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Advances in the use of CO_2 as a renewable feedstock for the synthesis of polymers

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Carbon dioxide offers an accessible, cheap and renewable carbon feedstock for synthesis. Current interest in the area of carbon dioxide valorisation aims at new, emerging technologies that are able to provide new opportunities to turn a waste into value. Polymers are among the most widely produced chemicals in the world greatly affecting the quality of life. However, there are growing concerns about the lack of reuse of the majority of the consumer plastics and their after-life disposal resulting in an increasing demand for sustainable alternatives. New monomers and polymers that can address these issues are therefore warranted, and merging polymer synthesis with the recycling of carbon dioxide offers a tangible route to transition towards a circular economy. Here, an overview of the most relevant and recent approaches to CO_2-based monomers and polymers are highlighted with particular emphasis on the transformation routes used and their involved manifolds.

1. Introduction

Polymers are versatile materials finding multiple, every day-life applications in the automotive industry, construction, packaging, medical devices, personal care products, and electrical and electronic applications among others. To date, most of the polymers have been produced from fossil resources. However fossil fuel depletion and the legislative requirement for a circular economy imposing sustainable and renewable plastics are forcing the chemical industry to find realistic alternatives to

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Bruno Grignard obtained his PhD in 2007 under the (co-)supervision of Prof. Robert Jérôme and Dr Christophe Detrembleur from CERM (ULiège, Belgium) in the field of CO_2 utilization for macromolecular engineering through controlled polymerization processes. Then, he continued in the same group as an associate R&D scientist in charge of the development of the Carbon Dioxide Utilization technologies for polymer processing (foaming, solvent, drying, anti-solvents) and polymer synthesis through novel conceptual routes of CO_2 conversion. He is also part of the team that created in 2017 the "FRITCO$_2$T" R&D platform dedicated to CO_2 capture, utilization and recycling at ULiège.

Sandro Gennen

Sandro Gennen obtained his PhD in 2018 under the supervision of Dr Christophe Detrembleur and Prof. Christine Jerome from CERM (ULiège, Belgium). His main research activities focused on CO_2 utilization as C1-feedstock to design novel (degradable) isocyanate-free polyurethanes. In 2018 he joined Celabor (Belgium) as a R&D scientist. His current activities are focused on the functionalization and the utilization of biomass (cellulose and lignin) to design sustainable coatings and in the use of pulsed electric field for extraction of bioactive additives.

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the production of renewable chemicals and polymers.[1–10] Non-edible biomass, such as lignocellulose (issued from wood), is one of the most abundant carbon sources on the earth, and thus represents one of the most promising renewable feedstocks for the chemical industry that does not compete with food production.[11–15] These lignocellulosic compounds are naturally formed by photosynthesis of plants, thus by the photochemical conversion of carbon dioxide (CO_2). Although essential to life on earth, CO_2 is, however, considered as a waste responsible for global warming and climate change. This is mainly the result of human activities that, associated with deforestation, generate larger quantities of CO_2 than plants and microorganisms can absorb to close the loop.

Taking inspiration from nature that is able to fix carbon dioxide into useful materials does not only constitute a way to valorize this abundant, inexpensive, safe, non-flammable and renewable gas but also to diversify our renewable resources for the sustainable production of chemicals and polymers. Major hurdles to the transformation of this C1 feedstock is its inertness towards many reagents, which requires both the use of high-energy reactants and suitable catalysts. In the past few years, a huge number of catalysts have been developed that allow for the successful conversion of CO_2 into commodity chemicals such as methanol, carboxylic acids, dimethyl carbonate (DMC) and urea,[16–25] and polymerisable building blocks and polymers.[26–33]

This review aims at establishing a clear roadmap of the most relevant CO_2-sourced polymers and highlights the novel conceptual routes, strategies and synthetic pathways that have been engineered for converting CO_2 into various macromolecules. This literature survey focuses both on the direct utilization of CO_2 or on the (co)polymerisation of (potentially) CO_2-based building blocks. In the direct approach, CO_2 is used as a monomer in combination with appropriate reagents and catalysts to produce polymers with a high CO_2 content such as polycarbonates, polyols, polyurethanes, polyureas and polyesters. In the second approach, CO_2 is transformed into organic molecules [(a)cyclic carbonates, carbamates and ureas among others] that enable the synthesis of a wide variety of polymers with specific and controlled properties. The synthesis of polymerisable building blocks compatible with existing infrastructures and industrial processes of plastic producers is a complementary key strategy to accelerate and facilitate a transition from existing fossil-based to CO_2-sourced plastics.

Special attention will thus be devoted to discussing the various polymerisation approaches that have been scrutinized taking advantage over versatile polymerisation techniques including ring-opening copolymerisation (ROCOP), ring-opening polymerisation (ROP), polycondensation reactions and terpolymerisations. The structural diversity that can be attained in CO_2-derived monomers is a testament of how the polymer properties can be regulated by a judicious choice of the reactants providing new

Christine Jérôme

Christine JEROME completed her PhD in the field of electropolymerization in 1998 at the University of Liege (ULIEGE, Belgium). In 2000, she joined the University of Ulm in Germany as a recipient of the Alexander von Humboldt scholarship and studied the synthesis of functional magnetic nanohybrids. In 2001, she was awarded permanent FNRS Research Associate at ULIEGE, became a Professor and the director of the Center for Education and Research on Macromolecules (CERM) in 2006, and was promoted full Professor in 2013. Her research interests include electropolymerization, biosourced polymers, functional macromolecular systems and advanced biomaterials. Christine has (co)authored around 390 publications.

Arjan W. Kleij

Arjan W. Kleij received his PhD in 2000 working on dendrimer- and hyperbranched based catalysts. In 2000, he joined Avantium focusing on biopolymer synthesis, and later on Hexion in the Epoxy & Phenolic Resins Division. He joined the group of Javier de Mendoza (Madrid) as a postdoc in 2002, and continued at the University of Amsterdam with Joost Reek in the field of catalysis. In October 2006 he joined the ICIQ, where he was promoted to ICREA professor in 2011. Arjan has (co)authored around 175 publications and 4 patents, and his research interests include CO_2 valorization catalysis and biopolymer development.

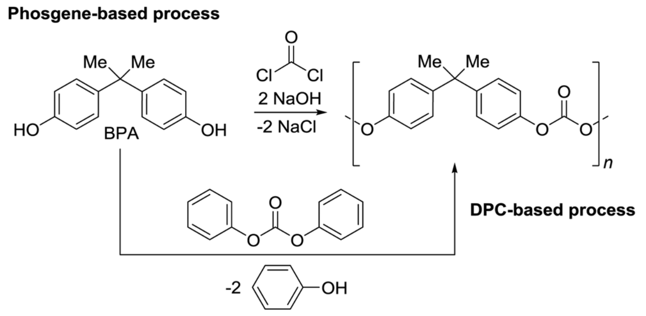
Christophe Detrembleur

Christophe Detrembleur obtained his PhD in 2001 from ULIEGE (Belgium) in the field of new controlled radical polymerization (CRP) techniques. He then moved to Bayer AG (Leverkusen, Germany) as a research scientist to develop new polymers from CRP and low viscous UV-curable formulations. In 2003, he joined ULIEGE as a permanent FNRS Researcher (currently as Research Director) to create his research group dedicated to the preparation of multi-functional (co)polymers by CRP and to the use of CO_2 as a C1-feedstock for the synthesis of low carbon footprint materials. Christophe has (co)authored around 270 publications and 25 patents.

impetus for the development of more sustainable plastics, and novel types of materials.

2. Polycarbonates from CO_2

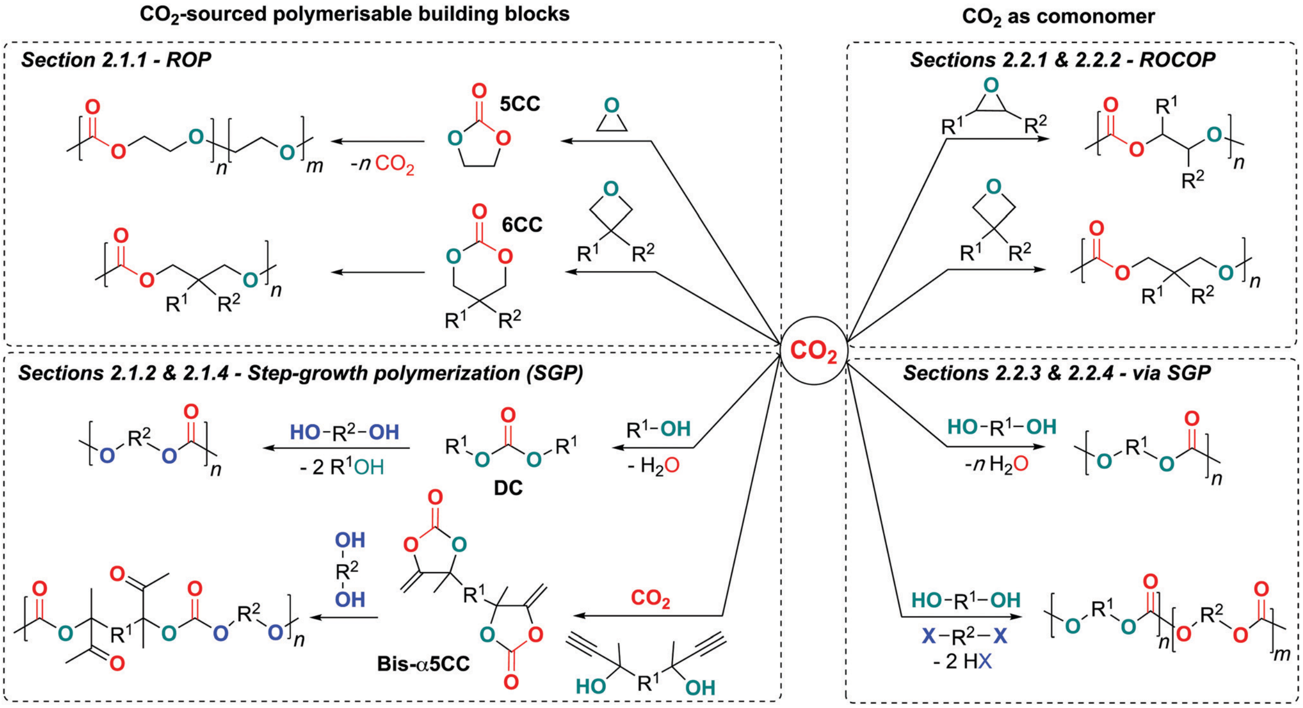
Polycarbonates (PCs) are polymers with $–(OCO_2R)–$ repeat units within their main backbone. Aromatic PCs with high impact resistance, stiffness, toughness, good thermal stability, transparency and flame retardancy are used as engineering plastics in automotive, electrical and electronic devices and in construction. Aliphatic PCs exhibit poor mechanical properties which restricts their scope of utilisation in packaging, as a binder in ceramics or as polyols for the formulation of polyurethane foams.[34–38] However, their biodegradability and biocompatibility make them useful candidates in the biomedical sector.[37,39–43] Industrially, these materials are largely produced from bisphenol A (BPA; *cf.*, aromatic PCs) or diols (*cf.*, aliphatic PCs) and phosgene or diphenyl carbonate (DPC; Asahi process) by melt polycondensation (Scheme 1).[44,45]



Scheme 1 Synthesis of aromatic PCs by a phosgene- or a DPC-based process.

Scheme 2 illustrates the most relevant alternative pathways to the industrial route that valorises CO_2-sourced building blocks or CO_2 as monomers for PC synthesis. These strategies include the ring-opening polymerisation (ROP) of cyclic carbonates, the ring-opening copolymerisation (ROCOP) of CO_2 with oxiranes, and various step-growth approaches, *i.e.* the polycondensation through transesterification of acyclic carbonates (dimethyl-, diethyl- or diphenyl carbonate; DMC, DEC and DPC respectively) with diols, the direct copolymerisation of CO_2 with diols or mixtures of diols and dihalides, and the polyaddition of activated bis-α-alkylidene five-membered cyclic carbonates and diols. As a general remark, it should be mentioned that it is not always clear whether the used monomers are produced from CO_2 or not because the synthetic procedures of the different CO_2-sourced building blocks are not always described in detail in the literature, and usually polymerisation reactions are performed using commercial monomers that may be produced from CO_2 or not.

To facilitate the understanding about the origin of CO_2 in the different polymerizable monomers, the most efficient strategies for the synthesis of CO_2-sourced building blocks were briefly reported before describing the different polymerisation methods that involve the corresponding CO_2-sourced monomers. As the current syntheses of the different organic carbonates used for PCs are well-developed using CO_2, we have also included the synthesis of PCs from carbonates of unknown synthetic procedures to illustrate the potential of CO_2-sourced



Scheme 2 Pathways for the synthesis of PCs from CO_2-sourced building blocks or from CO_2 directly.

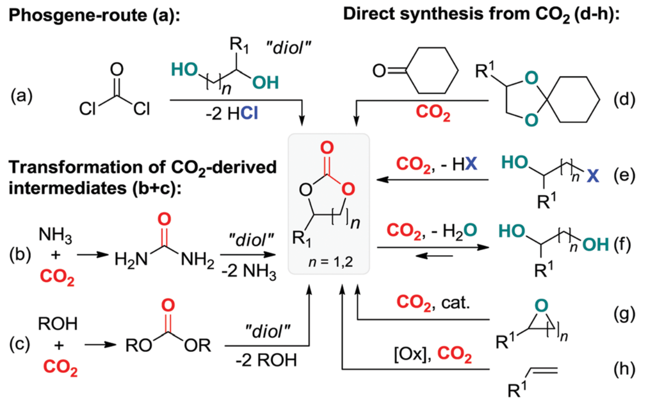
polymer synthesis from CO_2-sourced organic carbonates. This remark is also valid for the discussion related to the different polymerisation techniques used for polyurethanes (PUs) and polyureas (PUas), a class of polymers that will also be discussed in detail in this review.

2.1 Poly(carbonate)s from CO_2-sourced building blocks

2.1.1 Poly(carbonate)s by ring-opening polymerisation of five- or six-membered cyclic carbonates. Currently, 5- and 6-membered cyclic carbonates (5CCs and 6CCs) are mainly synthesized by ring-closing reactions of vicinal or 1,3-diols with phosgene[46,47] or phosgene derivatives such as 1,3-ethylchloroformate,[48,49] triphosgene,[50] carbonyldi-imidazole[51] and bis(pentafluorophenyl)carbonate[52] (Scheme 3a). Scheme 3 illustrates the various alternative pathways that have been developed to prepare 5- or 6CCs either by post-transformation methods, using CO_2-derived precursors or by direct use of CO_2 as a C1 reagent.

In the indirect approach, 5 or 6-membered cyclic carbonates have been synthesized by condensation of urea or dialkyl/diarylcarbonate with vicinal or 1,3-diols, respectively (Scheme 3b and c). Ethylene carbonate (EC), propylene carbonate (PrC), glycerol carbonate (GlC) and trimethylene carbonate (TMC) have been produced from urea and the corresponding diols in moderate to good yields (43 to 99%) at high temperature ($T > 140$ °C) in 0.5 to 4 h using (mixed) metal oxides,[53–55] metal ion-exchanged zeolites,[56] Au and Pd based nanoparticles,[57] and ionic liquids[58] as catalyst systems.

Using a similar strategy 5CCs (mostly GlC) were synthesized from dimethyl- or diethyl carbonate by transesterification with glycerol. This approach required demanding experimental conditions and generally afforded the cyclic carbonate products in high yields (>89%) in 0.5 to 2 h at 70 to 100 °C in the presence of various catalysts such as organic bases,[59] metal oxides[60] and ionic liquids.[61] With 1,3-diols, the synthesis of 6CCs follows an oligomerisation/thermally induced degradation process. Low molar mass oligocarbonates are first produced by transesterification of 1,3-diols with DEC at temperatures in the range of 110–170 °C followed by their thermal depolymerisation enabled by sodium,[62] sodium methoxide,[63] tin(II) 2-ethylhexanoate,[64] dibutyltin dilaurate[65] or NaH.[66] For both indirect routes, the formation of the 5- or 6-CCs is accompanied by the release of either ammonia or small alcohols such as methanol or ethanol.



Scheme 3 Synthetic pathways for the synthesis of CO_2-sourced 5- and 6-membered cyclic carbonates.

Various strategies for directly converting CO_2 into cyclic carbonates have been described (Scheme 3d–h). Aresta reported on the low-efficiency synthesis of 5CCs by coupling of CO_2 and ketals under supercritical conditions (T = 80–110 °C, p = 100–160 bar) for 8 h using metal oxides (based on Zr, Ti or Nb) or metal complexes (M = Fe, Cu, Zn) with perfluorinated ligands as catalysts (Scheme 3d).[67] Wang and Zhang utilized 1,2- and 1,3-halohydrins and CO_2 to produce EC analogues and TMC with yields between 8 and 95% at 1 to 35 bar for 4 to 15 h (Scheme 3e).[68,69] The reaction was promoted by bases such as K_2CO_3 and Cs_2CO_3 that deprotonate the hydroxyl group of the halohydrin. This deprotonation facilitates the formation of a linear carbonate nucleophile that triggers an intramolecular cyclization with elimination of an acid (HX).

Utilization of vicinal and 1,3-diols as precursors of 5- and 6CCs has also been investigated (Scheme 3f). 5CCs such as EC, PrC and GlC can be prepared by reaction of CO_2 with ethylene glycol, propylene glycol and glycerol, respectively.[70,71] These CO_2/diol coupling reactions are typically performed at high temperature ($T > 110$ °C) and high pressure (from 30 to 150 bar) in the presence of catalysts such as alkali carbonates, organotin compounds, zinc acetate and CeO_2–ZrO_2 catalysts. The major bottleneck of this approach is the concomitant formation of water that renders the CO_2/diol reaction reversible but moreover thermodynamically disfavoured. Despite the use of dehydrating agents such as nitrile compounds (acetonitrile, benzonitrile) or zeolites to push the equilibrium to the side of the carbonate product, 5CCs were obtained in low to moderate yields (1–61%).[71]

Recently, new catalytic systems were developed allowing the synthesis of 5CCs in higher yields and/or under milder conditions. As an example, EC and PrC in yields of 95% and 90%, respectively, were prepared in CH_2Cl_2 at 25 °C by the reaction of atmospheric pressure CO_2 with 1,2-diols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), followed by the addition of 1-bromobutane.[70] 5CCs in high yields (>99% for PrC and EC, and 78.9% for GlC) were obtained at 130–170 °C and 40–50 bar using CeO_2 as a catalyst in the presence of 2-cyanopyridine acting as a dehydrating agent.[72,73] Notably, the same catalytic system was also used for the synthesis of various 6CCs in high yields (62–97%) at 130–170 °C and 50 bar.

A more efficient catalytic system for the synthesis of 6CCs under ambient temperature/pressure conditions was developed by Buchard and co-workers.[74] An *in situ* leaving group approach was proposed to surpass the kinetic and thermodynamic limitations of the DBU catalyzed CO_2/diol coupling reaction. After insertion of CO_2 at 1 bar and rt, tosyl chloride was added to the reaction mixture to transform the unreacted alcohol into a tosylate leaving group that facilitated the ring closing to afford the carbonate product. This strategy enabled the synthesis of various polymerizable 6CCs, as well as 6CCs derived from CO_2 and thymidine[75] or raw sugars such as D-mannose.[76]

One of the most efficient routes towards formation of cyclic carbonates relies on the 100% atom-economy cycloaddition of

CO_2 to oxiranes (Scheme 3g). The synthesis of 5CCs from CO_2 and epoxides has been widely studied and reviewed in the literature.[77–84] At present, there are a number of highly efficient and selective metal-based and organo catalysts that enable the synthesis of 5CCs under mild conditions. As representative examples salen complexes of Al,[85,86] Cr,[86,87] and Zn,[88,89] bimetallic Al salen complexes,[90–93] Mg- and Al-centered porphyrins,[94] and aminophenolate complexes derived from Fe[95] and Al[96] have been developed as efficient homogeneous catalysts allowing (in the majority of these cases) the solvent-free synthesis of 5CCs at rt or low temperature (T = 25–80 °C) and CO_2 pressures in the range of 1–100 bar.[80,84]

In the past few years, several organocatalysts based on ammonium or phosphonium salts, ionic liquids, organic bases, and azaphosphatranes have also been developed for the synthesis of cyclic carbonates from epoxides and CO_2.[77–79,81] These catalysts are generally sufficiently active at temperatures between 50 and 140 °C and a CO_2 pressure between 10 to 100 bar. The catalytic activity of these types of organocatalysts can be significantly boosted by the addition of hydrogen-bond (HB) donor (co)catalysts such as phenol derivatives,[97] fluoroalcohols,[98] silanols,[99] boronic acids,[100] squaramides[101] or ascorbic acid,[102] or by designing two-component, bifunctional systems incorporating OH, COOH or NH_2 groups into ammonium or phosphonium salts and ionic liquids.[103–110] By correlation of DFT and experimental studies, D'Elia assessed recently the role of the Brønsted acidity of the hydroxyl protons in designing highly efficient HBD co-catalysts and concluded that the optimum acidity is in the range $9 < pK_a < 11$.[111] Heterogeneous catalysts are typically less efficient for cyclic carbonate synthesis as compared to homogeneous systems apart from those immobilized onto supports with residual hydrogen bond donor groups such as silica and cellulose: in those cases the HB groups are assumed to activate and facilitate the epoxide ring-opening of the epoxide.[81,112]

The synthesis of 6CCs by CO_2/oxetane coupling reactions is more challenging. In contrast to epoxides, oxetanes are less reactive though this is not (as sometimes assumed) due to large differences in ring strain: the strain energy difference between the simplest epoxide (EO) and oxetane is only 2 kcal mol^{-1}. The ring-opening of epoxides is simply more favored, as the smaller C–O–C angles increase the p-character of the nonbonding orbitals of the oxygen lone pairs, allowing for more efficient electron-delocalisation.[113] This in turn gives "aromatic" stabilisation in the ring-opening transition state by orbital-through-interaction bonds (OTIB), an effect that is not as pronounced for oxetanes.[114] Consequently, the transformation of oxetanes into 6CCs requires more demanding conditions ($T >$ 100–120 °C and $p >$ 10–100 bar) that obviously impact the chemoselectivity as attested by the concomitant formation of polycarbonates. However, these limitations can be surpassed by Cr,[115] Co,[116] Fe,[95] and Al[117,118] catalysts that are highly selective for 6CC formation at comparatively low temperature and pressure.

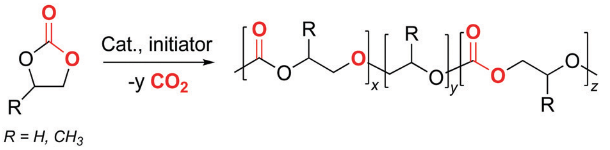
Finally, the oxidative carboxylation of olefins (Scheme 3h) has been proposed as a straightforward method towards the synthesis of 5CCs. This cascade reaction involves the *in situ* formation of an epoxide or halohydrin intermediate *via* olefin epoxidation or oxy-halogenation, followed by the reaction with CO_2 to afford the 5CC product.[119–121] The epoxidation step is generally performed with metal catalysts based on Au, Mn, Ti or Mo in the presence of *tert*-butyl hydroperoxide as an oxidant, whereas halides such as bromide are required for the subsequent cycloaddition.[119] Despite these promising developments, these catalysts are typically tested for the synthesis of styrene carbonate and not for the synthesis of EC and PrC, which are usually used as monomers in polyurethane and polycarbonate synthesis. However, Gao showed the successful synthesis of PrC with a yield of 99% from CO_2 and propylene using a binary quaternary ammonium heteropolyphosphatotungstate/tetrabutylammonium bromide (nBu_4NBr) catalyst system with H_2O_2 as the oxidant.[122]

Aliphatic polymers have been synthesized by catalytic ROP of cyclic carbonates. Considering the thermodynamic features of the ring-opening process and the reactivity of 5CC and 6CC monomers, the structures of the resulting polymers differ depending on the ring size of the precursors (*vide infra*).

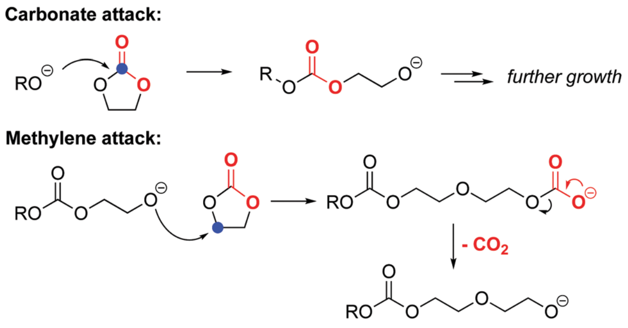
The ROP of 5CCs such as EC or PrC (Scheme 4) is thermodynamically disfavoured because of a high positive value of the polymerisation enthalpy (ΔH^p). For example, a ΔH^p of 125.6 kJ mol^{-1} was measured for the ROP of EC at 25 °C underlining the difficulty to polymerize EC by ROP.[123] However, the ROP of EC is possible if accompanied by some degree of decarboxylation. In fact, random polymers containing oxyethylene (EO) and EC units were synthesized at temperatures above 140 °C after several days in the presence of suitable catalysts such as tin or zirconium alkoxides,[123–125] sodium stannate hydrate,[124,126–128] and various other catalysts.[127]

Mechanistic understanding of this ROP process highlighted two competitive 5CC ring-opening pathways, *i.e.* a reversible and kinetically favoured nucleophilic attack of the active (propagating) species onto the carbonate group of the EC monomer, and an irreversible and slow attack onto the α methylene carbon next to the carbonate function, which is accompanied by the decarboxylation of the polymer chain-end (Scheme 5).[124,129,130] The loss of CO_2 induces the formation of an ethylene oxide unit at the chain end that increases the entropy of the system and furnishes a poly(ether-*co*-carbonate).[129,130]

Copolymers with a carbonate content of 10 to 50% have been obtained with bases, Lewis acids and transesterification catalysts.[129,130] A carbonate content lower than 50% is ascribed to the occurrence of two consecutive "methylene attacks" (Scheme 5) leading to carbonate–ether–ether triads.[124,126,130] By using KOH, Lee *et al.* prepared poly(ether-*co*-carbonate)s with number average molecular weights (M_ns) of up to 9000 g mol^{-1} with the polymer



Scheme 4 Synthesis of poly(ether-*co*-carbonate) by ROP of EC or PrC.

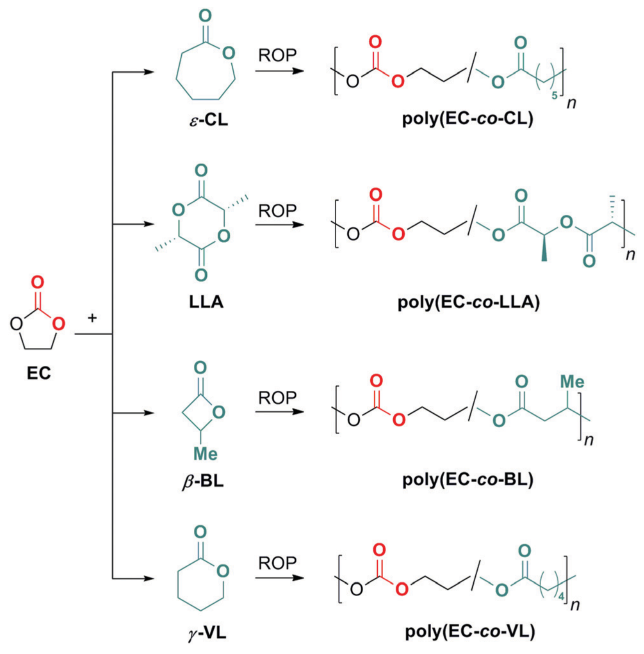


Scheme 5 Different mechanisms of nucleophilic attacks on EC.

