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THE BATTLE FOR THE “GREEN” POLYMER. Different approaches for biopolymer synthesis: Bioadvantaged vs. Bioreplacement.

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Biopolymers have been used throughout history; however, in the last two centuries they have seen a decrease in their utilization as the proliferation of inexpensive and mass-producible materials from petrochemical feedstocks quickly became better suited to meeting society's needs. In recent years, high petroleum prices and the concern of society to adopt greener and cleaner products has led to an increased interest in biorenewable polymers and the use of sustainable technologies to produce them. Industrial and academic researchers alike have targeted several routes for producing these renewable materials. In this perspective we compare and contrast two distinct approaches to the economical realization of these materials. One mentality that has emerged we term “bioreplacement”, in which the fields of synthetic biology and catalysis collaborate to coax petrochemical monomers from sugars and lignocellulosic feedstocks that can subsequently be used in precisely the same ways to produce precisely the same polymers as we know today. For example, the metabolic engineering of bacteria is currently being explored as a viable route to common monomers such as butadiene, isoprene, styrene, acrylic acid, and sebacic acid, amongst others. Another motif that has recently gained traction may be referred to as the “bioadvantage” strategy, where the multifunctional “monomers” given to us by nature are combined in novel ways using novel chemistries to yield new polymers with new properties; for these materials to compete with their petroleum-based counterparts, they must add some advantage, for example less cost. For instance, acrylated epoxidized soybean oil readily undergoes polymerization to thermosets and recently, thermoplastic rubbers. Additionally, many plants produce pre-polymeric or polymeric materials that require little or no post modification to extract and make use of these compounds.

1 Introduction

“Green” polymers, or “biopolymers”, are polymers produced partially or entirely from renewable natural resources other than petroleum. There are a wide variety of materials that can be described using the term “biopolymer”, nonetheless it usually refers to materials derived from biological sources such as microorganisms, plants, or trees. It may also refer to materials produced by synthetic chemistry from biological sources such as vegetable oils, sugars, fats, resins, proteins, amino acids, etc. . . ¹ Throughout history, humanity has made extensive use of biopolymers in everyday life. Millions of years B.C. humans used animal skins as a source of clothing; 24K years B.C. humans started using plant fibers; 10K years B.C. the use of flax, ramie, and jute was adopted; 9K years B.C. wool; 5K years B.C. silk, and 3K years B.C. cotton. ² In the 1220's, shellac, a thermoset resin secreted by the Asian lac bug, was used as a pigment for paintings, although there is evidence

that it may have been used thousands of years earlier. ³ Five centuries later in 1751, François Fresneau investigated the properties of natural rubber, a product extracted from the Para rubber tree indigenous to South America. The properties of natural rubber attracted interest amongst researchers and led, in 1860, to the discovery of isoprene by the English chemist Greville Williams who recovered it by distillation from natural rubber. In 1870 John Wesley Hyatt invented celluloid, a thermoset produced by combining camphor with cellulose nitrate. Celluloid was molded into toiletry items, collar stays, combs, photograph cases, and was used to make the first flexible photographic film. ⁴ In the early 1900's Swiss chemist Jacques E. Brandenberger invented cellophane, a thin transparent sheet made of regenerated cellulose utilized for packaging. During the same time rayon, also a product from regenerated cellulose, was being used in the apparel and furnishing markets. In the 1940's Henry Ford experimented with soybean-based composites for auto parts.

Nonetheless, these materials were costly by the standards of the day. The advent of the petroleum refining complex brought forth a dizzying array of economical small molecules;

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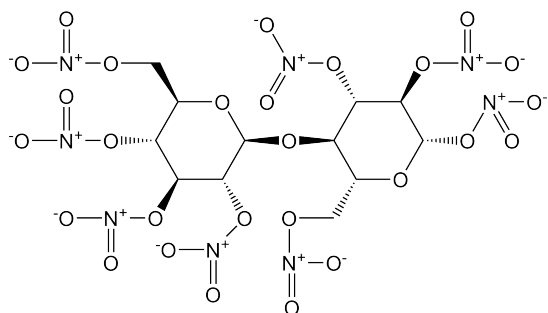


Fig. 1 Diagram of the cellulose nitrate molecule utilized by Count Chardonnet to produce the first synthetic fiber.

with the rapid development of synthetic chemistry and industrial processing technology it was only a matter of time before affordable synthetic polymers were brought to the masses.¹ In 1887, Count Hilaire of Chardonnet discovered a method to spin cellulose nitrate into fibers. These fibers were treated with an acid sulfide solution, which produced Chardonnet silk, the first synthetic fiber, see Figure 1. In the early 20th century Leo Baekeland, in search for a cheaper substitute for shellac, produced and patented Bakelite, the world's first fully synthetic plastic. Bakelite is a phenolic thermoset composite formed by combining formaldehyde with phenol and mixing it with fillers, see Figure 2. Wallace Carothers (1930's) at Dupont pioneered the use of a wide variety of polymeric materials brought forth by condensation chemistry, including polyesters, neoprenes, and nylons.⁴ Biopolymers continued to be supplanted by synthetics as chain growth chemistries and catalysis gave way to styrenics and eventually polyolefins. Today, polyethylene alone is a 17 billion pound industry.

In recent years, social, political, and economic pressures have resulted in a resurgence of interest in turning to nature to provide us with renewable and sustainable sources of energy, chemicals, and materials. Technologies providing renewable fuels are here, and in some cases are nearing economic parity with petroleum. However, high volume/low margin commodities such as fuels cannot support the fledgling biorefinery complex alone, at least not indefinitely. Just as the petroleum industry derives 90% of its value from specialty products comprising only 10% of the volume, so must the bioproducts industry. Biopolymers represent an important component of the value-added portfolio that sustainable and renewable technologies must include to thrive. Compared to today's synthetic polymers, biopolymers can potentially offer higher biodegradability, better recyclability, and lower process energy requirements, with a smaller environmental footprint overall. These attributes make them ideal candidates to replace 90 billion pounds of the petroleum-based polymers; in applications such as coatings, containers, packaging, textiles,

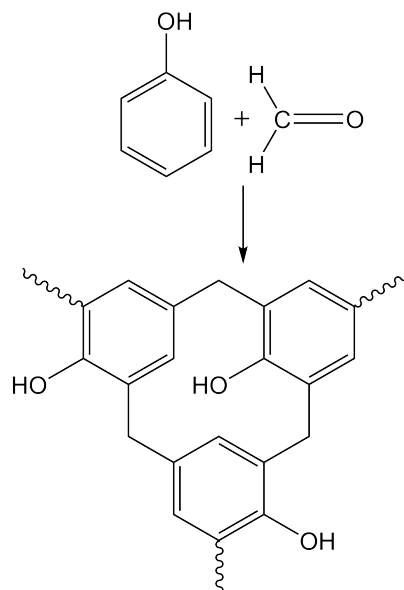


Fig. 2 Diagram representing the reaction to synthesize Bakelite by mixing a phenol with formaldehyde to form a phenolic thermoset.

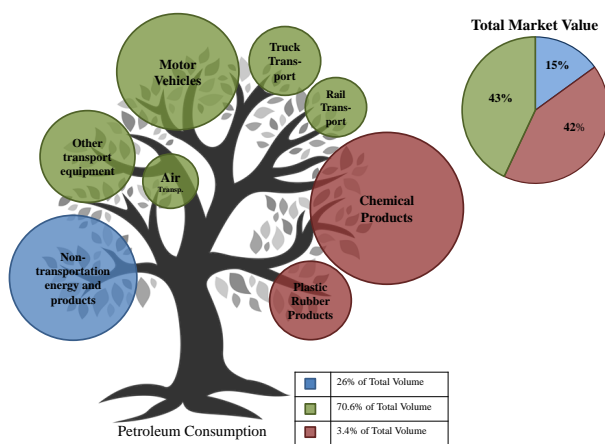


Fig. 3 Infographic derived from 9, depicting the “petroleum tree” with the main byproducts according to their petroleum consumption, as well as their market value share.

in the automotive industry, amongst others, see Figure 3.⁵⁻⁸ This exorbitant amount of petroleum-based products accounts, annually, for more than 300 million tons of the world's oil and natural gas supply.⁸ However, the shift to biopolymers will not occur until they represent a superior value opportunity for the industry when compared with their petroleum counterparts.

