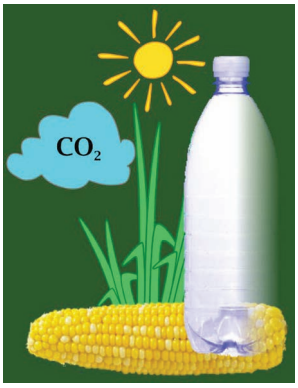
Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality

Rolf Mülhaupt*

Dwindling fossil resources, surging energy demand and global warming stimulate growing demand for renewable polymer products with low carbon footprint. Going well beyond the limited scope of natural polymers, biomass conversion in biorefineries and chemical carbon dioxide fixation are teamed up with highly effective tailoring, processing and recycling of polymers. "Green monomers" from biorefineries, and "renewable oil", gained from plastics' and bio wastes, render synthetic polymers renewable without impairing their property profiles and recycling. In context of biofuel production, limitations of the green economy concepts are clearly visible. Dreams and reality of "green polymers" are highlighted. Regardless of their new greenish touch, highly versatile and cost-effective polymers play an essential role in sustainable development.



1. Introduction

Modern polymer technology has green routes. In both natural and man-made technologies, polymers play a prominent role as extraordinarily versatile and diversified structural and multifunctional macromolecular materials. In 1920, the Nobel laureate Hermann Staudinger recognized that natural and man-made polymers are produced according to the same blueprint: a very large number of small monomer molecules are linked together to produce high-molecular-weight macromolecules. Properties are readily tuned by varying monomer type, sequence of monomer incorporation, polymerization processes, polymer superstructures, and processing technologies. Without polymers, modern life would be impossible because polymers secure the high quality of life and serve as pacemakers for modern technologies. During the early days of polymer sciences and engineering, almost all materials were based exclusively upon chemically modified biopolymers.[1,2] Among polymers, sugar-based cellulose, which is the major component of biomass, wood, and cotton, represents the most abundant organic compound produced by living organisms.[3] In biological cells and biotechnology labs, the incorporation of 20 amino acids is precisely controlled, producing polypeptides such as spider silk, wool, enzymes, insulin, and a great variety of other synthetic proteins for industrial and biomedical applications.[4]

In the 19th Century, natural raw materials such as casein, shellac, gum, natural rubber, and cellulose were chemically modified to convert them into useful macromolecular materials with new property profiles. An important objective was to render the infusible and frequently insoluble natural materials capable of being processed. The first horn-like plastic material was galalith, produced by reacting casein from milk (Greek *gala*) with formaldehyde to produce a stiff thermoset resin resembling stone (Greek *lithos*). Although the biodegradable and water-insoluble galalith was not moldable, sheets could be produced, thus enabling dyeing and machining. The latex of Brazilian rubber trees was collected, coagulated, dried, and vulcanized with sulfur to produce industrial rubber for making tires. Today, around 40% of rubber

R. Mülhaupt
Freiburg Materials Research Center and Institute for Macromolecular Chemistry of the University of Freiburg, Stefan-Meier-Str. 31, 79104 Freiburg, Germany
E-mail: rolfmuelhaupt@web.de

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

DOI: 10.1002/macp.201200439

raw materials are supplied by rubber tree plantations. When the highly flammable and explosive nitrocellulose, obtained by nitration of cellulose and used as smokeless gunpowder, was plasticized with camphor, it was rendered thermoplastic. In fact, plasticized nitrocellulose was the first thermoplastic material. Bio-based nitrocellulose, marketed as Parkesine™ and Celluloid™, was rather hazardous owing to its explosive character. Nevertheless, moldable nitrocellulose became a successful substitute for ivory and was used for making billiard balls, thus saving the lives of thousands of elephants. As a flexible carrier, Celluloid™ enabled manufacturing of photographic films. On the downside, nitrocellulose films represented a severe fire and safety hazard for cinemas during the early 20th Century.

The urgent demand of the growing population for textiles, natural rubber supply problems encountered during the time of the world wars, and emerging new technologies necessitated the development of new materials exhibiting property profiles unparalleled by any natural biomaterial. The breakthrough came in 1907 when Leo Hendrik Baekelite invented the first fully synthetic polymer (Bakelite™) by reacting phenol and formaldehyde.[5] As excellent electrical insulators, phenolic thermoset resins have revolutionized electrical engineering, paving the way for electrification and new communication technologies such as telephones, radio broadcasting, and television.

During the 20th Century, a great variety of synthetic polymers became available on the industrial scale. Strong technology base is petrochemistry, emerging in the 1950s. Exploitation of oil and gas as fossil raw materials for the chemical industry and polymer production greatly improved cost-effectiveness and simplified manufacturing of macromolecular materials. Since then the attractive combination of low cost with facile processing and innovation represents the key feature of plastics. In the 1990s, new recycling technologies enabled effective reuse of polymer products that had completed their first lifecycle. Polymer wastes thus became a valuable source of raw materials and energy. In today's highly efficient industrial polymerization processes, polymers are tailored to be stiff, soft, rubbery, conducting or insulating, optically transparent or opaque, permeable or impermeable, stable or (bio)degradable. Prominent examples of polymer applications include food and medical packaging materials, lightweight engineering plastics in the automotive and aerospace industries, damage-tolerant construction materials for modern architecture, high-strength fibers for textiles and composite materials, printed circuit boards and photoresists for microelectronics, solvent-free coatings for corrosion protection, adhesives, and new materials for biomedical applications such as wound dressing, membranes for artificial kidneys and water purification, dental fillings, drug delivery systems, artificial hearts, and implants. Plastics have become essential components of virtually any kind of consumer product that meets the highly diversified demands of human society.[6]

Unparalleled by any other class of materials, most polymers exhibit unique property combinations:

- Attractive cost/performance ratio.
- High versatility with respect to properties and applications.
- Low weight.
- Excellent corrosion resistance.
- Facile processing with short cycle times in injection molding, blow molding, fiber spinning, and extrusion.
- Highly cost-, resource-, eco-, and energy-effective mass production.
- Flexible base of raw materials (oil, coal, gas, and biomass).
- High energy content similar to that of oil and superior to wood.

Rolf Mülhaupt, born in 1954, studied chemistry at the University of Freiburg (1973–1978) and got his Ph.D. at the Swiss Federal Institute ETH Zürich (1978–1981) under the supervision of professor P. Pino. After conducting industrial research at Du Pont Central Research in Wilmington/Delaware, USA (1981–1985), and at Plastics and Additives Division of Ciba in Marly, Switzerland (1985–1989), he was appointed full professor of macromolecular chemistry and director of the Institute of Macromolecular Chemistry at the University of Freiburg in 1989. Since 1992, he is the managing director of the Freiburg Materials Research Center (FMF) and since 2012 also the managing director of the newly established Freiburg Center of Interactive Materials and Bioinspired Technologies (FIT). Since 2000, he is member of the Heidelberg Academy of Sciences. He published around 350 papers in refereed journals, filed 91 patent applications and was awarded the Piero Pino Gold Medal (2004) of the Italian Chemical Society and the Hermann Staudinger Price (2009) of the German Chemical Society. His research at the interfaces of basic and applied polymer sciences is concerned with polymer synthesis, polymerization catalysis, nanocomposites, tailoring polymers, blends and composites for applications in sustainable development and biomedicine, functional processing, 3D printing, specialty polymers, and additives.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

- Attractive ecobalance.
- Recycling as materials and sources of energy and chemical feedstocks.
- Substantial contributions to energy savings in applications.

Originally introduced as rather mediocre duplicates of natural materials such as silk, natural rubber, and ivory, modern plastics have emerged as advanced materials, enabling new technologies and securing a high quality of life. Synthetic polymers are engineered to satisfy basic human needs for shelter, health, food, communication, mobility, protection, as well as resource-, eco-, cost-, and energy-effectiveness. At present, around 7% of the annual oil production is used to produce plastics, which helps to save more than twice this amount of oil, lowers transportation weights, and improves energy effectiveness by thermal insulation of houses. Furthermore, the production of plastics requires much less energy than metals and ceramics. Due to their hydrocarbon nature, commodity plastics such as polyolefins preserve their high oil-like energy, which can be reused. Plastics wastes can be recycled by remolding or by facile thermal cleavage of their hydrocarbon backbone, enabling recovery of essentially quantitative yields of their oil and gas raw materials. Today plastic wastes, especially of large-scale commodity plastics, serve as a substitute for oil fuels in incineration plants and as feedstock for the production of chemicals or monomers. The high versatility of plastics combined with low cost, high performance, and facile processing renders high technology affordable for people living in industrialized as well as in developing countries. Baekeland's invention marks the birth of the modern Plastic Age. Unlike any other materials, plastics are highly beneficial to society, human health, and technological progress. Therefore, it is not surprising that the rapid growth of the global population is paralleled by a skyrocketing demand for advanced, cost-effective plastics. In fact, the amount of plastics produced during the first 10 years of the 21st Century is almost as large as the amount produced throughout the entire 20th Century.[7] But are dwindling oil reserves, global warming, and littering problems threatening the future of plastics? Do we need to exit petrochemistry and enter a new era of green technology with a renaissance of biomaterials?

