Novel polyesters from renewable resources

Résumé **Nouveaux polyesters biosourcés**

Les polyesters biosourcés présentent un intérêt croissant en tant qu'alternative aux polymères dérivés du pétrole dans le cadre du développement durable. Les polyesters aliphatiques sont biodégradables et souvent biocompatibles et, en raison de ces propriétés, présentent de nombreuses applications dans la vie quotidienne (emballages) mais également pour des marchés de niche (dispositifs biomédicaux). La copolymérisation par ouverture de cycle entre époxydes et anhydrides cycliques permet la synthèse de polyesters avec des architectures variables. Cette voie de synthèse est prometteuse grâce à une grande variété de monomères disponibles et la possibilité d'utiliser des monomères dérivant de la biomasse. Époxydes et anhydrides peuvent en effet être obtenus à partir de ressources naturelles telles que les polysaccharides cycliques, les acides gras et les terpènes.

Mots-clés **Chimie durable, polymères, bioressources, biodégradable, polymérisation par ouverture de cycle, époxyde, anhydride, biomasse.**

Abstract Bio-based polyesters attract a lot of interest with regard to sustainable development as alternatives to polymers derived from oil. Aliphatic polyesters are biodegradable and frequently biocompatible. Thanks to these properties, they have numerous applications in daily life such as packaging but also in niche markets (biomedical devices). Ring-opening co-polymerization between epoxides and cyclic anhydrides produces polyesters with variable architectures. This synthetic approach is promising thanks to the wide availability of monomers. A huge asset of the copolymerization is to use monomers from biomass. Epoxides and anhydrides can indeed be obtained from natural resources such as carbohydrates, fatty acids and terpenes.

Keywords **Sustainable chemistry, polymers, bio-based, biodegradable, ring-opening polymerization, epoxide, cyclic anhydride, biomass.**

Plastic materials are widely used in our modern society. In 2016, 335 million tons of plastics were produced worldwide, a 45% increase since 2005 [1]. It is a growing market in need of innovation. In this context, bio-sourced polyesters attract a lot of interest with regard to sustainable development as alternatives to polymers derived from oil [2-3]. One of the current challenges is to develop bioderived polymers with competitive performance properties (thermal resistance, mechanical strength, processability) and that are cost efficient.

Polyesters: an attractive class of polymers

According to the structure of the repeating units of the main chain, polyesters are classified as aliphatic, semi-aromatic and aromatic. Aromatic portions improve the hardness, rigidity, and heat resistance of the polymeric material, whereas aliphatic segments increase the flexibility and lower the melting temperature thus improving the processability.

The most important commercial polyesters are terephthalic polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) (*figure 1*). Both are semi-aromatic. They are thermoplastic materials that can be easily molded and, thanks to their good mechanical properties, they are largely used to obtain films and fibers (*figure 2*).

Aliphatic polyesters are materials with low melting and glass transition temperatures and poor hydrolytic stability. They are readily biodegradable and/or biocompatible. Traditionally, because of these properties, they have found applications in biomedical and pharmaceutical fields but recently their use has been extended to different industrial areas such as packaging and fibers. Some of the most successful aliphatic polyesters are certainly poly(glycolic acid) (PGA) and more recently poly(lactic acid) (PLA) (*figure 1*) thanks to the NatureWorks™ process

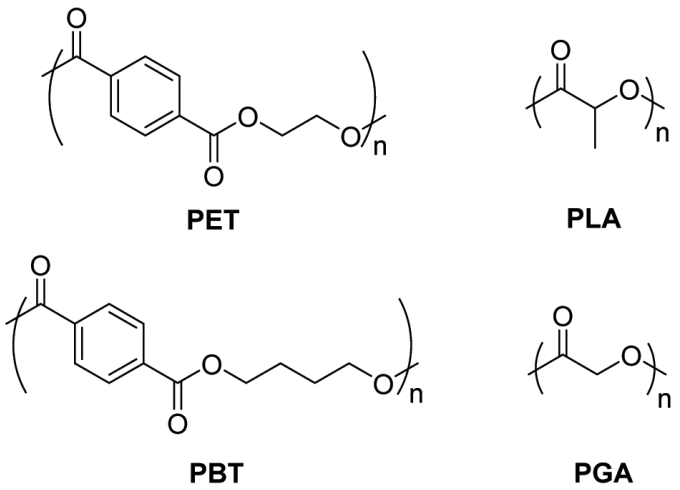

Figure 1 - Structures of some successful polyesters.

for the scalable production of PLA from corn *via* fermentation technologies [4-6]. Their common uses include plastic films, bottles, and biodegradable medical devices for drug release and tissue engineering [7].

