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Plastics Derived from Biological Sources: Present and Future: A Technical and Environmental Review

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1. INTRODUCTION

In the time period 2010−2015, the worldwide annual production of plastics is very likely to surpass 300 million tons,[1,2] requiring multiple amounts of petroleum and leading to hundreds of millions of tons of CO_2 in addition to health risks for the public due to the release of other types of emissions.[1,3] A large amount of plastics (at least 40% of the total consumption) is used in short-term applications, and the resulting waste can quickly lead to additional environmental damage unless adequate waste management systems are in place. For example, conventional petrochemical plastics are harmful for terrestrial and sea animals as well as birds that tend to eat plastic residues;[4] these impacts could be reduced by plastics that are biodegradable by microorganisms. In short, petrochemical plastics are not sustainable and bio-based sustainable plastics should be developed to avoid problems caused by the petrochemical plastics.

Materials derived from biological sources including starch, cellulose, fatty acids, sugars, proteins, and other sources can all be consumed by microorganisms, especially by bacteria which can convert these raw materials into various monomers that are suitable for polymer production including, for example, hydroxyalkanoic acids (with many structural variations), D- and L-lactic acid, succinic acid, bio-1,4-butanediol, (*R*)-3-hydroxypropionic acid, bio-ethylene (by dehydration of bioethanol), 1,3-propanediol, bio-propylene (from bio-isobutanol), and bio-ethylene glycol (from bio-ethylene) or even CO_2 (Figure 1).[5] These monomers have been used to produce various bio-based plastics including polyhydroxyalkanoates (PHA), polylactic acid (PLA), poly(butylene succinate) (PBS), polyethylene (PE), poly(trimethylene terephthalate) (PTT), polypropylene (PP), polyethylene terephthalate (PET), and poly(propylene carbonate) (PPC) (Figure 1).[5,6] Except for bio-based PE, PP, PTT, PET, and polyamides, all other bio-based polymers just mentioned are

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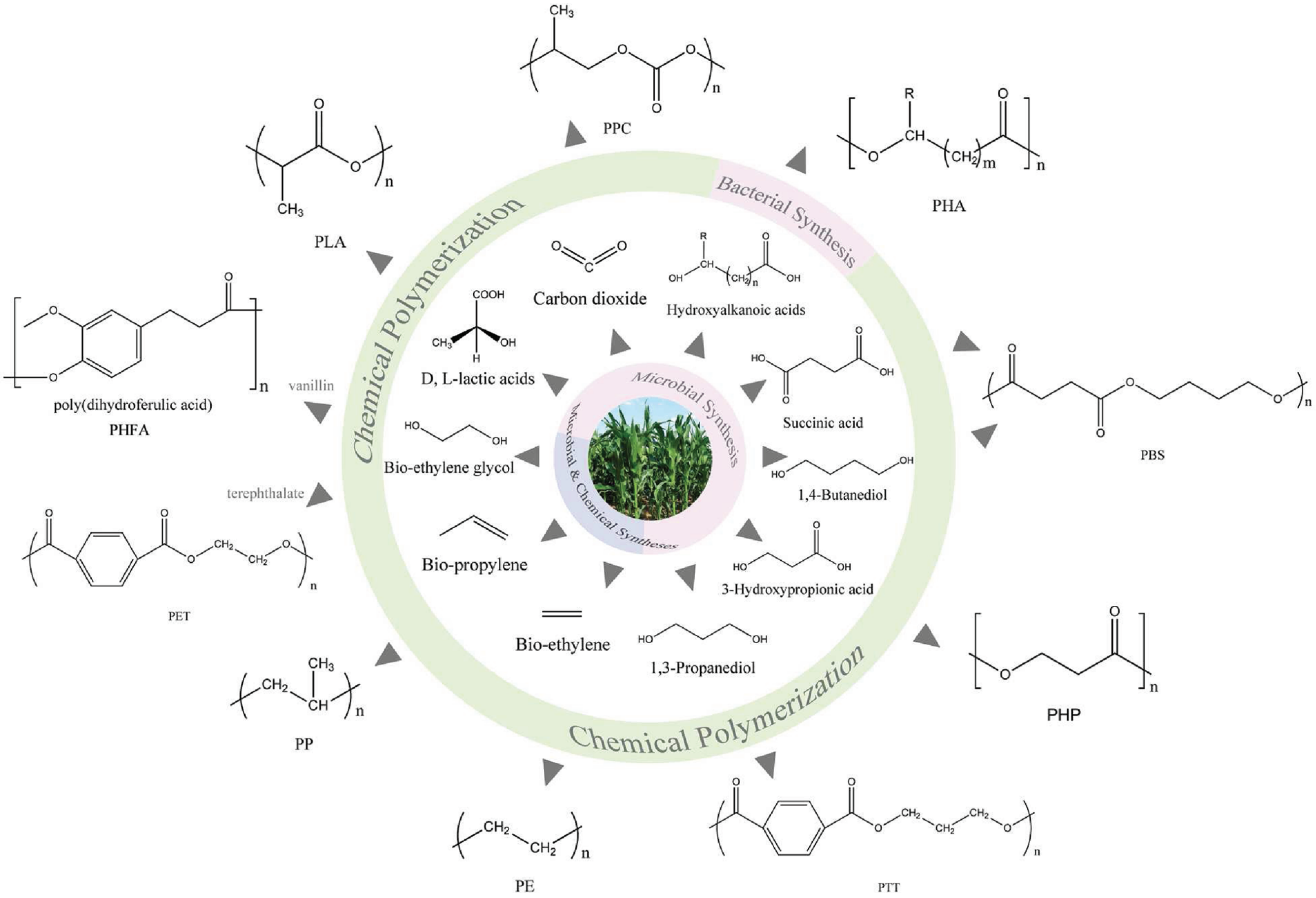

Figure 1. Bioplastics polymers and their monomers produced by microbial fermentations combined with chemical synthese.

biodegradable at different levels (Table 1). Since they are bio-based and biodegradable, PHA, PLA, PBS, and PPC have been proposed as sustainable, environmentally friendly, less petroleum dependent and low-carbon bioplastics for future applications.[5,6]

Because of the increased concern about the depletion of fossil reserves, supply security, greenhouse gas emissions, and feedstock costs, the area of "Plastics from Biological Sources" has been expanding rapidly. Among all bio-based plastics, possibly the most attention is currently being paid to polymers that involve a biotechnological conversion step. These plastics have therefore been chosen as the main focus of this article. They are normally produced by the combination of biological and chemical synthesis with the exception of PHA that are completely synthesized by microorganisms in an aqueous environment (Table 1). These bio-based plastics have been studied by medical experts, polymer scientists, and engineers for their different properties and applications (Table 2).[7] It has become a good example of multidisciplinary research. The purpose of this review is to discuss the production processes of important bio-based monomers and polymers, to compare the thermal and mechanical properties of the bio-based plastics, and to assess their environmental performance.

2. MONOMERS PRODUCED BY BACTERIA FOR POLYMERIZATION

Hydroxyalkanoic Acids

Hydroxyalkanoic acids (HA), monomers of PHA, can be produced via several routes including chemical synthesis, acidic hydrolysis of PHA, in vitro and in vivo enzymatic depolymerization of PHA (Figure 2),[8−10] conversion of 3-hydroxyalkanenitriles to 3-hydroxyalkanoic acids using a combination of nitrile hydratase and amidase.[11] However, metabolic engineering approaches for direct and extracellular production of various HA are believed to be more favorable since hydroxyalkanoates could then be directly obtained in the culture broth.[12−18] Although PHAs are completely synthesized by in vivo processes inside the bacteria, hydroxyalkanoic acids can also be used as building blocks for polymer synthesis.[19] Because of the difficulty of obtaining pure HA, the applications of using HA as new polymer building blocks have not been well studied. So far, only 3-hydroxybutyrate and its derivate butyrolactone, which is conveniently obtained from the most common PHA homopolymer, namely, polyhydroxybutyrate (PHB), was used as a monomer to chemically synthesize other polymers.[20]

Recently, metabolic engineering approaches were adopted to construct a *Pseudomonas putida* KT2442 based platform for production of various PHA homopolymers,[21,22] allowing the microbial production of various pure monomers instead of mixed monomers from either PHA degradation or in vivo hydrolyzation (Table 3). This will further permit us to create hydroxyalkanoates based new polymers.

D- and L-Lactic Acid

Lactic acid (LA) can be produced via chemical synthesis or microbial fermentation. However, the chemical processes produce a racemic (50:50) mixture of D-LA and L-LA (D-/L-LA),

Table 1. Bio-Based and Petrochemical Monomers for the Synthesis of Bio-Based Plastics

bioplastics	plastics biodegradability	bio-based monomers	starting substrates, monomer bioproduction and chemical conversion routes	petrochemical monomers	polymerization conditions	refs
PHA	yes	hydroxyalkanoates	glucose or fatty acids	no	substrate purity not required, aqueous phase, <40 °C	55, 56
PLA	yes	D,L-lactic acids	glucose	no	high lactate purity required, nitrogen atmosphere, >100 °C	23, 24
PBS	yes	succinic acid, 1,4-butanediol	glucose	no	high monomer substrate purity required, nitrogen atmosphere, >100 °C	25
PPC	yes	carbon dioxide	biorespiration or chemical oxidation	propylene oxide	high monomer substrate purity required, N_2 atmosphere, high pressure of 5 MPa, >80 °C	6
PTT	slow	1,3-propanediol	glycerol	terephthalate	high monomer substrate purity required, N_2 atmosphere, 50−210 °C	36
PE	very slow	bioethylene	glucose to ethanol to ethyelene	no	high monomer substrate purity required, N_2 atmosphere, high pressure, >80 °C	40
PP	very slow	bioisobutanol	glucose to isobutanol to butylenes to 2-butylene, and metathesis with ethylene to propylene	no	high monomer substrate purity required, N_2 atmosphere, high pressure, >70 °C	42−44
PET	very slow	bioethylene glycol	glucose to ethanol to ethylene to ethylene glycol	terephthalate	high monomer substrate purity required, N_2 atmosphere, >100 °C	45−48

