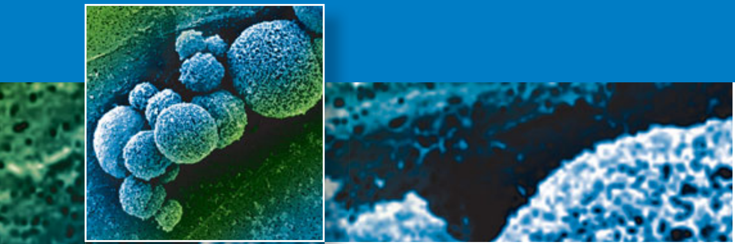

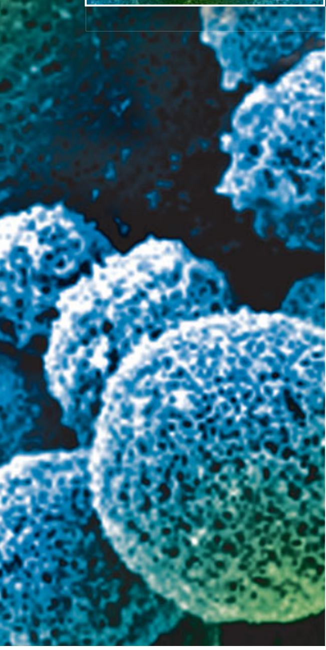

# Next-generation biopolymers: Advanced functionality and improved sustainability

**P.J. Halley and John R. Dorgan, Guest Editors**

A significant change is occurring in the global polymer industries. Development of a new generation of bio-based polymers, polymers derived from renewable resources, is progressing rapidly. Complementing historical biopolymers such as natural rubber and cellulosics, these new bioplastics include a growing number of commercial successes, including polylactides and polyhydroxyalkanoates. Many more bioplastics are on the near horizon, made possible by rapid advances in biotechnology. The molecular specificity of biochemical transformations is ideally suited for producing high purity monomers needed for making high molecular weight polymer molecules. Some of the newest developments involve the creation of well-established polymers (polyethylene, polybutlylene, poly(ethylene terephthalate)) via new biochemical pathways that start with renewable, rather than fossil, resources. This article highlights some recent advances in bio-based polymers. Specifically, this review includes topics ranging from novel biopolymer synthesis, new bio-based nanocomposites, novel processing, and holistic assessments of sustainability through quantitative life-cycle analysis. It is demonstrated that greener plastic materials can be produced through *eco*logically responsible conversion of renewable resources using industrial *bio*technology and enhanced by *nano*technology. This emerging approach represents a *triple technological convergence* that promises to significantly alter the value chains of the global plastics industries.

## Introduction

The worldwide production of plastics reached 260 billion lb/yr at the end of the 20th century, with a global value in excess of a trillion dollars and over $310 billion to the U.S. economy alone.[1] Large quantities of petroleum are used to produce plastics, but oil is of finite supply; as world economies develop, it will become more and more expensive.[2] Additionally, pollution results from the manufacture, use, and disposal of plastic materials. Emissions of greenhouse gases (GHGs) are of increasing concern due to issues relating to global climate change. As the world's light petroleum reserves are depleted, and as China, India, and other developing economies industrialize and drive demand, oil prices have shown great volatility. This same volatility is manifested in the prices of petroleum-derived plastics. Moreover, as the oil spill in the environmentally sensitive Gulf of Mexico demonstrates, drilling under challenging conditions such as deep water poses real risks, both environmental and financial. Simultaneously, lower-grade "heavy" crude oils, such as the Canadian oil sands, are being increasingly utilized; these carbon sources are less economical and potentially even more environmentally deleterious than off-shore drilling. However, plastics offer profound societal benefits, including increased agricultural production, reduced food spoilage, reduced fuel consumption in lighter-weight vehicles, better health care, and low-cost net shape manufacturing. Plastic materials are an indispensible part of modern societies, but the crisis consumers are faced with in the energy arena is also sharply impacting the plastics industries. What will happen to our environment, to human and animal health, and to the plastics industries—the fourth largest manufacturing sector of the U.S. economy, employing more than 1.2 million citizens[1]—if sustainable technologies are not developed and deployed?

