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Ring-Opening Copolymerization (ROCOP): Synthesis and Properties of Polyesters and Polycarbonates

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Abstract

Controlled routes to prepare polyesters and polycarbonates are of interest due to the widespread application of these materials and the opportunities provided to prepare new copolymers. Furthermore, ring-opening copolymerization may enable new poly(ester/carbonate) materials to be prepared which are inaccessible using alternative controlled polymerizations. This review highlights recent advances in the ring-opening copolymerization catalysis, using epoxides coupled with anhydrides or CO_2, to produce polyesters and polycarbonates. In particular, the structures and performances of various homogeneous catalysts are presented for the epoxide/anhydride copolymerization. The properties of the resultant polyesters and polycarbonates are presented and future opportunities highlighted for developments of both the materials and catalysts.

1. Introduction

Polyesters and polycarbonates are amongst the most widely applied oxygenated polymers. The majority of commercial materials are prepared by condensation polymerizations and include well-known polymers such as poly(ethylene terephthalate) (PET) and polycarbonate (PC) (from bisphenol A). These materials are found in applications spanning packaging, fibres, rigid plastics and engineering materials.

Currently, aliphatic polyesters and polycarbonates have fewer large scale commercial opportunities. This is partly due to their physical and chemical properties which are typically lower compared to materials containing aromatic/rigid functionalities in the polymer backbone. One interesting aliphatic polyester, produced on a several hundred thousand tonnes/annum scale, is poly(lactic acid) (PLA); this material is attracting considerable attention as a renewable and, in some cases, degradable alternative polymer for packaging, fibres, medical sutures/stents and in controlled release of active compounds.[1] Another promising class of aliphatic polyesters are the poly(hydroxyl alkanoates) (PHAs), once again applied for both commodity and niche medical applications.[2] Aliphatic polycarbonates prepared by the ring-opening copolymerization of epoxides and carbon dioxide are also attracting considerable attention, including commercialization ventures operating at pilot scale.[3] The polymerization can be controlled to enable the production of either low molar mass polycarbonates or poly(ether carbonates), which are subsequently applied as the polyol portion in polyurethane synthesis.[4] These materials are desirable as potential substitutes for conventional petrochemical polyols. Indeed, a recent detailed life cycle analysis shows that these materials consume ~20% less petrochemical raw materials and reduce carbon dioxide emissions by approximately 20% compared to the use of conventional petrochemicals.[5]

Another topical area is the development of ‘controlled’ polymerizations, which in this context refers to polymerizations resulting in the precise control of polymer molar mass (typically with narrow dispersity), composition, architecture and end-group functionality.[6] There is fundamental academic interest in understanding and developing such routes however, they are also essential for the production of (multi-) block copolymers and other sophisticated polymers.[6b-k] There are several controlled syntheses of aliphatic polyesters and polycarbonates, two of the most common are the ring-opening polymerization (ROP) of cyclic esters/carbonates and the ring-opening copolymerization (ROCOP) of epoxides and anhydride/carbon dioxide (Fig. 1). An alternative method, ring-opening polycondensation, to produce polyesters has been developed by Takasu and co-workers. However, the broad dispersity ($Đ_M > 2.0$) indicates that the polymerization is not well controlled.[7]

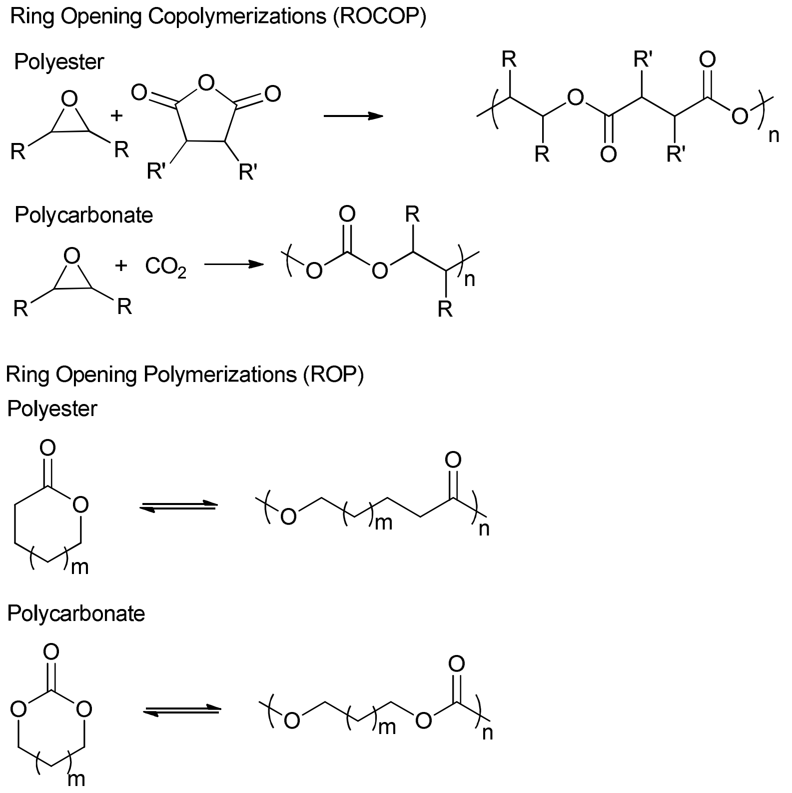


Fig. 1 Illustrates the generic reactions occurring during ring-opening copolymerization (ROCOP) and ring-opening polymerization (ROP) to prepare polyesters and polycarbonates. For the epoxides: where there is only one R group: R = alkyl, e.g. Me, Ph; CH_2Cl, CH_2OBn, and the other R group = H. Where both R groups are the same: R = cyclohexylene, cyclopentylene, naphthalene. For the anhydrides: where there is only one R' group: R' = Me, Ph, $=CH_2$, etc. and the other R' = H. Where both R' are the same: R' = absent (maleic), H (succinic), phenylene, cyclohexylene.

So far there have been a significant number of comprehensive reviews of ring-opening polymerization of lactones/cyclic carbonates, addressing areas spanning catalysis, new monomers, properties and applications for polyesters and polycarbonates.[1, 6d, 8] Although it is an excellent controlled polymerization for many applications, there are opportunities to broaden the range materials produced, and to overcome some of the limitations of the ROP method. In contrast to the bright lights shining on ROP, the sister polymerization method of ROCOP has received far less attention. One attraction of ROCOP is that the properties of the resulting materials can be easily manipulated by facile substitution of just one of the monomers: for example, switching the epoxide from propylene oxide to cyclohexene oxide, using the same ROCOP catalysts, it is possible to moderate the polycarbonate glass transition temperatures over the range 33-123 °C.[9] This facility to substitute different epoxides, using the same/very similar catalysts and conditions, stands in stark contrast to ROP methodologies, where changing the polymer repeating unit requires the preparation of new, functionalized lactones/cyclic carbonates.[8b] The synthesis of such functionalized monomers can be a very challenging undertaking, often requiring multiple steps.[8b] Furthermore, there are no guarantees that changing the lactone/cyclic carbonate will enable polymerization to occur at all, not least because this often reduces the ring strain, which is the thermodynamic driving force for polymerization.[8b] Furthermore, using ROP certain chemistries and repeating units are very difficult, and in some cases currently impossible, to incorporate into the polymer backbone. This is due to both thermodynamic limitations and the difficulty in preparing suitable lactones. One striking problem area for ROP is the production of polymers containing aromatic groups in the polymer backbone, a desirable goal to increase thermal and mechanical properties. ROCOP can overcome this limitation, in particular, it represents an attractive means to prepare semi-aromatic polyesters/polycarbonates.[10] A further advantage of ROCOP is the common availability of the epoxide and anhydride (co)monomers. Many are commercially produced, some on a large scale, or they are relatively straightforward to prepare from olefins or di-carboxylic acids, respectively.

This review will focus on the application of ring-opening copolymerization (ROCOP) to prepare aliphatic polyesters and polycarbonates. The ring-opening copolymerization of epoxides/anhydrides will be examined and the range of different catalysts for this transformation highlighted. In the field of epoxide/CO_2 copolymerization, there are already quite a range of reviews of different catalysts to which the reader is referred for more specific information.[6a, 9, 11] Furthermore, a recent review of stereocontrolled epoxide polymerizations and copolymerizations provides a complementary perspective.[12]

The first part of this review focuses on describing catalysts for epoxide/anhydride ROCOP, an area not yet comprehensively reviewed, so as to enable efficient polyester synthesis and on recent discoveries enabling the efficient production of copoly(ester carbonates). The second part, will describe the properties and performances of selected polyesters and polycarbonates, produced by ROCOP. This section seeks to illustrate both the range of materials already prepared, the possible chemistries and functionalities and to highlight areas in which future developments are expected. In particular, the emphasis will be on the influence that the polymer composition (epoxide/anhydride selection), tacticity and functional groups exert over the macroscopic properties. All the copolymerizations described in this review use epoxides as a co-monomer. Therefore, the reader may find Fig. 2 informative, as it illustrates the structures and abbreviations used for commonly applied epoxides and anhydrides.

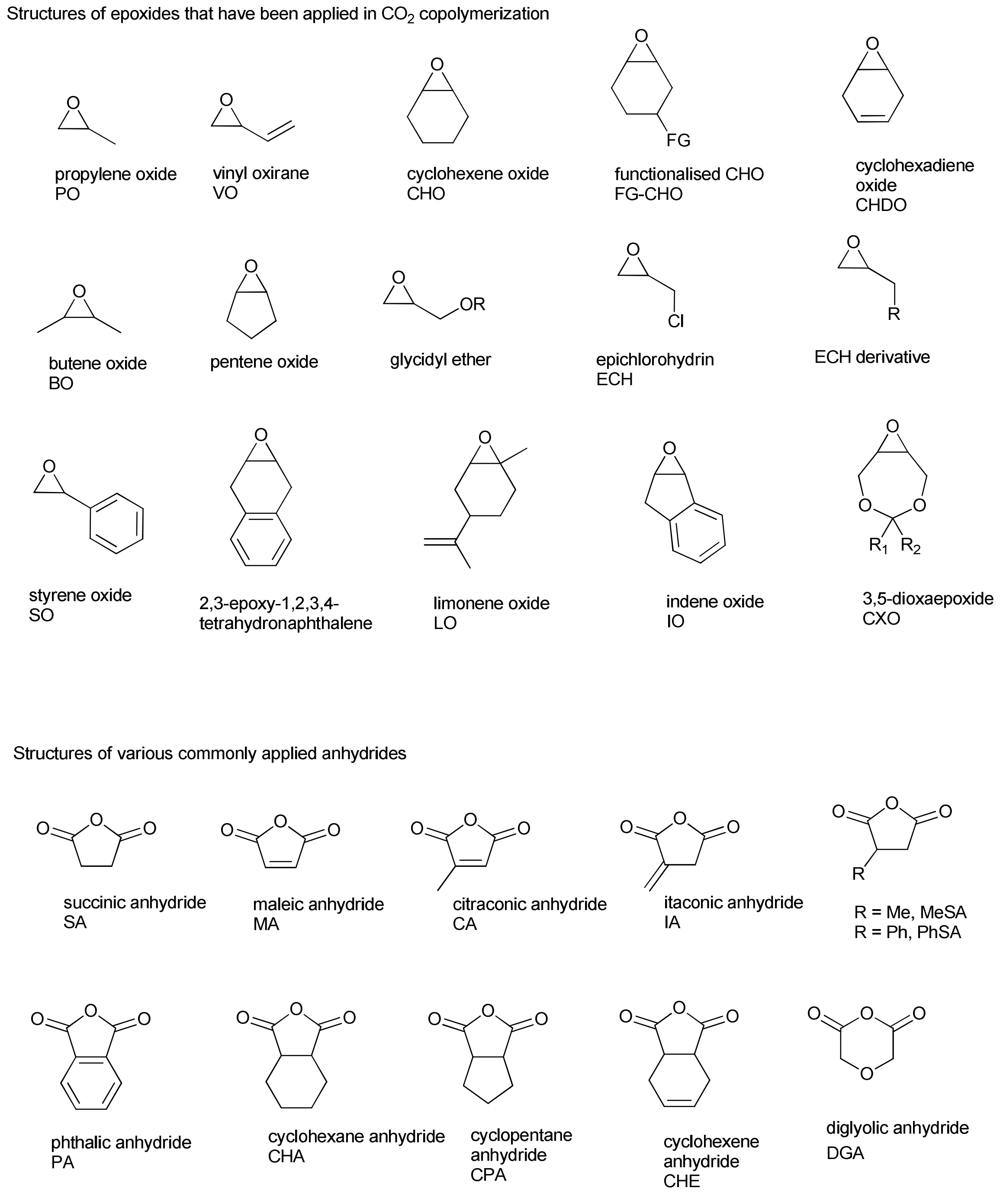


Fig. 2 Shows the structures of commonly applied epoxides and anhydrides.

