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Review

Carbon dioxide-based functional polycarbonates: Metal catalyzed copolymerization of CO_2 and epoxides

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ABSTRACT

Proof of principles studies by Inoue and coworkers in the late 1960s clearly illustrated the poorly controlled coupling of CO_2 and epoxides to provide polycarbonates. These early studies utilizing inadequately defined zinc catalysts derived from diethyl zinc and water have led to the development of a variety of catalysts for these processes over the last two decades. Numerous catalyst systems have been shown to be very effective and selective at affording perfectly alternating copolymers, including those with high levels of regio- and stereo-selectivity. The vast majority of the current literature reports upon the synthesis of hydrophobic polycarbonates which lack functionalities. In this review we will summarize the reports which utilize these well-developed metal-catalyzed CO_2/epoxides copolymerization processes to prepare high value-added functionalized polymeric materials for a variety of applications.

Contents

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1. Introduction

Polycarbonates (PCs) are a class of thermoplastic polymers containing carbonate units in their chemical structure. The most common type of polycarbonates on the market is bisphenol A (BPA) polycarbonate. It is an aromatic polycarbonate with a high glass transition temperature (T_g) of 140–155 °C. BPA polycarbonate is widely used in numerous industrial applications including automotive interiors, sunglasses, bulletproof windows, medical devices [1] et al. Compared to aromatic polycarbonates, aliphatic polycarbonates have received little commercial attention due to their low heat resistance and high susceptibility to hydrolysis. Their industrial applications are mostly limited to low molecular weight polycarbonate polyols for polyurethane production. Recently, aliphatic polycarbonates have attracted significant attention in the biomedical field due to their biocompatibility and biodegradability. One of the most investigated aliphatic polycarbonates is poly (trimethylene carbonate) (PTMC). Unlike other degradable polymers like polyester, PTMC degrades into non-acidic diols and carbon dioxide which are less likely to cause adverse effects such as inflammation. PTMC and its copolymers have been fabricated into nanoparticles [2,3], sutures [4,5] and hydrogels [6,7] for applications in tissue engineering and drug delivery.

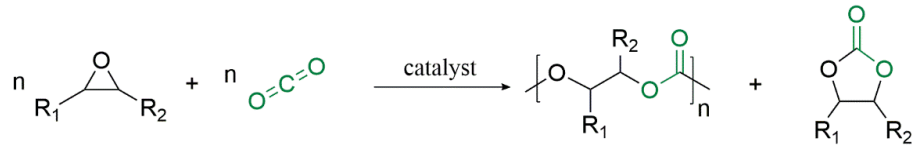
One attractive method to produce polycarbonates is the catalytic coupling of CO_2 and epoxides (Scheme 1), first discovered by Inoue in 1969 [8,9]. This synthetic route provides many advantages. It uses the nontoxic and inexpensive CO_2 as a carbonyl source instead of the toxic phosgene employed in traditional polycondensation methods. Polycarbonates made from this route can contain up to 50% (by moles) of CO_2 and therefore will rely less on fossil-based feedstocks and will have a significantly reduced carbon footprint. This process usually does not require extraneous solvent as many epoxides themselves are liquid and can dissolve the catalyst and the resulting polymer. Several side reactions that can occur in the process include the formation of ether linkages due to consecutive ring-opening of epoxides and production of cyclic carbonates due to a backbiting process. Along with the normal chain propagation process, chain transfer reactions also need to be considered. Chain transfer reactions, while reduce the chain length of the final products, can be exploited to achieve precise control of molecular weights which are determined by the concentration of both the catalyst and chain transfer agents.

Two of the most investigated epoxides are cyclohexene oxide (CHO) and propylene oxide (PO). Generally, copolymerization of CHO and CO_2 can proceed readily using a variety of catalysts under mild conditions and exhibits a high polycarbonate selectivity even at high temperatures. PO can also react with CO_2 quiet easily to form polycarbonate. However, in the latter instance, judicious choice of catalysts and reaction temperatures are usually required to eliminate formation of the cyclic by-products. Poly(cyclohexene carbonate) (PCHC) and poly(propylene carbonate) (PPC) burn cleanly and completely in air without emitting harsh residues, and thus can be used as sacrificial binders in electronics and ceramics manufacturing. Compared to PCHC, PPC exhibits more favorable mechanical properties and have found wider applications. For instance, PPC is already finding use as a degradable packaging material, and its low M_w polyols can substitute traditional petro-based polymers in polyurethane production. To date, PPC and PCHC have been commercially synthesized from CO_2 by many companies such as Saudi Aramco [10], Empower Materials [11], Econic Technologies [12] and Covestro [13].

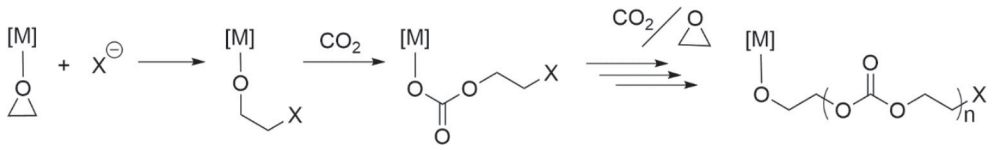
Despite the advantages of PPC and PCHC, their lack of functionalities and relatively low glass transition temperatures (T_g = 37 °C for PPC, 115 °C for PCHC) have limited their use in high value-added and functional materials. In order to expand the application scope of CO_2-based polycarbonates, two topics are of current interest. One is the synthesis of more diverse polycarbonates with different functionalities. For clarification, functional polycarbonates discussed here are not characterized by their thermal properties, but rather by their inherent functionalities. Both pendant and terminal functional groups can be incorporated into the polymer. The second topic of interest is the preparation of CO_2-PCs with high thermal resistance, characterized with a high glass transition temperature (T_g) and/or melting temperature (T_m). This report will focus on the current development of more diverse CO_2-derived polycarbonates with improved performance. In particular, synthetic strategies to expand polymer functionalities and to improve the thermal properties will be presented. Finally, recent applications of CO_2-based polycarbonates will be highlighted.

2. Catalysts development for the copolymerization of CO_2 and epoxides

The coupling reaction between CO_2 and an epoxide usually requires the application of a metal catalyst. The generally accepted mechanism for production of polycarbonates is depicted in Scheme 2. The copolymerization is initiated by the coordination of the epoxide and its subsequent ring-opening by the nucleophilic cocatalyst (X^-) to provide a metal-alkoxide species. This metal alkoxide intermediate then undergoes CO_2 insertion to form a metal-carbonate. The successive alternating incorporation of epoxides and CO_2 produces linear polycarbonates. It is generally proposed that the rate-determining step involves epoxide ring-opening by the growing anionic polymer chain rather than CO_2 insertion [14].



Scheme 1. Coupling between epoxide and CO_2 to yield the desired copolymer, and cyclic carbonate side-product.



Scheme 2. Generalized mechanism for the production of polycarbonates.

Inoue first discovered the coupling of CO_2 and propylene oxide in 1969 utilizing a heterogeneous catalyst based on diethyl zinc and water [8]. Since then, numerous catalysts, both heterogeneous and homogeneous, have been developed for this transformation. The most widely applied heterogeneous catalysts include zinc glutarate (or other carboxylates) and double metal cyanides [15–18]. These catalysts usually require more forcing reaction conditions (high catalyst loading, elevated temperature and CO_2 pressure) than homogeneous catalysts and often result in polymers with a significant amount of ether defects and broad molecular weight distributions. In addition, it is difficult to investigate the reaction mechanisms using these heterogeneous catalysts due to the lack of active-site control. Nevertheless, these catalysts are quite robust and easy to prepare from inexpensive starting materials, and thereby are currently applied in industrial processes for CO_2-based polycarbonate production. The first single-site catalyst for CO_2/epoxides copolymerization was discovered by Inoue and coworkers in 1986 [19]. In this instance, the catalyst system employed was an aluminum-porphyrin complex coupled with a quaternary organic salt or triphenylphosphine. Despite the low activity of these catalysts, they provided polymers with almost perfect alternating structures and narrow molecular weight distributions. Following Inoue's discovery, various homogeneous systems have been developed to achieve improved activity and polycarbonate selectivity. The representatives are zinc phenoxides [20,21], β-diiminate zinc alkoxides [22], metalloporphyrins [23,24], metal-salen or -salan complexes [25-27] as well as bimetallic macrocyclic derivatives [28].

To date, the most widely studied catalysts are derived from salen cobalt complexes [29]. The first generation of this type of catalysts is a binary system comprising of a (salen)$Co^{III}X$ complex (X = Cl^{-1}, N_3^{-1} or 2,4-dinitrophenolate, *etc.*) and an exogenous onium salt co-catalyst, typically quaternary ammonium ($^nBu_4NX$) or phosphonium salt (PPNX) (Fig. 1). Recent kinetic studies revealed a fractional reaction order between 1 and 2 in catalyst concentration [30–32], indicating concurrent bimetallic and monometallic pathways in the rate-limiting ring-opening step (Fig. 2). The binary catalysts yield copolymers with perfect alternating structures and can achieve good levels of regio- and stereochemistry control when chiral ligands are used. Unfortunately, a considerable amount of cyclic byproducts are produced at elevated temperatures and/or at higher degree of conversion. In addition, due to the binary nature, these systems typically exhibit a long induction period and low activity at low catalyst loadings.

To overcome these limitations, the second generation of (salen)Co^{III} catalysts were developed by covalently attaching the cocatalyst to the ligand backbone and as such were named bifunctional catalysts (Fig. 3) [33–37]. As the catalyst and cocatalyst are linked within one molecule, these compounds can maintain high activity at extremely low catalyst loadings. The appended ammonium arms can attract the dissociated anionic polymer chain through electrostatic interaction and prevent it from drifting into the bulk solution. This allows the polymeric chain to quickly return to the metal center and continue chain growth. Furthermore, the

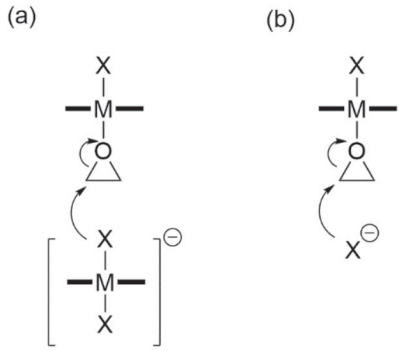


Fig. 2. Possible pathways for epoxide ring opening by binary catalysts: (a) bimetallic ring-opening and (b) monometallic ring-opening.

electrostatic interaction suppresses the back-biting process resulting in high polycarbonate selectivity (Fig. 3). These bifunctional catalysts are by far some of the most active catalysts for CO_2/epoxides copolymerization and unlike their simple counterparts can operate at high temperatures (70–120 °C) without losing polycarbonate selectivity.