Synthetic approaches to polyesters

Polyesters can be mainly produced *via* three synthetic methods (*figure 3*). The traditional one is the polycondensation between a diol and a diacid. However, this method requires high temperatures to remove the byproduct and achieve high molecular weight polymers with significant consequences on the energy costs and on the control of the polymerization process. Alternatively, the ring-opening polymerization (ROP) of the related cyclic esters enables the preparation of high

Figure 2 - An example of beverage packaging from PET.

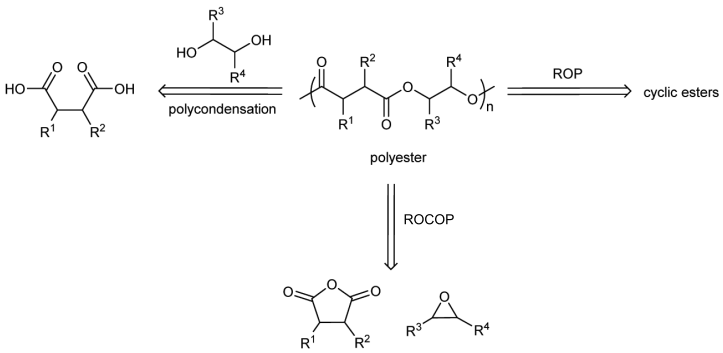

Figure 3 - Synthetic approaches to polyesters.

molecular weight polyesters with controlled microstructure. Its usefulness is restricted by the limited availability of structurally diverse monomers; in addition, it is difficult to synthesized semi-aromatic polyesters [8].

A more versatile way for producing polyesters with variable architectures is the ring-opening co-polymerization (ROCOP) between epoxides and anhydrides, but only a limited number of catalytic systems described in the literature can produce high molecular weight polymers with a perfectly alternating structure [9-10].

One of the first remarkable example of a catalyst able to promote this reaction was the 2-cyano-β-diketiminato zinc complex reported by Coates and co-workers in 2007 [11]. After this discovery, few successful single catalysts active in the ROCOP of epoxides and anhydrides have been reported. The most significant examples include complexes of trivalent metals such as Cr^{III}, Co^{III}, Mn^{III}, or Al^{III} with tetradentate dianionic ligands such as porphyrinate or bisphenoxide derivatives [9-10].

The huge asset of this synthetic way is the wide availability of relatively cheap monomers, that can also be sourced from renewable feedstocks including biomass. There is an incentive to develop synthetic routes to prepare epoxides and anhydrides from renewable feedstocks in order to produce fully renewable polymers.

Monomers from biomass

Bio-based materials are defined as materials made from biological and renewable resources such as grains, corn, potatoes, beet sugar, sugar cane or vegetable oils [1]. Such annually renewable material can potentially meet our future needs with a low carbon footprint if it can be efficiently converted into fuels, value added chemicals, or polymeric materials. Nonetheless, it is important to note that not all bio-derived material will be biodegradable, and *vice versa* [12].

There are many biomass sources that could be converted into renewable monomers to produce sustainable polymers, including simple sugars, starch, lignocelluloses, plant oils, and so on. Lignocellulosic materials such as grasses, trees, corn stover, or wheat straw, will definitely provide ample biorenewable resources for production of fuels and chemicals. The majority (60-90 wt%) of plant biomass are the biopolymer carbohydrates stored in the form of cellulose and hemicelluloses. Epoxides or anhydrides may be derived from naturally occurring sources such as carbohydrates, fatty acids, and terpenes (*figure 4*).

Carbohydrates

Most renewable carboxylic acids are prepared by fermentation of carbohydrates such as glucose. Glucose is produced from starch, cellulose, sucrose, and lactose by enzymatic hydrolysis or from woody biomass by chemical transformation. Glucose is transformed into building-block chemicals such as lactic acid or succinic acid which will be transformed into monomers (BioAmber process for the production of bio-based succinic acid). For example, lactic acid leads to lactide and succinic acid to succinic anhydride, one of the most studied anhydride in the ROCOP, since the early discovery by Maeda *et al.* in 1997 [13].

In 2005, Takasu *et al.* [14] epoxidized sugar-based alkenes and copolymerized the resulting epoxides with succinic anhydride and glutaric anhydride by using an aluminum alkoxide initiator to obtain fully renewable polyesters with low molecular weights.

