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Levulinic Acid as a Chemical Platform to Polymers

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Abstract: Levulinic acid (LA) is commonly obtained from acid hydrolysis of renewable biomass via dehydration of hexoses. Its bifunctionality is due to its structure's ketone and carboxylic acid groups. This turns LA a key compound for producing a biobased chemical platform, which products have a broad application range. The interest is due to the sustainable concept regarding LA production since its raw material is profusely available and renewable. Its production cost is competitive and attends the ecological appeal of the society, besides its great reactivity. Among the products generated from LA, monomers and biopolymers can be obtained that are of interest in the scientific community, such as methyl butanediol (MeBDO) and acrylic acid. The polymerization processes may be via direct polymerization with diamines to produce polyamides and ring-opening polymerization (ROP) of their lactones to obtain polyesters. The polymers formed have a green aspect aiming the replacement of fossil derivatives, such as diphenolic acid, which can replace the use of highly toxic bisphenol-A.

Keywords: biorefinery; levulinic derivatives, monomers; plasticizers; polymerization.

1. Introduction

The biorefinery is designed to reuse biomass residues for the production of high value-added value chemical derivatives (fine chemicals, solvents, polymers, pharmaceuticals, etc.) and energy (fuels, power, heat) [1–3]. In addition, there is an increasing trend to reduce the dependency on petroleum-based industries, since it causes pollution problems (carbon emission), price fluctuations due to the growing scarcity of fossil derivatives, summed to its rising consumption, and geopolitical crisis, being in accordance to the circular economy concept [4,5].

LA appears as an attractive chemical substance for the development of a renewable chemical platform, according to the United States Department of Energy (US DOE) [6]. The LA has a chemical versatility due to its bifunctionality; it has the functional groups carboxylic acid and ketone that give it high reactivity, providing a spectrum of marketable products (polymers, fuels, pharmaceuticals, solvents, fine chemicals, plasticizers, etc.) for different market segments [7–9].

In addition, LA is commonly produced by the acid hydrolysis of the lignocellulosic biomass, a renewable resource [10], as presented in Figure 1. The process generates hexoses

from the hydrolysis of the cellulose. The hexoses suffer isomerization in the acidic medium, through which successive dehydration leads to the production of 5-hydroxymethylfurfural (5-HMF), which is finally hydrated and generates LA and formic acid as products [11].

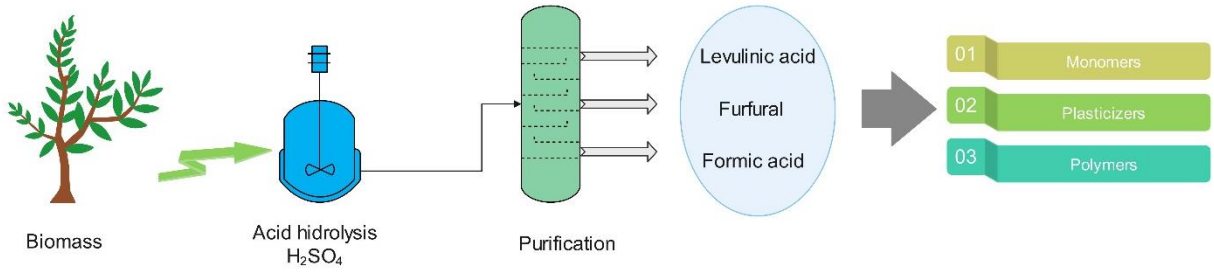

Figure 1. Levulinic acid production (based on info available in ref. [12]).

The chemical platform derived from the LA generate products of the interest of the polymer industry, such as monomers, polymers, and plasticizers [13]. This is possible through the reactions that happen in the carboxylic acid and ketone groups from LA (Figure 2) [14], which gives products with two or more functional groups that are required to expand the chain length of polymers [15]. Methyl and methylene groups also contribute to the development of polymer precursors. Furthermore, additional functional groups in the backbone structure improve intermolecular interactions, reflecting in the properties of the green polymers (chemical, physical, thermal, mechanical, and biodegradability) [16,17].

