

Synthesis of biodegradable polymers from renewable resources

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The vast majority of commodity materials are obtained from fossil fuels. However, many studies predict that all fossil resources will be depleted within a few centuries. Biomass represents an abundant carbon-neutral renewable resource for the production of materials. Using biomass for the production of new polymers can have both economic and environmental benefits. This review focuses on the use of biomass for the synthesis of biodegradable polymers.

Introduction

Commodity polymers such as polyolefins are ubiquitous in our societies. A combination of factors, including monomer cost and availability, synthetic ease, and excellent properties, have incited the widespread use of these materials. The vast majority of these commodity materials are obtained from fossil fuels and nowadays the utilization of non-renewable resources in the manufacture of plastics accounts for approximately 7% of worldwide oil and gas.^{1,2} However, these resources are limited and many studies predict that all fossil resources will be depleted within a few centuries.^{3–5} The growing environmental awareness over limited fossil fuel reserves (and consequently the increase of oil prices) has stimulated the search for novel polymeric materials and

production processes drawn from sustainable, renewable feedstocks and which minimize the detrimental environmental effects associated with their usage.⁶ In addition, from the widespread use of synthetic polymeric materials has emerged another major concern; indeed, despite the increasing popularity of plastic recycling, disposal of these undegradable materials has led to serious environmental pollution. From this point of view, the continuous depletion of landfill space available for discarded plastic wastes leads to the need for biodegradable polymeric materials to be used as substitutes for non-degradable conventional plastics. Such biocompatible and biodegradable polymers are thus currently emerging as valuable alternatives to conventional synthetic (petroleum-based) polymers and might be produced from raw materials.

Biodegradable polymers are defined as polymers that are degraded⁷ and catabolized, eventually to carbon dioxide and water, by naturally occurring microorganisms such as bacteria, fungi or algae. In addition, when they are degraded, these

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polymers should not generate any substances that are harmful to the natural environment.⁸ Generally, natural materials (*i.e.*, polysaccharides, proteins and bacterial polyesters) or synthetic polymers which contain hydrolyzable bonds in the backbone such as polyamides, polyurethanes, polyureas, polyethers, poly-anhydrides, polypeptides (and the corresponding copolymers) are interesting candidates for biodegradation.⁹ Among various families of biodegradable polymers, aliphatic polyesters have a leading position since hydrolytic and/or enzymatic chain cleavage yields hydroxy-carboxylic acids, which in most cases are ultimately metabolized.¹⁰ Several parameters have been reported to influence the degradation behavior of biodegradable polymers; the most important factors are the chemical composition, the molecular weight and molecular-weight distribution, the crystallinity, and the (micro)structure of the polymer. Recent studies have also evidenced the strong influence of ordered monomer sequences on degradation properties.¹¹ Other important properties of the polymer matrix that depend on the polymer composition, such as the glass transition temperature (T_g), have additional indirect effects on degradation rates.

Although the biodegradability of a material is independent of the origin of the starting raw materials used, biomass represents an abundant carbon-neutral renewable resource for the production of biodegradable materials. Nature produces over 200 billion tons of biomass by photosynthesis each year, 75% of which can be assigned to the class of carbohydrates. However, only 3.5% of these compounds are used by mankind.¹² It is crucial to exploit the vast biofeedstocks provided by Nature, through broad-scale basic research toward the development of efficient, environmentally benign, and economical process methodologies for the large-scale conversion of biomass (carbohydrates, proteins, fats, terpenoids) into industrially viable polymeric organic materials. There exists a real opportunity to discover new ways to produce novel materials within the context of sustainability issues that are beginning to permeate recent industrial thinking. Many of these renewable resource polymers

can also be rendered biodegradable under the appropriate conditions.^{1,2} However, except for polylactide, their high cost hampers their widespread use as bulk polymeric materials, relative to conventional petroleum-based plastics. More economically viable processes and the synthesis of new types of biodegradable polymers would clearly increase the number of applications for these polymers, as well as lower their cost. Recognizing that the raw material cost accounts for up to 50% of the overall production cost of biodegradable polymers,¹³ several research groups have directed investigative efforts toward the synthesis of new renewable monomers and the conversion of these monomers into their corresponding polymers.

The present review is concerned with those catalytic reactions that can help to transform carbohydrates and vegetable oils into valuable or potentially valuable materials. To avoid duplicity with the existing literature, herein we will comment on recent selected papers that have described methodologies and strategies that allow the synthesis of (potentially) biodegradable polymers from renewable resources.^{14,15} While most potential catalytic chemical routes have been considered, we have focused our attention on chemical routes through homogeneous catalysis; enzymatic processes are treated only marginally.

Lactide

Of the variety of biodegradable polymers synthesized from renewable resources, poly(lactide) (PLA) is certainly the most promising polymer today.^{1,16,17} These polymers, derived from 100% renewable resources such as corn or sugar beets, have recently become commercial materials, with the goal of supplanting traditional polyolefin-based materials in several applications.³ Indeed, polylactides are recyclable and compostable¹⁸ and their physical and mechanical properties can be manipulated through the polymer architecture.^{19–22} Tremendous progress has been made during the past decade in controlling the polymerization of synthetic PLA. Although several methods exist for the



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synthesis of PLAs,¹⁶ the most promising is the ring-opening polymerization of lactide.²³ Different strategies have been proposed for the ring-opening polymerization (ROP) of lactide involving anionic, nucleophilic, or cationic initiators. However, the controlled ring-opening polymerization of lactide by well defined metal-based catalysts is by far the most widely studied method. Therefore PLA can be obtained with homoleptic tin, aluminium and zinc-based systems but several drawbacks (*e.g.*, complicated equilibria phenomena and multiple nuclearities) have limited the control of the polymerization and the structural influence on catalyst activity. Homoleptic yttrium alkoxides were also studied in lactide polymerization. McLain and Drysdale were the first to demonstrate the high potential of yttrium complexes for the synthesis of poly(lactide) with a homoleptic complex described as “Y(OCH₂CH₂NMe₂)₃”, which was shown to polymerize *rac*-lactide in a rapid and controlled manner.²⁴ Also, Feijen *et al.* reported that Y₅(μ-O)(OⁱPr)₁₃ has a high activity in LA polymerization.²⁵ Finally, Tolman and co-workers reported that Fe₅(μ-O)(OEt)₁₃ displayed very high rates and excellent molecular weight control in lactide polymerization.²⁶

These complexes have contributed significantly to a better understanding of the factors that govern the polymerization, and spectacular improvements have thereby been achieved in terms of catalytic activity as well as polymerization control. However, although tin, aluminium and zinc-based systems proved to be quite convenient in the preparation of aliphatic polyesters, there is also no possible control of stereochemistry. As stereochemistry plays an important role in PLAs, determining their mechanical properties, biodegradability and ultimately the end use of the material, a second generation of heteroleptic metal-based complexes with fine ligand adjustment attracted interest for a better control, activity, and selectivity of the polymerization reaction.²⁷ Therefore, recent advances in catalyst design have led to a variety of PLA microstructures from the enantiomerically pure monomer, *racemic* mixture, or *meso* lactide. These lactide feedstocks can be used to construct various polymer

architectures (*i.e.* atactic, isotactic, heterotactic and syndiotactic) (Scheme 1).

