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Polymers from sugars: cyclic monomer synthesis, ring-opening polymerisation, material properties and applications

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Plastics are ubiquitous in modern society. However, the reliance on fossil fuels and the environmental persistence of most polymers make them unsustainable. Scientists are facing the challenge of developing cost-effective and performance-competitive polymers from renewable resources. Carbohydrates are a renewable feedstock with tremendous potential: sugars are widely available, environmentally benign and are likely to impart biocompatibility and degradability properties to polymers due to their high oxygen content. Sugars are also a feedstock with great structurally diversity and functionalisation potential that can enable fine tuning of the resulting polymer properties. In recent years, Ring-Opening Polymerisation (ROP) has emerged as the method of choice for the controlled polymerisation of renewable cyclic monomers, in particular lactones and cyclic carbonates, to allow the precise synthesis of complex polymer architectures and address commodity and specialist applications. This feature article gives an overview of sugar-based polymers that can be made by ROP. In particular, recent advances in the synthetic routes towards monomers that preserve the original carbohydrate core structure are presented. The performances of various homogeneous catalysts and the properties of the resultant polymers are given, and future opportunities highlighted for the development of both the materials and catalysts.

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1. Introduction

Today, plastic materials are widely used in countless industrial sectors, *e.g.* packaging, automotive parts, construction, and textile. With an ever-growing population, the demand for these light, strong and cheap materials is steadily increasing: in 2014, 311 megatonnes of plastics were produced worldwide, a 52% increase since 2002.[1] Polymers, the molecules of plastics, can also have sophisticated properties such as biocompatibility, conductivity or self-healing characteristics, which render them key in the development of emerging applications, including regenerative medicine and theranostics, flexible electronics and solar cells.

However, the environment is paying the price for this success.[2] The polymers that currently dominate the market (polyolefins such as polyethylene and polypropylene, or polyesters such as polyethylene terephthalate) are environmentally persistent, costly to degrade and rely on finite fossil resources, which make them unsustainable. Such concerns have spurred investigations into the development of sustainable alternatives, namely the cost-effective production from renewable feedstocks of both existing and novel polymers with performance competitive properties.[3] In addition, to address end-of-life issues, new polymers must be readily recyclable by degradation into environmentally benign products over a reasonable timescale. Alternatively, they must be safe to incinerate and allow for some energy recovery. Currently, sustainable polymers represent around 1% of the total global production annually.[4]

Monomers based on renewable feedstocks such as lignin,[5] terpenes,[6] amino-acids,[7] and carbon dioxide[8] have for example been used to produce novel sustainable polymers.[9] Amongst renewable resources, carbohydrates are also particularly promising raw materials[10] as they are widely available, environmentally benign, and they are likely to impart biocompatibility and degradability properties to polymers due to their high oxygen content. Sugars are also a feedstock with great structurally diversity and functionalisation potential that could enable fine tuning of polymer properties and unrivalled technical possibilities. In particular, carbohydrates bearing a cyclic structure can impart stiffness into the polymer chain, increasing the glass transition temperature[11] and leading to novel biodegradable and biocompatible materials, for applications in biomedical products and other sectors of greater consumption such as packaging.

The development of controlled polymerisation processes has been crucial in producing new polymers from renewable feedstocks, offering precise control over polymer molecular weight (typically with narrow dispersity $Đ$), composition, architecture and end group functionality. Such control is essential for the production of (multi-)block copolymers and other sophisticated polymer architectures (such as star-shaped, branched, as well as statistical copolymers), on which material properties and their applications depend. Ring-Opening Polymerisation (ROP) has emerged as one of the most efficient ways to produce controlled sustainable polymers. Since the pioneering work of Carothers on the thermally induced ROP of trimethylene carbonate in 1932,[12]

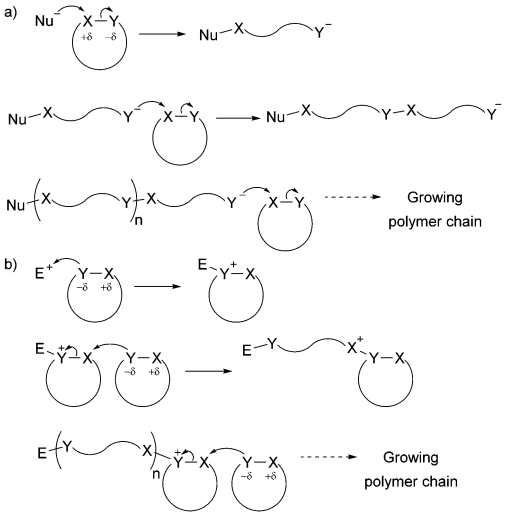

Fig. 1 General ionic ring-opening polymerisation mechanism (adapted from ref. 19): (a) anionic mechanism; (b) cationic mechanism (here S_N2 mechanism, S_N1 is also possible).

many ROP processes have been developed and are classified by their mechanism of action, namely anionic, cationic, zwitterionic, radical, metathesis and coordination–insertion processes. While Fig. 1 and Section 3 of this article give targeted insight into ROP processes, the reader is referred to the *Handbook of Ring-Opening Polymerization* edited by Dubois, Coulembier and Raquez for a comprehensive overview of the topic.[13] Most cyclic monomers are heterocycles that possess highly functionalised groups which can undergo heterolytic dissociation by a nucleophile (anionic ROP) or an electrophile (cationic ROP) (Fig. 1) (in contrast to the homolytic dissociation that occurs during ring-opening metathesis of cyclic olefins).

Due to the high oxygen content of most renewable feedstocks, a lot of renewable cyclic monomers are esters or carbonates, so that ring-opening transesterification polymerisation (ROTEP) processes and catalysts have formed much of the research focus. This was supported by the growing interest into the synthesis of poly(lactic acid), arguably the most successful example to date of a sustainable polymer.[14] The development of ROTEP catalysts has especially enabled controlled polymerisation of highly functionalised monomers under mild conditions (usually 6-, 7-, or strained 5-membered rings). There have been a significant number of comprehensive reviews of the ring-opening polymerisation of lactones and cyclic carbonates, focusing either on synthesis and catalysis,[15] new monomers[6d,16] or the properties and applications of the resulting sustainable polyesters and polycarbonates.[14c,17]

In parallel, several reviews have been published on synthetic sugar-based polymers, or glycopolymers.[18] Most of the time, these refer to poly(vinyls) and other polymers functionalised with sugars pendant from their main chain. A recent review has however reported recent progresses in the syntheses of polymers having sugar units incorporated into the main chain, but with a focus on polycondensation reactions.[20]

This feature article will provide a complementary perspective by giving a concise overview of how sugar feedstocks have

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been used to produce cyclic monomers and how these have been used to create novel sustainable polymers. The scope of cyclic sugar-based monomers and their ring-opening polymerisation is limited, not least because of the need for protection/deprotection steps, but also because the ROP thermodynamics can be limited by the presence of multiple substituents. There are however opportunities we will highlight, to broaden the range of materials produced, by taking advantage of the structural diversity, abundance and innocuousness of carbohydrate feedstocks, and of the recent developments in ROP and monomer synthetic methodologies.

The first part of this article will focus on the synthesis of cyclic monomers from sugars. We will distinguish between monomers that are indirectly synthesised from sugar crops (*via* oxygenated synthons obtained from biological or chemical routes, *e.g.* lactic acid or HMF) and do not conserve the original sugar structures, and monomers which are directly made from sugar molecules and retain most of the structure and functional groups of the original sugars. The second part will describe the catalytic ROP methods that have been used to produce polymers from these monomers. The last section of the article will report the characteristics of the resulting polymers and illustrate the applications of selected polymers. In particular, the emphasis will be on the applications of polymers where the structure and chemical complexity of the original sugar has been maintained, highlighting areas in which future developments are expected.

2. Cyclic monomers from sugars

2.1. Monomers which do not maintain the original sugar structure

Sugars have been used as feedstocks for chemical and fermentation processes to produce oxygenated synthons that can be used as monomers or monomer precursors, *e.g.* lactic acid or various dicarboxylic acids. In this case, the structure and chemical complexity, as well as the functionalisation potential of the original sugars, are not maintained. This section illustrates briefly such key sugar-derived cyclic monomers that have been reported in the literature and used to produce renewable polymers.

Lactide and lactic acid *O*-carboxyanhydride. Lactide (**1**) is a six-membered cyclic diester and the dimer of lactic acid (LA), the most widely occurring carboxylic acid in nature.[21] LA is produced by fermentation of biomass (in particular glucose and sucrose feedstocks).[22] Poly(lactic acid) (PLA)[23] can be prepared by direct polycondensation[24] of LA but the process is better controlled by ring-opening polymerisation of lactide. To prepare lactide, LA is first converted to a low molecular weight prepolymer (molecular weight ~1–5 kDa) and then depolymerised to lactide,[25] through an intramolecular esterification process or backbiting (Fig. 2). Typically, this uses a homogeneous catalyst, namely tin 2-ethylhexanoate (also known as tin octoate).[26] Recently a superior direct zeolite-based catalytic process was reported that converts LA into lactide.[27] The shape-selective properties of zeolites are essential to avoid both racemisation

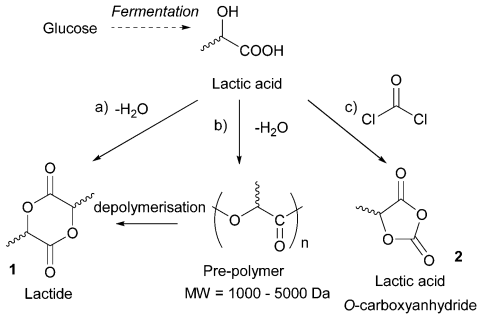

Fig. 2 Routes from LA to lactide *via* (a) zeolite-catalysed condensation and (b) oligomer depolymerisation (M_w: molecular weight). (c) Synthesis of lactic acid *O*-carboxyanhydride from LA.

and side-product formation. The existence of three different stereoisomers of lactide (L, D and *meso*) gives rise to tacticity considerations in PLA chains, which heavily impacts the polymer properties. Another cyclic LA derivative is lactic acid *O*-carboxyanhydride (LacOCA, **2**), which is prepared by reacting LA with phosgene.[28] Although high molecular-weight PLA is obtained by lactide ROP, the high ring strain in the five-membered LA derivative **2** gives access to PLA of controlled molecular weights with low polydispersities under milder conditions than with lactide.[29]

Glycolide. Glycolide (**3**) is the six-membered cyclic dimer of glycolic acid (GA) (Fig. 3). Although GA is not involved in the metabolic pathways of humans, it is metabolized by glycolate oxidase to oxalic acid or carbon dioxide.[7a] The vast majority of GA is produced by carbonylation of formaldehyde or by reaction of chloroacetic acid with sodium hydroxide. However, it can also be isolated from natural resources, such as sugarcane or fruit juices (*e.g.* banana, pineapple), or be produced biologically. The biological pathway starts from glucose, and other simple sugars, and uses a genetically modified microorganism to yield glycolate, amongst other products.[30] Recently it has been reported that Mo-containing heteropoly acid catalysts (HPAs) are effective for the conversion of cellulosic biomass materials in GA.[31] In particular, $H_3PMo_{12}O_{40}$ is capable of converting raw cellulosic materials, such as bagasse or hay, to GA with yields ~30%. Following hydrolysis of cellulose to glucose, successive retro-aldol reactions form glycolaldehyde, which is subsequently oxidised to glycolic acid. At the same time, isomerisation of glucose yields fructose which can be converted by retro-aldol reactions, through dihydroxyacetone and glyceraldehyde, into glycolaldehyde and formaldehyde, which yield GA and formic acid after oxidation. While the strong Brönsted acidity of these catalysts enables hydrolysis of cellulose, their moderate oxidation

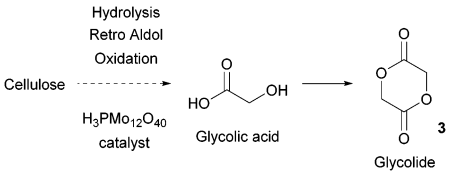

Fig. 3 Production of glycolic acid from fermentation of carbohydrates.