2. Ring-Opening Copolymerization of Epoxides and Anhydrides: Catalysis

2.1 Polymerization Pathway

Ring-opening copolymerization reactions are used to produce polyesters and/or polycarbonates. Such polymerizations require the application of a ‘catalyst’ or, more accurately, an initiator. This species is often a single site metal complex of the form LMX, where L is an ancillary ligand, M is the metal site at which catalysis occurs and X is the initiating group and site at which propagation proceeds. Fig. 3 illustrates the generic elementary reactions which are proposed to occur during epoxide/anhydride ROCOP.

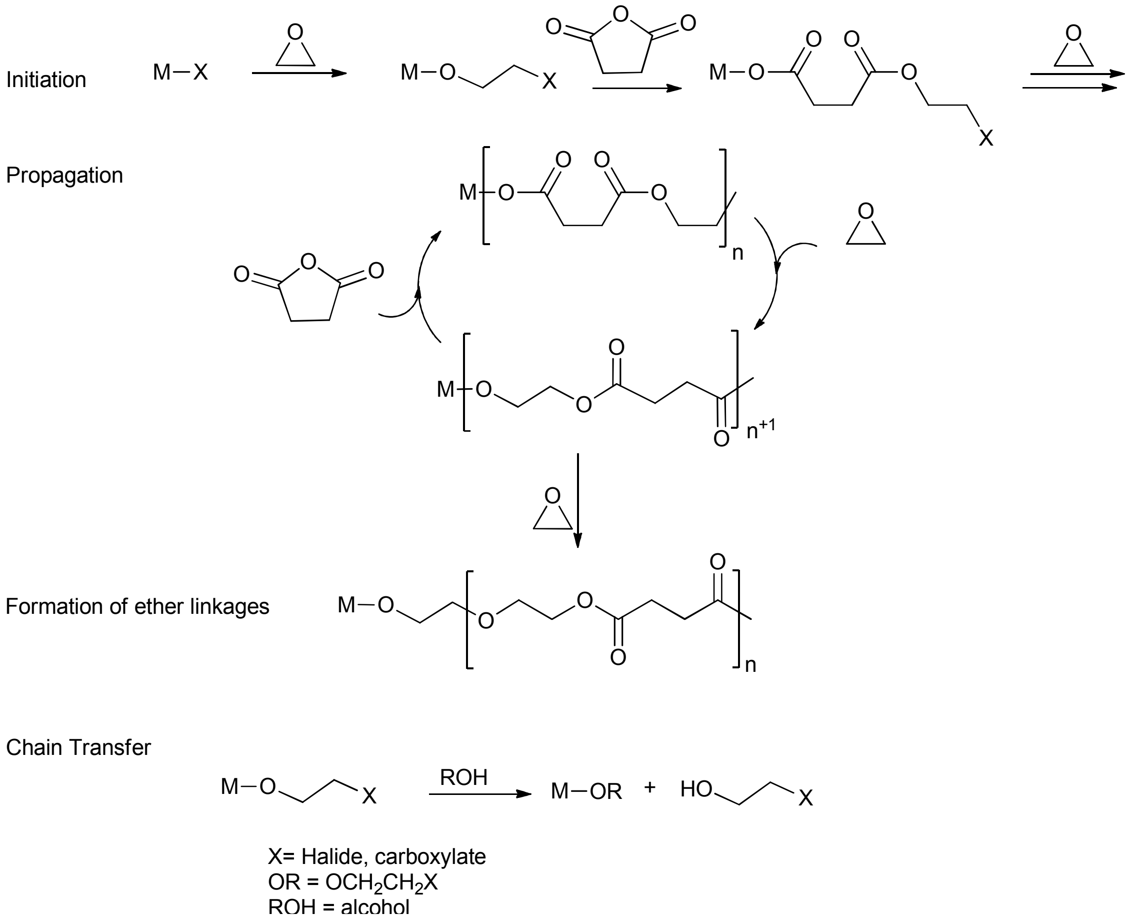


Fig. 3 Illustrates the elementary steps occurring during epoxide/anhydride ring-opening copolymerizations (ROCOP).

The **initiation** reactions involve a reaction between the MX initiator and the monomers, to generate metal alkoxide/carboxylate intermediates. The initiating group is commonly a carboxylate, alkoxide or halide group and, during controlled polymerization, this group becomes one of the chain end groups. The **propagation** reactions occur as monomers are sequentially enchained, this involves sequential formation of metal-alkoxide and carboxylate intermediates. The metal alkoxide intermediate attacks the anhydride to generate the metal carboxylate intermediate. The metal carboxylate intermediate attacks and ring-opens the epoxide co-monomer to (re-)generate the meal alkoxide. For this class of polymerizations, it is also important to consider **chain transfer reactions**. These are reactions in which the growing polymer chain equilibrates with added protic compounds, for example alcohols. The chain transfer reactions are typically assumed to occur more rapidly than propagation reactions; a hypothesis supported by the ability upon the addition of protic compounds, to control the molar mass and to narrow the dispersity of the polymers. Chain transfer reactions can be highly beneficial as they can be used to manipulate selectivity for a particular polymer end-group/molar mass. Other side reactions include sequential epoxide enchainment, leading to ether linkages. The **termination** of polymerization is frequently achieved by manipulating the conditions (reducing temperature, monomer removal) or by addition of water/acids.

Key parameters to consider when selecting a ROCOP catalyst include its productivity (often measured by its turn-over number, TON), activity (usually assessed as a turn over frequency, TOF), selectivity (against ether linkages), control of molar mass (and dispersity) and in some cases, control of regio- and stereochemistry during monomer enchainment.

2.2 Early Catalyst Discoveries

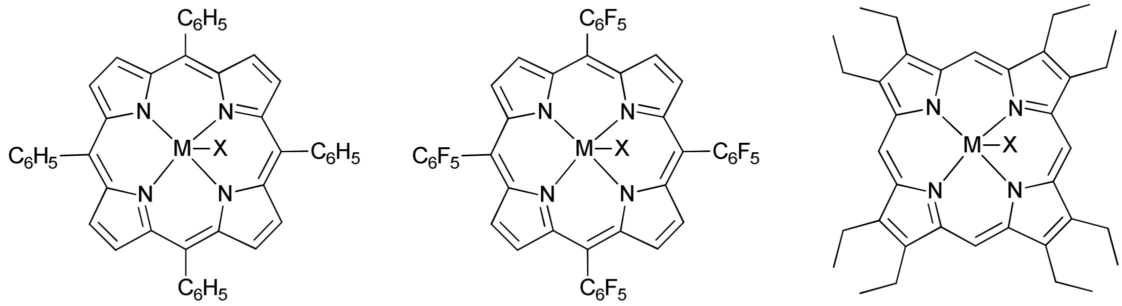
The first reports of the alternating copolymerization of epoxides and anhydrides were made in the 1960s.[13] A range of catalyst systems including inorganic salts, tertiary amines or metal-alkyl initiators were reported.[14] However, these copolymerizations were hampered by poor performance characteristics including low levels of polymerization control, poor activity and low molar mass products; additionally, in some cases, the catalysts exhibited poor selectivity resulting in significant quantities of ether linkages. In the mid-1960s, Inoue et al., investigated the preparation of polyesters using organometallic initiators.[14b, 14c, 14f] Thus, several metal alkyl initiators, together with added alcohol or water, were applied to epoxide (PO, ECH)/anhydride (PA, CaA) copolymerizations. An important mechanistic proposal, for

PA/CHO ROCOP initiated by dialkyl zinc, was that polymerization proceeded by sequential formation of zinc-carboxylate and zinc-alkoxide species.[14f] In 1973, Heisch et al. investigated the terpolymerization of epoxides, oxiranes and anhydrides, initiated by tri(alkyl)aluminium complexes.[14g] The resulting polymers consisted of alternating ABC blocks featuring ether-ester-ester linkages. In 1980, Kuran et al. reported MA/PO copolymerizations, using a series of organozinc catalysts of general formula RZnEt (R = alkoxide, aryloxide, carboxylate).[14h] Polyesters containing only 53 mol% incorporation of PO and of low molar mass ($M_n < 2000$ g/mol) were produced. Although these early discoveries laid the ground work for future catalyst developments, the catalysts were generally hampered by a lack of precise control and by an inability to accurately define the catalyst structure.

2.3 Well-Defined Metal Catalysts

The next major series of catalyst developments involved the preparation of well-defined metal complexes, via the use of ancillary ligands to control/minimise aggregation reactions. These single site species include catalyst systems which comprise both a (transition) metal complex and added co-catalyst (typically at a loading of 1-5 eq. vs. catalyst). Common co-catalysts include inorganic salts, such as ammonium or phosphonium halides, or Lewis bases, such as methyl imidazole or dimethylaminopyridine (DMAP). The precise role for the co-catalyst remains rather complex, but it is generally proposed that either the Lewis base or the anion coordinates to the metal catalyst, resulting in the labilizing of the initiating group, X or the propagating polymer chain (which is coordinated in a trans- position) and accelerating polymerization.

2.3.1 Metalloporphyrins



(TPP)M-X

1a: M = Al, X = Cl
1b: M = Al, X = OCOC$(CH_3)_3$
1c: M = Cr, X = Cl
1d: M = Co, X = Cl
1e: M = Mn, X = Cl

(TFPP)M-X

2a: M = Al, X = Cl, R = Ph
2b: M = Cr, X = Cl, R = Ph
2c: M = Co, X = Cl, R = Ph

(OEPP)M-X

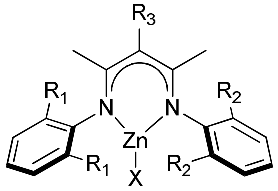
3a: M = Al, X = Cl,
3b: M = Cr, X = Cl,
3c: M = Co, X = Cl,

Fig. 4 Illustrates the structures of various metalloporphyrin initiators.

In 1985, Inoue *et al.,* reported the combination of porphyrinato aluminium complexes (**1a**-**b**) with quaternary ammonium/phosphonium co-catalysts, as catalytic systems (TOF = 5 d^{-1}) for the perfectly alternating PO (or CHO, SO, BO)/PA copolymerization.[15] Polymerization was controlled and yielded low molar mass polyester (2,300 < M_n < 3,000 g/mol) with a narrow dispersity ($Đ_M$ < 1.1). It was proposed that the polymerization reactions occurred from both sides of the metalloporphyrin plane and that the aluminium carboxylate attack at the epoxide was the rate limiting step. Very closely related porphyrin complexes were also some of the first examples of single site catalysts for CO_2/epoxide ROCOP and continue to attract significant attention in that field.[16] Recently, Duchateau *et al.* have thoroughly investigated porphyrinato chromium complex **1c,** in the presence of DMAP or N-MeIm as co-catalysts, for the copolymerization of CHO with different anhydrides (SA, CPra, CPA, PA).[10d] In the absence of the co-catalysts, **1c** is ineffective, however, on addition of DMAP the activity significantly increases (bulk: TOF = 95 h^{-1} at 100 °C) as does the selectivity (>99 % ester linkages). Once again, low molar mass polyester was produced (M_n = 1,500 g/mol), and this was ascribed to side reactions (chain transfer) involving water. Using a strained bicyclic oxirane (CPra, CPA) resulted in higher activities (bulk: TOF = 107 h^{-1}). Coates and co-workers also investigated the production of unsaturated polyesters, from MA/epoxide copolymerization however, under these conditions **1a** alone afforded significant ether linkage content.[17] Duchateau *et al.* also compared a series of metal porphyrin/salen catalysts, with DMAP as the co-catalyst, for SO/anhydride (PA, CPa, CPrA, SA) copolymerization.[10c] The chromium porphyrinato complex **1c** was substantially more active (TOF = 150 h^{-1}) than either the Co(III) or Mn(III) analogues **1d-e** (TOF ≤ 43 h^{-1}). Concurrently, Chisholm and co-workers, who had extensively investigated porphryrin complexes for CO_2/epoxide ROCOP,[16b-e] applied them in SO/anhydride copolymerization.[16f] [(TPP)CrCl] **1c,** with PPNCl co-catalyst, copolymerizes SO/SA leading to regio-random polystyrene succinate with a high TOF (~200 h^{-1}). As previously reported by Duchateau, they observed that phenyl acetaldehyde formed during polymerization, functions as a chain transfer agent, reducing the molar mass of the polyester.[10c]

Recently, Chisholm and co-workers have extensively investigated a range of metal (Al^{3+}, Cr^{3+}, Co^{3+}) porphyrins for PO/anhydride (SA, MeSa, PhSA, MA, PA) copolymerizations.[18] Comparing the metals, for MeSA/PO copolymerization, revealed that Cr(III) catalysts were significantly more active (TOF = 52 h^{-1}) than Co(III) and Al(III) analogues (TOF = 19 h^{-1} and 25 h^{-1}, respectively). Furthermore, the selectivity for ether/ester linkages was controlled by the quantity of co-catalyst and the ratio of monomers SO/MeSA. In addition, the chromium porphyrinato complexes were less affected by modifications to the porphyrin ligand than Al(III) and Co(III) counterparts, however in all cases the tetra(phenyl)porphyrin ligand was the best. The porphyrin substituents did affect the regioselectivity for PO/SA copolymerization, with the order being **1a>2a> 3a** and **2b > 3b > 1c** for the aluminium and cobalt complexes, respectively.