A wide variety of biopolymeric materials with different physical and mechanical properties have already been synthe-

sized using renewable resources; materials ranging from soft elastomeric rubbers to hard and rigid composites.¹⁰ However, many challenges (opportunities) remain in the development of biopolymers towards meeting or exceeding the physical and economical characteristics of petroleum based analogues. Two main approaches have emerged as prominent contenders to yield the “green” polymers of tomorrow that will help us to continue the process of weaning from reliance on petroleum:

“Bioreplacement” polymers: Production of bio-based monomers chemically identical to those currently derived from petroleum. Using the tools of synthetic biology and advanced catalysis, upgrade the sugars, starches, lignin, cellulose, and hemicellulose found in trees, plants, and animals to the monomers that we currently derive from petroleum. This approach starts with the complex molecules provided by nature, and breaks them down to the simple molecules abundant in oil. Assuming that a particular conversion is scalable and economical, the advantage is that producers and users of today’s polymers have nothing new to learn to become “green”. Success stories from this category, like the commercial production of succinic acid, have recently begun to appear, and will likely continue to be critical components of tomorrow’s integrated biorefinery.

“Bioadvantaged” polymers Polymers produced from biological monomers unheard-of in the petrochemical world: unmodified or minimally modified vegetable oils, proteins, cellulose, starch chitosan, chitin, alginates, and other polysaccharides.¹¹ In this realm, thousands of materials have yet to be discovered; some of them will be quite similar to their petroleum-based analogues, soy-based polyurethanes, for example. Others will have physical and chemical property combinations unmatched by any material known today. Of these, those that ultimately reach the marketplace must offer an “advantage”, some feature that presents a value opportunity that would be otherwise missed using the petrochemical alternative. Without such an advantage, there is no compelling reason for a producer or processor of polymers to leave behind the old materials that have served so well over the past century. Bioadvantaged polymers then, at least from our perspective, present both the greatest challenges but also the greatest opportunities for commercial success: without the need to break down complex molecules to simple ones, only to make them complex again through polymerization — should it not be less costly to start with these complex molecules as they are and simply upgrade them to new polymers?

Here in this Perspective we compare and contrast recent advances from both paradigms, with particular focus on efforts to upgrade plant oils into polymers mimicking those from



Fig. 4 Diagram of the different approaches of plastic production where the victor will be the one with the greatest economic opportunity.

petrochemicals (bioadvantaged) with parallel efforts to produce the petrochemical monomers from biological sources via metabolic engineering (bioreplacement); as Figure 4 suggests, the battle for the “green” polymer of tomorrow will be ultimately won by the almighty dollar.

2 “Bioreplacements”: Biomonomers from synthetic biology, catalytic and thermal conversion.

Many plant species naturally produce a mixture of different compounds that have the potential to be used as polymers. Moreover, plants and almost all bacteria have the metabolic machinery that can be engineered to synthesize a host of organic chemicals.¹² A variety of precursors—including lignocellulose, cellulose, hemicellulose, lignin, ash, starch, chitosan, chitin, alginates, or polysaccharides—can serve as the substrate for metabolic conversion into a commercially relevant monomer, often with the help of catalytic upgrades of the metabolized products. The most sought-after monomers in industry are: acrylic acid, adipic acid, butadiene, butanediol, butanol, furans, isoprene, propanediol, succinic acid, terephthalic acid, and a number of aromatic compounds (*e.g.* styrene).^{12–15} These monomers may then be polymerized

using existing techniques and often fully amortized capital equipment.

2.1 Metabolic engineering

Metabolic engineering has evolved extensively over the past few decades, increasing both the number of ways in which microorganisms can digest biological feedstocks into value-added chemicals, and the efficiency with which such conversions are completed. Table 1 provides a list of monomers with their corresponding starting materials as well as their uses, chemical formula, and an example of a metabolic engineered host used previously for their synthesis. Synthetic biology has been as a vehicle for the transformation of waste streams into the most common sought after monomers.¹⁴ Genetically modified organisms are designed to overproduce a preexisting metabolite or, through the insertion of heterologous genes, to produce altogether foreign compounds not found in wild types.¹⁴ Some of the most common host platforms are bacteria, such as *Escherichia coli* or *Pseudomonas putida*; fungi, for example *Penicillium camemberti*; and yeast such as *Saccharomyces cerevisiae*. Some of the main challenges for commercial viability in many cases are increasing the specificity of the target compound, mitigating the toxicity of the product so that the organisms can produce product concentrations high enough to be practical, and economically recovering the product at an acceptable purity level.

Myriant, a company that produces renewable chemicals, was able to successfully synthesize succinic acid (SA) using corn glucose (sorghum) and lignocellulosic sources as its feedstocks. Myriant's bio-plant located in Lake Providence, LA is able to produce 30 millions lb of SA a year based on a proprietary *E. coli* fermentation. Its high-yield process (95%) makes it cost effective and comparable to petroleum-based SA. In 2012 Reverdia, a joint venture between Roquette and DSM, began operations in Cassano Spinola, Italy to produce about 10,000 tonnes/yr of SA from glucose using a recombinant *E. coli*. Succinic acid can then undergo different transformations and produce chemicals such as: 1,4-butanediol, succinonitrile, dimethyl succinate, 2-pyrrolidone, tetrahydrofuran, γ -butyrolactone, 4,4-bionolle, N-methyl-2-pyrrolidone, 1,4-diaminobutane, succinamide, between others.¹⁶ Succinic acid can also be obtained in high concentrations and high yields in a three step continuous fermentation of glucose using *Anaerobiospirillum succiniciproducens* as the host platform, with conversions of up to 1.35 mol succinic acid per mol sugar and a slightly lower volumetric productivity of 10.4 g/L·h.^{16,17} *Mannheimia succiniciproducens* is also able to produce succinic acid from biorefinery sugars with high yields and without the formations of byproducts, such as lactic acid or acetic acid.¹⁸ In spite of the commercialization success of Myriant and Reverdia the vast majority of metabolic engi-

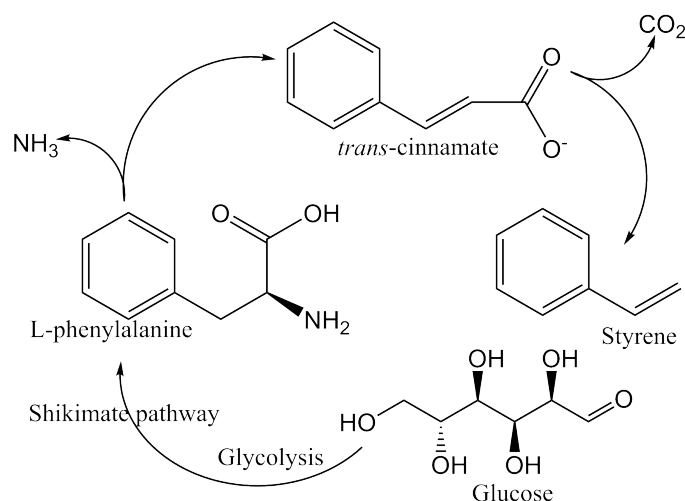


Fig. 5 Diagram of the enzymatic pathway for the conversion of styrene from renewable sugar (eg glucose). Image adapted from 15.

neering techniques require further study to make them economically feasible. Diols are comparatively simplistic to produce, at least from the biologist's perspective; a number of fermentation routes have been known for example to produce 1,3-propanediol from sugars and even glycerol, although the process failed to reach economic parity with petroleum-based feedstocks until significant breakthroughs in the separations technology were put into practice. Archer-Daniels Midland company was evidently the first company with the capability of producing this monomer, making use of a simulated moving bed chromatography process to cost-effectively recover the diol from the fermentation broth.¹⁹

In attempts to produce commodity petrochemicals from renewable substrates, McKenna *et al.* designed and developed a new biosynthetic pathway for the production of styrene from glucose.¹⁵ They accomplished this by the co-expression of phenyl alanine ammonia lyase and trans-cinnamate decarboxylase, using heterologous genes from *Arabidopsis thaliana* and *Saccharomyces cerevisiae* using *Escherichia coli* as the host organism. This method was able to produce up to 260 mg/L of styrene in flask cultures. This promising technique is the first to produce styrene directly from glucose. However, currently styrene's toxicity threshold was determined to be approximately 300 mg/L, a very small quantity when compared to the more than 60 million metric tons per year of styrene produced in the U.S. alone.¹⁵

