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The advent of recyclable CO₂-based polycarbonates

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Abstract.

Found in all sectors of applications, synthetic plastics have become ubiquitous and versatile materials in our modern life. However, most of them are produced from fossil resources and are responsible for a dramatic environmental pollution when not properly recycled/treated after utilization. Pushed by environmental incentives and legal obligations from the European Commission, there is an urgent need to reinvent the fabrication of plastics, ideally by exploiting raw biochemicals and waste effluents such as CO₂, while making the plastics more easily degradable or recyclable. This review discusses the chemical recycling pathways of a family of more sustainable polymers, i.e. polycarbonates, that are prepared by valorizing raw CO₂ as an inexhaustible, cheap and abundant C1-feedstock. In particular, this review draws briefly the fundamentals of the main synthetic approaches for the production of CO₂-based polycarbonates by the direct copolymerization of CO₂ with epoxides or by the (co)polymerization of CO₂-based monomers. The most relevant chemical re-/up-cycling scenarios of the different classes of polycarbonates are then addressed to illustrate the potential of these products to design more sustainable materials.

1. Introduction

Over the last century, the massive utilization of low cost commodity plastics has brought revolutionary progresses in our modern life. Their easy customizable properties have permitted their emergence for multiple purposes in very distinct fields including the automotive, packaging, pharmaceutical, electrical, electronical and building sectors.^{1,2} Despite their remarkable lightweight, flexibility, strength and durability, most of synthetic polymers lack of degradability by biological or abiotic means in landfills or the marine environment. Their persistency is now turning their initial magic into a major global ecological crisis. Moreover, most of the plastics are still produced from fossil resources making their carbon footprint dramatic. Recent predictions have highlighted a tripling of

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the actual plastics consumption at the horizon 2050.⁵ To abate the plastic pollution and decarbonize this industry, the European Commission recently adopted a vision specifying guidelines to rethink the fabrication and facilitate the recycling of plastics.³ On the path to circularity and sustainability, one key measure encourages the utilization of biorenewable chemicals and gaseous effluents to create new low carbon footprint polymers with thermo-mechanical performances analogues to existing ones. In this context, waste CO₂ is expected to become a cornerstone to fundamentally reinvent the fabrication of plastics.⁴ A recent prospective study has highlighted a brilliant future for these materials with a 25 fold volume increase representing ~ 25% of the market share at the horizon 2050.⁵ As second obligation, these new engineered plastics should display enhanced intrinsic mechanical or chemical recycling ability. If the revalorization/recycling of end-of-life plastics is mandatory to prevent the relegation of waste materials in the environment, it remains a huge bottleneck.^{6,7} Mechanical recycling often produces low performance 'downcycled' materials; such raw materials may need extensive additivation in order to be re-incorporated in consumer products.⁸ Chemical re- and upcycling can offer a more diverse spectrum of end-of-life reuse scenarios, either yielding the original monomers to refabricate the same plastic with virgin-like material properties in a close-loop approach, or producing building blocks for innovative, intrinsically circular materials (open-loop recycling).⁹⁻¹⁴ But, the inherent microstructure of (commodity) polymers with stable covalent carbon-carbon bonds still makes challenging their low-temperature selective chemical deconstruction. To date, only polymers containing C–O or C–N heteroatom linkages show sufficient lability and can be depolymerized through solvolytic approaches by employing nucleophiles or water or via thermal reversion into the native monomers or new chemicals.¹⁵⁻¹⁷ Herein, we review the state-of-the-art in the recycling of CO₂-based polycarbonates that belong to an important family of polymers. Fundamentals of the direct enchainment of CO₂ into polymer chains or the polymerization by well-established tools of prefabricated CO₂-based monomers will be briefly described, yet setting the foundations to the detailed discussions of the most relevant degradation/recycling pathways of these various polymers.

2. Few generalities on polycarbonates

Polycarbonates are polymers with easy customizable mechanical and thermal properties that vary from low thermal stability, poor mechanical properties and high susceptibility to hydrolysis/(bio)degradation for aliphatic PCs,¹⁸ to transparency, high impact resistance, high rigidity and good thermal stability for aromatic PCs. Today, PCs are key components of electronic, optical and biomedical devices, construction materials, cars manufacturing, Li-ion batteries. Progresses in the design of catalysts permit now the synthesis of PCs directly from CO₂ via ring-opening copolymerization (ROCOP) with

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epoxides or alternatively by ring-opening polymerization (ROP) of cyclic carbonates, which may in turn be synthesized using CO₂. Beside these (co)polymerization processes, a more traditional synthetic pathway consists in the polycondensation between diols and CO₂-sourced acyclic carbonates.^{1,19–22} Some of these synthetic approaches are reaching now the industrial maturity. For example, CO₂-sourced poly(propylene carbonate) of M_n up to 100,000 g/mol containing 43 wt% of CO₂ content is viewed as a green alternative to polyethylene, yet serving as disposable packaging and mulching films that are compostable and biodegradable upon burial in soil.²³ Low viscous hydroxytelechelic poly(carbonate-co-ether)s, also named polyols such as Cardyon®, are now utilized to manufacture polyurethanes for flooring and foam applications.²⁴ Asahi Kasei Chemicals has developed and licensed a technology to fabricate aromatic polycarbonates via polycondensation of bisphenol A and diphenyl carbonate (DPC). Through a sequential approach, ethylene oxide and CO₂ are first transformed into ethylene carbonate that further reacts with methanol to deliver dimethyl carbonate (DMC). DPC monomer is then obtained by transesterification of DMC with phenol.²⁵ In 2021, it has been estimated that a 750,000 ton polycarbonate production capacity exploiting this technology (at Asahi Kasei or via licensing) was installed across the world.⁵ To avoid the utilization of ethylene oxide, the same company has developed in 2016 a new so-called “dialkyl carbonate (DRC) process”, enabling the direct synthesis of DMC from CO₂ and methanol in a demonstration and validation plant, yet serving for DPC production.²⁵

3. ROCOP polycarbonates

3.1 *Fundamentals of CO₂/epoxide ROCOP.*

The ROCOP of CO₂ with propylene oxide has been pioneered by Inoue who utilized a water/diethylzinc catalytic system to produce poly(propylene carbonate).²⁶ This seminal work has given momentum to flourishing catalytic breakthroughs in ROCOP that are summarized in multiple comprehensive and much detailed reviews to which the reader is invited to read.^{1,27–30} Conceptually, the polymerization manifold responds to a well-established coordination–insertion mechanism involving first the activation of terminal or internal epoxides by a Lewis acid. The latest is selected among B(alk)₃, trivalent Co, Cr, Al or divalent Zn, Mg metal centers complexed by Porphyrin, Salen, Salphen, β-diimide, bimetallic macrocyclic phenolates or amino triphenolate ligands, as well as homo- and dinuclear- complexes (such as Mg(II)/Mg(II), Zn(II)/Zn(II), Al(III)/Al(III), Fe(III)/Fe(III), Mg(II)/Cr(II), Mg(II)/Zn(II), Mg(II)/Cu(II) or dual systems combining Zn(II) with a metal from Group 1 or 2) (Figure 1, non-exhaustive list, see general reviews for a complete overview of the various catalysts scope).^{30–43} Then, the resulting activated epoxy monomer undergoes a ring-opening via nucleophilic attack by a Lewis base acting as nucleophile to form an alkoxide-metal intermediate. The subsequent insertion

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of carbon dioxide into this intermediate creates a metal carbonate species prone to propagation by consecutive incorporation of epoxide units and CO₂ in an alternating fashion within the growing anionic chains (Scheme 1). The polymerization is terminated by adding a protic source furnishing a polycarbonate with an hydroxyl chain end. Mechanistically, it is commonly accepted that the rate-determining step for the PC formation lies in the ring-opening of the epoxide by the carbonate growing anionic polymer chain, rather than CO₂ insertion.^{30,44} The selection of the catalyst is of critical importance to control the microstructure of the polycarbonates. During the chain growth process, ether linkages may be formed by successive enchainment of epoxide molecules instead of alternated epoxide-CO₂ insertion. A second major impediment to the selective production of PCs by ROCOP of epoxides and CO₂ lies in the ease of the backbiting process from the free anionic growing PC chain, yet resulting in the formation of cyclic carbonate co-product.