Table 2. Comparison of Various Properties of Bio-Based Plastics[a]

								mechanical properties			
bioplastics	bio-based monomers	polymerization approach	$M_w \times 10^4$	poly- dispersity	T_m °C	T_g °C	$T_{d(5\%)}$ °C	Young's modulus MPa	elongation at break (%)	tensile strength MPa	refs
PHA	hydroxyalkanoates	biological	10−1000	1.2−6.0	60−177	−50 to 4	227−256	flexible	2−1000	17−104	5
PLA	D,L-lactic acids	chemical	5−50	1.8−2.6	175	60	339	2000−3000	5.2−2.4	61.6−49.6	23
PBS	succinic acid 1,4-butanediol	chemical	3−20	2.0−6.3	112−116	−33 to −36.6	353	268.0	175.2	24.8	25
PPC	carbon dioxide	chemical	5−36 (Mn)	1.72−2.79	125−140	35−36	190−250	993−6900	3−5	33.2	6
PTT	1,3-propanediol	chemical	3.8	2	227.55	42.6	364	727.88	159.48	49.24	36
PE (HDPE)	bioethylene	chemical	10−800	1.07−10	125−135	−133 to −113	350	413−1034	12−700	17.9−33.1	39, 118
PP	biopropylene	chemical	10−60	5−12	161−165	−13 to −2	330	1032−1720	500−900	29.3−38.6	122
PET	bioethylene glycol	chemical	2−3	2−5	265	69−115	420	2000−2700	180	50	51, 121, 122

[a] M_w: molecular weight measured by GPC. $T_{d(5\%)}$: temperature at 5% weight loss determined by TGA. T_m: melting temperature. T_g: glass-transition temperature. Mn: number average molecular weight. HDPE: high density PE.

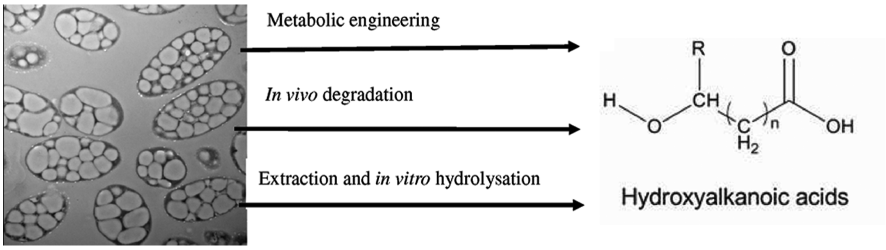

Figure 2. Microbial production of hydroxyalkanoic acids.

Table 3. Biotechnological and Chemical Conversions for the Production of Bio-Based Monomers

Bio-Plastics	Bio-based monomers	Production routes	Refs
PHA	Hydroxyalkanoates	Glucose or Fatty acids $\xrightarrow{\text{Bacterial fermentation-}}$ Hydroxyalkanoyl-CoA $\xrightarrow{\textit{In vivo}\text{ transformation}}$ Hydroxyalkanoates	5, 55,56
PLA	D, L-lactic acids	Glucose $\xrightarrow{\text{Fermentation of lactic acid bacteria}}$ D-lactic acids or L-lactic acids	23
PBS	Succinic acid, 1,4-butanediol	Glucose $\xrightarrow{\text{Fermentation of } \textit{Actinobacillus succinogenes, Anaerobiospirillum succiniciproducens} \text{ or } \textit{Mannheiminia succiniproducens}}$ Succinic acid Succinic acid $\xrightarrow{\text{Hydrogenation under the catalysis of activated carbon-supported Ru and Pd catalysts}}$ 1,4-Butanediol	25
PPC	Carbon dioxide	Bio-respiration or chemical oxidation	6
PTT	1,3-Propanediol	Glycerol $\xrightarrow{\text{Fermentation of } \textit{Klebsiella pneumoniae, Enterobacter agglomerans} \text{ or } \textit{Citrobacter freundii}}$ 1,3-Propanediol	36
PE	Bio-ethylene	Glucose $\xrightarrow{\text{Yeast fermentation}}$ Ethanol $\xrightarrow{\text{Dehydration under the catalysis of activated clay, phosphoric acid or activated aluminia}}$ Ethylene	40
PP	Bio-isobutanol	Glucose $\xrightarrow{\text{Fermentation of recombinant } \textit{E. coli}}$ isobutanol $\xrightarrow{\text{Dehydration}}$ butylenes $\xrightarrow{\text{Isomerization}}$ 2-butylene $\xrightarrow{\text{Metathesis with ethylene}}$ Propylene	42-45
PET	Bio-ethylene glycol	Glucose $\xrightarrow{\text{Yeast fermentation}}$ Ethanol $\xrightarrow{\text{Dehydration under the catalysis of activated clay, phosphoric acid or activated aluminia}}$ Ethylene $\xrightarrow{\text{Direct oxidation of ethylene followed by thermal hydrolysis}}$ Ethylene glycol	47, 49

which is not desirable for food, drink, and pharmaceutical industries due to the metabolic problems that D-LA may cause. For the polylactic acid (PLA) industry, typically lactic acid with high optical purity of over 98−99% of L-LA is required, and therefore, the chemical synthesis is not appropriate for this application.[23]

Many bacteria contain an enzyme called lactate dehydrogenase (LDH) which converts pyruvic acid to lactic acid. Depending on the bacterial species and its LDH specificity, the lactic acid fermentation process can produce very pure D-LA or L-LA or a mixture of them. Molecular biology tools have been employed to delete the D-LDH gene(s) in production strains to enhance the optical purity of its L-LA synthesis.[23]

The most significant cost for LA anaerobic fermentation comes from feedstocks such as carbohydrates. Two molecules of lactic acid are produced from one molecule of glucose via the "glycolysis" pathway. When lactic acid is accumulated in the broth, the pH is reduced, leading to inhibition of LA accumulation. An optimal pH can be maintained during the LA fermentation processes by adding $CaCO_3$, $Ca(OH)_2$, or ammonium hydroxide to the fermentation broth.[23]

Under high temperatures (>100 °C), D-LA or L-LA may be converted to each other through a racemization process, which eventually results in a racemic mixture with inferior optical properties (see section 2).[23,24] Therefore, processing at elevated temperature should be avoided.

Purified LA can be neutralized to form LA salt such as sodium lactate and calcium lactate. Water evaporation results in solid forms of LA salts after spray-drying, crystallization, and granulation.[23,24] LA esters can be produced by reacting LA with alcohols including methanol, ethanol, propanol, or butanol. LA can also be dehydrated to become lactide, which can be subsequently polymerized to poly(lactic acid) (PLA) (Table 3).[23]

Succinic Acid

By analogy with LA, succinic acid (SA) can be produced by means of a chemical process or by microbial fermentation. Several chemical synthesis processes for SA production are available.[25,26] For downstream processing, electrodialysis is a very promising technology due to its high yield, low cost, high purity, and very low or no waste formation. SA produced using this the electrochemical process is permitted for uses in food and pharmaceutical industries.[25]

Various microorganisms were reported to produce SA, including gastrointestinal bacteria, rumen bacteria, and *Lactobacillus* spp.[27] Bacteria such as *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, and *Mannheimia succiniciproducens* are commonly used for industrial SA production.[28−32] Feedstocks including corn starch, corn steep liquor, whey, cane molasses, glycerol, lignocelluloses, cereals, and straw hydrolysates could be utilized for microbial SA production.[25] The SA fermentation consumes 1 mol of CO_2 per mole of SA produced in theory: 1 mol of glucose and 2 mol of CO_2 are transformed into 2 mol of SA. In reality, fermentation byproducts including acetate and formate distort the above balance. Efforts have been made to develop more productive strains that can tolerate high SA concentration and utilize cheap feedstocks.

While improvements in the bioconversion step are aimed to reduce production costs, the costs related to downstream processing can also be very substantial (60−70% of the total production costs of SA).[25,33] Therefore, it is important to develop processes for low cost SA separation and purification for economic SA production.[25]

The Dutch chemical company DSM and the French starch and starch derivative producer Roquette have built a demonstration plant in France for production of several hundred tons of SA per year from starch using an innovative enzyme-based fermentation technology.[25] Also BASF and the Dutch company Purac are jointly pursuing SA production, and further players are BioAmber, Myriant and Amyris. Mitsubishi Japan has also attempted to industrialize SA microbial production for the company's PBS trade named GS Pla.[25] Recently, Myriant Technology based in the United States has joined the SA microbial production business.

1,4-Butanediol

San Diego based Genomatica Inc. developed a sucrose-based process for the manufacture of 1,4-butanediol, of which 1.3 million tons/year are nowadays produced from petrochemical feedstocks. Commercial production of 1,4-butanediol from sugar by an engineered microorganism is expected to bring about substantial cost advantages compared to current petrochemical processes next to lower energy use and greenhouse gas (GHG) emissions.[34] However, most 1,4-butanediol is still produced from chemical processes. Recently, an aqueous-phase hydrogenation of biomass-based succinic acid to 1,4-butanediol over supported bimetallic catalysts was reported, hence representing another production route to bio-based 1,4-butanediol.[35]

1,3-Propanediol

All chemical processes for preparation of 1,3-propanediol (PDO) use a similar intermediate: 3-hydroxypropionaldehyde, which is chemically synthesized and then chemically reduced to PDO via hydrogenation; this conversion step is usually easy compared to the preparation of 3-hydroxypropionaldehyde.[36]

Some bacteria are able to produce PDO using glycerol as a substrate, including *Klebsiella pneumoniae*, *Enterobacter agglomerans*, *Citrobacter freundii*, *Clostridium acetobutylicum*, *Clostridium butyricum*, *Clostridium pasteurianum*, *Lactobacillus brevis*, and *Lactobacillus buchneri*.[28] Among these organisms, *K. pneumoniae*, *C. freundii*, and *C. butyricum* showed higher PDO yields and productivities. Fungi *Aspergillus niger* and *A. oryzae* were also found to produce PDO from glycerol with low production ability.[37]

Production of PDO from glycerol is generally conducted anaerobically. Through the microbial oxidative pathway, glycerol is dehydrogenated by an NAD^+ linked glycerol dehydrogenase (GDH) to dihydroxyacetone (DHA), followed by phosphorylation under PEP- and ATP-dependent DHA kinases (DHAK). In a parallel reductive pathway, glycerol is dehydrated by coenzyme B_{12}-dependent glycerol dehydratase (GDHt) to form 3-hydroxypropionaldehyde (3-HPA), which is then reduced to PDO by $NADH_2$ linked PDO dehydrogenase (PDOR).[36]

Microbial PDO production is regulated by *glp* and *dha* regulons.[38] Gene expressions under the *dha* regulon can be induced by dihydroxyacetone (DHA).[39] Genes coding enzymes of glycerol metabolism including glycerol dehydratase (*dhaB*), PDO oxido-reductase (*dhaT*), glycerol dehydrogenase (*dhaD*), dihydroxyacetone kinase (*dhaK*), and a putative regulator *dhaR* have been cloned and sequenced,[36] allowing constructions of various PDO recombinant producers with enhanced production ability.

