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100th Anniversary of Macromolecular Science Viewpoint: Polymers from Lignocellulosic Biomass. Current Challenges and Future Opportunities

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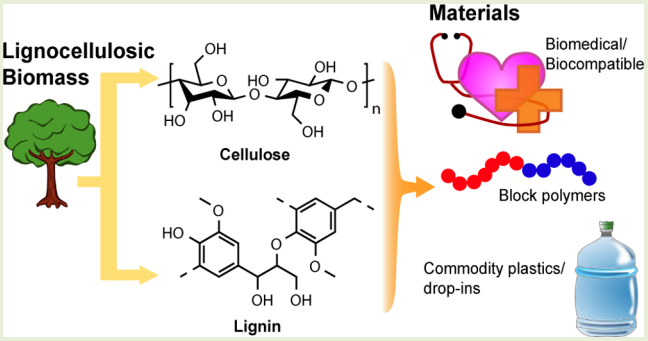
ABSTRACT: Sustainable polymers from lignocellulosic biomass have the potential to reduce the environmental impact of commercial plastics while also offering significant performance and cost benefits relative to petrochemical-derived macromolecules. However, most currently available biobased polymers are hampered by insufficient thermomechanical properties, low economic feasibility (e.g., high relative cost), and reduced scalability in comparison to petroleum-based incumbents. Future biobased materials must overcome these limitations to be competitive in the marketplace. Additionally, sustainability challenges at the beginning and end of the polymer lifecycle need to be addressed using green chemistry practices and improved end-of-life waste management strategies. This viewpoint provides an overview of recent developments that can mitigate many concerns with present materials and discusses key aspects of next-generation, biobased polymers derived from lignocellulosic biomass.



Polymer science has developed substantially over the past century, resulting in the creation of durable and versatile materials that greatly enhance our quality of life. However, these advances have come at a cost, in the form of ecological harm at both ends of the polymer lifecycle. The vast majority of the 8.3 billion metric tons of polymers produced since 1950 is derived from petrochemicals, and as such, polymer manufacturing is considered a major contributor to greenhouse gas emissions and other forms of environmental damage.[1] Additionally, many petroleum-based monomers are volatile and toxic, giving rise to both process safety and public health concerns. For example, styrene, used to make styrenic polymers, is a known carcinogen,[2] while bisphenol A (BPA), used to make polycarbonates and many epoxy resins, is a possible endocrine disruptor.[3] At the end of the polymer lifecycle, over 6.3 billion metric tons of plastic waste have been generated.[1] Only ∼9% of that plastic waste has been recycled, and another ∼12% has been incinerated for energy recovery.[1] The remaining ∼79% has been discarded, with much of it reaching the environment.[1,4] As the global standard of living increases and populations continue to grow, the demand for polymeric materials is increasing quickly, making these environmental and public health considerations ever more serious.[5] In response to the above-mentioned issues, macromolecular science has witnessed a steady increase in academic research and corporate interest in the generation of more sustainable polymers from renewable feedstocks.[6−13]

The production of biobased polymers accounted for 7.2 million metric tons of the 360 million metric tons of polymers produced in 2017,[14] just 2% of global production. The most widely manufactured biobased synthetic materials were bio-poly(ethylene terephthalate) (bio-PET), bio-polyethylene (bio-PE), and poly(lactic acid) (PLA) with annual productions of 600 000 t, 200 000 t, and 185 000 t, respectively, in 2017.[14] Bio-PET and bio-PE are drop-in replacements for petrochemical equivalents and are readily integrated into existing supply chains. It is worth noting, however, that only the ethylene glycol component of bio-PET is biobased, resulting in ∼30% renewable content in the final material.[14] Biobased ethylene glycol and bioethanol, the primary alcohol precursor to bio-ethylene, are typically produced via the fermentation of sugars. Several other monomers can be prepared from bioethanol, including vinyl chloride and ethylene oxide, but the commercial success of bioderived versions of these compounds

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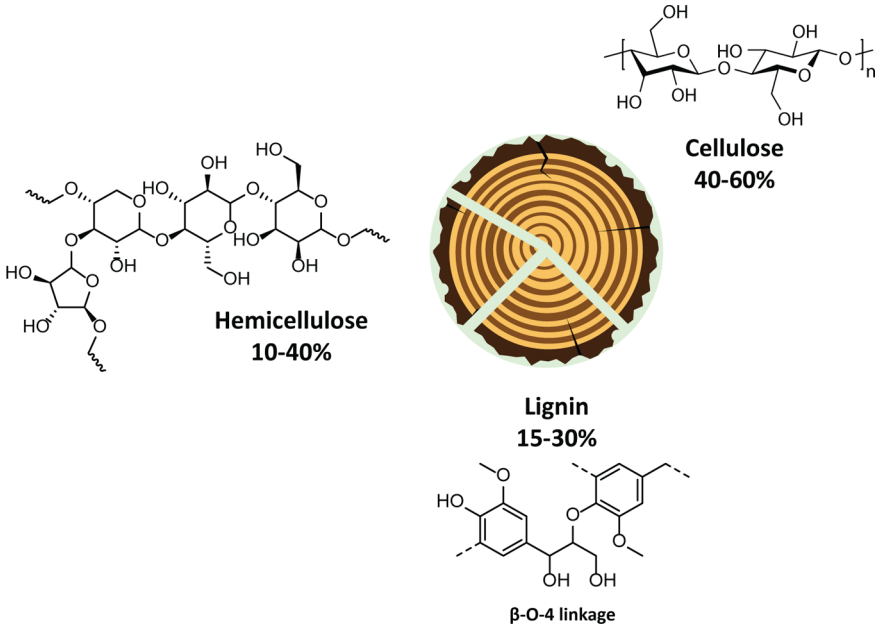

Figure 1. Composition of lignocellulosic biomass and representative chemical structures of each constituent. Hemicellulose and lignin are complex polymers with multiple types of subunits, and as such, the above structures are only to provide the reader with a conceptual overview.

is limited.[6,7,15,16] In contrast to bio-PET and bio-PE, PLA is a unique, biobased, and biodegradable thermoplastic that has achieved some commercial success.[17] The lactic acid monomer can be produced from the fermentation of sugars,[18] and an alternative monomer, lactide, can be prepared via the dehydration and dimerization of lactic acid.[19] Both monomers can be polymerized directly, and PLA is useful for many applications, such as disposable cutlery and food/drink containers.[20] PLA is only biodegradable in industrial composting facilities, however,[17] and many areas of the world do not have access to such facilities. Additionally, all of the above biobased monomers, or their precursors, commonly are derived from food resources, predominantly corn,[6,18,21] and in the case of drop-in replacements, biosourced monomers generally cost more than their petroleum-based counterparts.[14,18] The next generation of biobased materials should address these cost and sustainability issues without sacrificing or, better yet, by improving performance.

Lignocellulosic biomass (LCB), the most abundant biomass source on Earth,[22] is a promising feedstock for biobased monomer production, and polymers derived from LCB can address the aforementioned sustainability and cost issues while also providing performance advantages. LCB is comprised of three primary components, cellulose, hemicellulose, and lignin, as shown in Figure 1, and the typical composition ranges per component are 40−60%, 10−40%, and 15−30%, respectively,[23,24] with the exact composition depending on the feedstock.[25,26] Cellulose and hemicellulose are semicrystalline polysaccharides and, as such, are oxygen-rich materials, whereas lignin is a highly aromatic, amorphous polymer with a somewhat variable structure.[26] Significant strides have been made in the fractionation and subsequent depolymerization of LCB components, especially from nonfood resources like wood and industrial waste streams, to produce platform chemicals.[26−31] The resulting bioderived compounds have inherent chemical functionalities and polarity that can be exploited to design performance-advantaged materials with reduced environmental impacts. These top-down approaches that leverage the heteroatoms inherent in biomass are a deviation from traditional petrochemical processing in which molecules are built, bottom-up, from basic commodity chemicals with functionality being added as needed.