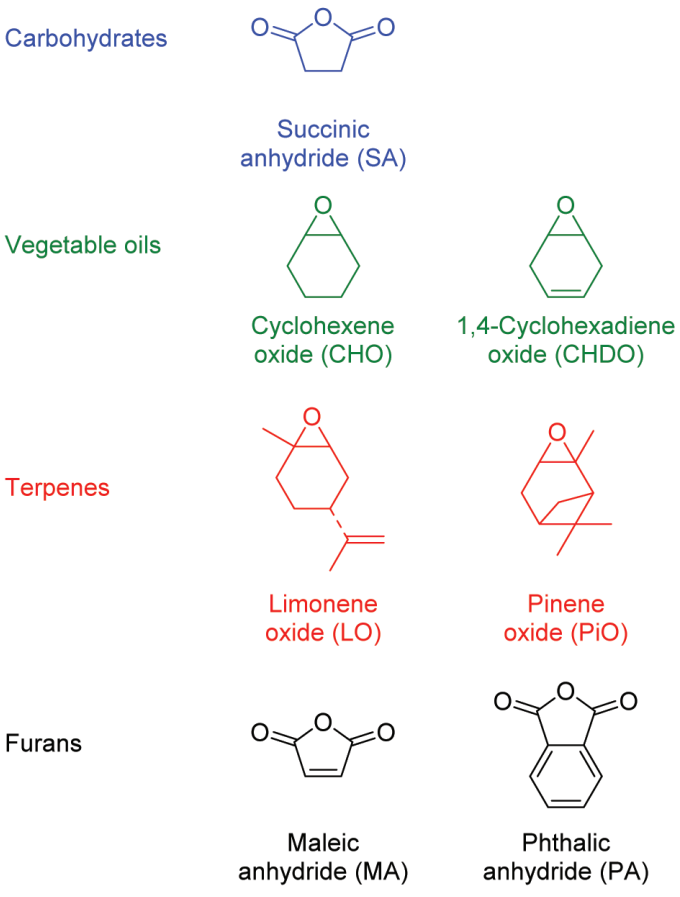

Figure 4 - Most investigated monomers in the ROCOP deriving from natural sources.

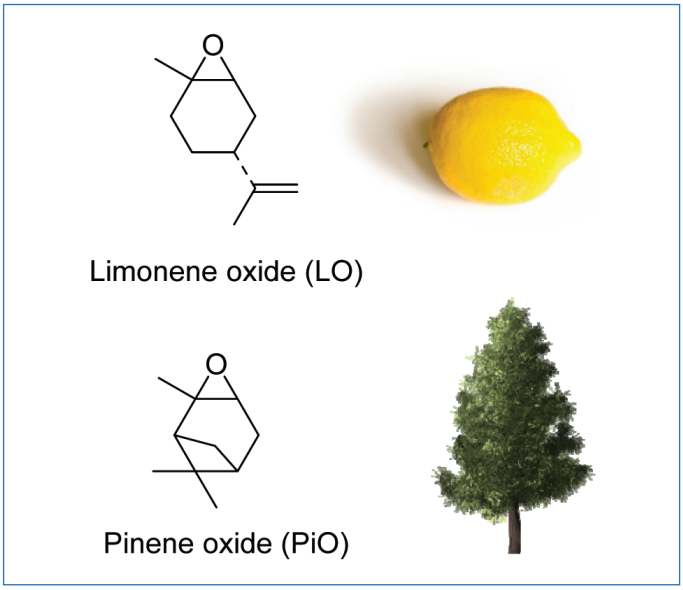

Figure 5 - Monomers from terpenes.

Thomas and co-workers reported in 2011 the synthesis of aliphatic polyesters *via* an auto-tandem catalytic transformation, where cyclic anhydrides are directly synthesized from dicarboxylic acids and subsequently copolymerized with epoxides [15]. The authors have been able to produce under mild conditions several renewable monomers (*e.g.*, camphoric, glutaric, pimelic, succinic anhydrides) and the resulting alternating copolymers.

Vegetable oils

Vegetable oils are an important class of abundant natural resources, and the literature already reports their use to make various monomers for polymerization.

In 2015, Williams and co-workers showed that epoxides derived from 1,4-cyclohexadiene such as cyclohexene oxide (CHO) and 1,4-cyclohexadiene oxide (CHDO) can be synthesized *via* self-metathesis of plant oil derivatives [16]. This represents a significant achievement since most of the published papers on ROCOP use epoxides such as cyclohexene oxide and propylene oxide.