2.3.2 β-Diiminate (BDI) Zinc Complexes



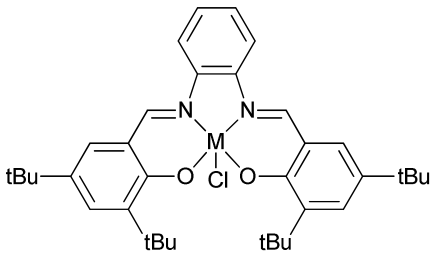
4a: R_1 = Et, R_2 = Et, R_3 = H
4b: R_1 = Et, R_2 = Et, R_3 = CN
4c: R_1 = Et, R_2 = Et, R_3 = Me
4d: R_1 = iPr, R_2 = Et, R_3 = CN
4e: R_1 = iPr, R_2 = iPr, R_3 = CN

Fig.5 Illustrates the structures of β-diiminate zinc catalysts.[10g]

Another major breakthrough was achieved by Coates and co-workers, in 2007, with the use of β-diiminate zinc or (BDI)Zn complexes (Fig. 5).[10g] These complexes were already known to be effective catalysts for a range of polymerizations, including CO_2/epoxide copolymerization,[19] cyclic ester[20] and cyclic carbonate ring-opening polymerization. These (BDI)Zn complexes show high activities for epoxide (VCHO, LO, PO, CBO, IBO)/anhydride (DGA) ROCOP, affording high molar mass (M_n < 55,000 g/mol), perfectly alternating, polyesters.[10g] The ligands' backbone and aryl substituents affected their stability and activity in polymerization, in common with previous observations for epoxide/CO_2

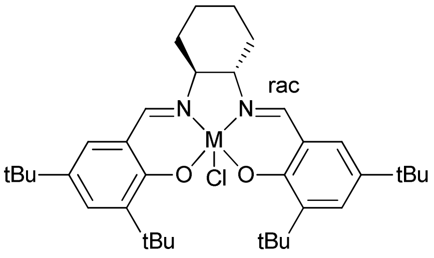
copolymerization.[19e] Complexes with R_3 = CN (**4b**, **4d**, **4e** in Fig. 5) were among the fastest and most tolerant.[10g] The use of **4d** for CHO/DGA copolymerization (TOF = 79 h^{-1}) afforded alternating polyesters with high molar masses (M_n = 23,000 g/mol) and narrow distributions (Đ_{M} = 1.2). In addition, a wide range of epoxides/anhydrides were investigated leading, in some cases, to unsaturated polyesters. These polyesters showed some promising features, including relatively high decomposition temperatures (~290 °C) and moderate glass transition temperatures (50-60 °C). The (BDI)ZnOAc complex shows low activity (TOF < 1 h^{-1}) for MA/PO copolymerization to afford polymers with high ether linkages (86 %).[17]

2.3.3 Metal Salen and Salan Complexes



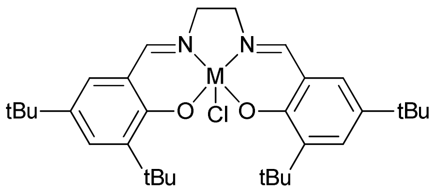
(salophen)M-X

5a: M = Cr, X = Cl
5b: M = Al, X = Cl
5c: M = Co, X = Cl
5d: M = Co, X = OAc
5e: M = Mn, X = Cl



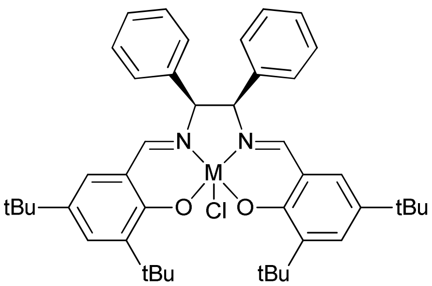
(salen)M-X

6a: M = Co, X = O2CPhF5
6b: M = Cr, X = Cl
6c: M = Co, X = Cl
6d: M = Al, X = Cl



(salen)M-X

7a: M = Cr, X = Cl
7b: M = Co, X = Cl
7c: M = Al, X = Cl



8a: M = Cr, X = Cl
8b: M = Co, X = Cl
8c: M = Al, X = Cl

Fig.6 Shows the structures of various metal salen and salophen complexes.

Metal(III) salen complexes (Fig. 6) have been widely applied in a range of catalyses, including in lactone polymerization and in CO_2/epoxide copolymerization.[25,26] Duchateau and co-workers reported the chromium salophen complex (**5a**)/DMAP system (Fig. 6) for CHO/anhydride (SA, CPra, CPA, PA) copolymerizations.[10d] As was observed for metalloporphyrins, the catalyst was ineffective without the addition of co-catalyst. Using DMAP as the co-catalyst, with **5a**, yielded better activity (Bulk: TOF = 64 h^{-1}) and led to low molar mass polymers (M_n < 1,800 g/mol) with moderate-good ester linkage content (< 73 %, in solution). Furthermore, the chromium salophen complex **5a** was less active than the chromium prophyrinato complex **1c**. Shortly after, Coates reported the successful use of cobalt and chromium salen complexes, **6a** and **6b**, for epoxide/MA copolymerizations.[17] Unusually, complexes **6a/6b** were effective, but slow initiators without any co-catalysts (TOF = 6 h^{-1} and 13 h^{-1} for **6a** and **6b**, respectively, at 45 °C, in toluene). Poly(propylene maleate) (PPM) of relatively high molecular weight was produced (M_n = 5,000 g/mol; 17,000 g/mol, **6a** and **6b**, respectively). The PPM was then successfully converted to poly(propylene fumarate) PPF by controlled *cis-trans* isomerization in the presence of dimethylamine. Complex **6b** was applied to a range of epoxide/MA copolymerizations (Fig. 6), always affording perfectly alternating polyesters (< 1% ether linkages) with high molar masses (21,000 < M_n < 31,000 g/mol), reasonably narrow distributions ($Đ_M$ < 1.7) and moderate activities (11 h^{-1} < TOF < 50 h^{-1}). By applying a range of epoxides, the polyester glass transition temperatures could be controlled from -29 to 50 °C.

Darensbourg and co-workers also investigated **6a**, with various onium salts as the co-catalysts, for epoxide/anhydride copolymerization.[21] They found that **6b** on its own is inactive for CHO/PA copolymerization. Using **6b**, PPN^+X^- ($X = Cl^-, N_3^-, DNP^-$) salts were slightly better co-catalysts than $NBu_4^+ X^-$ (X = Br-, I-) salts. The relative reactivity of various anhydrides, with CHO as co-monomer, were found to follow the order: CHA > PA > CHE. If CHA was applied as the anhydride, the relative order in epoxides was PO > CHO = SO. Once again, the most active metal was chromium, with **5a**/DMAP being significantly more active (Bulk: TOF = 150 h^{-1}) than analogous systems of Al(III), Mn(III) or Co(III). Duchateau and co-workers also reported an extensive study of metal salen/co-catalyst combinations for CHO/anhydride copolymerization.[22] Again, the chromium complexes outperformed cobalt and aluminium analogues. Duchateau and co-workers also investigated limonene oxide (LO)/PA copolymerization, catalyzed by metal salophen complexes (**5a**, **5b**, **5c**, **5e**), to yield partially renewable polyesters.[10a]

2.3.4 Dinuclear Catalysts

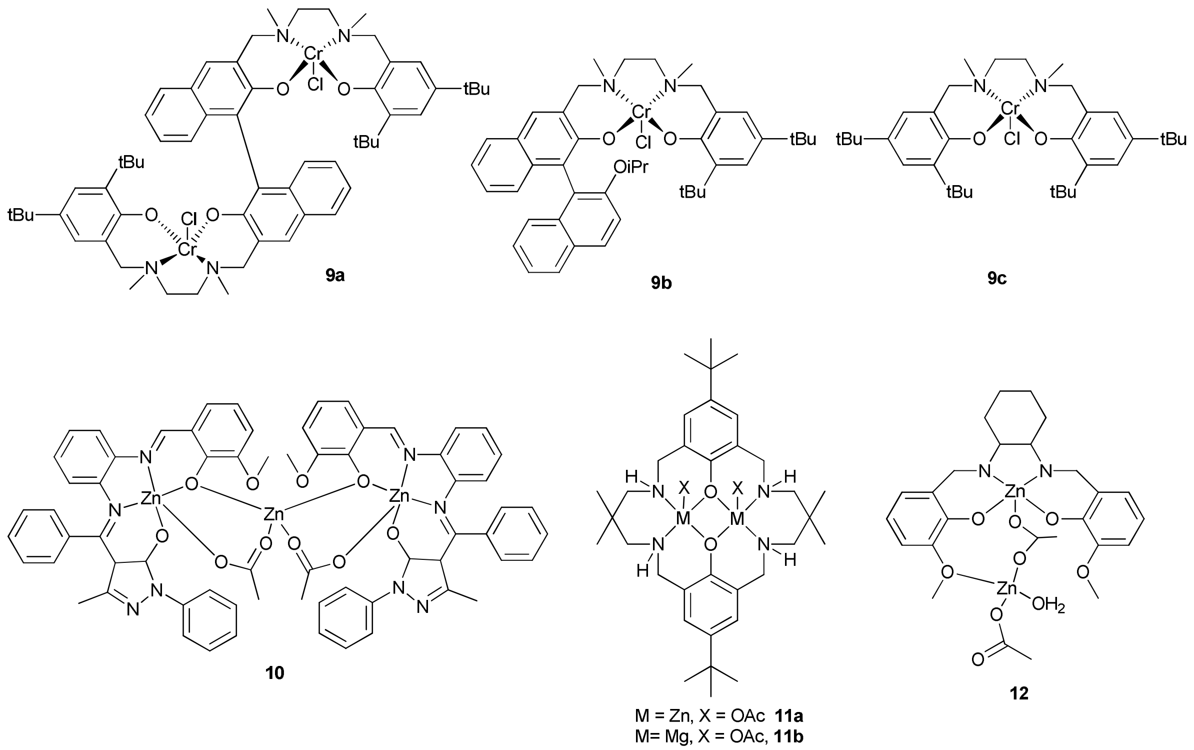
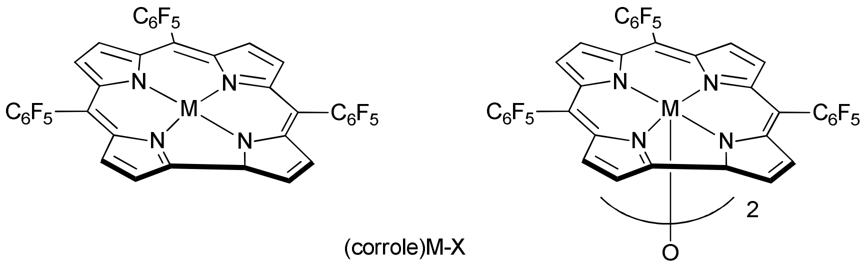


Fig.7 Illustrates the structures of various bimetallic catalysts.

In the parallel field of epoxide/CO_2 ROCOP it has been discovered that bimetallic or dinuclear catalysts frequently show superior performance compared to mononuclear analogues.[9, 11k, 19a, 19b, 19d, 23] This is proposed to be due to an improved facility to accommodate the monomers and lower barriers for metal carbonate attack on bound epoxide molecules. Given the recent focus on dinuclear catalysts for epoxide/CO_2 ROCOP, and the mechanistic parallels between the two copolymerizations, investigating dimeric catalysts was the logical next step for epoxide/anhydride ROCOP (Fig. 7).