Alan Berry was able to engineer *Escherichia coli*'s central metabolism to improve the production of aromatic compounds from glucose, *i.e.*, L-tryptophan and phenylalanine. These compounds can be used as precursors for the production of monomers such as styrene. Here, after 60 hours of

Table 1 Common biomonomers along with their starting material, chemical formula, uses, and metabolic engineered host.²⁰

| Monomer | Starting Material | Organism | Uses | Commercial Status |
|--------------------|--------------------|---|--|---|
| 1,3-propanediol | Glucose, Glycerol | <i>Clostridium acetobutylicum</i> and <i>Clostridium butyricum</i> , <i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i> | Adhesives, coatings, composites, carpeting, textiles | DuPont Tate & Lyle Bio Products, Archer-Daniels Midland Company |
| Glycerol carbonate | Glucose | <i>Candida antarctica</i> | Surfactants, coatings, polyurethane foams, hyperbranched polymers | Commercialized by Huntsman Performance Products |
| Isoprene | Mevalonate | <i>Bacillus subtilis</i> , <i>Bacillus amyloliquefaciens</i> | Thermoplastic elastomers, rubber | Pre-commercialization by Genencor and Goodyear |
| Lactic acid | Glucose | <i>Lactobacillus delbrueckii</i> | Production of biodegradable polymers (<i>polyesters</i> , <i>polylactic acid</i>) | Research stage |
| Styrene | Glucose | <i>Escherichia coli</i> | Thermoplastic elastomers, | Research stage |
| Succinic acid | Biorefinery sugars | <i>Anaerobiospirillum succiniciproducens</i> , <i>Mannheimia succiniciproducens</i> | Precursors for chemicals (<i>1,4-butanediol</i> , <i>tetrahydrofuran</i> , <i>γ-butyrolactone</i>) | Commercialized by Myriant |

fermentation, tryptophan yields achieved the theoretical maximum of 0.227 g/g.¹⁴ This was accomplished by diverting the flow of carbon through the central metabolism to the aromatic pathways. In a similar fashion, Guillermo Gosset reviews the production of 2-phenylethanol, *p*-hydroxycinnamic acid, *p*-hydroxystyrene, *p*-hydroxybenzoate, anthranilate, and cyclohexadiene-transidols, amongst others from bio-engineered *Escherichia coli* and *Pseudomonas putida*.¹² Lu *et al.* were able to produce viable yields of ω -hydroxyfatty acid, monomers that can be used to synthesize a unique family of polyethylene-like biobased polymers, from the engineering of the diploid yeast *Candida tropicalis*.^{21,22}

Isoprene, a highly sought-after hydrocarbon, used in the production of elastomeric materials, can also be produced by certain bacteria. Genencor and Goodyear formed a joint venture in 2008 to develop and commercialize “BioIsoprene”TM produced from *Bacillus subtilis* and *Bacillus amyloliquefaciens* (bacteria).²⁰ Nearly six years later, these efforts have been sufficiently fruitful to produce demonstration “bio-tires” at trade shows but are evidently still shy of economic parity with petrochemical isoprene. Lactic acid and 1,3-propanediol are products of the fermentation and neutralization of glucose using organisms such as *Lactobacillus delbrueckii* and *Clostridium acetobutylicum* respectively. Commercialization of lactic acid presents a waste disposal problem, as for every ton of lactic acid produced, approximately one ton of CaSO₄ is generated from the neutralization step.^{20,23} However, in recent years new yeast species such as, *Pichia stipitis*, have been modified to function at lower pH values, eliminating the need for subsequent neutralization. NatureWorksTM, an independent company invested in by Cargill and PTT Global Chemical is the largest producer

of biorefined lactic acid. They produce lactic acid from the fermentation of corn based dextrose. Their product is then sent to a continuous process, see Figure 6, which starts by removing water through a condensation reaction, producing low molecular weight polymer (LMW). This polymer is then catalytically converted into lactide and the polymerized into a high molecular weight (HMW) polymer using a ring-opening lactide polymerization. NatureWorks manufacturing facility, located in Blair, Nebraska, USA, as of 2002, had the capacity of producing 300 million pounds of HMW polylactide acid.²⁴ Lactide can be further used in the synthesis of thermoplastic elastomers, when combined with polymers with low *T_g* that will act as the soft and elastic segment.^{25,26} Polymers like: polymenthide,^{27,28} poly(trimethylene carbonate),²⁵ polyisoprene,²⁶ poly(3-hydroxybutyrate), poly(1,5-dioxepan-2-one), polyisobutylene, between others.^{25–27} Lactic acid base thermoplastic elastomers possess excellent physical properties that makes them suitable replacements of high *T_g* blocks, however newer technologies have to be developed to make copolymerization economically feasible.

Bozell and Petersen offer an extensive review of biobased products from biorefinery carbohydrates,²⁰ and provide a more exhaustive list of biomonomers that can-be/are-being synthesized through synthetic biology.

2.2 Catalytic Conversion

Chemical catalysis and thermochemical approaches have emerged as complements and also as alternatives to biosynthetic metabolic pathways in the upgrading of biomass to monomers. Table 2 provides a list of common monomers with their starting materials, production method, and uses.

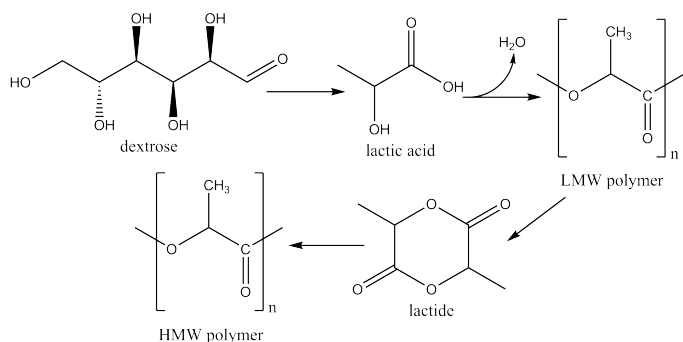


Fig. 6 Diagram of the pathway implemented by Natureworks® for the conversion of high molecular weight lactic acid from dextrose.

Avantium, the renewable chemical company behind the “green” packaging adopted by many in the beverage industry (including Coca-Cola), developed proprietary acid catalyst technology (YXY) capable of producing a wide range of materials by the conversion of plant-based sugars. Their proprietary catalyst is capable of dehydrating carbohydrate feedstocks, C6 and C5 sugars from non-food biomass, to make alkoxymethyl-furfurals (RMF), (*e.g.* methoxymethyl furfural) and levulinics (*e.g.* methyl levulinate).²⁹ Furanix, a division of Avantium, has developed solid acid catalysts that operate between 175–225°C that increase selectivity and conversion of ethoxymethylfurfural and acetoxymethylfurfural in their dehydration from fructose.²⁰ Catalytic oxidation of RMF produces the 2,5-furan-dicarboxylic-acid (FDCA) capable of producing polyethylene furanoate (PEF) when polymerized with monoethyleneglycol (MEG). In 2011, Avantium inaugurated a pilot plant for the production of furanics, see Figure 7, and levulinics in Geleen, in the Netherlands, with plans for a 30–50 kt/y facility to be operational in 2015.^{30,31}

The success of the biodiesel industry has brought with it a large supply of glycerol; it still remains a struggle for certain biodiesel producers to find value-added markets for this commodity. Acrolein, an important precursor to acrylic acid and other acrylic monomers, from glycerol has been a target of catalysis research since as early as 1948.³² Activity in this area has escalated substantially in the last decade, with reports of number of different (mainly solid acids and metal oxides) catalytic systems.^{33–41} A number of companies are piloting these technologies and it appears that “bio-acrylics” may be a commercial reality in the next few years.

