when Inoue and coworkers used a mixture of $ZnEt_2$ and H_2O to catalyze the alternating **copolymerization** (see Glossary) of propylene oxide (PO) and CO_2 [1,2]. Although these initial studies provided low yields of imperfect completely alternating copolymers, the findings subsequently stimulated extensive investigations by a number of academic and industrial groups. In the past 50 years, metal-based catalysts including alkaline-earth metals, transition metals, and group 13 metals have been developed for the synthesis of polycarbonates [3–19]. These metal complexes mediate the copolymerization process through a widely accepted coordination–activation insertion mechanism. That is, the metal complex copolymerization process is initiated by the coordination of the epoxide to the metal center followed by ring opening of the monomer by a nucleophile (Y^-) with the concomitant formation of a metal-bound alkoxide. This is illustrated in Figure 1, where, in the case of a monomer such as PO, this process may involve bond cleavage at the methylene or methine C–O bond and may or may not be regioregular. Subsequent **CO_2 insertion** without prior coordination to the metal center into the metal alkoxide to provide a metal carbonate is generally not rate determining. Successive alternating incorporation of epoxide and CO_2 produces linear polycarbonates.

During copolymerization of CO_2 and epoxides, two undesirable reactions can occur. First, successive incorporation of epoxide monomers leading to ether linkages in the main chain of the copolymer may take place. Second, cyclic carbonates can be formed via intramolecular elimination following backbiting of the displaced anionic growing polymer chain on epoxide binding in the rate-determining step. This process can be greatly retarded in the presence of bifunctional catalysts of type **2** [13]. Compared with linear polycarbonates, the corresponding five-membered cyclic carbonates are in general thermodynamically more stable and hence often are produced as side-products. The copolymerization activity, **regioselectivity**, **stereoselectivity**, and copolymer selectivity can be easily tuned by precisely designing the ligands bound to the

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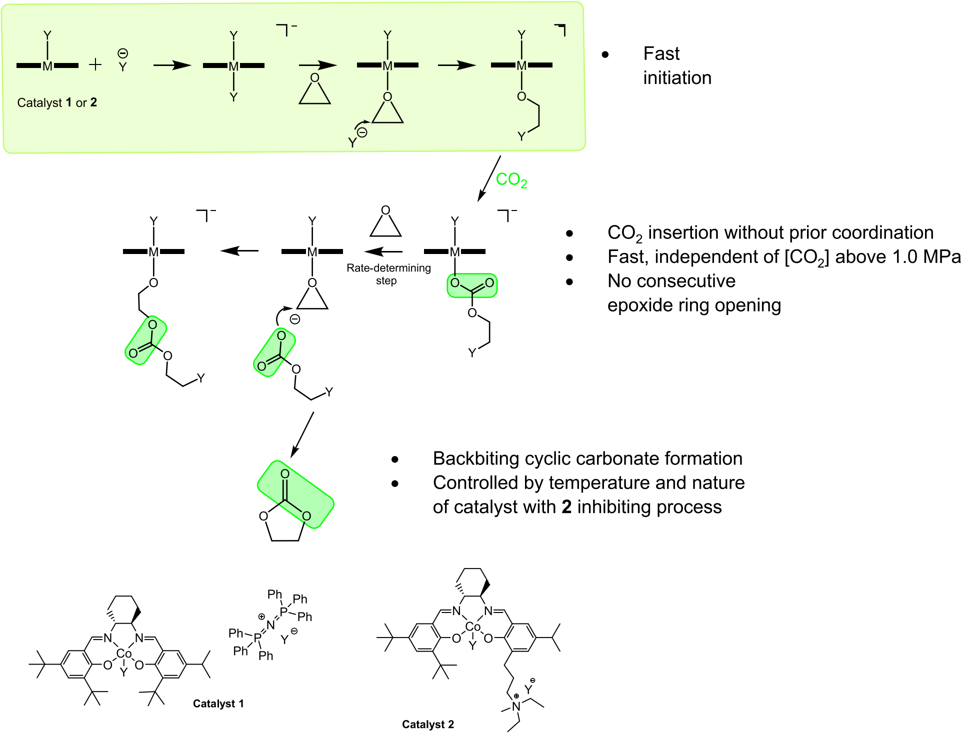

- Fast initiation

- CO_2 insertion without prior coordination
- Fast, independent of $[CO_2]$ above 1.0 MPa
- No consecutive epoxide ring opening

- Backbiting cyclic carbonate formation
- Controlled by temperature and nature of catalyst with **2** inhibiting process

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Figure 1. Mechanistic Aspects of the CO_2/Epoxide Copolymerization Process Illustrated for Typical Schiff Base Metal Catalysts.

metal center, the metal itself, and the reaction conditions – making CO_2-based polycarbonates attractive alternatives to phosgene-based analogs. Presently, the most researched epoxides, shown in Figure 2, are PO, 1,2-butylene oxide (BO), 1-hexene oxide (HO), allyl glycidyl ether (AGE), styrene oxide (SO), cyclopentene oxide (CPO), cyclohexene oxide (CHO), 4-vinylcyclohexene oxide (VCHO), and limonene oxide (LO). Nevertheless, the resultant polycarbonates, such as the commonly produced poly(propylene carbonate) (PPC) and poly(cyclohexene carbonate) (PCHC), are not likely to replace commodity plastics because of their inferior thermophysical properties as well as their lack of functionalities.

Topologies of Block Copolymers

To modify the properties of manufactured plastics for special needs, various strategies are used, among which the preparation of block copolymers by incorporating different macromolecular blocks is emerging as a useful method. Presently, many CO_2-based block copolymers with various molecular architectures have been designed and synthesized. However, only a minority

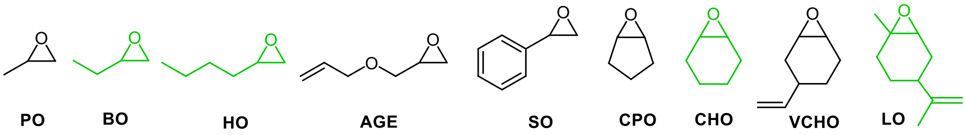

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Figure 2. The Most Widely Used Epoxides for Copolymerization with CO_2. Epoxides available from renewable resources are provided in green [16].

Glossary

Blocking efficiency: the purity of block copolymers (i.e., the mole or mass fraction of block copolymers relative to involved homopolymer impurities).

Chain-transfer/immortal polymerization: a polymerization of the monomer is performed by the propagating species that switches back and forth between the active and dormant states.

CO_2 insertion: a CO_2 molecule inserted into the M–OR (M, metal; R, alkoxy group) bond forms a growing metallic carbonate (M–OCO–OR) polymer chain.

Copolymerization/terpolymerization: an effective way of altering the physicochemical properties of a polymer via the incorporation of two/three monomers during chain-growth polymerization.

Regioselective: ring opening of an epoxide (e.g., PO) occurs at either its methylene carbon or methine carbon via nucleophile attack.

Reversible addition–fragmentation chain transfer (RAFT): a living radical polymerization technique for macromolecular design based on the interchange of xanthates.

Ring-opening copolymerization (ROCOP): an emerging polymerization strategy combining ROP and copolymerization to incorporate different monomers into the main chain of a predesigned polymer.

Stereoselective: for racemic epoxide, the polymerization proceeds by incorporating *R*-configuration epoxides or *S*-configuration counterparts; for mesomeric monomer, ring opening occurs at its *R*-configuration carbon or the *S*-configuration carbon.

have been studied for their potential applications, and fewer have been developed into commercial products. To enhance the functionality and properties of these materials for further usage, a vast array of block copolymers with various topologies have been exploited.

