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Chapter 1

RECOVERY OF MONOMERS AND BIOMACROMOLECULES FROM MUNICIPAL SOLID WASTE: STATE OF THE ART AND PERSPECTIVES

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ABSTRACT

This chapter reviews the current state of the art referring to the recovery and reuse of selected monomers and biomacromolecules (such as proteins and nucleic acids) from municipal solid waste. In fact, these recovered products, apart from representing a renewable source of energy, can gain a "second life," hence being valorized for different uses, also including the synthesis of biopolymers and the design of low

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environmental impact flame retardant additives. In particular, the chapter is aimed at providing the reader with an overall picture concerning i) the processes that can be exploited for the recovery of the aforementioned high added-value products from municipal solid wastes, ii) the most relevant recoverable chemical building blocks and biomacromolecules and iii) some of the most promising potentialities offered by them. Finally, the potential of some of the recovered products for synthesizing biopolymers, as well as the main current limitations concerning the recovery and reuse of selected monomers and biomacromolecules are discussed, highlighting the open challenges and future possible developments.

Keywords: municipal solid waste, biomacromolecules, chemical building blocks, biopolymers, flame retardants, recovery and reuse

INTRODUCTION

Sustainable development has become a priority for the world's policy makers, as humanity's impact on the environment has been greatly accelerated in the past century with rapidly increasing population and the concurrent unavoidable decrease of natural resources. Finding alternatives and more sustainable ways to live is our duty to pass on to future generations, and one of these important messages relates to waste. Waste from different sectors is produced day by day in extensive quantities, generating a significant problem in its management and disposal. In recent years, a widespread feeling of "environment in danger" has been created everywhere in our society, which, however, has not provoked a general consensus of cutting waste production in our daily lives yet.

Waste valorization is the process of converting waste/end of life materials into more useful products including chemicals, materials and fuels. Though this concept has already existed for a long time, quite recently it has been brought back to our society with renewed interest, due to the fast depletion of natural and primary resources, the increased waste generation and landfilling confinement worldwide and the need for more sustainable and cost-efficient waste management protocols.

The potential of valorizing wastes to produce valuable products is an attractive alternative solution that has gained the interest of both scientific and public opinion within a sustainability approach. However, the purification, processing and even the degradation of stable natural polymers into simple usable chemicals still remains a significant challenge.

Municipal solid waste (MSW) collected by municipalities includes wastes from households, separately collected waste from commerce, offices and public institutions and other wastes of similar nature or composition, such as bulky food and garden waste. Its biogenic fraction (biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises) ranges between 30 and 50% of total MSW, which represents more than 500 kg/capita (EU-27 average), 300 million tonnes overall every year in the EU-32, increasing at an annual 10% rate. Currently, approximately 50% of this volume is landfilled, 30% is recycled (materials separation and bio-waste recycling, including compost and digestion), while the remaining 20% is incinerated. In spite of the strong shift from MSW landfilling to recycling of such materials as plastics, wood or metals and energy production from the organic fraction (mainly by incineration), there is a challenge to turn the biogenic fraction into higher value products than bioenergy.

Although it could be an excellent substrate for upgrading to valuable products and energy, especially considering the availability of MSW, its handling shows some challenging issues. As an example, MSW presents a high variability in both regional and seasonal composition and volumes, which may affect the emissions generated during incineration. The high water content, which makes them prompt to microbial contaminations, is another challenge. This could potentially result in public health issues, as pathogens can also contaminate MSW. Furthermore, the high moisture content results in increased volumes and weight of MSW, making drying an important step to reduce the cost of transportation. In fact, drying and transportation are energy and cost demanding and, in turn, can significantly impact the total process cost. The generation of MSW is virtually present in every residual area: therefore, this can offer a solution to avoid both drying

and long-distance transportation. A decentralized system can be introduced where low-volume facilities locally use MSW.

At present, the society is facing a serious challenge for the effective management of the increasing amount of produced municipal solid wastes. The accumulated waste causes a series of environmental problems, such as uncontrolled release of greenhouse gases. Furthermore, the increasing amount of wastes results in a shortage of areas available for waste disposal, determining a non-sustainable waste management. These problems lead to serious public concerns, which, in turn, resulted in political actions aiming at reducing the amount of wastes that reach the environment. These actions aim at promoting sustainable waste management solutions. The main objective of these policies is to favor the recycling of municipal solid waste and the conversion of waste to energy and valuable chemicals. These conversions can be performed using either biological (e.g., anaerobic digestion) or thermochemical (e.g., pyrolysis) processes. Research efforts during the last years have been fruitful and many publications demonstrated the effective conversion of municipal solid waste to energy and chemicals. Energy and chemicals are mainly produced from fossil resources: this causes the release of CO_2 in the atmosphere, together with other toxic compounds. In addition, as these raw materials are finite, the processes utilizing them as feedstock are not sustainable; thus, the security of supply will be an important issue for humanity. Another important challenge is the rising accumulation of wastes in the environment. The waste accumulation in the environment has raised the public awareness because of the problems derived from the considerable amount of disposed wastes. However, the huge volumes that are produced globally, alongside the diversity that these wastes show, makes them ideal candidates useful for high-value applications.

MSW biowaste contains large amounts of polysaccharides (30-40% cellulose, hemicellulose, starch and pectin), lipids (10-15%) and protein (5-15%), depending on the origin and pre-processing steps. Efficient conversions of mixed and variable feedstocks are challenging. To date, mixed wastes have been transformed by thermochemical processes, such as hydrothermal liquefaction (HTL) and gasification, and by anaerobic

digestion, leading to methane and bio-hydrogen, fuels (ethanol and butanol), compost and fertilizers. The production of more complex chemicals is limited by large-scale economic feasibility, due to pre-treatment and conditioning costs of the recalcitrant raw materials. The use of the gases obtained by thermochemical processing and/or anaerobic digestion as substrates for fermentation of other products may represent one approach to overcome this issue. However, one more interesting method refers to the development of more cost-effective pre-treatment and fractionation methods that will open the use of MSW as a general fermentation substrate. For this reason, it is important to establish new technologies for pre-processing and fractionation of MSW for microbial conversions and for their subsequent transformation into marketable products, as well as to develop microbial strains, able to convert MSW to the targeted intermediate products with high productivities. The direct extraction of protein and lipids should also be explored, as they can be converted to other added-value products for further improving the process economy. For instance, lipids can be used as biofuels or biolubricants; hydrolyzed proteins can be exploited as biofertilizers; biosurfactants can be obtained from both lipids and amino acids. In this context, biotechnology is a promising solution. The biotechnological conversion of MSW involves the use of microorganisms, able to convert the organic fraction of the MSW into different molecules. The effective decomposition of complex polymeric molecules (such as cellulose and proteins) to simple molecules (such as sugars and amino acids) is often considered a rate-limiting factor of the process. The incorporation of these processes in biorefineries for the production of value-added products is an important contribution toward the world's highest priority target of sustainable development.

The major strength of biotechnology refers to its multidisciplinary nature and to the broad range of scientific approaches that it encompasses. Among the wide variety of technologies with the potential to reach the goal of sustainability, biotechnology could take an important place, especially in the fields of food production, renewable raw materials and energy, pollution prevention and bioremediation. A key factor in the achievement of a successful bio-based economy will be the development of biorefinery

systems that allow a highly efficient and cost-effective processing of biological feedstocks to a range of bio-based products, as well as their successful integration into existing infrastructure.

Therefore, this chapter is aimed at discussing all the aforementioned issues concerning the recovery of monomers and biomacromolecules from municipal solid waste, also providing the reader with an overview of the current limitations, the potentialities and the further possible developments of the technologies and applications of the recovered materials.

MSW: A SHORT OVERVIEW

Generally speaking, municipal solid waste (MSW) comprises any refuse or junk or other discarded materials, also involving solid, liquid, semi-solid, or contained gaseous products deriving from domestic, community, or human operations.

The generation rates of MSW and its composition change from country to country, according to different factors, also comprising the country economic condition, the presence and the activities of industrial structures, the waste management regulations and, of course, the life style. Both in developing and developed countries, the volume of produced MSW changes daily and seasonally.

As an example, Table 1 collects the per capita waste generation in developed countries. Furthermore, the composition of MSW in developed countries changes with the size and prosperity of the city. Therefore, the design of MSW management has to take into account several factors including the impact of recycling and composting activities, the programs of source reduction and the demographics as well. Besides, though either the consumer behavior or the product composition may affect the MSW stream, their effect is unpredictable and therefore it is only marginally taken into account.

However, in the last 5 to 10 years, it was possible to identify some general trends, especially in Europe and USA: in this context, the amounts of paper and plastics in the American MSW stream are expected to

continuously grow, unlike glass and steel, for which the replacement with lighter materials (i.e., plastics and aluminum alloys) is occurring.

Table 1. Per capita MSW generation in developed countries [3]

Country	**MSW generation rate (kg/capita/day)**
Australia	1.89
Austria	1.18
Belgium	1.10
Canada	1.80
Denmark	1.26
Finland	1.70
France	1.29
Germany	0.99
Greece	0.85
Hungary	1.07
Italy	0.96
Japan	1.12
Mexico	0.85
Norway	1.40
Poland	0.93
Portugal	0.90
Spain	0.99
Sweden	1.01
Switzerland	1.10
The Netherlands	1.37
Turkey	1.09
USA	2.00

Furthermore, over time, the demographics promoted some changes in the production of municipal solid waste, because of both the population changes and the per capita generation: this latter is strictly dependent on three main factors, namely household size, degree of urbanization and socio-economic status.

As far as the European situation is considered, the composition of mixed MSW changes from country to country and is strictly related to the differences in source separation methods. However, though it cannot be generalized, from an overall point of view, organics and paper represent the largest waste streams in Europe: all together, they account from 50 to 80% by weight of residential municipal solid waste. In addition, the relative amounts of metals, glass and plastics may change from country to country, in relation to the packaging mix, shifting from 10 to 25% by weight.

Table 2. Average physical composition (weight %) of municipal solid waste in developed countries [3]

Country	**Metals**	**Glass**	**Plastics**	**Paper**	**Organic**	**Other**
Australia	5	9	7	22	50	8
Canada	8	7	11	28	34	13
Denmark	9	6	7	30	37	17
Finland	3	6	0	26	32	35
France	6	12	10	30	25	17
Greece	5	5	9	20	49	1
Japan	8	7	9	46	26	12
Luxemburg	3	7	7	20	44	1
Mexico	3	6	4	14	52	20
Netherlands	5	4	9	27	43	8
Norway	5	4	6	31	18	36
Portugal	3	5	12	23	35	22
Spain	4	7	11	21	44	13
Switzerland	3	3	15	28	27	24
Turkey	1	2	3	6	64	24
USA	8	7	9	38	23	38
Average	*5*	*6*	*8*	*26*	*38*	*18*

It is worthy to note that the European household hazardous wastes (from 1 to 4% by weight) are much more significant because of their environmental implications, rather than for their absolute percentages. Finally, there are some differences between Western and Eastern European

countries, as the former tend to generate a waste stream higher in metals, plastics and glass and lower in putrescible components. Table 2 shows the average physical composition of municipal solid waste in developed countries.

The Organic Fraction of Municipal Solid Waste (OFMSW) mainly consists of proteins, lipids, carbohydrates, cellulose, lignin and ash. Therefore, it shows a high moisture content and high biodegradability, as it includes a great content of food waste, kitchen waste and scraps coming from residences, restaurants, factory lunch-rooms, cafeterias, and markets [4]. As a consequence, OFMSW signifies the main source of unfavorable environmental impacts and risks in traditional landfill confinement: in fact, it produces odours, fires, volatile organic compounds, groundwater contamination by leachate, global climate changes, and so on [5-7]. Therefore, both European and national waste management strategies have been working towards the seeking for possible alternatives from landfill confinement of OFMSW [8]: as a result, OFMSW can be stabilized by exploiting different technologies, including thermal (e.g., incineration) or, more frequently, biological processes (e.g., anaerobic digestion (AD) and composting). The former show significant limitations because of the low heating values of MSW organic fraction [9]; conversely, despite having been set as a well-established process, composting shows many drawbacks related to the energy consumption and to the compost market [10-11].

Besides, AD has shown an increasing interest over recent decades, also thanks to the diffusion of national programs pushing the communities towards the energy production from renewable resources. Besides, anaerobic digestion technologies can be also exploited for recovering and/or generating valued industrial precursors for fuels and plastic productions, apart from being considered as the best opportunity for the biological production of methane and hydrogen gases [12].

In this view, the next paragraphs will aim at providing the reader with a detailed description of the structure, properties and uses of the chemical building blocks and biomacromolecules, which can be recovered from OFMSW.

CHEMICAL BUILDING BLOCKS AND BIOMACROMOLECULES

Within the bio-based economy and the operation of a biorefinery, there are significant opportunities for the development of bio-based building blocks (i.e., chemicals and polymers). Taking into account MSW biowaste composition, biotechnological approaches and near-term market potentials, some relevant chemical building blocks have been selected to be included in this section. As MSW contains large amounts of polysaccharides (namely, cellulose, hemicellulose, starch and pectin), lipids and proteins, it is foreseeable that the main chemical building blocks that can be produced from MWS are those derived from lignocellulosic biomass. Therefore, a selection of some of them will be detailed in the next lines. As we are focusing our attention mainly on chemical building blocks suitable for obtaining bio-based polymers, we have not deepened on some compounds that represent the main components of biofuels or biogases. To facilitate the description, they have been classified according to the carbon number of each molecule, as shown in Table 3.

C3 Compounds

Lactic Acid

Lactic acid (LA, Figure 1) has been known since 1780, when Scheele isolated the compound from milk. Lactic acid has a long history of applications in the food and beverage sector as a preservative and pH adjusting agent [13]. It is used in the pharmaceutical and chemical industries, as a solvent and starting material in the production of lactate ester. Lactic acid is also utilized as a standard or active ingredient in personal care products, due to its moisturising, pH regulating and skin lightening properties [14].

Polymerisation of lactic acid produces polylactic acid (PLA), a biodegradable polymer that is used in food packaging including rigid

containers, shrink wrap and short shelf-life trays, as well as mulch films and rubbish bags, notwithstanding its use for biomedical applications (either as homopolymer or as copolymer).

The Dutch company Purac is the world leader in lactic acid production and is actively exploiting its technology base through partner collaborations.

LA has been produced by fermentative processes based on renewable resources. The great opportunity to produce a bio-based plastic from LA makes this monomer an interesting chemical feedstock. LA is biotechnologically produced exploiting the anaerobic fermentation of sugars. During this fermentation process, the enzyme called *lactate dehydrogenase* converts pyruvic acid into LA. This latter is optically active and exists in *L*- and *D*-forms. Advances in biotechnology enable the production of optically pure LA in both forms, or a mixture of them. The content of *D*- and *L*-enantiomers significantly influences the physical properties of the polymer. The current manufacture of PLA utilizes LA with a *L*-LA chiral purity beyond 98−99% [15]. Therefore, LA is mainly produced in the form of an optic isomer; only few producers manufacture racemic LA [16].

The most significant cost contribution in the production of LA relates to the expenses of the sugar feedstocks. Depending on the location, the sugar sources are either sucrose, dextrose corn syrups, or starch hydrolysates [16]. A great technological advantage originates from using cheap lignocellulosic hydrolysates as feedstocks. Hydrolysates of cellulose and hemicelluloses are fermentable to LA, with the only exception of lignin. A special pretreatment is necessary to disrupt the lignin and to destroy the crystalline structure of cellulose [17].

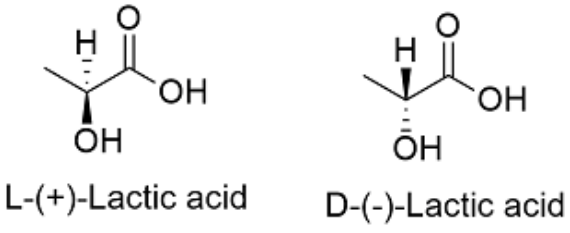


Figure 1. Lactic acid.

Table 3. Chemical building blocks useful to produce biopolymers

Number of carbons	Compound
C3	Lactic Acid
	Propylene Glycol
	1,3 Propanediol
	Epichlorohydrin
	Propylene
	Acrylic acid
	3-hydroxypropionic acid, acrylonitrile, acrolein
C4	Butanol
	Butanediol
	Succinic Acid
	Aspartic Acid
	Methyl methacrylate
	(R)-3-hydroxybutyric acid
	3-Hydroxybutyrolactone
C5	Furfural
	Levulinic acid
	Isoprene/Farnesene
	Xylitol/Arabitol
	Itaconic Acid
	Glutamic Acid
	1,5-pentanediamine
C6	5-hydroxymethylfurfural, 2,5-Furandicarboxylic acid (FDCA)
	Sorbitol
	Isohexides
	Lysine
	Adipic acid
	cis,cis-Muconic acid
	Glucaric and Gluconic acids
Cn	p-Xylene
	Fatty Acid derivatives
	Aromatic Monomers
	Lignin derivatives

With respect to the above-mentioned cost issue of substrates, the utilization of residues and waste materials became the focus of public attention [18]. Further efforts in R&D to achieve the provision of lactic acid, biotechnologically and commercially within the minimum cost, are still needed.

Propylene Glycol (1,2-Propanediol)

Industrially, propylene glycol (Figure 2) is derived from propylene oxide [19]. Propylene glycol can also be converted from glycerol, a biodiesel by-product. Alternative feedstocks for propylene glycol production include sorbitol and dextrose [13].

Propylene glycol has a wide range of uses, including some industrial applications such as for unsaturated polyester resins (45% of propylene glycol is used for this purpose), coolants and antifreeze, hydraulic and brake fluids, aircraft de-icing fluids, heat transfer fluids, paints and coatings, solvents, humectants (E1520), preservatives in food. Furthermore, it is utilized for tobacco products, e-liquid and cartridges used in electronic cigarettes, edible items such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda, vaporizers used for delivery of pharmaceuticals or personal-care products, artificial tears, oral treatments for hyperketonaemia in ruminants in veterinary medicine, etc. Besides, there is a huge market for high grade propylene glycol in fragrance, cosmetics and personal care applications, food and flavourings, pet food/animal feed and in pharmaceutical formulations.