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properties allow selective oxidation of the aldehyde groups in the fragmentation products.

ε-Caprolactone and ε-caprolactam. The majority of ε-caprolactone (ε-CL, **4**), a seven-membered ring ester is converted, by reaction with ammonia,[32] to ε-caprolactam (ε-CPL, **5**), its amide counterpart, for the production of Nylon-6. However, ε-CL, produced industrially by Baeyer–Villiger oxidation of cyclohexanone,[33] can also be converted to poly(ε-caprolactone) (ε-PCL) by ROP.[34] The commercial importance of Nylon-6 has led to the development of several methods for the synthesis of **5**, in particular, the conversion of cyclohexanone into an oxime followed by a Beckmann rearrangement. ε-CL and thus ε-CPL can also be produced from sugars *via* 5-(hydroxymethyl)furfural (5-HMF)[35] (Fig. 4), which can be obtained by dehydration of fructose,[36] glucose[37] or mannose[38] as well as directly from cellulose (Fig. 4).[39] From 5-HMF, Buntara *et al.* reported four different routes to 1,6-hexanediol (1,6-HDO) using various catalysts. Subsequent oxidation yields the corresponding monoaldehyde, which spontaneously cyclises to the lactol, dehydrogenation of which yields ε-CL.[40]

β-Methyl-δ-valerolactone. β-Methyl-δ-valerolactone (βMδVL, **6**) is a non-natural metabolite that can be synthesised from 3-methyl-1,5-pentanediol.[41] There are also two strategies for the preparation of βMδVL from glucose, either biological or semisynthetic (Fig. 5).[42] The artificial biosynthetic route relies on the mevalonate pathway using *Escherichia coli* strain. In the semisynthetic approach, the production of mevalonate is increased using *Escherichia coli* strain carrying genes from *Lactobacillus casei*, achieving a yield of 0.26 g per g of glucose. Addition of sulfuric acid to the fermentation broth and heating under reflux induces dehydration. The resulting anhydromevalonolactone is isolated by solvent extraction with chloroform and reduced to βMδVL using Pd/C as the catalyst. Distillation yields the monomer in polymerisation-grade purity. Chemo-enzymatic pathways have also allowed the preparation of optically enriched βMδVL from anhydromevalonolactone.[43]

Angelica lactone. Distillation of levulinic acid (LevA) under reduced pressure[44] or intramolecular dehydration in the presence of an acid catalyst such as acetic anhydride[45] or phosphoric acid[46] yields α-Angelica lactone (AL) monomer **7** (Fig. 6). A greener alternative using recyclable montmorillonite clay (K10) has also been reported.[47] LevA is a renewable keto-acid which can be prepared from polysaccharides (Fig. 6), *via* 5-(hydroxymethyl)-furfural (5-HMF)[48] or furfuryl alcohol (FFA).[49] It has also been identified as a platform molecule for the synthesis of several other value-added chemicals.[10a,50] Finally, α-AL (**7**) can also be isomerised to β-AL, the ROP of which is unknown.

γ-Butyrolactone and 2-pyrrolidone. γ-Butyrolactone (GBL, **8**) and 2-pyrrolidone (**9**) can be obtained from succinic acid (SA) produced by microbial fermentation from renewable feedstocks such as corn-derived glucose (Fig. 7). Microorganisms such as *Escherichia coli*, *Anaerobiospirillium succiniciproducens* and *Actinobacillus succinogenes* can produce SA in high yields (up to 1.3 moles succinate per mol of glucose).[51] Although the bulk

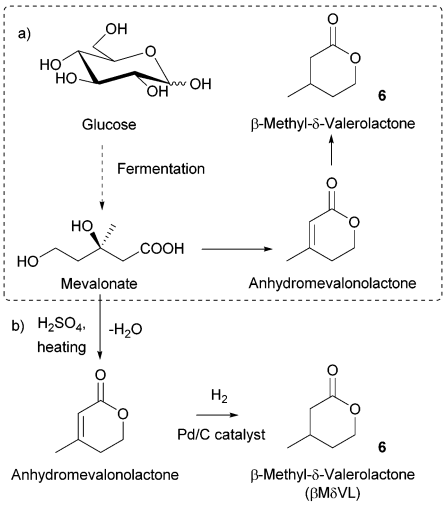

Fig. 5 (a) Biochemical synthesis of βMδVL; (b) semisynthetic production of βMδVL from mevalonate.

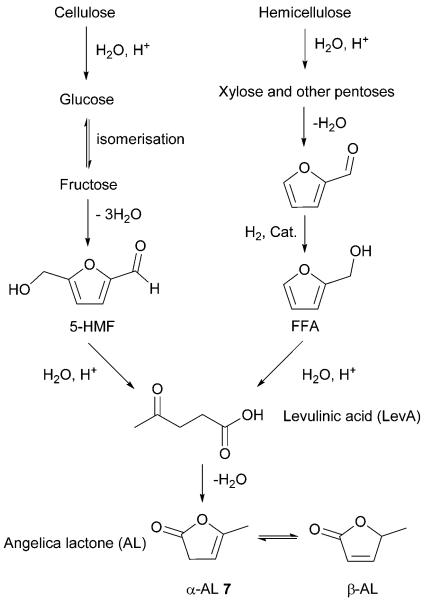

Fig. 6 Routes for the production of LevA from polysaccharides and its conversion to AL.

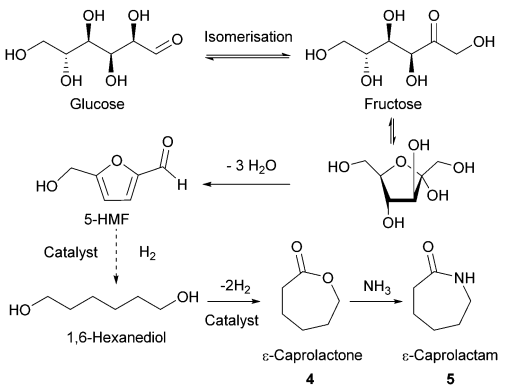

Fig. 4 Dehydration of glucose to 5-HMF and conversion to ε-CL and ε-CPL.

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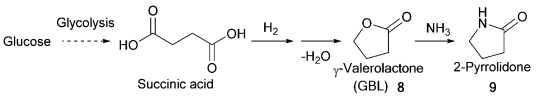

Fig. 7 Production of SA by microbial fermentation *via* phosphoenolpyruvate pathway. Preparation of GBL and preparation of GBL and 2-pyrrolidone from SA.

production of SA is carried out by hydrogenation of maleic anhydride obtained by oxidation of *n*-butane, the latter process is already operated on an industrial scale in Europe by Succinity, a joint venture between Corbion-Purac and BASF established in 2013. Alternative syntheses of SA from renewables has also been reported from LevA[52] or furfural,[53] albeit with less overall efficiency than the fermentation processes. The hydrogenation of SA to GBL can then be achieved on Au/TiO_2 catalysts[54] with a 97% selectivity in 97% conversion, with addition of small amounts of platinum favouring H_2 dissociation and resulting in higher activities. Pd-catalysts supported on mesoporous aerogels can also be used.[55] 2-Pyrrolidone can then be produced from GBL using ammonia. Recent technologies producing 2-pyrrolidone from sugars without involving GBL as an intermediate, through reductive amination of SA, have been described in patents,[56] including using heterogeneous metal catalysts.

β-Propiolactone. β-Propiolactone (**10**) can be produced from 3-hydroxypropionic acid (3-HPA).[57] Several chemical syntheses have been reported for 3-HPA production including oxidation of 1,3-propanediol[58] or 3-hydroxypropionaldehyde[59] using a palladium-containing supported catalyst, or by hydration of acrylic acid in the presence of a liquid or solid acid catalyst.[60] Production of 3-HPA using biological routes from renewable resources is more challenging. No known organism yields 3-HPA as a major metabolic end-product, so genetically modified metabolic pathways are required. Biosynthetic pathways for the production of 3-HPA using carbohydrates (glucose, sucrose, fructose) have been described,[56a,61] and operate *via* malonyl-CoA or β-alanine intermediates. Subsequent intramolecular condensation of 3-HPA, *e.g.* using an intramolecular Mitsunobu reaction and an ionic liquid-based chloroiminium reagent,[62] yields β-propiolactone (Fig. 8).

Malolactonate and L-malic *O*-carboxyanhydride. L-Malic acid is a natural α-hydroxy acid which can be obtained from carbohydrate feedstock *via* the metabolism of glucose. Currently, malic acid is produced through either the hydration of fumaric or maleic acid under high temperature and pressure, yielding a racemic mixture, or the biotransformation of fumarate using fumarase, producing L-malic acid. *Aspergillus flavus* can produce malic acid from carbohydrates but the intrinsic toxicity of this fungus and by-products formation have prevented its

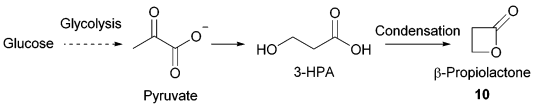

Fig. 8 Biocatalytic formation of 3-HPA from glucose and β-alanine and synthesis of β-propiolactone by condensation of 3-HPA.