Two types of control exist for the stereoselection in the coordination–insertion ring-opening polymerization: the chain end control and the enantiomeric site control. In a chain-end controlled mechanism, the chirality of the last unit in the growing polymer chain influences the chirality of the next monomer to be inserted. Enantiomeric site control, however, is demonstrated when the chirality of the catalyst, and not the chain end, dictates the chirality of the next insertion. Despite recent developments of achiral and chiral complexes for the ROP of lactide,²⁸ relatively few well-defined metal catalysts are able to achieve high stereochemical control in the ROP of *meso*- or *rac*-lactide. We will only discuss examples that allow the synthesis of highly stereocontrolled polymers.

Aluminium-catalyzed polymerization of lactide

Some of the most significant advances in stereocontrolled polymerization of lactide have been demonstrated using aluminium alkoxides stabilized by tetradentate bis(iminophenoxide) (*salen*-type)²⁹ or tetradentate bis(aminophenoxide) (*salan*-type)³⁰ ligands. Spassky *et al.* were the first to demonstrate that the aluminium methoxide complex bearing a binaphthyl Schiff-base ligand **1** induced a highly stereocontrolled polymerization of *rac*-LA to produce at low conversions (<19%) isotactic PLAs with 88% enantiomeric enrichment in (*R,R*) units (Fig. 1).³¹ At high conversions a stereocomplex between (*R,R*)- and (*S,S*)-enriched stereocopolymers was formed (*M_n* up to 12 700 g mol⁻¹). The polymerization reaction showed living type features, and narrow molecular weight distributions (*M_w*/*M_n* = 1.05–1.30), indicating that transesterification reactions do not occur significantly with this sterically hindered initiator.

The next reported initiators were essentially aluminium Schiff base systems and the corresponding polymerizations proceeded in a highly stereoselective manner and with a good control of the



Scheme 1 Lactide stereochemistry and typical PLA architectures.



Fig. 1 Stereoselective aluminium-based systems for the ROP of *rac*-lactide.

molecular weights (Fig. 1). It was shown that these initiators can be used to prepare PLA stereocomplexes and PLA stereoblocks, which showed enhanced thermal stability compared to the homochiral PLAs (T_m up to 210 °C). For instance, parallel stereocontrolled ROP of (*R,R*)- and (*S,S*)-LA from *rac*-LA was carried out with aluminium catalysts **2**³² and **3**³³ to give isotactic stereoblock PLA. The formation of a stereoblock PLA was explained by a polymer exchange mechanism where growing chains switch between (*R*)- and (*S*)-species.^{32a,34}

Other Al-based systems are able to generate isotactic PLAs from *rac*-lactide.³⁵ Some of them are achiral and operate *via* a chain-end control mechanism. Gibson and co-workers reported the formation of isotactic stereoblock PLA (P_m up to 0.79) with tetradentate *N,N'*-disubstituted bis(aminophenoxide) aluminium complexes **4a** and **4b**.^{35c} Remarkably, these aluminium initiators were demonstrated to generate a wide range of microstructures. Interestingly it was shown that isotactic PLAs were obtained in the presence of complexes bearing unsubstituted phenoxide groups whereas heterotactic PLAs were produced when the phenoxide units of the salen ligand contain substituents in the 3 and 5 positions (*e.g.* for complexes **4c** and **4d**). The authors proposed that the monomer selectivity is influenced by the alkylamino backbone substituents that can closely approach the site of polymer chain growth.

Also, syndiotactic, semicrystalline PLA can be formed by ROP of *meso*-lactide in the presence of the chiral aluminium isopropoxide complex **2**, which preferentially ring-opened one acyl-oxygen site, leading to a highly alternating arrangement of stereocenters in the polymer (M_n up to 15 400 g mol⁻¹, $M_w/M_n = 1.04$ –1.06).³⁶ The resulting PLA (syndiotacticity up to 96%) exhibited a melting temperature at 152 °C.

Indium-catalyzed polymerization of lactide

Hillmyer *et al.* have recently reported the ROP of *rac*-LA using a catalyst prepared *in situ* from indium trichloride, benzyl alcohol and triethylamine to prepare highly heterotactic PLA ($0.86 < P_r < 0.94$ at 25 °C, $P_r = 0.97$ at 0 °C).³⁷ The resulting



Fig. 2 Stereoselective indium-based initiator for the synthesis of isotactic PLA.

robust system was found to be active under a variety of reaction conditions to give heterotactic PLA with controlled molecular weight and a narrow molecular weight distribution (M_n up to 159 000 g mol⁻¹, $M_w/M_n = 1.06$ –1.62). Unlike the other stereoselective catalysts which contain sophisticated ligands critical to obtain highly tactic PLA, this system allowed the induction of stereocontrol without an added directing multidentate ligand.³⁸

Mehrkhodavandi and co-workers have recently published a chiral alkoxy-bridged dinuclear indium catalyst capable of active, living, and selective ROP of lactide (Fig. 2).³⁹ The authors demonstrated a possibility of functional-group-tolerant polymerization and catalyst recovery. In addition, even if the racemic catalyst **5** revealed modest isoselectivity in LA polymerization, the enantiopure catalyst **5** showed significantly decreased enantioselectivity in lactide ROP, thus highlighting the importance of a site-control mechanism.