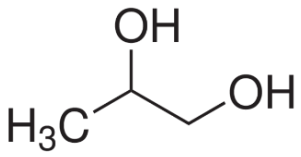


Figure 2. Propylene glycol.

1,3-Propanediol

1,3-Propanediol (Figure 3) can be formulated into a variety of industrial products including composites, adhesives, laminates, coatings, moldings,

aliphatic polyesters, copolyesters. It is also a solvent and used as an antifreeze and in wood paint. It is mainly used as a building block for the production of such polymers as polytrimethylene terephthalate.

1,3-Propanediol can be chemically synthesized through the hydration of acrolein, or by hydroformylating ethylene oxide to afford 3-hydroxy-propionaldehyde, which, in turn, is hydrogenated to 1,3-propanediol. In addition, the bioconversion of glycerol to 1,3-propanediol can be carried out by selected bacteria. Two other routes involve the bioprocessing by certain micro-organisms and the conversion from corn syrup and glycerol (a by-product of biodiesel production).

In 2004, DuPont gave rise to a joint venture with Tate & Lyle, an agriculture products company, to commercialize the production of 1,3-propanediol (PDO) from renewable resources (from corn syrup), under the trade names Susterra® and Zemea® [20]. Susterra® PDO is targeted at industrial application, while Zemea® is exploitable within the personal care sector. According to DuPont, the Bio-PDO process uses 40% less energy than conventional processes. Susterra® PDO is co-polymerised with terephthalic acid to produce poly(trimethylene) terephthalate (PTT), called Sorona®, which is targeted at clothing, carpet and automotive textile markets. Cerenol™ polyols based on PDO can be used in a variety of applications from personal care and functional fluids, to performance coating and elastomers [21].

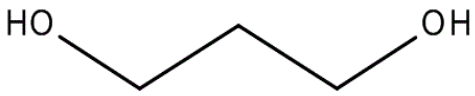


Figure 3. 1,3-Propanediol.

Epichlorohydrin

With a market size of 1.3 million tonnes, epichlorohydrin (Figure 4) is predominately utilized for the production of epoxy resins (76%), as it is mainly converted to bisphenol A diglycidyl ether. It is also used as a precursor of monomers in the synthesis of other resins and polymers (e.g., polyamide-epichlorohydrin resins). Niche applications include paper

reinforcement (e.g., tea bags and coffee filters) and water treatment. It is utilized as a solvent for cellulose, resins and paints, and also as an insect fumigant. It is a highly reactive compound: for this reason, it is a versatile precursor employed in the synthesis of many organic compounds. As an example, it can be converted to glycidyl nitrate and used in explosive and propellant formulations. An important biochemical application of epichlorohydrin refers to its use as crosslinking agent for the production of Sephadex size-exclusion chromatographic resins from dextrans. Furthermore, epichlorohydrin can be exploited for producing glycerol.

Global epichlorohydrin consumption is expected to grow. Solvay and several chemical producers including Zeachem, Spolchemie and DOW are working to commercialise bio-based epichlorohydrin [13].

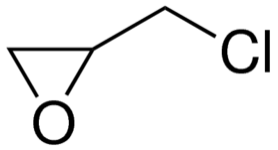


Figure 4. Epichlorohydrin.

Propylene

In 2013, the global propylene (Figure 5) demand was approximately 85 million tonnes. Though it is used mainly in the synthesis of polypropylene (60% of propylene demand), propylene is also consumed for the production of propylene oxide, cumene, butyraldehyde, acrylonitrile, acrylic acid and butanol. Furthermore, propylene is converted to acetone and phenol via the cumene process. Several routes have been suggested for the production of bio-based propylene [22].

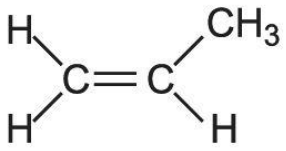


Figure 5. Propylene.

Acrylic Acid

Acrylic acid (AA, prop-2-enoic acid, Figure 6), is the simplest unsaturated carboxylic acid and one of the most important industrial chemicals. Acrylic acid is an important chemical building block utilized for the production of polyacrylates and commodity acrylates. The global petroleum-based acrylic acid market is worth US$8 billion (2011) and grows 3 to 4% per year. Commodity acrylates include methyl, ethyl, *n*-butyl and 2-ethylhexyl acrylate, which are used in a variety of industrial applications including coatings, adhesives and sealants, textiles and fibres, polymer additives/impact modifiers and films [23].

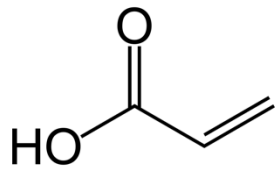


Figure 6. Acrylic acid.

New and innovative processes are required to establish a sustainable production of AA and to overcome fossil oil dependence in the future. Because of the little success in producing AA at considerable concentrations directly from sugars with microbes as biocatalysts, the indirect production via lactic acid is the most realistic approach. The simplicity of the LA pathway provides an effective opportunity to convert carbon sources from renewable resources in AA. Theoretically, 2 mol LA can be formed from 1 mol glucose, which serves as feedstock for the chemical conversion into AA. The opportunity to convert sugars from derived renewable resources into LA supports the concept of AA production from sustainable resources. After recovery and purification, LA can be chemically converted into AA through catalytic processes. However, more research is needed to increase the selectivity of catalytic conversion of LA into AA and to avoid or minimize the presence of unwanted side products that negatively affect the carbon balance [18].

Glycerol can also be chemically converted into acrylic acid, either by dehydration to acrolein followed by oxidation to the final product, or in a one-step oxydehydration. An example of the latter process is described in a patent by Arkema [24].

3-Hydroxypropionic Acid (3-HPA)

Bio-based acrylic acid can be obtained through the fermentation of carbohydrates to 3-hydroxypropionic acid (3-HPA, Figure 7); then, further dehydration of 3-HPA produces acrylic acid. The synthesis of 3-hydroxypropionaldehyde from glycerol, which can also serve as precursor, has been patented by Evonic [25].

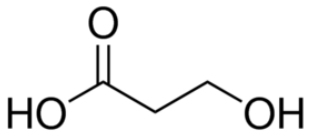


Figure 7. 3-Hydroxypropionic acid.

3-HPA is also a key building block for the production of high value products such as acrylonitrile, acrolein, acrylamide, 1,3-propanediol (PDO), propene, malonic acid, propiolactone, and 3-hydroxypropionic esters [26].

3-HPA can be chemically synthesized through the oxidation of PDO in the presence of Pd-containing supported catalyst, through the oxidation of 3-hydroxypropionaldehyde in the presence of Pd-containing supported catalyst, or by hydrating acrylic acid in the presence of acid catalysts. However, these chemical routes are too costly, hence requiring a biosynthetic pathway for large scale production of 3-HPA. In this consideration, cheap sugar feedstocks should be employed to obtain 3-HPA in a commercially efficient way. Even so, no known organisms can produce 3-HPA as a major metabolic end product from sugars. Hence, large scale production of 3-HPA can be carried out through fermentation of sugars by employing genetically modified microorganisms. The process necessitates an improved microbial biocatalyst, as well as a reduction in the production cost [27].

The production of acrylic monomers starting from 3-HPA is quite important, owing to the giant market size of acrylic polymers. Almost all commercially produced acrylic polymers contain acrylic acid and/or methacrylic acid at some extent. Hence, homo- or co-polymers of acrylic and methacrylic acids have a myriad of applications. Many companies have been involved in the production of these polymers.

Acrylonitrile (Figure 8) and acrolein (Figure 9) are the other two industrially important acrylic derivatives of 3-HPA. Acrylonitrile has unalterable status in the current fiber industry. It is the main monomer of Orlon, DuPont's first acrylic fiber. Besides, polyacrylonitrile (PAN) fibers, as well as the copolymers of acrylonitrile with other monomers such as styrene (SAN, ABS, ASA) are very interesting.

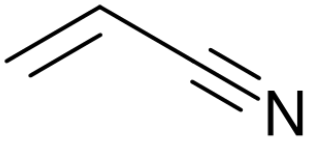


Figure 8. Acrylonitrile.

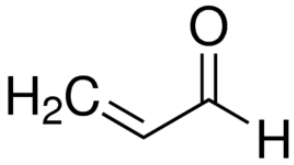


Figure 9. Acrolein.

Other C3 Based Building Blocks

Other C3 based building blocks that are of interest to be replaced by biobased equivalents include acetone (product in ABE – acetone butanol-ethanol - fermentations) and propionic acid (obtained through the reduction of lactic acid). All are currently used at scales around or beyond 1 Mton/year.

C4 Compounds

Butanol

Some companies are commercializing the production of *n*-butanol (Figure 10) and isobutanol. The bio-based production of *n*-butanol is an historic process dating back to the early 20th century [28]. *n*-Butanol is produced by fermentation (acetone butanol-ethanol (ABE) process), together with acetone and ethanol. Bio-based *n*-butanol production ceased in the 1980s, due to the low cost of crude oil and competing petrochemical routes; however, increasing oil prices and the importance in renewably-sourced chemicals have stimulated the interest in this technology again. The higher energy content and compatibility with existing infrastructure makes butanol an interesting biofuel proposition for the future. However, current production costs are high, leading producers to focus on the development of higher priced chemical applications. *n*-Butanol is used in a wide range of polymers and plastics and is also utilized as a solvent in paints and chemical stabilizers. It is also employed as a base for perfumes, though it has an intrinsic highly alcoholic aroma; besides, salts of butanol are chemical intermediates; as an example, alkali metal salts of tert-butanol are tert-butoxides.

Bio-based butanol production has been re-established in China to supply its growing chemicals market. In 2008, Cathay Industrial Biotech began supplying butanol under its BioSol brand; the production capacity is now approaching 100,000 tonnes. The production of isobutanol creates the opportunity for the synthesis of isobutylene and for a range of downstream products.

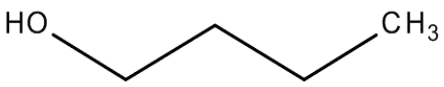


Figure 10. Butanol.

Butanediol

Diols are widely used in the polymer industry for the synthesis of polyesters and polyols. The efforts of biocatalytic investigations are currently focused on the synthesis of four diols that are utilized or can potentially be used for the manufacture of biobased polymers, namely: 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1,4-butanediol (1,4-BDO, Figure 11) and 2,3-butanediol (2,3-BDO). 1,2-PDO and 1,4-BDO are produced today as bulk chemicals based on petroleum resources. The microbial synthesis of 2,3-BDO was intensively investigated in the 1940s, mainly considering 2,3-BDO as an intermediate for the production of 1,3-butadiene. The development was carried out up to the pilot plant stage. Due to the availability of cheap petroleum feedstocks in the 1950s, these studies have not been continued [29]. At present, the interest in 2,3-BDO as a potential monomer and intermediate is revived. 2,3-BDO can be synthesized biotechnologically starting from a wide range of substrates. The advantages of the process comprise the possibility to reach a concentration of 2,3-BDO as high as 150 g/L [30]. To the best of our knowledge, no chemical biomass-based synthesis of 2,3-BDO has been proposed yet.

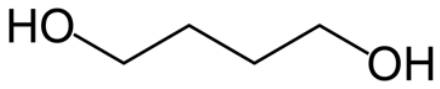


Figure 11. 1,4-Butanediol (1,4-BDO).

The production of 1,4-BDO from biomass has recently received a lot of attention [14]. Different routes leading to 1,4-BDO are schematized in Figure 12.

1,4-BDO is currently produced form acetylene or propylene oxide and has a market size of nearly 1 million tonnes [13]. It serves as a raw material for a range of important chemicals including polybutylene terephthalate (PBT) and polybutylene succinate (PBS).

Approximately 40% of 1,4-BDO is consumed in the production of tetrahydrofuran (THF). THF is a widely used performing solvent and a feedstock for the production of polytetramethylene ether glycol, employed

in the production of polyurethanes. It also acts as a precursor for a number of specialty chemicals used as solvents or as raw materials in the pharmaceutical and agrochemical sectors.

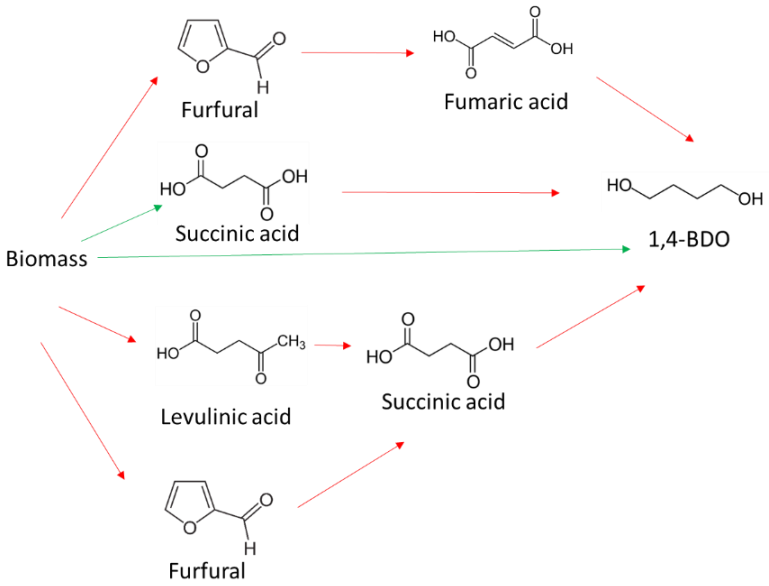


Figure 12. Proposed routes for biomass-based synthesis of 1,4-Butanediol (1,4-BDO) (Fermentation in green and catalytic reaction in red).

Either by employing metal catalysts or biocatalytic methods, 1,4-BDO can be converted into its diamine product, namely 1,4-butanediamine (putrescine, Figure 13). In the presence of metal catalysts, the primary alcohol firstly gives the corresponding carbonyl compound and hydrogen; then, the imine product is obtained. The subsequent hydrogenation of the imine leads to the desired amination product [31]. Putrescine has been extensively used in the synthesis of polyamides.

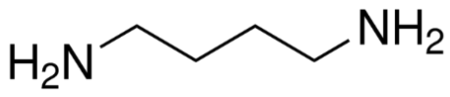


Figure 13. 1,4-Butanediamine.

Succinic Acid

Succinic acid (SA, Figure 14) is considered as one of the key intermediates for the production of biomass-based plastics. SA can be utilized as a monomer for the synthesis of polyesters (specifically poly(butylenesuccinate), PBS) and can be used as an intermediate for the synthesis of such important monomers as 1,4-butanediol or adipic acid [32]. Similarly to lactic acid, SA used to be of small interest for the naphtha-relying chemical industry. Therefore, the market of SA produced from fossil resources is only 15 kt per year, whereas the total capacity of SA production is currently estimated over 170 kt per year and gradually increases [33].

Succinic acid is currently a high-volume specialty chemical produced by catalytic hydrogenation of petrochemical maleic acid or anhydride. The traditional chemical synthesis requires heavy metal catalysts, organic solvents, high temperature and pressure: all these conditions make the petrochemical-based SA production process costly and ecologically questionable. In addition, the increasing cost of crude oil and the imminent need for green and renewable chemicals are the drivers for the demand of bio-based SA. However, large volume commodity markets could be accessed with cost reductions achieved through the production based on the bacterial fermentation of carbohydrates. Currently, the bacterial strain used for succinic acid production is *E. coli*, but the need for lower costs is moving companies towards other microorganisms such as *Coryne*-type bacteria and yeast. Mitsubishi Chemical has developed a *Corynetype bacterium* that shows a significantly higher productivity with respect to *E. coli*. Bio-based SA production has many benefits such as lower carbon footprint, higher cost efficiency, reduced price volatility, and the ability to reduce dependency on crude oil.

The production of succinic acid has attracted a number of industry players. BioAmber was the first to demonstrate the technological production feasibility of SA (at present, 30,000 tons of succinic acid per year). BioAmber is currently working together with Mitsubishi Chemical to further improve their technology and obtain low cost products. Other companies interested in commercializing succinic acid include Myriant Technologies

(technology developer), Reverdia (joint venture between Royal DSM and Roquette Frères), Purac (lactic acid producers) and BASF [13].

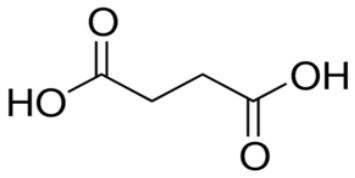


Figure 14. Succinic Acid.

In order to have an economically viable bio-based SA production process, the selection of appropriate production hosts and feedstocks is a key point. Yeasts could be one of the promising hosts for fermentative SA production in combination with metabolic engineering. The genetic modification of yeast for enhancing SA production should be carried out at the genomic level by combining metabolic and evolutionary engineering. Coupled biological and chemical processes would be an alternative strategy to improve SA yield. Thanks to the development of genome, transcriptome and synthetic biology, rational designs can be exploited for regulating the global metabolic pathways, in order to improve the production of succinic acid.

Succinic acid can be converted into 1,4-butanediol (BDO) and other products (fuel additives, plasticizers…). Gamma-butyrolactone (GBL) and THF can be also obtained through hydrogenation of succinic acid. Luque et al. proved that the selectivity of the formation of these products can be tuned by the proper choice of the catalyst [34, 35].

Aspartic Acid

Aspartic acid (Figure 15) is an α-amino acid used in the biosynthesis of proteins. In 2014, the global market for aspartic acid was $117 MM/year (50-60K MT/year). Current applications include the synthesis of polyaspartic acid, a biodegradable polymer that can replace polyacrylates, low calorie sweeteners (aspartame), scale and corrosion inhibitors, and resins. One area of aspartic acid market growth refers to biodegradable superabsorbent polymers (SAP) used mainly in disposable diapers and in

adult incontinence and feminine hygiene products. Aspartic acid has also applications in the fertilizer industry (where polyaspartate improves water retention and nitrogen uptake), in concrete floor coatings market (where polyaspartic is a low VOC, low energy alternative to traditional epoxy resins) and in corrosion inhibitors market.