2. Sustainable Plastics Entering the Green Economy

The rise of low-cost synthetic polymers with far superior properties, produced in highly energy- and resource-efficient polymerization processes, accounted for the declining use of the less competitive natural polymers, which amount to less than 1% of today's plastics production of 300 million tons per year. At the beginning of the 21st Century, we are experiencing a renaissance of renewable polymers and a major thrust towards the development of bio-based macromolecular materials. Is the future of plastics going to be green? There are several reasons for this paradigm shift and for the envisioned transition from petrochemistry to bioeconomy. From the economic point of view, after crossing the oil production peak, the dwindling oil supply is likely to further boost the oil price, especially in view of the expected surge in worldwide energy demand. This could drastically impact the cost-effectiveness and competiveness of plastics. Shifting chemical raw material production to renewable resources or coal could safeguard plastics production against this expected new future oil crisis. Hence, another even more important reason is the growing concerns of consumers regarding global warming, resulting in a surging demand for sustainable and "green" products. In addition, a tsunami of environmental legislation and regulations is propelling the development of environmentally friendly products with a low carbon footprint.

Today the world is facing mounting global crises, ranging from global financial market distress to extreme climate-induced weather events and skyrocketing costs for energy. At present, the world population exceeds 7 billion people and is projected to reach 9 billion people by 2050. People living in developing countries aspire to the living standards of the Western world and claim their rightful part of the world's resources and plastics production. The resulting drastically increasing hunger for energy, which is currently satisfied by consuming fossil fuels, will undoubtedly further increase emissions of the greenhouse gases, water vapor, methane, and carbon dioxide. The limits of growth, as already pointed out by the Club of Rome in 1972, are clearly visible at the horizon of our economy. Continued reckless depletion of natural resources and progressive global warming could trigger a sudden collapse of the biosphere.[8] The epoch of plentiful and cheap resources is over.[9] In euphoric visions, the path forward towards biofuels and biomaterials based upon biomass utilization, genetic engineering, and biotechnology is seen as the Holy Grail in a bright future.[10] The UN Earth Summit 2012 in Rio de Janeiro ("Rio+20") endorsed the concept of building a prosperous and strong "greenish" world economy within the context of sustainable development. The prime objective of sustainable development, as stated by the Brundtland Commission of the UN General Assembly in 1987, *"implies meeting the needs of the present without compromising the ability of future generations to meet their own needs."*[11] In European forestry, the concept of enabling a sustainable balance between wood consumption and wood production for safeguarding the sustainable economic success of the forestry business has a long tradition, dating back to the Middle Ages. Natural resources such as oil, gas, potable

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

water, clean air, fertile soil, rare metals, minerals, wood, and biodiversity are essential for human survival and for keeping the global economy functioning.

In green economy, it is imperative to reduce the demand for resources and energy, minimize wastes, prevent environmental pollution and hazards, reduce greenhouse gas emissions, optimize manufacturing processes, and establish effective recycling of wastes. These elements are an integral part of sustainable chemistry, which is also referred to as green chemistry, a term coined in the 1990s.[12] Important green principles of polymer production address the following issues:

- High resource effectiveness and high atom economy, maximizing the content of raw materials in the product.
- Clean and lean production processes, preventing wastes and reducing greenhouse gas emissions.
- High safety standards.
- No use of auxiliary substances such as organic solvents, blocking groups etc.
- High energy efficiency of materials' manufacturing and applications.
- No health and environmental hazards by minimizing toxicity.
- Use of renewable resources and renewable energy.
- Low carbon footprint.
- Controlled product lifecycles with effective waste recycling.

By this definition, "green" is not synonymous with biomaterials and biotechnology. In fact, many existing polymers and polymerization processes meet the demands of green chemistry. Prominent examples of successful sustainable materials are polyolefins such as polyethylene and polypropylene, which amount to around half of the global polymer production.[13] In the 1930s, the first industrial process for making polyethylene required temperatures above 150 °C and very high pressures exceeding 1000 bar. Catalytic olefin polymerization was discovered during the 1950s. This enabled olefin polymerization at low pressures below 10 bar and at temperatures below 100 °C. During the 1980s, in the aftermath of the first oil crisis in 1973, the energy-efficient catalytic copolymerization of ethylene and 1-olefins for manufacturing linear low-density polyethylene (LLDPE), used in food packaging, became a million ton business. Most likely, the marketing efforts by Union Carbide represent the first striking example of how the argument of improved energy effectiveness successfully triggered substantial changes in the market place, with catalytic ethylene copolymerization progressing at the expense of energy-intensive high-pressure ethylene polymerization.

In 1954, isotactic polypropylene became available as a highly versatile hydrocarbon resin with an extraordinarily wide spectrum of applications ranging from automotive bumpers to baby diapers, textiles, and food packaging.[14] Since then, a chain of breakthroughs in catalyst and process technology has greatly simplified polyolefin production, drastically enhancing energy- and resource-effectiveness. During the early 1960s, polypropylene was produced in a hydrocarbon slurry. Wasteful and costly purification was required to recover the solvent and to remove corrosive catalyst residues together with tacky atactic polypropylene byproduct wastes that were deposited in a landfill. Today, highly active and stereospecific supported catalyst generations polymerize propylene in solvent-free gas phase and in liquid pool processes without byproduct formation and without the need for waste disposition. Due to the extremely high catalyst activities, the very small amount of noncorrosive and nontoxic catalyst residues can be left in the polymer. Moreover, polypropylene granules can be produced in the reactor, thus eliminating the need for energy-consuming pelletizing melt extrusion. Modern olefin polymerization has set new standards for environmentally friendly polymer production. Polymer properties can be readily tuned as a function of catalyst type and process conditions to meet the demands of specific applications. Moreover, polypropylene is very effectively recycled either by remolding at temperatures around 230 °C or by facile thermal cleavage of the polypropylene backbone. At temperatures above 400 °C, polymer chain scission accounts for the quantitative recovery of the hydrocarbon feedstocks, which can be reused as a source of "renewable oil" for producing ethylene monomer (cf. Figure 8) or as source of energy. Polyolefins meet the demands of sustainable development, preserving resources for future generations. In terms of their favorable ecobalance, recycling, energy-, and resource-effectiveness as well as their attractive cost/performance ratio, polyolefins outperform all biopolymers and bio-based plastics. In principle, as will be discussed below, it is feasible to switch from fossil resources to bio-based feedstocks in polyolefin manufacturing to meet the demands of green chemistry. Today, polyolefin technology stands for the most effective and sustainable use of oil and gas, especially when compared with burning oil and gas in energy production. In contrast, most biotechnology processes consume significant amounts of water, produce byproduct wastes, and require energy-intensive biopolymer purification.

An integral part of the green economy concept is fostering the use of renewable resources and bio-based products. Figure 1 illustrates the politicians' and environmentalists' dream of using solar power in biological photosynthesis to convert greenhouse gas carbon dioxide and water into biomass, which then serves as a feedstock for biofuels, biopower, and bioplastics. Upon thermal

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

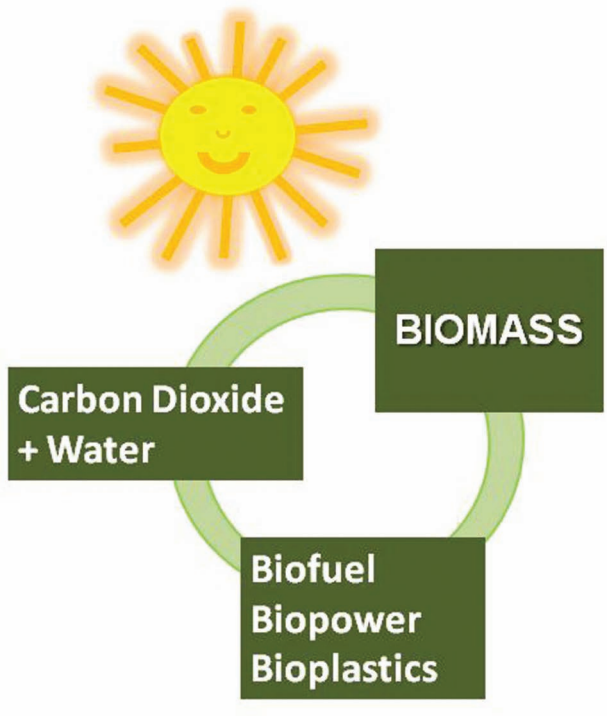


Figure 1. The illusion of a closed carbon cycle.

or biological degradation, water and carbon dioxide are recovered. In this perceived closed carbon dioxide cycle, in contrast to fossil resources, no additional greenhouse gas emissions would occur, accounting for a very low carbon footprint. From this extremely idealistic point of view, biodegradation appears to solve the littering problem encountered when highly durable synthetic polymers are not recycled. In the Northern Pacific Trash Vortex, also referred to as the Pacific Garbage Patch, which is driven by converging maritime and wind currents, floating plastic debris accumulates together with other garbage such as pesticides from agriculture and plentiful fishery wastes. As polymers are nontoxic and inert, partially degraded polymer particles may accumulate in marine organisms. Owing to their high porosity, which results from degradation and surface erosion, spongy polymer wastes are suspected to adsorb and concentrate low-molecular-weight toxic wastes such as pesticides. When marine organisms settle on such debris, they can travel far beyond their natural habitat.[15,16]

Should durable synthetic materials, especially those used in packaging applications with a short product lifetime, be banned and substituted by biodegradable bioplastics? This issue has triggered a hot and ongoing battle of the bag, fought by opponents of plastics bags and protagonists of paper. In order to address this question, a realistic disillusioned view of the real world is needed.

