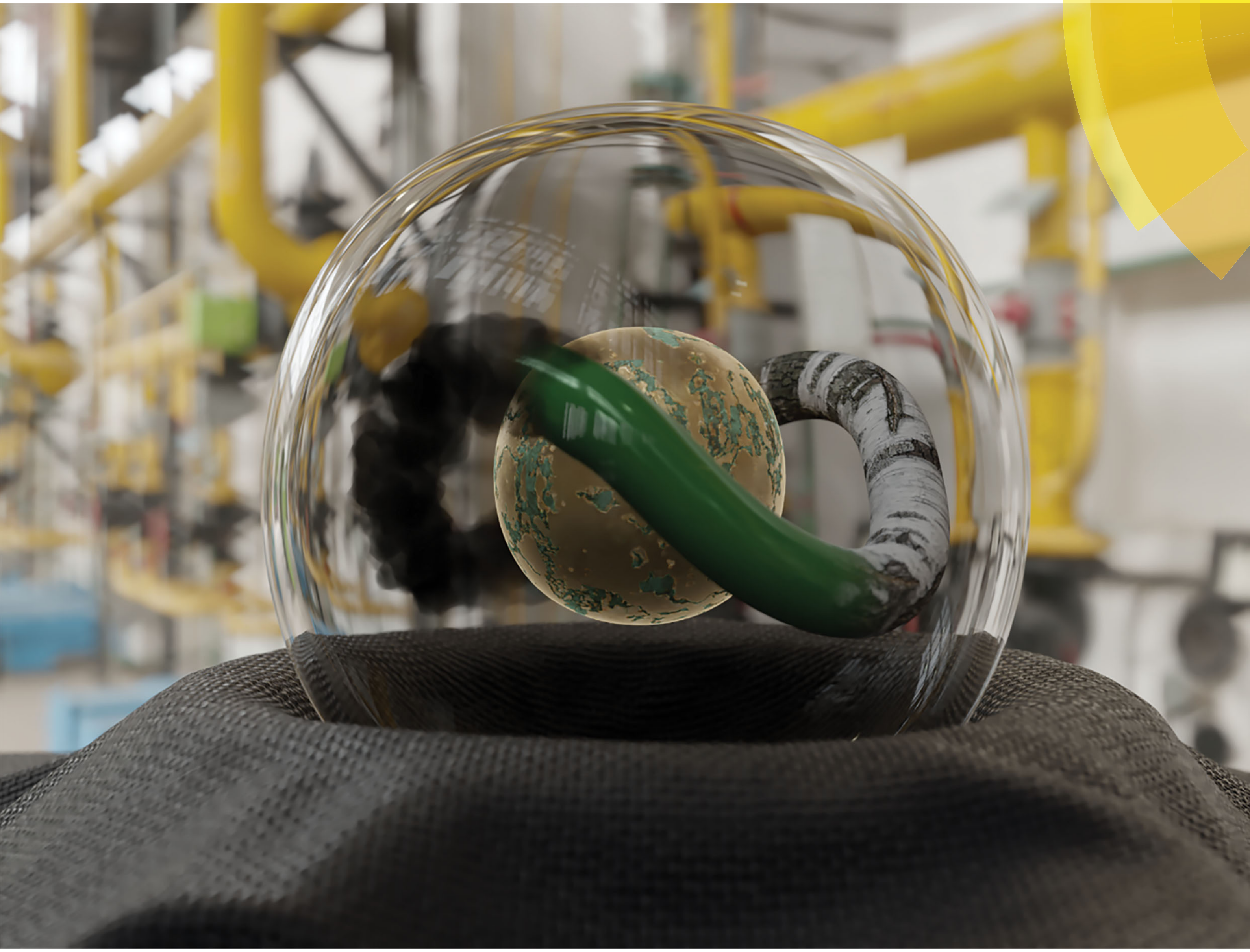
Volume 55 Number 10 4 February 2019 Pages 1347–1520

ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY | Celebrating IYPT 2019

FEATURE ARTICLE

Felix D. Bobbink *et al.*

En route to CO_2-containing renewable materials: catalytic synthesis of polycarbonates and non-isocyanate polyhydroxyurethanes derived from cyclic carbonates

ChemComm

FEATURE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2019, **55**, 1360

En route to CO_2-containing renewable materials: catalytic synthesis of polycarbonates and non-isocyanate polyhydroxyurethanes derived from cyclic carbonates

Felix D. Bobbink,* Antoine P. van Muyden and Paul J. Dyson

Combining CO_2-chemistry with biomass conversion allows renewable polymeric materials including polycarbonates and polyhydroxyurethanes (PHUs) to be generated. The demand for robust materials with modular properties that can be prepared on an industrial scale is important and, to date, the most important polymeric materials are derived from petrochemicals. These materials inevitably result in CO_2 emissions, and therefore making robust materials from renewable sources will contribute to a more sustainable society. An attractive way to address this challenge is to combine biomass transformations with CO_2-fixation and material science. An identified target that combines all three aspects involves the preparation of PHUs (or non-isocyanate polyurethanes, NIPUs) *via* the polymerization of fully renewable cyclic carbonates derived from biomass and CO_2 with a diamine compound that can also been derived from biomass sources. In this review, we critically analyze the progress in catalyst development for the efficient transformation of epoxides and CO_2 to cyclic carbonates and polycarbonates. We also discuss the synthesis of PHUs from cyclic carbonates and diamines (not restricted to fully renewable compounds), including challenges in regiocontrol and biodegradability, as well as the role catalysts play in the synthesis of these polymers.

Received 3rd October 2018,
Accepted 28th November 2018

DOI: 10.1039/c8cc07907b

rsc.li/chemcomm

Introduction

Today, most of society's chemicals, including chemical building blocks, fine chemicals, fuels and materials are derived from the petrochemical industry.[1] The intensive utilization of fossil resources has strongly impacted on the modernization of our society and our quality of life. However, the exploitation of these resources has also led to an imbalance in the carbon cycle and other environmental problems.[2,3] CO_2 is naturally involved in the carbon cycle, which balances the CO_2 in natural processes.[4] The concentration of CO_2 in the atmosphere before the industrial revolution was around 280 ppm and reached 410 ppm in July 2018. Human emissions of CO_2 have stabilized

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. E-mail: felix.bobbink@epfl.ch

Felix D. Bobbink

Felix Bobbink obtained his PhD from the École Polytechnique Fédérale de Lausanne (EPFL) in 2018, and is currently a post doc in Prof. Paul Dyson's laboratory at the EPFL. During his PhD, he developed ionic polymers and evaluated them as catalysts for CO_2-related transformations. His current work involves the preparation of polymers from cyclic carbonates and amines.

Antoine P. van Muyden

Antoine van Muyden obtained his MSc from the École Polytechnique Fédérale de Lausanne (EPFL) in 2016 and is currently a PhD student under the supervision of Prof. Paul Dyson at the EPFL. His work involves the preparation of heterogeneous bimetallic catalysts and their applications for biomass and CO_2 tranformations.

over the last few years at *ca.* 34 GTons. CO_2 acts as a greenhouse gas, which results in the warming of the earth, with potential catastrophic consequences.[5] Consequently, governments have recommended that the rate of emissions should be limited in order to contain global warming to 2 °C (decided in November 2015 at COP21 in Paris).[6] To achieve this goal, emissions should be limited in all possible areas of activity including electricity generation, heating, transport, construction and chemical production. This prerequisite rationalizes the efforts that are made in clean energy storage and production,[7] direct CO_2 reduction to fuels,[8] *etc.* Moreover, post-combustion technologies that aim at sequestering CO_2 at the source of emission have emerged.[9–11] These technologies are being implemented at the exhaust of power stations and rely, for example, on amine compounds that effectively form carbamate salts upon exposure to CO_2. Simultaneously, other technologies are emerging that aim to capture CO_2 directly from air, for example by relying on the affinity of atmospheric CO_2 with bases such as metal hydroxides or amines.[12,13] The aforementioned technologies are meant to capture CO_2 and then release it in pure form so that it can be stored underground or under the oceans.[14]

It would be advantageous to benefit from the CO_2 that is emitted to generate value-added products, as is the case for the synthesis of urea, which is prepared from CO_2 on an industrial scale.[15,16] A remarkable example of CO_2 valorization as a chemical reagent (or C1 source) involves the cycloaddition of CO_2 into epoxides (CCE reaction) to afford cyclic organic carbonates (COCs). This reaction was discovered in the early 1950s, has been industrialized,[17,18] and requires a catalyst (see below).[19] The production of the smallest COCs, propylene carbonate (PC) and ethylene carbonate (EC), is particularly important because of their diverse applications and low toxicity.[17,18,20] They find applications in cosmetics, as solvents,[21] and in batteries,[22] and, importantly, they are biodegradable.[23] The reaction between epoxides and CO_2 is not restricted to the formation of the smallest COCs, and various terminal epoxides have been employed.[24,25] Some of these epoxides can be derived from renewable sources such as cellulose, lignin, or vegetable oils and can subsequently be processed to polycarbonates (pCs), polyurethanes (PUs) and polyhydroxyurethanes (PHUs). In PUs the monomers are linked one to another *via* a urethane functional group. Typically, these are formed by reacting an isocyanate with a diol (or alternatively a diamine or an aminol) and have a rich history since their development in the 1930s.[26] The market for these compounds is enormous,[27,28] and currently all the precursors are derived from petrochemical sources. Moreover, the isocyanate group is moisture sensitive,[29] and isocyanates are notoriously toxic with, for example, the release of methyl isocyanate being responsible for the Bhopal catastrophe in India.[30] Therefore, finding alternatives to existing routes is ongoing, and routes involving bio-based or partially bio-based PUs/PHUs are under investigations.[31–35] Efforts to discover novel materials that are derived from biomass sources and that display properties comparable to those of existing materials is important *en route* towards a more sustainable chemical industry and society.

Paul J. Dyson

Paul Dyson joined the Swiss Federal Institute of Technology in Lausanne (Ecole Polytechnique Fédérale de Lausanne, EPFL) in 2002. He grew up in the UK, completing his doctoral thesis at the University of Edinburgh. Prior to his appointment at the EPFL he held appointments at Imperial College of Science, Technology and Medicine and the University of York as a Royal Society University Research Fellow.

In this review, we will present the state of catalyst research for the preparation of cyclic organic carbonates (COCs) and their corresponding polycarbonates. In addition, the synthesis of PHUs from COCs and diamines will be described and compared to the well-established PU synthesis. Throughout this review, the focus is directed to the available catalytic tools, the renewable aspects of the reaction and the biodegradability of the materials.