Glycerol metabolism is aerobically regulated by the *glp* regulon. Glycerol is first converted to glycerol-3-phosphate catalyzed by glycerol kinase, followed by oxidation to dihydroxyacetone phosphate catalyzed by dehydrogenase. The *glp* regulon contains six genes including *glpFK* encoding cytoplasmic membrane protein which facilitates the diffusion of glycerol into the cell and glycerol kinase, *glpTQ* encoding glycerophosphodiester phosphodiesterase, *glpABC* encoding anaerobic *sn*-glycerol-3-phosphate dehydrogenase, *glpD* encoding *sn*-glycerol-3-phosphate dehydrogenase with its regulator *glpR* close to *glpD* encoding an 33KD inhibitor, and two more genes *glpE* and *glpG* located between *glpD* and *glpR* without clear functions.[39] The above regulatory mechanisms have been used to construct enhanced PDO production recombinants.[36]

The production of bio-based PDO was developed and commercialized by the joint venture DuPont Tate & Lyle LLC. Today, bio-based PDO is produced by aerobic fermentation of glucose from corn starch, with a annual capacity of 45 000 tons (100 million pounds/year).

Bioethylene

Microbial ethanol is being produced at the multimillion ton scale (for application as biofuel) from starch (primarily from corn) and sugar (primarily from sugar cane), and major efforts are being made to reach the commercialization of bioethanol from lignocellulosic feedstocks such as wood, corn stalks, and other plant wastes via fermentation processes.[40]

Bioethanol can be catalytically dehydrated to ethylene with activated clay, phosphoric acid, sulfuric acid, activated alumina, transition metal oxides, transition metal composite oxides, and heteropolyacid zeolites as catalysts.[41] Currently, industrial ethanol dehydration to ethylene uses gas—solid phase dehydration. Ethanol is pretreated and then fed to the reactor in the gas state. The reaction of ethanol dehydration to ethylene is an endothermic reaction; column reactors were first used to improve the efficiency of heat transfer.[42] Ethanol dehydration to ethylene is a proven technology, and various processes were developed based on different catalysts.[40]

Biopropylene

The production of bio-based propylene is technologically more challenging than bio-based ethylene, explaining why bio-based propylene has not yet been commercialized. A route to bio-based propylene has been proposed which consists of the following steps: biotechnological production of isobutanol,[43] dehydration to butylenes, isomerization to 2-butylene,[44] and metathesis with ethylene to propylene.[45] The Brazilian company Braskem has plans to construct a biopropylene plant with a capacity of at least 30 000 tons by 2013. Another route may be the production of 1,2-propanediol or acetone via fermentation and the further conversion to 2-propanol, followed by dehydration to propylene.[46]

Bioethylene Glycol and Bioaromatic Monomers for Polyethylene Terephthalate (PET) and Its Mimics

Using bio-based ethylene, bio-based ethylene glycol can be produced via application of a well-known technology: oxidation to ethylene oxide followed by hydrolysis to ethylene glycol.[47,48]

To produce bio-PET and its mimics, aromatic or other ring-shaped components are needed. The most abundant biorenewable source of aromatic compounds is lignin which can be found in all vascular plants. Lignin is the second most abundant naturally occurring organic polymer, it makes up approximately 30% of wood.[49] The lignin extraction from wood is common in the paper pulping industry and can yield up to 5% of the aromatic aldehydes vanillin and up to 8% of syringaldehyde (Figure 3).[50] If produced at large scale, bio-based para-xylene could be converted to terephthalic acid (i.e., the second monomer of PET next to ethylene glycol) based on technology that is currently applied by the chemical industry. An alternative approach would be to replace terephthalic acid by a different chemical compound derived from biomass. A promising option is 2,5-furandicarboxylic acid (FDCA) which is produced in two steps: catalytic

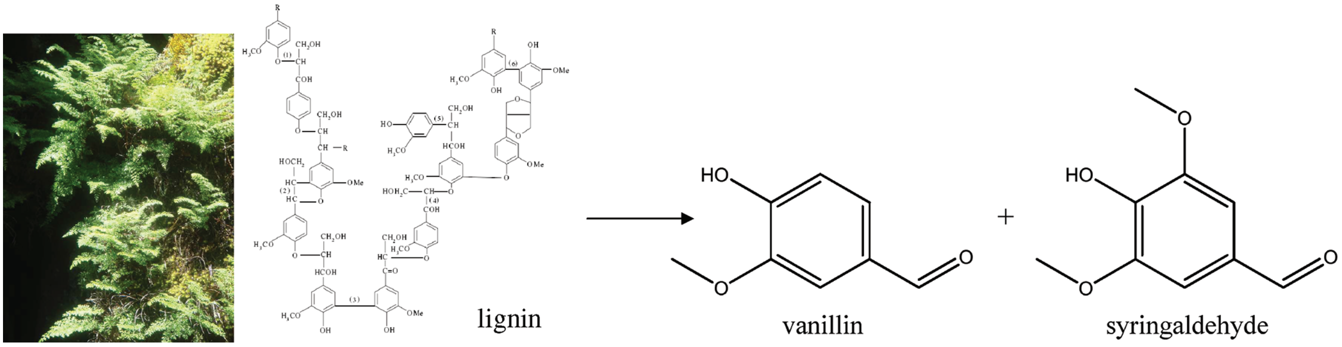

Figure 3. Aromatic compounds vanillin and syringaldehyde from lignin extraction during the production of paper.[48]

dehydration of fructose to 5-hydroxymethylfurfural,[51] which is converted to FDCA by another catalytic step.[52]

3. TECHNOLOGIES FOR POLYMERIZATION OF THE BIO-MONOMERS

In the following, the polymerization technology is described for bioplastics with substantial market potential.[53]

3.1. Polymers Produced Completely by Biosynthesis Processes

Polyhydroxyalkanoates (PHA), a family of biopolyesters with diverse structures, are the only bioplastics completely synthesized by microorganisms. PHA can be synthesized by over 30% of soil inhabiting bacteria.[54] Many bacteria in activated sludge, in high sea, and in extreme environments are also capable of making PHA.

PHA has diverse properties depending on the structure (Figure 1). Homopolymers, random copolymers, and block copolymers of PHA can be produced depending on the bacterial species and growth conditions. With over 150 different PHA monomers being reported, PHA with flexible thermo- and mechanical properties have been developed.[55] Such diversity has allowed the development of various applications including environmentally friendly biodegradable plastics for packaging purposes, fibers, biodegradable, and biocompatible implants and controlled drug release carriers.[55] PHA monomers can also be used to develop biofuels, drugs or chiral intermediates, and oligomers of PHA were reported to serve as valuable food additives for animals (Figure 4).[56] PHA associated proteins have also been used to develop applications for endotoxin removal[57] and surface modifications for better cell attachments and growth,[58,59] as well as for studying protein−protein interactions.[60] More and more applications are under intensive research. Globally more than 20 companies have been established to commercialize these developments.[55]

PHA can either be synthesized by chemical means or by biological approaches.[61,62] Biosynthesis of PHA leads to much higher molecular weight compared to chemical methods.[61] However, in the case of biosynthesis, it is difficult to control the monomer structures and ratios in the PHA polymers because the specificity of PHA polymerase (or PHA synthase) will influence the monomers to be incorporated into the polymers.[63,64] Recently, a *Pseudomonas putida* based platform has been successfully established for producing PHA homopolymers and block copolymers using related fatty acids,[21,22] and this has opened up new options to diversify PHA monomers and microstructures. Further, PHA development appears to be limited only by imagination and commonly applied practices.

3.2. Polymers Produced Using at Least One Monomer from Bioprocessing

Polylactic Acid (PLA). Polymerization of PLA has been conducted since 1932 by either a direct polycondensation of LA, or by a ring-opening reaction of lactide, a cyclic dimer of lactic acid.[23] Both processes rely on highly purified lactic acid or lactide for high molecular weights, and they both allow production of PLA with a high yield.