As a chemical building block, aspartic acid leads to the formation of many valuable compounds including fumaric acid, maleic acid, 2-amino-1,4-butanediol, β-alanine, aspartic anhydride and 3-aminobutyrolactone [36, 37]. In addition, aspartic acid based polymers, i.e., poly(amino acids) with free carboxylic groups, have attained the greatest commercial success as water soluble biodegradable polymers. Poly(aspartic acid)s (PASAs) can be produced by different routes. The thermal production of polyaspartate (TPA) is the simplest and oldest approach: in one of the involved steps, an intermediate, namely polysuccinimide (PSI), is produced, giving rise to the formation of TPA polymer. PSI has also been used as a polymer precursor for the production of polyaspartamide (PAA)-based polymers, apart from being an intermediate polymer for the production of commercial terephthalic acid (TPA).

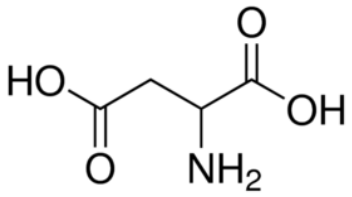


Figure 15. Aspartic Acid.

Methyl Methacrylate

Approximately 80% of methyl methacrylate (MMA, Figure 16) is exploited for the synthesis of poly(methyl methacrylate) (PMMA). Methyl methacrylate is also used for the production of methyl methacrylate-butadiene-styrene copolymer (MBS), employed as a modifier for PVC. Besides, MMA is utilized as bone cement in total hip replacements, as well as total knee replacements.

Given the scale of production, several chemical methods have been developed starting from different two- to four-carbon precursors. Two main routes appear to be commonly practiced, i.e., the cyanohydrin route and the methyl propionate routes.

MMA is a raw material for the manufacture of other methacrylates. These derivatives include ethyl methacrylate (EMA), butyl methacrylate (BMA) and 2-ethyl hexyl methacrylate (2-EHMA). Methacrylic acid (MAA) is used as a chemical intermediate, as well as in the manufacture of polymeric coatings, construction chemicals and textile applications.

Lucite International is the world's leading supplier of MMA. Methacrylates polymerize easily to form resins and polymers with excellent performances including exceptional optical clarity, strength and durability, especially in aggressive all weather or corrosive environments. They can also be copolymerized with other monomers to form a broader range of products typically used for paints, coatings and adhesives.

Lucite has developed Alpha, a two-stage, high-yield patented process route to MMA, which liberates the industry from its traditional dependence on acetone, hydrocyanic acid and isobutylene [13].

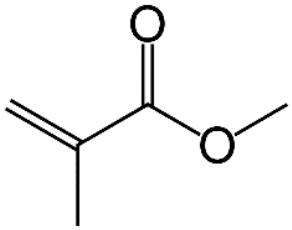


Figure 16. Methyl methacrylate.

(R)-3-Hydroxybutyric Acid

(R)-3-hydroxybutyric acid (Figure 17) is another interesting building block, which can be produced by the (enzymatic) hydrolysis of the biosynthesized poly(3-hydroxybutyrate) (PHB) or via direct biosynthesis routes [38]. It is the precursor to biodegradable polyesters. 3-

Hydroxybutyric acid produces PHB, which is also produced biologically by *Alcaligenes eutrophus* bacteria.

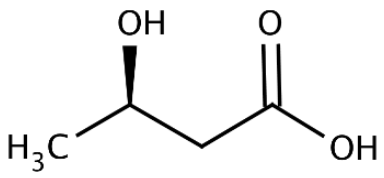


Figure 17. (R)-3-Hydroxybutyric acid.

3-Hydroxybutyrolactone

3-Hydroxybutyrolactone (3-HBL, Figure 18) is a versatile chiral building block utilized in the synthesis of a variety of pharmaceuticals, polymers and solvents. Enantiopure 3-HBL is an important precursor for chiral drugs (i.e., cholesterol reducing statins) and antibiotics (carbapenems and linezolid). In addition, the functional groups of enantiopure 3-HBL can be derivatized to yield chiral building blocks such as lactones, THFs, amides, nitriles, epoxides, and solvents [39, 40].

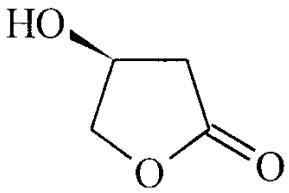


Figure 18. 3-Hydroxybutyrolactone.

C5 Compounds

Furfural

Furfural (FF, Figure 19) is one of the members of the furanics class, which also encompasses 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid and 2,5-dimethylfuran. The current world production of FF is estimated at ca. 250 000 tons/year, hence demonstrating its importance.

The chemical dehydration of five carbon carbohydrates (such as xylose and arabinose) yields furfural. Furfural is an established chemical product with a static market. China is the world's main producer of furfural, followed by the Dominican Republic. It seems that furfural production will increase in the upcoming years, probably lowering its costs and making traditional and new outlets of furfural economically attractive again [41].

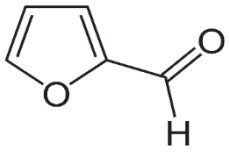


Figure 19. Furfural.

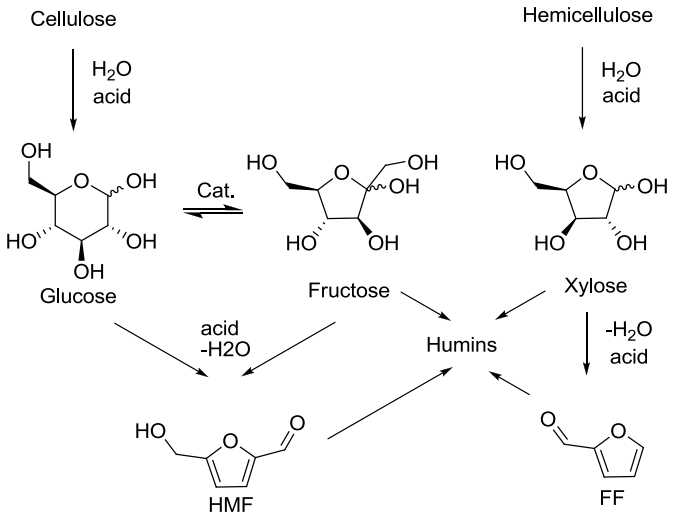


Figure 20. Routes to HMF and FF from cellulose and hemicellulose.

Furanics class bears formyl and/or hydroxymethyl groups. By means of both catalytic and synthetic organic pathways it can be converted to a variety of different functional groups that are suitable for polymerization reactions, as for hydroxymethylfurfural (HMF) (Figure 20) [42]. Excellent reviews on the large diversity of furanic monomers and their application in polymer chemistry have been published by Gandini et al. [43].

Levulinic Acid

Amongst the lignocellulosic biomass derived monomers, levulinic acid (LevA, Figure 21) has a critical importance, as its large-scale production from lignocellulosic biomass has already been achieved.

Levulinic acid can be obtained by means of acid treatment of starch or C6-carbohydrates in lignocellulosic biomass via hydration of hydroxyl-methylfurfural (HMF), a reaction intermediate. Formic acid, which is produced in equimolar amounts, is a side product of this reaction. It is also possible to obtain levulinic acid from the five carbon carbohydrates in hemicellulose (e.g., xylose, arabinose), by carrying out a reduction step (via furfuryl alcohol) subsequent to the acid treatment.

Avantium technology has developed a tunable process to convert plant-based carbohydrates into high purity methyl levulinate, which can be easily converted to LevA through a straightforward process [44]. Although these processes, for the first time, provide cost competitive and high-volume access to levulinics, the current LevA prices, remaining in between 5-8 $/kg, must be further decreased to 1 $/kg or below. Thereupon, the production of LevA as a giant commodity chemical can be achieved. For a further reduction of the LevA prices, its direct production from cheap cellulosic biomass feedstocks is more convenient: this issue is under intense investigation [45]. Levulinic acid has been promoted as an important biorefinery building block, due to its high yield from six carbon carbohydrates. LevA is the precursor of the levulinic family (Figure 22) and it branches too many valuable new compounds having novel applications. In particular, it is a significant precursor for many pharmaceuticals, plasticizers, and additives. Various companies recently launched the production of novel bio-polymers based on LevA or its derivatives, aiming at producing cost competitive and sustainable polymers [46].

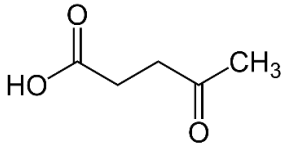


Figure 21. Levulinic acid.

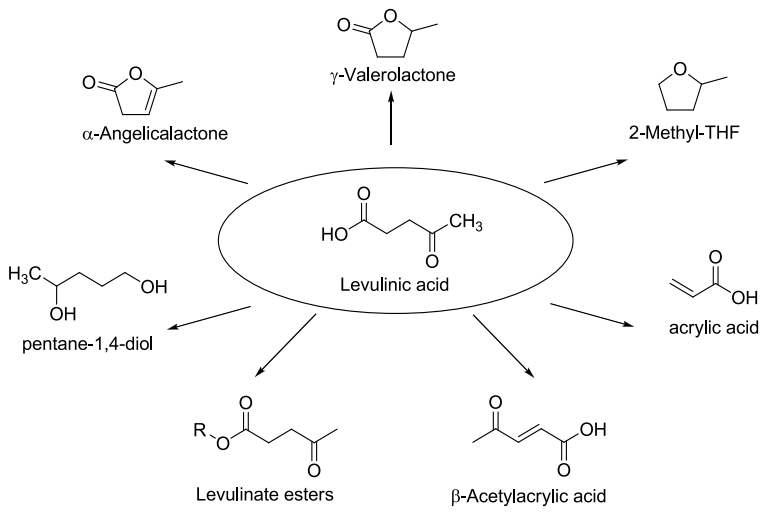


Figure 22. Levulinic acid derivatives.

It can be highlighted that LevA derived diphenolic acid (DPA) is considered as sustainable replacement for bisphenol A (BPA), due to the growing concern regarding the sustainability of BPA in consumer products and food containers (in fact, it may have a pseudo-hormonal effect on the body). It can be easily produced by reacting levulinic acid with two moles of phenol at 100°C in acidic conditions (Figure 23) [47]. Both these starting chemicals can be produced from lignocellulosic biomass. DPA has also attracted interest in the synthesis of poly(arylene ether ketone) (PAEK) and poly(ether ketone) (PEEK) based membranes for fuel cell applications [48].

In addition to DPA and levulinic ketals, LevA can be directly converted to levulinic esters [49], 5-aminolevulinic acid (DALA) [50], angelica lactones (ANLs) [51], 2-butanone [52], 4-hydroxy pentanoic acid or its esters [53] and gamma-valerolactone (GVL) [53]. Common applications of these direct derivatives of LevA are summarized in Figure 23. 5-aminolevulinic acid may represent a new interesting opportunity within the amino acid-based polymers. 4-hydroxypentanoic acid (4-hydroxyvaleric acid) is a monomer belonging to hydroxyalkanoates family. It can be polymerized into polyhydroxyalkanoates (PHAs) by chemical and/or biological methods.

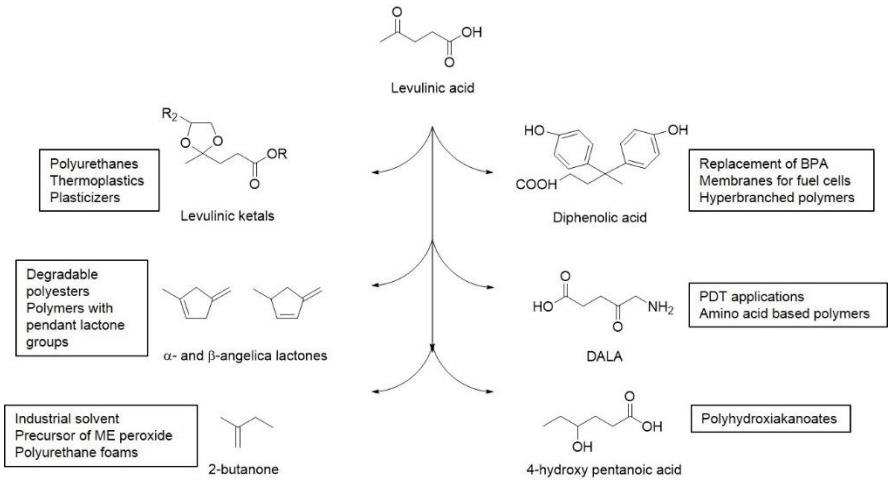


Figure 23. Scheme of synthetic routes for levulinic acid derivatives and applications of these derivatives.

LevA can be hydrogenated to GVL by employing either homogenous or heterogeneous catalysts that can produce several chemicals and fuels, including polymers, fuel additives, and jet fuels [52]. Levulinic acid platform can also open novel synthetic routes for the production of such giant monomers as butene and adipic acid (ADA).

Isoprene/Farnesene (Biohydrocarbons)

The fermentation of carbohydrates to biohydrocarbons is the latest wave of targets for bio-based chemical production. This opportunity is partly ascribed to the recent advances in synthetic biology that is allowing industry to design microbes for the production of a new range of molecules.

Isoprene (Figure 24) is a five carbon hydrocarbon used primarily in the production of polyisoprene rubber, styrenic thermoplastic elastomer block copolymers and butyl rubber. Isoprene is employed in products ranging from surgical gloves to car tyres. Isoprene has a market value of $1-2 billion. The production of isoprene from renewable resources (BioIsoprene™) is the target of a joint venture between the Goodyear Tire and Rubber Company and the biotechnology company Genencor [54]. Using BioIsoprene™, Goodyear has produced a synthetic rubber to be embedded in a concept tyre,

demonstrating the equivalence of BioIsoprene™ with the petroleum derived counterpart [55].

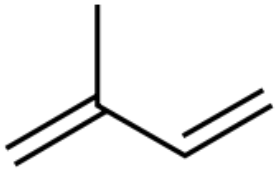


Figure 24. Isoprene.

Xylitol/Arabitol

Xylose and arabinose are the main pentoses or C5-carbohydrates in hemicellulose. The hydrogenation reaction of these carbohydrates yields two isomers, namely xylitol and arabitol. Xylitol (Figure 25) is presently used as a sustainable, naturally occurring sweetener with all the sweetness of sugar but with 40% less calories. At the moment there is limited commercial production of xylitol outside China and no commercial production of arabitol. Xylose and arabinose can be obtained from lignocellulosic biomass, though a major challenge is to obtain clean feed streams of these carbohydrates exploiting a low-cost procedure. However, these sugar alcohols have other potentialities, as they can be converted to glycols, namely ethylene glycol and 1,2 propanediol [13].

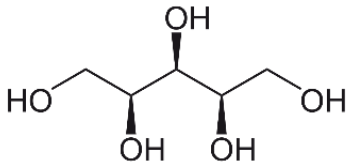


Figure 25. Xylitol.

Itaconic Acid

Itaconic acid (ITA, Figure 26) is one of the most attractive monomers for producing bio-based polymers, as it bears two functional acid groups, as well as a vinyl functionality. It is produced industrially via fermentation of carbohydrates (mainly glucose) by fungi; its recent market volume is about

15 kt/year. Though the chemical synthesis of ITA starting from different compounds, like citric acid, is also known, it is not economically and ecologically convenient for large scale production. According to Yao and Tang, itaconic acid may become a monomer replacing petrochemical-based acrylic or methacrylic acid, owing to its similarity in structure [56]. The current production of petroleum-based acrylic and methacrylic acid requires several chemical synthesis steps. In this consideration, ITA shows processing and ecological advantages, since it is a product derived from the direct fermentation of cheap carbohydrates. On the other hand, its market penetration requires a cost competitive production with respect to other acrylic monomers.

ITA has already been used in the production of synthetic fibers, coatings, adhesives, thickeners and binders. For instance, it is primarily used as comonomer in styrene butadiene polymers to provide dye receptivity in the fiber industry. Furthermore, its homopolymer, polyitaconic acid (PIA), is commercially available (Figure 27).

Apart from being a valuable monomer itself, ITA is also employed as a parent molecule for the production of other monomers: among them, 2-methyl-1,4-butanediol (2-MBDO) is a promising example. Upon a dehydration reaction carried out under acidic conditions and at high temperatures, the carbohydrate derived ITA can be converted to itaconic anhydride (ITAn). However, a faster synthesis process, which can proceed under milder conditions, is needed for this conversion. Itaconic acid is one of the unique monomers for designing cyclic anhydride copolymers, which can exhibit biodegradable characteristics and are derived from renewable resources.

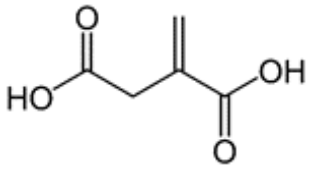


Figure 26. Itaconic acid.

The hydrogenation of the vinyl group of itaconic acid leads to the formation of hydroxyl acids. Then, intramolecular esterification of the hydroxyl acids yields two regioisomeric monomers, namely 2-methyl butyrolactone (2-MGBL) and 3-methyl butyrolactone (3-MGBL). Depending on the large-scale production of ITA from lignocellulosic biomass, these derivatives can provide a larger contribution to polymer research and industry.