Zinc-catalyzed polymerization of lactide

In the past decade, a new class of β -diiminate zinc complexes for ROP of lactides was described by Coates *et al.*⁴⁰ Such catalysts, like complexes **6** (Fig. 3), were found to act as single-site, living initiators for the polymerization of (*S,S*)-lactide, *rac*-lactide and *meso* lactide to PLA. These achiral complexes featured particularly high activities and selectivities, leading to the synthesis of highly heterotactic PLA (P_r up to 0.94 at 0 °C) from *rac*-LA by alternately incorporating the (*R,R*)- and (*S,S*)-LA. Among them, complex **6b** exhibited the highest activity and stereoselectivity for the polymerization of *rac*-lactide to PLA. Changing the ligand substituents from isopropyl to *n*-propyl groups resulted in a decrease of heterotacticity ($P_r = 0.76$).

Group 3 metal-catalyzed polymerization of lactide

In 2002 the catalytic behavior of a new salen yttrium alkoxide complex was investigated by Ovitt and Coates in the ROP of lactide.⁴¹ Although this complex revealed relatively higher activity than the parent aluminium derivative, no

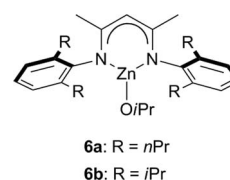


Fig. 3 Zinc systems for the heterotactic ROP of *rac*-lactide.

stereoselectivity was observed for the polymerization of *rac*-LA. However, from this early study, other research groups investigated the synthesis and reactivity of well-defined yttrium complexes supported by bis(phenoxide) ligands in order to achieve effective ROP of *rac*-LA.^{42,43} Among these, the yttrium amido and alkoxo derivatives **7a–d** (Fig. 4) have shown interesting performance for the heterotactic living polymerization of *rac*-LA. For instance, the PLA produced by **7b** and **c** was found to be highly heterotactic, with a P_r of 0.90 (M_n up to 87 000 g mol⁻¹, $M_w/M_n = 1.07$ – 1.34). Subsequently analogous alkyl yttrium derivatives **7e** and **7f** were synthesized and displayed higher stereoselectivity for the polymerization of *rac*-lactide to give heterotactic poly(lactide) with a P_r ranging from 0.97 to 0.99.⁴⁴ Finally, the yttrium systems **7a–c** are also able to act as *catalytic*-like species in the presence of excess alcohol, producing larger quantities of heterotactic PLA.⁴⁵

Okuda and co-workers reported the synthesis of several lanthanoid complexes such as **8** and **9** supported by 1,ω-dithiaalkanediy-bridged bis(phenoxide) ligands (Fig. 4).⁴⁶ Among these dichalcogen-bridged bis(phenoxide) derivatives, scandium complexes **8a** and **9a** exhibited high heterotactic selectivity (P_r up to 0.95) during the controlled ROP of *rac*-LA (M_n up to 28 500 g mol⁻¹, $M_w/M_n = 1.06$ – 1.89). The authors attributed the high selectivity of these complexes to a dynamic monomer-recognition process involving interconversion of the ligand configuration.

Organocatalyzed polymerization of lactide

Although metal-based catalysts can produce highly selective PLA, the contamination of the polymer by traces of metals can be a major drawback for polymers with biomedical applications. Therefore organocatalysis may be an alternative for the stereoselective ROP of lactide.⁴⁷ Most studies using organocatalysts for the ROP of lactide were carried out by Hedrick *et al.*⁴⁸ In particular, stereoselective ROP of *rac*- and *meso*-lactide was accomplished at low temperature with organocatalysts such as *N*-heterocyclic carbenes⁴⁹ and phosphazene base⁵⁰ ($P_m = 0.95$ at -75 °C). The use of chiral organocatalysts presents the advantage of potentially inducing kinetic resolution of *rac*-lactide. Indeed, Miyake and Chen reported recently the stereoselective ROP of *rac*-lactide and its first successful kinetic resolution using a cinchona alkaloid, β-isocupreide (ICD).⁵¹ In the presence of benzyl alcohol, ICD converted 86% of *rac*-lactide

to form an isotactic-enriched polymer ($P_m = 0.74$) with a good M_w/M_n of 1.12 at room temperature in dichloromethane (M_n up to 23 300 g mol⁻¹). Furthermore, it was shown that the ROP of (*S,S*)-lactide proceeded much faster than that of *rac*-lactide, indicating that the polymerization of (*R,R*)-LA was less favored. Indeed analysis of the unreacted monomer revealed a resolution of (*R,R*)-LA with 72% ee. The selectivity factor remains moderate but could be enhanced with further investigations.

Butyrolactone-based vinyl monomers

Polar vinyl molecules are interesting monomers for polymerization and methyl methacrylate (MMA) has been the most studied monomer to produce iso-, syndio- or atactic poly(methyl methacrylate) (PMMA) depending on the catalytic system used.⁵² Some renewable cyclic analogs of MMA (vinyl butyrolactones) are emerging as very interesting monomers. Indeed α-methylene-γ-butyrolactone (MBL) also called Tulipalin A is a natural product isolated from tulips.⁵³ A recent study reported its synthesis in high yield *via* enzyme-mediated conversion of tuliposide A, found in large quantities in tulip tissues (0.2–2% w/w fresh weight).^{53b} Its methyl derivative, γ-methyl-α-methylene-γ-butyrolactone (MMBL) is obtained in two steps using a method developed by DuPont⁵⁴ starting from levulinic acid, derived from biomass and produced in 450 tons per year.⁵⁵ Contrary to MMA, these vinyl butyrolactones are fixed in their *s-cis* form because of the ring strain, which increases their reactivity in free radical polymerization.⁵⁶ Polymerization of MBL and MMBL to produce PMBL and PMMBL respectively occurs *via* their double bond (Scheme 2).

PMBL and PMMBL present some advantages over PMMA due to the presence of the butyrolactone ring: they tend to have a better durability, a higher refractory index (interesting for optical applications) and glass transition temperatures T_g (194 °C and 227 °C respectively) and therefore can be used for the synthesis of thermoplastic elastomers. The first reports of MBL polymerization by radical and anionic mechanisms date back to the early 80's.⁵⁷ Group transfer polymerization⁵⁸ and copolymerization⁵⁹ have also been investigated. More recently, MBL was copolymerized with poly(ethyleneoxide) (PEO) by a radical mechanism⁶⁰ and with a cyclic ketene acetal, 2-methylene-1,3-dioxepane (MDO) by mixing the two monomers between 70 °C and 120 °C to produce high molecular weight copolymers. Two



Fig. 4 Lanthanoid complexes for the heterotactic ROP of *rac*-lactide.