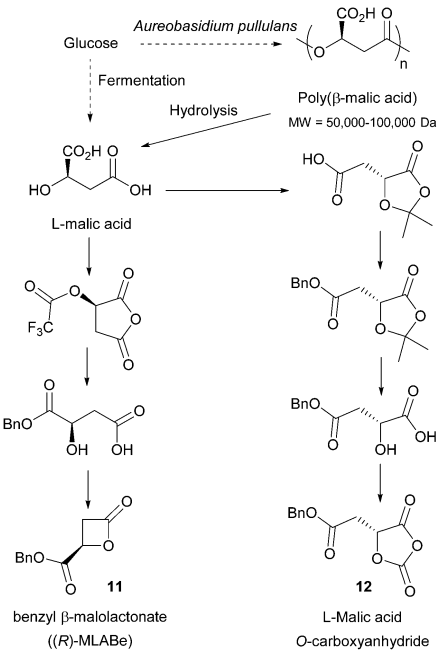

Fig. 9 Proposed pathway for the bioproduction of malic acid and conversion to 5-(*S*)-[(benzyloxycarbonyl)methyl]-1,3-dioxolane-2,4-dione (L-malOCA) monomer and to benzyl β-malolactonate.

industrial application.[63] Malic acid fermentation by genetically engineered *Escherichia coli*[64] and *Saccharomyces cerevisiae*[65] is possible but greatly limited by end-product inhibition. Recently, *Aureobasidium pullulans* was shown to be capable of producing large amounts of poly(malic acid) (PMA) from glucose. PMA was then easily hydrolysed to release malic acid.[66] PMA fermentation followed by acid hydrolysis offers a promising process for industrial malic acid production from carbohydrates. Benzyl β-malolactonate monomer (**11**) can then be efficiently synthesised from malic acid,[16d] on a 10 g scale (8% overall yield) using a procedure developed by Guerin and coworkers (Fig. 9).[67] Malic acid can also be converted into cyclic *O*-carboxyandride monomer **12**. To that end, Pounder and Dove described the protection of the α-hydroxy acid moiety with 2,2-dimethoxypropane and subsequent benzylation of the remaining β-carboxylic acid group followed by deprotection. Carbonylation of the α-hydroxyacid moiety using phosgene derivatives (diphosgene and triphosgene) yielded the OCA.[68]

Dihydroxyacetone and cyclic carbonate derivatives. Dihydroxyacetone (DHA) is the simplest of all ketoses and can be isolated from plants. DHA is also present in human metabolism during glycolysis as dihydroxyacetone phosphate (DHAP). DHAP is also an intermediate in the breakdown of other dietary sugars such as fructose, mannose or galactose. DHA can be produced by oxidation of glycerol using mild oxidants, such as hydrogen peroxide or palladium-based catalysts in the presence of oxygen,[69] or by microbial fermentation of glycerol over *Gluconobacter oxydans*.[70] However, production of glycerol from sugars is not industrially important, representing only 10% of the global production.[71]

In solution, DHA reacts intermolecularly to form a hemiacetal dimer.[72] This equilibrium and the reactivity of the ketone

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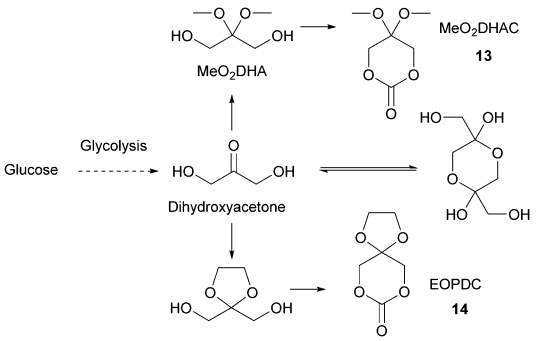

Fig. 10 Formation of DHA dimer and DHA derived cyclic carbonates (MeO_2DHAC and EOPDC) used in ROP.

function has so far prevented the direct polymerisation of a cyclic monomer derived from DHA without prior protection of the ketone group. Two ketone-protected DHA derivatives have been described for use in ROP: 2,2-dimethoxypropylene carbonate (MeO_2DHAC, **13**) and 2,2-ethylenedioxypropane-1,3-diol carbonate (EOPDC, **14**) (Fig. 10). Synthesis of MeO_2DHAC occurs in two steps; treatment of DHA with trimethylorthoformate and *p*-toluenesulfonic acid in methanol to yield dimethoxy protected DHA,[73] and subsequent cyclisation using triphosgene and pyridine[74] (or triethylamine and ethylchloroformate).[75] Waymouth and coworkers also used the oxidative carbonylation of MeO_2DHA with (neocuproine)$Pd(OAc)_2$ and sodium dichloroisocyanuric acid in acetonitrile to give **13**.[76] Similarly, the synthesis of EOPDC from DHA has been reported in a two-step process.[77]

Sugar-derived diols and cyclic carbonate derivatives. A common preparation of cyclic carbonate monomers involves the transesterification of diols with phosgene derivatives. Typically, focus has been centred on openable 6-membered ring monomers from propanediol and derivatives, including from sugars or glycerol (as seen with DHA).[78] Seven-membered cyclic carbonates (7CCs), namely 1,3-dioxepan-2-one, 4-methyl- and 5-methyl-1,3-dioxepan-2-one (7CC **15**, α-Me7CC **16** and β-Me7CC **17**) have also been reported as monomers. These carbonates can be synthesised from the corresponding α,ω-diols: 1,4-butanediol, 1,4-pentanediol and 2-methyl-1,4-butanediol, derived from succinic, levulinic or itaconic acids respectively (Fig. 11).[79] Itaconic acid is industrially produced from sugars *via* fungal fermentation of glucose, xylose, or arabinose, using *Aspergillus terreus*.[80]

2.2. Monomers which maintain the original sugar structure

This section focuses on the synthesis of monomers from sugars in which the structure and functionalisation of the original sugars has been preserved. This field is largely under-developed as the multiple functionalities in natural saccharides often require the use of protecting group chemistry during the monomer synthesis to avoid undesired side reactions.

Sugar-based lactones. Lactones derived from carbohydrates contain a cyclic sugar structure which is however lost on polymerisation. Yet, the large number of defined stereocentres offered by natural sugars results in polymers with specific stereochemistries. Carbohydrate derived 1,5-lactones are attractive as they can be

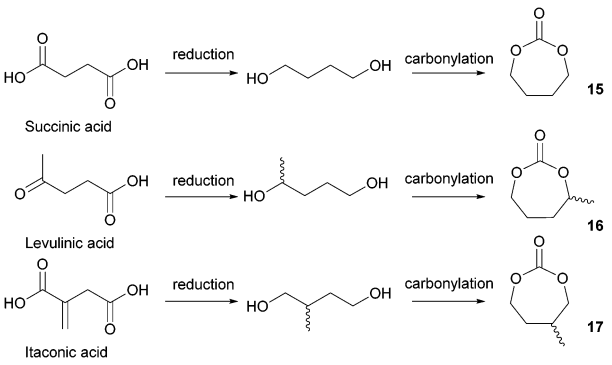

Fig. 11 Tetramethylene carbonate **15**, α- and β-methyl tetramethylene carbonates **16** and **17**, derived from succinic, levulinic and itaconic acids, respectively.

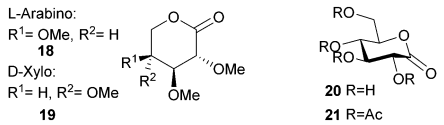

Fig. 12 Carbohydrate 1,5-lactones.

readily prepared in good yield by oxidation of the corresponding glycoside. Early work by Haworth and Drew[81] suggested evidence for the ROP of carbohydrate-1,5-lactones with tri-*O*-methyl-D-arabonolactone **18** (Fig. 12). Galbis and coworkers later[82] reported the synthesis of **19** and a 2002 patent claimed the ROP of D-glucono-1,5-lactone **20**.[83] Following the procedure outlined by Joseph *et al.*[83] tetra-*O*-acetyl-D-gluconolactone **21** (Fig. 12) was prepared by Williams and Haider in 90% yield by treatment of commercially available D-glucono-1,5-lactone with acetic anhydride and trifluoroacetic acid.[84] Also from D-gluconolactone, Williams and coworkers prepared carbohydrate lactone monomer **22** in two high yielding steps (Fig. 13). Diastereoselective hydrogenolysis with Pd/C of the product obtained from treatment of D-gluconolactone with acetic anhydride and pyridine yielded a racemic mixture of *syn* enantiomers. NOESY NMR experiments suggested that the boat conformation adopted by the carbohydrate ring in the X-ray crystal structure is maintained in solution.[85]

Synthesis of 1,6-lactones from carbohydrates requires more elaborate synthetic sequences and protecting group chemistry. *O*-Methyl protected D-glucono-1,6-lactone **23** was prepared by Galbis and coworkers *via* lactonisation of an ω-hydroxyacid intermediate, using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in the presence of DMAP·HCl (Fig. 14). The ω-hydroxyacid intermediate was synthesised in reasonable

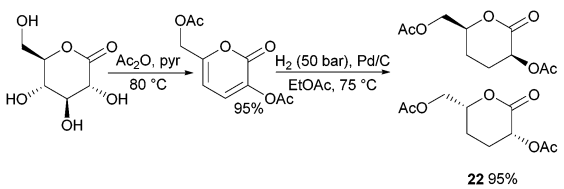

Fig. 13 Synthesis of racemic carbohydrate lactone **22**.

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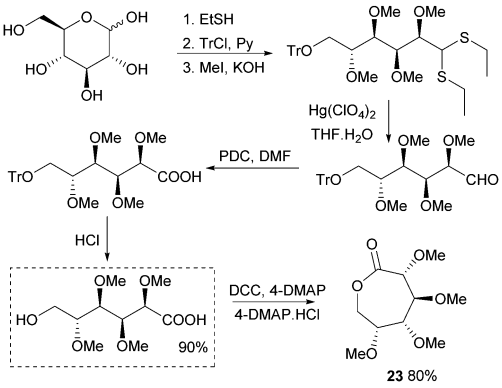

Fig. 14 Synthesis of ω-hydroxyacid precursor and lactone **23** *via* D-glucose diethylmercaptal intermediate.

yield by two different multi-step routes.[82] Route 1 to the pre-cyclisation intermediate from commercially available methyl-α-D-glucopyranoside involves selective, temporary protection of the primary hydroxyl group as the benzyl derivative. Acid hydrolysis and oxidation with acetic acid yields a lactone intermediate, which is ring-opened and subsequently deprotected (82% yield). With higher yields and fewer synthetic steps, route 2 (Fig. 14) requires treatment of fully protected D-glucose diethylmercaptal with $Hg(ClO_4)_2$ to form the aldehyde derivative, which is subsequently oxidised to the carboxylic acid. Acid removal of the triphenylmethyl group protecting the primary hydroxyl functionality yields the key ω-hydroxyacid intermediate.

Valera and coworkers prepared the analogous monomer **24** with D-galacto-stereochemistry in a shorter, 3-step synthetic route from D-galactono-1,4-lactone (Fig. 15).[86] The pre-cyclisation product, D-galactonic acid was prepared from the 1,4-lactone in an overall 47% yield, the final lactonisation being achieved as above. A racemic mixture of **24** was also prepared from reduced sugar D-dulcitol by Guan and Urakami (Fig. 15).[87] Lactonisation of the free primary hydroxyl groups in the otherwise *O*-methyl protected sugar was carried out with Na_2CO_3 and Shvo's catalyst in 60% yield. As dehydrogenation can happen at either primary alcohols, the cyclisation step produced both possible enantiomers.

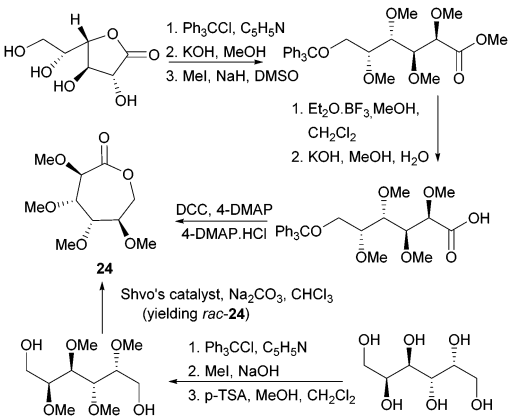

Fig. 15 Synthesis of D-galactono-1,6-lactone **24** from D-galactono-1,4-lactone D-dulcitol (yielding *rac*-**24**).

