

Review

# Recent Advances in RO(CO)P of Bio-Based Monomers

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**Abstract:** Synthetic polymers have a key role in modern society as they have allowed for great technological advancement since their discovery. However, the use of fossil-fuel-based raw materials and the pollution derived from plastics accumulation in the environment raised enormous concern, driving research efforts toward the identification of more sustainable alternatives. Bio-based functional molecules susceptible to ring-opening (co)polymerisation [RO(C)OP], such as lactones, cyclic carbonates, and oxiranes, represent an attractive source of monomers for the synthesis of more sustainable polymers. In this review, we describe the main advancement in this research field reported during the last seven years. In particular, we describe the preparation of monomers from (renewable) bio-sources such as sugars, terpenes, fatty acids, and carbon dioxide with a focus on structurally novel substrates. Both metal-mediated and organo-catalytic RO(CO)P methods are described, and the properties of derived functional polymers are discussed when relevant.

**Keywords:** ring-opening (co)polymerisation; catalysis; bio-based; monomer; polyether; polyester; polycarbonate



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## 1. Introduction

Technological and material advancements have been used to classify certain periods of human history, from ancient stone, bronze, and iron ages to the closer in time atomic, space and information ages [1]. There can be no doubt that synthetic plastics represent one of the greatest technological advancements in the modern era. Unfortunately, their use is accompanied by environmental pollution at such a level that the presence of plastic in non-bioturbated sediment could be used as a stratigraphic indicator for the Anthropocene [2].

Environmental accumulation of plastics due to the high stability of most commonly used polymers represents a priority problem and, at the same time, the vast majority of currently used polymers are based on non-renewable, fossil resources [3]. In the attempt to find a solution, besides recycling, the upcycling of waste polymers is emerging as highly promising strategy for mitigating plastic pollution [4]. In parallel, great attention has been directed to the identification of new, renewable alternative feedstocks for the production of (more) sustainable polymers [5]. In particular, the creation of renewable monomers has been proposed from numerous bio-sources such as terpenes [6], sugars [7], vegetable oils [8], lignin [9], cellulose [10], and starch [11].

Different classes of bio-based polymers have been obtained by means of several polymerisation techniques such as: polyhydroxyalkanoates (PHBs) by fermentation [12], polyolefins by anionic [13], and coordination-insertion polymerisation [14], polyacrilates by (controlled) radical polymerisation [15], and poly(hydroxyurethane)s by polyaddition reactions [16].

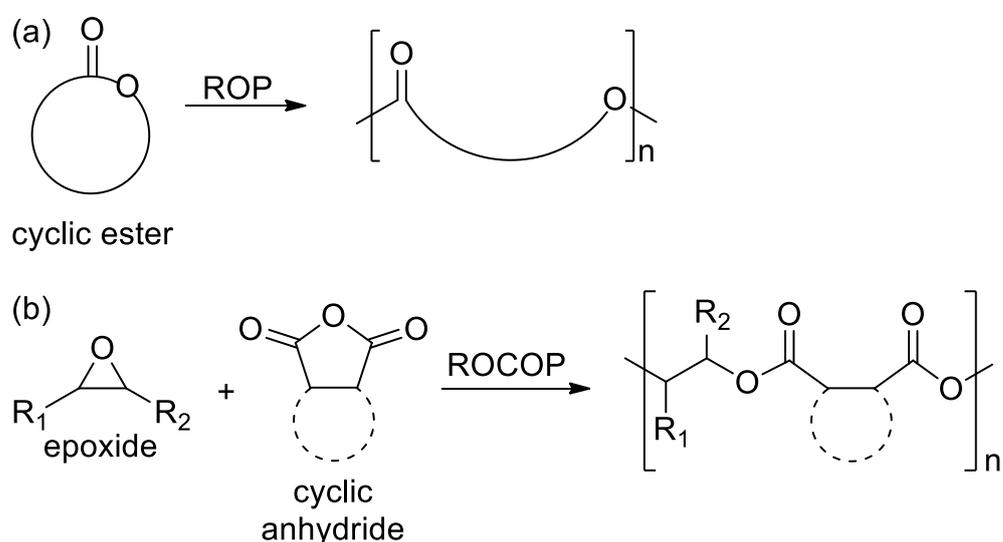
Among other polymerisation techniques, ring-opening (co)polymerisation [RO(CO)P] has been largely investigated in the last decades, and numerous catalytic systems have been developed to promote this reaction [17–24]. In particular, systems based on environmentally benign metals such as aluminium, zinc, magnesium, and iron are attracting high interest.

Depending on the chemical identity of the starting monomers, RO(CO)P gives access to the synthesis of polyethers, polyesters, and polycarbonates.

In this review, we summarize the major advancements in RO(CO)P application for the conversion of bio-based monomers. In particular, the description is divided on the basis of the polymer product identity. We mainly covered the period from 2015 to the beginning of 2022, to avoid overlapping with other exhaustive review papers.

## 2. Polyesters

One of the most appealing classes of sustainable polymers is represented by aliphatic polyesters (APEs), because of their general biocompatibility combined with a relatively easy hydrolytic degradation [25,26]. The synthesis of APEs can be conveniently performed via ROP of cyclic esters or ROCOP of cyclic anhydrides and epoxides (Scheme 1). Notwithstanding these methods have been deeply investigated, there is still a lack of suitable monomers from renewable resources. Hence, in this section, we divide the description of sustainable APEs into those obtained from bio-based lactones and those obtained from bio-based epoxides and cyclic anhydrides.

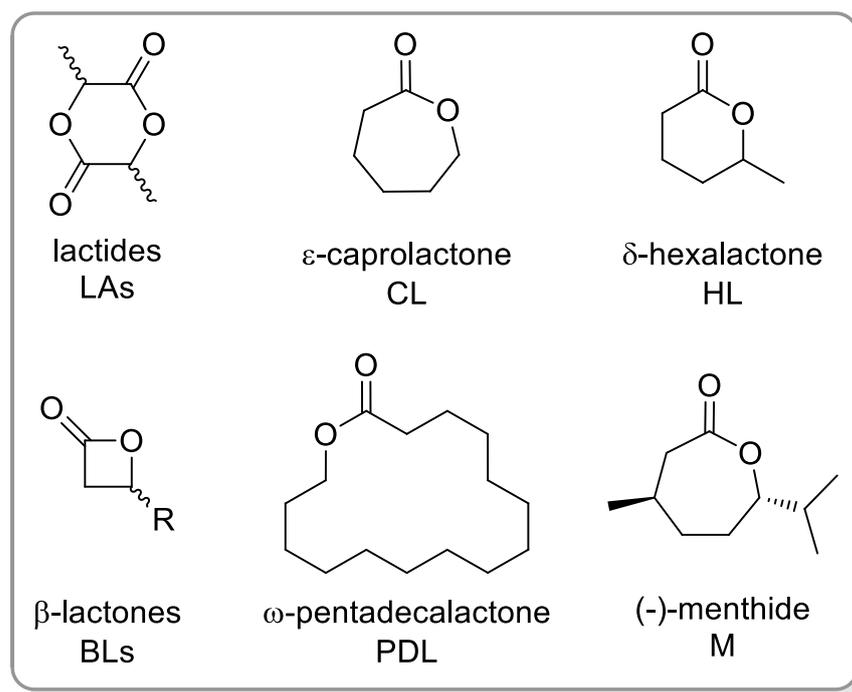


**Scheme 1.** General scheme for the ROP of cyclic esters (a) and ROCOP of epoxides with cyclic anhydrides (b).

### 2.1. Polyesters from ROP of Lactones

Monomers deriving from renewable biomass feedstocks, such as terpenes, sugars, and fatty acids, have been recognized as ideal candidates for the development of sustainable materials (Figure 1) [6,27,28].

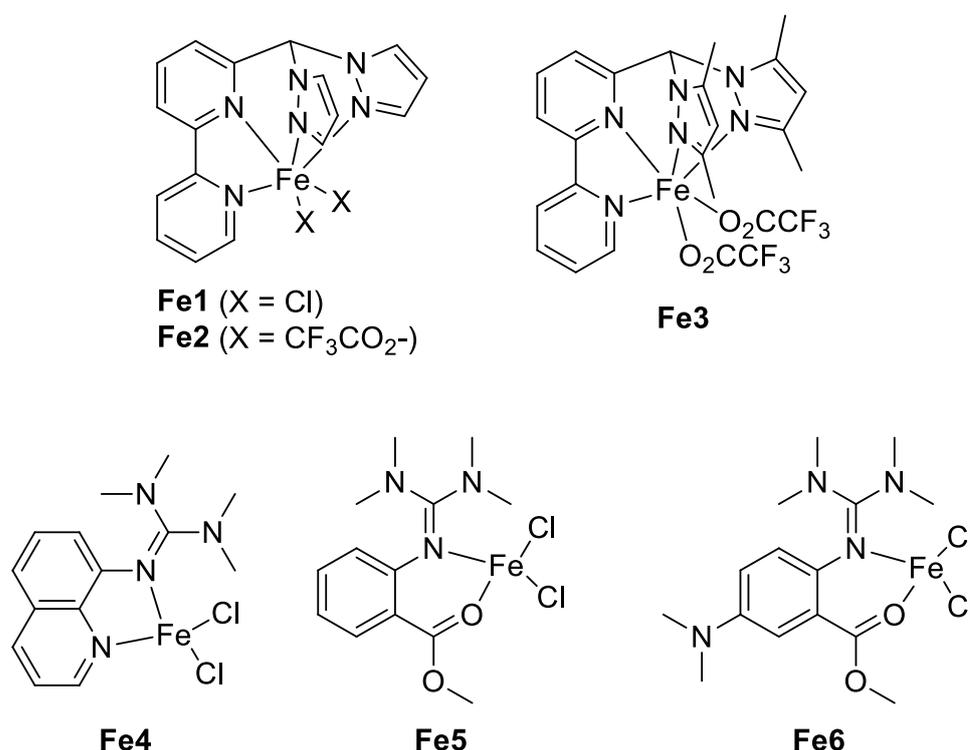
Although lactide (LA) and  $\epsilon$ -caprolactone (CL) are undoubtedly the most studied of the series, their congeners such as  $\delta$ -hexalactone (HA) and  $\beta$ -lactones (BLs) have been less investigated [29,30]. The corresponding polyesters are used in many fields, in particular for medicinal and pharmaceutical applications [31,32]. For this reason, important efforts have been dedicated to the development of catalytic systems based on non-toxic metals. Currently, the industrial production of polylactide (PLA) employs tin(II) octanoate ( $\text{Sn}(\text{Oct})_2$ ) as the catalyst, also approved by the U.S. Food and Drug Administration (FDA) [33]. Nevertheless, alternative systems capable of outperforming such catalysts have been developed during the past two decades. In this scenario, complexes based on Al, Mg, and Zn exhibit outstanding catalytic performances and have been extensively reviewed [34–36].



**Figure 1.** Main *sustainable* lactones employed as monomers in ring-opening polymerisation processes.

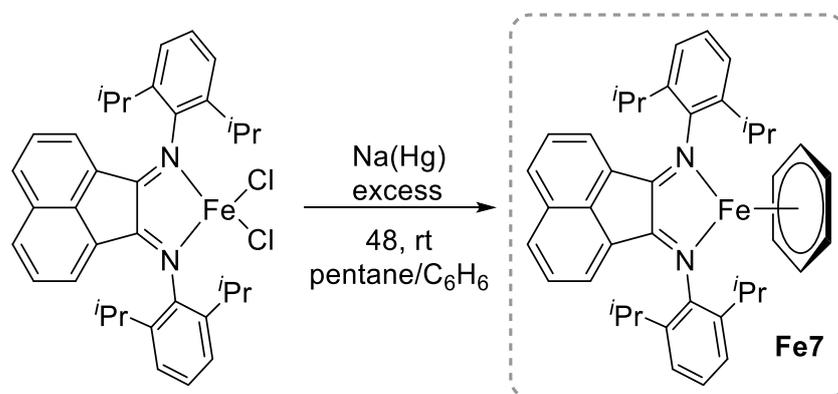
Along with these metals, Fe-based catalysts represent ideal candidates; nonetheless, applications of such systems as ROP catalysts are scant. Indeed, after the early reports by Tolman [37,38], and Gibson [39,40], the field has remained largely unexplored for almost a decade. In 2013, Byers et al. reported on the ROP of lactide promoted by bis(imino)pyridine Fe(II) bis(alkoxide) complexes [41]. The catalyst activity proved highly dependent on the nature of the exogenous alcohol employed as the co-activator. The obtained PLAs had relatively narrow molecular weight distribution (dispersity,  $\mathcal{D}$ , between 1.06 and 1.45), and the process exhibited a rather living character. Nevertheless, the systems proved poorly active, allowing for 60% conversion of 100 equivalents of monomer in 24 h. The analogous ferric compound was completely inactive, enabling the possibility of an on/off redox switchable process. Later, the same group disclosed analogue ferrous species bearing a bis(amidinato)-*N*-hetero-cyclic carbene ligand [42]. Compared to the previously reported bis(imino)pyridine-based congener, PLAs with higher  $M_n$  were achieved in shorter reaction times. This was accounted to faster activation rates granted by the more electron-donating NHC scaffold.