Terpenes

In terms of epoxides, so far, the only fully renewable options reported are limonene oxide and pinene oxide, derived from terpenes (*figure 5*). Terpenes are found in many essential oils and represent a versatile chemical feedstock. Many plants and trees produce this class of molecular biomass. The global turpentine production is more than 300 000 tons per year and its major constituents are α-pinene (45-97%) and β-pinene (0.5-28%), with smaller amounts of other monoterpenes. However, to date, the only example of a successful synthesis of aliphatic polyesters from these biorenewable substrates compounds was described by Thomas *et al.* who reported the alternating copolymerization of α-pinene oxide (α-PiO) and glutaric anhydride, to give the corresponding fully biodegradable copolymer [15].

Produced by more than 300 plants, limonene is the most common terpene [17]. The *(R)*-enantiomer constitutes 90-96% of citrus peel oil [18], and its world production is estimated to be more than 60 000 tons per year [19]. The corresponding epoxide is commercially available and its abundance, low cost, and structural similarity to CHO make *(R)*-limonene oxide (LO) an excellent choice as a nonfood biorenewable epoxide monomer.

Limonene oxide (LO) has been used as a comonomer for the synthesis of aliphatic polyesters by Coates [11] and Thomas [15]. More recently, Duchateau [20] and Mazzeo [21] reported the copolymerization of phthalic anhydride with LO to produce poly(limonene phthalate), a partially renewable semi-aromatic polyester. Additionally, bearing a vinyl pendant group as extra functionality, *(R)*-limonene offers the opportunity of post polymerization modifications to functional polymers, thereby increasing the range of potential uses. Taking advantage of these functional groups is the key to utilize raw natural biomass. This usually requires the use of highly efficient chemistry for functionalization.

Recently, Coates and co-workers reported the copolymerization of terpene-based cyclic anhydrides with propylene oxide using various metal salen catalysts. The copolymer of propylene oxide and the Diels-Alder adduct of maleic anhydride and α-terpinene exhibit T_g values up to 109 °C [22-23].

Furans

Furfural and 5-hydroxymethylfurfural (HMF), two widely developed furan-derived compounds, can be respectively prepared from C5 and C6 carbohydrate resources. For instance, cellulose is hydrolyzed to glucose, which can be dehydrated to HMF. One of major motivations to study furan-derived monomers is their suitability for Diels-Alder reactions. Furan and maleic anhydride were converted to phthalic anhydride (PA) in two reaction steps: Diels-Alder cycloaddition followed by dehydration. PA is of high interest since it allows the production of semi-aromatic polyesters thus improving the rigidity of the polymer backbone and the thermal properties [24].

Industrially, furan is produced by the decarbonylation of furfural in high yields and maleic anhydride can be obtained renewably by the oxidation of furfural using a VOx/Al_2O_3 catalyst or by the oxidation of 5-hydroxymethylfurfural in the liquid phase. The copolymerization of maleic anhydride with epoxides has been largely studied by Coates and co-workers, to produce unsaturated polyesters [25].

From all these bio-based chemicals, some are already encountering tremendous success. First one is lactic acid, used as the precursor of PLA, the leading bio-plastic which production capacities are predicted to grow up by 50 percent from 2017 to 2022 [26]. Bio-succinic acid has also been a hot topic the last few years with four companies working on its production: Myriant, BioAmber (mentioned earlier in this article), BASF-Purac (Succinity) and Reverdia (DSM-Roquette). It is considered one of the most valuable platform compound, leading to phthalic anhydride, adipic acid, maleic anhydride, and 1,4-butanediol, but also to polybutylene succinate, another bio-based, biodegradable and compostable material. The Dutch company Avantium developed a novel process for the synthesis of commercial furan polymers from 2,5-furandicarboxylic acid, a convincing alternative to terephthalic acid, the most studied being poly(ethylene-2,5-furandicarboxylate) (PEF). The large and ubiquitous availability of carbohydrates and terpenes, generally as waste from the food and wood industries, is an attractive key point for the development of new sustainable polymers with enhanced properties. More successes are on the way in the coming

decades, both for commodity polymers with high-tonnage productions or polymers for high-tech niche applications (biomedicine) [27].

Conclusions and outlook

This article aims to give a concise overview on how renewable feedstocks have been used to produce monomers and how these have been used to create novel sustainable polymers. By taking advantage of the structural diversity, abundance and innocuousness of renewable monomers, and of the recent developments in ROCOP, new opportunities for the production of polyesters are emerging. Using biomass can have both economic and environmental benefits. The discovery of efficient and selective processes for the synthesis of renewable polymers from biomass-derived feedstocks and that are suitable for recycling or biodegradation, is a crucial requirement for the sustained growth of the chemical industry.

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