In another example, ruthenium alkylidenes can self-metathesize unsaturated fatty acids yielding monosaturated diacids with even number of carbons. In a similar way, isomerizing alkoxycarbonylation, using palladium (II) complexes as catalyst, has proven to be an effective way to produce α,ω -diacid esters and their corresponding polycondensates from

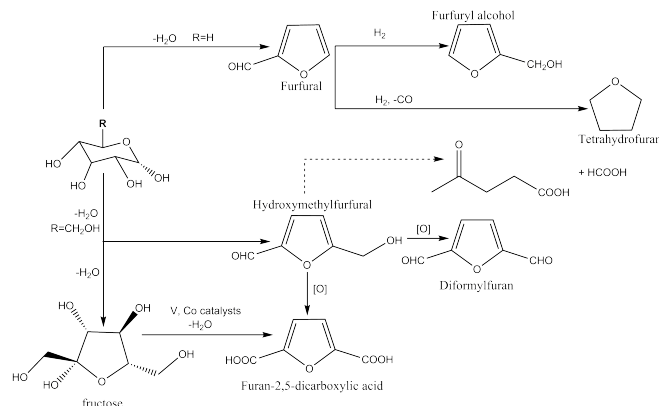


Fig. 7 Diagram of the different transformations of furans from sugars. Image adapted from 20.

fatty acids, *i.e.*, directly from vegetable oils.⁴⁴ Transition metal catalysts have also been used in the hydrogenolysis of petroleum feedstocks. Hydrogenolysis is a reaction in which a hydrogen is added to carbon-carbon or a carbon-heteroatom bond splitting the bond. At present, this technique is being used in the conversion of glycerol and other carbohydrates into higher value products such as propylene glycol and ethylene glycol.²³ Polaert *et al* proposed a method of dehydration of sorbitol to isosorbide in the presence of Amberlyst™ 35, a sulfonic acid ion exchange resin, by using a solvent-free system under microwave heating.⁴⁵ Azadi *et al* were able to produce a lignin derived solvent (LDS) that is effective for selective biomass conversion processes. They make use of LDS in their catalytic process to convert the hemicellulose and cellulose fractions of biomass into high value platform chemicals and biofuels (*i.e.* furfural, 5-hydroxymethylfurfural, levulinic acid, and γ -valerolactone).⁴⁶ Shanks *et al* made use a homogeneous Brønsted acid catalyst and a homogeneous Lewis acid catalyst to produce 5-hydroxymethylfurfural (HMF) from glucose.⁴⁷ The Center for Direct Catalytic Conversion of Biomass to Biofuels, at Purdue University, directed by Maureen McCann, has investigated the use of carbohydrates and other types of biomass and converted them into higher-value products. Maleic acid/zinc chloride is used to fractionate biomass (*i.e.* grasses, hardwood, and softwood) into water-soluble pentoses with high yields. Moreover they are able to produce aromatic co-products by deoxygenating monomeric and dimeric lignin with the use of modified Zn and Pd/C catalyst.⁴⁸ Isa K. Mbaraka and Brent H. Shanks recently reviewed the applications of a new mesoporous heterogenous catalyst in the conversion of oils and fats into chemicals and transportation fuels.⁴⁹

Table 2 Table of common biomonomers along with their starting material, production method, and uses.²⁰

| Monomer | Starting Material | Production Method | Uses |
|-----------------------------|-------------------|---|---|
| Furfural | Xylose | Dehydration using sulfonic acid groups to functionalized micro-mesoporous silica. | Organic solvent, precursor to different solvents (<i>i.e.</i> , furfuryl alcohol) |
| Furan-2,5-dicarboxylic acid | HMF | Oxidation over a Pt/Pb catalyst under strong alkaline conditions | Production of polyesters, as replacement of terephthalic acid |
| Glycerol carbonate | Glycerol | Reaction in diethylene glycol using urea as catalyst ⁴² | Surfactants, coatings, polyurethane foams, hyperbranched polymers |
| Hydroxymethylfurfural | Fructose | Dehydration using 1-H-3-methylimidazolium chloride as the catalyst. ⁴³ | Precursor for various building blocks |
| Isosorbide | Sorbitol | Dehydration of sorbitol in the presence of an acid catalyst | Medicine, biomonomer |
| Lactic acid | Glycerol | Catalytic hydrogenolysis | Production of biodegradable polymers (<i>polyesters</i> , <i>polylactic acid</i>) |
| Propylene glycol | Glycerol | Reduction at high pressured H ₂ over a copper chromite catalyst | Solvent, humectant, food preservative |
| Acrylic Acid | Glycerol | Dehydration/oxidation over acid catalysts | Acrylic polymers |

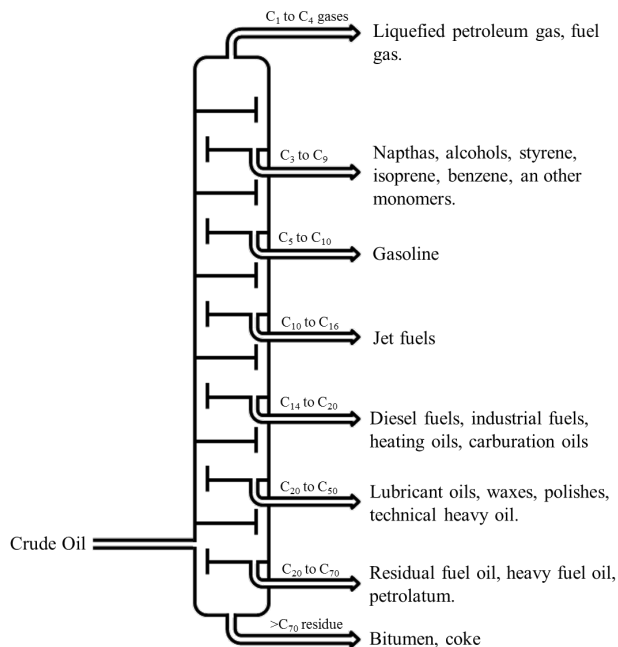


Fig. 8 Diagram with the main byproducts of petroleum.

2.3 Thermal Conversion

Thermal conversions, such as gasification or fast-pyrolysis, have shown promise as the basis of large-scale lignocellulosic biomass processing facilities that mimic the petroleum refin-

ing complex approach to product diversification, see Figure 8. Fast-pyrolysis thermally breaks down biomass into smaller molecules, producing char and a complex fluid known as “bio-oil”. Like petroleum, bio-oil is comprised of a broad distribution of chemical moieties and molecular weights; certain bio-oil fractions may have the potential to be upgraded and separated into monomers or small polymers.⁵⁰ Research in bio-oil derived monomers is still in early stages. Patwardhan *et al* pyrolyzed cellulose and obtained products like: 5-hydroxymethyl furfural, anhydro xylopyranose and 2-furaldehyde.⁵¹ However, a percentage of these products suffered from decomposition during the reaction indicating the need of further research in this area, focused in the optimization and selectivity of downstream products. To date, no bio-oil-based monomeric feedstocks are available in commercial quantities. Nonetheless certain pyrolytic conversions of well-defined substrates have been reported. For example, large quantities of monomers like undecylenic acid (UD) can be obtained by heating ricinoleic acid, see Table 3, under vacuum pyrolysis.⁵² Likewise, Carlsson *et al* were able to produce methacrylic acid from citric acid, see Figure 9. They reacted citric acid in 250 °C and 34.5 MPa water to form itaconic acid and citraconic acid with combined selectivity higher than 90%. At 360°C itaconic acid decarboxylates to form methacrylic acid.^{53,54}

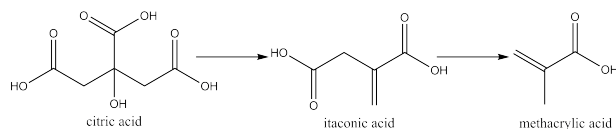


Fig. 9 Production of methacrylic acid from citric acid.

3 “Bioadvantaged” polymers produced directly from biofeedstocks.

Nature obviously has the ability to efficiently produce a diverse array of materials through plants, animals, etc... Raw feedstocks that have their origin in plants, especially in widely grown crops, such as corn or soybeans have received special attention as potential substitutes for materials traditionally derived from petroleum. Vegetable oils, cellulose, starch, chitosan, chitin, alginates, and other polysaccharides are all products and byproducts of plants. These compounds possess the capability, through some chemical modification and with the use of commonly used polymerization techniques, to produce a wide range on plastics.