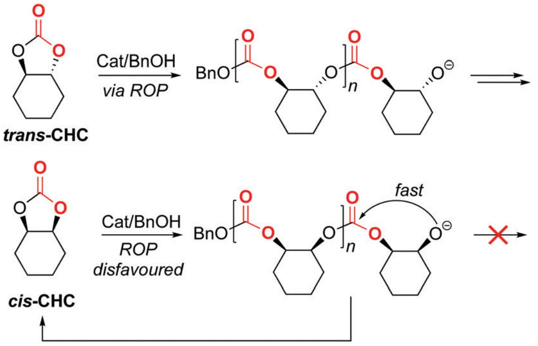
backbone composing mostly of carbonate–ether–ether repeat units.[130] Poly(ether-*co*-carbonate)s with higher M_n values (14 000 g mol^{-1}) and a carbonate content of up to 21% were obtained after 2.5 h at 180 °C in the presence of phosphazenes,[131] while oligomers with carbonate contents of up to 36 mol% were produced at temperatures between 80 and 120 °C using ionic liquids as catalysts.[132]

This concept was extended to the ROP of other 5CCs such as PC, cyclohexene carbonate (CHC) and sugar-based 4,6-*O*-benzylidene-2,3-*O*-carbonyl-*r*-D-glucopyranoside. Low molar mass poly(ether-*co*-carbonate)s with M_n in the range of 3200–4300 g mol^{-1} were obtained at 160–180 °C by ROP of PrC catalyzed by ZnEt$_2$.[133] Apart from ROP, also a ROCOP strategy was developed for facilitating the EC polymerisation. High molar mass polymers (up to 82 000 g mol^{-1}) with a carbonate incorporation of up to 22% were obtained by ROCOP of the 5CC monomer with ε-caprolactone (CL),[134–136] and L-lactide (LLA), see Scheme 6.[136]

One of the most interesting contributions was reported by Guillaume *et al.* who prepared a series of copolymers without loss of CO$_2$ by controlled ROCOP of EC with various lactones or lactide using zinc complexes or organocatalysts (1,5,7-triazabicyclo[4.4.0]dec-5-ene) and a protic source as an initiator.[137] Copolymers with M_n of up to 90 000 g mol^{-1} and an EC incorporation of up to 26, 23, 38 and 17% were respectively produced from EC and either β-butyrolactone (BL), δ-valerolactone (VL), CL and LLA (Scheme 6). Whereas the ROP of EC was not feasible without some degree of decarboxylation, other monomers could be polymerized by ROP without decarboxylation as is the case of *trans*-CHC. Compared with its *cis*-analogue, a *trans*-fused five-membered carbonate ring increases the ring strain of the cyclic carbonate thus favouring its ROP (Scheme 7).[138] In contrast, the *cis*-isomer did not polymerise due to a competitive and faster ring-closing reaction of a ring-opened carbonate intermediate.[139]



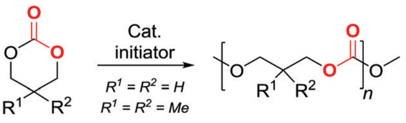
Scheme 6 ROCOP of EC with ε-CL, LLA, β-BL and δ-VL.



Scheme 7 ROP of *trans*- and *cis*-CHC.

ROP of monomers that comprise a *trans*-configured carbonate moiety such as *trans*-CHC and the more complex 4,6-*O*-benzylidene-2,3-*O*-carbonyl-*r*-D-glucopyranoside (MPCG) can be performed under mild reaction conditions. For example, Guillaume *et al.* prepared isotactically pure poly(cyclohexene carbonate) with M_n of up to 21 000 g mol^{-1} by ROP of enantiopure *trans*-(*R*,*R*)-CHC at 60 °C using a bulky Zn(diphenolate) complex combined with benzyl alcohol as an initiator.[139] Endo prepared ether-free PCs with M_n of up to 14 000 g mol^{-1} by anionic ROP of MPCG using DBU as a catalyst at 30 °C for 12 h.[140] Similar PC polymers with M_n of up to 16 000 g mol^{-1} were prepared at 25 °C in tetrahydrofuran (THF) after only 30 s, but rapidly degraded due to the occurrence of back-biting reactions.[141]

Monomers based on 6CCs are thermodyamically more prone to ROP as compared to 5CCs. Thermodynamically, the ring-strain of 6CCs such as TMC or functionalised analogues enables their polymerisation by ROP under relatively mild temperature conditions (Scheme 8). A wide diversity of aliphatic PCs with high molar masses and controlled microscopic architectures can be obtained through various ROP mechanisms including cationic, anionic, coordination–insertion, enzymatic or organocatalyzed approaches.[37,42,43,142,143]



Scheme 8 Example synthesis of two aliphatic PCs by ROP of 6CCs.

Activation of 6CCs by Brønsted acids such as methyl- or trifluoromethylsulfonic acid,[144–146] phosphoric acids,[147] phosphoramidic acids,[148] and Lewis acids including $BF_3{\cdot}(OEt)_2$[49,64,145] allowed for the synthesis of polymers with M_n of up to 23 000 g mol^{-1} and 70 000 g mol^{-1} prepared by solution phase or melt ROP processes, respectively. However, the PCs produced by cationic ROP are prone to (i) decarboxylation, resulting in 3–10% of ether defects in the PC backbone,[49,64,144,149] and (ii) intramolecular transesterification (*i.e.*, "back-biting").[144,146,149] However, PCs devoid of any observable ether linkages were obtained using either methanesulfonic acid,[144] phosphoramidic acids[148] or phosphoric acids.[150] Additionally, loss of CO_2 was suppressed by using methyl iodide as the initiator, thus forming an iodide counter-anion that reduces the risk of the CO_2 elimination pathway ability when compared to the presence of trifluoromethanesulfonate or triflate anions.[48,49]

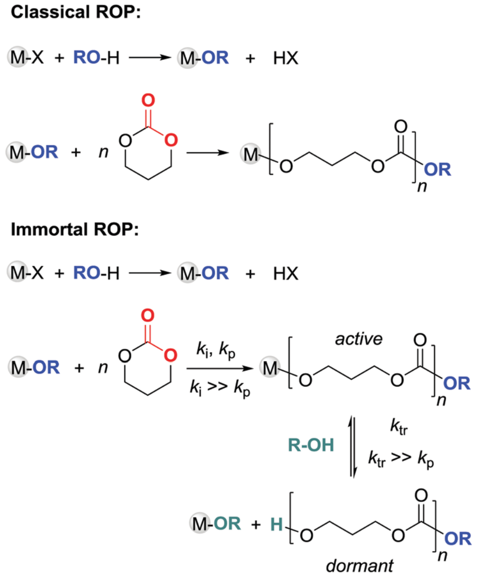
6-Membered cyclic carbonates undergo anionic ROP at low temperature (−30 °C to 0 °C) by using alkoxide or alkyllithium (*e.g.*, *sec*-BuLi) type initiators. This approach provided high molar mass PCs (35 000 g mol^{-1} $< M_n <$ 120 000 g mol^{-1}).[151] However, such prepared PCs were shown to be contaminated by cyclic oligomers resulting from the occurrence of back-biting side-reactions.[151–153] In coordination–insertion ROP, the synthesis of ether-linkage free PCs can be achieved by organometallic complexes derived from Sn, Al, Zn, Ca and lanthanides.[154–161] Through this type of mechanism, the occurrence of back-biting reactions typically observed in ionic approaches can be strongly reduced.[158] Interestingly, a linear increase in the polymer molar mass (M_n values) as a function of the monomer conversion was evidenced by Darensbourg *et al.* who used complexes composed of Ca(II) supported by tridentate and tetradentate Schiff base ligands.[154–156] Indeed, these polymerisation reactions exhibit a "quasi-living" nature enabling control over the molar mass and the micro-architecture of the PCs. Poly(trimethylene carbonate), PTMC, with very high molar masses of up to 355 000 g mol^{-1} was obtained at 130 °C using $Sn(Oct)_2$ as a catalyst.[162]

Recent progress made in ROP has enabled the synthesis of PCs by metal-free systems such as bio-friendly enzymes and organocatalysts. In enzymatic ROP, TMC was polymerised at 55–100 °C in the presence of various lipases such as *Candida antarctica*[163] and porcine pancreatic lipase[164] to afford high molar mass PCs with M_n of up to 169 000 g mol^{-1} with no observable loss of CO_2. However, a more precise control over the polymerisation process remained challenging as exemplified by the occurrence of transcarbonation reactions.

In the last decade, a broad diversity of efficient organocatalysts[165–167] including HB acceptors (guanidines, amidines),[168,169] N-heterocyclic carbenes or olefins,[165,168] and binary amine/thiourea based catalytic systems[168,169] have been developed for the ROP of TMC and more complex analogues. As for metal catalysts effective in the coordination–insertion approach, these organocatalysts allow for excellent control over the PC molar mass and polymer architecture.[168] Remarkably, these catalytic systems were efficient even at ambient temperature (T = 20–30 °C) as highlighted by fast polymerisations with limited transcarbonation side-reactions. In this context, Buchard *et al.* prepared novel PCs by TBD (1,5,7-triazabcyclo[4.4.0]dec-5-ene) catalysed ROP of CO_2-sourced *trans*-3′,5′-cyclic carbonate of thymidine (M_n of up to 17 000 g mol^{-1}), and a 6CC derived from the carboxylation of 2-deoxy-D-ribose producing PCs with M_n of up to 33 000 g mol^{-1}.[75,76] Recently, poly(glycocarbonate)s with various structures were prepared from CO_2-sourced 6-membered glycocarbonates produced by carboxylation of glucose analogues at the 4- or 6-position.[170] Linear and block copolymers with M_n of up to 9 000 g mol^{-1} were produced at rt with TBD acting as the catalyst, while macrocyclic homo- and diblock copolymers with M_n in the range of 3800–5000 g mol^{-1} were synthesized by a zwitterionic DBU/thiourea promoted ROP.

Previously mentioned ROP methods are all classified as "classical" approaches for which the number of growing chains equals the number of active sites provoked by the initiator. Based on the pioneering work of Inoue for the immortal ring-opening polymerisation (iROP) of epoxides,[171] Guillaume *et al.* extended this approach towards the synthesis of aliphatic PCs by iROP of 6CCs.[172–174] iROP can be performed in the presence of suitable metal complexes (*i.e.*, metal triflates, β-diiminate amido- and phenoxyalkyl zinc complexes) or organocatalysts (*e.g.*, 4-dimethylaminopyridine, TBD and phoshazenes) and a protic source such as alcohols, which act both as a chain transfer agent (CTA) and initiator (Scheme 9).

The iROP is essentially based on a reversible chain transfer reaction between active growing and dormant chains. Typically, the process is initiated by using a catalytic amount of a metal complex in the presence of an excess of a CTA, *i.e.* [CTA]/[catalyst] ≫ 1. Due to this excess of CTA, the number of growing chains depends on the initial amount of CTA and not on the concentration of the metal complex as is the case in classical ROP. iROP thus allows for high molar mass PCs with M_n of up to 185 000 g mol^{-1} and low dispersities ($Đ$) in the range 1.1–1.9



Scheme 9 Mechanism of classical ROP *versus* iROP of trimethylene carbonate to afford PTMC. M stands for the metal catalyst, k_i for the rate of initiation, k_p for the rate of polymerisation and k_{tr} for the chain transfer rate.

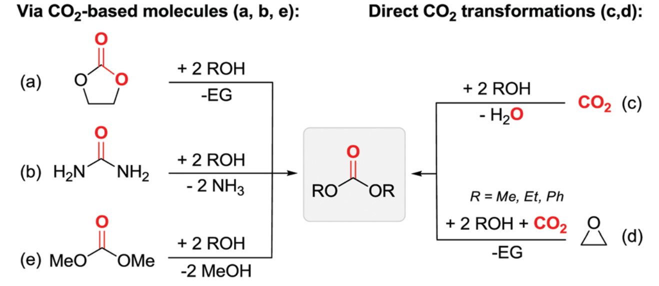
when PTMC is prepared from neat TMC at temperatures between 60–150 °C using a minute amount of catalyst and alcohols such as benzyl alcohol as the CTA.[173–177]

α,ω-Dihydroxy-telechelic PTMC with M_ns between 1300–109 500 g mol^{-1} were prepared by iROP in the presence of diols (1,3-propanediol or 1,4-benzenedimethanol) as CTAs.[172,175,177,178] Typically, these iROP reactions were performed under solvent-free conditions at 60–110 °C using catalysts including $ZnEt_2$, $[(BDI)Zn(N(SiMe_3)_2)]$, aluminum triflate and phosphazene (BEMP). Diols that can be accessed from CO_2-based building blocks (*i.e.*, cyclic carbonates) are interesting for the preparation of PUs by polyaddition approaches using diisocyanates as reaction partners, as will be discussed in Section 3.

2.1.2 Poly(carbonate)s by polycondensation of (a)cyclic carbonates with diols. Currently, the synthesis of acyclic dialkyl- and diarylcarbonates is carried out by phosgenation[179–182] or oxidative carbonylation (EniChem process) of alcohols,[180–185] and by carbonylation of alkylnitrite (UBE process).[180,183,184,186,187] These processes are exploited at the industrial scale to produce disubstituted acyclic carbonates such as dimethyl-, diethyl- and diphenylcarbonate (DMC, DEC and DPC). Besides these phosgene and carbon monoxide based routes, alternative strategies that valorise CO_2 or (potentially) CO_2-sourced intermediates have also been developed (Scheme 10).

A first example is the synthesis of DMC by the reaction of methanol (MeOH) with 5CCs, an approach which has been applied at an industrial scale by various companies including Texaco[188] and Asahi Kasai (Scheme 10a).[44] Another way to produce DMC is the alcoholysis of urea (Scheme 10b).[182,185,189,190] Through similar approaches, DEC can be produced by transesterification of DMC with ethanol[183,190] and by ethanolysis of urea (Scheme 10a and b).[183,189,191] In these processes, the formation of the targeted disubstituted acyclic carbonate is accompanied by the formation of by-products such as methanol, ethylene glycol or ammonia. The reactions are generally performed under vacuum at elevated temperatures in the presence of catalysts such as organotin, hydrotalcites and mixed metal oxides.

The straightforward transformation of CO_2 into disubstituted acyclic carbonates by reactions with alcohols (Scheme 10c) has gained attention in industry and various scientific communities. Various homogeneous and heterogeneous catalysts (ionic liquids, organotin compounds, metal carbonates, ZnO_2/ZrO_2) have been developed to surpass the limitations of this synthetic pathway that typically gives low reaction yields, as the reactions are thermodynamically limited.[70,182–184,192–194] In this regard, Tomishige and coworkers succeeded in the preparation of DMC and DEC with yields up to 96% and 91%, respectively, using CeO_2 as a reusable heterogeneous catalyst and 2-cyanopyridine as a dehydration agent at 120 °C and 20 bar.[195]

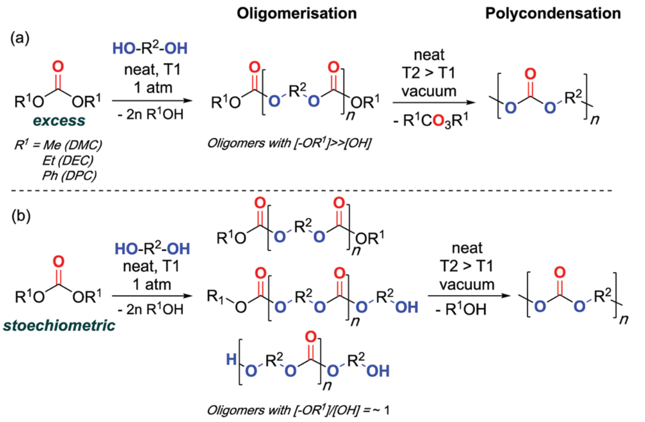


Scheme 10 Synthetic routes for the production of disubstituted acyclic carbonates. EG stands for ethylene glycol.

Apart from the direct synthesis of dialkyl carbonates from CO_2 and alcohols, the one-pot synthesis of dialkyl carbonates from CO_2, epoxides and alcohols presents another strategy for direct CO_2 utilization (Scheme 10d). DMC can be obtained through two subsequent steps that involve the reaction of CO_2 with epoxides to 5CCs, which in turn can be transformed into DMC and a diol by transcarbonation using alcohol reagents. *Via* such a strategy, DMC was produced in the presence of catalysts such as metal oxides and alkaline metal salts supported on oxides.[184,192] DEC was obtained with a yield of up to 64% by a one-pot reaction between CO_2, epoxides and ethanol using a KI-based binary catalyst at 170 °C and 30 bar.[196] DPC could be furnished by a catalytic reaction of (CO_2-sourced) DMC with phenol (Scheme 10e), with efficient homogeneous catalysts being tin alkoxides,[47,197] and MoO_3/SiO_2[198] or Pb–Zn oxides[199] as heterogeneous ones.[47,181] From mechanistic investigations it became evident that the phenol reagent first reacts with DMC to produce a methylphenyl carbonate (MPC) intermediate followed by the transformation of MPC into DPC *via* a second transesterification reaction with phenol or through disproportionation of MPC.[181] A few reports also describe the direct synthesis of DPC by coupling of CO_2 and phenol.[200–202] This latter reaction is generally performed at 100–130 °C and 80–90 bar using catalysts such as Co(salen)OAc containing quaternary phosphonium salts, $ZnCl_2$/triethylamine or silica-coated magnetic Fe_3O_4 nanoparticles. However, only low reaction yields of DPC ($<$32%) were obtained this way. Both DMC/DEC and DPC are key reagents in polycondensation approaches towards PCs, as will be discussed below.

The inherent advantage of polycondensation of acyclic carbonates *versus* ROP of 5- and 6CCs is the access to a larger variety of both aliphatic and aromatic PCs with tuneable properties.[44,203–212] However, the control over the molecular weight and the design of functional polymer architectures are more challenging. In a step-growth polymerisation procedure, PCs are usually synthesized by transcarbonation of diols with dialkyl carbonates (DMC, DEC) or diaryl carbonates (DPC), that can be both produced from CO_2 (Scheme 11a). First, α,ω-methylcarbonate telechelic low molecular weight oligomers are produced by transesterification of DMC with diols: these diols preferentially have a spacer between the OH groups containing more than three carbons to avoid the formation of cyclic carbonate by-products. The polycondensation is performed under atmospheric pressure at temperatures in the range of 80–140 °C to remove the liberated MeOH by distillation. A two- to three-fold excess of DMC compared to the diols was added in order to compensate for the carbonate fraction that evaporated during distillation.

In the second step, high molecular weight PCs are produced by applying higher temperatures (T = 150–240 °C) to induce



Scheme 11 Synthesis of PCs *via* transesterification between diols and (a) an excess of (CO_2-sourced) disubstituted carbonates, and (b) with an equimolar amount of (CO_2-sourced) disubstituted carbonate *versus* the diol reagent.

melt chain extension of the oligomers under (high) vacuum so as to allow elimination of the co-produced, volatile dialkyl carbonate and to favorably displace the polymerisation equilibrium.[212–214] This polycondensation method is facilitated by the use of various catalysts such as inorganic bases (K_2CO_3),[215] alkali metal acetylacetonates [Na(acac), Li(acac)],[207,209] metal-free catalytic systems (1-*n*-butyl-3-methylimidazolium-2-carboxylate, TBD and DMAP),[203,205,206,210,216] and heterogeneous catalysts based on mixed TiO_2/SiO_2 oxides.[211,217] Addition of these catalysts enabled the synthesis of linear and hyperbranched PCs[205,218] with M_n in the range of 16 000–100 000 g mol^{-1} when prepared from DMC and various aliphatic diols, including commercial acyclic diols (*e.g.*, 1,5-pentanediol)[203,205,206,210–212,216] or bio-based isosorbides.[209]

Via a similar approach as presented in Scheme 11a, Toshima and Gross prepared PCs with a weight average molar mass M_w of 2000–40 000 g mol^{-1} using DEC instead of DMC and lipase as the catalyst.[212,219] Lipase-catalysed polycondensations have to be performed at lower temperatures than the previously reported conditions using DMC, and thus required higher catalyst loadings (5–31 wt%).

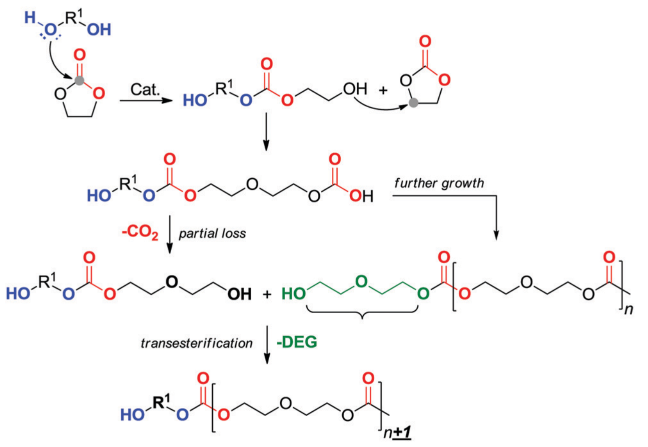
In 2013, Lee *et al.* succeeded in preparing PCs with M_ns of up to 150 000 g mol^{-1} by further optimising the experimental protocol.[208] By finely adjusting the DMC/diol molar ratio and using anhydrous reactants, oligomers bearing almost equal numbers of hydroxyl and methyl carbonate end-groups could be prepared (Scheme 11b). At the second stage of the process, chain extension occurs essentially by the reaction between the terminal hydroxyl and methyl carbonate groups of the low molecular weight intermediates thereby producing methanol that can be easily removed under vacuum, thus favoring the formation of the PC.

In contrast to the synthesis of PCs from dialkyl carbonates, diaryl carbonates such as DPC are used at an industrial scale for the commercial synthesis of aromatic PCs by a melt transesterification with bisphenol A.[44,220–222] However, more demanding experimental conditions are required to efficiently remove the released phenol and to adjust the viscosity of the melt during the polymerisation process. Typically, basic catalysts such as $LiOH{\cdot}H_2O$ are used for the commercial melt transesterification process between DPC and bisphenol A.[220–223] In a first step, oligomers are synthesized at 180–250 °C under reduced pressure (20–100 mm Hg; 30–130 mbar), followed by a second step that encompasses chain extension at a temperature between 260 and 300 °C under high vacuum (1 mm Hg; 1.3 mbar).

In addition to this procedure, Asahi Kasai Corporation reported the first commercial process for the synthesis of an aromatic PC by a phosgene-free process using CO_2 as a starting material.[44] Initially CO_2 is reacted with epoxides resulting in the formation of EC which is then converted into DMC by a reaction with MeOH. Then, DMC is treated with phenol to afford DPC, which in turn is used as a monomer for the synthesis of a CO_2-sourced aromatic PC by polycondensation with bisphenol A. Transcarbonation between DPC and different aliphatic diols has also been developed in academic laboratories. Wang *et al.* prepared PCs by a one-pot melt transcarbonation of DPC with 1,4-butanediol in equimolar amounts at 200–220 °C.[224,225] They obtained PCs with M_w of up to 156 200 g mol^{-1} and 182 200 g mol^{-1} using $Zn(OAc)_2$ or MgO as a catalyst, respectively. Moreover, bio-based PCs with M_w close to 40 000 g mol^{-1} were obtained using isosorbide as a diol and Cs_2CO_3 as a catalyst.[226]

2.1.3 Poly(carbonate)s by polycondensation of 5-membered cyclic carbonates with diols. Attempts to produce pure PCs by polycondensation between 5CCs and diols have also been reported (Scheme 12). Similar to polymers produced by ROP of 5CCs, this polyaddition approach faces similar limitations, *i.e.* the lack of site-selective nucleophilic attack by the diol that (partially) results in decarboxylated chain-ends and rather low molecular weight poly(ether-*co*-carbonate)s. Despite these limitations, Harris *et al.* prepared alternating poly(ether-*co*-carbonate)s with high CO_2 content from an excess of EC and diethylene glycol (DEG).[227]

In a first step, low molecular weight poly(ether-*co*-carbonate) polyols with M_n between 300–1000 g mol^{-1} were obtained at 135–170 °C using sodium stannate trihydrate as a catalyst. Then, chain extension was performed at a higher temperature (T = 185–227 °C) leading to polymers with M_n of 2000–3000 g mol^{-1}. Mechanistic investigations suggested that polymer formation



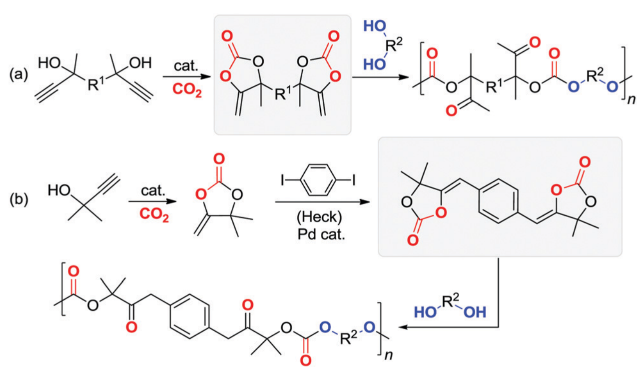
Scheme 12 Transesterification between diols and EC.

occurs *via* transesterification reactions between the hydroxyl chain-ends of an oligomer with a carbonate group of a second oligomer (Scheme 12). This chain extension is accompanied by the release of DEG that can be removed under reduced pressure.

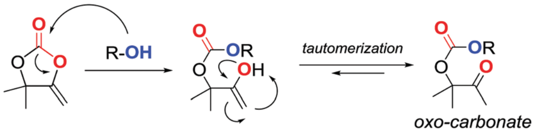
By a judicious choice of the 5CC and the utilization of azeotropic solvents (heptane or xylene), Rokicki *et al.* were able to tune the polymer (micro)structure. Pure α,ω-hydroxyl-telechelic oligocarbonates were prepared from PrC using tin catalysts or alkali metal iodides, while oligo(ether-*co*-carbonate) diols were prepared from EC.[228,229] This difference in backbone composition arises from the different preferred nucleophilic attack on the carbonate monomer (EC or PrC). While the nucleophilic attack only occurs onto the carbonate carbon center of the cyclic carbonate in the case of PrC, EC is ring-opened either by nucleophilic attack onto the β-methylene carbon or the carbonate fragment. Regardless of this difference in reactivity at the ring-opening stage of the cyclic carbonate, the molecular weight of the polymeric products did not exceed 3000 g mol^{-1} through this high temperature chain extension approach.

2.1.4 Poly(oxo-carbonate)s by polyaddition between 5-membered bis(α-alkylidene cyclic carbonate)s and diols. Recently, Detrembleur and coworkers developed a new conceptual route to access regioregular and functional PCs from CO_2-sourced 5-membered bis(α-alkylidene cyclic carbonate)s (bis-α5CCs) and diols by facile, ambient temperature organocatalysed polyaddition (Scheme 13).[230,231] In contrast to conventional 5CCs, 5-α-alkylidene cyclic carbonates show high reactivity towards alcoholysis. This difference in reactivity relies on the presence of the exo-cyclic olefinic group that facilitates and selectively directs the regio-selective ring-opening of the carbonate ring through the establishment of a keto–enol equilibrium (Scheme 14).

Two bis-α5CCs with internal or terminal exocyclic double bonds were prepared. The bis-α5CC with a terminal exocyclic double bond was obtained by a catalysed carboxylative coupling between a bis-propargylic alcohol and CO_2 (Scheme 13a), whereas the one with internal double bonds was prepared by a Heck coupling of 1,4-diiodobenzene and the CO_2-sourced cyclic carbonate 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (Scheme 13b). Defect-free regioregular poly(β-oxo-carbonate)s incorporating ketones within the polymer backbone and/or as pendant groups were obtained with M_n of 5500 to 25 000 g mol^{-1} at 25 °C by a DBU-catalyzed polyaddition between 1,4-butanediol and the bis-α5CC in DMF. The scope of polymers was recently extended to aliphatic polycarbonates with M_ns in the range 45 000–60 000 g mol^{-1} *via* an ambient organocatalysed polyaddition of CO_2-sourced bis-αCC with polyethylene oxide diols in DMSO. These materials have shown great promise as solid electrolytes for all-solid Li-ion batteries.[231]



Scheme 13 Synthesis of regioregular functional poly(β-oxo-carbonate)s by polyaddition of diols and CO_2-sourced bis(α-alkylidene) 5CCs.



Scheme 14 Formation of (β-oxo-carbonate)s by tautomerization.

2.2 Direct synthesis of PCs by use of CO_2 as a comonomer

Despite the enormous progress that has been made in the development of CO_2-sourced PCs obtained from CO_2-sourced building blocks (Section 2.1), environmentally more friendly and economical procedures have been explored to avoid the additional steps associated with the preparation of the CO_2-sourced monomers that decrease time and resource efficiency. A more sustainable solution comprises polymerisation methods that directly valorise CO_2 as an environmentally-benign carbon feedstock. Several strategies for PC synthesis from CO_2 have been identified over the years, including the ROCOP of CO_2 and epoxides, the step-growth polymerisation between diols and CO_2, and the stepwise polymerisation between CO_2, dihalides and diols (Scheme 2). Among these strategies, the CO_2/epoxide copolymerisation leading to (mostly) aliphatic PCs is the most intensively studied process. Therefore, in this section the ROCOP of CO_2 and epoxide will be first discussed, with special attention to propylene oxide, functional epoxides and procedures leading to oligomeric carbonate diols of interest in the area of novel polyurethane synthesis.