The introduction of chemically dissimilar block types and additional numbers of blocks (*n*) can rapidly expand the number of unique sequences and the possibilities of cyclic and branched architectures (selected topologies of block copolymers by varying the number of blocks are shown in Figure 3) [20]. This opens the door to the creation of many new and innovative functional materials. For example, to construct nanomaterials using AB [e.g., polyisoprene-*block*-polystyrene (PI-*b*-PS)] copolymers, typically, four familiar microphase structures (spheres, cylinders, lamellae, and double gyroid) can be obtained by varying the A/B fraction, the degree of polymerization, and the temperature. If more abundant microphase structures are needed, new block components C and other block types may be introduced, which can dramatically expand the spectrum of the accessible nanostructured morphologies. To prepare nanoarchitectures of A/B block copolymers with smaller size, the optimization of molecular morphologies is also necessary. Hawker and Fredrickson have reported the synthesis of PLA/PS miktoarm block copolymers; the results showed that AB_2 and A_2B_2 were effective molecular architectures for simultaneous tuning of domain feature sizes [21]. For building materials with elasticity and fracture toughness, multiblock copolymers will be suitable. Prominent among these are the commercialized styrene-butadiene-styrene (SBS) elastomers.

The development of new and versatile synthetic methods continues to provide approaches to a broad portfolio of architectures of block copolymers. In the following portion of this review, we mainly focus on the design and synthesis of linear block copolymers. At the end of this report, applications of some linear block copolymers are also introduced. Although the applications of these polymers remain in their infancy, we believe that these examples will have a significant impact on the development of new applications of these polymers in the future.

Construction of CO_2-Based Block Copolymers

In this section, we mainly divide the strategies into three cases: sequential monomer addition, chain-transfer polymerization, and kinetic controlled polymerization. Other strategies are

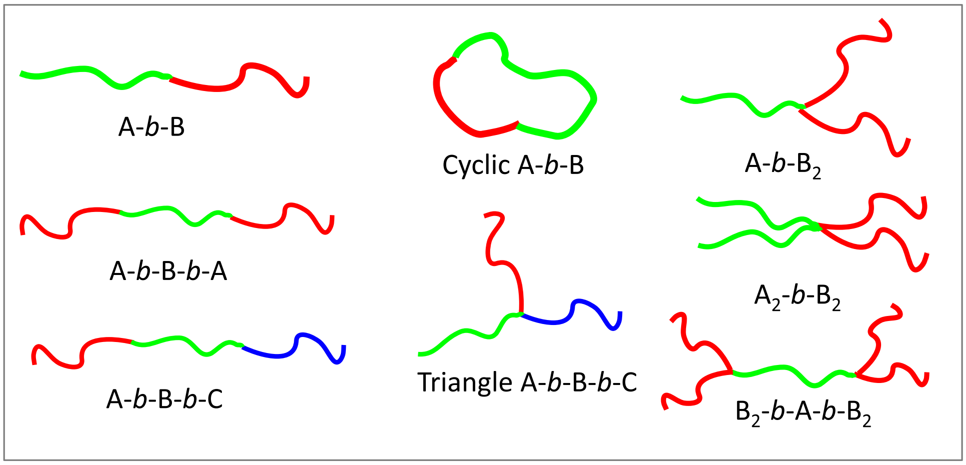

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Figure 3. Selected Topologies of Block Copolymers by Varying the Number of Blocks (Linear, Cyclic, Trilateral, and Branched Topology for Di-, Tri-, Tetra-, and Pentablock Copolymers).

seldomly used; for example, chain end coupling which has been reported by Xiao and Meng for the construction of multiblock PPC/PBS block copolymers [22].

Sequential Monomer Addition

Sequential monomer addition is regarded as the most general strategy for the formation of CO_2-based block copolymers (Figure 4). To construct well-defined block copolymers, attention should be paid to the following aspects. First and foremost, the initial monomer used should be completely consumed or removed prior to the addition of the second monomer. Second, the order of monomer addition should be rational in consideration of the relative nucleophilicity of the propagating center; hence, it is hard to vary the block sequence in many instances.

The first polycarbonate-*b*-polycarbonate derived from carbon dioxide using the sequential approach was reported by Nozaki and coworkers [23]. This was achieved by the quantitative conversion of PO/CO_2 in 1,2-dimethoxyethane in the presence of a bifunctional (salen)Co(III) catalyst, followed by the addition of 1-hexene oxide/carbon dioxide for formation of the second polycarbonate block. Similarly, Darensbourg and coworkers synthesized the PPC-*b*-poly(cyclohexene carbonate) (PPC-*b*-PCHC) block polymer using a binary (salan)Cr(III)/PPNCl catalyst system [24].

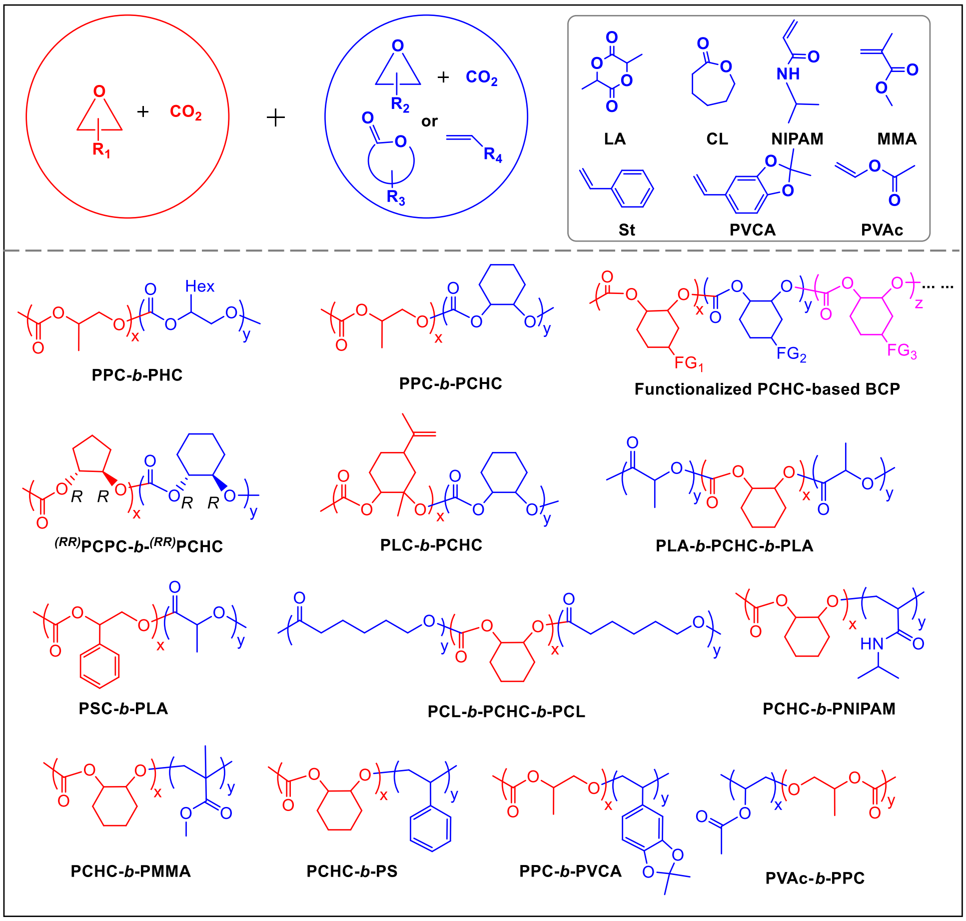

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Figure 4. Sequence Control Incorporating Different Monomers to Construct CO_2-Based Block Copolymers by a One-Pot Synthetic Strategy. Given the limited space, the junction unit is omitted for clarity.