This viewpoint will discuss how platform chemicals arising from reasonably straightforward and commercially relevant LCB fractionation and depolymerization schemes can be used to generate both renewable drop-in replacements for current products, along with novel materials with unique properties. Emphasis will be given to chemocatalytic processing techniques that enable efficient utilization of all components of LCB. In comparison to other LCB conversion routes (e.g., biotechnological or pyrolytic), catalytic approaches enable greater range and flexibility in reaction conditions and result in more selective product formation with simpler separation schemes.[28,32−35] These processes are well-suited for next-generation biorefineries, and the depolymerization products highlighted herein are commercially relevant building blocks for more sustainable materials. Separate sections will be devoted to the platform chemicals and associated polymers derived from the cellulosic and lignin components of biomass.

Also, it is worth highlighting that the continued development of sustainable polymers from biomass resides at the intersection between catalysis, process engineering, biology, and polymer science. Thus, the viewpoint presents an outlook on the future opportunities and challenges in LCB valorization that are a result of this nexus. For example, many current-generation biobased materials are costly and lack in performance, durability, and/or scalability, motivating the need for new performance-advantaged and economically feasible biobased polymers. The momentum behind sustainable materials is growing, and a focused and integrated approach to develop improved predictive capabilities, more efficient biomass processing techniques, greener functionalization chemistries, and suitable recycling strategies for materials lifecycle management are key steps along the path to a sustainable materials ecosystem.

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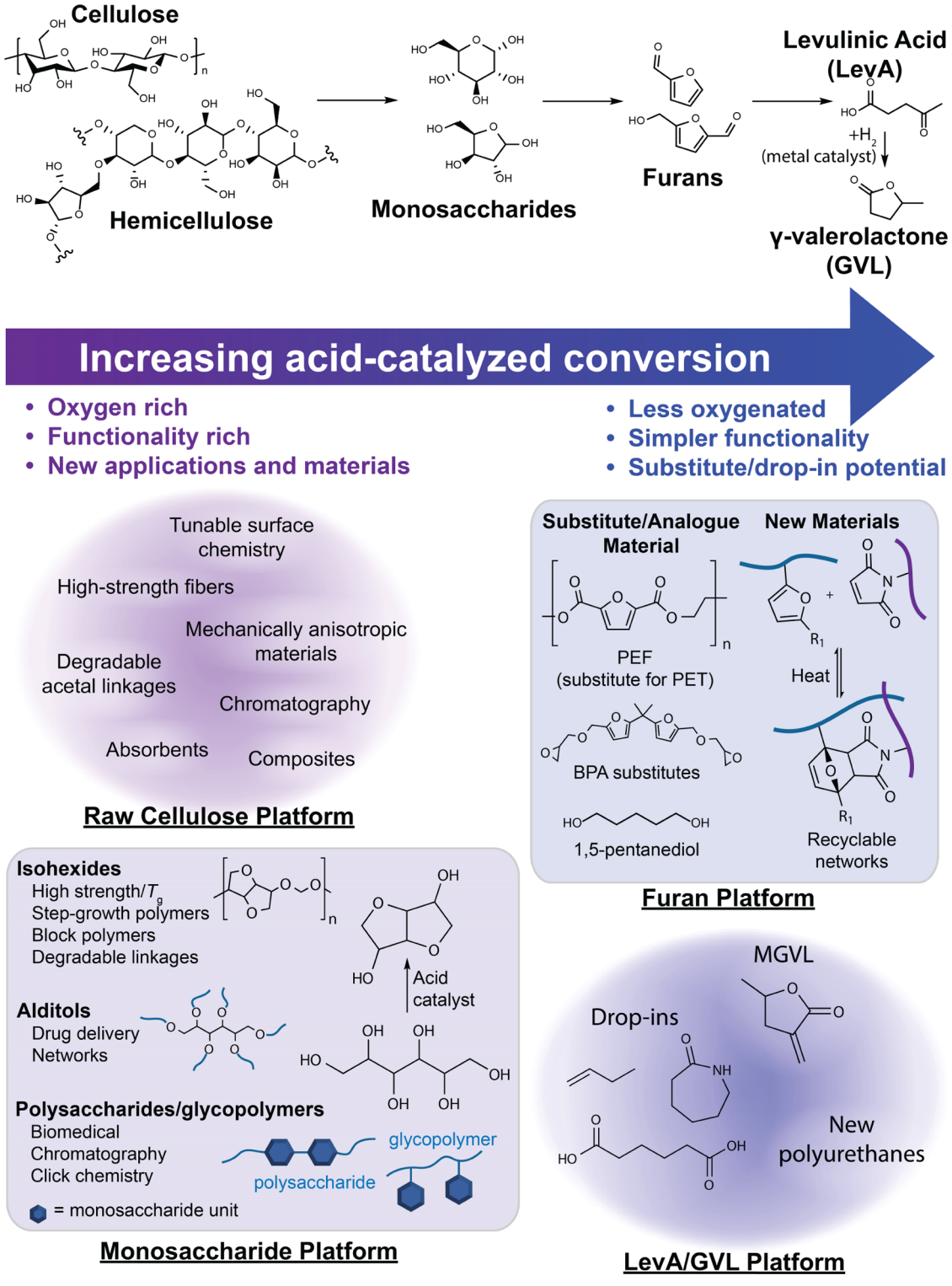

Figure 2. Classes of compounds from acid-catalyzed conversion of cellulosic biomass and potential materials applications.

Cellulosics. Cellulose and hemicellulose comprise the bulk of LCB, accounting for ~65−80% of the material by dry mass.[36] Through the fractionation and depolymerization of cellulose and hemicellulose, saccharide-based building blocks have become available for the synthesis of valuable materials. With a high degree of functionalization relative to native petrochemical building blocks, saccharides are promising starting materials for both the design of new macromolecules and the efficient synthesis of current staple polymers. Many techniques have been developed for the depolymerization of cellulosic biomass; in general, these techniques can be classified as biocatalytic, thermochemical, or chemocatalytic.[15,33,37−39] The biocatalytic conversion of cellulosic biomass is centered primarily on microbial action on simple sugars,[39−42] and biotechnological routes have been developed for the production of polymer building blocks such as succinic acid,[15,43] itaconic acid,[15,44] and various amino acids.[15] Bioprocessing of cellulosic streams are challenging because of

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trade-offs between productivity and the health of the microbial system, and extensive pretreatment often is needed for efficient conversion.[11,39−42,45] Thermochemical conversion methods, such as pyrolysis, have the advantage of being low cost and simple, but these techniques require extensive energy input and complex product separations, detracting from overall process sustainability.[15,42,46]