Producing "green" polymers and composites has been a goal for some time, but significant technical and economic problems have kept this approach from being pursued on a large scale.[3] While there is clearly a need to develop bioplastics and biocomposites, the materials must be competitive on a price-performance basis. In the past, renewably based plastics were

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either too expensive or they simply lacked the properties required for many applications. Recently, commercial successes in new bioplastics have emerged, and these advancements are reflective of a larger trend toward the successful application of industrial biotechnology. Examples include the commercialization of polylactides (PLA) for compost bags and flexible films and Mirel (family of polymers known as polyhydroxyalkanoates) for injection-molded products such as cutlery. Soy oil-based materials (polyols) are also now commercially produced by a number of companies for use in the urethanes industries, and some polyamides are also bio-based (Nylon-11 and Nylon 6–10 with biocontent). It is also noteworthy that a number of companies from around the globe are working to commercialize renewably sourced PBS (poly(butylene succinate)) for flexible agricultural and packaging films, and large soft drink manufacturers have committed to securing PET (polyethylene terephthalate) from renewable resources. These successes are indicative of the overall opportunity to replace significant fractions of the billions and billions of pounds of plastics produced using petroleum each year.

Fortunately, sustainable polymeric materials are becoming increasingly possible. The science of industrial ecology, through the tools of quantitative life-cycle analysis (LCA), now enables a better understanding of the environmental impacts of plastic materials. Simply described, LCA defines the scope of impact, the specific material flows and their impacts, and improvement strategies for the impacts from a process. For example, utilizing crops with low inputs of water and fertilizer that can be grown on marginal lands reduces deforestation and pressures on food supplies.[4] Similarly, the recent rapid developments in industrial biotechnology are making the conversion of biomass into useful chemicals and fuels increasingly feasible.[5,6] Finally, advances in nanotechnology are enabling increased materials performance. This emerging combination represents a triple technological convergence, which is represented in **Figure 1**.[7]

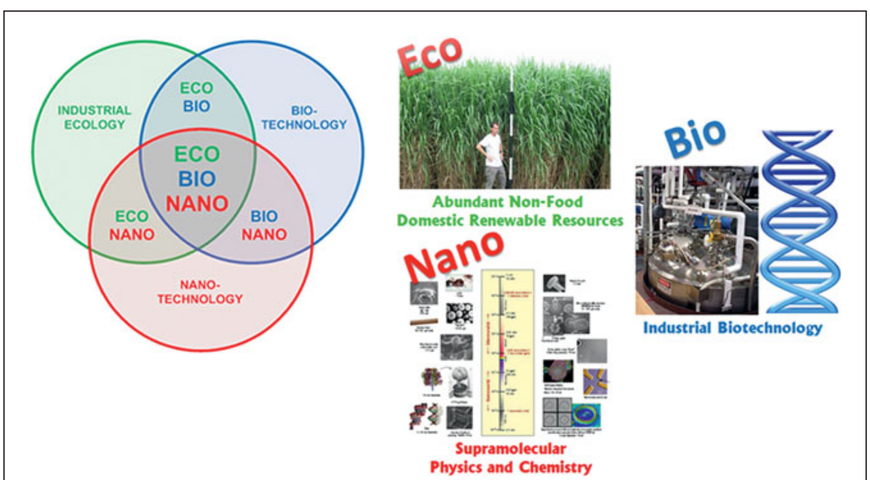


**Figure 1.** Cross-cutting science and technologies are converging to impact the way plastic materials are obtained. *Eco*logically responsible use of renewable resources aided by industrial *bio*technology and optimization of material properties using *nano*technology can create a new foundation for a sustainable plastics manufacturing industry.

## Sustainable polymer options

A number of strategies for developing sustainable plastics have been pursued. Photodegradable plastics contain a balance of antioxidants and photodegradation catalysts that enables controlled degradation (maintaining performance properties while undergoing degradation) after a photo-initiated degradation stage.[8] Their advantages are that they have performance characteristics similar to conventional polymers at similar cost structures; however, the disadvantages of oxodegradable materials (at present) are their continued use of non-renewable fossil fuels and their inability to degrade fully to $CO_2$ and $H_2O$ in the soil.[9] Additionally, if not controlled, photofragmentation, which increases litter, rather than photodegradation of these materials may occur.[10] Degradable polymers have been developed without antioxidant packages or with pro-oxidants that allow slow degradation over time. They present similar advantages and disadvantages to photodegradable polymers in their cost structure, performance properties, use of non-renewable resources, and the production of degradation products other than $CO_2$ and water such as ketones, branched alkenes, alcohols, and esters.[9] Because of these drawbacks, both biodegradability (i.e., compostability) and renewable content are desirable goals in developing sustainable plastics (for additional perspective, see the article by Narayan in this issue).