3. Development of functional polycarbonates from CO_2

Introduction of pendant functional groups allows for the tailoring of material properties, such as solubility, biodegradability, stimuli-response, and self-healing ability. Functional polycarbonates with pedant functionalities can be prepared *via* i) direct copolymerization of a functional monomer with CO_2, or ii) post-polymerization modification of polymer scaffolds bearing reactive groups. End functionalized polycarbonates are also of interest. The presence of terminal functional groups can lead to block copolymer formation, or for some applications such as coatings and adhesives, can improve the compatibility between different polymers. For CO_2-epoxides copolymers, end functionalities can be introduced through addition of chain transfer agents.

3.1. Direct polymerization of functional monomers

With the development of highly efficient catalyst systems, a large family of functional epoxides has been successfully copolymerized with CO_2 to produce polycarbonates with pendant functionalities. The functional epoxides can be classified into four main categories based on their structures: terminal epoxides, glycidyl ethers, 4-substituted cyclohexene oxides, and other functional alicyclic epoxides. Some of these epoxide monomers can be prepared from renewable feedstocks [38].

3.1.1. Terminal epoxides

Copolymerization of CO_2 and terminal epoxides (Fig. 4) with electron-withdrawing groups (EWG), such as styrene oxide (SO) [39–43], epichlorohydrin (ECH) [44–47] and 2-vinyloxirane (VIO)

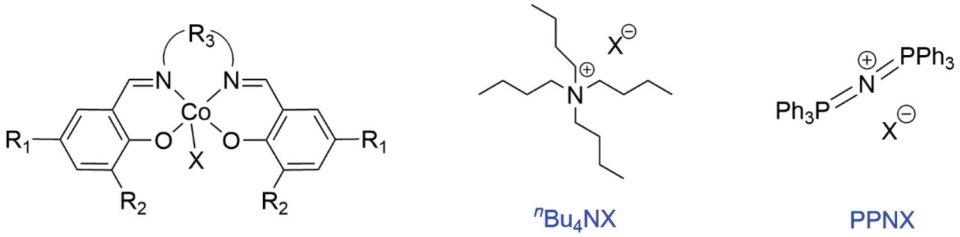


Fig. 1. (Salen)$Co^{III}X$ catalyst (left) with onium salt cocatalysts (right).

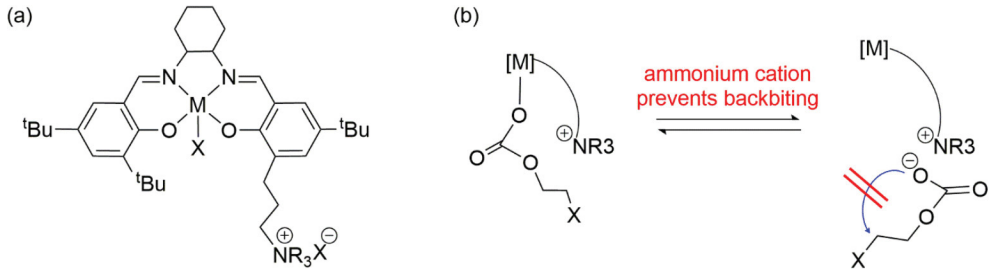


Fig. 3. (a) Bifunctional (salen)Co^{III} catalyst, (b) proposed mechanism for preventing backbiting by bifunctional catalysts.

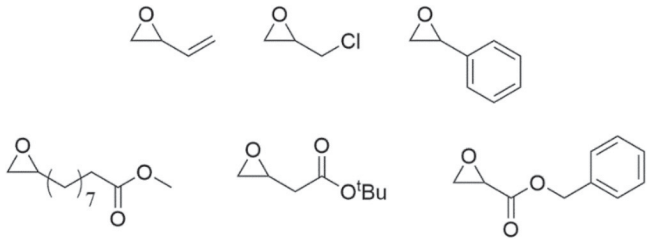


Fig. 4. Selected terminal epoxides used in CO_2 copolymerization reactions.

[48], has been extensively studied, in comparison with propylene oxide/CO_2 coupling, to understand the influence of substituents on reaction activity, regioselectivity, and product selectivity. Generally, electron-withdrawing substituents reduce the epoxides' coordination ability to the metal center, resulting in a higher activation energy compared to propylene oxide. With regard to regioselectivity, the methine C—O bond is more prone to ring-opening due to a more electrophilic carbon center. This in turn would facilitate the formation of cyclic carbonate byproducts *via* backbiting to the methine carbon of the adjacent carbonate unit. When the binary (salen)Co^{III}X/PPNX (X = 2,4-dinitrophenolate (DNP)) catalyst system was employed, copolymerization of CO_2 and VIO [48] or ECH [44] produced significant amounts of cyclic carbonates at 25 °C, the latter one showing only 10% polymer selectivity. On the other hand, the bifunctional (salen)Co^{III}X complex exhibited much higher polymer selectivities (92–100%), affording high molecular weight copolymers with low polydispersities. For SO/CO_2 coupling reactions, whereas both the binary and bifunctional systems (DNP as the initiating anion) yielded polymers with more than 99% selectivity, the latter catalyst showed a much higher activity and could maintain its high performance at very low catalyst loadings [43].

Several terminal epoxides containing ester functionalities have been applied to produce CO_2 copolymers. In 2014, Qi et al. reported the catalytic coupling of epoxy methyl 10-undecenoate (EMU) and CO_2 using a double metal complex [Zn-Co^{III} DMCC] to produce an ester functionalized polycarbonate [49]. Notably, the epoxy monomer can be obtained from a bio-renewable feedstock. The EMU/CO_2 copolymers displayed low T_g values of −38 °C to −44 °C depending on the molecular weights as a result of the long alkyl side chain.

Another two ester functionalized CO_2 copolymers, poly(benzyl glycidate carbonate) (PBGC) [50] and poly(*tert*-butyl 3,4-dihyroxybutyrate carbonate) ($P^tBuDHBC$) [51], have been prepared by the Grinstaff group and the Darensbourg group, respectively (Fig. 5). The monomers employed in both studies carried a bulky substituent at the methine carbon which in turn promoted ring-opening to occur predominantly at the sterically less hindered C_β—O bond during the copolymerization reactions. Hydrogenolysis of PBGC afforded poly(glyceric acid carbonate) (PGAC) which was shown to degrade in aqueous solutions. Similarly, the *tert*-butyl group in $P^tBuDHBC$ could be cleaved to produce degradable poly (3,4-dihydroxybutyric acid carbonate) (PDHBAC) which compared to PGAC contained one extra carbon between the polymer backbone and the COOH group. Of importance, a detailed degradation study of PDHBA showed that it could degrade readily in basic solutions into 3,4-dihyroxyl butyric acid, which is a normal human

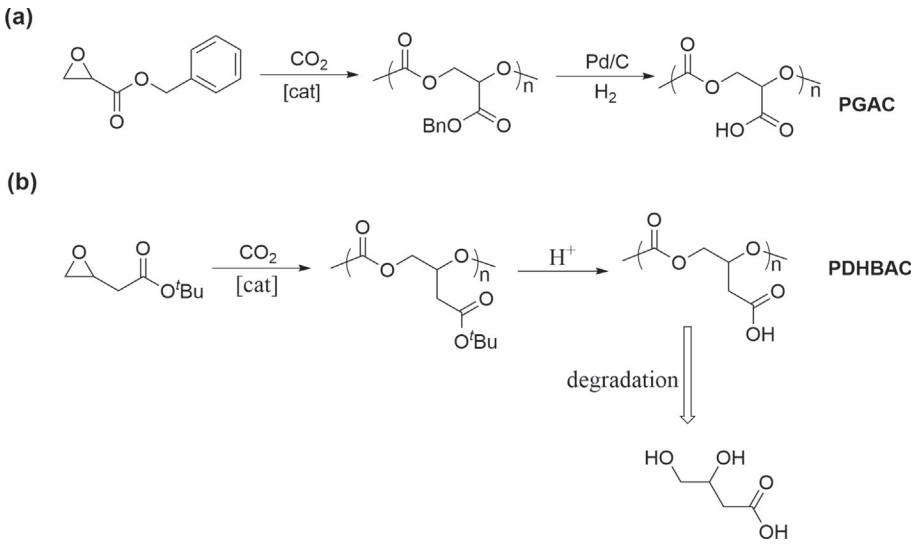


Fig. 5. (a) Synthesis of poly(glyceric acid carbonate) (PGAC) through copolymerization of benzyl glycidate and CO_2 followed by hydrogenolysis [50]; (b) synthesis of poly(3,4-dihyoxyl butyric acid) (PDHBA) through copolymerization of *tert*-butyl 3,4-epoxybutanoate and CO_2 followed by hydrolysis [51].

metabolite. PDHBA provides a human-friendly and environmentally benign platform for biomedical applications.

3.1.2. Glycidyl ethers

Glycidyl ethers can be readily prepared from substitution reactions between epichlorohydrin and functional alcohols. To date, a large family of glycidyl ethers (Fig. 6) have been successfully copolymerized with CO_2 using Co or Zn catalysts to produce functional polycarbonates [52]. The structure versatility of glycidyl ethers allows access to various copolymers with desired physicochemical properties suitable for different applications. Moreover, using monomers containing reactive groups as alkyne [53], alkene [54–59] and furfuryl [60] enables introduction of multiple different functionalities onto a single polymer chain through post polymerization functionalization. A few representative functional polycarbonates derived from glycidyl ethers will be highlighted below; these polycarbonates all bear hydrophilic moieties along the polymer backbone. For a full summary of glycidyl ether and CO_2 copolymers, see the excellent review by Frey and Scharfenberg [52].

The groups of Frey [61] and Grinstaff [62] independently reported the synthesis of poly(1,2-glycerol polycarbonate) through copolymerization of benzyl glycidyl ether (BGE, **B**) or ethoxyethyl glycidyl ether (EEGE, **K**) with CO_2 followed by cleavage of the protecting groups (Fig. 7). Of note, synthesis of poly(1,2-glycerol carbonate) from direct coupling of glycidol and CO_2 is not feasible due to the interference of chain transfer reactions. Poly(1,2-glycerol carbonate) was not soluble in common organic solvents like dichloromethane, toluene and chloroform, indicating its enhanced hydrophilicity due to the presence of hydroxyl pendant groups. In contrast to poly(1,3-glycerol carbonate) prepared from ring-opening polymerization (ROP), poly(1,2-glycerol carbonate) exhibited a strikingly faster degradation rate with a $t_{1/2} \approx 2$–3 days [62]. The increase in degradation was attributed to the lower activation energy required for the pendant primary OH in poly(1,2-glycerol carbonate) to undergo intramolecular attack onto the carbonate linkage, compared to the secondary OH in the 1,3 isomer.