Fig. 5 Half-sandwich indenyl rare earth metal dialkyl catalysts.

with the sandwich $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ complex) though a moderate M_w/M_n of 1.64 was obtained. MBL is often considered more active than MMBL but in this case the authors explained that the excellent activity of the methylated analogue is due to the higher electron density of the monomer which can bind more tightly to the rare earth metal catalyst. Moreover, catalyst **13c** being less sterically hindered than the sandwich catalyst, the access of the larger monomer is facilitated.

Contrary to PMBL, PMMBL is soluble in CH_2Cl_2 and the polymerization of MMBL can therefore be carried out in this solvent. Results also followed the same trend as in DMF: **13c** was the most active catalyst and gave a syndiotactic-enriched polymer (42.4% *rr*, 44.8% *mr*, 12.8% *mm*) with a T_g of 218 °C, similar to that obtained for atactic PMMBL with $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ (221 °C). Kinetic studies in CH_2Cl_2 revealed a second order reaction law in respect to the catalyst concentration, suggesting a bimolecular propagation. A catalytic cycle involving a Michael addition was proposed, similar to the mechanism described for polymerization of methacrylates with non-bridged group 4 metallocene catalysts.⁷⁵ MALDI-TOF mass spectrum analysis of an unpurified low molecular weight PMMBL ($[\text{M}]/[\text{13c}] = 20$) revealed that one of the two mass distributions corresponded to PMMBL with one chain-end group being the alkyl CH_2SiMe_3 and the other a proton resulting from the acidic work-up procedure. Furthermore, the efficiency coefficient for the polymerization with these catalysts was found to be over 100%, suggesting the two alkyl species CH_2SiMe_3 participated in chain initiation but only one chain grew at a time since a first order dependence to MMBL was observed.

It can also be mentioned that homoleptic lanthanide silylamide $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Sm, La, Nd, Er}$), cationic zirconocene and half titanocene complexes, which are efficient for the polymerization of MMA, were chosen as catalysts for the polymerization of (M)MBL. However the polymerization was much slower than with $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ and not well controlled.^{70a}

Polymerization of MBL and MMBL catalyzed by $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ and dysprosium catalyst **13c** respectively was studied in the presence of an external chain-transfer agent (CTA). A CTA is supposed to cleave the growing polymer from the active species and reinitiate the polymerization by anchoring to the polymer chain.⁵² Enolizable organo acid 3-methyl-2-butanone (MBO), methyl isobutyrate (MIB) and dimethyl malonate (DMM) were chosen as potential CTAs but only MBO can be considered as a suitable agent in the polymerization of MBL with $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ giving an efficiency coefficient of 1060% with a turn over number (TON) of 10 with 20 eq. of the CTA.^{70a} On the contrary,

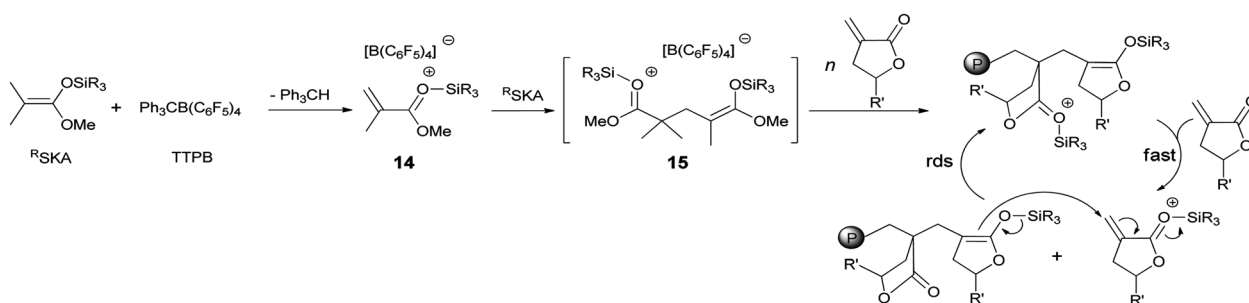
both MBO and MIB were ineffective for the polymerization of MMBL in the presence of Dy catalyst **13c**.^{70b}

Although most studies dealing with the polymerization of (M) MBL involved metal-based catalysts, Chen and co-workers have also reported the use of ambiphilic silicon propagators⁷⁶ and frustrated Lewis pairs.⁷⁷ The ambiphilic silicon catalyst system was recently successfully developed for (meth)acrylate polymerization⁷⁸ and consequently has been applied to the methylene butyrolactones polymerization. Ambiphilic silicon propagating species consist of both the nucleophilic silyl ketene acetal (^RSKA) initiating moiety and the electrophilic silylium catalyst. The first step consists in the oxidative activation of a silyl ketene acetal by a catalytic amount of [trityl tetrakis(pentafluorophenyl)borate] (TTPB) to form an electrophilic silylium cation **14** which undergoes a Michael addition of a second ^RSKA to lead to the active propagation species **15** (Scheme 4). In the proposed propagation mechanism, the monomer captured a silylium cation in a fast step followed by the rate determining step consisting in the intermolecular Michael addition of the polymeric SKA to the silylated monomer. With ^{tBu}SKA as the initiator, MBL polymerization in CH_2Cl_2 gave a bimodal polydispersity because of the insolubility of PMBL in that solvent. As already mentioned, PMMBL is soluble in CH_2Cl_2 ; thus its polymerization was controlled with quantitative yields obtained in 10 min at room temperature with excellent M_w/M_n between 1.01 and 1.06 depending on the ratio $[\text{M}]/[\text{SKA}]$. For $[\text{M}]/[\text{SKA}] = 400$, a syndio-enriched PMMBL was produced (45.8% *rr*, 39.9% *mr*, 14.3% *mm*). Moreover, when increasing to 600 equivalents of MMBL, characteristics of living polymerization were observed and for 800 equivalents, a high molecular weight of 548 000 g mol^{-1} was produced. Investigations with ^{Me}SKA (best initiator for MMA polymerization) and activators other than TTPB (TRISPHAT and $\text{HB}(\text{C}_6\text{F}_5)_4$) did not lead to better catalytic systems.

Copolymerization studies with the best catalytic system ^{tBu}SKA/TTPB produced the block copolymer PMMBL-*b*-PMBL displaying two glass transition temperatures of 197 and 212 °C (similar to the ones of isolated PMBL and PMMBL, respectively) and statistical PMMBL-*co*-PMBL with one T_g at 213 °C.