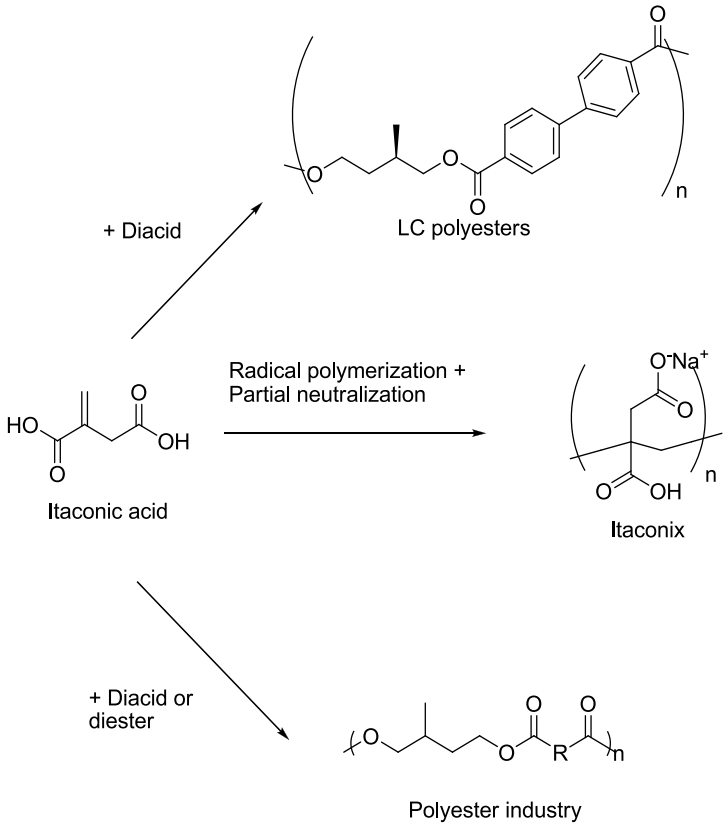


Figure 27. Itaconic acid derivatives polymerization.

Glutamic Acid

Currently, the global production capacity of glutamic acid (Figure 28) is more than 200 kt per year; most of this production is achieved through

fermentation. Although glutamic acid is produced from cheap feedstocks, there are certain limitations in its large-scale production process. The main limitation stems from its complex processing, which consists of a number of downstream treatment schemes like precipitation, conventional filtration, acidification, carbon adsorption and evaporation. All these treatments are essential to obtain high purity glutamic acid but they greatly increase the overall production cost. Thus, a new process is required to produce glutamic acid in a more eco-friendly and economically way. In this consideration, a membrane-based processing is envisioned to eliminate the need for separate purification units and to reduce the overall production cost [57]. Thus, a shift from the current complex processing to a membrane-based technology might be observed in the glutamic acid market in the near future.

The industrial production of glutamic acid is quite important for obtaining the C5 compounds and their corresponding polymers. So far, the most successful commercial polymer form of glutamic acid is poly-γ-glutamic acid (γ-PGA), an anionic biopolymer formed via gamma-amide linkage. A structurally different polymer of glutamic acid is poly-α,L-glutamic acid (α,L–PGA), which is generally synthesized starting from poly(-benzyl-L-glutamate) (PBLG, Figure 29).

Hence, PGA and its derivatives have been of interest in the past few years, especially in food, cosmetics, medicine, and water treatment industries. The glutamic acid platform can provide bio-based monomers for polyamides and polyesters. Its hydrogenation product, 1,5-PDO, has already been used as a common plasticizer in today's modern polymer industry, owing to its fairly long carbon chain [58].

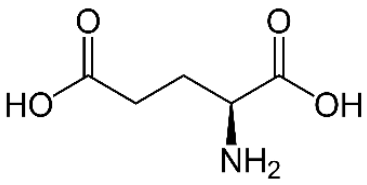


Figure 28. Glutamic acid.

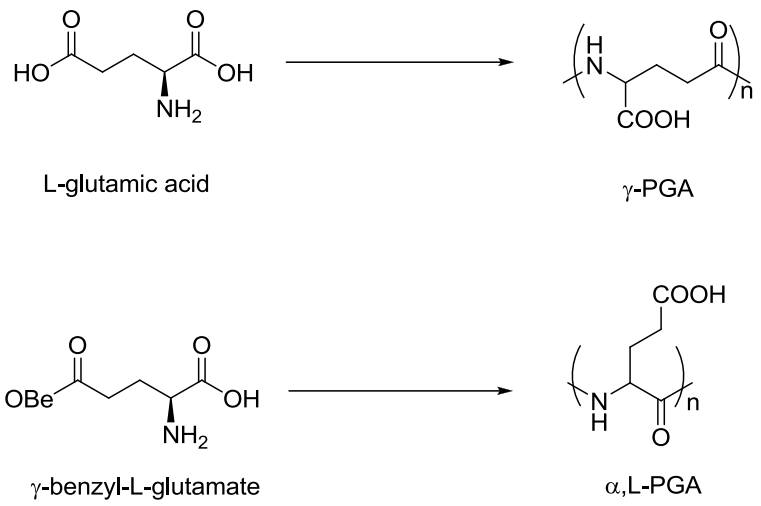


Figure 29. γ-PGA from L-glutamic acid and synthesis of α,L–PGA.

1,5-Pentanediamine (Cadaverine)

From the chemical viewpoint, 1,5-pentanediamine (Figure 30) is a linear aliphatic diamine with five carbons. It has been isolated and described for the first time more than 100 years ago during systematic experiments on the putrefaction of human cadavers, obviously providing rather directly its trivial name cadaverine [59]; it is a minor member of the group of biogenic polyamines.

1,5-pentanediamine is an important industrial platform chemical with a variety of applications including the production of polyamides or polyurethanes, chelating agents, or additives. In the rising era of bio-economy, 1,5-pentanediamine is receiving increasing interest as chemical platform, especially as innovative building block for bio-based polymers. The vital interest in bio-based supply of 1,5-diaminopentane has strongly stimulated research on the development of engineered producer strains. Particularly, it is relevant for bio-polyamides derived from renewable feedstocks to replace conventional polyamides from petrochemical routes, which suffer from shortage and rising prices of the fossil resources, as well as low eco-efficiency. As an example, using 1,5-pentanediamine derived from microbial biosynthesis, polymerization with appropriate bio-blocks

such as succinate from microbial fermentation, or sebacic acid from natural plant oils, allows the production of completely bio-based polyamides [60].

Though 1,5-pentanediamine is currently mainly manufactured by oil-based chemical synthesis, the microbial conversion of sugars, molasses, methanol and other carbon sources into 1,5-pentanediamine was demonstrated recently. 1,5-pentanediamine can be produced by a single step decarboxylation of L-lysine, one of the largest biotechnological bulk products (2 million tonnes in 2015). Large global producers of L-lysine, like Ajinomoto, Cathay and Evonik Industries AG, have patented production processes. Bio-based diamine is produced from 100% plant sugars using a patented process developed by Cathay Biotech and by Ajinomoto in collaboration with Toray. The most prominent *L*-lysine and 1,5-pentanediamine producing host is currently *Corynebacterium glutamicum*, which for decades has been subject for classical mutagenesis and genetic engineering, aiming at increasing the production levels of various amino acids or the ability to metabolize alternative carbon sources, e.g xylose and methanol. Though the technologies for engineering of bacterial strains for 1,5-pentanediamine production are known, the highest reported yields on glucose in the open literature are still only around 10%, while the yield for lysine is between 50 and 60%. Increasing the yields and obtaining competitive productivities are therefore a challenge.

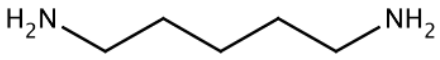


Figure 30. 1,5-Pentanediamine.

C6 Compounds

Hydroxymethylfurfural (HMF) and 2,5-Furandicarboxylic Acid (FDCA)

Hydroxymethylfurfural (HMF, Figure 31) is produced by the chemical dehydration of six carbon carbohydrates. HMF has driven its derivatives to

become potential building blocks for step-growth polymers. In addition, the development of inexpensive vinyl polymers from biomass derived 5-HMF can introduce new substituents for commodity polymers.

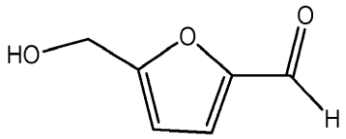


Figure 31. Hydroxymethylfurfural.

HMF can be converted by chemical manipulation to a range of furan derivatives. The oxidation of HMF gives 2,5-furandicarboxylic acid (FDCA, Figure 32), which has been suggested as a replacement for terephthalic acid in the production of polyesters. The range of potential furanic products and the possible uses in novel polymer structures suggests the potential for good market growth if commercialisation can be achieved. The Dutch company Avantium is building a platform technology, branded as "YXY," to commercialize bio-based furanics. Furanics are green building blocks for a range of materials, chemicals and fuels. In the scientific literature, furanics are referred to as "sleeping giants," because of their enormous potential for the production of green plastics and chemicals. Furanics were also listed in the top 12 high-potential green building blocks published by the US Department of Energy. Until today, furanics had not been commercialized because their production was not cost-effective yet [61]. Thus, the "sleeping giants" have already woken-up and started to claim their place in today's market. As an example, Avantium has developed 100% bio-based polyethylene-furanoate (PEF) bottles, fibers and films under the mentioned brand of "YXY," by using plant sugar derived 2,5-FDCA.

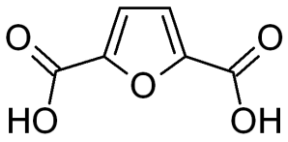


Figure 32. 2,5-Furandicarboxylic acid.

Such platform chemicals as 5-hydroxymethylfurfural (HMF) and furfural (FF) are the starting point for the synthesis of furan-based monomers (Figure 20). In short, the production of HMF relies on an acid-catalyzed hydrolysis of cellulose and hemicellulose to the corresponding carbohydrate monomers (namely, glucose and xylose). A subsequent treatment of glucose and xylose under acidic conditions leads to their corresponding dehydration products, HMF and FF.

The HMF production is much more problematic than that of FF, due to further transformation to levulinic acid and formic acid via a rehydration reaction. This can be largely avoided by switching to nonaqueous solvents; however, since biomass fractionation processes mostly employ water, a large energy penalty has to be paid for the water removal. These problems aside, HMF has received considerable attention as its oxidation product (2,5-furandicarboxylic acid, FDCA) represents a suitable replacement for terephthalic acid (TPA) and isophthalic acid [62]. TPA is mostly used in the large-scale synthesis of polyesters (e.g., poly(ethylene terephthalate) (PET)) and polyamides (e.g., poly(phthalamides), aramids), which are employed in textiles and beverage containers. In theory, the use of FDCA as a substitute for TPA, together with biomass-based ethylene glycol, allows the preparation of completely renewable polyesters, leading to a significant reduction of greenhouse gas emissions [63].

Other potential applications of FDCA include its use in the production of polyureas [64] and polyester polyols [65]. As a result, new and improved routes, as well as scale-up of processes for the production of HMF are actively being researched. In 2013, AVA Biochem BSL AG built up the first industrial HMF production facility with a small capacity of 20 tons/year. Furthermore, Avantium is currently building a pilot plant for the production of FCDA with a capacity of 50 000 tons/year, which is expected to come on stream in the next years. Besides this application, furanic monomers possess a big potential for the replacement of various fossil-based monomers.

Sorbitol

Sorbitol (Figure 33) is produced at a large industrial scale by catalytic hydrogenation of glucose. It is a batch process with a production volume of

1.1 Mton/year [13]. Though fermentative routes are also suggested [66], it seems that these approaches cannot replace the technically mature catalytic hydrogenation process. Besides food, sorbitol is also the raw material for other products such as surfactants and polyurethanes. Sorbitol can also be further derivatized into ascorbic acid (80.000 ton/year by combined biotechnological/chemical process), sorbitan (50.000 ton/year), isosorbide (selective dehydration) and 1,2-propanediol by hydrogenolysis (900.000 ton/year) [67].

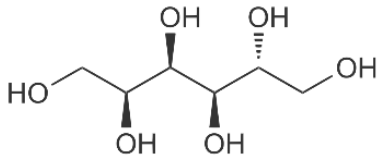


Figure 33. Sorbitol.

Isohexides and Derivatives

Due to their two functional hydroxyl groups, the isohexides pose a great potential for further functionalization. Examples of these diols comprise isomannide (1,4:3,6-dianhydro- *D*-mannitol), isosorbide (1,4:3,6-dianhydro-*D*-glucitol/-sorbitol) and isoidide (1,4:3,6-dianhydro-*L*-iditol) (Figure 34).

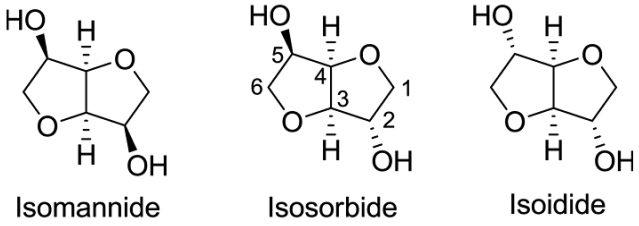


Figure 34. Three different isohexide isomers exhibiting different configurations of the 2-C and 5-C hydroxyl groups.

A huge number of stoichiometric, as well as catalytic approaches has been reported to be suitable for grafting the hydroxyl groups with differently functionalized organic residues, via ether or ester bond formation [68].

However, the direct replacement of the hydroxyl groups in positions 2 and 5 by alternative functional groups is of utmost importance, since it shows the advantage of using the rigid isohexide backbone with much higher flexibility as compared to other aliphatic monomers. Thus, in the following, synthetic and catalytic examples are discussed, focusing on the production of isohexide-based dicarboxylic acids, diamines, and diisocyanates.

Derivatives of isohexides are investigated for numerous applications. In particular, application of nitrates as pharmaceuticals, aliphatic esters and ethers as high-boiling solvents and fuel additives, monosubstituted derivatives as surfactants with the isohexide being a sterically demanding polar headgroup, chiral auxiliaries or even ionic liquids and deep eutectic solvents have been reported.

Isosorbide is a diol obtained by dehydration of sorbitol (a derivative of glucose), for which Roquette is the leading world producer. Isosorbide is used for the manufacture of specialty polymers belonging to the polyester (the so-called PET-like polymers), polycarbonate and polyurethane families. Thanks to its rigid structure, isosorbide is the only biobased diol that improves resistance to heat, UV rays and chemicals and provides the obtained materials with excellent optical and mechanical properties.

Lysine

The production of nitrogen-containing bulk chemicals from biomass is in a less advanced state with respect to oxygenated bulk chemicals such as glycols. Biobased routes from lysine to caprolactam for the production of nylon have perhaps received the highest attention. In the 1950s, the fermentation with *Corynebacterium glutamicum* was found to be a very efficient production route to *L*-glutamic acid. Since that time, biotechnological processes involving bacteria of the species *Corynebacterium* were developed and became among the most important in terms of tonnage and economical value. Nowadays, *L*-lysine (Figure 35) is a bulk product with a production volume of 640 kton/year [67] and a cost price of 1200 €/ton. Other routes that are currently under investigation refer to the development of genetically modified plants with elevated levels of certain amino acids such as lysine. This way, amino acids that are naturally

produced by plants can be produced at higher concentration levels by overexpression of specific structural genes [13].

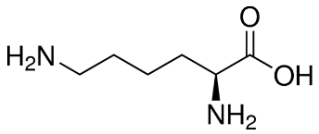


Figure 35. L-Lysine.

Adipic Acid

Adipic acid (hexanedioic acid or 1,4-butanedicarboxylic acid, Figure 36) is the most important aliphatic dicarboxylic acid. It is a white crystalline powder, primarily used for the production of polyamide 6,6. The current market for adipic acid is close to 3 million tons per year, worth approximately $8 billion at current market prices [13].

Though several fossil-based processes for the production of adipic acid have been reported, only one involves a biomass substrate, i.e., the biosynthesis of *cis,cis*-muconic acid by fermentation of glucose, followed by catalytic hydrogenation to adipic acid [69]. Apart from the optimization of production organisms, the recovery of adipic acid from aqueous medium at the purity levels needed for polymer-grade products and the catalytic conversion of muconic acid to adipic acid need to be further investigated. Since then, several companies have claimed processes for adipic acid.

Verdezyne Inc. demonstrated the feasibility of the production and recovery of adipic acid by a yeast microorganism from an alkane feedstock [70]. BioAmber, one of the market leaders in biobased succinic acid, has entered into an exclusive licensing agreement with Celexion LLC for the technology related to the production of adipic acid and other chemical intermediates [71]. A recent patent describes how to produce a "green" version of key intermediate chemicals for obtaining nylon, utilizing renewable feedstocks such as commercially-available carbohydrates, instead of crude oil or natural gas [72]. These organisms directly produce adipic acid and 6-aminocaproic acid (6-ACA), which can be exploited for the synthesis of polyamide 6,6 and polyamide 6, respectively. Rennovia is

also working on the production of adipic acid from renewable raw materials, becoming competitive with the conventional DuPont/Invista cyclohexane-based oxidation process.

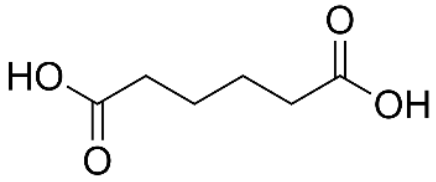


Figure 36. Adipic acid.

The ultimate motivation of these companies towards the synthesis of bio-ADA is to produce 100% bio-based polyamides. In this consideration, ADA is a critical monomer. About 85% of the total produced ADA is utilized for the production of PA-6,6 [73]. PA-4,6 is another important commercial polymer of ADA. Apart from the polyamides, esters and polyesters comprise the second most important class of ADA derivatives. Esters of ADA can be obtained from alkylpenteonates [74]; furthermore, ADA can be readily reacted with alcohols to give either its mono- or diesters [75]. Moderately long-chain esters of ADA find large applicability as plasticizers, particularly for poly(vinyl chloride) (PVC) [73]. As an example, BASF manufactures and markets di-2-ethylhexyl adipate and di-isononyl adipate derivatives of ADA under the trend name of Plastomoll® [76].

cis,cis-Muconic Acid

cis,cis-Muconic acid (*cis,cis*-MA, Figure 37) can be converted by hydrogenation into adipic acid or turned into terephthalic acid (with a global market of 71 million tons), which is the main component of polyethylene terephthalate (PET). Besides, *cis,cis*-MA could be exploited for the production of other compounds, such as diamines or mercapto acids and esters.