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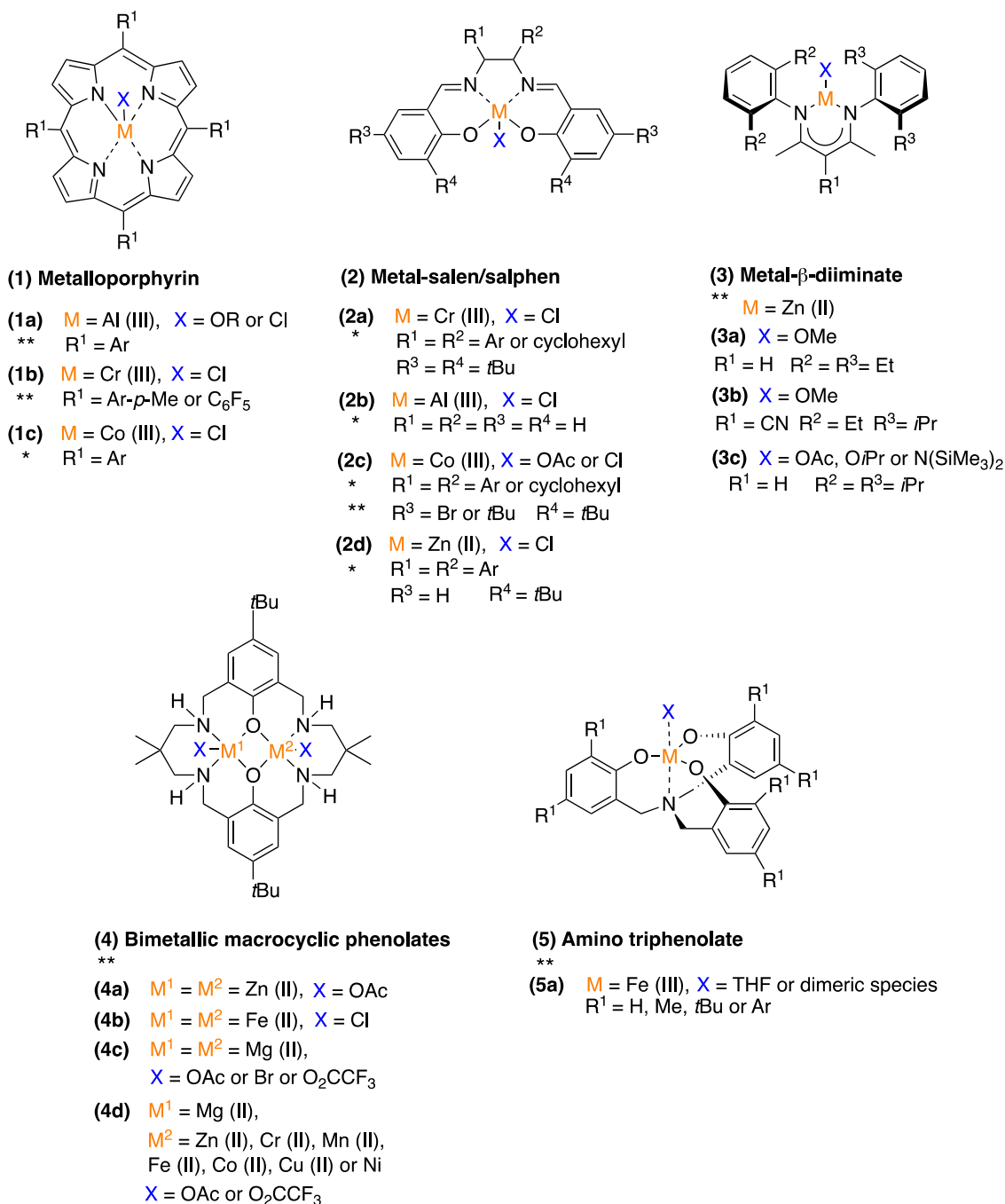
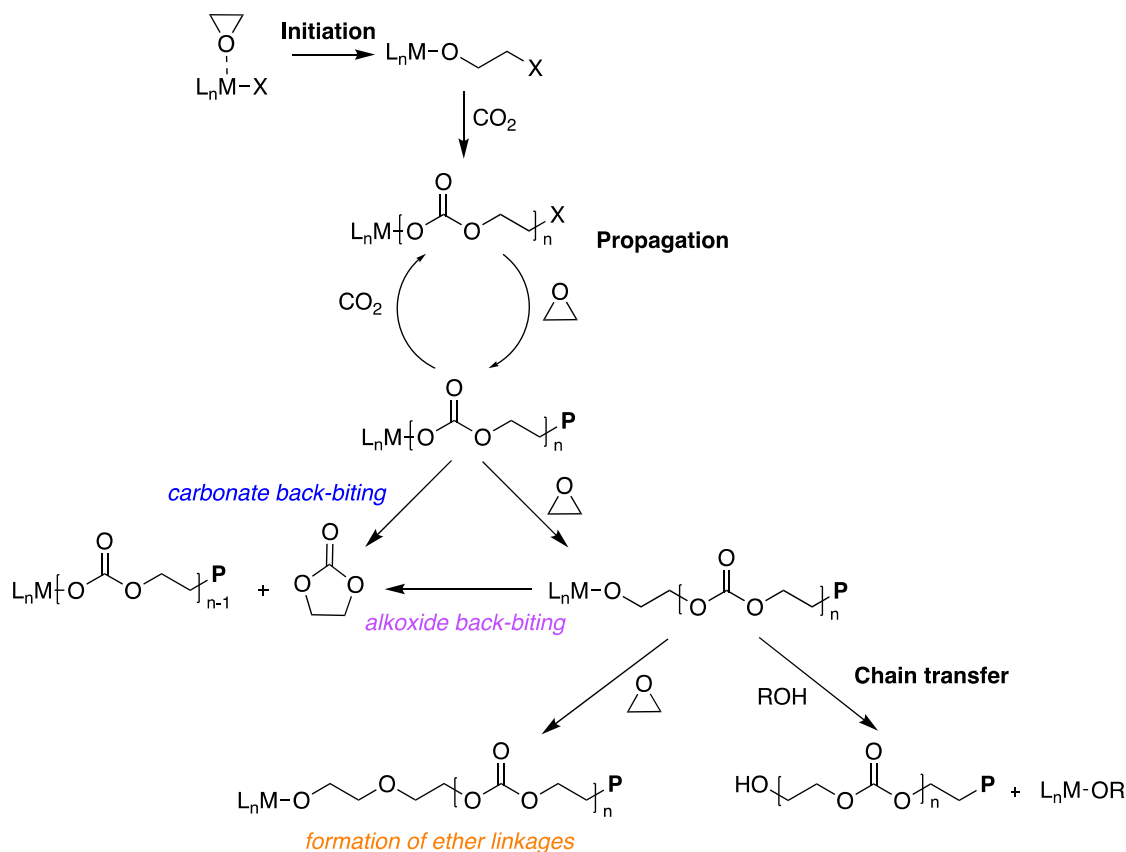


Figure 1. Non-exhaustive list of representative metal catalysts used for the ROCOP of CO₂ with epoxides. Catalyst active for the ROCOP of CO₂ with (*) terminal epoxides (such as ethylene or propylene oxide) and (**) with internal epoxides (such as cyclohexene, limonene or indene oxide). Reproduced from ref. 31 with permission from Royal Society of Chemistry, copyright 2023.

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Scheme 1. General mechanism of synthesis of PCs by ROCOP of epoxide with CO₂.

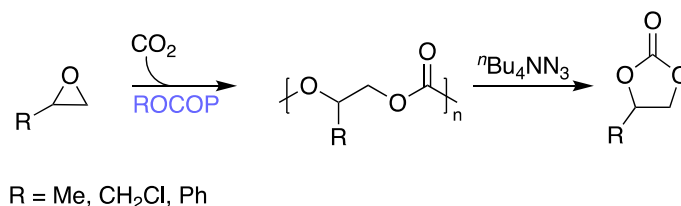
ROCOP polycarbonates degrade via two main scenarios, either via their thermal (decarboxylative) reversion into added value chemicals or offspring monomers, or through solvolysis and hydrogenolysis.

3.2 Thermal tail-to-head reversion of ROCOP PCs.

The construction/deconstruction loop of ROCOP PCs is mainly governed by the polymer energetics with a major influence of the ceiling temperature below/above which the polymer chains grow/depolymerize.^{4,11,45} Following the deprotonation of the OH chain-ends, aliphatic CO₂-based polycarbonates depolymerize into 5-membered cyclic carbonates. The process responds to the unzipping of the resulting anionic chains in a backbiting fashion leading to a steady curtailing in the PC molar mass while maintaining a low dispersity. To illustrate this concept, Darensbourg has reported on the thermal anaerobic decomposition of series of aliphatic ROCOP polycarbonates derived from epoxides bearing both electron donating or electron withdrawing substituents, i.e. styrene oxide, epichlorohydrin and propylene oxide.⁴⁶ By employing a strong nitrogen

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base like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a rapid and complete depolymerization of poly(styrene carbonate) to styrene carbonate is accomplished at 22 °C in less than an hour. By switching to tetrabutylammonium salts with an azide counter-anion ($n\text{Bu}_4\text{NN}_3$), the same polymer is decomposed in less than 10 min at 70 °C, while its reversion to styrene carbonate was strongly slowed down with Cl anion or even not observed with bromide (Scheme 2). This reflects the vital role of the basicity of the anion or the base in the aliphatic PC deconstruction which endwise scission is initiated by the chain-end deprotonation. Similarly, the deconstruction of poly(CO_2 -*alt*-epichlorohydrin) and poly(propylene carbonate) promoted by $n\text{Bu}_4\text{NN}_3$ furnished exclusively and quantitatively the corresponding 5-membered cyclic carbonates. The depolymerization activation energies, obtained through kinetic studies, increases in the order poly(styrene carbonate) (46.7 kJ/mol) < poly(CO_2 -*alt*-epichlorohydrin) (76.2 kJ/mol) < poly(propylene carbonate) (80.5 kJ/mol).⁴⁶



Scheme 2. Synthesis of PCs by ROCOP of CO_2 with substituted-epoxides and their thermal degradation into 5-membered cyclic carbonates.

Through computational studies, Darensbourg has highlighted that the metal-free backbiting reaction of aliphatic PCs, promoted by a free anionic polycarbonate chain-end, is inhibited by bulky groups at the methine carbon of the polymer microstructure, however it is accelerated by resonance stabilization.⁴⁷ The thermal reversion of aliphatic PCs into cyclic carbonates is strongly retarded in the presence of a binary catalyst (a combination of a base ($n\text{Bu}_4\text{NN}_3$) and a (Salen)CrCl complex). This presumably arises from the binding of the anionic copolymer to the coordinatively unsaturated metal center. The emergence of new generations of ROCOP catalysts is now an asset to the construction of aliphatic ROCOP PCs displaying thermal tail-to-head reversion ability. They enable the construction of polymers free of ether linkages defects that were acting as termination nodes for the complete deconstruction of the chains.

Unlike aliphatic PCs, the ROCOP of CO_2 with (geometrically constrained) epoxides fused with cyclopentene, indene, cyclohexene, limonene or cycloheptene rings provides alicyclic PCs which thermal deconstruction features and products selectivity are governed by the judicious choice of the catalyst, the size of the alicyclic ring and/or the

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operative conditions. At the exception of poly(indene carbonate) (synthesized by ROCOP of **1**, Scheme 3)⁴⁸ that depolymerizes into the corresponding *cis*-cyclic indene carbonate (Scheme 3, pathway *i*), PCs derived from CO₂ and epoxides fused with a 5-membered alicyclic ring such as cyclopentene⁴⁹ or *O*- and *N*-heteroepoxide (*N*-aryl pyrrolidine oxide)^{50,51} revert preferentially into the parent epoxide (**2** and **3** respectively) and CO₂ via a decarboxylative ring closure depolymerization pathway (Scheme 3, pathway *i'*). This is exemplified by the depolymerization of poly(cyclopentene carbonate). Aided by DFT calculations, Darensbourg has demonstrated that the backbiting of these PCs to the corresponding epoxide monomers possesses a free energy barrier 6.6 kcal mol⁻¹ lower than the one of the *trans*-cyclopentene carbonate (Scheme 3, pathway *ii*), claimed by the author as the kinetic product. Moreover, this latest is 19.9 kcal mol⁻¹, higher in enthalpy than its *cis*-boat conformer.⁴⁹ Therefore, the *trans*-conformation of cyclopentene carbonate is highly unstable due to the strain energy of the two five-membered fused rings and this product should not be observed upon depolymerization. This correlates with the depolymerization experiments. Bases such as ⁿBu₄NN₃ and DBU are ineffective in deconstructing poly(cyclopentene carbonate). Employing the stronger, non-nucleophilic base sodium bis(trimethylsilyl)amide (NaHMDS) enables the slow reversion of the chains into cyclopentene oxide and *cis*-cyclopentene carbonate in a nearly equimolar ratio after 300 h at 110 °C (polymer degradation of 30 %).⁴⁹ Extending the degradation time to 60 days changed the product distribution, with the formation of the cyclic carbonate specie being favored. The *in-situ* release of CO₂ creates an environment that not only changes the product selectivity but also slows down the depolymerization rate, as confirmed by control depolymerization experiments driven under 0.7 bar. When reproducing the same experiment under reduced pressure, the PC deconstruction is enhanced with a polymer deconstruction yield of ~ 50 % in 70 h, yet furnishing cyclopentene oxide (**3**) as the major product. Recently, Wu et al. has reported a bifunctional dinuclear organoboron catalyst for the depolymerization of poly(cyclopentene carbonate) assisted by potassium hydroxide. By a pathway combining end-chain scission and chain unzipping, the degradation provides the near-quantitative formation of cyclopentene oxide (**3**) in 24 h and at 110 °C.⁵²

It is assumed that cyclohexene oxide (**4**) arises from alkoxide endwise backbiting, whereas the *cis*-cyclic carbonate scaffold results from backbiting by a carbonate chain end. Unlike aliphatic ROCOP PCs, the metal-assisted depolymerization process accelerates the polymer deconstruction with a product distribution favoring the parent alicyclic epoxide monomer. Using a dual (Salen)Cr(II)Cl/ⁿBu₄NN₃ catalytic system for 30 h at 110 °C, 86 % of poly(cyclopentene carbonate) is reverted into cyclopentene oxide with a selectivity of 92 %. With (Salen)Cr(III)Cl/bis(triphenylphosphine)iminium azide (PPNN₃), the PC is fully degraded in 40 min via pyrolysis at 200 °C, yet delivering cyclopentene oxide with a 94 % selectivity.⁵³ Rather similar in concept is the loop