Tetradentate bis(imino)pyridine iron(II) complexes active in the ROP of lactide were lately reported by Herres-Pawlis et al. (Fe1–3, Figure 2) [43]. Such species allowed for high conversion (87%) of technical grade monomer within 30 h under solvent-free conditions, affording PLAs with a number average molecular weight ( $M_n$ ) lower than the theoretical values and rather large dispersity ( $1.5 \leq \mathcal{D} \leq 1.9$ ). Two years later, the same group disclosed novel iron-guanidine complexes exhibiting superior catalytic activity in the ROP of lactide (Fe4–6, Figure 2) [44]. Remarkably, such species outperformed Sn(Oct)<sub>2</sub> under industrially relevant conditions (i.e., technical grade monomer and bulk), affording high molecular weight PLA ( $M_n > 90$  kDa) having thermal properties matching those reported in the literature. Analysis of the polymer chain ends indicated that, in the absence of an external co-activators (alcohol), the reaction could be initiated either by adventitious water or by the guanidine moiety of the complex.



**Figure 2.** Bis(imino)pyridine-**Fe1–3**, and guanidine-based Fe(II) **Fe4–6** complexes active in the ROP of lactide.

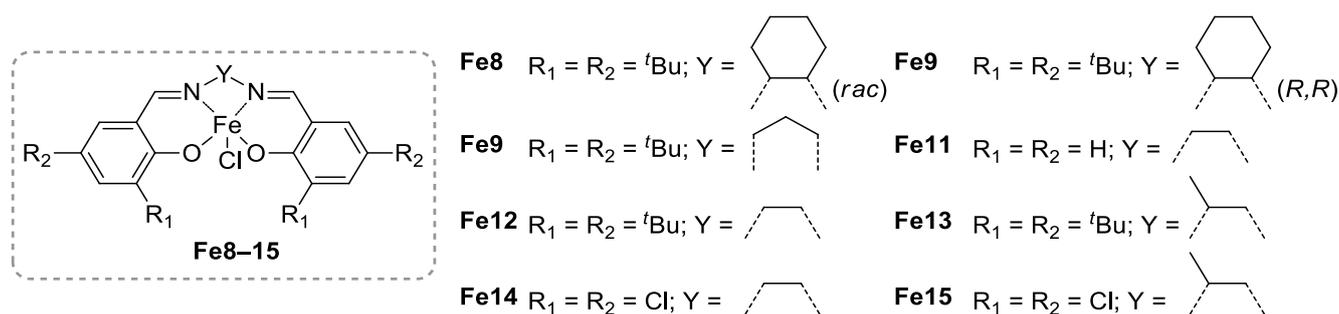
In 2017, a Fe( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)-bis(arylimino)-acenaphthene (BIAN) system was reported by Long et al. (**Fe7**, Figure 3) [45].



**Figure 3.** Synthesis of Fe( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)-bis(arylimino)-acenaphthene complex **Fe7**.

Complex **Fe7** was tested in the ROP of L-LA, affording high molecular weight PLLA ( $M_n$  up to 300 kDa) in the absence of exogenous alcohol with moderate dispersity values ( $D = 1.7$ ). Upon introducing 4-methoxyphenol as the co-activator, a drop of polymer  $M_n$  consistent with the concentration of alcohol was observed. In turn, <sup>1</sup>H NMR spectroscopy analysis revealed the presence of 4-methoxyphenoxy-terminal groups, indicating the alcohol as the actual initiator of the process. Nevertheless, no clear evidence of in situ formation of iron alkoxide species was obtained. The actual polymerisation mechanism, as well as the role of the iron complex, could not be clarified due to the formation of paramagnetic species hampering in-depth NMR spectroscopy analyses.

Concomitantly, Pang et al. disclosed a series of air-stable Fe(III)-salen catalysts for the ROP of *r*-LA and CL (**Fe8–15**, Figure 4) [46,47].

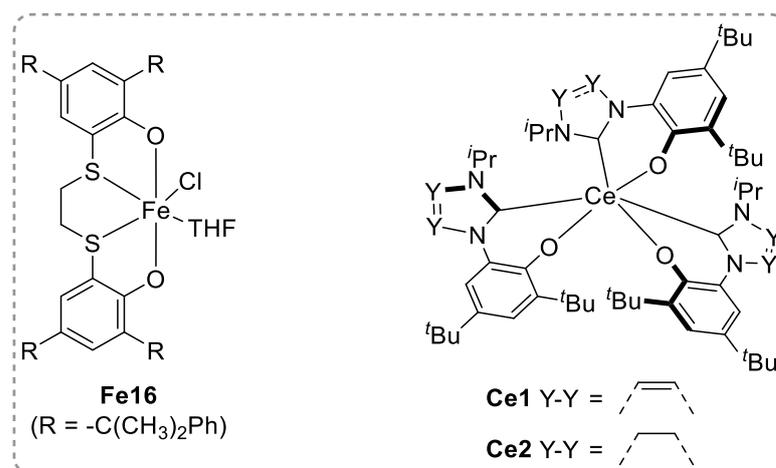


**Figure 4.** General representation and structural variation of Fe(III)-salen complexes **Fe8–15**.

Although no polymerisation was achieved in toluene, all complexes proved active upon using propylene oxide (PO) as the solvent. MALDI-ToF analysis of the polymers revealed chain terminations compatible with chloropropanol moieties, suggesting that the catalyst activation proceeds by ring-opening of the epoxide affording a Fe-alkoxide species. Remarkably, the presence of poly(propylene oxide) blocks was not observed, indicating that, aside from the activation step, the epoxide remains completely unreacted. This was in striking contrast with the reactivity observed with analogues Al-complexes. In addition, the Fe-compounds proved better performing than Al-systems with similar structures. This was accounted for by a stronger donor property of the Fe(III) centre. The activity of **Fe9** was higher than that of **Fe8**, possibly because of the greater flexibility of the  $C_3$  bridging unit. On the other hand, all polymers exhibited comparable  $M_n$  and  $D$ . The unsubstituted complex **Fe11** exhibited the lowest activity, while the presence of an electron-withdrawing substituent in **Fe14–15** determined an improvement of the catalytic performance due to the reduced electronic density around the metal centre. In turn, *tert*-Bu substituted complexes **Fe12–13** allowed for narrow polydispersity and moderate  $M_n$  (1.13 and 10.5 kDa, respectively). The obtained PLAs were somewhat isotactic ( $0.68 < P_m < 0.78$ ) or heterotactic depending on the ligand structure. In particular, hindered aromatic moieties granted higher isotacticity. Extensive mechanistic studies indicated that the stereoselectivity of *r*-LA polymerisation proceeds according to a chain-end control mechanism.

Along with linear polyesters, polymers with cyclic structures are attractive materials due to their interesting properties and absence of terminations [48]. Although relevant examples are present in the literature [49–51] the synthesis of cyclic polyesters remains challenging. For example, Sn-based species allowed for the synthesis of cyclic poly(L-lactide) (*c*PLA) displaying  $M_n$  as high as 31 kDa, albeit with very broad dispersity ( $D > 6$ ) [52,53]. Remarkably, the industrial catalyst  $\text{Sn}(\text{Oct})_2$  also proved to produce *c*PLA with good activity under specific conditions [54].

In this scenario, Capacchione and co-workers showed that the bis-thioether-bis-phenolate [OSSO]-type Fe(III) complex **Fe16** (Figure 5) is capable of producing *c*PLA at 80 °C with LA:Fe ratios as high as 10,000 in either PO or cyclohexene oxide (CHO) as the solvent [55]. Moreover, in this case, the epoxide acted as the co-activator of the polymerisation. In fact, the first step of the mechanism was proposed to be the activation of the epoxide by the Fe-catalyst, as previously observed with the same system [56,57]. The  $M_n$ 's of the polymers were as high as 6.4 kDa with rather narrow dispersity ( $1.16 < D < 1.45$ ). Interestingly, kinetic investigations indicated a zero-order dependence on the monomer concentration. The complex was also capable of affording cyclic poly( $\epsilon$ -caprolactone) (*c*PCL) and cyclic poly( $\beta$ -butyrolactone) (*c*PBL).



**Figure 5.** Fe-complex **Fe16**, and Ce-complexes **Ce1–2** affording cyclic polyesters.

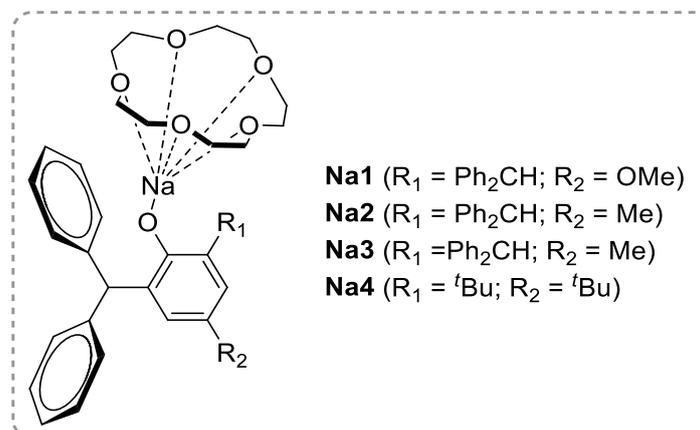
Lately, Williams, Arnold et al. reported on the synthesis of *c*PLA promoted by N-heterocyclic carbene (NHC) Ce(III) complexes (**Ce1–2**, Figure 5) [58].

Complex **Ce2**, bearing a saturated NHC backbone, proved more active than its unsaturated congener **Ce1**. Nevertheless, both complexes exhibited high polymerisation rates at very low catalyst loading (200 ppm), allowing for the isolation of *c*PLA displaying  $M_n$  up to 250 kDa and rather narrow polydispersity ( $\mathcal{D} = 1.59$ ). In addition, CL and BL were also successfully converted into cyclic polyesters. Interestingly, linear polymers could be obtained upon introducing exogenous alcohol (*i*PrOH), albeit with a lack of control and lower  $M_n$  (73 kDa)

Homo- and hetero-multimetallic complexes have often exhibited higher activities in the ROP of LA and CL when compared to their monometallic counterparts [59,60]. Such difference is thought to arise from cooperative effects between the different metal centres. A comprehensive overview of such systems has been recently reported by Garden and Gruszka [61].

Polyesters derived from the homo/copolymerisation of larger lactones (i.e.,  $\omega$ -pentadecalactone, PDL), have been proposed as viable biodegradable alternatives to polyolefins. Indeed, the mechanical and thermal properties of poly(pentadecalactone) (PPDL) were found to be comparable to that of low-density polyethylene (LDPE) [62]. As for LA and CL, most of the catalytic systems employed in the ROP of PDL are based on Al- [63], Zn- [64], and Mg-complexes [65,66].

Very recently, a family of sodium complexes bearing a dibenzhydryl-substituted phenoxide and 15-crown-5-ether ligands exhibited interesting activity in the ROP of PDL (**Na1–4**, Figure 6) [67].