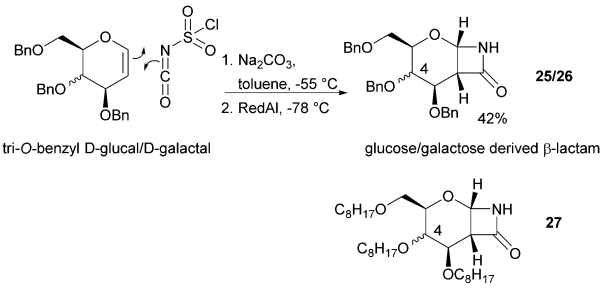

Fig. 16 Synthesis of D-glucose and D-galactose derived β-lactam monomers.

The one-step synthesis of previously reported[88] glucose-derived β-lactam **25** (Fig. 16) from benzyl protected D-glucal and chlorosulfonyl isocyanate was reported by Grinstaff and coworkers in 2012.[89] Following a stereoselective [2+2]-cycloaddition between the glucal and isocyanate, *in situ* reductive removal of the sulfonyl group gave the monomer in 42% yield. This was an improved procedure over the original synthesis using trichloroacetyl isocyanate.[90] Later, Grinstaff and coworkers prepared, using the same synthetic methodology, the corresponding galactose derivative **26**, which only differs in the axial, rather than equatorial, configuration of the C-4 substituent.[91] The glucose derived β-lactam monomer could also be prepared with octyl ether chains in place of benzyl protecting groups (**27**) in similar yield (43%).[92] β-Lactam **28** was synthesised by Galbis and co-workers *via* cyclisation of 3-amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic acid.[93]

A carbohydrate derived *N*-carboxyanhydride **29** (Fig. 17), was prepared in a multi-step synthesis from 2-acetamido-2-deoxy-D-glucose, involving methyl protection of the hydroxyl groups and temporary *t*-butyloxycarbonyl (Boc) protection of the amine group. Subsequent cyclisation of a protected D-gluconic acid intermediate with trichloromethyl chloroformate afforded the sugar based monomer in high yield.[94] **29** could also be prepared from D-glucosamine.[95]

Cyclic carbonates. Synthesis of cyclic carbonate monomers for ROP often involves the use of phosgene or phosgene derivatives. Phosgene is a highly toxic reagent synthesised from CO and Cl_2 in an energy intensive process.

Typically, 5-membered cyclic carbonates do not undergo ROP or require forcing conditions that result in elimination of CO_2 and formation of polyether linkages. Nevertheless, *trans*-configured 5-membered cyclic carbonates fused to pyranose sugar rings serve as highly strained monomers. Cyclisation using ethyl chloroformate and triethylamine of the *trans*-vicinal hydroxyl groups in methyl-4,6-*O*-benzylidene-α-D-glucopyranoside to prepare **30** was reported originally by Rist and coworkers.[96] A molar ratio of saccharide: carbonating agent: base of 1 : 30 : 10 gave an 89% yield of the desired product. A mixture of products

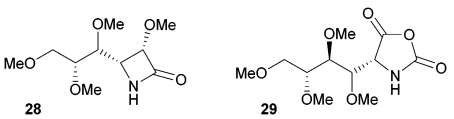

Fig. 17 Synthesis of *N*-carboxyanhydride monomer from D-glucose derivative.

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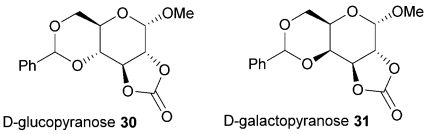

Fig. 18 *trans*-Fused 5-membered cyclic carbonates with a pyranose core for ROP.

was obtained if a different ratio was used. Comparison with the galacto-(**31**) and mannopyranoside analogues revealed that the *cis*-configuration of the latter, mannose based, 5-membered cyclic carbonate resulted in insufficient ring strain for ROP (Fig. 18).[97]

In 1999, Gross and Chen reported a 6-membered cyclic carbonate of D-xylose (Fig. 19). (1,2-*O*-Isopropylidene-D-xylofuranose (IPXTC, **32**)).[98] After ketal-protection of the 1,2-diol, cyclic carbonation of the remaining 1,3-diol was achieved using ethyl chloroformate phosgene derivative in 41% yield. Gross and coworkers also reported the cyclic carbonate derived from D-glucose in its furanose form requiring both acetonide and benzyl protection. Cyclisation was again achieved using ethyl chloroformate in 65% yield to produce 1,2-*O*-isopropylidene-3-benzyloxy-pentofuranose-4,4′-cyclic carbonate (IPPTC, **33**) (Fig. 19).[99]

Following the original report in 1970,[100] which used ethyl chloroformate and triethylamine, the *trans*-fused 6-membered cyclic carbonate of D-glucopyranose (**34**) was more recently isolated by Mikami *et al.* using bis(pentafluorophenyl) carbonate with catalytic amounts of CsF in 36% yield (Fig. 20).[101] Cyclic carbonation of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside with

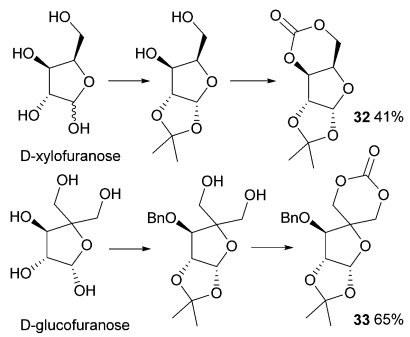

Fig. 19 Cyclic carbonation with ethyl chloroformate of furanose sugars to yield 6-membered cyclic carbonate monomers.

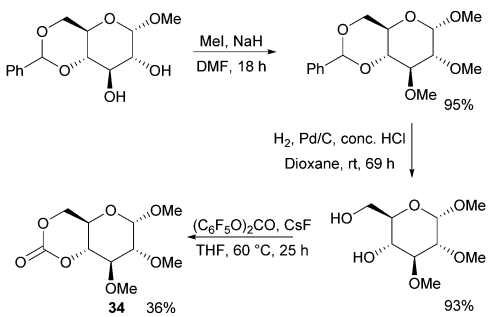

Fig. 20 Three step synthesis of D-glucopyranose derived cyclic carbonate monomer.

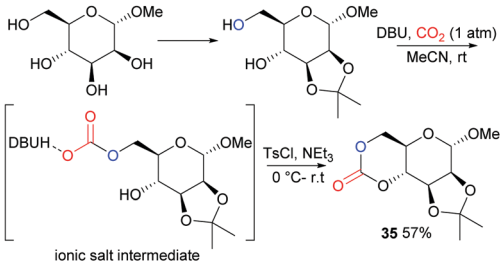

Fig. 21 Synthesis of D-mannose derived cyclic carbonate using CO_2 as a feedstock.

ethyl- or 4-nitrophenyl chloroformate in the absence of base gave only mono-carbonated products. Overall, monomer synthesis was achieved in three steps from commercially available methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. Prior to cyclisation, methylation of the free hydroxyl groups with methyl iodide in dimethylformamide and removal of the benzyl group by hydrogenolysis were achieved in high yields. The monomer could also be prepared using triphosgene and pyridine at 30 °C in CH_2Cl_2 but in only 25% yield.[102]

Following on from some of our work to find a safer alternative to phosgene derivatives for the synthesis of cyclic carbonates from diols,[103] we reported the novel synthesis of D-mannose based monomer **35** (Fig. 21) using CO_2 as a safe, renewable C1 synthon at 1 atm pressure and room temperature (rt).[104] Starting from commercially available 1-*O*-methyl-α-D-mannopyranose, the 1,2-diol motif could be temporarily protected as the isopropylidene ketal for removal post-polymerisation. CO_2-insertion, predominantly into the primary hydroxyl group, was facilitated by 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) reagent to form a carbonate salt. Addition of a tosyl chloride (TsCl) leaving group alongside triethylamine led to formation of the cyclic carbonate product *via* a nucleophilic addition–elimination mechanism. Conditions of high dilution and cold temperatures were key in favouring the desired unimolecular cyclisation over competing dimerisation reactions giving an isolated yield of 57%.

3. Ring-opening polymerisation

3.1 Thermodynamic and kinetic considerations

The ability of a cyclic monomer to be polymerised by ROP is determined by two important factors.

First, regardless of the mechanism, the conversion of the monomer molecules into macromolecules (of linear or more complex topologies) must be allowed thermodynamically. As the entropy term of the polymerisation reaction is generally positive, the relief of the ring strain must be large enough to overcome the unfavourable entropic term and yield a negative free enthalpy of reaction. The structure of the monomer has therefore a large impact on the polymerisation behaviour. The presence of multiple substituents thus does not generally favour polymerisation. On the contrary, low temperatures and high monomer concentration favour polymerisation equilibrium thermodynamics.

Secondly, the polymerisation process must be allowed kinetically. The use of a catalyst can considerably influence this factor

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by decreasing activation barriers and promoting a particular mechanistic path.

3.2 ROP of monomers which do not maintain a sugar structure

Table 1 shows selected examples of polymerisation of the monomers seen in Section 2.1. This table, though not comprehensive, aims to show polymerisation potential in terms of control, yield, reaction conditions and choice of catalytic and initiating system. The following section highlights the key features of each monomer ROP and provides the reader with references for further study.

ROP of lactide. The subject has been extensively investigated and reviewed,[14b,e,f,105] the key parameter being the possibility of controlling the tacticity of the polymer from a mixture of lactide stereoisomers (usually racemic). Indeed, the physical and thermomechanical properties of the polymer depend on its tacticity. Atactic PLA is amorphous ($T_g \sim 50$ °C) whereas isotactic PLA is crystalline with a melting point of 170–180 °C. Lactide polymerisation has been accomplished with a broad range of metal catalysts, organometallic promoters but also organic compounds. Preparation of PLA *via* biocatalytic routes using *Pseudomonas cepacia* lipase has also been reported.[106] Industrially, tin octoate is used in the monomer melt (140–180 °C), in the presence of an alcohol initiator, for between a few minutes to several hours, but with no stereocontrol of tacticity. Many single site catalytic systems have been reported to induce stereoselective polymerisation of lactide.[14g] Metal complexes, (*e.g.* (R-SalBinap)AlOMe)[107] but also organocatalysts,[108] are known for producing isotactic and crystalline PLA from *rac*-LA.

ROP of lactic acid *O*-carboxyanhydride. The ROP of LacOCA yields PLA under milder conditions, compared to lactide.[109] For example, PLA of controlled molecular weights and low polydispersities can be obtained at 35 °C within minutes by the ROP of LacOCA using DMAP[28,29] or lipase (Novozym 435 and lipase PS)[110] compared to a few days for lactide. Organometallic complexes, *e.g.* tin(II) carboxylates, Al(III) and Co(III) complexes with Schiff base ligands,[111] and zinc β-diketiminates[112] are also effective ROP catalysts for LacOCA.