3.1 Multifunctional Biopolymers

3.1.1 Triglyceride based biopolymers

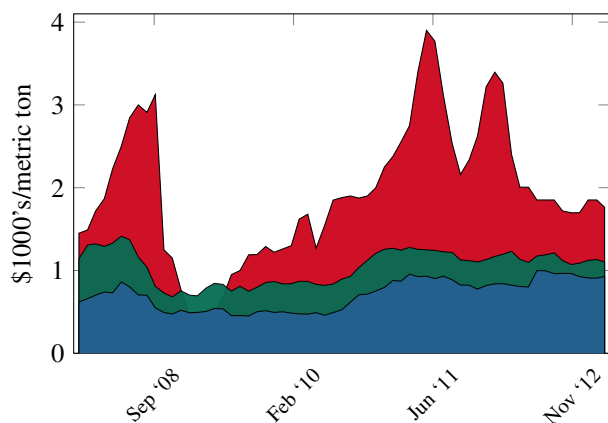


Fig. 10 Spot commodity prices for butadiene (red) and soybean oil (green), and distiller's corn oil (blue).

Vegetable oils are attractive as biomonomers due to their natural abundance of double bonds that serve as facile starting points for the economical transformation into a range of higher-value products. Vegetable oils have been considered as monomeric feedstocks for the plastics industry for over 20 years. In recent years, the market pricing of many vegetable oils has become highly competitive with—and in many cases

more economical than—petrochemical feedstocks. Over the past five years, thanks to government policies like the Energy Independence and Security Act of 2007 that seeks to move the United States toward energy independence by providing subsidies to farmers, spot prices of many vegetable oils, (*e.g.*, soybean oil), have experienced only moderate fluctuations near \$1,000/mt; important monomers such as butadiene, in contrast, have been extremely volatile, reaching well over \$4,000 per mt, as the trends illustrate in Figure 10.

Vegetable oils are essentially composed of triacylglycerols (TAGs), also commonly referred to as triglycerides. TAGs are three-armed fatty esters as shown in Figure 11, tethered at the center with glycerol (glycerine); the three different fatty acids vary significantly by cultivar, and to a lesser extent growing conditions. Their names often arise from their plant or animal sources.⁵⁵ Table 3 provides a list of the industry's most commonly used fatty acids found in vegetable oils, as well as their most usual occurrences. Vegetable oils contain a mixture of saturated and unsaturated fatty acids. Unsaturated fatty acids possess at least one carbon-carbon double bond that can be used to synthesize a broad range of materials with little or no chemical modification.^{5,6,10,55,56}

Naturally occurring oils typically place the oleic and linolenic acid chains on the C₂ carbon of the glycerol, which renders them less sterically accessible. As such, natural triglycerides polymerize quite slowly under typical chain-growth polymerization schemes. The reactivity can be substantially enhanced through chemical modification. Larock *et al* pioneered the use of catalytically conjugated vegetable oils using a rhodium-catalyzed isomerization process.^{5,10,56} Conjugation of double bonds increases the reactivity of the oils, making them more susceptible to polymerization, such as free radical or cationic copolymerization.

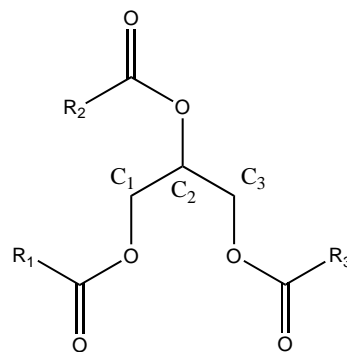
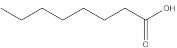
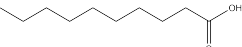
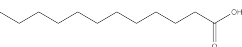


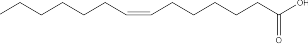
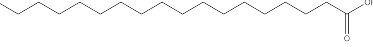
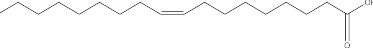


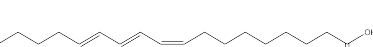






Fig. 11 Structure of a triacylglycerol (TAG) found in vegetable oils, where R_1 , R_2 , and R_3 represent fatty acid chains.

Oleic, linoleic, and linolenic double bonds can be easily epoxidized using hydrogen peroxide through acid-catalyzed or chemoenzymatic routes^{58–60}. Epoxidized soybean oil

Table 3 Table of common fatty acids along with their corresponding formulas and vegetable or animal oil's sources.⁵⁷

| Fatty Acid | Formula | Structure | Occurrence |
|-----------------------|--|---|---|
| Caprylic | C ₈ H ₁₆ O ₂ |  | Coconut oil, babassu oil, milk fat |
| Capric | C ₁₀ H ₂₀ O ₂ |  | Coconut oil, palm kernel oil, milk fat |
| Lauric | C ₁₂ H ₂₄ O ₂ |  | Coconut oil, laurel oil, palm kernel oil, milk fat |
| Myristic | C ₁₄ H ₂₈ O ₂ |  | Coconut oil, palm oil, nutmeg oil |
| Palmitic | C ₁₆ H ₃₂ O ₂ |  | Palm oil, Animal fats (<i>i.e.</i> , lard, tallow) |
| Palmitoleic | C ₁₆ H ₃₀ O ₂ |  | Marine oils (<i>i.e.</i> , sardine or menhaden oil), Macadamia nuts |
| Stearic | C ₁₈ H ₃₆ O ₂ |  | Most animal and plant fats |
| Oleic | C ₁₈ H ₃₄ O ₂ |  | Most animal and plant fats (<i>i.e.</i> , olive oil, pecan oil, canola oil, peanut oil, macadamia nut oil, sesame oil) |
| Linoleic | C ₁₈ H ₃₂ O ₂ |  | Seed oils (<i>i.e.</i> , safflower oil, sunflower oil, soybean oil, cottonseed oil) |
| α -Linolenic | C ₁₈ H ₃₀ O ₂ |  | Linseed oil and in lower levels in many other seed oils |
| α -Eleostearic | C ₁₈ H ₃₀ O ₂ |  | Tung oil, bitter gourd seed oil |
| Ricinoleic | C ₁₈ H ₃₄ O ₃ |  | Castor oil |
| Vernolic | C ₁₈ H ₃₂ O ₃ |  | Vernonia oil |
| Lesquerolic | C ₂₀ H ₃₈ O ₃ |  | Seed oils from the genus <i>Lesquerella</i> |
| Timnodonic | C ₂₀ H ₃₀ O ₂ |  | Marine oils (<i>i.e.</i> , sardine, cod liver, herring, mackerel, salmon, menhaden oil) |

(ESO) has many commercial uses (*e.g.*, as a plasticizer in poly(vinyl chloride)); hydrolysis of the epoxy groups yields diols, which can then be used to produce polyurethanes.⁶¹ The market entry of soy-based polyurethane foams has steadily gained traction over the past decade, now appearing in cushions in the automotive, furniture, and bedding industries.^{62,63} Moreover, the glycidic moieties readily undergo ring opening and condensation with acrylic acid to form acrylated oils, see Figure 12. Acrylated epoxidized soybean oil (AESO) is commercially produced by Allnex by the name of Ebecryl®860. Due to their intrinsically multifunctional nature,

TAGs rapidly approach gelation under typical free radical or cationic polymerization conditions. For this reason, until recently only thermoset plastics have been considered based on vegetable oils. Without copolymerization, polymerized vegetable oils range from soft rubbers with $T_g \approx -40^\circ\text{C}$ to low modulus plastics with T_g near or slightly above room temperature. These properties can be further customized with statistical copolymerization during the cure process.^{64,65} The conjugated acrylic bonds attached to the triglyceride backbone open the possibility of using controlled radical polymerizations, *i.e.*, atom transfer radical polymerization (ATRP) or

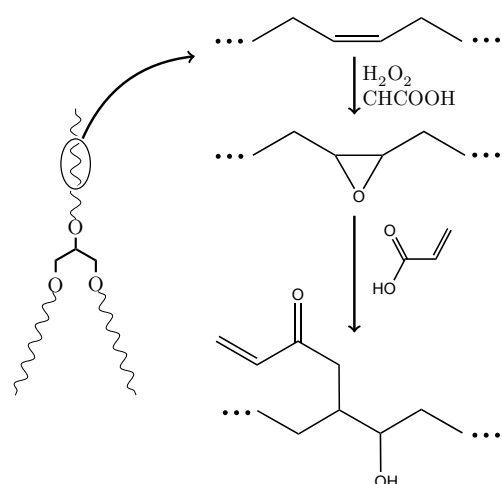


Fig. 12 Epoxidation and acrylation process of triglycerides using formic acid catalyzed oxidation with hydrogen peroxide, followed by base-catalyzed ring-opening with acrylic acid.