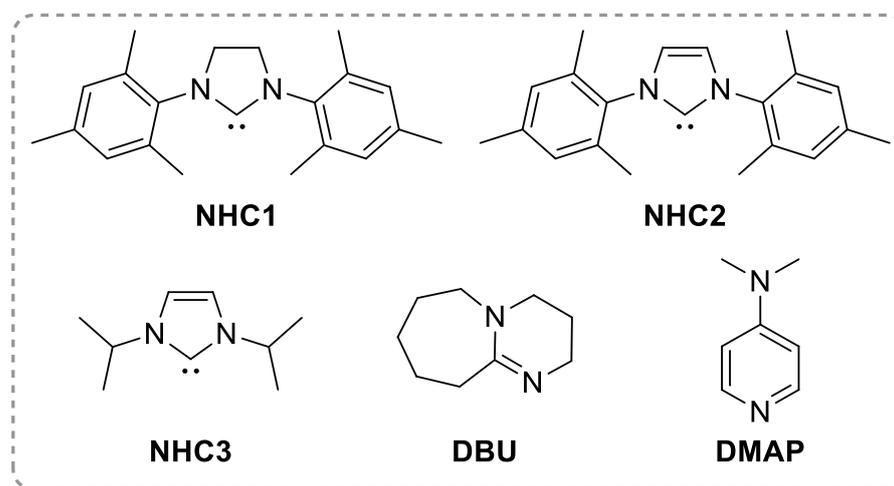
**Figure 6.** Sodium complexes **Na1–4** active in the ROP of  $\omega$ -pentadecalactone.

Such systems allowed for a complete conversion of 100 equiv. of monomer within 5 h in the presence benzhydrol as co-activator. In terms of catalytic activity, all complexes proved equally performing, affording polymers with  $M_n$  as high as 50 kDa and polydispersity values spanning from 1.69 to 2.57. The size of the crown-ether cavity was thought to allow only for the polymer chain growth, inhibiting undesired transesterification processes.

With respect to organocatalyzed routes, phosphazane superbases proved viable ROP promoters [68,69]. Indeed, PPDL having  $M_n$  matching the theoretical values has been obtained with moderate to good conversions even at room temperature in the presence of exogeneous alcohol (BnOH) as the co-activator. Interestingly, the melting temperatures of the polymers (spanning from 90 to 93 °C) were found close to that of liner PE.

A dual catalyst approach involving an organic base in combination with a Lewis acid has been developed by Dove et al. [70]. In this case, N-heterocyclic carbenes (NHC1–3), 1,8-diazabicycloundec-7-ene (DBU) and 4-dimethylaminopyridine (DMAP) were selected as the bases (Figure 7), while  $MgX_2$  ( $X = Cl, Br, I$ ),  $FeCl_3$ ,  $ZnCl_2$ ,  $B(Ph)_3$ ,  $Bi(OTf)_3$ ,  $YCl_3$  and  $AlCl_3$  were employed as the Lewis acids. For the latter, the activity order was found to be  $Mg > Y > Al$ , while the other species proved completely unreactive. Such trend was tentatively explained considering the moderate solubility of such reactants in the reaction medium (toluene); nevertheless, the occurrence of processes leading to the saturation of the electronic vacancy of the Lewis acid in competition with monomer coordination was not excluded. In turn,  $MgI_2$  proved more active than its bromide- and chloride analogues, allegedly because of its cationic character resulting from the dissociation of one iodine ligand.

Concerning the organic base different NHCs, in combination with  $MgX_2$ , allowed for similar reaction rates and monomer conversions. Nevertheless, the use of the more donating carbene NHC3 led to a broadening of the molecular weight distribution, indicating a lack of control. Finally, the combination of  $MgI_2$  and DBU exhibited the highest catalytic activity, allowing for a complete conversion of 200 equiv. of PDL within 30 min at 110 °C in the presence of BnOH as the co-activator, affording a polymer having  $M_n$  and  $\bar{D}$  of 71 kDa and 1.80, respectively.

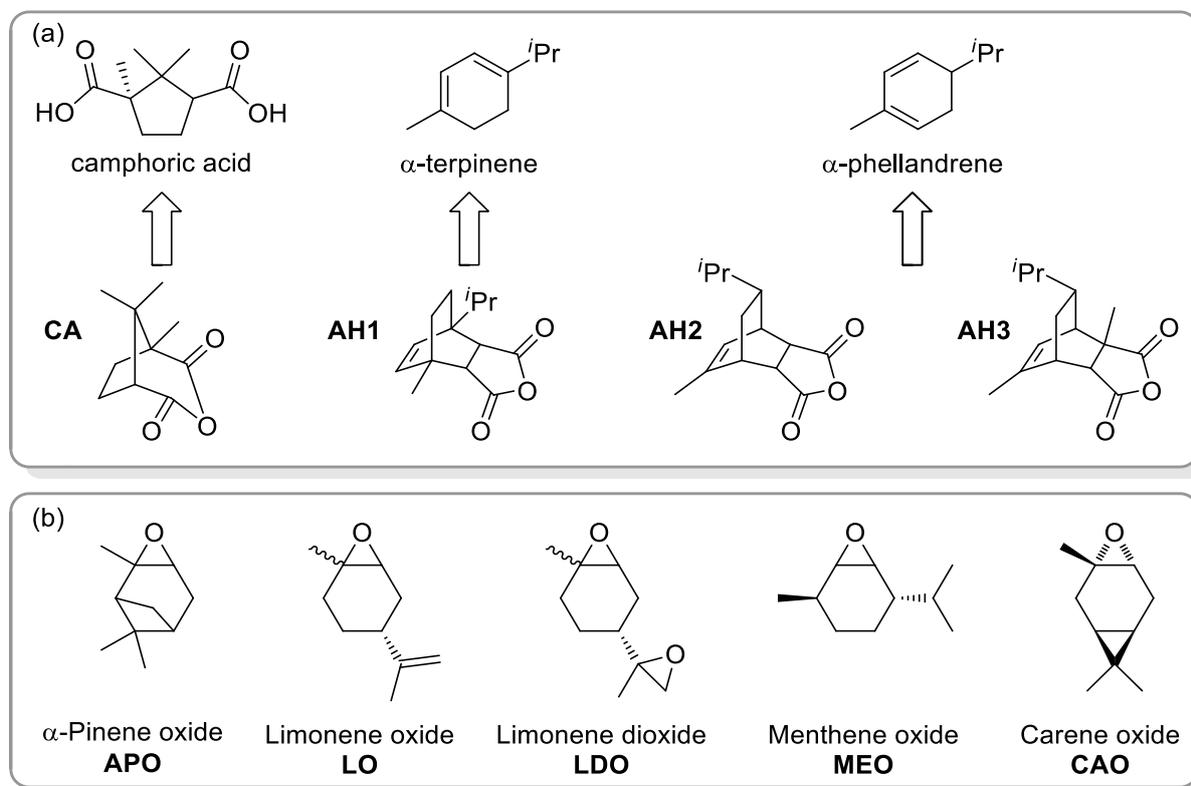


**Figure 7.** Organic bases used in the dual catalyst approach proposed for the ROP of lactones.

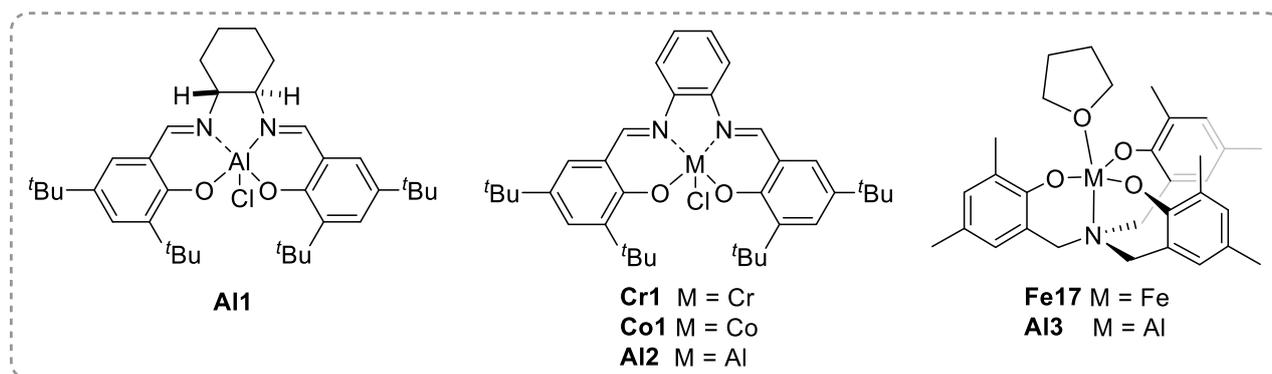
## 2.2. Polyesters from ROCOP of Epoxides and Cyclic Anhydrides

The ROCOP of epoxides and cyclic anhydrides is another effective approach to access polyesters [20,71]. Aside from benchmark monomers such as propylene oxide (PO), cyclohexene oxide (CHO) and phthalic anhydride (PA), terpene-anhydrides and epoxides have been gaining increasing attention (Figure 8). An example of fully terpene-based polyester was reported by Thomas et al. in 2011 [72]. Indeed, the ROCOP of camphoric anhydride (CA) and limonene oxide (LO) was achieved in the presence of Al-salen complex

**AI1** (Figure 9). Attempts to post-functionalize the polymer by olefin cross-metathesis were unsuccessful [73].



**Figure 8.** Terpene-based anhydrides (a) and epoxides (b).



**Figure 9.** Complexes employed in the ROCOP of epoxides and anhydrides.

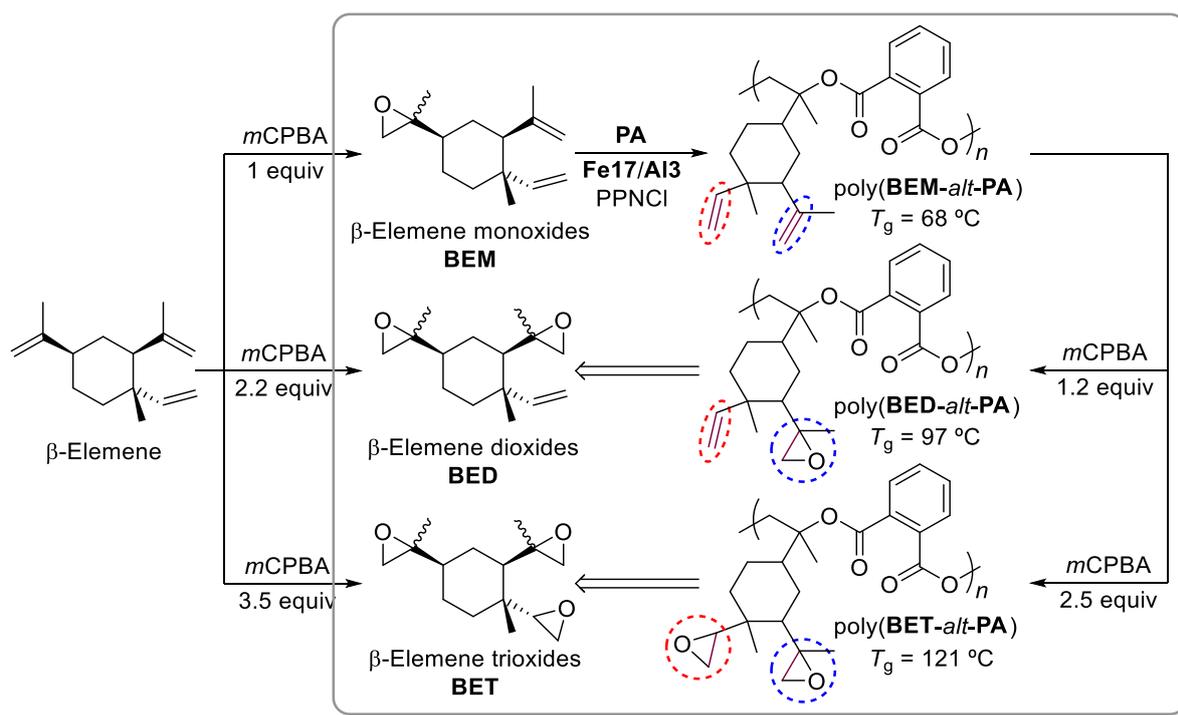
Tricyclic anhydrides **AH1** and **AH2**, derived from  $\alpha$ -pinene and  $\alpha$ -phellandrene, respectively, have been employed in the ROCOP with PO to afford polyesters exhibiting high  $T_g$  [74]. Catalysts investigated in such a study were Cr-, Co- and Al-complexes bearing a salen scaffold (Figure 9). Improved thermal properties (higher  $T_g$  values) have been achieved upon replacing PO with a more rigid epoxide such as CHO [75]. Reports concerning the use of terpene-derived epoxides (i.e., **APO**, **LO**, Figure 8b) remain scant since their reactivity is generally hampered by steric congestion.