The most common chemocatalytic approach toward cellulosic biomass depolymerization relies on simple, acid-catalyzed hydrolysis reactions.[28−30,32,36,47−50] Acid-catalyzed cellulose deconstruction also dovetails nicely with the "lignin-first" reductive catalytic fractionation (RCF) strategy summarized in the next section because the cellulose stream from RCF can be subsequently valorized through a separate acid-catalyzed depolymerization process. Furthermore, acid-catalyzed cellulose processing has been accelerated by recent innovations such as biphasic systems for extraction of desired products and mitigation of side reactions,[32,51] ionic liquids or molten salt hydrates as solvents to facilitate cellulose dissolution,[32,51−54] microwave heating to improve reaction kinetics,[32,51,53] microreactors to minimize heat and mass transfer resistances,[55] adsorbents and membranes for improved product separation and purification,[56] and heterogeneous acid catalysts for more efficient catalyst recovery and reuse.[31,32,47,53,57] Representative approaches to the acid-catalyzed conversion of cellulosic biomass are depicted in Figure 2. One attractive feature of the acid-based routes is that the extent of the hydrolysis can lead to the production of different classes of compounds that serve as platforms for materials synthesis.[28,30−32,48,49,51,58−62] These compounds can be generated in the following sequence: (1) raw cellulose;[28,30,36,51,60] (2) monosaccharides and immediate derivatives;[28,30−32,36,48−51,58−61,63] (3) furanics;[31,32,48−51,58−61,63] and (4) levulinic acid (LevA),[48−50,59−62] γ-valerolactone (GVL),[60,62] and associated derivatives.[60,62] The products that arise earlier in the conversion sequence tend to be more highly functionalized and are amenable as building blocks for more complex materials and applications, whereas products that arise later in the process usually are less functionalized and thus approach the application range of traditional petroleum-based monomers. This diversity in available building blocks provides excellent versatility in materials generation from a single process stream.

Raw cellulose, which can be isolated from LCB via various fractionation processes,[28,30] is an intriguing product with properties that make it advantageous in materials applications. Cellulose has a high degree of crystallinity,[52,64] being comprised of stiff and well-oriented chains.[52] These molecular characteristics enable the fabrication of high-strength cellulose fibers[65−67] that can function as a reinforcement in composite materials.[68−72] Chain alignment also creates mechanical anisotropy in materials.[64] Leveraging this behavior, Chen et al. used carbonized, conductive, cellulose fibers to create flexible strain sensors with excellent directional strain resolution for possible use in wearable technologies and robotics.[73] Furthermore, cellulose can be chemically modified through manipulation of the hydroxyl functionalities.[52,74] To complement this strategy, regioselective reactions are being developed;[52,75] for example, Edgar and co-workers used a catalytic scheme to deacylate cellulose acetate that effectively enabled regioselective acylation of hydroxyl groups in cellulose.[75] Additionally, the acetal linkages in cellulose serve as convenient centers for hydrolytic attack to assist in degradation,[9,11] even in neutral and slightly basic aqueous media.[9,76] Drawing inspiration from this behavior of cellulose, Miller and co-workers modified PLA with acetal linkages.[76] The resulting polymer exhibited modest degradation rates in challenging environments, including distilled water and slightly basic seawater.[76] With an extrapolated total degradation time of 5−10 years, the overall decomposition profile strikes a reasonable balance between utility and longevity for common disposable plastics designed for short-term use. Clearly, cellulose and cellulose-inspired components have great potential in materials applications due to their unique mechanical properties, chemical exploitability, and amenability to degradation in common natural environments. Identification of simpler derivatization schemes with better regiocontrol and enhanced processing techniques to overcome solvent resistance are keys to unlocking the full potential of cellulosics.[52,75]

The second class of compounds accessible through the acid-catalyzed conversion of cellulosic biomass is 5- and 6-carbon monosaccharides (see Figure 2).[28−30,32,36,60] Some benefits of the direct use of monosaccharides in polymer synthesis stem from their high functionality, low toxicity, and biodegradability.[15,77] Therefore, it is not surprising that saccharide-based polymers are considered for numerous biomedical applications,[15] such as drug delivery,[15,78] biosensing and bioimaging,[79] protein recognition,[15,77] and tissue engineering.[15,80] A salient example comes from the work of Nagahama et al., which demonstrated how saccharides can bridge the gap between synthetic and biological materials.[80] "Living" hydrogels were fabricated from live cells covalently cross-linked with modified polysaccharides using click chemistry.[80] These gels were generated *in vivo* and accelerated tissue regeneration in injured areas of live mice.[80] Challenges remain, especially in regio- and stereocontrol of monosaccharide connectivity, but the high degree of chemical functionality in fully synthetic polysaccharides and glycopolymers can be leveraged to broaden the available structures and functions of biobased materials.[81]

In addition to raw monosaccharides, sugar derivatives have been used in polymer synthesis. For instance, the multihydroxylated structure of alditols—or sugar alcohols—has been leveraged to create biobased epoxy prepolymers and amine hardeners,[82] polyurethane networks by reaction with diisocyanates,[83] and amphiphilic polymers with useful self-assembly characteristics.[84] The alditols also can be transformed into isohexides via acid-catalyzed dehydration and cyclization.[11,37,85−87] Incorporation of these rigid and inflexible diols into polymer architectures tends to increase the mechanical strength, stiffness, and glass transition temperature (T_g) of the associated polymers.[15,86−90] As an example, the Hillmyer and Reineke groups produced isosorbide acrylates as the high-T_g block in block polymer pressure-sensitive adhesives (PSAs).[91,92] These materials showed comparable performance to commercial PSAs.[91,92] Isohexides also are suitable for step-growth polymerizations; however, secondary alcohols usually require modification to enhance reactivity.[11,87,88,93−95] Similar to the above-mentioned chain-growth polymers, isohexides can improve the thermomechanical properties of step-growth systems. For example, fully biobased isohexide-containing polyesters have been reported, and the properties were tunable based on the structure of the comonomer(s).[96] These systems have broad utility as alternatives to, or additives for, commercial polymer systems with rigid groups, such as terephthalic acid (TPA)-derived polyesters or BPA-based