In the context of developing frustrated Lewis pair (FLP) catalytic systems,⁷⁹ Chen and co-workers have reported the use of the sterically encumbered Lewis acid and Lewis base Al(C_6F_5)₃ and 1,3-di-*tert*-butylimidazolin-2-ylidene (^{tBu}NHC) respectively, as a catalytic system for the polymerization of (M) MBL in CH_2Cl_2 at room temperature.⁷⁷ MBL and MMBL polymerized quantitatively but again, PMMBL was produced more rapidly than PMBL (in 1 min vs. 1 h) with narrower M_w/M_n (1.15 vs. 1.28) and a TOF almost 70 times higher (48 000 vs. 704 h^{-1}). However, atactic PMMBL is formed while in the same conditions, syndiotactic PMMA is observed.

In 2011 Chen *et al.* also investigated the anionic polymerization of (M)MBL using potassium salts (hydride, enolate and allyl) associated to tris(pentafluorophenyl)alane Al(C_6F_5)₃.⁸⁰ Potassium salts are less studied as anionic initiators than their lithium analogues but the authors justified their choice by describing the advantages of using a non-toxic (resorbable) and larger cation. Again MMBL was reported to be more active than MBL. A $[(\text{M})\text{M}]/[\text{I}]$ ratio of 400 was chosen for the study. The most efficient initiator KH/Al(C_6F_5)₃ (in 1 : 2 ratio) produced



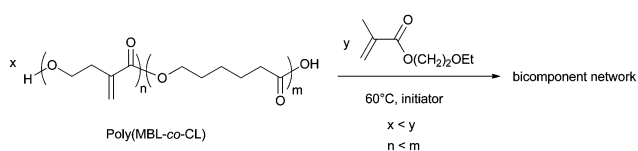
Scheme 4 Proposed mechanism for the polymerization of (M)MBL with ambiphilic silicon propagators ($R' = \text{H}$ or CH_3).

PMMBL at room temperature in 50 min with high TOF (482 h^{-1}), M_n ($209\,000 \text{ g mol}^{-1}$) and M_w/M_n of 1.56 whereas PMBL was obtained quantitatively after 24 h (TOF 4 times lower) with a broader M_w/M_n of 1.87. The enolate potassium salt $\text{Me}_2\text{C}=\text{C}(\text{O}^i\text{Pr})\text{OK}$ with 2 equivalents of $(\text{C}_6\text{F}_5)_3\text{Al}$ led to longer reaction times (4–24 h), TOF around 5 times lower and similar M_w/M_n (1.79–1.84). Finally, the allyl salt $\text{K}[(1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3)]$ only polymerized MMBL in 24 h with a narrower M_w/M_n of 1.42. Atactic P(M)MBL was produced with the three catalytic systems while syndiotactic PMMA was obtained in the same conditions.

All the catalytic systems described above enable the polymerization of α -methylene butyrolactone to proceed *via* its double bond without any ring opening polymerization. The first example of ROP with MBL was described only recently by copolymerization with ϵ -caprolactone (ϵ -CL) in the presence of bismuth trifluoromethanesulfonate.⁸¹ One of the interests of synthesizing poly(MBL-*co*-CL) resides in the *exo*-vinylidene moiety of MBL which can be used for instance for cross-link reactions with methacrylates to form bicomponent networks with a shape memory effect. The elasticity and the T_g of the polymers can be controlled from -26°C to $+29^\circ\text{C}$ (Scheme 5).

Polymers obtained from the ROP of MBL such as poly(MBL-*co*-CL) can be considered as biodegradable polymers due to the presence of the ester linkage in the backbone. In contrast, P(M)MBL obtained from the polymerization of the double bond without ring opening possesses the ester function only on the side chain (lactone). A preliminary degradation study of a copolymer poly(MBL-MDO) with a ratio MBL/MDO = 97 : 3 was carried out in a basic methanolic solution.⁶¹ A polymer containing hydroxy acid side chains resulting from the hydrolysis of the lactones was characterized by NMR spectroscopy. This hydrolyzed polymer is in part soluble in the alcoholic solution, suggesting a potentially slow degradation of the backbone.

In summary, ATRP can be used to successfully prepare copolymers containing the MBL moiety with thermal properties suitable for thermoplastic elastomers. Other catalytic systems showed that the polymerization of MMBL generally proceeds



Scheme 5 Synthesis of bicomponent networks by radical cross-linking reaction using poly(MBL-*co*-CL).

more rapidly and in a more controlled manner compared to that of MBL mainly because of the poorer solubility of PMBL in common polymerization solvents. It was also shown that both vinyl butyrolactones displayed different reactivity compared to MMA. Future investigations may focus on the selective polymerization of MBL and MMBL *via* their double bond to form *iso*- or *syndio*- rather than *atactic* polymers and on the ring-opening polymerization of the butyrolactones.

Fatty acids

Today plant oils are the most important renewable raw materials for the chemical industry. The annual global production of the major vegetable oils (from palm, soy, rapeseed, cotton, peanut, sunflower, palm kernel, olive, and coconut) amounted to 84.6 million tons in 1999/2000 and increased to 137.3 million tons in 2009/10.⁸² Vegetable oils are heavily used as raw materials for surfactants, cosmetic products, and lubricants. In addition, plant oils have been used for decades in paint formulations, as flooring materials and for coating and resin applications.⁸³ Triglycerides contained in vegetable oils are triesters of glycerol and fatty acids. Only five major fatty acids are contained in vegetable oils as the triglyceride (Fig. 6): two saturated acids, stearic acid and palmitic acid and three unsaturated, oleic acid, linoleic acid and linolenic acid containing one, two and three carbon-carbon double bonds respectively. Ricinoleic acid, namely *cis*-12-hydroxyoctadeca-9-enoic acid produced from hydrolysis of castor oil is of interest, as it is a bifunctional fatty acid containing a hydroxyl group on the fatty chain.

Fatty acids are good candidates for biocompatible and biodegradable polymers preparation, as they are natural body components containing hydrolyzable bonds.⁸⁴ Several types of materials were prepared by direct copolymerization/insertion of bio-derived oil with other matrices to get bio-based nanocomposites⁸⁵ or biodegradable materials (*e.g.*, polyester and polyanhydrides).^{86,87} Due to the presence of a carbon-carbon double bond, triglycerides containing unsaturated fatty acids can be directly polymerized or copolymerized to get biopolymers, biocomposites and biocoatings.⁸⁸ Also, biopolyamides derived from castor oil especially are industrially produced from chemical companies such as Arkema (Rilsan® PA11), Rhodia (Technyl® eXten) or BASF (Ultramid® Balance).⁸⁹

However, well-defined polymers can only be prepared from pure monomers. Therefore further purification/separation and/or functionalization of the monomer issued from vegetable oils is always needed, increasing the final cost of the material.