Although the vision for green technology, displayed in Figure 1, is intriguing and inspiring, severe disillusionment sets in when facing reality. There is a growing recognition that "bio" does not automatically imply "green." Prospects and problems concerning the use of biofuels and biofeedstocks are listed in Table 1 and are illustrated in

Table 1. Prospects and problems of bio-based feedstocks and biofuels.

Pro Bio	Contra Bio
Renewable resources conserve non-renewable fossil raw materials	Competition with food production
Lowering of carbon dioxide greenhouse gas emissions by switching from fossil fuels to biofuels	Intensified farming, extensive use of fertilizers, deforestation, and grassland conversion cause drastic increases of greenhouse gas emissions
Domestic energy supply and less dependence on oil imports	Energy crop monocultures threaten biodiversity
Plant cells and bacteria serve as solar microreactors for producing chemicals	Use of transgenic plants and genetically modified bacteria
Energy crops as nonfood incentives for farmers in industrialized countries with surplus food production	Rising costs of food because farmers abandon food production in developing countries that are unable to feed their rapidly increasing population
Use of agricultural and forestry wastes	A portion of the biomass must remain on agricultural land to secure soil quality and natural habitats for animals
Biodegradation	No biodegradation in the absence of water and oxygen. Disintegration may cause nanoparticle emissions.
No toxicity and no health hazards	Spongy degrading biopolymer particles are food sources and breeding grounds for bacteria and spores, which could be inhaled.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

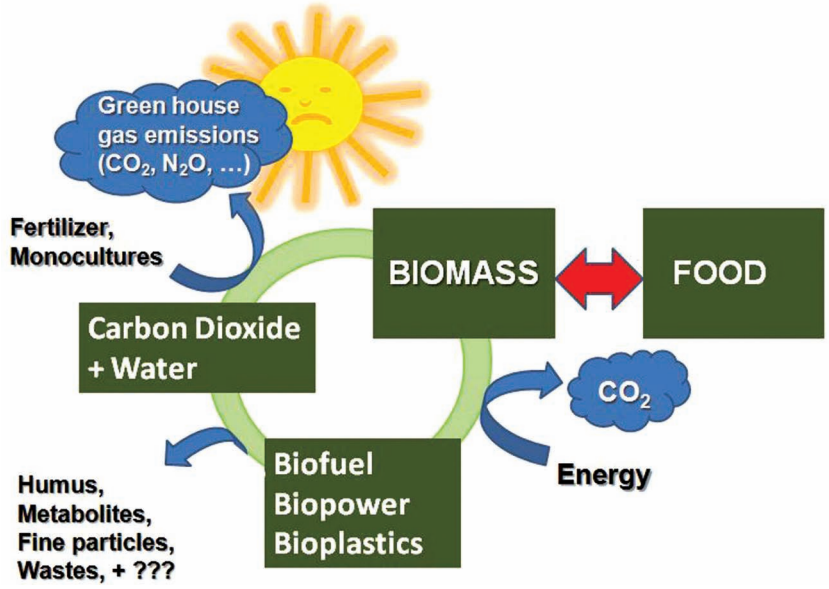


Figure 2. The reality of green economy.

Figure 2. First of all, even the partial substitution of fossil oil and gas for biomass would require intensified farming of energy crops in competition with food production. In view of the surging energy demand and rising energy costs, farmers are tempted to abandon cheap food production in favor of producing higher value-in-use energy crops offering much higher profits. In 2007, the US thrust for exploiting maize-based bioethanol as a biofuel was accompanied by a surge of financial speculation on maize, which triggered a dramatic rise in the cost of maize in the neighboring Mexican food industry. What became known as the "Mexican Tortilla Crisis," threatening the health and sustenance of the country's poor, is a foretaste of what is yet to come in the event of uncontrolled biofuel production.[17] Stepping up energy crop production and intensifying production and worldwide trading of biofuel and biofeedstocks could severely threaten the biosphere. The skyrocketing demand for biofuel and biofeedstocks is likely to accelerate deforestation of rainforests and cultivation of grasslands, both of which are very effective in carbon dioxide sequestering. Due to intensified use of fertilizers, emissions of the very potent N_2O greenhouse gas are expected to drastically increase. Ultimately, in spite of replacing fossil fuels, the surging use of biofuels will probably accelerate global warming and biosphere collapse. According to recent modeling studies, the anticipated conversion of rainforest and grassland into new cropland for producing biodiesel and bioethanol could release 17 to 420 times more carbon dioxide greenhouse gas for many decades and even centuries when switching from fossil to biofuels.[18] Intensified farming of energy crops, irrigation, and the use of pesticides endangers the natural habitats of many plants and animals. Severe losses of biodiversity are imminent together with alarming socioeconomic implications of biofeedstock competition with food production.

According to the 2020 forecast of the German Agency for Renewable Energy ("Agentur für Erneuerbare Energien") and the Federal Association of Renewable Energy ("Bundesverband Erneuerbare Energie"), in an industrialized country like Germany, bioenergy production could supply 9.1% of the electrical power, 13.1% of the thermal energy, and 21.4% of the fuel used in transportation, including around 50% of imports from other countries.[19] Important pillars are biogenic wastes from forestry and farming. In contrast to energy production, it would be easy to supply the much lower demand of biomass required for switching from fossil to renewable raw materials in plastics production. However, although the demand for bioplastics is orders of magnitude lower with respect to the demand for bioenergy, both bioplastics and bioenergy production are closely interconnected because they compete for the same biomass feedstocks. The imbalance of demand and supply of biomass is likely to trigger future "biocrises" similar to the oil crisis when the oil supply was low in 1970s. In order to avoid conflicts with securing food supplies, it is imperative to focus on exploiting agricultural and forestry wastes for the production of bioplastics and to avoid conversion of rainforests and grasslands.

Today it is recognized that "bio" does not imply quantitative and rapid degradation to produce exclusively carbon dioxide and water. Biodegradation can also produce water-soluble and even toxic metabolites that are washed away by rain and thus pollute groundwater. In landfills, cellulose of paper and other biodegradable materials do not degrade and survive for many decades when oxygen and water are absent. Moreover, biodegradation and bioerosion render polymers brittle so that they readily disintegrate when exposed to mechanical stresses. Most likely, they form much smaller dust-like micron- and nanometer-sized particles, which are carried away by wind or rain. Although the biodegrading plastics are no longer visible to the human eye, the resulting fine and invisible particles can accumulate in the air and cause inhalation hazards. Most biodegradable polymers are a coveted source of food for bacteria, other microorganisms, for example fungal spores, and even small animals, such as insects, bugs, mice, and rats. As a consequence, applications of truly biodegradable materials frequently require

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

chemical lines of defense using rather aggressive antimicrobial additives and poisons. Yet another consequence is that bacteria and spores can settle on such particles, which may then be inhaled, causing severe health problems. At present, there is very little research addressing such potential inhalation hazards and the role of climate-dependent biodegradation with respect to nanoparticle emissions.

The battle of the bag—plastics against paper—is a nuisance because both packaging materials represent a severe source of pollution when recycling fails. Whereas paper consists of the natural polymer cellulose, most synthetic packaging polymers are based on polyethylene, which is still fossil-based but has a much lower weight, higher strength, and causes less pollution during production. Moreover, polyolefins as hydrocarbon resins have a significantly higher energy efficiency. Polyethylene bags are produced in a blow-molding process by melt extrusion of polyethylene granules, which are produced by highly energy-efficient catalytic polymerization of ethylene in solvent-free gas-phase processes. To produce paper, trees are stripped of their bark, shredded, washed, and chemically digested for many hours at elevated temperatures in aqueous sulfurous acid to separate cellulose and lignin. Pulp production requires a very large amount of water. After bleaching and further washing, the suspension of cellulose fiber pulp is pressed into finished paper. Polyolefin bags, on the other hand, have a low weight and a high energy content, and are thus attractive for saving energy due to weight savings in transportation and effective energy recovery in recycling. On heating above 400 °C, the high-molecular-weight hydrocarbon polymers degrade to produce low-molecular-weight hydrocarbons, equivalent to crude oil, that can be used as source for renewable oil and gas, and as a substitute for fossil resources. As durable hydrocarbons, the non-biodegradable plastic wastes can be easily collected and stored, enabling effective energy recycling without serving as a food source and a breeding ground for microbial organisms. There is no competition between polyethylene and other plastics. In fact, modern packaging of milk and fruit juices makes extensive use of both materials, which are joined together with paper serving as the carrier and polyethylene as the barrier to water and flavor permeation. Synthetic polymers are not marine villains that threaten marine life. Littering problems result from a lack of recycling and illegal dumping of garbage, especially in shipping. The issues of ineffective recycling and intolerable burdening of the biosphere by wastes are not solved by banning non-biodegradable materials, but by demands to change human attitudes.