Cis,cis-muconic acid has a high commercial potential when produced from biomass. Some integrated biochemical production routes are being developed as carbon source with glucose and lignin, as the first and second

generation biomass, respectively [77]. To transform glucose into *cis,cis*-MA, the substrate is first converted via the shikimic acid pathway to dehydroshikimate, which can be further transformed into cis,cis-MA via, subsequently, *3-dehydroshikimic acid dehydratase* (AroZ), *protocatechuic acid decarboxylase* (AroY), and *catechol 1,2-dioxygenase* (CatA) [78]. These three enzymes are heterologously expressed. On the other hand, *Arthrobacter sp*. and *Pseudomonas sp*. can convert benzoate into *cis,cis*-MA via the ortho-cleavage pathway, which is a part of the ß-ketoadipate pathway [79]. At present, the further industrial usage of *cis,cis*-MA is hampered by its high price. Compared with the top sugar-derived building blocks and new top chemical potentials from biorefinery carbohydrates, *cis,cis*-MA is relatively unknown [80]. Of all the *cis,cis*-MA produced, 85% is processed into adipic acid [81]. The opportunity to develop processes for the production of MA from lignin paves the way for the biotechnological utilization of the waste materials-derived components. With further microbial strain and process optimizations, the concentration of MA obtained from biotechnological processes might reach an industrially relevant value.

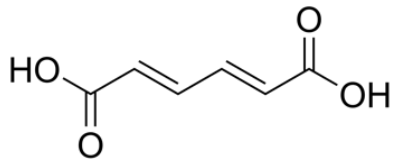


Figure 37. *Cis,cis*-muconic acid.

Glucaric and Gluconic Acids

The main contribution of the glucaric acid (Figure 38) platform to the polymer chemistry would be in the design and synthesis of novel sugar-containing polymers. In terms of linear monosaccharide derivatives, *D*-gluconic acid (Figure 39) has an estimated market size of 60 kt/year. It is usually produced by enzymatic oxidation of *D*-glucose, which is facilitated by the enzyme glucose oxidase and glucose dehydrogenase. *D*-gluconic acid is considered as an interesting source of comonomers to synthesize functionalized polyesters for biomedical and pharmaceutical applications.

However, the polyesters are not suitable for large scale production, as several laborious and expensive steps are required to synthesize the dilactone monomer. Other polymers that can be produced from *D*-gluconic acid comprise polyurethanes, hydrogels, hydroxylated polyamides and novel initiators. Their research and industrial utilization can extend from composites to cosmetic and biomedical materials [82].

As another linear monosaccharide derivative, glucaric acid can be obtained by oxidation of the primary hydroxyl group of gluconic acid on Pt/C catalysts. The recent literature on polymers of glucaric acid is mainly based on poly(*D*-glucaramidoamine)s (PGAAs). Efficient and degradable gene delivery vehicles consist of three main functionalities: carbohydrate groups, secondary amines and amide bonds. Nobes et al. synthesized and tested a number of poly(glucaramides) that were used as an additive in fiber-reinforced panels. The water resistance of the panels increased dramatically with increasing the amount of poly(glucaramide) in the formulation [83].

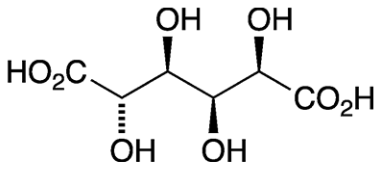


Figure 38. Glucaric acid.

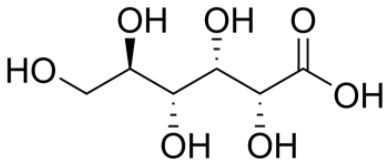


Figure 39. *D*-Gluconic acid.

Other C6 Based Building Blocks

Several other C6 based building blocks are currently used at scales around 100 kton/year and beyond. Important examples comprise ascorbic

acid (formed by combined biotechnological/chemical process), sorbitan (formed by dehydration of sorbitol) and phenols (from lignin).

Cn Compounds

p-Xylene

The production of *p*-xylene is industrially significant, with annual demand estimated at 37 million tons in 2014, and still increasing. *p*-Xylene is produced by catalytic reforming of petroleum naphtha as part of the BTX aromatics (benzene, toluene and the xylene isomers) extracted from the catalytic reformate. The reaction of dimethylfuran and ethylene to produce *p*-xylene has been disclosed in a patent by Honeywell/UOP [84]. The dimethylfuran can be produced from such carbohydrates as glucose or fructose. Virent, the latest in line, claims to have produced *p*-xylene in its pilot plant made through a patented catalytic process that converts plant-based carbohydrates into *para*-xylene molecules [85]. However, in spite of all this activity, none of these technologies are close to being commercial and it seems it will take a lot of time before they will be cost competitive with fossil-based alternatives.

p-Xylene (Figure 40) is an important chemical feedstock. Among other industrial applications, it is a raw material suitable for the large-scale synthesis of various polymers. In particular, it is a component in the production of terephthalic acid for polyesters (namely, polyethylene terephthalate). Besides, it could be polymerized directly to produce parylene.

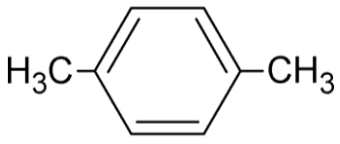


Figure 40. *p*-Xylene.

Fatty Acid Derivatives

Oils, fats and their derivatives have already been used for a long time in the chemical industry. Compared to other major plant constituents such as carbohydrates, proteins and lignins, fatty acid derivatives are the easiest to handle in the current hydrocarbon-based chemical infrastructure, due to their often liquid nature and their low oxygen content. Palm, palm kernel and coconut oil, being rich in C12-C18 saturated and monounsaturated fatty acids, are important sources for a broad range of surfactants in soaps, detergents and personal care products. 'Drying oils' such as soybean, sunflower and linseed oil contain high levels of polyunsaturated fatty acids and are major raw materials for thermosetting systems such as coatings and ink resins, lacquers and linoleum. Epoxidized soybean and linseed oils are used as (secondary) plasticizers and stabilizers in PVC. Rapeseed oil has a high level of oleic acid: thus, it is a favoured source for biolubricants, for which low viscosity combined with high oxidative and thermal stability are important properties. Although their number is currently relatively small, a few bifunctional building blocks derived from fatty acids are commercially applied. Sebacic acid is used for the preparation of such polyamides as polyamide 4,10 (EcoPaXX® by DSM), polyamide 10,10 (VESTAMID® Terra DS by Evonik; Zytel RS 6/10 by DuPont) and polyamide 6,10 (VESTAMID® Terra HS by Evonik; Ultramid® BALANCE by BASF and Technyl eXten by Rhodia). 10-Undecenoic acid is converted by Arkema to 11-aminoundecanoic acid, the monomer for polyamide 11 (Rilsan®). Arkema also produces sebaic acid-based polyamides 10,10 and 10,12 under the name Hiprolon. DSM also produces a thermoplastic copolyester (Arnitel Eco) based on rapeseed oil, while BASF/Elastogran produces castor oil-based polyols (Lupranol® BALANCE 50). Cognis produces azelaic acid, a C9 dicarboxylic acid, by ozonolysis of oleic acid. Azelaic acid is used as a monomer in polyamide 6,9. Dimerised fatty acids or dimer acids represent a well-known class of branched difunctional oleochemical products: they are C36 dicarboxylic acids obtained by treating unsaturated fatty acids at high temperature with clay catalysts [13].

Aromatic Monomers

Renewable phenolic compounds can be obtained from various biomass species and components, such as lignin, tannin and extracts from cashew nut shell, palm oil, and coconut shell. Lochab et al. comprehensively reviewed the naturally occurring phenolic sources, the isolation process of desired phenol compounds and their utilization for polymer production [86].

Lignin Derivatives

Lignin offers a significant opportunity for enhancing the operation of a lignocellulosic biorefinery. It is an extremely abundant raw material contributing as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass. The native structure of lignin suggests that it could play a key role as a new chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals [87]. Up to now, the vast majority of industrial applications has been developed for lignosulfonates. These latter are isolated from acid sulfite pulping and are used in a wide range of low value applications, where the form – instead of the quality – is important. The solubility of this type of lignin in water is an important requirement for many of these applications. Around 67.5% of world consumption of lignosulfonates in 2008 was for dispersant applications followed by binder and adhesive applications (32.5%). Major end-use markets include construction, mining, animal feeds and agriculture uses. So far, the use of lignin for chemical production has been limited due to contamination from salts, carbohydrates, particulates, volatiles and the molecular weight distribution of lignosulfonates. The only industrial exception refers to the limited production of vanillin from lignosulfonates [13].

Besides lignosulfonates, Kraft lignin is produced as commercial product at about 60kton/year. New extraction technologies, developed in Sweden, will lead to an increase in Kraft lignin production at the mill side, foreseeing uses as external energy source and for the production of value added applications [88].

Biomacromolecules as "Green" Flame Retardants (FRs)

Quite recently, some selected biomacromolecules (namely, caseins, hydrophobins, whey proteins and nucleic acids) turned out to exhibit flame retardant properties [89, 90], suitable for improving the fire behaviour of different textiles (namely cotton, polyester and their blends) [91-99] and of some thermoplastic polymers (such as polyolefins and EVA copolymers) [100, 101]. It is worthy to note that, in some cases, the fire performances of these biomacromolecules are comparable to those observed for standard phosphorus-based FRs.

Besides, the use of the selected biomacromolecules in flame retardancy is definitely related to their low environmental impact and toxicity: in fact, when applied to fabric substrates, these products are usually dissolved or suspended at low concentrations in aqueous media, hence limiting the release of VOC (Volatile Organic Carbon) species. On the other hand, their melt compounding in low melting thermoplastics can be carried out using the standard processing techniques (extruders, Brabender mixers …).

In addition, some of the investigated biomacromolecules (namely, caseins and whey proteins) are considered as by-products or even wastes from the agro-food industry and their recovery and subsequent use as flame retardants may fulfil the current needs towards the valorization of agro-food crops, limiting and/or avoiding their landfill confinement. Besides, despite the considerably high cost of deoxyribonucleic acid (DNA) with respect to traditional chemical FRs, its availability has become competitive with those of other FRs, thanks to the large-scale method quite recently developed [102], which involves the extraction and purification of the biomacromolecule from salmon milt and roe sacs.

The mode of action of these substances is connected to their chemical composition. For instance, nucleic acids contain the three ingredients typical of an intumescent formulation, namely: the phosphate groups able to produce phosphoric acid, the deoxyribose units acting as a char carbon source and blowing agents and the nitrogen-containing bases (i.e., adenine, guanine, cytosine and thymine) that may release ammonia. Besides, whey proteins comprise sulfur-containing structures, like methionine and cysteine, which are quite effective for fire retardant purposes. Caseins are phosphor-

proteins that represent the main fraction of milk proteins (around 80%) and, perhaps, the most widely studied food proteins, obtained as co-products during the production of skim milk: once again, their chemical composition can be successfully exploited for providing flame retardant properties to polymeric matrices. Finally, the structure of hydrophobins comprises sulphur (as cysteine structures) and nitrogen (as amino acid residues), which can be successfully exploited for flame retardant purposes.

In some cases, the biomacromolecules were blended with other natural materials, such as clays and crab shells, to improve the flame retardancy in a synergistic way [103]. Very recently, it was demonstrated that it is possible to recover nucleic acids from vegetable scraps and spent brewer's yeasts, at a lab scale, using "green" recovery methods and to use the recovered biomacromolecules as effective flame retardant additives for cotton fabrics [104]. Thus, some of the selected biomacromolecules can be considered as high added value materials, which can be recovered from wastes, by-products and co-products from the agro-food industry. Therefore, their recovery and use as effective FRs may comply with the current needs towards the valorization of agro-food crops, avoiding their landfill confinement.

Despite the flame retardant efficiency observed for the aforementioned biomacromolecules, there are still some challenging issues that justify further investigation.

First, the possibility of scaling up the technology involving the biomacromolecule at least to pre-industrialization is still under evaluation and the final decision will be certainly established on the cost-effectiveness of the proposed biomacromolecules. In fact, nucleic acids are presently very expensive: therefore, their use as FRs could be expected on the basis of a significant cost reduction. It is worthy to note that the production capacity of the industrial extraction plants for these biomacromolecules is being projected to grow in the forthcoming years, because of the enhancement of the extraction processes and technologies that should provide higher yields, keeping the purity of the extracted biomacromolecules at the suitable level required for their use in flame retardant textiles.

Besides, one of the current limitations of the use of flame retardant biomacromolecules refers to their low thermal stability that does not comply with the processing temperatures (beyond 180-200°C) required for most of the flame retarded thermoplastics: therefore, the possibility of improving their thermal stability is a key factor for making these biomacromolecules suitable as effective flame retardants for thermoplastic matrices, including polyamides.

Bio-Based Polymers from the Most Relevant Chemical Building Blocks

In this section, the most relevant bio-based polymers produced from the chemical building blocks described in the previous section are presented.

Figure 41 shows some of the most relevant biopolymers that can be obtained from biomass [14].

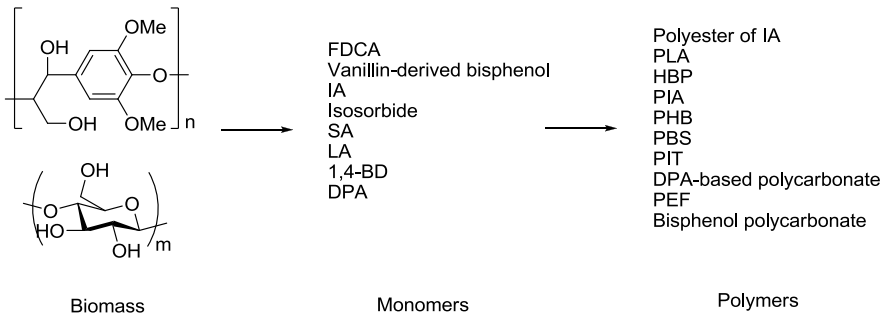


Figure 41. Production of biobased polymers. Abbreviations for the monomers: LA (lactic acid), IA (itaconic acid), SA (succinic acid), 1,4-BDO (1,4-butanediol), DPA (diphenolic acid), and FDCA (2,5-furandicarboxylic acid). Abbreviations for the polymers: PLA (poly(lactic acid)), HBP (hyperbranched polymer), PIA (poly(itaconic acid)), PHB (poly(3-hydroxybutyrate)), PBS (poly(butylene succinate)), PIT (poly(isosorbide terephthalate)), and PEF (poly(ethylene 2,5-furandicarboxylate)).

Similarly to what was done in the last section, in order to make easier their description, the polymers will be segmented on the basis of the number of carbons of the chemical building block involved.

C3 Compounds

Lactic Acid Based Biopolymers

As it was mentioned in the last section, the polymerization of lactic acid produces poly(lactic acid) (PLA), which is used in food packaging, as well as mulch films, rubbish bags, fibres in clothes and in other industrial applications. In addition, materials based on PLA and its copolymers have extensive applications in the biomedical field as drug delivery capsules, suture and bone fixation materials, tissue engineering, etc.

PLA was first synthesized over 150 years ago, but its instability under humid conditions retarded the introduction into the market. In the 1960s, the usefulness of PLA in medical application became apparent. After intensive research in 1980 – 1990s, Cargill developed a continuous process for the production of high purity lactide based on reactive distillation [105]. Since then, the capacity of the PLA production has gradually increased, while its market augmented drastically. The global leader in PLA production is NatureWorks. Other companies active in PLA include Futerro, Teijin Fibers, Toyobo, HiSun and Pyramid Bioplastics [106]. The development of PLA applications has been hampered by some of its functional characteristics. These short-comings are now being overcome through the use of additives and, importantly, through the controlled polymerization of defined isomers of lactic acid.

Figure 42 shows two existing procedures of PLA synthesis, namely direct polycondensation and ring-opening polymerization of lactides. Both processes rely on a substrate of very high purity: therefore, the purification of crude LA is a crucial operation step. Direct polycondensation is an organic solvent-based process under azeotropic removal of water by distillation. The removal of water at a high degree of polymerization is challenging, due to the very slow diffusion of moisture out of the highly viscous polymer. Importantly, the presence of water is detrimental as it decreases the molecular weight of PLA. Therefore, only a few companies use the direct polycondensation process for the production of PLA. Most of the manufacturers of PLA employ ring-opening polymerization catalyzed by organometallic catalysts. First, LA is oligomerized at high temperature and

reduced pressure to remove water. Then, the catalytic depolymerization of these oligomers under low pressure yields lactide. Vacuum distillation or crystallization is carried out to remove the residual LA from lactide. Finally, the polymer is produced via catalytic ring-opening polymerization of lactide in the melt (Figure 42). Poly(*L*-LA) and poly(*D*-LA) are semicrystalline in nature. The molecular weight of PLA varies from 100 to 300 kg/mol, which is similar to that of a conventional polymer such as poly(ethylene terephthalate) (170-350 kg/mol). It is worthy to note that a higher molecular weight of PLA results in an increase of the strength owing to a decrease in the relative motion of the chains as they become longer. PLA exhibits good transparency, glossy appearance, high stiffness and biodegradability.

Propylene Glycol (1,2-Propanediol) Based Biopolymers

Propylene glycol has a wide range of uses, including industrial applications (i.e., for unsaturated polyester resins). In fact, 45% of the produced propylene glycol is used as chemical feedstock for the synthesis of these polymers. In this regard, propylene glycol reacts with a mixture of unsaturated maleic anhydride and isophthalic acid to give a copolymer. This partially unsaturated polymer undergoes further crosslinking to yield thermos settings. Regarding this application, propylene glycol reacts with propylene oxide to give oligomers and polymers that are exploited for obtaining polyurethanes.

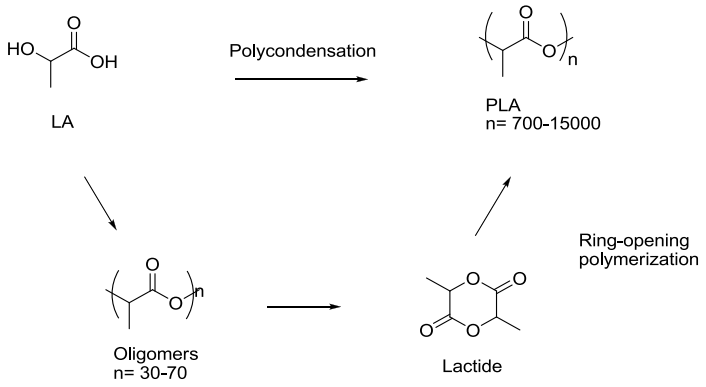


Figure 42. Lactic acid polymerization routes.