### *Classification of biopolymer production methods*

Bio-based plastics are obtainable through a variety of pathways and can be generalized according to the scheme in **Figure 2**. Here, the number of distinct chemical transformations needed to pass from the raw biomass resource to the final polymer is counted as a "stage." For example, polylactides can be considered three-stage bioplastics, as in this technology, corn sugars are derived from plant matter (stage 1), these sugars are fermented to lactic acid (stage 2), and then the lactic acid is polymerized (stage 3).[11,12] In a two-stage production process, the plant-derived material is converted by fermentation directly to a polymer; the polymer may be present intercellularly, as with polyhydroxyalkanoates/polyhydroxybutyrates (PHAs/PHBs),[13–16] useful for consumer packaging, or secreted extracellularly as in the case of xanthan gum, a polysacharide useful as a rheology modifier and food additive. Also, Nylon-11 (poly(aminoundecanoic acid)) is produced in a two-stage process, whereby castor oil is extracted from the castor bean and subsequently chemically converted. Finally, in a one-stage process, the biomass itself contains the valued polymer; the most-used biopolymers (starch, cellulose, and natural rubber) come from one-stage processes. Due to biotechnological advances, trans-species genetic engineering is now possible, by moving genes from one species, for example the bacteria that produce PHAs, into another species, such as


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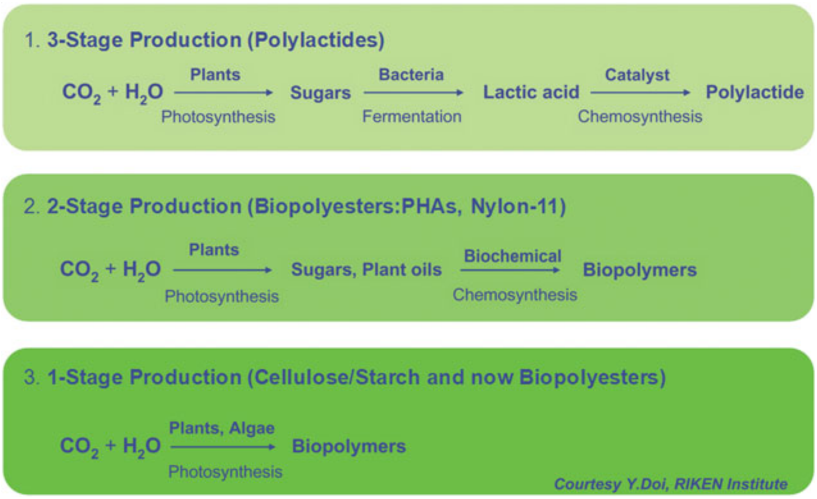


**Figure 2.** Characterization of bioplastics depending on the number of distinct biochemical transformations needed to obtain the final polymer. (Image courtesy of Y. Doi, RIKEN Institute). PHAs, polyhydroxyalkanoates.

sugarcane.[17,18] Producing desired polymers directly from $CO_2$ and sunlight via photosynthesis has a number of appealing features; however, these must be evaluated from a LCA perspective, and this route also faces a number of environmental, social, and regulatory issues.

## Starch-based plastics

Starch-based polymers have a variety of industrial uses, such as food packaging, flexible films, and injection molded pots.[19] Thermoplastic starches (TPS), developed since the 1980s,[20,21] are composed of starch, plasticizers, and additives. The low cost of these materials, their inherent biodegradability, and their large renewable resource content make them an attractive choice in terms of economy and sustainability. However, disadvantages include water sensitivity and poor product performance in extreme environments. Recent research[22–25] has extended their application by improving water resistance via blending while still maintaining biodegradability. Commercial grades are currently available; **Figure 3** shows a disposable candy tray made from TPS. Starch blends with synthetic commodity polymers (such as starch-polyethylene and starch-ethylene vinyl acetate) have been extensively investigated.[26–29] Their advantages include low cost, good packaging and mechanical performance, and the ability to process on conventional equipment. Disadvantages include incorporation of the non-renewable blend component, partial degradability, and residual non-biodegradable byproducts.[9] Starch-based polymers are discussed further in the Glenn et al. article in this issue.