In their synthetic process, an internal epoxide (CHO) was added for the formation of the second PCHC block at 60°C subsequent to evacuation of the excess PO and CO_2. The block structure was confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and differential scanning calorimetry (DSC) measurement as it differed from the random copolymer analog. In this manner, the triblock copolymer PPC-*b*-PCHC-*b*-poly(4-vinylcyclohexene carbonate) (PPC-*b*-PCHC-*b*-PVCHC) can be constructed via the sequential addition of PO, CHO, and VCHO. Coates and coworkers have utilized a similar method to prepare multiblock copolymers of functionalized cyclohexene oxides and CO_2 using β-diiminate zinc (BDI Zn) catalysts [25,26]. In this work, all of the polymerization processes proceeded to >99% conversion of the epoxides and the sequence of blocks was interchangeable due to the similarities of the propagating centers. In related studies, an isotactic poly(pentene carbonate)-*b*-PCHC (PCPC-*b*-PCHC) copolymer was synthesized by sequential addition of the *meso*-monomers using an enantioselective BDI Zn catalyst by this group [27]. More recently, Grenier and Schmalz, utilizing a BDI Zn complex as a catalyst, prepared biobased poly(limonene carbonate)-*b*-PCHC (PLC-*b*PCHC) diblock copolymers with molecular weights up to *ca* 120 kg/mol by sequential addition of *trans*-LO and CHO in the catalyzed copolymerization with carbon dioxide [28].

Cyclic esters can be ring opened in succession following the formation of CO_2-based polycarbonates to synthesize diblock polyester-*b*-polycarbonate copolymers. An easy method involves the straightforward addition of lactones following the complete consumption of epoxides, on the condition that the catalysts for **ring-opening copolymerization (ROCOP)** of epoxides/CO_2 are also effective for ring-opening polymerization (ROP) of lactones or lactides. For example, Williams and coworkers have reported a triblock polylactide-*b*-PCHC-*b*-polylactide (PLA-*b*-PCHC-*b*-PLA) polymer [29]. This was achieved by first producing the telechelic HO-PCHC-OH by using a dizinc catalyst with the addition of a small quantity of water (*vide infra*) to the CHO/CO_2 copolymerization system; afterwards, lactide was added to construct the PLA block catalyzed using an yttrium amide complex. In other cases, additional catalysts were needed for cyclic ester consumption. Darensbourg and Lu have published a tandem strategy for the preparation of poly(styrene carbonate)-*b*-PLA (PSC-*b*-PLA) using a (salen)CrX catalyst for the styrene oxide/CO_2 copolymerization process [30]. Subsequently, a small amount of water was added as a chain-transfer agent (CTA) to provide PSC with an end-capped hydroxyl group, which could be used as a macroinitiator for the sequential organocatalyzed lactide ROP. Notably, although a strong base, DBU, was used as the organocatalyst for the ROP of LA, no degradation of PSC was detected.

Block copolymers can also be synthesized when both monomers are simultaneously present in the reaction mixture. In this manner, Williams and coworkers have reported the construction of polycaprolactone (PCL) and PCHC block copolymers using a dizinc complex, which is efficient for both ROCOP of epoxides with CO_2 and ROP of lactone in the presence of epoxide [31]. CHO first reacts with the zinc carboxylate species to afford a zinc alkoxide, which catalyzes the ROP of caprolactone (CL). Following PCL formation, the addition of CO_2 served as an exogeneous switch reagent, directing the copolymerization of CHO and CO_2. This one-pot, two-step process allows the production of PCL-*b*-PCHC. Interestingly, the reverse sequence of polymer formation was achievable by first adding CO_2 along with CHO to generate the PCHC block, since CO_2 undergoes facile insertion into the zinc alkoxide initiator and the resulting zinc carbonate is nonreactive with CL. Subsequently, replacing CO_2 with N_2, formation of the PCL block occurs. Sequential addition of carbon dioxide was also applied in the formation of a pentablock polymer resulting from a mixture of cyclic anhydride, epoxide, and lactone [32].

Recent progress involving sequential monomer addition for the formation of block polymers has made it possible to combine different polymerization mechanisms to provide the construction of several novel polymeric materials. Namely, Wu and coworkers have described a one-pot sequential construction of a block copolymer from epoxide/CO_2 and vinyl monomers using a bifunctional BDI Zn complex [33]. The initiator present in the BDI Zn complex was designated a **reversible addition–fragmentation chain-transfer (RAFT)** agent 3-(benzylthiocarbonothioylthio) propionate, thus providing the ability to initiate ROCOP of CHO and CO_2 as well as homopolymerization of the vinyl monomer following the addition of a radical initiator. PCHC-*b*-PNIPAM was prepared in this manner by the tandem addition of CHO/CO_2 and NIPAM. Several other block polymers, including PCHC-*b*-PS, PCHC-*b*-PMMA, and PCHC-*b*-PVCA, were constructed using this method [34]. Wang has reported an oxygen-triggered switchable polymerization pathway for the synthesis of CO_2-based block copolymer [35]. This methodology utilizes (salen)Co(II) as an effective catalyst for the formation of polyvinyls via an organometallic-mediated radical polymerization process, followed by using (salen)Co(III)X as a catalyst for ROCOP. In this work, the cobalt(II) on addition of oxygen is converted to cobalt(III). Thereby, polyvinyl acetate (PVAc) was initially synthesized using the (salen)Co(II) species as a catalyst, following treatment with oxygen to afford (salen)Co(III)X, which on the addition of epoxide/CO_2 affords the block polymer.

The sequential monomer addition pathway, which minimizes the interference of the different monomers during the formation of block copolymers, provides the most versatile approach for the synthesis of a broad scope of CO_2-based block polymers. However, this technique is time consuming and there is a need for catalyst development for efficient construction of block copolymers. Undoubtedly, this will involve combination polymerization mechanisms to provide methods for the synthesis of a wider array of useful functional polymers.

Chain-Transfer Polymerization

An alternative, very useful method for the synthesis of CO_2-based block polymers is **chain-transfer polymerization**, which is usually referred to as **immortal polymerization**. This approach is illustrated in Figure 5, along with several of the block polymers thus far reported for this methodology. As indicated in Figure 5, chain propagation is first initiated by ring opening of the coordinated epoxide by the nucleophilic anion (X) to afford a metal-alkoxide intermediate followed by alternating CO_2/epoxide enchainment. The growing anionic polymer chain can undergo protonation by the CTA, to afford a metal-CTA intermediate, which serves to initiate the alternating incorporation of an epoxide and CO_2. The released dormant chain can reenter the chain-propagation process as it is reversely deprotonated. Importantly, all of these reactions are rapid and reversible, and the rate of chain transfer >> rate of propagation, leading to nearly uniform molecular weight and a narrow molecular weight distribution.

Telechelic polycarbonates with hydroxyl end groups can be formed by the addition of water as the CTA. Wu and Darensbourg have reported that the true chain transfer during the copolymerization of PO and CO_2 in the presence of water is propylene diol [36]. In general, this will be true if the catalytic rate of epoxide hydrolysis significantly exceeds that of the CO_2/epoxide enchainment. The first formed HO–PC–OH segment acts as a macroinitiator for the sequential ROCOP of the next epoxide/CO_2 or ROP of cyclic ester or cyclic phosphate monomers. This process has led to the formation of ABA triblock copolymers, such as PAGEC-*b*-PPC-*b*-PAGEC [37,38], PLA-*b*-PC-*b*-PLA [31,39,40], PCL-*b*-PCHC-*b*-PCL [41], PCHC-*b*-PAGEC-*b*-PCHC [42], PCHC-*b*-PPC [43], and polyphosphoester-*b*-PPC-*b*-polyphosphoester (PPE-*b*-PPC-*b*-PPE) [36].