1,3-Propanediol Based Biopolymers

1,3-Propanediol (PDO) has been copolymerized with terephthalic acid to produce poly(trimethylene) terephthalate (PTT), commercialized by DuPont under the trade name Sorona® [21]. It was patented in 1941. Sorona® PTT has been targeted at clothing, carpet and automotive textile markets. It is produced by a method called condensation polymerization or transesterification. In general, polyols based on PDO can be also used for coatings and elastomers.

PTT value as a commercial polymer has improved, due to more economical and efficient methods to produce 1,3-propanediol developed in the 1980s by Degussa, via acrolein and by Shell via the hydroformylation of ethylene oxide [107]. DuPont has successfully commercialized the synthesis of this polymer via 1,3-propanediol obtained by fermentation. These developments may allow PTT to effectively compete against PBT and PET, two polyesters that have been far more successful than PTT to date.

Epichlorohydrin Based Biopolymers

Epichlorohydrin is predominately used in the production of epoxy resins (76%) and other resins and polymers, such as polyamide-epichlorohydrin resins (PAE). These latter are water soluble and the most used permanent wet strength additive in alkaline conditions for preparing wet strengthened papers and in the food industry to manufacture tea bags, coffee filters, and sausage/salami casings, as well as for water purification.

Propylene Based Biopolymers

The main use of propylene is for the production of polypropylene (60% of propylene demand). There are several routes for bio-based propylene production. Polypropylene end uses include films, fibers, containers, packaging, caps and closures.

Acrylic Acid Based Biopolymers

Acrylic acid is utilized for the production of polyacrylates and commodity acrylates (methyl, ethyl, n-butyl and 2-ethylhexyl acrylate), which have industrial uses as coatings, adhesives and sealants, textiles and

fibres, polymer additives/impact modifiers and films. Polyacrylates are widely used as super absorbent polymers.

3-Hydroxypropionic Acid (3-HPA) Based Biopolymers

3-HPA is a key building block for the production of valuable monomers that can be polymerized, such as acrylics, propanediol, acrylonitrile, etc. The production of acrylic monomers starting from 3-HPA is quite important owing to the giant market size of acrylic polymers. Therefore, the importance of its homo- and co-polymers and its derivatives, produced by several companies, is quite relevant.

Acrylonitrile Based Biopolymers

Acrylonitrile is employed for manufacturing polyacrylonitrile (PAN) fibres and for obtaining different copolymers, namely: styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styreneacrylate (ASA), acrylonitrile-butadiene (ANB) and acrylonitrilemethyl acrylate (AN/MA).

C4 Compounds

Butanol Based Biopolymers

Although considered as a potential biofuel, *n*-Butanol is also used in a wide range of polymers and plastics, among other applications. In particular, butanol is utilized for producing butyl acrylate, a primary ingredient of water-based acrylic paints.

Butanediol Based Biopolymers

As other diols, butanediol is useful for the synthesis of polyesters and several polyols, namely: 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1,4-butanediol (1,4-BDO), and 2,3-butanediol (2,3-BDO). Relevant polymers for 1,4-BDO are poly(butylene terephthalate) (PBT) and polybutylene succinate (PBS). In fact, the production of PBT is the second largest use of 1,4-BDO.

At present, there are more than 50 companies engaged in the production of PBT. Among these companies, Toray has recently manufactured a partially bio-based PBT, using 1,4-BDO made with Genomatica's bio-based process technology. PBT exhibits excellent thermal stability, high strength, high chemical resistance and good durability. It is also easily manufactured into yarn that exhibits a natural stretch similar to Lycra®. These characteristics of PBT polyester resins and yarns justify its numerous uses. Many efforts have also been devoted to further broaden its current applications by changing its crystallinity and crystallization rate [108].

Besides, 1,4-BDO can be transformed into 1,4-butanediamine that has been extensively used in the production of polyamides. DSM Engineering Plastics currently uses putrescine to produce PA-4,6 and PA-4,10, which have been marketed as Stanyl™ and EcoPaXX™, by using adipic acid and sebacic acids as co-monomers, respectively [109]. These polyamides have led to the rise of novel technologies. As an example, EcoPaXX™ has started to be used in the engine cover of Mercedes Benz A-Class engine. Furthermore, Bauser, an injection molding company located in Wehingen (Germany), has successfully introduced a production process for automotive gears using Stanyl™. PA-4I (I: isophthalic acid), PA-4T (T: terephthalic acid) and PA-4,2 are the other extensively studied polymers of putresine [110].

Succinic Acid Based Biopolymers

Succinic acid (SA) can be utilized as a monomer for the production of polyesters (specifically poly(butylenesuccinate), PBS). Various polyamides (PA), polyesters (PE), and poly(ester amide)s (PEA) can be produced via the condensation reaction of succinic acid or succinic acid diesters with diamines or diols. Referring to polyamides, the literature generally reports on polyamides derived from either 1,4-butanediamine or succinic acid [111]. Certain types of succinic acid based polyesters, particularly poly(alkylene succinate)s (PAS), can also be manufactured. Poly(ethylene succinate) (PES), poly(propylene succinate) (PPS) and poly(butylene succinate) (PBS) are the mostly studied polyesters of succinic acid. From these set of polyesters, PES and PBS are successfully commercialized due to their

relatively high melting temperatures, controllable biodegradation rate and good processability. They have polyethylene (PE) like crystallization behavior and their elongation at break and tensile strength are comparable with those of polypropylene (PP) and low-density polyethylene (LDPE) [112]. PBS and its copolymers have been receiving a special interest in the current polymer market. Poly(butylene succinate) (PBS) is a biodegradable polyester consisting of SA and 1,4-BDO as building blocks. The bulk production of PBS derived from biobased SA and petrochemical-based 1,4-BDO started at the beginning of the 2000s [113]. Before that, PBS was manufactured exclusively relying on fossil feedstocks. Due to the development of 1,4-BDO synthesis from renewable feedstocks, the manufacturers recently announced the shift towards a fully biomass-based production of PBS. Owing to the excellent mechanical properties of PBS and its blends, this polymer is very likely to replace some conventional polymers such as polypropylene (PP) or poly(ethylene terephthalate) (PET). PBS is a semicrystalline polymer with a Tg of −32°C and a Tm of 115°C [114]. Currently, PBS-based materials are utilized as barrier films, for packaging, as dishware and as drug encapsulation systems. Besides, PBS is used as a component of blends or copolymers.

Gamma-butyrolactone (GBL) is obtained through hydrogenation of succinic acid; the reaction product can be employed for obtaining poly(4-hydroxybutyrate) (P4HB) through ring opening polymerization (ROP).

Aspartic Acid Based Biopolymers

Polyaspartic acid, the polymerization product of aspartic acid, is a biodegradable substitute for polyacrylates: however, the polyaspartate market comprises a small fraction (est. < 1%) of the total market of superabsorbent polymers (SAP) used in disposable hygiene products. Besides, polyaspartic acid is used in the fertilizer industry, improving water retention and nitrogen uptake.

Biopoly(amino acids) with free carboxylic groups can be obtained from aspartic acid: these polymers have attained the greatest commercial success in terms of water soluble biodegradable materials. Aspartic acid can also be utilized as a polymer precursor for the production of polyaspartamide

(PAA)-based polymers. Recent literature studies regarding PAA-derived polymers mainly focused on their use as drug carriers and stimuli-responsive polymeric materials [115].

Fumaric and Malic Acid Based Biopolymers

Homopolymers of these diacids, either alone or in combination with other polymers, have been used for general biomedical applications. Unlike succinic acid, the presence of a double bond in fumaric acid allows the formation of crosslinked, degradable polymer networks with tunable material properties. Among them, poly(propylene fumarate) (PPF) has been widely investigated, as PPF-based polymers can be *in situ* crosslinked to form solid polymer networks for injectable applications. Recently, Kasper et al. reported a novel protocol for the synthesis of PPF by a two-step reaction of diethyl fumarate and propylene glycol, aiming at its potential utilization in the fabrication of orthopedic implants, scaffolds for tissue engineering, controlled bioactive factor delivery systems and cell transplantation vehicles [116]. By providing high water solubility, poly(malic acid) was specifically studied for the design of targeted drug delivery systems [117].

Methyl Methacrylate Based Biopolymers

The main part of MMA is used to obtain poly(methyl methacrylate) (PMMA), also known as acrylic or acrylic glass, as well as by the trade names Plexiglas, Acrylite, Lucite and Perspex, among several others. It is a transparent thermoplastic often used in form of sheets as a lightweight or shatter-resistant alternative to glass. The same material can be utilized as a casting resin, in inks and coatings, and has many other uses. PMMA is an economical alternative to polycarbonate (PC) when tensile strength, flexural strength, transparency, polishability and UV tolerance are more important than impact strength, chemical and heat resistance.

Methyl methacrylate is also used for the production of such copolymers as methyl methacrylate-butadienestyrene (MBS), which is used as a modifier for PVC. Methacrylates polymerize easily to form resins and polymers with excellent performance characteristics including exceptional

optical clarity, strength and durability, especially in aggressive all weather or corrosive environments. They can also be copolymerized with other monomers to form a broader range of products typically used for paints, coatings and adhesives.

C5 Compounds

Furfural Based Biopolymers

Furfural (FF) contains formyl and/or hydroxylmethyl groups that are suitable for polymerization reactions via both catalytic and synthetic organic pathways as published by Gandini [43]. See "H5-hydroxymethylfurfural (5-HMF) and 2,5-Furandicarboxylic acid (FDCA) based biopolymers" in C5 compounds group of this section.

Levulinic Acid Based Biopolymers and Polyhydroxyalkanoates

Several companies recently launched the production of novel bio-polymers based on LevA or its derivatives.

Diphenolic acid (DPA) (a derivative of LevA) has attracted interest in the synthesis of poly(arylene ether ketone) (PAEK) and poly(ether ether ketone) (PEEK) for fuel cell applications.

Another of its derivatives, 5-aminolevulinic acid (DALA), can provide novel opportunities in amino acid-based polymers.

4-hydroxypentanoic acid can be used for hydroxyalkanoate (PHAs) biopolymers by means of chemical and/or biological methods.

GVL is used to obtain polymeric materials with potential biodegradability with alkali metal alkoxides and alkali metal supramolecular complexes based initiator systems. Its copolymerization with various monomers, including diglycidyl ether of BPA [118] and *L*-lactide [119], was also thoroughly investigated (Figure 43).

Poly-γ-methyl-α-methylene-γ-butyrolactone (PMMBL) is very easily obtained via vinyl polymerization of MMBL that occurs even spontaneously at room temperature [120].

Polymers based on diphenolic acid (DPA) can be rather versatile. The structure of DPA resembles that of bisphenol A (BPA), which is a petroleum-derived monomer for the synthesis of polycarbonates. An alternative exploitation of DPA as monomer refers to the preparation of hyperbranched polymers (HBPs), i.e., highly branched macromolecules with a three-dimensional dendritic architecture [121].

α-Angelica lactone (AL) can be polymerized according to the two pathways shown in Figure 44. The first possibility concerns a vinyl polymerization, while the second route is a ring-opening polymerization yielding polyesters. Due to the presence of a double bond, polyesters of AL are not very stable [122].

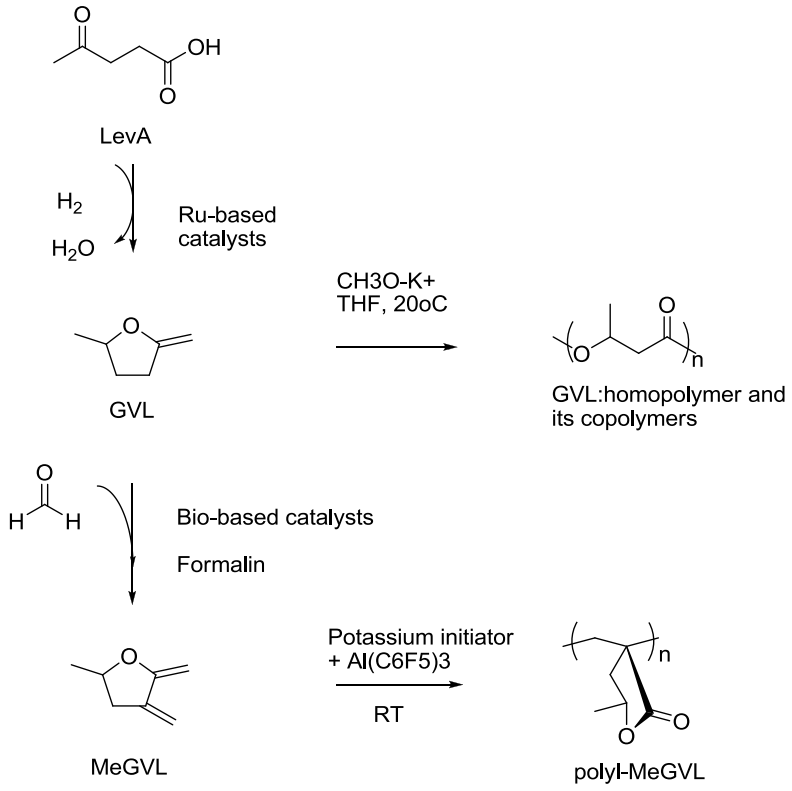


Figure 43. GVL synthesis from LevA and GVL polymers and copolymers.

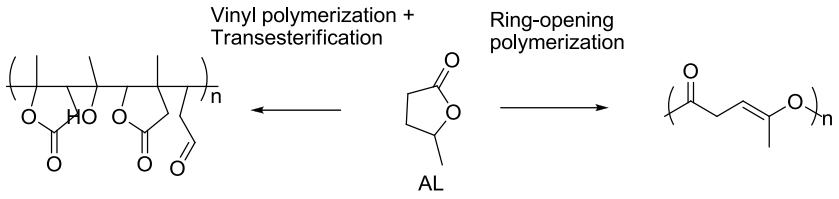


Figure 44. Vinyl and Ring-Opening Polymerization of α-Angelica Lactone (AL).

An important biobased group of polymers refers to polyhydroxyalkanoates (PHAs), which can be obtained from levulinic acid through 4-hydroxypentanoic acid, among others. They represent a group of microbial polyesters with a history of production dating back over 50 years. Unlike most of the bio-based polymers, which are produced by chemical polymerization methods using bio-based monomers, PHAs are produced directly by fermentation. PHAs are based on renewable materials and are biodegradable, hence attracting the interest of several companies. Although over 150 types of PHAs are known, only 3 are produced in significant quantities. The global capacity for PHA production is around 100,000 to 130,000 tonnes but could expand significantly, given the increasing demand for bio-based and biodegradable materials. Companies active in the production of PHAs include Mitsubishi Gas Chemical in Japan, PHB Industrial in Brazil, Tianjin Green Bio-Science in China and Metabolic Explorer in France [88].

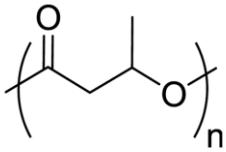


Figure 45. PHB.

Polyhydroxyalkanoates (PHA) are the most well-known family of polymers synthesized directly inside cells. Traditionally, the biotechnological synthesis of polymers implies a fermentative production of monomers with a subsequent chemical polymerization. The production of PHA does not require an intermediate isolation of the monomers: in fact, the polymers are accumulated in the cytoplasm under growth limiting

conditions, in the presence of a carbon source [123]. Poly(3-hydroxy-butyrate) (PHB) was the first representative of PHA uncovered in 1926 (Figure 45).

This polymer received a great attention, although PHAs containing more than 150 different monomers have been synthesized since then, mainly at the laboratory scale. Depending on the type of bacteria and synthesis conditions, PHA monomers can bear carbon chain lengths ranging from 3 to 14. In some cases, the monomer structure contains such functionalities as halogens, benzene, unsaturated bonds, epoxides and cyclic groups. Obviously, the great variation potential of the monomer structure confers different properties to PHA. In vivo synthesis provides different types of PHA polymers, i.e., homopolymers, copolymers and block copolymers [14].

The production of PHA includes three steps, namely: (1) fermentation, (2) isolation, and (3) purification. Despite the very attractive properties of PHA, these polymers have not entered the bulk market yet, owing to high production costs.

Currently, PHA and their copolymers are predominantly used as biodegradable plastics for food packing. Being biocompatible and nontoxic, PHAs are suitable for several biomedical applications. PHAs can be utilized in the chemical industry as sources of valuable optically pure acids available via hydrolysis of PHA. In addition, after use as bioplastics, the transformation of PHA into biofuels via successive hydrolysis and esterification has been suggested.

PHAs are semicrystalline polymers with molar masses within 200 and 3000 kg/mol, Tm in between 60 and 177°C and Tg values ranging from -50 to 4°C. PHB is the most produced polymer of the PHA family. It exhibits very good thermoplastic properties (Tm = 180°C); articles made of PHB retain their shape in the temperature range from -30 to 120°C. Unlike most of the biobased polymers, PHB is water-insoluble and relatively resistant to water degradation. Some applications of PHB are restrained by the high stiffness and brittleness of the polymer, as well as by a narrow processing temperature range, the tendency to "creep" and the slow crystallization. However, the properties of PHB can be improved when copolymerized with other monomers, namely 3-hydroxyvaleric or 3-hydroxyhexanoic acid [14].

Isoprene Based Biopolymers

Isoprene is used primarily in the production of polyisoprene rubber, styrenic thermoplastic elastomer block copolymers and butyl rubber. Goodyear has produced a synthetic rubber for a concept tyre, demonstrating the equivalence of BioIsoprene™ with the oil-derived counterpart [54].

Itaconic Acid Biopolymers

The two acid groups and the vinyl functionality of itaconic acid (ITA) make it an ideal monomer for producing bio-based polymers via either vinyl polymerization or formation of polyesters (Figure 46). The former option has been more studied and the synthesis of polyesters received much less attention.