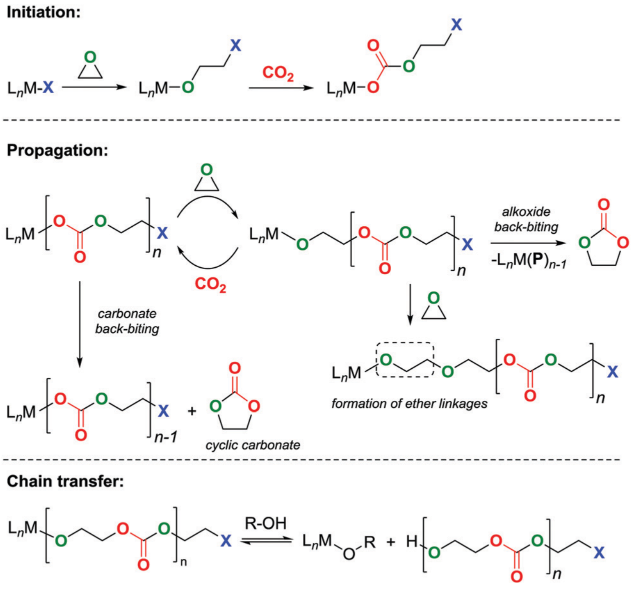
2.2.1 Poly(carbonate)s by ROCOP of CO_2 and propylene and cyclohexene oxide. Probably the most attractive epoxide monomer used to prepare PCs is PO since it represents a cheap and readily available starting material, aspects of high industrial importance. Apart from that, cyclohexene oxide (CHO) is likely to be the single most studied epoxide monomer in the area of ROCOP affording PCs, and it represents in many contributions an attractive substrate to benchmark catalyst performance. Therefore, in this sub-section the focus will be primarily on PO and CHO monomers, including the principal manifolds and families of catalysts that have been developed over the years.

Ever since the pioneering work of Inoue *et al.* who prepared poly(propylene carbonate) (PPC) from CO_2 and propylene oxide (PO) using a water/diethylzinc heterogeneous catalytic system,[232] the ring opening copolymerisation (ROCOP) of epoxides and CO_2 has been extensively developed both at bench and commercial scales. Examples of successful larger scale PO/CO_2 copolymerisation processes were developed by Novomer[233] and Empower.[35] A wide range of metal complexes (Zn, Cr, Co, Al, Fe) with the general formula "L_nMX" (L_n is a suitable, often multidentate ligand; X is typically a halide or other suitable initiating group; M is typically a di- or trivalent metal cation) have been designed to promote the ROCOP of CO_2 with epoxides.[28,228,229,232–240]

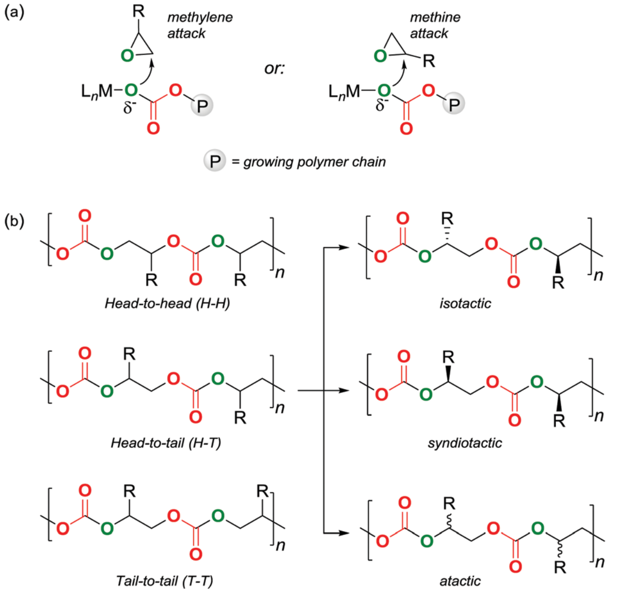
Generally, this type of copolymerisation reaction has a number of attractive features: (i) it represents an atom-economical and controlled process with a linear increase of the polymer molar mass with the epoxide conversion; (ii) the resultant PCs are typically characterized by a low dispersity with the initiation step being faster as compared to the propagation step; (iii) this ROCOP process allows for easy variation of the epoxide monomer and thus the properties of the PCs. The polymerisation manifold proceeds through a well-established coordination–insertion mechanism. A Lewis acidic metal center first activates the epoxide through coordination, after which the activated monomer undergoes a ring-opening *via* nucleophilic attack of the initiating species (X). The resulting metal alkoxide is then transformed into a metal carbonate by a formal CO_2 insertion (Scheme 15, initiation).

In a second step, chain propagation occurs by repetitive and sequential insertion of epoxides and CO_2 leading to (fully alternating) PCs. Depending on the metal, the ligand and/or epoxide structure, the chain propagation is accompanied by potential reactions which may include: (i) two or more consecutive chain enchainments that involve epoxide monomers resulting thus in the formation of ether linkages (Scheme 15, propagation); (ii) intramolecular back-biting reactions that involve alkoxide- or carbonate-terminated chain-ends producing thermodynamically more stable five-membered cyclic carbonates as by-products;[239] (iii) the presence of protic impurities (such as H_2O) may induce chain transfer reactions that affect the produced molecular weight of the PCs.

The PC properties are also influenced by the regioselectivity of the epoxide ring-opening and the stereochemistry of the carbonate sequences. The ring-opening of terminal epoxides such as PO can occur at both C–O bonds to an extent that depends on several factors such as the type and the stereochemistry of the catalysts as well as the presence of co-catalysts. Ring-opening of the methylene C–O bond retains the stereochemistry at the adjacent methine carbon after copolymerisation with CO_2 whereas two possibilities exist for the ring-opening occurring at the methine C–O bond, *i.e.* retention or inversion of the original stereochemistry (Scheme 16a).[239,241]



Scheme 15 General coordination–insertion mechanism for the synthesis of PCs by ROCOP of CO_2 and epoxides. P stands for a propagated polycarbonate chain. For the sake of simplicity, the epoxide monomer is devoid of any substituents.

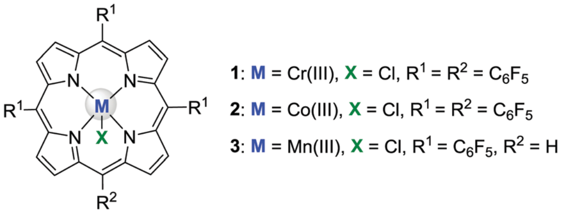


Scheme 16 (a) Regiochemistry of epoxide ring-opening, and (b) structures of different carbonate diads and their respective tacticities.

Depending on the regioselectivity in the epoxide ring-opening, head-to-head (H–H) and tail-to-tail (T–T) carbonate linkages are produced by sequential ring-opening at the methine C–O bond followed by ring opening at the methylene C–O bond, whereas head-to-tail (H–T) linkages are obtained by successive ring opening at the same carbon center of the epoxide monomer (Scheme 16b).[239,241] Besides its influence on creating different PC properties, the stereochemistry is also affected by the regiochemistry of the epoxide ring opening.[246] For the H–T linkages, three distinct stereochemistries can be operative affording either isotactic, syndiotactic or atactic polymer domains (Scheme 16b).

A second way to produce enantiomerically enriched PCs is the desymmetrisation (asymmetric) ROCOP of CO_2 with *meso*-compounds such as CHO in the presence of chiral catalysts or reagents that cause inversion of configuration at one of the two chiral centers.[239,241,244] As the ROCOP of CO_2 and epoxides has been extensively reviewed in the past few years, here the emphasis will be on the most efficient catalyst systems (*vide infra*) for the copolymerisation reactions that involve either PO or CHO as substrates. For a more comprehensive overview, the reader is referred to these previous accounts.[28,228,229,233–236,238–240,242–249]

In 1978, Inoue reported the first ROCOP process of PO and CO_2 catalysed by homogeneous aluminum tetraphenylporphyrin complexes.[250] Later, binary catalysts composed of air- and water-stable tetraphenylporphyrin aluminum chloride [Al(TPP)Cl] and



1: M = Cr(III), X = Cl, $R^1 = R^2 = C_6F_5$
2: M = Co(III), X = Cl, $R^1 = R^2 = C_6F_5$
3: M = Mn(III), X = Cl, $R^1 = C_6F_5$, R^2 = H

Scheme 17 Some selected metallo-porphyrins/corroles.

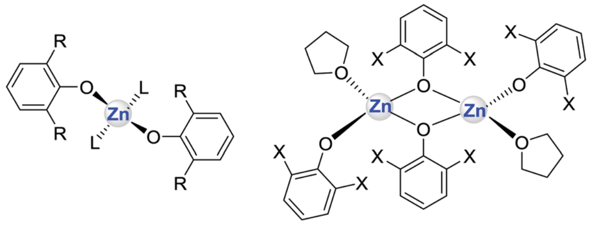
quaternary ammonium halide salts or triphenylphosphine were shown to promote the ROCOP of CO_2 with PO and CHO at rt and a CO_2 pressure of 50 bar. Alternating PCs with low molecular weights of 3500–6200 g mol^{-1} and dispersities (*Đ*'s) as low as 1.06 were obtained after 12–23 days.[251] In addition to this sluggish reactivity, the concomitant formation of a 5CC (*cf.*, PC backbiting, Scheme 14) was also observed.

Various strategies were then engineered to enhance the activity of metalloporphyrins while (i) suppressing back-biting side reactions, and (ii) preventing the formation of ether linkages in the ROCOP of either CO_2 and PO or CO_2 and CHO. To achieve better catalyst performance, its structure was systematically varied: (1) various substituents such as pentafluorophenyl, octaethyl and *p*-tolyl were introduced onto the periphery of the porphyrinato ligands; (2) the X anion of the L_nMX complex was modulated (in most reported cases: X = Cl, Br, I, AcO); (3) the Al was substituted by other (trivalent) metal ions such as Cr, Co and Mn (Scheme 17; **1–3**); and (**4**) the addition of alternative co-catalysts such as different onium salts and bases (pyridine, 4-dimethylaminopyridine, *N*-methylimidazole) was also probed.[252–256]

However, generally some irregularities in the PC backbones derived from PO are observed as revealed by the presence of predominant head-to-tail (around 90%) relative to a minor amount of head-to-head and tail-to-tail defects (around 10% in total). With metalloporphyrin complexes (Scheme 17), poly(propylene carbonate)s with molecular weights between 1500–115 000 g mol^{-1}, a carbonate content between 29–99% and with chemoselectivities (*i.e.*, polymer *versus* cyclic carbonate) higher than 95% were produced at pressures in the range 1–50 bar and temperatures between 25–80 °C.[252,253,257,258] With the less reactive, internal epoxide CHO the ROCOP furnished lower molecular weight PCs (M_n = 600–25 900 g mol^{-1}) at pressures and temperatures between 1–227 bar and 40–110 °C, respectively.[252–255] By fine-tuning of the catalytic system, poly(cyclohexene carbonate)s, PCHCs, with a carbonate content of up to 99% were produced by using the Co(TPP)Cl/DMAP (**2**) binary catalyst or the Mn-based corrole complex (**3**) in combination with a suitable co-catalyst of the type [PPN]X [PPN = bis(triphenylphosphine)iminium, and X = Cl, $OBzF_5$, AcO].[252,253]

Zinc (bis-phenoxide) complexes were identified as the first active discrete zinc complexes for the ROCOP of epoxides and CO_2.[235,243] Holtcamp and Reibenspies indepedently designed such complexes by combining Zn and phenoxide ligands substituted in the 2 and 6-positions by phenyl or halide groups (Scheme 18, **4** and **5**).[259,260]

Catalysts of type **4** afforded PCs from CHO and CO_2 with M_n of 38 000 g mol^{-1} and a dispersity of 4.5 at 55 bar and 80 °C.[260]



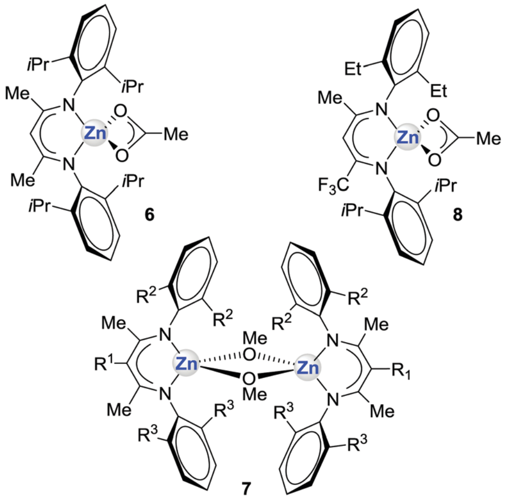
4: R = Ph, L = Et_2O

5a: X = F
5b: X = Cl
5c: X = Br

Scheme 18 Zn-Based bis-(phenoxides) active in the ROCOP of epoxides and CO_2.

The microstructure of the polymer revealed the presence of 9% ether linkages. Substitution of the phenyl groups in the 2- and 6-positions by sterically less crowded, electron-withdrawing halides (F, Cl and Br) provided dimeric phenoxide derivatives **5a–5c**.[259] PCHC with M_n of up to 42 000 g mol^{-1} and a dispersity of 6 were produced at 80 °C and 55 bar using **5a**. Interestingly, a completely alternating PCHC without observable ether linkages was obtained. The authors suggested that this absence of ether linkages originates from the availability of only one epoxide binding site at the Zn center in complexes **5** opposed to the two available binding sites in catalyst **4**. Reibenspies also established a reactivity trend of the halogenated phenolate complexes **5**, following the order **5a** > **5b** > **5c**. The catalytic activity thus decreased in the presence of less electronegative halide substituents, which increased the electron density on the Zn center and decreased the affinity of the metal to bind the epoxide monomer. In contrast to the selective synthesis of PCHC, the ROCOP of CO_2 with terminal epoxides such as PO was more challenging due to the occurrence of back-biting reactions observed at higher temperatures (80 °C).[235,244,259]

In 1998, Coates identified novel efficient CO_2/epoxide copolymerisation catalysts based on a Zn-centred β-diiminate (BDI) structure (Scheme 19, **6**) with the metal embedded in a sterically



Scheme 19 Successful β-diiminate zinc complexes used as ROCOP catalysts.

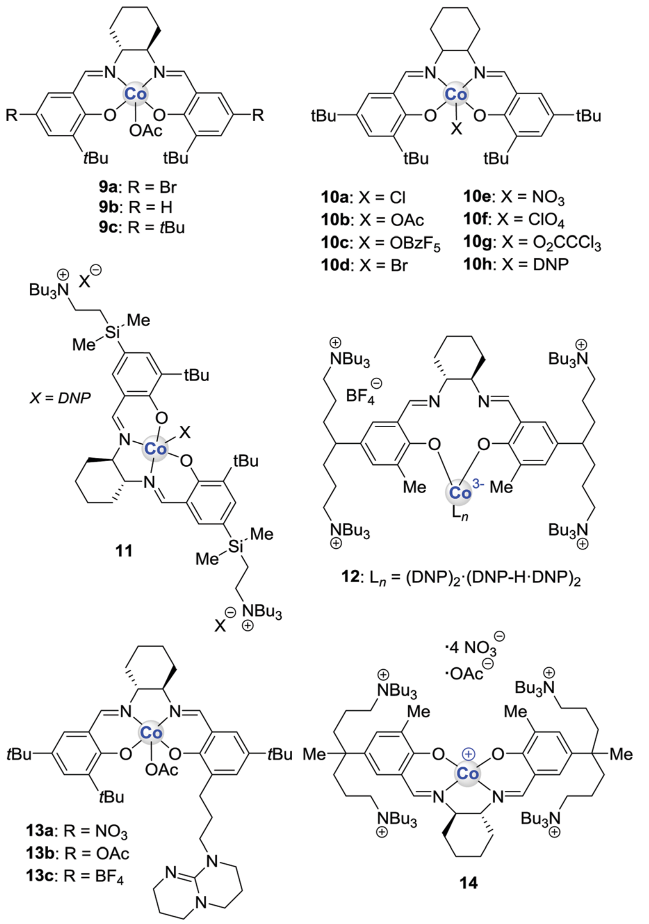
demanding environment.[261] The initiation ability of the Zn(BDI)X complexes is dictated by the anion (X = OAc, OMe, OiPr or $N(SiMe_3)_2$), while the copolymerisation activities are drastically affected by subtle steric and electronic variations within the β-diiminate ligand structure.[262–265] The geometric requirements of the β-diiminate ligands are essential to design high performance catalysts by (1) introduction of bulky iso-propyl or ethyl substituents in the *ortho*-position of the *N*-aryl-ring,[262,265] or (2) installing electron withdrawing CN or CF_3 groups[262,264] making the epoxide coordination more efficient resulting in increased copolymerisation rates.[264]

By using well-designed β-diiminate zinc complexes (Scheme 19, 7), alternating PCHCs with M_n of up to 32 000 g mol^{-1}, low dispersities ($Đ$ values as low as 1.15) and a carbonate content in the range of 90–99% were obtained at 25–80 °C and relatively low CO_2 pressures of 7–20 bar.[261,262,264,265] The acetate complex **8** (Scheme 20) was also shown to be active for the ROCOP of CO_2 and PO: regioirregular PPCs with M_n of up to 36 700 g mol^{-1} were obtained at 25 °C and 7 bar with a PPC chemoselectivity of 75%.[263] Interestingly, by increasing the pressure to 35 bar the formation of PrC through back-biting was suppressed to afford PPCs with a significantly higher (93%) chemoselectivity.[263]

Salen-type metal complexes of the general formula M(salen)X (with M = Cr, Co, Al, Zn, Yb, Sc, Y and Ti; X is typically a halide) represent a large group of catalysts with high potential for the ROCOP of CO_2 and epoxides.[243–245,266–268] The synthetically facile variation of the salicylidene fragments of the ligand has enabled the construction of a broad variety of catalyst structures and fine-tuning of their activity. Compared to other types of catalysts, these salen complexes generally exhibit high selectivity towards polymer formation and excellent regioselectivity. The catalysts shown in Scheme 20 (**9–14**) are the most widely investigated complexes in the ROCOP of CO_2 and epoxides, and display improved catalytic activity and higher polymer selectivity compared to other salen complexes.[239–241,243–245]

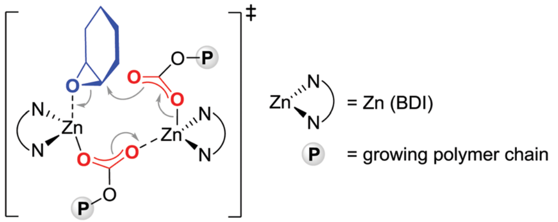
PPCs without any observable formation of PrC (chemoselectivity >99%) were prepared at 25–40 °C and 55 bar using a [Co(salen)OAc] catalyst, **9**.[269] Detailed characterisation of the PPCs showed a microstructure with 70–80% of head-to-tail linkages. The catalytic activity of [Co(salen)X] as well as the regio- and stereoselectivity can be increased by combining this type of complex with ammonium salts (NR_4Y; Y typically a halide, OAc or ClO_4; R = alkyl) or organic base co-catalysts such as *N*-methylated TBD.[270–272]

The preparation of PPCs with high chemoselectivity (>99%), high carbonate content (>99%), M_n of up to 30 400 g mol^{-1} and with >95% head-to-tail enchainment was accomplished at 25 °C and 20 bar by using n-Bu_4NCl as a co-catalyst.[272] Coates and coworkers obtained defect-free PPCs having M_n of up to 43 000 g mol^{-1} at 22 °C and 14 bar in the presence of PPN-Cl (PPN = bis(triphenylphosphine)imine).[271] Importantly, the Co(salen) based catalyst structure and activity could be further engineered by grafting the co-catalyst onto the [(salen)CoX] backbone (Scheme 20, **11–13**).[273–277] These bifunctional, single component catalysts displayed high activity at $T > 50$ °C producing high molecular weight PPCs without the formation of cyclic carbonate by-products. As a seminal example, Lee *et al.* prepared a [Co(salen)X] (X = 2,4-dinitrophenolate, DNP) complex **11** decorated with two quaternary ammonium cations.[276] Complex **11** showed high catalytic activity at 50–90 °C and 20 bar producing with high chemoselectivity (>90%) ether-free PPCs with M_n in the range 53 000–90 000 g mol^{-1} at low catalyst loading (PO/**11** = 25 000 : 1). The high selectivity and activity of **11** was assigned to coulombic interactions between the quarternary ammonium cations and the anionic growing PPC chain.[240,276] These interactions minimise the risk of a diffusion of the growing polymer out of the coordination sphere of the metal cation preventing thus the occurrence of competitive back-biting.



Scheme 20 Binary and bifunctional [Co(salen)X] catalysts for the ROCOP of CO_2 and epoxides. DNP stands for 2,4-dinitrophenolate.

Anchoring four quaternary ammonium cations to the Co(salen)X structure (**12**) further improved the catalytic performance and overall selectivity parameters.[275] PPCs with M_n of up to 300 000 g mol^{-1} and a chemoselectivity of >99% were obtained at 80 °C and 20 bar at a high PO/**12** ratio of 100 000 : 1. The high catalytic activity of **12** is due to a unique binding mode of the Co ion facilitated by a relatively small methyl group in the *ortho*-position in the salen backbone (see Scheme 20) rather than a "classical" and sterically more congested *tert*-butyl group.[239,273] The direct anchoring of co-catalytic units onto the chelating salen framework helps to maintain high activity of the catalyst



Scheme 21 Bimetallic transition state structure reported for a Zn(BDI) complex.

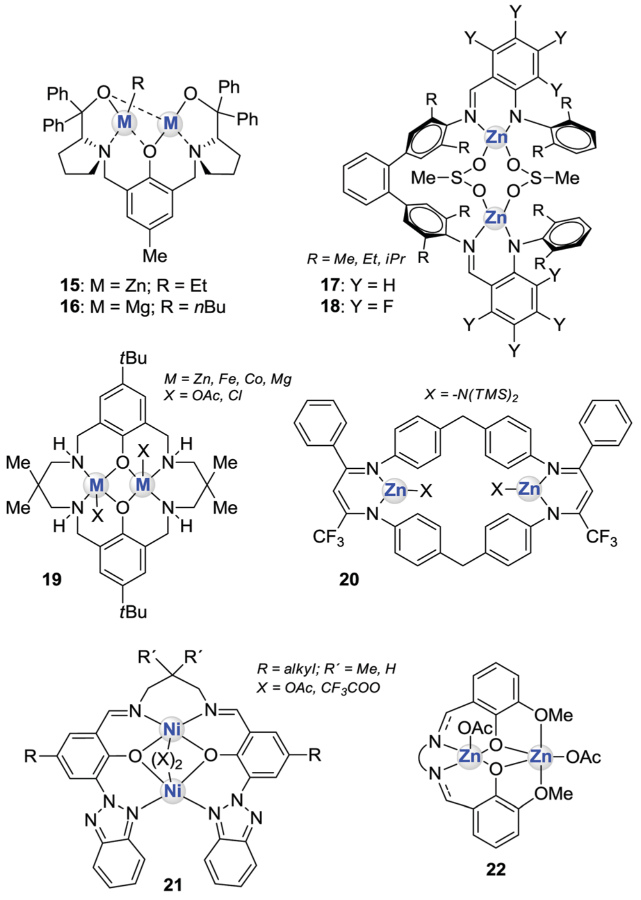
while preventing thermal decomposition.[274] Such observations were reported for **13** that mediated the formation of PPCs with a carbonate content of >99%, M_n of up to 112 000 g mol^{-1} and a chemoselectivity of 97% at 90 °C and 20 bar. The versatility and efficiency of Co(salen)X complexes as catalysts for PCHC formation has also been demonstrated.[278,279]

In-depth comprehensive studies reported by Coates supported that the most active zinc β-diiminate (BDI) complexes (*cf.*, Scheme 19) adopt dimeric structures and operate *via* a bimetallic mechanism.[262] One Zn centre activates the epoxide while the second one provides a nucleophile in the form of a growing polycarbonate chain that aids the epoxide ring-opening (Scheme 21). This pivotal finding and similar results disclosed by Nozaki *et al.*[280] inspired the design of novel highly active Zn, Co, Fe, Mg and Ni based dinuclear catalysts (Scheme 21, **15–22**) for the ROCOP of CO_2 and CHO using various ligands analogous to the ones described in the previous sections. These systems have been largely reviewed by Rieger and Williams.[234,243,244]

Thanks to mechanistic studies based on density functional theory (DFT) calculations and spectroscopic analyses, the intermetallic distance, the flexibility of the bridging spacer and the steric and electronic environment of the metal centres were identified as key features that have enabled designing highly efficient bimetallic catalysts. The first example of bimetallic complexes was developed by Ding *et al.* who succeeded in the synthesis of PCHC from CHO and CO_2 under 1–20 bar CO_2 pressure at 60–80 °C using di-Zn complexes of type **15**, which can be generated *in situ* by treatment of Trost's phenolate ligand with $ZnEt_2$ followed by the addition of alcohols.[281] By replacing the Zn for Mg ions (*cf.* **16**), the catalytic activity was reduced but, regardless of the type of metal ion, copolymers with M_ns in the range 20 000–40 000 g mol^{-1}, excellent carbonate content (>99%) and moderately low dispersities of 1.6 were obtained.[282]

A series of di-Zn anilidoaldimine complexes (**17–18**) possessing impressive activity for the ROCOP of CO_2 and CHO were reported by Park *et al.*[283] At a low 1 : 17 000 **17**/CHO ratio, PCHCs with M_n of up to 284 000 g mol^{-1}, carbonate content of up to 91% and $Đ$ values in the range 1.3–1.7 were produced at 80 °C and 14 bar. As reported for the BDI ligands (see Scheme 19), the catalyst activity could be further optimized by steric and electronic variations within the anilidoaldimine ligand structure. General structure–activity relationships established that the introduction of methyl, ethyl and isopropyl substituents in the *ortho*-position of the diaryl-N donor group improved the activity of the catalyst.[283] A similar trend was observed by replacing anilidoaldimine ligands by fluorinated analogues (**18**).[284] The presence of the electron-withdrawing fluorine atoms reduced the electron density at Zn, thereby increasing the epoxide binding affinity and increasing the catalytic activity.[244] With **18**, high molecular weight PCHCs with M_n of 100 000–200 000 g mol^{-1} were obtained at **18**/CHO molar ratios of 1 : 50 000. However, the increase in catalytic activity occurred at the expense of chemoselectivity as evidenced by a carbonate content that was reduced to 65–86%, and by higher polydispersities of 1.2–2.5.

In 2009, the Williams group prepared air-stable di-Zn complexes (Scheme 22, **19**) with the two Zn(II) metal centers coordinated within a macrocyclic Robson-type ligand.[285] These complexes efficiently promote the ROCOP of CO_2 and CHO at only 1–10 bar CO_2 pressure and at temperatures of 80–100 °C, yielding PCHC with a M_n of 6000 to 14 000 g mol^{-1} with no noticeable ether defects. However, concomitant formation of low amounts of cyclic carbonate content (CHC, 6%) was observed as well as a bimolecular weight distribution for the PCHC polymer. The macrocyclic environment of the ligand and the bimetallic nature of these complexes were crucial to the observed catalyst efficiency as monometallic and ''open''



Scheme 22 Structures of different reported dinuclear complexes **15–22** used in ROCOP.