Functional CTAs can also be introduced into the catalyst system to provide an exciting new strategy for the synthesis of block copolymers. For example, Wang and Xie utilized a trithiocarbonate compound bearing a carboxylic group as a bifunctional CTA, which serves as an initiator for both RAFT polymerization and ROCOP [44]. In this manner, they were able to synthesize CO_2-based

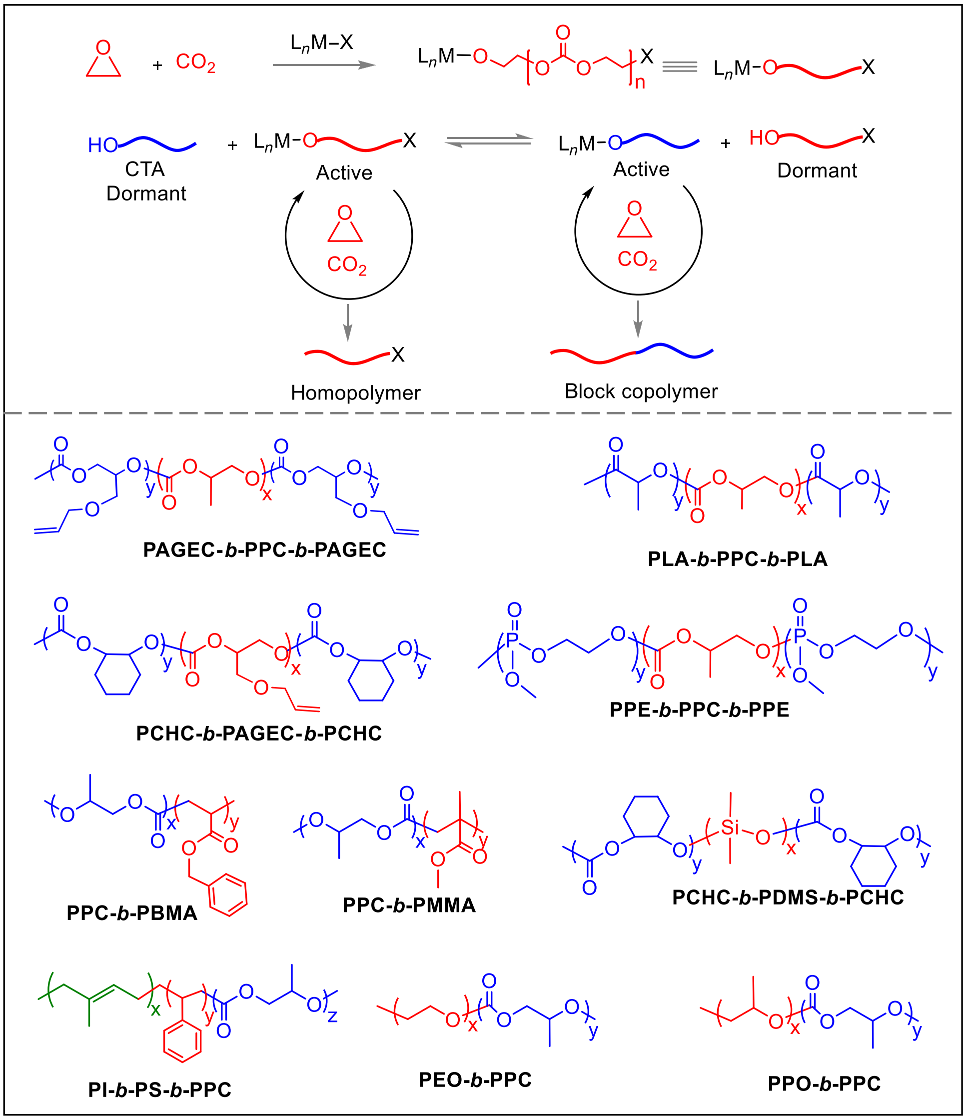

Figure 5. Direct Construction of CO_2-Based Block Copolymers Using Macro-Chain-Transfer Agents. Given the limited space, the junction unit is omitted for clarify.

block copolymers including PHC-*b*-PMMA, PCHC-*b*-PMMA, PPC-*b*-PS, and PPC-*b*-PBMA. These block copolymers were afforded in a one-step route because of the good compatibility of the ROCOP of epoxide/CO_2 and RAFT polymerization of vinyl monomers. Similarly, Nakano and co-workers have reported the usage of α-halocarboxylic acids as bifunctional CTAs, which can initiate both the ROCOP of epoxides and CO_2 and atom-transfer radical polymerization (ATRP) of vinyl monomers [45]. This approach has enabled these researchers to prepare (PPC-*b*-PMMA), PCHC-*b*-PMMA, and PPC-*b*-PMMA-*b*-PS block copolymers. Recently, functionalized CTAs comprising protic ionic liquids or metal carbonyl-containing diols have been used in the preparation of block copolymers [46,47]. In the latter instance, triblock polymers containing one metal complex per polymer chain were obtained, which on functionalization by thiol-ene click chemistry provided micelles in aqueous solution [48].

Polymers bearing hydroxyl and other protic groups at chain ends can be fed into a ROCOP system to serve as a macro-CTA for the construction of block copolymers. In 2010, Lee and coworkers reported the preparation of di- and triblock copolymers by introducing various polymer initiators during the copolymerization of CO_2 and epoxides [49]. This approach has utilized poly(dimethylsiloxane) [50], poly(ethylene oxide) [51], and polyolefins [52] as macro-CTAs to synthesize new CO_2-based block copolymers. Using this methodology, the thermoresistance, brittleness/softness, and hydrophilicity performance of CO_2-based polymers were significantly modified by the incorporation of distinctly different blocks. Zhang and coworkers have reported a chain-shuttling polymerization of CL and epoxide/CO_2 using a zinc-cobalt double metal cyanide complex (DMC) and $Sn(Oct)_2$ as catalysts [53]. In the presence of benzyl alcohol, chain transfer-polymerization can occur on either catalyst. Hence, the two independent chain propagations were connected by the two cross-chain exchange reactions, thereby, producing multiblock polyester/polycarbonate copolymers.

Despite the fact that the use of chain-transfer polymerization processes for the construction of block copolymers is easily achieved, allowing the growth of several polymer chains from a single catalyst site, the catalytic activity and blocking efficiency are compromised. Wu and Darensbourg have systematically examined the influence of the size, nature, and ratio of [macro-CTA]:[cat] on the catalytic activity and blocking efficiency for the formation of block copolymers [36]. Using various macro-CTAs (including PPG, PEG, and PS) in the presence of the two most common catalyst systems, (BDI)ZnOAc and (salen)CoTFA/PPNTFA, the results showed that these variables have a significant influence on the activity and blocking efficiency of the processes. For example, increasing the quantity of a macro-CTA provides higher blocking efficiency at the expense of reaction activity. However, larger macro-CTAs will decrease both block efficiencies and reaction activities. Thus, when constructing block copolymers using this method, multiple factors should be taken into consideration, including the dosage of catalyst as well as the reaction and blocking efficiencies.

Kinetic Controlled Polymerization

The preparing of ordered copolymers from mixtures of monomers can be challenging, especially when the catalyst is active for all monomers. In this section, we introduce a kinetic controlled polymerization that has been shown to be a facile synthetic route to block copolymers, where the block copolymer can be constructed in a one-pot or even one-step strategy. Many of the copolymers produced via this synthetic technique are illustrated in Figure 6.

In 2008, Coates and coworkers reported a novel method for the block **terpolymerization** of epoxides, cyclic anhydrides, and CO_2 in a simple one-step, one-pot procedure under mild reaction conditions [54]. Using a β-diiminate zinc catalyst with monitoring of the polymerization by *in situ* IR spectroscopy, the epoxide reacted with the zinc catalyst is the rate-determining step to provide a zinc alkoxide intermediate. Subsequent reaction of this intermediate with cyclic anhydride provided the polyester block until the cyclic anhydride was completely consumed, followed by the copolymerization of epoxide and CO_2 to form the polycarbonate block. Interestingly, copolymerization of epoxides and CO_2 occurs at a faster rate than polyester formation as monitored by *in situ* IR spectroscopy. Since the polyester block is formed prior to the polycarbonate block, it can be concluded that insertion of the anhydride into the common zinc alkoxide intermediate is much faster than the insertion of CO_2. On the basis of these predicted reactivities, the observed block construction is consistent with a product-determining step that is pre-rate determining. Similar monomer selectivity and block copolymer formation have been observed in terpolymerization processes using salophen chromium [55], salen chromium [56,57], porphyrin aluminum [58], porphyrin chromium [55,58], porphyrin cobalt [58], salen cobalt [59], and di-magnesium and di-zinc macrocyclic complexes [60] as catalysts.