Role of catalysis in CO_2-containing COCs and pCs

COC synthesis

Prior to discussing the synthesis of COCs from bio-based epoxides some general remarks on the catalyzed CO_2-epoxide coupling (CCE) reaction are provided. The CCE reaction proceeds according to Fig. 1 and represents a successful application of CO_2 chemistry.[36] As mentioned above, the reaction has been intensively investigated, and numerous efficient catalysts have been developed and described.[37–40] For example, ionic liquids (ILs) have been identified as potent catalysts for this reaction that operate under mild, solvent-free conditions. Typical examples involve simple ammonium salts such as *N*-tetrabutylammonium bromide/iodide (Fig. 1, catalyst **1**) or 1-butyl-3-methylimidazolium chloride (Fig. 1, catalyst **3**). Similarly, alkali metal salts combined with a polar aprotic solvent have also been used (Fig. 1, catalyst **5**).[19,41–43]

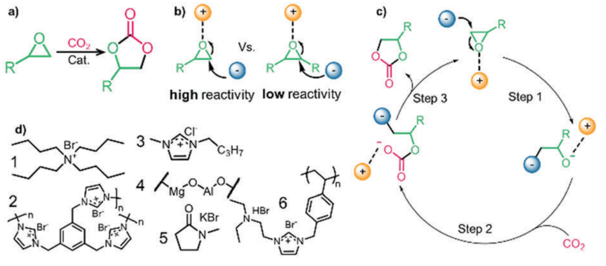


Fig. 1 (a) General CCE reaction. (b) Key mechanistic step for IL catalyzed CCE reaction. (c) Mechanism for IL-catalyzed reaction. (d) Selected catalysts.

For processing purposes, heterogeneous versions of the catalysts have been developed, such as imidazolium-based polymers used in place of ILs (see Fig. 1, catalysts **2** and **6**).[44–47] It should be noted that while the reaction is considered "green", little emphasis has been put on the sustainability of the catalyst itself. In this context, it has been shown that ILs are not necessarily biodegradable and that their synthesis poses problems.[48–50] ILs often require dichloromethane, tetrahydrofuran (THF) or diethyl ether during synthesis, all of which are towards the bottom of the solvent sustainability scale.[51] Note, ILs based on naturally occurring cations can potentially be obtained from renewable sources.[52] In contrast to organocatalysts, metal composites are not derived from petrochemical resources even if their extraction can produce a significant amount of waste. These catalysts are based on available materials and can, to some extent, be considered green (Fig. 1, catalyst **4**).[52,53] Advances in the catalysts and the mechanism of the reaction have been reviewed several times in recent years.[54–56] The CCE reaction is often considered a reaction that requires harsh conditions to proceed, but recent studies have shown that simple and cheap catalysts convert epoxides into cyclic carbonates under atmospheric pressure of CO_2 at temperatures well below 100 °C.[57] Notably, a study from 1993 demonstrated that the reaction takes place at atmospheric pressure.[58] The mechanism of the transformation proposed for IL and organic salt catalysts proceeds *via* ring opening of the epoxide (Fig. 1, step 1) by the anion of the salt, followed by insertion of CO_2 into the alkoxide (Fig. 1, step 2). Finally, the product is formed *via* a ring-closing step (Fig. 1, step 3).[59] The mechanism and the rate determining step can vary according to the nature of the catalyst.[60]

The reactivity of epoxides with CO_2 is dependent upon the structure of the epoxide with the typical reactivity of different epoxides depicted in Fig. 2. Epichlorohydrin (ECH) is among the most reactive epoxides for the CCE reaction (converted to (chloromethyl)ethylene carbonate, which will be referred to as epichlorohydrin carbonate, EpC) and can be converted at 50 °C under 1 atm of CO_2 using a simple homogeneous IL catalyst.[57] It should be noted that ECH can be prepared from glycerol, a renewable chemical obtained during biodiesel production (*via* the Epicerol® process).[61] Despite the renewable aspect of ECH, it is very toxic and must be handled with care, and this may hinder industrial development.[62]

Complete solubility/miscibility of the salt catalyst in the reaction solution is crucial for high activity, a feature that is frequently overlooked in organic-salt catalyzed reactions (ILs are not necessarily soluble in the epoxide under solvent-free conditions, and can therefore be considered as heterogeneous catalysts rather than homogeneous). Furthermore, propylene oxide (PO) and ethylene oxide (EO) are somewhat inconvenient to use on a laboratory scale due to their low boiling points, thus necessitating the use of pressure reactors and, consequently, they are not exclusively used as model substrates, despite their high industrial importance. The utilization of internal epoxides such as cyclohexene oxide (CyO) or limonene oxide (LO) requires harsher reaction conditions because of the lower reactivity of the tertiary carbon compared to secondary carbons in terminal epoxides (steric hindrance). Notably, both internal and terminal epoxides can be derived from renewable sources.[63]

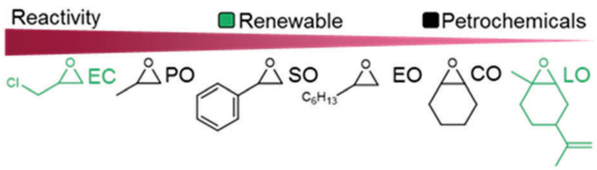


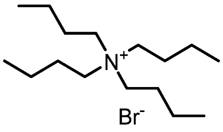
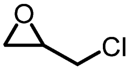
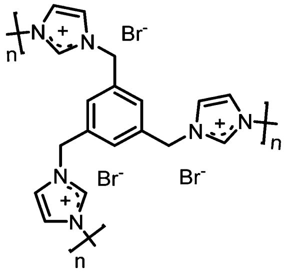
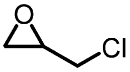
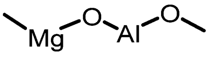
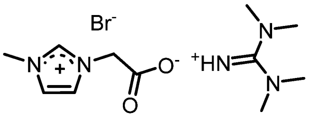
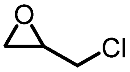
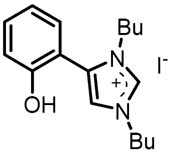
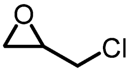
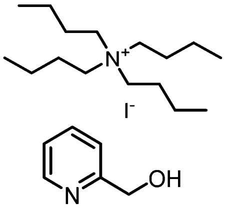
Fig. 2 Epoxides derived from non-renewable and renewable sources and their relative reactivity for COC synthesis.

Table 1 compiles reaction conditions for selected CO_2-epoxide cycloadditions, including examples of homogeneous and heterogeneous salt catalyzed reactions (Table 1, entries 1, 2, 4 and 5), as well as a Mg-Al-oxide catalyst (Table 1, entry 3). The table compiles one simple organic salt (Table 1, entry 1), one heterogeneous salt (entry 2), and three examples of H-bond donor salts (entries 4–6). The example of inorganic catalyst (entry 3) is included as a reminder that many classes of catalysts have been developed over the past decades. Direct comparison between catalysts is hampered by the absence of benchmark experimental reaction conditions. Typical reaction conditions for propylene oxide conversion require pressures of 5–10 atm at temperatures ranging from room temperature to 100 °C (Table 1, entry 3). When other epoxides are employed, the reaction can conveniently be conducted at atmospheric pressure at temperatures ranging from 25 °C to 100 °C (Table 1, entries 1, 2, 4 and 5). The difficulty to compare different catalysts has been identified previously and benchmark conditions have been proposed,[57,64] as it is difficult to assess the extent of progress that has been made between the catalysts reported between 1999 (Table 1, entry 3) and 2018 (Table 1, entries 4 and 5). Nonetheless, it appears that the most promising systems in terms of catalytic efficiency are composed of an onium salt combined with an external H-bond donor, allowing the reaction to proceed at room temperature under atmospheric pressure (Table 1, entry 6).[57,64,65] It should be noted that the catalysts for COC synthesis presented above are most often not oxygen sensitive and the reaction does not require anhydrous conditions and water can even accelerate the reaction rates of certain IL catalysts.[66] Epoxides possess a stereogenic center and hence stereoselective reactions are possible using chiral catalysts that afford optically pure COCs,[67–69] although optically pure COCs may also be obtained from the catalytic chiral resolution of racemic epoxides.[70]

pC synthesis

Catalysts have also been developed that convert epoxides and CO_2 directly into pCs. The mechanistic pathway of the reaction differs and, for the direct polymerization, a metal catalyst is usually required (see Fig. 3 for representative examples).[74] The main epoxides that are converted into pCs are PO, CyO and LO and lately efforts have been devoted to the development of tailored epoxides for the reaction.[75] Co-polymerization of PO with CO_2 leads to polypropylene carbonate (pPC), a polymer that finds applications in ceramics (as a binder), in adhesives and as a propellant.[76,77] Polymerization of CyO with CO_2 leads

Table 1 Selected reaction conditions and yields for COC synthesis catalyzed by organic salts and Mg-Al oxide

Entry	Catalyst	Epoxide	Reaction parameters	Yield [%]	Ref. year
1	 homogeneous		1 atm, 60 °C, 22 h, 2 mol%, 30 g epoxide	78	42, 2002
2	 heterogeneous		1 atm, 100 °C, 24 h, 5 mol%, 76 mg epoxide	99	44, 2017
3	 heterogeneous		5 atm, 100 °C, 24 h, 0.5 g cat, 0.232 g epoxide	88	53, 1999
4	 homogeneous		1 atm, 30 °C, 12 h, 25 mol%, 0.185 g epoxide	84	71, 2018
5	 homogeneous		10 atm, 80 °C, 1 h, 0.75 mol% cat., 148 mg epoxide	99	72, 2018
6	 homogeneous		1 atm, 25 °C, 20 h, 8 mol% cat., 348 mg epoxide	86	73, 2016

to polycyclohexene carbonate (pCyC). The pC prepared from LO and CO_2 is a viable bio-based polymer candidate for industrial applications since the resulting polymer displays excellent properties including high thermal resistance, hardness and transparency as well as having a low polydispersity index (PDI < 1.2) and high molecular weight (108.6 kDa).[78] Moreover, in contrast to many other polymers (polyethylene for example), pCs are often biodegradable, a major advantage as plastic waste is heavily polluting the environment.[79–82]

As discussed above, the CCE reaction to prepare COCs is most efficient with terminal epoxides, and mechanistic studies show that internal epoxides (CyO for example) result in a more controlled polymerization reaction than terminal epoxides and decreases the selectivity towards COCs.[74] Furthermore, the use of CyO (or LO) facilitates co-polymerization while avoiding the formation of unwanted polyethers (pEs) derived from the epoxide.[83–85] While pEs are unwanted in the context of pC synthesis, these polymers are also valuable in their own right and are obtained from the polymerization of epoxides in the absence of CO_2. For instance, polypropylene oxide (pPO) is used as a component in PU synthesis.[86] Efforts to produce isospecific polymers by catalytic routes are ongoing.[87] Interestingly, the catalysts employed in the synthesis of pC and pE tend to be structurally related. For example, mono- and bimetallic cobalt salen complexes have been employed as effective catalysts to transform PO into pPO.[88,89] Bimetallic Cr-based catalysts afford isospecific polyethers containing alcohol end-groups,[90] and the resulting polymers are semi-crystalline and display average molecular weights (M_n) in the range 2–15 kDa. Active catalysts for the co-polymerization of CO_2 and epoxides are typically metal-based and may contain ionic sites directly attached to the ligands.[91,92] Alternatively, when no ionic part is present in the metal-catalyst, a co-catalyst