ROP of glycolide. Poly(glycolide) (PGA) is a highly crystalline polymer ($T_g \sim 30$–50 °C, $T_m \sim 220$–230 °C),[17b] poorly soluble in most common organic solvents except hexafluoroisopropanol, which has hindered its characterisation. ROP of glycolide[14f] has been performed using anionic, cationic and nucleophilic promoters, including organocatalysts[113] and metal catalysts, *e.g.* calcium acetylacetonate,[114] tin octoate or tin alkoxides,[115] and diphenyl bismuth bromide.[116] Industrially, the reaction is carried out using tin octoate in the melt, at 180–230 °C, close to the melting and decomposition temperature (255 °C) of PGA.[117] Supercritical CO_2 has also been used to lower the reaction temperature (120–150 °C), and maintained polymers of high molecular weight.[118]

ROP of ε-caprolactone. Thielemans *et al.* have extensively reviewed the ROP of ε-CL into poly(ε-caprolactone) (PCL),[34a] a biodegradable, semi-crystalline polyester ($T_g \sim -60$ °C, $T_m \sim 60$ °C).[34b] Metal-based catalysts are among the most used catalysts for the ROP of ε-CL, including alkali metals, alkaline earth metals, main group metal catalyst (based on aluminium or tin) and transition metals (Ti, Zr). Rare-earth metals are especially good catalysts (Sm,[119] La, Y or Lu).[120] Organic bulky

Table 1 Selected polymerisation data and polymer properties

M[a]	Catalyst [cat. mol%]	Initiator	$[M]_0$ (mol L^{-1})	$[M]/[I]^b$	Time (h)	Conv. (%)	T (°C)	Solvent	M_n[c] (kDa) [$Đ$][d]	T_g (°C)	T_d (°C) [% mass loss][e]	Ref.
1 (L)	Tin octoate $Sn(Oct)_2$ [0.011]	1-Dodecanol	Bulk	13 000	10	95	140	N/A	110	51–59	260 [5][161]	115
2	DMAP [1]	*neo*-Pentanol	0.9	600	19	>96	25	CH_2Cl_2	62.3 [1.18]	55[111]	231 [5]	29*b*
3	DBU [1]	—	1.42	—	1	34	−20	CH_3CN	31.9[f] [2.0]	38	268 [10]	113*b*
4	$Sm(OAr)_2(THF)_3$[g] [0.05]	—	1.0	—	0.08	100	25	Toluene	626 [1.56]	−60[87]	325[162]	119
5	EtMgBr [0.1]	*N*-Acetyl-ε-caprolactam	Bulk	3333	5	100	150	N/A	700[h] [2.3]	49[129a]	~425[130]	128*c*
6	TBD [0.2]	Benzyl alcohol	Bulk	289	—	86	18	N/A	70.0 [1.13]	−51	240[41b]	42
7	$Sn(OCt)_2$ [0.33]	—	5	—	30	79.8	130	Toluene	29.4 [1.25]	—		133
8	$La[N(SiMe_3)_2]_3$ [0.5]	1,4-Benzene-dimethanol	10	133	12	29	−40	THF	30.2 [2.4]	−52	273[i135]	139
9	*t*BuOK [1]	*N*-Benzoyl-pyrrolidone	Bulk	100	75	59.9	40	N/A	166.3	52/72[j 163]	273[164]	144
10	$(T(2,4,6\text{-}MeO)_3PP)AlCl$[k] [2]	—	3.8	—	0.4	51	30	CH_2Cl_2	2 [1.19]	−4[155c]	230[165]	153
11	$(BDI^{iPr})Zn(N(SiMe_3)_2)$ [1]	Isopropanol	Bulk	50	4	95	60	N/A	2.0 [1.26]	30[156a]	—	16*d*
12	4-Methoxypyridine [5]	*neo*-Pentanol	0.32	250	8	92	25	$CHCl_3$	24.5 [1.03]	—	—	68
13	$(BDI^{iPr})Zn(N(SiMe_3)_2)$ [0.2]	Benzyl alcohol	Bulk	250	1	98	90	N/A	38.8 [1.36]	39	225 300 [60]	160
14	Tin octoate [0.1]	—	Bulk	1000	12	93	110	N/A	55 [1.46]	49	—	77
15	$HCl{\cdot}Et_2O$ [2.5]	*n*-Butanol	1	60	24	99	25	CH_2Cl_2	6.2 [1.14]	—	—	166
16	$(BDI^{iPr})Zn(N(SiMe_3)_2)$ [0.5]	Benzyl alcohol	2.0	200	0.5	93	60	Toluene	10.75 [1.33]	−14	—	79
17	$(BDI^{iPr})Zn(N(SiMe_3)_2)$ [1]	Benzyl alcohol	2.0	100	5 min	100	20	Toluene	5.7 [1.11]	30	—	79

[a] M = monomer. [b] I = initiator. [c] M_n = number average molecular weight, as determined by size-exclusion chromatography (SEC). [d] M_w/M_n (M_w = weight average molecular weight). [e] Degradation temperature (onset unless % mass loss is precised). [f] M_p peak value of molecular weight. [g] Ar = $C_6H_2{}^tBu_2$-2,6-Me-4. [h] M_w. [i] For the particular system: γ-BL/$La[N(SiMe_3)_2]_3$/Ph_2CH_2OH in a 100/1/1 ratio. [j] Depending on water content. [k] $(T(2,4,6\text{-}MeO)_3PP)AlCl$ = tetrakis((2′,4′,6′-trimethoxyphenyl)porphinato)aluminium chloride.

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bases (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD), 7-methyl-TBD (MTBD)),[121] phosphazene bases[122] or organic acids (such as diphenyl phosphate (DPP))[123] have also been reported for the ROP of ε-CL. Some enzymes have been used albeit yielding smaller molecular weights. Notably, *Candida antarctica* can achieve high conversions in less than 24 h while other lipases need more than 10 days.[124]

ROP of ε-caprolactam. In 1938, IG Farben patented a process for the ROP of ε-CPL producing polycaprolactam, also known as Nylon-6, a semicrystalline (T_g = 47 °C, T_m = 215 °C) polyamide of high commercial importance.[125] ε-CPL can undergo thermal ROP by heating above 260 °C for several hours under an inert atmosphere. However, anionic ROP of ε-CPL can be performed at a faster rate and lower temperatures (*e.g.* 150 °C),[126] with better conversion and higher molecular weights.[127] Strong bases like alkaline metals, hydrides, or Grignard reagents are used to initiate the anionic ROP of ε-CPL. The utilisation of activators (*e.g. N*-acyllactam, *N*-carbamoyllactams) enables higher rates.[128] ε-CPL can also undergo cationic ROP initiated by amines, carboxylic acids or even water.[129] ROP of ε-CL and ε-CPL under microwave irradiation, using tin octoate and ω-aminocaproic acid catalysts respectively, has been reported.[130]

ROP of β-methyl-δ-valerolactone. ROP of βMδVL has been performed using TBD organocatalyst and benzyl alcohol (BnOH) initiator. Poly(βMδVL) was produced after 1 hour at rt in 75% monomer conversion, giving polymer molecular weights between 4.1 and 70 kDa ($Đ$ 1.05–1.3).[42] Poly(βMδVL) is an amorphous polymer with a low glass transition temperature (−51 °C). The bulk ROTEP of βMδVL has also been reported using acid catalyst DPP and various alcohols initiators.[131] More recently, Hillmyer and coworkers polymerised βMδVL using TBD in the absence of an alcohol initiator.[41b] Isotactic poly((−)-βMδVL), obtained by ROP of (−)-βMδVL with BnOH initiator and DPP catalyst, was shown to remain amorphous with similar T_g to the atactic polymer.[43]

ROP of angelica lactone. α-AL (**7**) features two functional groups capable of polymerisation: the lactone ring and an endocyclic carbon–carbon double bond. The double bond enhances the strain energy of the five-membered ring and improves ROTEP thermodynamics. Addition of sodium isopropoxide to AL yielded polyesters with number average molecular weights (M_n) of up to 19.5 kDa after heating at 60–65 °C for 40–60 min. A 20–32% lack of double bonds in the polymer backbone revealed that part of the monomer was polymerised *via* the vinyl pathway.[132] The ROP of α-AL was also achieved using tin octoate as catalyst, at 130 °C for 30 h, yielding a polyester with a molecular weight of 29.4 kDa and a dispersity of 1.25. The resulting polymer showed good degradability under light and acidic/basic conditions.[133]

ROP of γ-butyrolactone. High-molecular weight polymers of γ-BL **8** were long thought unachievable due to the monomer low ring strain.[134] Various methods[135] such as lipase catalysts,[136] ultrahigh pressure and temperature (20 000 atm and 160 °C),[137] or a triflic acid catalyst and high pressure (1000 MPa)[138] combination resulted in 8 kDa polymers at best.[138b] However, recently, Chen and coworkers found that ROP of γ-BL could be performed at −40 °C under ambient pressure using La[N(SiMe$_3$)$_2$]$_3$ as catalyst (amongst others) and alcohol initiators.[139] Conducting the reaction below the ceiling temperature of γ-BL was vital to overcome the unfavourable ROP entropy. Solvent choice (THF) and high lactone concentration also drove the equilibrium, including by precipitation of the polymer. Molecular weights of up to 30.2 kDa and conversion of up to 90% in 6 hours (using an amino-bisphenolate yttrium initiator) could be achieved. Hong *et al.* further later reported the efficient organocatalysed ROP of γ-BL using phosphazene superbase *tert*-Bu-P$_4$.[140]

ROP of 2-pyrrolidone. ROP of 2-pyrrolidone **9** produces poly(pyrrolidone), also known as Nylon-4, a highly crystalline polymer (T_m ∼ 250 °C) that can be degraded by some bacteria,[141] but which is difficult to process as it reverts to its monomer upon melting.[142] Anionic ROP can be achieved at low temperatures using alkali metals, basic catalysts (*e.g.* potassium hydroxide, potassium *tert*-butoxide) or alkali salts of lactams.[143] The polymerisation can also be accelerated using *N*-acyl-2-pyrrolidone activators, (*e.g. N*-benzoyl-2-pyrrolidone).[144]

ROP of β-propiolactone. Poly(β-propiolactone) (PβPL) is a degradable polyester that can be produced by heating β-propiolactone **10** at 130–150 °C. However, the use of catalysts allows polymerisation to proceed under milder reaction conditions.[145] Several enzymes (*e.g. Candida cylindracea*)[146] as well as anionic[147] (*e.g.* alkali-metal alkoxides combined with a cation cryptand)[148] and cationic[149] (*e.g.* electron-deficient organosilicon species)[150] catalysts are known for the ROP of β-propiolactone. The mechanism for anionic ROP is generally accepted to proceed *via* acyl-oxygen or alkyl-oxygen scission of the monomer. ROP of β-propiolactone by a coordination–insertion mechanism is also reported for several metal complexes (for example based on nickel,[151] aluminium,[152] including coordinated to tetraphenylporphyrins,[153] and zinc[154]). Degradation of PβPL can be achieved thermally or by the actions of enzymes.[155]

ROP of malolactonates. Advances in the synthesis of poly(MLABe) (PMLABe) and its copolymers, including with other alkyl β-malolactonates, have been subject to a recent comprehensive review.[16d] Deprotection of PMLABe yields poly(β-malic acid). Although the ROP of MLABe **11** can be carried out using various cationic and anionic initiators/catalyst, control is limited. Nucleophilic catalysts (metal-based or metal-free), operating through a coordination–insertion or activated monomer mechanism respectively, afford much better control, at 40–60 °C, in solution or in bulk. It is worth noting that most reports concern the ROP of *rac*-MLABe. There are therefore opportunities to investigate further the stereoselective ROP of MLABe enantiomers to deliver polymers with different tacticities and thermal properties.[156]

ROP of L-malOCA. To the best of our knowledge, the ROP of L-malOCA **12** has only been reported by Dove and coworkers.[68] Building on the pioneering work of Bourissou and coworkers on lac-OCA ROP, *para*-substituted pyridines were investigated as catalysts in combination with *neo*-pentanol initiator, in $CHCl_3$ at rt. 4-Methoxypyridine provided the best balance between activity (95% conversion after 90 min) and selectivity, while affording a well-controlled ROP process. Deprotection of the benzyl ester

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side groups of the polymer yielded poly(α-malic acid), which was shown to fully hydrolyse to L-malic acid in 10 days.