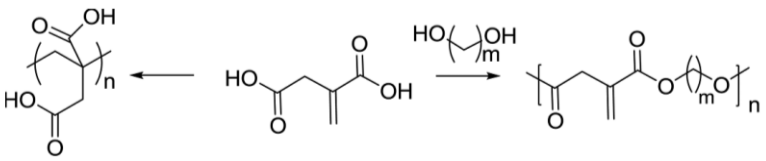


Figure 46. Polyesters of itaconic acid.

Its homopolymer, polyitaconic acid (PIA), is commercially available and it is primarily used as comonomers in styrene-butadiene polymers to provide dye receptivity in fiber industry. For a long time, PIA as an alkaline salt or in sulfonated form has been used as component of cleansing agents and shampoos. From the 1990s, the application field of PIA and copolymers of IA was extended to the medical field, specifically for drug delivery purposes [124]. Easily polymerizable alkyl itaconates are used as plastics, adhesives, elastomers and coatings. The copolymers of IA with unsaturated compounds, e.g., acrylic acid, aconitic acid and butadiene, have been known for a long time. Many copolymers of IA find application for the production of synthetic fibers, coatings, adhesives, thickeners and binders. As an example, IA, at small concentrations (1-5%), is utilized as a comonomer of rubber-like resins. IA can also be used for synthesis of biobased epoxy resins. Another promising application of IA relates to the production of

glass-ionomer dental cement that contains a copolymer of IA with acrylic acid.

The capability of IA-containing polyesters to undergo cross-linking enables tailoring the polymers by introducing some IA as comonomer. For example, IA amounts below 10% were copolymerized with PBS, 3 poly(propylene carbonate) [125], and a polyester containing maleate and 3-methyl-1,5-pentanediol units [126]. In all cases, cross-linked polymers were successfully obtained even at a low IA content. Interestingly, Tang et al. first copolymerized a polyester containing IA, maleate and 3-methyl-1,5-pentanediol and then performed a selective photo-crosslinking of the exotype double bonds of itaconates, whereas the double bonds of maleate were preserved [124].

IA derivatives are also quite important. More specifically, itaconic anhydride (ITAn) is one of the unique monomers for designing cyclic anhyride copolymers, which can exhibit biodegradable characteristics and are derived from renewable resources. 2-methyl butyrolactone (2-MGBL) and 3-methyl butyrolactone (3-MGBL) can be polymerized; this reaction is rarely exploited, since 5-membered lactones are thermodynamically stable. Depending on the large-scale production of ITA from biomass, these derivatives can give a wide contribution to polymer research and industry [80].

Glutamic Acid-Based Biopolymers

Poly-γ-glutamic acid (γ-PGA) is the most successful comercial polymer form of glutamic acid. PGA is isolated particularly from various strains of *B. licheniformis* and *B. subtilis*. γ-PGA is water-soluable, edible, bio-degradable, biocompatible and non-toxic for humans and the environment. Hence, this polymer and its derivatives have been of interest in the past few years, especially in food, cosmetics, medicine and water treatment industries. Poly-α,L-glutamic acid (α,L–PGA), which is generally synthesized starting from poly(α-benzyl-L-glutamate) (PBLG) is a structurally different polymer of glutamic acid. α,L–PGA shows the general features of γ-PGA; additionally, its carboxylic group provides functionality for drug attachment. Thus, anticancer drug conjugates of α,L–PGA have

been studied extensively. α,L–PGA-based anti-cancer drug conjugates were reviewed in detail by Li [127].

Further, glutamic acid can be used for obtaining polyamides and polyesters.

Gluconic/Glucaric Acids Based Biopolymers

D-gluconic acid is an interesting comonomer for the synthesis of functionalized polyesters for biomedical and pharmaceutical applications. The ROP of the cyclic dilactone obtained from D-gluconic with lactide yields novel degradable polyesters with higher glass transition temperatures than poly(lactic acid-co-glycolic acid) polymers, which are routinely used for sutures, bone prostheses and drug delivery systems [128]. However, nowadays, these polyesters are not suitable for large scale production. Other polymers that can be produced from *D*-gluconic acid comprise polyurethanes, hydrogels, hydroxylated polyamides, etc. Biomedicine is the most relevant sector of application of all these polymers.

Referring to glucaric acid, the main polymers are poly(*D*-glucaramidoamine)s (PGAAs) and poly(glucaramides).

1,5-Pentanediamine (Cadaverine)-Based Biopolymers

1,5-pentanediamine is an attractive building block for innovative polyamides. At present, polyamides comprise various success materials such as polyamide 6 or polyamide 6.6 (nylon 6,6), as well as different high-performance polyamides of altered composition; they share an annual global market size of 6 million tons. The production of new polyamides could promote an enormous market. The secret of polyamide properties relies on a large degree found in the basic monomers, polyamides consist of. Hereby, polyamides based on 1,5-pentanediamine reveal long-known excellent materials properties. Polymerizing 1,5-pentanediamine derived from microbial biosynthesis with appropriate bio-blocks such as succinate [129] or sebacic acid from castor oil [130], provides completely bio-based polyamides such as PA 5.4 and PA 5.10, respectively (Figure 47). Sebacic acid is thereby obtained by extracting or expressing the seed of the castor oil plant, followed by saponification and pyrolysis. It is interesting to note that

the bio-based PA 5.10 shows excellent materials properties (Table 4), including a high melting temperature and low water absorption. In some important characteristics, it competes even with the conventional nylon. In particular, PA 5.10 has a lower density, relevant for use in energy friendly transportation. Besides, the lower water absorption provides a better long-term dimensional stability, attractive in cases where exact geometrical shapes of the polymer have to be maintained. Other advantages comprise improved flow characteristics and a better visual surface quality. Thus, polyamides from 1,5-pentanediamine open new opportunities for bio-based polymers with advanced material properties, for example in the automotive industry or in high-value consumer products.

C6 Compounds

Hydroxymethylfurfural (5-HMF) and 2,5-Furandicarboxylic Acid (FDCA) Based Biopolymers

The development of vinyl polymers from biomass derived 5-hydroxy-methylfurfural (5-HMF) can introduce new substituents for commodity polymers. The recent progress in the synthesis, characterization and physical properties of 5-HMF derived furanoic polymers including polySchiff-bases, polyesters, polyamides, polyurethanes, polybenzo-imidazoles and polyox-adiazoles, was thoroughly reviewed by Amarasekara [131].

5-HMF gives 2,5-furandicarboxylic acid (FDCA) by oxidation, which can be used for replacing terephthalic acid in the production of polyesters (Figure 48). TPA is mostly used in the large-scale synthesis of polyesters (poly(ethylene terephthalate) (PET)) and polyamides (poly(phthalamides), aramids), which find applications in textiles and beverage containers. FDCA has been suggested as a substitute for TPA, together with biomass-based ethylene glycol, for obtaining completely renewable polyesters. Thus, in particular, the preparation, the materials properties and the applications of poly(ethylenefuranoate) (PEF) and poly(butylenefuranoate) (PBF) are studied very intensively. It is important to highlight the enormous market potential of the “sleeping giants” of renewable intermediate chemicals. In

this context, Avantium has developed 100% bio-based polyethylene-furanoate (PEF) bottles, fibers and films by using plant sugar derived 2,5-FDCA. The application of polymeric furanoate esters in beverage containers and textiles imposes high demands on the quality of the polymer in terms of physical appearance, processability, mechanical strength, thermal and chemical stability, etc. It can be also employed for synthesizing polyureas and polyester polyols (with linear and cyclic diols).

Table 4. Materials properties of fossil-based polyamide PA6 and bio-based polyamide PA5.10

	PA 6	**PA 5.10**
Bio-based content	0	100
Melting point (°C)	220	215
Glass Transition Temperature (°C)	54	50
Density (g/cm^3)	1.14	1.07
Water sorption (%)	3.0	1.8

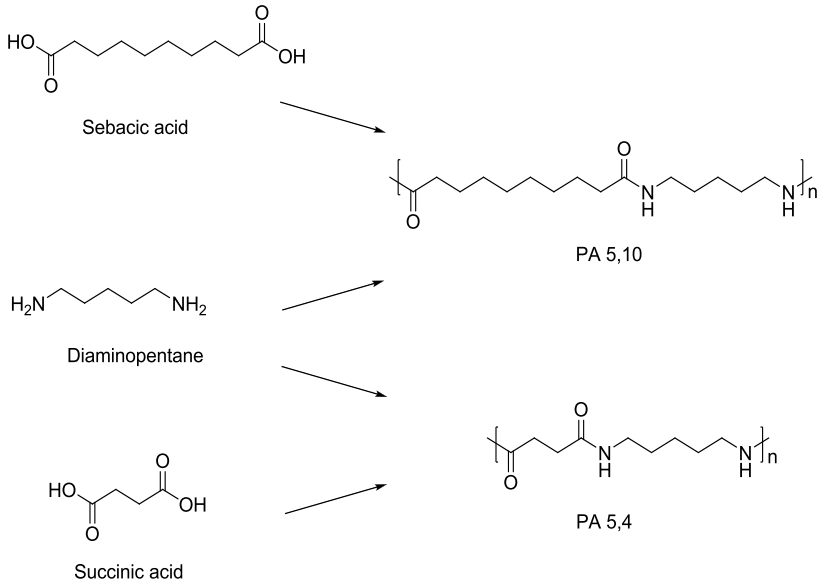


Figure 47. Polymerization of 1,5-diaminopentane with succinic acid or sebacic acid to build PA 5.4 or PA 5.10.

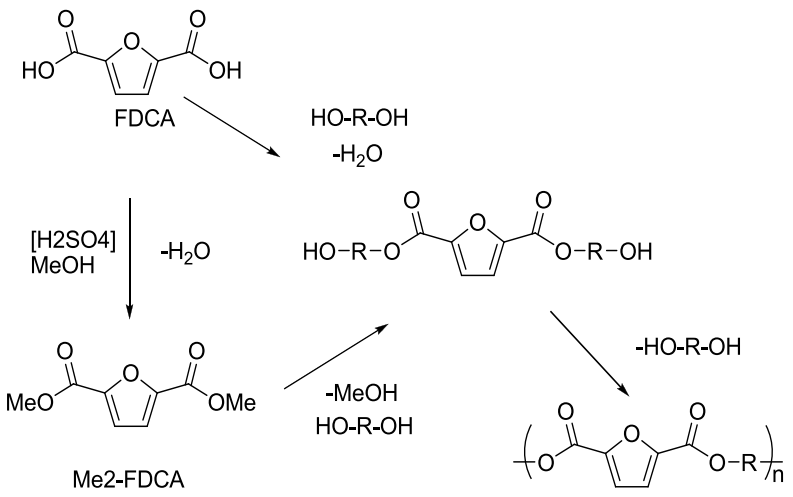


Figure 48. Polymerization of 2,5-furandicarboxylic acid (FDCA) and its dimethyl ester with glycols.

Other monomers derived from furfural containing six or more carbons have been applied to synthesize polymers and are also worthy to mention. As an example, 2,5-diformylfuran (DFF) has been chosen for obtaining phenolic resins and linear poly(imines); 2,5-Bis(hydroxymethyl)-furan (BHMF) has been used as homopolymer in formulations for poly (isocyanurate) foams, furan resin-based binding compositions for glass fibers and polyurethane foams. Besides, its application as a comonomer in poly(acrylonitrile) and polyethers has also been reported; the polymerization of 2,5-bis(aminomethyl)furan (BAMF) and 2,5-bis(carboxyl chloride)furan for the preparation of furan-containing polyamides has been described: a patent application by BASF discloses the use of BAMF as a hardener for epoxy resin; Rodia also claims the preparation of polyamides from BAMF. Furthermore, previous studies by Gandini et al. demonstrated that the dimers of FCA can be successfully applied as monomers in the transesterification reaction with ethylenglycol and 1,4-BDO. Further, more recently, FCA dimers have been used in the synthesis of various copolymers, namely: block copoly(esters) with PET, random copolymers with TPA by melt condensation, copolymers with sulfonated isophthalic acids and copolymers with hexamethylene diamine and ethylene glycol. The most studied

application of the furfuryl amine dimer is its conversion to the diisocyanate and subsequently to polyurethanes; this monomer can be employed for the preparation of poly(imides) by reaction with aromatic anhydrides (e.g., pyromellitic dianhydride) and polyureas by reaction with diisocyanates. As for BAMF, the conversion to poly(imines) is also feasible [14].

Isohexides (and Derivatives) Based Biopolymers

Isohexides have been used to synthesize polyester, polyamides, polycarbonates and polyurethanes.

Polyesters based on isohexides can generally be divided into two groups, depending on the fact that isohexides serve as the diol monomer or as the dicarboxylic acid monomer. For the latter, isohexides have to be converted into their carboxylic acid derivatives. Polyterephthalates are very promising polymers based on isohexides as the diol monomer. Since their discovery, these compounds found a great interest, especially with isosorbide as a co-monomer. This is due to the excellent thermal properties of the polymers, which can be obtained by the polymerization of terephthalic acid with isohexides instead of ethylene glycol. Depending on the synthesis, glass transition temperatures between 150 and 200°C can be achieved, i.e., well beyond the Tg (70°C) of standard poly(ethylene terephthalate) (PET). Thus, bottles made of poly(isosorbideterephthalate) (PIT) tolerate hot fillings in contrast to PET bottles. However, lower molecular weights are obtained with isosorbide; in addition, the amount of unreacted terephthalic acid groups remaining in PIT is higher than in PET. Therefore, research also concentrates on copolymers based on different ratios of isohexides with other dialcohols. One example is poly(ethylene-co-isosorbide terephthalate) (PEIT, Figure 49).

As far as isohexides in polyamide synthesis are considered, in the early 1990s, Thiem et al. reported on the preparation of polyamides based on isohexides by interfacial polycondensation with dicarboxylic acid dichlorides [132]. Interestingly, isoidide and isosorbide yield polyamides with relatively high molecular weights when reacted with isophthaloyl chloride; conversely, high molecular weight polyamides cannot be synthesized using isomannide. Jasinska et al. developed semicrystalline

polyamides using diamineoisoidide (DAII) or diaminoisosorbide (DAIS) with sebacic or brassylic acid, as well as copolyamides in the presence of 1,4-diaminobutane (DAB) [133].

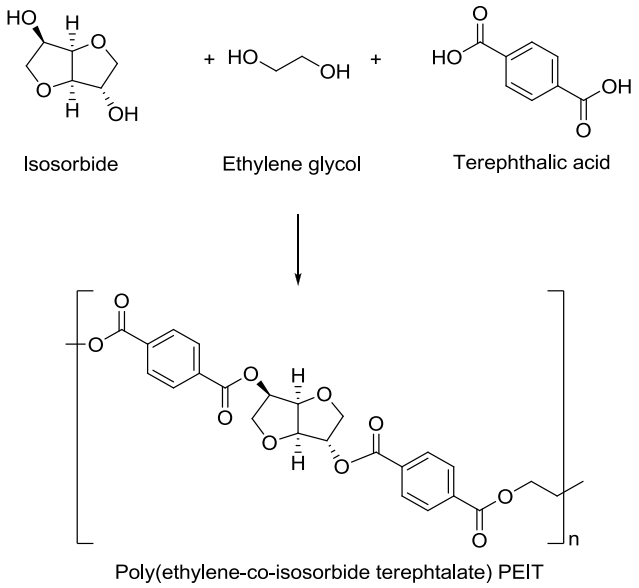


Figure 49. Synthesis of Poly(ethylene-co-isosorbide terephthalate) (PEIT), starting from Isosorbide, Terephthalic Acid, and Ethylene Glycol.

Finally, polyurethanes based on isohexides can be synthesized starting from their diamine compounds as reported by Thiem and Lüders already in 1986 [134]. It is noteworthy that, conveniently, they serve more often as the diol monomer. In one recent example, the isohexide is not only the diol monomer, but also its backbone is found in the isocyanate [135].

Adipic Acid Based Biopolymers

Adipic acid (ADA) is primarily used for the production of polyamides and mainly for polyamide or nylon 6.6. A recent patent describes how to produce a "green" version of key intermediate chemicals for the synthesis of nylon, utilizing renewable feedstocks such as commercially-available carbohydrates [72]. PA 4.6 is another important commercial polyamide of ADA. Apart from the polyamides, esters and polyesters comprise the second

most important class of ADA derivatives; some moderately long-chain esters of ADA find large applications as plasticizers, particularly for poly(vinyl chloride) (PVC).

Thus, ADA can be exploited for synthesizing bio-polyamides. At present, in the production of commercially available bio-based PA, castor and palm oils are used as a renewable feedstock. 11-aminoundecanoic acid and sebacic acid are products from chemical conversion of ricinoleic acid, the major fatty acid component of castor oil. Their modifications, such as sebacic acid, aminoundecanoic acid or decamethylene diamine, may lead to the synthesis of polyamide building blocks. Besides, some polyamides can be produced from sugars. For example, PA 6 could be synthesized by ring opening polymerization of caprolactam produced by glucose fermentation. However, the production of bio-based PA from carbohydrates is not cost-effective. Figure 50 schematizes some of commercial bio-based polyamides and their percentage on renewable source and main properties. The properties of polyamides increase with increasing the length of the monomer chain. More specifically, long-chain PAs have lower density, lower water absorption but also significantly lower strength and stiffness, lower melting temperature and continuous operating temperature than standard polyamides (Figure 50). Few companies have already introduced different kinds of long-chain bio-based polyamides into the market. Polyamide 11 (Rilsan from Arkema) is commercially available and applied in different industrial sectors (i.e., automotive, textile, electronics), mainly in coatings. Polyamide 10.10 (produced by DuPont, EMS-Chemie, Evonik and Suzhou Hipro (now Arkema) [136]) has properties close to PA 11. Both PA 11 and PA 10.10 are fully made from castor oil. Polyamide 5.10 is now produced by BASF, but not yet commercially available. Its dicarboxylic acid part is synthesized from castor oil, while the diamine is obtained by glucose fermentation, via lysine as intermediate. Polyamide 6.10 (BASF, DuPont, EMS, Rhodia, Evonik, Toray, Suzhou Hipro (Arkema), Akro-Plastic) with about 60% of renewable-source content has recently raised a great interest, as it combines high mechanical properties (typical of PA 6) with low density and high chemical resistance (typical of PA 10.10). Other partially biobased polyamides available on the market are PA 4.10 (up to 70% biobased, DSM

Company) and PA 10.12 (about 40% biobased, Evonik, Suzhou Hipro (Arkema)). The Chinese company Cathay Industrial Biotech Ltd has also provided long-chain diacids and 1,5-pentanediamine to the polymer industry. Biopolyamide 5.6 has the same strength and heat resistance as conventional polyamide made from the petrochemical derivative HMDA. Its current percentage of biobased source is 45% (according Cathay Company).

cis,cis-Muconic Acid Based Biopolymers

Of all the *cis,cis*-Muconic acid produced, 85% is processed into adipic acid, an intermediate for polyamide 6.6 [79]. Caprolactam (employed for obtaining polyamides) and terephthalic acid (used for polyesters) are the second and third bulk chemicals, which, as expected, can significantly increase the market for cis,cis-MA. Currently, there are no processes for bio-based production of this compound from MSW in the market. The processes that are under development utilize primary food-chain sugars or vegetable oils.

