



# Sustainable polymers from biomass: Bridging chemistry with materials and processing



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## ABSTRACT

Renewable natural resources, such as plant oils, fatty acids, cellulose, and lignin, have been widely pursued as precursors for manufacturing sustainable polymers. There are many challenges in the production of biobased plastics. This Trend article provides a succinct overview of three major areas: lignin chemistry and polymers, biobased polyolefins, and long-chain aliphatic polycondensates. The emphasis is placed on how chemistries of monomers and polymers improve materials properties in conjunction with processing methods. Each section concludes with challenges and prospects toward better sustainable polymers.

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**Abbreviations:** AIE, aggregation-induced emission; ATRP, atom transfer radical polymerization; ACC, 1-aminocyclopropane-1-carboxylic acid; ADMET, acyclic diene metathesis polymerization; DMTO, dimethyl ether to olefins; EFE, ethylene-forming enzyme; FCC, fluid-catalytic cracking; FDM, fused deposition modeling; MEP, 5-methyl erythritol phosphate; MTO, methanol to olefins; MTP, methanol to propylene; MVA, mevalonate; PA 6, nylon 6; PA 11, nylon 11; PA 12, nylon 12; PA 15, nylon 15; PA 16, nylon 16; PA 66, nylon 6,6; PA 410, nylon 4,10; PA 610, nylon 6,10; PA 1010, nylon 10,10; PA 1012, nylon 10,12; RAFT, reversible addition fragmentation chain transfer polymerization; ROP, ring-opening polymerization; SAM, S-adenosyl-methionine; SLS, selective laser sintering;  $\Phi$ , dispersity;  $T_g$ , glass transition temperature.

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## 1. Introduction

The global demand on energy, chemicals, and materials continues to increase as the world population expands. Most chemicals and polymers are derived from fossil resources. Currently, there are about 8 % of the total fossil oils used to manufacture polymers. It is predicted that this number could increase to 20 % by 2050 [1–4]. With the increasing concern on undesirable environmental and socioeconomic consequences of petrochemicals and limited fossil resources, there is a significant interest in using natural biomass as raw resources for chemical, polymer, and material development [5–9]. Moreover, many sustainable polymeric materials possess commendable biocompatibility, which could bring additional benefits for expanded applications [10].

With the advent of the 100th anniversary “Macromolecular hypothesis” that was conjectured by Staudinger [11], who could have imaged the extraordinary impact of polymers on humankind. Polymers have tremendously transformed almost every aspect of our daily life. While polymers have brought enormous benefits and convenience to the society, they inadvertently have some undesirable consequences on environments and climate change, for which the scientific communities did not intend from the very beginning. This Trend article aims to delineate some possible solutions to mitigate the negative influence and to promote a more sustainable development.

Sustainable polymers are classified into two major categories: natural polymers and synthetic biobased polymers. Natural polymers, such as cellulose, lignin, hemicellulose, starch, protein, and modified biopolymers, have been widely consumed for the preparation of bioplastics and composites, and for other applications [12]. Synthetic biobased polymers can be derived from a variety of molecular biomass such as plant oils, fatty acids, furan, terpenes, rosin acids, and amino acids [13–15]. It is worth noting that sustainable polymers are not necessarily biodegradable. On the contrary, most of them do not biodegrade. The use of sustainable polymers can avoid the dependence on petroleum resources and reduce carbon emissions [16–19].

Different from carbon-carbon and carbon-hydrogen bond-based petrochemical feedstocks, a variety of natural biomass possess chemical structures such as carbon-oxygen bonds that are not economical to produce from fossil feedstocks. These unique structures could be used as new platforms to design functional and readily compostable polymers bearing new and improved properties. However, there are many hurdles, including cost, environmental impact, and thermomechanical performance, to be overcome before sustainable polymers will have more substantial economic impact.

Significant progress has been made in the area of sustainable chemistry to transform biomass into polymers. Molecular biomass can be well utilized toward biobased polymers in a way similar to the highly successful molecular engineering of petrochemicals. However, a key challenge is the realization of materials with comparable or even improved properties in terms of sustainability and economics. Processing, often neglected by chemists, can actually play an important role to significantly enhance material properties.

In this Trend article, we highlight three areas that are critical for sustainability (Fig. 1): (1) **Lignin**. It is not only the second most abundant biomass but also among the most challenging due to its complexity. There are tremendous potentials and gains to transform lignin into polymers. (2) **Biobased polyolefins**. Given the gigantic volume of polyolefins in the market, it is a necessity to explore various means to prepare biomass-derived polyolefins. (3) **Long-chain aliphatic polycondensates**. This is an emerging class of polymers that could combine the benefits of polyolefins and condensation polymers. We will emphasize how to bridge chemical designs with materials based on their functions and properties. In

addition, a largely neglected area is how the processing methods can enhance the properties of sustainable polymers, which will be also discussed. There are many other classes of biomass such as terpenes, CO<sub>2</sub>, and furfural that are also widely pursued as precursors for manufacturing sustainable polymers. However, it is not the intention of this Trend to provide an exhaustive review on the various forms of biomass. Readers interested in this aspect should refer to a few recent reviews [1,9,10,13,14,20].

## 2. Lignin

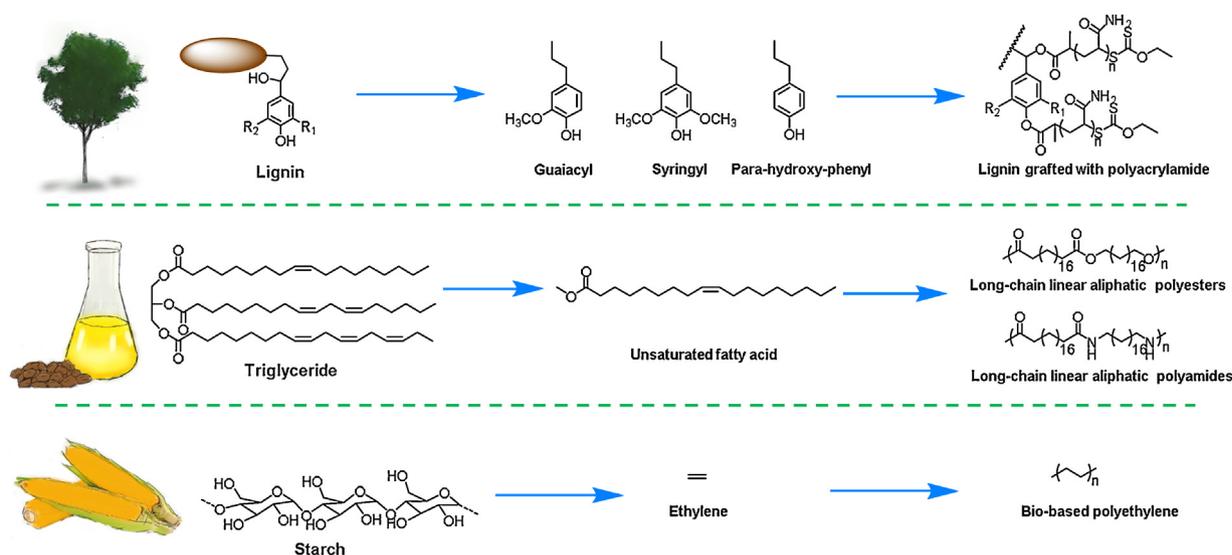
Lignin, a component of the lignocellulosic biomass only second to cellulose in natural abundance, has high prospects as a greener, non-food alternative to petroleum sources. Lignin serves as a three-dimensional polymeric networking agent providing structural support to cell walls. It is estimated that over 300 billion tons of lignin is present in the biosphere and about 20 billion tons annually biosynthesized throughout the world [21]. Although lignin is a recalcitrant substrate, certain microorganisms such as white-rot fungi can degrade lignin, facilitating the formation of soil organic matter, thus making lignin a biodegradable natural polymer [22]. Currently, lignin is under-utilized for chemical and material development, mostly (~98 %) burnt as fuel. Some of its macromolecular applications include agricultural and dye dispersants, emulsifiers, cement additives, pelleting aids, battery expanders, binders, chelants, etc. (Fig. 2) [23].