ROP of sugar-diol derived cyclic carbonates. Advances on the polymerisation of cyclic carbonates have been reviewed recently.[157] The development of ROP catalysts[15g] has enabled controlled polymerisation of highly functionalised monomers[17a,158] under mild conditions. Tin octoate and aluminum isobutoxide have been used for the ROP of EOPDC **14**[77] and MeO_2DHAC **13**.[159] β-Diketiminate zinc complex, aluminium triflate or DMAP in combination with an alcohol/diol initiator have also been investigated.[160] TBD is the fastest catalyst reported for the ROP of **13** reaching 95% conversion in 5.5 min at rt.[74] Deprotection of the ketal then afforded poly(dihydroxyacetone carbonate), a crystalline polymer with a melting temperature of 246 °C. The controlled ROP of 7-membered ring α-Me7CC **16** and β-Me7CC **17** was successfully carried out by Carpentier, Guillaume and coworkers using various metal catalysts (based on Al, Zn and Y) and organocatalysts (DMAP, TBD and superbase BEMP), in bulk conditions (at 20 °C for **16**, and 60 or 110 °C for **17**).[79] The nature of the monomer and of the catalyst used influenced the regioselectivity of ring-opening. Preferential ring-opening at the most hindered oxygen-acyl O–C(O)O bond was seen for α-Me7CC with zinc and yttrium catalysts but not with Al. Conversely, no regioselectivity was observed for β-Me7CC, irrespective of the catalyst system used. Polymer thermal analyses highlighted the impact of the methyl substituent position on the glass transition temperature.

3.3 ROP of monomers which maintain a sugar structure

Table 2 shows selected examples of polymerisation of monomers seen in Section 2.2.

ROP of sugar-based lactones. In contrast to the readily ring-openable β-lactams and cyclic carbonates and despite their facile synthesis, homopolymerisation of sugar-1,5-lactones to aliphatic polyesters has proved challenging. Trimethyl arabonolactone **18** was deduced to undergo polymerisation upon exposure, over several weeks, to trace amounts of acetyl chloride or HCl, reaching an estimated molecular weight of 1.9 kDa.[81] Characterisation of the products obtained from the ROP of D-gluconolactone **20** was also limited. However, Péter and coworkers[167] reported the lipase-catalysed copolymerisation of the un-derivatised carbohydrate lactone **20** with 3-hydroxybutyric acid.

ROP of neat tetra-*O*-acetyl protected monomer **21** only formed low molecular weight oligomers of up to 1.47 kDa with $Sn(Oct)_2$ and 1,4-butanediol initiator, after 8 h at 80 °C (Fig. 22).[84] MALDI-ToF analysis of these mono-, di and tri-aldaric esters, isolated by column chromatography in 30% yield, showed two hydroxyl end groups and no cyclic or carboxylic acid terminated species. Hence, the oligoesters could serve as macroinitiators in the ROP of D- and L-lactide with an alkyl zinc initiator (LZnEt) to form triblock ABA copolymers. Carbohydrate co-initiators specifically aldonate esters have also been reported from glucose, xylose and 2-deoxy-D-ribose, containing one hydroxyl group for chain propagation in the ROP of lactide.[168] D-Manno and galactono-analogues of **21** alongside tetra-*O*-methyl/benzyl-D-gluconolactone and tri-*O*-methyl/acetyl/benzyl-D-xylono/L-arabonolactone are also reported to yield only dimers and trimers.[85]

Nevertheless, less substituted carbohydrate-1,5-lactone **22** undergoes ROP with catalytic amounts of $Sn(OBu)_2$ initiator to form atactic amorphous polyesters with M_n ranging from 1.8–7.3 kDa.[85] MALDI-ToF spectrometry showed the major product to be a cyclic species at all conversions and for initial monomer concentrations of 0.5–1.5 M (Fig. 23). This is reasoned to be due to the relatively low ring strain of the monomer and thus slow ROP, taking days or weeks to reach equilibrium at 80 °C. Subsequently the rate of propagation was comparable to the rate of transesterification leading to cyclic formation by backbiting reactions. The polymer (M_n 2.9 kDa, $Đ$ 1.26) showed a high thermal stability with the onset of degradation not occurring until 250 °C but loss of the rigid sugar ring upon

Table 2 Sugar-derived polymerisation data and thermal properties

M[a]	Catalyst [cat. mol%]	Initiator	$[M]_0$ (mol L^{-1})	$[M]/[I]^b$	Time (h)	Conv. (%)	T (°C)	Solvent	M_n[c] (kDa) [$Đ$][d]	T_g (°C)	T_d (°C) [% mass loss][e]	Ref.
18	HCl	—	Neat	—	Weeks	—	—	None	1.9[f,g]	—	—	81
21	$Sn(Oct)_2$ [17]	1,4-Butanediol	Neat	3	8	—	80	None	1.47[f]	—	—	84
22	$Sn(OBu)_2$	—	1.0	122	680	78	80	Toluene	4.3 [1.41]	18[h]	250–400 [94][h]	168
24	$Y(O^iPr)_3$ [1.25]	—	1.0	240	18	95	25	Toluene	13.7 [1.16]	52[i]	—	87
25	LiHMDS [1.25]	ArCOCl	0.1	200	0.5	>99	0	THF	56.2 [1.1]	—	—	89
26	LiHMDS [5]	ArCOCl	0.1	50	0.5	>99	0	THF	28.8 [1.1]	—	—	91
27	LiHMDS [2.5]	ArCOCl	0.1	100	1	>99	0	THF	47.4 [1.1]	15–25	200–500 [99%]	92
28	*t*-BuOK [5]	*N*-Boc,4-Me, 4-Ph, azetidine-2-one	0.15	55	48	80	25	CH_2Cl_2	10.5 [1.56]	—	—	93
29	—	NEt_3	1.6	26	2880	—	25	DMF	10[f]	—	225	95
30	—	*t*BuONa	0.25	200	2	—	25	THF	20.2 [1.82]	—	—	170*b*
31	—	^{t}BuOK	3.0	25	12	—	90	DMF	4.0 [1.60]	—	—	97
32	$Y(O^iPr)_3$ [1]	—	4.63	300	3	—	70	Dioxane	13.2 [1.69]	128	—	171
33	—	$Sn(Oct)_2$	Bulk	—	—	—	—	None	7.88	69	—	99
34	TBD [1]	4-MeBnOH	1.0	51	7	>98	25	CH_2Cl_2	14.7 [1.15]	122	250–320 [98]	101
35	TBD [1]	4-MeBnOH	1.0	50	1	>99	25	CH_2Cl_2	13.6 [1.17]	152	170–350 [98]	104

[a] M = monomer. [b] I = initiator. [c] M_n = number average molecular weight, as determined by size-exclusion chromatography (SEC). [d] M_w/M_n (M_w = weight average molecular weight). [e] Degradation temperature (onset unless % mass loss is precised). [f] M_w. [g] Estimated by elemental analysis. [h] Refers to polymer of M_n 2.9 kDa ($Đ$ 1.26). [i] Refers to polymer M_n 40 kDa ($Đ$ 1.14).

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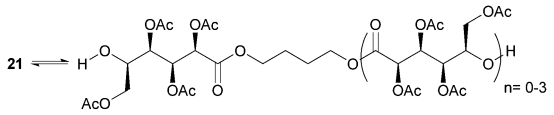

Fig. 22 ROP of **21** with $Sn(Oct)_2$ and 1,4-butanediol to yield dimers and trimers.

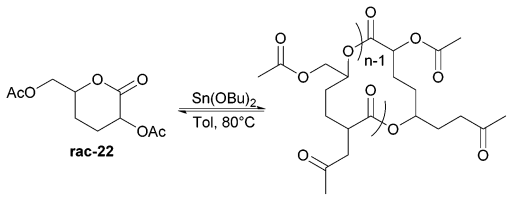

Fig. 23 ROP of **22** with $Sn(OBu)_2$ to form highly stable cyclic polyesters.

polymerisation resulted in a T_g of only 18 °C. In addition, the materials showed enhanced hydrophilic character compared to PLA, swelling on addition of water and a static water contact angle of ~33°. Use of a zinc ethoxide initiator with an ancillary ligand (LZnOEt) greatly reduced the polymerisation time to 1 h or less, and at rt.

Tetra-substituted 1,6-lactone **23** could only be copolymerised with L-lactide in the bulk at 110 °C using tin octoate.[82] A maximum sugar monomer incorporation of 2.2% was reported. Homopolymerisation of enantiopure aldono-1,6-lactone **24** was also unsuccessful with $Al(O^iPr)_3$ (decomposition) or $Sc(OTf)_3$ (no reaction) catalysts but 10% could be incorporated into the polyester chain of poly(ε-caprolactone).[86]

However, Guan and Urakami[87] reported the living ROP of racemic **24** using $Y(O^iPr)_3$ in toluene at rt (Fig. 24). Homopolyesters were isolated in yields of 85–95% with M_n estimated by SEC ranging from 5.3–40.1 kDa ($Đ$ 1.12–1.17). The racemic nature of the monomer and thus lack of stereoregularity resulted in an amorphous polymer for which Differential Scanning Calorimetry (DSC) analysis showed a T_g of 52 °C.

ROP of sugar-based lactams and *N*-carboxyanhydrides. Anionic ROP of β-lactam glucopyranose monomer **25** was carried out with LiHMDS catalyst under mild reaction conditions of 0 °C in THF solvent (Fig. 25).[89] Complete conversion to enantiopure poly-amido-saccharides (PASs) was observed in less than 0.5 h for all initiator (0.5–4 mol%) and catalyst loadings (1.25–8 mol%). Thus, polymerisation proceeded rapidly and in high yield (89 ± 5%) despite the steric bulk of the benzyl protecting groups, to give well-defined molecular weights, up to 56.2 kDa (M_n) with narrow dispersities ($Đ$ 1.1). A good agreement between NMR, SEC and theoretical M_n at lower monomer/initiator ratios of

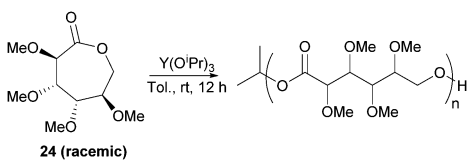

Fig. 24 Rare-earth metal initiated ROP of racemic **24**.

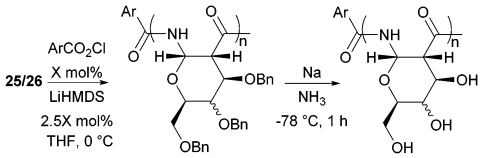

Fig. 25 Anionic ROP of β-lactam sugar monomers and subsequent benzyl deprotection with sodium metal in ammonia.

26 and 50 was found. Dynamic Light Scattering (DLS) was also used. The initiator was prepared *in situ* from the monomer by addition of 4-*tert*-butylbenzoyl chloride. Birch reduction was used post-polymerisation to achieve complete debenzylation of the PASs. Aqueous SEC *versus* dextran standards showed little broadening or decrease in chain length after deprotection for the smaller polymers ($M_{n,SEC} \leq 16.7$ kDa). Poor solubility made the analysis of longer chains difficult.