Early examples of **LO** copolymerisation with phthalic anhydride catalysed by **Cr1** required high temperatures [76]. In turn, the use of the Fe-aminotriphenolate complex **Fe17** allowed for the copolymerisation of PA with various terpene-derived epoxides (Figure 8b) under mild reaction conditions, both in solution and in bulk [77].

In 2020, Della Monica and Kleij reported the ROCOP of new terpene-based epoxides obtained from  $\beta$ -elemene in the synthesis of highly functional semi-aromatic polyesters (Figure 10) [78]. This terpene, naturally occurring in citrus fruit, is usually extracted from ginger root and demonstrated to have anticancer activity [79]. Thanks to the different reactivity of the double bonds in  $\beta$ -elemene, it was possible to obtain the corresponding mono-, di- and tri-epoxides (**BEM**, **BED**, and **BET** respectively). In particular, **BEM** was obtained as a regio-isomers mixture in a 7:3 composition. Copolymerisation of **BEM** with PA was investigated using complexes **Fe17** and **Al3**, activated by (triphenylphosphine)-iminium chloride (PPNCl), obtaining poly(**BEM-alt-PA**) with  $3.5 \leq M_n \leq 8$  kDa and  $1.13 \leq \mathcal{D} \leq 1.28$ .

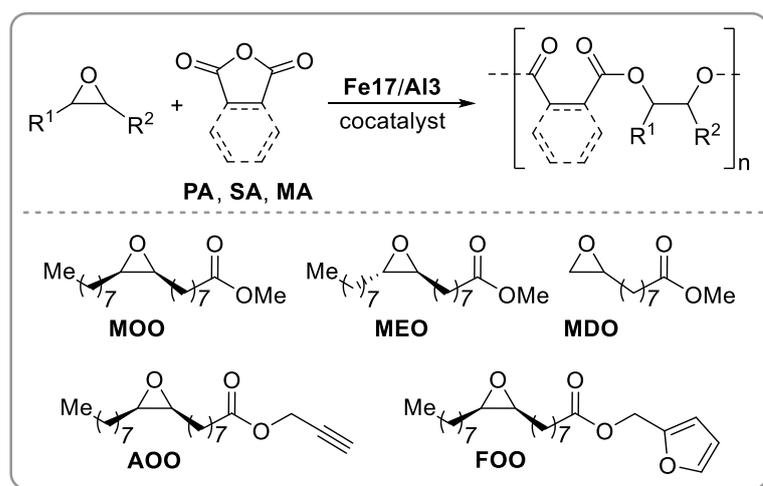
The functional polyester poly(**BEM-alt-PA**), bearing two pendant double bonds with different reactivity, was subject to post-functionalization via epoxidation, obtaining the corresponding poly(**BED-alt-PA**) and poly(**BET-alt-PA**) that cannot be prepared by direct reaction of **BED** or **BET** (Figure 9). Indeed, ROCOP of **BED** with PA was also performed under conditions similar to **BEM**, but an insoluble, crosslinked polyester was obtained, with a  $T_g$  of 125 °C. Notably, the post-synthetic epoxidation affects the thermal properties, with the  $T_g$  raising from 68 to 121 °C.

Fatty acids represent a highly attractive renewable feedstock for chemical industries [80] and became interesting also for the development of sustainable polymers [81,82]. For example, an efficient approach is the valorisation of epoxidized-products derived from fatty acids [83–85].



**Figure 10.** Synthesis of  $\beta$ -elemene-based epoxides, corresponding functional semi-aromatic polyester poly(**BEM-alt-PA**), and its post-modification.

In this regard, very recently the ROCOP of epoxidized fatty acids esters for the synthesis of functional polyesters was also described [86]. First, copolymerisation of methyl oleate oxide (**MOO**) with PA was investigated, using combinations of **Fe17** and **Al3** with PPNCl and DMAP as the catalytic system, obtaining polyesters with  $4 \leq M_n \leq 12$  kDa and  $1.15 \leq \mathcal{D} \leq 1.19$ . Notably, the reaction was also possible using **MOO** based on oleic acid obtained from food industry waste. Structurally different polyesters were obtained starting from various epoxides/cyclic anhydrides combinations (Figure 11), and the flexible nature of the pendant side-chains resulted in materials with  $-45 \leq T_g \leq -5$  °C.

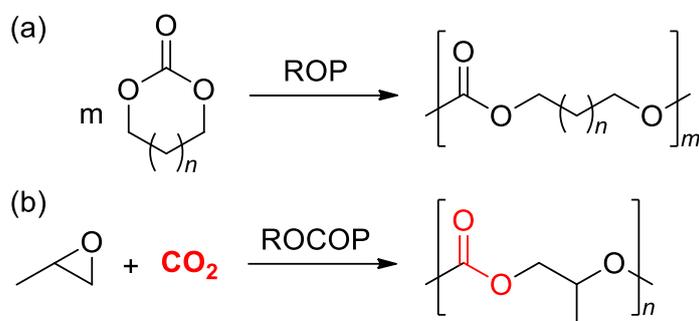


**Figure 11.** Fatty acid-based epoxides, and synthesis of corresponding functional polyesters.

In addition, two different methods were used for the creation of thermally stable, and thermo-reversible cross-linking networks. In the first case, the polymer based on allyl oleate oxide (**AOO**) was reacted with a bis-azide via Cu(I)-catalyzed azide–alkyne cycloaddition, obtaining an insoluble material with  $T_g$  of 37 °C, higher than that of the pristine polyester ( $T_g = -22$  °C). In the second case, the polymer based on furfuryl oleate oxide (**FOO**) was reacted with bis-maleimide in Diels-Alder (DA) reaction. In this case, the crosslinked polyester also showed an increase in  $T_g$  (from  $-19$  to 95 °C), however thermal curing at 160 °C for 16 h induced a retro-DA reaction giving PE with the same properties as the original sample.

### 3. Polycarbonates

Polycarbonates (PCs) are classified into aromatic PCs and aliphatic PCs. Commercial aromatic PCs are known as BPA-PCs, based on bis-phenol A (BPA) structural motif. In recent years, concern has arisen regarding BPA-PC because it degrades under environmental temperature and normal pH, releasing BPA which is known to act as an endocrine disruptor [87]. In addition, industrial PC production relies on the use of highly toxic phosgene. On the contrary, aliphatic PCs seem to represent a more sustainable alternative, due to their general biodegradability and biocompatibility [88,89]. However, most common aliphatic PCs, such as poly(propylene carbonate), suffer from scarce material properties limiting their possible applications [90]. In this context, the successful synthesis of aliphatic polycarbonates achieved either via direct ROP of cyclic carbonates (CCs) or ROCOP of epoxides and carbon dioxide is highly attractive (Scheme 2) [17–22,91,92].



**Scheme 2.** Polycarbonates synthesis via ring-opening of cyclic carbonates (a) and ring-opening copolymerisation of carbon dioxide and epoxides (b).

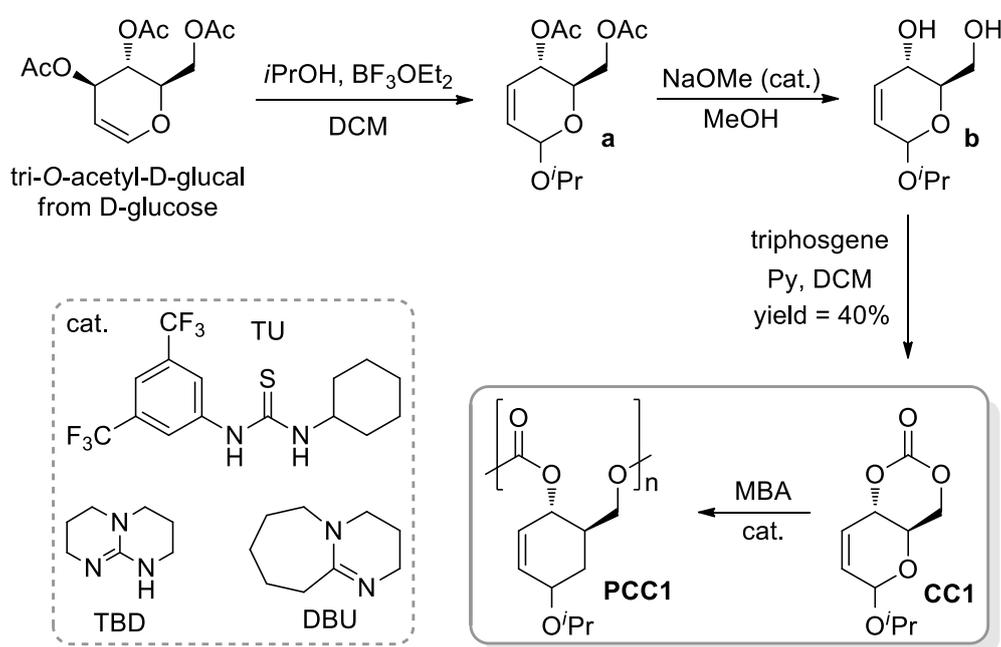
Notwithstanding these methods are highly attractive, they both present some critical aspects to be considered when designing new monomers. In the case of CCs, it is important

to notice that not all CCs can be polymerised, and the success of the reaction often depends on ring-size, substitution pattern and stereochemistry of the monomer. For example, it is well known that the *trans*-form of cyclohexene carbonate can be polymerised while the *cis*-isomer is inert toward polymerisation [93,94]. In the case of ROCOP, the epoxide nature also plays an important role in directing the reaction toward the formation of PC or CC [95]. In addition, the search for catalytic systems based on sustainable metals is still highly active since the most active systems producing PCs are based on metals such as Co and Cr. Hence, in this section, we divide the description of sustainable PCs into those obtained from bio-based CCs and those obtained from bio-based epoxides.

### 3.1. ROP of Cyclic Carbonates

The synthesis of bio-based cyclic carbonates for application in ROP is largely based on sugars, which are converted into cyclic carbonates thanks to the presence of multiple hydroxyl groups. Thanks to their large availability and biocompatibility, carbohydrates represent one of the more attractive feedstocks in sustainable polymer chemistry [96]. Indeed, they combine a wide structural diversity with the presence of oxygenated functional groups, ideally offering the possibility to design materials with enhanced material properties and biodegradability. In the last years, the research groups of Wooley and Buchard reported the synthesis of several sugar-based CC monomers for PC synthesis. Bicyclic and tricyclic structures were obtained, containing cyclic carbonates moieties with both *cis*- and *trans*-configuration. This results in good reactivity of such sugar-based monomers, which can be polymerised in the presence of simple organocatalysts.

In 2017, the multistep synthesis of D-glucose-based monomer **CC1** was described (Figure 12) [97].

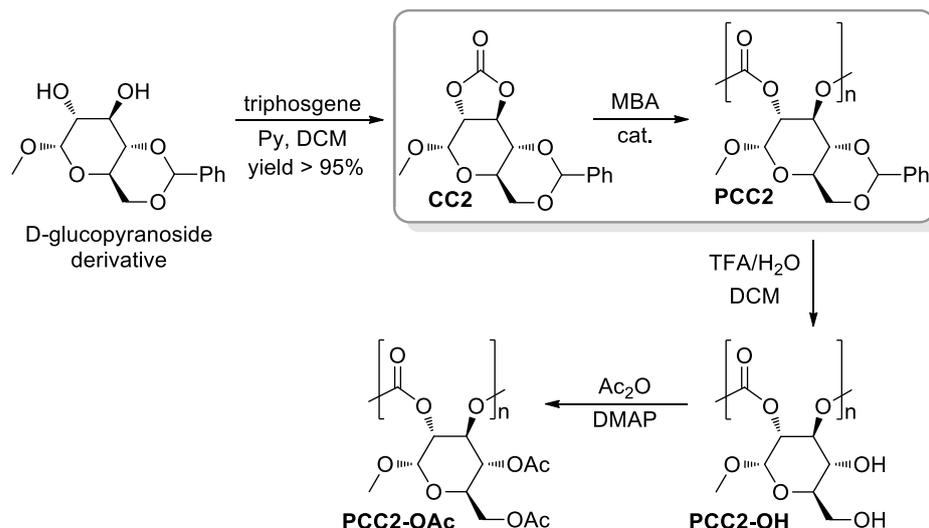


**Figure 12.** Synthesis of D-glucose-based monomer **CC1** and corresponding polycarbonate **PCC1**. Organo-catalysts structures are also shown for clarity.