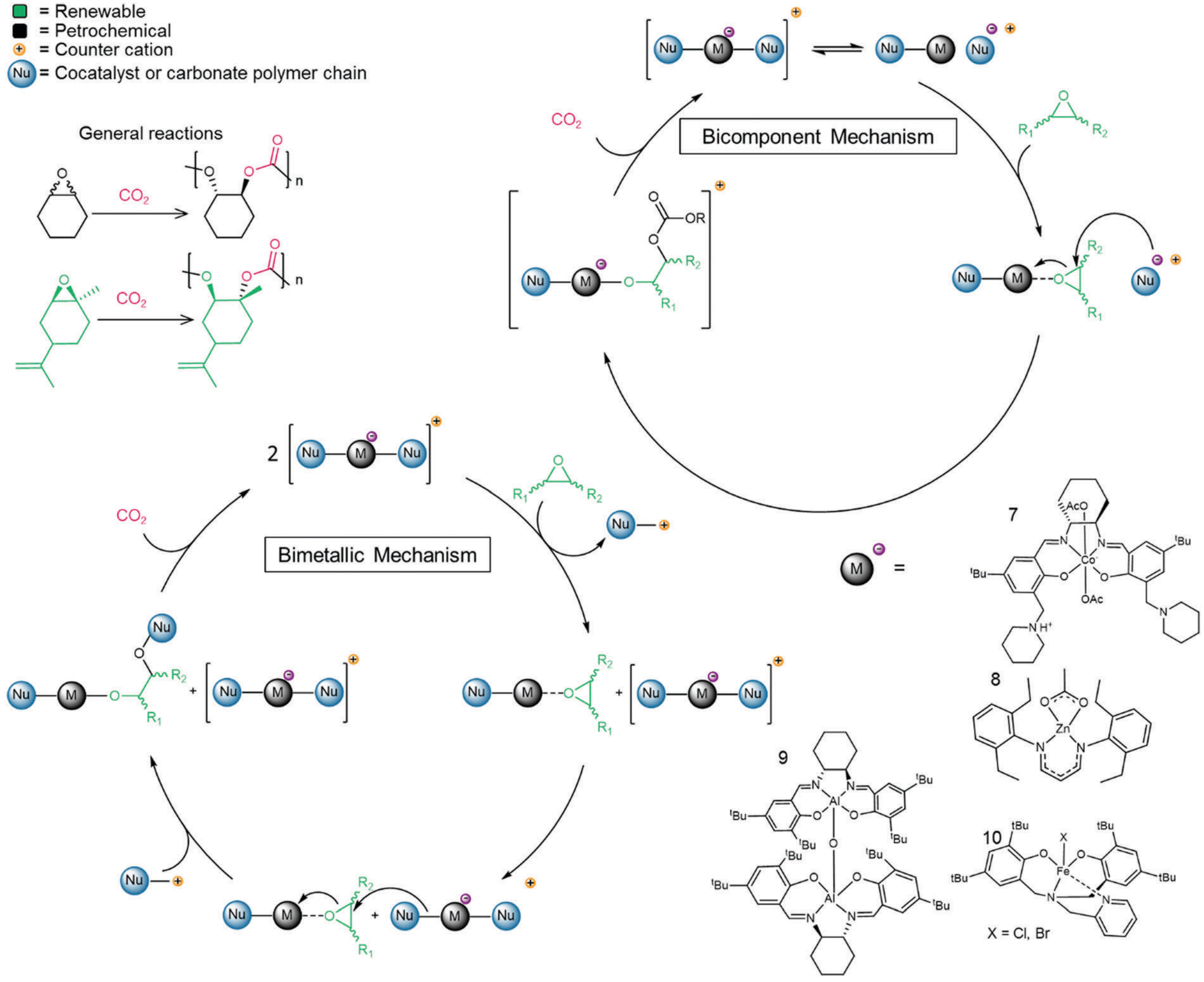
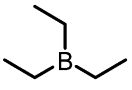
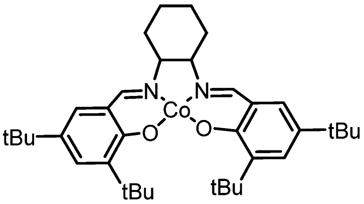
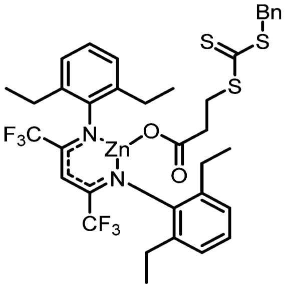
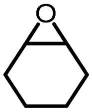
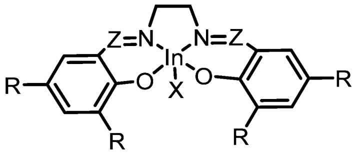
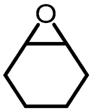


Fig. 3 Co-polymerization of epoxides and CO_2 to afford pCs, representative catalysts and the generally accepted bicomponent and bimetallic catalytic cycles.[64,74,78,97,98]

is required to promote the reaction, typically TBAB or PPNCl or other salts that are commonly used in COC synthesis (see examples in Table 2). Several metal complexes have been successfully applied for this reaction including Co,[74,93] Zn,[94] Al[64] and Cr,[95,96] and examples of Fe[97] and In[98] complexes have also been reported (see Fig. 3, structures **7–10** as examples).[99] The reaction proceeds *via* either a bicomponent or bimetallic pathway, and this typically depends on the catalyst and reaction parameters.[100,101] In this context, evidence for a monometallic pathway has been provided for an In catalyst (see Fig. 3 for general catalytic cycle).[98] Recently, an example of a metal-free, salt catalyst has been reported for the polymerization reaction, which is of interest towards the development of a sustainable, metal-free process.[102]

The increasing importance of CO_2-epoxide derived pCs has also led to their application in other types of polymerization reactions. For example, living reversible addition–fragmentation chain transfer (RAFT) has been applied to the reaction, which leads to polymers with very narrow PDIs (<1.11). RAFT polymerization has been achieved using a β-diiminate Zn catalyst (see Fig. 4, the structure is structurally related to that of catalyst **8** in Fig. 3).[94] Living polymerization methods also allow more complex block co-polymers to be prepared. In this respect, CO_2-epoxide ring-opening copolymerization (ROCOP) has been combined with RAFT polymerization of vinyl monomers.[103] Achieving controlled polymerization and block co-polymerization could, in turn, lead to polymers with superior properties, since pure pCs based on PC or limonene carbonate suffer from low rigidity and brittleness, respectively.[79] Furan-containing monomers have been prepared and converted into their corresponding pC. This is particularly relevant in terms of sustainability because the furan ring is present in 5-hydroxymethylfurfural (5-HMF), a platform chemical obtained from cellulose (see Fig. 9, right).[104] A useful feature of furan rings is that they react *via* well-established Diels–Alder (DA) chemistry (see Fig. 4 for an example), which enables post-polymerization functionalization.[104–106] In the example given in Fig. 4 (top), the polymer is reacted with 10 equivalents of maleimide for 48 h at 60 °C (maleimides may be obtained from renewable resources). A retro-DA reaction proceeds at 100 °C and restores the furan-containing polymer. Interestingly, if the polymer contains both an olefin and a furan ring, reversible cross-linking of the polymer can be achieved using the DA reaction.[107]

Table 2 Selected reaction conditions and yields for CO_2-epoxide copolymerization

Entry	Catalyst	Epoxide	Reaction parameters	Remarks	Ref, year
1	 [PPN]Cl		10 atm, 60 °C, 10 h, THF solvent	Yield = 35%, M_n = 37 kDa, PDI = 1.1	102, 2016
2	 [PPN]X X = dinitrophenolate		15 atm, 22 °C, 2 h	TON = 802 ± 26, M_n = 27 kDa, oxidant = $FcPF_6$	113, 2016
3			30 atm, 50 °C, 3 h, 1 mL toluene	M_n = 28.6 kDa polymer, PDI = 1.11, T_g = 112 °C, block-polymer achieved with addition of *N*-isopropylacrylamide	94, 2018
4	 R = cumyl, Z = PPh_2, X = O^tBu		1 atm, 80 °C, 23 h, 0.1 mol%	>99% carbonate linkage, TON = 350, M_n = 3400 Da	98, 2018

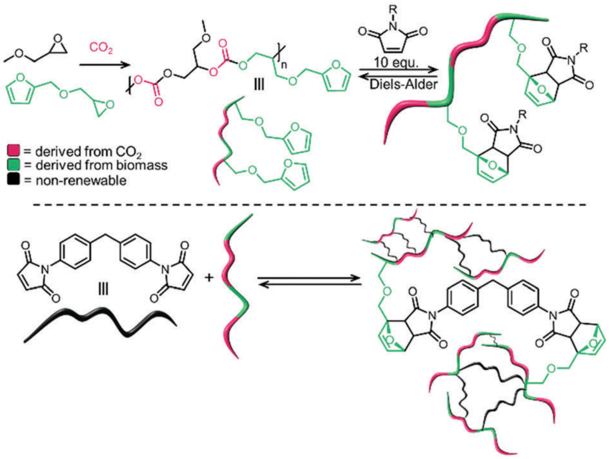


Fig. 4 Schematic representation of post-polymerization functionalization of furan-containing pC using the DA reaction.

Another reversible cross-linking strategy is to react the furan containing polymer with a bis-maleimide (Fig. 4, bottom).[106,108] In the example shown, however, only 50% of the native polymer could be recovered following the retro-DA reaction. Moreover, the reaction requires a large excess of the dienophile when no catalyst is employed (10 eq. for the example in Fig. 4, top).[109]

Table 2 compiles the reaction conditions required by selected catalysts to copolymerize CO_2 and epoxides. As for COC synthesis discussed above, no straightforward analysis is possible due to the vastly different reaction conditions employed. However, salen ligands are privileged ligands for the copolymerization reaction (Table 2, entries 2 and 4, as well as catalysts **7** and **9**, Fig. 3). In most cases, an ionic/basic co-catalyst is required, and in some cases is covalently linked to the ligand (for example in catalyst **7**, Fig. 3). Typically, the co-polymerization reaction is conducted at low temperatures and pressures (<100 °C, <30 atm, Table 2, entries 1–4). The resulting polymers often display a high M_n (for example 27 kDa, Table 2, entry 2) and narrow PDIs (<1.2). Notably, the Zn catalyst depicted in Table 2, entry 3, affords high M_n (28.6 kDa) homodispersed polymers (PDI = 1.11) at 50 °C and a moderate CO_2 pressure (30 atm). The examples discussed above were presented without taking into account that the polymerization leads to two different stereoisomeric products as the epoxide starting material possesses a chiral center. Advantageously, catalysts have been developed that lead to a single, highly crystalline isotactic product. Producing isotactic polymers confers different properties to a material compared to a material displaying low or no tacticity, and highlights the crucial role of the catalysis in the polymerization reaction.[110,111] Obtaining fully regio- and

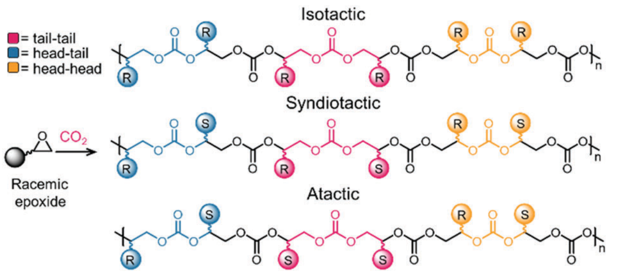


Fig. 5 Example of stereoselective control during pC synthesis. Top: All-*R* stereocenter. Middle: Alternating *R*–*S* stereocenters. Bottom: Random *R*–*S* distribution.[111]

stereo-controlled polymers usually also leads to higher glass transition temperatures.[92] A generic example of isotactic polycarbonate is shown in Fig. 5. Control over the stereoselectivity requires an appropriate catalyst, although the substituents on the epoxide can play a role as well. For instance, using a Co(III) catalyst, it has been shown that an electron withdrawing group on the epoxide can lead to highly isotactic polymers, allowing semi-crystalline and crystalline polymers to be obtained.[112]