Thermal-responsive polymers have been widely studied for their biomedical applications, such as drug delivery and tissue engineering [63]. The first examples of thermal-responsive polycarbonates derived from CO_2 were reported by Wang and coworkers [64]. Epoxides (ME_nMO, **J**) containing pendant oligo(ethylene glycol) groups were copolymerized with CO_2 using the binary (salen)Co^{III} catalyst (Fig. 8). The copolymer derived from ME_2MO/CO_2 coupling exhibited a rapid and reversible thermo-responsive phase transition in water, possessing a lower critical solution temperature (LCST) of ~44.7 °C [64]. Furthermore, terpolymerization of $ME_2MO/ME_1MO/CO_2$ were conducted with various feeding ratios, yielding terpolymers with a wide range of LCST values from 0 °C to 43 °C. Soon after this work, the same group reported the synthesis of $PO/ME_3MO/CO_2$ terpolymers, which also exhibited thermal-responsive solubility in water [65]. This new class of 'smart' materials could provide a powerful platform for biomedical applications.

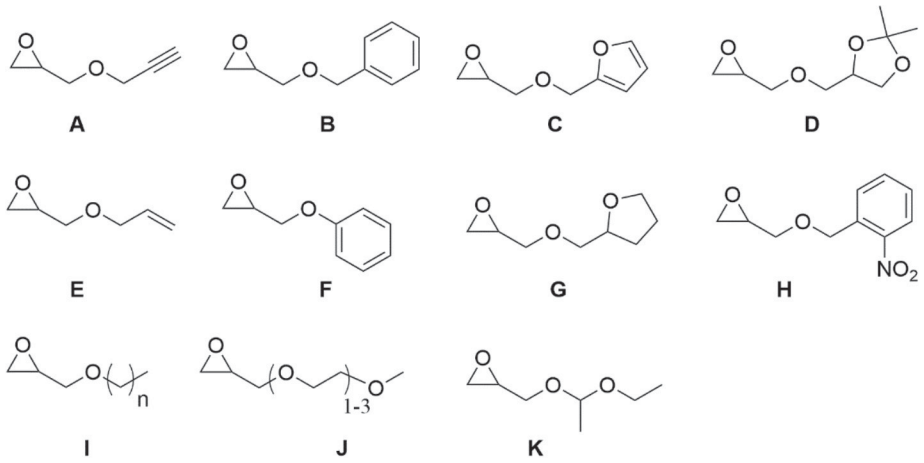


Fig. 6. Selected glycidyl ethers used in CO_2 copolymerization reactions.

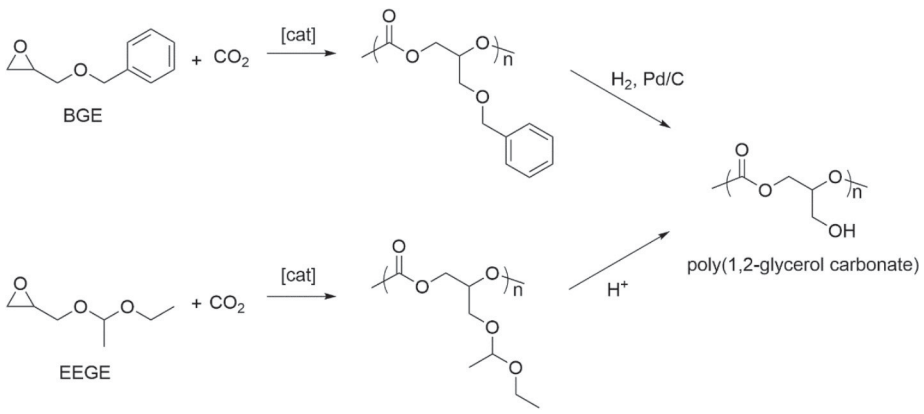


Fig. 7. Synthesis of poly(1,2-glycerol carbonate) *via* copolymerization of BGE or EEGE with CO_2 followed by deprotection [61,62].

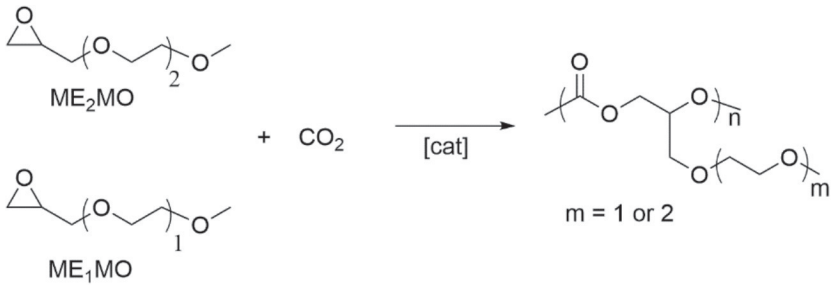


Fig. 8. Synthesis of thermo-responsive polycarbonates through coupling of ME_nMO and CO_2 [64]. ME_1MO: 2-((2-methoxyethoxy)methyl)oxirane; ME_2MO: 2-((2-(2-methoxyethoxy)ethoxy)methyl)oxirane.

3.1.3. 4-Substituted cyclohexene oxides

4-Substituted cyclohexene oxides (Fig. 9) have also been investigated in the copolymerization reaction with CO_2 to produce functional polycarbonates. An interesting example was reported by the Darensbourg group, describing the coupling of CO_2 and 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane to form a CO_2 soluble polycarbonate [66]. Upon dissolution of the crude polymer in supercritical CO_2 and subsequent release of CO_2 pressure, the metal catalyst was effectively removed. Furthermore, the trimethoxysilane functionality could be utilized to prepare a cross-linked network through Si—O—Si bond formation.

Coates and co-workers employed a [(BDI)ZnOAc] complex to study the catalytic coupling of CO_2 with a variety of 4-substituted cyclohexene oxides containing vinyl, ketal, triethylsiloxy, polyethylene glycol (PEG), alkyl and fluorophilic functionalities [67]. The copolymerization reactions were demonstrated to behave in a living manner. Furthermore, various multiblock copolymers containing lipophilic, hydrophilic and fluorophilic units in a single chain were prepared by sequential addition of different monomers upon complete consumption of a former monomer.

Two ester-functionalized PCHC derivatives were synthesized by Gruter and co-workers through copolymerization reactions between CO_2 and 3,4-cyclohexene-oxide-1-carboxylic acid methyl ester or 3,4-cyclohexene-oxide-1-carboxylic acid phenyl ester using a BDI zinc catalyst [68]. A thorough MALDI-TOF-MS analysis of the isolated polycarbonates revealed the occurrence of transesterification side reactions. Consequently, branched and cyclic polymer structures were formed, which led to a broadening of the molecular weight.

3.1.4. Other functional alicyclic epoxides

Several other functional alicyclic epoxides (Fig. 10) in addition to 4-substituted cyclohexene oxides have been employed in the copolymerization reactions with CO_2. The Darensbourg group and others reported the synthesis of fully renewable functional polycarbonates from the catalytic coupling of CO_2 and a bio-derived epoxide, 1,4-cyclohexadiene oxide (1,4-CHDO, **L**) [69–71]. Several catalyst systems have been employed for the copolymerization reaction, including di-zinc and di-magnesium macrocyclic catalysts [71], Cr- and Co-based salen complexes [69,71], and a (porphyrin)$Co^{III}Cl$/4-dimethylaminopyridine (DMAP) system [70]. The highest activities were observed with the binary (salen)$M^{III}X$/PPNX (M = Co or Cr, X = Cl^{-1} or 2,4-dinitrophenolate) catalysts. In the process catalyzed by Co^{III} catalyst, high copolymer selectivity (>99%) was observed, whereas employing the Cr^{III} system at its operation temperatures of 80–90 °C, the reactions gave a significant amount of cyclic carbonates in addition to the desired polymer [69]. Both *cis*- and *trans*-cyclic carbonates were produced (Fig. 11).

1,3-Cyclohexadiene oxide (1,3-CHDO, **M**), an isomer of 1,4-CHDO, was also investigated in the copolymerization reaction with CO_2 to produce polycarbonates [72]. Notably, under the same reaction conditions, 1,3-CHDO exhibited a strikingly faster rate in the

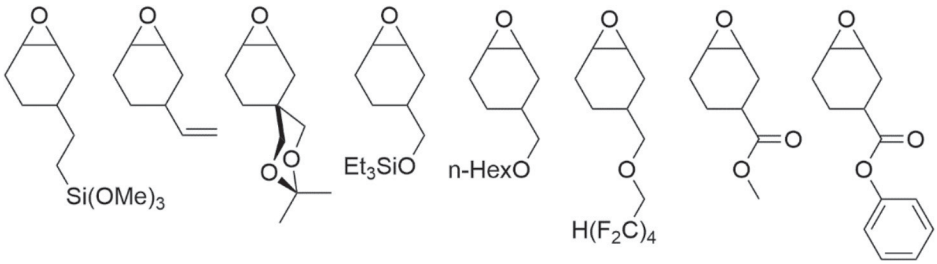


Fig. 9. Selected 4-substituted cyclohexene oxides used in CO_2 copolymerization reactions.

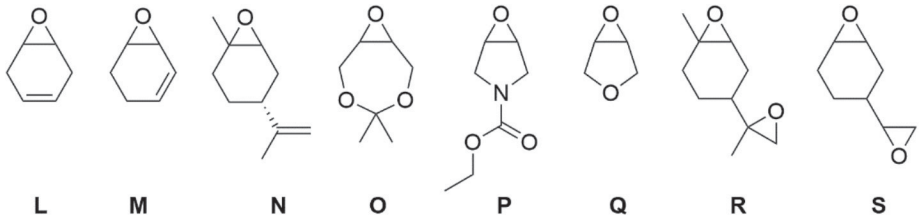


Fig. 10. Functional alicyclic epoxides used in CO_2 copolymerization reactions.