Formation of α-1,2-amide linked polymers of galactose derived β-lactam monomer **26** and octyl ether functionalised **27** was achieved similarly using 4-nitrobenzoyl chloride as an *in situ* generator of initiator (entries 2 and 3, Table 2).[91] The minor change in stereochemistry of the galactose-based repeat unit resulted in highly water soluble PASs compared to the glucose-derived analogue. Investigation into the structure of the glucose and galactose derived PAS by NMR spectroscopy, circular dichroism and molecular dynamic simulations suggested that the relatively rigid chair conformation adopted by the pyranose repeat unit contributes towards the formation of a defined helical secondary structure.[169] Thermogravimetric analysis (TGA) of the hydrophobic glucose octyl ether (GOE) PASs from **27** showed thermal stability up to 200 °C. DSC revealed T_gs of 15–25 °C for the larger polymers (M_n 26.3–47.4 kDa). Further endothermic transitions, associated with small enthalpy changes (1–2 J g^{-1}) indicated mesophases with low translational order.[92]

ROP of **28** was carried out in dichloromethane for 2 days at rt, using potassium *tert*-butoxide as catalyst. The resulting polyamide was optically active, amorphous and soluble in water. The weight-average molecular weight (M_w) was estimated by SEC to 10.5 kDa, with a dispersity of 1.59.[94] However, intrinsic viscosity measurements of the polyamides suggested higher molecular weights of 25 kDa. ^{13}C NMR spectroscopy revealed no epimerisation under the polymerisation conditions and thermal analysis showed decomposition occurred above 225 °C.[95]

Finally, treatment of *N*-carboxyanhydride **29** with triethylamine in DMF gave poly(glucoamides) with molecular weights (M_w) of 10 kDa by SEC after 2 days stirring at rt.[93]

ROP of sugar-based cyclic carbonates. Polycarbonate formation from 5-membered cyclic carbonate **30** was achieved *via* anionic ROP with DBU or metal alkoxide initiators (*t*-BuOK, *n*-BuLi, *t*-BuOLi and *t*-BuONa) in DMF or THF solvent.[170] Polymerisation of the highly strained *trans*-configured monomer proceeded at mild reaction temperatures of 25–60 °C without elimination of CO_2. *n*-BuLi and *t*-BuONa showed the highest polymerisation activity. Formation of both linear and cyclic polymeric species (from backbiting) was revealed by MALDI-ToF spectrometry, even at low concentrations of 0.25 mol L^{-1}.

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Higher reaction temperatures of 90 °C were required for the anionic ROP of **31**, to aid solubility in DMF.[97] With *t*-BuOK initiator, an aliphatic polycarbonate of M_n 4 kDa ($Đ$ 1.68) was isolated in 89% yield after 12 h.

Homopolymerisation of ring glucose pentofuranose based 6-membered cyclic carbonate **33** was readily achieved with $Sn(Oct)_2$, yielding polymer of M_n 7.88 kDa exhibiting a T_g of 69 °C.[99] A host of anionic, cationic and coordination–insertion catalysts were used in the more difficult homopolymerisation of D-xylose derived cyclic carbonate **32**.[171] ROP with yttrium isopropoxide in dioxane solvent at 70 °C gave the best results, yielding polycarbonates of M_n up to 13.2 kDa ($Đ$ 1.69) after 3 h. Extended reaction times led to a broadening of the molecular weight distribution and decrease in M_n associated with chain backbiting reactions. Three different carbonate environments in a roughly 1 : 2 : 1 ratio were observed in the ^{13}C NMR spectra of the polycarbonates. This suggested random cleavage of the acyl–oxygen bond at either side of the asymmetrical carbonate to give three different linkage types (Fig. 26): head–head (H–H); head–tail (H–T) and tail–tail (T–T). Wide-angle X-ray diffraction (WAX) analysis showed the polymer was semi-crystalline, with melting domains at 228 °C.

In contrast to the dominant use of metal-based catalysts, the ROP of D-glucose based and D-mannose derived monomers (**34**[101] and **35**[104] respectively) were carried out with TBD organocatalyst (Fig. 27). The *trans*-configuration of these 6-membered cyclic carbonates fused to a pyranose ring resulted in highly strained monomers, which readily underwent controlled polymerisation at rt with 4-methylbenzyl alcohol initiator. For example, the mannose monomer **35** reached full conversion in 1.3 h with 1 mol% catalyst and a monomer-to-initiator feed ratio of 100. Analogous to the D-xylose based cyclic carbonate, ^{13}C NMR spectroscopy supported by ESI tandem MS analysis by electron transfer dissociation (ETD) indicated non-selective propagation of the glucose based monomer **34** to form a regio-random polymer with a distribution of all three linkage types in the polymer backbone.

In contrast, one distinct carbonyl environment was observed for ketal-protected D-mannose based polycarbonates and supported by DFT calculations, suggesting a preference for H–T regiochemistry. Homopolymerisation of the mannose derived monomer was also possible with industrially relevant $Sn(Oct)_2$ catalyst under melt conditions (140 °C). The onset of thermal degradation was observed at 170 and 250 °C for amorphous glucose and mannose derived polymers, respectively resulting in near complete mass loss (98%) by 320–350 °C. Restricted rotation about the polymer chain imposed by retention of the furanose and pyranose rings revealed high T_g values for the sugar-based polycarbonates: 122 °C for glucose (14.7 kDa), 128 °C for xylose (13.2 kDa) and 152 °C for mannose (13.6 kDa). A higher T_g for the latter was attributed to the ketal protecting group which could be readily removed by treatment of the polymer with 80 : 20 TFA : H_2O. This introduces free hydroxyl groups along the polymer backbone to modify polymer properties and serve as a handle for further functionalisation.

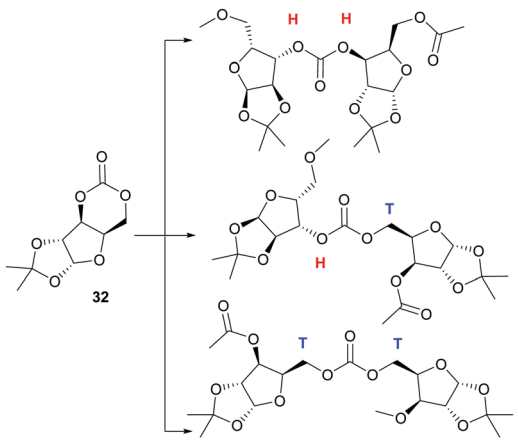

Fig. 26 Different regiochemistries in the homopolymer of **32** (H: head, T: tail).

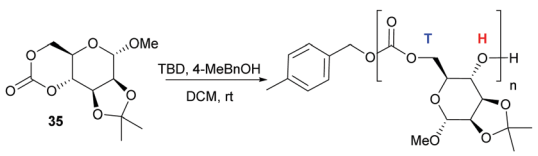

Fig. 27 Organocatalytic ROP of D-mannose derived cyclic carbonate **35** with head–tail regioselectivity.

4. Material properties and applications

Synthetic polymers can overcome some of the limitations of natural polymers such as source variability, contamination with biological toxins and need for extensive purification as well as provide access to unique properties that go beyond those found in nature. The basic thermal properties of the polymers obtained by ROP in Section 3 can be found in Tables 1 and 2. Next we will briefly present the various applications that these materials have found and the different strategies used to overcome limitations and address end-user applications. In this section, the emphasis is put on polymers which conserve a core carbohydrate structure (from Section 3.3).

4.1 Applications of polymers without a core carbohydrate structure

Most of the described sugar-derived polymers (as homo or copolymers) are interesting biomaterials for applications in the biomedical field (wound repair, drug delivery, tissue engineering, *etc.*).[172] Lactide and glycolide-based polymers have been widely used to this end due to their biocompatibility and biodegradability. These features also makes them suitable candidates for the construction of materials that require end-of-life degradation to environmentally benign components, such as those employed in packaging,[14c] washing products, fertilisers, insecticides *etc.*[173] Poly(α-malic acid), which was shown to fully hydrolyse to L-malic acid in 10 days, is also a promising degradable material.[68] Besides, the biomedical applications of aliphatic polycarbonates have been recently highlighted.[17c]

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Likewise, other emerging renewable polymers show promise. Poly(β-methyl-δ-valerolactone) provides a renewable rubbery polymer which can act as the soft segment in novel thermoplastics and elastomers.[131] It was for example recently used in the preparation of biobased recyclable polyurethanes for the fabrication of adhesives, foams, and coatings,[131] as well as in degradable cross-linked elastomers.[41b] Poly(γ-butyrolactone) is also interesting as it displays different melting-transition temperatures depending of its topology (~63 °C for the linear polymer and ~52 °C for the cyclic polymer). It is furthermore a truly recyclable polymer which gives back its monomer upon heating.

In general, the design of novel synthetic materials that can be tailored at the monomer level for a targeted application is highly desirable. There is therefore a growing interest in functionalised cyclic monomers.[17a,158b,c,174] However, most of the previous monomers are difficult to functionalise, conversely to monomers which have retained a core carbohydrate structure and part of the original sugar functionalisation potential.

4.2 Applications of polymers from sugar-based monomers

In addition to sustainability considerations, the biocompatibility, stereoregularity and functionalisation potential of sugar-based polymers can allow the structural features of natural polysaccharides to be mimicked and even expanded upon for specific polymer applications.

Owing to the anticipated biocompatibility and potential for derivatisation of free hydroxyl groups, many of the applications of sugar-based polymers obtained by ROP fall within the biomedical field. The use of aliphatic polyesters such as PLA, polyglycolide, poly(ε-caprolactone) and their copolymers as degradable sutures, bone pins, stents, tissue engineering scaffolds and drug delivery carriers rely on their degradation profile. However, the lack of functionality and hydrophobicity of some polymers can result in poor cell attachment properties. Such applications can thus be limited by the ability to control polymer properties for example, in the controlled release of an active compound. Copolymerisation serves as a very powerful tool for tuning polymer properties for a desired application.

Targeting tissue engineering applications,[175] where degradation of the polymer scaffold should correspond to the rate of tissue regeneration, copolymers of lactone **22** with L-lactide were prepared to address the slow degradation of PLLA (Fig. 28). Random copolymers composed of 1–25 wt% of lactone **22** with M_n 88–44 kDa ($Đ$ 1.36–1.51) were prepared using LZnOEt at rt.[176] Higher loadings of the functionalised lactone resulted in an increased degradation rate constant and decrease in the degradation temperature from 290 (1 wt%) to 255 °C (25 wt%). The T_g also decreases with increased proportion of **22** from 55.1 to 46 in line with predictions. These enhanced degradation properties are reflected in the loss of crystallinity upon copolymerisation. At 25 wt%, no melting temperature is observed by DSC compared to at 6 and 11 wt%, were semicrystalline regions were present.

A decrease in the static water contact angle to 71.4° at 25 wt% from ~79.1° for PLA reveals the accompanying increase in hydrophilicity upon incorporation of functional substituents. Cell viability and attachment studies were carried out on electrospun fibres of the copolymers using human osteogenic sarcoma Saos-2 cells. At all copolymer compositions, 90% of the cells were deemed viable but SEM images indicated a greater spread of cells on the copolymer with the highest ratio of **22** due to the increased hydrophilicity of the scaffold.