PHU synthesis from COCs and diamines

Definition of PUs and conventional synthesis methods

As mentioned in the Introduction, the definition of PUs is not restricted to polymers containing only urethane linkages. Rather, many classes of polymers are referred to as PUs because they contain urethane groups. Block polymers containing polyethers, polyesters or silicone polymers, in addition to PU segments, may be classified as PUs.[114] Consequently, PUs have a large number of applications. PUs typically contain both rigid and flexible parts, and it is this combination that confers their thermoplastic properties (see Fig. 6).[115,116] The chemistry of PUs has been intensively studied and numerous reviews and books describe the properties and applications of PUs.[26,115,117–119] Similarly to PUs, PHU elastomers comprising rigid and flexible segments can be conveniently obtained from the COC-diamine route described below.[120]

The most common route to prepare PUs is *via* the reaction of isocyanates with diols (Fig. 7).[121] The isocyanate functional group is water sensitive and the reaction between isocyanate and water leads to the release of CO_2. For processing of PUs into foam-like structures, water is added intentionally to the process,[122] but this method requires using an excess of isocyanate and may be less economically viable than other methods.[123] The addition of water leads to a decrease in the density of the polymer, which is an important parameter for foams. PUs are routinely prepared on an industrial scale, and the materials find applications as sponges, in foams for car seats, in mattresses, and even in medicine.[79,123] Fig. 7 shows selected monomers (isocyanates, diols and diamines) and catalysts that are routinely employed in the synthesis of PUs.[26] In general, N-containing bases are used as catalysts (*e.g.* DABCO, BDMAEE, *etc.*, see Fig. 7).[124] Notably, the reaction produces a single product and, unlike pC synthesis, a chiral catalyst is not needed for the reaction.

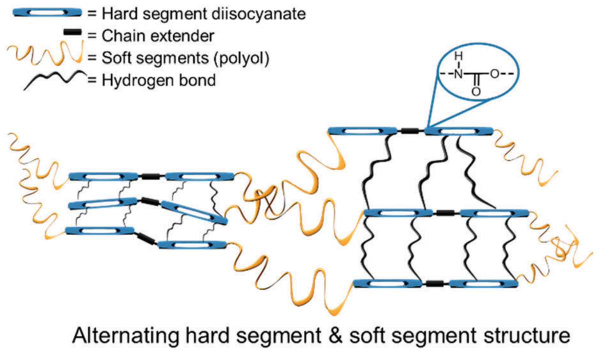


Fig. 6 Schematic structure of a typical PU.[119]

PHU synthesis from COCs and diamines and their applications

In contrast to PUs, PHUs (also referred to as "non-isocyanate polyurethanes", NIPUs) prepared from COCs and diamines have been less well investigated, but several excellent contributions demonstrate their high potential.[125–129] Similar to PUs, PHUs derived from COCs and diamines have been prepared by combining different COCs and amine precursors, some examples of which are illustrated in Fig. 7.[130] Examples of COCs employed include bisphenol A diglycydyl ether carbonate (BPAC) and diglycerol dicarbonate (DGC); the former is not derived from biomass sources but has been used routinely in pC packaging for decades. Unfortunately, BPA is harmful (it is being banned in food packaging), and alternatives are being investigated,[131,132] for example DGC, a presumably less toxic molecule that can be derived from (renewable) glycerol.[133]

Any diol can be reacted with ECH to generate bis(epoxides) that can be converted to the corresponding COCs.[134] The diols can be derived from biomass sources (for example cellulose or

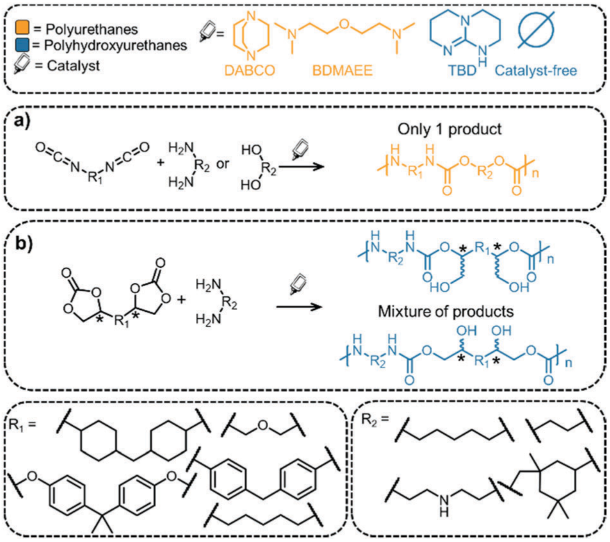


Fig. 7 Synthesis of PUs and PHUs and selected functional groups and catalysts that have been used.

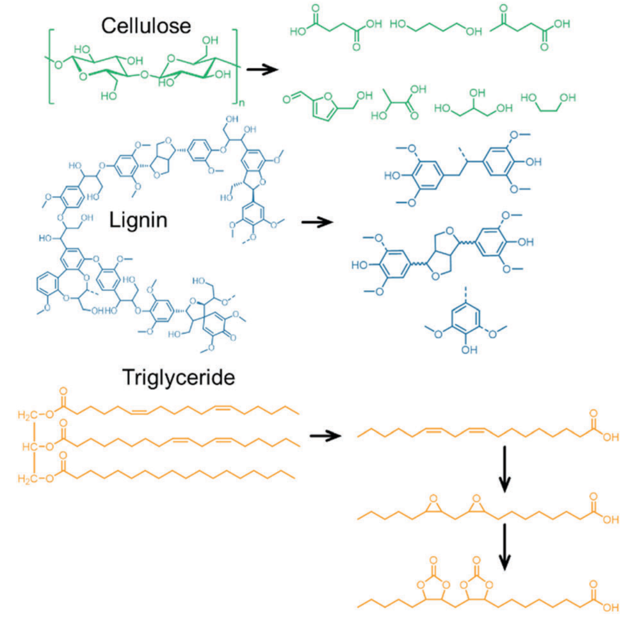


Fig. 8 Examples of alcohols/diols derived from cellulose and lignin (top, middle) after hydrogenation/hydrogenolysis reaction. Example of a carbonated vegetable oil (linoleic acid, bottom) obtained from a natural triglyceride.

lignin, see Fig. 8 for examples).[135–137] Biomass conversion can lead to a variety of functional groups including acids, ketones, and others (alcohols, amines).[138] Acids and ketones can be converted to alcohols by hydrogenation, and subsequently to COCs using ECH and the CCE reaction presented above. Note that acids or ketones obtained from biomass can also be used as platform chemicals for other polymeric products, such as poly lactic acid (pLA, one of the most important bio-based polymer that is biodegradable) or poly γ-valerolactone (pGVL).[139] Diols can be obtained from lignin containing biomass sources by catalytic reductive fractionation with hydrogen and typically employ supported metal catalyst (Pd, Ni, Ru, Rh). Fig. 8 contains examples of structures of diols that may be obtained from biomass sources.[140,141]

1,2-Diols obtained from carbohydrate sources are converted to COCs using the highly toxic phosgene route or dimethyl carbonate (transesterification reaction).[142] Notably, 1,2-diols can also be converted to COCs using CO_2 as the C1 source, although this reaction is hindered by the release of water as a by-product (thermodynamic limitation, the reverse reaction is employed to generate EG from EC and water),[143,144] which leads to moderate yields and significant amounts of waste because of the water capture strategies (utilization of alkyl halides as dehydrating agents, for example). COCs can also be obtained from vegetable oils or fatty acids because they contain olefin bonds. The olefins are first epoxidized and further transformed into their corresponding COC (see Fig. 8, bottom).[122] These oil-based COCs can then be converted to a PHU by reaction with a suitable amine.[145,146] This strategy is attractive because of the availability of the vegetable oil starting material and the properties of the resulting material that can be used as coatings and thermal insulators, *etc.*[122,147]

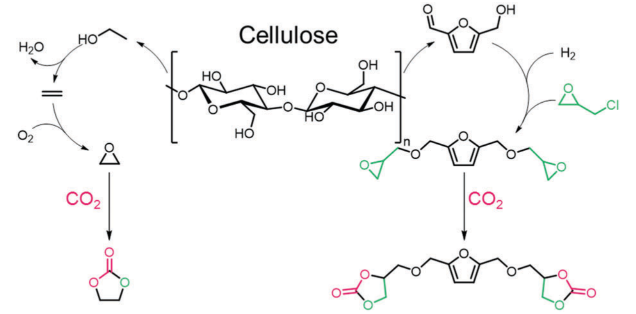


Fig. 9 Preparation of renewable EC (left) and 5-HMF derived bis(carbonate) (right) from cellulose.

The dehydration of ethanol (obtained from cellulosic feedstock) yields ethylene, which can be oxidized to afford ethylene oxide,[148] a substrate in the CCE reaction. Sugar-based polymers have attracted attention due to the availability of non-edible cellulosic feedstocks (which can be broken down into sugars), and examples of the polymerization of glucose and related compounds have been reviewed elsewhere.[149,150] The hydrolysis/dehydration of cellulose leads to carbohydrates that can be further converted into 5-hydroxymethylfurfural (5-HMF, see Fig. 9, right),[151] that can be transformed into a bis-epoxide and subsequently converted into a bis(carbonate).[72,152,153] To make the material fully renewable, the coupling partner to the COC must also be derived from renewable sources.[154] The formation of bio-based diamines is also possible from lignin derivatives when ammonia is added into the reaction mixture as a reagent.[155,156] Currently, ammonia is generated from the Haber–Bosch (HB) process, but efforts to produce more sustainable ammonia are underway.[157] The synthesis of ammonia (Haber–Bosch) is energy-intensive and, therefore, the biopolymers chitin and chitosan are being investigated as alternative sources of nitrogen containing compounds. Chitin is the second most abundant biomass source after cellulose.[154,158] Efforts to prepare bio-based amines from chitin have been reviewed previously.[155,159] Fig. 10 shows a generic strategy to obtain COCs and diamines from biomass sources and catalysts that have been employed in the synthesis of PHUs.