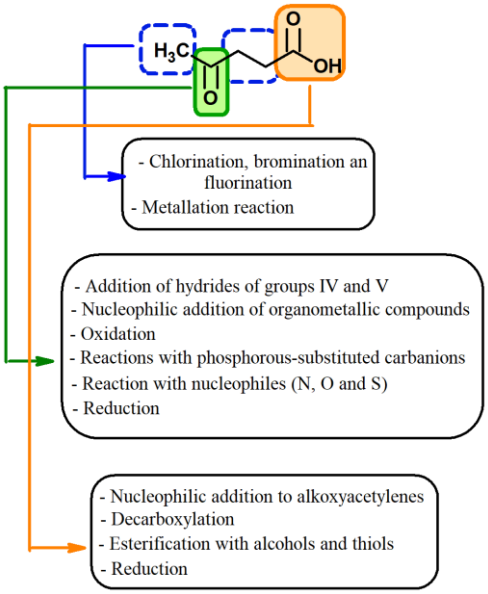

Figure 2. Levulinic acid reactivity (based on info available in ref. [14, 15]).

A range of monomers (Figure 3) can be obtained through the LA to obtain renewable biomass-based polymers, such as polyesters [18], polyamides [19], polycarbonates [20], polyurethanes [21], among others. The polymers produced with LA have different behaviors (thermoplastics, thermoplastic elastomers, and thermosetting) and a wide variety of desirable characteristics relative to the polymers: degree of crystallinity, flexibility, ductility, biodegradability, biocompatibility, bioadhesion, physical-chemical-thermal-mechanical properties, which makes the LA be a promising polymer engineering pathway.

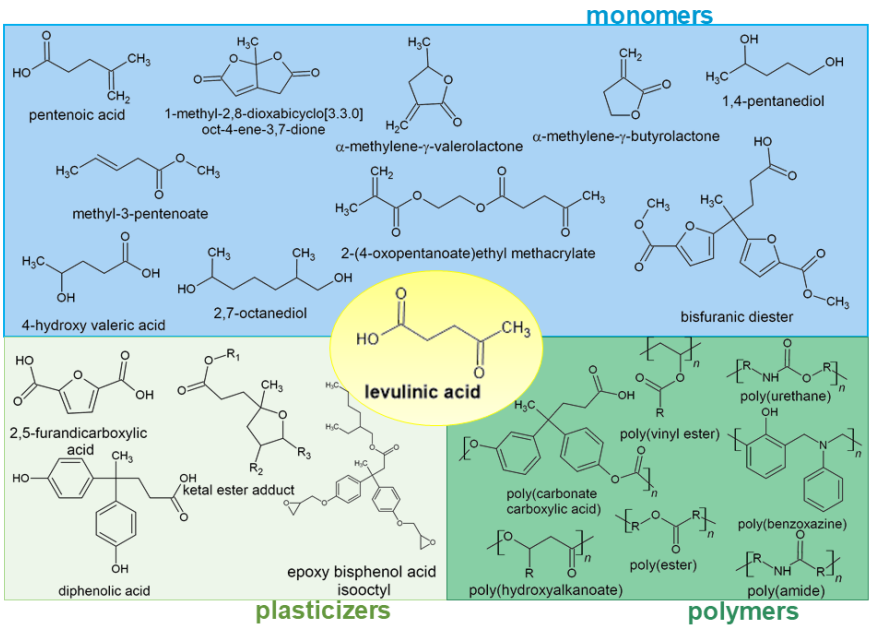

Figure 3. Polymer chain derived from LA.

Many studies have been carried out to develop plasticizers and monomers to replace Bisphenol-A (BPA) [22]. This is caused by the ban on the use of BPA in Europe, the USA, and other countries [23], mostly because of the researches reporting the exposure of BPA as a factor of incidence of neurological diseases (Parkinson and Alzheimer), cancer, cardiovascular diseases, disorders in the endocrine and reproductive system, obesity, diabetes, and others [24,25]. Substitutes for BPA can be synthesized from LA through its condensation with two molecules of phenol-producing diphenolic acid (DPA) [26,27]. Other LA-based plasticizers can be obtained via LA reaction with epoxidized unsaturated fatty acid esters derived from vegetable oils [28] or via its oxidation to obtain 2,5-furan dicarboxylic acid (FDCA) [29], which can be used in the formulation of a variety of polymers.