Lu *et al.* compared a dinuclear chromium salan catalyst, **9a**, with two mononuclear analogues **9b** and **9c**.[24] The dinuclear catalyst, **9a**, was approximately four times faster for epichlorohydrin/MA (TOF = 7.8 h^{-1}vs 0.9 h^{-1}) and approximately seven times faster for glycidyl phenyl ether/MA compared to the mononuclear analogue **9c** (TOF = 6.0 h^{-1} vs 0.4 h^{-1}). Furthermore, the polyesters showed perfectly alternating structures and were of high molar masses (M_n = 32,500 g/mol, $Đ_M$ < 1.6). The hydrolysis of the polymer obtained by (S)-GO/MA copolymerization shows an *ee* of 98.5% suggesting that ring-opening predominantly occurs at the methylene carbon. A novel trinuclear zinc complex, **10**, with DMAP as co-catalyst, showed good activity for CHO/MA co-polymerisation (TOF = 116 h^{-1} at 110°C in toluene).[25] However, the polymerization conditions were important: in bulk there were ether linkages (> 29%), these could be reduced using a solvent (toluene/DMF). Our group have reported di-zinc and di-magnesium catalysts for CO_2/epoxide copolymerizations.[9, 23a-h] The di-zinc and magnesium catalyst, **11a** and **b**, are also effective for CHO/PA copolymerizations; representing the first example of a well-defined magnesium catalyst for this polymerization.[26] The optimum performance was in bulk, where the complexes show moderate/good activities (**11b**, TOF = 97 h^{-1}, 100 °C) and produced perfectly alternating semi-aromatic polyesters. Dizinc complex **12** with DMAP as a cocatalyst was shown to selectively copolymerise CHO and MA at 110 °C.[27] The polymer produced is perfectly alternating polyester (< 1% ether linkages). Polymerization was controlled and yielded low molar mass polyester (M_n = 4,000 g/mol) with a narrow distribution ($Đ_M$ < 1.1). The activity was good (TOF = 130 h^{-1}), but longer reaction times lead to broader distributions and increased amounts of ether linkages.



13a: M = Mn
13b: M = MnCl
13c: M = Fe(Et_2O)$_2$
13d: M = FeCl

13e

Fig.8 Illustrates the structures of various metal corrole catalysts.[23j]

Very recently, Nozaki and co-workers have reported metal-corrole complexes **13a-e** (Fig. 8), some of which are dimeric, for the homopolymerization of epoxides, as well as epoxide/anhydride or epoxide/carbon dioxide ROCOP.[23j] Manganese (**13a-b)** and iron corrole complexes (**13d-e**), with the co-catalyst (PPN)OBzF_5, were slow systems for PO/GA copolymerization (**13e**, TOF = 3 h^{-1}, in bulk, at 30 °C) affording perfectly alternating polyesters ($5{,}700 < M_n < 8{,}000$ g/mol and $Đ_M \leq 1.2$). Interestingly, in toluene solutions poly(ester-*co*-ether) products formed, whereas no activity was observed in THF. Furthermore, the same catalyst system was suitable for use with other epoxides, including PO or ECH, and anhydrides, including GA.

2.4 Copoly(ester-carbonate): Combining ROCOP and ROP Processes

Recently, interest in copoly(ester-carbonates) has intensified, driven by the opportunities to modify and improve upon the polymer properties. A range of different copolymer microstructures/architectures have been investigated, including block, graft and multi-branched/star copolymers. The syntheses applied depend on the desired microstructures and include sequential monomer addition (for block copolymers), the use of macro-initiators (for graft/star polymers) and the application of various multi-functional or polymeric chain transfer agents. There has been a particular focus on the development of so-called 'one-pot' methods, i.e. where all monomers are combined and copolymer selectivity results from catalysts/polymerization control.

2.4.1 ROCOP Terpolymerizations

An early report (2006) of the terpolymerizations of PO, CO_2 and MA, using a polymer supported double metal cyanide heterogeneous catalyst, resulted in the preparation of a poly(ester-carbonate), although the structure of the material was not defined.[28] In 2008, Coates and co-workers reported that the terpolymerizations of diglycolic anhydride (DGA), CO_2 and cyclohexene oxide (CHO) using catalyst **4b** (X= OAc).[29] Detailed in situ ATR-IR spectroscopic analysis revealed that epoxide/anhydride ROCOP occurred first, and, only once the anhydride was nearly completely consumed, did epoxide/CO_2 ROCOP occur. This was surprising because when conducted independently the epoxide/CO_2 copolymerization occurs significantly faster than epoxide/anhydride copolymerization. It was proposed that the selectivity is due to a relative faster rate of anhydride insertion vs. CO_2 insertion into the zinc alkoxide intermediate; both reactions are pre-rate determining steps in the catalytic cycles. Fig. 9 illustrates the combination of polymerization cycles which are proposed to be occurring. During initiation, the (BDI)ZnOAc complex reacts with an equivalent of epoxide to generate the zinc alkoxide species (A). At this stage, the reaction with anhydride (B) is proposed to occur faster than the reaction with CO_2 (C), leading to the dominant intermediate in terpolymerizations being a zinc carboxylate species. This intermediate reacts with epoxide (D) to form a zinc-alkoxide and the polymerization cycle progresses around the ester cycle (steps B, D). Only when the anhydride is almost fully consumed, does the insertion of CO_2 into the zinc alkoxide intermediate (C) become competitive. Once this occurs, a zinc carbonate intermediate is formed, which ring opens an epoxide to re-generate an alkoxide (E). Therefore, in this polymerization the formation of the second block occurs faster than the first block because reaction E is faster than D.

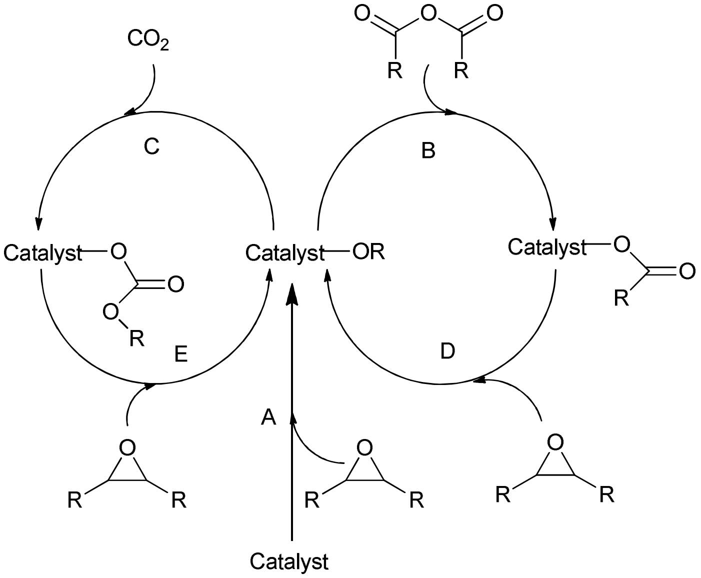


Fig. 9: Shows the proposed mechanism for the formation of copoly(ester-*b*-carbonate), as reported by Coates and co-workers.[29]

Subsequently, other catalysts have also been shown to exhibit the same selectivity and produce copoly(ester-*b*-carbonates) group.[10b, 10d, 21, 26, 28, 30] Duchateau and co-workers used **5a** with DMAP as the co-catalyst for the terpolymerisation of CHO/anhydrides (SA/CPrA/CPA or PA) and CO_2.[10b, 10d] By monitoring the reaction they found that ~90 % of the anhydride is converted before any carbonate functionalities are formed. It was also found that the presence of CO_2, suppresses the formation of ether linkages, even in the ester blocks. It was suggested that the coordination of CO_2 to the metal, may reduce its Lewis acidity and thereby quench sequential epoxide enchainment. The resulting copolymers show a single glass transition temperature, proposed to be due to block miscibility. Darensbourg and co-workers also prepared block copolymers from CHO/PA/CO_2, using a chromium salen catalyst **6b** with PPNCl/N_3 as the co-catalyst, however, in this case two glass transition temperatures were observed, consistent with phase separation of the blocks (T_g = 48 °C and 115 °C).[21] A Cr(III)salen catalyst with a tethered ammonium co-catalyst, was also successfully applied, by the Darensbourg group, to copolymerize PO/NA/CO_2.[30a] Duchateatu and co-workers reported that metal porphyrin catalyst **1c** with DMAP (as co-catalyst), was effective for the terpolymerisation of CHO, anhydrides (SA/CPrA/CPA or PA) and CO_2.[10d] In this case however, there was concurrent carbonate linkage formation during the enchainment of ester linkages, leading to tapered block structures. This was attributed to relatively similar rates of anhydride and CO_2 insertion into the metal-alkoxide bonds. In contrast, Chisolm et al. also used the same catalyst, **1c** with PPNCl as co-catalyst, for the terpolymerization of PO/SA/CO_2 and reported the formation of diblock copoly(ester-carbonates).[18] Our group have reported that the di-zinc and di-magensium catalysts, **11a/b**, are also selective in the terpolymerizations of CHO, PA and CO_2 producing block copoly(ester-carbonates).[26] Heterogeneous catalysts such as zinc glutarate or double metal cyanides (DMC) have also been investigated. Using zinc glutarate for PO/MA/CO_2 copolymerizaiton produced tapered block copoly(ester-carbonates).[30b] This is proposed to be due to similarities in the rate of insertion of the anhydride and CO_2 co-monomers. A similar result occurs using double metal cyanide catalysts.[30c] The polymerisation of CHO/MA/CO_2 gave a sequence where initially polyester forms, together with the random insertion of carbon dioxide. Once the MA is mostly consumed (> 90%), the carbonate block forms. In contrast, the polymer supported double metal cyanide showed a different selectivity.[28] During the polymerisation of PO/MA/$CO_{2,}$ only polycarbonate formed, with occasional, random insertion of MA, there was no formation of polyester blocks.

2.4.2 Combining ROCOP and ROP: Tandem and Switch Catalysis

Another interesting route to copoly(ester-carbonates) involves the copolymerization of epoxides, CO_2 and lactones. This is conceptually distinct as it requires the combination of two different polymerization catalytic cycles: ROCOP and ROP. There have been a few reports of the use of heterogeneous catalysts for such transformations, including zinc glutarate[31] and double metal cyanides,[32] in all cases leading to rather low lactone uptake and random or undefined polymer structures. A (BDI)ZnOAc catalyst was reported for the terpolymerisation of CO_2/CHO/lactide (LA), resulting in the formation of a statistical copolymer.[33] The authors observed that using *rac*-lactide resulted in higher carbonate content than using S-lactide.

Earlier this year, our group reported a novel ‘Switch’ catalysis which enabled the two polymerization cycles to be combined and controlled.[34] Using the di-zinc catalyst, **11a**, for the terpolymerization of CHO, CO_2 and ε-caprolactone (CL) led to the selective formation of block copoly(ester-carbonates) (Fig. 10).[35] The reactions were monitored using in situ ATR-IR spectroscopy which showed that firstly the ROCOP reaction occurred leading to formation of only polycarbonate, subsequently, after carbon dioxide removal, the lactone ROP occurred leading to a block copoly(carbonate ester). The selectivity was interesting and unexpected because the rate of ROCOP was significantly slower than the rate of ROP, however, it was controlled by the pre-rate determining step (carbon dioxide insertion into the metal alkoxide bond). This is comparable to the earlier findings on epoxide/anhydride/CO_2 copolymerisation. It was discovered that the catalyst selectivity could be easily manipulated, thus under a nitrogen atmosphere the combination of CHO and CL led to the exclusive formation of polyester. When the gas atmosphere was changed to CO_2, the only product was the polycarbonate. The polymerizations were easily controlled, in one-pot, by adding different monomers at selected time points and this enabled the production of block copolymers.