An example of a renewable PHU is depicted in Fig. 11, bottom, where the diamine is derived from the 5-HMF platform (furfural) by reaction with NH_3 and the COC is derived from lignin.[135] The polymer obtained from the compounds depicted in Fig. 11 is prepared in the molten phase, in the absence of a catalyst at 160 °C, and has a molecular weight of 5.3 kDa and a high PDI of 3.2. The polymer exhibits a glass transition temperature of 73 °C and decomposes at 267 °C, comparable to that of a bisphenol A polymer prepared under the same conditions (T_g = 79 °C and T_d = 276 °C). PHUs obtained from isosorbides and Jeffamine (a polyetheramine based on propylene oxide/ethylene oxide) display properties suitable for coatings (low glass transition temperature of −8 to 59 °C).[160] PHU vitrimers (polymers networks whose cross-links undergo associative exchange at elevated temperatures) have been prepared from COCs and diamines that possess similar mechanical properties to PU

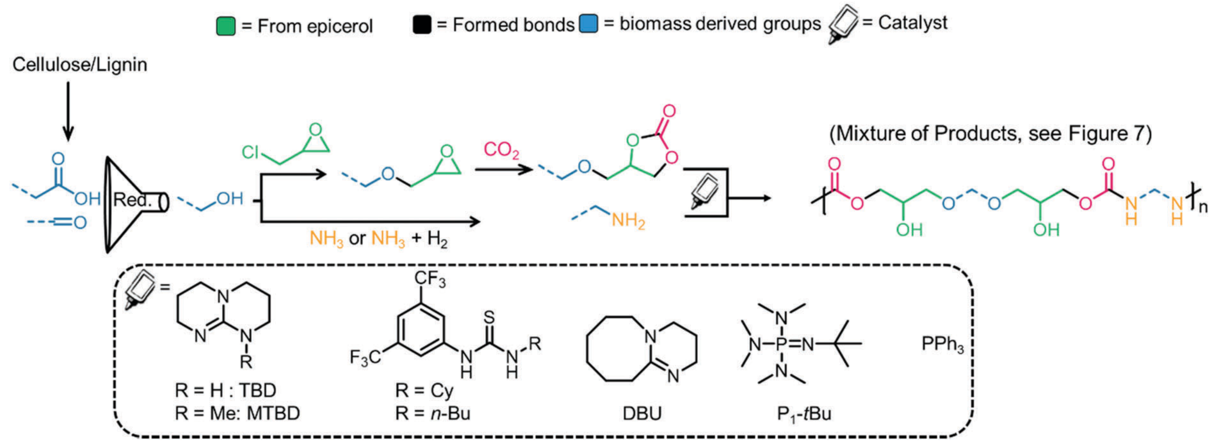


Fig. 10 Generic strategy for the preparation of renewable PHUs from biomass sources and catalysts that have been used for PHU synthesis. The product is the result of the reaction between a bis-carbonate and a diamine. Only one side is presented for clarity.[135,162,163]

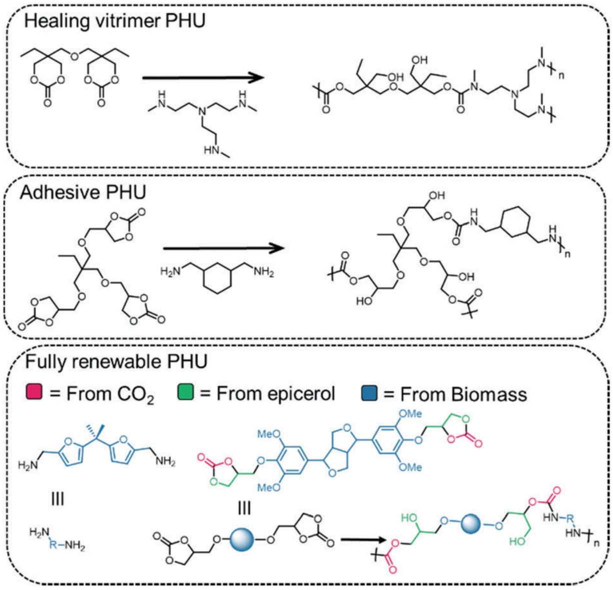


Fig. 11 Examples of PHUs and their applications.

thermosets, but with enhanced reshaping and repair properties by compression molding (Fig. 11, top).[129] The PHUs prepared from trimethylolpropane tris-carbonate (TMPTC) and commercial diamines such as 1,3-cyclohexanebis(methylamine) (CBMA) are used as adhesives and effectively bind to wood, aluminum and glass supports (Fig. 11, middle).[161]

Challenges in regiocontrol of PHUs

The structural difference between PUs and PHUs (*i.e.* one pendant alcohol group) confers very different properties to the polymers (more extensive H-bonding in the latter usually leads to higher glass transition temperatures, for example).[164] It should be noted that it is difficult to control the regioselectivity during PHU synthesis and that often several different polymers (that differ in their regioselectivity or stereoselectivity) are formed (see Fig. 7).[165] Chiral centers are also present in COCs and in the polymeric materials derived from them and a lack of stereocontrol leads to poorly defined polymers, which explains why PHUs are generally amorphous.[127] PHUs typically have low molecular weights, which is attributed to the many side reactions that can occur during their synthesis, especially at higher temperatures. However, the presence of a pendant hydroxyl group in PHUs enables post-polymerization modifications.[166,167] The side reactions that hinder high polymerization degrees of PHUs include the formation of ureas[168] and oxazolidinones,[20] (see Fig. 12 for representative side-reaction pathways that can occur in catalyzed and non-catalyzed reactions).[127] At the same time, it is the relatively high reactivity of the urethane C–O bond that renders these polymers biodegradable.[114,169] Foaming of PHUs is also problematic, since no gas is released during the synthesis (addition of water to isocyanate-based PUs forms CO_2 – the foaming agent) which makes processing more challenging.[122] Nevertheless, foaming strategies for non-isocyanate PUs have been proposed, using, for example, poly(methylhydrogenosiloxane) as a blowing agent.[170,171]

The catalysts used to prepare PHUs comprise a few N-bases, metal salts and thiourea compounds (see Fig. 10, examples include TBD and DABCO).[162,165,172–174] While catalysts accelerate the reaction they currently do not solve the regioselectivity issues. Moreover, it was shown that if the catalyst is highly basic (for example TBD), then the selectivity can decrease and the reaction can lead to the formation of urea or COC functional groups rather than urethane linkages (see Fig. 12, bottom, for the mechanism of the TBD-catalyzed transformation).[175]

Strategies that lead to regioregular polymers are being investigated. It appears that one promising approach to obtain such polymers is to use/design suitable monomers. For example, using COCs and amines with bulky substituents leads to regioselective polymers when TBD is employed as a catalyst.[176] Furthermore, when α-alkylidenes are used as the starting materials, regioregular PHUs are obtained (Fig. 13, top).[177] Note that if two equivalents of EC is reacted with a diamine, then it is possible to avoid the pendant hydroxyl group and hence the regioselectivity issues. The resulting product is a diurethane diol that can be

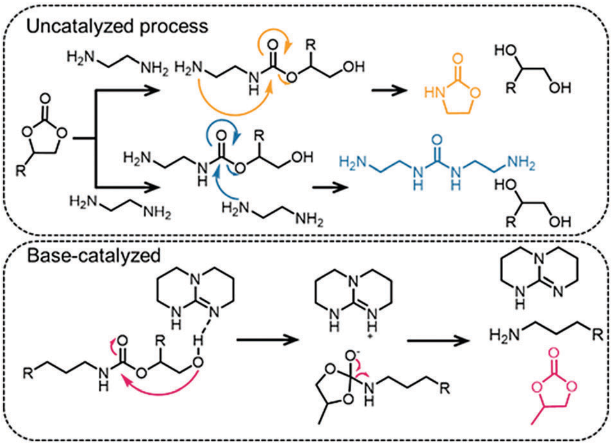


Fig. 12 Unwanted side-reactions that take place during PHU synthesis from COCs and ethylenediamine.

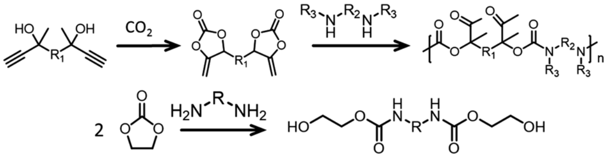


Fig. 13 Example of regioregular poly(oxourethane) (top) and diurethane diol (bottom).[177]

transformed into polyesters–polyurethanes (Fig. 13, bottom).[178] Recently, *trans*-carbamates were obtained by taking advantage of existing tools for pC synthesis (see above). Incorporating an amine into an epoxide:CO_2:catalyst mixture leads to *trans*-carbamate products in the presence of chiral aluminum or cobalt catalysts (Fig. 14).[179,180] Presumably, this strategy could open a way to controlled polymerization by reacting the epoxide:CO_2 mixture with diamines.

Biodegradation of the polymers/polymer end-of-life

It is not only important that future polymers are based on renewable sources, but that they do not pose long-term environmental problems. Therefore, designing tomorrow's materials will require a better understanding of (bio)degradation pathways and how to ensure polymers degrade within reasonable time scales and do not release toxic by-products into the environment. Biodegradation requires chemical bonds to be cleaved by enzymes (present in microorganisms). Other degradation pathways such as oxidation, hydrolysis or irradiation are often considered as biodegradation, even if these pathways do not require enzymes/microorganisms.[80] The behavior and degradation of polymers under physiological conditions, for example, has been extensively studied in the context of implants.[181–183] Biodegradation often relies on a depolymerization step followed by a mineralization step. The first step converts the polymer into its monomer, and in the second step digestion of the monomer into (ideally) CO_2 and water, takes place.[184] Biodegradation is often limited as polymers cannot be readily accessed by the enzyme capable of cleaving the polymer bonds. Hence, polymers are required that can penetrate within the active site of enzymes. For instance, not all pCs are necessarily biodegradable and care must be taken when referring to pCs as biodegradable. In this respect, the pC based on bisphenol A is not readily degradable and persists in the environment.[80]

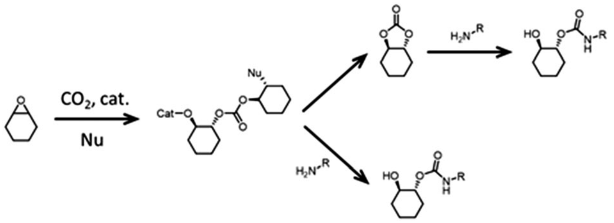


Fig. 14 Trapping of a *trans*-carbamate product *via* a pC intermediate.