This review aims to show the potential to develop a renewable bio-based chemical platform for polymers through LA and the possible applications to these novel polymers. This is a trending topic nowadays since, over the decade, has increased the research in the area of chain plastic production materials derived from LA (Figure 4).

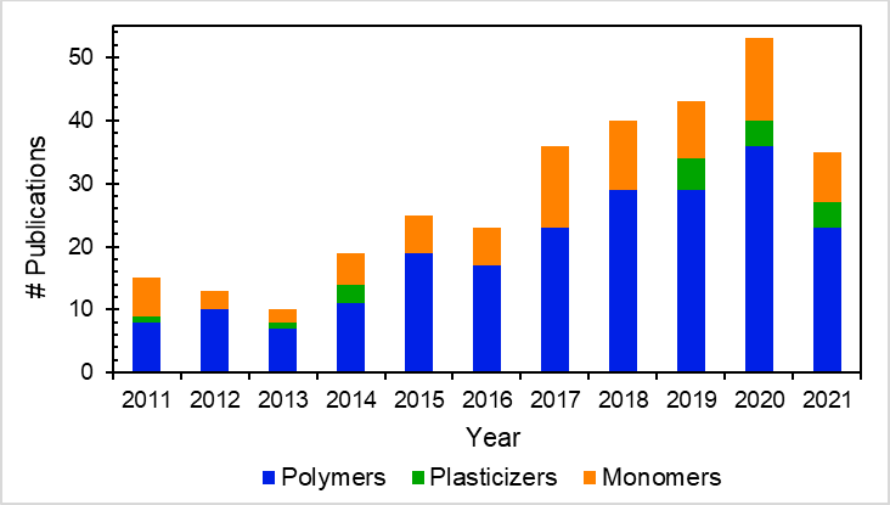

Figure 4. The number of publications of the decade based on the plastic production chain derived from LA. Info was available on Web of Science [30].

2. Monomers

4-hydroxyvaleric acid (4-HVA), a biomonomer for polyesters, can be synthesized via enzymatic reduction using 3-hydroxybutyrate dehydrogenase (3HBDH) from *Alcaligenes faecalis*. 3HBDH can also be engineered in an *Escherichia coli* strain, producing 4-HVA with LA as substrate [31]. This monomer is used as a fuel precursor (γ-valerolactone, GVL) [32], [33].

1-methyl-2,8-dioxabicyclo[3.3.0]oct-4-ene-3,7-dione is a versatile monomer for polyester synthesis that can be obtained through acid-catalyzed condensation of LA with glyoxylic acid followed by a reduction reaction [34].

2,5-furandicarboxylic acid (FDCA) can be produced via oxidation of LA in the presence of a catalytic system (cobalt/manganese/bromide, 1:1:4) and oxidative gas (O_2). Due to its chemical structure, FDCA has been discussed as a green alternative to phthalates plasticizers and as a raw material for terephthalate derivatives [29].

α-methylene-γ-valerolactone (MGVL), an acrylic biomonomer, structurally similar to methyl methacrylate, may be synthesized through LA in two steps. Firstly, GVL is obtained via LA hydrogenation using Ru/C as a catalyst, and secondly, the GVL suffers a condensation with formaldehyde using basic catalysts (metal salts on silica – K, Ba, Rb, Cs) [35]. The MGVL is an attractive monomer since it is highly reactive (polymerizes rapidly), and it adds thermal stability to the acrylic polymer [36]. Equivalent presumption works with γ-methyl-α-methylene-γ-butyrolactone (MMBL) [37,38].

γ-hydroxy(amino)amide (HAA) compounds were produced from GVL through ring-opening with amine compounds catalyzed with Lewis acids. This reaction gives an amine into the GVL' carbonyl lactone, producing a building block to addition-elimination reactions, leading to obtaining polyethers, polyesters, and polyurethanes [39].

Nylon intermediates (adipic acid, dimethyl adipate, or caprolactam) may also be produced by methyl-pentenoates (MP) [40,41]. In a catalytic distillation process, this compound can be derived from a GVL via acid-catalyzed transesterification with methanol [37]. Also, a ring-opening reaction of GVL using ZrO_2/SiO_2 as a catalyst and adding CH_3OH yields methyl 2-, 3- and 4-MPs [41].