Commercial lignin-based thermoplastics, thermosets, and composite polymeric products are almost negligible in volume, though significant research efforts have been reported [24–27]. It is worth exploring two major directions, which are, however, ill-pursued in many scenarios: (1) lignin as a whole: the challenge is either inferior performance of products or low volume use of lignin; (2) defragmented lignin as monomers: the challenge is either too costly to make selected functional molecules or the use of model compounds that is far from the reality of lignin.

### 2.1. Fractionation and depolymerization processes of lignin

The transformation of lignin into value-added chemicals and materials involves many processes such as lignocellulose fractionation, lignin depolymerization, and chemical upgrading [23]. Industrial lignin production via biomass fractionation is traditionally carried out in paper pulping mills, generating over 50 million metric tons of lignin per year. During the paper-pulping process, lignin is dissolved in alkaline media under high temperature and high pressure. According to production methods, lignin can be classified as kraft lignin, lignosulfonates, soda lignin, organosolv lignin, and others. Only about 2 % of isolated lignin is used for chemicals, and the rest is used as fuel in pulp mill recovery boilers in order to recover pulping chemicals and provide energy. However, the paper-pulping industry is shifting toward integrated lignin recovery systems to harness the chemical value of lignin and lignosulfonates rather than burning as low margin fuel. Novel extraction routes including lignin-first method and biorefinery concepts are gaining ground [28]. Especially, large quantities of (non-sulfonated) lignin could be generated from ethanol biorefineries [29].

Special focus is given to the depolymerization of industrial lignin into small molecules via various routes including reductive, oxidative, base- and acid-catalyzed, solvolytic, and thermal pathways [23]. However, it is not an easy task to increase monomer yields from lignin depolymerization. Further technological development is needed toward lignin-derived value-added products such as carbon fibers, activated carbons, engineering plastics, thermoplastic elastomers, polymeric foams and composites, chemicals such as vanillin, and high-value aromatic compounds.



**Fig. 1.** Sustainable polymers from renewable resources: (1) lignin, its basic structural units, and chemistry; (2) triglycerides, fatty derivatives, and polymers; (3) polysaccharides, conversion into olefins and polyolefins.



**Fig. 2.** Lignin-based materials in the current market and for future applications.

## 2.2. Structure and properties

Lignin is a highly oxygenated complex amorphous polymer having both aliphatic and aromatic units. It is formed through biochemical processes that involve radical crosslinking polymerization of *p*-coumaryl, coniferyl or sinapyl alcohols (Fig. 3). Various types of covalent bonds such as  $\beta$ -O-4 linkages keep the integrity of the network structure. During the paper pulping processes, the alkyl-aryl ether linkages are broken, resulting in lower molecular weight fragments with phenolic structures as well as new C-C bonded units. Preventing structural alteration/degradation of lignin during fractionation from lignocellulosic biomass is a key challenge.

Depending on the isolation methods, lignin has a molecular weight in the range of 500–50,000 g/mol, a dispersity of  $D = 2$ –8, glass transition temperature in the range of  $T_g = 90$ –170 °C [24,30,31]. Lignin belongs to the class of semi-polar polymers and has a glassy structure at room temperature. It softens above its  $T_g$  and further heating (>250 °C) results in self-condensation, decomposition, and produces charcoal, tar, and small molecular fragments. Functional groups such as carboxylic acids, phenolic and aliphatic alcohols, carbonyls, and aromatic units make lignin suitable as a substrate of many chemical modifications.

## 2.3. Polymer-based lignin composites

Lignin has useful properties such as antioxidant, UV protector, and reinforcing support. Therefore, many approaches have been developed to make polymeric materials containing lignin. There are three major routes to produce lignin-based polymers (Fig. 4). **The first route** is to use lignin as a biopolymer component in thermoplastic polymer blends. Blending with off-the-shelf polymers where lignin is used as a “drop-in” material has considerable potential to increase the content of renewable resources in an economically favorable way. Lignin-polymer blends are described in a few recent reviews [31,32]. The incompatibility of lignin with many synthetic and biobased polymers makes it challenging to produce blends/composites with enhanced properties. In addition, the high  $T_g$  and the self-condensing propensity of lignin at high temperature complicate the development of polymer blends. The polarity of lignin results in strong self-interactions and hinders miscibility with non-polar polymers [32]. Lignin blends with polyolefins, vinyl polymers, polyesters, polyurethanes, and natural and synthetic rubbers have attracted the most attention [33]. Lignin-polymer blends are produced mostly via melt-mixing processes at high temperature and mechanical blending followed by thermal extrusion. Depending on the compatibility between lignin

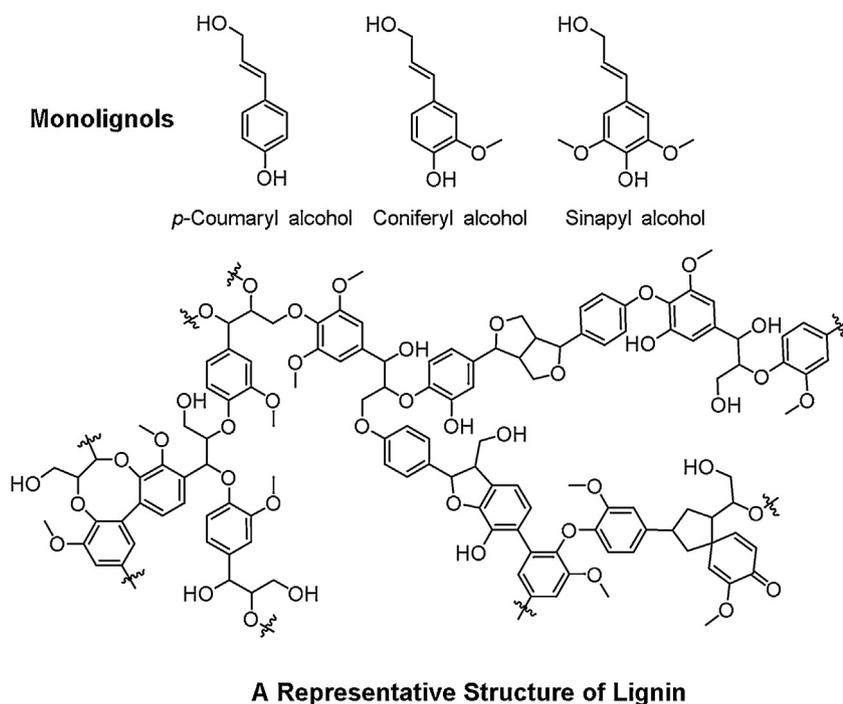


Fig. 3. Monomeric units and a representative structure of lignin.