## Biopolyesters

Polyesters from either renewable or fossil resources are often degradable due to the relative ease of hydrolyzing the ester bond. As already mentioned, both PLAs[12,30,31] and PHBs[32] are now commercially available from renewable resources. PBS based on fossil resources is available commercially, is easily processed, and has excellent material properties and biodegradation; however, it is more expensive and, at present, made from non-renewable resources.[33] However, the starting succinic acid monomer (one of the starting butylene and succinic acid monomers) is readily available from *Actinobacillus succinogenes, Anaerobiospirillum succiniciproducens, Mannheimia succiniciproducens,* and recombinant *Escherichia coli*, and there is presently significant commercial activity to produce PBS from renewable resources.[34] There is broad and growing literature on polymer blends incorporating biopolyesters, both with other bioplastics and with a variety of petroplastics. Avérous and Pollet discuss biopolyesters in this issue.

## Biocomposites and bionanocomposites

Biocomposites using natural fiber reinforcement have also received considerable attention recently; reinforcing fibers derived from abaca, flax, hemp, jute, kenaf, oil palm, sisal, and many other plants have been used to make biocomposites with both bioplastic and petroplastic matrices.[35] Among natural fibers, kenaf is very promising for a variety of reasons, including, importantly, low odor emissions. To date, biocomposites have primarily been developed for sheet applications suitable for fabrication into interior auto parts such as

**Figure 3.** Thermoplastic starch food packaging.



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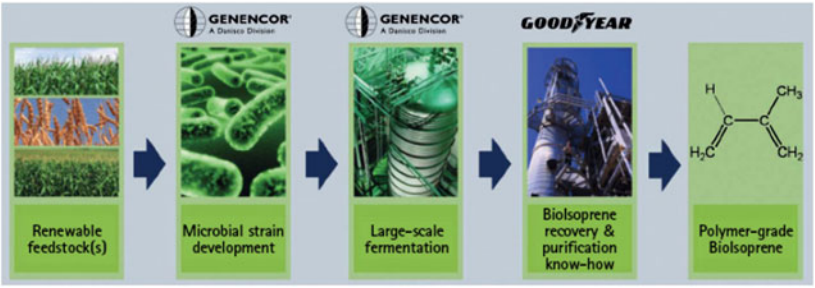


**Figure 6.** Isoprene is being produced starting from renewable resources due to the successful metabolic engineering of the isoprene pathway.[45]

headliners.[36,37] Truss discusses biocomposites in this issue.

Nanocomposites can overcome some of the drawbacks of bioplastics and biocomposites, but key developmental challenges remain. Extensive work has been completed on nanoclay reinforced bioplastics.[38] Reactive grafting of biopolymers to nanocellulose or carbon nanotubes improves a suite of thermophysical properties.[7,39,40] Nanocellulose is a topic of increasing interest in the bio-based materials community,[41–43] because if processing costs can be kept to between \$0.20–\$0.25/lb, then nanocellulose reinforced bioplastics will be less expensive than many common plastics derived from petroleum. Avérous and Pollet discuss various bionanocomposites in this issue.

## *Traditional polymers made from renewable resources*

For many applications, such as building materials and automobiles, rapid degradability is undesirable, but the use of renewable resources is desirable. Also, as petroleum prices escalate and show volatility, there is an economic incentive to find alternative routes to traditional materials. Great progress has been made in recent years in developing alternative routes to traditional materials, starting with renewable resources.

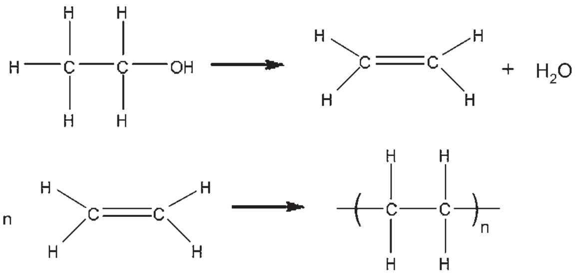

**Figure 4.** Ethanol from biomass provides a feedstock for producing polyethylene. Figure shows ethanol conversion to ethylene to polyethylene.