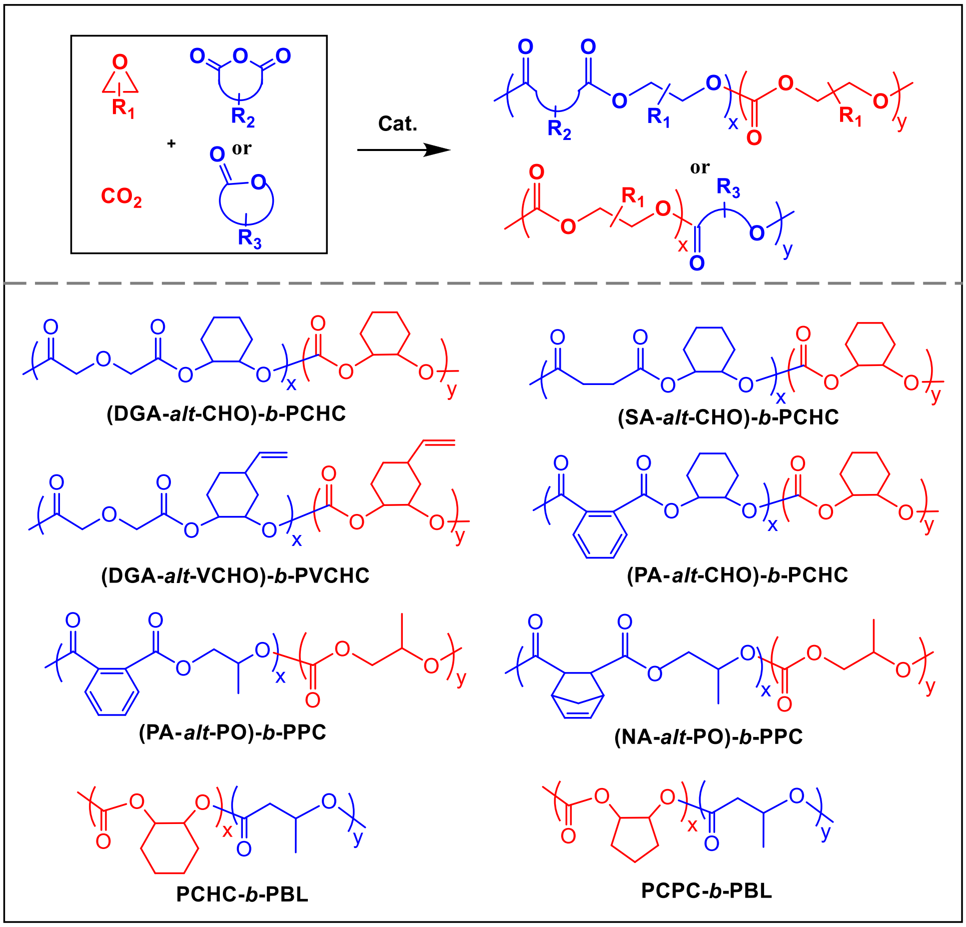

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Figure 6. Sequentially Constructed CO_2-Based Block Copolymers by Terpolymerization of Cyclic Anhydrides, Epoxides, and CO_2 and in a One-Pot/One-Step Strategy Using Kinetic Controlled Polymerization.

Kinetic controlled polymerization can also be applied to the production of block CO_2-based polymers from mixtures of epoxides, CO_2, and lactones. In particular, Williams and coworkers have reported the synthesis of PCHC-*b*-PCL block copolymers [31]. In this reaction system, PCHC formation is preferential because CO_2 insertion into the metal-alkoxide species is faster than lactone ring opening and the afforded metal-carbonate species is not active for the ROP of PCL. Therefore, a well-defined PCHC block is formed, followed by a second PCL block produced on the release of CO_2. Similarly, Rieger's group has published a terpolymerization process involving β-butyrolactone (BBL), epoxides, and CO_2 for the production of block copolymers [61,62]. Using a BDI zinc complex as the catalyst, the PCHC-*b*-PBL and PCPC-*b*-PBL copolymers were prepared using the aforementioned strategy, where the CO_2 pressure was 4.0 MPa for polycarbonate formation and released for PBL production. Interestingly, in this instance, CO_2 acts as a controlling agent. Under a low CO_2 pressure of 0.3 MPa, the similar reaction rates of the two polymerization processes result in terpolymers with statistical compositions. The block sequence can also be reversed by the addition of CO_2 to the reaction following the formation of PBL, to afford PBL-*b*-PCHC block copolymers in the manner described previously for sequential polymerization. Currently, the monomer scope for kinetic controlled polymerization is limited to epoxide/CO_2, epoxide/cyclic anhydride, and cyclic esters. The related blocks are usually formed in the order [32,63,64] epoxide/cyclic anhydride > epoxide/CO_2 > cyclic esters. Notably, an opposite selectivity in polymerizations of epoxide/CO_2 and epoxide/cyclic anhydride was reported recently by Williams and Mathers [65]. The requirement for the successful construction of block copolymers and minimizing of tapered segments in the polymers is to optimize the pressure of CO_2.

Kinetic controlled polymerization – more precisely, kinetic resolution polymerization here – can also be applied for the formation of stereoblock polycarbonates. In this manner, stereogradient PPC has been prepared by Nozaki and coworkers, although with moderate tapering segments due to small values of k_{rel} [the relative rate constant of (S)-PO vs (R)-PO or (R)-PO vs (S)-PO] [66]. Nevertheless, the thus-provided stereogradient PPC shares similar thermal properties with the stereoblock PPC prepared by sequential monomer addition. Presently, no perfect stereoblock polycarbonate has been reported via kinetic resolution. Hence, there exists a need to discover robust catalyst systems for the construction of well-defined stereoblock polycarbonates.

Applications of CO_2-Based Block Copolymers

Recent advances in the synthesis of CO_2-based block copolymers have modified the thermal properties and improved the behavior in micro-phase separation of the PC-based polymers. These synthetic techniques can provide a means for the introduction of a wide variety of functional groups into these polymeric materials. Nevertheless, in contrast to the rapidly growing body of synthetic literature, the applications of these materials are seldom discussed. In this concluding section, we introduce recent progress in the applications of CO_2-based block copolymers for the construction of high-value-added and functional materials (Figure 7).

Block copolymers with amphiphilic blocks can undergo self-assembly into many microphase structures. For example, by designing copolymers with hydrophilic and hydrophobic blocks, these materials can be assembled into micelles in water. These include, PPC-*b*-PEO [51], PPE-*b*-PPC-*b*-PPE [36], PCHC-*b*-PNIPAM [33], and modified PAGEC-*b*-PPC-*b*-PAGEC [37], which show hopeful platforms for biomedical applications. Recently, Li and associates have utilized a CO_2-based amphiphilic block polycarbonate for cancer diagnosis and treatment in laboratory mice that has a low-toxicity pathway [67]. These researchers first synthesized a cysteine-modified amphiphilic PAGEC-*b*-PPC-*b*-PAGEC triblock copolymer using sebacic acid as the CTA involving tandem immortal copolymerization of CO_2/epoxide and thiol-ene click reactions. Subsequently, the cysteine-modified block copolymer was reacted with diethylenetriaminopentaacetic acid (DTPA) dianhydride as the chelating agent. On coordination with the gadolinium salt ($GdCl_3$), the resulting polymeric micelles (APC-DTPA/Gd) exhibited nano-self-assembly behavior, and provided excellent magnetic resonance imaging performance for tumor diagnosis with a cytotoxic immune response.

