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Introduction

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1.1 Introduction

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The discovery and development of synthetic polymeric materials in the twentieth century is undisputedly recognized as one of the most significant inventions humans have made to improve the quality of life. Durability, light weight, processability, and diverse physiochemical properties are just a few merits why polymeric materials are widely used for the manufacture of simple water bottles to setting up modern space stations. Outstanding processability features along with adequate physical properties have resulted in polymeric materials displacing many other materials, such as wood, metal, and glass to a considerable extent. Packaging, construction, transportation, aerospace, biomedical, energy, and military are few examples of industrial sectors, where polymeric materials prevail. Global production of plastic has risen from 204 million tons in 2002 to about 299 million tons in 2013 [1]. Manufacture of non-natural polymers is largely associated with the utilization of essentially non-renewable fossil feedstocks, either natural gas or petroleum. Approximately, 5–8% of the global oil production is used for plastic production [2]. Accompanying environmental problems include, but are not limited to, generation of solid waste that accumulates in landfills and oceans, production pollution and related environmental problems [3]. A major underlying issue in the use of plastics is the enormous carbon footprint associated with their production as portrayed by burning 1 kg of plastics to generate about 3–6 kg of CO_2 (including production and incineration) [2]. In addition, their impervious nature to enzymatic breakdown and “linear” consumption as opposed to natural counterparts results in relentless generation of solid waste from most commercial polymers. Although polymers can be recycled to produce new materials or incinerated to recover its heating source value, such an endeavor is neither clearly understood by the majority of consumers nor technological advances are available in most parts of the world. Depleting oil reserves as well as these detrimental environmental impacts observed in the twentyfirst century have driven government, academia, private sectors, and non-profit organizations to explore sustainable polymers from renewable biomass as a long-term alternative. In addition, the consumers’ preference as well as the governmental landscape has shaped in favor of sustainable products for a greener

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environment. Significant advancements have been made to discover sustainable polymers that are cost-effective to manufacture, as well as compete or out-perform traditional materials in mechanical aspects as well as from environmental standpoints [4]. The valuable contributions to the field by several recent books [5, 6] and reviews [7–11] broadly discuss about sustainable polymeric materials. Our objective is to provide a perspective of the efforts to convert small molecular biomass into sustainable polymers in different continents. This introductory chapter overviews sustainable polymers in general and briefly summarizes the content of each chapter afterward.

1.2 Sustainable Polymers

Given the influence of polymers as an indispensable resource for the modern society, it should be taken as a firm concern for sustainable development. There are many statements to define the term of sustainability. For example, “Development that meets the needs of the present without compromising the ability of future generations to meet their own needs” is the working definition provided by the report *Our Common Future*, published in 1987 by the World Commission on Environment and Development [12]. In most cases, the terms renewable polymers and sustainable polymers are used with overlapping meanings and without any distinction. Contrary to common belief, it should be noted that not all renewable polymers are sustainable. Typically, renewable polymers are made from renewable chemical feedstocks. However, to be sustainable, those renewable polymers should be more environmentally friendly to produce and use. Sustainable polymers should demand less non-renewable chemicals or energy for their synthesis and processing, make less pollution emissions, and be amenable to be decomposed and even composted after reaching their service lifetime (Figure 1.1).

The past two decades have overseen a great level of scientific advancements that have paved paths toward the primary stages of an era of sustainability, carbon neutrality, and independence from petroleum sources for making polymeric materials. Rapid expansion of this field can be visualized by the exponential

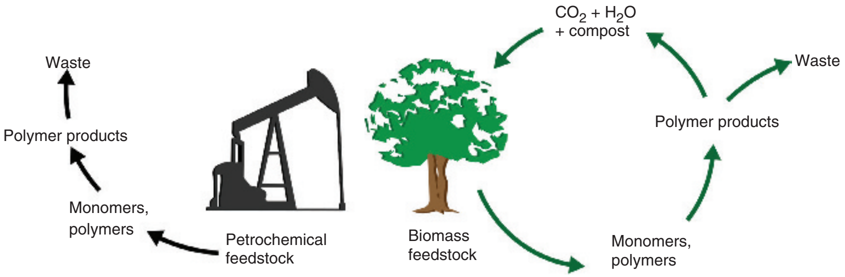


Figure 1.1 A comparison between traditional petrochemical-based polymers and sustainable polymers.