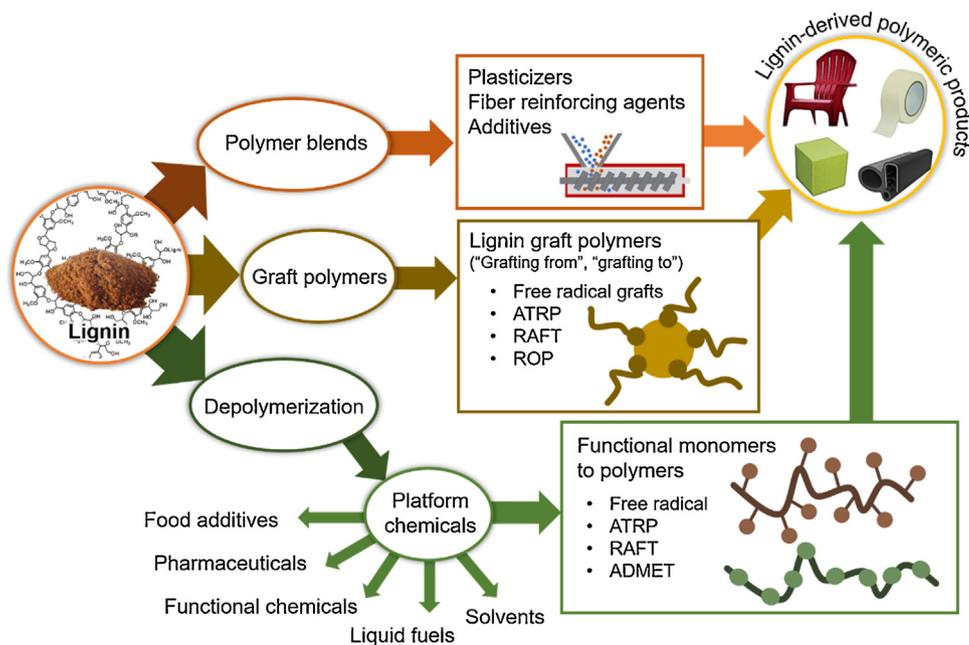


Fig. 4. Strategies for lignin upgrading into value-added polymeric materials.

and the polymer matrix, miscible blends or phase-separated systems are observed. For example, poly(ethylene oxide) (PEO) blend of lignin is miscible while polypropylene blend shows immiscibility [25]. More compatible polymeric blends are reinforced by lignin via lignin-polymer and lignin-lignin interactions. Plasticization, chemical modification, and coupling can be used to control such interactions [32]. Arboform, a commercially produced melt-processable thermoplastic material, consists of lignin, cellulose, plasticizers, and other additives [34]. A new class of renewable thermoplastic elastomers was reported from nanoscale-dispersed lignin in nitrile rubber via a high shear melt-phase preparation route. These products had high yield stress (15–45 MPa), strain

hardening properties, and outstanding recyclability [35]. Recently, melt-stable hardwood lignin composites with 3D printability were developed through incorporating lignin, conventional low-melting nylon, and carbon fiber [36].

As **the second route**, chemical modifications and graft polymers of lignin are of great interest to improve the interfacial properties of lignin for better compatibilization with synthetic polymers. Although grafting polymers from lignin have a long history [37], the lack of molecular control made little to no progress. Recent advances in controlled polymerization methods, such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and

ring-opening polymerization (ROP), facilitate the synthesis of lignin-based graft polymers with predictable properties [12]. Lignin graft polymers can be developed via “grafting from” or “grafting to” methods. We and others recently reviewed controlled polymerization methods-based lignin graft polymer research [24,38]. Tang et al. used “grafting from” ATRP to produce rosin polymer-grafted lignin hydrophobic polymer composites with  $T_g$  ranging from 20 °C to 100 °C [39]. Furthermore, they developed lignin-based multi-arm star thermoplastic elastomers with UV absorbing and improved mechanical properties [40]. A ‘one-component’ route based on ATRP towards thermoplastic lignin composites was reported by Washburn and coworkers [41]. The grafted nanocomposites have toughness greater than lignin/polymer blends. Polymer grafted lignin fillers have extraordinary toughening and strengthening effects in polymer nanocomposites [42]. Wang et al. developed lignin-graft-poly(methyl methacrylate) via ARGET ATRP [43]. Venditti et al. reported UV curable lignin thermoplastic copolymers [44]. In addition, ATRP-based responsive materials [45–47], self-healing hydrogels [48], UV protectants [49], RAFT-based superplasticizers [50], surfactants [51], flocculants [52], and biocomposites [53] have been reported. The presence of hydroxyl groups enables the ROP of various cyclic monomers including caprolactone [54], lactide [55],  $\beta$ -butyrolactone [56], and ethylene oxide [57] for applications as lignin composites, biomaterials, coatings, surfactants, etc. Tang et al. utilized azide-alkyne cycloaddition coupling chemistries to grafting polymers onto lignin and produce various copolymers [58,59].

**The third route** is to depolymerize lignin into platform chemicals, which can be converted into monomers and then polymers. There are many recent reports on the use of lignin model compounds such as vanillin, guaiacol, and eugenol to prepare various polymers by polymerization techniques. Epps et al. conducted several investigations on lignin polymers based on RAFT [60–62]. They recently developed lignin-derived RAFT polymers by direct biomass depolymerization and functionalization with minimal purification steps [63]. Acyclic diene metathesis (ADMET) polymerization is also utilized to generate polymers using lignin-derived monomers [64,65]. Du Prez et al. conducted ADMET polymerization of lignin-inspired phenolic  $\alpha,\omega$ -dienes followed by post-modification and crosslinking via TAD chemistry [66]. Cramail et al. reviewed thermoset and thermoplastic materials prepared from lignin-derived aromatic compounds [67]. Typically, these bottom-up routes have better control over chemical and physical properties of final materials and avoid the complexity of macromolecular lignin.

#### 2.4. Challenges and outlook

Understanding the challenges in the path of future development on lignin-based polymeric materials, including thermoplastics, thermosets, adhesives, and foams, is critical for large-volume use of lignin [68]. There are at least three levels of challenges worthy for innovation:

(1) Purification of lignin. Recovered technical lignin, such as kraft lignin and liginosulfonates, is dark in color and contains significant amounts of various forms of sulfur. This requires deodorization and decolorization for many applications, for example, as thermoplastics used in the automotive industry. Monomeric sugars and other impurities in lignin have negative impacts on the direct functionalization of lignin, for example, ring-opening polymerization. There are efforts in developing more pure lignin by innovative purification and fractionation methods [69,70]. It must combine with chemical processing to remove undesirable impurities.

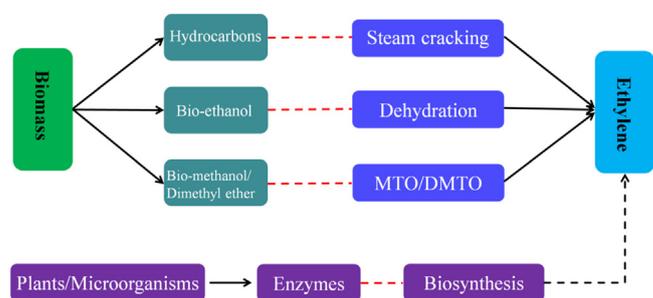


Fig. 5. Processes of bio-ethylene production [20]. Copyright 2018. Adopted with permission from Multidisciplinary Digital Publishing Institute.