Other useful materials can be formed by careful design of the corresponding block copolymers. Coates and Wiesner, using the as-synthesized PI-*b*-PS-OH block copolymer as the macro-CTA, have prepared a triblock copolymer, PI-*b*-PS-*b*-PPC [52]. Because of the incompatibility of these three blocks, the triblock polymer can self-assemble into co-continuous network morphologies. The PI and PPC blocks were removed orthogonally using UV light or NaOH, followed by deposition of Au, Ni, and Cu metals into the related mesoporous channels. These materials may be used in tandem and size-selective catalysis. In 2017, Yang and coworkers reported the use of PS-*b*-PPC as a new material for lithography [68]. The PS/PPC block copolymer exhibited a Flory–Huggins interaction parameter (χ) of 0.079 at 150°C, which is significantly higher than that of PS/PMMA ($\chi = 0.029$ at 150°C). Hence, this polymeric material can self-assemble into much smaller nanostructures. On the application of directed self-assembly of the diblock copolymer

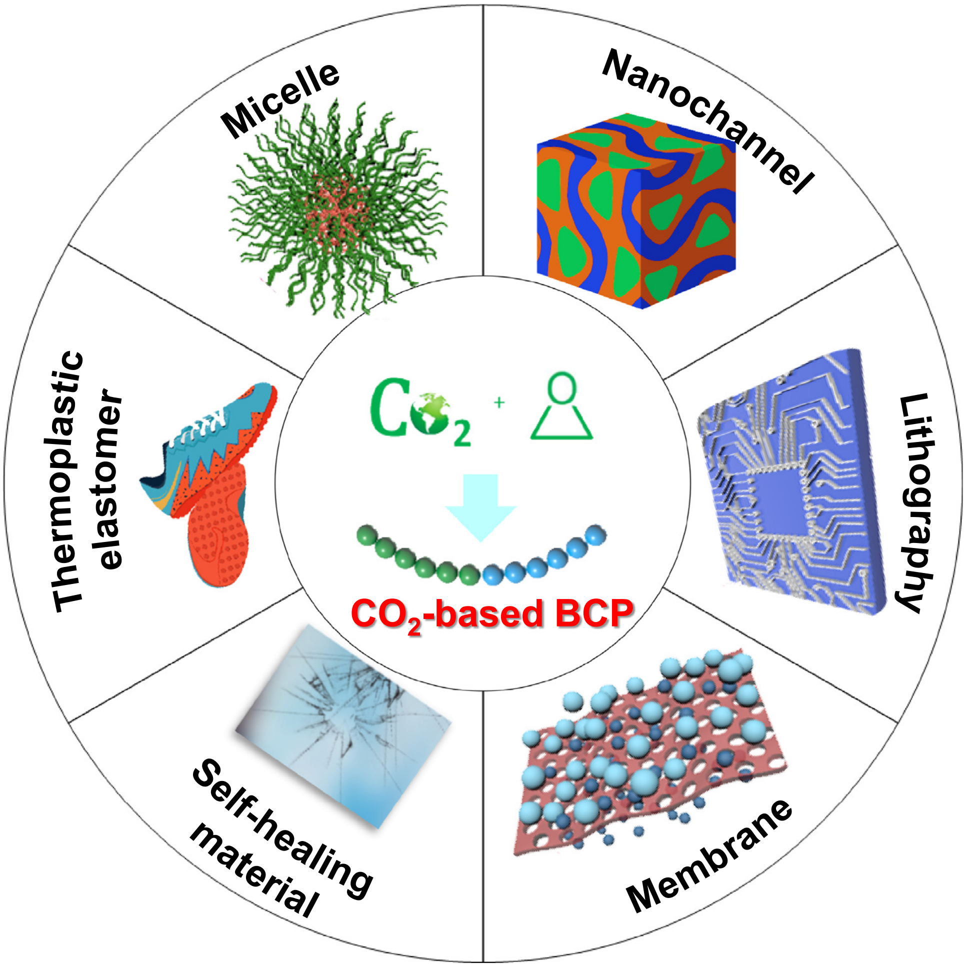

Figure 7. Applications of the CO_2-Based Block Polymers.

via thermal annealing, a well-defined lamellar structure was obtained. Since the PPC block is easily removed by etching with O_2 RIE, a sub-10-nm pattern was achieved, thereby making this material an attractive candidate for next-generation lithography. More recently, Wu and coworkers have reported the preparation of nanoporous membranes for water treatment from CO_2-based block copolymers [34]. A designed block copolymer of poly(propylene carbonate)-*b*-poly(4-vinylcatechol acetonide) (PPC-*b*-PVCA) was shown to self-assemble into a cylinder morphology by solvent annealing. The water-treatment membrane is suggested to be simply manufactured since the PPC block is easily removed by alkali. This allows the PVCA block to provide the bioinspired catechol group, where an ultrathin ZrO_2 layer can be delivered by a biomineralization process. In addition, Greiner and Schmalz recently reported the self-assembly of PLC-*b*-PCHC into disordered cylinders, cylinders, hexagonally perforated lamellae, and lamellar structures [28]. These hold great potential for further nanoapplications.

CO_2-based block copolymers can also be used as mechanical materials. In this regard, Feng and coworkers reported that a PCL-*b*-PPC-*b*-PCL triblock copolymer can be utilized as a toughening agent for epoxy thermosets, as a result enhancing tensile elongation and fracture toughness [69].

Wu and Darensbourg have described a self-healing material prepared from the post-polymerization reaction of PAGEC-*b*-PPC-*b*-PAGEC with the radical-mediated thiol-ene click reaction to introduce 2-(acetylamino)ethanoethiol (AET) across the double bond of the PAGEC segment [38]. In these polymeric materials, the PPC phase serves as the stiff domain to maintain the mechanical strength, while the PAGEX soft phase provides hydrogen bonding for self-healing. The phase separation between the two blocks results in the hard PPC polymer chains aggregating together, thereby providing physical crosslinks in the material. The homohydrogen bonds (between amide groups) and the heterohydrogen bonds (between amide groups and carbonate groups) are regenerated after the two damaged faces are contacted, demonstrating an excellent autonomic self-healing ability. Soon thereafter, Wu and his group disclosed an effective synthesis of a thermoplastic elastomer, a closely related process [41]. Besides the elastomeric property, this material exhibited autonomic self-healing ability at room temperature using dynamic covalent bonds. Finally, Müller and coworkers have synthesized transparent ABXBA poly(ether carbonate) multiblock polymers, which are highly interesting for new coating applications [70]. Most recently, Williams and coworkers synthesized a series of PCHC-*b*-polydecalactone-*b*-PCHC (PCHC-*b*-PDL-*b*-PCHC) copolymers. By tuning the ratio and molecular weight of PCHC:PDL triblock copolymers, these materials were shown to exhibit desirable thermal stability (decomposition temperature ~280°C), toughness (112 MJ m^{-3}), and elongation at break (>900%), enabling them to be suitable candidates for adhesives, elastomers, and toughened plastics [71].

Concluding Remarks and Future Perspectives

Recent developments in synthetic methodologies for the synthesis of well-defined CO_2-based block copolymers have thus far been sustainable and degradable platforms for applications in filtration, catalysis, and drug delivery. From early studies of the properties of CO_2-based block copolymers, it has become clear that many of the physical weaknesses that exist in homopolymers derived from CO_2 and cyclic ethers can be overcome by the production of well-defined block copolymers. Please see Outstanding Questions for a concise summary of the important issues that must be addressed prior to CO_2-based copolymers being competitive with other polymeric materials. It is anticipated that, with the current capability for the synthesis of a wide variety of polymeric materials, a plethora of new utilizations will become available in the not-too-distant future.

Outstanding Questions

How can we construct more versatile topologies of CO_2-based block polymers and how might these topologies impact the materials?

Represented by the progress in organic catalysis development, can the use of organocatalysts overcome the dominance of metal-based catalysts, thereby making the process greener?