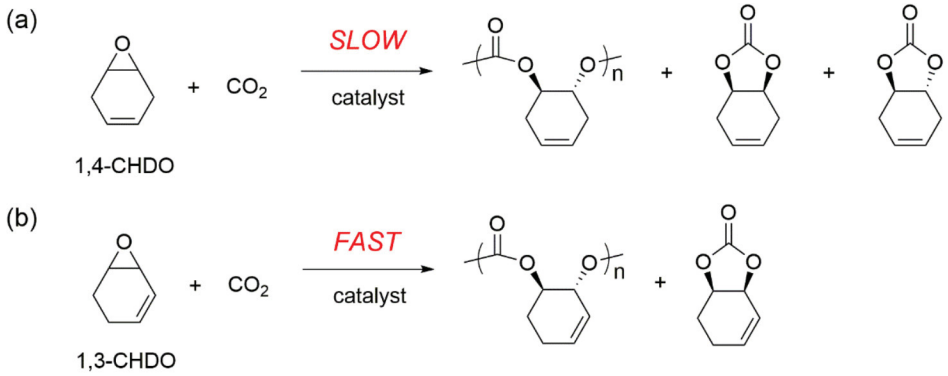


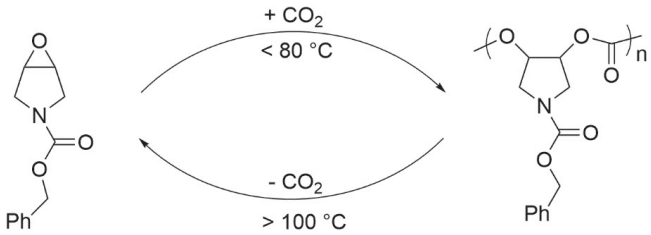
Fig. 11. (a) Copolymerization of 1,4-CHDO with CO_2 to produce polycarbonate and *cis*- and *trans*-cyclic carbonate byproducts [69]. (b) Copolymerization of 1,3-CHDO with CO_2 to yield polycarbonate and *cis*-cyclic carbonate byproduct [72].

coupling reaction with CO_2 than its 1,4-analogue. In reactions catalyzed by Cr^{III} catalysts, cyclic carbonate byproducts were observed, but only existing in the *cis*-form. This is in stark contrast to the copolymerization of 1,4-CHDO and CO_2. A detailed computation study was performed to understand the dramatic behavioral differences between the two epoxide isomers. Poly(1,3-cyclohexadiene carbonate) displayed a T_g of 104–108 °C, about 15 °C lower than its 1,4-copolymer counterpart.

A particularly attractive epoxide for polycarbonate production is *R*-limonene oxide (LO, **N**) as it can be readily obtained from a bio-derived precursor (limonene, which is a major component of citrus oils) [73,74]. Catalytic coupling of *R*-LO and CO_2 was first achieved by Coates and co-workers in 2004 using BDI zinc catalysts, affording copolymers with moderate molecular weight (10.8 kg/mol) and high regio- and stereo-regularity [75]. Very recently, significant progress has been made in poly(limonene carbonate) (PLC) production. New catalysts based on BDI zinc derivatives [76] and aluminum amino-triphenolate complexes [77] were developed and showed moderate to high activities towards *R*-LO/CO_2 copolymerization. Notably, Greiner was able to scale up PLC production to kilograms per batch and achieve high molecular weights of >100 kg/mol [78]. Moreover, the thermal, mechanical and gas permeability properties of PLC have been fully analyzed by Reiger and co-workers [78,79]. High M_w PLC exhibits a wide range of attractive properties, *e.g.* high thermal stability, excellent transparency, good hardness as well as high gas permeability, rendering PLC a promising material for 'breathing glass' applications [79].

Limonene dioxide (LDO, **R**), the diepoxide counterpart of LO, was reported to undergo chemoselective alternating copolymerization with CO_2 in the presence of a BDI Zn catalyst to yield poly(limonene-8,9-oxide carbonate) (PLOC) with epoxy pendant groups [80]. No branching or crosslinking were observed. The resultant polycarbonate PLOC displayed a high T_g of up to 135 °C. In a separate report by Kleij, PLOC was synthesized by epoxidation reaction of PLC [81].

Lu and co-workers reported the copolymerization of CO_2 with a number of functional epoxides fused with five- or seven-membered rings [82–84]. For instance, they synthesized a series of *meso*-3,5-dioxaepoxides and investigated their coupling reactions with CO_2 using chiral catalyst systems based on biphenol-linked dinuclear $Co^{(III)}$ complexes [83]. For the dimethyl substituted dioxaepoxide, 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO, **O**), its CO_2 copolymer PCXC was highly isotactic (ee >99%) and semicrystalline possessing a high T_m of 242 °C. Moreover, PCXC could undergo hydrolysis to generate pendant hydroxyl groups and was subsequently applied as macroinitiators for lactide ring-opening. Very recently, the same group prepared a completely



Scheme 3. Temperature-dependent copolymerization and depolymerization of poly(BEP carbonate) [84].

recyclable polycarbonate based on a N-hetero-epoxide, 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine (BEP, **P**) [84]. At 60 °C, BEP was selectively converted to the corresponding polycarbonate using dinuclear chromium complexes coupled with a PPNX (X = NO_3^{-1}, N_3^{-1}) cocatalyst. Upon heating up to 100 °C, the copolymer degraded readily back into the epoxide monomer in quantitative yield. Remarkably, this copolymerization/depolymerization process could be recycled several times by simply switching the temperature (Scheme 3).

3.2. Postpolymerization functionalization

Postpolymerization functionalization provides a powerful synthetic tool to access multiple functional polymers through a single scaffold and more importantly allows the introduction of functionalities that are incompatible with the polymerization process. As mentioned earlier, CO_2-derived polycarbonates containing reactive alkyne, alkene, furfuryl and epoxy groups have been prepared by many research groups. These copolymers can be modified *via* postpolymerization functionalization to yield polymers with a wide range of properties.

With advantageous features like high efficiency, little oxygen inhibition, quantitative conversion and absence of side products [85], thiol-ene click chemistry has been widely employed to anchor new functionalities onto the polymer backbone. For instance, the Darensbourg group functionalized poly(1,2-vinyloxirane carbonate) *via* thiol-ene click chemistry with —OH and —COOH functionalities [48]. As a result, the hydrophilicity of the polymer was greatly enhanced. Following this work, the same group demonstrated the modification of a block copolymer P(allyl glycidyl ether carbonate)-*b*-PPC-*b*-P(allyl glycidyl ether carbonate) with various thiols to yield amphiphilic polycarbonates with negatively- or positively- charged functionalities [54]. These amphiphilic polymers were shown to undergo self-assembly to form micelles upon dissolution in deionized (DI) water. To our knowledge, this marked

the first time that polymeric nanoparticles have been prepared from CO_2-derived block polycarbonates. Another example of this thiol-ene chemistry is the functionalization of poly(4-vinyl cyclohexene carbonate) to generate pendant hydroxyl groups [86]. Subsequent ring-opening polymerization of ε-caprolactone initiated by the —OH yielded well-defined brush copolymers.

Fully renewable poly(limonene carbonate) (PLC) was also subjected to thiol-ene click chemistry (Scheme 4), affording polymers with a wide range of properties [87]. Modification of PLC with 2-mercaptoethanol or mercaptoacetic acid greatly enhanced its hydrophilicity; the latter functionality endowed the material with pH-dependent solubility in water. Addition of butyl-3-mercaptopropionate followed by curing transformed the engineering thermoplastic into an elastic rubber, resulting in a decrease in Young's modulus by three orders of magnitude and a T_g drop by 125 °C. PLC was also treated with 2-(diethylamino)ethanethiol and subsequent quaternation with benzyl bromide produced a cationic polymer possessing antibacterial properties. Besides thiol-ene reactions, the double bond of PLC can undergo acid-catalyzed electrophilic addition with OH-end capped polyethylene glycol to enhance its hydrophilicity. However this reaction was limited to short reaction times and thereby only partial (~18%) conversion of the double bond was achieved.

As discussed previously, poly((limonene-8,9-oxide carbonate) (PLOC) carrying epoxide functionalities was synthesized through chemoselective copolymerization of limonene dioxide and CO_2 [80]. PLOC can be modified by epoxide ring-opening reactions using various nucleophiles including thiols and carboxylic acids, without causing degradation of the polycarbonate backbone (Scheme 4). Moreover, the pendant epoxide can undergo CO_2 insertion to produce a poly(limonene)dicarbonate (PLDC) with cyclic carbonate functionalities. T_g values of these resulting PLOC derivatives expand a wide temperature range of 13–146 °C depending on the structure of the anchored functionalities. Remarkably, PLDC (M_n = 11.2 kg/mol) exhibited a high T_g of 146 °C, very close to that of BPA-based polycarbonates. Alternatively, PLDC was synthesized by a 'two-step' process from PLC by Kleij [81]. The polymer had a higher molecular weight of 15.0 kg/mol and its T_g was reported to be up to an unprecedented 180 °C.

The Frey group prepared propargyl-functional poly(carbonate)s through terpolymerization of glycidyl propargyl ether (GPE), glycidyl methyl ether (GME) and CO_2 using a simple zinc-pyrogallol catalyst system [53]. Further functionalization of the polymer was achieved through copper-catalyzed Huisgen 1,3-dipolar cycloaddition reaction between the pendant alkyl groups and benzyl azide.

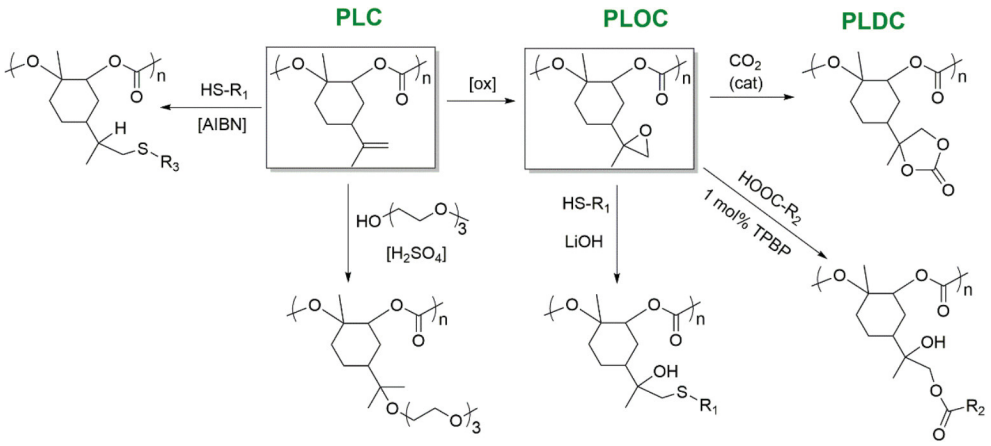
The Wang group utilized Diels-Alder (DA) reactions to post-modify a furfuryl glycidyl ether (FGE)/CO_2 copolymer (PFGEC) [88]. PFGEC tends to cross-link upon exposure to air due to the presence of furfuryl functionalities. Stabilization of the copolymer was achieved by DA reaction between the furfuryl ring and N-phenylmaleimide. Frey and co-workers prepared terpolymers of FGE, GME and CO_2 and later functionalized these terpolymers *via* Diels-Alder chemistry using various maleimide derivatives [60]. Furthermore, this transformation was demonstrated to be reversible.

