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MINI-REVIEW

Recent developments in non-biodegradable biopolymers: Precursors, production processes, and future perspectives

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Abstract

During the last decades, biopolymers experienced a renaissance. The increasing limitation of fossil resources in combination with a public demand for environmental-friendly and sustainable processes has led to the formation of a market for biobased plastics. Especially non-biodegradable bioplastics are very interesting materials, as they combine the benefits of reduced carbon footprint during production and increased resource efficiency with the persistence to microbial degradation. Consequently, persistent biomass-derived plastic materials are highly promising to substitute conventional fossil-based plastics in applications, which require durability and longevity. Non-biodegradable bioplastics derived from renewable resources represent 57% of all bioplastics with partially biobased polyethylene terephthalate currently leading the market, followed by biobased polyamides and fully biomass-derived polyethylene. An exceptional biopolymer with thermoplastic properties was discovered only two decades ago, when—for the first time—polythioesters were synthesized by microbial fermentation. Though synthesized by bacteria, it turned out that polythioesters are non-biodegradable by microorganisms in contrast to all other biopolymers and thus, represent a novel non-biodegradable bioplastic material. This review gives an overview about the recent development and progress regarding bioplastics with special focus on persistent bioplastics. We describe the generation of the respective monomers from biomass-derived substrates and summarize the current status of production, which range from the laboratory-scale up to large-scale industrial processes.

Keywords Bioplastic · Non-biodegradable biopolymer · Polyamides · Polyethylene · Polyethylene 2,5-furandicarboxylate · Polyethylene terephthalate · Polypropylene · Polythioester · Polytrimethylene 2,5-furandicarboxylate · Polytrimethylene terephthalate · Polyurethanes

Introduction

Polymer materials are universal and indispensable elements in everyday life. The term <polymer> is derived from the Greek words <*polus*> and <*meros*> meaning "many parts" and refers to molecules composed of a large number of covalently linked repeated units. Polymers ranging from naturally occurring biopolymers to synthetic polymers are obtained by chemical polymerization reactions or—in case of biopolymers—synthesis is conducted by enzymes or living cells, respectively. Biopolymers are divided into eight classes: nucleic acids, polyanhydrides, polyamides (PAs), polyisoprenoids, polyphenolic biopolymers, polysaccharides, polyoxoesters, and polythioesters (PTEs). These classes include DNA and RNA, proteins, as well as rubber, lignin, and cellulose. The latter are the most abundant biopolymers on earth with an estimated annual amount of about 100 billion tons (Kirk and Fenn 1982).

Synthetic polymers comprise beside other specialty polymers primarily seven commodity materials: polyethylene (PE), polypropylene (PP), polyvinyl chloride, polyethylene terephthalate (PET), polystyrene, polycarbonate, and poly(methyl methacrylate) with an annual production of more than 330 million tons in 2015 (PlasticsEurope 2016). These most widely used polymers are also designated as plastics, which refers to materials that can be molded by applying heat and pressure. Owing to their low cost, the ease of manufacture,

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and their versatile properties, including imperviousness to water and persistence to biodegradation, synthetic plastics are used in many different products.

Most plastics are produced from petrochemical resources, thus leaving a negative environmental footprint due to high greenhouse gas (GHG) emissions. The increasing environmental awareness together with a limitation of fossil resources has led to the formation of a market for biobased plastics, which combine the benefits of reduced carbon footprint during production with increased resource efficiency or even improved material properties. The term <bioplastic> is defined by European Bioplastics as either biodegradable plastic materials (recently reviewed in Jambunathan and Zhang 2016; Emadian et al. 2017; Rujnić-Sokele and Pilipović 2017) and/or plastics that are produced from renewable resources. Bioplastics currently only account for about 1% of the total plastic materials produced annually, but according to estimations about the future development, the total production capacity of 2.05 million tons in 2017 will reach an amount of 2.25 up to 5.95 million tons by 2021 (Table 1). The major growth drivers in the field of biodegradable bioplastics are polyhydroxyalkanoates (PHAs) and polylactide (PLA) (European Bioplastics 2016a, 2017).

Non-biodegradable bioplastics derived from renewable resources represent 57% of all bioplastics with biobased PET leading the market. These so-called drop-in bioplastics are chemically identical to their petrochemical counterparts, but consist at least partially of biobased components. As their specifications allow biobased conventional plastics to easily enter the market due to existing infrastructure and applications, extensive investment is usually avoided. Non-biodegradable bioplastics combine two major benefits: first, their improved carbon footprint in comparison to conventional plastic materials because they are produced from renewable resources. Second, their persistence towards biodegradation, which facilitates conventional applications requiring durable materials.

Almost two decades ago, an exceptional novel biopolymer was discovered, when PTEs were synthesized by microbial fermentation for the first time. However, it turned out that PTEs are non-biodegradable by microorganisms in contrast to all other biopolymers (Lütke-Eversloh et al. 2001; Elbanna et al. 2003; Kim et al. 2005). Thus, PTEs clearly contradict the paradigm postulated by Martin Alexander, one of the leading environmental microbiologist of his time, that "all naturally occurring compounds are degradable by microbes" (Alexander

Table 1 Production volumes of persistent biobased plastics

Bioplastic material	Monomer	Precursor	Production volume[a]
Polythioester (PTE)	Mercaptoalkanoic acids	Acrylic acid, H_2S	–
Polyethylene (PE)	Ethylene[b]	Ethanol	199,000 t (2017)
Polypropylene (PP)	Propylene[b]	Ethanol, *n*-butanol	–
Polyethylene terephthalate (PET)	Ethylene glycol[b]	Ethylene, glycerol	539,000 t (2017)
	Terephthalic acid[b]	p-Xylene	
Polytrimethylene terephthalate (PTT)	1,3-Propanediol[b]	Sugars	–
	Terephthalic acid[b]	p-Xylene	
Polyamides (PAs)	1,4-Butanediamine	Succinic acid	244,000 t (2017)
	1,6-Hexanediamine	Propylene, butadiene	
	1,10-Decanediamine[b]	Castor oil	
	Adipic acid	Cyclohexane	
	Sebacic acid[b]	Castor oil	
	11-Aminoundecanoic acid[b]	Castor oil	
Polyurethanes (PURs)	Polyols[b]	Natural oils, sugars	1,714,000 t (2016)
	Isocyanates	Toluene, methylenedianiline	
Polyethylene 2,5-furandicarboxylate (PEF)	Ethylene glycol[b]	Ethylene	–
	2,5-Furandicarboxylic acid[b]	Fructose	
Polytrimethylene 2,5-furandicarboxylate (PTF)	1,3-Propanediol[b]	Sugars	–
	2,5-Furandicarboxylic acid dimethyl ester[b]	Fructose	

[a] Source: European Bioplastics, nova Institute 2017/2018

[b] Monomer produced from biomass or biomass-derived compound

1965). This unique characteristic of PTEs is caused by the thioester linkages in the polymer backbone, which are indeed resistant to microbial degradation. Only in one case, the enzyme-catalyzed cleavage of such a thioester linkage could be shown so far (Kato et al. 2005). Like their oxoester analogs PHAs, PTEs exhibit thermoplastic properties and are consequently classified as non-biodegradable bioplastics (Lütke-Eversloh et al. 2002; Kawada et al. 2003).