The procedure involves the Ferrier rearrangement of starting tri-O-acetyl-D-glucal to yield intermediate **a**, followed by deprotection of the alcohol groups. Finally, the 1,3-diol **b** was converted into the desired monomer **CC1** using triphosgene in the presence of pyridine. The corresponding polycarbonate **PCC1** was successfully obtained via ROP of **CC1** by using 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1-(3,5-bis-(trifluoromethyl)-phenyl)-3-cyclohexyl-2-thiourea (TU) in the presence of 4-methylbenzyl alcohol (MBA) as the initiator. Almost complete conversion was achieved

in short times (1–10 min) with all the catalysts, obtaining the highest  $M_n$  of about 10 kDa with TBD. However, bimodal molecular weights distribution was observed in this case, probably due to *trans*-carbonation side-reaction. The **PCC1** shows a relatively high  $T_g$  of about 69 °C, likely due to the presence of a rigid six-membered ring. Interestingly, this sugar-based polymer presents a double-bond that could be further used in post-synthetic transformations.

Soon after, direct synthesis of the five-membered cyclic carbonate monomer **CC2** was described by reaction of a commercially available D-glucopyranoside derivative with the same procedure reported for **CC1**, but a very high yield (95%) was obtained in this case (Figure 13) [98].

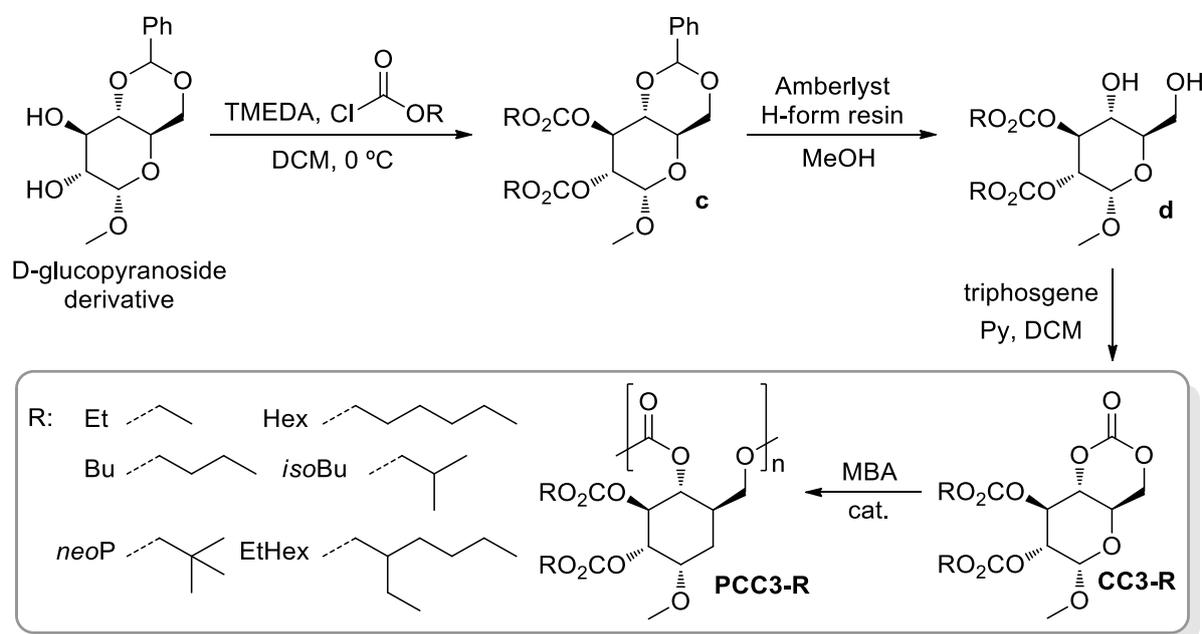


**Figure 13.** Synthesis of D-glucose-based monomer **CC2** and corresponding polycarbonate **PCC2**, followed by post-functionalization toward hydroxylated- and acetate-polycarbonates **PCC2-OH** and **PCC2-OAc**, respectively.

It is important to note that, in general, five-membered CCs do not react under ROP catalytic conditions. On the contrary, in this case, the combination of *trans* stereochemistry with the presence of fused rings provided enough ring-strain for a successful ROP. Indeed, polycarbonate **PCC2** was readily obtained under conditions similar to **PCC1**. However, a longer reaction time of 5 h was needed and  $M_n$  in the range of 3–6 kDa were obtained. Interestingly, **PCC2** was modified by post-synthetic reactions. Indeed, removing the benzylidene protecting groups under acidic conditions led to the formation of hydroxy-functionalized **PCC2-OH**, which was further converted into the acyl protected **PCC2-OAc** using acetic anhydride. Measurement of water contact angle revealed, as expected, that the hydroxy-functionalized polycarbonate **PCC2-OH** is significantly more hydrophilic ( $38^\circ \leq \text{contact angle} \leq 58^\circ$ ) than the protected polycarbonates ( $94^\circ \leq \text{contact angle} \leq 128^\circ$ ).

More recently, the synthesis of a series of differently substituted six-membered CCs (**CC3-R**, Figure 14) was described, starting from the same glucopyranose derivative used for the preparation of **CC2** [99]. In this case, the initial hydroxyl groups were converted into linear carbonates **c** by reaction with various chloroformates. Removal of benzylidene acetal protecting group, forming 1,3-diols **d**, followed by cyclic carbonate formation with triphosgene yield the desired **CC3-R** monomers. The ROP of **CC3-R** led to the formation of the corresponding **PCC-R** polycarbonates with narrow distributions ( $1.04 \leq D \leq 1.06$ ) and similar molecular weights ( $15 \leq M_n \leq 16$  kDa). Remarkably, the presence of structurally different substituents resulted in the fine-tuning of  $T_g$  in a wide thermal window, from 38 to 125 °C. Very interestingly, the authors were able to analyse the relationship between  $T_g$  and molecular weight for two selected polycarbonates, **PCC-neoP** and **PCC-EtHex**. In detail, the analysis was conducted at the level of discrete oligomers (from monomers to

tetramers) and polymers with a polymerisation degree from 10 to 40, finding that the variation of  $T_g$  with  $M_n$  is very well described by the Flory-Fox theory [100].

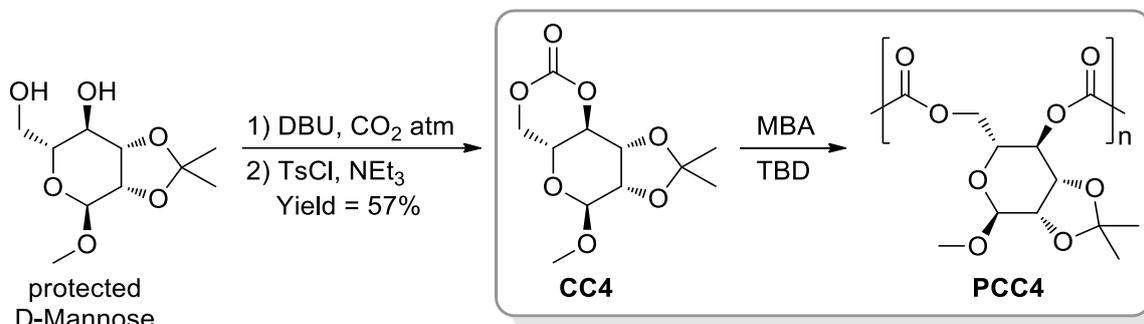


**Figure 14.** Synthesis of D-glucose-based monomer **CC3-R** and corresponding polycarbonate **PCC3-R**.

Notably, the same research group analysed the regio-chemistry of **CC3-R** ROP, combining NMR analyses and DFT investigations, finding that the presence of carbonate pendant groups is crucial for the formation of regio-regular polymers [101]. Indeed, analogous monomers bearing ether pendant groups were also polymerized but in a regio-irregular fashion, and the pendant carbonate moieties seem to be involved in the stabilization of the transition state via intermolecular hydrogen-bonding with TBD.

All the examples of sugar-based CCs described so far demonstrated the high potential of this class of monomers but, unfortunately, their preparation is based on the use of phosgene derivatives. Consequently, the search for more sustainable reaction procedures for the synthesis of structurally complex cyclic carbonates is a topic of high interest [83]. In this regard, Buchard's research group reported a new method for the synthesis of six-membered CCs from diols, using carbon dioxide, an organic base, and tosyl chloride (TsCl) [102,103]. This procedure was successfully applied for the synthesis of sugar-based cyclic carbonate monomers.

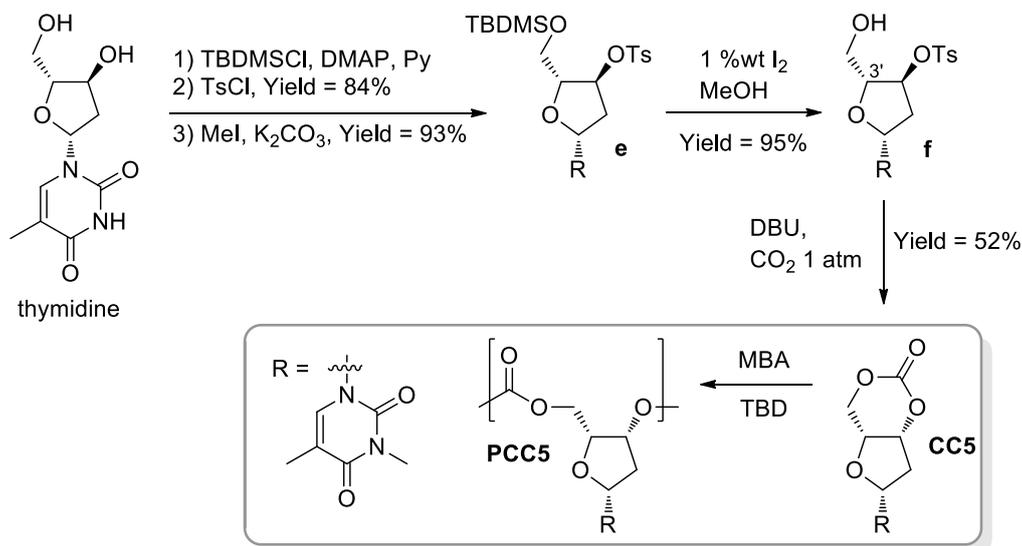
In 2016, the synthesis of D-mannose-based monomer **CC4** was described, and its structure was also confirmed by X-ray analysis (Figure 15) [104].



**Figure 15.** Synthesis of D-mannose-based monomer **CC4** and corresponding polycarbonate **PCC4**.

As previously described, also in this case the *trans*-stereochemistry and the presence of a fused tricyclic structure resulted in a good reactivity of **CC4** in the organocatalytic ROP promoted by TBD. The resulting **PCC4** was obtained with  $M_n$  in the range 6–33 kDa and with narrow distributions ( $1.10 \leq \bar{D} \leq 1.19$ ). However, using **CC4**/TBD ratio higher than 150 and reaching  $M_n > 15$  kDa, back-biting of the polymer chain forming smaller cyclic species was observed, supported by MALDI analysis. Notably, the ROP of **CC4** proceeds in a regioselective manner probably due to the steric hindrance of the 2,3-O-isopropylidene protecting group. In addition, **PCC4** exhibits a high  $T_g$  of 152 °C likely due to the rigidity of its structure. Deprotection of the 1,2-hydroxyl groups was also explored, and it was possible to remove 70% of protecting groups by treating with  $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$  mixture.