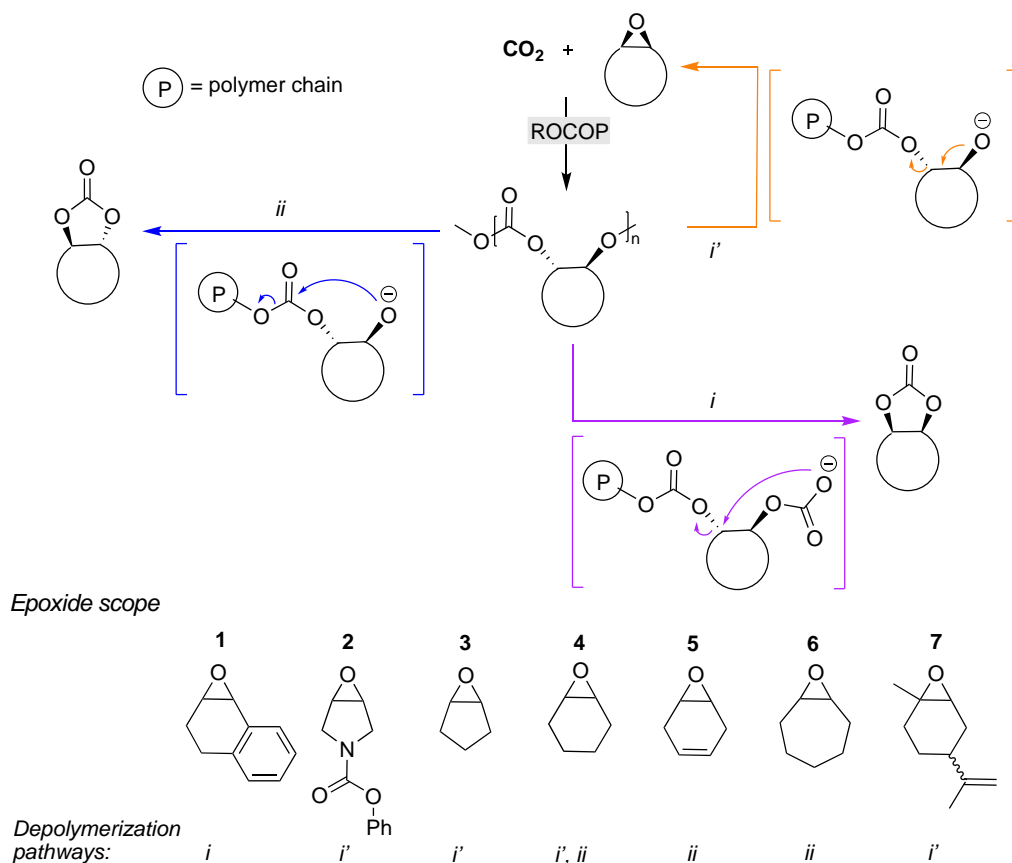
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synthesis of defect-free PCs of M_n up to 27,000 g/mol from CO_2 and 1-benzyl- or alkyl-oxycarbonyl-3,4-epoxy pyrrolidine driven by dinuclear Cr(III)-complex/PPNX or (Salen)Co(III)Cl/PPNX system (PPN=bis(triphenylphosphine)iminium) (with $X = \text{NO}_3^-$ or 2,4-dinitrophenoxide) at 25-80 °C. This PC has been quantitatively recycled at 100-110 °C (in solution) or via vacuum thermolysis at 200°C into the offspring epoxide by a ON/OFF reversible temperature switch.^{51,54} If the formation of alicyclic carbonates with two fused five-membered rings in a *trans* conformation is energetically unfavorable due to the ring strain (as observed for poly(cyclopentene carbonate), such conformers become the competitive degradation products when reducing the ring strain via an increase of the fused alicyclic ring size. These *trans* scaffolds might be revalorized as monomers for ROP polymerization (see section 4). Moreover, the judicious choice of the catalyst and operative conditions also allow for controlling the PC degradation into the native epoxide and CO_2 , or into the *trans*-alicyclic carbonate. These features are illustrated for the depolymerization of poly(cyclohexene carbonate) which endwise scission (Scheme 3, pathway *i'*) initiated by a (Salen)Cr(III)Cl/PPN₃ catalytic system provides exclusively and quantitatively cyclohexene oxide (**4**) in bulk conditions at 200 °C in 20 min under static vacuum.⁵³ In contrast, *trans*-cyclohexene carbonate is selectively and quantitatively produced in solution at 110 °C after 170 h when PPNN₃ was replaced by ⁿBu₄NN₃ (Scheme 3, pathway *ii*).⁴⁶ Similarly, Buchard further extended the utilization of a dinuclear Mg(II) complexes, known to promote the CO_2/CHO copolymerization,⁵⁵ to the depolymerization of poly(cyclohexene carbonate) into the native epoxide (**4**) at 120 °C in 24 h with a high degree of selectivity (92-98%).⁵⁶ Interestingly, the mononuclear counterpart catalyst is less efficient and selectively furnishes the *trans*-cyclohexene carbonate (Scheme 3, pathway *ii*). Very recently, the utilization of a homogeneous dinuclear methyl zinc catalyst (BDI-ZnMe)₂ has given access to poly(cyclohexene carbonate) by ROCOP of *meso*-cyclohexene oxide (**4**) with CO_2 . In the presence of water traces, the catalyst is converted into heterogeneous multinuclear zinc catalyst (BDI-(ZnMe₂ • 0.1H₂O))_n, which selectively degrades the polymer into the starting monomer in 9 h at 150 °C (Scheme 3, pathway *i'*).⁵⁷ Recent breakthrough discovery by Williams et al. employs a heterodinuclear Co(II)Mg(II) catalyst to deconstruct ROCOP PCs made from CO_2 and series of alicyclic epoxides at the solid state, yet delivering the native epoxides in up to 95 % yield with >99 % selectivity at 100-140 °C. Remarkably, the catalyst itself could also be recycled up to 4 times without compromising its activity or selectivity.⁵⁸

Trans-cyclohexadiene and *trans*-cycloheptene carbonates are identified as the sole degradation products of the corresponding ROCOP poly(hexadiene carbonate) and poly(cycloheptene carbonate) (Scheme 3, pathway *ii*, from compound **5** and **6**) when depolymerizations are assisted by the strong base NaHMDS and/or (Salen)Cr(III)Cl/ⁿBu₄NN₃ at 110 °C in solution.^{59,60} Beside, biorenewable limonene oxide (LO) (**7**) has

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been copolymerized at r.T. with CO₂ using β-diiminate (BDI) zinc catalyst to produce poly(limonene carbonate) with exclusive carbonate linkages. This PC reverts back exclusively in 5 h to LO, even under 40 bar of CO₂, at 110 °C when catalyzed by the strong base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).⁶¹ Detailed mechanistic studies have shown a dominating endwise degradation of the chains through decarboxylative ring closure. Meanwhile, TBD catalyzes competitive intra- and intermolecular transcarbonation reactions between the alkoxide chain ends and the PC skeleton. This creates “dead” polymer strands which only degrade slowly when involved in new transcarbonation reactions.



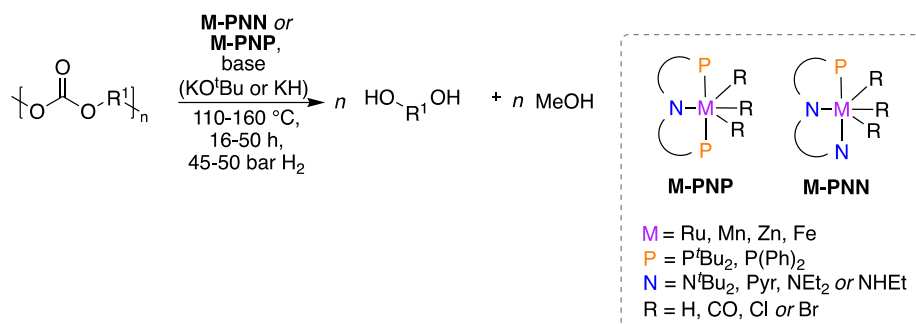
Scheme 3. Polycarbonates synthesis by ROCOP of various alicyclic epoxides with CO₂ and their depolymerization pathways.

3.3 Hydrogenation of PCs.

Recycling end-of-life ROCOP polycarbonates by metal-catalyzed hydrogenation offers an indirect route to convert CO₂ into methanol with the co-production of vicinal diols. This hydrogenative depolymerization scenario is illustrated for poly(propylene carbonate) of M_n up to 100,000 g/mol.⁶² Various noble or earth abundant metal

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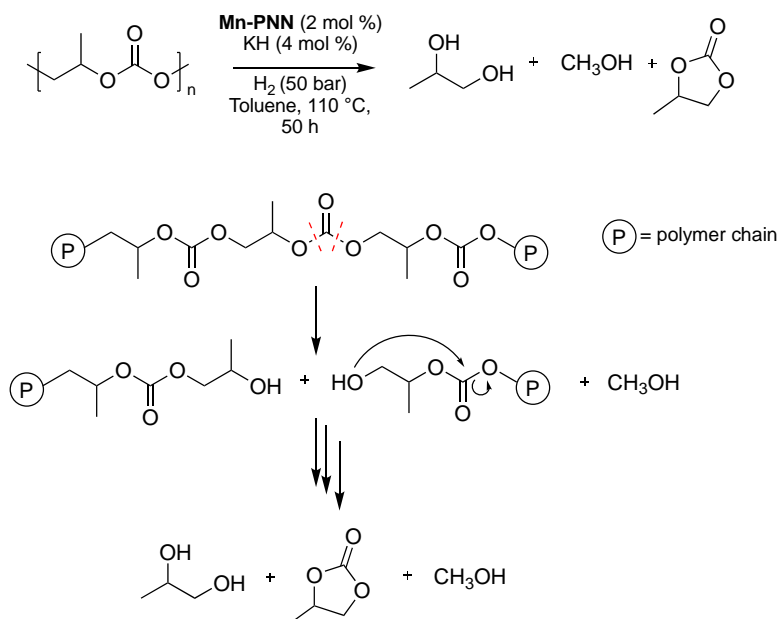
complexes derived from Ru, Mn, Zn or Fe ligated by bis(di-alkyl/phenyl-phosphine)-2,6-diaminopyridine (PNP) or (alkyl/aryl-phosphine)methyl)-2,2'-bipyridine (PNN) pincer ligands have been engineered and used in combination or without additional bases (KO^tBu, KH) to promote the PC hydrogenation at 110-160 °C, in 16 to 50 h, under 45-50 bar of H₂ (Scheme 4).⁶²⁻⁶⁵



Scheme 4. Metal-PNP or PNN catalyzed hydrogenation of PCs.