The petrochemical industry is causing a major part of air pollution and GHG emissions, which already have led to severe and irreversible damages of the environment (EPA 2018). The global concern about these negative impacts led to a change of philosophy about chemical processes, and the principles of "green chemistry" were developed with the purpose to reduce GHG emissions, the consumption of water and energy, and the generation of industrial waste (Allison and Bassett 2015; Fasciotti 2017). Since the rapid development of genomic sciences in the 1990s enabled major advances in genetic and metabolic engineering techniques (Cañestro et al. 2007), biotechnology became an important tool for industrial production processes. Synthesis of chemicals by microorganisms and the use of enzymes for in vivo or in vitro syntheses are naturally in compliance with the clean principles of green chemistry, while also improving the selectivity of chemical processes, lowering production costs, and using safer and more sustainable materials (Wenda et al. 2011). This field of "white biotechnology" is now established for the production of fine chemicals, biofuels, and agricultural products by sustainable processes with reduced GHG emissions, water and energy consumption, and generation of industrial waste (Gupta and Raghava 2007). The so-obtained renewable biopolymers are predicted to exhibit a great potential to replace conventional synthetic polymers (Fasciotti 2017). For a detailed overview of industrially relevant biopolymers—both biodegradable and persistent—with regard to technical aspects such as material properties and applications, see Nakajima et al. (2017).

This review gives a comprehensive compilation of non-biodegradable biopolymers, which are under development, already produced at the laboratory scale or even commercialized. First, biomass-derived feedstocks for biopolymer production and established biotechnical processes to produce biobased monomers are summarized. Then, persistent bioplastics will be discussed in detail, with a particular focus on the current state of the production processes.

Biobased plastic production from renewable resources

Petroleum-derived chemicals are still the precursors for the production of almost all conventional plastic materials, which is expected to triple by 2050, so that 20% of the annual global oil consumption would be required for their synthesis (World Economic Forum 2016). The associated release of vast amounts of CO_2 into the atmosphere as well as the depletion of fossil resources has raised public concerns about the economic and environmental sustainability (Cherubini et al. 2009). Consequently, the production of plastics from renewable biological resources has gained major attention and is experiencing rapid development during the last decade.

Currently, most biobased precursors utilized for bioplastic production are obtained from first-generation biomass resources, like glucose or starch, which directly compete with food and feed production for agricultural land. In order to establish a biobased economy, non-edible feedstock must be used for the production of biomonomers (Kawaguchi et al. 2017).

Lignocellulosic biomass is a highly abundant renewable resource, but requires pretreatment and enzymatic hydrolysis to release fermentable sugars of glucose and xylose, which can then be used by metabolically engineered microorganisms to produce monomers (Fernandes et al. 2013; Kawaguchi et al. 2016; Kawaguchi et al. 2017). Corn stover, sugarcane, wheat straw, and kraft pulp have already been successfully applied for the production of ethanol (Hasunuma and Kondo 2012). Moreover, monomers obtained by microbial fermentation from renewable feedstocks as precursors for biobased polyesters and polyamides (Reddy et al. 2013) expanded from aliphatic compounds, such as dicarboxylic acids, ω-amino acids, diols, and diamines to aromatic compounds (Koma et al. 2012).

In theory, it is technically possible to produce all major commonly used bioplastics from biomass. Replacing all petrochemical-derived chemicals applied in polymer materials by monomers produced from biomass would significantly contribute to a change towards a biobased economy (Harmsen et al. 2014). With decreasing cost for biotechnological processes, feedstock costs will start to weigh more heavily on the total production costs. Consequently, strategies for the efficient conversion of cheap renewable resources to biobased building blocks will attract major interest. Ten years ago, only 2% of all the chemicals were produced from biomass (Shen et al. 2010), which is predicted to increase to approximately 22% by 2025 (Philp et al. 2004, 2013). Biomass-derived chemical production has the potential to increase added values in an economy with a simultaneous decrease of GHG emissions, thus leading to a sustainable and environmental-friendly economy (Kikuchi et al. 2013). Harmsen and coworkers presented a comprehensive summary of biobased alternatives for chemical building blocks typically required in the production of plastics, such as vinyl polymers, polyesters, polyamides, polyurethanes, and synthetic rubber (Harmsen et al. 2014).

Classification of bioplastics: biobased, biodegradable, persistent

Today, there are bioplastic alternatives for most conventional plastic materials and their corresponding applications with a

great potential to substitute petrochemical plastics. The term 'bioplastic' is on the one hand used for plastic materials that are produced from biological resources and on the other hand to summarize all plastics that are biodegradable including those materials that are made from petrochemical resources. Thereby, the term 'bioplastic' is used in different meanings. At present, biodegradable biopolymers attract major attention of researchers, companies, and the public, as the environmental pollution by vast amounts of plastic waste became a huge concern. Among biodegradable bioplastics, the most promising and already well-established representatives are PLA and the various members of PHAs (Peelman et al. 2013; Lettner et al. 2017). However, the introduction of biodegradable plastics will not be the only solution to our world's waste problem, as there is barely infrastructure for separate collection schemes or the controlled composting processes needed for the complete biodegradation of bioplastics (Rujnić-Sokele and Pilipović 2017). Moreover, many present applications of plastics require durable materials, which can therefore not be substituted by biodegradable plastics. These durable plastics are conventionally produced based on fossil raw materials. The depletion of fossil resources is another important issue, which has to be encountered by finding alternative precursors for the chemical industry. Especially in the field of plastic materials, there have been numerous innovations and new products over the last years, aiming at the production of bioplastics, which are based on renewable resources, yet not or barely biodegradable and thus meet the requirements of durable plastic materials. Non-biodegradability as such of any material can admittedly only be presumed under reservation. Indeed, first studies have been published recently showing the microbial degradation of a plastic material (PET), which has been and is still termed non-biodegradable (Yoshida et al. 2016). As long as such biodegradation activities are insignificantly low, they will not influence the application range or waste treatment processes. However, non-biodegradability is only a postulation, which is valid until there is clear evidence to the contrary.

Fully or partially biobased, persistent bioplastics accounted for 1.2 million tons in 2017, which was 56% of the total bioplastics production capacities (European Bioplastics 2017). This group of plastic materials, which are produced from biomass-derived substrates, but are—from today's point of view—non-biodegradable, can be subdivided into two classes (Fig. 1): first, there are primarily petroleum-based conventional plastic materials, which now became bioplastics due to the utilization of renewable precursors derived from biomass, such as biobased PE and PP. These bioplastics and their biobased precursors are so-called drop-in solutions, as their properties and performance are exactly the same compared to the fossil-based materials (European Bioplastics 2017).

Second, there are bioplastics, which are originally synthesized by microorganisms and yet non-biodegradable by any organisms or enzymes tested so far. PTEs are up to now the only biopolymers belonging to this second class of persistent bioplastics. As there is no established petrochemical counterpart, neither production nor distribution infrastructure exist and properties as well as performance of these new biomaterials must still be assessed prior to application. However, PHAs as the biodegradable oxoester analogs of PTEs are already established bioplastic materials. This could help to clear the way for a market introduction of persistent PTEs, which are synthesized via the PHA biosynthesis systems.

Microbial polythioesters

Since their discovery as bacterially synthesized polymers in 2001, PTEs form the eighth class of biopolymers (Lütke-Eversloh et al. 2001). PTEs exhibit comparable thermoplastic and elastomeric properties, like their oxoester analogs PHAs, while, in contrast to PHAs, being non-biodegradable due to the unique thioester linkages in the polymer backbone (Lütke-Eversloh et al. 2001; Elbanna et al. 2003; Kim et al. 2005). The resulting biological persistence of PTEs to microbial or enzymatic degradation is their most remarkable characteristic, making them ideal bioplastics to replace conventional petrochemical plastics in applications requiring durable materials (Uhrich 2003; Steinbüchel 2005).