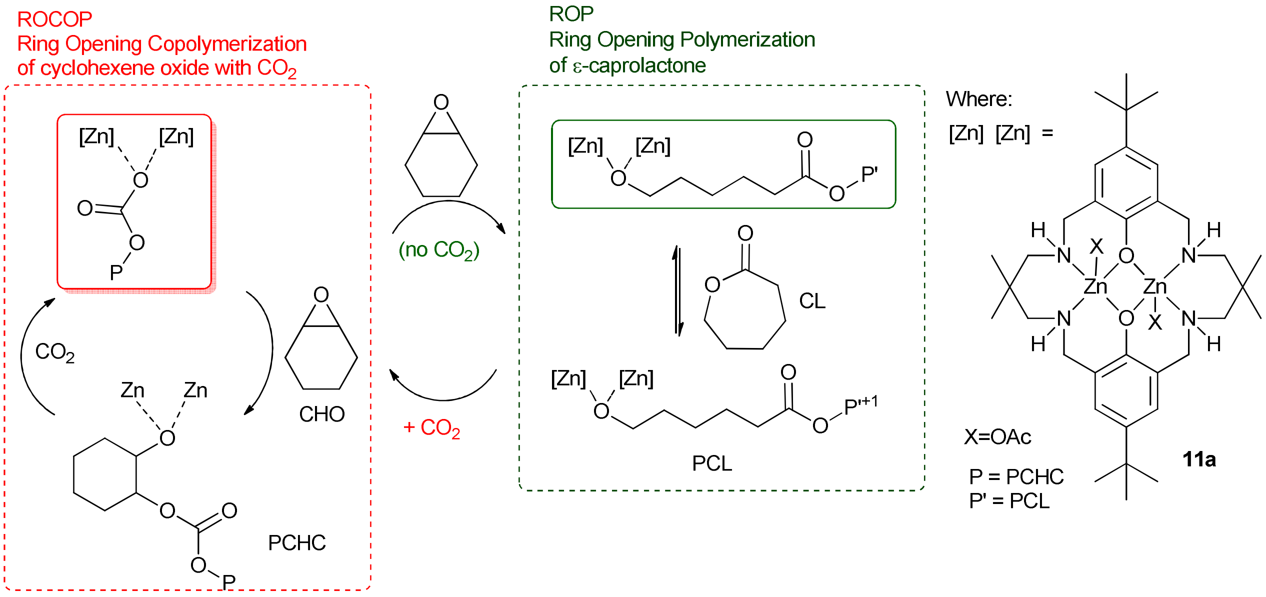


Fig.10 Illustrates the combination of ROCOP and ROP reactions, using a single catalyst as reported by Williams and co-workers.[34]

The polymerization is initiated by reaction between the metal carboxylate species and cyclohexene oxide, resulting in the formation of a metal alkoxide species. This intermediate can enter into either catalytic cycle (ROP or ROCOP). Despite the fact that the overall rate for ROP is significantly faster than ROCOP, in the presence of all three monomers the catalyst selectively enchains carbonate units. This is because the fastest reaction for the alkoxide intermediate is with carbon dioxide (1 bar pressure), leading to the formation of a zinc carbonate intermediate. The zinc carbonate species cannot react with lactones, thus it can only react with epoxide to (re)-generate the metal alkoxide species. The polymerization progresses through the ROCOP cycle. Upon removal or consumption of the carbon dioxide, in the presence of excess cyclohexene oxide, the catalyst can switch to ring-opening polymerization and selectively produce copoly(carbonate-*b*-ester). An attraction of this one-pot, single catalyst, switch catalysis is the potential to use it to prepare multi-block materials.

An alternative route to such copolymers is by carrying out the CO_2/epoxide ROCOP in the presence of (di)hydroxyl terminated polymeric chain transfer agents. In 2010, Lee and co-workers carried out an extensive study of CO_2/epoxide ROCOP, using cobalt salen catalysts, and the in presence of various macromolecular chain transfer agents.[36] Hydroxyl terminated polymers, including PCL and PEG, were used to prepare di or triblock co-polymers (AB or ABA type). An indication of the promising properties for such terpolymers is that the copoly(carbonate-ether) PPC-PEG block copolymer was less brittle than the homopolycarbonate (PPC).

In an alternative strategy, our group and the Darensbourg group have both applied polycarbonate macro-initiators in the ring-opening polymerization of lactones. In both cases, two catalysts were required and it was important to ensure compatibility between the different species and cycles. In 2011, we reported a di-zinc catalyst which was highly selective for the preparation of telechelic dihyroxyl terminated polycyclohexene carbonate (PCHC).[23c] The telechelic PCHC was subsequently applied, together with an yttrium initiator, for the ring-opening polymerization of *S*- or *rac*-lactide, leading to the formation of ABA block copoly(lactide-*b*-PCHC-*b*-lactide). Subsequently, Darensbourg and co-workers applied a cobalt(III) salen catalyst, featuring a tethered ammonium co-catalyst, for the ROCOP of SO/CO_2.[37] Once the ROCOP was complete, water was added to quench the ROCOP reaction and form, *in situ*, the hydroxyl terminated polymer. This addition was followed by the addition of LA, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the ROP catalyst; in the second phase a block copoly(carbonate-ester) was produced. This initial report was followed by the discovery that a related cobalt(III) salen catalyst, featuring a tethered co-catalyst, could catalyse the polymerisation of PO and CO_2 in the presence of water to give dihydroxyl terminated PPC.[38] This telechelic polymer was subsequently applied as a macroinitiator for LA polymerisation using the same sequence of additions as previously. This year, Coates and co-workers reported the copolymerization of various epoxides, including PO, CHO, CPO and various glycidyl ethers, with dihydrocoumarin.[39] This novel copolymerization produced perfectly alternating, atactic polyesters; it was surprising that two of these polyesters showed significant crystallinity.

3. ROCOP: Polymer Properties

The recent focus and development of ring-opening copolymerization (ROCOP) catalysts is significant because the product polyesters differ considerably in backbone structure and functionality compared to those accessible by ROP. Most importantly, simply by changing the epoxide or cyclic anhydride, the properties of the resulting material can be easily controlled, including the thermal properties (glass transition temperature (T_g), thermal decomposition temperature) as well as properties such as the lower critical solution temperature (LCST) and UV-stability.[2c, 10a, 10g, 17, 40] In 2014, Coates and co-workers communicated the first example of a polyester stereocomplex, prepared by catalytic and regio-selective ROCOP.[41] In the following sections, the structures/properties of this novel class of polyesters and polycarbonates will be outlined.

3.1 Polyesters

3.1.1 Thermal Properties: Glass Transition Temperature (T_g)

Understanding the influence of the polymer structure and its concomitant effect on the glass transition temperature (T_g) is a critical parameter, particularly as it influences the materials' mechanical properties. One important limitation for aliphatic polyesters is their low thermal stabilities, in particular low glass transition temperatures (T_g). It is especially difficult using ROP to prepare polyesters with glass transition temperatures in excess of 100 °C; where this has proved possible the monomer syntheses are often extremely challenging and include multiple steps.[42] One attraction of ROCOP is the facility to prepare materials with tuneable glass transition temperatures, including those approaching or exceeding 100 °C.[21] Thus, by selecting the epoxide/anhydride combination, it is relatively straightforward to modify the thermal properties of the resulting polyester.

The nature of the polymer backbone linkages exerts a significant influence, also, the presence of ether linkages is often proposed to introduce backbone flexibility leading to a lower glass transition temperature. Nishimura and co-workers, reported that for poly(itaconic anhydride-*co*-1,2-epoxybutane), the T_g decreased upon the increasing the content of ether linkages (from 11 to -9 ^{o}C).[43] It is notable that although isomerization from the itaconic to citraconic configuration occurred during the polymerization, the molar ratio of the two configurations hardly affected the T_g. In addition, it was noted that the T_g of the polyester could be further increased by the crosslinking of the polymer through the itaconic units.

ROCOP using maleic anhydride has been quite widely investigated (*vide supra*) and is attractive from the property perspective because moderation of the maleic group enables control of the T_g.[44] Poly(maleic anhydride-*alt*-propylene oxide) had only Z-configuration C=C bonds (Fig. 11a). However, these can be isomerized to the E-configuration, using morpholine (Fig. 11b). In addition, by varying the isomerization reaction time, the ratio of Z- to E- was easily controlled. The T_g increased from -14 ^{o}C to 4 ^{o}C with the increasing content of the E-configuration (from 0 to 92 mol%).

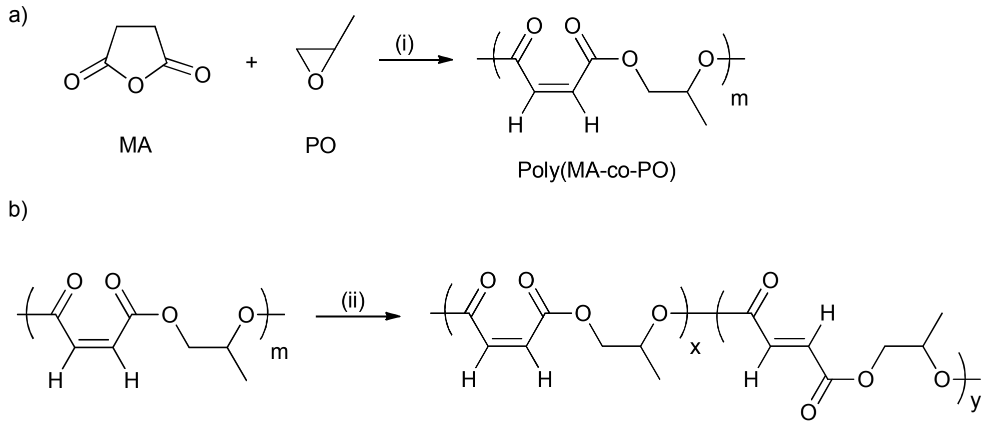


Fig. 11 (a) Ring-opening copolymerization of maleic anhydride with propylene oxide; (b) isomerization of poly(maleic anhydride-*co*-propylene oxide) catalyzed by morpholine.[44] Reagents and Conditions: (i) $Mg(OEt)_2$, toluene; (ii) Morpholine, dichloroethane.

As mentioned, Coates and co-workers reported a range of polyesters synthesized from maleic anhydride and various epoxides, including PO, epichlorohydrin, glycidyl ethers, perfluoroalkyl substituted epoxides, via ROCOP.[17] The T_g of the poly(alkylene maleate) was tuned from -26 ^{o}C to 41 ^{o}C by simply changing the epoxide co-monomer. The highest T_g was observed using perfluoro alkyl substituted epoxides, whilst epoxides with diethylene glycol substituents afforded materials with the lowest T_g. Furthermore, the isomerization of poly(propylene maleate) to poly(propylene fumarate) slightly increased the T_g of the polyesters.

Since the choice of epoxide affects the T_g of the resulting polyester, several epoxides with a range of anhydrides were selected for investigation by Darensbourg and co-workers.[21] They pointed out that for a particular anhydride, the T_g of the resultant polyesters increases in the order PO < SO < CHO, whilst for a particular epoxide, the T_g increases in the order SA < MA < CHA ≤ PA < CHE. Thus, as expected, the steric effect of the pendant groups and the rigidity of the repeating unit exert a significant influence on the T_g of polyesters [from -39 ^{o}C (SA/PO) to 95 ^{o}C (CHE/CHO)]. Moreover, two different T_g values were obtained for MA/PO copolymer due to photo-isomerization reactions.

A further influence on the polyesters T_g is the molar mass of the polymer. Duchateau and co-workers, reported that the T_g of poly(styrene oxide-*alt*-phthalic anhydride) increases from 43 to 73 ^{o}C as the molar mass increases from 4,500 to 9,000 g/mol.[10c]

In 2014, Coates and co-workers reported the first example of a polyester stereocomplex, prepared by the ROCOP of enantiopure epoxides/anhydrides (Fig. 12).[41] Using highly regio-selective chiral cobalt salen catalysts, with ionic-cocatalysts, the ROCOP of enantiopure *R*- or *S*-propylene oxide, with succinic anhydride enabled preparation of highly regio-regular, isotactic poly(propylene succinate). The thermal properties of the two enantiopure polymers showed very slow crystallization (T_m: 50 °C, with a smaller amount of high melting polymorph 70 °C). However, by mixing the two polymers a stereocomplex or co-crystallite between the two isotactic (enantiomeric) polymers was formed. The stereocomplex showed a higher melting temperature (120 °C) and the $t_{1/2}$ of recrystallization was three orders of magnitude faster than for the separate enantiomers. This very promising result shows the potential to manipulate the stereo- and regiochemistry of ROCOP to enable the preparation of polyesters with a melting temperature approaching that of low density polyethylene.