As reported by Ding et al., the catalytic activity of Ru-PNP complexes for the hydrogenative depolymerization of poly(propylene carbonate) furnishes methanol and propylene glycol with yields >99%.⁶² Alike Ru systems, Mn complexes furnish propylene glycol and methanol but with lower yields of 91% and 84%, respectively.^{63,64} By using KH as a base, the product selectivity is affected by side reactions delivering propylene carbonate by-product (30%) (Scheme 5), that is assumed to come from the competitive thermal reversion of the PC by unzipping or the carbonylation of the vicinal propylene glycol by the polymer chains.⁶⁴ Recent catalytic discoveries have permitted the improvement of the hydrogenation process of poly(propylene carbonate), yet quantitatively delivering methanol and propylene glycol under mild conditions using an efficient Fe pincer complex that operates without requiring a base.⁶⁵

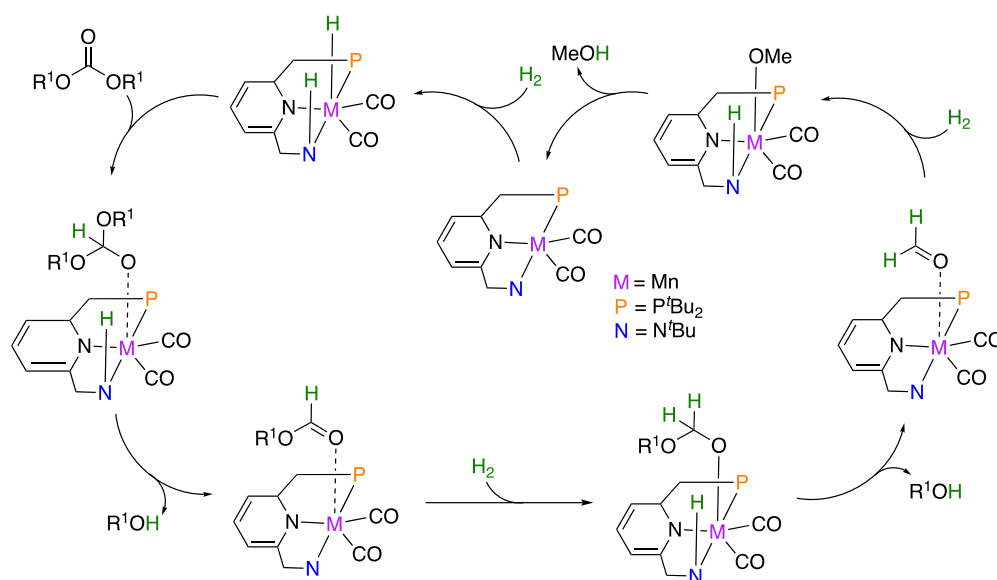
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Scheme 5. Hydrogenative depolymerization of poly(propylene carbonate).

The overall deconstruction mechanism of PCs chains proceeds via domino hydrogenation events (Scheme 6).^{63,64} Following the creation of a 16 electrons metal complex upon addition of a base, the heterolytic cleavage of H_2 enables the hydrogenation of the catalytic species via hydride addition onto the metal center as well as the protonation of the ligand. In a second step, the catalyst promotes the reduction of the carbonyl moiety of the PCs via transfer of the hydride to the sp^2 atom of the substrate. This creates two strains being end-capped either by a formate or an alcohol. Then, the formate species is involved in a novel hydrogenation event producing an alcohol terminated chain and formaldehyde. Formaldehyde is finally reduced into methanol co-product. The repetition of the depolymerization process at each carbonate linkage leads ultimately to the formation of the vicinal diol and methanol.

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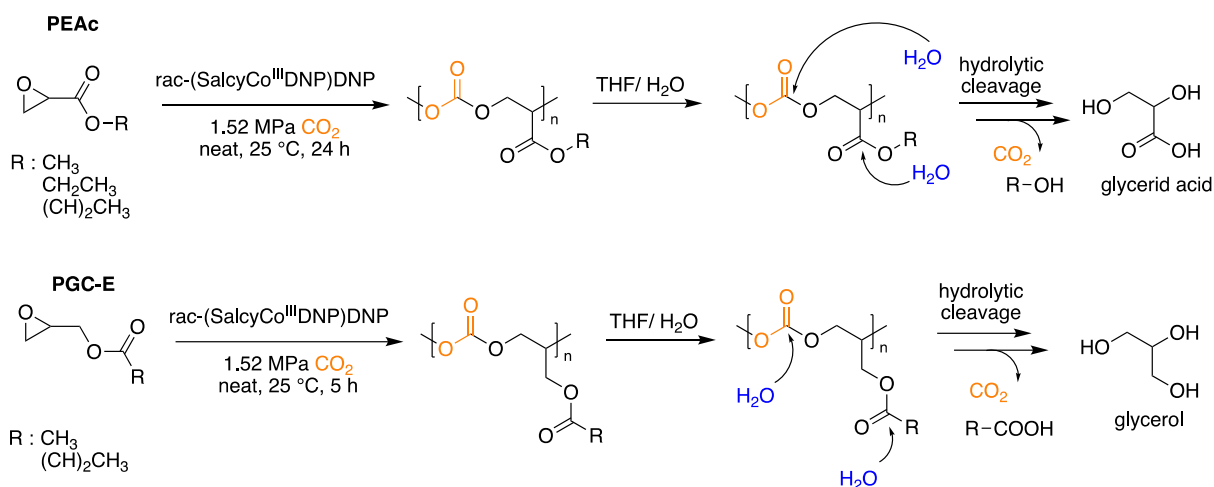


Scheme 6. Deconstruction mechanism of PCs via metal-PNN catalyzed hydrogenation.

3.4 Solvolysis of PCs

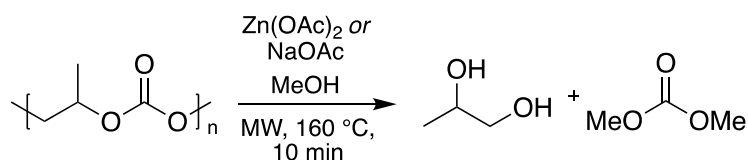
Curiously, despite being one of the simplest means to degrade O-C(O)-O containing polymers, the hydrolysis of ROCOP PCs has been rarely reported. Grinstaff has created a library of novel hydrolysable aliphatic PCs from structurally diverse alkyl glycidate and glycidyl ester type oxiranyl monomers and CO_2 .⁶⁶ PCs of M_n of 5,900 – 10,600 g/mol were synthesized under 15 bar of CO_2 using a trivalent cobalt Salicyl complex at 25 °C (Scheme 7). The orientation of the ester linkage within the monomer dictates the polymerization features, glycidyl ester type epoxides being more reactive due to the low steric congestion and the suppression of the electron withdrawing effect of the carbonyl moiety. Hydrolytic cleavage in a 3/1 v/v THF/water solution of the ethyl glycidate poly(carbonate)s (PEAc), viewed as the degradable version of commercial poly(acrylate)s, furnishes glyceric acid with co-production of ethanol and CO_2 . The glycidyl ester counterpart (PGC-E) degrades into glycerol concomitantly with acetic acid and CO_2 . Both PCs have shown appreciable degradation rates that are controlled by the pH. At low pH value of 5, both PCs display $t_{1/2}$ above 35 days, while the glycidyl ester polycarbonate shows a fast degradation rate with $t_{1/2}$ of only 2 days at pH = 9. Comparative studies have also highlighted the easier degradation ability of the glycidyl ester PC than the constitutional isomeric glycidate material.

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Scheme 7. Synthesis and degradation of PEAc and PGC-E.

Methanolysis of poly(1,2-propylene carbonate) has been recently investigated by Enthaler. By using a cheap $\text{Zn}(\text{OAc})_2$ or NaOAc catalyst, the depolymerization at $160\text{ }^\circ\text{C}$ under microwave generates 1,2-propanediol and dimethyl carbonate after 10 min (Scheme 8).⁶⁷



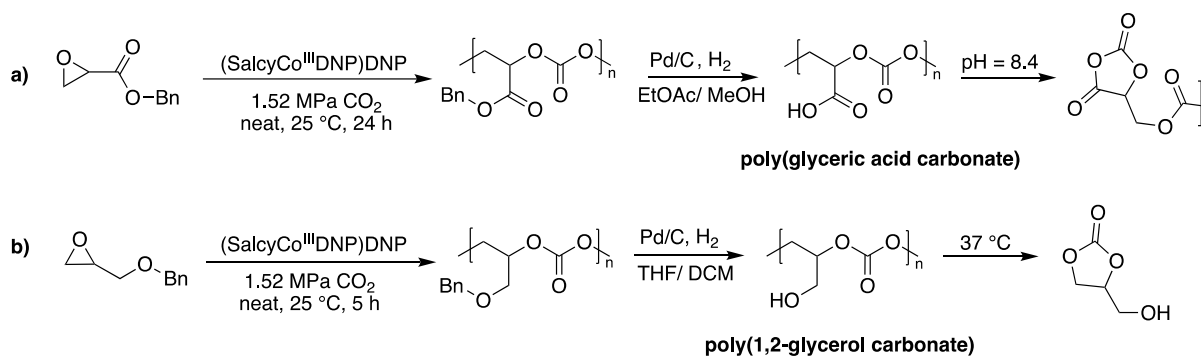
Scheme 8. Methanolysis of poly(1,2-propylene carbonate).

3.5 Self-immolative PCs

Self-immolative polymers refer to materials prone to end-to-head degradation upon cleavage of their backbones or end-caps. They differentiate from degradable polymers by their ability to amplify a response to an external stimulus, yet translating a single cleavage event into the total deconstruction of the chains via cascade events into new chemicals. Notably, such features have propelled self-immolative aliphatic polycarbonates as attractive materials for biomedical and pharmaceutical applications.¹⁸ In the continuation of his previous works, Grinstaff has designed series of PCs of controlled tacticity showing self-immolation properties. Racemic benzyl glycidate and benzyl glycidyl ester, i.e. oxiranyl monomers bearing respectively protected carboxylic acid and alcohol moieties, have been copolymerized with 15 bar of CO_2 at $25\text{ }^\circ\text{C}$ using racemic trivalent cobalt Salen complex with 2,4-dinitrophenolate (DNP) axial ligand, yet furnishing atactic PCs.⁶⁸ Applying a similar polymerization procedure to the *R*-

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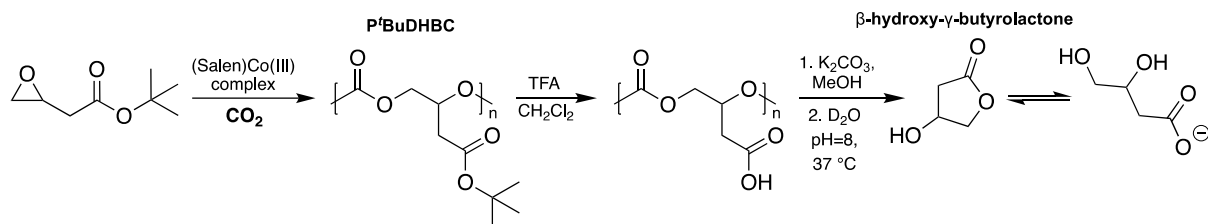
enantiomers in the presence of (chiral) Salen cobalt complexes provides the chiral isotactic version of the polymer.⁶⁹ All PCs have been characterized by M_n of 14,000 to 41,000 g/mol with a 99 % carbonate linkage selectivity and high regioregularity with a head-to-tail connectivity > 92-97 %. Deprotection of the carboxylic acid or alcohol by hydrogenolysis provides poly(glyceric acid carbonate) (Scheme 9a) as degradable mimetic of poly(acrylic acid) and poly(1,2-glycerol carbonate) (Scheme 9b), a degradable substitute to poly(1,3-glycerol carbonate). Poly(glyceric acid carbonate) remains stable for months in the dry state, however unlike poly(acrylic acid), degrades in 26 days in water. Remarkably, by dissolving the PC in a buffer solution at pH = 8.4, the polymer readily self-immolates in 8 h with formation of *O*-carboxyanhydride structures that result from an intramolecular cyclization of the carboxylate moiety onto the adjacent carbonate linkage. Beside, by simple thermal treatment at 37 °C, poly(1,2-glycerol carbonate) spontaneously self-degrades ($t_{1/2}$ = 2-3 days) to produce the thermodynamically stable glycerol carbonate through repetitive intramolecular cyclizations, in line with Frey's similar work.⁷⁰



Scheme 9. Synthesis and hydrogenolysis of poly(benzyl glycidate carbonate)s and poly(benzyl 1,2-glycerol carbonate)s to form poly(glyceric acid carbonate) and poly(1,2-glycerol carbonate).