Fig. 6 Main fatty acids issued from vegetable and castor oil.

Nowadays, triglycerides and fatty acids can be obtained in high purities and are commercially available from chemical suppliers. A series of papers investigated the functionalization of fatty acids to get interesting monomers by epoxidation,⁹⁰ hydroxylation,⁹¹ hydroformylation,⁹² ozonolysis⁹³ and isomerization⁹⁴ of the olefinic moiety. For instance, polymerization of epoxy fatty acids was reported by cationic ring opening polymerization of the epoxide function to form polyether–polyols.⁹⁵ A focus on selected recent examples describing the synthesis of polymers from renewable fatty acids will be presented as follows. Firstly, polyester synthesis from fatty acids is discussed. Secondly, polyurethanes obtained by self-condensation of functionalized fatty acids are commented.

Polyesters by ring-opening polymerization of macrolactones

Increasing interest was given to polymers derived from long chain ω -hydroxy fatty acids, mainly produced by polycondensation methods.⁹⁶ Enzyme polymerization, including ring-opening polymerization was already reviewed and won't be discussed in detail.⁹⁷ The synthesis of macrolactones, not necessarily derived from bioresources, was reported and reviewed. For instance, efficient procedures were developed to prepare the C8 to C17 lactones by cyclization of the corresponding hydroxyacids.⁹⁸ However, few examples of ring-opening polymerization of such monomers were reported. Chemical ring-opening polymerization and enzymatic ring-opening polymerization are methods of choice for controlling the polymer characteristics (molecular weight, polydispersity and microstructure). It is accepted that the driving force behind the chemical ROP is the release of the ring strain of the cyclic monomer to give the polymer chain. Thus an increase of the lactone ring size decreases the ring strain. Duda *et al.* compared thermodynamics and kinetics for chemical ROP and enzymatic ROP and demonstrated that contrary to chemical ROP, the rate of enzymatic ROP increases with the ring size of the lactone monomers from δ -valerolactone to 16-hexadecanolide: in enzymatic ROP, the rate determining step involves the formation of the lipase–lactone complex, promoted by the hydrophobicity of the lactone monomer, which is higher for larger lactone rings.⁹⁹

Thus, lipases were already reported as highly active initiators of macrolactone ROP affording high molecular weight polymers, the main drawback of the enzymes being their high price and temperature sensitivity.¹⁰⁰ Pentadecalactone (PDL), a cyclic ω -hydroxy fatty acid used in the fragrance industry and belonging to the class of naturally occurring macrocyclic musks, is often used as a macrolactone model monomer. Polypentadecalactone (PPDL), obtained by ROP of pentadecalactone with Novozym 435, was reported having M_n up to 150 000 g mol⁻¹ ($M_w/M_n = 2.1$).^{100f} In comparison, metal-catalyzed ROP of PDL generally gave polyesters with lower molecular weights ranging from 30 000 to 40 000 g mol⁻¹ ($M_w/M_n = 1.6$) with rare-earth initiators, such as Y(OⁱPr)₃ and Ln(BH₄)₃(THF)₃.¹⁰¹ Anionic ROP of macrolactones^{102,103} such as PDL with ^tBuOK as the initiator was also successfully reported; a high molecular weight polymer was obtained ($M_n = 92\,000$ g mol⁻¹, $M_w/M_n = 2.1$).¹⁰³

To our knowledge, the first example of a polymer with high molecular weight ($M_n = 155\,000$ g mol⁻¹, $M_w/M_n = 2.0$), obtained by chemical ROP of macrolactone, such as pentadecalactone was reported very recently by Heise and Duchateau *et al.* using an aluminium–salen complex as the initiator.¹⁰⁴ However, these metal initiators were inactive at temperatures below 60 °C contrary to Novozym 435 and ^tBuOK, which polymerized PDL at room temperature.

An interesting work using ricinoleic acid (RA) was reported by Slivniak and Domb in 2005,¹⁰⁵ taking advantage of the two functional groups of ricinoleic acid, a hydroxyl and a carboxylic function in order to form large macrolactones. The corresponding lactone was formed by intramolecular esterification of ricinoleic acid by the classical method (dicyclohexylcarbodiimide, dimethylaminopyridine and hydrochloric acid).^{98g} Formation of the expected C12 lactone as well as macrocyclic lactones containing up to 6 ricinoleic units was observed (Scheme 6). The ratio of lactones is dependent on the initial concentration of the ricinoleic acid; low RA concentration (up to 10 mg mL⁻¹) yielded mainly the C12, C24 and C36 lactones (the C12 lactone is obtained pure in 46% yield after purification) and higher RA concentration yielded larger rings.

Afterwards, ring-opening polymerization of the lactones C12, C24 or C12–C72 mixture was investigated with different initiators such as Y(OⁱPr)₃ and Sn(octoate)₂, which were inactive for the pure C12 lactone ROP but also for the lactone mixture (Scheme 7, (a)). However the tin initiator gave low molecular weight polymers by ROP of C24 lactone ($M_n = 4400$, $M_w = 5700$ g mol⁻¹, representing up to 15–20 RA units). Unfortunately, only oligomers were also obtained using Y(OⁱPr)₃.

Copolymerization of ricinoleic lactone mixture and L-lactide (Scheme 7, (b)) was reported and low molecular weight polymers in the range of 5000–16 000 g mol⁻¹ were synthesized containing a low ratio of RA unit in the polymer chain as the ROP of ricinoleic lactone derivative is much slower than the one of lactide. The ratio of the RA unit in the polymer can be tuned by varying the initial RA lactone to lactide ratio; it was determined by ¹H NMR spectroscopy that up to 17% of RA was inserted in the polymer chain using a 1 : 1 weight ratio of the two monomers. Domb also observed that the molecular weight of the polymer decreased with an increase in the content of the RA unit. They also studied the hydrolytic degradation properties of the P (RA–LA) copolymers obtained and pointed out that the material



Scheme 6 Formation of lactones and macrolactones mixture (up to $n = 5$). (i) Reaction conditions: dicyclohexylcarbodiimide, dimethylaminopyridine, hydrochloric acid in chloroform.