The physical and mechanical properties of PLA as well as its degradation properties are intimately dependent on the chain stereochemistry. For example, isotactic poly(L-lactide) (PLLA) is a semicrystalline polymer with a melting transition near 180 °C, while atactic poly-(*rac*-LA) (*rac*-LA is a 1:1 mixture of L-lactide and D-lactide) and poly(*meso*-lactide) are amorphous polymers.[65]

Interestingly, the equivalent mixture of L-PLA and D-PLA forms a crystalline stereocomplex with a high melting temperature at 230 °C. A monoethylaluminum Schiff base complex,[61] enolic Schiff base aluminum(III) complexes,[66] and several other aluminum Schiff base catalysts[67,68] were synthesized and found to achieve stereoselective ring-opening polymerization of rac-lactide (*rac*-LA). The polymerization yielded crystalline poly (*rac*-LA) with a high melting temperature (193−201 °C).[65−68] The relationship between the *rac*-LA conversion and molecular weights of the polymer was linear so that the polymerization could be well controlled.[65,69]

Crude lactic acid with impurities could strongly impact the polymerization process, the yield, and PLA properties. Therefore, purification of lactic from the industrial fermentation process is of key importance for producing a PLA with good quality.[23]

The direct polycondensation process (DPC) dehydrates LA to form oligomers which are further polymerized to PLA under simultaneous dehydration to avoid the degradation of polymer in the presence of moisture. Removal of water generated by the LA condensation is usually very difficult during the final stage of polymerization as the diffusion of moisture in a highly viscous polymeric melt is very slow. The residual water trapped in the PLA melt will reduce PLA molecular weights. As a result, the direct polymerization process is reported to be used only by two companies, namely, Tongji (Shanghai) and Mitsui Chemicals (Japan).[23,70]

Most industrial PLA production processes employ the conversion of lactide, a cyclic dimer of LA, to PLA via a ring-opening polymerization process (ROP) catalyzed by organometal catalysts.[23,65−68] During the process, LA is dehydrated and condensed into its oligomers at high temperature under a vacuum to remove moisture. Subsequently lactide is obtained from catalytic depolymerization of these short polylactic acid chains under reduced

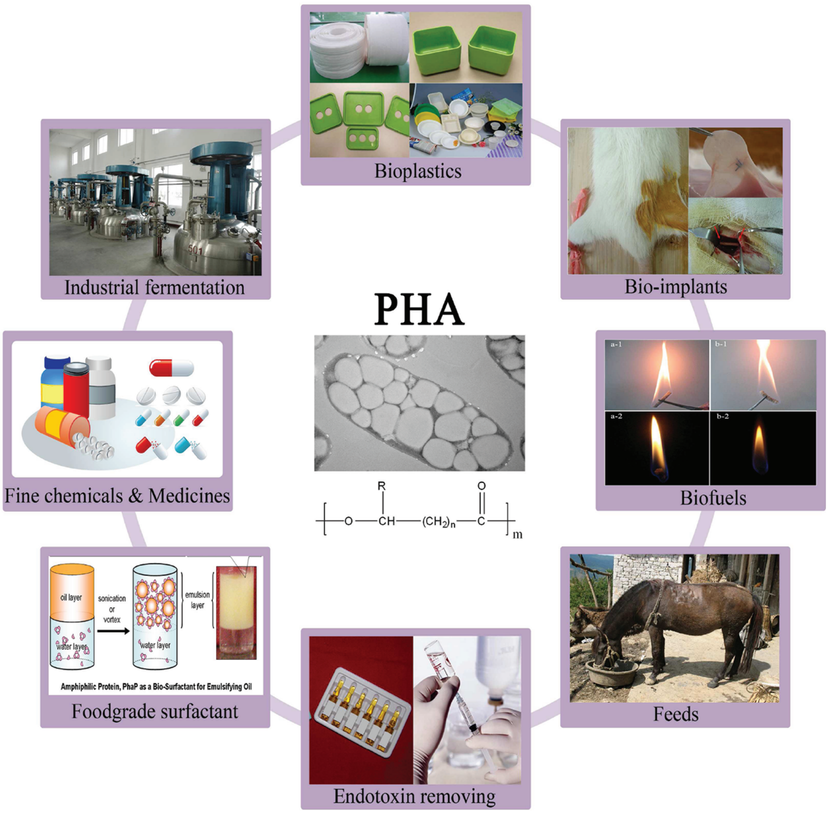

Figure 4. PHA industrial value chain ranging from industrial fermentation, bioplastics, medical bioimplants, biofuels, feed additives, endotoxin removal, food grade surfactant, fine chemicals, and medicines.

pressure. Residual LA is removed from lactide via distillation or crystallization. The purified lactide is polymerized by a ring-opening reaction into PLA at temperatures above the melting point of lactide and below the degradation temperatures of PLA. The resulting PLA resin is solidified and/or crystallized into pellets. During the ring-opening polymerization of lactide, there is no moisture to be removed from the melt PLA resin.[23] Purified PLA is compounded with additives and extruded to form resin pellets for crystallization and packaging as a final product.[23]

Generally, polymer-grade L-LA as used for commercial PLA production contains over 98−99% L-LA and less than 1−2% of D-LA. When L-LA is dehydrated at high temperature into L-lactide, some L-LA may be isomerized to D-LA. D-LA mixed in L-LA contributes to formation of meso-lactide, the cyclic dimer of one D-LA and one L-LA, leading to PLA heteropolymer containing both D-LA and L-LA monomers. PLA heteropolymers have slower crystallization kinetics and lower melting points compared to their PLA homopolymers consisting of only L-LA or D-LA monomer.[23] Heteropolymers should be avoided.

Poly(butylene succinate) (PBS). The pioneer synthetic method for PBS is transesterification polycondensation,[25] in which PBS is synthesized by melt polymerization starting from stoichiometric amounts of dimethyl succinate and 1,4-butanediol, or by using an excess of 1,4-butanediol not above 10%, in the presence of catalyst such as tetra-*n*-butyl-titanate, tetra-isopropyl titanate.[25] The reactor is first filled with nitrogen in order to remove air and avoid oxidation during the transesterification process. The process is started under intensive mixing at 150−190 °C under nitrogen atmosphere. After the removal of most of the methanol resulting from transesterication, the polycondensation process is initiated under a vacuum at 200 °C and beyond in order to remove the resulting butanediol and to polymerize the oligomers. PBS with M_n of 60 000 and M_w of 100 000 can be synthesized from such a process.[25,70]

Direct melt polymerization of succinic acid and butanediol to PBS can be carried out via two approaches: one starts the polymerization directly in the melt of succinic acid and butanediol (melt polymerization); another initiates the polymerization in the solution of raw materials (solution polymerization). Direct melt polymerization is simple in operation and it yields PBS with high molecular weights. Therefore, direct melt polymerization is considered as a promising process for production of PBS aimed for food contact packaging applications.[25]

A chain extender with two functional groups can react with the terminal −OH or COOH groups of PBS, leading to PBS with high molecular weight. Ideally, a chain extender can couple two PBS chains.[28,29] Because of biosafety and biodegradability considerations, chain extended PBS is not allowed to be used as a food-contact packaging material.[25]

Poly(trimethylene terephthalate) (PTT). PTT is a semi-crystalline polymer synthesized by condensation of PDO with either terephthalic acid or dimethyl terephthalate, followed by polymerization. Studies of PTT remained an academic interest until PDO became available at a reasonable cost. Recent breakthroughs in PDO production allow PTT to be available in industrial quantities, offering new opportunities for PTT markets in applications of carpets, textiles, films, packaging, and engineering thermoplastics.[36]

PTT synthesis is similar to that of PET involving direct esterification and ester interchange polymerization. During the

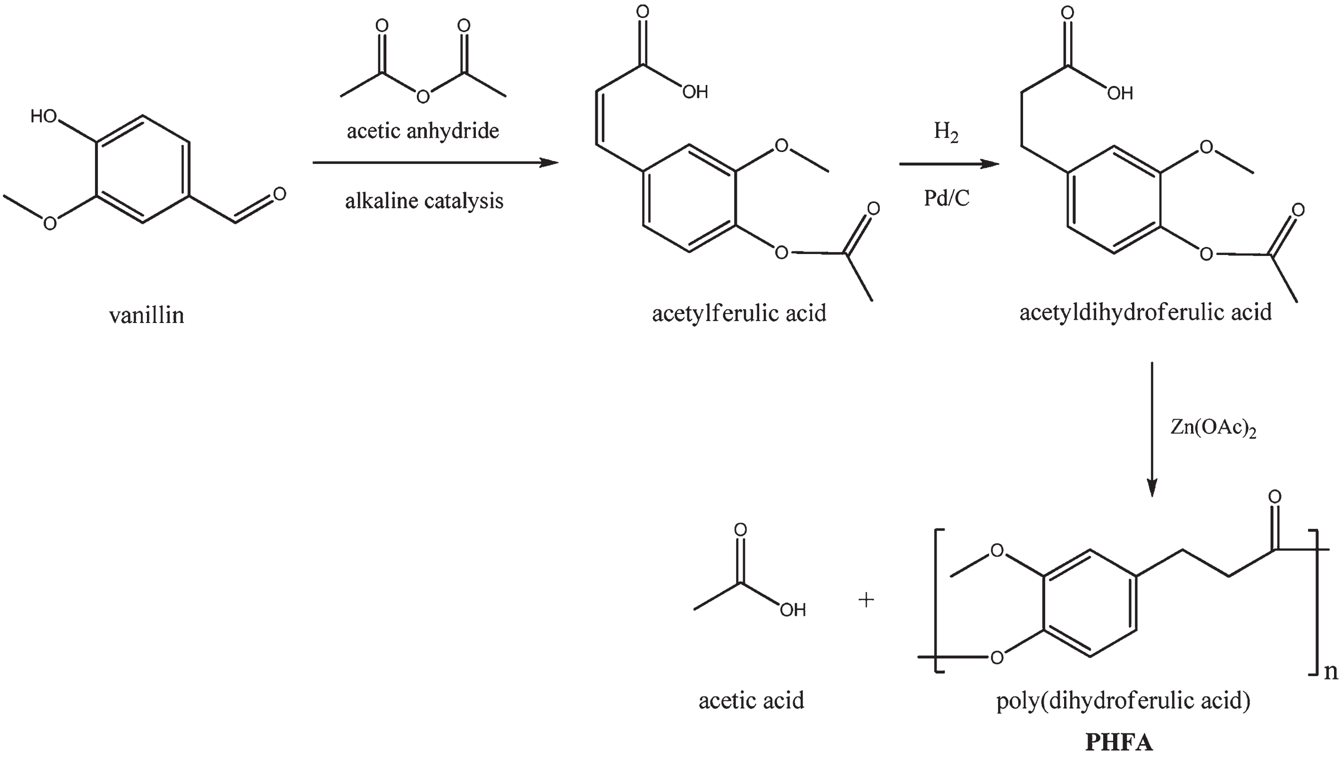

Figure 5. Synthesis of the PET like aromatic/aliphatic polyester poly(dihydroferulic acid), PHFA, from vanillin and acetic anhydride.[48]

first stage of polymerization, TPA (terephthalic acid) or DMT (dimethyl terephthalate) is mixed with PDO to form oligomers of up to six monomers. In the second stage, this oligomer is polycondensed to form PTT consisting of 60−100 monomers. The catalyst used in the first step accelerates the polycondensation reaction. DuPont is currently producing PTT from bio-based PDO (see section 2) and petrochemical TPA.