reverse addition-fragmentation chain transfer polymerization (RAFT), to synthesize polymers.⁶⁶ Evidently these methods shift the gel point to high conversion such that thermoplastic rubbers and even block copolymers thereof may be produced from multifunctional monomers such as AESO. Triglyceride molecules can undergo methanolysis to form monoglycerides and diglycerides that can also be subject to the mentioned modifications. These fatty esters can be prepared to have only a single functional site per molecule, and also form thermoplastics, although the costs associated with separations may be prohibitive for commercialization.^{67,68} Lligadas *et al* made use of diols from oleic acid (OL) and undecylenic acid (UD) as platform chemical for thermoplastic polyurethanes. They were able to combine isocyanates with vegetable oil based polyols to produce polyurethanes with characteristics similar to the petroleum derived polyols.⁵²

3.1.2 Polyols Molecules with multiple hydroxyl groups (polyols) like: glycerol, sorbitol, arabinitol, or xylitol, can be subject to modification by: acrylation, alkylation, or chlorination of their alcohol groups making them suitable of polymerization or copolymerization by different synthetic approaches. Free radical polymerization, photopolymerization, controlled radical polymerization, acceptor-donor polymerization are some of the routes being adopted to produce polyol based polymers.⁶⁹ However due to the multifunctional nature of these molecules controlled radical polymerization techniques such as: atom-transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), or reversible addition-fragmentation chain transfer polymerization (RAFT) have been only applied to monofunctional modified

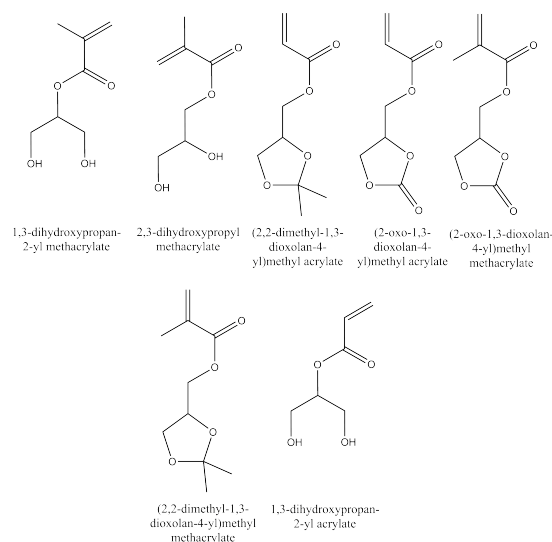


Fig. 13 Examples of monofunctional modified glycerol molecules.

olecules, see Figure 13. Pham *et al.* review various radical polymerizations techniques for monofunctional and multifunctional glycerol-based monomers.⁶⁹

Polycondensation of polyols a more traditional and widely used way of synthesizing polymers and copolymers.^{69–72} This relatively simplistic chemical reaction has produced a wide variety of biodegradable biopolymers such as poly(ethylene glycol-*co*-citric acid),⁷³ poly(polyol sebacate),⁷⁴ poly(glycerol citrate),⁷⁵ poly(sorbitol citric sebacate),⁷⁰ poly(sorbitol tartaric sebacate),⁷⁰ poly(1,2-glycerol carbonate),⁷¹ between others. These polymers are considered to be the new generation of materials for biomedical applications.⁷⁰

3.1.3 Polymerization Techniques

For the past several decades polymerization of vegetable oils was reserved to the application of traditional cationic and free radical polymerization techniques. Larock *et al* pioneered research in a variety of polymers, from vegetable oils, ranging from soft rubbers to hard, rigid materials.^{5,8,10,55,56,76,77} Beginning with commercially available soybean oil (SBO) and low saturation soybean oil (LSS), they first conjugated the C=C double bonds, followed by the use cationic polymerization with boron trifluoride diethyletherate as their catalyst. Lu *et al* synthesized soybean-oil-based waterborne polyurethane films with different properties ranging elastomeric polymers to rigid plastics by changing the polyol functionality and hard segment content of the polymers.⁷⁸ They were also able to create thermosetting resins synthesized from SBO that have the potential be used in sheet molding compound applications. These resins were synthesized

by introducing acid functionality into the triglycerides. The acid groups reacted with divalent metallic oxides or hydroxides forming the sheet, while the C=C groups were subject to free radical polymerization.⁷⁹ Andjelkovic *et al* were able to synthesize homopolymers from SBO which usually resulting in viscous oils or soft elastic materials with limited industrial application, nonetheless they have copolymerized SBO with divinylbenzene and styrene to enhance the properties of the materials.⁵ Incorporation of fillers (*i.e.*, organoclays) and bio-fillers (*i.e.*, kenaf fiber, wood flour, hemp, flax) into vegetable oils has also been studied as ways of reinforcing and improving mechanical properties of polymers.^{76,80,81} The Affordable Composites from Renewable Resources Group at the University of Delaware (ACRES) led by Richard P. Wool, has also pioneered the use of vegetable oils to synthesize different bio-based materials, such as sheet molding composites, elastomers, coatings, foams, etc. Bunker *et al* were able to synthesize pressure sensitive adhesives using miniemulsion polymerization of acrylatedmethyl oleate, a monoglyceride derived from SBO. The polymers produced were comparable to their petroleum counterparts.^{67,82} Zhu *et al* were able to generate an elastic network based on acrylated oleic methyl ester through bulk polymerization using ethylene glycol as the crosslinker. Obtaining a high molecular weight linear polymer using miniemulsion polymerization.⁸³ Bonnaillie *et al* were able to create a thermosetting foam system using a pressurized carbon dioxide foaming process of AESO.⁸⁴ Wool *et al.* were able to synthesize liquid molding resins that are able to cure into high modulus thermosetting polymers and composites using triglycerides derived from plant oils.^{85,86} Castor oil was reacted with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride to give a norbornenyl-functionalized bicyclic castor oil (BCO) derivative, see Figure 14. BCO was then copolymerized, by ring-opening metathesis polymerization, with cyclooctene catalyzed by a G2 catalyst, producing rubbery thermosets with T_g values from -14 to 1 °C.⁵⁵ Richard Marvey reviews the use of sunflower-based feedstocks for nonfood applications, where it has been used in the production of bio-fuels, biopolymers, and other fine chemical applications.⁸⁷

For the past several decades research done on vegetable oils yielded highly crosslinked materials. Uncontrolled chain branching and crosslinking is inevitable using conventional polymerization routes (*i.e.*, cationic and free radical) due to the multifunctional nature of triglycerides, multiple initiation sites along the chain backbone, and chain transfer/termination reactions. Each polytriglyceride repeat unit has the potential to crosslink with at least one other polytriglyceride; when approximately a fraction of $1/N$ of such units have crosslinked (N denotes the number of repeat units in a polymer chain), the polymers are said to be at their “gel point” at which an infinite polymer network has formed and the material is a thermoset. This characteristic limits the applications in which they can

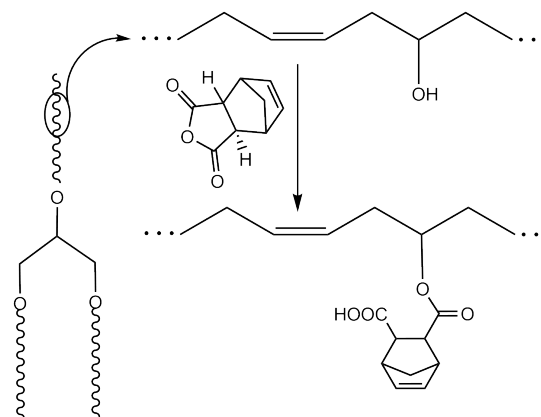


Fig. 14 Image of a the addition of the norbornene by the reaction of castor oil with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride.

be used. Ford Motor Company has pioneered in the use of bio-based thermosets with the use of soy-based polyurethane foams. They are replacing 40% of the standard petroleum-based polyol, substance that makes up a vehicle's seat cushions, seat backs, armrests and head restraints.