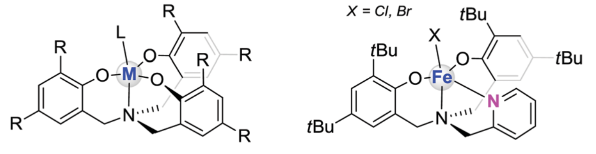
bimetallic analogues displayed no activity.[285] The catalytic performances were further improved by substituting the divalent Zn for Co(II) or a combination of Co(II) and Co(III) ions that increased the nucleophilicity of the propagating metal-stabilized carbonate-terminated chains. Consequently, a 9-fold increase of the catalytic activity compared to diZn analogues was observed, together with a higher chemoselectivity for polycarbonate formation and virtually no cyclic carbonate was detected.[286] Low M_n below 9000 g mol^{-1} and a bimodal molecular weight distribution remained, however, bottlenecks to overcome. By introducing Fe(II) metal centers in the macrocyclic structure, the catalytic performance was shown to be identical to the one witnessed for the di-Zn(II) analogue, apart from the observation of a significantly lower carbonate content (66%) in the PCHC when the copolymerisation was performed at 1 bar.[287] The PCHC selectivity and carbonate content were both increased to 99% upon increasing the pressure to 10 bar. Irrespective of the nature of the bimetallic catalyst, MALDI-ToF mass spectrometric characterisation of the PCHCs revealed the presence of different end-groups including acetate (from the initiator), hydroxyl (through chain transfer) or alcohols (cyclohexanol, cyclohexenol or cyclopentanol) produced from Meerwein–Ponndorf–Verley–Oppenauer side reactions and subsequently acting as chain transfer agents.[244,285–288]

Rieger *et al.* introduced a new type of dinuclear Zn complex by linking two Zn(BDI)s by two flexible methylene bridges (Scheme 22, **20**).[289,290] With these di-Zn complexes very high catalytic activities were achieved for the ROCOP of CO_2 and CHO reaching TOFs of 1255–9130 h^{-1} at 10–40 bar. Such high activities are the result from a shift of the rate-determining step (RDS) from the ring-opening of the epoxide to CO_2 insertion. This shift in the RDS originates from an acceleration of the epoxide ring-opening step due to the presence of a flexible tether.[290] PCHCs with M_n amounting to 228 000 g mol^{-1} were produced at 30 bar and 100 °C after 20 min.[289] The catalytic activity could be further increased by the introduction of EWD CF_3 groups allowing the synthesis of PCHCs with M_n of 280 000 g mol^{-1} and providing TOFs of 155 000 h^{-1}; the latter is the highest polymerisation rate ever reported for the ROCOP of CHO and CO_2.[289] Additional variations of the BDI ligand structure were considered to increase the bimetallic catalyst performance by placing the two Zn sites in parallel or "face to face" configurations.[291] While the parallel orientation did not lead to any significant polymerisation activity, the "face to face" configuration allows for efficient catalysis at 10 bar and 60 °C with the formation of PCHCs having a M_n in the range 45 000–100 000 g mol^{-1}, dispersities of 1.2–1.4 and polymer chains with 99% carbonate linkages.[291]

Bimetallic salen-like complexes were designed by Williams, Ko and Lin for the ROCOP of CHO and CO_2 (Scheme 22, **21** and **22**).[268,292,293] Divalent metals such as Co, Ni and Zn can be incorporated into these ligand scaffolds with one metal ion being N_2O_2-chelated while a second metal ion is complexed in a "second coordination sphere" by phenolate and either neutral O- or N-donor atoms. Generally, all catalysts gave excellent copolymerisation selectivity (>99% carbonate linkages, CHC < 1%) but their activities remained rather moderate at 80–130 °C and 20–30 bar: the molecular weights obtained ranged from 400 to 52 000 g mol^{-1}.

Despite the notable progress made in the design of efficient dinuclear complexes, the ROCOP of CO_2 and PO using this class of catalysts remains poorly investigated. This may be due to the competition between preferential formation of cyclic (PrC) over polycarbonate (PPC) under the experimental conditions. Indeed, Rieger *et al.* demonstrated the incapacity of di-Zn catalysts of type **19** to promote PPC synthesis[294] and assumed that the formation of PrC by back-biting is faster than copolymerisation. The ROCOP of CO_2 and PO was shown to be feasible in the presence of dinuclear Co(salen) complexes, dinuclear Cr(salphen) complexes and dinuclear Co(porphyrins).[295–297] With dinuclear Co(salen) complexes, Nozaki and coworkers were able to prepare PPCs with M_n between 9800–36 700 g mol^{-1} and carbonate content of 84–97% at 22–40 °C and 53 bar.[296] Rieger prepared PPCs with M_n of up to 22 000 g mol^{-1} and a chemoselectivity of >98% using dimeric Cr(salphen) complexes.[297] Later on, the same group created binary catalytic systems based on dicobalt porphyrin complexes and ammonium chloride.[295] They highlighted that the spatial separation of the two metal centers within the ligand framework strongly affected the polymer/cyclic carbonate selectivity though the overall activity remained very low. PO conversion reached only 3 to 39% and polymers with M_n of 1500 to 23 000 g mol^{-1} with $Đ$ values of 1.2–1.4 were prepared at 20 bar with concomitant formation of PrC (1–8%). By virtue of mechanistic and comparative studies with monometallic analogues, the authors showed that in this case there is no benefit of dinuclearity, suggesting that propagation of the polymer chains occurs at a single metal center.

Complexes based on readily accessible aminotriphenolate ligands coordinated to low-toxic, cheap and earth-abundant metals such as Al and Fe were introduced in 2012 by Kleij *et al.* as a novel class of catalysts (Scheme 23, **24–26**) for epoxide/CO_2 coupling reactions.[95,96,118] In combination with organic halide co-catalysts, these complexes were found to be highly efficient and robust in promoting the solvent-free synthesis of different PCs by ROCOP of CO_2 with internal epoxides such as CHO.[298–300] By changing the co-catalyst type, the catalyst/co-catalyst ratio, catalyst and co-catalyst loading as well as the steric and electronic environment of the aminophenolate ligand, the selective synthesis of ether-linkage free PCHC was achieved. The polymer features included M_n of up to 6000 g mol^{-1} realised at 85 °C and 80 bar by using a binary **24**/PPNCl catalyst. By applying strictly



24a: M = Fe; R = Me; L = thf
24b: M = Fe; R = *t*Bu; L = H_2O
25: M = Al; R = Me; L = thf

26

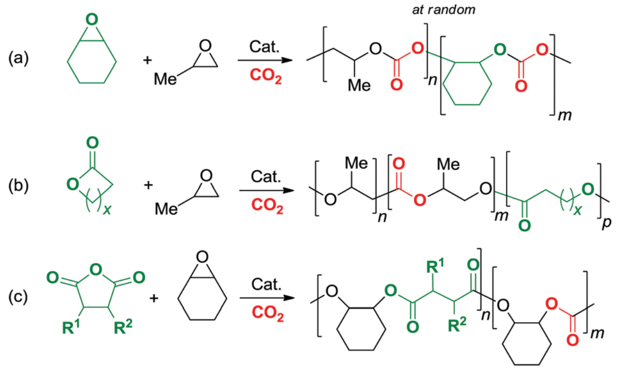
Scheme 23 Fe(III) and Al(III) centred aminodi- or triphenolate complexes.

anhydrous conditions, the polymer molecular weight could be increased to almost 19 000 g mol^{-1}, pointing at chain transfer effects by trace amounts of water under standard conditions. PCHCs with a lower polymer selectivity (<88%) and significantly lower molar masses (<1600 g mol^{-1}) were formed with iron(III) pyridylamino-bis(phenolate) **26**.[299]

Apart from a much wider array of available homogeneous catalysts, also heterogeneous systems have been developed for the ROCOP of epoxide and CO_2. Among these, zinc glutarate (ZnGA) represents a cheap and non-toxic catalyst, and is one of the most widely used heterogeneous systems for the formation of polycarbonates even on an industrial scale.[243,244,301] The key parameters boosting the catalytic performance of ZnGA are its degree of crystallinity, the size of the crystallites and the addition of ethylsulfinate groups.[302,303] These parameters are easily modulated by the synthetic protocols, by the nature of the Zn precursor and the glutarate source. The best-performing, crystalline catalyst showed alternating layers of Zn and glutarate ions, whose surface composition included unsaturated Zn centers and reversible binding sites for CO_2.[301,304] This catalyst generally operates under mild temperature conditions (60 °C) and 40–50 bar to mediate the ROCOP of CO_2 and PO,[305,306] converting 90% of PO in 40 h into PPC with a molecular weight exceeding 100 000 g mol^{-1}. The selectivity towards polymer formation was rather good, even though some ether defects and a low amount of cyclic carbonate by-products were observed. A more detailed discussion of the catalyst synthesis and activity for ROCOP was published by Luinstra.[301]

Double metal cyanides of the general formula $Zn_3[M(CN)_6]_2$ (M = Fe(III), Co(III), Ni(III) or Cr(III)) used in combination with complexation agents including salts, alcohols and ethers are a second important class of heterogeneous catalysts used in the ROCOP of CO_2 and epoxides.[307–316] From mechanistic studies, it was postulated that the Zn metal centre is the active site, whose coordinative interactions are adjusted by the second metal centre that influences the electron-donating features of the cyanide ligands. These catalysts showed rather good activity at 10–55 bar and 40–130 °C, and PCs with M_n in the range of 2000–130 000 g mol^{-1} (ref. 307–309, 311, 314, 316 and 317) and 2000–41 000 g mol^{-1} (ref. 310, 312–315, 318 and 319) were produced from PO and CHO, respectively.[308,310,311,318] In contrast to the previously reported homogeneous and ZnGA catalysts, PPCs and PCHCs with a lower carbonate content of 74% and 95.5% were obtained, respectively. The lower carbonate content when PO was used as the substrate was explained by a competition between the thermodynamically driven ROCOP of CO_2 and PO opposed to the kinetically driven PO homopolymerisation. Lower observed molecular weights resulted from the competitive formation of a substantial amount of cyclic carbonate. The microstructure of copolymers produced from PO and CO_2 showed predominant head-to-tail junctions (>75%).[316]

Terpolymerisation strategies of CO_2 with two different epoxides have been explored to adjust the thermo-mechanical and degradation behaviour of PCs or to introduce functional groups along the main backbone such as olefins, alkynes, halogens and protected alcohols.[278,279,304,320–324] The difference in epoxide reactivity, especially when considering aliphatic PO and cyclic CHO, makes the choice of the catalyst essential for proper incorporation of both monomers producing ideally two types of carbonate repeat units.[259] The CO_2/CHO/PO terpolymerisation (with [CHO]/[PO] = 1 : 1) promoted by a bis(2,6-difluorophenoxide)zinc catalyst at 55 °C and 40–50 bar gave rise to PCs enriched in CHC linkages and presenting ether defects (85% cyclohexene carbonate linkages, 12% propylene carbonate linkages, 3% propylene ether linkages) as well as the concomitant formation of propylene carbonate.[259]

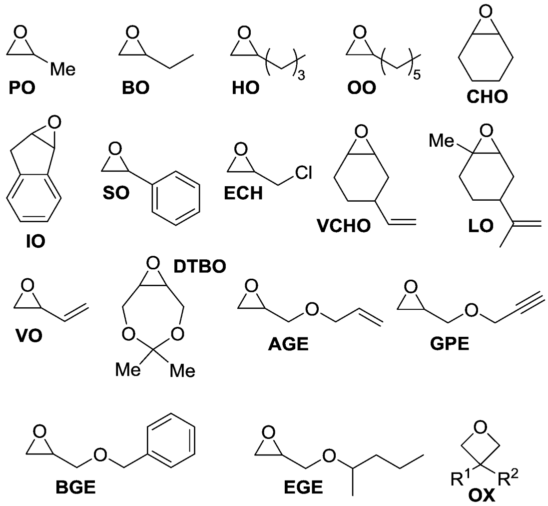


Scheme 24 Strategies used for fine-tuning of the properties of PCs derived from PO, CHO and CO_2.

Increasing the amount of inserted PO within the polymer chain was achieved by using binary catalysts based on quaternary ammonium salts and either Co- or Cr(salen) type complexes.[278,279,324] At 25 °C and 15 bar, PO, CHO and CO_2 were randomly distributed in the polymer with no deviation from the initial [CHO]/[PO] molar ratio (Scheme 24a). These terpolymers had M_ns of up to 24 000 g mol^{-1}, $Đ$ values of around 1.25 and a carbonate content of >99%.[279] From the available literature, salen-type (*cf.*, Scheme 20, **10g** and **12**) and aminophenolate metal complexes (**25**) appeared as the most appropriate catalysts to perfectly control the incorporation of both types of oxiranes within the terpolymeric structure.[278,279,298,324]

Besides the terpolymerisation of CO_2 with two different epoxides, the terpolymerisation between CO_2, an epoxide and monomers other than epoxides showed also the potential to adjust the properties of (partial) PCs. In fact, several terpolymers were produced by the one-pot, one-step terpolymerisation of PO, CO_2 and cyclic esters such as L-lactide, ε-caprolactone or γ-butyrolactone (Scheme 24b).[325–328] In contrast to the pure PPCs, these produced terpolymers are characterised by an improved degradability as well as enhanced thermal and/or mechanical properties. Another variation concerns the terpolymerisation of CO_2, CHO and cyclic anhydrides (*e.g.*, diglycolic anhydride, succinic anhydride and phthalic anhydride) using a one-pot procedure (Scheme 24c). Typically, block poly(ester-*co*-carbonate)s were obtained this way due to a faster insertion of the more reactive cyclic anhydride monomers as compared to the insertion of CO_2.[329–332]

These strategies (Scheme 24a–c) represent some of the commonly used strategies to tune the properties of PCs. For a more detailed and comprehensive overview of the most relevant



Scheme 25 Amplified scope of epoxide monomers used in the ROCOP with CO₂. For completion and structural comparison, also PO and CHO are included. Abbreviations: BO = 1-butene oxide, HO = 1-hexene-oxide, OO = 1-octene oxide, CHO = cyclohexene oxide, IO = indene oxide, SO = styrene oxide, ECH = epichloro hydrin, VCHO = 1,2-epoxy-4-vinylcyclohexane, LO = limonene oxide, VO = vinyl oxirane, DTBO = 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane, AGE = allyl glycidyl ether, GPE = glycidyl propargylic ether, BGE = benzyl glycidyl ether, EGE = ethoxyethyl glycidyl ether, OX = 3,3-disubstituted oxetane.

advances in this area, the reader is kindly referred to a recently disclosed review on this topic.[238]

2.2.2 Poly(carbonate)s by ROCOP of CO_2 and other (functional) cyclic ethers. Apart from the use of PO and CHO, a lot of efforts have been devoted to the use of other types of epoxides to allow preparation of PCs with different properties, some of these having built-in functionalities in the repeat units that allow for curing or post-polymerisation modification of these copolymers (Scheme 25). In 2018, the Darensbourg group reviewed the preparation of functional, CO_2-based PCs derived from functional, rigid and less rigid cyclic and acyclic epoxide monomers and their (potential) applications.[333] For this reason, only some selected examples of functional PCs are discussed in detail, and they are included to provide a complete picture of the area of CO_2-based PC formation.

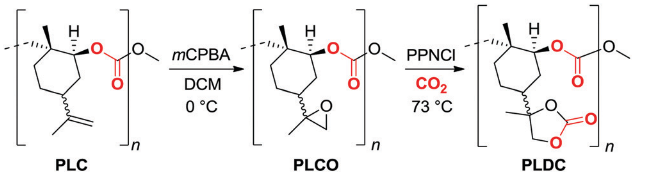
Apart from the use of readily available acyclic (functional) epoxides such as ECH,[334] SO,[335–337] and substituted CHOs[338,339] (Scheme 25) as more prominently used monomers in ROCOP with CO_2, here attention is focused on two specific examples: LO and IO. The use of LO (being a functional epoxide monomer that can be obtained from a renewable resource) was first used by Coates *et al.* to produce poly(limonene carbonate), PLC, under Zn(BDI) catalysis.[340] This copolymerisation process occurred under rather mild conditions (25 °C, around 7 bar CO_2 pressure) providing fully alternating PLCs with M_n of up to 25 000 g mol^{-1} ($Đ$ values <1.2). After this seminal publication, various other groups used similar types of Zn-catalysts producing different PLC grades with M_n of over 100 000 g mol^{-1} and glass transitions of 130 °C.[340–342] The incorporation of synthetically useful olefin bonds in the PLC repeat units allowed easy modification of these PCs to a large extent, giving them either antibacterial activity, hydrophilic properties, pH-dependent solubility or gas separation potential.[343,344] Further to this, Coates and Auriemma reported that complementary enantiomeric forms of PLC allow access of crystalline, stereocomplexed materials.[345,346]

The only other known type of catalyst for the synthesis of PLC is based on an Al(III) aminotriphenolate complex (Scheme 23, **25**).[347] The conformation flexibility of **25** and related complexes is crucial for the coordination of sterically more congested epoxides such as LO. Complex **25**, in combination with PPNCl, is able to convert both *cis* and *trans* LO isomers, and the ROCOP of both monomers with CO_2 resulted in virtually perfect alternating (carbonate content $>99\%$) PLCs with M_ns of up to 10 600 g mol^{-1} ($Đ = 1.43$) under mild temperature (25–45 °C) and pressure conditions (5–10 bar). The observed stereoregularity was extensively investigated by computational methods (DFT) showing that the origin for this is a preferred propagation that furnishes *trans*-configured carbonate repeat units, and higher reactivity of the *cis*-LO monomer while using **25**. Generally speaking, the formation of PLCs is fully chemoselective, and the formation of cyclic limonene carbonate is not favored due to severe steric strain upon back-biting of a propagating PLC as supported by DFT calculations.[347]

In the presence of the binary catalyst **25**/PPNCl, PLCs with M_n between 1300 and 15 000 g mol^{-1} were prepared at 45 °C and 15 bar using either commercially 40 : 60 mixture of *cis*- and *trans*-LO, or 100% *cis*-LO.[348] The prepared PLCs could be transformed into poly(limonene dicarbonate), PLDC, *via* a sequential approach involving an epoxidation and carbonation step resulting in PLDCs with T_g up to 180 °C (Scheme 26), which is among the highest glass transitions known for PCs.

Additionally, the binary catalyst **25**/PPNCl was also efficient for the synthesis of partially bio-based PCs *via* terpolymerisation of CHO, *cis*-LO and CO_2.[298] Terpolymers with high carbonate content ($>95\%$) and M_ns in the range 3580–8220 g mol^{-1} containing 10 to 40% of incorporated LO-based carbonate repeat units could be prepared at 40 °C and 15 bar. The incorporation of the LO monomers proceeded more slowly giving rise to gradient PCs with higher limonene carbonate content towards the end of the ROCOP process. MALDI-ToF mass analysis further provided detailed information of the highly complex distribution of PC polymer chains, and their end-group analysis. The potential of low molecular weight PLCs to serve as a starting point for new coating applications was recently disclosed by Koning and Williams who used photo-initiated, thiol–ene based crosslinking reactions.[349]

High T_g polycarbonates were also reported by Darensbourg, who used a rigid epoxide monomer (IO, Scheme 24) to access PCs.[350,351]

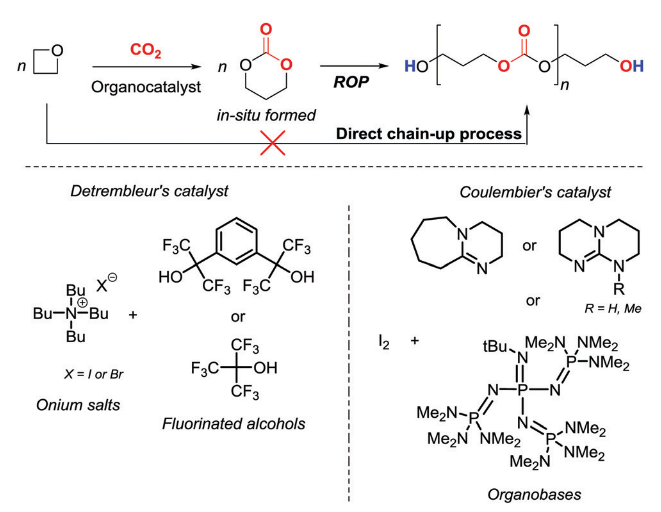


Scheme 26 Synthetic pathway for the preparation of PLDC from PLC.

The ROCOP of IO and CO_2 delivered poly(indene carbonate)s with a M_n of up to 9700 g mol^{-1} ($Đ$ = 1.12), with high chemoselectivity for PC formation (>99%) and a T_g of up to 138 °C.[350] Bifunctional Co(salen) catalysts (Scheme 20; *cf.*, similar to **11–14**) gave higher molecular weights operating at 0 °C and 34 bar; however, one drawback is that these ROCOP reactions take several days to give decent IO conversion levels as a likely result of the steric impediment of the epoxide monomer.

Another monomer suitable for the preparation of PCs is based on a different type of cyclic ether, *viz.* oxetanes. As already discussed in Section 2.1.1, oxetanes are less prone towards nucleophilic ring opening reactions, in particular those having a substitution at the 3-position. Darensbourg and coworkers demonstrated that Cr(salen)X complexes (X = halide) in the presence of nucleophilic additives such as NBu_4N_3 (*i.e.*, an "onium" azide) are effective catalysts for oxetane/CO_2 coupling reactions being performed at 110 °C and a pressure of 35 bar.[115,352,353] The formation of poly(trimethylene carbonate) *via* ROCOP of OX (Scheme 27) and CO_2 was shown to partially proceed through *in situ* formation of a cyclic carbonate following ROP of the latter: the larger the steric bulk at the 3-position of the oxetane monomer, the higher the chemo-selectivity for the cyclic carbonate product.[117,354] The PCs derived from simple oxetane, the unsubstituted monomer, had molecular weights of up to 14 500 g mol^{-1} ($Đ$ = 1.30) under Cr(salen)X catalysis using neat conditions.[352]

In a more recent approach, Detrembleur *et al.* showed the feasibility of organocatalyzed CO_2/oxetane copolymerisation. Low molar-mass α,ω-hydroxyl telechelic oligocarbonates (M_n < 2000 g mol^{-1} with >99% carbonate linkages) were produced at 100–130 °C and 20–100 bar by using an onium salt in combination with a fluorinated alcohol as a hydrogen bond donor cocatalyst (Scheme 27).[355] Through in-depth DFT calculations and spectroscopic analyses, they demonstrated the *in situ* formation of trimethylene carbonate (TMC). A small fraction of TMC was then rapidly hydrolyzed by residual water into 1,3-propanediol that initiated the ROP of TMC, giving the telechelic oligomers (Scheme 27). Both the oxetane/CO_2 coupling and TMC ring opening were facilitated by hydrogen bond activation by fluorinated alcohols. The scope of organocatalysts was extended by Coulembier by using a combination of iodine and organic superbases such as TBD.[356] This organocatalytic system operated at 105 °C under 10–30 bar of CO_2 pressure within 1 to 7 days, and also afforded α,ω-hydroxyl telechelic poly(TMC) with slightly higher M_n (1360–6500 g mol^{-1}) with 5 to 20% of ether defects. Mechanistic studies suggested that TMC was produced *in situ*, and subsequently polymerised *via* an activated chain-end mechanism initiated by an I_2/oxetane adduct.



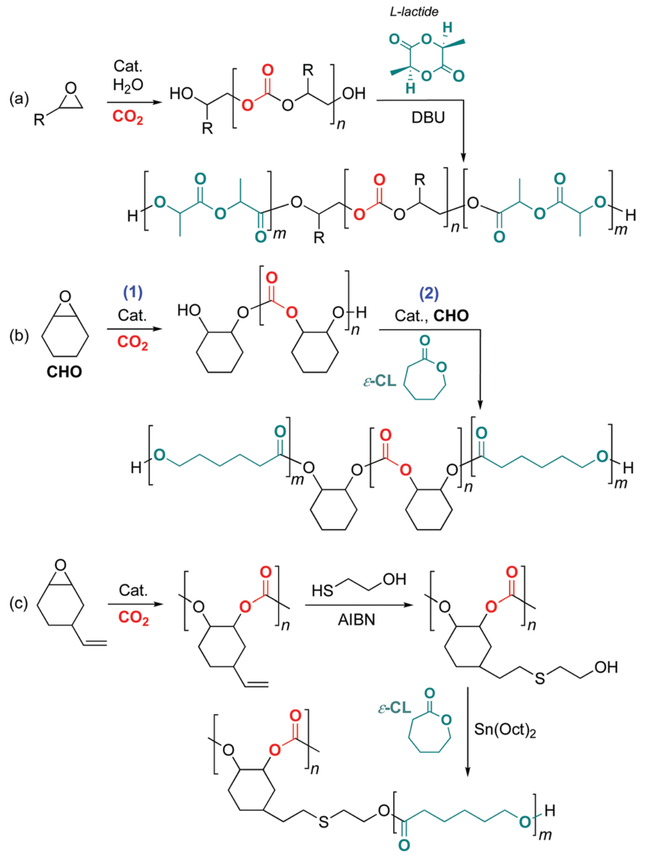
Scheme 27 Organocatalysed CO_2/oxetane copolymerisation *via in situ* formation of trimethylene carbonate and its subsequent ROP.

2.2.3 Synthesis of CO_2-based polyols. One of the advantageous properties of small molecular weight PCs is that they can be used for the preparation of, for instance, polyurethanes and block copolymers provided that the PCs are α,ω-hydroxy-terminated. Typically, the molecular weight of these polyols can be controlled by the addition of CTAs such as water, acids or alcohols and can provide superior properties to the final polymer targets as compared to the use of polyether polyols.

Wang, Qin and coworkers reported extensively on the controllable formation of oligomeric poly(ether-*co*-carbonate) based diols from PO and CO_2 using various types of CTAs and typically Zn/Co double metal cyanides (ZnCoDMCs) as highly effective catalysts.[357–361] In these contributions, the poly(ether-*co*-carbonate)s were produced using CTAs including diacids (oxalic acid, malonic acid),[357,358,361] triacids (trimesic acid)[360] and tetraacids (1,2,4,5-benzenetetracarboxylic acid)[359] while Liu reported the presence of BPA as a CTA.[362] The versatility of using ZnCoDMCs as catalysts with a range of CTAs allowed precisely controlling the molecular weight of chain-extended diols, and typically the desired oligo(carbonate-*co*-ether) diols had a M_n of 1000–13 000 g mol^{-1}, a carbonate content of 15.3–75% and were obtained *via* ROCOP of PO and CO_2 at 50–95 °C and 10–60 bar.

Salen-type metal complexes based on Co have also been exploited for the synthesis of low molecular weight poly(propylene carbonate) based diols, which can be exploited for the synthesis of PUs by further reaction with diisocyanates (see Section 3). As an example, Lee *et al.* prepared PPC based diols with M_n of 2000–10 000 g mol^{-1} by immortal CO_2/PO copolymerisation at 75 °C and 25 bar using catalyst **14** (Scheme 20) and with dicarboxylic acids or diols as CTAs.[363] Through a similar approach, Darensbourg prepared PPC based diols having M_n of ~4500 g mol^{-1} at 25 °C and 15 bar using binary catalysts of type **10** (Scheme 20; with X = Y = trifluoroacetate) and water as both CTA and hydrolyzing agent for the trifluoroacetate end-groups.[364,365] Williams *et al.* used catalysts of type **19** (Scheme 22) to prepare dihydroxyl-terminated PCs based on CHO. Poly(cyclohexene carbonate) based polyols with M_n of 1700–9200 g mol^{-1} at 80–100 °C and 1 bar could be prepared using a dinuclear Mg or Zn catalyst system having a trifluoroacetate initiating group (X = CF_3COO) coordinated with H_2O serving as a CTA.[361,366]

AB and ABA block type copolymers, with A being a polyester block and B a CO_2-based polycarbonate block, were obtained by combining two different polymerisation techniques (Scheme 28a). The first polymerisation step involves the preparation of

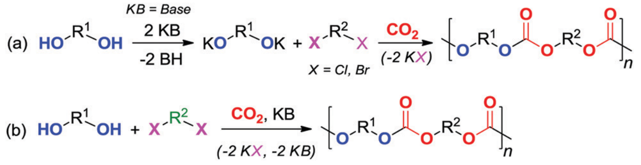


Scheme 28 *In situ* formation of PC-based polyols and their copolymerisation with L-lactide (a) or ε-CL (b and c).

monofunctional or difunctional hydroxyl-terminated PCs by ROCOP of CO_2 and an epoxide in the presence of water as CTA. In a second step, the prepared OH-mono/di-functionalised PC serves as a macroinitiator for the organocatalytic ROP of L-lactide resulting in AB or ABA triblock copolymers depending on the origin of the macroinitiator.[337,361,364] A similar strategy was used by Darensbourg for the preparation of an ABA triblock copolymer designated as poly(phosphate-*b*-carbonate-*b*-phosphate)s using α,ω-dihydroxyl end-capped PCs and a cyclic phosphate monomer.[365]

Williams *et al.* further developed a one-pot strategy allowing for the selective preparation of ABA poly(ester-*b*-carbonate-*b*-ester) triblock copolymers from a mixture of CHO, ε-CL and CO_2 and catalyst **19** (M = Zn; see Scheme 22) containing acetate initiating groups (Scheme 28b). In a first step, a PCHC diol was prepared by a selective ROCOP of CO_2 and CHO in the presence of ε-CL. After removing the excess of CO_2, the selective ROP of ε-CL initiated by the PCHC diol occured in the presence of non-reacted CHO, and gave a triblock copolymer as indicated.[367,368]

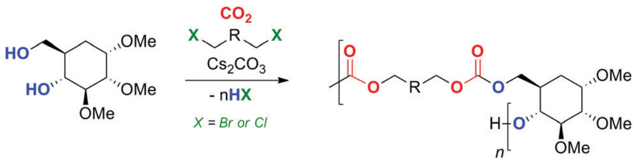
Additionally, in some contributions, the synthesis of "grafted" PCs was described (Scheme 28c). In a first step, 4-vinylcyclohexene oxide was copolymerised with CO_2 resulting in a PC having pendent, terminal olefin groups. Then, a radical initiated thiol–ene reaction with 2-mercapto-ethanol introduced pendent primary alcohols that can be exploited to initiate the ROP of ε-CL in the presence of tin octoate as the catalyst yielding a PC grafted with PCL chains.[369] Lu *et al.* developed a different method avoiding the use of a thiol–ene reaction. A chiral, isotactic PC was first prepared by ROCOP of CO_2 and the protected monomer DTBO (see Scheme 25) followed by deprotection of the cyclic ketal. The resulting free OH groups acted as macroinitiators for the ROP of lactide.[370]



Scheme 29 Synthesis of CO_2-sourced PC by (a) terpolymerisation of CO_2, dihalides and diolates or diphenolates, and (b) terpolymerisation of CO_2, dihalides and diols.