Fig. 15 depicts a conceptual representation of enzymatic biodegradation. Biodegradation pathways are complex and a simple change in the polymeric structure can lead to major changes in the decomposition pathway. For example, polyethylene glycols (PEGs) and polypropylene glycols (PPGs) decompose *via* different routes.[185]

The mechanism of biodegradation of PUs has been studied and several pathways are possible including oxidative biodegradation. If the PU contains polyesters or polyureas, then esterases or ureases are able to cleave the bonds and degrade the polymer. The prerequisite is that the polymer can reach the active site of the enzyme.[186] In fact, including PUs in the structure of functional materials represents a strategy to increase the degradability of polymers that would otherwise not degrade. This strategy is employed in the preparation of biodegradable conducting polymers for biomedical applications.[187,188] Notably, even if the materials are bio-derived, there is no guarantee that the resulting polymer will be degradable (for example if the material is highly cross-linked and hydrophobic).[189] Thermal degradation pathways of the polymers can result in the release of toxic chemicals. The decomposition products from the thermal degradation of a PHU is depicted in Fig. 16.[190] The main reactions

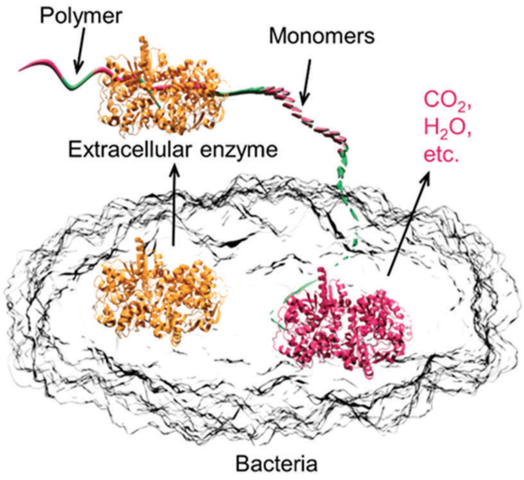


Fig. 15 Representation of enzyme catalyzed polymer degradation.[80]

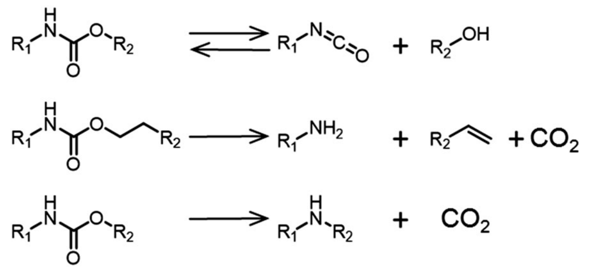


Fig. 16 Decomposition pathways of urethane linkages at 200–300 °C.[190]

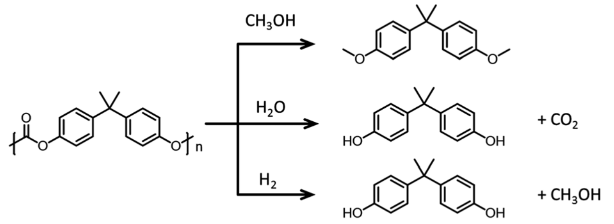


Fig. 17 Chemical depolymerization of bisphenol A carbonate. Top: Methanolysis. Middle: Hydrolysis. Bottom: Hydrogenolysis.

include the reversible depolymerization reaction of the urethane bond to form an isocyanate and an alcohol. CO_2 is also liberated upon degradation of the polymer, as well as amines and olefins.

Chemically converting polymers into their monomers in order to reuse the monomers is an attractive recycling concept. This approach has been extensively studied for polyesters and pCs, where the polymeric linkages (esters or carbonates) can be disrupted by hydrolysis,[191] alcoholysis,[192] glycolysis[193] or hydrogenolysis (see Fig. 17 that illustrates the chemical pathways for bisphenol carbonate depolymerization).[194] Currently, it is more cost-effective to dispose of the waste and generate new polymers from petrochemicals than to recycle and reuse existing materials.[195]

Current limitations, future perspectives and conclusions

The preparation of COCs has been extensively studied due to the wide range of uses of liquid COCs such as PC and EC. COCs are also used as reactive precursors to PUs and PCs. Terminal epoxides react smoothly in the presence of easily accessed catalysts and does not require elevated CO_2 pressures, high temperatures or prolonged reaction times. Indeed, the reaction can be conducted under diluted, continuous-flow reaction conditions at atmospheric pressure.[196,197] Hence, thermally robust catalysts that are resistant to water, oxygen, and industrial contaminants such as H_2S are sought after.

Suitable terminal epoxides can be derived from waste biomass sources. Importantly, for the process to be sustainable the use of waste (inedible) biomass is essential rather than using biomass from crops specifically grown to produce a chemical (non-food) product.

The reaction between COCs and diamines (or aminols/diols) leads to PHUs (or pCs), and it seems likely that bio-derived PHUs will find large-scale applications in the future. Although PHUs are prepared from COCs and diamines in the absence of a catalyst, discovering catalysts that enable a higher degree of regio- and stereo-control should afford polymers with more homogeneous properties and will accelerate the utilization of renewable PHUs at an industrial level.

The catalysts described herein are derived from petrochemicals. The catalysts are not used in the same quantities as the chemicals they are used to produce, but if the preparation of renewable materials must become fully sustainable, the development of renewable catalysts becomes relevant. In this respect, catalysts based on lecithin,[198,199] chitosan[200] or animal-based wool have been used for COC synthesis[100] and natural catalysts/supports are being exploited in other applications.[201,202]

Finally, a thorough life-cycle analysis (LCA) of the obtained polymers is required to assess the sustainability of the process. For example, CO_2-containing materials do not necessarily decrease the net amount of CO_2 since energy is required for their transformations.[203] Further, at the "end-of-life", the polymers will typically be converted into CO_2 again, as mentioned in the section on biodegradation. An extensive review on the LCA of CO_2-derived chemicals has been published very recently and these types of analysis are extremely relevant to pursue the quest of catalytically produced sustainable materials.[204]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the EPFL, the CTI Swiss Competence Center for Energy Research (SCCER) on Heat and Electricity Storage, and the Swiss National Science Foundation for financial support.

Notes and references

1 A. W. Kleij, M. North and A. Urakawa, *ChemSusChem*, 2017, **10**, 1036–1038.
2 S. A. Zimov, E. A. G. Schuur and F. S. Chapin III, *Science*, 2006, **312**, 1612–1613.
3 C. Le Quéré, R. Moriarty, R. M. Andrew, G. P. Peters, P. Ciais, P. Friedlingstein, S. D. Jones, S. Sitch, P. Tans, A. Arneth, T. A. Boden, L. Bopp, Y. Bozec, J. G. Canadell, L. P. Chini, F. Chevallier, C. E. Cosca, I. Harris, M. Hoppema, R. A. Houghton, J. I. House, A. K. Jain, T. Johannessen, E. Kato, R. F. Keeling, V. Kitidis, K. Klein Goldewijk, C. Koven, C. S. Landa, P. Landschützer, A. Lenton, I. D. Lima, G. Marland, J. T. Mathis, N. Metzl, Y. Nojiri, A. Olsen, T. Ono, S. Peng, W. Peters, B. Pfeil, B. Poulter, M. R. Raupach, P. Regnier, C. Rödenbeck, S. Saito, J. E. Salisbury, U. Schuster, J. Schwinger, R. Séférian, J. Segschneider, T. Steinhoff, B. D. Stocker, A. J. Sutton, T. Takahashi, B. Tilbrook, G. R. Van Der Werf, N. Viovy, Y. P. Wang, R. Wanninkhof, A. Wiltshire and N. Zeng, *Earth Syst. Sci. Data*, 2015, **7**, 47–85.
4 P. Falkowski, *Science*, 2013, **291**, 290–296.
5 T. P. Hughes, J. T. Kerry, M. Álvarez-Noriega, J. G. Álvarez-Romero, K. D. Anderson, A. H. Baird, R. C. Babcock, M. Beger, D. R. Bellwood, R. Berkelmans, T. C. Bridge, I. R. Butler, M. Byrne, N. E. Cantin, S. Comeau, S. R. Connolly, G. S. Cumming, S. J. Dalton, G. Diaz-Pulido, C. M. Eakin, W. F. Figueira, J. P. Gilmour, H. B. Harrison, S. F. Heron, A. S. Hoey, J. A. Hobbs, M. O. Hoogenboom, E. V. Kennedy, C. Kuo, J. M. Lough, R. J. Lowe,

G. Liu, M. T. McCulloch, H. A. Malcolm, M. J. McWilliam, J. M. Pandolfi, R. J. Pears, M. S. Pratchett, V. Schoepf, T. Simpson, W. J. Skirving, B. Sommer, G. Torda, D. R. Wachenfeld, B. L. Willis and S. K. Wilson, *Nature*, 2017, **543**, 373–377.

6 C. McGlade and P. Ekins, *Nature*, 2015, **517**, 187–190.

7 B. Smit, A.-H. A. Park and G. Gadikota, *Front. Energy Res.*, 2014, **2**, 2013–2015.

8 K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller and G. Laurenczy, *Chem. Rev.*, 2018, **118**, 372–433.

9 M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Müller, *ChemSusChem*, 2011, **4**, 1216–1240.

10 B. Walsh, *Energy Environ. Sustain.*, 2013, **325**, 1652–1655.

11 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082.

12 R. Socolow, M. Desmond, R. Aines, J. Blackstock, O. Bolland, T. Kaarsberg, N. Lewis, M. Mazzotti, A. Pfeffer, K. Sawyer, J. Siirola, B. Smit and J. Wilcox, *Am. Phys. Soc.*, 2011, 100.

13 N. R. Stuckert and R. T. Yang, *Environ. Sci. Technol.*, 2011, **45**, 10257–10264.

14 V. Favero and L. Laloui, *Int. J. Greenhouse Gas Control*, 2018, **71**, 133–141.

15 I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384–1405.

16 J. Meessen, *Chem. Ing. Tech.*, 2014, **86**, 2180–2189.

17 B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554–4581.

18 B. Schäffner, S. P. Verevkin and A. Börner, *Chem. Unserer Zeit*, 2009, **43**, 12–21.

19 J. Peng and Y. Deng, *New J. Chem.*, 2001, **25**, 639–641.

20 J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663–674.

21 T. Yamada and H. Ono, *Bioresour. Technol.*, 1999, **70**, 61–67.

22 M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet and F. Guittard, *Green Chem.*, 2013, **15**, 283–306.

23 Huntsman Corporation, *Tech. Data Sheet*, 2011, 2509.

24 S. Sopeña, G. Fiorani, C. Martín and A. W. Kleij, *ChemSusChem*, 2015, **8**, 3248–3254.

25 C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij and M. A. Pericàs, *Green Chem.*, 2014, **16**, 1552–1559.

26 A. L. Silva and J. C. Bordado, *Catal. Rev.: Sci. Eng.*, 2004, **46**, 31–51.

27 G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R. J. Kumpf, H. Orzesek, H. G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Appl. Catal., A*, 2001, **221**, 303–335.

28 R. B. Seymour and G. B. Kauffman, *J. Chem. Educ.*, 1992, **69**, 909–910.

29 C. Six and F. Richter, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2003, pp. 264–322.

30 J. R. Bucher, *Toxicol. Sci*, 1987, **9**, 367–379.

31 F. Zia, K. M. Zia, M. Zuber, S. Kamal and N. Aslam, *Carbohydr. Polym.*, 2015, **134**, 784–798.

32 A. Usman, K. M. Zia, M. Zuber, S. Tabasum, S. Rehman and F. Zia, *Int. J. Biol. Macromol.*, 2016, **86**, 630–645.

33 A. Noreen, K. M. Zia, M. Zuber, S. Tabasum and A. F. Zahoor, *Prog. Org. Coat.*, 2016, **91**, 25–32.

34 N. Mahmood, Z. Yuan, J. Schmidt and C. Xu, *Renewable Sustainable Energy Rev.*, 2016, **60**, 317–329.

35 Y. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, **540**, 354–362.

36 Y. Li, X. Cui, K. Dong, K. Junge and M. Beller, *ACS Catal.*, 2017, **7**, 1077–1086.

37 M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiaridi, J. T. Hupp and O. K. Farha, *Front. Energy Res.*, 2015, **2**, 1–10.

38 M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2014, **136**, 15861–15864.

39 T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Y. Hasegawa, *J. Am. Chem. Soc.*, 2014, **136**, 15270–15279.

40 C. Miceli, J. Rintjema, E. Martin, E. C. Escudero-Adán, C. Zonta, G. Licini and A. W. Kleij, *ACS Catal.*, 2017, **7**, 2367–2373.