Chemical synthesis of PTEs was firstly reported in 1951; however, the rather complex and inefficient processes requiring toxic and expensive reagents were not suitable for upscaling and commercialization (Marvel and Kotch 1951; Kricheldorf and Schwarz 2007). More recently, PTEs have been chemically obtained by ring-opening polymerization of 1,4-thiazine-2,5-diones (Ura et al. 2009) or by polycondensation of 2,5-bis(sulfanylmethyl)-1,4-dithiane with 1,3-adamantanedicarbonyl dichloride or cyclohexanedicarbonyl dichloride (You et al. 2010).

In vitro production of PTEs applying enzymatic approaches represents promising alternatives to chemical PTE synthesis, as high selectivity is achieved under mild conditions, thus meeting the criteria of green chemistry. Among others, PTEs were efficiently synthesized by copolymerization of lactones with mercaptoalkanoic acid (Iwata et al. 2003), polycondensation of 11-mercaptoundecanoic acid or dithiols and dicarboxylic acids (Kato et al. 2005, 2006), (trans)thioesterification of α,ω-alkanedithiols (Weber et al. 2006), and ring-opening polymerization of cyclic thioesters (Kato et al. 2007; Shimokawa et al. 2011), all applying immobilized lipases of *Candida antarctica* or *Rhizomucor miehei* as biocatalysts (Kobayashi 2010).

Microbial (in vivo) biosynthesis of PTE homopolymers is established in three bacterial strains (Fig. 2; reviewed in Wübbeler and Steinbüchel 2014): (1) *R. eutropha* H16 is

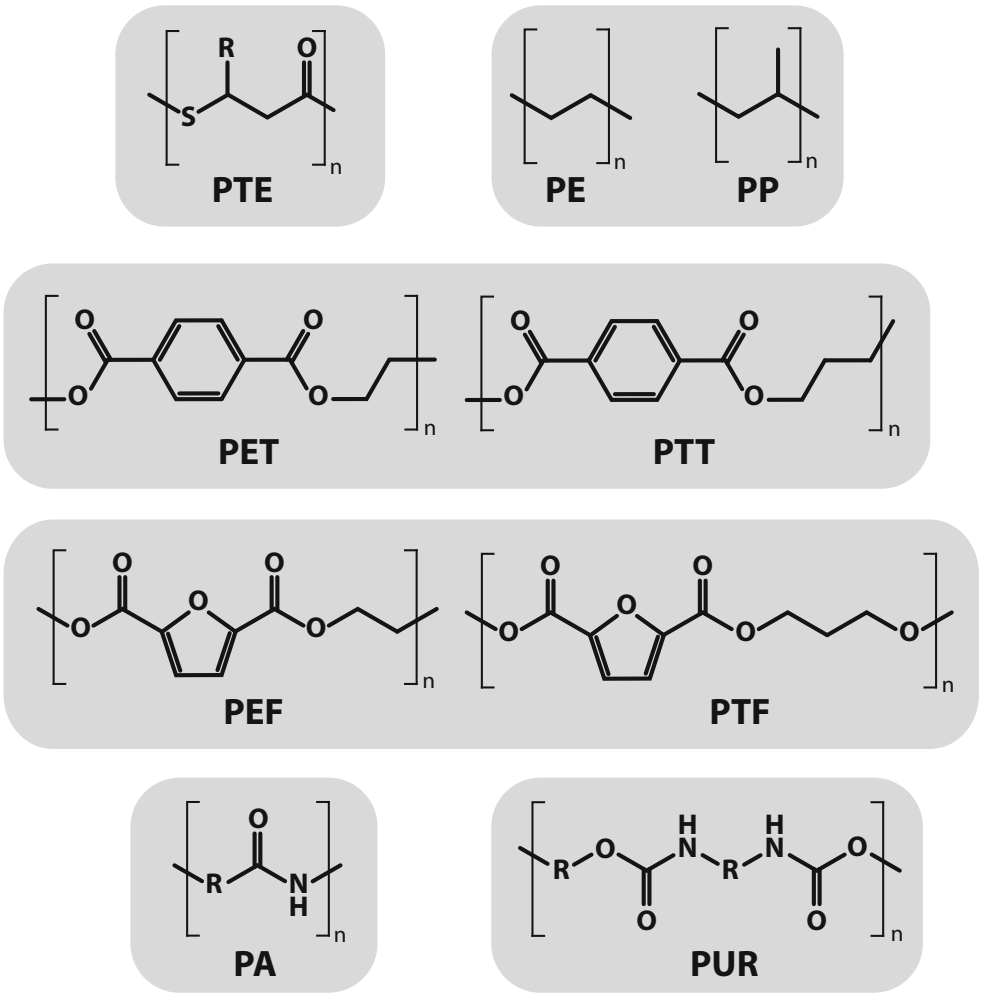

Fig. 1 Chemical structures of persistent bioplastics. Abbreviations: PA, polyamide; PE, polyethylene; PEF, polyethylene 2,5-furandicarboxylate; PET, polyethylene terephthalate; PP, polypropylene; PTE, polythioester; PTF, polytrimethylene 2,5-furandicarboxylate; PTT, polytrimethylene terephthalate; PUR, polyurethane

naturally capable of synthesizing PTE copolymers consisting of 3-hydroxybutyric acid (3HB) and 3-mercaptoalkanoic acids (3MAs). (2) Recombinant strains of *Escherichia coli* JM109 expressing the artificial BPEC pathway, which employs butyrate kinase (Buk) and phosphotransbutyrylase (Ptb) from *Clostridium acetobutylicum* as well as PHA synthase (PhaEC) from *Thiocapsa pfennigii*, PTE homopolymers can be produced. By feeding 3-mercaptopropionic acid (3MP), 3-mercaptobutyric acid (3MB), or 3-mercaptovaleric acid (3MV) as substrates with gluconate as cosubstrate, the corresponding PTEs poly(3MP), poly(3MB), and poly(3MV), respectively, can be synthesized (Lütke-Eversloh et al. 2002). Optimized large-scale fermentation with glycerol as carbon source yielded poly(3MP) at a concentration of up to 6.4 g/l (cellular content of 30% *w*/*w* of the cell dry weight) with a 49% conversion rate of supplied 3MP (Thakor et al. 2005). (3) Ten years after the discovery of PTEs as biopolymers, the BPEC pathway was also implemented in a metabolically engineered strain of *Advenella mimigardefordensis* to synthesize poly(3MP) with a content of 25% (*w*/*w*) of the cell dry weight using glycerol and 3,3′-dithiodipropionic acid (DTDP) as substrates (Xia et al. 2012).

As mentioned above, the most outstanding property of PTEs regards their (non-)biodegradability; while the heteropolymer poly(3HB-*co*-3MP) could be degraded microbially (Elbanna et al. 2003), the homopolymer poly(3MP) exhibited persistence to microbial degradation although bacterially synthesized as well (Kim et al. 2005). In contrast, the PTE poly(11-mercaptoundecanoic acid) was shown to be synthesized as well as degraded by lipase-catalyzed mechanisms (Kato et al. 2005). Poly(β-thioesters), which are polymerized by the thiol-ene click reaction, were shown to be degraded by chemically induced hydrolysis of the ester linkages in the polymer chain (Vandenbergh et al. 2012).