2.2.4 Poly(carbonate)s by polycondensation between CO_2, α,ω-dihalides and diols. In the 1970s, Ikeda reported the synthesis of CO_2-sourced PCs by terpolymerisation of CO_2, dihalides and alkali metal diolates or diphenolates (Scheme 29a).[371,372] These polymerisations were performed in dioxane at 40–120 °C for 48 h in the presence of the macrocyclic ether 18-crown-6 that favoured the diolate-alkali metal ion pair dissociation by forming stable complexes with the cations. Kielkiewicz proposed a mechanism based on this approach by optimising the PC synthesis and a model reaction between CO_2, potassium phenolate and a dihalide.[373] In the first step of this proposed manifold, an alkyl carbonate anion is formed by the reaction between CO_2 and the alkoxide formed by the dissociation of the diolate-alkali metal ion pair promoted by the crown ether. Then, PCs are obtained through the nucleophilic attack of the produced alkyl carbonate anions on the dihalide reagents.

Later, this initial concept was improved by the direct polycondensation between CO_2, dihalides and diols in the presence of an excess of K_2CO_3 (Scheme 29b).[374] PCs free of any observable ether defects and with M_n values between 3300 and 15 800 g mol^{-1} were prepared by Inoue at 80 °C under 1 bar CO_2 pressure in the presence of polar aprotic solvents such as (*N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylacetamide). PCs of higher molecular weight with M_n up to 43 000 g mol^{-1} were prepared by a one-pot polycondensation of various diols, dihalides and CO_2 at 100 °C and 10 bar in the presence of an excess of Cs_2CO_3.[375] From this study, it was noticed that the terpolymerisation process is affected by the nature of the diolates and dihalides. PCs of higher molecular weight and with a monomer conversion >96% were obtained using dihalides with a spacer comprising more than four carbons and diols with a spacer containing a number of carbons different from four. Additionally, a slight excess of dihalides was required to produce high molecular weight PCs. In fact, the authors suggested that these halides may be replaced by the carbonate anion of Cs_2CO_3 through nucleophilic substitution. The generated carbonated compounds can then react with the dihalide reagents producing carbonate linkages, which are incorporated into the polymer by self-polycondensation.

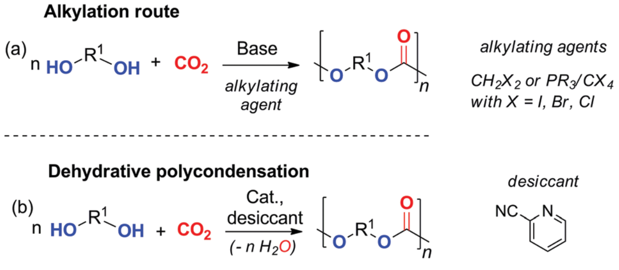


Scheme 30 Synthesis of poly(glycocarbonate)s by polycondensation of α-methyl-2,3-di-*O*-methyl-D-glucopyranoside with CO_2 and aliphatic or aromatic dihalides.

Interestingly, this previously developed methodology is also efficient for the synthesis of CO_2-sourced poly(glycocarbonate)s. These poly(glycocarbonate)s with M_ns between 7000–14 000 g mol^{-1} could be prepared by polycondensation of α-methyl-2,3-di-*O*-methyl-D-glucopy-ranoside with CO_2 and aliphatic or aromatic dihalides at 100 °C and 10 bar in *N*-methyl-2-pyrrolidone, NMP (Scheme 30).[376]

2.2.5 Poly(carbonate)s by polycondensation between CO_2 and diols. The synthesis of PCs by polycondensation of diols and CO_2 shares conceptual similarities and comparable bottlenecks as generally observed for the synthesis of 5- or 6-membered cyclic carbonates (Scheme 31) from diols, with the major difference being the proper selection of the diol reagents. Chain extension is favoured by using aromatic diols or (cyclo)aliphatic 1,*x*-diols (with $x > 4$), whereas cyclic carbonates are generally obtained with 1,2- or 1,3-diol substrates.[377]

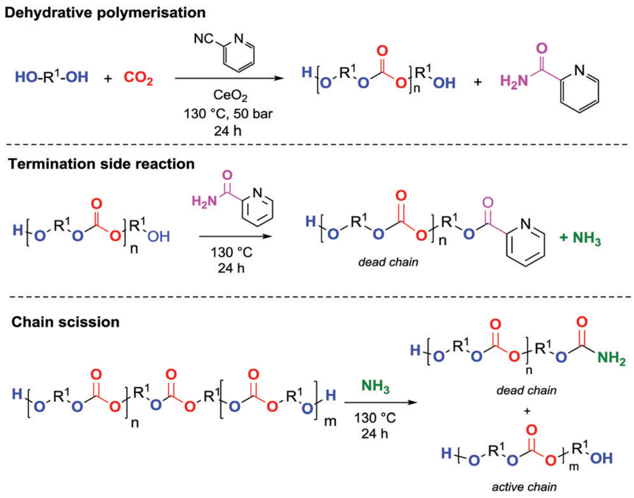
Polyadditions through the alkylation route (Scheme 31a) are typically conducted in organic solvents and require the presence of an excess of base for the deprotonation of the diols, following the formation of a carbonate anion by reaction with CO_2. The carbonate anion reacts further with the alkyl halide to produce an ''activated'' carbonate that is attacked by another carbonate anion generating a carbonate linkage. This approach was exploited by Du *et al.* who prepared low molecular weight PCs and poly(ether-*co*-carbonate)s (M_n up to 5000 g mol^{-1}) from various diols using a combination of Cs_2CO_3 in excess and CH_2Cl_2.[378] Polymerisations were performed at 1 bar CO_2 pressure and 100 °C for 12 h in NMP. Depending on the diol structure, polymers of different compositions were obtained. PCs with a carbonate content higher than 90% were obtained using benzylic diols, whereas poly(ether-*co*-carbonate)s with alternating carbonate/ether units were prepared using aliphatic diols. Recent insights into the mechanism and the polymer structure highlighted a key role of the dihalomethanes (CH_2X_2) and dihaloethanes $(CH_2X)_2$ (X = Cl, Br or I) and more specifically of the halide atom in the formation of the PC backbones when promoted by Cs_2CO_3.[379] The alkoxide generated upon partial deprotonation of the OH groups acts as a nucleophile and adds CO_2 to form a carbonate intermediate. Then, both the unreacted alkoxide and the carbonate anions attack the dihalide forming two halogenoalcohols that subsequently react with a diol or a second alkoxide/carbonate anions creating poly(ether-*co*-carbonate) or polycarbonate. Due to the good leaving group ability of iodide, Du postulated that the alkoxide created upon deprotonation preferentially reacted with CH_2I_2 compared with CO_2 making polyether chains rich in –CH_2–ORO– units with low incorporation of CO_2. With dichloro- and dibromo(m)ethane alkylating agents, the various panel of cross-reactions between all reactive intermediates led to chains of M_n of up to 9800 g mol^{-1} with random enchainment of the carbonate, or methylene oxide units. Interestingly, despite a low activity of the chlorinated alkylating agents that limited the M_n to 2000–6400 g mol^{-1}, no –CH_2–ORO– polyether segments were detected within the polymer microstructure and all chains were end-capped by chlorine groups at both α and ω chain ends.



Scheme 31 Synthesis of CO_2-sourced PCs by polycondensation between CO_2 and diols.

According to a similar strategy, Gnanou prepared bio- and CO_2-sourced water-soluble poly(glycocarbonate)s of low molecular weight (∼2000 g mol^{-1}) by polycondensation of methyl glucopyranoside and CO_2 in the presence of CH_2Br_2 and DBU acting as a dual catalytic system.[376] Competitive depolymerisation promoted by the catalytic system was assumed to be responsible for the low molecular weights that were produced.

A slightly different strategy combined a base with a mixture of trisubstituted phosphine and carbon tetrabromide instead of using an alkyl halide. This process enabled the synthesis of poly(xylylene carbonate)s with M_n between 1000–3800 g mol^{-1} by a polycondensation of CO_2 with *p*-xylylene glycol or *m*-xylylene glycol at rt in DMF.[380,381] However, the selected condensing agent was not effective for lower reactive diols such as diethylene glycol. Thus, the authors introduced a condensing agent consisting of triphenylphosphine, bromotrichloromethane and *N*-cyclohexyl-*N*′,*N*′,*N*″,*N*″-tetramethylguanidine, which permitted the synthesis of low molecular weight PCs (M_n of 4700–6600 g mol^{-1}) from various diols at rt in $CHCl_3$.[380] Finally, Tomishige prepared oligocarbonates with a selectivity >99% by a direct copolymerisation of CO_2 with various 1,*x*-diols (with $4 < x < 10$) in the presence of CeO_2 as a catalyst and 2-cyanopyridine as a dehydrating agent (Scheme 31b).[382] PCs with M_n of up to 1650 g mol^{-1} were obtained at 50 bar and 130 °C. The origin of the low molar masses was recently explained by the esterification of the hydroxyl chain ends of the PCs with the amide produced by the *in situ* hydration of the cyano-derivatives (Scheme 32).[383] This side-reaction left ester end-capped chains with no further ability for chain extension. It was accompanied by the concomitant release of ammonia that induced the scission of the carbonate linkage of PC with the formation of shortest dead chains end-capped by a carbamate moiety and active PCs with alcohol chain end functionality. To limit the termination and the scission of the chains while maximizing the PC molar masses, the scope of dehydrating agent was enlarged to other nitrile derivatives. Amongst the broad range of tested



Scheme 32 CeO_2/2-cyanopyridine promoted polycondensation of diols with CO_2.

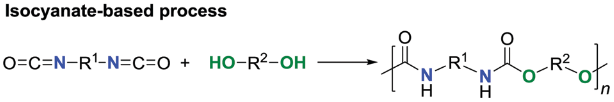
compounds, 2-furonitrile was identified as the most active dehydrating agent offering diol conversions close to 100% and PC chains with M_n of 1600–5000 g mol^{-1} at 50 bar CO_2 pressure and 130 °C for 24 h. The origin of this enhanced efficiency was not only assigned to the suppression of the ester chain ends, but also to a weaker adsorption of the nitrile group of 2-furonitrile onto CeO_2 which facilitated the access of the growing PC macrodiols to the active sites of the catalyst.

3. Polyurethanes from CO_2

Discovered by Otto Bayer in 1937, polyurethanes (PUs) have become one of the most important polymers finding everyday life applications such as in coatings, adhesives, sealants, elastomers and foams, heart valves, and cardiovascular catheters, among others.[384–388] Industrially, PUs are produced by polyaddition between diisocyanates and di- or polyols (Scheme 33).[389] Recent focus in the field of PUs has been on establishing isocyanate-free routes for their production as illustrated in Scheme 33; carbon dioxide can play a crucial role in this important transition (see Scheme 34).

3.1 Poly(urethane)s from CO_2-sourced building blocks

3.1.1 Poly(urethane)s by polyaddition of CO_2-sourced polyols with diisocyanates. CO_2-Sourced polyols generally refer to low-viscous α,ω-hydroxyl telechelic short- and long-chain poly(carbonate)s or poly(ether-*co*-carbonate)s made by CO_2/epoxide copolymerisation, immortal ROP of 6CCs or depolymerisation of high M_n PCs. Their step-growth polymerisation with diisocyanates gives access to CO_2-sourced PUs, as exemplified below.



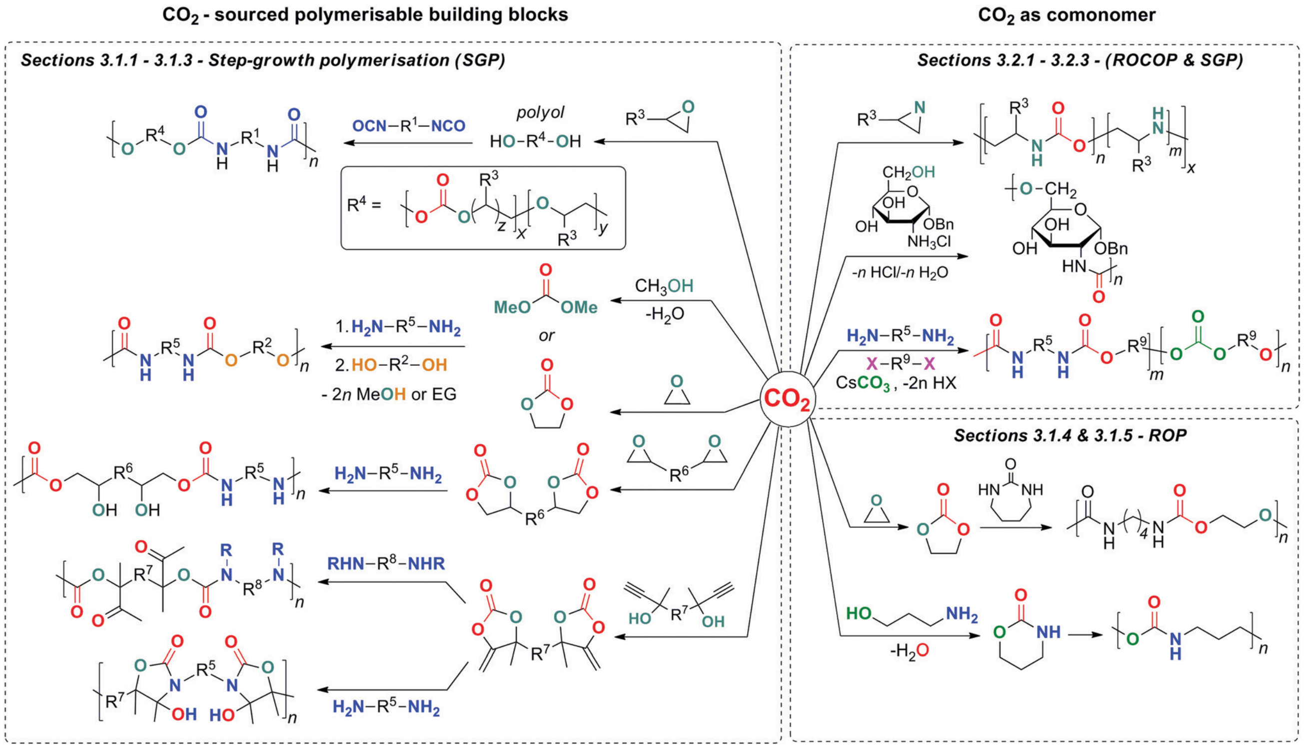
Scheme 33 Industrial synthesis of polyurethanes from isocyanates.

Thermoplastic polyurethanes (TPU) were synthesized in a one-pot, two-step procedure by first preparing low molar mass poly(propylene carbonate) diols (M_n ~ 4100 g mol^{-1}) by the ROCOP of CO_2 and using a salen-type catalyst and different diprotic CTAs at 70 °C and 30 bar, followed by the addition of diisocyanates at 70 °C. The molar masses (M_ns in the range 15 700–49 000 g mol^{-1}) and the T_gs (40–60 °C) of the poly(carbonate-*co*-urethane)s could be adjusted by varying the structure of the diisocyanates (*i.e.*, 4,4′-methylene diphenyl diisocyanate (MDI), toluene-2,4-diisocyanate (TDI) or 1,4-phenylene diisocyanate) and the CTAs.[390,391] Recently, Hong fabricated CO_2-based TPUs (M_ns: 22 600–35 300 g mol^{-1}) for anticorrosion applications using different formulations containing poly(tetrahydrofuran)diol (M_n ~ 2000 g mol^{-1})[392] and commercially available PPC diols (M_n ~ 2000 g mol^{-1}).[233] TPUs were obtained *via* a two-step polyaddition reaction. Initially, a reaction of the polyol with an excess of 4,4′-methylenebis(cyclohexyl isocyanate) was conducted at 80 °C in DMF, followed by chain extension using 1,4-butanediol (BDO) in the presence of dibutyltin dilaurate as a catalyst at 80 °C. Based on similar concepts, a poly(trimethylene carbonate) based diol with low molar mass (M_n ~ 2000 g mol^{-1}; prepared by either organocatalytic oxetane/CO_2 copolymerisation[393] or $[(BDI)Zn(N(SiMe_3)_2)]$ catalyzed iROP of TMC)[394] was exploited for the production of aliphatic PUs at 25–75 °C with the products having M_ns between 5700 and 50 000 g mol^{-1}.

The (immortal) ROCOP of CO_2 and PO catalysed by double metal cyanide-based zinc hexacyanocobaltate was also employed to prepare a series of poly(ether-*co*-carbonate) based polyols (with M_ns of 1600–5500 g mol^{-1}, CO_2 content of 9–55 wt%) by using either di-, tri- or tetracarboxylic acid[357–360,395] or di- or trialcoholic poly(ethylene glycol) starters.[396,397] Some of these polyols were incorporated by Gürtler *et al.*[38] and Nagridge *et al.*[398] into isocyanate-based PU formulations as soft segments to design flexible foams (that are now trademarked by Covestro under the name Cardyon™)[399] or adhesives.[400]

(Commercially available) poly(ether-*co*-carbonate) based polyols were introduced in waterborne PU formulations.[360,401–403] One of the most relevant examples was reported by Wang who prepared a series of oligo(ether-*co*-carbonate)s (M_n ~ 1350–2200 g mol^{-1}) with a carbonate content of 30–66 wt% by the ROCOP of CO_2 and PO using Zn–Co double metal cyanide catalysts and sebacic acid as the initiator and chain transfer agent.[360,401–403] The combination of these latter polyols with MDI, BDO and 2,2-dimethylol propionic acid gave access to waterborne polyurethanes after neutralization of the acid groups by triethylamine. The mechanical and thermal properties of the PUs were easily tuned by the ether and carbonate contents of the polyols. These PUs displayed improved thermal, hydrolysis and oxidation resistance compared with analogous waterborne PUs made from polyester macrodiols such as poly(butylene adipate glycol). Leading chemical companies such as Repsol, Econic, and Novomer have launched demo-plants or even commercialised low M_n polyols produced from CO_2 for PU applications.[392,398,400]

Recently Meng adopted a "top to bottom" approach to prepare CO_2-polyols by using a controlled depolymerisation approach.[397] The thermal alcoholysis of high molar mass PPC (M_n = 82 000 g mol^{-1})



Scheme 34 Synthetic pathways for the synthesis of polyurethanes from CO_2 and/or from CO_2-sourced building blocks.

into lower molar mass macrodiols ($M_n \sim 3000$ g mol^{-1}) was optimised using various diols (1,2-propanediol, 1,4-butanediol or 1,6-hexanediol). The presence of Zn catalyst residues (from the Zn-glutarate used for PPC synthesis by the ROCOP of CO_2 and PO), the excess of diol feed and the high reaction temperature accelerate the alcoholysis reaction and the random chain scission of the polycarbonate. This PPC decomposition was also accompanied by unzipping or decarboxylation side-reactions producing propylene carbonate and polyether segments, rendering the alcoholysate composition rather complex. By controlling the carbonate/ether balance within the macrodiols, the CO_2-sourced building blocks found utility in the formulation of PUs with an adjustable mechanical performance and hardness.

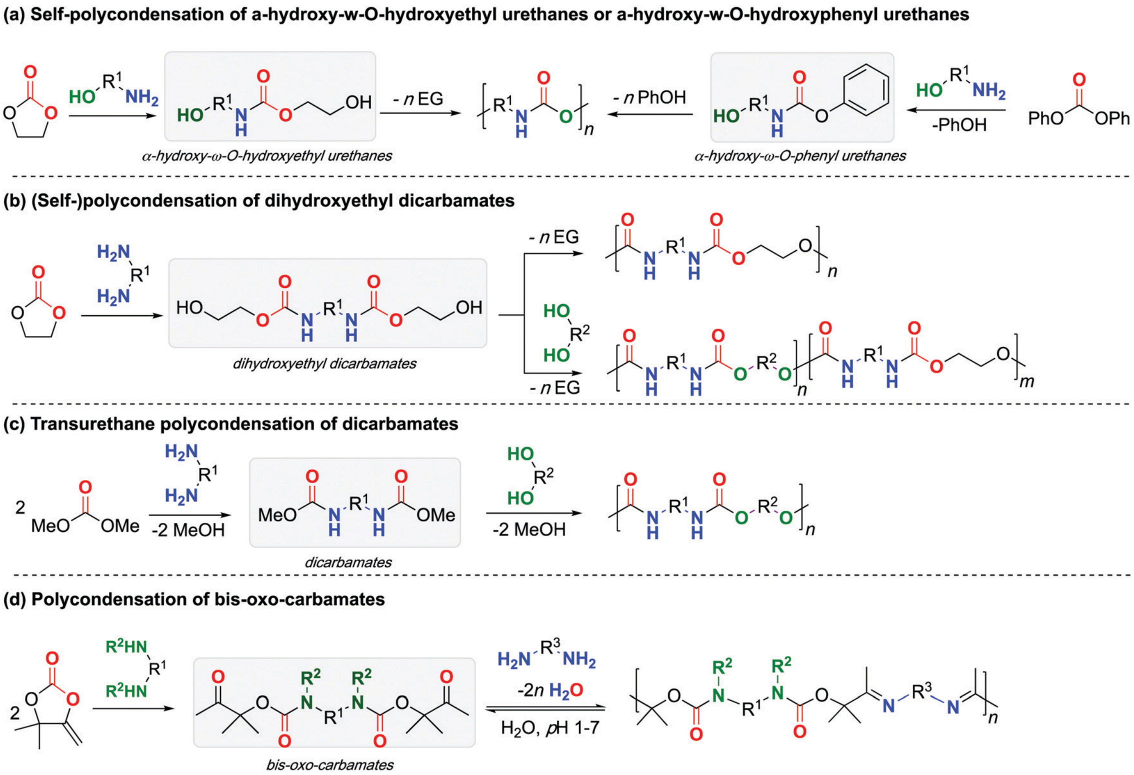
3.1.2 Poly(urethane)s from (a)cyclic carbonates by transurethanisation and polycondensation methods.

Melt transurethanisation and polycondensation of (bis)carbamates derived from (a)cyclic carbonates provide routes towards CO_2-sourced, non-isocyanate based PUs (Scheme 35); this field has been partially reviewed by Cramail *et al.*[404]

Self-polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes (Scheme 35a) or dihydroxyethyl dicarbamates (Scheme 35b) made respectively by aminolysis of ethylene carbonate with aminoalcohols[405] or diamines (1,4-butanediamine,[406] 1,6-hexanediamine,[406,407] 1,12-dodecanediamine,[408] isophorone diamine[409] or piperazine[410]) is mediated by Bu_2SnO or $SnCl_2$ catalysts at 100–150 °C. The removal of ethylene glycol (EG) by-product by vacuum or azeotropic distillation furnished PUs with M_ns of 1600 to 31 000 g mol^{-1}. This PU polymer contained 15 to 35% of urea defects arising from back-biting reactions releasing ethylene carbonate, and giving polymer chains end-capped by primary amine groups. Subsequent aminolysis of a urethane linkage by these primary amine groups furnishes urea defects as shown in Scheme 36. The urea content could be decreased to 5% by replacing α-hydroxy-ω-*O*-hydroxyethyl urethane reagents for hydroxy-ω-*O*-phenyl urethane ones that can be prepared from DPC and amino alcohols. The better leaving group ability of the phenoxy group allowed suppressing the back-biting reactions. PUs with M_ns of 1500 to 16 000 g mol^{-1} were prepared at a lower reaction temperature in the range 90–120 °C.[405,411–413]

In addition to their self-polycondensation, dihydroxyethyl dicarbamates are easily copolymerised with different diols (such as short- and long-chain diols derived from poly(ethylene glycol)),[409,414–416] nylon-6 oligomers,[407] poly(1,4-butylene-adipate),[417] poly(tetramethylene glycols)[418] and polycaprolactone[419] to form semi-crystalline, thermoplastic or thermoplastic elastomer segmented PUs. PUs with M_ns ranging from 7500 to 64 000 g mol^{-1} and some urea defects were prepared at 170–180 °C under reduced pressure using $SnCl_2$ as a catalyst.

A major advance in the field of PU synthesis using melt transurethane polycondensation methods was realised in the copolymerisation of dimethyl dicarbamate monomers (DMDC) with diols (Scheme 35C).[420–425] Unlike in other pathways, the alcoholysis of DMDC releases MeOH that is easier to remove than ethylene glycol. Also, a proper selection of the diol comonomer (1,*x*-diols with $x > 3$) prevents the formation of urea defects by suppressing the back-biting side reactions, that are responsible for the aminolysis of the urethane linkages (Scheme 36). Various DMDC monomers were produced by reactions of diamines (1,4-butanediamine, 1,6-hexanediamine, 1,10-decanediamine, isophorone diamine and Priamine 1047)

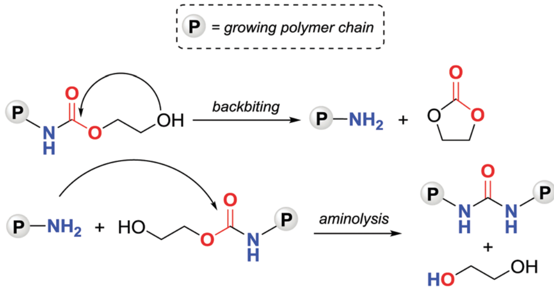

(a) Self-polycondensation of a-hydroxy-w-O-hydroxyethyl urethanes or a-hydroxy-w-O-hydroxyphenyl urethanes

(b) (Self-)polycondensation of dihydroxyethyl dicarbamates

(c) Transurethane polycondensation of dicarbamates

(d) Polycondensation of bis-oxo-carbamates

Scheme 35 Routes to isocyanate-free PUs from linear or cyclic carbonates by transurethanisation and polycondensation methods.