3. Strategies for Renewable Plastics

In principle, there are three different strategies towards renewable plastics that are useful in a green economy. In strategy (i), biorefining of biomass and chemical conversion of carbon dioxide are employed to produce synthetic crude oil ("renewable oil") and green monomers for highly resource- and energy-effective polymer manufacturing processes without impairing established recycling technologies. In strategy (ii), which goes well beyond the green routes of polymers, living cells are converted into solar-powered chemical reactors, exploiting genetic engineering and biotechnology routes to produce biopolymers as well as bio-based polymers. In strategy (iii), carbon dioxide is activated and polymerized. The basic strategies and material flow cycles are shown in Figure 3 and discussed below. Whereas Nature needs more than 300 million years to convert biomass into oil, there are several options for producing synthetic bio-based renewable oil and even "green coal" on a large scale that require only a few minutes.

In analogy to petrochemistry, in which petroleum is refined to obtain monomers, in strategy (i) biorefinery and

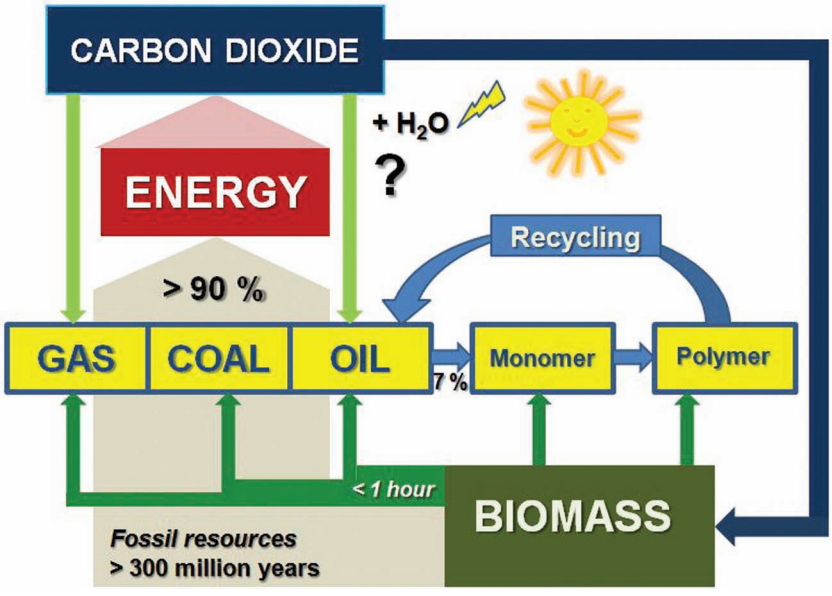


Figure 3. Exploiting biomass as renewable resource for making renewable oil, green coal, gas, monomers, and renewable polymers without a delay of many million years typical for fossil raw materials. Recycling of polymer wastes can be used to recover oil and gas feedstocks from wastes.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

biofuel technologies are developed to refine biomass to produce renewable oil and green monomers.[20] Inspired by coal liquefaction and gasification, biomass-to-liquid (BtL) conversion is based on the Fischer–Tropsch process to convert biomass into a mixture of carbon monoxide and hydrogen (syngas), which is an important feedstock for chemicals. Although the entire plant can be gasified, this process is energy-intensive, especially when producing nonpolar olefin monomers. Less favorable energy and problematic ecobalances are typical for biodiesel, prepared by transesterification of vegetable oils with methanol, accompanied by glycerol byproduct formation.[21] Among emerging biofuels, bioethanol is produced by fermentation of sugar obtained from sugarcane or cellulose. Bioethanol represents a very versatile raw biomaterial for producing olefin and diolefin monomers such as ethylene, propylene, and butadiene.[22] Both BtL and bioethanol processes possess rather poor atom economy because only part of the raw material is incorporated into the polymer product. In recent research innovations, biomass is directly converted into renewable coal and oil in a single process step. In the catalytic pressureless liquefaction of wood and plastics wastes (KDV, "katalytische Direktverölung"), developed by AlphaKat in Germany, high-quality diesel fuel is produced without requiring the high temperatures and pressures typical for coal gasification and the Fischer–Tropsch processes.[23] In hydrothermal carbonization, developed by Antonietti, aqueous slurries of virtually any kind of biomass and agricultural waste are converted into "green coal" using very moderate reaction conditions. This process is exothermic and tolerates high salt contents, which are detrimental to most other catalytic processes. Moreover, this carbonization enables highly effective and simultaneous dehydration of the biomass.[24] Several processes have been developed to convert carbon dioxide into carbon monoxide, methanol, formic acid, and formaldehyde. In a recent advance, photocatalysis was employed to convert aqueous carbon dioxide into carbon monoxide using in situ water splitting as a hydrogen source.[25] Going well beyond the scope of biomass utilization, the direct chemical fixation of carbon dioxide is commonly recognized as an attractive green feedstock and green solvent for the chemical industry.[26]

4. Biopolymers and Bio-based Polymers

In strategy (ii), renewable polymers are obtained either from natural biopolymers or by polymerization of bio-based monomers. As shown in Figure 4, carbohydrates, terpenes, proteins, and polyesters are prominent representatives of biomaterials that are chemically modified in manifold ways to meet the demands of polymer processing and applications. Recent progress in preparing and processing renewable polymers was reviewed by Gandini, Mittal, Rieger and co-workers.[27–30]

5. Wood/Plastics Composites and Cellulose

Cellulose is the most abundant biopolymer in the world, serving as a renewable polymer and as a sustainable carbon source for the green economy.[31] Traditional applications of cellulosic materials include wood as building materials, cotton for textiles, and hemp for ropes and sails—of strategic importance in naval history. Natural fibers, such as flax, jute, hemp, and sisal provide excellent fiber reinforcement for thermosets and thermoplastics. The German automotive company Daimler has developed polypropylene composites reinforced with abaca fibers for interior applications.[32] Novel families of thermosetting and thermoplastic wood/plastics composites, such as injection-moldable wood/plastic compounds, have been developed to reduce processing costs and improve performance.[33] Over the last decade, microfibrillated cellulose from wood and cellulose nanowhiskers have been developed as nanofillers for polymer nanocomposites, including applications in medical implants.[34] Wood is composed of cellulose that is chemically attached to lignin. As a phenolic resin, lignin protects cellulose against thermo-oxidative degradation and microbial attack. Most chemical processes for separating cellulose from lignin are cost- and energy-intensive and do not meet all the requirements of green chemistry. The major market for purified cellulose is the paper industry. Hydrolysis of lignocelluloses represents an attractive source of sugars, which are in demand as a food source for bacteria in various biotechnology and biorefinery processes, including biofuel production.

Lignin is a million ton phenolic byproduct from pulping and serves as renewable energy source in paper manufacturing, as a dispersing agent for cement, and as a biofeedstock for biorefining of aromatic compounds such as vanillin.[35] Lignins with a low sulfur content are of interest as fillers for various polymers and rubbers. Aiming at fulfilling the dream of injection-moldable wood, the German company Tecnaro has introduced moldable lignin-based polymer compounds, marketed as Arboform™, consisting of a pelletized and moldable mixture of thermoplastic lignin with flax, hemp, and other natural fibers. This "liquid wood" product is claimed to combine the advantages of wood materials with facile molding typical of synthetic thermoplastics. Applications include furniture, automotive parts, and heels of the "Eco pump" shoe, commercialized by Sergio Rossi/Gucci.[36]

Starch, formed as a granular energy reserve in plant cells, is highly water soluble, readily biodegradable, and consists of a mixture of linear amylose and highly branched amylopectine. Present in maize, potatoes,

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

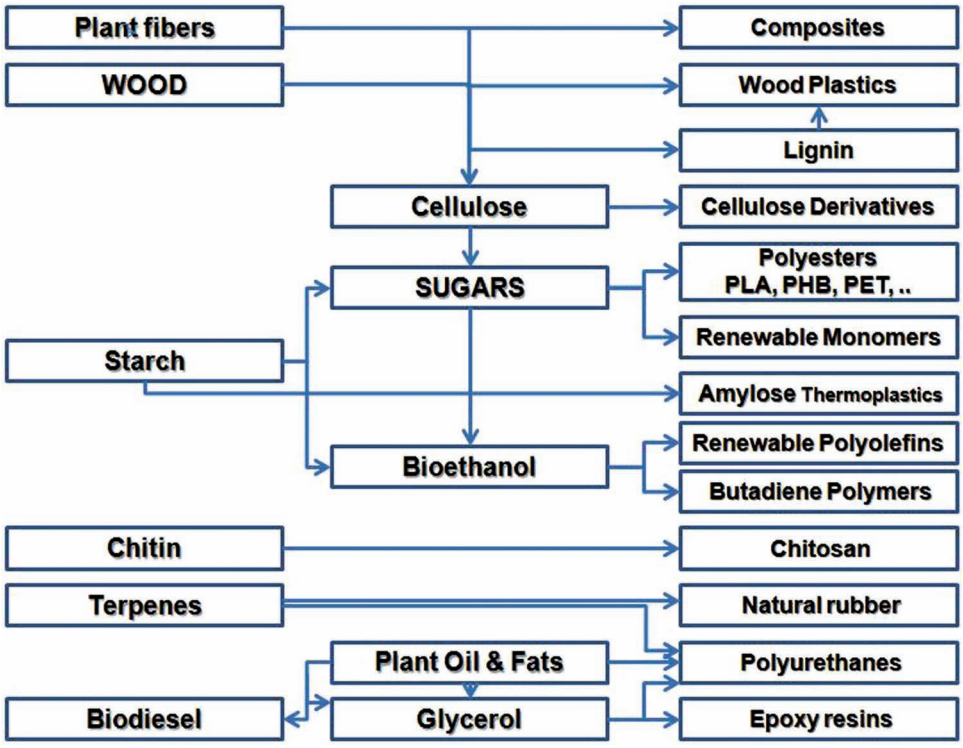


Figure 4. Renewable polymers based upon carbohydrates and terpenes, illustrated by selected examples.