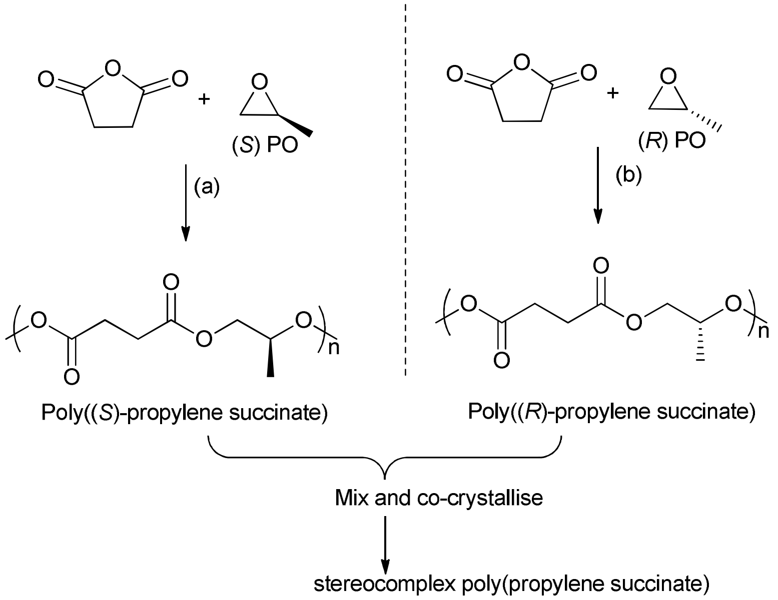


Fig. 12 Illustrates the formation of stereocomplex poly(propylene succinate) by co-crystallisation of poly((*S*)-propylene succinate) and poly((*R*)-propylene succinate). Reagents and Conditions: (a) [(*R*,*R*)-(Cl-salcy)CoNO$_3$], [PPN][NO$_3$], 30 °C, 36 h. (b) [(*S*,*S*)-(Cl-salcy)CoNO$_3$], [PPN][NO$_3$], 30 °C, 36 h.[41]

3.1.2 Thermo-responsive polyesters

Thermo-responsive polymers such as poly(*N*-isopropylacrylamide) (PNIPAAM) are attracting attention, particularly in bio-medical contexts.[45] However, so far, the common thermo-responsive materials are not degradable, and PNIPAAM has been implicated in some cytotoxic mechanisms.[46] It would be of significant value to design polymers with both thermo-responsivity and biodegradability. To address this problem, thermo-responsive polyesters were synthesized by Hao and coworkers.[47] Epoxides bearing oligo-ethylene glycol pendant chains (with different chain lengths) were copolymerized with succinic anhydride (Fig 13). A lower critical solution temperature (LCST) was observed in all three samples, with a narrow transition temperature window; the temperature was dependent on the chain length (m = 1, 2, 3 corresponding to LCST values of 17.8 ^{o}C, 49.2 ^{o}C and 73.3 ^{o}C, respectively). Under physiological pH conditions, the polyesters displayed comparable degradation rates to some clinically applied materials. Interestingly, the degradation rate also depends on the ether side chain length, a finding that has been attributed to the increases in hydrophilicity and aqueous solubility.

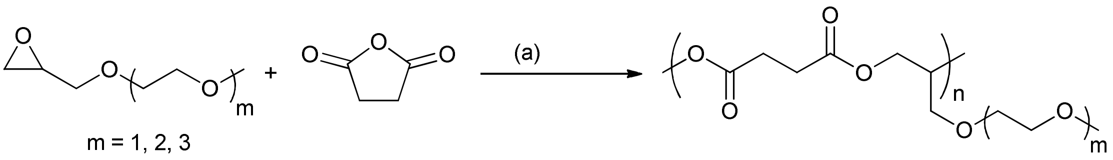


Fig. 13 Shows the synthesis of the thermo-response polyesters prepared by ROCOP. Reagents and Conditions: (a) Al(O^{i}Pr)$_3$.[47]

Although these initial results are promising, the successive tuning of the LCST cannot be easily achieved. In order to achieve finer degrees of control, a mixture of MEMO/ME$_2$MO epoxides were copolymerized with SA.[40] By changing the molar ratio of MEMO/ME$_2$MO (from 0 to 100 mol %), fine control of the LCST of the polyester was possible over the range 17.8 to 49.2 °C. Importantly, a linear increase of LCST was observed with the increasing ME$_2$MO content in the initial feed.

3.1.3 Energy Storage Polyesters

The photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) derivatives has long been known as an efficient means to convert and store solar energy.[48] Polyesters which can store solar energy were prepared by ROCOP of epoxide monomers bearing a norbornadiene (NBD) moiety and various anhydrides.[49] The photoisomerization of these NBD groups (Fig. 14) was possible either in thin films or in solution. The stored energy can be directly released through photoirradiation of the sample above its T_g. The polymers were able to release approximately 90 kJ/mol energy.

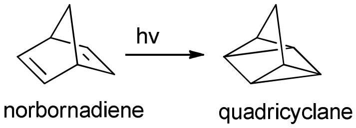


Fig. 14 Shows the photoisomerization process from norbornadiene to quadricyclane.

A photosensitizer addition was required to achieve the conversion, however, Nishikubo *et al.* successfully synthesized a self-photosensitizing polyester using a mixture of epoxides, with norbornadiene (NBD) and benzophenone substituents, copolymerized with PA.[50] The reactivity of photoisomerization was increased, while the energy storage capacity remains the same (90 kJ/mol). Nevertheless these polymers are hampered by relatively low photoreactivity and material fatigue. To solve this problem, polyesters bearing donor-acceptor norbornadiene (NBD) moieties in both the main chain and the side chain were prepared via ROCOP.[51] The rate of photoisomerization using these donor-acceptor NBD derivatives is increased 5-8 times compared to earlier generations of materials. They also demonstrate the highest storage capacity ~150-190 J/g.

3.1.4 Mechanical properties of Polyesters

While the ROCOP of cyclic anhydrides and epoxides has aroused intensive research interest recently, the study of the polyesters' mechanical properties has rarely been reported. As a class of polymers with tuneable backbone substituents, polyesters, prepared via ROCOP, might be capable of exhibiting controllable mechanical properties by simply changing the combination of anhydrides/epoxides. A pioneering study has been conducted by Wang et al.[52] Three representative anhydrides: succinic anhydride (aliphatic), phthalic anhydride (aromatic), and maleic anhydride (unsaturated), were copolymerized with propylene oxide using a double metal cyanide complex catalyst, to afford poly(ether-esters) (polyesters with ether linkages) polyols. After the chain extension reaction using 4,4'-diphenylmethanediisocyanate (forming a polyurethane segment), the mechanical properties of these three poly(ether-ester) polyurethanes were investigated. By changing the aliphatic anhydride (succinic anhydride) to the aromatic one (phthalic anhydride), the mechanical property was significantly increased from 19.1 to 23.5 MPa. Also, a high ester content in soft segments was found to be important to achieve the best mechanical properties of the polyurethanes.

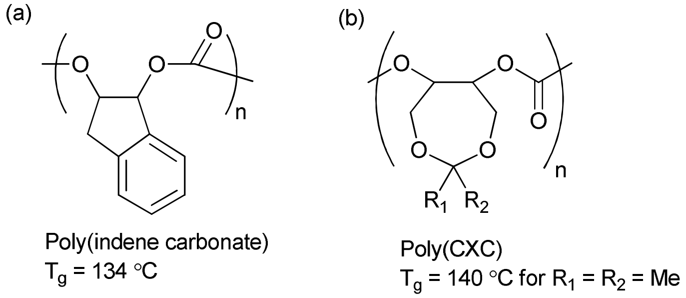
3.2 Polycarbonate and Terpolymer Properties

As mentioned above, there is a plethora of comprehensive reviews of catalysts for CO_2/epoxide ROCOP.[6a, 9, 11] Rather than any further catalysts review, this section will review the material properties of these aliphatic polycarbonates, prepared by ROCOP, as well as the potential for copoly(ester-carbonates). In our 2011 review of catalysts for CO_2/epoxide copolymerisation, we wrote that "so far, polycarbonates produced from CO_2 cannot match the properties of conventional polycarbonate (from bisphenol A)."[9] Three years on, the outlook is markedly different.

It has been known since the initial discovery of ROCOP, by Inoue, that various epoxides, including styrene oxide (SO),[53] epichlorohydrin,[53] 3-phenyl-1,2-epoxypropane,[54] cyclohexylepoxyethane,[55] 1,2- and 2,3-epoxybutane,[56] isobutylene oxide,[14f] and various glycidyl ethers, bearing functional moieties including methyl, ethyl, benzoate and cholestryl,[57] could be copolymerised (Fig. 2). Inoue and co-workers also showed that ROCOP using trimethylsilyl protected glycidyl ethers, with aluminium porphyrin systems (**1a**-**e**), could furnish hydroxyl-functionalised polycarbonates after deprotection.[58] Inoue's approach showed great foresight, marking an important milestone and enabling further functionalization (post-polymerization) of the hydroxyl groups to give a greatly expanded range of polycarbonates. Other epoxides that have been investigated for ROCOP include cyclopentene oxide,[23o, 59] 2,3-epoxy-1,2,3,4-tetrahydronaphthalene,[60] limonene oxide,[61] indene oxide,[10f] isomers of butane oxide and functionalized 3,5-dioxaepoxides.[62]

3.2.1 Thermal Properties

The two most common aliphatic polycarbonates prepared by ROCOP are poly(propylene carbonate) PPC and poly(cyclohexylene carbonate) PCHC. These are usually produced as amorphous materials and typically show T_g values of approximately 30-40 °C (PPC) and 80-115 °C (PCHC).[9] A recent exciting development in this field has been the discovery of other polycarbonates with high thermal resistance, as evidenced by high glass transition temperatures. Darensbourg and co-workers also investigated indene oxide for ROCOP and reported significantly higher thermal resistance of the resulting polycarbonates (Fig. 15).[10f]



Poly(indene carbonate)
T_g = 134 °C

Poly(CXC)
T_g = 140 °C for $R_1 = R_2$ = Me

Fig. 15 Highest T_g polycarbonates reported to date from ROCOP of CO_2 and (a) indene oxide (IO)[10f] and (b) 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO).[62]

Following optimization, medium molar masses were achieved, yielding poly(indene carbonate) with a high T_g of 134 °C; the second highest T_g for any CO_2 derived polycarbonate reported to date and approaching that of the polycarbonate prepared form bis(phenol) A (T_g= 154 °C).[10e] The polycarbonate molar mass was an important factor, with a variation of > 20 °C in T_g depending on the chain length (M_n) of poly(indene carbonate).[10b] The authors extrapolated the maximum T_g to a value of 153 °C, although they were unable to achieve sufficient molar masses to realise this result. In contrast, the structurally similar 2,3-epoxy-1,2,3,4-tetrahydronaphthalene was difficult to polymerise,[60] resulting only in trace amounts of polymer and formation of the cyclic by-product.

Lu and co-workers synthesized a range of 3,5-dioxaepoxides (Fig. 15b) which were copolymerized with CO_2, using a range of enantioselective dinuclear catalysts.[23o, 62] For the dimethyl substituted dioxaepoxide, an isotactic polymer (PCXC) with >99 % enantioselectivity and high crystallinity was prepared, exhibiting a melting temperature of 242 °C. When the achiral analogue of the dinuclear cobalt salen catalyst was used, the polymer was atactic and notably, demonstrated the highest T_g yet reported (140 °C). This study once again highlights the importance of both tacticity control and polymer backbone rigidity in achieving the optimum thermal properties. The polymers are also highly suited to post-polymerization modification producing polycarbonates with pendant hydroxyl groups; which can subsequently be applied as macro-initiators for the ring-opening polymerization of lactide.[62] The number of branch points, and therefore the thermal and mechanical properties of the polymer, could be altered by simple variation of the feed ratio of dioxaepoxides, CHO and CO_2. This strategy could be of interest in biomedical applications, since the PLA regions introduce degradability and biocompatibility into the polymer.

3.2.2 Tacticity Control

Controlling the stereochemistry of epoxide enchainment in ROCOP affects the tacticity of the resulting polycarbonate, which influences the macroscopic properties.[12, 23i, 23o, 63] There have been numerous results of stereoselective copolymerisation of racemic epoxides and CO_2.[12, 64] The focus here will be on highlighting significant recent advances in the field and the influences on the material properties.