What is the impact of being able to synthesize block copolymers containing different stereoregular (iso-, syndio-, or/and hetero-tactic) segments?

Although it is possible to construct ~7-nm-sized features using CO_2-based block copolymer lithography under thermotreatment, what is the limit of the microphase separation for these materials?

How can the cost-effectiveness of CO_2-based block copolymers be made more competitive with current degradable materials?

What impact does the direct use of CO_2 from point sources have on the production of CO_2-derived polycarbonates, and are they biodegradable materials?

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References

1. Inoue, S. *et al.* (1969) Copolymerization of carbon dioxide and epoxide. *J. Polym. Sci. B Polym. Lett.* 7, 287–292
2. Inoue, S. *et al.* (1969) Copolymerization of carbon dioxide and epoxide with organometallic compounds. *Makromol. Chem.* 130, 210–220
3. Darensbourg, D.J. and Holtcamp, M.W. (1996) Catalysts for the reaction of epoxides and carbon dioxide. *Coord. Chem. Rev.* 153, 155–174
4. Coates, G.W. and Moore, D.R. (2004) Discrete metal-based catalysts for the copolymerization of CO_2 and epoxides: discovery, reactivity, optimization, and mechanism. *Angew. Chem. Int. Ed.* 43, 6618–6639
5. Sugimoto, H. and Inoue, S. (2004) Copolymerization of carbon dioxide and epoxide. *J. Polym. Sci. A* 42, 5561–5573
6. Darensbourg, D.J. *et al.* (2004) Copolymerization of CO_2/epoxides catalyzed by metal salen complexes. *Acc. Chem. Res.* 37, 836–844
7. Chisholm, M.H. and Zhou, Z. (2004) New generation polymers: the role of metal alkoxides as catalysts in the production of polyoxegenates. *J. Mater. Chem.* 14, 3081–3092
8. Darensbourg, D.J. (2007) Making plastics from carbon dioxide. Salen metal complexes as catalysts for the production polycarbonates from epoxides and CO_2. *Chem. Rev.* 107, 2388–2410
9. Klaus, S. *et al.* (2011) Recent advances in CO_2/epoxide copolymerization – new strategies and cooperative mechanisms. *Coord. Chem. Rev.* 255, 1460–1479
10. Kember, M.R. *et al.* (2011) Catalysts for CO_2/epoxide copolymerization. *Chem. Commun.* 47, 141–163
11. Lu, X.-B. and Darensbourg, D.J. (2012) Cobalt catalysts for the coupling of CO_2 and epoxides to provide polycarbonates and cyclic carbonates. *Chem. Soc. Rev.* 41, 1462–1484
12. Lu, X.-B. *et al.* (2012) CO_2 copolymers from epoxides: catalytic activity, product selectivity, and stereochemistry control. *Acc. Chem. Res.* 45, 1721–1735
13. Darensbourg, D.J. and Wilson, S.J. (2012) What's new with CO_2? Recent advances in its copolymerization with oxiranes. *Green Chem.* 14, 2665–2671
14. Paul, S. *et al.* (2015) Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* 51, 6459–6479

15. Trott, G. *et al.* (2016) Catalysts for CO_2/epoxide ring-opening copolymerization. *Philos. Trans. R. Soc. A* 374, 20150085
16. Poland, S.J. and Darensbourg, D.J. (2017) A quest for polycarbonates provided via sustainable epoxide/CO_2 copolymerization processes. *Green Chem.* 19, 4990–5011
17. Kozak, C.M. *et al.* (2018) Copolymerization of carbon dioxide and epoxides by metal coordination complexes. *Coord. Chem. Rev.* 376, 565–587
18. Kamphuis, A.J. *et al.* (2019) CO_2-fixation into cyclic and polymeric carbonates: principles and applications. *Green Chem.* 21, 406–448
19. Huang, J. *et al.* (2020) Update and challenges in carbon dioxide-based polycarbonate synthesis. *ChemSusChem* 13, 469–487
20. Bates, C.M. and Bates, F.S. (2017) 50th Anniversary perspective: block polymers – pure potential. *Macromolecules* 50, 3–22
21. Shi, W. *et al.* (2015) Producing small domain features using miktoarm block copolymers with large interaction parameters. *ACS Macro Lett.* 4, 1287–1292
22. Qin, J. *et al.* (2017) Novel multiblock copolymer of CO_2-based PPC-*mb*-PBS: from simulation to experiment. *ACS Sustain. Chem. Eng.* 5, 5922–5930
23. Nakano, K. *et al.* (2006) Selective formation of polycarbonate over cyclic carbonate: copolymerization of epoxides with carbon dioxide catalyzed by a cobalt(III) complex with a piperidinium end-capping arm. *Angew. Chem. Int. Ed.* 45, 7274–7277
24. Darensbourg, D.J. *et al.* (2009) Highly selective and reactive (salan)CrCl catalyst for the copolymerization and block copolymerization of epoxides and carbon dioxide. *Macromolecules* 42, 6992–6998
25. Kim, J.G. *et al.* (2011) Tailored living block copolymerization: multiblock poly(cyclohexene carbonate)s with sequence control. *Macromolecules* 44, 1110–1113
26. Kim, J.G. and Coates, G.W. (2012) Synthesis and polymerization of norbornenyl-terminated multiblock poly(cyclohexene carbonate)s: a consecutive ring-opening polymerization route to multisegmented graft polycarbonates. *Macromolecules* 45, 7878–7883
27. Ellis, W.C. *et al.* (2014) Copolymerization of CO_2 and meso epoxides using enantioselective β-diiminate catalysts: a route to highly isotactic polycarbonates. *Chem. Sci.* 5, 4004–4011
28. Bailer, J. *et al.* (2019) Synthesis and self-assembly of biobased poly(limonene carbonate)-*b*-poly(cyclohexene carbonate) diblock copolymers prepared by sequential ring open copolymerization. *Green Chem.* 21, 2266–2272
29. Kember, M.R. *et al.* (2012) Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate). *Polym. Chem.* 3, 1196–1201
30. Wu, G.-P. *et al.* (2012) Tandem metal-coordination copolymerization and organocatalytic ring-opening polymerization via water to synthesize diblock copolymers of styrene oxide/CO_2 and lactide. *J. Am. Chem. Soc.* 134, 17739–17745
31. Romain, C. and Williams, C.K. (2014) Chemoselective polymerization control: from mixed-monomer feedstock to copolymers. *Angew. Chem. Int. Ed.* 53, 1607–1610
32. Chen, T.T. *et al.* (2018) Pentablock copolymer from tetra component monomer mixture using a switchable dizinc catalyst. *Macromolecules* 51, 5346–5351
33. Zhang, Y.-Y. *et al.* (2018) A bifunctional β-diiminate catalyst with CO_2/epoxides copolymerization and RAFT polymerization capacities for versatile block copolymers construction. *Macromolecules* 51, 3640–3646
34. Zhou, H.J. *et al.* (2018) Bioinspired block copolymer for mineralized nanoporous membrane. *ACS Nano* 12, 11471–11480
35. Zhao, Y. *et al.* (2019) Oxygen-triggered switchable polymerization for the one-pot synthesis of CO_2-based block copolymers from monomer mixtures. *Angew. Chem. Int. Ed.* 58, 14311–14318
36. Wu, G.-P. and Darensbourg, D.J. (2016) Mechanistic insights into water-mediated tandem catalysis of metal-coordination CO_2/epoxide copolymerization and organocatalytic ring-opening polymerization: one-pot, two steps, and their catalysis cycles for triblock copolymers synthesis. *Macromolecules* 49, 807–814
37. Wang, Y. *et al.* (2015) Construction of versatile and functional nanostructures derived from CO_2-based polycarbonates. *Angew. Chem. Int. Ed.* 54, 10206–10210
38. Yang, G.W. *et al.* (2018) Construction of autonomic self-healing CO_2-based polycarbonates via one-pot tandem synthetic strategy. *Macromolecules* 51, 1308–1313
39. Darensbourg, D.J. and Wu, G.-P. (2013) A one-pot synthesis of a triblock copolymer from propylene oxide/carbon dioxide and lactide: Intermediary of polyol initiators. *Angew. Chem. Int. Ed.* 52, 10602–10606
40. Zhang, Y.-Y. *et al.* (2014) Synthesis of fully alternating polycarbonate with low T_g from carbon dioxide and bio-based fatty acid. *RSC Adv.* 4, 36183–36188
41. Paul, S. *et al.* (2015) Sequence selective polymerization catalysis: a new route to ABA block copoly(ester-*b*-carbonate-*b*-ester). *Macromolecules* 48, 6047–6056
42. Yang, G.-W. and Wu, G.-P. (2019) High-efficiency construction of CO_2-based healable thermoplastic elastomers via a tandem synthetic strategy. *ACS Sustain. Chem. Eng.* 7, 1372–1380
43. Jiang, Y.-J. *et al.* (2019) Synthesis of polycarbonate block terpolymers using robust cobalt catalyst systems. *Chin. J. Polym. Sci.* 37, 1200–1204
44. Wang, Y. *et al.* (2018) One-step route to CO_2-based block copolymers by simultaneous ROCOP of CO_2/epoxides and RAFT polymerization of vinyl monomers. *Angew. Chem. Int. Ed.* 57, 3593–3597
45. Mizuno, Y. and Nakano, K. (2018) Block copolymers of aliphatic polycarbonates: combination of immortal epoxide/carbon dioxide copolymerization and atom transfer radical polymerization of vinyl monomers. *Chem. Lett.* 47, 580–583
46. Huang, Z. *et al.* (2018) One-pot synthesis of ion-containing CO_2-based polycarbonates using protic ionic liquids as chain transfer agents. *Macromolecules* 51, 9122–9130
47. Folsom, T.M. *et al.* (2019) Approach for introducing a single metal complex into a polymer chain. Metallo-chain transfer agents in CO_2 or COS/epoxide copolymerization processes. *Macromolecules* 52, 5217–5222
48. Bhat, G.A. *et al.* (2020) Placing single metal complexes into the backbone of CO_2-based polycarbonates chains. Construction of nanostructures for prospective micellar catalysis. *Organometallics* 39, 1612–1618
49. Cyriac, A. *et al.* (2010) Immortal CO_2/propylene oxide copolymerization: precise control of molecular weight and architecture of various block copolymers. *Macromolecules* 43, 7398–7401
50. Reiter, M. *et al.* (2016) *In situ* generated ABA block copolymers from CO_2, cyclohexene oxide, and poly(dimethylsiloxane)s. *ACS Macro Lett.* 5, 419–423
51. Hilf, J. *et al.* (2013) CO_2-based non-ionic surfactants: solvent-free synthesis of poly(ethylene glycol)-block-poly-(propylene carbonate) block copolymers. *Macromol. Chem. Phys.* 214, 2848–2855
52. Cowman, C.D. *et al.* (2015) Multicomponent nanomaterials with complex networked architectures from orthogonal degradation and binary metal backfilling in ABC triblock terpolymers. *J. Am. Chem. Soc.* 137, 6026–6033
53. Li, Y. *et al.* (2015) Highly efficient one-pot/one-step synthesis of multiblock copolymers from three component polymerization of carbon dioxide, epoxide and lactone. *Chem. Sci.* 6, 1530–1536
54. Jeske, R.C. *et al.* (2008) Pre-rate-determining selectivity in the terpolymerization of epoxides, cyclic anhydrides and CO_2: a one-step route to diblock copolymers. *Angew. Chem. Int. Ed.* 47, 6041–6044
55. Huijser, S. *et al.* (2011) Ring-opening co- and terpolymerization of an alicyclic oxirane with carboxylic acid anhydrides and CO_2 in the presence of chromium porphyrinato and salen catalysts. *Macromolecules* 44, 1132–1139
56. Darensbourg, D.J. *et al.* (2012) Kinetic studies of the alternating copolymerization of cyclic acid anhydrides and epoxides, and the terpolymerization of cyclic acid anhydrides, epoxides, and CO_2 catalyzed by (salen)Cr(III)Cl. *Macromolecules* 45, 2242–2248
57. Liu, Y. *et al.* (2018) Making various degradable polymers from epoxides using a versatile dinuclear chromium catalyst. *Macromolecules* 51, 771–778
58. Bernard, A. *et al.* (2013) The influence of the metal (Al, Cr, and Co) and the substituents of the porphyrin in controlling the reactions involved in the copolymerization of propylene oxide and