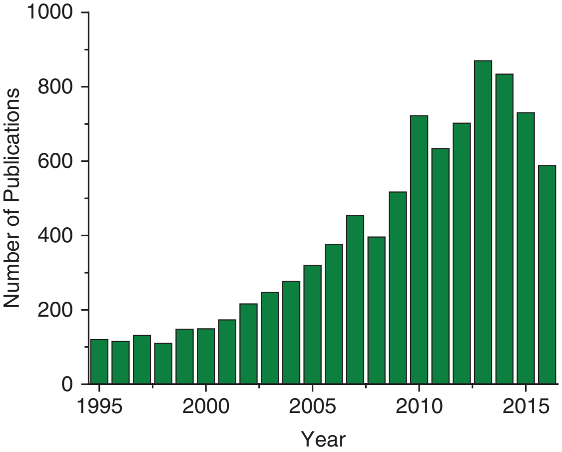


Figure 1.2 Scientific publications with the keyword "sustainable polymers" published from 1995 to 2016. (SciFinder.)

increase in the number of scientific reports published on sustainable polymers in recent years (Figure 1.2), appearance of dedicated scientific journals such as *ACS Sustainable Chemistry and Engineering* and the steady increase of the market share of renewable bio-based material products, for example, NatureWorks Ingeo™, DuPont™ Sorona®. Although the worldwide production capacity of bio-based polymers is only 5.7 million tons (2% of total polymer capability) in 2014, it is expected to triple to nearly 17 million tons by 2020. The compound annual growth rate (CAGR) for the production capacity of bio-based polymers is impressive at about 20%, whereas the CAGR for the petroleum-based polymers is at 3–4% [13].

The principal aspects of the concept of sustainable materials are to utilize renewable biomass resources for raw materials as opposed to petrochemical sources and to ideally incorporate degradability to the novel materials such that sustainable polymers inherit a cyclic life cycle considering the time factor.

As illustrated in Figure 1.3, the plastic industry has a considerable influence on global carbon cycle. "Fossil-sourced" carbon dioxide release is so overwhelming that natural photosynthesis or other natural sinks cannot effectively moderate for the equilibration of the global ecosystem. However, a material feedstock transition from fossil-based chemicals to the renewable biomass-derived compounds for the production of sustainable polymer materials would diminish their contribution to the greenhouse effects because of their low carbon or carbon neutral characteristics. As against the geographically uneven distributions of world-wide fossil oil resources, natural biomass is widely available in many geographic areas for the development of local or regional supply of chemical and material feedstock resources without significant technological intervention. In addition, the market price fluctuations would be much favorable compared to those from crude oil resources and can provide a steady and stable supply over a long period of time.