So far, fermentative production of PTEs is performed only at a laboratory scale, as it depends on the provision of organic sulfur compounds, which are expensive and impair cell growth. In order to make the production process of PTEs economically feasible, alternative substrates are required. As the ultimate future goal, biosynthetic pathways must be

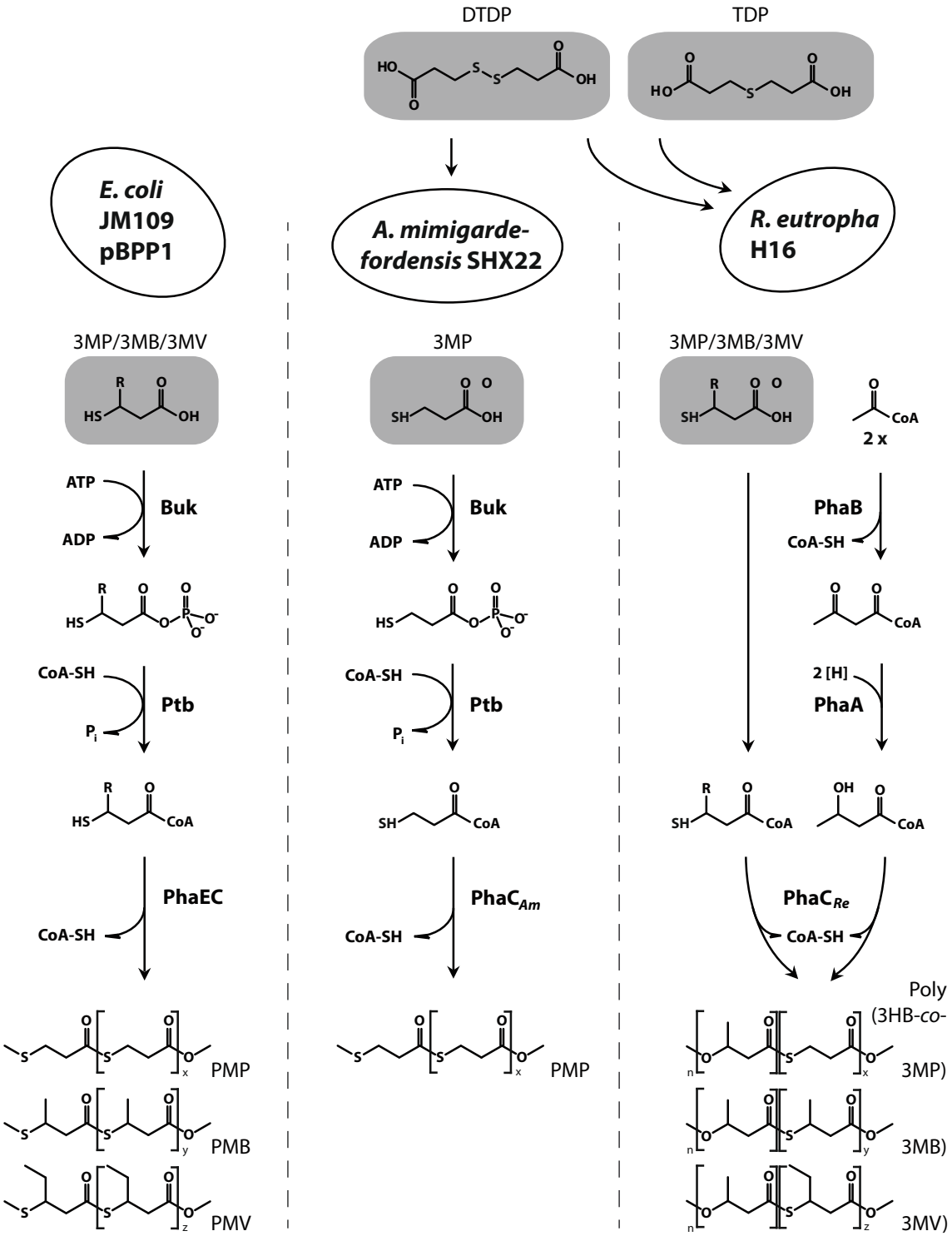

Fig. 2 Biosynthesis of polythioesters (PTEs) by microbial fermentation. Abbreviations: *Am*, *Advenella mimigardefordensis*; Buk, butyrate kinase of *Clostridium acetobutylicum*; DTDP, 3,3′-dithiodipropionate; PhaA, β-ketothiolase; PhaB, acetoacetyl-CoA reductase; PhaC, polyhydroxyalkanoate synthase; PhaEC, PHA synthase of *Thiocapsa pfennigii*; PHB, poly(3-hydroxybutyrate); Ptb, phosphotransbutyruylase of *C. acetobutylicum*; PTE, polythioester; *Re*, *Ralstonia eutropha*; TDP, 3,3′-thiodipropionate; 3MB, 3-mercaptobutyric acid; 3MP, 3-mercaptopropionic acid; 3MV, 3-mercaptovaleric acid

implemented in PTE-producing microorganisms by means of metabolic engineering in order to biotechnically produce 3MAs, thereby combining the processes of biomass-derived substrate synthesis with the subsequent production of bioplastics (Wübbeler and Steinbüchel 2014; Andreeßen et al. 2017, 2018).

Fully biobased conventional biopolymers

Conventional plastic materials, which are nowadays produced from renewable resources, usually combine a two-step process, wherein the polymer precursors are synthesized based on alternative raw materials by metabolically engineered microorganisms (Fig. 3). The polymerization typically proceeds via the conventional chemical process analogous to the production of the petrochemical counterpart.

Polyethylene

PE is the most common plastic with primary use in various packaging applications, due to its special mechanical properties such as high ductility and impact strength as well as low friction, hardness, and rigidity as well as chemical resistance. PE synthesized from renewable feedstock is also referred to as "bio-PE" or "green" PE. During production of biobased PE, biotechnological and chemical processes are combined.

In a first step, ethanol is produced by fermentation, most efficiently of sucrose or starch, respectively. Ethylene can then be manufactured from ethanol via dehydration, thus providing a biobased alternative for fossil-based ethylene, which is by far the most important chemical with 127 million tons produced globally (E4tech et al. 2015). Industrial plants for the production of ethylene from first-generation biobased ethanol are already operating (Mohsenzadeh et al. 2017). Production of ethanol via fermentation is majorly located in the USA and Brazil with an overall annual capacity of 86 billion liters in 2016, which accounts for 83% of the total production of ethanol from renewable resources. The most important feedstocks are corn starch, sugarcane, and wheat starch (Barros 2016), which are used as sugar sources for the fermentative conversion to ethanol by microorganisms (Bai et al. 2008; Naik et al. 2010; Chandel et al. 2011; Kang and Lee 2015). Second- or third-generation biobased ethanol from lignocellulosic substrates or waste materials, respectively, is under development (Taherzadeh and Karimi 2007; Balat 2011; Dubey et al. 2016), but has not been commercialized yet, as the required pretreatment and hydrolysis processes are much more complicated and elaborate (Sun and Cheng 2002; Shupe and Liu 2012).

After chemical conversion to ethylene, the second step of conventional catalyst-driven polymerization yields PE (Morschbacker 2009). In 2016, approximately 200,000 tons of PE were produced from renewable resources, which is 4.8% of the total amount of the global bioplastics production (European Bioplastics 2017). Production of biobased ethylene is majorly realized in Brazil and India using sugarcane and molasses, respectively. The largest production plant for ethylene and subsequently PE (under the trade mark "I am green™") from sugarcane-derived ethanol is operated by Braskem in Brazil with an annual production capacity of 200,000 tons per year (Mohsenzadeh et al. 2017).