- (2) Grafting and/or blending. It needs more high-level utilization of lignin as a whole with the aid of minor chemical modifications and effective blending. Grafting polymers from lignin is scientifically important, but not practically prevalent due to low volume use of lignin (e.g. 1–5 %). One must consider the economy of these modifications, which should be focused on the hydroxyl groups.
- (3) Defragmentation or depolymerization of lignin. It is insightful to understand chemistry and polymerization of model compounds. However, transformational progress is needed to develop more powerful synthetic strategies to convert a mixture of numerous chemical entities from the depolymerization of lignin. One should be more aware of the common structures of these entities, for example, they all possess phenolic functionality. In addition, new polymerization techniques should be more tolerant to multiple functionalities.

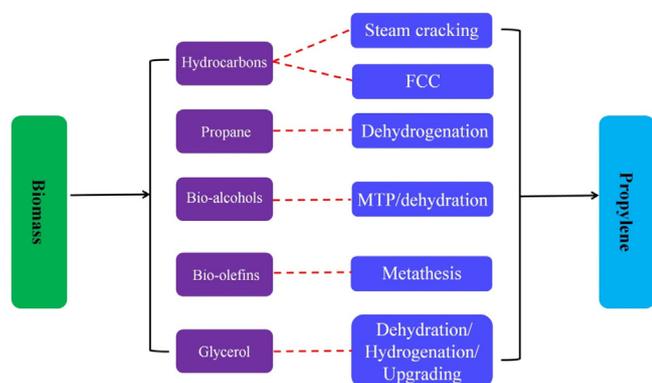
Repurposing lignin as value-added products requires collective efforts from chemistry, materials, and processing. A more fundamental understanding of the molecular structures and physical properties of lignin is required to develop high-value materials.

### 3. Biobased polyolefins

As the most volumetric commodity and engineering plastics, polyolefins are used in a wide variety of fields due to their excellent mechanical properties, high chemical stability, and good electrical insulation [71–73]. Commercial polyolefins are derived from fossil resources. Without alternative products, it is scientist’s consciousness to explore biobased polyolefins from renewable resources [74]. It is not only carbon neutral, but also important to achieve a sustainable economy [75].

#### 3.1. Biobased polyethylene

Traditionally, ethylene is produced by steam cracking of naphtha [20]. During recent years, the substitution of naphtha and other fossil resources by biomass has made progress. The synthetic pathways of bio-ethylene are shown in Fig. 5. Besides steam cracking of biomass, catalytic conversion of bio-ethanol into ethylene is an attractive approach [76,77]. Biobased alcohols can be obtained by fermentation of biomass such as starch, sucrose, and cellulose. Rapid cracking of biomass produces syngas, which can be converted to olefins via Fischer-Tropsch reaction [78]. A few companies, including Braskem (Brazil), Dow (USA), and Axens (France), have developed processes for the production of biobased polyethylene. Biomass derivatives such as methanol and dimethyl ether are also converted into ethylene through approaches, so-called methanol to olefins (MTO) and dimethyl ether to olefins (DMTO) [79–81]. With the commercialization of biobased polyethylene, their utilization



**Fig. 6.** Processes of bio-propylene production [20]. Copyright 2018. Adopted with permission from Multidisciplinary Digital Publishing Institute.

in packaging, automobile manufacturing, and construction is being actively explored.

Plants and microorganisms can produce ethylene through metabolisms [82,83]. In plants, ethylene is produced in a two-step reaction. *S*-adenosyl-methionine (SAM) is first converted to 1-aminocyclopropane-1-carboxylic acid (ACC) by ACC synthase, which is then catalyzed to release ethylene and cyanide via ACC oxidase [84]. However, the productivity of olefins from plant metabolisms is limited. In addition, microorganisms are also important sources for olefin synthesis. One of the metabolic proteins used by microbes is an ethylene-forming enzyme (EFE), which uses  $\alpha$ -ketoglutarate and arginine as substrates. EFE is a promising biotechnology target because the expression of a single gene is sufficient for ethylene production in the absence of toxic intermediates [85]. However, biosynthetic technology for ethylene production is still in its infancy, as the scalability and economy are far from being competitive with the mature petrochemical industry of ethylene.

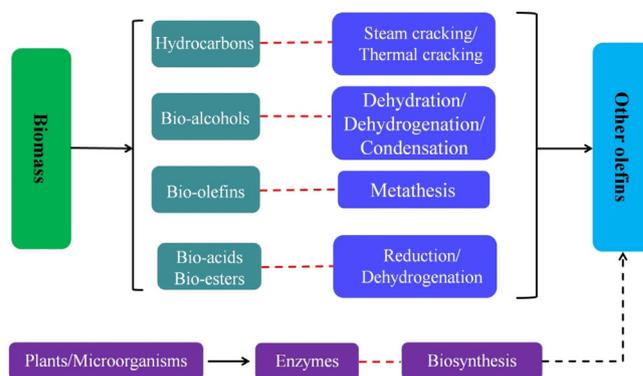
### 3.2. Biobased polypropylene

Compared with polyethylene, polypropylene enjoys higher mechanical strength and heat resistance, and is almost equally used in various fields. As shown in Fig. 6, biomass can be converted into biobased propylene by multiple processes, such as cracking, gasification, fermentation, metathesis, and dehydrogenation [86]. Propylene mainly comes from by-products of ethylene production by steam cracking of hydrocarbons. By controlling reaction temperature and catalysts, the yield of propylene could be optimized [87]. Similarly, fluid-catalytic cracking (FCC) is a pathway to convert hydrocarbons into propylene using modified zeolites as catalysts [88].

The success in biobased methanol production provides an opportunity for propylene synthesis, an approach called “methanol to propylene” (MTP). MTP technology was successfully developed by Lurgi in 1990s. Recently, Zhang and coworkers developed a modified ZSM-5/SiC foam catalyst, which showed high activity and high selectivity for propylene production [89]. Other bio-alcohols, such as isopropanol, ethanol, butanol, and glycerin, are also good candidates for propylene synthesis [90–92]. Biobased propylene could be obtained by metathesis reaction of all biobased butylene and ethylene. Moreover, glycerol can be selectively converted to propylene under the action of highly efficient catalysts [93].

### 3.3. Other biobased polyolefins

In addition to polyethylene and polypropylene, other polyolefins such as polybutylene, polybutadiene, and polyisoprene can be also derived from biomass (Fig. 7). Although the main prod-



**Fig. 7.** Processes of other bio-olefin production [20]. Copyright 2018. Adopted with permission from Multidisciplinary Digital Publishing Institute.

ucts of biomass steam cracking are ethylene and propylene, there is still a small portion of other olefins [94]. Moreover, biobased ethylene and propylene can be converted into long-chain biobased olefins via metathesis. Likewise, such olefins can be synthesized via dehydration of biobased alcohols. Dehydration of butanol leads to 1-butene. Isobutene can be obtained by isomerization of 1-butene. Besides biobased alcohols, itaconic acid can be converted to methyl tetrahydrofuran and subsequently to isoprene by dehydration [95]. Similar to the ethylene biosynthesis, several olefins can be obtained through biological metabolisms. Compared with chemical synthesis, the biosynthesis of biobased alkenes is a promising method. For example, biobased isoprene can be obtained through the mevalonate (MVA) and 5-methyl erythritol phosphate (MEP) pathways by *E. coli* [96]. Using biobased butadiene and isoprene as raw materials, biobased rubbers have been recently commercialized [97].