Similar strategy has been embraced by Darensbourg for the chemical depolymerization of acetyl-capped poly(*tert*-butyl 3,4-dihydroxybutyrate carbonate) (P^{*t*}BuDHBC).⁷¹ The polymer has been obtained by cobalt(III) salen complex catalyzed ROCOP of racemic-*tert*-butyl 3,4-epoxybutanoate and CO₂, followed by a deprotection by trifluoroacetic acid (TFA) and subsequent deprotonation with K₂CO₃ in MeOH. Dissolving the polymer in water (pH = 8) at 37 °C promotes the full degradation into β -hydroxy- γ -butyrolactone and 3,4-dihydroxybutyrate (Scheme 10).

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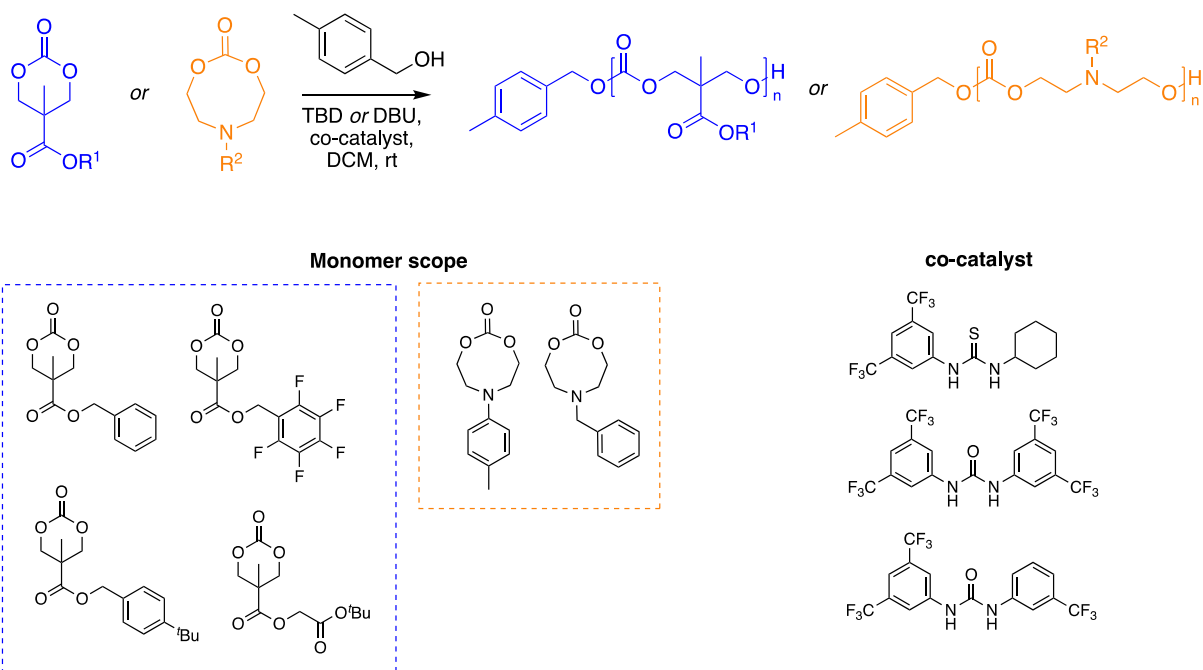
Scheme 10. Synthesis and degradation of poly(tert-butyl 3,4-dihydroxybutyrate carbonate).

4. ROP Polycarbonates

4.1 Access to CO₂-sourced cyclic carbonates and fundamentals of their ROP

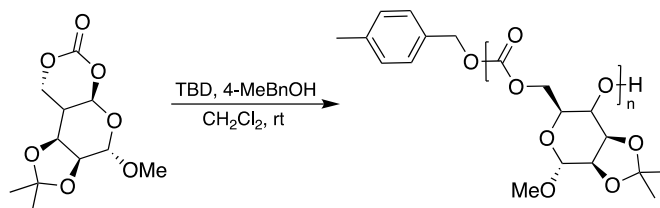
The last decade has seen the emergence of non-reductive coupling methods of CO₂ to afford cyclic carbonates, yet potentially serving as monomers for the construction of aliphatic polycarbonates via ionic, coordination-insertion, enzymatic or dual chain-end-monomer activation ROP mechanisms, as extensively reviewed elsewhere.^{1,18,72} The well-established [3+2] coupling of CO₂ with epoxide provides a large portfolio of five-membered cyclic carbonates (5CCs) under very attractive process conditions.^{22,31,73–76} These heterocycles with small ring strain are stable and their ring-opening polymerization is thermodynamically disfavored and typically accompanied by the elimination of CO₂ to deliver poly(ether-co-carbonate)s (Scheme 11a).⁷² The in-chain ether linkage defects are suppressed by polymerizing five-membered cyclic carbonates fused in the *trans*-fashion to a six-membered ring (*trans*-cyclohexene carbonate (CHC)) (Scheme 11b). Such alicyclic carbonates, produced for instance by thermal reversion of CO₂-sourced poly(cyclohexene carbonate) (see section 3.2), dispose of sufficient ring-strain to deliver the aliphatic polycarbonates without decarboxylation upon anionic⁷⁷ or coordination-insertion^{33,78} ROP conditions. For example, the ^tBuOK-initiated anionic polymerization of *trans*-cyclohexene carbonate produces the corresponding PC of M_n = 11,000 g/mol with > 99 % carbonate linkages. For this system, the associated thermodynamics ($\Delta H^\circ_{\text{polym}} = -23 \text{ kJmol}^{-1}$ and $\Delta S^\circ_{\text{polym}} = -63 \text{ Jmol}^{-1}\text{K}^{-1}$) compare favorably with those reported for the easy polymerizable trimethylene carbonate (TMC).⁷⁷

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Scheme 12. The ROP of six and eight-membered cyclic carbonates.

Another relevant example by Buchard exploits a CO₂-sourced cyclic carbonate fused with a *D*-mannose unit in a *trans* configuration to deliver regioregular PCs (*M_n* up to 33,000 g/mol) at ambient temperature by TBD controlled ring-opening polymerization (Scheme 13).⁸⁷

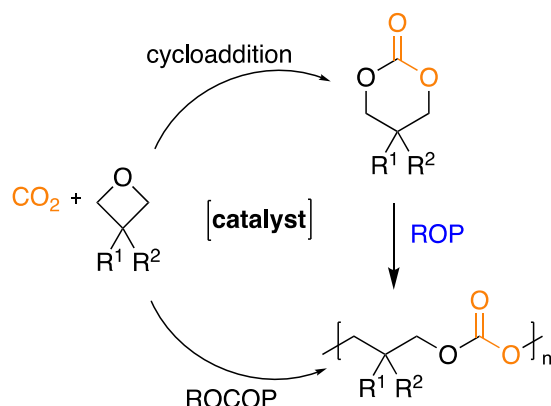


Scheme 13. ROP of CO₂- and *D*-mannose-sourced cyclic carbonate.

The catalytic ring expansion of (substituted) oxetanes with CO₂ is another mean to access TMC and functional analogues.^{88–95} As the six-membered cyclic carbonate is thermodynamically less stable than the resulting PC, affording high cyclic vs linear co-product is strongly dependent on the catalyst and operating conditions (Scheme 14). Various metal complexes including (Salen)CoCl^{96,97} or VO(acac)₂ /onium salts⁹⁰, Al(III)- and Fe(III)-based amino-(triphenolate)s^{88,98,99} and dual organocatalysts such as alkyl boranes/onium or phosphonium halide,⁹³ ammonium acetate/I₂⁸⁹ are reported for such transformation. Selectivity for TMC > 85–99 % was generally achieved at low CO₂

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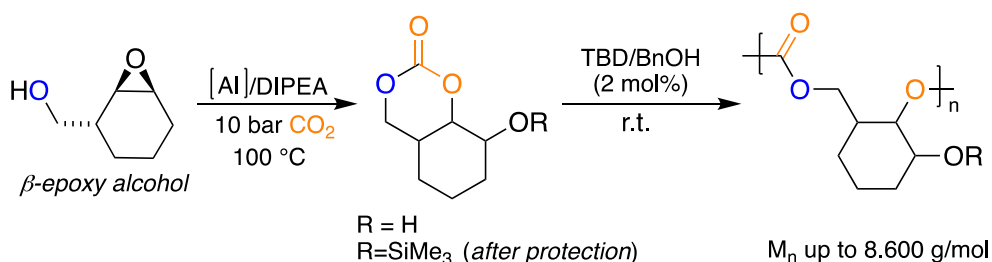
pressure and low temperature. As illustrated by Coulembier for the ammonium acetate/I₂ catalytic system⁸⁹, the energetic barriers for TMC vs poly(TMC) formation by oxetane/CO₂ coupling is estimated to 36.9 kJ/mol vs 49.9 kJ/mol. This sufficient 13 kJ/mol difference in energetic barrier suggests a thermally controllable product selectivity, the formation of TMC being favored at low temperature while poly(TMC) is produced at higher temperature (generally > 75-100°C). Besides, increasing the steric congestion of the oxetane improved the selectivity towards the cyclic carbonate formation.^{97,100} Despite the ROP of the so-produced six-membered heterocycles is not reported, additional contributions have highlighted the formation of poly(TMC) from CO₂ and oxetane through the enchainment of *in-situ* formed TMC by using DBU/I₂⁹⁵ or ⁿBu₄Ni/fluoroalcohol dual catalysts.¹⁰¹ Aided by DFT studies, the CO₂/oxetane ROCOP mechanism has been excluded due to unfavorable polymerization energetics. The formation of the resulting PC with M_n < 10,000 g/mol and the presence of low (or no) ether linkage defects have been attributed to the *in-situ* formation of TMC followed in a domino fashion by its ROP.



Scheme 14. Synthesis of poly(TMC) from CO₂ and oxetanes.

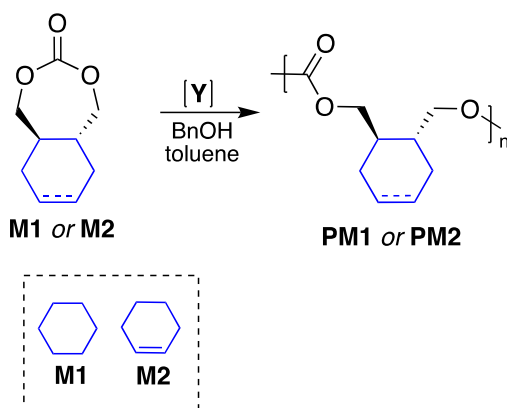
Recently, Kleij has discovered that β -epoxy alcohols with an *anti*-configuration delivers hydroxy-functional densely substituted bicyclic 6-membered carbonates upon direct coupling with CO₂ (Scheme 15).¹⁰² This breakthrough concept employs a binary catalysis involving an aluminum aminotriphenolate complex (AlL(THF)) (where L= tris(2-oxy-4,6-di-tert-butyl-benzyl)amine) and *N,N*-Diisopropylethylamine (DIPEA) as nitrogen base additive and operates at low CO₂ pressure of 10 bar in 22 h at 100 °C. The diversification of the substrate scope furnishes a portfolio of new scaffolds with yields of 44 to 91 %. One representative bicyclic carbonate heterocycle and its *O*-protected version by a silyl group have been subjected to ROP using TBD as catalyst at r.T., yet providing respectively oligomers of low M_n = 1,700 g/mol (for R=H) or short PCs chains with M_n = 8,600 g/mol in 20 h (for R = SiMe₃) (Scheme 15).

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Scheme 15. ROP of β -epoxy alcohols derived six-membered cyclic carbonates.