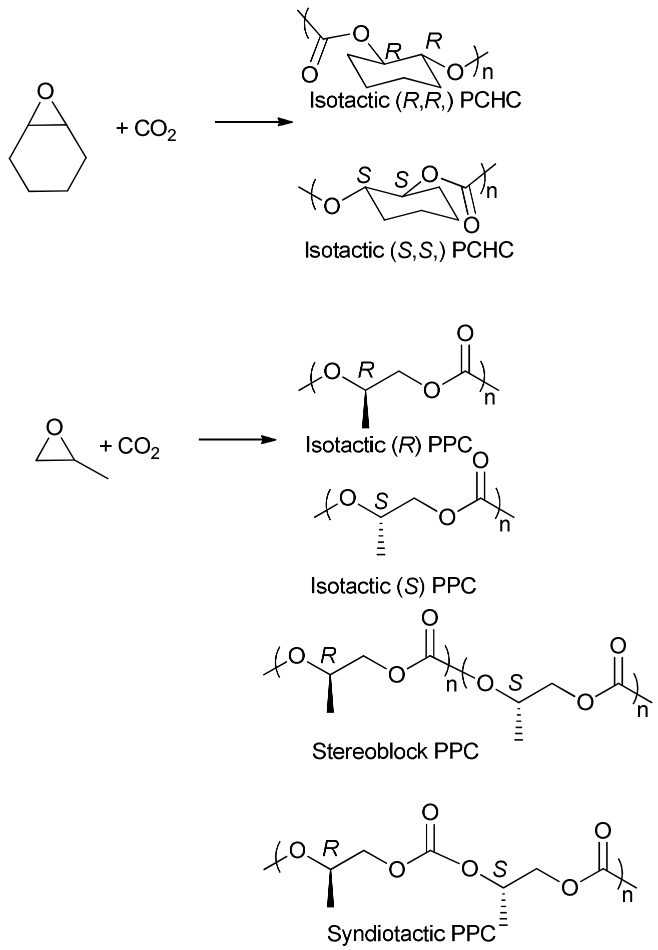


Fig. 16 Selected structures of stereocontrolled polycarbonates (considering head-to-tail enchainment for PPC).

Isotactic PCHC has been synthesised by several groups,[23i, 23o, 63f, 63i, 65] usually with chiral catalysts such as Co/Cr salen catalysts and ZnBDI catalysts (Fig. 16).[23i, 23o, 63i, 63k, 66] The degree of isoselectivity is usually determined by comparing the integrals of various tetrad/carbonyl signals in the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra or by polymer hydrolysis and analysis of the chirality of the diol degradation products. An elegant study by Lu and co-workers[23o] demonstrated the highest *ee* values (> 99%) for isotactic PCHC through careful modification of an asymmetric cobalt salen catalyst system. For iso-enriched PCHC (*ee* $\geq$ 92%), a T_g of 124 °C was observed. For isotactic PCHC (*ee* > 99%), there was no amorphous region and a T_m value of 272 °C was observed. Equivalent degrees of iso-selectivity were also recently demonstrated by Coates and co-workers by systematic modification of the (BDI)Zn catalysts, particularly applying C1 symmetric complexes.[23i] Very recently Guillaume, Carpentier and co-workers have demonstrated that the ring-opening polymerization of *trans*-

cyclohexene carbonate, using a range of metal/organo-catalysts, and provides an alternative route to prepare isotactic PCHC, showing a similarly high degree of stereoselectivity and melting temperature.[67] This latter result is particularly important as it had previously been assumed to be thermodynamically unfeasible for five-membered ring cyclic carbonates to undergo ring opening polymerization.

The preparation of isotactic PPC has also been widely investigated and various chiral cobalt and chromium salen catalysts have been developed (Fig. 16).[23m, 63j, 66b, 68] One very interesting result was achieved by Nozaki and co-workers who used chiral cobalt salen catalysts to prepare a tapered stereoblock (isotactic) poly(propylene carbonate) from *rac*-PO (Fig. 16).[63h] The finding was particularly significant as it had previously not been known that PPC could form stereoblock structures and it offers the intriguing potential to prepare a stereocomplex PPC in the future. The stereoselective PPCs prepared by Nozaki and co-workers were semi-crystalline, showing T_g of 33 °C (M_n = 15,000 g/mol), and increased the thermal decomposition temperatures. Syndiotactic PPC, having 79-96% of head-to-tail linkages, was also synthesised by Coates and co-workers.[68b] Other epoxides have been copolymerised stereoselectively with CO_2, including 1,2-hexene oxide,[68g] 1,2-butene oxide,[68g] styrene oxide,[63c, 69] phenyl glycidyl ether[63a, 63b] and epichlorohydrin.[70]

3.2.3 Post-polymerization Modification

Post polymerisation modification allows the introduction of secondary groups, which alter the properties of the polymer. This requires the polymer to contain a functional group which can be modified. The most common groups are hydroxyl groups, alkynes and vinyl groups or epoxy groups. The functional groups can be terminal (at the end of the polymer chain) [33, 37-38, 71] or pendant (along the backbone). [62, 72]

When the functional groups are terminal this leads to block copolymers. Terminal hydroxyl groups can be obtained by use of specific catalysts or the addition of chain transfer agents.[23b, 71] The hydroxyl terminated polymers (polyols) can then be used as chain transfer agents for further polymerisations (see 2.4.2). Polyols can also be reacted with isocyanates to synthesise polyurethanes.[4, 52, 73] This is proposed as a readily accessible way to displace a fraction of conventional petrochemically derived polymer with renewable CO_2 based polymers. CO_2 based polyols have been shown to perform favourably on a life cycle basis (relative to conventional polyols),[5] with production now reaching industrial scales.[3]

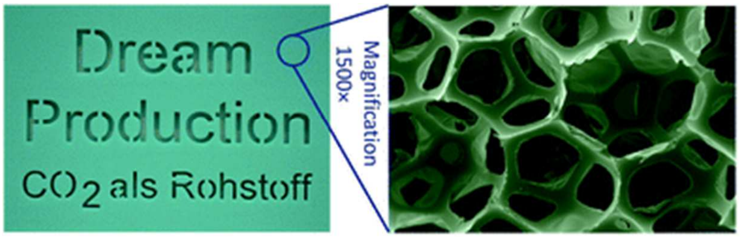


Fig. 17 Shows an image of a polyurethane foam and micrograph showing the foam structure. The foam was prepared by the reaction between poly(ether carbonate) polyol (10.5 wt% CO2) and toluene di-isocyanate. The images are reproduced from reference 4.

When the functional groups are pendant or 'mid chain', further modification leads to graft or brush copolymers. Pendant functional groups occur from the ROCOP of functionalised monomers. The main challenge with using functionalized epoxides in ROCOP is ensuring that the functional group does not interfere with the polymerization. This becomes a particular problem with hydroxyl groups which are highly effective chain transfer agents and thus should be considered as reactive functionalities. Instead, functionalised monomers that can be modified after polymerization to give hydroxyl groups are used.

A range of different glycidyl ethers have been copolymerized with CO_2 to give various poly(1,2-glycerol carbonates).[57, 63a, 74] These polymers, which are often modified post polymerization to produce hydroxyl functionalized polycarbonates, are reported to be biodegradable and biocompatible – contrasting with poly(propylene carbonate), which has been shown to be resistant to enzymatic attack.[75] Ren and co-workers have prepared regio-regular (HT), isotactic poly(phenyl glycerol carbonate) which is a semi-crystalline material with a melting temperature of 75 ^{o}C. In contrast, its atactic counterpart exhibited a T_g of 50 ^{o}C.[63a] Deng and co-workers used epichlorohydrin[47] to produce a series of epoxides that gave polycarbonates with oligo(ethylene glycol) side chains which were thermo-responsive materials.[74i, 74j] A common strategy has been to use various protecting groups to enable efficient polymerization and after polymerization to effect deprotection without degrading the polymer backbone, for example by the hydrogenation of benzyl groups or acid hydrolysis of alkyl groups (Fig. 18). The nature of the protecting group is important and a reactivity series for the production of polymer using various protecting groups has been established: allyl > butyl > isopropyl.[74h] Using glycidyl ethers to prepare polycarbonates, followed by deprotection produces poly(1,2-glycerol carbonate), which is substituted with primary hydroxyl groups, in contrast to the ROP of cyclic carbonate which affords poly(1,3-glycerol carbonate) that contains only secondary hydroxyl groups. Poly(1,2-glycerol carbonate) was shown to be ‘highly degradable with a $t_{1/2}$ of 3 days by Grinstaff and co-workers.[74d] Luinstra, Theato and co-workers applied a 2-nitrobenzyl glycidyl ether in copolymerization, the resulting polycarbonates were deprotected using ultra-violet light, without any backbone degradation, to prepare poly(1,2-glyercol carbonates).[76]

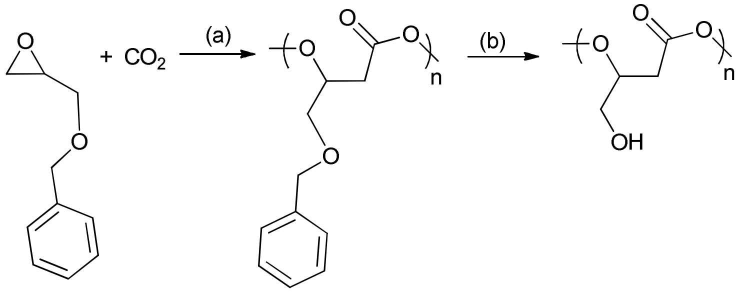


Fig. 18: Shows the preparation of poly(1,2-glycerol)carbonate as reported independently by Frey and co-workers and Grinstaff and co-workers.[74a, 74b, 74d] Reagents and conditions: (a) zinc pyrogallol catalyst (Et_2Zn:pyrogallol, 2:1), 20 bar, 40 h or [Co(salcy)(O_2CCCl_3)]PPNCl, 40 bar, 22 °C, 4 h. (b) H_2 (40 bar), Pd/C, ethyl acetate, 24 h.

Using other functionalized glycidyl ether monomers allows access to polycarbonates with controllable reactivity. Frey and co-workers copolymerized propargyl glycidyl ether with CO_2 to produce polycarbonates.[74l] The alkyne functional groups on the polymer were reacted with benzyl azide, using the copper-catalyzed Huisgen-1,3-dipolar addition, to produce functionalized polycarbonates.[74e, 74l] The same group also prepared various random copolycarbonates containing different ratios of glycidyl methyl ether and 1,2-isopropylidene glyceryl glycidyl ether units. The acetal functional group was deprotected, under acidic conditions, to yield polycarbonates functionalized with side-chain diol groups.[74e, 74l]

Ester functionalization of epoxides while potentially useful for post polymerisation modification, is rare for these polymerizations as the ester functional group can react by transesterification processes. The copolymerisation of glycidyl esters/CO_2, to give acrylate functionalized PC was achieved using a heterogeneous zinc-cobalt double metal cyanide complex.[77] Although epoxide homopolymerization also occurred, resulting in formation of a poly(carbonate-*co*-ether). Duchateau and co-workers copolymerised an ester functionalised CHO using a (EtBDI)ZnOEt catalyst, however significant amounts of transesterification occurred both from the pendant ester and the carbonate unit.[78]

As discussed previously, 3,5-dioxaepoxides (CXO) can be copolymerised with CO_2 to give isotactic and semicrystalline polycarbonate (Fig. 15). The polymer can be easily deprotected to produce a polymer with pendant hydroxyl groups. This was used as a macro-initiator in the ring-opening polymerisation of lactide to give graft copolymers.[62]

One potential draw-back of using protecting groups is the need for deprotection strategies which do not compromise the polymer backbone. Alternatively, the copolymerization of vinyl functionalized epoxides enables alternative post-polymerization functionalization. Coates and co-workers carried out a comprehensive investigation of the copolymerisation of CO_2 with 4-vinyl cyclohex-1,2-ene oxide (VCHO), and other functionalised CHOs with vinyl, triethylsiloxy, PEG, ketal, alkyl and fluorophilic substituents at the 4 position.[79] They employed a [Zn(BDI)(OAc)]complex that was both tolerant of the functional groups, and enabled production of high molar mass polymers with narrow distributions ($\text{Đ}_M < 1.1$). A range of multiblock copolymers, were prepared by addition of different functionalized ~~-~~CHOs upon full consumption of the previous monomer. It was possible to prepare multi-block copolycarbonates featuring lipophilic, hydrophilic and fluorophilic units in the same linear chain. The authors highlight that this method could provide a ready means for the systematic study on the effect of block miscibility on polymer nanostructure.[78, 80]

Frey and co-workers, copolymerized various epoxides possessing terminal vinyl groups, e.g. 1,2-epoxy-5-hexene (EH) and 1,2-epoxy-9-decene (ED), with PO and CO_2.[72a] The frequency of pendant vinyl groups to the PC backbone could be controlled through adjusting the proportion of PO in the feed ratio, although neither ED nor EH could be directly copolymerised with CO_2. Carboxyl and hydroxyl moieties were introduced using the thiol-ene reaction. The hydroxyl functionalised polycarbonates were used as macro-initiatiors for lactide ROP, giving graft copolymers with thermal properties, linked to the PLA branch length.[72a]

In 2014, Darensbourg and co-workers reported ROCOP using vinyl-oxirane, PO and CO_2, with cobalt(III) salen catalysts to produce a range of polycarbonates (Fig. 19).[80c] These were modified using post-polymerization thiol-ene 'Click' reactions to produce amphiphilic and water soluble polycarbonates with multiple hydroxyl or carboxyl functionalities.[80c]

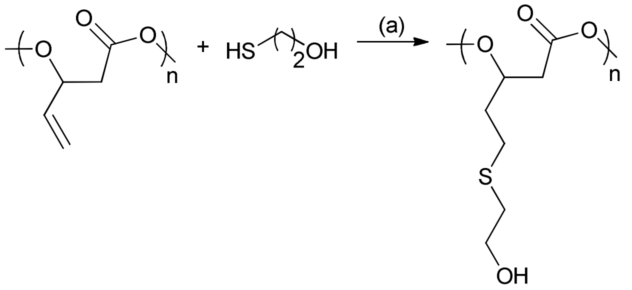


Fig. 19 Illustrates the functionalization of poly(2-vinylpropylene carbonate) using the thiol-ene reaction. Reagents and Conditions: (a) AIBN, THF, 24 h, 70 °C.[80c]

Zhang and co-workers, also investigated the post-modification of poly(VCHC) *via* the thiol-ene reaction to generate OH groups. These were subsequently used as initiators in the ROP of ε-caprolactone to give graft copolymers.[72c]

An interesting possible alternative to the ROCOP between epoxides and carbon dioxide was presented in 2014 by Nozaki and co-workers who reported the copolymerization of carbon dioxide and butadiene via a lactone intermediate.[81] They applied a palladium catalyst to prepare a metastable lactone intermediate, in addition to various side-products, via the condensation of carbon dioxide and buta-1,4-diene. The lactone was reacted by free radical polymerization to afford polymers. So far, this reaction represents a proof of principle, with a range of different repeating units present in the polymer backbone, but further research may enable its application to prepare functionalized polycarbonates.