3.3. Terminal functionalization via addition of chain transfer agents

It is desired to synthesize polycarbonates with multiple hydroxyl end functionalities (PC polyols) as they can be used as building blocks to obtain more complex polymer structures. Typically, the hydroxyl end groups are introduced by addition of chain transfer agents (CATs), such as water [54,89–91], diols [92], dicarboxylic acids [92,93] or other compounds containing —OH or —COOH groups. One of the potential applications of the PC polyols is in the industrial production of polyurethane (PU).

While most CO_2-derived polycarbonate polyols reported are telechelic polymers due to ease of synthesis, it is also of interest to investigate multifunctional branched polymers. To date, several groups have been able to synthesize star-shaped [94–98] and hyperbranched [99,100] polycarbonate polyols. These structures possess unique rheological, mechanical and self-assembly properties, and exhibit improved solubility due to the large number of functional groups [101]. Very recently, Frey and co-workers employed hyperbranched poly(ethylene oxide) (*hb*PEO) or poly (butylene oxide) (*hp*PBO) polyether polyols as macro CATs in the copolymerization reaction of CO_2 and ethylene oxide or 1,2-butylene oxide [95]. Multiarm star polymers with high content of hydroxyl end groups were synthesized; their glass transition temperatures and intrinsic viscosity could be tuned in a broad range by varying the ratio of polyether units and polycarbonate units.

Hyperbranched polymers can be synthesized by employing an 'inimer' (initiator-monomer) in the copolymerization reaction [99,100]. Using this strategy, again the Frey group prepared hyperbranched polycarbonate polyols from terpolymerization of CHO, (4-hydroxymethyl)cyclohexene oxide (HCHO) and CO_2 (Fig. 12) [100]. HCHO is an inimer as it contains a polymerizable epoxy ring and an initiating (through chain transfer) hydroxyl group. Consequently, the incorporation of HCHO in the coupling reactions leads to the branching of the polymers. By varying the ratio of HCHO and CHO, the degree of branching and the number of hydroxyl end



Scheme 4. Modifications of poly(limonene carbonate) and poly(limonene-8,9-oxide carbonate [80,81,87].

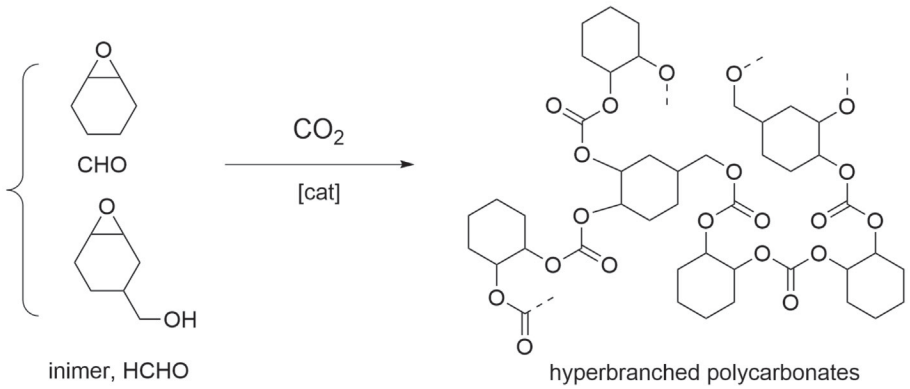


Fig. 12. Synthesis of hyperbranched polycarbonates based on (4-hydroxymethyl)cyclohexene oxide (HCHO), cyclohexene oxide (CHO), and CO_2 [100].

groups could be adjusted. Compared to their linear counterpart, the hyperbranched polycarbonates displayed lower glass transition temperatures and intrinsic viscosities. These multifunctional polycarbonate polyols can be used in rigid polyurethane foam applications.

4. Development of CO_2/epoxides copolymers with improved thermal properties

Most CO_2-based polycarbonates are amorphous, and their low glass transition temperatures have prevented their use in many applications, especially as structural materials. In order to improve the thermal deformation resistance of CO_2-PCs, several synthetic strategies have been employed, including (i) incorporation of bulky and rigid monomers, (ii) controlling the stereochemistry of epoxide enchainment, (iii) construction of terpolymers or block polymers, and (iv) formation of cross-linked networks.

4.1. Incorporation of bulky and rigid monomers

The rigidity of the polymer backbone exerts a significant influence on the glass transition temperature of the material. The presence of a bulky rigid moiety along the backbone can hinder segmental mobility of the polymer and therefore increase its T_g. By introducing a bulky epoxide in the copolymerization reaction, it is relatively straightforward to enhance the thermal resistance of the resulting polycarbonate. Thanks to the development of novel transition metal catalysts, several challenging epoxides with bulky structures have been successfully copolymerized with CO_2 to produce polycarbonates (structures see Fig. 13) with T_g values that are comparable to that of industrial BPA polycarbonate.

In a seminal study, Darensbourg and Wilson reported the catalytic coupling of indene oxide (IO) and CO_2 to produce the corresponding poly(indene carbonate) (PIO) with a T_g of up to 138 °C [102,103]. This is the first example of incorporating an aromatic group in the backbone of CO_2-based polycarbonates. Both the binary and bifunctional (salen)Co^{III} catalysts were employed for the copolymerization; with the latter catalyst exhibiting a much higher polymer selectivity under the same reaction conditions. However, the catalytic activity still remained low (TOF = 12 h^{-1}) and only moderate molecular weights (no more than 9700 g/mol) were achieved. Moreover, the asymmetrical nature of IO renders difficulty to further tune the thermal properties by controlling the stereochemistry of the ring-opening process.

Later, the same group investigated the copolymerization reaction of 1,4-dihydronaphthalene oxide (CDO) and CO_2 using various Cr^{III} catalysts [104]. It was found that the copolymer formation was highly dependent on the steric environment around the active

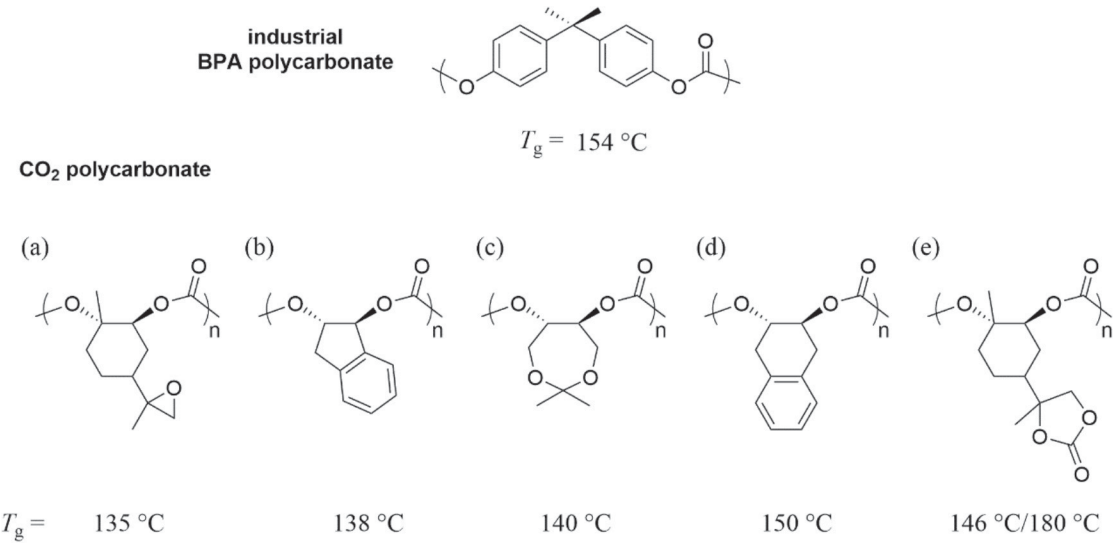


Fig. 13. (a) Poly(limonene-8,9-oxide carbonate) (PLOC), (b) Poly(indene carbonate) (PIO), (c) PCXC, (d) poly(1,4-dihydronaphthalene carbonate) (PCDC), and (e) poly (limonene)dicarbonate.

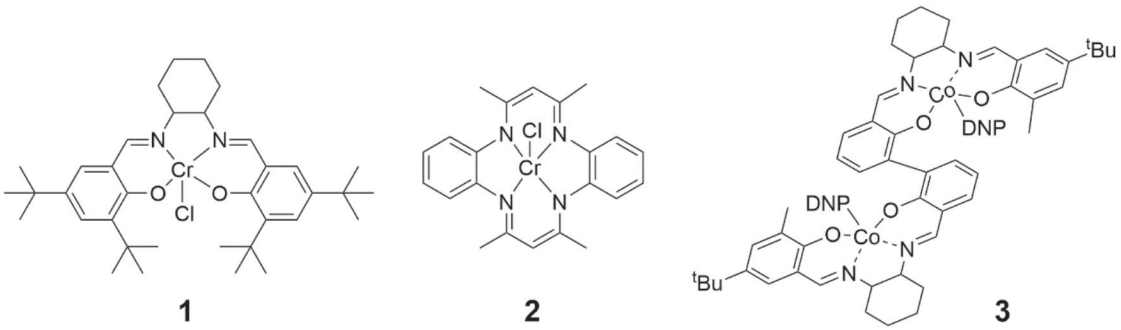


Fig. 14. Catalysts utilized for the copolymerization of 1,4-dihydronaphthalene oxide (CDO) with CO_2: the sterically crowded catalyst (salen)$Cr^{III}Cl$ **1**, tetraazaannulene-derived (tmtaa)$Cr^{III}Cl$ **2**, and biphenol-linked dinuclear (salen)$Co^{III}DNP$ **3**.

metal center. Traditional (salen)$Cr^{III}Cl$ (Fig. 14, **1**)/PPNCl system bearing bulky *tert*-butyl groups exhibited a low TOF of 8 h^{-1} at a 0.2% loading and yielded polycarbonate with 78% selectivity. In contrast, when a less sterically demanding tetramethyltetraazaannulene (tmtaa) catalyst, (tmtaa)$Cr^{III}Cl$ (Fig. 14, **2**) was employed for the copolymerization reaction, catalytic activity was increased by two folds and polymer selectivity was increased to ~89%. The highest molecular weight that was obtained in this study was 6.7 kg/mol and displayed a T_g of 136 °C. Parallel to this work, Lu and co-workers studied the catalytic coupling of CDO and CO_2 using chiral biphenol-linked dinuclear Co^{III} complexes [105]. At a 0.2% loading, the dinuclear cobalt complex **3** (Fig. 14) coupled with 2 equiv of PPNDNP cocatalyst showed a very high activity of 247 h^{-1}, yielding only the copolymer with ≥98% enantioselectivity at 25 °C. Moreover, high molecular weight of up to 40.7 kg/mol could be achieved. An intramolecular bimetallic synergistic effect was proposed to account for **3'**s excellent catalytic activity, polymer selectivity and enantioselectivity [117]. High M_W isotactic poly(1,4-dihydronaphthalene carbonate) (PCDC) exhibited a high T_g of 150 °C, which is very close to that of BPA polycarbonate.