Pentenoic acids (PEA) are precursors to nylon monomers, which can be obtained through acid-catalyzed reactive distillation with GVL. Adipic acid, a nylon monomer, can be produced via hydroxycarbonilation of PEA, and via self-metathesis followed by its hydrogenation. The ethenolysis of PEAs produces acrylic acid, which is important to acrylic polymers production [42]. Another route to produce alkenoic acids (monomers) consists in the LA functionalization with alkyltriphenylphosphonium halide under basic medium (Wittig reaction), inducing the reduction of the LA' ketone group [43].

LA can also provide a diol bio-based monomer via LA's electrochemically coupled reaction. It gave 2,7-octanedione, that after hydrogenation produces 2,7-octanediol. This diol is very appropriate to produce polyesters through its reaction with diacid chlorides and its transesterification with diesters; besides, it can suffer copolymerization with isosorbide and diacid chlorides [44].

3. Polymers

3.1. Polyesters.

Polyhydroxyalkanoates (PHAs) are a group of bacterial polyesters synthesized with a range of prokaryotic microorganisms. PHAs are produced as intracellular carbon for the energy storage of bacteria. It is produced in a medium with unbalanced nutritional conditions, with an excess of carbon sources [45]. PHAs can be classified as short-chain length (3-5 carbons) that has high crystallinity and brittleness, or medium-chain length (6-14 carbons) that has lower crystallinity and are more flexible; they can also have no crystallinity and be flexible [46]. Common PHA monomers are hydroxybutyric (HB), hydroxyvaleric (HV), hydroxyhexanoic (HHx), hydroxyoctanoic (HO), hydroxydecanoic (HD), and hydroxydodecanoic (HDD) acids; which have a varying number of carbons and at least one chiral center [47]. These monomers are used in reactions of homopolymerization and copolymerization, providing a variety of polymer properties (thermoplastic to elastomeric) [46,48].

The PHAs have different physical, chemical, thermal, mechanical, and biological properties according to its production' procedure, the microorganism, and carbon nutrient used; but its biodegradability is inherent, which turns PHA good for medical applications biodegradable plastic packaging, among other applications [49]. These characteristics also make the PHAs attractive as alternatives for the common petroleum-based plastics since they are environmentally friendly bio-based plastics and present tunable properties. Many companies produce PHAs around the world [50], which have improved the bioplastics economy.

LA can be used as a carbon source for microorganisms to produce PHAs. Biopolyesters containing 4-HVA and medium-chain-length hydroxy alkanoic acids were produced with a recombinant strain of the PHA-negative mutant GpP104 of *Pseudomonas putida* using LA as a precursor substrate for the 4-HVA [51]. The PHAs synthesized with medium chains (C6 – C12) behaved as thermoplastic elastomers with high molar mass and elongation to rupture. Posterior studies from this research group produced biopolyester based on 4-HVA on a large scale with recombinant strains of *Pseudomonas putida* and *Ralstonia eutropha* [52]. These biopolyesters showed lower molar mass and elongation at break, indicating a higher crystallinity [52], making this elastomer suitable for medical applications, especially in coatings.

Glycerol and LA were used as co-substrates in the fermentation process of *Pseudomonas oleovorans* and *Ralstonia eutropha* to produce PHAs biopolymers with short chains. This system produced PHAs with pure 3-HB varying to pure 3-HV depending on the ratios of glycerol and LA used to feed the microbiological medium. The biopolymers produced showed a high molar mass and wide melting temperature, making them attractive for various commercial applications [53,54]. Another condensation reaction involving the direct use of LA and glycerol using Sb_2O_3, p-toluenesulfonic acid, and 1-(1-propylsulfonic)-3-methylimidazolium chloride as catalysts, produced oligomers with ketal and ester linkages, making them suitable to be biodegradable, useful as plasticizers, and as raw material for copolyester synthesis [55].

The copolymer poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) can be produced using *Ralstonia eutropha* with LA as the precursor for 4-hydroxyvalerate [56]. Another work obtained PHBV via *Burkholderia cepacia fermentation* with xylose and LA as co-substrates [46,57]. These routes are interesting since the higher content of HV units reduces the PHB

crystallinity, which originally is a highly crystalline and brittle polymer. It also improves its thermal and mechanical behavior by increasing the temperature difference between decomposition and melting, besides its flexibility and ductility, making them suitable for commercial applications [58].