The increase of the commercial production of PE predicted in a short report published by The International Renewable Energy Agency (IRENA) and the Energy Technology Systems Analysis Programme (ETSAP) in 2013 has not been realized, until today (Harmsen et al. 2014). In 2015, Braskem stopped further investment in the production of biobased ethylene and, moreover, Dow Chemical and Mitsui Chemicals have been postponing their joint venture announced in 2011 (Plastics Today 2011), to construct the respective production plant with a capacity of 900,000 t/year (Nikam 2017). Critical points about plastic production based on starch-derived ethanol include on the one hand the suboptimal resource efficiency, since carbon is lost as CO_2 during ethanol production (Fasciotti 2017). On the other hand, most of the ethanol is still a first-generation product from raw materials, which compete with the food industry, resulting in both ethical and political dilemmas (Gnansounou and Dauriat 2005). Therefore, second-generation biobased ethanol must be produced employing non-edible feedstocks like agricultural waste (Sarkar et al. 2012; Aditiya et al. 2016).

Life cycle analyses (LCA) to assess the environmental performance of the production and consumption of PE produced

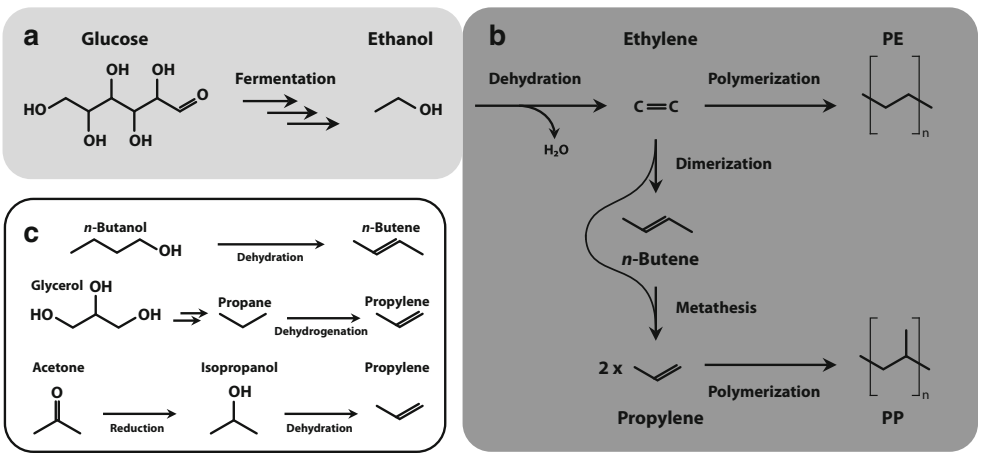

Fig. 3 Production routes for biomass-derived polyethylene (PE) and polypropylene (PP)

from renewable resources demonstrated that the substitution of fossil-based PE by biomass-derived PE is suitable to reduce GHG emissions, which generally originate from PE production (Kikuchi et al. 2013). Although uncertainties in the agricultural processes impact the potential of the fermentative production, they do not negate the benefits of the produced PE. Indeed, PE production from sugarcane-derived ethanol was shown to have the largest effect on GHG emission mitigation, in direct comparison to biomass-derived PP or ethanol (Kikuchi et al. 2018).

PE has been considered to be a plastic material remarkably persistent to degradation and is still classified as non-biodegradable (European Bioplastics 2017). Although the utilization of this polymer by microorganisms is physically limited by its insolubility in aqueous media, lack of functional groups, and high molecular weight (Arutchelvi et al. 2008), the ability of microorganisms to use virgin PE as a carbon source has been established during the last decade (e.g., *Rhodococcus*, *Bacillus*, and *Pseudomonas* strains, Sivan et al. 2006; Sudhakar et al. 2008; Balasubramanian et al. 2010; Yoon et al. 2012; Harshvardhan and Jha 2013; Yang et al. 2014; reviewed in detail in Restrepo-Flórez et al. 2014). The exact catabolic pathway still needs to be elucidated. Breakdown and oxidation of the PE molecule by enzymatic action were shown to be catalyzed by laccase (Santo et al. 2013), while an alkane hydroxylase from the AlkB family was able to oxidize PE (Yoon et al. 2012). The most efficient approach to biodegrade PE was only recently achieved by a combination of chemical PE oxidation applying anionic surfactants followed by microbial degradation by *Lysinibacillus fusiformis* (Mukherjee et al. 2016; Mukherjee et al. 2017). Nevertheless, studies that provide sufficient evidence for the incorporation of PE-derived carbon into the microorganism's metabolism and macromolecules are missing, until today. Moreover, the development of an effective process to address the issue of PE waste treatment is not likely to be realized in the near future.

Polypropylene

PP is the commodity plastic material with the second highest production volume after PE and applied in a wide variety of areas from packaging to automotive components and medical devices. Properties of PP are comparable to PE, with better mechanical stability and thermal resistance owing to its methyl groups, which also leads to decreased chemical resistance. Following successful establishment of renewable-derived PE, PP was the next promising conventional plastic to be produced from biomass (Kikuchi et al. 2018). Biobased propylene can be produced via several processes (Harmsen et al. 2014): (1) in order to synthesize propylene entirely from biomass-derived ethanol, ethylene is dimerized into 2-butene followed by metathesis of ethylene and 2-butene. (2) Propylene is obtained from n-butanol by dehydration to 1-butanol, subsequent isomerization into 2-butene, and metathesis of ethylene and 2-butene. (3) Propane derived from glycerol, as the main by-product of biodiesel production, can be converted to propylene by dehydrogenation. (4) Acetone produced by fermentation of sugars can be reduced to isopropanol or (5) isopropanol directly derived from sugar fermentation can be further dehydrated yielding propylene. Propylene obtained from biomass via one of these routes is identical to fossil-based propylene and therefore processed accordingly via conventional catalyst-driven polymerization to produce biomass-derived PP. So far, the market for PP from renewable resources is in its nascent stage as production processes are still in development and expected to be commercially realized by 2020–2022 with a strong growth potential due to the widespread application of PP (European Bioplastics 2017).

Due to the growing demand of the packaging industry and especially automobile manufacturers for eco-friendly lightweight materials, the market growth for renewable-derived PP is predicted to boost from an estimated size of USD 32.3 million in 2016 with a compound annual growth rate of 5.1% over the next years (Grand view research 2017). Key players operating in the establishment of fermentative PP production are Trellis Earth Products, Biobent Polymers, Dow Chemicals, Braskem, and Global Bioenergies. Currently, companies pursue the development of processes to synthesize biobased propylene, as the poor availability of precursors produced from biomass, such as n-butanol or isopropanol represents the major limitation of PP production (Grand view research 2017). The manufacturing of propylene from sugarcane-derived ethanol is already established by Braskem (Brazil). However, the plan to construct a production facility for PP with a capacity of about 30–50 kt announced in 2011 was later frozen for economic reasons, which included the increasing availability of shale gas as feedstock for petrochemical production. Further future restraints in the market of PP produced from biomass are expected to be potential advantages of competing bioplastics such as biobased PET and PLA (Grand view research 2017). LCA analysis confirmed the superior environmental performance of sugarcane-derived over petrochemically produced PP, showing that biobased PP is suitable to mitigate GHG emissions. Compared to PE derived from sugarcane, the reduction rate of GHG emissions is lower, as the increased number of reaction steps during PP production leads to higher energy consumption (Kikuchi et al. 2018).