The protein resistant properties of the homo- and block copolymers of tetra-substituted racemic lactone **24** and ε-caprolactone were quantified using surface plasmon resonance (SPR) spectroscopy.[87] Nonspecific protein adsorption onto self-assembled monolayers of the polymers were evaluated using fibrinogen (a model hydrophobic protein) and lysozyme (a model for electrostatic protein adsorption). Strong adsorption of both proteins was observed onto the hydrophobic surface of poly(caprolactone) but introduction of hydrophilic methoxy side groups along the polymer backbone by copolymerisation with **24** resulted in a reduction in non-specific protein adsorption (Fig. 29). A 27 : 73 diblock copolymer of **24**: **ε-CL** (M_n 8.23 kDa) resulted in a fully protein resistant material. Thermal analysis of the copolymers showed they were fully miscible, exhibiting a single T_g from 10 to −17 °C depending upon the composition.

The biological activity of the deprotected glucose-derived PASs was investigated by Grinstaff and coworkers[89] through their ability to interact with natural carbohydrate receptors. Recognition and binding by readily available carbohydrate binding protein, Concanavalin A was demonstrated by a measured increase in turbidity of the solution upon aggregate formation and inhibition of glucose binding. The latter confirmed binding at the same pocket as natural glucose derivatives. High molecular weight polymers were required to form multiply binding interactions and elicit a response. Subsequent work, subjected the debenzylated glucose PAS to TEMPO-mediated oxidation to introduce an ionisable carboxylic acid group at the primary C-6 position of the repeat unit (Fig. 30).[177] This mimics natural polysaccharides such

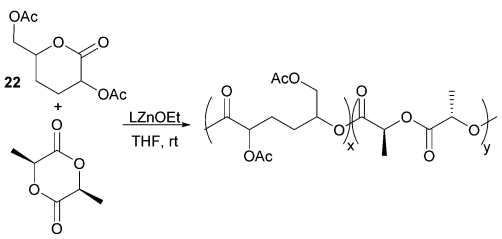

Fig. 28 Protein-resistant materials by copolymerisation of tetra-substituted and unsubstituted caprolactone monomers.

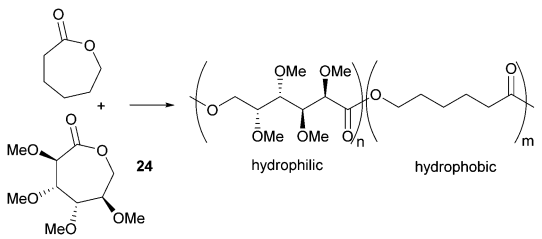

Fig. 29 Protein-resistant materials by copolymerisation of tetra-substituted and unsubstituted caprolactone monomers.

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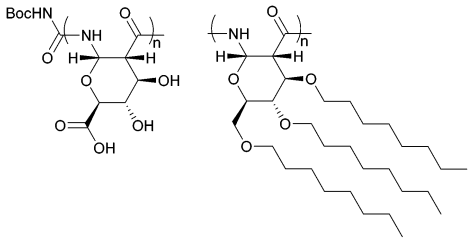

Fig. 30 OxPASs (left) as protein stabilising agents and GOE-PASs (right) as LC materials.

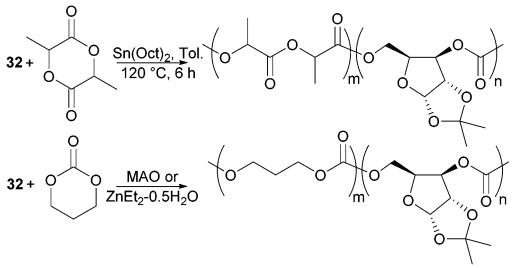

Fig. 31 Copolymers of sugar-based cyclic carbonates **32** with L-LA and TMC.

as hyaluronic acid, aliginic acid and oxidised forms of cellulose, which have been investigated and used for a variety of applications.

The resulting oxidised PAS (OxPASs) showed promise as protein stabilising agents. Protein stability and retention of activity during storage are important concerns within research and the pharmaceutical industry. Using lysozyme as a model protein, OxPAS was found to be significantly more effective at lessening the loss of activity during a repeated freeze-drying process compared to trehalose, a commonly used protein stabilising agent. Gel electrophoresis suggested formation of a complex between the protein and oxPAS accounting for the stabilising effect.

Aside from biomedical applications, translation of the liquid crystalline (LC) properties of small molecules, widely used in display technologies, to form functional polymeric materials is of immense interest. Derivatisation of the hydroxyl groups in glucose β-lactam with hydrophobic long chain alkyl groups imparted self-assembly properties to the resulting PASs (Fig. 30). The octyl ether substitutes served as a molten phase against the rod-like carbohydrate backbone, promoting formation of LC phases at rt and up to 120 °C. Depending upon the temperature and polymer chain length, lamellar and hexagonal columnar mesophases were formed.[92]

The galactose-derived PASs, which differ from the glucose analogues only by the configuration of the C-4 substituent, display higher water solubility, and showed potential application in drug delivery, hydrogel formation and surface passivation.[91] These materials were found to be non-cytotoxic to HeLa, HepG2 and CHO cell lines after incubation for 48 h. Cellular uptake studies into human hepatocyte cells expressing a galactose specific receptor were carried out with fluorescently labelled PASs. Uptake by endocytosis was observed by confocal microscopy after a 24 h incubation time and found not to be dependent on the type of receptor.

The biodegradability and when functionalised, biocompatibility of APCs makes them attractive synthetic polymers for biomedical applications. Unlike PLA which degrades *in vivo* to lactic acid, degradation of APCs does not lead to the formation of an acidic environment which can be problematic to surrounding tissues and loaded drugs. Copolymerisation of D-xylose based cyclic carbonate **32** and pentofuranose monomer **33** served to overcome challenges in both their homopolymerisation by decreasing the steric hindrance along the polymer chain as well as to tailor the material properties of PLA or poly(trimethylenecarbonate) (PTMC) (Fig. 31). Among the organometallic catalysts evaluated, $Sn(Oct)_2$ was preferred for the formation of high molecular weight co-polymers of **32** with L-lactide (L-LA).[98]

Compared to the xylose monomer, L-LA showed a much higher (20-fold) reactivity and after 6 h at 120 °C, polymers of M_n 78.4 kDa ($Đ$ 1.9) were reported consisting of 7% xylose repeat units. Higher xylose content, up to 39 mol% resulted in higher T_g values but lower M_n (13.9 kDa, $Đ$ 1.7) and polymer yields (48% *vs.* 82% above). In all cases, a single T_g was observed, reported at 89 °C for the copolymer with 39 mol% xylose units compared to 71 °C at 15 mol%. At 130 °C, the bulk copolymerisation of **33** with L-LA yielded a polymer of M_n 77.8 kDa composed of 4 mol% glucose sugar, which exhibited a T_g of 59 °C.[99] Selective removal of either the benzyl or ketal protecting groups could be achieved to strategically place 1, 2 or 3 hydroxyl groups along the polymer backbone. This is important for the fine-tuning of the physical, hydrophilicity and biodegradability properties of functional materials for biomedical applications. MAO, IBAO and $ZnEt_2{\cdot}0.5H_2O$ catalysts at 90 °C gave the most promising molecular weights and yields for the copolymerisation of xylose cyclic carbonate **32** with TMC.[178] The random amorphous copolymers showed a single T_g dependent upon the xylose content. At 29 mol% a T_g of 37 °C (M_n 21.7 kDa) was reported, which increased to 109 °C with 83 mol% of xylose repeat units. A more comparable polymerisation rate of **32** with TMC cyclic carbonate compared to L-LA enabled copolymers with higher xylose content to be prepared. Ketal deprotection resulted in a decrease in T_g.

Materials that undergo triggered and reversible supramolecular assembly and disassembly to nanostructures have broad applications in medicine, controlled released and diagnostic imaging. Transformation of the alkyne functionality in the polyphosphoester used as a macro-initiator in the TBD catalysed polymerisation of D-glucose-based cyclic carbonate **34** imparted an amphiphilic character to the polymers resulting in temperature sensitive phase behaviour (Fig. 32).[102] Below a lower critical solution temperature (LCST), the functionalised cationic,

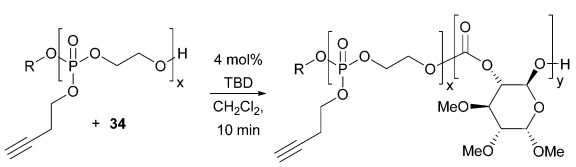

Fig. 32 Block copolymers of **34** showing stimuli sensitive phase behaviour (R = 4-MeBn).

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anionic and zwitterionic block co-polymers were observed to self-assemble into spherical micelles of the order of 20 nm diameter by TEM.

Perspectives

Amongst the approaches to prepare sustainable polymers from renewable feedstocks, the utilisation of sugar resources (either through fermentation and/or chemical routes) provides access to a wide range of cyclic monomers, namely lactones, lactams, *O* and *N*-carboxyanhydrides and cyclic carbonates. However, apart from PLA, the resulting polymers are currently niche products (often in the biomedical field), because of their cost and intrinsic limitations as materials.

Strikingly, the majority of these sugar-derived cyclic monomers do not preserve the functionalities and the core structure of their parent carbohydrates. Multiple functional groups can be detrimental to the thermodynamics of the ROP but at the same time provides opportunities for functional and tailored materials that could compete with traditional polymers. Synthesis of monomers directly from sugars often involves protection/deprotection steps that can be seen as limiting in practice and for price, but that ultimately can be used to tune the material properties (*e.g.* amphiphilicity, biodegradability, thermal-response). Combined with the use of renewable building blocks for functionalisation, these should be seen as opportunities to provide new sustainable materials. There is significant scope for the development of new benign methods, with functional group tolerance, to produce monomers from sugar structures, in particular under-developed cyclic monomers.

The ROP of cyclic monomers provides indeed a powerful precision method to deliver in a controlled fashion, polymers with various properties and tailored applications. In particular, ring-opening copolymerisation allows for the modification of the material properties by incorporation of another monomer to yield block or statistical polymers. These structures are particularly useful in the fine tuning of properties. Recent years have seen many great advances, in particular in the development of inexpensive and abundant metal homogeneous catalysts, as well as organocatalysts, which can catalyse even the most reticent monomers under the right conditions (including with multiple substituents), and yield polymers of predictable molecular weight, with narrow dispersities. There remains however a need for fundamental catalyst development, including for more active and selective catalysts. In particular, the control of stereo and regiochemistry is of great interest to moderate the crystallinity of polymers obtained by ROP. Stereoselective ROP has been so far limited to PLA synthesis, but the area should expand upon the development of novel monomers with stereochemical diversity. To this end, the use of sugar feedstock is particularly interesting. Heterogeneous catalysts have also received significantly less attention, although they could facilitate catalyst recycling and reduce cost (thus promoting applications), as well as facilitate the synthesis of complex structures using flow processes.

The next chapter in the quest for sugar-based polymers will require that challenges in monomer synthesis be overcome before seeking improved control over the polymerisation and post-polymerisation processes. Only then the engineering of advanced polymer architectures towards cost and performance competitive materials, but with controlled degradability, will be realised and sustainable polymers based on sugar feedstocks will find widespread applications and displace current petroleum-based engineering and commodity plastics.

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