Recently, our group has been able to synthesize thermoplastic elastomers using AESO and styrene with the use of controlled radical polymerization (ATRP and RAFT).^{66,88} Controlled radical polymerization such as ATRP limits the number of initiation sites and drastically reduce the rate of chain transfer and termination reactions introducing the capability of producing custom chain architectures such as block copolymers (BCPs). The poly(styrene-*b*-AESO-*b*-styrene) (PS-PAESO-PS) triblock copolymers produced had similar physical properties as their petroleum counterparts. They have the ability to microphase separate demonstrating that there is a strong incompatibility between the two blocks, hence the formation of a rich AESO and styrene microdomains. The TEM image of the PS-PAESO-PS triblock stained with osmium tetroxide OsO_4 reveals a semi-periodic microstructure having black colored styrene islands surrounded by the lighter AESO regions.

This accomplishment widens the applications vegetable oil can be used in, as the materials produced can be processed thanks to their thermoplastic qualities. Initial trials were conducted to replace styrene-butadiene-styrene (SBS) type polymers used in asphalt (bitumen) modification. Bitumen modified with different soybean-based triblock copolymers was compared to asphalt modified with two commercially available SBS polymers and with neat bitumen. Rheological laboratory testing results of the bitumen-polymer blends show the biopolymers improves the complex shear modulus of the asphalt to a similar and even greater extent as the commercially available SBS polymers, see Figure 16, even when using 1% less polymer by weight.

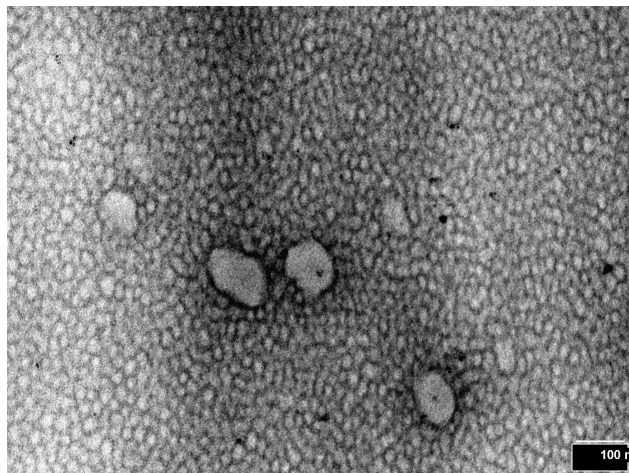


Fig. 15 TEM image of the poly(styrene-*b*-AESO-*b*-styrene) triblock copolymer, image shows a semi-ordered structure where the black islands are styrene and the lighter regions are the AESO.

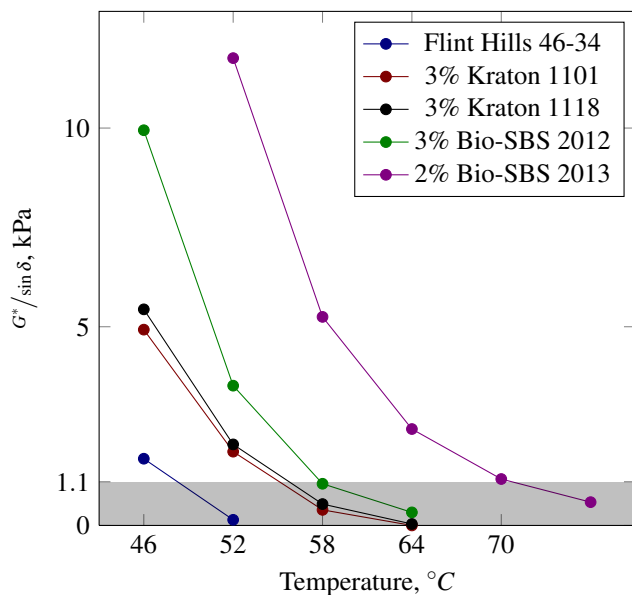


Fig. 16 Graph showing the complex shear modulus as a function of temperature of Flint Hills 46-34 neat bitumen, bitumen modified with 2% and 3% by mass of poly(styrene-*b*-AESO-*b*-styrene) triblock, and of bitumen modified with 3% *Kraton* 1101 and *Kraton* 1118. The shadowed area represents industry's failure specification.

3.2 Biomass: lignin, cellulose, hemicellulose, and starch

Crop residues like: straw, stems, hulls, and milling byproducts (*e.g.*, brans) from barley, corn, oat, rice, soybean, wheat, amongst others, are composed of components like cellulose, starch, lignin, and pentosan.⁸⁹ These molecules can have the

capability of being able to serve as prepolymeric materials when modified (*e.g.* acrylation of the hydroxyl groups) and as monomers when broken down by techniques such as: pyrolysis, hydrolysis, etc.

3.2.1 Lignin Lignin which constitute ca. 95% of the total plant biomass is mainly composed of phenylpropane units containing methoxy and hydroxyl groups, see Figure 17.⁹⁰ These groups can be modified to yield both thermoplastic and cross-linked polymers (*i.e.*, etherified lignin with methyl methacrylate). Although lignin can also be modified with acetonitrile, chloroacetic acid, and alkyl chlorides among others broadening the possibilities of polymerization and copolymerization. Properties of these thermoplastic polymers can be compared to petroleum-based polymers.⁹¹ Glasser *et al* devised a method to use lignin as a prepolymeric material. They hydroxyalkyl modified lignin making it almost non-phenolic and solvent soluble making it suitable to polymerization by known methods.⁹² Hydroxybutyl lignin as well as lignin were modified by reaction with isocyanatoethyl methacrylate (IEM) and copolymerized with styrene and methyl methacrylate. These reactions produced network polymers with gel structures that showed an increase in the soluble fraction as the percent of vinyl equivalents increased.⁹³

Current technology is able to transform lignin in chemicals like: acetylene and ethylene through fast thermolysis, acetic acid, phenol, methane, etc. through pyrolysis, phenols, cresols, etc. through hydrogenation, phenol and substituted phenols through hydrolysis, vanillin, dimethylsulfide, methyl mercaptan, etc. through oxidative transformation, ferulic, vanillic, coumaric and other acids and highly polymerized lignin through microbial conversions, oxidized lignin (used in paints and coatings) through enzymatic oxidation, and phenolic acids and catechol through alkali fusion.¹⁶ These bio-based monomers are chemically identical to those currently derived from petroleum.

3.2.2 Cellulose and Hemicellulose Cellulose (hemicellulose, a shorter version of cellulose) is the primary structural component of green plants, see Figure 18, and the most abundant renewable resource on the planet. It is estimated that 830 million tons of cellulose are produced every year product of photosynthesis.^{91,94} Cellulose has been used to make cellophane and more recently modal, a bio-based textile. Its hydroxyl groups can be chemically modified to allow polymerization and produce derivatives with useful properties (*i.e.*, carboxymethylcellulose, methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, cellulose acetate, cellulose acetate propionate, or cellulose xanthate). These products can be then used in the manufacturing of fibers, films and thermoplastics for injection molding.^{89,94-96}

3.2.3 Starch Starch, a molecule composed of a large number of glucose molecules (Figure 19), has been used since

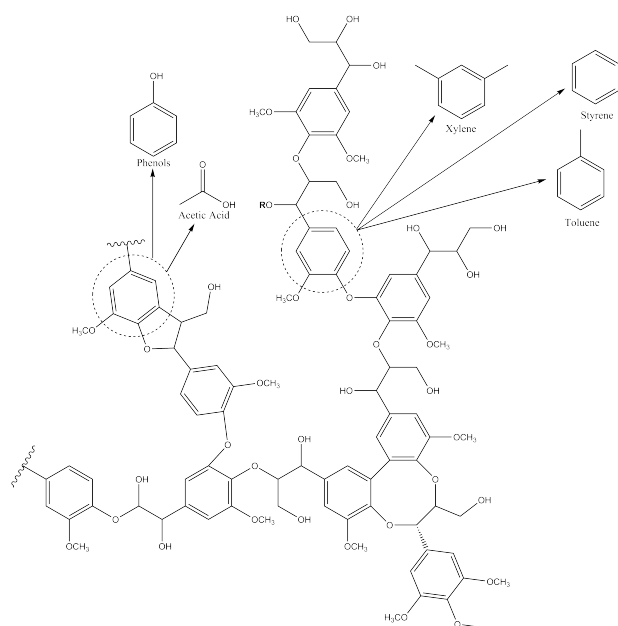


Fig. 17 Representation of a lignin molecule with potential chemicals that can be derived from it.