Scheme 36 Side reactions in the self-polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes or dihydroxyethyl dicarbamates.

and a large excess of DMC (6–11 eq.) in the presence of sodium methoxide,[424,425] $Zn(OAc)_2{\cdot}2H_2O$,[421] Na-MCM-41[423] or TBD based catalysts.[420,422] The condensation reaction between DMDC monomers and diols generally proceeds by an oligomerisation step at relatively low temperature (T = 100–150 °C) followed by chain extension at higher temperature (T = 150–185 °C) and/or under vacuum in the presence of a catalyst such as $Ti(OBu)_4$,[424,425] Bu_2SnO,[423] TBD, K_2CO_3 or dibutyltin dilaurate.[420] This procedure was exploited by Jayakannan to synthesize PUs from different DMDC monomers and (cyclo)-aliphatic or macrodiols giving rise to polymers with M_ns of up to 20 000 g mol^{-1}.[420,424,425] Hengshui fabricated poly(carbonate-*co*-urethane) elastomers with M_ns of 30 000–50 000 g mol^{-1} by transurethanisation between dimethyl 1,6-hexamethylene dicarbamate and oligo(carbonate) macrodiols (with M_ns of 1000–2000 g mol^{-1}) as soft segments.[423] This synthetic procedure was further exploited to design thermoplastic polycarbonate-modified polyether polyurethanes (with M_n of up to 64 000 g mol^{-1}) from formulations composed of DMDC, polycarbonate diol, poly(oxytetramethylene)glycol and BDO as a chain extender.[421]

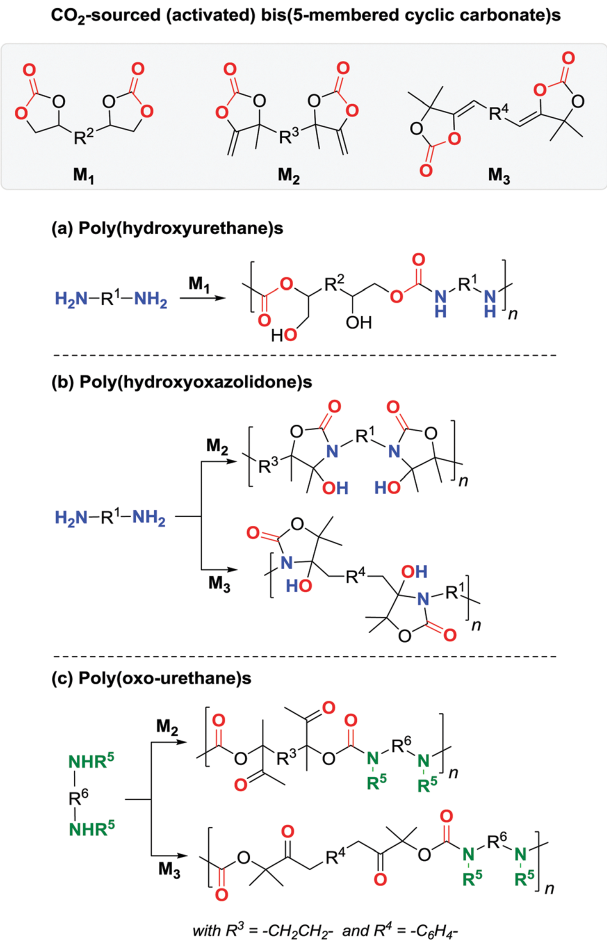
Burel and coworkers prepared thermoplastic polyether polyurethane elastomers (M_w = 7500–17 200 g mol^{-1}) from various DMDC monomers and blends of PEG diol (used as a soft segment) and BDO.[420] Additional examples can be found in Cramail's review and they are all based on similar procedures to those reported in the previously discussed selected examples. The main difference between all examples is the basis of the PU formulation, with some of these formulations being based on bio-based reactants such as limonene, ricinoleic acid and fatty-acid-derived diols.[404,422,426,427]

Recently, Detrembleur engineered a synthesis pathway towards degradable PUs incorporating reversible imine linkages within their main skeleton by polycondensation of CO_2-sourced monomers (Scheme 35d).[428] Two bis-oxo-carbamates were prepared at rt by catalyst-free regioselective aminolysis of a 5-membered cyclic carbonate having an exo-cyclic double bond (4,4-dimethyl-5-methylene-1,3-dioxolan-2-one) with secondary diamines including piperazine and *N*,*N*′-dimethyl-1,6-hexanediamine. Polycondensation of these bis-oxo-carbamates with primary diamines afforded poly(urethane-*co*-imine)s (PUIs, M_n in the range 3000–8500 g mol^{-1}) at 60 °C in the presence of $Ti(OEt)_4$ acting as a Lewis acid catalyst and dehydrating agent. These polymers could be easily hydrolysed under acidic and neutral pH conditions (1 < pH < 7) and allowed recovery of the starting monomers.

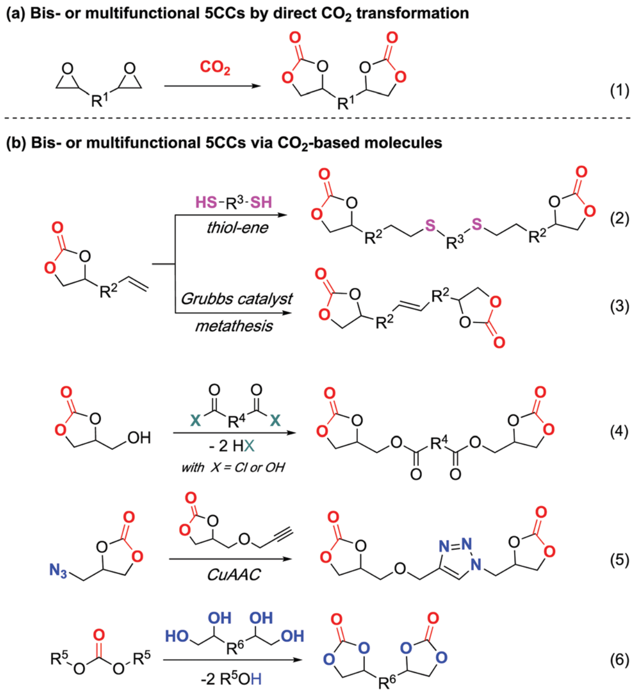
3.1.3 Poly(hydroxyurethane)s, poly(oxo-urethane) and poly(hydroxy-oxazolidone) by polyaddition of bis(5-membered cyclic carbonate)s with diamines.

Poly(hydroxyurethane)s, abbreviated as PHUs, are emerging as one of the most promising alternatives to isocyanate-based PUs.[404] These PHUs differ from conventional PUs by the presence of primary and secondary hydroxyl pendant groups along the main –NH–(C═O)–O–R– skeleton and the absence of biuret and allophanate defects.[429,430] The hydroxyl groups can form inter- and intramolecular hydrogen bonds with the urethane groups and impart to the polymer higher chemical resistance and lower gas permeability than observed for conventional PUs. However, the real influence of the hydrogen bonds on properties such as water absorption and thermal stability still remains a controversial subject.[431] PHUs are synthesized by the polyaddition of bis(5-membered cyclic carbonate)s to diamines (Scheme 37a).

Thanks to the huge progress made in the transformation of CO_2, most of the PHUs are now accessible from a large diversity of CO_2-sourced bis- or multifunctional 5CCs produced by various strategies (Scheme 38). The most relevant pathway involves the direct [3+2] cycloaddition of CO_2 to bis- or multifunctional (biorenewable) epoxides mediated by (organo)catalysts such as LiBr,[432,433] ammonium salts[434–439] or binary systems such as NaI/PPh_3,[440] Fe(*N*,*N*-bis-2-pyridinylmethyl-cyclohexane-1,2 diamine)/*n*Bu_4NBr[441] and *n*Bu_4NI/fluorinated alcohols[98,442–449] (Scheme 38, route 1). The reader is invited to refer to Section 2.1.1 or to consult some recent comprehensive reviews devoted to catalysts used for CO_2/epoxide coupling reactions for further information.[77,78,80,84]



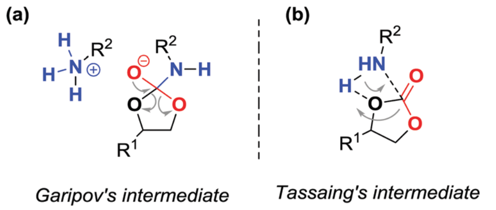
Scheme 37 Isocyanate-free PUs prepared by polyaddition of CO_2-sourced (activated) bis(cyclic carbonate)s to diamines.



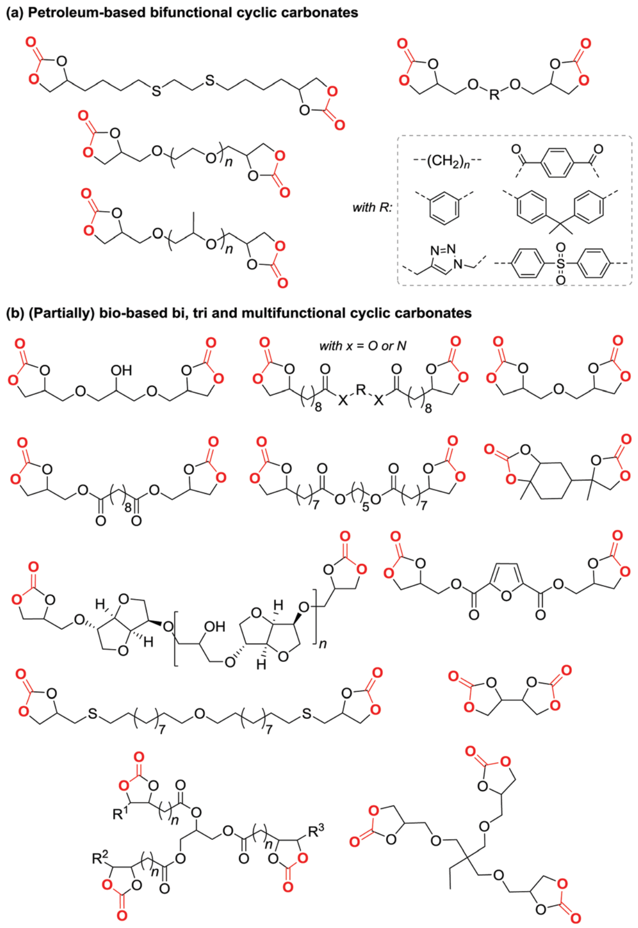
Scheme 38 Pathways for the synthesis of CO_2-sourced bis- or multifunctional 5CCs for PHU synthesis.

Alternative procedures for the synthesis of bis(5CC)s focus on the transformation of monofunctional CO_2-sourced 5CCs (Scheme 38, routes 2–5). Endo[450] and Boutevin[451,452] prepared bis(5CC)s by radical or photochemical thiol–ene reactions between 4-vinyl-1,3-dioxolan-2-one and dithiols at 60–70 °C (Scheme 38, route 2). Cramail produced a difunctional monomer through dimerization of the same vinylic precursor *via* olefin metathesis driven by the 1st generation Grubbs catalyst (Scheme 38, route 3).[453] Bis(5CC)s were also prepared by (trans)esterification of CO_2-sourced GlC with diacylchloride such as sebacoyl chloride in the presence of triethylamine[454] or with dicarboxylic acids (*e.g.* sebacic acid, terephthalic acid) in the presence of *N*,*N*-dicyclohexylcarbodiimide and DMAP (Scheme 38, route 4).[455,456] More recently, Endo exploited the ambient Cu-catalysed azide–alkyne "click" cycloaddition to design triazole-linked bis(5CC)s from azide- and alkyne-functionalized 5CCs (Scheme 38, route 5).[457] By using a condensation concept, Meuldijk and Mülhaupt prepared difunctional monomers from CO_2-sourced dialkyl- or diaryl acyclic carbonates (DMC or DPC) and diglycerol or *meso*-erythritol (Scheme 38, route 6).[435,458]

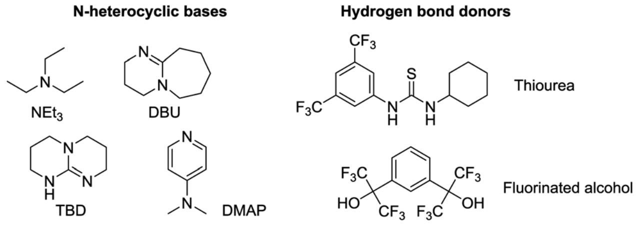
Garipov was the first to propose mechanistic insights into hydroxyurethane formation[459] and suggested a three-step mechanism involving the initial formation of a tetrahedral



Scheme 39 Possible intermediates formed during the synthesis of hydroxyurethane bonds.



Scheme 40 Structures of the main (bio-based) bis(5CC)s used in PHU formulations.



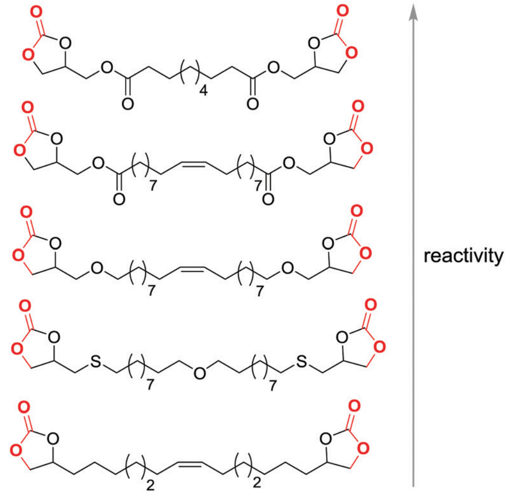
Scheme 41 Examples of selected organocatalysts used for PHU synthesis.

intermediate by a nucleophilic attack of the amine at the carbon center group of the carbonate unit, followed by deprotonation of the intermediate by a second amine. Finally, the C–O link was cleaved, resulting in the formation a hydroxyurethane with a primary or secondary hydroxyl group (Scheme 39a). Based on this mechanism, several authors suggested that the presence of electron withdrawing groups in the α, β and γ positions of bis(5CC) contributes to an enhanced stabilisation of the transition state, thus favoring the formation of hydroxyurethanes with secondary OH groups.[430,432,460,461] Recently, Tassaing *et al.* revisited the hydroxyurethane synthesis by modelling the aminolysis of PrC by DFT calculations.[462] They concluded that a concerted one-step mechanism is involved with a transition state formed by H-bonding of the amine to the carbon atom of the carbonate group accompanied by a proton transfer of the amine to the adjacent O-atom of the carbonate before the ring-opening of PrC (Scheme 39b).

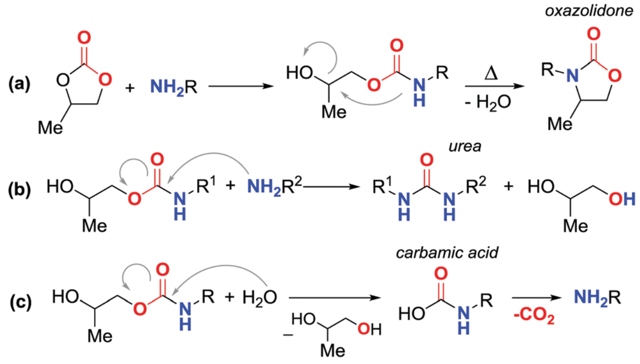
Many bis(5CC)/diamine formulations that are based on petroleum- or bio-based precursors (Scheme 40) have been explored to adjust the polymer properties.[393,398,401,404,405,407,410,415,416,419,423,424,426,427,430,432,441,442,449,451,452,459,466–470] Polymerisations were performed in organic solvents (DMF, DMSO, DMAc)[432,439,440,451,452,457,471–473] or in aqueous (dispersed) media,[474,475] in bulk or in the melt.[425–427,430,431,433–436,443,459,462,469,470,476,477] Generally, linear PHUs with low to high M_n values in the range of 1000–30 000 g mol^{-1} or thermoset materials were obtained at 60–140 °C. The advances in PHU synthesis were extensively reviewed by others, and are thus not discussed in great detail here.[389,404,431,463–465,478–480]

The slow aminolysis rate of 5CCs represents one of the major bottlenecks for this polyaddition strategy to be able to compete with the chemistry of conventional PUs. To improve these kinetic limitations, addition of Lewis acids (LiCl, LiF, LiBr, $MgBr_2$ and $Yb(OTf)_3$ among others),[460,481,482] organic bases (including triethylamine, TBD, DBU, DMAP and phosphazenes),[481–484] hydrogen bond donors (thiourea, fluorinated alcohols)[442,481,482,485] or dual catalysts (TBD/lithium triflate),[486] Scheme 41, has been shown to accelerate the aminolysis of 5CCs by activation of the carbonyl group of 5CCs and/or by activation of the NH_2-group of the amine. As an illustrative example, Endo identified LiCl as an efficient catalyst for PHUs synthesis.[460] Polymers with M_ns of up to 36 000 g mol^{-1} were produced in DMSO at 70 °C using 10 mol% LiCl whereas lower molar mass polymers (M_n 19 000 g mol^{-1}) were obtained under catalyst-free conditions. Organocatalysts such as thiourea and TBD showed higher efficiency than LiCl.[482] As an example, PHUs with M_ns of 53 000 g mol^{-1} and 5430 g mol^{-1} were produced in DMSO at rt with and without TBD, respectively.

To accelerate the aminolysis rate of 5CCs, some authors designed activated cyclic carbonates by introducing electron-withdrawing groups such as ethers,[453,461,487] esters[453,487] or sulfur atoms[488] near the 5-membered ring (Scheme 42). For instance, Caillol observed that a 5CC activated by an ester group strongly increased the aminolysis reaction (up to 6.5-fold rate enhancement) at 25 °C compared to 5CCs bearing an alkyl chain.[487] This observation was explained by the negative inductive and mesomeric effects of the ester group that favours the carbonate ring opening, and to the interaction of amines with the ester groups



Scheme 42 Observed reactivity order of substituted 5CCs.



Scheme 43 Possible side-reactions occurring during PHU synthesis.

through hydrogen bonding. Cramail reported similar trends with a 14.7-fold increase of the aminolysis rate of ester-activated cyclic carbonates at 70 °C in DMSO.[453] These results were confirmed for the synthesis of PHUs with higher M_n (12 000–13 700 g mol^{-1}) using an ester-activated bis(5CC) compared to polymers produced from ether-activated (M_n = 7500 g mol^{-1}) and non-activated analogues (M_n = 6000 g mol^{-1}).[453]

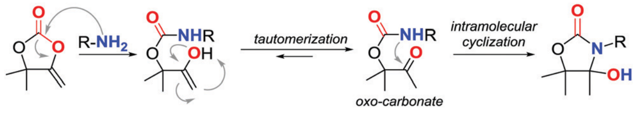
As a last exemplary case, Endo showed that increasing the carbonate ring size from five to six induces a 28 to 62-fold acceleration for the aminolysis reaction at 30 and 70 °C, respectively.[429] The higher reactivity of 6CCs was proposed to result from a higher ring-strain. This increase in the rate of aminolysis was further confirmed by Caillol,[487] Cramail[489] and Sardon[490] who benchmarked the reactivity of EC and TMC with *n*-hexylamine in DMSO at 50 °C and found that the ring-opening of TMC was 2.5–3.6 times. The benefit of increasing the carbonate ring size was illustrated for the copolymerisation of various bis(6CC)s/diamine combinations.[450,451,489,491] Endo demonstrated that PHUs prepared from a bis-6CC and 4,9-dioxadodecane-1,12-diamine exhibited higher M_n values than those synthesized from bis(5CC)s having an analoguous structure (M_n = 26 000 *versus* 12 000 g mol^{-1}) after copolymerisation at 50 °C in DMAc.[450] Similar trends were observed by Boutevin for the polyaddition of bis(6CC)s with diethylenetriamine.[451] However, developing facile transformation pathways of CO_2 into 6-membered cyclic carbonates remains difficult. To date, the only known general route towards CO_2-sourced bis(6CC)s was reported by Kleij *et al.* who used a CO_2/bis-oxetane coupling reaction promoted by Al(III) aminotriphenolate complexes and TBAB.[117]

A second major limitation of the PHU chemistry is the occurrence of side reactions that render the selective synthesis of high M_n polymers challenging. In a model reaction, Caillol evidenced the concomitant formation of oxazolidinone and urea by-products, which originate from the dehydrative intramolecular cyclization of the NH group of the urethane link having a neighboring hydroxyl group, and the aminolysis of a urethane bond (Scheme 43a and b), respectively.[453,488,492]

Urea formation yields non-reactive hydroxyl-terminated PHU chains. Water may hydrolyze the PHU chains, thus leaving non-reactive hydroxyl-terminated PHU fragments but also carbamic acid end groups that rapidly decarboxylate to afford reactive amine-terminated polymer chains (Scheme 43c). All these side reactions induce a deviation from an ideal stoichiometry of the reactants, and consequently prevent the formation of high molar mass PHUs. Recently, Sardon nicely exploited the formation of ureas to synthesize segmented poly(urea-*co*-hydroxyurethane)s upon thermal treatment of the PHU in the presence of catalytic amounts of strong organic bases.[493]

Caillol postulated that intra- and inter-chain hydrogen bonds might also prevent the formation of high molar mass PHUs by limiting monomer diffusion and conversion.[494] They suggested that the addition of plasticisers (glycerol, diglycerol) or polar protic solvents (such as methanol and ethanol) should interfere with the inter- and intramolecular hydrogen bonding network formation and restore the monomer mobility. The hypothesis was examined by comparative kinetic studies of aminolysis model reactions in various solvents that showed higher 5CC conversion in MeOH.[487,494] However, the enhanced reactivity of 5CCs also arises from its activation by the protic solvent through H-bonding with the heteroatoms of the carbonate group.[454,487] This interaction increases the electrophilicity of the cyclic carbonate and thus facilitates its susceptibility towards ring-opening. Currently, the potential influence of this intra- and inter-chain bonding on the course of the polymerisation reaction and the molar mass is still under debate.

An interesting advancement in the area of isocyanate-free PU formation demonstrates the facile synthesis of novel functional and regio-regular PUs (Scheme 37b and c) by exploiting the high reactivity of new CO_2-sourced 5-membered bis(α-alkylidene cyclic carbonate)s.[230] Two bis-αCCs monomers, with an external or internal exo-cyclic olefin bond, were prepared from CO_2 (see Section 2.1.4). Their polyaddition reaction that involves secondary diamines yielded regio-regular functional poly(β-oxo-urethane)s bearing either pendent oxo-groups (when bis-αCCs with external double bonds were used), or ketones within the polymer backbone when the polymerisation was carried out with bis-αCCs having internal double bonds. On the other hand, the polyaddition of bis-αCCs with primary diamines yielded poly(β-hydroxy-2-oxazolidone)s that originate from an intra-molecular



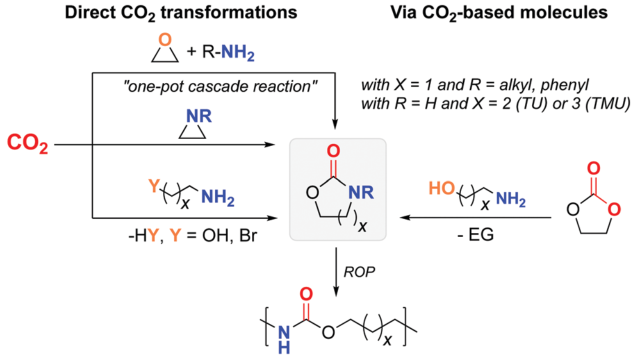
Scheme 44 Mechanism of oxazolidone formation.

cyclisation after the ring-opening of bis-αCCs with the diamine (Scheme 44).

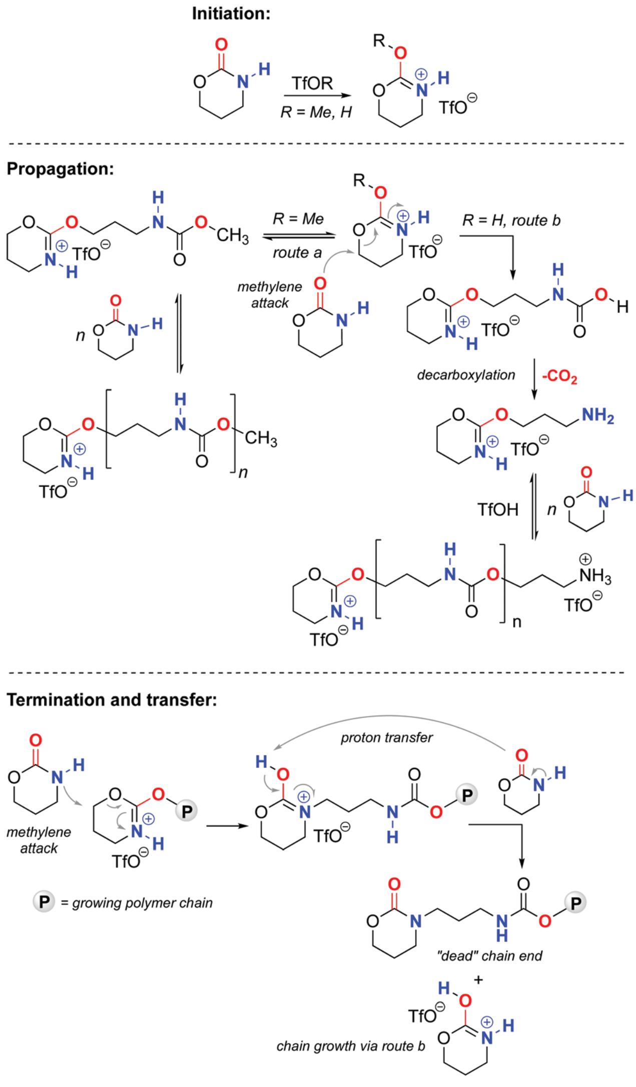
Remarkably, these latter polyadditions were feasible under ambient conditions without any catalyst though addition of DBU accelerated these polymerisations. Linear poly(β-oxo-urethane)s with M_ns of up to 25 000 g mol^{-1} and poly(β-hydroxy-2-oxazolidone)s with M_ns of up to 22 000 g mol^{-1} were produced without any noticeable defects. At present, efforts are devoted to optimise the protocols for the synthesis of these α-alkylidene cyclic carbonates from carbon dioxide and propargylic alcohols, mainly by developing high performance and selective (organo)catalysts.[489–521] This is a necessary step for the potential industrial implementation of this technology that is receiving interest from various polymer producers, such as BASF and Henkel, in the context of both PU and PC production (see Section 2.1.4).[20,515,522]

3.1.4 Poly(urethane)s by ring-opening polymerisation of cyclic urethanes. Cationic ROP of 6- and 7-membered cyclic urethanes such as trimethylene urethane (TU) and tetramethylene urethane (TMU) were proposed for the preparation of PUs (Scheme 45) but examples remain rare.

TU[406,523,524] and TMU[406] were produced by the reaction of CO_2-sourced EC with amino alcohols, *i.e.* 3-amino-1-propanol and 4-amino-1-butanol, respectively. Piotrowska proposed a two-step mechanism that involves an aminolysis reaction of EC followed by an intramolecular cyclisation by transurethanisation.[406] When performed in an azeotropic solvent by using $Bu_2Sn(OMe)_2$ as a catalyst, TU was obtained in a yield of 64% while the TMU yield was limited to only 10%. The direct synthesis of cyclic urethane from 3-amino-1-propanol and CO_2 afforded TU with a yield of 95% in acetonitrile at 150 °C and 50 bar using a heterogeneous CeO_2 catalyst.[525] TMU (15%) could be prepared directly from CO_2 and 4-amino-1-butanol in ethanol at 7 bar and 160 °C in the presence of ceria nanoparticles.[526] In another variant, TU was produced in quantitative yield by coupling CO_2 with γ-haloamines such as 3-chloropropylamine or 3-bromopropylamine in ethanol at 65 °C and 35 bar CO_2 pressure using KOH as a catalyst.[527]



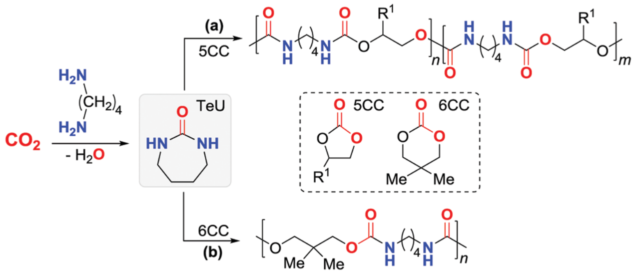
Scheme 45 Synthesis of CO_2-sourced cyclic urethanes and their ring-opening polymerisation to afford polyurethanes.



Scheme 46 Mechanism of the cationic ring-opening polymerisation of TU.

TU and TMU polymerisations were carried out by cationic ROP that are thermodynamically favored because of negative $\Delta G^0_{\text{Polym}}$ values (Scheme 46).[528–530] Alkylation of the carbonyl moiety of TU by electrophilic initiators (TfOH, TfOMe or $BF_3 \cdot OEt_2$) afforded an active species which underwent *O*-alkyl scission by the nucleophilic attack of the carbonyl oxygen of a second TU.[523,531] The chain propagation occurred by repetition of these steps leading eventually to PUs. The polymerisation was affected by transfer and termination reactions resulting from the nucleophilic attack of the nitrogen atom of TU onto the active species, and a subsequent proton transfer gave unreactive chains. PUs free of urea or carbonate defects and characterised by M_ns of 14 300–34 800 g mol^{-1} and 1200–5200 g mol^{-1} were respectively prepared from TU[523,531] or TMU[532] in bulk at 70–120 °C.

In 2019, Thomas introduced a straightforward methodology to access aliphatic PUs with novel structures by anionic ring-opening polymerisation of 5-membered cyclic carbamates.[533]

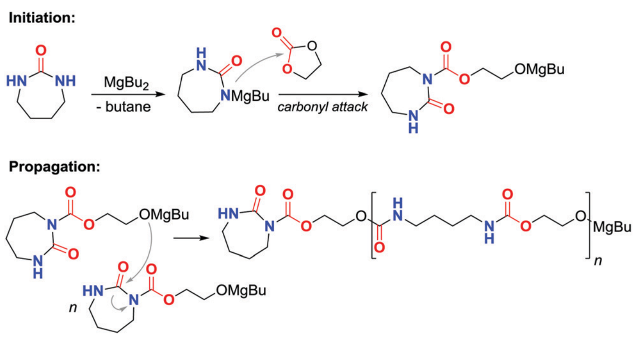


Scheme 47 Synthesis of PUs by ring-opening copolymerisation of a cyclic urea with cyclic carbonates.