41 T. Sakai, N. Kihara and T. Endo, *Macromolecules*, 1995, **28**, 4701–4706.

42 V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561–2563.

43 T. Iwasaki, N. Kihara and T. Endo, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 713–719.

44 W. Zhong, F. D. Bobbink, Z. Fei and P. J. Dyson, *ChemSusChem*, 2017, **10**, 2728–2735.

45 F. D. Bobbink, A. P. Van Muyden, A. Gopakumar, Z. Fei and P. J. Dyson, *ChemPlusChem*, 2017, **82**, 144–151.

46 F. D. Bobbink, Z. Fei, R. Scopelliti, S. Das, P. J. Dyson and J. Paul, *Helv. Chim. Acta*, 2016, **99**, 821–829.

47 S. Ghazali-Esfahani, H. Song, E. Păunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan and P. J. Dyson, *Green Chem.*, 2013, **15**, 1584–1589.

48 T. P. Thuy Pham, C. W. Cho and Y. S. Yun, *Water Res.*, 2010, **44**, 352–372.

49 D. Coleman and N. Gathergood, *Chem. Soc. Rev.*, 2010, **39**, 600–637.

50 A. Jordan and N. Gathergood, *Chem. Soc. Rev.*, 2015, **44**, 8200–8237.

51 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.

52 K. R. Roshan, T. Jose, D. Kim, K. A. Cherian and D. W. Park, *Catal. Sci. Technol.*, 2014, **4**, 963–970.

53 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526–4527.

54 F. D. Bobbink and P. J. Dyson, *J. Catal.*, 2016, **343**, 52–61.

55 Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis and F. M. Kerton, *Catal. Sci. Technol.*, 2014, **4**, 1513–1528.

56 C. Martín, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370.

57 F. D. Bobbink, D. Vasilyev, M. Hulla, S. Chamam, F. Menoud, G. Laurenczy, S. Katsyuba and P. J. Dyson, *ACS Catal.*, 2018, **8**, 2589–2594.

58 N. Kihara, N. Hara and T. Endo, *J. Org. Chem.*, 1993, **58**, 6198–6202.

59 S. Marmitt and P. F. B. Gonçalves, *J. Comput. Chem.*, 2015, **36**, 1322–1333.

60 S. Gennen, M. Alves, R. Méreau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome and B. Grignard, *ChemSusChem*, 2015, **8**, 1845–1849.

61 G. M. Lari, G. Pastore, C. Mondelli and J. Pérez-Ramírez, *Green Chem.*, 2018, **20**, 148–159.

62 W. H. Lawrence, M. Malik, J. E. Turner and J. Autian, *J. Pharm. Sci.*, 1972, **61**, 1712–1717.

63 S. J. Poland and D. J. Darensbourg, *Green Chem.*, 2017, 4990–5011.

64 J. Rintjema and A. W. Kleij, *ChemSusChem*, 2017, **10**, 1274–1282.

65 M. Hong, Y. Kim, H. Kim, H. J. Cho, M. Baik and Y. Kim, *J. Org. Chem.*, 2018, **83**, 9370–9380.

66 J. Sun, J. Ren, S. Zhang and W. Cheng, *Tetrahedron Lett.*, 2009, **50**, 423–426.

67 P. Yan and H. Jing, *Adv. Synth. Catal.*, 2009, **351**, 1325–1332.

68 R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622–1623.

69 M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood and X. Wu, *ACS Catal.*, 2015, **5**, 3398–3402.

70 X. B. Lu, B. Liang, Y. J. Zhang, Y. Z. Tian, Y. M. Wang, C. X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 3732–3733.

71 J. Hu, J. Ma, H. Liu, Q. Qian, C. Xie and B. Han, *Green Chem.*, 2018, **20**, 2990.

72 J. A. Castro-Osma, J. Martínez, F. De La Cruz-Martínez, M. P. Caballero, J. Fernández-Baeza, J. Rodríguez-López, A. Otero, A. Lara-Sánchez and J. Tejeda, *Catal. Sci. Technol.*, 2018, **8**, 1981–1987.

73 L. Wang, G. Zhang, K. Kodama and T. Hirose, *Green Chem.*, 2016, **18**, 1229–1233.

74 K. Nakano, T. Kamada and K. Nozaki, *Angew. Chem., Int. Ed.*, 2006, **45**, 7274–7277.

75 M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1–16.

76 Y. Qin and X. Wang, *Biotechnol. J.*, 2010, **5**, 1164–1180.

77 X. B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484.

78 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760–770.

79 M. Taherimehr and P. P. Pescarmona, *J. Appl. Polym. Sci.*, 2014, **131**, 1–17.

80 T. Artham and M. Doble, *Macromol. Biosci.*, 2008, **8**, 14–24.

81 F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis and G. W. Coates, *Angew. Chem., Int. Ed.*, 2015, **54**, 1215–1218.

82 O. Hauenstein, S. Agarwal and A. Greiner, *Nat. Commun.*, 2016, **7**, 1–7.

83 E. H. Lee, J. Y. Ahn, M. M. Dharman, D. W. Park, S. W. Park and I. Kim, *Catal. Today*, 2008, **131**, 130–134.

84 H. Sugimoto, H. Ohshima and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3549–3555.
85 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760–770.
86 L. S. Morris, M. I. Childers and G. W. Coates, *Angew. Chem., Int. Ed.*, 2018, **57**, 5731–5734.
87 M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. Lapointe and G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129–8152.
88 W. Hirahata, R. M. Thomas, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2008, **130**, 17658–17659.
89 R. M. Thomas, P. C. B. Widger, S. M. Ahmed, R. C. Jeske, W. Hirahata, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2010, **132**, 16520–16525.
90 M. I. Childers, A. K. Vitek, L. S. Morris, P. C. B. Widger, S. M. Ahmed, P. M. Zimmerman and G. W. Coates, *J. Am. Chem. Soc.*, 2017, **139**, 11048–11054.
91 K. N. Eun, J. N. Sung, S. Sujith, S. W. Kim and Y. L. Bun, *J. Am. Chem. Soc.*, 2007, **129**, 8082–8083.
92 Y. Xu, L. Lin, M. Xiao, S. Wang, A. T. Smith, L. Sun and Y. Meng, *Prog. Polym. Sci.*, 2018, **80**, 163–182.
93 J. Y. Jeon, J. J. Lee, J. K. Varghese, S. J. Na, S. Sujith, M. J. Go, J. Lee, M.-A. Ok and B. Y. Lee, *Dalton Trans.*, 2013, **42**, 9245–9254.
94 Y. Y. Zhang, G. W. Yang and G. P. Wu, *Macromolecules*, 2018, **51**, 3640–3646.
95 R. K. Dean, K. Devaine-Pressing, L. N. Dawe and C. M. Kozak, *Dalton Trans.*, 2013, **42**, 9233–9244.
96 J. Gurnham, S. Gambarotta, I. Korobkov, L. Jasinska-Walc and R. Duchateau, *Organometallics*, 2014, **33**, 4401–4409.
97 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.
98 A. Thevenon, A. Cyriac, D. Myers, A. J. P. White, C. B. Durr and C. K. Williams, *J. Am. Chem. Soc.*, 2018, **140**, 6893–6903.
99 G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618–6639.
100 Y. L. Bun, Y. K. Heon, Y. L. Su, J. N. Sung, S. I. Han, H. Yun, H. Lee and Y. W. Park, *J. Am. Chem. Soc.*, 2005, **127**, 3031–3037.
101 M. Cozzolino, K. Press, M. Mazzeo and M. Lamberti, *ChemCatChem*, 2016, **8**, 455–460.
102 D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *J. Am. Chem. Soc.*, 2016, **138**, 11117–11120.
103 Y. Wang, Y. Zhao, Y. Ye, H. Peng, X. Zhou, X. Xie, X. Wang and F. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 3593–3597.
104 J. Hilf, M. Scharfenberg, J. Poon, C. Moers and H. Frey, *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
105 A. Dag, M. Aydin, H. Durmaz, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4476–4483.
106 M. J. Barthel, T. Rudolph, S. Crotty, F. H. Schacher and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4958–4965.
107 Z. Mou and E. Y. X. Chen, *ACS Sustainable Chem. Eng.*, 2016, **4**, 7118–7129.
108 E. Slavko and M. S. Taylor, *Chem. Sci.*, 2017, **8**, 7106–7111.
109 V. Froidevaux, C. Negrell, S. Caillol, J. P. Pascault and B. Boutevin, *Chem. Rev.*, 2016, **116**, 14181–14224.
110 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, **15**, 3083–3090.
111 N. Kielland, C. J. Whiteoak and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2115–2138.
112 W. M. Ren, T. J. Yue, X. Zhang, G. G. Gu, Y. Liu and X. B. Lu, *Macromolecules*, 2017, **50**, 7062–7069.
113 M. Hatazawa, K. Nakabayashi, S.-i Ohkoshi and K. Nozaki, *Chem. – Eur. J.*, 2016, **22**, 13677–13681.
114 E. M. Christenson, J. M. Anderson and A. Hiltner, *Corros. Eng., Sci. Technol.*, 2007, **42**, 312–323.
115 J. O. Akindoyo, M. D. H. Beg, S. Ghazali, M. R. Islam, N. Jeyaratnam and A. R. Yuvaraj, *RSC Adv.*, 2016, **6**, 114453–114482.
116 A. M. Nelson and T. E. Long, *Macromol. Chem. Phys.*, 2014, **215**, 2161–2174.
117 X. Zhou, Y. Li, C. Fang, S. Li, Y. Cheng, W. Lei and X. Meng, *J. Mater. Sci. Technol.*, 2015, **31**, 708–722.
118 I. Yilgör, E. Yilgör and G. L. Wilkes, *Polymer*, 2015, **58**, A1–A36.
119 C. Prisacariu, *Polyurethane Elastomers*, Springer, 2011.
120 J. Nanclares, Z. S. Petrovic, I. Javni, M. Ionescu and F. Jaramillo, *J. Appl. Polym. Sci.*, 2015, **132**, 7–14.
121 E. Delebecq, J. P. Pascault, B. Boutevin and F. Ganachaud, *Chem. Rev.*, 2013, **113**, 80–118.
122 B. Grignard, J. M. Thomassin, S. Gennen, L. Poussard, L. Bonnaud, J. M. Raquez, P. Dubois, M. P. Tran, C. B. Park, C. Jerome and C. Detrembleur, *Green Chem.*, 2016, **18**, 2206–2215.
123 M. Thirumal, D. Khastgir, N. K. Singha, B. S. Manjunath and Y. P. Naik, *J. Appl. Polym. Sci.*, 2008, **108**, 1810–1817.
124 P. Król, *Prog. Mater. Sci.*, 2007, **52**, 915–1015.
125 H. Tomita, F. Sanda and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 3678–3685.
126 B. Nohra, L. Candy, J.-F. Blanco, C. Guerin, Y. Raoul and Z. Mouloungui, *Macromolecules*, 2013, **46**, 3771–3792.
127 V. Besse, F. Camara, F. Méchin, E. Fleury, S. Caillol, J. P. Pascault and B. Boutevin, *Eur. Polym. J.*, 2015, **71**, 1–11.
128 E. K. Leitsch, G. Beniah, K. Liu, T. Lan, W. H. Heath, K. A. Scheidt and J. M. Torkelson, *ACS Macro Lett.*, 2016, **5**, 424–429.
129 D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer and W. R. Dichtel, *J. Am. Chem. Soc.*, 2015, **137**, 14019–14022.
130 J. Ke, X. Li, F. Wang, S. Jiang, M. Kang, J. Wang, Q. Li and Z. Wang, *RSC Adv.*, 2017, **7**, 28841–28852.
131 E. J. Hoekstra and C. Simoneau, *Crit. Rev. Food Sci. Nutr.*, 2013, **53**, 386–402.
132 M.-Y. Chen, M. Ike and M. Fujita, *Environ. Toxicol.*, 2002, **17**, 80–86.
133 J. L. J. Van Velthoven, L. Gootjes, D. S. Van Es, B. A. J. Noordover and J. Meuldijk, *Eur. Polym. J.*, 2015, **70**, 125–135.
134 F. Ng, G. Couture, C. Philippe, B. Boutevin and S. Caillol, *Molecules*, 2017, **22**, 149.
135 M. Janvier, P. H. Ducrot and F. Allais, *ACS Sustainable Chem. Eng.*, 2017, **5**, 8648–8656.
136 C. Luo, S. Wang and H. Liu, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 7636–7639.
137 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem., Int. Ed.*, 2008, **47**, 8510–8513.
138 A. Corma Canos, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
139 K. Yao and C. Tang, *Macromolecules*, 2013, **46**, 1689–1712.
140 W. Schutyser, S. Van Den Bosch, T. Renders, T. De Boe, S. F. Koelewijn, A. Dewaele, T. Ennaert, O. Verkinderen, B. Goderis, C. M. Courtin and B. F. Sels, *Green Chem.*, 2015, **17**, 5035–5045.
141 S. F. Koelewijn, S. Van Den Bosch, T. Renders, W. Schutyser, B. Lagrain, M. Smet, J. Thomas, W. Dehaen, P. Van Puyvelde, H. Witters and B. F. Sels, *Green Chem.*, 2017, **19**, 2561–2570.
142 M. S. Kathalewar, P. B. Joshi, A. S. Sabnis and V. C. Malshe, *RSC Adv.*, 2013, **3**, 4110–4129.
143 F. D. Bobbink, W. Gruszka, M. Hulla, S. Das and P. J. Dyson, *Chem. Commun.*, 2016, **52**, 10787–10790.
144 M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa and K. Tomishige, *ACS Catal.*, 2014, **4**, 1893–1896.
145 L. Maisonneuve, A. S. More, S. Foltran, C. Alfos, F. Robert, Y. Landais, T. Tassaing, E. Grau and H. Cramail, *RSC Adv.*, 2014, **4**, 25795–25803.
146 M. Bähr and R. Mülhaupt, *Green Chem.*, 2012, **14**, 483–489.
147 R. Pathak, M. Kathalewar, K. Wazarkar and A. Sabnis, *Prog. Org. Coat.*, 2015, **89**, 160–169.
148 K. Kaneda, S. Haruna, T. Imanaka, M. Hamamoto, Y. Nishiyama and Y. Ishii, *Tetrahedron Lett.*, 1992, **33**, 6827–6830.
149 J. A. Galbis, M. D. G. García-Martín, M. V. De Paz and E. Galbis, *Chem. Rev.*, 2016, **116**, 1600–1636.
150 X. Feng, A. J. East, W. B. Hammond, Y. Zhang and M. Jaffe, *Polym. Adv. Technol.*, 2011, **22**, 139–150.
151 J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
152 J. Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, J. A. Castro-Osma, A. Lara-Sánchez and A. Otero, *ChemSusChem*, 2017, **10**, 2886–2890.
153 X. Shen, X. Liu, J. Wang, J. Dai and J. Zhu, *Ind. Eng. Chem. Res.*, 2017, **56**, 8508–8516.
154 F. D. Bobbink, J. Zhang, Y. Pierson, X. Chen and N. Yan, *Green Chem.*, 2015, **17**, 1024–1031.
155 M. Pelckmans, T. Renders, S. Van de Vyver and B. F. Sels, *Green Chem.*, 2017, **19**, 5303–5331.
156 M. Pelckmans, W. Vermandel, F. Van Waes, K. Moonen and B. F. Sels, *Angew. Chem., Int. Ed.*, 2017, **56**, 14540–14544.