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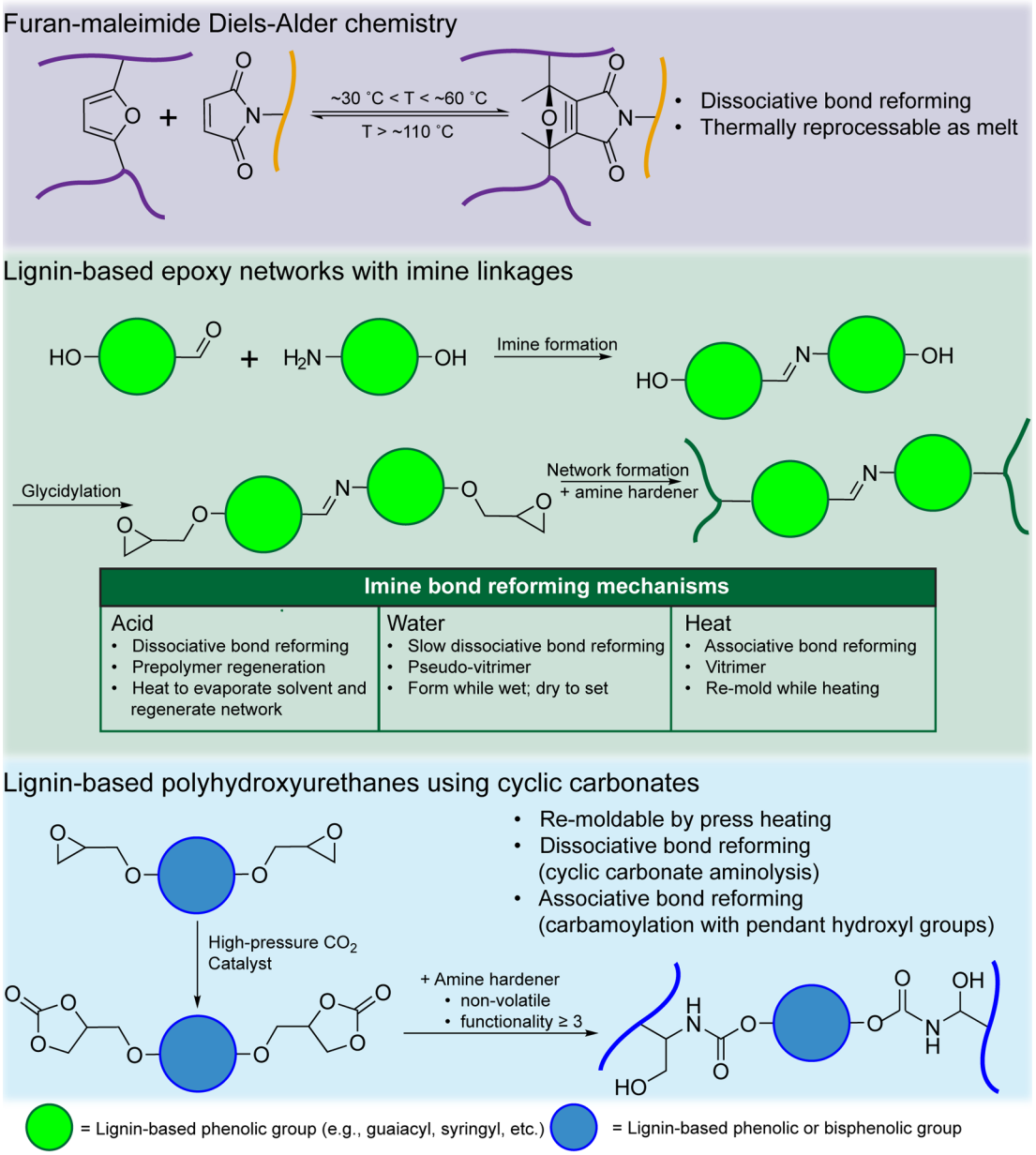

Figure 3. Strategies for the incorporation of recyclability into biobased thermoset networks. All strategies rely on bond-reforming mechanisms, which may be dissociative or associative.

materials, to provide enhanced sustainability while maintaining or improving material properties.

Furans are generated next in the acid-catalyzed conversion sequence of cellulosic biomass (see Figure 2) through continued dehydration of the monosaccharides,[31,32,37,48,49,51,58−61,63,97,98] and they are comparatively less oxygenated and less functionalized. As a result, furans are an intriguing starting point for the development of materials that act as improved analogues or substitutes for petroleum-based materials. For example, furfural can be subjected to reductive catalytic hydrogenation and hydrogenolysis to form 1,5-pentanediol (PDO), and PDO has general utility in step-growth polymers.[99,100] Additionally, polyesters based on furandicarboxylic acid (FDCA) have been proposed as potential replacements for petroleum-based polyesters derived from TPA,[15,86,88,98,101−103] and some FDCA-based polyesters have property profiles that rival or outperform TPA-based polyesters such as PET.[15,97,101−107] There are even examples of commercial FDCA-based polyesters;[101] for instance, Netherlands-based Avantium aims to scale up production of poly(ethylene furanoate) (PEF) to 5000 t/year by 2023.[108]

In addition to the increasing promise of furan-based materials that may function as analogues or substitutes for petroleum-based polymers, other interesting chemistries associated with furans may be exploited for new materials applications. For instance, epoxidized FDCA has been used to create high-modulus epoxy networks,[109−112] while Abu-Omar and co-workers employed lignin-derived catechols linked by furfural or 5-hydroxymethylfurfural (HMF) to create epoxy prepolymers that are structurally reminiscent of BPA.[113] Another route to new furan-based polymers relies on reversible Diels−Alder (DA) reactions between furan rings and maleimides, generating furan-maleimide adducts.[114−121] These DA adducts can be formed at modest temperatures

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ACS Macro Lett. 2020, 9, 476−493

and are thermally reversible upon heating (>∼110 °C).[114−119,122] Networks with furan-maleimide cross-links can have mechanical properties comparable to traditional thermoset materials, such as epoxies and unsaturated polyester networks.[123,124] Yet, the reversible cross-links can be leveraged for convenient processing, self-healing,[116−119,122] and recycling (similar to thermoplastics).[116−119] The production of reversible thermosets is a powerful tool to enhance the sustainability of polymer systems, and several reversible chemistries have been reported that are applicable to both cellulose- and lignin-based materials (see Figure 3). Continued focus on the integration of furanic units into diverse polymeric structures, especially chain-growth polymers, will lead to a greater understanding of the impact of furan incorporation on polymer properties and broaden the applicability of furanic platform compounds.

Levulinic acid (LevA) and γ-valerolactone (GVL) constitute the final monomer platform in the acid-catalyzed conversion of cellulosic biomass described in Figure 2. LevA and GVL are functionally simpler than the compound classes described earlier and, as a result, are precursors to monomers that are typically derived from petroleum.[62,125−131] LevA is generated through the continued acid-catalyzed transformation of furans, especially HMF,[48−50,59−61] and formation of GVL from LevA requires an additional reductive catalytic step typically accomplished with a supported ruthenium catalyst.[60,132−135] Several schemes have been developed that use LevA or GVL as starting materials for the synthesis of drop-in replacements to petrochemical monomers. For example, Bond et al. demonstrated that butenes can be generated from GVL in high yields (>90% of theoretical molar yield) through catalytic decarboxylation.[128,129] Butenes have drop-in potential in polyolefin process streams.[136−142] This GVL-to-butenes decarboxylation route also can be modified to produce adipic acid[62,125,131] and ε-caprolactam,[126,127,130,131] both of which are commercially relevant in the production of polyamides (e.g., nylon-6 and nylon-6,6, respectively). Finally, new materials derived from the LevA/GVL platform have been reported, including high-T_g (>200 °C) α-methylene-γ-valerolactone (MGVL)-based polymers[135] and related polyurethanes.[143,144]

The great strength of the acid-catalyzed conversion process of cellulosics lies in the ability to generate many interesting classes of compounds from a single process stream with reasonably straightforward chemistry. A variety of material properties are possible through these different platforms, and this diversity in available products aligns well with the idea of the biorefinery[5,6] because it provides improved flexibility to respond to economic changes and enables accessibility to more industries and markets. This strategy integrates nicely with lignin-associated RCF, as will be discussed below, to fully utilize every component of LCB.

Lignin. Lignin is the most abundant natural polymer, after cellulose, and is one of the only renewable sources of aromatic compounds.[145] Yet, unlike cellulose, it is an underutilized materials resource, as its valorization to chemicals and designer macromolecules is both technically and economically challenging. Lignin is isolated from raw biomass in industrial pulping processes (e.g., Kraft, organosolv, and soda pulping) at a rate of ∼70 million tons annually,[145] but only a small fraction of technical lignin finds use in value-added applications—upward of 98% is burned for energy.[145,146] The remaining 2% often is employed as a filler in tires, concrete, and asphalt,[147,148] with some specialized efforts focused on upgrading technical lignin to higher-value materials,[149−168] such as polymer composites,[149−154] epoxy resins,[153−158] and several other macromolecular systems.[150,154,159−166] Although it is possible to incorporate lignin into polymeric materials, dark colors, unpleasant odors, and limited functional handles hinder the use of lignin in high-performance materials applications.[146,149,154,169] Value-added products from lignin are necessary for a cost-competitive bioeconomy,[170] and in general, lignin depolymerization to small-molecule (non-macromolecular) compounds is a critical component of effective valorization.