Larger ring-strained carbonates are also prone to ROP. To the best of our knowledge, only one example from Zhu focuses on the synthesis of 7-membered cyclic carbonates fused in a *trans*-fashion with a cyclohexyl or cyclohexadiene ring by carbonylation of *trans*-cyclohexane-1,2-diyldimethanol or *trans*-cyclohexadiene-1,2-diyldimethanol (Scheme 16).¹⁰³ Thanks to the high ring strain, this new class of highly reactive monomer polymerizes in the presence an yttrium alkyl complex ($\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})$) ligated by tetradentate aminobisphenolate chelant. The ROP is expedient in toluene and approaches a 100 % monomer conversion within 30 seconds, furnishing PCs with M_n up to 673,000 g/mol (Scheme 16). In the continuation of his work on the carbonylation of diols by CO_2 ,¹⁰⁴ Hedrick has reported series of 8-membered heterocycles furnishing PC of $M_n = 1,250 - 7,500$ g/mol in 1.5 – 24 h at r.T. using appropriate (binary) organocatalysts (Scheme 12).⁸⁶



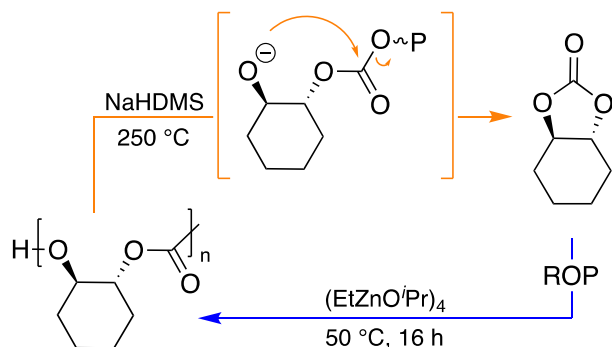
Scheme 16. ROP of seven-membered *trans*-cyclohexane or cyclohexadiene cyclic carbonate using $[\text{L}]\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ complex.

4.2 Thermal tail-to-head reversion of ROP PCs

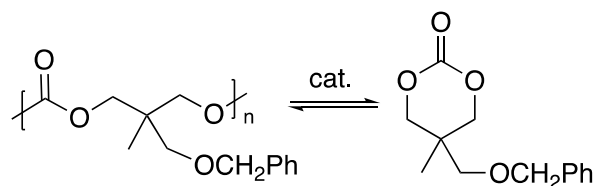
Examples of thermal reversion of CO_2 -derived ROP PCs into repolymerizable scaffolds remain rare. The close loop recycling of CO_2 -sourced PCs made by ROP is illustrated by Coates with isotactic poly(cyclohexene oxide) with hydroxyl end caps.³³ The endwise thermal unzipping of this PC is promoted by NaHMDS base at 250 °C and delivers the

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corresponding enantiopure 5-membered cyclic carbonate fused in a *trans* configuration with a cyclohexene ring, i.e. (*S,S*)-2,2-cyclohexene carbonate (Scheme 17). This monomer is repolymerized following a ROP scenario into isotactic poly(cyclohexene carbonate) using ethyl zinc isopropoxide as a catalyst at 50 °C for 16 h. Rather similar in concept is the depolymerization of poly(5-methyl-5-benzyloxymethyl-1,3-dioxan-2-one), a functional version of poly(TMC) with benzyloxymethyl moieties pending along the main skeleton (Scheme 18).¹⁰⁰ This CO₂-sourced PC reverts by a backbiting pathway into the corresponding six-membered cyclic carbonate (5-methoxymethyl-5-methyl-1,3-dioxan-2-one) in the presence of (salen)Cr(III)chloride complexes and ⁿBu₄NN₃ additive, at 110 °C in 16 h. Under argon atmosphere, the depolymerization is slow, delivering the heterocycle with a yield of 30 % in 200 h, while the depolymerization is strongly retarded, even inhibited, under 7 bar of CO₂. Despite their close loop recycling is not illustrated, the ROP of cyclic carbonates of similar structure has been demonstrated in the presence of a Ti(*i*OPr)₄ catalyst at 210 °C, yet potentially completing the virtuous polymer-to-monomer-to-polymer cycle.¹⁰⁵



Scheme 17. Thermal reversion of CO₂-derived ROP PCs into repolymerizable cyclohexene carbonates.

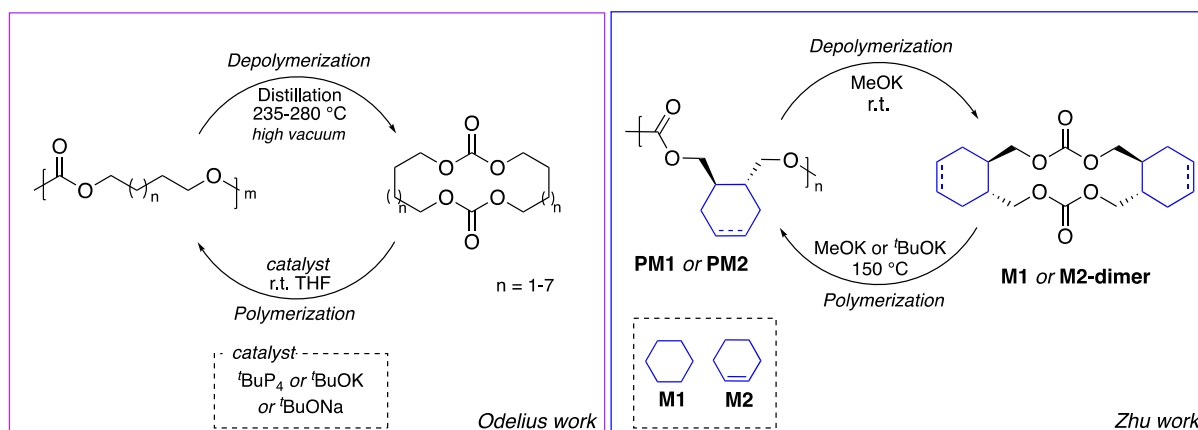


Scheme 18. Depolymerization of poly(3-benzyloxymethyl-3-methyloxetane carbonate) into six-membered cyclic carbonate.

As illustrated above, 7-membered cyclic carbonates containing *trans*-cyclohexyl-fused rings afford high molar mass PCs that follow complete depolymerization at room temperature into new cyclic dimers by simple use of MeOK (Scheme 19). These polymers degrade in a stereoselective manner at high selectivity and yield into

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enantiomerically pure (*R,R,S,S*) cyclic carbonate dimers identified as the stable thermodynamic configuration. As oligomer intermediates have been identified during the process, and by analogy with Odellius' contribution on the ROP of similar macrocycles and their polymer-to-monomer regeneration (Scheme 19), it is supposed that an *in-situ* transesterification depolymerization mechanism governs the deconstruction of the chains.¹⁰⁶ By simple temperature switch to 150 °C, the new dimeric macrocyclic carbonates reenter into the polymerization loop through anionic ROP (using MeOK or ^tBuOK as a base), yet reforming PCs with microstructure identical to the native material, but of significant lower molar mass ($M_n < 7,600$ g/mol)(Scheme 19).¹⁰³

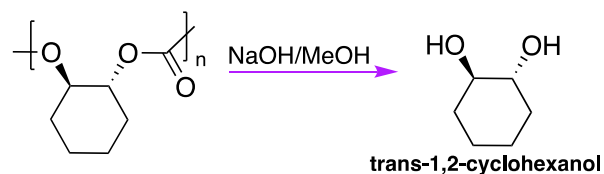


Scheme 19. Depolymerization of poly(*trans*-cyclohexane or cyclohexadiene)carbonates into macrocyclic carbonates.

4.3 Solvolysis of ROP PCs

Beside their thermal reversion to the *trans*-cyclohexene carbonate, isotactic poly(cyclohexene carbonate) is quantitatively degraded by hydrolysis into *trans*-1,2-cyclohexanol and CO₂ by using a NaOH/MeOH mixture (Scheme 20). To the best of our knowledge, the hydrolytic degradation of CO₂-based poly(cyclohexene carbonate) is applied to polymers synthesized by ROCOP. However, considering the polymeric structure, it should be possible to extend such methodology to poly(cyclohexene carbonate) and other CO₂-sourced ROP polymers.^{107–109} One also underlines that poly(trimethylene carbonate) and functional analogues are now easily accessible by ROP of CO₂-sourced monomers. Thanks to their easy tunable degradation properties and biocompatibility, these aliphatic PCs are widely explored for biomedical use for drug delivery, tissue regeneration or the design of vascular grafts. Despite not being the topic of the review, one invites the reader to refer to the excellent review of Dove illustrating all the degradation pathways of such materials via hydrolysis, oxidation, *in-vivo*/enzymatic deconstruction.¹⁸

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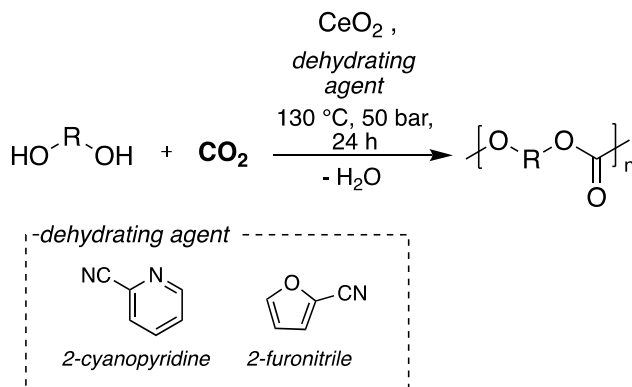


Scheme 20. Solvolysis of poly(cyclohexene carbonate).

5. Step-growth copolymerization (SGP) PCs

5.1 Fundamentals of CO₂-sourced PCs by SGP

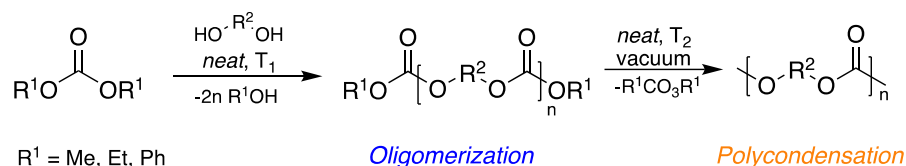
The direct copolymerization of CO₂ and diols is an appealing but challenging method to fabricate PCs, while avoiding using toxic phosgene. The condensation of CO₂ and diols leads to water by-product formation which removal is mandatory to construct PCs chains with reasonable molar masses.^{110,111} The most relevant contribution in this research area has been reported by Tamura et al who describes the direct copolymerization of CO₂ with a wide scope of 1,*x*-diols (*x* > 4) by using CeO₂ heterogeneous catalyst and 2-cyanopyridine as desiccant (Scheme 21).¹¹⁰ Such approach furnishes only oligomers (M_n up to 1,650 g/mol) as a result of the occurrence of various side reactions. The concomitant hydration of the cyanopyridine in presence of the cerium catalyst leads to the formation of the corresponding amide that interferes with the chain growth process. Its reaction with diol chain-ends provides the corresponding ester with release of NH₃ further involved in the ammonolysis of the carbonate linkages and consequently, the PC chains scission.¹¹¹ The formation of ester chain ends is slightly minimized by switching from 2-cyanopyridine to 2-furonitrile, yielding polymers with slightly higher molar masses (M_n up to 5,000 g/mol). Different dehydrating agents/processes (e.g. membranes, molecular sieves, chemical agents) have been also explored, but with moderate success to fabricate PCs of higher molar masses.^{112,113}



Scheme 21. Polycondensation of CO₂ with diols.