wheat, and other plants, starch is a major energy source for living organisms. Whereas most starch products are consumed in the food industry, nonfood applications include cosmetics, adhesives, textile sizing, and provision of sugar and dextrose feedstocks for biotechnology. In contrast to cellulose, amylose can be rendered thermoplastic by adding water, glycols, glycerol, or sorbitol as a plasticizer.[37] For example, thermoplastic high-amylose starch has been developed by Cardia Bioplastics for injection-molding, blow-molding, extrusion, films, and coating applications.[38] In view of the high water solubility of starch, several companies have developed biohybrids using starch as a blend component with hydrophobic nondegradable polyolefins and compostable polyesters such as terephthalic acid/adipic acid/1,4-butanediol copolyesters (Ecoflex™ from BASF SE).[39]

Chitosan contains glusosamine repeat units and is derived by partial or full deacetylation of chitin, which is obtained from the shells of shrimps, crabs, and lobsters. Its annual production quantity is very similar to that of cellulose. Applications of chitosan include drug release, encapsulation, wound dressings, and water purification.[40]

Terpenes include the natural rubber poly(*cis*-1,4-isoprene), which makes up more than 40% of the rubber market.[41] In the terpene family, fats and oils are valuable intermediates for the chemical industry, especially for the production of ionic and non-ionic surfactants. Hydroxyl-functionalized castor oils have been used for many years as polyol components in polyurethane syntheses. Unsaturated fatty acids are dimerized and trimerized to produce di- and trifunctional carboxylic acids, also known as dimer and trimer acids. They are used in polyester synthesis and in hotmelt adhesives as flexibilizing segments. Unsaturated fatty acids are modifiers for alkyd resins and air-drying finishes. Transesterification of vegetable oils with methanol yields methyl esters ("biodiesel") and glycerol as a byproduct, which can be used as a biofeedstock for a variety of monomers such as 1,3-propane diol and bio-based acrylic acid and even epichlorohydrin for the production of epoxy resins.

Proteins such as collagen are abundant in mammals. Protein fibers such as silk and wool have been used in the textile industry for centuries. Gelatin, which is denatured collagen, is one of the preferred materials for drug encapsulation. Casein, produced from cow's milk, is used as a binder and as an adhesive.

Biopolyesters such as poly(L-lactic acid) (PLA), poly(hydroxybutyrate) (PHB), and other poly(hydroxalkanoates), produced by bacteria as chemical energy storage in cells, are fully biodegradable and decompose to produce water, carbon dioxide, and humus when air and water are present. It is possible to tailor stiff, soft,

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

and elastomeric polyesters as a function of their molecular architecture. Bacteria and transgenic plants have been successfully used to produce biopolyesters on a large scale.[42] For two decades, PLA, produced by bacteria and especially by lactide polymerization, has been the approved material of choice for resorbable sutures in surgery. As a function of the stereoisomer composition, PLA can be amorphous or crystalline, melting at temperatures up to 185 °C. The thermal stability is rather low with degradation starting below 230 °C. During the 1980s, ICI introduced biodegradable poly(hydroxybutyrate-*co*-hydroxyvalerate), marketed as Biopol™. It targeted polypropylene, but failed to match the attractive cost/performance ratio typical for polypropylene, even when taking into account today's increased oil price. Although significant progress has been made in biotechnology since then, separation of polyesters from cell proteins and purification is rather expensive and energy intense. Contrary to the demands of green chemistry, biopolyesters are often extracted using chlorinated solvents. It should be noted that biodegradation is not the domain of biotechnology. Biodegradable PHB can also be produced by the catalytic conversion of propylene oxide with carbon monoxide.[43] When account is taken of the entire product lifecycle, biopolymers are not always by definition superior in terms of low carbon footprint, resource-, eco- and energy-efficiency when compared to the same polyesters prepared from fossil feedstocks.[44] In bacterial polyesters, it is rather difficult to fine-tune molecular polyester architectures with respect to improving shear thinning and crystallization rate of polyesters in melt processing.

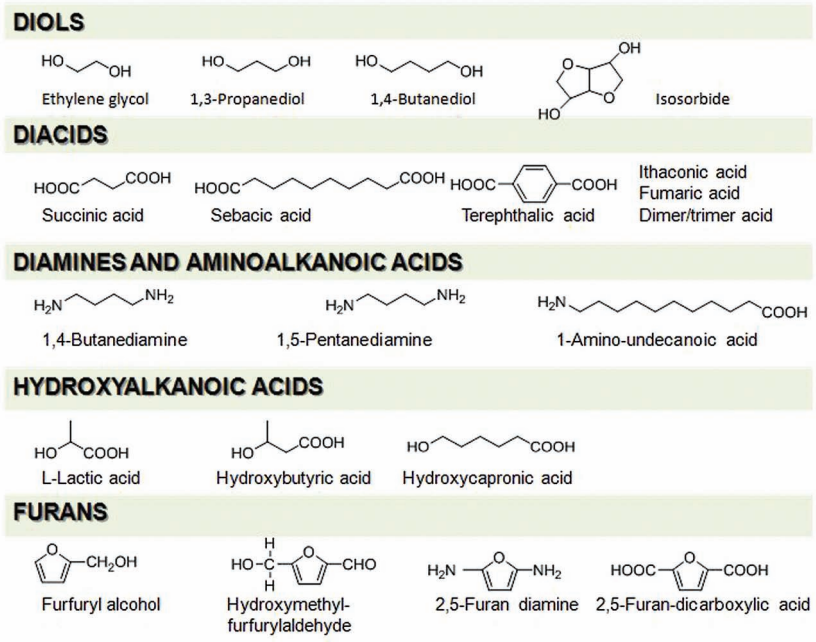


Figure 5. Selected examples of renewable polymers supplied by biotechnology.

6. Bio-based Monomers

Instead of developing new biotechnology routes to biopolymers with rather tedious polymer purification and difficult tuning of processing properties, biotechnology and biorefinery processes are employed to supply renewable monomers, which are polymerized in highly effective conventional melt- or gas-phase polymerization processes. Compared to polymers, monomers are much easier to purify. Moreover, the resulting bio-based polymers combine the advantages of a low carbon footprint, typical for renewable feedstocks, with the recycling capability and high resource- and energy-effectiveness of solvent-free melt-, and gas-phase polymerization processes. Biofeedstocks such as agricultural and forestry wastes are used preferentially to order to avoid conflicts with food production. Fermentation of glucose, obtained from lignocelluloses and starch, can be used to produce a great variety of bio-based monomers. Selected examples are listed in Figure 5. For example, bioethanol is readily converted into ethylene, propylene, and also butadiene that can be used to synthesize bio-based polyolefins and butadiene rubber. Also available are diols, polyols, diacids, hydroxyalkanoic acids, aminoalkanoic acids, and diamines that can be used in melt polycondensation reactions to produce bio-based polyesters, polyamides, polycarbonates, as well as thermoset resins such as unsaturated polyesters and air-drying finishes. Starting from glucose, it is possible to obtain sorbitol, isosorbide, and also a large variety of furans, most of which are not natural products. Furan derivatives offer attractive opportunities for preparing bio-based thermoset and thermoplastic resins from furfuryl alcohol, furfuryl aldehyde, hydroxymethyl furfuryl aldehyde, and 2,5-furandicarboxylic acid. Side-products of biofuel production, such as glycerol, are also attractive bioresources for producing bio-based monomers such as acrylic acids, epichlorohydrine, 1,3-propanediol, and acrolein. Selected examples for the production of bio-based polymers are presented below.