Employing an achiral dinuclear (salen)Co^{III} catalyst, the Lu group synthesized atactic PCXC from copolymerization of dioxaepoxide CXO and CO_2. Atactic PCXC, with fused seven membered rings in the backbone structure, displayed a high glass transition temperature of 140 °C [83]. When the chiral analogue of the dinuclear cobalt catalyst was used, the resultant polycarbonate is highly isotactic, possessing a semicrystalline structure with a T_m of 242 °C (*vide supra*). This influence of tacticity on the thermal properties of CO_2-based polycarbonates will be discussed later in more detail.

Despite the high thermal stability of PIO, PCDC and PCXC, these polymers are based on petroleum feedstocks, and thus it is of great interest to develop high performance CO_2-based polycarbonates from sustainable natural resources. Notably, poly(limonene-8,9-oxide carbonate) (PLOC), derived from biorenewable limonene dioxide (LDO), displayed a T_g of up to 135 °C [80] and could be further modified through CO_2 insertion onto to its pendent oxirane to produce a PLDC with an even higher T_g of 146 °C [80]/180 °C [81] (*vide supra*).

4.2. Controlling the stereochemistry of epoxide enchainment

The relative stereochemistry of neighboring chiral centers within polymeric chains (also referred to as tacticity) has a significant effect on the physical properties of the material. Considering that stereoselective copolymerization of epoxides and CO_2 have been reviewed in numerous articles [29,106–110], the focus here will be on highlighting recent advances in the field, including stereocomplexed polycarbonate formation, with an emphasis on the improvement of thermal properties.

As alicyclic polycarbonates usually possess relatively high T_gs, much effort has been made to tune their stereoregularity for further improvement of the thermal properties, hoping to match the performance of some commercial engineering plastics. In this respect, stereoselective copolymerization of CHO and CO_2 has been widely investigated and several chiral catalysts of Zn(II) [111–115], Co(III) [116–118] and Al(III) [119] have been developed. Notably, both Lu [117] and Coates [111] were able to achieve high enantioselectivity (90–98% ee) and precise molecular weight control for CHO/CO_2 coupling under mild reaction conditions by employing chiral dinuclear (salen)Co^{III} catalysts and C_1-symmetric ZnBDI catalysts, respectively. It was worth noting that the use of chiral dinuclear Co^{III} catalysts predominantly provided polymer products with the same stereochemistry, *i.e.* (*S,S,S,S*)-configured catalysts yielded *S,S*-configured repeating units, whereas chiral ZnBDI complexes afforded polymers with opposite configurations. Unlike atactic PCHC which is an amorphous polymer, highly isotactic PCHC has a semicrystalline structure and its melting point is greatly effected by the ee% of the polymer chain. Interestingly, a systematic thermal analysis performed by Coates showed that T_m of isotactic PCHC increased almost linearly with ee% over the tested tacticity range (78% to >99%) [111]. Highly isotactic PCHC (M_n = 11 kDa, >99% ee) displayed a T_m of 267 °C.

Following their success with preparing highly isotactic PCHC, Lu and co-workers have synthesized a series of highly enantiopure alicyclic polycarbonates from asymmetric copolymerization of CO_2 and various *meso*-epoxides utilizing the same chiral dinuclear $Co^{(III)}$ complexes (Fig. 15) [82,83,105,117,120,121]. Both (*R,R*)- and (*S,S*)-polycarbonates were formed from the corresponding chiral catalysts. Among these isotactic polycarbonates, some are semicrystalline polymers possessing T_ms of 179–271 °C depending on the structure. Now with both (*R,R*)- and (*S,S*)-configured isotactic polycarbonates in hand, the same group investigated the stereocomplexation between enantiomers of opposite configuration. Various crystalline stereocomplexes have been prepared from both crystalline and amorphous isotactic polymers, resulting in a significant improvement in thermal properties. For instance, the 3,4-epoxytetrahydrofuran (COPO)/CO_2 copolymer (PCOPC) stereocomplex exhibits a T_m of 300 °C, some 30 °C higher than its parent isotactic enantiomer [120]. Upon mixing equal amounts of amorphous (*S,S*)- and (*R,R*)-PCDC, a crystalline stereocomplex was formed and displayed a very high T_m of 373 °C, the highest T_m yet reported in the field [105]. A summary of the thermal properties of selected isotactic polymers and their corresponding stereocomplexes can be found in Table 1. Furthermore, the same group demonstrated that amorphous enantiomeric polymers having different chemical structures can cocrystallize to form hetero-stereocomplexes [105]. Wide-angle X-ray diffraction (WAXD) analysis revealed that hetero-stereocomplexes have different crystalline structures from those of the corresponding homo-stereocomplexes.

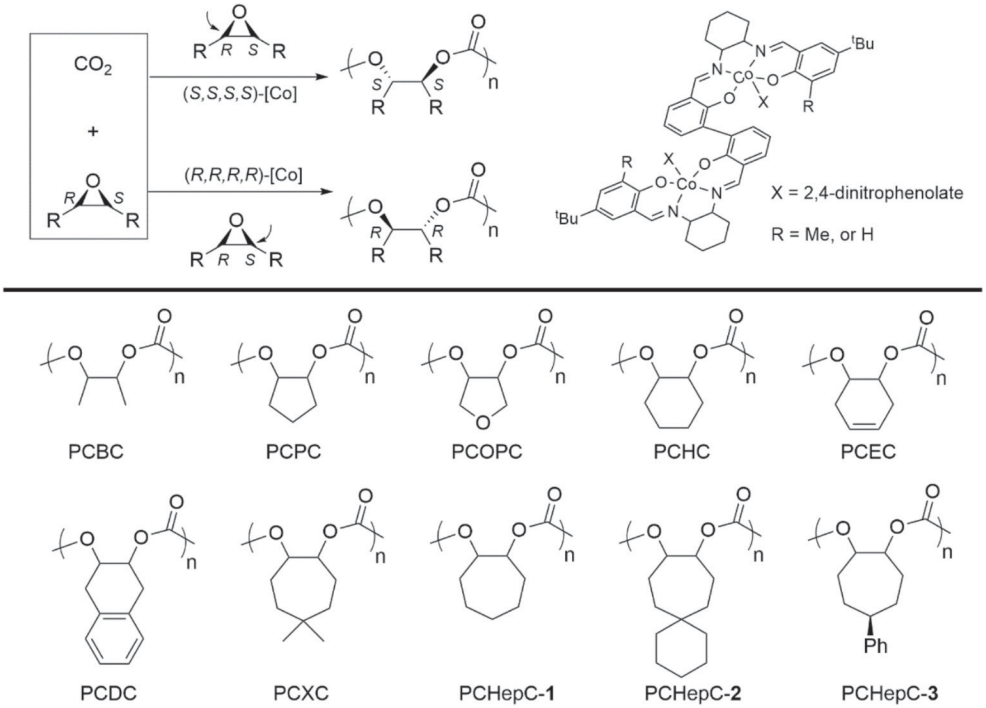


Fig. 15. Enantioselective copolymerization of CO_2 and *meso*-epoxides to enantiopure isotactic polycarbonates.

Table 1
Thermal properties of selected isotactic polycarbonates (Fig. 15) and their stereocomplexes.

	Isotactic PC			Stereocomplex	Refs.
	M_n (kg/mol)[a]	ee (%)	T_g/T_m (°C)	T_m (°C)	
PCBC	39.3	99	73/–[b]	177	[120]
PCPC	29.8	99	85/–[b]	199	[120]
PCOPC	10.9	99	–[c]/271	300	[120]
PCHC	35.6	98	–[c]/272.4	–[f]	[117]
PCEC	29.8	99	130/–[b]	314[e]	[105]
PCDC	24.5	99	150/–[b]	373[e]	[105]
PCXC	17.5	99	–[c]/242	–[d]	[120]
PCHepC-**1**	7.4	92	118/–[c]	–[f]	[83]
PCHepC-**2**	12.6	>99	–[c]/179	–[f]	[83]
PCHepC-**3**	8.9	–[f]	123/257	–[f]	[83]

[a] Reported M_n of (*S*)-polycarbonate. The corresponding (*R*)-polycarbonate has similar M_n.
[b] Amorphous polymer.
[c] Not detectable.
[d] $T_d > T_m$.
[e] Measured by fast-scan chip-calorimeter (FSC).
[f] Not applicable.

Coates et al. prepared a novel crystalline stereocomplex by mixing equal amounts of isotactic poly(*R*-limonene carbonate) (PRLC) and poly(*S*-limonene carbonate) (PSLC) [122]. PRLC and PSLC were synthesized from regioselective copolymerization of CO_2 and (*R*)- and (*S*)-limonene oxide, respectively. Both enantiomers were amorphous with a T_g of ~120 °C and a decomposition temperature (T_d) of ~250 °C. On the other hand, their stereocomplex had a crystalline structure and exhibited a 15 °C increase in decomposition temperature, although its T_g remained the same as the individual enantiomer. T_m of the stereocomplex was not observed in DSC as the polymer started to degrade before reaching the transition. A detailed structural analysis revealed that the formation of stereocomplex was promoted by the tight interdigitation between alternating PRLC and PSLC chains and by the dipolar interaction between carbonyl groups [122,123].

Stereoselective copolymerization of mono-substituted aliphatic epoxides and CO_2 has also been investigated. In this case, formation of highly isotactic polymers requires regioselective ring-opening at the methylene C_β—O bond of the terminal epoxides (Fig. 16). By tuning the chiral and steric environment around the active metal center, high regio- and stereo-selectivity can be achieved. Many research groups have reported the synthesis of isotactic PPC, by either the enantioselective polymerization of racemic monomers, or the simple regioselective polymerization of enantiopure substrates [124–131]. The thermal properties of PPC are greatly enhanced by controlling the stereochemistry of the polymer chain. Highly isotactic PPC was reported to have a glass transition temperature of 47 °C, which is 10–12 °C higher than that of completely atactic PPC [131]. And a stereogradient PPC prepared by Nozaki et al. displayed a much higher decomposition temperature (T_d = 273 °C) than its stereoirregular counterparts (T_d ~240 °C) [128].