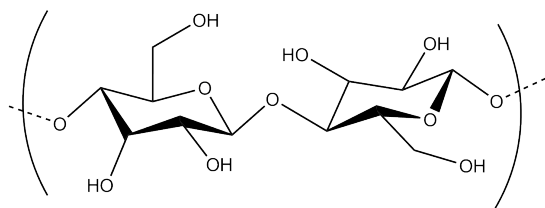


Fig. 18 Image of a cellulose molecule. The molecule possesses several hydroxyl groups capable of being modified to allow different polymerization techniques. Hemicellulose is composed of only five to six carbon sugars.

the 1980s combined with plasticisers and additives to produce starch-based thermoplastic polymers. Large amounts of starch can be obtained from tubers, cereals, and seeds. Chaleat *et al* at the University of Queensland, have developed thermoplastic starch polymers (TPS) blends and nanocomposite blends with enhanced properties. They were able to process TPS at higher temperatures (without suffering degradation by fragmentation) which enabled better melt mixing, increase clarity and improve tensile properties.⁹⁷ Starch acetate product of the acetylation of starch has been used to cast films impermeable to water but impermeable to water vapor. Acetylated starch is more soluble and is considerably more hydrophobic than native starch and according to Chandra *et al.* has shown better retention of tensile properties when exposed to water.⁹⁸ Starch

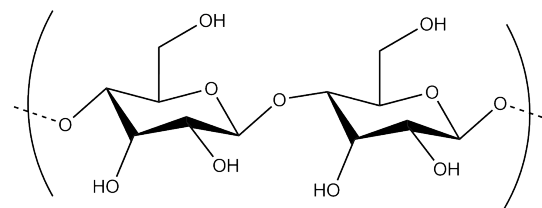


Fig. 19 Diagram representing a starch molecule. Starch molecules are made of α -glucose repeat unit while cellulose molecules are composed of β -glucose molecules.

has also been used as a filler into disposable polyvinyl chloride (PVC) plastics and used in agricultural applications.⁹⁹ Hydroxyl groups in starch have been reacted with isocyanates to produce resins with improves solvent resistance and strength qualities.^{94,98}

3.3 Plant extraction

Plants have the capability of naturally producing monomers and polymers. Natural rubber, the most known polymer extracted from plants, has been widely studied and characterized throughout the years. Latex, the main source of natural rubber, is a milky colored sap extracted from trees. It posses a complex composition, that includes alkaloids, terpenoid compounds, resins, starch oils, and a large number of proteins and other enzymes. Its composition is greatly dependent on its extraction source. Currently, the main source of natural rubber comes from latex extracted from the *Havea brasiliensis* tree a member of the *Euphorbiaceae* family.¹⁰⁰ Nonetheless there are many other tree sources for latex: *Parthenium argentatum*, *Taraxacum kok-saghyz*, *Scorzonera tau-saghyz*, *Scorzonera uzbekistanica*, *Ficus benghalensis*, the fig tree *Ficus elastica* and *Ficus carica*, in lettuces species such as *Lactuca seriola* and *Lactuca sativa*, and in other shrub species such as *Euphorbia etherophylla*, *Euphorbia lactiflua*, and *Euphorbia characias*.¹⁰⁰ Common extraction methods, of natural rubber, include the use of acetone, trichloroacetic acid, octyl phenol ethoxylate, or acetic acid, followed by cycles of solubilization in cyclohexane and precipitation in ethanol. Extraction yields tend to be low, less than 15% by weight of the latex collected from the plant, *i.e.* the *Euphorbia characias*.¹⁰⁰

Other natural polymers extracted from plants include: gum acacia or gum arabic, extracted from the stems and branches of the *Acacia senegal* plant, and it is used in oral and topical pharmaceutical formulas as a suspending and emulsifying agent. Agar, extracted from the cell walls of some species of red algae or sea weed (*Gelidium*, *Gracilaria*, *Acanthopeltis*, *Ceramium*, *Pterocladia* found in the Pacific and Indian oceans) and used as culture media in microbiology.⁹⁵ Alginate is obtained from the *Phaeophyceae* brown seaweed and used as

controlled-release systems of drugs. Carrageenan obtained by the extraction from members of the Rhodophyceae class (*i.e.*, *Kappaphycus cottonii*, *Eucheuma spinosum*, and *Gigartina stellata*) is used as gelling and thickening agents. Guar gum obtained from the ground endosperms of the *Cyamopsis tetragonolobus* plant and used as a drug delivery system because of its high water swellability, non-toxicity, and low cost. These polymers, and others listed by Rajesh *et al.*, are currently used mainly for drug-delivery applications, thanks to their excellent biocompatibility and biodegradability properties.⁹⁵

Plant derived vinyl monomers can be classified into three categories according to their chemical structure: olefinic, styrenic, and (meth)acrylic monomers. An example of a methacrylic monomer originated from plants is: α -Methylene- γ -butyrolactone (MBL) or Tulipalin A, present in white tulips. MBL belongs to the sesquiterpene lactone family and is considered as an analog to methyl methacrylate (MMA).¹⁰¹ Table 4 lists several plant derived monomers with their corresponding petroleum derived counterparts.

4 Conclusions

Concerns in the availability of petroleum feedstocks has increased the research and development of new biomaterials, however only a very low volume of renewable is being used to manufacture consumer goods.¹⁶ Due to the fact that industry is mostly driven by economics, production processes tend to be chosen according to their potential revenue. Different ways of making renewable monomers and polymers are currently studied, each one having their advantages and disadvantages.

The primary advantage of “Bioreplacement” monomers is clear: provided that product purities are brought to an acceptable level the polymers produced with these technologies are indistinguishable from their petroleum-based counterparts. Decades of research in biocatalysis and synthetic biology are beginning to be commercially fruitful. We feel it will be some number of decades, however, before all of the challenges in the complete replacement (with economic parity) of our portfolio of petrochemical monomers has been replaced with their equivalents from biomass.

“Bioadvantaged” materials face an altogether different set of challenges. The “food vs. fuel” debate is an important component of the public perception. The polymers that arise from this arena are in many cases similar to, but not equivalent, in terms of properties or cost. New products, even when very similar in performance and/or cost to the *status quo*, must navigate through a battery of certifications and regulatory obstacles before reaching the market; soy-based polyurethanes and the poly(ethylene terephthalate)-like materials produced by Avantium serve as examples that these hurdles can in fact be surmounted. Moreover, the high-value polymers produced in this arena will be an important component in the long-term

economic stability of tomorrow’s biorefinery complex. Innovative applications of chemistry will continue to transform the waste streams of today into the coproduct stream of tomorrow.

As time and technology progress, additional opportunities will arise for biopolymers to replace their petroleum-based counterparts. Sadly, these technologies will only be adopted if the price is right and there is money to be made. Nonetheless, the future for biopolymers looks brighter as more resources are being allocated in the development of the ultimate “green” polymer.

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Table 4 Table of plant derived monomers with their corresponding petroleum derived counterparts.¹⁰¹

| Plant based monomer | Type | Chemical Structure | Petroleum Counterpart |
|---------------------|---------------------|--------------------|--|
| α -pinene | Olefinic monomer | | Ethylene, propylene, 1,3-butadiene, etc. |
| β -pinene | Olefinic monomer | | Ethylene, propylene, 1,3-butadiene, etc. |
| Limonene | Olefinic monomer | | Ethylene, propylene, 1,3-butadiene, etc. |
| Myrcene | Olefinic monomer | | Ethylene, propylene, 1,3-butadiene, etc. |
| Anethole | Styrenic monomer | | Styrene, α -methyl styrene, etc. |
| Isosafrole | Styrenic monomer | | Styrene, α -methyl styrene, etc. |
| Isoeugenol | Styrenic monomer | | Styrene, α -methyl styrene, etc. |
| Cinnamates | Styrenic monomer | | Styrene, α -methyl styrene, etc. |
| MLB | Methacrylic monomer | | Methyl methacrylate, n-butyl acrylates, etc. |
| Itaconic acid | Methacrylic monomer | | Methyl methacrylate, n-butyl acrylates, etc. |

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Table of Contents



In this perspective we compare and contrast two distinct approaches to the economical realization of biomaterials.