This seminal work offered a new way to valorise oxazolidinones that are easily produced by a [3+2] cycloaddition reaction between CO_2 and aziridines,[74,534–547] *via* the condensation of CO_2 with 1,2-aminoalcohols[525,526,548] or 1,2-haloamines[527] or by three-component cascade reactions between CO_2, amines and epoxides[549–556] or CO_2, amines and dihalides.[557]

3.1.5 Poly(urethane)s by ring-opening copolymerisation of cyclic ureas with cyclic carbonates. The significant developments made in the area of CO_2 conversion opened a new route to prepare PU precursors employing tetramethylene urea (TeU) that can be polymerised by ROCOP in the presence of 5- or 6-membered cyclic carbonates (Scheme 47). Garcia produced TeU by dehydrative coupling of CO_2 with 1,4-diaminobutane using ceria nanoparticles as a catalyst.[558] Höcker reported on the ROCOP of TeU with 5CCs (EC or PrC) using dibutylmagnesium ($MgBu_2$) as an initiator (Scheme 47, path a).[405] The copolymerisation was performed in bulk at 100 °C using a 3-fold excess of 5CC compared to TeU and furnished PUs having M_ns of 8600, 12 200 or 9800–18 200 g mol^{-1} in the presence of EC, PrC or EC/PrC mixtures as comonomers, respectively.

The proposed mechanism involves the formation of a nucleophilic TeU–MgBu salt that mediates the ring-opening of the 5CC to form an active species bearing a nucleophilic (alcoholate) and an electrophilic (carbonyl) site. Chain propagation occurs *via* repetition of the nucleophilic addition of the alcoholate onto the carbonyl carbon of the dimer (Scheme 48). The resultant PU microstructure showed a perfect alternating TeU/5CC sequence with no observable ether or carbonate defects. This concept was further extended to the ROCOP of TeU with a 6-membered cyclic carbonate (*e.g.*, 2,2-dimethyltrimethylene carbonate) using *N*,*N*′-dimethylpropylene urea as a solvent (Scheme 47, path b). PUs with a fully alternating microstructure and M_ns between 3000 and 22 000 g mol^{-1} were produced at 80–140 °C.[559,560]

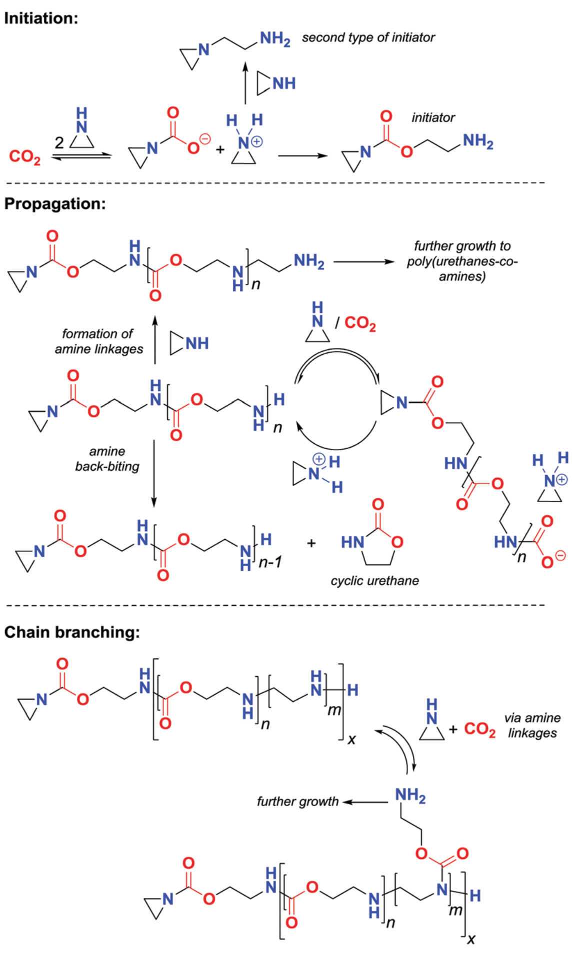


Scheme 48 Mechanism of the ring-opening polymerisation of TeU with 5CCs.

3.2 Direct synthesis of PUs by use of CO_2 as a comonomer

Synthesis routes to PUs from direct polymerisation of CO_2 are limited to the ROCOP of CO_2 and aziridines, the dehydrative polycondensation of amino alcohols with CO_2 and the terpolymerisation of CO_2, diamines and dihalides.

3.2.1 Poly(urethane)s by the ROCOP of CO_2 and aziridines. Conceptually, the ROCOP of aziridines with CO_2 represents an attractive method to produce aliphatic PUs. However, ever since the seminal work from Ikeda,[561–563] this strategy remains scarcely explored. The proposed polymerisation mechanism proceeds through a reversible capture of CO_2 by the aziridine reagent to form an aziridinium–carbamate zwitterionic adduct (Scheme 49).[564] The aziridinium cation is then ring-opened by nucleophilic attack of either the carbamate anion or another equivalent of aziridine, leaving in both cases a reactive amine initiating species. In a second step, propagation occurs *via*



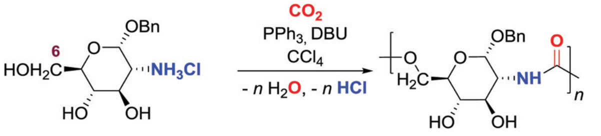
Scheme 49 General mechanism for the ring-opening copolymerisation of aziridines with CO_2. For the sake of simplicity, the aziridine monomer is devoid of any substituents.

repetition of the reversible carboxylation of the amine chain ends followed by nucleophilic attack onto the aziridinium cation to form a subsequent urethane linkage. Depending on the CO_2 pressure and the presence of a Lewis acid catalyst,[565] chain propagation is accompanied by some side reactions: (i) the consecutive insertion of two or more aziridine units resulting in the formation of polyamine segments; (ii) intramolecular back-biting reactions that involve the amine chain ends, releasing the thermodynamically stable five-membered cyclic urethane (oxazolidinone) as by-product; and (iii) the formation of zwitterionic complexes between CO_2 and the amine defects within the main skeleton promoting the branching of the polymer.

As in the ROCOP of CO_2 and epoxides (see Section 2.2.1), one may expect the formation of PU chains with different properties induced by the regioselectivity of the ring-opening of terminal aziridines such as propylene- or *N*-phenylethylene imine, that can occur at both the methylene or methine carbon centre. However, none of the reported contributions so far investigated the occurrence of different insertion modes of the aziridine monomer. The exact microstructure of the polymer (*cf.*, head-to-head, head-to-tail or tail-to-tail enchainments) has thus far not been elucidated.

Ikeda fabricated PUs from various aziridines such as *N*-phenylethylene imine, 2-methylaziridine and ethylene imine.[561–563] PUs with a urethane content of 47–59% were synthesized from CO_2 and *N*-phenylethylene imine at 100 °C in *n*-hexane using divalent Mn catalysts such as $Mn(acac)_2$ and $MnCl_2{\cdot}4H_2O$.[561] The urethane content could be increased to 80% by conducting the copolymerisation at 120–150 °C. Moreover, PUs with a CO_2 content of 10–35 mol% and urethane content of 8–53 mol% were produced by a catalyst-free ROCOP of 2-methylaziridine and CO_2 performed at 0–100 °C in organic solvents or under solvent-free conditions.[563] The same group also reported the solvent- and catalyst-free synthesis of PUs having a 13–31 mol% urethane content by the ROCOP of CO_2 and ethylene imine at 80 °C.[562] The formation of polyamine segments was suppressed by using a series of one- or two-component organozinc catalysts including $ZnEt_2$, EtZnOMe, $ZnEt_2$/pyrogallol, $ZnEt_2$/resorcinol, $ZnEt_2$/*o*-aminophenol and $ZnEt_2$/*o*-phenylenediamine[565] that enabled the incorporation of both monomers in a perfectly alternating fashion. However, only oligomers with M_ns of 400–600 g mol^{-1} were produced at 35 °C and 60 bar CO_2 pressure.

Significant progress in the ROCOP of CO_2 and aziridines was communicated by Ikariya *et al.* who highlighted the beneficial nature of using supercritical conditions to control the urethane/amine content of the PU products, and to access to high molar mass polymers.[564,566] PU chains with M_ws of 27 000 to 150 000 g mol^{-1} were produced from CO_2 and 2-methylaziridine at 80–140 °C and 100–220 bar. The urethane content improved from 33 to 61% by increasing the CO_2 pressure from 30 to 220 bar.[566] The concept was further improved by adding DMAc as a co-solvent that enhanced the PU solubility in supercritical CO_2 and favoured the formation of polymers with M_ns of up to 210 000 g mol^{-1} with a urethane content of up to 74% when the reactions were carried out at 220 bar and 100 °C. The urethane content could be further increased to 85% in the presence of a $Y(CCl_3COO)_3$–$ZnEt_2$–glycerine catalyst but at the expense of the observed M_w (3500–4500 g mol^{-1}).[567]



Scheme 50 PUs obtained through polycondensation of benzyl-2-amino-2-deoxy-α-D-glucopyranoside hydrochloride and CO_2.

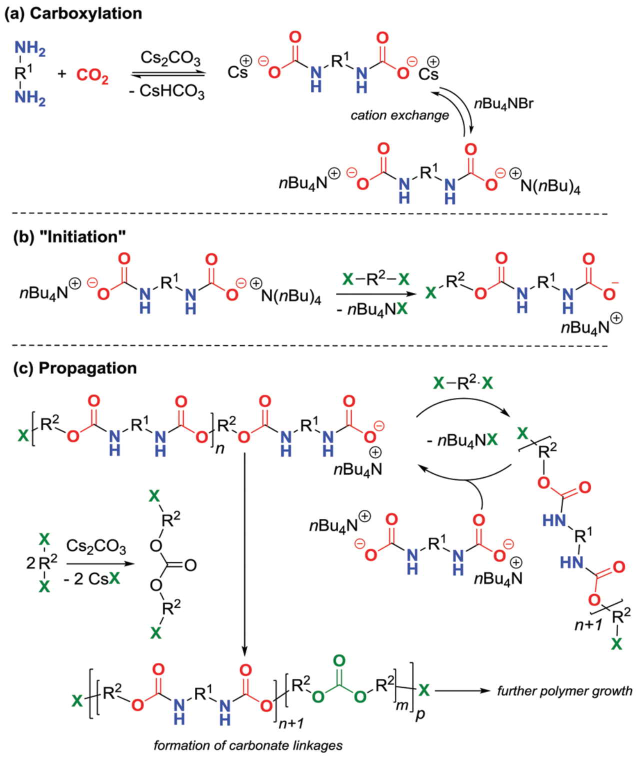
3.2.2 Poly(urethane)s by polycondensation between CO_2 and amino alcohols. The synthesis of PUs by dehydrative polycondensation of CO_2 with 1,*x*-aminoalcohols shares conceptual similarities and bottlenecks with those reported for the direct coupling of CO_2 and diols (see Section 2.2.5). To the best of our knowledge, Chiba reported the only example of PU synthesis by polycondensation of CO_2 and benzyl-2-amino-2-deoxy-α-D-glucopyranoside hydrochloride as the amino alcohol (Scheme 50).[568] The polymerisations were performed in DMF at 25 to 100 °C under an ambient CO_2 atmosphere using a ternary condensing agent composed of PPh_3, CCl_4 and DBU. The resulting polymers were acetylated prior to characterisation. Acetylated PUs with low M_ns of 2000–3000 g mol^{-1} were produced by this strategy. The authors demonstrated that the polycondensation proceeded regioselectively *via* the primary OH group at the C6 position of the sugar molecule.

3.2.3 Poly(urethane)s by terpolymerisation of CO_2, diamines and dihalides. In 2017, Gnanou prepared PUs by a direct one-pot, two-step terpolymerisation process using CO_2, various diamines and dihalides.[569] This polycondensation approach was promoted by a dual system composed of an excess of base (Cs_2CO_3) and an ammonium halide salt at 80 °C and 10 bar of CO_2. The mechanistic proposal (Scheme 51) has the amines first deprotonated by the Cs_2CO_3 to form a carbamate salt in the presence of CO_2. A cation exchange then takes place between the Cs and ammonium cations. This exchange is thought to be crucial to push the polymerisation towards completion by preventing side reactions such as *N*-alkylation of the amines or alkylation of the carbonates by the alkyl halide reagents.

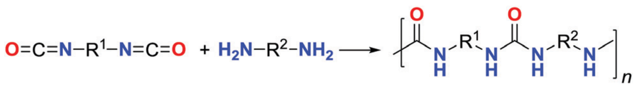
The carbamate intermediate readily reacts with the dihalides by means of nucleophilic substitution to generate a urethane bond. Repetition of this reaction sequence leads to chain propagation, though accompanied by some carbonate defects. These defects originate from the direct replacement of a halide by the carbonate anion of Cs_2CO_3, that further reacts with a second dihalide to afford carbonate linkages. Typically, poly(urethane-*co*-carbonate)s with M_ns of 2500–4000 g mol^{-1} and a PU/PC ratio of around 6 : 1 were produced at 60–100 °C at 10 bar CO_2 pressure. By varying the nature of the dihalide and the diamine, poly(urethane-*co*-carbonate)s with M_ns ranging from 1000 to 23 000 g mol^{-1} and PU/PC ratios of 14 : 1 to 3.3 : 1 were prepared.

4. Polyureas from CO_2

Polyureas (PUA)s are polymers containing urea linkages (*i.e.*, having –NH–C(=O)–NH– groups) within the polymer backbone.



Scheme 51 PUs by terpolymerisation of CO_2, diamines and dihalides.



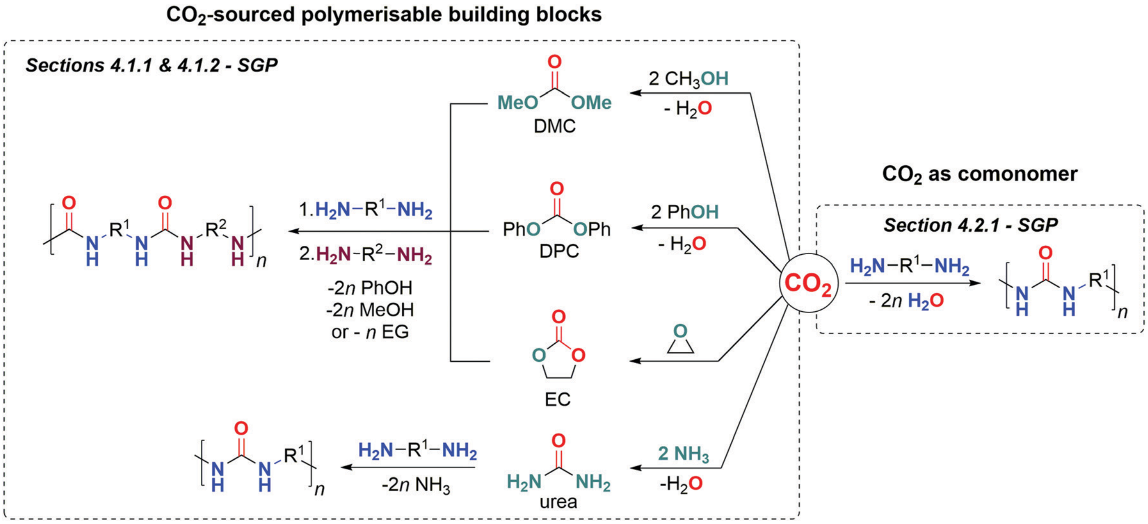
Scheme 52 Industrial synthesis of PUAs by polyaddition of isocyanates and diamines.

They find applications as linings, joint sealants, and microcapsules among others in numerous sectors such as in the automotive industry, construction, household products and marine-related technologies. Due to their corrosion, abrasion and chemical resistance, PUAs are also ideal (spray) coating materials for the protection of different substrates such as steel and concrete.[570–574] Industrially, PUAs are prepared by polyaddition using diisocyanate and diamine reagents (Scheme 52).[573,575,576] As for the conventional synthesis of PUs, non-isocyanate routes have been engineered to synthesize these polymers from CO_2-sourced (a)cyclic carbonates or urea, or *via* direct copolymerisation of CO_2 with diamines (Scheme 53).

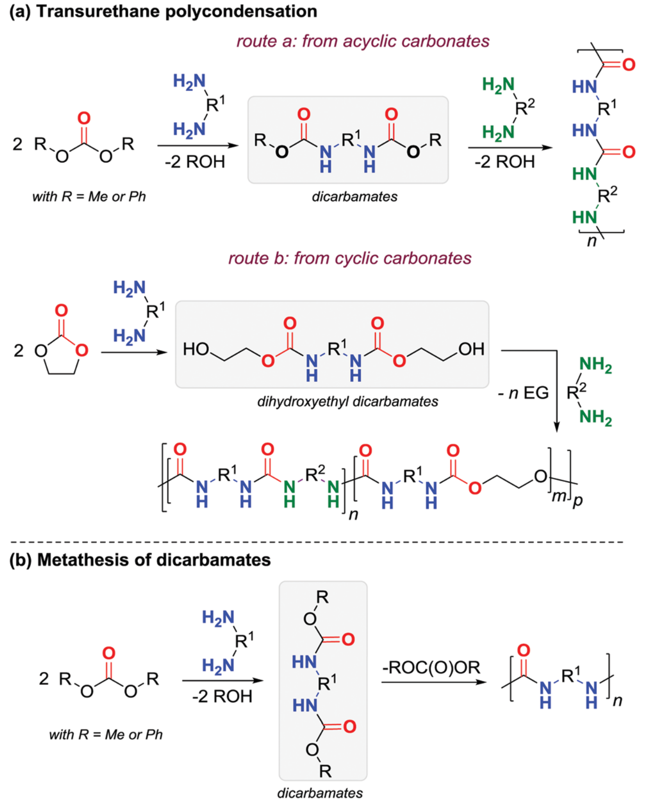
4.1 Polyureas from CO_2-sourced building blocks

4.1.1 Polyureas from (a)cyclic carbonates by melt-transurethanisation and polycondensation methods. As in PU chemistry, CO_2-sourced organic carbonates (both cyclic and acyclic ones) show great utility as building blocks for the synthesis of polyureas (Scheme 54a). In (melt) transurethanisation methods, the aminolysis of (a)cyclic organic carbonates furnishes bis-carbamate monomers or oligoureas by using alkali bases (KOMe, KOtBu or potassium bis(trimethylsilyl)amide),[577] alkaline oxides (GeO_2, SrO_2), transition metal complexes (based on Ti, Sn or Sc) or organic superbases (DBU, TBD, phosphazene) as catalysts.[577–579] Upon addition of the diamine reagent and removal of the alcohol by-product, the polymer chains propagate at high temperature (100–200 °C) to afford PUAs.

As representative examples for the strategy using acyclic carbonates (Scheme 54a, route a), the copolymerisation of poly(propylene glycol)-bis(2-aminopropyl)ether with butylene bis-carbamate created PUAs with M_ns ranging from 15 000 g mol^{-1} up to 90 000 g mol^{-1} at 130 °C with TBD or alcoholate derived catalysts, respectively. *N*,*N*′-Diphenyl-4,4′-methylene diphenylcarbamate was prepared from 4,4′-methylenedianiline and an excess of DPC using benzoic acid as a catalyst at 80 °C.[580] This intermediate was used to produce segmented PUA elastomers (M_w in the range 57 000–130 000 g mol^{-1}) by transurethanisation with blends of a long-chain polyether diamine and primary (cyclo)aliphatic or aromatic diamine chain extenders at 140 °C.



Scheme 53 Synthetic pathways towards CO_2-sourced polyureas.

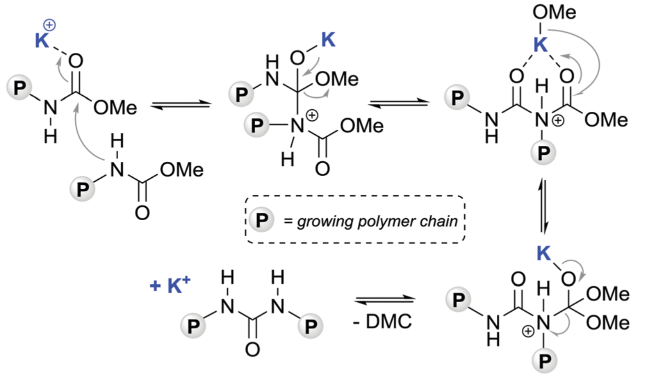


Scheme 54 Synthesis of CO_2-sourced PUAs by (a) (melt) transurethane polycondensation or (b) dialkylcarbamate metathesis.

When cyclic carbonates were the precursors (Scheme 54a, route b), β-dihydroxyalkyl-bis-carbamate intermediates were produced by the aminolysis of 5CCs (EC or PrC) with piperazine or 1,6-hexanediamine.[410,581] Their melt polycondensation with isophorone diamine at 130–170 °C released the vicinal diol that was removed under vacuum to furnish PUAs with M_ns of 3300 to 15 000 g mol^{-1}.[410]

However, the PUA microstructure revealed substantial urethane linkage defects (1.2 to 41%). These defects could be suppressed by Rieger *et al.* by combining the use of a superbase (TBD) catalyst and microwave irradiation (at fixed mode, power 10–20 W, 15–120 min) for propylene carbonate/1,6-hexanediamine copolymerisation that promoted the *in situ* formation of the bis-carbamate intermediate that underwent further aminolysis and provided as such the targeted PUAs.[582]

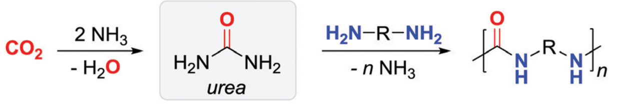
Burel introduced a synthetic approach towards PUAs by alkylcarbamate metathesis (Scheme 54b).[579] Oligoureas were first produced from various dimethyl dicarbamate intermediates at 160–200 °C, followed by K_2CO_3 mediated chain growth with a concomittant release of DMC. The authors suggested that the weak Lewis acidic potassium cation interacts with the oxygen atom of the carbonyl group of the carbamate thereby increasing its electrophilicity. This carbonyl group is then attacked by the nitrogen atom of a second carbamate. The resultant tetrahedral intermediate rearranges into a potassium stabilised tridentate chelated complex with release of methoxide. A subsequent attack of the methoxide anion on the newly created carbonyl carbon affords a new tetrahedral intermediate which rearranges into urea with the release of DMC (Scheme 55). The so-produced PUAs were found to be poorly soluble in the solvents used for SEC analysis, rendering the determination of their M_ns impossible. However the polymers displayed enhanced thermal properties compared with their analogues produced by melt transurethane polycondensation, suggesting a higher M_n or a lower content of carbonate defects.



Scheme 55 Proposed mechanism for the formation of PUAs by a metathesis reaction.

4.1.2 Polyureas by (melt) polycondensation methods of urea and diamines.

To date, urea is the organic compound that uses the highest amount of CO_2 at an industrial level. Known for more than a century, its synthesis is based on the reaction of CO_2 with ammonia by a high temperature/high pressure two-step process (T = 190–210 °C and p_{CO_2} = 150 bar).[583,584] Ammonia reacts with CO_2 to form ammonium carbamate that is then dehydrated to give urea. The polycondensation of diamines with urea provides an isocyanate- and phosgene-free pathway to polyureas (Scheme 56). Abdolmaleki prepared PUAs from urea and various primary diamines under microwave conditions (400 W, 12 min) in DMAc in the presence of a catalytic amount of p-toluenesulfonic acid.[585] Polymers were obtained from both aromatic and aliphatic diamines. Later, Long synthesized PUAs by catalyst-free melt polycondensation between urea and blends of 1,8-octanediamine and 2,2-(ethylenedioxy)bis(ethylamine).[586] The mixtures of monomers were heated at 170–250 °C followed by the removal of the by-produced ammonia under vacuum at 250 °C. The thermo-mechanical properties of these PUAs were easily tuned by the ratio between the diamine and urea or by modulating the composition of the diamine mixture. However, in both these latter studies, no mention was made on the molar masses of the prepared PUAs likely due to the poor solubility of these polymeric products.



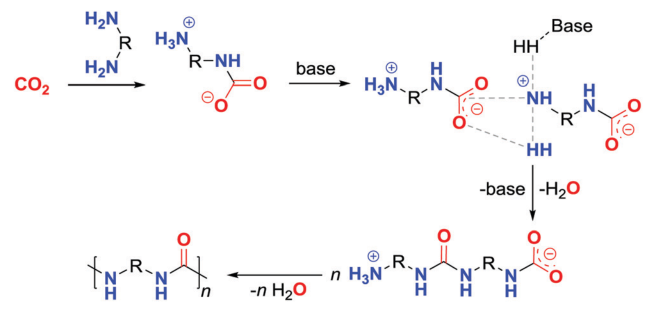
Scheme 56 Synthesis of PUAs by polycondensation between urea and primary diamines.

4.2 Direct synthesis of polyureas by use of CO_2 as a comonomer

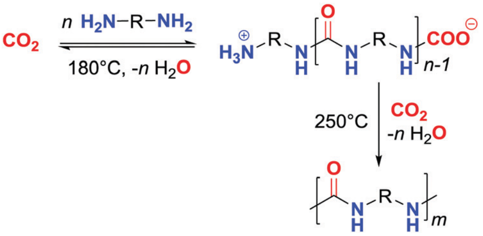
4.2.1 Polyureas by polycondensation between CO_2 and diamines. The direct polycondensation of CO_2 with primary 1,*x*-diamines into PUAs was pioneered by Higashi in the 1970s (Scheme 57).[587–589] Polymerisations generally occured at 40–80 °C and a pressure of 10–50 bar in an organic medium (pyridine, DMF, NMP or hexamethylphosphoramide).[587–592] The use of catalysts/reagents such as the carbamoyl-*N*-phosphonium salt of pyridine[593] or diethyl *N*-acetyl-*N*-methylphosphoramidite/imidazole[594] was required to yield PUAs under milder conditions (T = 40 °C and 20 bar). However, this approach faced several hurdles such as: (i) the use of stoichiometric amounts or an excess of catalyst/reagent, (ii) only aromatic diamines could be copolymerised with CO_2 using phosphorous-containing catalysts (triphenyl phosphate or ethylene chlorophosphite) or ionic liquids, and (iii) diamines of high basicity promoted the formation of unreactive ammonium carbamates, which limited the PUA yield.[588,594]

Most of these limitations were overcome by Deng and Zhao who opened up a way for the copolymerisation of CO_2 with primary diamines under catalyst-free conditions at high temperature (T = 180 °C),[595,596] or by using alkali bases (NaOH, KOH, K_3PO_4, K_2HPO_4, K_2CO_3, CsOH, Cs_2CO_3),[592,597,598] ionic liquids or salts (hexafluorophosphate, acetate, triazolate, halide salts of hexyltributylphosphonium or 1-ethyl-3-methylimidazolium)[599] or organic superbases (TBD, DBU).[592] Diamines reacted spontaneously with CO_2 to form a zwitterionic ammonium carbamate intermediate that underwent dehydrative condensation ensuring chain propagation. Addition of a base activated the ammonium carbamate cation that further facilitated the reaction (Scheme 57).

Recently, Zhao slightly improved this synthetic procedure by introducing a two-step approach.[592,596] It consisted of a metal or organocatalysed synthesis of oligoureas from CO_2 and diamines at 180 °C and 55 bar followed by an *in situ* high temperature dehydrative post-polymerisation (T = 250 °C) under continuous CO_2 flow of 1 bar (Scheme 58). As a general trend, Deng correlated the catalyst activity with their basicity and the efficiency of various alkali bases was in the order CsOH > Cs_2CO_3 > K_3PO_4 > K_2CO_3 > K_2HPO_4 > $KHCO_3$ > KH_2PO_4,[597] while for ionic liquids hexyltributylphosphonium salts proved to be more reactive than 1-ethyl-3-methylimidazolium based ones with the anion influence on the raectivity following the series [OAc] > [Triz] > [BF_4] > [PF_6] > [Cl].[598,599]



Scheme 57 Proposed mechanism for PUA synthesis by polycondensation between CO_2 and primary diamines.



Scheme 58 PUA synthesis by chain extension of CO_2-sourced oligoureas *via* a one-pot, two-step process.

The choice of the solvent also had a crucial impact to reach high PUA yields. Polar solvents with basic features such as NMP proved to be priviledged ones. The carbonyl group in NMP interacts *via* hydrogen bonding with the hydrogen atoms of the diamine, thereby assisting the nucleophilic attack of the amine and the dehydration processes.[597] The authors also noticed that, besides the basicity of the amine that impacted the formation of the carbamate salt, the PUA yields were dependent on the structure of the diamine (*i.e.*, spacer between the amine moietie, and the steric hindrance).[597,599] Low PUA yields (7–12%) were obtained in the copolymerisation of CO_2 with ethylenediamine (C_2 spacer) but increased up to 64% and 97% employing diamines having a C_4 or C_6 spacer, respectively. Substitution of the C_6 linear spacer by a cyclohexyl one slightly reduced the PUA yield (∼90%), while no polymer was formed in the presence of aromatic diamines or 4,4′-diaminodiphenyl methane.