3.2.4 Bio-derived Epoxides

One attraction of epoxide/CO_2 copolymerization is the ability to use, or even recycle, carbon dioxide in the polymer backbone. Naturally, there is also significant interest in the possibility to prepare epoxides from biomass to provide a route to fully renewable aliphatic polycarbonates. The epoxides or anhydrides may be derived from three naturally occuring sources: carbohydrates, fatty acids (triglycerides) and terpenes.

Teperenes contain double bonds which can be epoxidised, such epoxides include Limonene oxide and pinene oxide. The first success of terpene derived epoxide/CO_2 ROCOP came from Coates and co-workers, in 2004, who reported the successful copolymerization of limonene oxide/CO_2, using a BDIZnOAc catalyst.[61] The polymer was highly regio-and stereoregular, and moderate-good activity was possible (TOF = 37 h^{-1}). The catalyst is highly selective for the ROCOP of the trans-epoxide diastereoisomers (leaving the cis-epoxides unreacted). In 2014, Coates and co-workers reported on the application of closely related catalysts to prepare enantiopure isotactic poly(limonene carbonates) (Fig 20).[82] These were prepared by reacting *cis*/*trans* mixture of (*R*)- or (*S*)- limonene oxide with CO_2. The catalyst was found to only polymerize the *trans* diastereoisomer letting the *cis* isomer unreacted. It results in highly regio-, diastereo-, and enantiopure polymers which were found to have amorphous structures. However, mixing an equal proportion of the two enantiomers (i.e. the racemic mixture of poly(*R*)- and poly(*S*)-limonene carbonate) enabled the preparation of a co-crystallite or stereocomplex poly(limonene carbonate) which had a crystalline structure (as determined by powder XRD measurements).

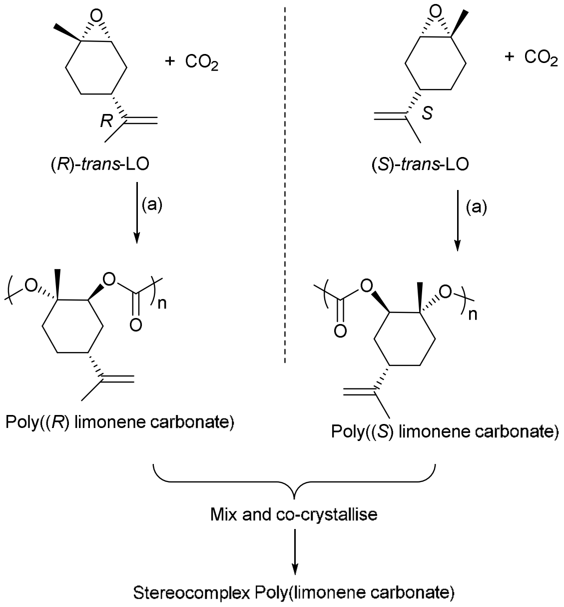


Fig. 20 Shows the preparation of stereocomplex poly(limonene carbonate). Reagents and Conditions: (a) $[(BDI)Zn(N(SiMe_3)_2]$, 22 °C, 7 bar pressure CO_2.[82]

Thomas and co-workers used a clever tandem catalysis method to form polyesters from a range of diacids, produced from renewable resources. Dicarboxylic acids were cyclized to give anhydrides, which then underwent ROCOP with epoxides. In the cases were the epoxides are limonene oxide and pinene oxide (anhydrides are CA and GA respectively) then the polyester is fully renewable.[83]

Fatty acids, derived from vegetable oils, contain unsaturated groups which can be epoxidised. Recently, our group in collaboration with the group of Meier have reported the preparation of various cyclohexene(diene) oxides derived from fatty acids (Fig. 21).[84] This provides a bio-based route to prepare PCHC, as well as functionalized polycarbonates.

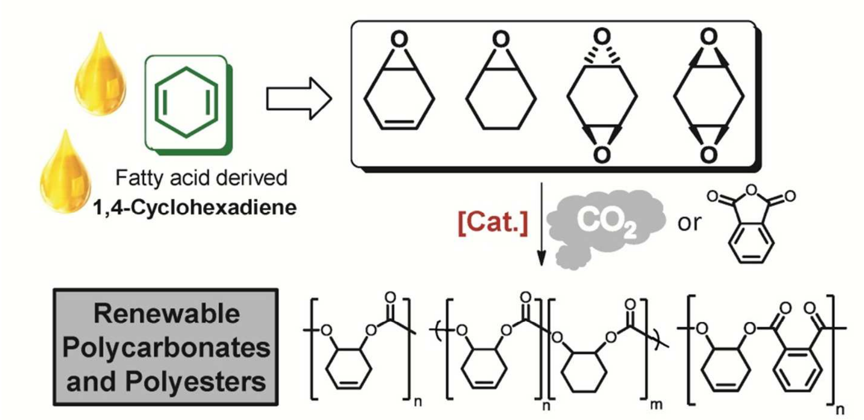


Fig. 21 Illustrates the structures of various polycarbonates and polyesters which can be prepared from fatty acids, via ROCOP reactions, where [Cat.] represents the di-zinc and di-magnesium catalysts (**11a/b**) illustrated in Fig. 7.[84]

Carbohydrates can be transformed into fufuraldehyde by a range of acidic treatments. Wang and co-workers reported the preparation of furfuryl glycidyl ether by reaction between epichlorohydrin and furfuryl alcohol.[85] The same group investigated the copolymerization of furfuryl glycidyl ether with CO_2 to produce a carbohydrate derived polycarbonate. The post-polymerization functionalization was possible by a Diels-Alder (DA) reaction between the furan and *N*-phenylmaleimide; it resulted in a polycarbonate with higher T_g (from 6.8 ^{o}C to 40.3 ^{o}C) and decreased the rate of polymer degradation. Maleic anhydride can be synthesised from furfuraldehyde using VO_x/Al_2O_3 catalysts.[86] Furthermore, phthalic anhydride can be synthesised by the Diels Alder reaction of furan, derived from carbohydrates, and maleic anhydride, followed by dehydration.[87] Many different anhydrides can be synthesised by cyclisation of dicarboxylic acids, available from carbohydrates, including SA, GA, IA, MA, and PA.[88]

Epichlorohydrin, is produced on a 1.8 million tons/yr scale worldwide from petrochemicals, however it can be derived from glycerin,[89] and therefore polymers derived from epichlorohydrin have the potential to be renewable. Epichlorohydrin, can be directly copolymerized with CO_2,[70, 74m, 90] or used as a monomer precursor to other epoxides – in particular glycidyl ethers.[74a, 74e, 74j-m] Darensbourg and co-workers used ROCOP to producing crystalline and perfectly alternated epichlorohydrin/CO_2 copolymers.[70, 90]

4. Conclusions

Amongst the approaches to prepare polyesters and polycarbonates, ring-opening copolymerization (ROCOP) provides a large scope to modify the properties of the materials by facile substitution of at least one of the monomers (epoxide/anhydride/CO_2). The polymerizations require the application of catalysts; various homogeneous and hetereogeneous catalysts have been reported. Although the field of CO_2/epoxide catalysis is well developed, and has not been reviewed here, the contrasting area of epoxide/anhydride catalysis remains under-developed and there is much scope to increase activity, selectivity and molar mass of the target polyesters. The polymerizations catalyzed using single site homogeneous metal complexes are generally controllable, yielding polymers of predictable molar masses, with narrow dispersities. There remains a need for fundamental understanding of the polymerization kinetics and the elementary steps occurring during these polymerization pathways so as to enable the preparation of more highly active and selective catalysts.

In terms of the product properties, there are indications of the significant potential for this class of polymer with superior thermal properties. Although the range of materials explored is still a fraction of those which could be prepared from available epoxide/anhydride/heterocumulene precursors, there have already been some promising properties. For example, in the field of polyester synthesis, the application of ROCOP may prove an attractive means to prepare semi-aromatic materials which are otherwise very difficult to synthesise (e.g. using ring-opening polymerization). Such polymers, together with those with rigid polymer repeat units, show higher glass transition temperatures, than aliphatic polyesters prepared by ROP. It is possible to control aspects such as amphiphilicity, biodegradability, thermal-response and, in future, it is anticipated that more detailed understanding and study of the polymer properties will result from the advances in catalyst control.

Following from a period of intense catalyst development in the field of CO_2/epoxide ROCOP, there is now significant interest and scope for exploring the limits of polycarbonate properties. Recent highlights include the potential to access glass transition temperatures well above 100 °C, indeed maximum values of 140 °C are close to those for some commercial polycarbonate materials (although other material property aspects are not yet optimised). In the area of tacticity control, the combination of advances in organometallic chemistry and the application to polymerization have enabled the production of isotactic polycarbonates, some of which are crystalline materials. As an example of the potential to moderate properties, isotactic poly(cyclohexene carbonate) has shown a melting temperature in excess of 272 °C. Such a high melting temperature, combined with high degrees of stereocontrol (> 99% *ee*) offer much promise in the quest for the next generation of polycarbonate materials. In the field of functionalized epoxides and bioderived epoxides there has been significant recent activity and it is feasible, by a number of approaches, to prepare polycarbonates with pendant hydroxyl groups (via post-polymerization modifications). Such polymers are proposed as interesting materials for bio-medicine or as macro-initiators for further functionalization, for example by ring-opening polymerization with cyclic esters to produce partially degradable poly(ester carbonates).

There are many opportunities for the future development of aliphatic polycarbonates, including the expansion of the range of epoxides, the application of tacticity control to moderate crystallinity and the ability to control polymer properties either by post-polymerization modification or by copolymerization. The next chapter in the quest for advanced CO_2-based polycarbonates will require improved control over the polymerization of epoxides, in order that high degrees of polymerization may be reached and the true thermal and mechanical properties of these materials may be evaluated. It is clear that a number of synthetic challenges need to overcome so that the engineering of advanced polymer architectures can be realised.

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Graphical Abstract For:
Ring-Opening Copolymerization (ROCOP):
Synthesis and Properties of Polyesters and Polycarbonates

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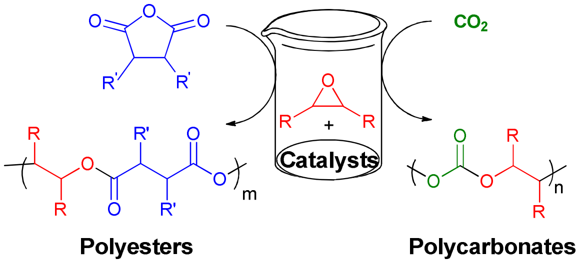

This feature article highlights the opportunities presented by ring-opening copolymerization (ROCOP) as a controlled route to prepare polyesters and polycarbonates. Ring-opening copolymerization is attractive as it can be well controlled and produces a range of polymer structures using widely available epoxides and anhydrides. The review highlights and summarizes recent advances in the polymerization catalysis and the properties of the polymers.