**Figure 5.** Ethanol can be converted to ethylene glycol, which when polymerized with terephthalic acid produces a polyethylene terephthalate that is 30% bio-based. This is the basis of the present PlantBottle technology.

The United States is now the world's largest producer of ethanol from biomass,[44] and ethanol provides a building block for two important non-degradable bioplastics: bio-polyethylene (bio-PE) and bio-polyethylene terephthalate (bio-PET). **Figure 4** shows the route to bio-PE; ethanol is dehydrated to ethylene, which can then be polymerized by many different mechanisms using a wide variety of catalysts. This route is being commercialized by a chemical company in Brazil that is providing flexible film and extrusion grades of bio-PE to global markets (as seen in typical products such as that shown in **Figure 5**).

The widely used butyl rubber, a copolymer of isobutylene and isoprene, will soon be available from renewable resources. Genencor has pioneered the metabolic engineering of the isoprene pathway to express it in *E. coli*, thus resulting in an industrial biochemical process that produces high purity isoprene.[45] This renewably resourced isoprene is also being incorporated into tires; a schematic is shown in **Figure 6**.

The other needed component for butyl rubber, isobutylene, is available via the dehydration of isobutanol. Like many organic acids and alcohols, isobutanol can be derived via fermentation from starch or cellulose derived sugars. **Figure 7** presents schemes for converting isobutanol first into isobutylene and subsequently into a number of interesting compounds, including terepthalic acid. The combination of renewable isoprene and isobutylene yielding butyl rubber provides the perplexing reality of being able to produce what might be called all-natural synthetic rubber.

Another notable monomer available from renewable resources is 3-hydroxypropionic acid (3-HP). This monomer may be polymerized to produce a biodegradable biopolyester poly(3-HP) or dehydrated to produce acrylic acid. Thus, a route to renewable poly(acrylic acid), a key component in paints and superabsorbancy materials, is also emerging. Many other examples can be cited.

Nylons (polyamides) are tough plastics with desirable properties that command relatively high prices. Historically, polyamide-11 has been produced from castor oil as the starting


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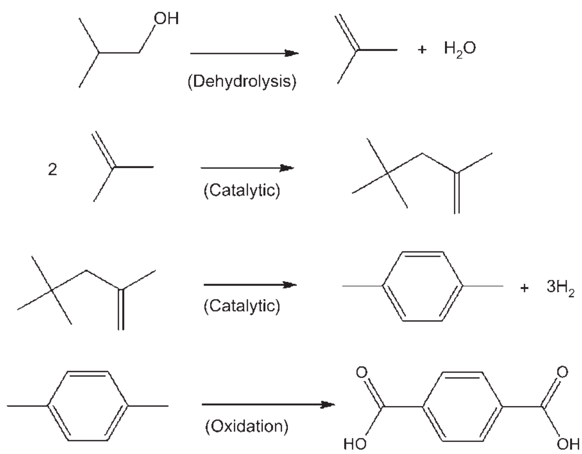


**Figure 7.** Isobutanol from renewable resources can provide monomers for polyisobutylene, butyl rubber, and polyethylene terephthalate.

material. Presently, a number of research groups are working on developing other nylons from renewable resources; for example, Nylon-4 can be produced starting from monosodium glutamate, a food additive widely produced via fermentation. The modern tools of industrial biotechnology are sure to yield new organisms with metabolically engineered pathways that produce other polyamide precursors.

## Conclusions

Societal demands and the technological convergence of industrial ecology, biotechnology, and nanotechnology are altering the way in which plastic materials are produced. The development of bio-based polymers ("bioplastics") is on an exciting trajectory—scientific research is leading to rapid commercialization. The articles in this issue highlight current research trends that are pushing bioplastics to the next level of performance. In the evolving realities of the global economy, an important performance metric is the environmental footprint of a material. Accordingly, commensurate developments in newly developed assessment tools for sustainability are also discussed. The confluence of higher fossil resource prices, new technologies, and consumer demand for more environmentally conscientious materials is rapidly changing polymeric materials science.

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