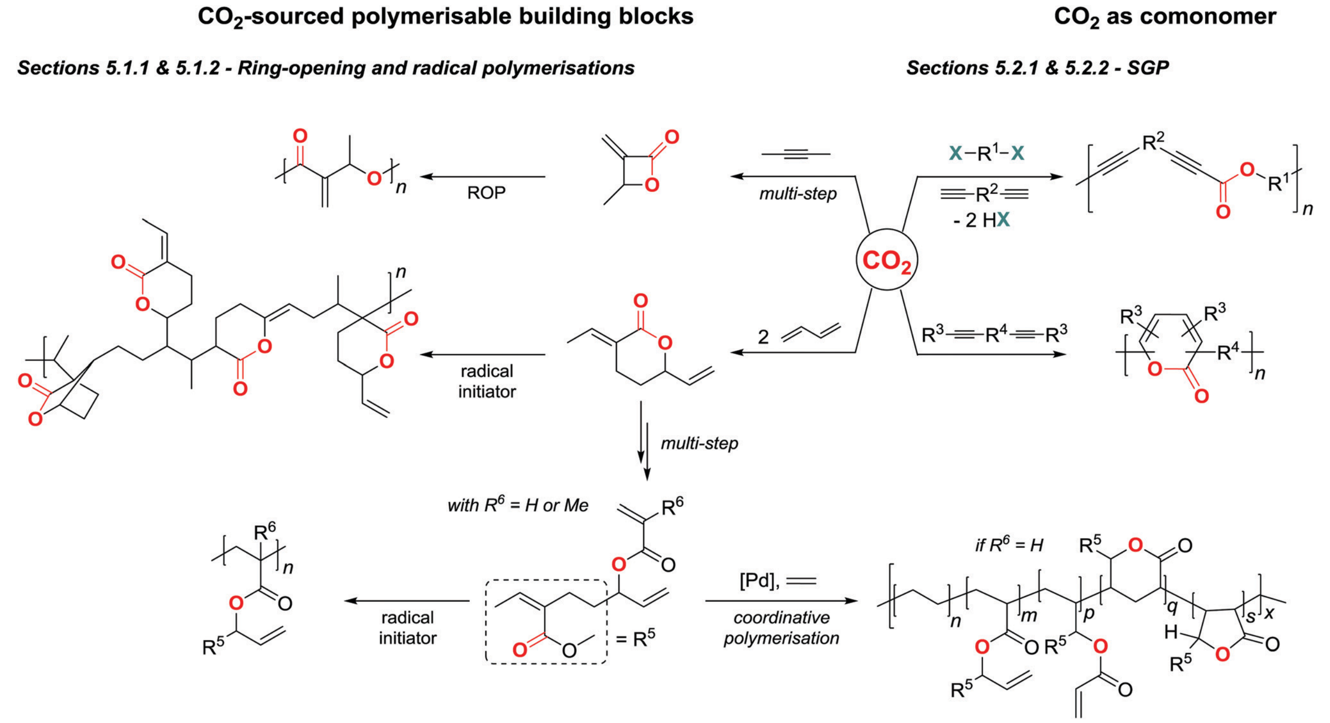
In all studies, strong intermolecular hydrogen bonding between the chains rendered the PUAs insoluble in common organic solvents, which prevented any determination of their molar mass by SEC/GPC analysis.[600] To the best of our knowledge, only water-soluble, amine-terminated oligoureas prepared from CO_2 and 4,7,10-trioxa-1,13-tridecanediamine at 180 °C and 110 bar and (macrocyclic) oligoureas were characterised by MALDI-TOF mass spectrometry providing an indication of the molecular weights being in the range 2200–3700 g mol^{-1}.[592,601,602]

5. Polyesters from CO_2

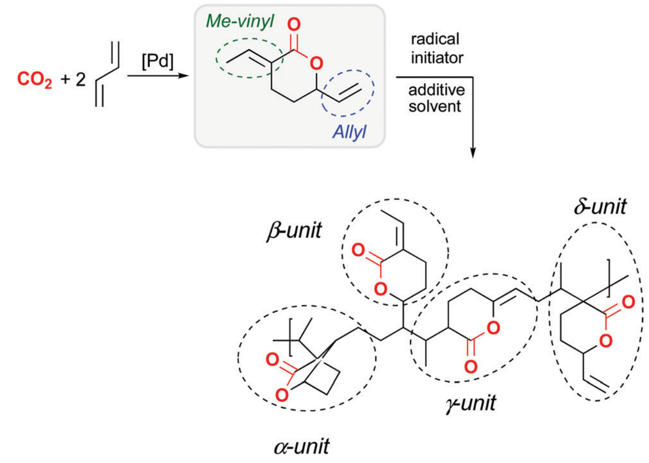
Poly(ester)s are polymers containing –C(=O)–O– linkages within the polymer backbone. They are widely used in packaging, fabrics and in surgery/therapeutic applications due to their excellent (bio)degradability and biocompatibility features.[603–606] Their industrial production is based on the ROP of lactones/lactides,[166] the dehydrative polycondensation of dicarboxylic acids with diols or the self-polycondensation of α-hydroxyacids.[607–610] The synthesis of this important class of polymers from CO_2 remained long elusive but new conceptual routes for their production are now emerging as illustrated in Scheme 59.

5.1 Polyesters from CO_2-sourced building blocks

5.1.1 Polyesters from CO_2 and olefins. The copolymerisation of CO_2 with ethylene or other olefins in an alternating fashion by metal-catalysed coordination–insertion is considered to be the most straightforward route towards CO_2-sourced polyesters. However, this approach faces thermodynamic and kinetic



Scheme 59 Synthetic pathways towards CO_2-sourced polyesters.



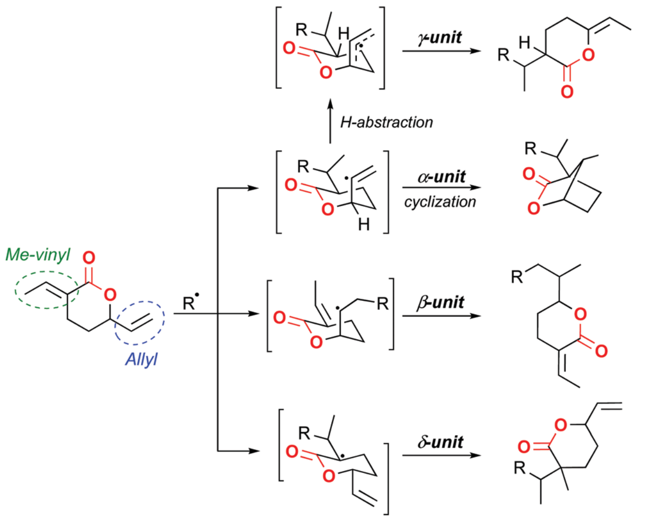
Scheme 60 Synthetic pathway towards CO_2-sourced polyesters.

hurdles that are difficult to surpass. Computational studies predicted that a perfect alternating ethylene/CO_2 polymerisation reaction is endothermic by 9.4 kcal mol^{-1} and suggested that an excess of ethylene monomer insertion (>63%) is required to ensure endergonic CO_2 incorporation.[611–613] Kinetically, the high activation energy for CO_2 insertion within the growing chain competes with the facile homopolymerisation of ethylene. To date, only Zhou has been able to produce high molar mass polyesters by random copolymerisation of CO_2 with ethylene with a CO_2 content of up to ~30% using late transition metal complexes of Fe(II or III) or Co(I, II or III).[614] However, Miller's attempts to reproduce these results using MAO activated pyridine or diimine complexes of Fe, Co, Ni or Cu failed.[611]

To circumvent the kinetic and thermodynamic barriers, Nozaki employed an innovative strategy to design polyesters with 29% of inserted CO_2 *via* anaerobic radical polymerisation of a metastable δ-lactone, *i.e.* 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (Scheme 60).[612] This vinyl-functionalised cyclic ester was prepared with up to 95% selectivity and in 67% yield by Pd(II)/phosphine promoted telomerisation of CO_2 and butadiene at 40–100 °C and CO_2 pressures up to 40 bar.[615–623]

The radical polymerisation of this monomer mediated by conventional azo-initiators (*e.g.* 2,2-azobis(isobutyronitrile), AIBN) allowed the formation of polyesters with M_ns in the range 2200–5700 g mol^{-1} at 100 °C.[612] Addition of acetic acid increased the M_n to 19 000 g mol^{-1}. The polymer structure was composed of bicyclic "α-units" (Scheme 60) produced by alternating chain propagation *via* the methyl-vinyl- and allyl-type olefinic moieties, and the cyclisation of the radical intermediate (Scheme 61). The use of a combination of Lewis acid additive ($ZnCl_2$) with EC as the solvent significantly improved the M_ns of the polymers to 85 000 g mol^{-1} but also affected the polymer morphology showing the presence of isomeric α, β and γ units. The monocyclic β and γ structures were produced by propagation through an allyl ester radical intermediate or *via* hydrogen abstraction from the allylic ester group by a radical formed from the methyl vinyl moiety, respectively (Scheme 61).

An elegant one-pot two-step domino process was then developed based on the formation of the δ-lactone followed by its polymerisation.[612] However constitutional isomers of the δ-lactone (*i.e.*, 5-membered lactone by-products) acted as polymerisation retardants. The versatility of the process was demonstrated by extending the strategy to the terpolymerisation of



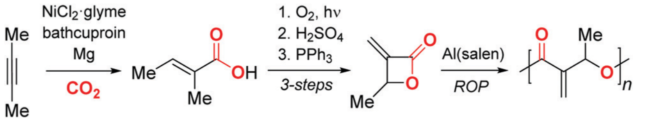
Scheme 61 Proposed reaction pathways for the formation of the isomeric units.

CO_2 with mixtures of butadiene and other 1,3-dienes such as isoprene or 1,3-pentadiene, giving rise to novel polyesters with CO_2 contents up to 20 and 24 wt%, respectively.[612]

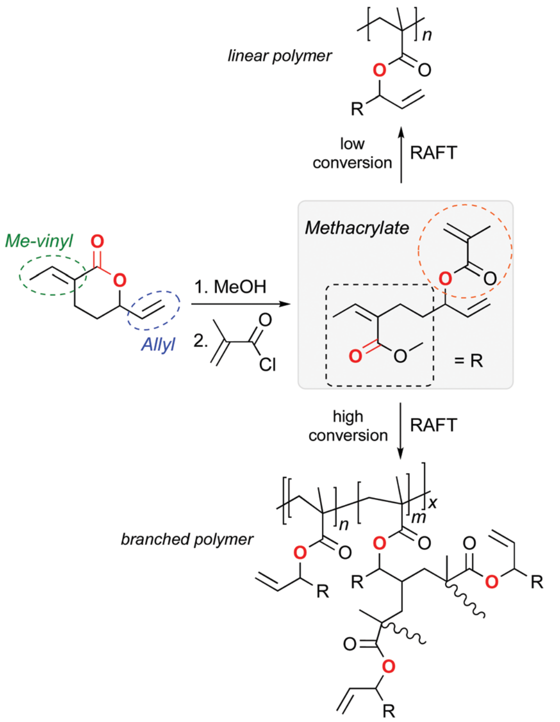
In 2017, Lin investigated the catalyst-free air initiated bulk polymerisation of this δ-lactone at 180 °C.[624] Surprisingly, polymers with M_ns of up to 239 000 g mol^{-1} and quantitative monomer conversions were obtained in 24 h. Through various control experiments, the authors suggested that the polymerisation of the lactone occurs *via* a radical mechanism, with O_2 acting as a radical initiator at low concentration. They postulated that the allylic C–H bond underwent facile H-atom abstraction creating an active radical species/initiator by the reaction with oxygen. Interestingly, a fourth isomeric unit (δ-unit) was identified within the polymer structure. The formation of this alternative constitutional isomeric unit was ascribed to the radical polymerisation of the monomer through the methyl vinyl moiety without subsequent intramolecular cyclisation.

These polyesters bearing double bounds were modified by "thiol–ene" click reactions to introduce hydroxyl, amine or carboxylic acid functionalities or to design gels,[616,625] offering thus new perspectives in the field of polymer science and materials.

Alkynes can also be exploited for the design of polyesters by using CO_2 as a co-reagent (Scheme 62). Indeed, Lu prepared a racemic mixture of a 4-membered lactone (α-methylene-β-butyrolactone) by a four-step strategy starting from 2-butyne and CO_2.[626] The controlled ROP of the lactone monomer using achiral Al(salen) complexes afforded syndiotactic semi-crystalline polyesters with predictable M_ns of up to 24 000 g mol^{-1} at 20–100 °C.



Scheme 62 Polyesters obtained by ROP of CO_2-sourced α-methylene-β-butyrolactone.



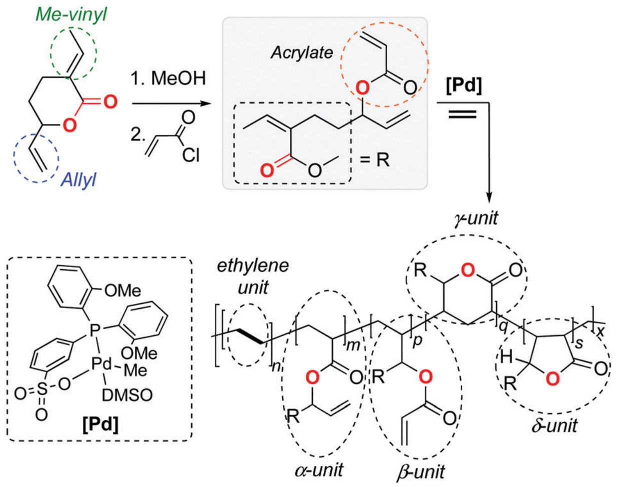
Scheme 63 Polyesters formed by radical polymerisation of CO_2-sourced methyl-2-ethylidene-5-hydroxy-hept-6-enoate methacrylate.

5.1.2 Vinyl-type polyesters. To enlarge the possibilities of the CO_2-sourced δ-lactone used by Nozaki in macromolecular engineering, Shen modified it into a novel ester-type trivinyl monomer, *i.e.* methyl-2-ethylidene-5-hydroxy-hept-6-enoate methacrylate (Scheme 63).[627]

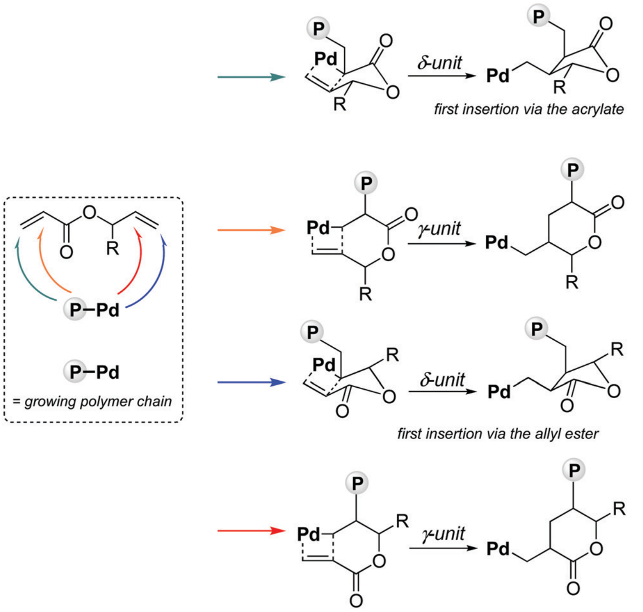
This compound was polymerised under anaerobic conditions at 70 °C *via* a so-called addition–fragmentation chain transfer radical (RAFT) polymerisation technique. As the methyl vinyl and allyl ester groups displayed no or weak reactivity towards the radicals, the polymerisation of the trivinyl monomer proceeded by chemoselective addition to the methacrylate moieties, at least at low (32%) to moderate conversion (69%), leading to a polymethacrylate bearing a pendant ester groups. At higher conversions, the growth of the polymer chains propagating *via* the methacrylate moiety competed with the insertion of monomer units *via* the allylic ester group. Chain branching was thus observed with a marked increase of the M_ns up to 108 000–150 000 g mol^{-1} for conversions in the range 70–92%. Esters within the branches were thus introduced.

Recently, Jiang developed novel functional polyethylenes incorporating noncyclic and cyclic ester units by coordination–insertion copolymerisation of ethylene with an acrylate analogue of the ester-type trivinyl monomer derived from the δ-lactone (Scheme 64).[628]

This copolymerisation of olefins with a polar monomer only occurs with late transition metal complexes.[629–635] By using the functional group tolerant dual catalyst based on the Drent-type phosphine-sulfonate Pd complex and NaBArF in weakly coordinating DMSO as a solvent, polymers with M_n values between 7400 and 27 500 g mol^{-1} and an ester content varying



Scheme 64 Ester-functional polyethylenes from CO_2-sourced ester-type trivinyl and ethylene monomers.

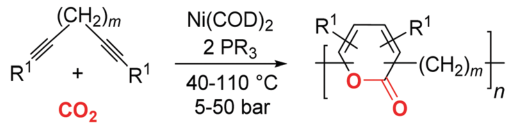


Scheme 65 Proposed reaction pathways for the formation of the isomeric units.

between 1.3 to 3.8% were prepared at 35–85 °C and 6 bar ethylene pressure. As the methyl vinyl moiety did not polymerise, the trivinyl monomer was incorporated within the growing chain *via* the allyl ester and acrylate groups. Four constitutional isomeric ester units were identified within the main skeleton. The α and β linear isomers resulted from the direct enchainment of the monomer *via* the acrylate or the allyl ester groups, while γ and δ cyclic units were formed by an additional intramolecular cyclization (Scheme 65).

5.2 Direct synthesis of polyesters by use of CO_2 as a comonomer

5.2.1 Poly(2-pyrone)s from CO_2 and diynes. In 1992, Tsuda introduced novel poly(2-pyrone)s by applying alternating copolymerisation of CO_2 with (a)cyclic diynes at 60–110 °C under a CO_2 pressure of 5 to 50 bar (Scheme 66).[636,637]

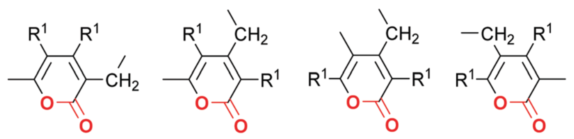


Scheme 66 Synthesis of poly(2-pyrone)s by alternating CO_2/diyne copolymerisation.

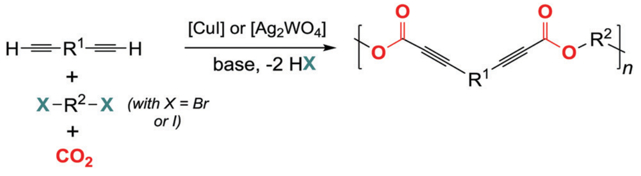
The Ni(0)/trialkylphosphine-catalysed polymerisation follows a coordination–insertion mechanism. It is based on the oxidative coupling of the Ni(0) precursor with the alkyne and CO_2 to form a five-membered nickelactone intermediate that then undergoes the insertion of a second alkyne. An intramolecular ring closure and the reductive elimination of the metal provides the pyrone unit.[638] Polymers with M_ns of 1700 g mol^{-1} to 17 900 g mol^{-1} were produced. The authors also showed a dependence of the poly(2-pyrone) molar mass on the CO_2 pressure that proved to be optimum at 20 bar. A too high CO_2 pressure (*i.e.*, $p_{CO_2} > 50$ bar) favored the deactivation of the catalyst through disproportionation of CO_2 into inactive $NiCO_3$ and carbon monoxide. The structural characterisation of the chains evidenced the presence of four regioisomeric units within the polymer backbone (Scheme 67), whose formation depended on the insertion mode and the steric hindrance/rigidity of the diyne monomer.

5.2.2 Poly(alkynoate)s *via* terpolymerisation of CO_2, diynes and dihalides. Inoue introduced a convenient synthesis of poly(alkynoate)s by a CuI/K_2CO_3 catalysed terpolymerisation of diynes with a 1,4-dihalobutane under a CO_2 atmosphere (Scheme 68).[639] In the presence of a 6-fold excess of base, the diynes and CuI afford a copper actylide species that undergoes carboxylation with CO_2. The copper carboxylate intermediate reacts with the dihalide to produce ester linkages and regenerates the catalyst (Scheme 69). All polymerisation reactions were performed in DMAc at 80 °C, affording polymers with M_ns of up to 8400 g mol^{-1}.

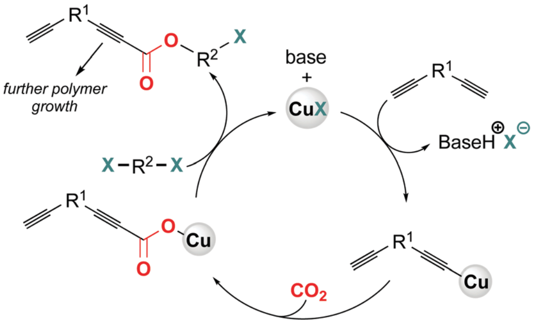
The polymerisation process was accelerated by addition of 1,10-phenanthroline, but the polyester yields decreased when



Scheme 67 Structure of the four regioisomers that are possibly formed during the synthesis of the poly(2-pyrone)s.



Scheme 68 Synthesis of poly(alkynoate)s by CO_2/diyne/dihalide terpolymerisation.



Scheme 69 Proposed manifold for the terpolymerisation of CO_2/diynes/dihalides.

using aliphatic diiodide or secondary aliphatic bromide, or when aromatic diynes were replaced by aliphatic ones. Further polymerisation improvement was achieved by substituting the dual CuI/K_2CO_3 catalyst for Ag_2WO_4/Cs_2CO_3.[640] Polymers with yields >95%, a CO_2 content of 15–24 wt% and M_ns of up to 31 400 g mol^{-1} were produced at 80 °C under atmospheric CO_2 pressure. The presence of ester linkages endowed the polymer with favorable degradability features while the alkyne moieties of the main backbone were suitable for post-polymerisation modification by amine-yne click reactions to produce nitrogen-containing regio- and stereo-regular materials.

6. Concluding remarks

The recycling of CO_2 and turning this waste into value has become a major goal in contemporary science. In particular, catalysis has presented itself as a key enabling technology providing new opportunities to turn this carbon feedstock into valuable engineering plastics while diversifying renewable resources for the sustainable production of consumer materials. Therefore, fostering novel routes to turn CO_2 into polymers will become a key driver to accelerate and facilitate the transition from existing fossil-based to future generations of more sustainable materials trying to meet the requirements of a circular economy for consumer plastics.

In this review, we have described the most relevant conceptual routes, strategies and synthetic pathways (including the mechanistic aspects where available) to prepare four important classes of polymers, *i.e.* polycarbonates, (non-isocyanate based) polyurethanes, polyureas and polyesters using CO_2 as a renewable feedstock. Two main modes of transformations are discussed: (i) direct copolymerisation of CO_2 with appropriate co-monomers such as oxiranes, aziridines, alcohols, amines, alkynes and others, and (ii) the synthesis of CO_2-based building blocks including (a)cyclic carbonates, carbamates, urea and lactones followed by their (co)polymerisation.

By applying the first direct strategy, the copolymerisation of CO_2 with various comonomers allows for the preparation of polymers with a high CO_2 content. The success of this approach depends highly on the catalyst design, and the current state of the art is testament of the development of a large diversity of highly efficient and selective metal-based catalysts. Organocatalysts are now also emerging in the field; however, they are still not competitive enough compared to the metal-based ones in terms of substrate activation potential and scope, but breakthroughs are expected in the near future. The ROCOP of CO_2 and epoxides is the most widespread method for preparing CO_2-based polymers. Mainly aliphatic polycarbonate polyols are now commercialized by some chemical companies for their incorporation into polyurethane (PU) formulations. These CO_2-based polymers, however, suffer from low glass transition temperatures and insufficient mechanical strength, limiting their exploitation in a broader range of applications/products.

Recent breakthroughs in catalyst engineering have permitted the precise synthesis of highly stereo-regular PCs with improved thermo-mechanical properties that are expected to drastically widen the application potential of CO_2-based PCs. Availability, low cost and high productivity and stability (*cf.*, high TOFs and TONs) are important prerequisites for these catalysts to become industrially relevant and attractive. The copolymerisation of CO_2 with epoxides and anhydrides or lactones is also largely explored to provide polyesters, as well as emerging methods for CO_2/oxetane copolymerisation that furnish aliphatic PCs. Besides these ROCOP techniques, many current efforts are dealing with the polycondensation of CO_2 with a broad range of co-monomers (such as diols or diamines) that are accessible at low cost, in large volumes, and that can be partially or fully bio-sourced. These processes are potentially relevant for the large-scale production of polymers; however, they are all associated with major challenges, *i.e.* slow reactions are typically noted and the release of equimolar amounts of small molecules (such as water, alcohols and acids) that have to be removed to drive the reaction to completion. Routes to solve these limitations are intensively investigated for pushing this attractive technology towards realistic utility.

In the second strategy, CO_2-based monomers, being either cyclic or not, are first prepared by metal- or organocatalysed reactions of CO_2 with suitable substrates such as oxiranes, alkenes, diols, alkynes and ammonia. These CO_2-based monomers are then applied in polymerisation reactions following mechanisms that depend on the nature and functionality of the respective monomer. Although the homo-polymerisation of monocyclic CO_2-sourced monomers (such as cyclic carbonates, urethanes and ureas) mainly follows catalysed ROP, some of the CO_2-sourced monomers are also able to copolymerise with diols to form PCs or PUs, or with diamines to yield PUs or PUAs by polycondensation reactions. These polymerisations most often require elevated temperatures and/or a catalyst, and the released small molecules (alcohols, ammonia) have to be removed during the process. Di- or poly(5-membered cyclic carbonate)s are amongst the most easily accessible CO_2-sourced monomers that have been largely exploited for the sustainable construction of non-isocyanate PUs through polyaddition to diamines. The high stability of these cyclic carbonates, however, require reaction conditions that concomitantly induce structural defects in the PUs, thereby limiting their molar mass. It thus remains difficult to design PU at rt starting from cyclic carbonate precursors, in contrast to the commercially applied isocyanate-based variants.

Due to the importance of PUs in daily-life materials, intensive research is still devoted to solve these aforementioned problems, by designing easily accessible more activated cyclic carbonates that do not require forcing conditions for their copolymerisation. Five-membered cyclic carbonates bearing exo-cyclic vinylic groups have recently emerged as promising candidates for the facile production of PUs and PCs under attractive, ambient conditions. Many examples also illustrate that polycondensation of non-cyclic CO_2-sourced compounds (linear carbonates, carbamates, ureas) with diols or diamines at elevated temperatures is a feasible polymerisation route to provide a large diversity of PCs, PUs or PUAs. Amongst the major breakthroughs in the past few years, a vinyl-functionalised δ-lactone, obtained by Pd-catalysed telomerisation of CO_2 with butadiene, can be copolymerised by various pathways to provide novel types of polyesters.

This review has shown that a multitude of important polymers are now accessible by exploiting CO_2 as a renewable C1 feedstock. Many different routes exist for producing a single family of polymers, and the choice for a specific polymerisation approach not only depends on the target molar mass and functionality, but also on the level of structural defects that can be tolerated in the final product. Most of the reported techniques are still in the early stage of development and require more sophisticated optimisation to furnish polymers at low cost and under conditions that are compatible with existing industrial production sites. Recent attention for legislative requirements that can help to transition to a circular economy and impose to the production of sustainable and renewable plastics present a strong incentive to push this research field forward.

It should be noted that the current level of technology does not allow for the exploitation of large volumes of CO_2 in polymer production while solving the problem of global warming and CO_2 accumulation/emissions. Indeed the content of carbon dioxide that can be converted into polymers will be too low compared to what is currently emitted annually, even if the entire plastic production would be based on using CO_2 as a monomer. However, changing our way of producing plastics by exploiting CO_2 (and potentially replacing other monomers that have a negative carbon footprint) will indisputably decrease our dependency on fossil resources that are for the time being the main resources for the production of chemicals. A transition from fossil to CO_2 carbon feedstock will only be a success if the new conversion routes are atom-efficient, are characterised by low energy consumption, are cost effective and industrially scalable. The role of catalysts is crucial for the success of the implementation of CO_2 as a monomer in polymer production. Finally, this overview of the state-of-the-art has demonstrated that CO_2 based technologies are also able to provide unprecedented access to polymers with new functionalities and structures, which prospectively will contribute to the exploration and development of new (niche) applications.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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