Glucaric Acid Based Biopolymers

Glucaric acid can also be polymerized, although the commercialization of the related polymer is probably some years away.

Cn Compounds

Polymers Based on Bioaromatic Monomers from Lignin

Organosolv lignin, Kraft lignin, and lignosulfonate are abundant wastes from the pulp industry. Their application is of great economical interest and environmental advantages. Several reviews reported on the direct application of lignins in composite materials [137-139]. This section will mainly focus on the synthesis of polymers from lignin monomers [14].

Polyesters Based on Vanillin Monomers

A two-step conversion of vanillin could produce dihydroferulic acid, which contains a carboxylic group and an acetyl protected hydroxyl group.

The bifunctional molecule can be used for replacing both glycol and terephthalate for PET production.

Application of Diphenolic Monomers in Polyurethanes

The cardanol derived diphenolic compound is able to react with MDI to produce polyurethane (PU). The PU material is stable under UV radiation and also exhibited good thermal stability below 290°C [140].

Polycarbonates Based on Vanillin Monomers

Based on bisphenol obtained from vanillin, a polycarbonate was synthesized through its transesterification with diphenyl carbonate. The material exhibited a Tg of 86°C, lower than that of conventionally prepared bisphenol polycarbonate (120°C) [141].

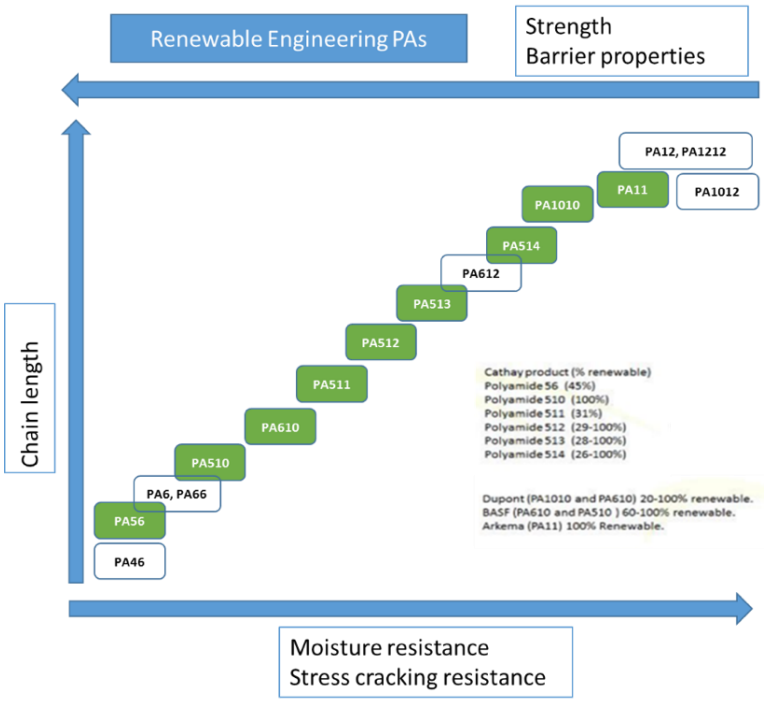


Figure 50. Scheme of some of commercial bio-based polyamides and their percentage on renewable source and main properties.

Polyacrylates

Replacing styrene with vanillin derived methylacrylester, various polymeric materials could be prepared. Although methyl acrylated vanillin is solid at room temperature [142], a low viscous resin could be prepared via adding glycidyl methyl acrylate to the mixture of methyl acrylated vanillin and methyl acrylate [143].

Polyethers

A spirocyclic polyether was synthesized by the condensation of pentaerythritol with vanillin derived dialdehyde. This way, seven cyclic polyethers with Tg ranging from 68 to 129°C were prepared from lignin-related dialdehydes and tetraols [144].

Epoxy Resins

The curing of vanillin-based epoxy resins using isophorone diamine as hardener provided a solid material with a Tg of 117°C, indicating that the epoxy resin is promising to replace the reprotoxic bisphenol A epoxy resin [145]. Similarly, the cardanol-based epoxy resin was cured in the presence of an aromatic polyamine and the composites based on this material were applied as anticorrosive paints [146].

Polybenzoxazines

They are a relatively new class of high performance polymers. The benzoxazine synthesized from vanillin, furfuryl amine, and formaldehyde could be polymerized at 179−232°C; the Tg of the vanillin derived polybenzoxazine is 270°C [147].

Polycyanurate

The (bis)cyanate ester prepared from vanillin was amenable to thermal cure under mild conditions. A DSC study showed that the monomer started to cure below 200°C, yielding a thermoset material with a Tg of 202°C: this finding indicated that the material was comparable to some of the most-performing petroleum-derived epoxy resins [141].

TECHNICAL BARRIERS, LIMITATIONS FOR SOME BIO-BASED CHEMICAL BUILDING BLOCKS

The main technical barriers, limitations and some considerations for this kind of products relating to their polymerization strategy have been discussed in the work of Petersen et al. [61], who investigated the top value-added chemicals from biomass: this concept also applies to monomers from MSW. Some of them have been included in this section. This analysis demonstrates that there is a significant market opportunity for the development of these biobased products and their polymers.

1,4-Diacids (Succinic, Fumaric and Malic)

The major challenges are primarily associated with the reduction of the overall cost of the fermentation. In order to become competitive with petrochemicals derived products, the fermentation cost needs to be at or below $0.25/pound. This is a significant technical challenge and should be undertaken with a long-term perspective.

When considered in aggregate, the diacid family offers access to a wide range of products that address a number of high volume chemical markets.

2,5-Furan Dicarboxylic Acid (FDCA)

The primary technical barriers towards production and use of FDCA include the development of effective and selective dehydration processes for sugars. The control of sugar dehydration could be a very powerful technology, leading to a wide range of additional, inexpensive building blocks, but it is not yet well understood. Currently, dehydration processes are generally nonselective, unless, immediately upon their formation, the unstable intermediate products can be transformed into more stable materials. Necessary R&D will include development of selective

dehydration systems and catalysts. FDCA formation will require the development of cost effective and industrially viable oxidation technology that can operate in concert with the necessary dehydration processes.

A number of technical barriers also exist with respect to the use of FDCA (and related compounds) in the production of new polymers. Thus, the development and control of esterification reactions and the control of the reactivity of the FDCA monomer will be of great importance. Understanding the link between the discrete chemistry occurring during polymer formation and how this chemistry is reflected in the properties of the resulting polymer, will provide useful information for industrial partners seeking to convert this technology into marketplace products.

The utility of FDCA as PET/PBT analogue offers an important opportunity to be addressed to a high volume, high value chemical market. To achieve this opportunity, selective oxidation and dehydration technologies will have to be developed. However, the return on investment might have applicability of interest to an important segment of the chemical industry.

3-Hydroxypropionic Acid (3-HPA)

The major challenges include the development of a low-cost fermentation and a family of catalysts for the conversion of 3-HPA to the desired products. In order to be competitive with petrochemical routes to acrylates, both the fermentation and catalysis must afford high yields.

Aspartic Acid

Improved fermentation for the direct production of aspartic acid or improved fermentation for reducing the costs of fumaric acid will depend on the utilization of both genetic engineering and traditional strain improvement technology.

Novel biodegradable specialty polymers (polyaspartic acid and polyaspartates) offer new potential markets as substitutes for polyacrylic acid and polycarboxylates. Applications may include detergents, water treatment systems, corrosion inhibitors, and super-absorbent polymers.

Glucaric Acid

Selective oxidation of an inexpensive sugar or sugar source to a single compound is analogous to the conversion of complex starting petrochemicals to single and much simpler building blocks. Success in the development of glucaric acid production and of new derivatives will favor a broad application to the sugar platform and will address high volume and high value markets. Technology specific to glucaric acid will also be applicable to the production of xylaric and arabinaric acids, two other compounds highly ranked within this evaluation, making this portion of the biorefinery R&D effort significant.

Glutamic Acid

The major challenges are primarily associated with reducing the overall cost of the fermentation process. In order to be competitive with products derived from petrochemicals, the fermentation cost needs to be at or below $0.25/pound. This is a significant technical challenging issue, but has the potential to be reached in the midterm, since there is substantial experience working with the organism for glutamic acid production.

Itaconic Acid

The major challenges are primarily associated with reducing the overall cost of the fermentation. In order to be competitive with petrochemical-derived products, the fermentation cost needs to be at or below $0.25/pound.

This is a significant technical challenge and should be undertaken with a long-term perspective.

Levulinic Acid

The family of compounds available from levulinic acid is quite broad and addresses a number of large volume chemical markets. This monomer offers one of the largest families of potential industrial derivatives among the compounds included in the top 10. Its low cost and ready availability from both 5-carbon and 6-carbon sugars suggest that it could be a building block of central importance within the biorefinery. R&D will be necessary, especially to determine which of the many potential derivatives offer the best opportunities for partnering with industry.

3-Hydroxybutyrolactone

Ring opening reactions can produce hydroxyl equivalents of succinic acid as potential derivatives. Other potential derivatives include gamma-butenyl-lactone (via dehydration) and acrylate-lactone (via esterification).

The research and market opportunities for 3-hydroxybutyrolactone come from its potential to create new derivative compounds. Since it is produced as a specialty chemical for fairly high value uses, little attention has been paid to producing it as a commodity chemical intermediate and all the attendant issues with such development. This would be a challenging product to develop, but one showing some exciting opportunities. Engineering analyses would be required, aiming at better defining the metrics needed to achieve cost efficient production of this molecule.

CHALLENGES AND OPPORTUNITIES

Waste valorization is an attractive concept that has gained increasing popularity in many countries nowadays, due to the rapid increase in

generation of such waste residues. Because of this, researchers are not only developing valorization strategies but also focusing on the design of greener materials utilizing a range of green technologies.

Waste valorization is currently geared towards three sustainable paths: the production of fuel and energy to replace common fossil fuel sources and, in parallel, the production of high-value platform chemicals, as well as useful materials. Another direction of waste valorization aims at producing high-value chemicals from residues, such as MSW. The production of biomass-derived chemicals is a sustainable approach, as it maximizes the use of resources and, at the same time, minimizes waste generation.

Increasingly tighter regulations regarding organic waste and the demand for renewable chemicals and fuels are pushing the manufacturing industry towards higher sustainability to improve cost-effectiveness and meet customers demand. Therefore, the large amounts of waste generated globally represent an attractive sustainable source for industrially important chemicals.

MSW is generally characterized by a high diversity and variability, a high proportion of organic matter, and high moisture content. Due to these properties, waste disposal constitutes a significant problem due to the growth of pathogens and rapid autoxidation. The high moisture contents also increase the cost of waste transportation. Besides, MSW with high lipid content is also susceptible to rapid oxidation. Further, the release of foul-smelling fatty acids adds difficulties as far as the storage of this waste is concerned. For these reasons, in recent years, problems associated with the disposal of MSW to landfills lead to increased interest in searching for innovative alternatives, due to the high proportion of organic matter in the food waste contained in MSW.

Valorization research has evolved through the years, with many techniques and developments achieved in recent decades. In a recent review by Pfaltzgraff et al. [148], it was noted that the valorization of food wastes into fine chemicals is a more profitable and less energy consuming approach as compared to its possibilities for fuels production. Because of this, related waste processing technologies, particularly referring to the production of

fuels, have also been proposed to address energy efficiency and profitability from a range of different feedstocks.

It has been seen that municipal solid waste is still a highly underutilized source for microbial conversion to valuable chemicals. This is a challenge and therefore opens an interesting range of opportunities for the development of more cost-efficient pre-treatments and fractionation methods that will open the use of MSW as a general fermentation substrate, utilizing either the carbohydrates only, or the complete organic fraction. Furthermore, another challenge refers to the establishment of new technologies for pre-processing and fractionation of MSW for microbial conversions, aiming at developing microbial strains able to convert MSW to the targeted intermediate products with high productivities and suitable for their subsequent transformation into marketable products.

The purpose of pre-treatment is to facilitate extraction of different fractions required for further revalorization, and to prepare MSW biomass for optimal fermentation. Therefore, the development of advanced pre-treatments will be essential to obtain a cost-efficient fermentation and downstream process. So far, the purpose of pre-treatment has been to overcome the intrinsic characteristics of the waste, including recalcitrance, heterogeneity, multicomposition, and diversity.

Biotechnological processes are promising alternatives to petrochemical routes for overcoming the challenges of resource depletion in the future in a sustainable way. Renewable resources, such as agricultural residues or residues from food production, such as MSW, are produced in large amounts and have been shown to be promising carbon and/or nitrogen sources. Biotechnological processes for the production of bio-based chemicals are auspicious alternatives to petrochemical routes for overcoming the challenges of resource depletion in the future within a sustainable pathway. The change from a fossil oil-based to a bio-based economy requires the development of innovative utilization processes to fully exploit the potential of biomass.

Biotechnological approaches are essential to achieve the goals, involving enzymatic hydrolysis of the feedstocks, development of microbial strains designed for conversion of the feedstocks to diamines and diacids

and setup of efficient fermentation processes. The production of more complex chemicals is limited by large-scale economic feasibility due to pre-treatment and conditioning costs of the recalcitrant raw materials. The use of the gases obtained by thermochemical processing and/or anaerobic digestion as substrates for fermentation reactions may represent a suitable approach for overcoming this challenge. Though some of these approaches have proven to be valuable to increase the availability of polysaccharides to enzymatic hydrolysis and fermentation to biofuels, a specific and optimized process must be developed to work with MSW.

Strategies to handle varying MSW composition should also be developed, and integrated with the strain and fermentation process development.

An additional effort has to be put on the lipid and protein fraction, as biomass pre-treatment procedures have mostly been developed for cellulose or lignin components. Since there is no ideal pre-treatment procedure for MSW, attending to the requirements of the different fractions for further revalorization, combination of different pre-treatments should be applied. The direct extraction of protein and lipids for conversion to other added-value products to further improve the process economy, should be also explored. For instance, lipids can be used as biofuels or biolubricants; hydrolyzed proteins can be used as biofertilizers; biosurfactants can be obtained from both lipids and amino acids, etc.

Obviously, it should be also necessary to consider the environmental impact of the processes and their sustainability. This will probably restrict the choice of chemicals used and the energy requirements of individual units operations.

However, we must not only focus on the MSW, but also bear in mind that there is still a lot to do in terms of lignocellulosic derivatives. We have to take into account that the development in the valorization of lignocellulosic biomass still remains a big challenge together with many opportunities. Thus, extensive research is currently being undertaken all over the world to convert lignocellulosic biomass to value-added chemicals and polymers at high selectivities and yields at economical costs. One of the most important goals is to fractionate lignocellulose into its three major

components, namely cellulose, hemicelluloses and lignin. Once these components are isolated, target compounds can be obtained through either chemocatalytic or microbial production processes.

This is the reason, for which future developments in the valorization of lignocellulosic biomass are directly correlated to improvements in the fields of chemical and microbial synthesis. Owing to the recent advancements in these fields, the number and diversity of lignocellulosic biomass-based commodity and specialty chemicals have been rapidly increasing. Furthermore, biorefinery and biofuel technologies have been developed to refine lignocellulosic biomass in analogy to petrochemistry for producing green fuels, chemicals and polymers. The number of biorefinery-related pilot and demonstration plants has been increasing. All these technological advances will allow to isolate interesting chemical building blocks, from lignocellullosic derivatives or directly from MWS, which could be utilized to produce many conventional and novel polymers. Therefore, current commodity polymers are expected to be replaced by their bio-derived counterparts in the near future.

However, the ultimate commercial success of biopolymers will depend on three factors; economics, performance and environmental factors. The first factor seems to be more significant, since biopolymers have been proven to exhibit similar performance and more environmental friendliness in comparison with their petroleum-based counterparts. Economic considerations can be improved via continued research and development, as well as government and private sector investment. Fortunately, the recent trends suggest that we are on the path of establishing a worldwide bio-based economy and lignocellulosic biomass and MSW may have a great contribution in this context.

The conversion of a range of feedstock into valuable products including chemicals, biomaterials and fuels has been demonstrated to highlight the significant potential of advanced waste valorization strategies. The incorporation of these and similar processes in future biorefineries for the production of value-added products and fuels will be an important contribution towards the world’s highest priority target of sustainable development.

However, perhaps, currently way overlooked, society itself is the main and most important issue to be addressed for the sake of future generations. The most extended perception of waste as a problem, as a residue, as something not valuable needs to give way to a general awareness of society that waste is a valuable resource, which obviously entails a significant complexity (from its inherent diversity and variability). Nevertheless, waste can provide at the same time an infinite number of innovative solutions and alternatives to end products, by exploiting advanced valorization strategies. These will need joint efforts from a range of different disciplines ranging from engineering to biochemistry, biotechnology, environmental sciences, legislation and economics, in order to come up with innovative alternatives that we hope to see leading the way towards a more sustainable bio-based society and economy.

ACKNOWLEDGMENTS

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