cyclic anhydrides by porphyrin metal (III) complexes. *Polymer* 54, 2639–2646

59. Wang, X. *et al.* (2014) Highly active bifunctional cobalt-salen complexes for the synthesis of poly(ester-block-carbonate) copolymer via terpolymerization of carbon dioxide, propylene oxide, and norbornene anhydride isomer: roles of anhydride conformation consideration. *J. Polym. Sci. A Polym. Chem.* 52, 789–795
60. Saini, P.K. *et al.* (2014) Di-magnesium and zinc catalysts for the copolymerization of phthalic anhydride and cyclohexene oxide. *Polym. Chem.* 5, 6068–6075
61. Kernbichl, S. *et al.* (2017) CO_2-controlled one-pot synthesis of AB, ABA, block and statistical terpolymers from β-butyrolactone, epoxides and CO_2. *J. Am. Chem. Soc.* 139, 6787–6790
62. Kernbichl, S. *et al.* (2019) Terpolymerization of β-butyrolactone, epoxides and CO_2: chemoselective CO_2-switch and its impact on kinetics and material properties. *Macromolecules* 52, 8476–8483
63. Zhu, Y. *et al.* (2015) Selective polymerization catalysis: controlling the metal chain end group to prepare block copolyesters. *J. Am. Chem. Soc.* 137, 12179–12182
64. Stößer, T. and Williams, C.K. (2018) Selective polymerization catalysis from monomer mixtures: using a commercial Cr-salen catalyst to access ABA block polyesters. *Angew. Chem. Int. Ed.* 57, 6337–6341
65. Saini, P.K. *et al.* (2017) Zinc versus magnesium: orthogonal catalyst reactivity in selective polymerizations of epoxides, bio-derived anhydrides and carbon dioxide. *Chem. Eur. J.* 23, 4260–4265
66. Nakano, K. *et al.* (2011) Stereocomplex of poly(propylene carbonate): synthesis of stereogradient poly(propylene carbonate) by regio- and enantioselective copolymerization of propylene oxide with carbon dioxide. *Angew. Chem. Int. Ed.* 50, 4868–4871
67. Li, Y. *et al.* (2017) CO_2-based amphiphilic polycarbonate micelles enable a reliable and efficient platform for tumor imaging. *Theranostics* 7, 4689–4698
68. Yang, G.-W. *et al.* (2017) Directed self-assembly of polystyrene-*b*-poly(propylene carbonate) on chemical patterns via thermal annealing for next-generation lithography. *Nano Lett.* 17, 1233–1239
69. Chen, S. *et al.* (2015) Exploring the application of sustainable poly(propylene carbonate) copolymer in toughening epoxy thermosets. *ACS Sustain. Chem. Eng.* 3, 2077–2083
70. Subhani, M.A. *et al.* (2016) Transparent films from CO_2-based polyunsaturated poly(ether carbonate)s: a novel synthesis strategy and fast curing. *Angew. Chem. Int. Ed.* 55, 5591–5596
71. Sulley, G.S. *et al.* (2020) Switchable catalysis improves the properties of CO_2-derived polymers: poly(cyclohexene carbonate-*b*-ε-decalactone-*b*-cyclohexene carbonate) adhesives, elastomers, and toughened plastics. *J. Am. Chem. Soc.* 142, 4367–4378