Lignin depolymerization can be accomplished either pyrolytically,[171] enzymatically,[172,173] or catalytically,[26,174−178] and the products and efficiencies of these methods depend upon the structure of the initial biomass and the specific lignin breakdown process. The vast majority of lignin consists of three primary subunits (*p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)) linked together by several families of C−O and C−C bonds (β-O-4, 5−5, β-5, etc.).[26] The distributions of these subunits and linkages are a function of the type of biomass and processing history (i.e., virgin biomass or technical lignin). Hardwoods contain a mixture of G and S units with mostly β-O-4 linkages, softwoods contain mostly G units with fewer β-O-4 linkages than hardwoods, and grasses/herbaceous lignins consist of a mixture of H, G, and S units with more variable linkage structures.[25] In general, the C−O bonds are significantly weaker than the C−C bonds, and lignins with higher C−O bond content, particularly β-O-4 linkages, are more susceptible to selective depolymerization.[179,180] Thus, hardwoods and some grasses (e.g., miscanthus) are ideal LCB feedstocks as they can be broken down more efficiently than both softwoods and more recalcitrant varieties of herbaceous biomass.[181−183]

The primary differences between the three depolymerization strategies are complexity, energy intensity, yield, and product distribution. Depolymerization generally produces substituted aromatic compounds that correspond to the three lignin subunits—phenol, guaiacol (2-methoxyphenol), and syringol (2,6-dimethoxyphenol). As with intact lignin, the distribution of these product types and the specific substituent groups are influenced by the structure of the original feedstock and type of processing.[26] The typical depolymerization product mix includes the above-mentioned small-molecule families, oligomers, and some side products from cellulose/hemicellulose degradation (e.g., sugars).[26] Among the three depolymerization process classes, pyrolysis is the simplest and does not require solvent; however, pyrolysis is energy intensive as it typically requires high temperatures (>600 °C).[26,171,184] Additionally, pyrolysis produces complex mixtures at only moderate yields.[26,171,184] Thus, extensive separation schemes are necessary to obtain sufficiently pure chemicals that easily can be sold or further modified for enhanced valorization.[26] Enzymatic depolymerization, on the other hand, is a biological process that generates substituted phenolics under mild conditions, but it does require extensive pretreatment to produce low-molecular-weight, aqueous feed streams and to manage impurities like glucose and oligomers.[172,185] The purification of biological depolymerization products also is a major challenge.[172] The toxicity of aromatic products necessitates low concentrations, and product streams often are multiphase mixtures or emulsions.[172] Because of the above-mentioned considerations, catalytic depolymerization processes likely are the most scalable and

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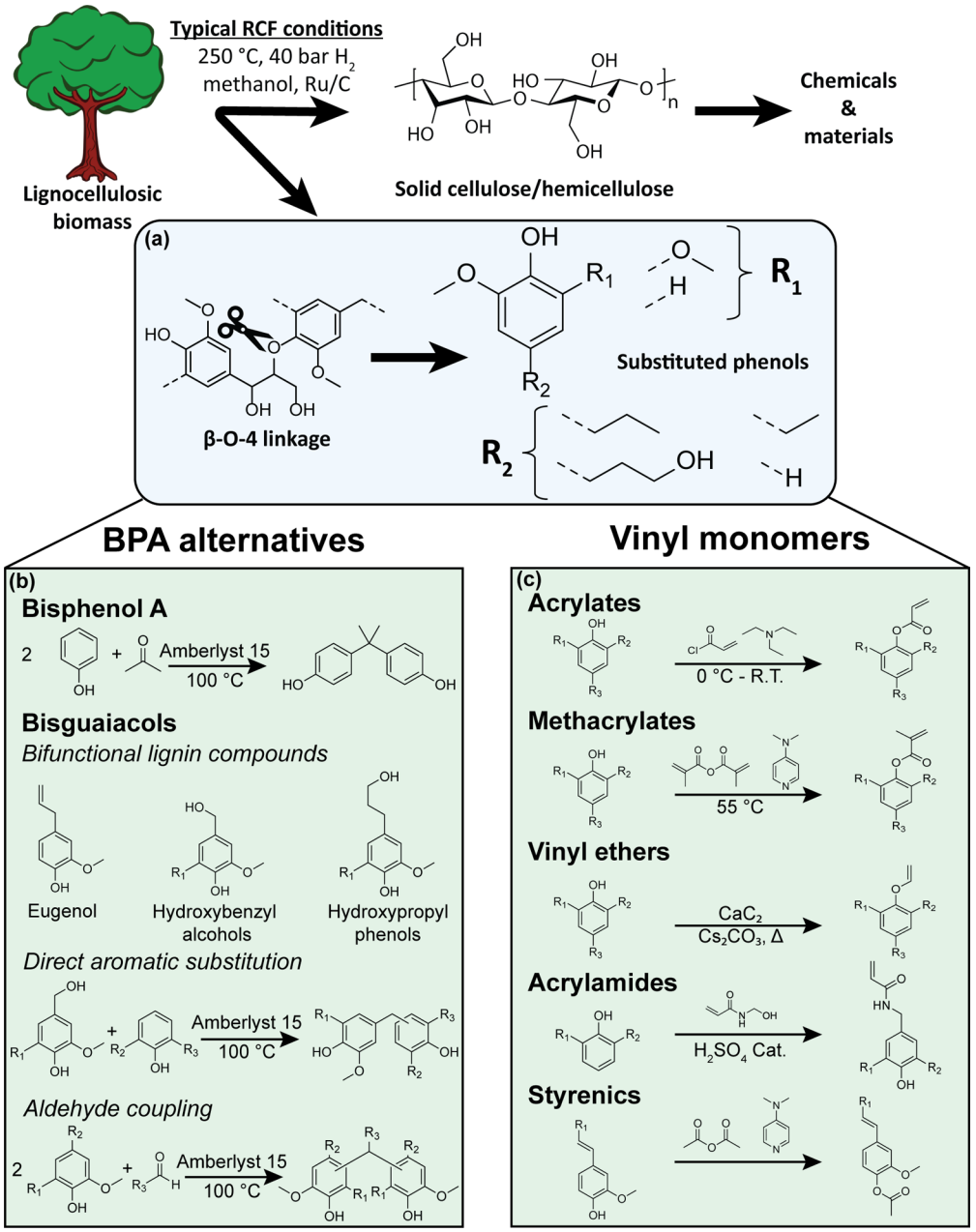

Figure 4. (a) RCF of LCB to solid cellulosics and substituted phenols. The R_1 and R_2 groups are influenced by the type of biomass and processing conditions. (b) BPA alternatives from lignin derivatives, including monoaromatics and coupled compounds. (c) Vinyl monomers from lignin derivatives and model compounds.

cost-effective due to narrow product distributions, relatively high yields, and modest energy requirements.[26,186] Several types of catalytic processes exist, but the focus of this section will be RCF.[26,186]

RCF, illustrated in Figure 4a, is an attractive process for the valorization of raw biomass in a biorefinery-compatible "lignin-first" approach.[26,174,186] In a typical RCF process, lignin is concurrently separated from cellulosics and depolymerized at moderate temperatures (~250 °C).[174,186−188] The catalyst stabilizes reactive intermediates to inhibit the recombination or condensation events that result in the formation of recalcitrant C−C linkages (i.e., oligomer formation).[175,186,189] Furthermore, the cellulosic pulp remains intact and can be further upgraded to chemicals and polymers as discussed above. The ability to selectively upgrade the entire biomass feedstock gives RCF a significant advantage over other processing techniques and improves the economics of biomass valorization.[186] Efforts to reduce catalyst costs are necessary, as RCF typically employs expensive metals like ruthenium or palladium. Robust, environmentally benign, and inexpensive catalysts, such as copper-based and other systems, could be evaluated as less costly alternatives.[178,187,190] Additionally, strategies to upgrade depolymerization products to valuable monomers and polymers, including BPA alternatives,[191−194] epoxy resins,[194−199] and performance-advantaged thermoplastics,[168,174,200−211] are necessary as will be discussed below.