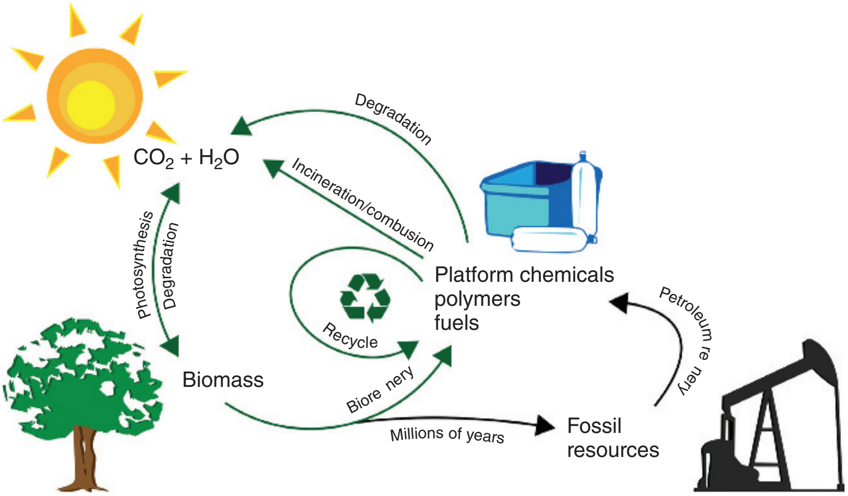


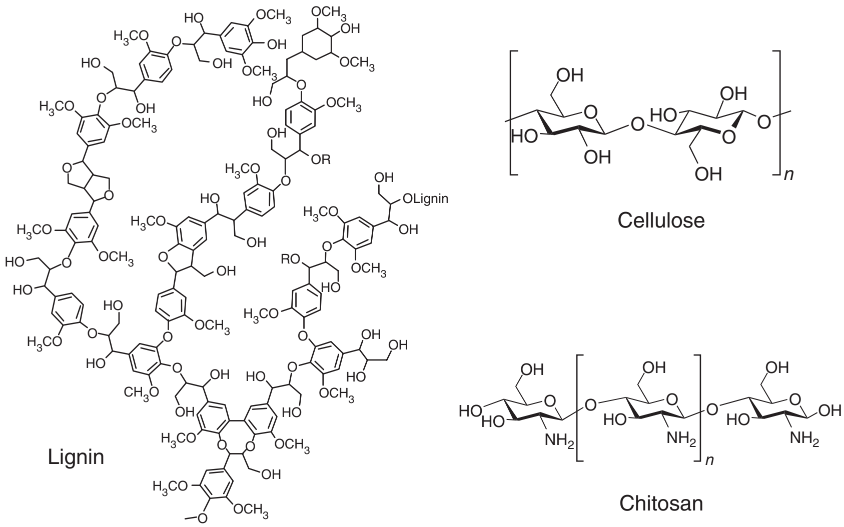
Figure 1.3 A schematic diagram to illustrate the concepts of sustainable polymers from biomass.

1.3 Biomass Resources for Sustainable Polymers

Global primary production of the biosphere exceeds 100 billion metric tons of carbon per year, which include contributions from both terrestrial and marine communities [14]. It is obvious that this primary production either mostly ends up in food chains or decays and sediments. Useful raw materials for making sustainable polymers are hidden in the biomass. Unfortunately, the utilization of biomass for sustainable polymer production is lagging behind largely due to the price and property competitiveness of fossil oil counterparts, as well as their well-established routine processing technologies for polymer industry. In addition, as the human population grows rapidly, the demand for biomass usage for food and energy purposes has perceived an escalating interest. Nevertheless, a modern "gold rush" is witnessed in recent years to unlock the true potential of biomass chemicals. Generation of sustainable polymers from agricultural feedstocks such as sugar cane, soybean, corn, potatoes, and other plants has limitations due to competing food necessities. Therefore, there are significant efforts that focus on developing nonfood renewable biomass including waste resources, such as lignocellulosic resources, paper mill waste, agricultural waste, and food waste.

1.3.1 Natural Biopolymers

Naturally occurring biopolymers such as rubber, cotton, and starch were used extensively for a long time before the invention of synthetic polymers less than a century ago. In recent years, the reviving efforts of biopolymer research in materials science have been very active. In particular, there is enormous growth in the research on biopolymers such as cellulose, chitosan, and lignin (Figure 1.4) to discover novel hybrid materials with improved properties as well as for commercialization.



Lignin

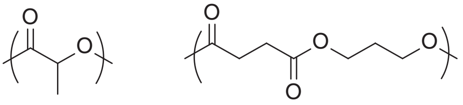
Cellulose

Chitosan

Figure 1.4 Examples of a few naturally occurring biopolymers.

Chapter 2 of this book by George Chen *et al.* is dedicated to the description of the research frontiers of polyhydroxyalkanoates (PHAs), a family of biodegradable linear polyesters, which are produced by bacterial fermentation of sugars and lipids [15]. Their structural diversity and analogy to plastics makes them viable candidates to replace synthetic thermoplastics. With modern technologies, the PHA research has expanded to produce block copolymers and graft copolymers to tailor the thermal and other physical properties of PHAs using a variety of bacteria including new isolates and metabolically engineered species.