157 J. Wang, L. Yu, L. Hu, G. Chen, H. Xin and X. Feng, *Nat. Commun.*, 2018, **9**, 1795.

158 Y. Pierson, X. Chen, F. D. Bobbink, J. Zhang and N. Yan, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2081–2089.

159 V. Froidevaux, C. Negrell, S. Caillol, J. P. Pascault and B. Boutevin, *Chem. Rev.*, 2016, **116**, 14181–14224.

160 R. Besse, S. Auvergne, G. Carlotti, B. Boutevin, S. Otazaghine, J. Caillol and B. Pascault, *React. Funct. Polym.*, 2013, **73**, 588–594.

161 A. Cornille, G. Michaud, F. Simon, S. Fouquay, R. Auvergne, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2016, **84**, 404–420.

162 M. Blain, L. Jean-Gérard, R. Auvergne, D. Benazet, S. Caillol and B. Andrioletti, *Green Chem.*, 2014, **16**, 4286–4291.

163 W. Schutyser, T. Renders, S. Van Den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 852–908.

164 N. Kihara and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 2765–2773.

165 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chem. Rev.*, 2015, **115**, 12407–12439.

166 G. Beniah, W. H. Heath and J. M. Torkelson, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 3347–3351.

167 T. J. Farmer, J. W. Comerford, A. Pellis and T. Robert, *Polym. Int.*, 2018, **67**, 775–789.

168 Q. W. Lu, T. R. Hoye and C. W. Macosko, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2310–2328.

169 M. Cregut, M. Bedas, M. J. Durand and G. Thouand, *Biotechnol. Adv.*, 2013, **31**, 1634–3647.

170 A. Cornille, S. Dworakowska, D. Bogdal, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2015, **66**, 129–138.

171 A. Cornille, R. Auvergne, O. Figovsky, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2017, **87**, 535–552.

172 C. Duval, N. Kébir, R. Jauseau and F. Burel, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 758–764.

173 M. Blain, H. Yau, L. Jean-Gérard, R. Auvergne, D. Benazet, P. R. Schreiner, S. Caillol and B. Andrioletti, *ChemSusChem*, 2016, **9**, 2269–2272.

174 V. M. Lombardo, E. A. Dhulst, E. K. Leitsch, N. Wilmot, W. H. Heath, A. P. Gies, M. D. Miller, J. M. Torkelson and K. A. Scheidt, *Eur. J. Org. Chem.*, 2015, 2791–2795.

175 A. Bossion, R. H. Aguirresarobe, L. Irusta, D. Taton, H. Cramail, E. Grau, D. Mecerreyes, C. Su, G. Liu, A. J. Müller and H. Sardon, *Macromolecules*, 2018, **51**, 5556–5566.

176 S. Sopeña, V. Laserna, W. Guo, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Adv. Synth. Catal.*, 2016, **358**, 2172–2178.

177 S. Gennen, B. Grignard, T. Tassaing, C. Jérôme and C. Detrembleur, *Angew. Chem., Int. Ed.*, 2017, **56**, 10394–10398.

178 L. Han, J. Dai, L. Zhang, S. Ma, J. Deng, R. Zhang and J. Zhu, *RSC Adv.*, 2014, **4**, 49471–49477.

179 Y. Liu, W. M. Ren, K. K. He, W. Z. Zhang, W. B. Li, M. Wang and X. B. Lu, *J. Org. Chem.*, 2016, **81**, 8959–8966.

180 W. Guo, V. Laserna, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Chem. – Eur. J.*, 2016, **22**, 1722–1727.

181 B. D. Ulery, L. S. Nair and C. T. Laurencin, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 832–864.

182 Q. Liu, L. Jiang, R. Shi and L. Zhang, *Prog. Polym. Sci.*, 2012, **37**, 715–765.

183 Y. Hong, J. Guan, K. L. Fujimoto, R. Hashizume, A. L. Pelinescu and W. R. Wagner, *Biomaterials*, 2010, **31**, 4249–4258.

184 A. A. Shah, F. Hasan, A. Hameed and S. Ahmed, *Biotechnol. Adv.*, 2008, **26**, 246–265.

185 A. Zgoła-Grześkowiak, T. Grześkowiak, J. Zembrzuska and Z. Łukaszewski, *Chemosphere*, 2006, **64**, 803–809.

186 G. T. Howard, *Int. Biodeterior. Biodegrad.*, 2002, **49**, 245–252.

187 N. Lucas, C. Bienaime, C. Belloy, M. Queneudec, F. Silvestre and J. E. Nava-Saucedo, *Chemosphere*, 2008, **73**, 429–442.

188 B. Liu, *Biomacromolecules*, 2018, **19**, 1783–1803.

189 T. Garrison, A. Murawski and R. Quirino, *Polymers*, 2016, **8**, 262.

190 A. Cornille, C. Guillet, S. Benyahya, C. Negrell, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2016, **84**, 873–888.

191 D. Carta, G. Cao and C. D'Angeli, *Environ. Sci. Pollut. Res.*, 2003, **10**, 390–394.

192 M. Genta, F. Yano, Y. Kondo, W. Matsubara and S. Oomoto, Mitsubishi Heavy Ind. Ltd., *Technol. Rev.*, 2003, **40**, 1–4.

193 F. R. Veregue, C. T. Pereira da Silva, M. P. Moisés, J. G. Meneguin, M. R. Guilherme, P. A. Arroyo, S. L. Favaro, E. Radovanovic, E. M. Girotto and A. W. Rinaldi, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12017–12024.

194 S. Westhues, J. Idel and J. Klankermayer, *Sci. Adv.*, 2018, **4**, eaat9669.

195 X. Zhang, M. Fevre, G. O. Jones and R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 839–885.

196 P. Izák, F. D. Bobbink, M. Hulla, M. Klepic, K. Friess, Š. Hovorka and P. J. Dyson, *ChemPlusChem*, 2018, **83**, 7–18.

197 A. Barthel, Y. Saih, M. Gimenez, J. D. A. Pelletier, F. E. Kühn, V. D'Elia and J.-M. Basset, *Green Chem.*, 2016, **18**, 3116–3123.

198 J. Song, B. Zhang, P. Zhang, J. Ma, J. Liu, H. Fan, T. Jiang and B. Han, *Catal. Today*, 2012, **183**, 130–135.

199 Y. Hu, J. Song, C. Xie, H. Wu, Z. Wang, T. Jiang, L. Wu, Y. Wang and B. Han, *ACS Sustainable Chem. Eng.*, 2018, **6**, 11228–11234.

200 J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A. C. Kathalikkattil and D.-W. Park, *Catal. Sci. Technol.*, 2012, **2**, 1674–1680.

201 S. Das, F. D. Bobbink, S. Bulut, M. Soudani and P. J. Dyson, *Chem. Commun.*, 2016, **52**, 2497–2500.

202 A. Laca, A. Laca and M. Díaz, *J. Environ. Manage.*, 2017, **197**, 351–359.

203 N. von der Assen, J. Jung and A. Bardow, *Energy Environ. Sci.*, 2013, **6**, 2721–2734.

204 J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434–504.