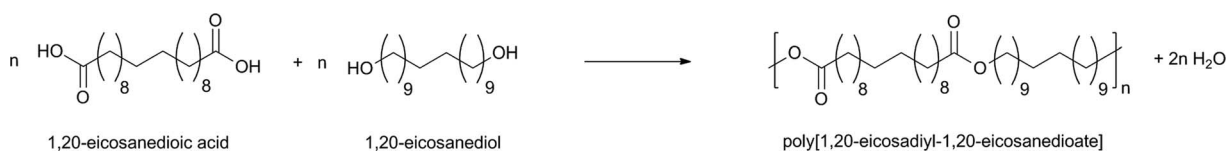
Scheme 7 ROP of ricinoleic acid derived lactone. (a) $\text{Sn}(\text{octoate})_2$ or Me_3SiONa , THF, 40 °C; (b) $\text{Sn}(\text{octoate})_2$, bulk, 135 °C.

with a low RA content degraded slower than pure PLA of similar molecular weight.

Quinzler and Mecking reported a convenient route to high molecular weight poly(dodecyloate) (M_n up to 22 000 g mol^{-1}) by step growth polymerization of undec-10-en-1-ol and carbon monoxide.¹⁰⁶ By using a cobalt catalyst system known for alkoxycarbonylation ($[\text{Co}_2(\text{CO})_8]/\text{pyridine}$), the authors were able to prepare a semicrystalline polyester by copolymerization of CO and undec-10-en-1-ol which was first obtained in two high-yield steps from ricinoleic acid.¹⁰⁷

Very recently, Mecking *et al.* published an interesting study on undecenoic acid, also produced from ricinoleic acid.¹⁰⁸ 1,20-Eicosanedioic acid was obtained by self-metathesis of undecenoic acid followed by hydrogenation. The corresponding diol, eicosane-1,20-diol, was formed by reduction of eicosanedioic acid. Subsequently, the diacid and the diol, obtained from the same renewable resource, were polycondensed to give a high molecular weight C20 polyester with a T_m of 108 °C. The reaction was carried out in bulk and catalyzed by titanium alkoxides (Scheme 8).

Gross *et al.* reported the melt-polycondensation of the ω -hydroxyl tetradecanoic acid (C14), a new monomer available



Scheme 8 Synthesis of the 20,20-polyester by melt polycondensation.

by a fermentation process,¹⁰⁹ catalyzed by titanium tetraisopropoxide. High molecular weight poly(ω -hydroxytetradecanoate) was prepared with good control (up to 140 000 g mol^{-1} with a M_w/M_n of 1.8).¹¹⁰ The mechanical properties of the obtained polymer were studied and compared to linear high-density polyethylene (LHDPE) and authors concluded that such poly(ω -hydroxyalkanoate), such as C14, C16 and C18 polyesters, have the potential to function in similar ways to PE, possessing a potential biodegradability advantage. Meier *et al.* reported the synthesis of different polyethylene-like copolymers from renewable platform chemicals (castor oil derived chemicals: 11-bromo-1-undecene and 10-undecenol) using thiol-ene addition as well as Acyclic Diene METathesis (ADMET) polymerization.¹¹¹

Polyurethane synthesis by self-condensation

Polyurethanes are an important class of polymers used in several different fields such as footwear, coatings and paintings, elastic fibers and medical devices.¹¹² Recently several works dealing with polyurethanes based on vegetable oils were published and reviewed.^{93,95,113}

In 2010 Cramail and co-workers reported an interesting approach to synthesize polyurethane (PU) from methyl oleate (derived from sunflower oil) and ricinoleic acid using the AB-type self-polycondensation approach.¹¹⁴ In this work, three novel AB-type monomers, namely, a mixture of 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz), 12-hydroxy-9-*cis*-octadecanoyl azide (HODEAz) and methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (MHHDC) were prepared from methyl oleate and ricinoleic acid using simple reaction steps (Scheme 9). Then, HMODAz and HODEAz monomers were polymerized by the acyl-azido and hydroxyl AB-type self-condensation approach. The acyl-azido and hydroxyl self-condensations were carried out at various temperatures (50, 60, 80 and 110 °C) in bulk with and without a catalyst. It was demonstrated that the polymerization of the acyl azide occurred through its thermal decomposition to isocyanate, known as the “Curtius

rearrangement", which further condensed with the hydroxyl group to form the polyurethane. A FT-IR study of the polymerization, using HMODAz at 80 °C without a catalyst, indicated *in situ* formation of an intermediate isocyanate group in the first minutes of the reaction. Also, MHHDC monomer was polymerized through AB-type self-condensation. In this case, a transurethane reaction was used to obtain a similar PU (which was obtained by AB-type acyl-azido and hydroxyl self-condensation of HODEAz) in the presence of titanium tetrabutoxide as a catalyst at 130 °C.

The self-condensation of these bifunctional monomers led to polymers with low molecular weight. This was explained by the formation of macrocycles, detected by MALDI-TOF analyses of the polyurethanes. Due to the presence of soft and hard segments, poly(HMODAz) and poly(HODEAz) showed two glass transition temperatures respectively at -22 °C, 27 °C and -53 °C, 26 °C.

Also, Cramail *et al.* reported polyaddition of diamines with vegetable-based biscarbonates to prepare new polyurethanes (Scheme 10).¹¹⁵ The starting material **16a** was obtained from **16b** by a metathesis reaction with Hoveyda's catalyst. Then the epoxy ester dimers **18a-b** were obtained from **16a-b** in two steps (Scheme 10). The biscarbonates **19a-b** were prepared from **18a-b** and CO₂ and further self-polycondensed with ethylene diamine and isophorone diamine to form polyurethanes. The optimal conditions for the carbonation reaction appeared to be in the presence of tetrabutylammonium bromide (TBABr) as the catalyst. The average molecular mass of the polyurethane reached 13 500 g mol⁻¹ with a good control over the chain length ($M_w/M_n < 1.5$) and their glass transition temperature T_g ranging from -25 to -13 °C.