Recent advances in biotechnology have made the use of biochemical means such as microbial fermentation of various biomass feedstocks in the production of bio-based monomers such as lactic acid, succinic acid, and itaconic acid to be more cost-effective. These monomers are then polymerized using conventional methods. Examples of polymers include poly(lactic acid), poly(butylene succinate), poly(ethylene), and poly(itaconic acid) (Figure 1.5). Polylactide or poly(lactic acid) is a type of thermoplastic polyester that is one of the most promising commercialized renewable polymers due to its biodegradability, biocompatibility, and sufficient mechanical properties. Long chain branched polylactides (LCB PLAs) have been introduced to overcome shortages of linear versions. In Chapter 3, Zhigang Wang *et al.* summarize and discuss the recent



Poly(lactic acid)

Poly(butylene succinate)

Figure 1.5 Sustainable polymers derived from biotechnologically derived monomers.

advances in the fabrication and structural characterizations of LCB PLAs from the "bottom-down" strategy.

1.3.2 Monomers and Polymers from Biomass

Compared to chemicals from fossil oil refinery, one major drawback in biomass feedstocks is its direct conversion into high value chemicals that can be used for polymerizations [16]. Technological infancy for such enterprises as well as the operating cost makes it far from feasible for large-scale production. However, modern chemists and material scientists have cracked down most of these problems and have achieved varying degrees of success. Top biomass platform molecules produced from sugars, which were recognized by the US Department of Energy, are shown in Figure 1.6 [17]. A recognized approach for transforming raw biomass into marketplace chemicals is provided by the concept of biorefinery [18]. In a biorefinery, raw biomass feedstock is processed to generate value-added platform chemicals. The products from biorefinery are expected to replace fossil oil-based products resulting from petrochemical refinery.

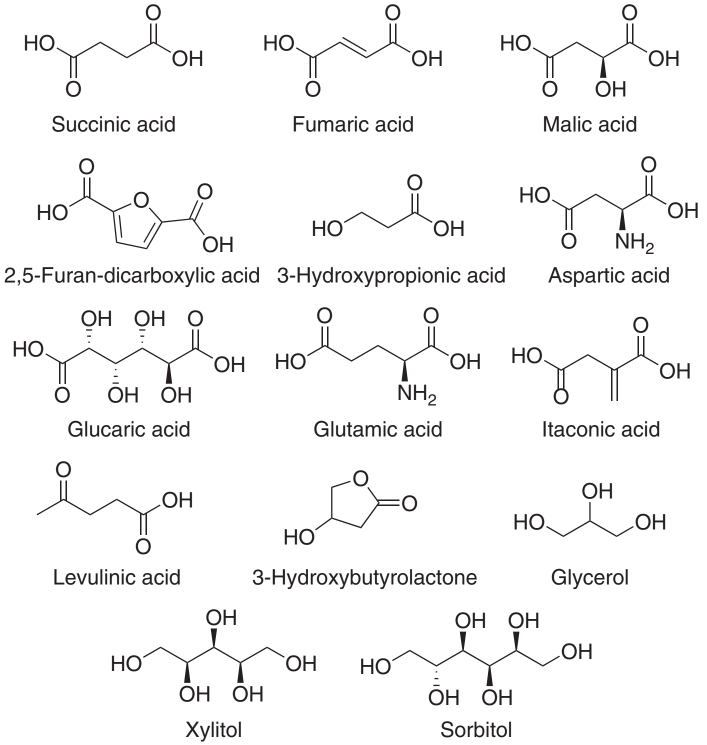


Figure 1.6 Top biomass platform molecules produced from sugars recognized by the US Department of Energy.

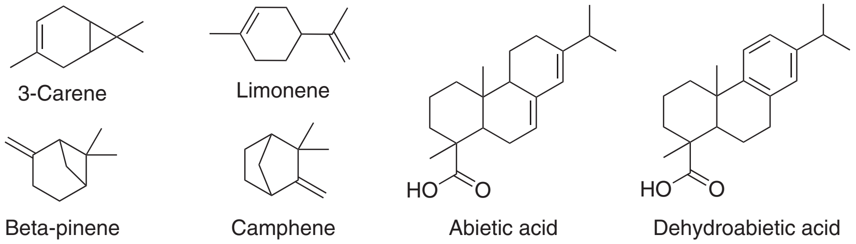


Figure 1.7 Terpene-based compounds used in renewable polymers.

Besides these chemicals, hydrocarbon-rich biomass such as terpenes including pinene, limonene, resin acids (Figure 1.7), and furans, as well as fatty acids from vegetable oils, cashew nut shell liquid are promising candidates for sustainable polymer preparation [7, 8, 11, 19, 20].