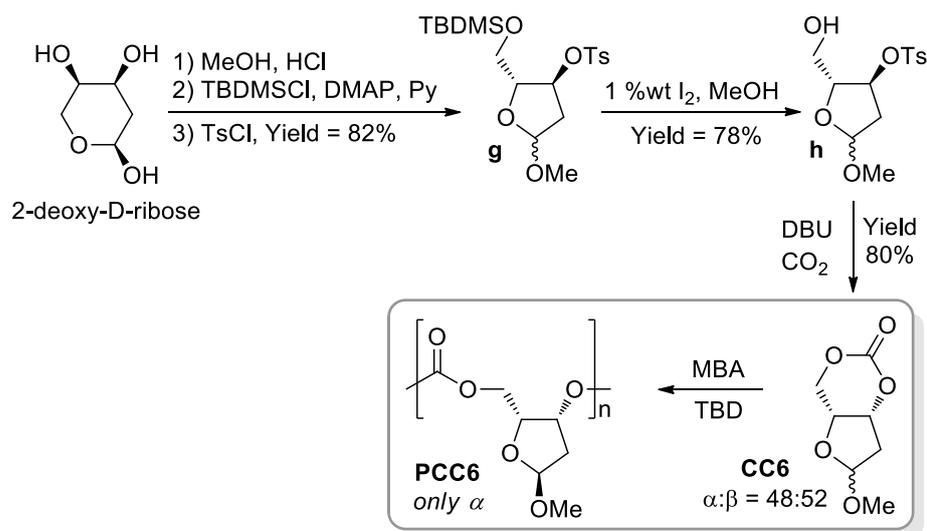
Later, the same group investigated the use of thymidine in polycarbonate synthesis [105]. Attempts to obtain a cyclic carbonate monomer using both phosgene-reagents and the  $\text{CO}_2$  method described before were unsuccessful. This result was attributed to the high strain of the thymidine-base carbonate in the *trans*-configuration. Interestingly, a different multistep approach was adopted involving the protection of the secondary alcohol moiety with a tosyl group, followed by an  $\text{S}_{\text{N}}2$ -type intramolecular reaction that, by involving the stereochemistry inversion in a 3' position, yielded the desired **CC5** monomer (Figure 16).



**Figure 16.** Synthesis of thymidine-based monomer **CC5** and corresponding polycarbonate **PCC5**.

The ROP of **CC5** to obtain the corresponding **PCC5** was achieved in the presence of TBD, and the polymerisation proceeds until the establishment of the monomer–polymer equilibrium (e.g., 80% conversion at 25 °C), so the temperature dependence of the equilibrium was studied, and the polymerisation thermodynamic parameters determined equal to  $\Delta H_p = -12.3 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta S_p = -29 \pm 1.1 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ . As for the case of **CC4**, back-biting of the polymer chain was observed, however  $M_n$  up to 17 kDa with  $\bar{D} = 1.3$  were obtained. The hydrolytic stability of **PCC5** was also investigated and, while stable in 1 M HCl for one week, the polymer hydrolyses in 1 M NaOH in 4 h to the *cis*-diol of 3-N-methyl thymidine. A cell attachment study was conducted with a human osteoblast cancer cell line (MG-63) to explore the possibility to use **PCC5** as a tissue engineering scaffold indicating promising results, but further structural modifications are needed to obtain better results.

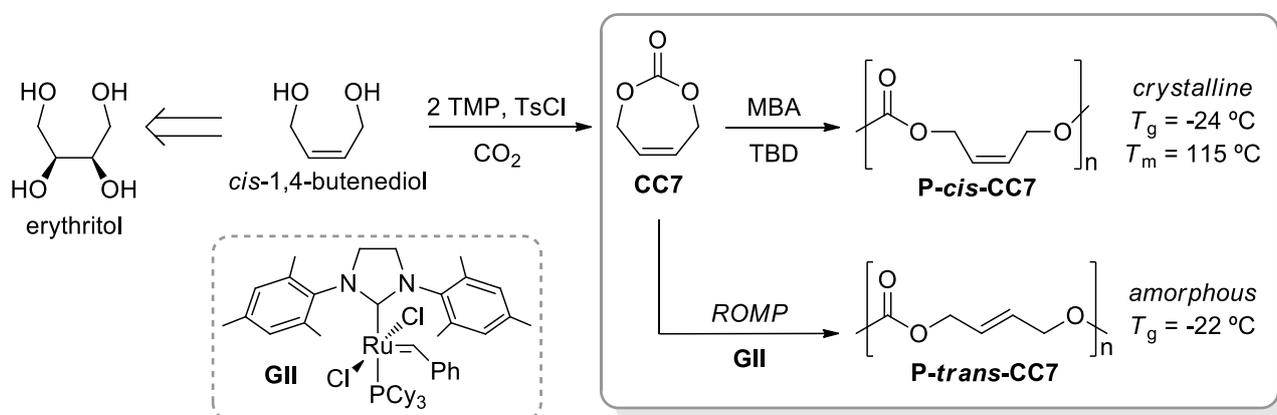
Soon after, the synthesis of 2-deoxy-D-ribose-based monomer **CC6** was reported with a procedure similar to that used for monomer **CC5** [106]. Using this method, the desired carbonate was obtained in 80% yield in the two  $\alpha$  and  $\beta$  anomeric forms (Figure 17).



**Figure 17.** Synthesis of 2-deoxy-D-ribose-based monomer **CC6** and corresponding polycarbonate **PCC6**.

Polymerisation studies conducted with TBD as the catalyst revealed that only the  $\alpha$ -form of **CC6** is susceptible to ROP, yielding the insoluble polycarbonate **PCC6** with  $M_n$  as high as 26 kDa, while the  $\beta$ -form cannot polymerise. This difference was rationalized by DFT investigations, finding that the overall thermodynamics of  $\beta$ -**CC6** ROP is unfavourable ( $\Delta\Delta G = +1.4/+2.0 \text{ kcal} \cdot \text{mol}^{-1}$ ) compared with that of  $\alpha$ -**CC6** ( $\Delta\Delta G = -0.9 \text{ to } -1.9 \text{ kcal} \cdot \text{mol}^{-1}$ ). MALDI analyses of **PCC6** revealed the presence of cyclic species in high concentrations ( $\approx 50\%$ ). Copolymerisation of **CC6** with trimethylene carbonate (TMC) was investigated, obtaining random copolymers with **CC6**:TMC composition from 93:7 to 14:86,  $43 \leq M_n \leq 57 \text{ kDa}$  and  $1.37 \leq D \leq 1.35$ . The poly(**CC6-co-TMC**) copolymers showed  $T_g$  values comprised between those of **PCC6** and **PTMC** homopolymers (58 and  $-25 \text{ }^\circ\text{C}$ , respectively), depending on composition in agreement with the Fox equation.

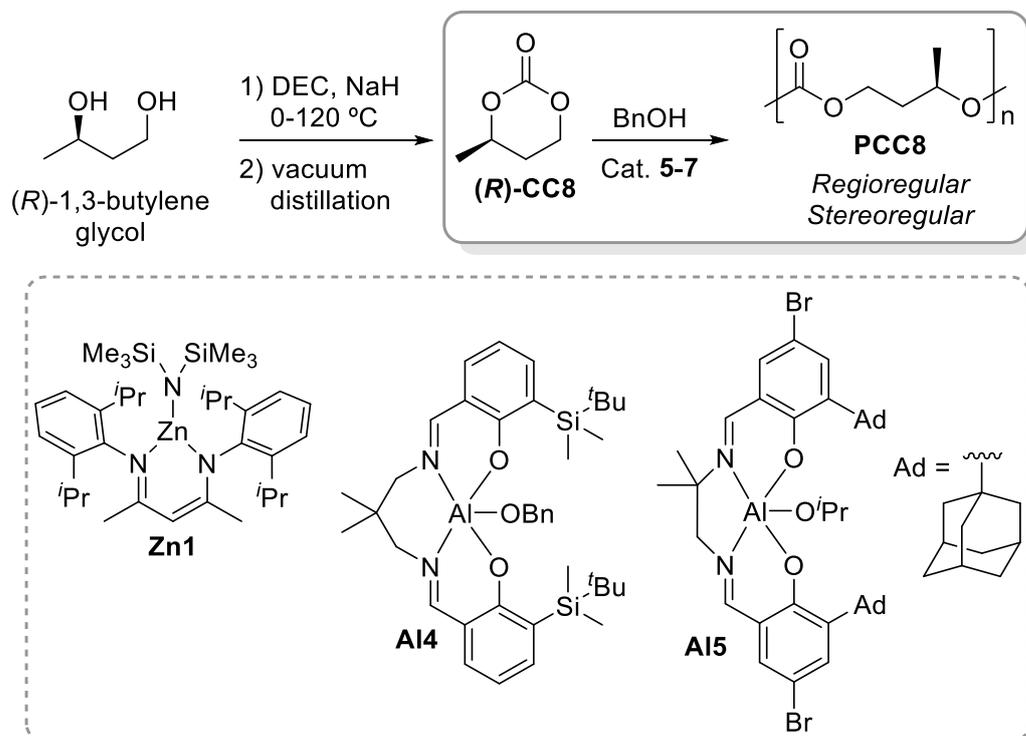
In 2019, Buchard et al. demonstrated that monomer **CC7**, prepared from glucose-derived erythritol, can be used in two different stereoselective polymerisation processes (Figure 18) [107]. In the case of TBD-mediated ROP, the original stereochemistry of the double bond is retained, yielding **P-cis-CC7**. In contrast, the ring-opening metathesis polymerisation (ROMP) performed with the Grubbs second-generation catalyst (**GII**, Figure 17) inverts the original stereochemistry, producing **P-trans-CC7** with stereoselectivity up to 95%.



**Figure 18.** Synthesis of erythritol based monomer **CC7** and corresponding polycarbonates **P-cis-CC7** and **P-trans-CC7**.

The two polymers have different material properties, indeed **P-trans-CC7** is a soft amorphous material ( $T_g = -22\text{ }^\circ\text{C}$ ) while **P-cis-CC7** is a hard, semicrystalline material ( $T_g = -24\text{ }^\circ\text{C}$ ;  $T_m = 115\text{ }^\circ\text{C}$ ).

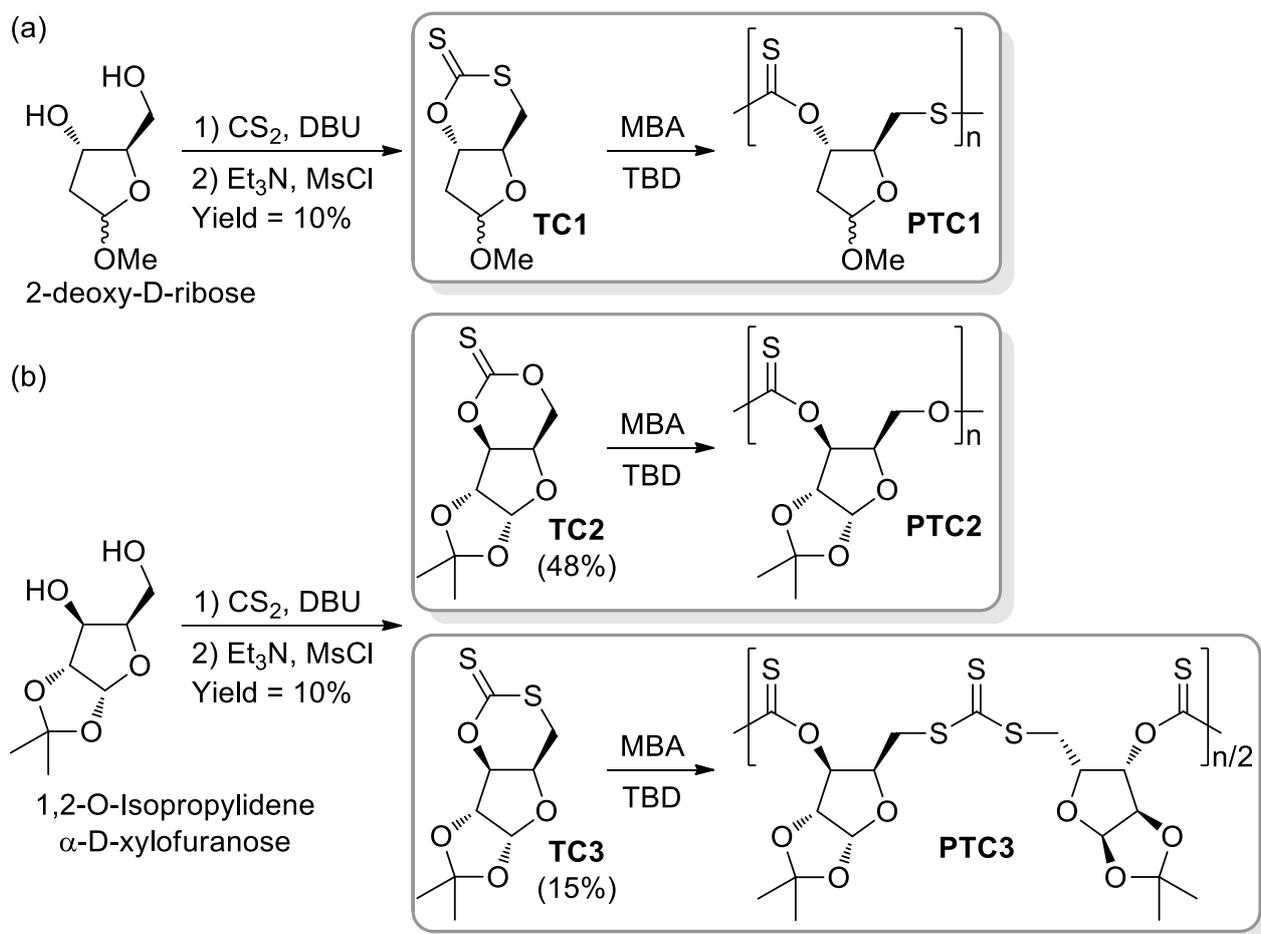
Another interesting sugar-based precursor is represented by (*R*)-(-)-1,3-butanediol, obtained via glucose fermentation with very high stereoselectivity [108]. Recently Hillmyer et al. reported the preparation of carbonate monomer (*R*)-**CC8**, based on (*R*)-(-)-1,3-butanediol, and its ROP toward polycarbonate **PCC8** (Figure 19) [109].