Polyethylene (PE). There is a long history of producing bio-based ethylene by dehydration of ethanol including first developments in Western Europe in the early 20th century and industrial application until the 1980s in a few countries including India and Brazil before being replaced worldwide by petrochemical steam cracking.[71,72] Some of this ethylene was converted to polyethylene, but it was also produced for other purposes such as polyvinyl chloride (PVC) and styrene. The polymerization of bio-based ethylene is identical with the process for polymerizing petrochemical ethylene, which has been applied at a very large scale for decades.

The Brazilian company Braskem is the first company to offer bio-based polyethylene at a commercial scale.

Polypropylene (PP). While the production of bio-based propylene is not straightforward, it consists of the following steps including biotechnological production of isobutanol,[43] dehydration to butylenes, isomerization to 2-butylene,[44] and metathesis with ethylene to propylene.[45] Its conversion to bio-based polypropylene (PP) is based on the same technology as petrochemical PP which is produced at a very large scale. Brazilian Braskem has planned to construct a plant of at least 30 000 ton green bio polypropylene by 2013 using biopropylene derived from ethylene.

Polyethylene Terephthalate (PET). Polyethylene terephthalate (PET), which was first commercialized in the 1940s, is nowadays primarily produced via direct esterification of terephthalic acid (TPA) with ethylene glycol.[47,48] Using bio-based ethylene glycol, partially bio-based PET can easily be synthesized. Bio-based PET has been used since recently for selected markets by Coca-Cola and other beverage companies.[73] So far, the TPA continues to be produced from petrochemical feedstocks, although, in principle, it can also be produced from biofeedstocks: Ryan (2010) proposes to convert biotechnologically produced isobutanol to *p*-xylene via dehydration, dimerization, and aromatization.[72] Other options may be to use bio-based xylene produced by depolymerization of lignin, to make it from 2.5-furandicarboxylic acid (FDCA) or to directly replace TPA by FDCA.[49,50]

Lignin-based vanillin and acetic anhydride are subjected to the Perkin reaction and then hydrogenation to produce acetyldihydroferulic acid. Polymerization of this monomer yields poly(dihydroferulic acid), which exhibits thermal properties functionally similar to those of polyethylene terephthalate (PET) (Figure 5).[51]

Poly(propylene carbonate) (PPC). There are different opinions on whether the use of CO_2 as a raw material for generating chemicals is “green chemistry”. The current use of polymers and worldwide fossil fuel consumption differ by 2 orders of magnitude. Therefore, the fixation of CO_2 into polymers will not substantially contribute to reduce anthropogenic CO_2 emissions.[6] Nevertheless, using CO_2 as feedstock meets the requirements of sustainable development, and it offers opportunities to produce some biodegradable compounds.[74] From this viewpoint, this reaction can be considered as “green chemistry”.[6]

Though currently many CO_2 copolymers have been prepared in the lab, only a few of them have the potential for commercialization in view of the complexity of the production process, cost, and property limitations. Among them, poly(propylene carbonate) (PPC) is perhaps the most important one, receiving a lot of attention both in academy and in industry. PPC can be prepared via terpolymerization of carbon dioxide, propylene oxide and diepoxide using $Y(CCl_3OO)_3$-$ZnEt_2$-glycerine coordination catalyst.[75] When equimolar $ZnEt_2$ and diepoxide are used, double propagation active species are generated in situ by nucleophilic attack of metal alkoxide on diepoxide, leading to PPC with doubled molecular weight. PPC molecular weights have a strong influence on polymer thermal and mechanical performances: PPC with an average molecular weight M_n of 23 000 Da (kDa) shows a Young's modulus of 6900 MPa at room temperature, while the Young's modulus of PPC with M_n of 11 kDa has only 4300 MPa. Moreover, when Mn increases from 11 to 23 kDa, a 37 °C increase in the onset degradation temperature is observed.[6]

The thermal and mechanical performance of these CO_2 copolymers is not satisfactory.[6] Intrinsic properties of these polymers are difficult to change. Therefore, the development of improved catalyst systems and new CO_2-based polymers with a better performance are two important objectives. Other options of CO_2 usage for the production of intermediates and polymers are its conversion to polycarbonates and polyurethanes.[76]

4. PROPERTIES OF THE BIO-BASED POLYMERS

4.1. Thermal and Mechanical Properties

Although the plastics discussed above are bio-based, their properties are often very similar to traditional petroleum-based plastics.

PHAs are most diverse in structure, resulting in wide ranges of melting temperatures (T_m, from 60 to 177 °C), glass transition temperatures (T_g, from −50 to 4 °C), and thermo-degradation temperatures ($T_{d(5\%)}$, from 227 to 256 °C).[5] Mechanical properties including very flexible Young's modulus, their elongation at break and tensile strength range from 2 to 1000% and 17−104 MPa, respectively (Table 2).

In comparison, low cost PLA, typically consisting of more than 4% of D-LA next to L-LA, is brittle with an elongation to break of 5.2−2.4%; however, its tensile strength is the highest among the studied plastics, ranging from 49.6 to 61.6 MPa together with a Young's modulus of 384−481 MPa (Table 2).[5] A T_g of 60 °C of this type of PLA has been a weak point as articles made from this material change their shapes at this temperature; as mentioned above, this problem can be overcome by stereochemistry.

PBS has a melting temperature (T_m), a glass transition temperature (T_g), and a thermo-degradation temperature ($T_{d(5\%)}$) ranging from 112 to 116 °C, −33 to −37 °C, and 353 °C, respectively.[5] Young's modulus, elongation at break, and tensile strength of PBS are around 268 MPa, 175%, and 25 MPa, respectively. In addition, PBS is thermally quite stable with a $T_{d(5\%)}$ of 353 °C. It is a quite flexible material with considerable strength, making it suitable for many applications (Table 2).

PE based on bioethanol has the same properties as petroleum-based PE; that is, it also has a high elongation at break of 298% with a T_g around −133 and −113 °C.[5] As a consequence, bio-based and petrochemical PP have identical properties.

Partially bio-based PTT is a reasonably elastic material (159% elongation at break)[5,29] with the highest Young's modulus among all plastics mentioned here.[36]

There are several routes to improve the thermal stability of PPC. One of them is to raise the molecular weight of PPC in order to reduce the hydroxyl group concentration in PPC. However, the thermal degradation temperature does not increase linearly when the molecular weight increases from 50 kDa to 360 kDa; instead, the thermal decomposition temperature at 5 wt % loss increases by only 30 °C.[77−79]

4.2. Biodegradability and Biocompatibility

Enzymes and microorganisms such as bacteria and fungi are involved in the degradation of both natural and synthetic plastics (Table 1).[79−81] The biodegradation proceeds differently under different soil conditions depending on their different properties. PHA are natural plastics, which microorganisms can produce and store under nutrient limited conditions, they can be degraded and metabolized when the carbon or energy source is in limitation.[79] The first metabolite of the biodegradation of PHB is $R\bar{3}$-hydroxybutyric acid, while extracellular degradation of PHBV yields both 3-hydroxybutyrate and 3-hydroxyvalerate. The PHA monomers are water-soluble and small enough to passively diffuse through bacterial cell walls, where they are metabolized by β-oxidation and tricarboxylic acid cycle (TCA) to produce carbon dioxide and water under aerobic conditions.[5]

Abiotic hydrolysis is the most important reaction for initiating the environmental degradation of synthetic polymers such as PE,[79,81] PTT,[82] PLA, and their copolymers.[83,84] The degradation of most synthetic plastics in nature is slower than natural polyester. This process involves environmental factors, followed by the action of microorganisms in their surroundings.[5,85,86]

PLA is fully biodegradable under composting conditions at temperatures of 60 °C and above.[87] PBS is hydro-biodegradable and begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages and it reduces the molecular weight of the polymer, allowing for further degradation by much more microorganisms.[23,88] Biodegradation of polyethylene, if it does happen, probably proceeds by two mechanisms: hydro-biodegradation and oxo-biodegradation.[5,88]

PPC has been regarded as a biodegradable polymer due to the existence of a carbonate group in the backbone. However, research on its biodegradability is still in the preliminary stage, especially for PPC with a high molecular weight. It is accepted that PPC of high molecular weight degrades slowly in soil or in neutral buffer solution. Under standard composting conditions at 60 °C, however, PPC can be degraded at an observable rate during a period of 69 days.[88]

5. ENVIRONMENTAL ASSESSMENT OF PLASTICS PRODUCED BY APPLICATION OF BIOTECHNOLOGY

5.1. LCA Methodology and Specific Aspects Related to Bio-Based Carbon

Life cycle assessment (LCA) is the most widely applied and accepted method for the environmental assessment of products and services. It is a **standardized method** for the compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle. The LCA methodology has been standardized by the International Standards Organisation (ISO) in the ISO-14040 series (ISO, 2006).[89,90] ISO distinguishes the following steps:

- *Goal definition and scoping:* In this step, the purpose and the methodology of the LCA is explained, including the products to be compared; moreover, the functional unit (describing in quantitative terms the primary function/s fulfilled) and the system boundaries are defined and a decision is made about the environmental impacts taken into account.