Terpenes are the largest and most abundant class of natural hydrocarbons found in nature. Various olefinic terpenes have been incorporated into polymeric materials. Sustainable vinyl polymers prepared via controlled polymerization of terpenes is discussed in Chapter 4 by Masami Kamigaito *et al.* Resin acids are naturally produced by conifer trees and the production is more than 1 million tons annually. This largely overlooked resource is gaining interest as a source for the polymer industry. Chapter 5 by Jinwen Zhang *et al.* delivers a general overview of properties and novel applications of rosin and turpentine-based polyurethane materials. Fuxiang Chu *et al.* provide a well-detailed discussion about rosin-derived monomers and their progress in polymer application in Chapter 6. Chapter 7 by Phil Hurd *et al.* is based on the progression of crude tall oil feedstock to fractionated products including terpenes isolated from crude sulfate turpentine, tall oil fatty acids, and rosin acids from the distillation process involved in pine chemicals industry.

Triglycerides from natural plant oils are a widely abundant source of biomass to produce sustainable polymers and materials. Various types of thermoset polymers have been developed using plant oils. In Chapter 8, Chuanbing Tang *et al.* review recent advances on mono-functional monomers derived from plant oils that have been pursued for the preparation of re-processable linear polymers with pendent fatty chains. Energy efficient and environmentally attractive technologies such as photo-initiated cationic polymerization are in demand for sustainable polymer research. Structure–property relationships of epoxy thermoset networks developed for UV-cure coating applications using photoinitiated cationic polymerization of epoxidized vegetable oils are provided in Chapter 9 by Chang Y. Ryu *et al.*

Lignocellulosic biomass originated during soybean harvesting and industrial soybean grain and sugarcane are useful sources of chemicals and polymers such as cellulose micro/nanofibrils and nanocrystals, polyols, and lignin. Chapter 10 by Delia R. Tapia-Blácido *et al.* describes the recent advances in biopolymers from sugarcane and soybean lignocellulosic biomass. Starch-based thermoplastic products have been used in many areas, such as food packaging, coating/adhesions/laminations. Renewable and biodegradable polymer materials

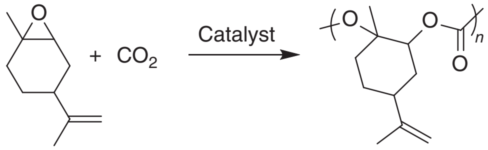


Figure 1.8 Copolymerization of limonene oxide and CO_2.

developed utilizing wheat gluten has provided a promising area of sustainable polymers from biomass. In Chapter 11, Xiaoqing Zhang *et al.* discusses in detail about the current status of investigation on wheat gluten-based materials.

Non-hydrocarbon molecular biomass including carbon dioxide (CO_2), carbon disulfide (CS_2), and carbonyl sulfide (COS) is useful in the preparation of copolymers with epoxides that afford C1-based polycarbonate polymers (Figure 1.8). Such polymers could be promising to directly reduce the impact of excessive levels of CO_2 produced by burning of fossil resources. However, the major drawback is the poor activity of the reactants to undergo polymerization. To circumvent that, copolymerization optimization and new catalysts are being investigated.

Chapter 12 by Xing-Hong Zhang *et al.* introduces the recent efforts on the C1 copolymerization of CO_2 and its sulfur analogs (COS and CS_2), covering catalyst systems, and a variety of epoxides including several biomass-derived molecules. In Chapter 13, Darbha Srinivas *et al.* put forth advancements made about double-metal cyanide catalyst design in CO_2/epoxide copolymerization.

1.4 Conclusions

This book intends to give an overview of sustainable polymers from renewable biomass with specific areas of research that are worthy of a comprehensive discussion. As plastics are becoming increasingly ubiquitous materials in our modern society for a wide range of applications from commodity to advanced technology, our quality and style of living depends on the increasing development and usage of polymers from renewable sources. We envision that, in the future, sustainable polymers from natural biomass will significantly replace the petroleum-derived polymers. It is simply a matter of time for modern polymer science and technology to be relieved of its dependence on petroleum, as the fossil oil resources will be geographically localized and eventually depleted. Therefore, this book is written to highlight the significant achievements that have been made on our quests to transform technology from petrochemical-based polymers to bio-based sustainable polymers.

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