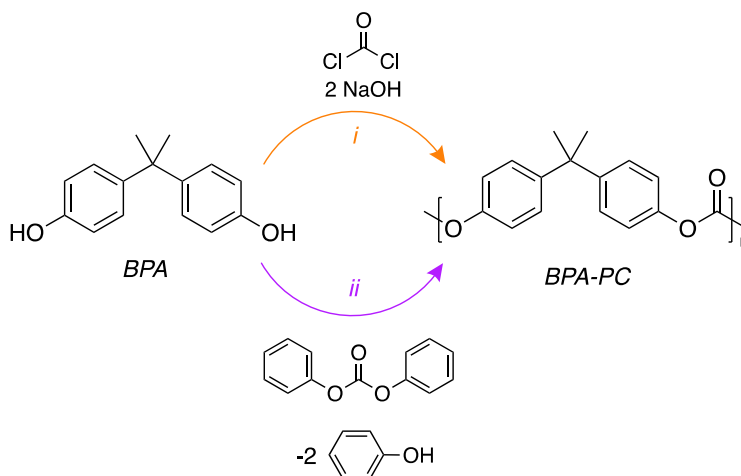
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The step-growth copolymerization (SGP) between diols and a carbonyl source (such as phosgene) is a well-established methodology to deliver high molar mass PCs with diverse microstructures and side-chain functionalities.¹ Alternative synthetic pathways to produce PCs have been developed by using ecofriendly CO₂-derived precursors such as dimethyl- (DMC) or diphenyl- (DPC) carbonates. The polycondensation of CO₂-sourced acyclic aliphatic or aromatic carbonates with diols is a common synthetic strategy that permits to access a large palette of PCs with tunable properties. It is generally performed following a two-steps process involving first the preparation of oligocarbonates of low molar mass by transcarbonation reaction at moderate temperature (T₁ between 80 and 140 °C) followed by chain extension at higher temperature (T₂ between 150 and 300 °C) under high vacuum to remove methanol (for DMC) or phenol (for DPC), thus permitting the chains growth (Scheme 22).^{114–120}



Scheme 22. Polycondensation of acyclic carbonates and diols.

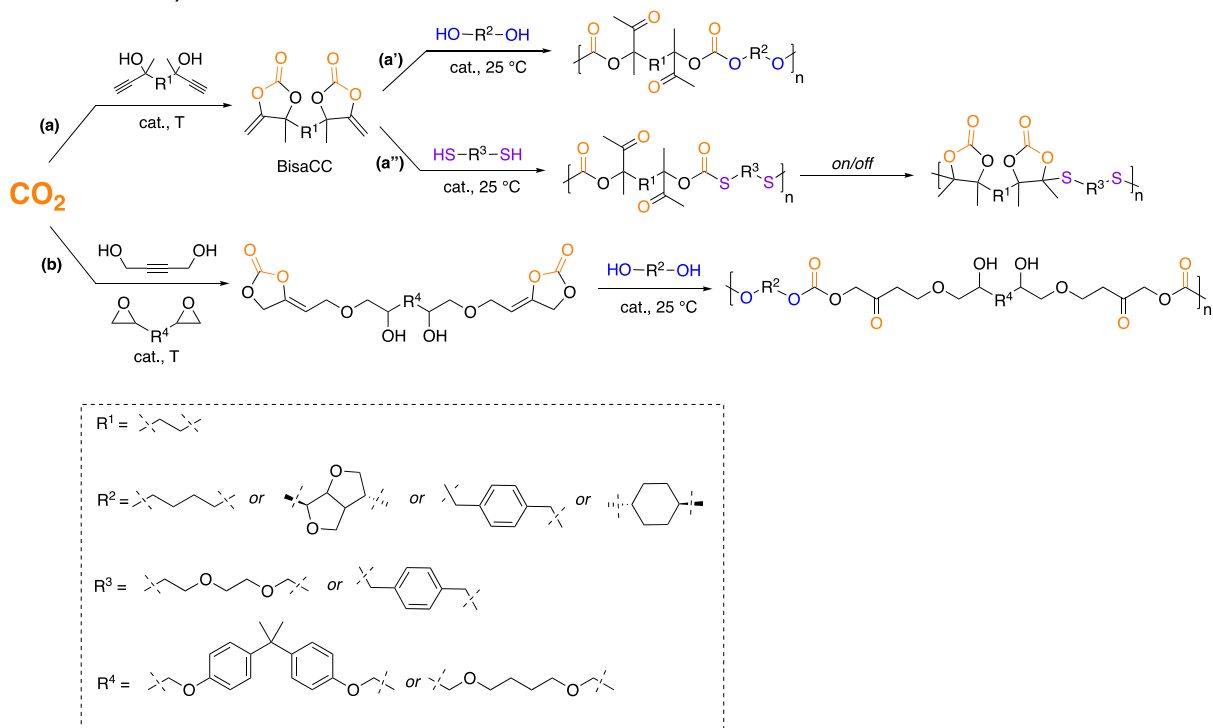
Due to their outstanding thermo-mechanical properties, aromatic PCs are largely exploited in a plethora of applications. The industrial production of aromatic PCs follows the phosgenation of bisphenol A (BPA) (Scheme 23, pathway *i*). However, the phosgene process presents non-negligible safety issues which pushed the scientists to replace it by diphenyl carbonate (DPC). The first process from CO₂ has been developed by Asahi and Kasei group reporting a two-steps procedure of polycondensation between DPC as carbonyl source and BPA to furnish BPA-PCs (Scheme 23, pathway *ii*).^{118,121}



Scheme 23. Synthetic pathways for BPA-PC.

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In 2017, Detrembleur and co-workers have pioneered a versatile and appealing conceptual approach to produce PCs from novel CO₂-based monomers, i.e. bis(α -alkylidene carbonate)s (bis α CCs) and diols through organocatalyzed step-growth copolymerization under mild reaction conditions (Scheme 24a).¹²² The presence of the exovinylene group enhances the reactivity of these 5-membered cyclic carbonates, including against alcohols, and their organocatalyzed ring-opening is regio-selective as the result of the keto-enol tautomerism.¹²³ Defect-free poly(oxo-carbonate)s are thus easily obtained with M_n up to 25,000 g/mol at room temperature. Biorenewable and CO₂-based (semi-crystalline) polycarbonates are also easily accessible by copolymerizing bis α CCs with sugar- (1,4-butanediol or isosorbide) or lignin- (1,4-benzenedimethanol or trans-1,4-cyclohexanediol) based diols (Scheme 24a').¹²⁴ The scope of the polymers has been extended to poly(ethylene glycol) (PEG) diols to produce poly(carbonate-co-ether)s of M_n up to 60,000 g/mol of potential interest as solid electrolytes for battery applications.¹²⁵ Novel poly(cyclic carbonate-co-thioether)s are also accessible by the organocatalyzed copolymerization of bis α CCs with dithiols at r.T. (Scheme 24a'').^{126,127} Similarly, Schaub et al. has designed recently new bis α CCs from the tricomponent reaction between 1,4-butanediol, epoxides and CO₂, and has successfully tailored low molar mass poly(oxo-carbonate)s (M_n < 3,000 g/mol) by polyaddition with 1,4-butanediol (Scheme 24b).¹²⁸

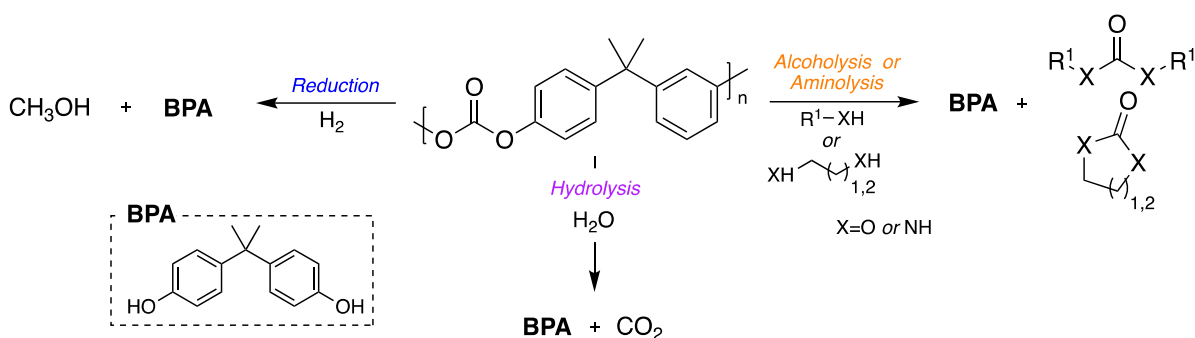


Scheme 24. Synthesis of PCs by step-growth copolymerization of bis α CCs with diols or thiols.

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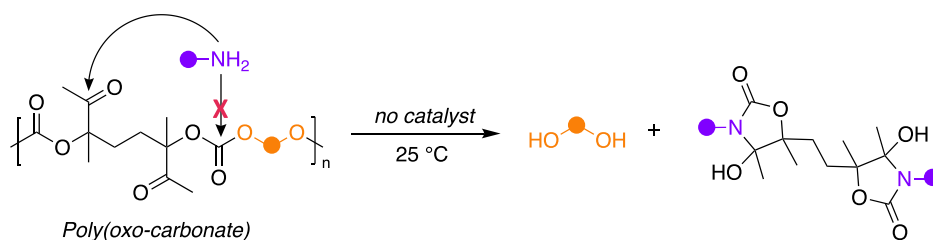
5.2 Chemical degradation of SGP PCs

During the last decade, a strong effort has been exerted on the BPA-PC depolymerization. Thanks to the presence of the carbonyl moieties within the chain, the BPA-PC backbone is prone to easy cleavage by suitable reagents. Using adapted catalysts, BPA-PC can be deconstructed by hydrolysis, alcoholysis or aminolysis, further releasing the native BPA monomer and some useful co-products such as (a)cyclic carbonates, urea, carbamates or methanol (Scheme 25).^{129–138} In addition, the catalyzed hydrogenative depolymerization has been investigated by using iron-complex catalysts and permitted to recover BPA as well as methanol.⁶⁵ The BPA-PC degradation is largely described in dedicated reviews.¹³⁹



Scheme 25. Chemical degradation of BPA-PC.

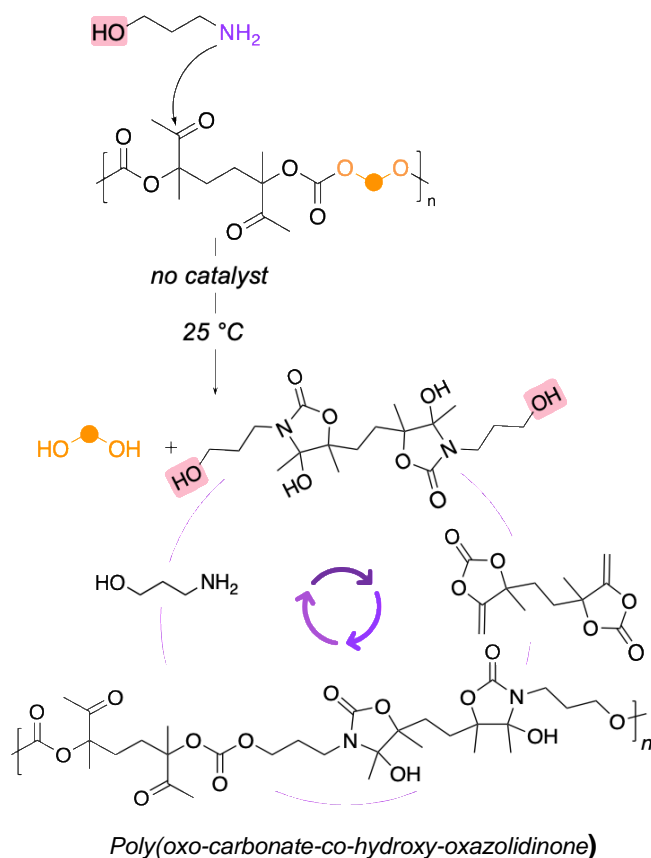
Structurally, poly(oxo-carbonate)s differ from conventional analogues by the presence of additional acetyl moieties which high electrophilic character vs the carbonyl group of the carbonate linkage is an asset for the polymer deconstruction. Their presence, combined to the regioregular and defects-free nature of the chains, endows the polymers with an easy degradability by facile chemo-selective addition of *N*- or *O*-nucleophiles. This is exemplified by the complete deconstruction of series of poly(oxo-carbonate)s derived from bis α CCs and various biobased diols (1,4-butanediol, 1,4-benzenedimethanol, 1,4-hexanediol) which r.T. aminolysis furnished the starting diol and novel bis(oxazolidinone) scaffolds (Scheme 26).¹⁴⁰



Scheme 26. Catalyst-free and chemoselective aminolysis of poly(oxo-carbonate).