BPA and its analogues are manufactured at a scale of ~7 million tons annually and are precursors to a wide variety of polymers.[212] Demand for BPA-based products is increasing, and BPA production is expected to reach 9.6 million tons in

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ACS Macro Lett. 2020, 9, 476−493

2020.[212] This classic bisphenol is formed via condensation of two phenols and acetone as shown in Figure 4b, and although BPA and other bisphenols are valuable constituents in polymer materials, they are petroleum derivatives and present significant concerns from a human and animal health standpoint.[3,213−219] BPA is a suspected endocrine disruptor, and exposure is associated with several poor health conditions, including cancer, obesity, and heart disease.[3,213−219] Because of these health concerns, the U.S. Food and Drug Administration banned the use of BPA in baby bottles in 2012,[193] and the European Commission placed restrictions on BPA in food contact materials in 2018.[220] Several compounds have been marketed as safe alternatives to BPA, but many exhibit some degree of endocrine disruption potential.[221] Thus, efforts to generate a suitable BPA replacement that reduces both environmental and health impacts are still necessary, particularly for food contact applications,[222] and recent work on model compounds and lignin derivatives has yielded promising results for safer, biobased BPA analogues.[191,192,194−199,223−226]

Lignin-derived BPA alternatives have been produced through a number of approaches, including direct modification of bifunctional compounds,[195,197] aromatic substitution,[194] aldehyde condensation,[113,191,192] and imination,[199] among others.[195,196,225,227−229] Several examples are shown in Figure 4b. The simplest BPA alternatives are bifunctional lignin molecules that can be used directly (i.e., without coupling).[176,177] Vanillyl alcohol and eugenol have been modified and incorporated in epoxy[197] and diacrylate resins;[225] however, the thermal and mechanical properties, namely, T_gs and Young's moduli, of the resulting polymer networks were lacking. These compounds only contain a single aromatic ring per molecular unit, whereas the more rigid BPA analogues (described below) have two in close proximity. BPA alternatives in which lignin "single-aromatic" molecules are coupled often result in improved thermomechanical properties and offer numerous options to fine-tune structure/function through linker and precursor choice. For example, the direct condensation of substituted hydroxybenzyl alcohols and substituted phenols yielded several bisguaiacols (BGs) with varying *o*-methoxy contents (Figure 4b).[194] Additionally, formaldehyde,[191,192,198] vanillin,[230] furfural,[113] and HMF[113] have been used to couple lignin-based substituted phenols via condensation reactions, and eugenols have been coupled by thiol−ene click chemistry,[225] etherification,[196] and isomerizing metathesis.[229] Lignin-based benzoxazines,[227] imines,[199] and cyclic carbonates[228] also have been reported. These compounds have been used as building blocks for several types of macromolecules, including epoxy resins,[113,154,194−198,226,230] polycarbonates,[192,205,229] polyesters,[105,168,191,204,231,232] polyacrylates,[225] polybenzoxazines,[227] polyhydroxyurethanes,[228] and others.[159,204] The thermal and mechanical properties of the synthesized polymers varied widely, and several of the reported materials were recyclable/reprocessable thermosets—imine-based epoxy resins were easily recycled in the presence of water,[199] polyhydroxyurethanes were catalytically reprocessable,[233] and succinic anhydride-linked epoxy vitrimers were thermally recyclable.[196] The above-mentioned reversible chemistries can enhance sustainability because they impart greater recyclability to materials, and they can generate more durable, self-healing polymers and minimize waste generation by improving product longevity.[234] Additionally, as alluded to above, health considerations are important, and the BGs produced by direct substitution and the coupled eugenols prepared by isomerizing metathesis have been evaluated for estrogenic activity and demonstrate potential as safer alternatives to BPA and its analogues.[223,229] As one example, mixtures of bisguaiacol F isomers exhibited significantly lower estrogenic activity than either BPA or an estradiol control in both cell proliferation and gene expression assays,[223] and the eugenol derivatives showed no activity in yeast estrogen screens.[229]

Biobased BPA alternatives that ameliorate waste management and safety concerns will enable the development of more versatile, durable, and sustainable macromolecules, but next-generation BPA alternatives also need to perform at least as well as BPA in materials applications. The development of structure−property relationships will provide key insights to aid in the design of compounds with advantageous properties. Future work is needed to improve the thermal and mechanical properties of materials prepared from biobased BPA alternatives by evaluating different bridging structures between biobased aromatic units. As an example, the production of more benign BPA alternatives from lignin-derived phenols and biobased acetone would improve renewability and offer performance benefits over the reported BPA alternatives with methylene bridging structures.[194] Macromolecular thermal and mechanical properties typically improve when substituting BPA for bisphenol F because of the additional steric hindrance in the bridging structure, and this trend is expected to apply to biobased BPA alternatives as well.[194] Additionally, efforts to screen a wider variety of BPA surrogates for endocrine disruption potential would elucidate structure−activity relationships and enable the design of substitutes with reduced negative-health implications. Finally, the implementation of reversible chemistries will improve the longevity of biobased materials and enable facile recycling/reprocessing of thermosetting polymers, but these new functionalities cannot significantly reduce overall material properties/performance. With some development, materials derived from biobased BPA alternatives could outperform incumbents from the beginning to the end of the polymer lifecycle.

Lignin-based phenolics also have been functionalized to generate monomer classes that can be polymerized by several additional methods, including atom transfer radical polymerization (ATRP),[235] along with bulk and solution free radical, reversible addition−fragmentation chain-transfer (RAFT),[236] ionic,[237,238] and other polymerization techniques.[239−241] Controlled/living polymerizations (e.g., ATRP, ionic polymerization, etc.) are attractive because these methods enable the precise manipulation of macromolecular architecture, composition, and molecular weight; however, many chain growth approaches tend to be rather sensitive to oxygen and other impurities.[242] Thus, polymerization strategies that are tolerant to impurities found in biomass streams must be applied to biobased materials. RAFT polymerization is particularly promising, in the chain-growth arena, for the polymerization of complex biobased mixtures,[236,243] and it has been applied to a number of model and real biomass systems to generate biobased or bioderivable polymers and explore their resultant properties.[200−202,207−211]

Lignin-derived compounds can be functionalized for addition polymerization at the phenolic hydroxyl groups, or in some cases, the existing functionality can be used for polymerization. Several monomers for addition polymerization are shown in Figure 4c. The most widely studied monomers