Epoxides with electron withdrawing substituents have also been copolymerized stereoselectively with CO_2 [39,132–134]. Wu

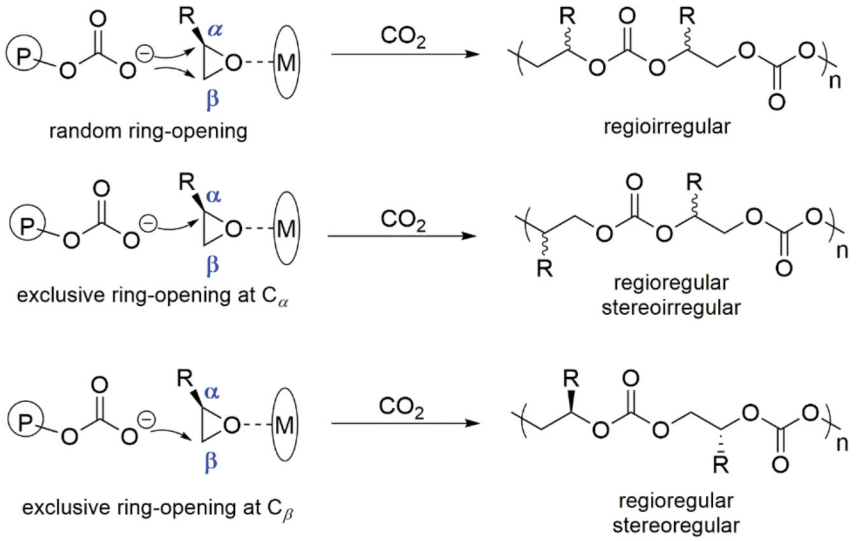


Fig. 16. Stereochemistry involved in the copolymerization of CO_2 and enantiopure mono-substituted aliphatic oxides.

et al. reported the coupling reaction of epichlorohydrin and CO_2 using bifunctional (*S,S*)-(salen)Co^{III} catalysts [133]. It was found that bulkier substituents on the ligand promoted ring-opening at the least hindered C_β—O bond. The highest regioselectivity was observed when complex **4** (Fig. 17) bearing an adamantane group and an appended bulky dicyclohexyl ammonium salt was used as the catalyst. When enantiopure (*R*)-epichlorohydrin is utilized in the coupling reaction, **4** predominantly ring-opens at the methylene carbon, allowing for the retention of the stereochemistry at the methine carbon. Isotatic poly(chloropropylene carbonate) (94% ee) is a typical semicrystalline polymer with an improved T_g of 42 °C (T_g = 31 °C for the atactic polymer) and a T_m of 108 °C.

Very recently, the Lu group prepared highly stereoregular poly (styrene carbonate) (PSC) and its derivatives from regioselective copolymerization of (*R*)-configured epoxides and CO_2 using a multichiral (*S,S,S*)-(salen)Co(III) complex **5** (Fig. 17) coupled with a PPNX (X = DNP) cocatalyst [132]. Ring-opening predominantly occurred at the methylene carbon to afford (*R*)-configured polycarbonates (Fig. 18). Similarly, (*S*)-configured polymer were synthesized from regioregular coupling of (*S*)-epoxides and CO_2 with the (*R,R,R*)-(salen)Co(III) catalyst system. Highly isotactic poly (styrene carbonate) and PSC-OCH_3 are typical semicrystalline polymers with T_ms of 137.3 and 90 °C, respectively. On the contrary, isotactic polymer PSC-Cl is amorphous possessing a T_g of 83.8 °C. Interestingly, a 1:1 mixture of (*R*)-PSC and (*S*)-PSC can cocrystallize to form a stereocomplex with an enhanced T_m of 164.1 °C, about 27 °C higher than its parent enantiomers. A crystalline stereocomplex with a T_m of 147.3 °C was also formed after mixing amorphous (*R*)-PSC-Cl and (*S*)-PSC-Cl in equal mass. Of importance, these are

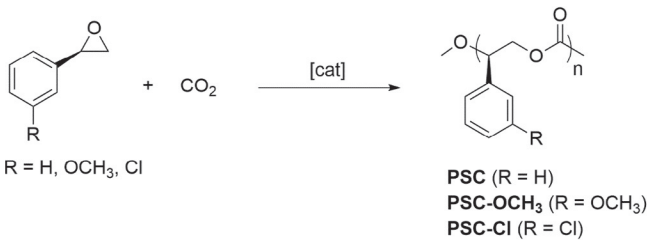


Fig. 18. Regioselective copolymerization of CO_2 and (*R*)-configuration styrene oxide and its derivatives [132].

the first examples of stereocomplex formation that is based on terminal epoxides/CO_2 copolymers. Attempt to cocrystallize PSC-OCH_3 of different configurations was not successful.

4.3. Construction of terpolymers or block polymers

Modification of thermal properties can be achieved by combining different monomers to form either random (statistical) copolymers or block copolymers. Generally, a random copolymer displays only one glass transition temperature that falls between the T_g values of each homopolymer and is dictated by the fraction of each component. On the other hand, a block copolymer can display one T_g or two distinctive T_gs depending on the compatibility between different blocks. Various catalysts and synthetic strategies have been developed to prepare these two types of copolymers with enhanced thermal properties.

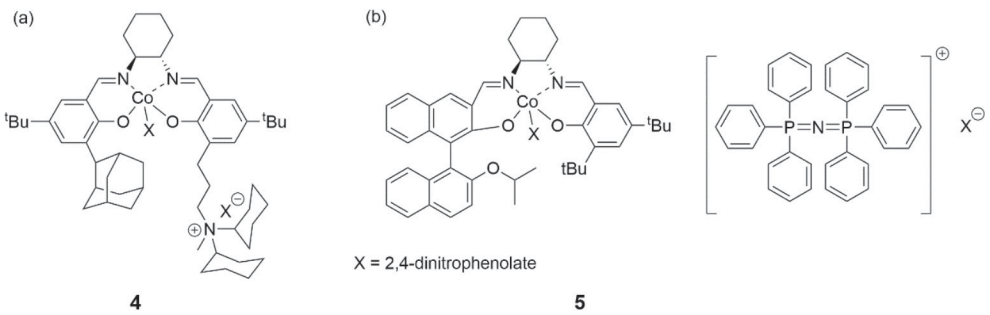


Fig. 17. Catalyst systems utilized in the stereospecific copolymerization of enantiopure terminal epoxides and CO_2.

As discussed previously, PPC has good mechanical properties but its application as structural materials has been marred by a low T_g of 35–45 °C. To address this problem, there has been a lot of interest in the terpolymerization of PO, CHO and CO_2. In 2006, the Lu group reported the synthesis of random PO/CHO/CO_2 terpolymers utilizing a (salen)Co^{III} catalyst system [118]. With about 40 mol% of PCHC, the terpolymer exhibited a single T_g of 68.8 °C. (Note that a block polymer PPC-*b*-PCHC prepared by the Darensbourg group exhibited two T_gs [27].) The T_g value could be adjusted between 50 and 100 °C by controlling the molar fraction of PCHC. Although PO/CO_2 copolymerization occurs much faster (~6 times) than CHO/CO_2 coupling under the same conditions, a matched reactivity for the two epoxides was observed during the terpolymerization reaction. This was attributed to a balanced coordination ability and ring-opening reactivity of the two epoxides, *i.e.* CHO has a stronger coordination ability but its ring-opening rate is slow, PO the opposite. Later the same group utilized a bifunctional (salen)Co^{III} catalyst bearing a quaternary ammonium arm for the PO/CHO/CO_2 terpolymerization reaction [37]. This catalyst exhibited a high reactivity (TOF = 3590 h^{-1}) and polymer selectivity at 90 °C and provided high molecular weight terpolymers. The Lee group also investigated the terpolymerization of PO, CHO and CO_2 using a (salen)Co catalysts tethered by four quaternary ammonium salts [135]. Reactivity ratio of PO and CHO was studied using Fineman-Ross analysis to reveal that the terpolymer had a tapered structure. Nevertheless, only one T_g was observed for the terpolymer.

Terpolymerization of PO, 1,3-cyclohexadiene oxide (1,3-CHDO) and CO_2 has been investigated by Darensbourg and Chung [72]. Fineman-Ross kinetic analysis revealed a matched reactivity between the two epoxides. The resultant polymer with about 20% 1,3-cyclohexadiene carbonate units displayed a T_g of 68.9 °C, approximately midway between the T_gs of the respective copolymers. An attempt to incorporate 1,4-CHDO into PPC failed due to the much lower copolymerization activity of 1,4-CHDO than PO.

Liu and co-workers studied the terpolymerization of PO, 4-vinyl cyclohexene oxide (VCHO) and CO_2 using a bifunctional salcyCo^{III}-NO_3 complex [136]. It was found that the feed ratio of VCHO had a great effect on both the catalytic activity and polycarbonate selectivity. A PO/VCHO/CO_2 terpolymer with 27% vinyl cyclohexene carbonate (VCHC) units displayed a T_g of 56 °C, about 20 °C higher than that of PPC. Moreover, the thermal properties of the terpolymer can be further improved by transforming the pendant alkene groups into epoxide or cyclic carbonate functionalities.

Block copolymers have also been prepared to modify the thermal properties of PPC. Darensbourg and Wu reported the one-pot synthesis of novel poly(lactide-*b*-propylene carbonate-*b*-lactide) triblock copolymers [91]. Copolymerization of PO and CO_2 was carried out in the presence of water utilizing a binary (salen)CoTFA/PPNTFA (TFA = trifluoroacetate) system to generate PPC polyol intermediate. PPC diols were subsequently used as a macroinitiator for 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-catalyzed ring-opening polymerization of *D*-lactide (LA). The resulting block polymers exhibited a much higher thermal resistance ($T_g \approx 45$ °C, T_m >110 °C) than the parent PPC diols.

4.4. Formation of cross-linked network

Another effective way to increase the thermal stability of polymers is to form cross-linked networks (thermosets) by interconnecting polymer chains *via* covalent bonds or ionic bonds. Other properties such as mechanical strength and chemical resistance can also be improved through crosslinking. As discussed before, a wide range of epoxides have been coupled with CO_2 to produce polycarbonate bearing different side chain groups, such as hydroxyls, carboxylic acids, alkynes, alkenes and epoxies. These pendant functionalities have been exploited through a variety of chemical reactions to form cross-linked polycarbonate networks.

In an interesting study, Coates reported the transformation of linear polycarbonates with pendant vinyl groups into organic nanoparticles through intramolecular olefin cross-metathesis reactions [137]. At 76% cross-linking, the T_g of the particles increased to 194 °C from an initial value of 114 °C. In 2015, the Frey group utilized well-established Diels-Alder reactions to transform polycarbonates bearing pendent furfuryl groups into a cross-linked gel [60]. The cured samples exhibited much higher T_gs (~50 °C) than their linear counterparts (T_gs are below 0 °C). Furthermore, this cycloaddition transformation was shown to be fully reversible and offers promise for the development of self-healing materials.