Biodegradable poly(3-hydroxypentanoic acid) (PHP) may be produced using LA as a carbon source in a biotechnological process with *Rhizobium s*. The reaction mechanism has a hypothesis involving the conversion of LA into propionyl Co-A that condenses with acetyl Co-A forming the PHP [59].

Poly(5-hydroxylevulinic acid) (PHLA) can be obtained via polycondensation of the 5-hydroxylevulinic acid using stannous chloride dehydrate ($SnCl_2.2H_2O$) and p-toluenesulfonic acid as catalysts. The oligomers produced are hydrolytically degradable with satisfactory thermal stability, which encouraged the polymerization studies of 5-hydroxylevulinic acid with polyols aiming to produce biopolymers with pendant functional groups interactions [60]. Since these biodegradable polymers contain aliphatic ester linkages, they degrade into nontoxic 5-hydroxy levulinic acid and a diol, making it promising to be biocompatible and appropriate for applications such as biomedical materials and useful as polymers for food (chewing gum) [60].

Poly(4-ketovalerolactone) (PKVL) is another polyester obtained by ring-opening polymerization of a monomer produced by the bromination and cyclization of LA. PKVL has a great potential for applications because its structure resembles polyglycolide (PGA), a well-established biopolymer [61].

A bio-based bisfuranic diester monomer (BFD) was synthesized via acid-catalyzed condensation of LA with methyl-2-furoate in the presence of zinc acetate. These BFD, an aromatic-aliphatic polyester, presented excellent thermal stability due to the chain composition [62]. Additionally, it was found that LA-modified furan resins with zinc phosphate hydrate films can be used as protective coatings on carbon steels surfaces [63].

3.2. Polyurethanes.

The reduction of LA leads to GVL production, which is an interesting monomer precursor for polyurethane (PU) synthesis [64]. The ring-opening reaction of GVL with aminoethanol and ethylenediamine produced GVL-derived polyols, N,N'-1,2-ethanediylbis-(4-hydroxypentanamide) and 4-hydroxy-N-(2-hydroxyethyl)-pentanamide [65], respectively, which can react with diisocyanates (hexamethylene, 1,4-phenylene, and 2,4-toluene) [21]. These reactions produced polyurethanes with high molar masses, making it possible for their use in common PUs commercial applications [21].

Aqueous polyurethane dispersions can be produced via the reaction of LA with epoxidized vegetable oils, which gave polyketone-polyols oligomers. Such polymeric dispersion improves film formation for coating applications, besides having low volatile organic compounds and being an environmentally friendly product. On the other hand, the polyols produced via epoxide ring-opening with LA are suitable to react with hydrazines, producing polyurethane pre-polymers [66].

3.3. Polyamides.

Polyamides can be directly obtained from LA via UGI multicomponent reaction. This was possible because of the bifunctional nature of LA (carbonyl and carboxylic acid), which can react with diamines and diisonitriles [67].

Other polyamides can be obtained through condensation polymerization of hexamethylenediamine or decamethylenediamine with furan-2,5-dipropionic acid or tetrahydrofuran-2,5-dipropionic acid (LA derivative monomers), which are synthesized via LA and furfural reaction [19]. Diethyl 1-methylpyrrolidine-2,5-di-β-propionate was synthesized in a multi-step reaction of LA and furfural; this biomonomer led to the production of homo and copolymers through the polycondensation of diethyl 1-methylpyrrolidine-2,5-di-β-propionate with hexamethylenediamine and or with diethyl adipate, azelate, sebacate [68].

3.4. Other polymers.

Polycarbonate carboxylic acid (PCA) was synthesized with DPA, in a reaction system that firstly involved the protection of the carboxylic acid of the DPA with tert-butanol through esterification, secondly occurred the condensation with phosgene to produce homo-polycarbonate, and finally, the product was deprotected with trifluoroacetic acid [20].