PP belongs to the group of non-biodegradable plastic materials and consists of hydrocarbons with methyl side chains. The lack of functional groups and its hydrophobicity prevent hydrolysis and biodegradation by microorganisms. Nevertheless, several examples can be found in the literature, where pretreated PP or PP combined with a biodegradable polymer, such as starch or natural fibers, was biodegraded, although with very limited efficiency (Kaczmarek et al. 2005; Fontanella et al. 2013; Khoramnejadian 2013; Sepperumal and Markandan 2014). Only very recently, the mesophilic

bacterium *Stenotrophomonas panacihumi* PA3-2., which is able to degrade PP without any additives, has been isolated from soil (Jeon and Kim 2016). However, the biodegradative activity was rather slow and will neither endanger stability of products made from PP, nor offer real options to develop a biological waste treatment process.

Partially biobased conventional biopolymers

Until now, PE and PP are the only conventional plastic materials, which can be completely produced from biomass. As the demand for renewable-derived plastic is growing with the increasing public environmental awareness, companies are searching for strategies to also produce bulk plastic materials like PET, PTT, PAs, and PURs at least partially based on biomass-derived precursors.

Polyethylene terephthalate

Economically, PET partially produced from renewable resources is the most relevant bioplastic material, although the production of fully biomass-derived PET is not realized, yet. Applications of PET range from packaging, most commonly bottles and containers, to fibers as in fleece materials. In 2017, the total production of partially biobased PET accounted for 540,000 tons or 26.3% of the total annual bioplastics production (European Bioplastics 2017) and is predicted to reach about 7 million tons by 2020 using ethanol as biomass-derived precursor (Prieto 2016). In this case, the synthesis of PET is based on ethanol from sugarcane or corn starch, which is converted to monoethylene glycol (MEG) and further combined with fossil-based terephthalic acid (TPA) by conventionally applied transesterification to yield partially (23% of the carbon) biobased PET. The relatively high demand for PET produced from renewables is essentially driven by the 'Plant PET Technology Collaborative' including Coca Cola, Ford, Heinz, Nike, and Proctor & Gamble, which also has the declared objective to develop commercial processes for PET fully derived from biomass (Fig. 4) (Plastics Today 2012). With the investment of these companies in research and development, the production of the aromatic PET-compound TPA from renewable resources is rapidly progressing. During petrochemical synthesis, TPA is obtained by oxidation of *para*-xylene, which is the main focus of ongoing research to establish routes for its commercial production from biomass. Besides isolation from BTX (mixtures of benzene, toluene, and xylene), either by pyrolysis or by aqueous phase reforming (Komula 2011; Benner et al. 2012; Anellotech 2013), also the fermentative production of TPA via isobutanol and isobutylene is close to commercialization (Harmsen et al. 2014; Smith 2015). In 2015, Coca Cola presented the first PET bottle (PlantBottle™) fully derived from renewable precursors at the World Expo in Milan (Bioplastics magazine 2015).

As polyester with a high content of aromatic components, PET plastic is particularly resistant to microbial degradation, which also promotes its accumulation in the environment (Kint and Muñoz-Guerra 1999; Müller et al. 2001). Very recently, the new bacterium *Ideonella sakaiensis* 201-F6 was described, which is able to utilize PET as its main source of carbon and energy by enzymatically hydrolyzing the polymer to its two environmentally uncritical monomers, TPA and ethylene glycol. The development of environmental bioremediation strategies or the biological recycling of waste PET could become a highly interesting research field in the future (Yoshida et al. 2016).

Polytrimethylene terephthalate

The copolyester polytrimethylene terephthalate (PTT), also designated as polypropylene terephthalate (PPT), with main applications as fibers for carpet and textiles, exhibits optimized properties as engineering thermoplastic by combining the desirable mechanical stability and resistance of PET with the good processability and surface appearance of polybutylene terephthalate (PBT). PTT can be produced from biomass-derived 1,3-propanediol (PDO) and petroleum-based TPA to yield partially biobased PTT (Fig. 4). The fermentative production of PDO is already largely industrialized with a global capacity of 90 kt/year in 2014. (Harmsen et al. 2014). In 2000, DuPont began the commercial production of PTT based on renewable-derived PDO under the trade name Sorona™ (DuPont 2018).

Polyamides

Within the large group of PAs, also known under the generic name nylons, there are partially as well as fully biobased materials available, including drop-in PAs derived partially from biomass and also completely novel polymers (Fig. 5). PAs partially produced from renewable precursors accounted for 11.9% of the global annual bioplastic production in 2017, which are approximately 240,000 tons. Hence, PAs currently represent the bioplastic with the second highest production volume after PET (European Bioplastics 2017). Biomass-derived PAs exhibit processing and application properties identical to conventional PAs and are likewise obtained by either ring-opening polymerization of cyclic amides (homopolymers), polycondensation of aminocarbonic acids (homopolymers) or various diamines and dicarbonic acids (heteropolymers) (Harmsen et al. 2014). Examples for 100% biobased PAs are PA 6 from fermentatively produced ε-caprolactam, PA 11 (Arkema 2018) from castor oil or undecanoic acid, respectively, PA 10.10 (EMSGrivory 2018; Evonik 2011; JEC Group 2013) from castor oil and castor oil-derived 1,10-decamethylenediamine (DMDA) and PA 10.12 obtained from biobased DMDA and dodecanoic acid. Partially biobased PA 4.10, PA 5.10, and PA 6.10 can be obtained from DMDA and fossil-derived 1,4-tetramethylenediamine (TMDA),