7. Bio-based Polyesters

In 1997, Cargill and Dow formed a joint venture aiming at converting PLA into a commodity plastic. The L-lactic

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

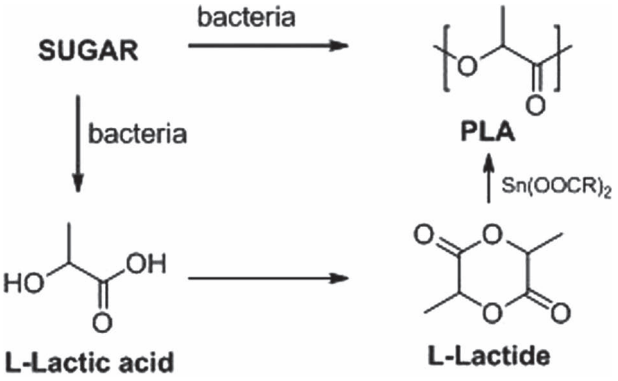


Figure 6. Poly(L-lactic acid) from bacteria and by melt polymerization of lactide, prepared from bio–based L-lactic acid.

acid monomer was produced by fermentation of dextrose from forage maize or other plant sources for sugar without requiring genetically modified plants. In a separate step subsequent to fermentation, lactide was formed and polymerized by ring-opening polymerization to produce PLA, which was globally marketed in 2003 by the newly formed company NatureWorks under the trade name Ingeo™. In contrast to the one-step biotechnology route to PLA, the lactide ring-opening polymerization (cf. Figure 6) in the melt phase enables facile tuning of the PLA molecular architectures to substantially improve PLA melt processing and property profiles.[45] Incorporation of small amounts of the D-isomer led to self-nucleation and very fast PLA crystallization during rapid cooling in injection-molding applications. Long-chain branching enabled melt strengthening during foaming and extrusion coating. In 2009, NatureWorks established an annual nameplate production capacity of 140 000 tons of the Ingeo biopolymer.[46] Going well beyond the scope of biodegradable plastics, PLA applications include packaging, durable plastics, and fibers. Similar to paper, PLA does not degrade in landfills. NIR probes can be used to detect PLA wastes so that they can be separated from plastics recycling streams.

In 2011, the world's largest beverage company Coca-Cola Co. announced a partnership with three biotechnology companies with the aim of producing plastic bottles made from 100% bio-based materials.[47] In 2009, the first generation of PlantBottle™ was introduced as the first recyclable PET bottle using up to 30% bio-based monomers. Bio-based ethylene glycol and recycled PET are employed in PET production. In the new generation of 100% bio-based PlantBottle™, the terephthalic acid will also be bio-based. As shown in Figure 7, at Virent and Gevo terephthalic acid is produced using bio-based *p*-xylene as an intermediate. This route does not interfere with established PET recycling. At the Dutch company Avantium, R&D focuses on the development of bio-based poly(ethylene furanoate) (PEF) using bio-based ethylene glycol and furandicarboxylic acid as monomers.

8. Bio-based Polyolefins

Polyolefin materials are prominent examples of a successful sustainable development. Produced by highly effective solvent-free olefin polymerization processes, they conserve their oil-like energy content and can be tailored to meet the demands of highly diversified markets. At the end of their product life, polyolefins can be recycled by remolding or thermal decomposition. Upon heating above 400 °C, thermal chain scission of the hydrocarbon backbone of polyolefins produces low-molecular-weight fragments that are equivalent to crude oil. Today and for many years to come, petrochemical feedstocks such as ethane and propane will continue to be major and efficient raw materials for synthesizing polyolefins. In principle, as described above, biorefinery concepts offer new opportunities for the green future of renewable polyolefins. In September 2010, Braskem in Brazil inaugurated a 200 kton/year plant producing green ethylene from sugarcane bioethanol for the production of green polyethylene by means of catalytic low-pressure ethylene polymerization. Braskem expects a 30 kton/year green polypropylene plant to go on stream in 2013 as soon as bio-based propylene is available from bioethanol. Marketed by Braskem as Green Polyethylene™, the green polyolefins are identical to non-renewable polyolefins based upon fossil resources, both of which are 100% recyclable. According to Braskem, for each ton of green polyethylene produced, 2.5 tons of carbon dioxide are captured and sequestered.[48]

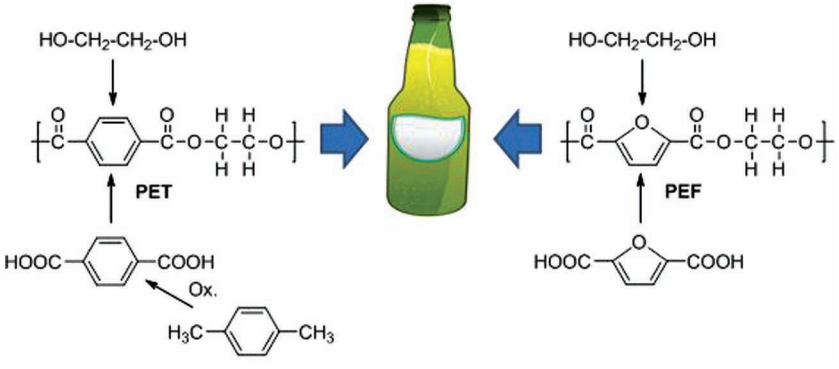


Figure 7. Bio-based polyester for bottles (PlantBottle™ technology from Coca Cola Company).

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

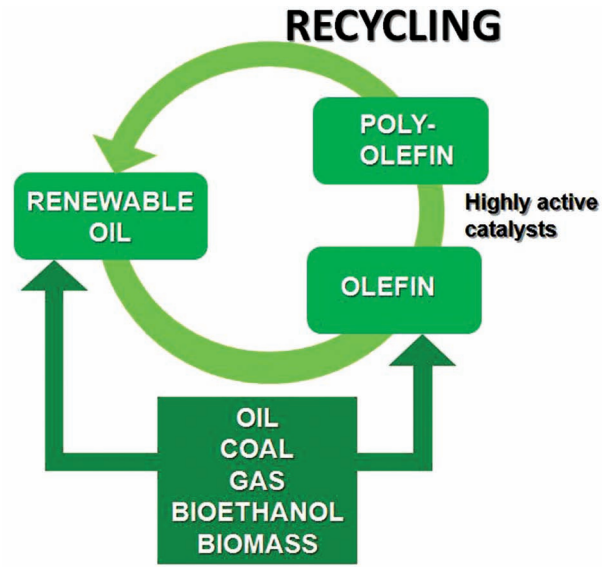


Figure 8. Green polyolefins: Renewable oil is obtained from biomass and also from thermal degradation of polyolefin wastes. Olefin monomers are produced from various raw materials including bioethanol.

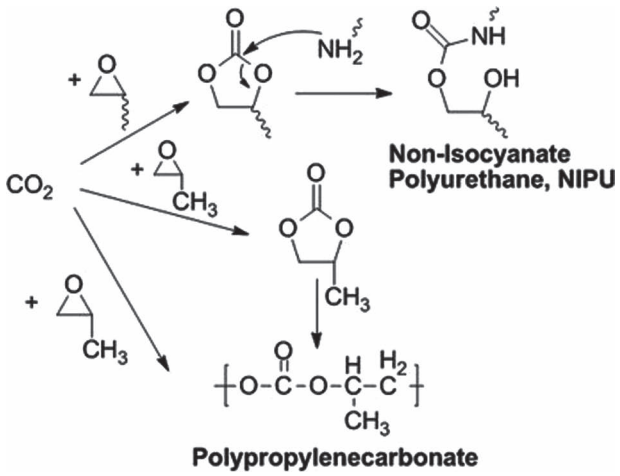


Figure 9. Non-isocyanate polyurethanes (NIPU) and polypropylenecarbonates prepared from cyclic carbonates.

9. Polymers From Carbon Dioxide

As a naturally occurring, abundant, inexpensive, nonflammable, and renewable chemical compound, carbon dioxide is an attractive feedstock for the chemical industry. Apart from fermentation, cement production, and combustion processes, most carbon dioxide originates from continental drift and volcanic eruptions when calcium carbonate, for example, formed by carbon dioxide fixation in corals, is exposed to the high temperatures of magma. Carbon dioxide can be recovered on a large scale in carbon capture of power plants, burning fossil fuels, and in steam-reforming to produce hydrogen from water and coal. To enable its industrial use, energy is required for the activation of carbon dioxide. In industrially viable processes, carbon dioxide is reacted with energy-rich strained rings, for example, oxiranes, to produce cyclic carbonates. The nontoxic and biodegradable cyclic carbonates with their high boiling and flash points are readily produced from oxiranes such as ethylene oxide and propylene oxide in the presence of tetrabutylammonium bromide.[49] Applications include their use as green solvents for degreasing oily steel, paint stripping, and various other cleaning applications. Formation and reactions of cyclic carbonates are shown in Figure 9. At temperatures well above 100 °C, cyclic carbonates are green nontoxic alkylating agents for phenolics and alcohols, producing hydroxyethyl ethers. In recent years, they have played a prominent role as polar solvents and components of electrolytes, promoting electrical conductivity of lithium ion batteries.[50] At lower temperatures, polycyclic carbonates, prepared from epoxy resins or by polymerization of vinyl carbonates, were cured with polyamines to produce poly(*N*-hydroxyethyl-urethanes) without using toxic isocyanates as in conventional polyurethanes.[51] Albeit produced from fossil resources such as commercial epoxy resins, the non-isocyanate polyurethanes are marketed by Nanotech Industries under the trade name of Green Polyurethane™. In addition to safety and health benefits, green polyurethanes are 100% solids based, exhibit zero emission of volatile organic compounds, are claimed to be thermally more stable and solvent-resistant than conventional polyurethanes and can also be applied in the cold cure condition.[52]