- *Inventory analysis:* A flow diagram is developed. All resource requirements and the emissions to air, water, and soil are quantified.
- *Impact assessment:* determines the (potential) environmental impacts (e.g., global warming) caused by the environmental releases analyzed in the inventory analysis.
- *Interpretation:* the results of the inventory analysis and the impact assessment are discussed, conclusions are drawn, and recommendations are made.

In this LCA review the chosen **functional unit**, that is, the basis of all comparisons, is 1 metric ton of plastic. It is acknowledged that this is not necessarily a fair starting point, especially when the quality of the plastics studied differs and therefore different amounts of materials are required in order to fulfill the same purpose. One way of overcoming this drawback would be to assess individual end products (e.g., cups, trays, etc.). In view of the enormous number of applications this is, however, not a viable way forward. Another option could be to apply methods that reflect the differences in material properties, for example, the methods developed by Ashby (2005) in order to correct for differences in material properties for specific functions (e.g., beam or panel) in a generic way.[91] Since several material properties need to be considered for each application, this would be very challenging in methodological terms and with regard to the data requirements. It would be commendable to perform this type of exercise for the most relevant combinations of products and applications,[92] but this would exceed the scope of this publication. The functional unit chosen for this article is hence based on practical considerations, but further work is required to draw conclusions at the level of end products.

The chosen system boundary is the **system "cradle-to-factory gate"** which covers all processes from the extraction of resources and/or agriculture up and until the plastic is delivered at the factory gate of its producer. For most applications, the environmental impacts (and benefits) caused by plastics in the use phase (e.g., a flower pot) can generally be neglected; the main exception are products used in vehicles (next to other moved objects), where lightweight construction substantially improves the efficiency. Since the savings very much depend on the concrete application (e.g., car versus airplane) we exclude the use phase from our further analysis. We also exclude post-consumer waste management. Another reasoning behind the choice of the system "cradle-to-factory gate" is that the producers of plastics are primarily responsible for environmental impacts related to this system, while the conversion to end products and their use is in the hands of their clients and of the consumer, and finally, end-of-waste management is typically subject to national policy.

When deciding about scope of the analysis, the chosen **environmental impact categories** should ensure that the analysis is relevant and comprehensive. In this context, comprehensiveness means that all (relevant) environmental impact categories, such as the contribution to climate change, acidification, or human toxicity, are covered. Full coverage is generally not possible given data gaps and the lack of LCA methodologies for several environmental impact categories, for example, for pollution by light or by invasive species. For this reason, even full-fledged LCA studies generally do not cover all potentially important environmental impacts. It has been shown that fossil energy demand is a good first approximation for overall environmental impacts including, for example, climate change, acidification, and eutrophication.[93] On the basis of this finding and due to the diverse coverage of environmental impact categories across the studies reviewed, we present in this paper only results for non-renewable energy use (NREU, i.e., the total of fossil energy and nuclear energy) and greenhouse gas emissions (GHG, 100 year time period). It should be noted that fossil energy demand and consequently also NREU may be unreliable proxies for some impact categories, for example, human toxicity, if toxic chemicals are released by the chemical process. In-depth analyses and comparative assessments of impact categories such as human toxicity are therefore urgently needed for the products studied in this paper. Because of the very limited coverage of environmental impact categories, this paper should not be referred to as review of LCA studies but rather as review of non-renewable energy use related to selected plastics made by industrial biotechnology and their impact on climate change.

When assessing the GHG emissions there are, in principle, two ways of dealing with **bio-based carbon** (always based on the assumption that the biomass used is sustainably grown). Bio-based carbon can either be considered as carbon-neutral because the CO_2 withdrawn from the atmosphere during photosynthesis is returned to the atmosphere within a limited period of time. This is the approach that is generally applied for bioenergy. For bio-based materials – the topic of this article – either the same approach is found in the literature or an alternative approach is used which assumes carbon storage (at least for applications that are in use for more than one year); the reasoning behind this approach is that carbon is extracted from the atmosphere during plant growth and is then embedded in bio-based products (CO_2 from fossil fuels required for transport, processing the crops and producing auxiliaries, e.g., fertilizers, are accounted for separately). The principle of carbon storage is endorsed by International Reference Life Cycle Data System (ILCD) Handbook (Eur. Commission/JRC, 2010)[94] and by the "Publicly Available Specification" PAS 2050 (2008),[95] however with somewhat different approaches for how to consider the time period of carbon storage.

In this review we uniformly apply the principle of carbon storage. Since the functional unit plastic is 1 metric ton of plastic without any distinction between different types of end-use applications, we assume for simplicity full carbon storage over the entire time period (the default period for assessing the greenhouse effect is 100 years). We only account for the bio-based carbon sequestered in the plastic, that is, not in the biofeedstock. As a consequence of accounting for bio-based carbon as storage for the system "cradle-to-factory gate", the release of this bio-based carbon during incineration must be accounted for as greenhouse gas emission.

Throughout this article the assumption is made that the agricultural crops (or other forms of biomass) are grown in a sustainable manner. This is, however, not necessarily the case, with land use change being one possible reason. Two types of land use change can be distinguished, that is, direct land use change (dLUC) and indirect land use change (iLUC).

- An example for **direct land use change (dLUC)** is the direct conversion of tropical rainforest into sugar cane plantations supplying crops for the production of bio-based materials; this can, in principle, be avoided by good management (e.g., by means of certification schemes).
- This is not the case for the so-called **indirect land use change (iLUC)**, which can be explained by the following example describing a domino effect: (i) rapeseed is cultivated in Europe and is converted to bio-based products;

(ii) the land used for this purpose was originally used to grow food crops for human consumption; (iii) these food crops are now imported and a part of them is cultivated on agricultural areas that were originally pristine land such as tropical rainforest.

It should be noted that neither dLUC nor iLUC has been taken into account in the studies reviewed in this article.

So far no fully **harmonized data sets** are available, partly because LCA methodology development is partly still in flow and partly because alternative methodological choices can be equally justifiable depending on the specific circumstances. This concerns, for example, the application of **allocation principles** to processes with multiple outputs. In general, most authors apply the rules laid down by ISO (2006),[89,90] but since these offer some flexibility, the authors of some of the studies discussed in this paper are likely to have used deviating approaches. This leads to uncertainty which we are not able to systematically correct for nor quantify.

R&D is currently ongoing to use lignocellulosics as a feedstock for products made by industrial biotechnology, but so far nearly all commercially available products are made from **starch crops or sugar crops** as feedstock source. Following agriculture, the first step in the process chain is therefore extraction of sugars or starch. This is achieved either by processing sugar crops (sugar cane or sugar beet) or starch-containing crops, such as maize (corn), wheat, or tapioca. In the case of starch crops, the starch is subsequently converted to fermentable sugar by enzymatic hydrolysis or by acid hydrolysis. The fermentable sugar is processed by means of industrial biotechnology to produce bio-based alcohols, acids, or other monomers. These are then chemically processed and often combined with other monomers (ideally bio-based, if available) in order to arrive at the desired polymer.

5.2. Results for NREU and GHG Emissions

Polyhydroxyalkanoates (PHA). As explained above (section 3.1), PHA are produced directly via a biosynthesis process and the polymer accumulates within the microorganism. There are two common methods used for extraction of this PHA, namely, solvent extraction and the so-called enzyme cocktail extraction.[96−98] Variants and combinations of the two approaches are also possible.[96]

The body of the published environmental assessments of PHA production indicates that fermentation and especially downstream processing require substantial amounts of process energy and also auxiliary materials, including, for example, detergents resulting in substantial indirect energy use.[97−101] This is a consequence of the effort that needs to be made to isolate PHA from the interior of the microorganism. Simpler processes can be conceived that involve less process steps and require less process energy and auxiliary materials, but they lead to a product of lower quality (no publicly available detailed information is available on the options and the related trade-offs).

Most of the available environmental assessments reflect the technology at a very early stage of development, including upscaling results from lab research for the fermentation step and assuming a variety of options for downstream processing. Tables 4 and 5 present NREU and GHG values from selected analyses for the system cradle-to-factory gate (further data can be found in Tables S-1 and S-2 of the Supporting Information, which is available online); the first and the last data set for PHA do *not* assume the use of biomass waste, that is, crop residues such as maize stover, for providing heat or power, while the second does make this assumption (in Tables 4 and 5 reported as Kim and Dale, "Near future, *with* use of agricultural residues").[102] The NREU and GHG values for the latter are by far the lowest. But even *excluding* residue use and limiting ourselves to the former data sets, we find widely ranging values, for example, for NREU from less than 40 GJ/t to more than 110 GJ/t. Both of these extreme values originate from the BREW project,[101] and the difference between them is purely related to downstream processing, demonstrating that this is where the challenge lies for PHA. Kim and Dale (2005) prepared their analysis in collaboration with PHA producers Metabolix, ADM and Telles, which makes their results more reliable than other studies.[102] For the case *with* the use of agricultural waste, which Kim and Dale refer to as "integrated system",[102,103] they assumed that 60% of the maize stover or corn stover is removed from the field and that it is used to generate process heat and power with the remaining 40% left on the maize field to avoid soil erosion. While Kim and Dale's results *without* use of crop residues for energy supply (Tables 2−4) fall into the wide range of values according to earlier studies,[101−108] their results *with* use of agricultural waste are very advantageous compared to petrochemical processes. This is possible because substantial amounts of process heat and power are provided from biomass.

Kim and Dale (2008) discuss the possible implications of the removal of 50% of the maize stover on soil carbon, and they conclude that soil organic carbon levels decrease by about 40 kg of carbon (C) per ton of PHB for current tillage practices.[108] It is commendable that this aspect was included, while hardly any other environmental assessments do so.[109,110] However, other publications indicate that the uncertainties of soil carbon estimates are very substantial.[111] Moreover, it is not straightforward to interpret the result: while a soil organic carbon reduction by about 40 kg of C per ton of PHB may seem acceptable with regard to the effect on global warming,[108] the question to be answered is whether it is sustainable regarding the soil quality and soil quantity if this cultivation method is applied over many decades.