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ACS Macro Lett. 2020, 9, 476−493

are based on methacrylates[200,201,207,208,244] and acrylates,[174,225] prepared through acylation of the −OH groups, and phenolic cinnamics[211] and styrenics[209,210] that make use of conjugated (i.e., polymerizable) double bonds, typically para to the hydroxyl group. Other functionalization strategies have been reported, such as acrylamides prepared by a Friedel−Crafts alkylation of guaiacol with *N*-hydroxymethylacrylamide.[245] A broad range of properties are accessible by polymerizing these diverse monomers. For example, a library of methacrylate monomers was developed from lignin model compounds (e.g., guaiacol, vanillin, syringol, syringaldehyde) and mixtures thereof.[200−202,207,208] The compounds were functionalized via reaction of the phenolic hydroxyl groups with methacrylic anhydride in the presence of 4-dimethylaminopyridine.[207,208] RAFT polymerizations were carried out in all cases, and interestingly, the reaction kinetics were not significantly impacted by monomer structure or *o*-methoxy content.[207] The T_gs of the homopolymers ranged from ∼116 °C for monomethoxy-based poly(4-ethylguaiacyl methacrylate)[200] to ∼205 °C for dimethoxy-based poly(syringyl methacrylate).[201] Structure−property relationships were developed for model systems and showed that *o*-methoxy content drives the enhanced thermal, mechanical, surface, and tribological properties (e.g., friction and adhesion).[200,202] A range of styrenic monomers, such as substituted vinylphenols and cinnamic compounds, also have been studied in model systems.[209−211] Vinylphenols are a particularly interesting class of compounds, and polymers with unprotected phenolic hydroxyl groups display promising antibacterial properties in guaiacol-based polyacrylamides.[245] Polymerizing monomers with free phenolic hydroxyl groups is difficult, however, as these functional groups are considered inhibitory in typical chain-growth polymerization approaches and often facilitate branching.[203,245] Thus, protection of phenolic −OH groups is necessary for well-controlled polymerizations, and biobased vinylphenols have been protected with easily reversible chemistries such as acetylation.[209−211] Protected vinylguaiacol and vinylcatechol were studied when made into homopolymers via RAFT polymerization,[210] but for bulky monomers like isoeugenol acetate and cinnamic monomers, homopolymerization was not possible.[209,211] In these cases, nearly alternating copolymers with common comonomers (e.g., acrylates, styrene) were produced,[209,211] with T_gs above 100 °C for the cinnamic and vinylphenol versions of the polymers.[209,210] The hydroxyl protection/deprotection scheme also did not harm the terminal chain transfer agents in polyvinylcatechol, and block polymers with common acrylic monomers and styrene were readily generated by chain extension.[210] These model systems demonstrate the broad range of accessible properties from lignin-based polymers, including high T_gs, antibacterial properties, and block polymerizability, and they also suggest strategies to mitigate the challenges with biobased monomers, such as using robust polymerization techniques, polymerizing mixtures, protecting reactive groups, and copolymerizing bulky monomers.

Other recent efforts have been directed at using monomers and monomer mixtures from real biomass, but lignin-based mixtures, particularly pyrolysis oils, typically have multiple functional handles that can lead to cross-linked polymers. Qu et al. overcame this limitation through the partial functionalization of pyrolysis oil feedstocks to methacrylates, which allowed them to control the degree of cross-linking and produce either thermoset or thermoplastic materials.[203] RAFT polymerization was used in this case because it is relatively tolerant to unprotected functional groups in bio oil (e.g., carboxylic acids, hydroxyl groups).[236,243] As in other cases, protection of the residual hydroxyl groups via acetylation was necessary for well-controlled polymerizations,[210,211,245] and after residual −OH groups were acetylated, well-controlled RAFT polymerizations (i.e., low dispersity) were possible.[203] This effort extended the learnings from model systems to generate well-defined polymers from real biomass and demonstrated that complex and costly separation schemes are not necessary to make biobased performance materials.

Lignin derivatives are particularly well-suited as the high-T_g constituents in nanostructured block polymers, and potential applications include rubbers, PSAs, and coatings. Substituting higher-T_g biobased blocks for common petroleum-based blocks, such as polystyrene and poly(methyl methacrylate), can generate performance-advantaged materials that maintain their mechanical properties at elevated temperatures; however, the ability to produce nanostructured block polymers from lignin-derivable monomers previously was uncertain. Relatively low Flory−Huggins interaction parameters (χ-parameters) were expected between proposed biobased blocks (e.g., vanillin methacrylate and lauryl methacrylate) on the basis of the similarity in oxygen content, relative to a more conventional case such as styrene and lauryl methacrylate. Several block polymers that exhibit microphase separation have been prepared using lignin model compounds. For instance, poly(vanillyl methacrylate)-*b*-poly(lauryl methacrylate) was prepared by RAFT polymerization and formed a microphase-separated, spherical morphology.[244] Vinylcatechol was block polymerized with various acrylates, methyl methacrylate, or styrene, and some of the resulting block polymers exhibited two distinct T_gs, indicative of phase separation.[210] These studies with model compounds demonstrate that lignin-derivable monomers have potential for block polymer applications. As one example, Wang et al. synthesized an ABA triblock polymer PSA from real biomass via RCF of poplar wood followed by product extraction, acrylation, and block polymerization.[174] The glassy end-blocks of the polymer were a mixture of 4-propylsyringyl acrylate and 4-propylguaiacyl acrylate monomer segments, and the rubbery block was composed of *n*-butyl acrylate, a potential derivative of biobased butanol.[174] This lignin-derived copolymer bore resemblance to a triblock polymer PSA that consisted of an *n*-butyl acrylate midblock and acetylated acrylic isosorbide end blocks produced from commercially sourced isosorbide.[92] In both PSA systems the adhesive behavior was competitive with several commercial tapes and was performance advantaged in that no additives (e.g., tackifiers) were required for desirable properties in standardized loop tack, peel, and shear tests.[92,174] These PSAs are only one example of performance-advantaged biobased materials, but the broadly tunable thermal and mechanical properties present an exciting opportunity for tailor-made polymers for numerous applications.

Future Opportunities. There are numerous future opportunities and challenges associated with fundamental research and commercial advancement toward LCB valorization. An overview of several such examples is provided below.

The development of feedstock-dependent process models for LCB valorization in addition to robust, translatable structure−property relationships will enable the prediction of material properties linked directly to the original biomass

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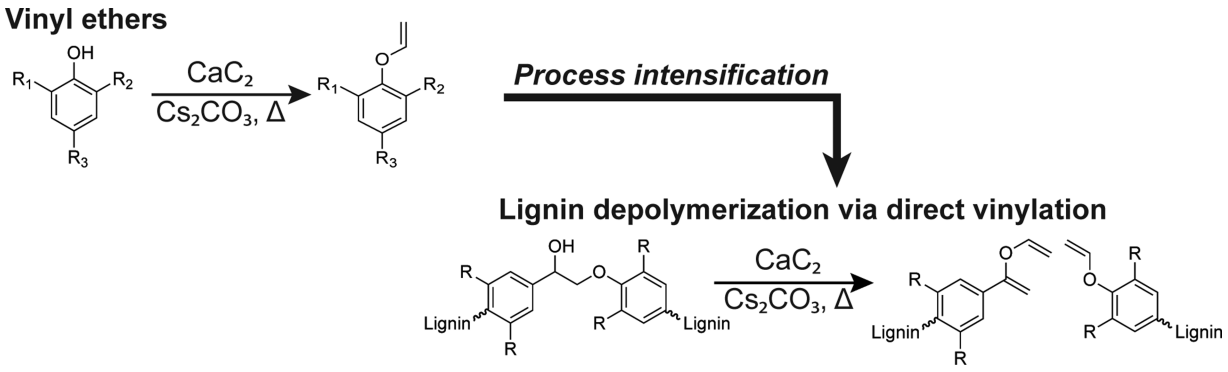