Functionalized lactones

Poly(lactides) may lack chemical functional groups which can modify the hydrophilic properties and degradation rate;¹¹⁶ however, functionalized aliphatic polyesters issued from bio-resources are not broadly available. Even if ring-opening polymerization of lactide, previously described, and lactones can be well controlled,^{23,117} only few examples of ring-opening of functionalized and/or bioderived lactones were reported.¹¹⁸ Moreover, syntheses of functionalized lactones are often multi-step reactions using complex procedures and/or purification methods. Carbohydrate 1,5-lactones seem to be interesting monomers, but very few studies were reported on their polymerization. In 1927, Drew and Haworth reported the formation of "polymeride" when tri-*O*-methyl-D-arabino-1,5-lactone was reacted with acids.¹¹⁹ More recently, in 2002, a methodology for the polymerization of D-gluconolactone was patented but the characterization of the resulting material was limited.¹²⁰ An attempt to polymerize such monomers undertaken by Haider and Williams revealed a dimerization or trimerization of the previously mentioned monomers.¹¹⁸ Recently, Williams *et al.* reported the ROP of a carbohydrate lactone, obtained in 90% yield in two steps from the commercially available D-gluconolactone.¹²¹ D-Gluconolactone is derived from gluconic acid (the latter being obtained from glucose) and is used as a food additive.^{12e,g} The new lactone **20** was obtained as a racemic mixture of the two *syn* enantiomers *S,S* and *R,R* (Scheme 11).

The ring-opening polymerization was studied with "classical initiators" derived from Sn(OR)₂ and LZn(OEt). The tin catalyst showed a slow conversion of lactone (from 140 to 680 h to convert 30–120 eq. of lactone) while the reaction was much faster



Scheme 9 Polyurethane prepared from functionalized oleic acid and ricinoleic acid (a) 80 °C, 24 h (for clarity only the 10-hydroxy-9-methoxy isomer of HMODAz is presented); (b) CH₃OH, reflux, 4 h; (c) Ti(OBu)₄, 130 °C, 6 h.



Scheme 10 Polyurethane from methyloleates.

with the Zn catalyst (1 h to convert 100 eq. of lactone). A large disparity between the expected mass and the calculated one was obtained for the corresponding polyesters due to the formation of cyclic polyesters (observed by MALDI-TOF analysis) and transesterification reaction.

Recently, dihydrocarvone obtained from carvone, a natural terpenoid found in both *Mentha spicata* (spearmint) (up to 60–70% of oil content) and *Carum carvi* (caraway) (only small percent) oils, was used as the starting material for the synthesis of lactone monomers.¹²² Compared to production of fatty acids, carvone stays quite marginal as spearmint and caraway oil world markets are estimated to be 1500 t per year and 10 t per year respectively.¹²³ Thus, Hillmyer *et al.* prepared two new lactone

monomers from dihydrocarvone (Scheme 12). Carvomenthide (**22**) was obtained in good yield (~70%) in two steps consisting in hydrogenation of dihydrocarvone to carvomenthone followed by oxidation. In the case of dihydrocarvone (**21**), obtained by a direct selective Baeyer–Villiger oxidation of dihydrocarvone with Oxone®, purification of the product was more challenging as **21** was obtained in 42% yield still containing epoxide impurities. Both lactones were ring-opening polymerized with $\text{ZnEt}_2/\text{nBuOH}$ as the initiator system.

Polymers polycarvomenthide (PCM) with a M_n up to 50 000 g mol^{-1} were obtained with good polymerization control ($1.08 < M_w/M_n < 1.26$). In the case of polydihydrocarvone (PD), the olefinic bond remained intact after the polymerization but



Scheme 11 ROP of a carbohydrate derived lactone.



Scheme 12 Formation of polyesters with lactones derived from dihydrocarvone.

a disparity was observed between the expected molar mass and the determined one. This was explained by the fact that **21** self-polymerizes due to the presence of polymerization initiating impurities, probably epoxides. No transesterification reactions were observed, as M_w/M_n remained low; thus high molecular weight can be reached contrary to that obtained with ϵ -caprolactone.¹²⁴ Both polymers PCM and PD exhibited low glass transition temperatures (less than -20 °C). It was also shown that copolymerization of **21** and PD as well as cross-linking polymerization of the PD polymer after epoxidation of the olefinic moiety was possible. This points out the versatility of these monomers for the preparation of renewable materials by post-polymerization functionalization and/or copolymerization strategies. Block copolymers were also reported by copolymerization of carvomenthide and polylactide to give elastomers.¹²⁵

Conclusion and perspectives

We have reviewed renewable structures that can be turned into viable biodegradable macromolecules. Using biomass for the production of new polymers can have both economic and environmental benefits. The discovery of efficient and selective processes for the synthesis of renewable polymers is a crucial requirement for the sustained growth of the chemical industry. In this area, promising results have been obtained using catalytic processes. However, despite recent significant advances, some major points remain to be addressed and improved.

For instance, preparation of high molecular weight polyesters from renewable resources remains challenging due to the presence of functional groups on the monomers, relative stability of the monomer (large ring lactone for instance) and side-reactions (cyclization, transesterification). Therefore focus on the development of ligand and initiators, tolerant to functional groups, efficient and stable is needed to promote a wide use and applications of bioderived monomers and polymers.

Whereas carbon dioxide is not plant-derived, the utilization of CO_2 for the production of polymers could be critically important given its widespread abundance. In particular, there has been considerable interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides to

produce polycarbonates. As a result, a significant amount of recent research has focused on the discovery and development of new catalysts for this process.¹²⁶ While CO_2 is an ideal synthetic feedstock since it is abundant, inexpensive and nontoxic, most epoxide/ CO_2 copolymerization systems focus on petroleum derivatives such as propylene oxide or cyclohexene oxide. However, a major breakthrough has recently been achieved by Coates *et al.* who reported the alternating copolymerization of CO_2 with limonene oxide, which is derived from limonene, the major component of oils from citrus fruit peels (*e.g.* 95% of the oil from orange peels).¹²⁷ Another way to produce polycarbonates issued from renewable resources is ring-opening polymerization of cyclic carbonates. Indeed, such carbonate monomers can be derived from biomass. For instance, trimethylene carbonate can be prepared from glycerol. Also, Carpentier *et al.* used levulinic and itaconic acids as a naturally occurring source to produce two 7-membered cyclic carbonates as monomers. Subsequent ring-opening polymerization using various (organo)metallic and organic catalysts afforded the corresponding polycarbonates with quite good control and activities.¹²⁸

Finally a recent study reported a new strategy to obtain biodegradable polyesters.¹²⁹ This was achieved by tandem catalysis, which confers great interest to this approach. Commercially available complexes were used as efficient catalysts for cyclization of dicarboxylic acids followed by alternating copolymerization of the resulting anhydrides with epoxides. Given an operationally simple method, this tandem catalysis is an attractive strategy for the production of new renewable materials.

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