### 3.4. Challenges and outlook

Given the gigantic volume of petrochemical olefins, there is a clear demand on biobased polyolefins. One of the most important advantages for the development of biobased polyolefins is the well-practiced polymerization of olefins and processing of polyolefins. Thus, most innovations reside on the preparation of biobased olefin monomers. Once natural resources are converted to biobased olefins, the polymerization and processing in industrial scales can be well achieved. However, the production of biobased olefins faces a lot of challenges. Increasing the yield from biomass and reducing the production cost are most critical for the development of biobased olefins. Choosing non-edible biomass as sources should be favorably considered. The development of efficient and selective catalysts and greener procedures is indispensable to promote the commercialization of bio-olefins. It is obvious that future research should focus on the design of chemical catalysts with high selectivity for olefins. Microbial synthesis of olefins is a very promising method [98,99]. The discovery of new strains is the key step to realize industrial production.

A long-standing challenge in the polyolefin industry is the incompatibility between polyethylene and polypropylene, which is a big hurdle for recycling of polyolefins. Regardless of the sources of olefins, it is imperative to improve the processability of polyolefin blends for promoting sustainability. Recent work by Coates and Bates demonstrated an approach to enhancing the compatibility of PE and PP [100,101]. They designed block copolymers of ethylene and propylene to reinforce the interface between PP and PE and allow blending of the two polymers. Biobased polyolefins could adopt similar strategies by developing block copolymers of olefins from renewable resources. It could include not only ethylene and propylene, but also other olefins such as isoprene, butylene,

and butadiene. One could also attempt the use of other copolymer compositions such as random copolymers.

#### 4. Long-chain aliphatic polymers

Polyolefins represent the most prominent synthetic polymers that possess aliphatic backbones. Compared with polyolefins, aliphatic polycondensates such as polyamides, polyesters, and polyethers have polar groups on the polymer main chain, which provide unique properties such as degradability, compostability, and biocompatibility. Usually, aliphatic polycondensates contain six or fewer linear carbon per repeating unit, where the polar groups largely determine physical properties. For example, the presence of amide groups provides polyamide 6 with excellent thermal and mechanical properties. However, high densities of polar groups could induce high processing temperature and poor water resistance.

There is a growing incentive to develop long-chain aliphatic polyesters, polyamides and polyurethanes, which bridge the gap between conventional polyolefins and polycondensates. This class of polymers has great potential in pursuing green bioplastics by coupling with renewable natural resources. The major approach is to prepare linear  $\alpha$ ,  $\omega$ -difunctional monomers, particularly encouraged by recent advances in catalytic conversions of plant oils. Plant oils are one of the most abundant renewable resources, which have been widely applied in oleochemical industry [102]. The main components of plant oils are triglycerides, a class of esters combining glycerol and various fatty acids (Fig. 8). Fatty acids make up about 90 % of the total weight of triglycerides. Various functional groups provide ample possibilities for synthesizing polymers [102–104]. We have invested major efforts in using plant oils as renewable feedstocks [53,59,68,105–114]. Long-chain aliphatic polymers are one of the most important fatty acid-based products. They possess unique structures and properties, which have been described in recent reviews [115–117]. We focus on how chemical design and physical processing improve material properties. This section is divided into three major parts: (1) long-chain aliphatic polyamides, (2) long-chain aliphatic polyesters, and (3) long-chain aliphatic polyurethanes.

##### 4.1. Long-chain aliphatic polyamides

Polyamides have been widely utilized in various fields such as aerospace, electronics, automobile, and clothing due to their excellent mechanical and thermal properties [118,119]. However, the high-water absorption and poor low-temperature properties still limit the application of traditional polyamides. Long-chain polyamides possess long aliphatic chain and low amide group densities [117]. At the same time, there is an increasing interest in the development of biobased polyamides. Fatty acids are extremely important biobased precursors to prepare long-chain aliphatic polyamides. As an example, polyamide 11 (PA 11) from castor oils has been commercially used for decades, which is synthesized via polycondensation of 11-amino-undecanoic acid [118].

Long-chain aliphatic polyamides are mainly synthesized via polycondensation of diamines and dicarboxylic acids or amino acids (Fig. 9) [117,119]. In general, polyamides have high crystalline structures due to strong intermolecular hydrogen bonding between amide groups, which dominates the formation of crystalline phases. Melting points and mechanical properties of polyamides can be adjusted via tuning the density of amide groups. For example, compared to PA 6 and PA 66, the melting point of PA 11 is reduced by  $\sim 40^\circ\text{C}$ . In addition, PA 410, PA 610, PA 1010, and PA 1012 are synthesized based on castor oils [120]. Biotechnological processes have been used to prepare long-chain aliphatic polyamides from

fatty acids such as PA 12 and PA 16 [119,121]. PA 15 can be also synthesized from fatty acid [122]. Numerous attempts have been explored to prepare long-chain aliphatic polyamides with excellent properties and energy-economic processing conditions.

Guan and coworkers designed a mild, clean process to synthesize polyamides via catalytic dehydrogenation of diols and diamines [123]. A straightforward and efficient method to prepare various long-chain polyamides from plant oils was presented by Meier et al. [124]. Polyamides with tunable properties could be obtained via copolymerization of traditional monomers. Koning and coworkers synthesized biobased semicrystalline polyamides via solid-state polymerization [125]. These polyamides have adjustable polarities and melting points.

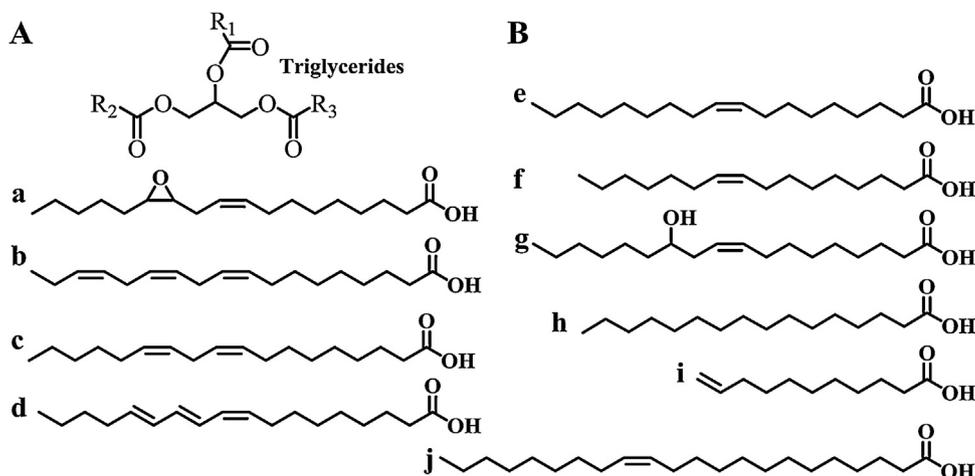
The introduction of functional pendant groups is an alternative method to tune properties of polyamides with additional advantages that most main-chain approaches lack of. Functional polyamides with alkyne groups in the main chain were presented by Du Prez and co-workers. Side groups can be further introduced via thiol-yne click reaction [126]. They extended thiolactone to AB type monomers, which were converted into polyamides [127,128]. Mecking et al. prepared polyamides with pendant thiol groups via reactions between bis(thiolactone) and diamines. The thiol groups were then reacted with various acrylates via Michael addition to obtain functional polyamides [129]. Another approach is to use multicomponent reactions to prepare polyamides with different side groups [130–133]. However, the development of high molecular weight polyamides with functional side groups, tunable crystallization, and excellent mechanical properties is still a challenge.