**Figure 19.** Synthesis of bio-1,3-butylene glycol-based monomer **CC8** and corresponding polycarbonate **PCC8**. Structures of catalysts **Zn1**, **Al3** and **Al4** are also shown on the bottom.

The ROP of **CC8** was already reported before, however, only amorphous polycarbonates were obtained because of the scarce regiochemistry control [110,111], or the use of racemic monomer mixtures leading to atactic **PCC8** [112,113]. On the contrary, the polymerisation of (*R*)-**CC8** promoted by bulky Zn- $\beta$ -diiminate, and Al-salen complexes (**Zn1**, and **Al4–5**, Figure 18) proceeds with virtually perfect regioselectivity (99%) under operationally simple reaction conditions (bulk,  $70\text{ }^\circ\text{C}$ ), with  $M_n$  up to 150 kDa and  $D = 1.2$  in the case of **Al4**. The **PCC8** obtained in this way is semicrystalline, with a  $T_m = 73\text{ }^\circ\text{C}$ . Interestingly, an attempt to form a stereocomplex by mixing **PCC8** prepared from (*R*)- and (*S*)-**CC8** only resulted in a little enhancement with  $T_m = 80\text{ }^\circ\text{C}$ .

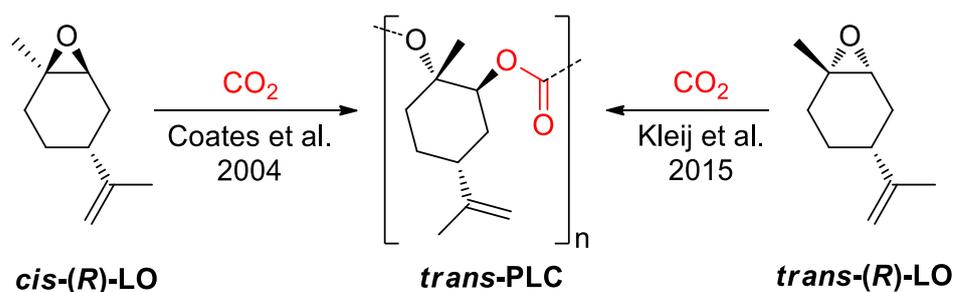
Replacing  $\text{CO}_2$  with  $\text{CS}_2$  in the DBU-based procedure described above discloses the access to structurally related thiocarbonate monomers **TC1–3**, derived from 2-deoxy-D-ribose or D-xylofuranose (Figure 20) [114]. Poly-thiocarbonates **PTC1–3**, were obtained by organocatalytic ROP of **TC1–3**, with  $3 \leq M_n \leq 31\text{ kDa}$  and  $1.3 \leq D \leq 2.2$ . The interest in these polycarbonate analogues is based on the observation that the substitution of some oxygen atoms with sulphur ones may result in the enhancement of certain material properties [115–117]. However, in this case, the  $T_g$  were similar to or lower than those of the corresponding sugar-based polycarbonates.



**Figure 20.** Synthesis of 2-deoxy-D-ribose-based monomer **TC1** (a), D-xylofuranose-based monomers **TC2** and **TC3** (b), and corresponding poly-thiocarbonates **PTC1**, **PTC2** and **PTC3**.

### 3.2. ROCOP of Carbon Dioxide and Oxiranes

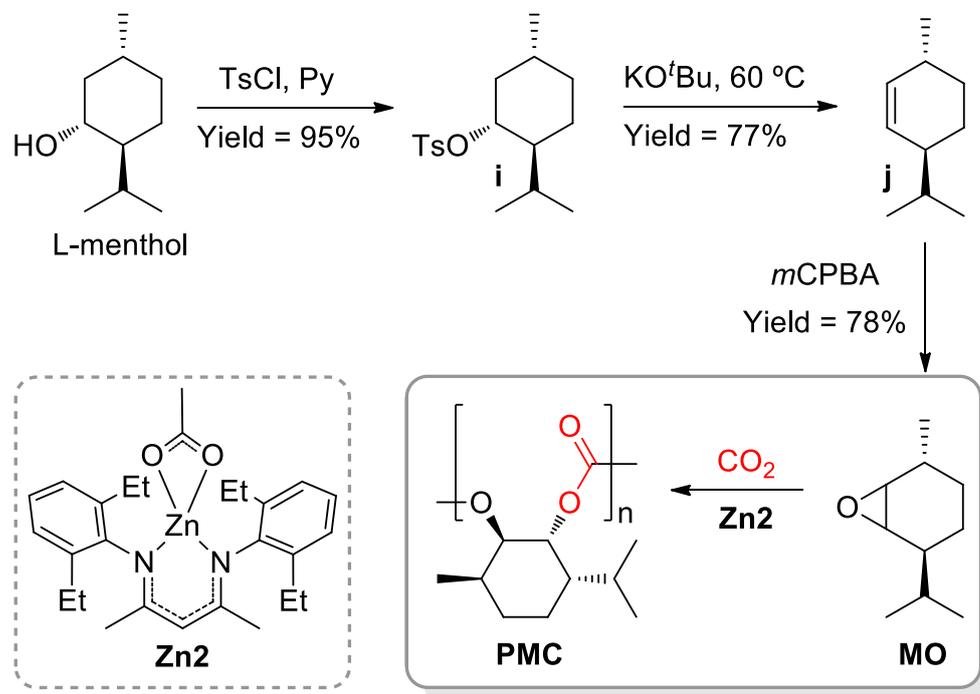
The sustainable synthesis of polycarbonates via the direct use of carbon dioxide involves the identification of suitable bio-based co-monomers. As mentioned in the introductory paragraph, not all oxiranes can be copolymerized with CO<sub>2</sub>, because of the preferential formation of the corresponding cyclic carbonates. Consequently, the use of bio-sourced epoxides is quite limited and an exemplary case is given by limonene oxide (**LO**) for which, to date, only two catalytic systems are known to promote the formation of the corresponding poly(limonene carbonate) (**PLC**) (Figure 21) [118,119]. This topic has been recently reviewed by some of us [6].



**Figure 21.** Conversion of the *cis*- and *trans*-forms of limonene oxide to poly(limonene carbonate).

However, in the last few years, some interesting cases of bio-based PC obtained from the ROCOP of CO<sub>2</sub> with properly designed monomers have been reported.

In 2020, Greiner et al. reported the synthesis of menth-2-ene oxide (**MO**) and its copolymerisation with CO<sub>2</sub> promoted by a zinc β-diiminato catalyst (**Zn2**), obtaining the new poly(menthane carbonate) **PMC** (Figure 22) [120].



**Figure 22.** Synthesis L-menthol-based epoxide **MO**, and corresponding polycarbonate **PMC**. Structure of catalyst **Zn2** is also shown.

The monomer was obtained starting from L-menthol, which was first converted to menth-2-ene **j**, and then epoxidized to the desired **MO** obtaining a mixture of the two possible stereoisomers in a 3:7 ratio. Using catalyst **Zn2**, copolymerisation of **MO** with CO<sub>2</sub> at 25 bar and 25 °C in toluene gave good results, yielding **PMC** with  $7 \leq M_n \leq 23$  kDa and  $1.11 \leq D \leq 1.23$ . Bulk polymerisation was also possible, but with a lower degree of control over the copolymerisation process obtaining bimodal molecular weights distributions. Importantly, both **MO** isomers were incorporated in **PMC**, as confirmed by NMR analyses of polycarbonate hydrolysis products. This is in contrast with the case of **Zn2**-promoted **LO**/CO<sub>2</sub> ROCOP where the *trans*-epoxide is preferentially converted. The **PMC** has a high  $T_g$  of 144 °C and did not show any crystallinity. However, this polycarbonate exhibits a particularly high decomposition temperature ( $T_d = 308$  °C) if compared with structurally related **PLC** ( $T_d = 229$  °C) prepared with the same catalyst.

Very recently, Wooley et al. described the use of a D-xylose derived oxetane in polycarbonate synthesis using an interesting dual-pathway approach [121]. First, the desired xylose oxetane (**XO**) was prepared via intramolecular cyclization of intermediate **I**, obtained from D-xylose as in Figure 23.

At this point, the first approach was based on the copolymerisation of **XO** and carbon dioxide promoted by the combination of Cr-salen complex **Cr2** with a suitable cocatalyst, which is known to catalyse this reaction for structurally related substrates (Figure 24) [122,123]. Under the best conditions (i.e., 140 °C, and 3 MPa of CO<sub>2</sub>), it was possible to obtain **PXC** with 80% selectivity,  $M_n = 7.4$  kDa, and  $D = 1.12$ . In parallel, the xylene carbonate **XC** is also formed during the reaction. In order to maximise the polycarbonate selectivity, a second approach was adopted based on the initial formation of **XC** followed by ROP (Figure 24). The cycloaddition reaction of CO<sub>2</sub> to **XO** was performed, using ZnI<sub>2</sub> and tetra-butylammonium iodide as the catalytic system, obtaining **XC** with 99% selectivity. Next, the ROP of **XC** catalysed by TBD in the presence of MBA gave **PXC** with  $M_n = 10$  kDa and  $D < 1.2$ . The polycarbonate obtained with the two different approaches has the same

structure and shows similar thermal behaviour ( $122 \leq T_g \leq 125 \text{ }^\circ\text{C}$ ). However, MALDI analyses showed that different chain-end groups are present depending on the approach employed. In the **XO**/ $\text{CO}_2$  ROCOP case, **PXC** was initiated with a halide group, while a 4-methylbenzyl group was observed in the case of **XC** ROP.

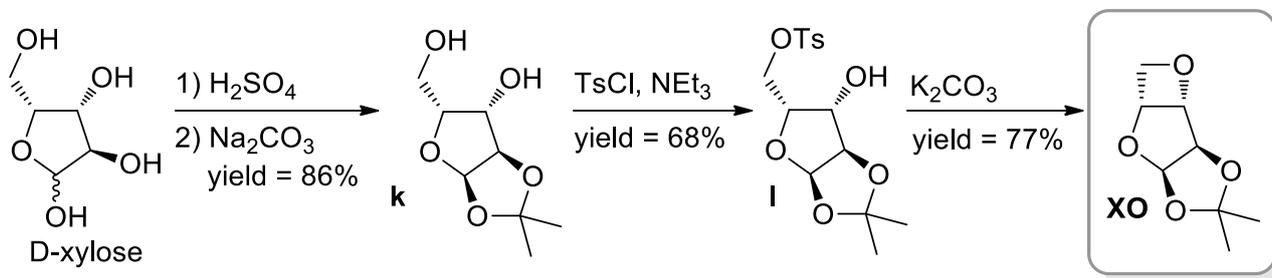


Figure 23. Synthesis D-xylose-based oxetane **XO**.