Polylactic Acid (PLA). Since the early 1980s several companies have worked on new, energy-saving and waste-free recovery technologies to manufacture pure, thermostable lactic acid. Among these concepts, electrodialysis, adsorption with ion exchange resins, solvent extraction, membrane separation, crystallization and distillation have been studied.[99,100] All these novel processes avoid the generation of large amounts of gypsum as byproduct and can be combined with continuous fermentation.

As explained in Section 3.2, two main routes have been developed to convert lactic acid to PLA, i.e. the indirect route via lactide and direct polymerization by polycondensation. The first route is applied by today's two most important producers of PLA, i.e., NatureWorks and PURAC.[23,101−103]

Publicly available life cycle assessment data for PLA is scarce. NatureWorks recently published cradle-to-factory gate energy and CO_2 data for PLA production from corn[99,100] Tables 4 and 5 report data on the currently implemented technology (referred to as "Ingeo 2009"; Ingeo is NatureWork's trademark) in comparison with results of our calculations from the BREW project[100,101] and data for petrochemical polyethylene terephthalate (PET; somewhat more detailed information can be found in Tables S-3 and S-4 of the Supporting Information). The values from the BREW project by and large endorse those published by NatureWorks.[101] For the petrochemical PET, we report data that were released recently by PlasticsEurope (2010);[104] these

Table 4. Non-renewable Energy Use (NREU) for Productions of Various Bio-Based Plastics As Compared to Petrochemical Polyethylene (PE), Polypropylene (PP), Polyethylene Terephthalate (PET) and Polytrimethylene Terephthalate (PTT), for the System Cradle-to-Factory Gate

	PHA[101,108]																	
	Kim & Dale (2008) Maize[108] use of agri. residues			PLA[99,100]		Bio-PE (this study)		Pchem. PE[118]	Bio-PP (this study)	Pchem. PP[122]	Bio-PET (this study)		Pchem. PET[a127]	Bio-PTT[101,127]		Pchem. PTT[101,127]		PBS
NREU (GJ/t plastic)	without	with	BREW (2006)[101] Maize	Ingeo 2009 Maize	BREW (2006) Maize	Maize today	Sugar cane (2005/2006)	Pchem. today	Maize medium term	Boustead (2005)	Maize today	Sugar cane (2005/2006)	Pchem. today	DuPont (2006)[127] Maize	BREW (2006)[101] Maize	DuPont (2006)[127]	BREW (2006)[101]	this study From Bio-SA
cradle-to- factory gate	68.6[b]	17.8[c]	37.5−111.6[d]	42	41−52	43.4	9.1	72.7−76.7	>41−43	73.4	58.7	51.3	69.4	77.3	62.3	88.1−94.7	67 to 88	65−92

[a] New data set released by PlasticsEurope in 2010 (IFEU, 2010).[104] For comparison, the NREU value of petrochemical PET published by PlasticsEurope in 2005 was 80.75.[105] [b] Value for near future according to Kim & Dale (2008),[108] without use of agricultural residues; this total consists of the following process steps (all values in GJ/t plastic): Cultivation (7.8), wet milling (10.7), fermentation and downstream processing (53.7), stover harvest and transport (1.3), alternative system for coproducts wet milling (−3.6), alternative system for electricity (0.0), alternative system for steam (−1.3), and carbon content (n.a.). [c] Value for near future according to Kim & Dale (2008),[108] with use of agricultural residues; this total consists of the following process steps (all values in GJ/t plastic): Cultivation (7.8), wet milling (10.7), fermentation and downstream processing (2.9), stover harvest and transport (1.3), alternative system for coproducts wet milling (−3.6), alternative system for electricity (0.0), alternative system for steam (−1.3), and carbon content (n.a.). [d] Without use of agricultural residues.

are substantially lower than the data released by PlasticsEurope in 2005,[105] e.g., for NREU 69.4 GJ/t as opposed to 80.75 GJ/t and GHG emissions of 2.15 t CO_2 eq./t as opposed to 3.3 t CO_2 eq./t, reflecting the substantial improvement in efficiency of the petrochemical process. Nevertheless the NREU and GHG emissions of the current PLA process (Ingeo 2009/NatureWorks, 2009)[100] are approximately 40% lower for the system cradle-to-factory gate compared the latest data for petrochemical PET. NatureWorks announced that they will further improve their process, with a target value for NREU of 35 GJ/t PLA and a GHG value of 0.8 t CO_2 eq./t PLA (both for cradle-to-factory gate); this would increase the savings to approximately 50% for NREU and 65% for GHG in comparison with the latest petrochemical PET values for the system cradle-to-factory gate.[99,100]

The values discussed so far refer to the production from starch crops while the requirements of non-renewable energy and the release of greenhouse gases are substantially lower if sugar cane is used.[100] This is demonstrated by Purac's LCA study for PLA (with published values of 30.5 GJ NREU/t and 0.5 t CO_2 eq./t) and also by the BREW study.[101]

Polyethylene (PE). Any comprehensive discussion about the environmental impacts of bio-based PE must be based on the environmental assessment of its precursor, that is, bioethanol. Because of its large-scale use for fuel purposes there is an extensive body of work on the environmental performance of bioethanol, but only few publications are transparent concerning the process data used and the methodology applied. As a basis for the analyses presented here, we used the process information provided by the companies Lurgi[112] and Vogelbusch.[113] Complementing this information with data from other sources, we were able to estimate the non-renewable energy use and greenhouse gas emissions from cradle to factory gate. According to our calculations, advanced bioethanol plants which have a high level of heat integration and are operated with maize just about comply with the EU's Directive on renewable energy (Directive 2009/28/EC),[114] according to which bioethanol for fuel purposes must save at least 35% of greenhouse gases compared to petrol. We use a data set from the BREW project[101] which fulfills this requirement and matches well with the Vogelbusch and the Lurgi data also with regard to steam and other process energy use (BREW data set "BioEtOH-Anaer-GA-Fd"; we refer to this data set as "Best practice today"). For ethanol from sugar cane we base our calculations on a publication by Macedo et al. (2008)[115] who provide data for Brazil and distinguish two cases, that is, the current state of technology with limited use of bagasse for heat and power generation (denoted in Tables 4 and 5 as "2005/2006"). For catalytic dehydration of ethanol to ethylene, we approximate process energy use with the theoretical heat of reaction calculated from heats of formation due to lack of plausible industrial data. Finally, for ethylene polymerization, data from PlasticsEurope were used,[116−118] which is also the chosen data source for petrochemical polyethylene (data for polymerization were calculated as the difference between the cradle-to-factory gate values for ethylene and polyethylene).[116−118]

The results displayed in Tables 4 and 5 (see Tables S-5 and S-6 in the Supporting Information for additional data) show substantially lower energy requirements and greenhouse gas emissions for bio-based as compared to petrochemical PE. Compared to PE production from maize, the impacts are lower for sugar cane-based production due to the more favorable climate conditions and the resulting larger amounts of biomass waste that is available for covering the process energy

Table 5. Greenhouse Gas (GHG) Emissions of Various Bio-Based Plastics As Compared to Petrochemical Polyethylene (PE), Polypropylene (PP), Polyethylene Terephthalate (PET), and Polytrimethylene Terephthalate (PTT) for the System Cradle-to-Factory Gate

	PHA[101,108]																	
	Kim & Dale (2008) Maize Use of agricultural residues			PLA[99,100]		Bio-PE (This study)		Pchem. PE[118]	Bio-PP (This study)	Pchem. PP[122]	Bio-PET (This study)		Pchem. PET[a127]	Bio-PTT[101,127]		Pchem. PTT[101,127]		PBS
GHG emissions ($t\ CO_2$ eq./t plastic)	without	with	BREW (2006) Maize	Nature- Works (Ingeo 2009) Maize	BREW (2006) Maize	Maize today	Sugar cane (2005/2006)	Pchem. today	Maize medium term	Boustead (2005)	Maize today	Sugar cane (2005/2006)	Pchem. today	DuPont (2006) Maize	BREW (2006) Maize	DuPont (2006)	BREW (2006)	this study from Bio-SA
Cradle-to- factory gate	1.7 [b]	−1.2 [c]	−0.7 to 4.2 [d]	1.3	0.4 to 1.3	−0.34	−2.05	1.8 to 2.1	>−0.2 to −0.3	2.0	1.4	1.0	2.15	2.51	1.6	3.17 to 3.55	1.9−3.2	2.3 to 3.9

[a] New data set released by PlasticsEurope in 2010 (IFEU, 2010).[104] For comparison, the NREU value of petrochemical PET published by PlasticsEurope in 2005 was 80.75.[105] [b] Value for near future according to Kim & Dale (2008),[108] without use of agricultural residues; this total consists of the following process steps (all values in t CO_2 eq./t plastic): Cultivation (0.3), wet milling (0.7), fermentation and downstream processing (3.1), stover harvest and transport (0.1), alternative system for coproducts wet milling (−0.4), alternative system for electricity (−0.1), alternative system for steam (−0.1), and carbon content (−2.0). [c] Value for near future according to Kim & Dale (2008),[108] with use of agricultural residues; this total consists of the following process steps (all values in t CO_2 eq./t plastic): Cultivation (0.3), wet milling (0.7), fermentation and downstream processing (0.2), stover harvest and transport (0.1), alternative system for coproducts wet milling (−0.4), alternative system for electricity (−0.1), alternative system for steam (−0.1), and carbon content (−2.0). [d] Without use of agricultural residues.

requirements and for generating excess power. The results in Table 5 show that the production of bio-based PE is a net CO_2 sink (resulting in negative values) for the system cradle-to-factory gate.