Since the early advances during the 1960s, several highly active catalyst generations have been developed for alternating copolymerization of propylene oxide with carbon dioxide to produce high-molecular-weight polypropylene carbonates.[53–55] As expected for amorphous polymers with glass transition temperatures slightly above room temperature, most amorphous polypropylene carbonates are rather soft materials and are of interest as blend components with a low carbon footprint. Dihydroxy-terminated polypropylene carbonates are of special interest as a substitute for conventional polyester polyols in polyurethane synthesis.[55] As illustrated in Figure 10, novel families of 100% bio-based plastics can be derived from citrus fruits and carbon dioxide. Extraction of orange peels is an industrial process for producing limonene oils, which are then oxidized to form mono- as well as difunctional epoxides. Subsequent catalytic copolymerization of limonene monoxide with carbon dioxide affords thermoplastic polylimonene carbonates with properties resembling those of polystyrene.[56] Limonene-based polyesters were prepared by copolymerization of limonene monoxide with dicarboxylic acid anhydrides such as succinic anhydride to yield limonene-based polyesters.[57] Novel

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

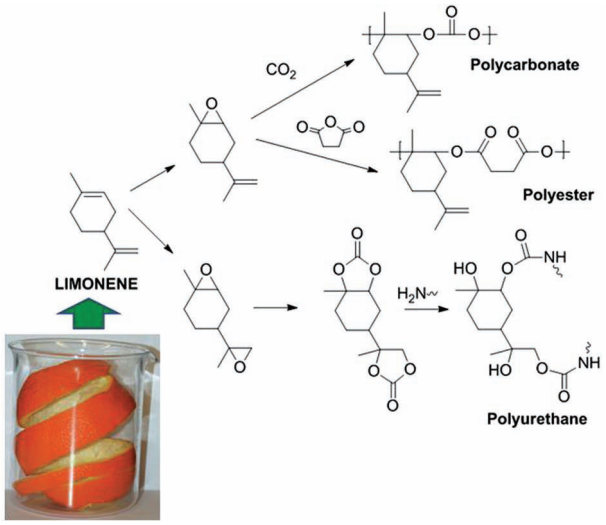


Figure 10. Bio-based polymers from orange peels.

limonene dicarbonates, produced from limonene dioxide, enable chemical fixation of 34 wt% carbon dioxide. They were cured with polyfunctional amines, such as citric aminoamides, to produce a wide variety of crosslinked terpene-based green polyurethanes without requiring the use of isocyanates.[58] Because it uses wastes from orange juice production, the production of limonene-based polymers does not interfere with food production.

10. Conclusions

Since their pioneering days over a hundred years ago, plastics have greatly improved human living conditions and are indispensable and irreplaceable in modern everyday life and in advanced technologies. As a result of their highly energy-, cost-, eco-, and resource-efficient production processes, facile processing, and high versatility in terms of tunable properties and broad range of applications, they render high technology affordable for all humankind. The production of commodity plastics meets the demands of green chemistry for lean and clean production by using solvent-free processes with efficient use of resources, no byproduct formation, waste management, and even exploitation of renewable resources. In sharp contrast to burning oil to generate energy, the use of oil in plastics manufacturing represents the most sustainable and effective use of oil and gas. Many plastics have an oil-like energy content. On heating above 400 °C, plastics degrade producing low-molecular-weight hydrocarbons, which then serve as a source of renewable oil and gas. This is an ideal route to meeting demands to secure resources for future generations in sustainable development. In lightweight engineering, food packaging, and thermal insulation of buildings, plastics innovations contribute to substantial energy savings, amounting to more than twice the amount of energy needed to produce the plastics. In industrialized countries, polymer packaging secures the food supply chain, whereas in less developed countries around half the food is lost in transportation. As electrical insulators of power cables, components of batteries and fuel cells, in corrosion protection applications, and in rotor blades of windmills, they claim an active part in securing the energy supply. Farmers use plastic films to enhance food production by creating a local warm climate directly on the fields, making more effective use of solar energy in agriculture. In highly diversified medical applications ranging from advanced drug release systems to dental fillings, artificial kidneys, and sensors for medical diagnostics, plastics are significantly improving human health. Moreover, polymer innovations contribute towards protecting our natural resources. For instance, polymer membranes have been developed for water desalination and purification, cleaning air, and recovering rare metals from wastes. At the beginning of the 21st Century and unlike any other class of materials, sustainable plastics with an attractive balance of low costs and high performance are essential for meeting the demands of the growing global population with respect to health, shelter, clothing, communication, mobility, and securing food and energy supplies. Without plastics, most blessings of modern technologies would be unaffordable for the poor and for people living in developing countries. Plastics play a key role in sustainable development.[59]

Do skyrocketing energy costs and dwindling oil resources threaten cost effectiveness and the future of plastics? Do we need to ban nonrenewable plastics, exit petrochemistry, and embark on a glorious journey leading to a green future by using biofuels and biomaterials based upon biomass utilization, genetic engineering, and biotechnology processes? There are considerable misconceptions and illusions concerning the prospects of the term "bio." Bio does not by definition imply green and biodegradable. In landfills, neither synthetic polyolefins nor cellulose and polylactic acid are biodegradable in the absence of air and water! Biodegradation is not the exclusive domain of nature. Furthermore, the majority of biodegradable polymers do not instantaneously degrade, producing exclusively carbon dioxide and water. Biodegradation is slowed down dramatically in dry climates. It is well known that degradation renders polymers brittle, thus accounting for their disintegration into much smaller micro- and nanoparticles that can be carried away by the wind. Although these wastes are no longer visible, their degrading dust-like particles are still present, floating around in the air. Spongy biodegradable polymers represent an attractive food source and a cozy habitat for a variety of microbes that may cause health problems

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

upon inhalation. More research is needed to clarify the role of climate-dependent micro- and nanoparticle emissions in biodegradation and the potential health hazards of microbe-loaded biodegradable biopolymer particles. Serving as a food source for microbes and small animals, such as mice, bugs, and rats, many biodegradable polymers used in packaging applications must be defended against infestation and attack using powerful chemical weapons such as antimicrobial additives and poisons. Biodegradation is an important issue in applications such as drug release, resorbable surgical sutures, and composting of plastic wastes. In future, it is highly unlikely that composting will be a substitute for recycling materials and energy typical for most plastics wastes. Hence, biodegradation in packaging is counterproductive with respect to recycling efforts and reuse of durable polymers as valuable and energy-rich renewable raw materials as a substitute for fossil oil. Knowing that plastics wastes are biodegradable may open the door to unrestrained littering of all kinds of nondegradable wastes. Marine littering is a problem associated with illegal waste dumping, especially in shipping and fishing, which is not solved by developing biodegrading materials.

The majority of biomaterials such as cellulose and wood are infusible and cannot be injection-molded without chemical modification. Inspired by the attractive physical properties of wood, many attempts have been made to combine the prospects of biomaterials and synthetic resin, aiming at synergies between wood-like properties and facile processing typical for man-made polymers. In the early days of polymer technology, Baekeland used wood flour to reinforce and toughen his rather brittle phenolic resins. Nowadays, plant fiber-reinforced polymers continue to be a very attractive composite material in lightweight engineering. New classes of thermoplastic and thermosetting wood/plastic compounds with a high wood content ("liquid wood", "wood rubber", "injection-moldable wood") are emerging as potentially cost-effective composite materials.

In the past, many biopolymers produced in bacteria or transgenic plants were not commercially successful because of their rather poor processability and inferior properties. Owing to the very high precision of biosyntheses, it is rather difficult to adapt molecular architectures in biosyntheses to the demands of polymer molding. With respect to the very fast cycle times in injection molding, the crystallization rate of many biopolymers, for example polyhydroxybutyrate, is too slow. In nature, all polymers have identical chain lengths, whereas industrial polymers demand much broader customizable molar mass distributions with controlled short- and long-chain branching as well as a self-nucleation capability in polymer crystallization. Yet another problem in most biotechnology polymer syntheses is the rather tedious separation of biopolymers from cell proteins that are formed as byproducts. Many polyhydroxyalkanoates are extracted using chlorinated solvents. Whereas biotechnology polymer biosyntheses require water and extensive water purification, all commodity polymers are produced in the melt or the gas phase without using solvents and wastes, meeting the demands of both green chemistry and polymer processing. In spite of remarkable progress made in biotechnology, it would be tedious and expensive to fine-tune biopolymers by genetic engineering and enzyme modifications to meet the diversified demands of individual polymer applications. Therefore, a much more viable approach towards the manufacturing of commercially successful bio-based polymers is to produce monomers in biotechnology or biomass conversion processes combined with subsequent melt- and gas-phase polymerization processes. There are many examples of how this team play affords green materials with attractive processing and material properties. Today, bio-based monomers are used to render conventional plastics like PET and polyolefins renewable and green without impairing their attractive properties and recycling capability.