Polybenzoxazine (PBZ) resins were obtained using DPA and a methyl ester DPA derivative (MDPA) as monomer precursors, which were further reacted with 2,4,6-triphenyl-1,3,5-triazine and paraformaldehyde to form DPA-Bz and MDPA-Bz monomers. These monomers were used to produce thermosetting resins through cure and low-density rigid foams via decarboxylation at high temperature and pressure [69].

Ketone functionalized poly(vinyl esters) were obtained through the copolymerization of vinyl levulinate with vinyl acetate by alkyl cobalt (III)-mediated radical polymerization (CMRP). The ketone groups of poly(vinyl acetate-co-vinyl levulinate) were functionalized by ketoxime click chemistry with O-benzylhydroxylamine [70].

The monomer 2-(4-oxopentanoate)ethyl methacrylate (PAEMA) was obtained via LA esterification with 2-hydroxy ethyl methacrylate. The PAEMA was further polymerized by reversible addition-fragmentation chain transfer (RAFT) and had its chain extended with ethylene glycol; the copolymer obtained showed no cytotoxicity [71].

1,4-pentanediol obtained from the LA reduction was used to produce cyclic ketene acetals (CKA), 2-methylene-4-methyl-1,3-dioxepane (MMD), which can suffer ring-opening polymerization in the presence of azobisisobutyronitrile (AIBN) to produce polyesters (PMMD) [72].

Poly amine co-esters (PAEs) can be synthesized using four different monomers with methyl levulinate: N-methyl aminoethanol, L-prolinol, Sarcosine methyl ester, and L-proline methyl ester. The routes to produce PAEs are by polycondensation or ring-opening polymerization [73].

4. Plasticizers

Plasticizers are utilized in polymer's formulation to give more flexibility to the chain polymer structure, lowering their transition glass temperature (Tg) and making the polymer's processing [74].

Ketal adducts are produced in the reaction with alkyl esters of levulinate and epoxidized unsaturated fatty acid esters derived from vegetable oils. These ester products can be used as secondary plasticizers in poly(vinyl chloride) (PVC) formulation, or they can be used as a base polymer for vinyl chloride polymers, P3HA, poly(lactates), and polysaccharide polymers formulations [28]. They present epoxidized fatty acid fragments in their structure, which act as scavengers of acidic in the polymer medium, preventing thermal decomposition and oxidation

[75], besides the fact of being an environmentally friendly alternative to the common BPA plasticizers utilized in the polymer's industry, such as flexible polymers, laminates, pipes, coatings, flooring, and others.

LA ester derivatives obtained from the esterification with polyols can be used as reactive plasticizers or coalescent solvents in polymers formulations [76]. It means that giving flexibility to the polymer chain helps the polymer solution to produce a uniform film when used in coatings compositions, besides having lower volatility, which is of great interest in the industry.

DPA can be obtained by condensing LA with phenol; such compound has a similar structure to BPA, a highly toxic plasticizer. Therefore, DPA has compatible properties to be an alternative plasticizer, less toxic, and derived from renewable sources [13].

The epoxy bisphenol acid isooctyl ester (EBAIE) is a promising LA-based plasticizer used in PVC manufacturing. The blend PVC/EBAIE at 30:100 wt% had good mechanical properties and thermal stability [77].

5. Conclusions

Levulinic acid is a versatile chemical compound due to its bifunctionality (carboxylic acid and ketone groups), making it an attractive building block to produce polymers with different functionalities and applications. Besides these facts, levulinic acid is obtained through acid hydrolysis of renewable feedstocks (lignocellulosic biomass), making it an appropriate raw material as an alternative to the commonly petroleum-based polymers. The great reactivity of the levulinic acid allows the production of a range of biomonomers and biopolymers (polyester, polyurethane, polyamide, polycarbonate, etc.) with commercial and special such as commodity polymer to biomedical applications. The polyhydroxyalkanoates (PHAs) derived from levulinic acid are particularly appropriate for biomedical and tissue engineering due to their biocompatibility and inherent biodegradability. The levulinic acid can also offer environmentally friendly plasticizers used in polymers composition, such as diphenolic acid (DPA) or (epoxidized esters vegetable oils derivatives). In summary, levulinic acid can be used in all-polymer chain production (synthesis, formulation), representing a green alternative to the plastic industry.

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Conflicts of Interest

The authors declare no conflict of interest.

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