The choice of the theoretical reaction enthalpy to approximate the process energy for catalytic dehydration may lead to underestimation of the estimated NREU and GHG values because additional energy (from external sources) may be needed for product separation and purification. Assuming instead an upper NREU value for dehydration of 10 GJ/t ethylene (equivalent to 0.56 t CO_2 eq. assuming natural gas) has a notable effect on the final results (e.g., by increasing the NREU of the maize-based process by 20%), but it does not alter the final conclusion about the attractiveness of bio-based PE compared to petrochemical PE.

While an advanced plant with optimized heat integration has been assumed, the company Vogelbusch reports that a *traditional* (i.e., *not* optimized) ethanol plant requires nearly 5 tons more steam per ton of ethanol, translating to nearly 14 GJ more NREU and approximately 0.75 additional tons of CO_2.[119] This would reduce the advantage of the bio-based process very substantially demonstrating that the implementation of bio-based processes as a goal in itself is insufficient and that it needs to be combined with advanced, energy efficient process design.

Polypropylene (PP). This section presents the environmental impacts of bio-based PP made from isobutanol as a first intermediate. We approximate the energy use for producing isobutanol by replacing in our model for the acetone-butanol-ethanol (ABE) process the yield, concentration, and selectivity data by the values given by Glassner for the gevo process.[120] Because of a lack of industrial data for the subsequent conversion steps, we use theoretical heats of reaction for the dehydration of isobutanol to butylene and for the subsequent metathesis of butylene and ethylene to propylene. We have chosen to prepare this rough estimation due to the outstanding importance of PP next to PE, as PP accounts for 21% of the worldwide demand for plastics with PE for another 31%.[121]

Our results are very similar to those presented for bio-based polyethylene (Tables 4 and 5; see also Supporting Information). One reason is that the NREU and GHG values of bio-based isobutanol (approximately 27 GJ/t and −0.7 t CO_2 eq./t) are rather close to bioethanol which is approximately 20 GJ/t and −0.6 t CO_2 eq./t. A further reason is that the process energy for some steps of polypropylene production has been approximated by means of the reaction enthalpy.[122] The *real* energy use and greenhouse gas emissions for the production of bio-based polypropylene are therefore very likely to be larger than the values calculated in the way described and hence also compared to bio-based polyethylene. Nevertheless, they can be expected to still be lower compared to petrochemical PP.

Polyethylene Terephthalate (PET). The non-renewable energy use and greenhouse gas emissions for three options of producing (partially) bio-based PET were estimated, that is, the esterification of (i) bio-based ethylene glycol with petrochemical TPA; (ii) petrochemical ethylene glycol with bio-based TPA produced via the isobutanol route[73] mentioned above (see Section 3.1); and (iii) bio-based ethylene glycol with bio-based TPA (via isobutanol). For case (i) Tables 4 and 5 show the results for bio-based PET from maize and from sugar cane (see Supporting Information for case (ii) and (iii)). Since ethylene glycol represents only 27 wt % of the total input for producing PET (with terephthalic acid representing the remaining 73%), the NREU savings are only in the range of 15% for PET from maize and 25% for sugar cane-based PET (system cradle-to-factory gate); the respective GHG savings are 35% and beyond 50%, respectively. The petrochemical data refer to the most recent data set released by PlasticsEurope (IFEU Institute, 2010),[110] which are substantially lower than the values published in 2005 by PlasticsEurope.[117,118,122,123] For bio-based PET, we used newly estimated data on terephthalic acid which are consistent with the new PlasticsEurope data set (Tables 4 and 5).

Poly(trimethylene terephthalate) (PTT). The production of bio-based PDO, one of the two monomers leading to PTT, was commercialized by the joint venture DuPont Tate & Lyle Bio Products LLC. Its polymerization together with terephthalic acid to PTT, which is also referred to as PTMT (polytrimethylene terephthalate) or PPT (polypropylene terephthalate), has been developed by DuPont under the trade name Sorona.[36]

Tables 4 and 5 show the values reported by DuPont and the outcome of our calculations for PTT based on the BREW project[101] (further information including the comparison with nylon can be found in the Supporting Information). The values were adapted for bio-based PTT in order to make the input data on terephthalic acid and for esterification consistent with the other calculations in this paper. As the comparison across different materials on a mass basis (per ton of plastic) is not necessarily adequate, caution is also required when comparing results of studies with different scopes, for example, European industry average data for PlasticsEurope's PET versus design data for a single DuPont plant.

The NREU data for PTT from maize are approximately 25% larger for DuPont's data set compared to the BREW study. The main reasons are (i) different assumptions regarding steam raising and power generation (partly by combined heat and power in BREW), (ii) different allocation methods for corn wet milling (while mass allocation is applied in BREW, DuPont assigns credits according to the system expansion method), (iii) different models regarding the use of biomass waste products, (iv) differences in the use of auxiliary chemicals, (v) slight differences in process data for PDO production and polymerization. Petrochemical PTT data according to DuPont are somewhat larger than the values according to BREW. The savings (in percent) for bio-based PTT compared to petrochemical PTT (arithmetic mean of the two petrochemical routes) are smaller according to the DuPont data as opposed to the BREW data, for example, 15% and 20%, respectively, for NREU savings. DuPont's NREU and GHG results for bio-based PTT are somewhat above the values for polyethylene terephthalate (new PET data for petrochemical process according to PlasticsEurope), while PTT offers small savings according to BREW. In terms of NREU and GHG values, partially bio-based PTT made from bio-based propanediol and petrochemical terephthalic acid is much more attractive than petrochemical nylon and it scores better than petrochemical PTT.[124]

We limit the discussion to PTT from bio-based PDO and exclude considering the additional substitution of bio-based for petrochemical terephthalic acid in view of the large uncertainties discussed above.[125,126]

Other Polymers. For the remaining polymers, that is, PBS and PPC, it is not or hardly possible to estimate energy and GHG values due to lack of data. For PBS, a first estimate has been made using an NREU value of 80.6 GJ/t for 1,4 butanediol (BDO) according to Cooper and Vigon (2001),[127] and using data for succinic acid and lactic acid from the BREW project.[101] For succinic acid, two different processes were considered due to their very differing energy requirements, that is, a process assuming crystallization for downstream processing (bioSA-Anaer-GA-Tc) and another assuming electrodialyis (bioSA-Anaer-GA-Ted). This results in NREU values of 65 to 92 GJ/t for PBS and GHG values of 2.3 to 3.9 t CO_2 eq./t assuming natural gas as fuel contrary to Cooper and Vigon.[127] These values are rather high due to the large energy requirements for BDO according to the source used which may, however, be outdated. For PPC, no estimate could be made.

6. CONCLUSIONS

In the past years, R&D spending for bio-based products has increased substantially, with the most important drivers being (expected further) price increases for fossil fuels, supply security considerations, and greenhouse gas emission reduction. Many bio-based polymers have been developed, of which some are already in industrial production, including the bioplastics PHA, PLA, PBS, PE, and PPC which are discussed in this review. Each polymer has its strengths and weaknesses, which can be compensated by blending with other bio-based polymers or with common petrochemical plastics. At the moment, bio-based plastics are more expensive than petrochemical plastics, with important reasons being the low efficiency of the microbial fermentation processes and/or expensive chemical catalysts, challenging downstream processing, and economies of scale. With the rapid advancement of microbial technology including the omics and synthetic biology, we are now in a better position to change the metabolic pathways of production microbes. Together with the rising cost of petroleum, this will contribute significantly to the further reduction of production costs and to improved competitiveness of PHA and monomers of other bio-based plastics. At a certain moment not far away from now, bio-based polymers can be sold at similar prices to petroleum-based polymers.

Given the rapid technological progress, this review cannot provide more than a snapshot of the non-renewable energy use and GHG emissions of plastics which are based on biotechnologically produced monomers. Among the most attractive products are PLA and bio-based PE, with NREU values of 40 GJ/t plastic up to a maximum of 50 GJ/t and GHG values of up to around 1 ton CO_2 eq./t plastic (values for production from maize). These values translate to savings of around 40% compared to the petrochemical counterparts. The results for fully bio-based PET and bio-based PP seem somewhat less attractive. Both of these polymers are in an early stage of development and the results are therefore rather uncertain; even though the number of conversion steps is substantial, PP is an interesting polymer to pursue given its very large market volume. In terms of NREU and GHG values, partially bio-based PTT made from bio-based propanediol and petrochemical terephthalic acid is much more attractive than petrochemical nylon, and it scores better than petrochemical PTT, while the comparison with petrochemical PET is less clear. PHA is in a similar range as bio-based PTT. The energy and carbon profile can be substantially improved by using agricultural waste (e.g., maize stover) to provide process energy. This opportunity should be made use of on a large scale for all bio-based polymers once there is more certainty about the long-term effects of the removal of agricultural waste on erosion and soil organic carbon. The results discussed in this paper do not allow a transparent discussion about the fact that there is a trade-off between NREU and GHG on the one hand and the amount of biomass use and land requirements on the other; this deserves deeper analysis. The results do show that the implementation of bio-based processes as a goal in itself is insufficient and that it needs to be combined with advanced, energy efficient process design. Such advanced processes for bio-based products are then very likely to offer significantly lower NREU and GHG values than their petrochemical counterparts.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available for section 5.2 (results for non-renewable energy use and GHG emissions). Data from additional sources are presented, results for the system cradle-to-factory gate are broken down into the contribution of the various process steps, and results are presented for the system cradle-to-grave. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Professor Guo-Qiang (George) Chen received his B.Sc. and Ph.D. from South China University of Technology in 1985 and Graz University of Technology (Austria) in 1989. He also conducted research from 1990 to 1994 as a postdoc at University of Nottingham in U.K. and University of Alberta in Canada. He has been focusing his research on microbial metabolic engineering and bio-based polymers since 1986. After joining Tsinghua University in 1994, he has been actively promoting the microbial Bio- and Material Industries in China. Professor Chen has more than 25 years of basic research as well as R&D experience in microbial physiology, microbial production, and applications of polyhydroxyalkanoates (PHA). Technologies developed in his lab have been provided to several companies that succeeded in mass production of microbial polyhydroxyalkanoates (PHA).

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