Processing can be well utilized to enhance properties of biobased polymers. Recently, Wang, Tang, and coworkers combined new chemical structures with unidirectional processing to prepare ultra-strong polyamide elastomers derived from castor oils (Fig. 10) [134]. A diene monomer possesses twenty linear carbons and two amides. Thiol-ene addition polymerization was carried out. The presence of an additional hydroxyl group allows the control of crystallinity, which can tune mechanical properties. These polyamides with an ultimate tensile strength at  $\sim 200$  MPa were obtained, while maintaining good elasticity. Moreover, the formation of amide clusters of these elastomers led to aggregation-induced emission (AIE) with strong luminescence. The mechanical and thermal properties and crystallinity of polyamides can be precisely controlled by simple adjustment of feed ratios of monomers.

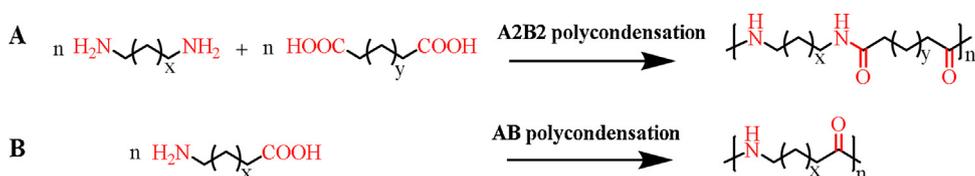
##### 4.2. Long-chain aliphatic polyesters

Due to the promise of degradability and compostability, long-chain aliphatic polyesters derived from fatty acid have attracted intensive attention in recent years. Most of them were prepared via condensation polymerization of diols with dicarboxylic acids or diesters, intrinsic hydroxycarboxylic acids, or ring-opening polymerization of lactones, and ADMET polymerization (Fig. 11) [135,136]. Long hydrocarbon chains in polyesters can promote crystallization. Like polyamides, physicochemical properties can also be adjusted via controlling the ester group density.

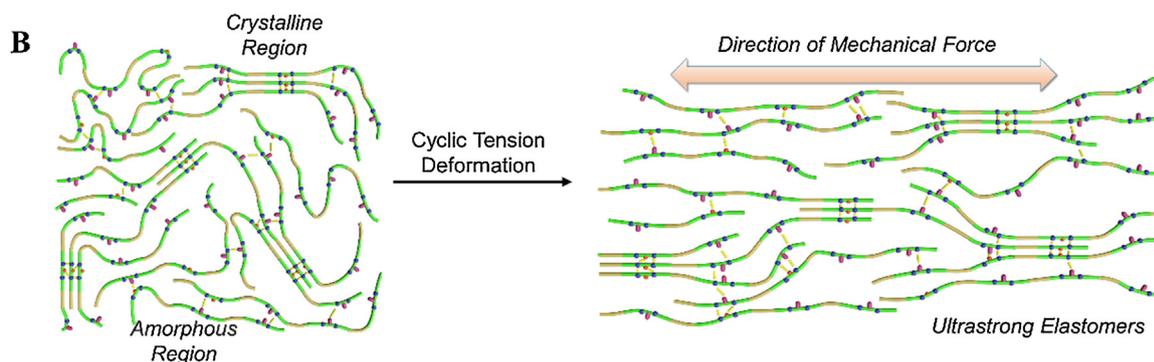
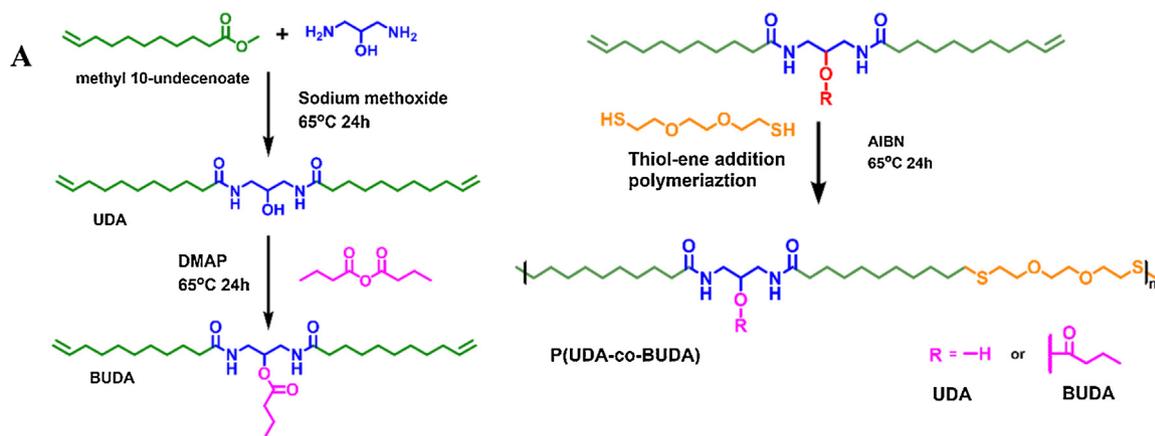
Isomerizing alkoxyacylation is a useful method to prepare dicarboxylic acids from unsaturated fatty acids. C19 and C23 dicarboxylic acid monomers were prepared and polymerized by the Mecking group [137]. These polyesters can be processed into a wide range of materials via injection molding, hot-press, and electrospinning [138]. Olefin metathesis is another effective approach to preparing long-chain aliphatic polymers from fatty acids [139]. C20 long-chain polyester was prepared via olefin metathesis [139]. Mecking and coworkers synthesized polyesters from algae oil via transesterification [140]. In addition, ADMET polymerization with subsequent hydrogenation was also used to synthesize long-chain



**Fig. 8.** (A) A general structure of triglycerides, where R represents various fatty groups; (B) Fatty acids chemical structures: (a) vernalic acid, (b) linolenic acid, (c) linoleic acid, (d)  $\alpha$ -eleostearic acid, (e) oleic acid, (f) palmitoleic acid, (g) ricinoleic acid, (h) palmitic acid, (i) 10-undecenoic acid, (j) erucic acid.



**Fig. 9.** Conventional routes to prepare long-chain aliphatic polyamides.



**Fig. 10.** (A) Synthesis of functional polyamides with pendant groups via thiol-ene addition polymerization; (B) A proposed microstructure illustrates the alignment of crystalline domains via unidirectional cyclic tensile deformation [134]. Copyright 2018. Adopted with permission from Nature Publishing Group.