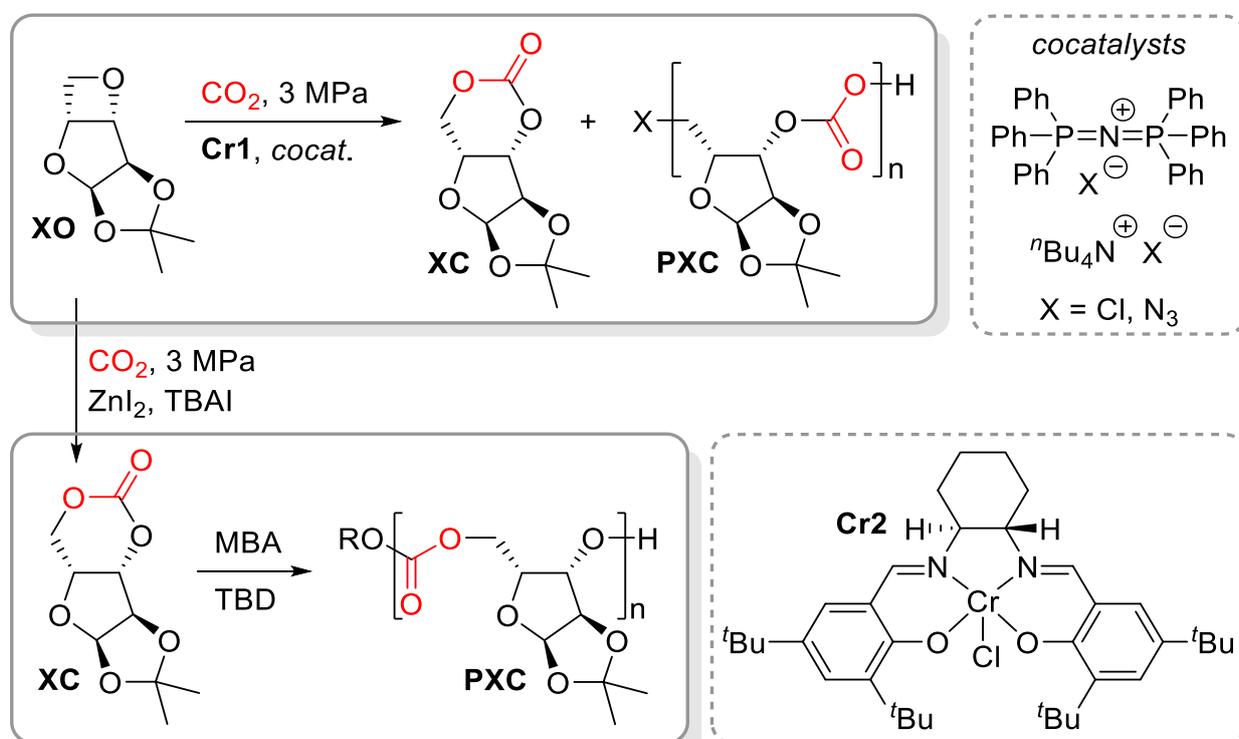


Figure 24. Synthesis D-xylose-based carbonate **XC**, and corresponding polycarbonate **PCC** via **XO**/ $\text{CO}_2$  ROCOP (top), and **XC** ROP (bottom). Structure of catalyst **Cr2**, and cocatalysts are also shown.

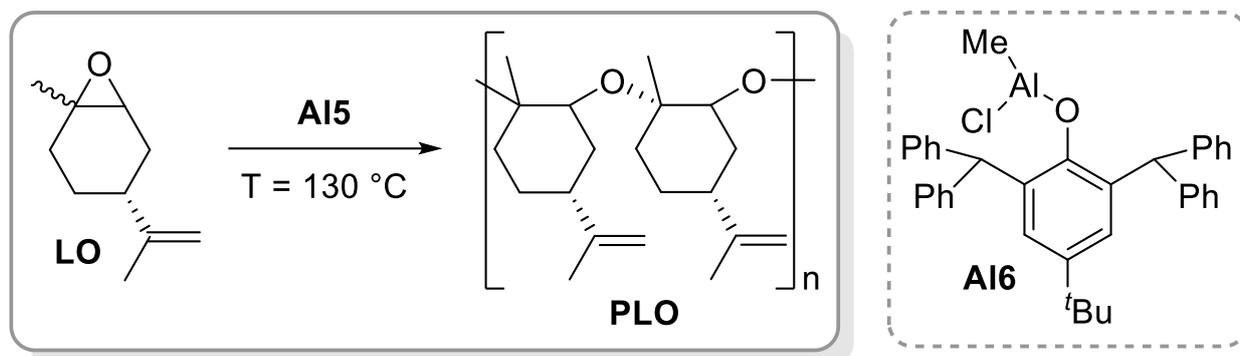
#### 4. Polyethers

Polyethers and polyols are commonly synthesized via ROP of cyclic esters. With respect to sustainable monomers, terpene-derived epoxides represent excellent candidates for green polyethers. In this scenario, limonene oxide is widely explored, since it can be easily produced from limonene, an abundant monoterpene readily extracted from the peel of citrus fruits. However, studies regarding the homo-polymerisation of **LO** are scant as only a few catalysts can overcome the kinetic barrier for the activation of its internal trisubstituted epoxide group.

The cationic photoinitiated ROP of **LO** using diaryliodonium or triarylsulphonium salts as photoinitiators was reported by Crivello et al. [124]. Nonetheless, the process led to a mixture of low molecular weight products derived from several side reactions. In turn,  $\alpha$ -pinene oxide ( $\alpha$ -**PO**) displayed higher reactivity compared to **LO**, allegedly

because of the simultaneous double ring-opening reaction involving both its epoxide and cyclobutene rings. However, side reactions occur also, in this case, limiting the use of  $\alpha$ -PO in homopolymers production.

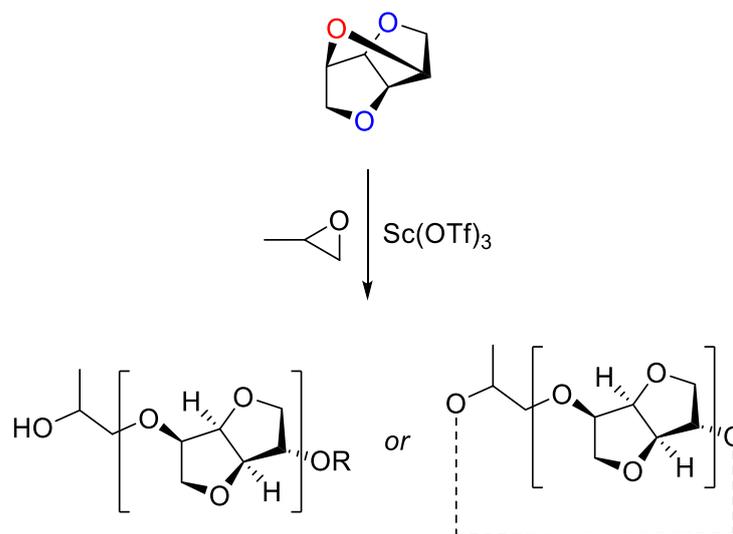
More recently, the aluminium-based catalyst **A16** was successfully employed in the synthesis of poly(limonene oxide) (**PLO**) by coordination/insertion ROP (Figure 25) [125]. The produced polyether shows low molecular weights, up to 1300 Da, and moderate dispersity ( $1.37 \leq D \leq 1.42$ ).



**Figure 25.** Polymerisation of LO to PLC catalysed by A16.

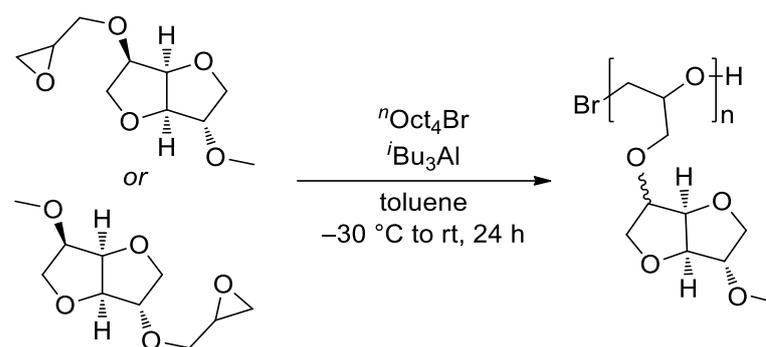
However, despite the scarce literature on LO homo-polymerisation, several studies are reported on the ROCOP of anhydrides and terpene-derived epoxides (vide supra).

Another attractive bio-based monomer for polyethers synthesis is isosorbide, a molecule derived from sorbitol. Reineke et al. reported on a cationic and quasi-zwitterionic ROP of an annulated isosorbide derivative (1,4:2,5:3,6-trianhydro-D-mannitol) in the presence of  $\text{Sc}(\text{OTf})_3$  and propylene oxide. Depending on the reaction conditions, it was possible to selectively direct the polymerisation towards either linear or cyclic macromolecular architectures (Figure 26) [126].



**Figure 26.** Cationic ROP of 1,4:2,5:3,6-trianhydro-D-mannitol.

Vares and co-workers reported on the synthesis of isosorbide mono-epoxides with the remaining hydroxyl group capped as a methyl ether, in order to avoid difficulties in subsequent polymerisations to linear polymers. The novel isosorbide epoxides, polymerised by anionic ROP, afforded polyethers with  $T_g$  around 10–15 °C and molecular weights in the range of 13–17 kDa (Figure 27) [127].



**Figure 27.** ROP of isosorbide epoxides.

Most polyether polyols are synthesized via ROP of oxiranes such as ethylene oxide (EO), propylene oxide (PO) or butylene oxide (BO). When oxiranes are obtained from renewable sources, they are considered bio-based monomers. To this end, EO can be synthesized from biomass-derived ethanol (e.g., from sugar cane), PO and BO can be bio-synthesized using a multistep process from glucose or via fermentation of biomasses, respectively [128,129]. Oxiranes can be polymerised via anionic, coordination, and cationic ROP as well as by metal-free ROP. PEO and PPO are mainly synthesized by oxanionic polymerisation. However, due to the drawbacks of such a process, studies on the coordination polymerisation reaction aiming to achieve high molecular weight polymers have been carried out. In this regard, the effect of many initiators on kinetics and molecular weight control has been investigated. Excellent overviews are reported on the polymerisation of EO, PO and other alkylene oxides, classically considered non-bio-based monomers, hence out of the scope of this review [130].

Similarly, THF can also be considered a bio-based monomer polymerisable by ROP to produce a polyether polyol. The preparation of poly(tetrahydrofuran) (PTHF) is known since the 1930s but nowadays, PolyTHF<sup>®</sup> commercialized by BASF is produced using THF obtained from the bio-based 1,4 butanediol cyclisation [131].

## 5. Conclusions

We discussed the synthesis of different classes of bio-based polymeric materials by ring-opening (co)polymerisation, with a high focus on polyesters, polycarbonates and polyethers. In particular, the great tolerance toward the presence of various functional groups on the starting monomers allows for the synthesis of structurally complex and functional materials. This, in turn, offers a wide range of possibilities in terms of possible applications, from commodity plastics to fine applications such as tissue engineering. Nevertheless, several significant aspects still need to be addressed.

With respect to the polylactones, relevant monomers such as  $\epsilon$ -caprolactone and  $\delta$ -valerolactone are still synthesized mainly from petrochemicals while polylactide, despite being biodegradable and biomass-derived, finds limited applications due to its poor mechanical properties. Polyesters derived from fully renewable higher lactones (i.e.,  $\omega$ -pentadecalactone) are considered possible solutions to these issues, albeit their large-scale production is still limited. Moreover, the biodegradation behaviour of this class of polymers is still widely unexplored; indeed, further insights are required to evaluate the long-term impact of such materials on the natural environment.

In the case of the polyethers, the identification of suitable monomers exhibiting good reactivity also in homopolymerisation reactions is highly desirable. This problem is related to that of polycarbonates. Indeed, in the latter case, bio-based epoxides could serve as starting material for the production of bio-based PCs. In addition, the amount of bio-based cyclic carbonates suitable for ring-opening polymerisation is still limited.

In general, there is still a tremendous lack of concrete sustainable monomers for the synthesis of oxygenated polymers.

Another aspect is related to the possibility to obtain controlled molecular weights suitable for real applications. Indeed, molecular weights are often reported in the range from 2 to 20 kg/mol and, notwithstanding these values are sufficient for certain uses like polyols in polyurethane production [132], they are too low for other applications. For example, industrial production of PLA by ROP with Sn(Oct)<sub>2</sub> gives  $M_n$  spanning from 20 to 220 kg/mol with  $D = 1.6$ – $2.0$  [133,134].

In conclusion, with this review, we demonstrated that the use of ring-opening (co)polymerisation processes is a highly promising approach for the assessment of new sustainable polymers obtained from bio-based, renewable feedstocks, and we hope that this will trigger more significant advancements in this direction.

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