Thiol-ene click chemistry have been widely employed to prepare cross-linked materials by connecting the olefin groups present in the polycarbonate chains. Pescarmona et al. reported the curing of poly(vinylcyclohexene carbonate) with 1,3-propanedithiol [138]. The resultant crosslinked polymer exhibited a substantial increase in T_g from 75 °C to 130 °C. The group of Darensbourg prepared crosslinked polycarbonate films using various ratios of a tetrafunctional thiol linker [55]. The films exhibited an increase in T_g with increasing cross-linking densities.

Recent efforts have been focused on developing new cross-linked materials derived from renewable feedstocks. In this context, both Kleij [139] and Koning [140] have utilized 'thiol-ene' chemistry to prepare thermoset materials based on poly(limonene carbonate). Kleij and co-workers prepared a series of LO/CHO/CO_2 terpolymers with a variable ratio of limonene carbonate units [139]. The terpolymers were cured with a stoichiometric amount of a dithiol reagent under concentrated conditions to obtain cross-linked materials with improved thermal properties. Compared to the parent terpolymers, the decomposition temperatures of these cross-linked polycarbonates are increased by 15–77 °C and the glass transition temperatures by 19–54 °C. The Koning group synthesized low M_W poly(limonene carbonate)s and subsequently cured them with a trifunctional thiol reagent [140]. A detailed kinetic study by ATR-IR was performed to investigate the effects of different variables, *i.e.* polymer molecular weight, ene/thiol stoichiometry and curing temperatures, on the extent of network formation. The resultant thermosets exhibited high T_gs of >100 °C and good homogeneity. The PLC/thiol system was also evaluated for coating applications, showing promising properties such as high transparency, good acetone resistance and high pencil hardness.

Besides the aforementioned methods, other types of chemical reactions have also been employed to form cross-linked polycarbonate networks, including free radical coupling [141], thiol-epoxy addition [80], hydrolysis and polycondensation of alkoxy silane [66], isocyanate-hydroxy reaction [142–144] as well as ring opening of aziridine with carboxylic acids [61].

5. Application of CO_2-derived polycarbonates: recent examples

During the past decade, tremendous progress has been made in the formation of CO_2 copolymers. Notably, numerous epoxides, including those derived from renewable feedstocks, have been successfully copolymerized with CO_2 to produce polycarbonates with a wide range of physicochemical properties, *i.e.* hydrophilicity/hydrophobicity, degradability, degree of crystallization, and glass transition temperatures. Moreover, the development of various synthetic strategies, like post-polymerization functionalization, stereocomplex formation and terpolymerization, has enabled further improvement of key properties. With the synthetic advances, it is possible to expand the application scope of CO_2 copolymers by exploiting specific structural features. To date, these copolymers

have been utilized in various fields ranging from commodity structural materials to biomedical and electronic devices, and so forth.

One of the most important applications of CO_2-based polycarbonates is low molecular weight polyols as a feedstock for polyurethane (PU) production [145–147]. These polyols can be used in a wide range of polyurethane applications, such as foams, adhesives, sealants, coatings and elastomers [10]. Compared to traditional feedstocks, polycarbonate diols offer many performance advantages, including improved hydrolytic stability when compared to polyesters and better oxidative stability when compared to polyethers. Industrial production of CO_2-derived polyols have been realized by several companies worldwide, including Covestro [13], Empower Materials [11], Saudi Aramco [10] and Repsol [148]. Polycarbonate polyols (Converge®) from Aramco contain up to 50% of CO_2 in mass while polyethercarbonate polyols (cardyon™) from Covestro have a CO_2 content of 20%. To access the environmental impacts of CO_2-based polyol production, a detailed cradle-to-gate life cycle analysis was performed based on a real industrial pilot plant [149]. Compared to conventional polyether polyols, production of polyols with 20 wt% CO_2 can reduce greenhouse gas emissions by 11–19% and cut fossil fuel consumption by 13–16%. However, it is important to note that this production does not act as a net CO_2 sink as 2.65–2.86 kg CO_2 are still emitted per 1 kg polyol formed. Regardless, CO_2-polycarbonate polyols presents an excellent economic opportunity for CO_2 utilization.

Owing to their biocompatibility and (bio)degradability, aliphatic polycarbonates have been widely studied for biomedical applications like tissue engineering and drug delivery. To date, most of these polycarbonates investigated are prepared through ring-opening polymerization (ROP) of cyclic monomers [150,151]. Only rarely have been reports of using CO_2-derived polycarbonates for relevant applications. Compared to ring-opening polymerization, this alternative route from directive CO_2/epoxides copolymerization eliminates the need for the separate preparation of cyclic carbonates and therefore has great potential for large-scale production.

An interesting example of developing CO_2-based polycarbonate biomaterials came very recently from Grinstaff et al. [152] They used poly(1,2-glycerol carbonate) (PGC) as a degradable scaffold for paclitaxel (PTX) conjugation, achieving high and controlled drug loadings of up to 74 wt%. Sub-100 nm nanoparticles (NPs) were produced from the PGC-PTX conjugates and displayed favorable features like narrow dispersity, high storage stability and sustained drug release. 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. The authors highlight that these polycarbonate-PTX conjugates could serve as an ideal replacement for current chemotherapeutic dosing strategies by providing a sustained release of high doses of therapeutic agents.

Based on the work of Darensbourg et al. [54], Lu and co-workers prepared micelles of amphiphilic polycarbonates conjugated with gadolinium (Gd^{3+}) and investigated their application in tumor imaging [153]. Compared to a simple chelated Gd^{3+} complex, the polymer-Gd conjugates exhibited higher MRI signal in tumor regions due to enhanced permeability and retention effect of cancer cells. Furthermore, these conjugates were shown to degrade readily into small cyclic products that could be cleared from the body in a short time without inducing toxicity.

Recently, CO_2-derived aliphatic polycarbonates have attracted considerable attention as polymer electrolyte materials for lithium-ion battery applications. Aliphatic polycarbonates contain a large fraction of polar carbonyl groups to facilitate salt dissociation and have low glass transition temperatures (favorable for ion transport). In addition, these polymers have similar structure to cyclic carbonates used in traditional liquid electrolytes, suggesting that they may be compatible with commonly used electrodes.

Poly(propylene carbonate) (PPC), one of the most studied and also industrially produced CO_2 copolymer, has been fabricated into both solid polymer electrolytes (SPEs) [154–156] and gel polymer electrolytes (GPEs) [157,158]. For instance, Wu et al. introduced PPC into gel polymer electrolytes based on poly(vinylidene fluoride) (PVdF) [158]. The presence of amorphous PPC reduced the crystallinity of PVdF. Consequently, PVdF/PPC electrolytes exhibited a much higher ionic conductivity than pure PVdF electrolytes. Poly(ethylene carbonate) (PEC) has also been investigated as polymer electrolytes [159–163]. It was demonstrated that a large amount (188 mol)% of Li^+ can be incorporated into PEC to afford polymer electrolytes with relatively high ionic conductivity and extremely high Li transference numbers [162].

Glycidyl ether-based polycarbonates have been widely studied as polymer electrolytes due to their structural versatility, low T_gs and higher O/C ratio compared to other types of aliphatic polycarbonates. Grinstaff and co-workers prepared poly(ether 1,2-glycerol carbonate)s with long alkyl pendant chains and investigated their potential as thermally stable solid polymer electrolytes [152]. In particular, poly(butyl glycerol carbonate) (T_g = −24 °C) containing 65 wt% lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) displayed comparable conductivity to optimized PEG-based electrolytes. Tominaga et al. have prepared a series of poly(ether 1,2-glycerol carbonate)s containing both alkyl and oxyethylene side chains, and investigated the influence of side group structure on ionic conductivity [164–166]. Recently, the Meng group reported the synthesis of single-ion-conducting polymer electrolytes based on PO/AGE/CO_2 terpolymers [167]. The pendant alkene groups were functionalized with mercaptopropionic acid followed by lithiation with LiOH to afford novel poly(lithium carboxylate)-type polymer electrolytes. With 41.0 mol% lithium content, the electrolytes exhibited a high ionic conductivity of 1.61×10^{-4} S/cm at 80 °C and a high Li transference number of 0.86.

Besides these described applications, polycarbonates and their copolymers have also been used as a toughening additive for epoxy resins. Typically these polycarbonate modifiers have two active hydroxyl end groups that can react with the epoxy or curing agents to ensure good adhesion to the matrix. The first example of toughening epoxy with poly(propylene carbonate) was reported by Cong and co-workers [168]. With the incorporation of 20 wt% of PPC, the fracture toughness increased by 45%. Very recently, Misra and co-workers explored the toughening effect of PPC in a bio-based epoxy/poly(furfuryl alcohol) interpenetrating network [169]. It was found that the addition of 20 and 30 wt% of PPC could effectively improve the Izol strength and tensile toughness. Feng et al. prepared a triblock copolymer of PPC and poly(ε-caprolactone) (PCL), and investigated its toughening effect in epoxy resins [170]. Compared with neat epoxies, the thermosets with 30 wt% modifiers exhibited a 320% increase in tensile elongation and a 180% increase in fracture toughness. This significant toughness improvement was attributed to the enhanced interfacial adhesion between the modifier and the epoxy as the PCL block were miscible with the epoxy matrix. Despite the improvement in toughness showed in all three examples, it is accompanied by a decrease in glass transition temperature and tensile strength due to the plasticizer effect of soft PPC. To overcome this challenge, Feng introduced 0.25 wt% of reduced graphene oxide into the modified epoxy thermosets and achieved a good balance of toughness, strength and thermal properties [171].

6. Conclusions

This review has highlighted efforts to develop synthetic routes to a diverse array of functionalized polymeric materials. It is possible to achieve these polymers via direct copolymerization of

functional epoxide monomers with CO_2, or by post-polymerization modifications of polymer scaffolds bearing reactive groups. These latter processes have been widely achieved by efficient and highly versatile synthetic tools such as thiol-ene click chemistry and Diels-Alder reactions. The rapidly expanding range of functionalities has enabled access to polycarbonate materials with promising properties, such as hydrophilicity, rapid degradation, and thermal-response. One important limitation for aliphatic polycarbonate is their low thermal stabilities, often characterized by low glass transition temperatures. In this review, we have also summarized the synthetic strategies to improve the thermal properties of CO_2-based polycarbonates. Indeed, several CO_2 copolymers with superior thermal properties have been developed, exhibiting T_g values well above 140 °C (close to those for some commercial BPA polycarbonate materials). Moreover, semi-crystalline aliphatic polycarbonates have also been prepared through careful tacticity control. Overall, these recent development in the field could provide new application opportunities for CO_2-derived polycarbonates.

Declaration of interest

None.

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