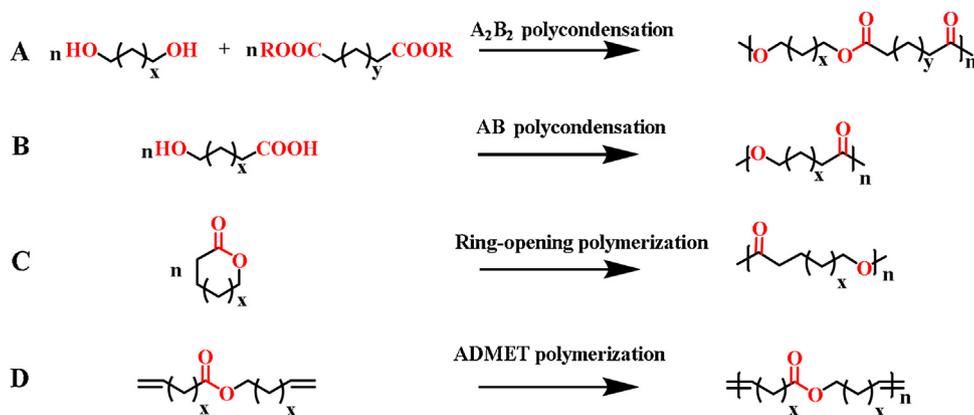


Fig. 11. Strategies for synthesis of long-chain aliphatic polyesters.

aliphatic polyesters [141]. Ether and thioether were introduced into the main chain of polyesters to improve hydrophilicity [142]. Ricinoleic acid and sebacic acid were also mixed to prepare long-chain polyesters [143]. The resulting copolymers can be injection molded. Moreover, long-chain polyester-based thermoplastic elastomers can be prepared, where the crystalline long methylene chain between ester groups can act as hard domains in phase-separated soft matrix [144].

Functional polyesters with active side groups may extend applications of polyesters. Bai and coworkers designed a highly effective and facile strategy to synthesize functional polyesters with various side groups from castor oil at room temperature. Dicarboxylic acid monomers derived from 10-undecenoic acid were prepared via thiol-ene addition reaction. Then condensation polymerization of diacid monomers with dihalide monomers was conducted at room temperature using 1,1,3,3-tetramethyl guanidine as a promoter. By choosing different dihalide monomers, functional polyesters with various side groups were obtained (Fig. 12) [145]. Moreover, a two-step strategy was also developed to introduce epoxide groups and unsaturated double bonds into long-chain polyesters [146].

By using processing such as solvent casting, molding, injection, and 3D printing, polyesters can be processed into various products. The processing method could modify the properties of final polyester products. Solvent casting is the most convenient method, which is limited in a laboratory scale due to the use of mass organic solvents [147]. Moreover, organic solvents are not eco-friendly [148]. Thus, it is unsuitable for large-scale processing. 3D printing is among the most popular additive manufacturing in recent years. Fused deposition modeling (FDM) and selective laser sintering (SLS) are important technologies in 3D printing for products used in tissue engineering [148]. Compared with solvent casting, 3D printing technology not only eliminates the negative effect of organic solvents, but also provides opportunities in manufacturing devices with complex shapes [149]. The SLS technique can be used to prepare materials with high mechanical strength and low porosity. Polyester materials with different mechanical properties can be obtained via tuning manufacturing parameters [149,150].

#### 4.3. Long-chain aliphatic polyurethanes and others

Polyurethanes are widely used in biomedical and packaging applications due to their potential degradability and excellent mechanical properties. A green approach to preparing polyurethanes from oleic acid and undecylenic acid was reported in 2011 [151]. The yield of polyurethanes was up to 99%. Like long-chain polyamides, long-chain polyurethanes are usually semicrystalline. The melting points also decrease with the increasing length of the methylene chain between urethane groups.

Diisocyanates used in the production of polyurethanes are not environmentally benign. Thus, the development of a greener strategy on the preparation of diisocyanates is particularly important. The Narine group reported the synthesis of 1,16-diisocyanatohexadec-8-ene and 1,7-heptamethylene diisocyanate from oleic acid via Curtius rearrangement [152,153]. Cramail and co-workers reported a facile method to prepare fatty acid-based diisocyanates (1-isocyanato-10-[(isocyanatomethyl)thio]decane and 1,8-diisocyanatoctane) [154].

In addition, there are many non-isocyanate approaches to preparing polyurethanes, such as polyhydroxyurethanes and poly(ester urethane) by reacting cyclocarbonate with amine [156,157]. Polyurethanes from soft/flexible to brittle properties were obtained via tuning molecular structures between urethane groups. Meier et al. prepared renewable non-isocyanate based thermoplastic polyurethanes via base-catalyzed Lossen rearrangement and polycondensation of dimethyl dicarbamates and diols [158]. Polyurethanes with high molecular weight and excellent thermal properties were obtained.  $\alpha, \omega$ -Diene urethane monomer synthesis and ADMET polymerization were applied to prepare polyurethanes [159]. Ring-opening polymerization of cyclic carbonate-methyl ester was used to prepare poly(amide-hydroxyurethane)s from plant oil (Fig. 13) [155]. Cyclic carbonate-methyl ester was prepared via epoxidation and carbonation of plant oil-based methyl 9-decanoate. This work provides the first example on linear isocyanate-free polyurethanes with mechanical integrity and processability. Moreover, AB-type monomers from ricinoleic acid were used to prepare polyurethanes via self-polycondensation [160]. The AB-type monomers from oleic acid and undecylenic acid were also used as raw materials to synthesize semicrystalline polyurethanes, and various synthetic routes were carried out to obtain polyurethanes with desired molecular weight [161].

Beside long-chain aliphatic polyesters, polyamides, and polyurethanes, a variety of polyureas, polyacetals, polycarbonates, and polyanhydrides were also synthesized from fatty acids and their derivatives. It is not our intention to have an extensive elaboration on these materials, but to give a few examples. Cramail and coworkers converted oleic acid into an AB type monomer with a carbonate group and a hydroxyl group, which was then polymerized via self-polycondensation to obtain long-chain aliphatic polycarbonates [162]. Mecking and coworkers converted fatty acid-derived  $\alpha, \omega$ -diols into polyacetal directly via acetal metathesis polymerization [163].

#### 4.4. Challenges and outlook

The conversion of natural abundant fatty acids into value-added long-chain aliphatic polymers has been actively explored