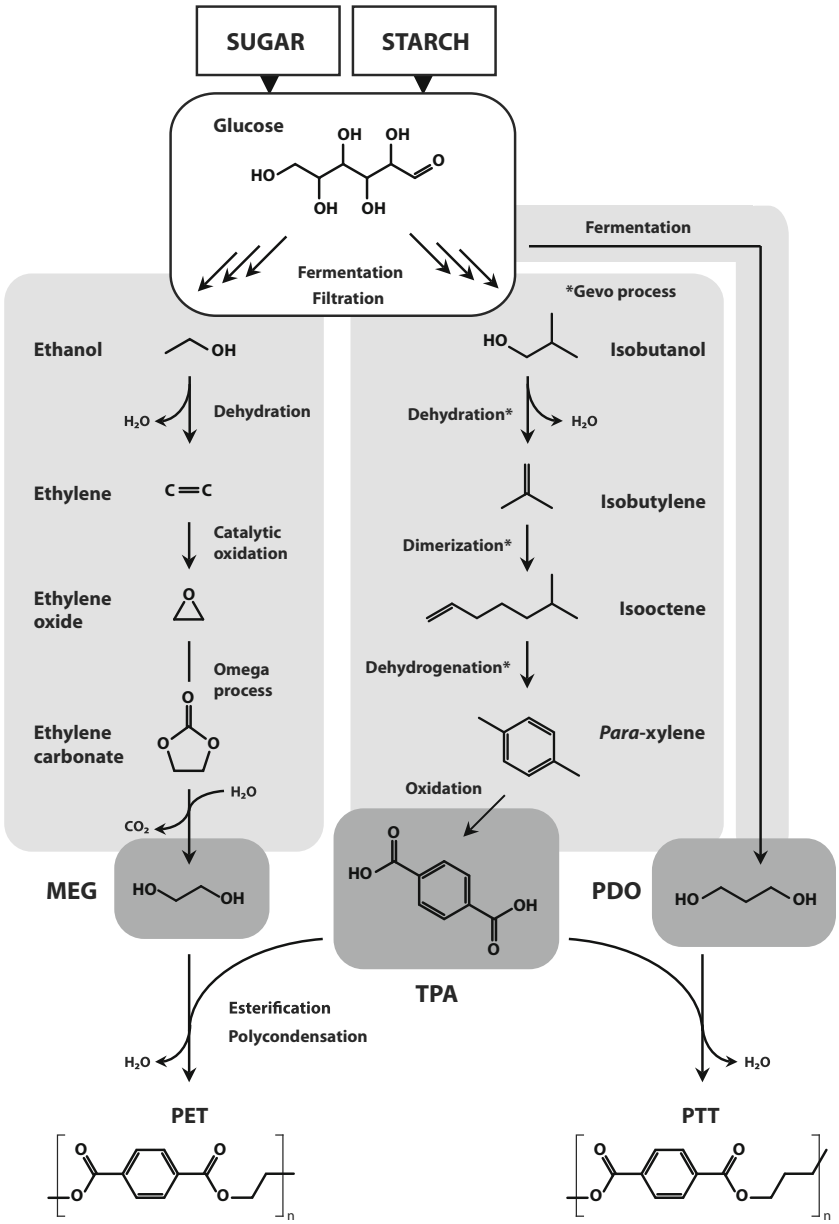

Fig. 4 Production routes for fully biobased polyethylene terephthalate (PET) and polytrimethylene terephthalate (PTT). Biomass-derived substrates are marked by white boxes, biobased synthesis of monomers is highlighted in light gray, key monomers in dark gray. Abbreviations: MEG, monoethylene glycol; PDO, 1,3-propanediol; TPA, terephthalic acid

1,5-pentamethylenediamine (PMDA), or 1,6-hexamethylenediamine (HMDA). Research on further fully renewable-derived PAs is ongoing, including the utilization of PMDA obtained from glucose fermentation, polymerization of biobased HMDA and azelaic acid to obtain PA 6.9 and biotechnologically produced succinic acid to generate PA 4.4 or PA 6.4 (Harmsen et al. 2014).

Polyurethanes

PURs are a diverse family of polymers with a total production of 14,000 kt/year (Kersh 2011). Production of PURs occurs via polyaddition of polyols and isocyanates, resulting in linear, branched, or even cross-linked polymers with a wide range of properties according to the many different precursors and hence, applications range from foams to coatings, adhesives and sealants (Harmsen et al. 2014). The synthesis of monomer components from biomass was successfully established for diols and polyols, while the isocyanate supply (most importantly: toluene diisocyanate, methylene diphenyl isocyanate, hexamethylene diisocyanate) still depends on petrochemicals (Fig. 5). PURs partially based on biomass are obtained by employing polyols from renewable resources, such as natural oils, PDO and 1,3-butadiene, sugars or diacids (Cargill 2018), but were commercially produced only with an annual capacity of 28 kt in 2013 (Kersh 2011). Biobased polyols, so-called "natural-oil polyols" (NOPs), are obtained from vegetable oils, such as soybean, palm, sunflower, rapeseed, or castor oil, by

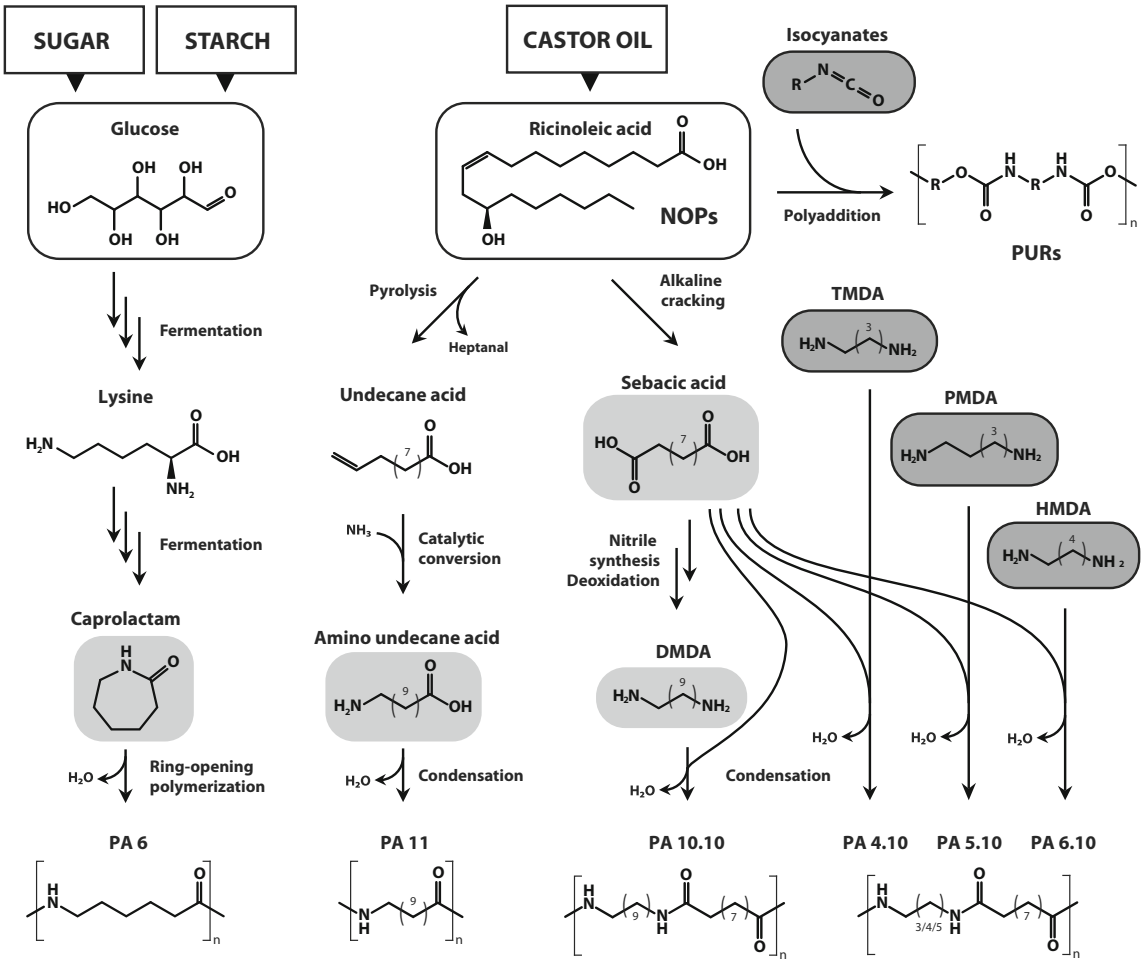

Fig. 5 Production routes for fully and partially biomass-derived polyamides (PAs) and polyurethanes (PURs). Biomass-derived substrates are marked by white boxes, petrochemical precursors by dark gray boxes. Biobased key monomers are highlighted in light gray. Abbreviations: DMDA, 1,10-decamethylenediamine; HMDA, 1,6-hexamethylenediamine; NOP, natural oil polyol; PMDA, 1,5-pentamethylenediamine; TMDA, 1,4-tetramethylenediamine

oxidation and epoxidation, esterification, hydroformylation, or ozonolysis (Endres and Siebert-Raths 2011). In order to produce PURs, which are fully derived from biomass, the synthesis of isocyanates from renewable substrates has to be established (Harmsen et al. 2014). Biobased PUR have huge production capacities with a well-established market and are expected to grow faster than the conventional PUR market due to their versatility in the future (European Bioplastics 2017).