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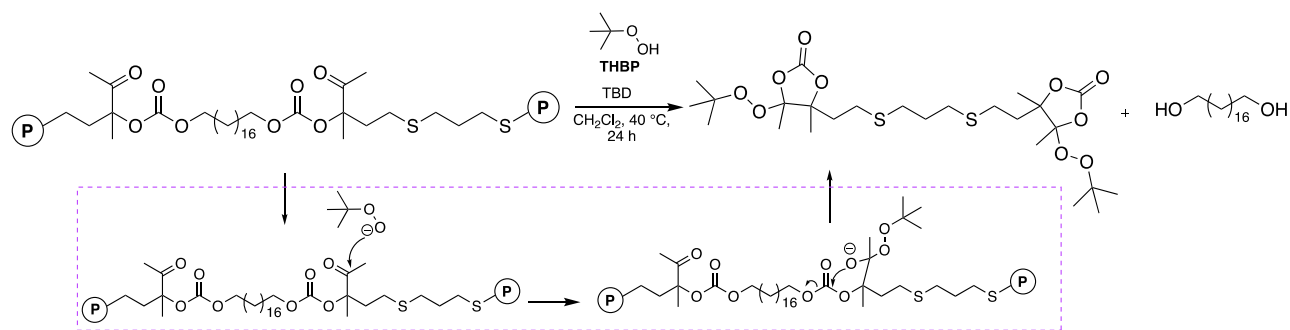
The depolymerization is even found expeditious (< 30 min at r.t.) when the amine is used as the reagent and solvent. Switching to functional amine (e.g. propanolamine) yielded again the offspring diol together with a repolymerizable bis(oxazolidinone) bearing two reactive primary alcohols groups (Scheme 27). Upon SGP with bis α CC, a new "hybrid" polymer alternating oxo-carbonate and oxazolidinone linkages has been designed. This polymer is easily deconstructed by propanolamine into the starting hydroxy-functional bis(oxazolidinone) as unique depolymerization product that could be repolymerized with bis α CC into the same polymer, offering a close-loop recycling scenario to this product (Scheme 27).¹⁴⁰



Scheme 27. PC aminolysis using propanolamine and formation of closed-loop system.

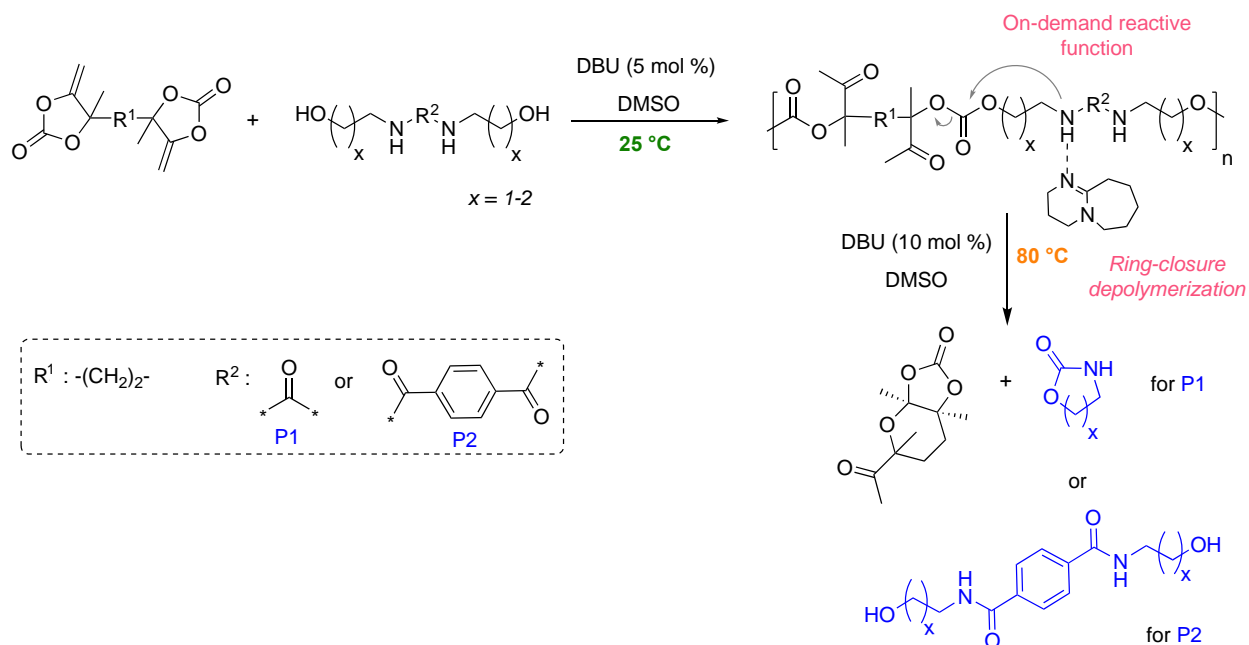
Rather similar in concept is the depolymerization of poly(oxo-carbonate)s employing unstable hydroperoxides as nucleophiles; yet providing the native diol and bicyclic carbonate with peroxides substituents (Scheme 28). However, this depolymerization pathway is slow and required an organobase (up to 20 mol%) as catalyst and thermal conditions (40 °C) to ensure the complete chains degradation.¹⁴¹

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Scheme 28. Depolymerization of poly(oxo-carbonate)s employing unstable hydroperoxides as nucleophiles.

By introducing urea or amide groups within the poly(oxo-carbonate) backbone (Scheme 29), Detrembleur et al. has edited polymers prone to degradation via cascade ring-closing events catalyzed by DBU at 80 °C.¹⁴² This polymer deconstruction provides the native precursor (the diol) or added-value offspring oxazolidinones, together with a hemiacetal cyclic carbonate. When the urea functional poly(oxo-carbonate) is mixed with a common polyester (PCL or PET), the depolymerization of the poly(oxo-carbonate) is selective when the same treatment is applied, leaving intact the polyesters.



Scheme 29. Synthesis of urea or amide functionalized poly(oxo-carbonate)s and on demand cascade ring-closure depolymerization.

6. Conclusions

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Synthetic plastics have become ubiquitous and versatile materials in our modern life. Notwithstanding their considerable presence, *non*-treated plastic wastes lead to *non*-negligible ecological and biological-health issues, but also to economical damages due to the loss of potential resources. The fossil origin of plastics also makes their carbon footprint dramatic. Pushed by environmental incentives, new European resolutions and legal obligations¹⁴³ from the European Commission, there is now an urgent need to reinvent the fabrication of plastics, ideally by exploiting raw biochemicals and waste effluents such as CO₂, while making them more easily degradable/recyclable. This review illustrates where scientists are shifting their gaze for the development of more sustainable plastic materials using raw CO₂. In particular, it summarizes the most relevant synthetic approaches for the production of CO₂-based polycarbonates and highlights their emerging end-of-life scenario. Thanks to catalytic breakthrough discoveries, there is now an impressive body of knowledge on how to construct and control the PCs microstructure via the R(OC)OP approaches, yet imparting desired properties often guided by the need of the final application. Their thermal *tail-to-head* reversion is multi-factors dependent (ceiling temperature, catalytic system, the presence of defects within the main skeleton,...) and provides either the native monomers or (macro)cyclic carbonate products. Aliphatic ROCOP PCs undergo fast and facile base promoted deconstruction by endwise unzipping to deliver exclusively 5-membered cyclic carbonates. Generally, ROCOP PCs derived from (geometrically constrained) epoxides fused with aliphatic ring necessitate binary catalysts composed of a strong base and a Salen complex to deconstruct slowly the chains even under high thermal conditions. PCs derived from CO₂ and epoxides fused with 5-membered ring such as cyclopentene revert preferentially into the parent epoxide and CO₂ through decarboxylative ring closure depolymerization. The release of CO₂ enables to accommodate the strain-induced distortions in these fused systems, minimizing the energy of the two five-membered fused rings. Besides, the formation of alicyclic carbonates with a *trans* conformation becomes energetically favorable when i) reducing the ring strain via an increase of the fused alicyclic ring size (6- or 7-membered rings) and/or ii) driving the chains depolymerization under CO₂ atmosphere, so limiting/preventing the formation of the corresponding fused epoxide by decarboxylative ring closure depolymerization.

The close loop recycling of CO₂-sourced PCs made by ROP has been rarely illustrated. Hydroxyl terminated PCs derived from 5-membered alicyclic carbonates or 6-membered rings revert via *tail-to-head* backbiting above their ceiling temperatures (T > 200-250 °C) into the native cyclic monomers in the presence of appropriate base (NaHMDS) or dual catalyst systems (e.g. azide salt/Salen complex). Beside, ROP PCs derived from 7-membered cyclic carbonates degrade at r.T. using MeOK in a stereoselective manner at high selectivity and yield into enantiopure cyclic carbonate dimers. Their polymer-to-

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monomer regeneration is governed by an *in-situ* transesterification depolymerization mechanism.

The chemical degradation of PCs via hydrolysis, solvolysis or hydrogenolysis is more versatile as it is virtually adaptable to all types of PCs, whatever their origin and microstructures. All approaches require appropriate catalysts and thermal activation, yet leading to the total deconstruction of the chains with concomitant formation of mixture of diols and CO₂ (hydrolysis), (a)cyclic carbonates and ureas (solvolysis) or methanol (hydrogenolysis).

Finally, designing PCs that are intrinsically degradable on demand is an alternative way to overcome the accumulation of plastic waste. Such concept is illustrated for ROCOP PCs designed from oxiranyl monomers bearing protected carboxylic acid and alcohol moieties in which the introduction of a protected active group along the chain skeleton permits to trigger depolymerization upon deprotection. The chain degradation is initiated *via* an intramolecular cyclization, leading to the formation of cyclic compounds such as O-carboxyanhydride, glycerol carbonate or β -hydroxy- γ -butyrolactone.

Depolymerizing PCs into high-value-added products that can be upcycled is a new direction for a more sustainable plastic development. It is noteworthy that almost all current recycling/upcycling strategies focus on RO(CO)P made PCs, with only few studies exploring the chemical degradation of PCs made by SGP. The recently developed poly(oxo-carbonate)s obtained by SGP are offering new perspectives in the field by their facile complete deconstruction by aminolysis at r.T. under catalyst-free conditions or by using hydroperoxide in the presence of an organobase at moderate temperature. By a smart design of their microstructure, self-degradable poly(oxo-carbonate) were recently fabricated by unifying conflicting SPG with on-demand ring-closure depolymerization.

CONFLICTS OF INTEREST

The authors declare no competing financial interest.

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