Figure 5. Direct vinylation of substituted phenols and process intensification to couple lignin depolymerization and monomer synthesis.

source. Studies in that direction have been reported by Broadbelt and co-workers, who used lignin structural information and a kinetic Monte Carlo framework to predict pyrolysis product compositions.[246,247] The calculated product distributions were in good agreement with experimental data, and the overall effort represents a significant step forward in the development of accurate lignin libraries for the optimization of depolymerization conditions.[246] The efforts also investigated the modeling of fast pyrolysis kinetics, which enabled the prediction of low molecular weight and macromolecular products,[247] along with polymer outputs following radical polymerization.[248,249] These predictive capabilities can be merged with structure−property relationships for biobased polymers to predict final materials properties drawn from the biomass feedstock and processing method. For example, the process-related predictions can be combined with the relevant macromolecular information, such as relationships uncovered by Holmberg et al. for a library of lignin model compounds.[200] The model studies can be expanded to include other common depolymerization products, such as *n*-propyl-substituted phenolics and vinylphenols/styrenics. Future experiments could be conducted to encompass a wider variety of biomass sources and depolymerization techniques, including reductive catalytic depolymerization, to gain greater insight into the complex chemical processes and to facilitate improved prediction and control of product distributions. Structure−property relationships should be expanded in conjunction with these computational processing efforts to then predict the thermal, mechanical, chemical, and tribological properties of polymers with only the composition and structure of the biomass feedstock as the major variables.

Dovetailing with the above efforts, biomass processing is inherently complex, and several aspects of current strategies are ripe for improvement. For example, more effective catalyst systems are needed to increase product selectivity and overall yields. In addition to the less expensive systems mentioned above,[178,187,190] novel processing approaches like microwave and plasma depolymerization should be explored for LCB valorization. Furthermore, small-molecule additives should be studied as promoters and homogeneous co-catalysts—formaldehyde is known to stabilize reactive intermediates in lignin depolymerization to improve product yields.[250] These strategies have the potential to simplify separations and minimize waste, impacting process economics beyond direct catalyst costs. The optimization of biomass fractionation/depolymerization processes for different feedstocks, including technical lignins and biomass mixtures, would increase the versatility of depolymerization strategies.

Process intensification is another promising strategy to improve LCB valorization. One pathway to lignin-based monomers is direct vinylation using calcium carbide, and lignin model compounds have been used to synthesize various vinyl ether monomers via direct vinylation at near-quantitative yields.[251] Vinylation with calcium carbide breaks β-O-4 linkages in model lignin systems—the same linkage targeted in reductive catalytic processes.[26,251] If this approach is successful in real biomass systems, a process intensification scheme in which lignin depolymerization is coupled with vinyl ether monomer synthesis could be possible as shown in Figure 5. To the authors' knowledge, no polymers have been prepared from lignin-based vinyl ethers (including model compounds), and future work should explore other process intensification schemes and the utility of the resulting compounds for polymer synthesis.

New biobased materials also should be designed with overall lifecycle sustainability as a priority. This holistic approach includes sustainable chemistries for monomer functionalization, novel end-of-life waste management strategies, and improved recycling strategies for existing "nondegradable" or "nonreprocessable" polymers. Renewable materials, such as those derived from lignin or cellulose, do not address entirely the sustainability issues in the overall product lifecycle[8,252,253] because the functionalization strategies mentioned above yield undesirable byproducts and employ petroleum-based, hazardous, and expensive chemicals such as acyl chlorides and epichlorohydrin. Significant effort should be undertaken to eliminate unsustainable functionalization routes in favor of entirely biobased schemes that minimize the environmental impacts and hazard profiles of biomass valorization. Materials that are designed for facile recycling, such as those depicted in Figure 3, are valuable for end-of-life waste management. This approach is particularly valuable for thermosets as current recycling methods are generally ineffective for cross-linked polymers. For materials that cannot be designed with reversible or easily degradable chemistries, new recycling strategies are needed. Existing mechanical methods (e.g., re-extrusion, shredding, etc.) typically degrade polymer chains and require blending with fresh material to maintain thermal and mechanical properties,[254] and chemical methods, such as PET depolymerization via hydrolysis, generate high-quality monomers but generally are polymer-specific.[254] Next-generation recycling strategies that do not sacrifice material properties, and are not limited to certain polymers, include biodegradation[255] and catalytic or biological depolymerization.[12,254] Biodegradation is attractive because it can be carried out under mild conditions and usually is environmentally

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ACS Macro Lett. 2020, 9, 476−493

benign, but biodegradable materials must be designed to withstand normal use cycles without premature degradation.[255] Additionally, it is somewhat challenging to recover monomers directly from traditional biodegradation approaches. Biological and catalytic depolymerization processes can play a role here as depolymerized monomers can be recovered and then repolymerized to generate virgin polymers. This approach can reduce the demand for new monomer production and lower the environmental impact of both petroleum- and bioderived materials; however, reported catalysts are neither efficient nor selective enough for effective implementation.[12,254,256−258] The knowledge gained from the depolymerization schemes for lignin and cellulose can be applied to design catalysts and find enzymes that selectively degrade both conventional and biobased materials. The evaluation of polymers on a cradle-to-grave basis will build a more thorough understanding of sustainability and is an enormous opportunity for future research.

CONCLUSION

Over the past 100 years, polymer science has enabled many of the materials that are key to modern life, but now, sustainable alternatives to conventional polymers are needed to mitigate environmental damage and reliance on petroleum resources. In this pursuit, LCB is a promising feedstock, especially as approaches to fractionation and depolymerization of LCB into useful monomers with rich chemical functionalities continue to improve in selectivity and efficiency. Efforts to integrate RCF and acid-catalyzed cellulose depolymerization will enable the effective valorization of the entirety of LCB feedstocks and potentially bring a sustainable bioeconomy to fruition. Polymers derived from LCB depolymerization products are environmentally benign, and the high degree of chemical functionality of the constituent building blocks can be leveraged for more versatile and performance-advantaged materials. These benefits can range from facile recycling through selective degradation to particularly high T_gs and potentially less hazardous compounds. When juxtaposed with traditional, petroleum-based materials, which are typically persistent and potentially toxic, the sustainability benefits of LCB-based materials become evident. Clearly, there is an enormous opportunity for the adoption of biobased polymers, and a holistic, integrated approach to addressing the challenges in biomass processing, monomer preparation, and lifecycle management will ensure a bright future for sustainable materials.

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Notes

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ABBREVIATIONS

ATRP: Atom transfer radical polymerization; BPA: Bisphenol A; BG: Bisguaiacol; DA: Diels−Alder; FDCA: Furandicarboxylic acid; G: Guaiacyl unit; GVL: γ-valerolactone; H: *p*-hydroxyphenyl unit; HMF: 5-hydroxymethylfurfural; LCB: Lignocellulosic biomass; LevA: Levulinic acid; MGVL: α-methylene-γ-valerolactone; PDO: 1,5-pentanediol; PE: Polyethylene; PEF: Poly(ethylene furanoate); PET: Poly(ethylene terephthalate); PLA: Poly(lactic acid); RAFT: Reversible addition−fragmentation chain-transfer; RCF: Reductive catalytic fractionation; S: Syringyl unit; T_g: Glass transition temperature; TPA: Terephthalic acid

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