"New" fully biobased bioplastics

In contrast to conventional plastic materials, which are fully or partially produced from biomass-derived substrates, so-called drop-in bioplastics, other bioplastic materials are based on renewable resources but represent new biopolymers (Fig. 6). These "new" bioplastics probably face a more challenging introduction to the markets, as the required infrastructure has to be established first. However, these new biobased plastic materials have a great potential to substitute conventional plastics due to their superior properties.

Polyethylene 2,5-furandicarboxylate

Polyethylene 2,5-furandicarboxylate (PEF), also referred to as polyethylene furanoate, is produced by polycondensation of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol and represents a chemical analog of PET as aromatic polyester. PEF can be manufactured into films and plastic bottles for food and beverage packaging, thus representing a promising alternative to PET (European Bioplastics 2016b). The biotechnological process to convert biomass into FDCA was patented by Avantium, who, in 2014, closed a deal with leading companies in the field of food, beverage, and plastics packaging production (including Coca-Cola and Danone) to develop bottles made of 100% biobased PEF. Recently, Avantium and BASF announced their partnership to construct a reference plant in Antwerp with an annual production capacity of

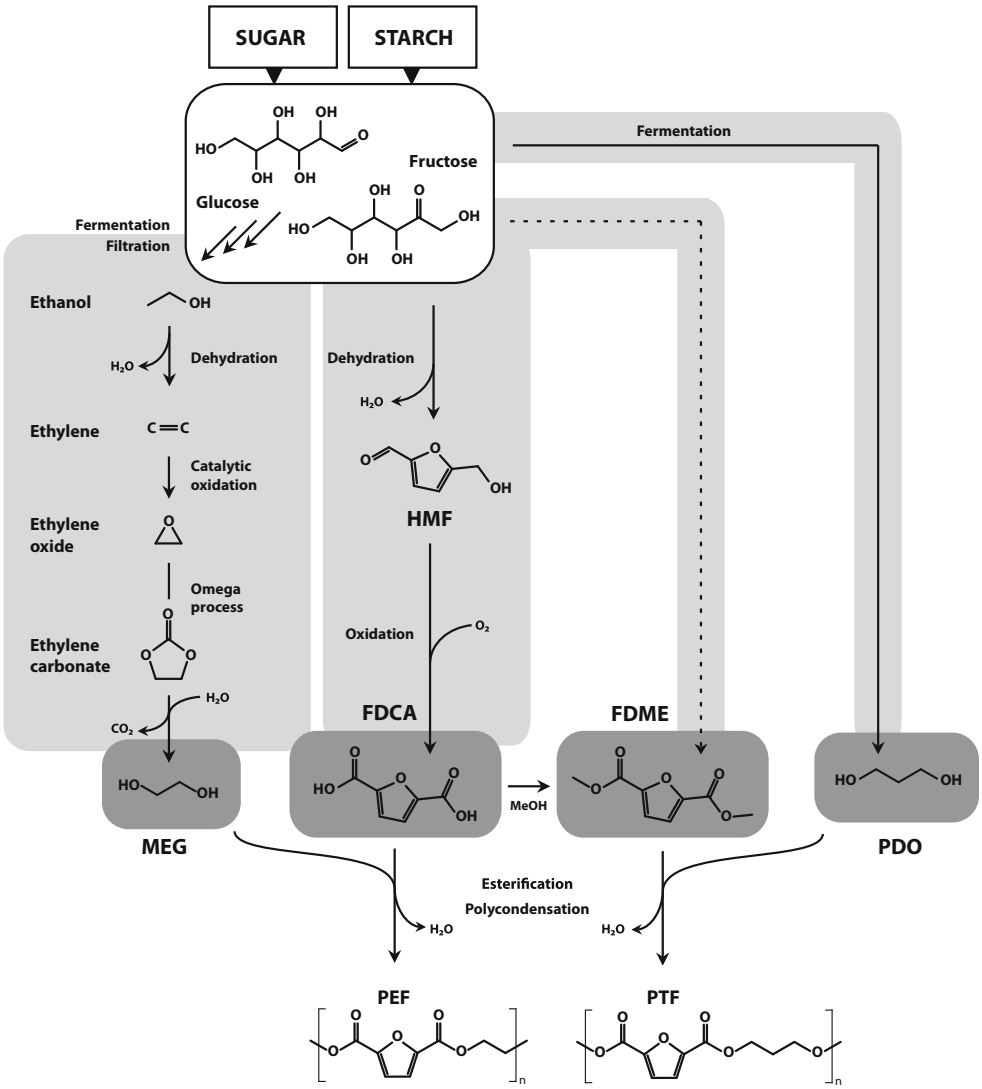

Fig. 6 Production routes for fully biomass-derived polyethylene 2,5-furandicarboxylate (PEF) and polytrimethylene 2,5-furandicarboxylate (PTF). Biomass-derived substrates are marked by white boxes, biobased synthesis of monomers is highlighted in light gray, key monomers in dark gray. Abbreviations: FDCA, 2,5-furandicarboxylic acid; FDME, 2,5-furandicarboxylic acid dimethyl ester; HMF, 5-hydroxymethylfurfural; MEG, monoethylene glycol; PDO, 1,3-propanediol

50,000 tons to produce FDCA from renewable resources and consequently PEF. Another approach to produce biobased FDCA is pursued by Avalon Industries. The Hydrothermal Processing technology patented by AVA-CO2 Switzerland to industrially produce biobased 5-hydroxymethylfurfural (HMF) was developed further to yield FDCA, which facilitates competitive production of biobased PEF for applications as films, bottles, and potentially open new markets not served by any other plastics materials, so far (Plazzo 2017). The launch of an industrial production plant by AVA-CO2 with an annual capacity of 120,000 tons of FDCA is planned for 2019 (K-Zeitung online 2016).

Polytrimethylene 2,5-furandicarboxylate

Besides PEF, polytrimethylene 2,5-furandicarboxylate (PTF) represents another biobased alternative to conventional PET with improved gas barrier properties, which is advantageous for food packaging applications. DuPont and Archer Daniels Midland (ADM) plan to produce PTF by reacting fructose-derived 2,5-furandicarboxylic acid dimethyl ester (FDME) with PDO. *DuPont* and ADM announced construction of a demonstration plant in Decatur (Illinois, USA) with an annual capacity of 60 tons to produce FDME for further testing and research (Tullo 2016).

Conclusions and future perspectives

The production of bioplastics is stably growing, and processes to yield the required precursors from renewable resources as well as the polymerization techniques are constantly improving. As there is a high demand for biobased plastic materials from various industries ranging from consumer goods and packaging to automobile manufacturers, companies invest in research and development of bioplastics as well as in production facilities to enhance their capacities for established biomass-derived plastic materials or to industrialize new

processes for bioplastics production. In the early phase of the bioplastics industry, mainly biodegradable plastic materials were developed for short-term applications with the purpose of solving the problem of plastic waste. Nowadays, the production of bioplastics focuses on applications requiring durable materials with the benefit of using sustainable processes, which involve biomass-derived substrates, thereby reducing GHG emissions and depletion of fossil resources. Moreover, the production of biobased plastics is no longer only interesting to substitute their petrochemical counterparts, but the development of new applications is conceivable due to improved or even new properties. In general, further growth and development on the bioplastics market are expected in the future regarding variety and quantity of biobased materials. Especially, progress in the processes to make lignocellulosic biomass, which accumulates as a waste product, available for biopolymer production will drastically lower production costs and render renewable-derived plastics even more attractive.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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