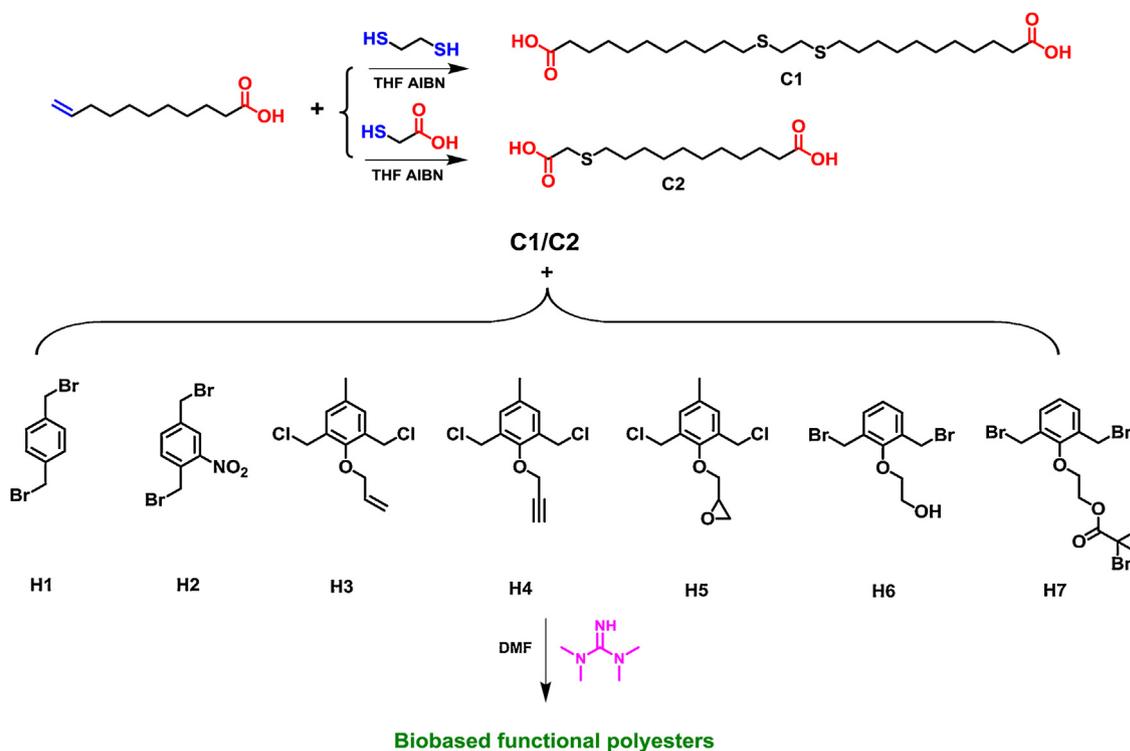


Fig. 12. Synthesis of functional polyesters with various side groups [145]. Copyright 2016. Reproduced with permission from American Chemical Society.

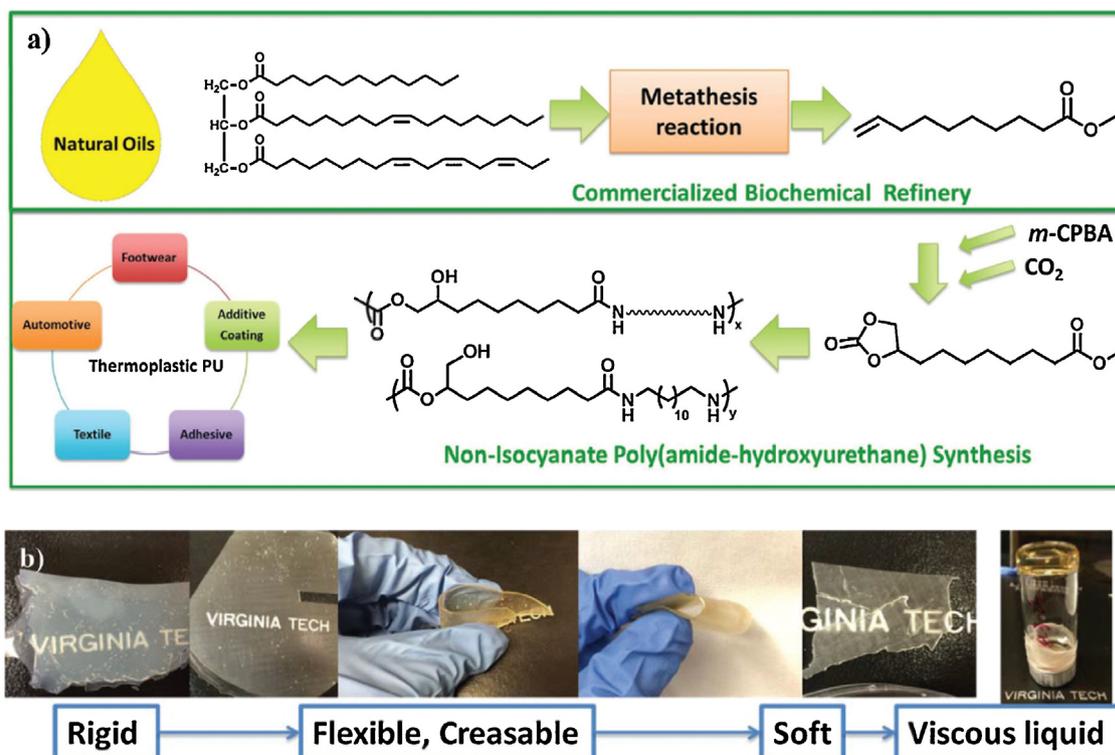


Fig. 13. (a) Synthesis of linear segmented PA<sub>12</sub>HU-PTMO; (b) Melt-compression molded films of thermoplastic polyurethanes [155]. Copyright 2016. Reproduced with permission from the Royal Society of Chemistry.

in recent years. Various monomers were developed, which were further converted into greener long-chain aliphatic polyesters, polyamides and polyurethanes. In most cases, the physical properties of these long-chain aliphatic polymers cannot compete with commercial polymers, in some scenarios, most chemistry has

been reported without characterization of critical thermal and mechanical properties. Several key aspects need to be considered: new strategies towards high purity and low-cost monomers derived from fatty acids should be explored; high molecular weight long-chain aliphatic polymers are required to assess physicochem-

ical properties; the microstructures and properties of long-chain aliphatic polymers should be finely controlled for specific applications. In addition, the chemical design is preferred in combination with processing to achieve better physical properties.

## 5. General conclusions and future perspectives

Sustainable polymers derived from renewable biomass have enormous opportunities to replace or complement with some of petrochemical counterparts. Among them, lignin-derived polymeric materials, biobased polyolefins, and long-chain aliphatic polymers are being intensively pursued in both academia and industry. Although some of the sustainable polymers, such as PA 11, have been commercialized, the overall share of market is still very small. In order to stimulate a sustainable economy, sustainable polymers should grow at an outpacing speed to meet the ever-increasing challenges. However, it cannot be achieved until the following challenges are overcome. First, properties of biobased polymers should be comparable or even better than commercial polymers. Second, the cost of biobased polymers should be more competitive. Two possible approaches are proposed as follows: (1) Synthesize polymers or analogues to replace commercial polymer counterparts, such as polyolefins, from renewable biomass via greener processes; (2) Design novel polymeric materials with unique structures, excellent performances, and innovative processing.

Raw origins of biomass such as lignin, cellulose, and fatty acid are low-cost, readily available, and chemically modifiable. To obtain higher value-added or greener commodity products, how to take advantage of unique chemical structures of renewable resources should be carefully considered for designing monomers and polymers. The rigid aromatic ring of lignin is a good candidate for making glassy polymers. Fluorescent materials can be obtained via a facile processing method from lignin due to the existing of aromatics [164]. More fundamental research on lignin's molecular structures, chemical modification, polymer materials design and their processing methods is required to obtain high-value materials. Fatty acids contain reactive functional groups such as double bonds, hydroxyl, and carboxyl. Thus, they are ideal candidates in designing long-chain aliphatic polymers. In part, long-chain aliphatic polymers are analogues to linear polyethylene due to the existing of long methylene chains. More importantly, the functional groups such as ester and amide endow them with special properties (polarity, degradability, compostability, etc.), which distinguish them from polyethylene – they hence deserve attention.

Sustainable polymers from biomass are an emerging subject that is rapidly gaining more attention worldwide. Interdisciplinary cooperation within material science, biology, chemistry, bionics, and materials processing is of great importance. In the near future, with the progress of chemical synthesis, bio-refinery, and analytical techniques, more active components from renewable resources can be discovered and used as raw materials. It is expected that more sustainable polymeric materials with desirable properties will soon appear in the marketplace.

## Author contribution

The study was conceived by Z.W., M.S.G. and C.T. All coauthors wrote the manuscript.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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