In principle, the production of renewable oils and monomers, produced either by recycling hydrocarbon polymers or by chemical conversion of biomass and carbon dioxide, has been demonstrated to be technologically feasible and capable of substituting petrochemical feedstocks. However, in spite of surging oil prices, the cost/performance ratio still presents a problem. Although the markets ask for green products, it remains to be seen whether the market is willing to tolerate higher prices. An open question and the topic of heated debates is the impact of bio-based materials on global warming and on society. Certainly, at first glance, the substitution of fossil oil and gas by carbon dioxide and biomass as raw materials translates into reduced total carbon dioxide emissions, as expressed by a lower carbon footprint. In recent years, the quest for a low carbon footprint became trendy and is now even employed as a marketing tool. With respect to carbon dioxide emissions in energy production, the emission of carbon dioxide in polymer production, which consumes only around 7% of the oil, is rather small. Hence, the reduced carbon dioxide emissions are likely to have marginal impact on preventing global warming. At a second glance, switching from petrochemistry to biorefinery has to be seen within the context of producing biofuels such as ethanol, which are also raw materials for many bio-based monomers. In spite of its apparent abundance, biomass available from agricultural and forestry products that lie well outside the food chain is rather limited and insufficient to supply the high demands of biopower and biofuel production. With progressing use of biomass, the imbalance of biomass demand and supply could trigger a new crisis that resembles the oil crisis in the 1970s. There are growing concerns that replacing fossil carbon by biocarbon

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

is problematic. In green economy, the demand for biopower, biofuel, and biomaterials competes with food production, depriving the world's poor of their food, and simultaneously increasing carbon dioxide emission and accelerating global warming when green lands and rainforests are converted ("green paradox"[17]). Without doubt, switching from food to energy crop production, increasing use of fertilizers and pesticides, irrigation of agricultural monocultures together with the transformation of grasslands and rainforests poses a severe threat to the biosphere and biodiversity. Whereas burning carbon to produce energy is very problematic for the future of Planet Earth, the production of recyclable plastics, regardless of whether they are bio-based or fossil, represents a sustainable use of fossil and green carbon sources. For many years to come, petrochemistry- and bio-based plastics will coexist and play a prominent role in the development of sustainable and cost-effective materials, thus meeting the needs of modern society.

Received: July 27, 2012; Revised: September 7, 2012; Published online: November 19, 2012; DOI: 10.1002/macp.201200439

Keywords: bio-based polymers; carbon dioxide; green; green chemistry; renewable resources

[1] R. Mülhaupt, *Angew. Chem. Int. Ed.* **2004**, *43*, 1054.
[2] R. Mülhaupt, *Macromol. Chem. Phys.* **2010**, *211*, 121.
[3] D. Klemm, B. Heublein, H. Fink, A. Bohn, *Angew. Chem. Int. Ed.* **2004**, *44*, 3358
[4] *Protein Engineering Handbook*, (Eds: S. Lutz, U. T. Bornscheuer), Wiley-VCH, Weinheim,Germany **2008**.
[5] D. Braun, G. Collin, *Chem unserer Zeit* **2010**, *44*, 190.
[6] A. L. Andrady, *Plastics and Environment,* Wiley–Intersciences, Hoboken,Germany **2003**.
[7] R. C. Thompson, C. J. Moore, F. S. vom Saal, S. H. Swan, *Phil. Trans. R. Soc. B* **2009**, *364*, 2153.
[8] A. D. Barnosky, E. A. Hadly, J. Bascompte, E. L. Berlow, J. H. Brown, M. Fortelius, W. M. Getz, J. Harte, A. Hastings, P. A. Marquet, N. D. Martinez, A. Mooers, P. Roopnarine, G. Vermeij, J. W. Williams, R. Gillespie, J. Kitzes, C. Marshall, N. Matzke, D. P. Mindell, E. Revilla, m A. B. Smith, *Nat. Rev.* **2012**, *486*, 52.
[9] D. Meadows, J. Randers, D. Meadows, *Limits of Growth–The 30 Years Update*, Earthscan, Bath Press, London **2004**.
[10] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484.
[11] General Assembly Resolution 42/187, "Report of the World Commission on Environment and Development", United Nations General Assembly 96th plenary meeting, 11th December 1987).
[12] P. T. Anastas, J. C. Warner, *Green Chemistry. Theory and Practice*Oxford University Press, Oxford **1998**.
[13] J. L. White, D. Choi, *Polyolefins*, Hanser Publishers, Munich **2004**
[14] *Polypropylene Handbook*, (Ed: N. Pasquini), Hanser Publishers, Munich **2005**
[15] http://en.wikipedia.org/wiki/Great_Pacific_Garbadge_Patch, accessed July 11, 2012
[16] O. J. Dameron, M. Parke, M. A. Albins, R. Brainard, *Marine Pollution Bull.* **2007**, *54*, 423.
[17] *The Green Paradoxon–A Supply–Side Approach to Global Warming*, (Ed: H. W. Sinn), Massachusetts Institute of Technology, Boston **2012**, p. 113
[18] J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Hawthorne, *Science* **2008**, *319*, 1235.
[19] http://www.unendlich-viel-energie.de/de/bioenergie/detailansicht/article/105/potenziale-der-bioenergie.html, accessed July 15, 2012.
[20] M. Stöcker, *Angew. Chem. Int. Ed.* **2008**, *47*, 9200.
[21] A. Sivasany, K. Y. Choo, P. Fornasiero, F. Kemausuor, S. Zinoviev, S. Miertus, *ChemSusChem* **2009**, *2*, 278.
[22] A. Morschbacker, *Polym. Rev.* **2009**, *49*, 79.
[23] M. Odenwald, *Focus* **2011**, *41*, 127. http://www.alphakat.de, accessed July 15, 2012.
[24] M.-M. Titirici, A. Thomas, M. Antonietti, *New J. Chem.* **2007**, *31*, 787.
[25] K. Teramura,* S. Iguchi, Y. Mizuno, T. Shishido, T. Tanaka, *Angew. Chem. Int. Ed.* **2012**, *51*, 1.
[26] M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, Germany **2010**.
[27] M. N. Belgacem, A. Gandini, *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Oxford **2008.**
[28] A. Gandini, *Macromolecules* **2008**, *41*, 9491.
[29] *Renewable Polymers*, (Ed: V. Mittal), Scrivener Publishing and John Wiley & Sons, Hoboken, Salem **2012**.
[30] Synthetic biodegradable polymers, (Eds: B. Rieger, A. Künkel, G. W. Coates, R. Reichardt, E. Dinjus, T. A. Zevaco), *Adv. Polym. Sci. 245*, Springer, Berlin **2012**.
[31] M. Rose, R. Palkovits, *Macromol. Rapid Commun.* **2011**, *32*, 1299.
[32] A. K. Bledzki, O. Faruk, V. E. Sperber, *Macromol. Mat. Eng.* **2006**, *291*, 449.
[33] A. Ashori, *Bioresource Technol.* **2008**, *99*, 4661.
[34] D. Klemm, F. Kramer, S. Moritz, T. Lindstöm, M. Ankerfors, D. Gray, A. Dorris, *Angew. Chem. Int. Ed.* **2011**, *50*, 5438.
[35] J. E. Holladay, J. J. Bozell, J. F. White, D. Johnson, Top Value-Added Chemicals from Biomass Volume II - Results of Screening for Potential Candidates from Biorefinery Lignin, Report of the Pacific Northwest National Laboratory prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830, October 2007.
[36] http://www.tecnaro.de, accessed July 15, 2012.
[37] L. Janssen, L. Moscicki, *Thermoplastic Starch: A Green Material for Various Industries*, Wiley-VHC, Weinheim, Germany **2009**.
[38] http://www.cardiabioplastics.com, accessed July 15, 2012.
[39] K. O. Siegenthaler, A. Künkel, G. Skupin, M. Yamamoto, in [30], p.91.
[40] M. N. V. R Kumar, *Reactive Functional Polym.* **2000**, *46*, 1.
[41] T. Kurian, N. M. Mathew, in *Biopolymers: Biomedical and Environmental Applications*, (Eds: S. L., Kalia Avérous), Scrivener Publishing and John Wiley & Sons, New York **2011,** Ch. 14.
[42] Y. Poirier, C. Nawrath, C. Sommerville, *Nat. Biotechnol.* **1995**, *13*, 142.
[43] R. Reichardt, B. Rieger, in [30], p. 49.
[44] S. Mecking, *Angew. Chem. Int. Ed.* **2004**, *43*, 1078.
[45] R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841.
[46] http://www.natureworksllc.com, accessed July 15, 2012.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

[47] http://www.thecoca-colacompany.com/dynamic/press_center/2011/12/plantbottle-partnerships.html, accessed July 15, 2012.
[48] http://www.braskem.com.br/plasticoverde/eng/braskem.html, accessed July 15, 2012.
[49] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* **2002**, *4*, 2561.
[50] J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663.
[51] D. C. Webster, *Progr. Org. Coatings* **2003**, *47*, 77.
[52] http://www.nanotechindustriesinc.com/GPU.php, accessed July 15, 2012
[53] S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284.
[54] a) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388; b) R. Eberhardt, M. Allmendinger, B. Rieger, *Macromol. Rapid Commun.* **2003**, *24*, 194.
[55] G. Luinstra, *Polym. Rev.* **2008**, *48*, 192.
[56] C. M. Byrne, S. D. Allen, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 11404.
[57] C. Robert, F. de Montigny, C. M. Thomas, *Nat. Commun.* **2011**, *2*, 586.
[58] M. Bähr, A. Bitto, R. Mülhaupt, *Green Chem.* **2012**, *14*, 1447.
[59] M. Tolinski, *Plastics and Sustainability*, Scrivener Publishing LLC and Wiley, Hoboken, USA **2012**.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim