

# Nature or Petrochemistry?—Biologically Degradable Materials

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## Keywords:

environmental chemistry · green chemistry · petrochemistry · plastics · polymers

*Naturally occurring polymers have been utilized for a long time as materials, however, their application as plastics has been restricted because of their limited thermoplastic processability. Recently, the microbial synthesis of polyesters directly from carbohydrate sources has attracted considerable attention. The industrial-scale production of poly(lactic acid) from lactic acid generated by fermentation now provides a renewable resources-based polyester as a commodity plastic for the first time. The biodegradability of a given material is independent of its origin, and biodegradable plastics can equally well be prepared from fossil fuel feedstocks. A consideration of the overall carbon dioxide emissions and consumption of non-renewable resources over the entire life-cycle of a product is not necessarily favorable for plastics based on renewable resources with current technology—in addition to the feedstocks for the synthesis of the polymer materials, the feedstock for generation of the overall energy required for production and processing is decisive.*

## Introduction

The evolution and the success of the chemical industry in the second half of the 19th century was intimately related to the introduction of fossil feedstocks as a basis for synthesis. With synthetic dyes made from coal replacing scarce naturally occurring dyes, light-stable colorants became accessible to larger portions of the population for the first time. Today fossil feedstocks in the form of oil and gas are by far the most important raw materials for the chemical industry, accounting for more than 90%. After energy generation (54% in the OECD countries) and transportation (35%), the chemical industry follows in third position as user of fossil feedstocks

(12%, of which approximately equal shares are used as raw materials for syntheses and for energy generation).<sup>[1]</sup> In the chemical industry, the larger part of the raw materials is converted to polymers. The success of commodity plastics over the past 50 years can be attributed not only to the reliable raw materials basis and to

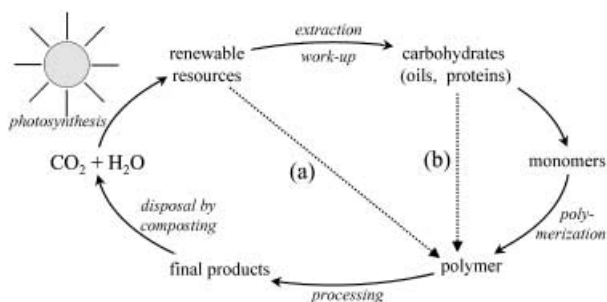
their versatile applications properties, but also to their thermoplastic processability. Processing from the melt enables a cost effective and environmentally benign fabrication of mass products such as films and molded articles.

As a result of the oil crisis in 1973, alternative energy and raw materials sources such as biomass were propagated and investigated intensely. With decreasing crude oil prices public interest diminished again. Contemporary geopolitical and economical developments have brought back to mind the disadvantages of a dependence on crude oil and also its limited availability. The range of proven oil reserves accessible with conventional recovery techniques is currently estimated to be 40 years.<sup>[2]</sup> Albeit past estimates of this type have always proven to be pessimistic in hindsight, on the other hand without doubt the dependence on the oil reserves in the Middle East will increase substantially. The ultimate formation of the greenhouse gas CO<sub>2</sub> from fossil feedstocks has unpredictable and irreversible consequences on the global climate. A disposal of traditional plastics in landfills will occupy the latter for indefinite amounts of time due to the very slow degradation. A cycle according to Scheme 1 based on renewable resources therefore appears attractive, and would also satisfy the general desire for “natural” products.

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**Scheme 1.** Simplified schematic materials cycle for biologically degradable materials based on renewable resources.

In the following discussion the term of biodegradability will be defined. Subsequently the synthesis and properties of biologically degradable materials based on naturally occurring polymers, polyesters from microbial synthesis, lactic acid as a monomer prepared from renewable resources, and petrochemical monomers will be presented. Finally, materials based on renewable resources and petrochemistry-based materials are compared with respect to their ecological potential.

### Biological Degradability

Biologically degradable materials are currently receiving considerable attention. In this context, biodegradability and the preparation from renewable resources should be differentiated from one another. While it is true that naturally occurring polymers, such as cellulose or natural rubber, are also biodegradable, the degradability of a given chemical structure will be independent of whether it was generated from renewable resources or from fossil resources.

As a definition of the term biodegradability, a German standard test method exists since 1998, which is entitled “test of the compostability of plastics” (Figure 1).<sup>[3,4]</sup> In addition to an analysis of the chemical composition (e.g. of any heavy metals present) this standard test includes probing the



**Figure 1.** Symbol for the certification of biodegradability of plastics according to the German standard test method DIN V54900.

complete degradability in laboratory experiments, probing the degradability under real-life conditions and the quality of the resulting compost, and probing the ecotoxicity of the compost for barley, rain worms, and daphnia. To be classified as biodegradable, in laboratory experiments more than 60% of the organic carbon must be converted within a maximum of six months; moreover under real-life conditions of composting more than 90% of the plastic is required to be degraded to fragments not more than 2 mm in size.

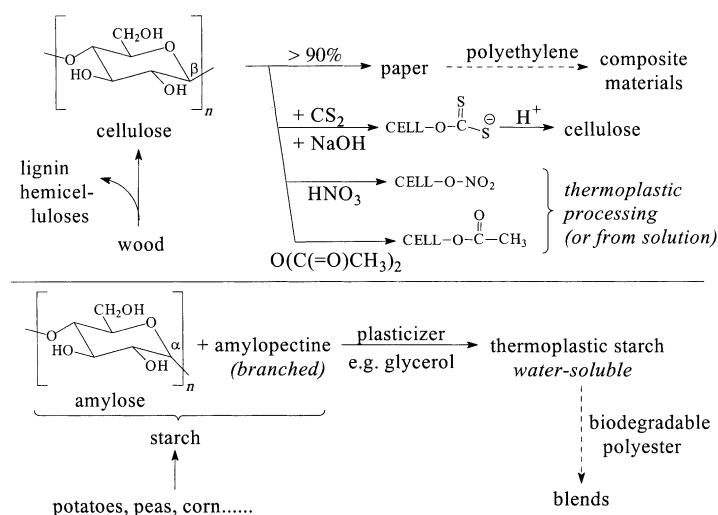
Besides naturally occurring polymers, the use of microbially or chemically prepared polyesters as biodegradable materials is currently the center of attention. Degradation occurs in two steps: An initial extracellular enzymatic or chemical hydrolysis results in low molecular weight fragments, in some cases this can proceed to the original monomers. These fragments can be resorbed by cells, and are ultimately mineralized to carbon dioxide and water. As erosion usually occurs much faster in the amorphous regions of the polymer than in the crystalline regions, crystallinity and crystallite sizes can have a strong impact on the degradation rate.<sup>[5]</sup> The predominance of structures with a high crystallinity amongst traditional polyesters and polyamides is certainly related to the corresponding desirable mechanical properties, which, for example, enable their use as molded parts and in fibers. In addition it can be speculated that the non-degradability and the resulting stability towards undesired environmental influences during the useful lifetime of the products contributed to establishing them in the early days of the polymer industry.

### Naturally Occurring Polymers

More than  $10^{11}$  t of biomass is formed by photosynthesis annually, consisting for the most part of cellulose, starch, other polysaccharides, and lignin. Paper has been known for more than 2000 years. The current annual worldwide production of paper and cardboard amounts to  $320 \times 10^6$  t, clearly exceeding that of petrochemical plastics ( $200 \times 10^6$  t).<sup>[6]</sup> However, the hydrophilicity and the resulting sensitivity of the mechanical properties towards water limits the utility as a material—a soaked paper bag is of little use. Moreover, unlike commodity plastics such as polyolefins, cellulose cannot be processed thermoplastically. Thus, cellulose fibers (viscose) or sheets (cellophane) are manufactured from solution by decomposition of cellulose xanthogenate



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**Scheme 2.** Materials based on cellulose and starch.

(Scheme 2).<sup>[7,8]</sup> Derivatization can yield materials suited for thermoplastic processing, for example, cellulose acetate or celluloid (that is cellulose nitrate with camphor as a plasticizer).<sup>[8,9]</sup> However, this requires additional synthetic steps which today consume fossil resources, and the degradability of these derivatives is less than that of unmodified cellulose.

Pulp (which consists primarily of cellulose) for paper production or serving as a raw material for the chemical industry is made from wood by separating the hemicelluloses and lignin. The processes currently applied for pulp production consume significant amounts of energy and water, and pollutants such as sulfur compounds are released into the environment.<sup>[10]</sup> Accordingly, for example, paper bags offer no advantage over polyethylene bags with regard to the overall environmental impact from the raw materials to their disposal.<sup>[11]</sup>

Composite materials can combine the low cost of pulp with the water stability of polyethylene. In beverage containers, marketed under the tradename Tetrapak in Europe on a very large scale, a thin polyethylene film protects both sides of the cardboard container. Upon “recycling” after use, the pulp is dissolved and employed for other applications less demanding with regard to fiber quality, and the polyethylene is burnt to generate energy.<sup>[12]</sup>

In contrast to cellulose, starch can be processed thermoplastically without the need for modification if it has a suitable water content. In addition to its water sensitivity, the overall mechanical properties of starch pose a strong limitation, however. Both issues can be improved upon by blending with thermoplastics, such as polyethylene or polyesters. Blends with biologically degradable polyesters are completely compostable. Such blends are produced by Novamont under the tradename Mater-Bi on a scale of 20 000 t per year.<sup>[13]</sup>

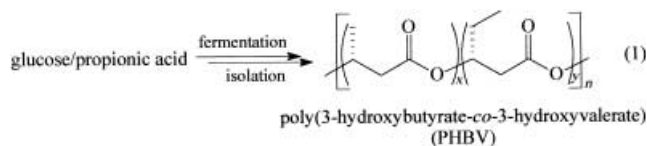
Naturally occurring polymers perform versatile vital functions in living organisms, and they represent highly attractive materials. Employing naturally occurring polymers as materials is a beneficial “shortcut” (route a) in terms of Scheme 1. The necessity for their isolation from biomass and

their limited processability impose significant limitations. Therefore other thermoplastic biodegradable materials, mostly polyesters—prepared microbially or chemically—have become the focus of attention in recent years.<sup>[14–16]</sup>

## Microbially Synthesized Polyester

Poly(3-hydroxybutyrate) (PHB) is produced by various bacteria by fermentation of carbohydrates under controlled nutrition conditions. Similar to the function of starch or glycogen in other organisms, it serves as an energy-storage reservoir. It is located in the cytoplasm in the form of granules of approximately 0.5  $\mu\text{m}$  size. Under suitable conditions, up to 90% polymer can be accumulated with respect to bacteria dry mass. Isolation of the PHB requires breaking of the cell walls by means of mechanical shear or by enzymatic digestion, followed by extraction of the polymer. This extraction can be performed by means of washing in centrifuges, or with organic solvents such as dichloromethane.<sup>[17]</sup>

As early as the 1960s, PHB was produced on a kilogram scale temporarily, motivated by potential commercial applications as a biodegradable plastic based on renewable resources.<sup>[18]</sup> During the oil crisis in 1973 interest in PHB reintensified, and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was successfully prepared by a fermentative route [Eq. (1)].<sup>[19]</sup> By comparison to (stereoregular) PHB,



which melts at 180 °C, the melting point of PHBV can be lowered to 137 °C by introduction of 25 mol% of hydroxyvalerate units. This strongly improves thermoplastic processability. In addition, mechanical stability (impact strength) is improved by an order of magnitude. Overall properties are comparable to those of polypropylene. With the stabilization of oil prices, interest in commercial uses of PHBs decreased again for some time. However, in the late 1980s PHBV was commercialized by ICI under the tradename Biopol. In Germany a blowmolded shampoo bottle was marketed. An example of another potential application is commercial fishing nets, which upon loss sink to the bottom of the ocean where they degrade. In 1996 the Biopol technology was acquired by Monsanto, which investigated the direct synthesis of polyhydroxyalkanoates in transgenic plants intensively. The production was stopped by Monsanto in 1998.<sup>[20,17c]</sup> The company Biomer in Munich has been producing PHB with their own proprietary bacteria strains since 1994. Current annual production amounts to several tons per year, with prices around € 15 to 20 per kg. The material is applied for instance in fireworks rockets, which degrade in the environment.<sup>[21]</sup>

A direct synthesis of carbohydrates again represents a favorable “shortcut” (route b) in terms of Scheme 1. A

disadvantage of the current syntheses of polyhydroxyalkanoates is the necessity to use glucose as a relatively costly substrate, which is converted to PHBV with limited yield (ca. 40%), as well as the effort required to isolate the polymer. Designed bacteria with a lower demand with regard to the substrate, or a direct production of polyhydroxyalkanoates in genetically modified plants could provide potential future alternatives.<sup>[22]</sup>

### Poly(lactic acid)

The synthesis of higher molecular weight poly(lactic acid) (PLA) was reported by Carothers et al. already in 1932.<sup>[23]</sup> Since the 1970s copolymers based on lactic acid and glycolic acid have been utilized for medical applications, for example, as a degradable matrix for the slow release of drugs.<sup>[24]</sup> A broader larger scale application as a biodegradable material has only become reality very recently.

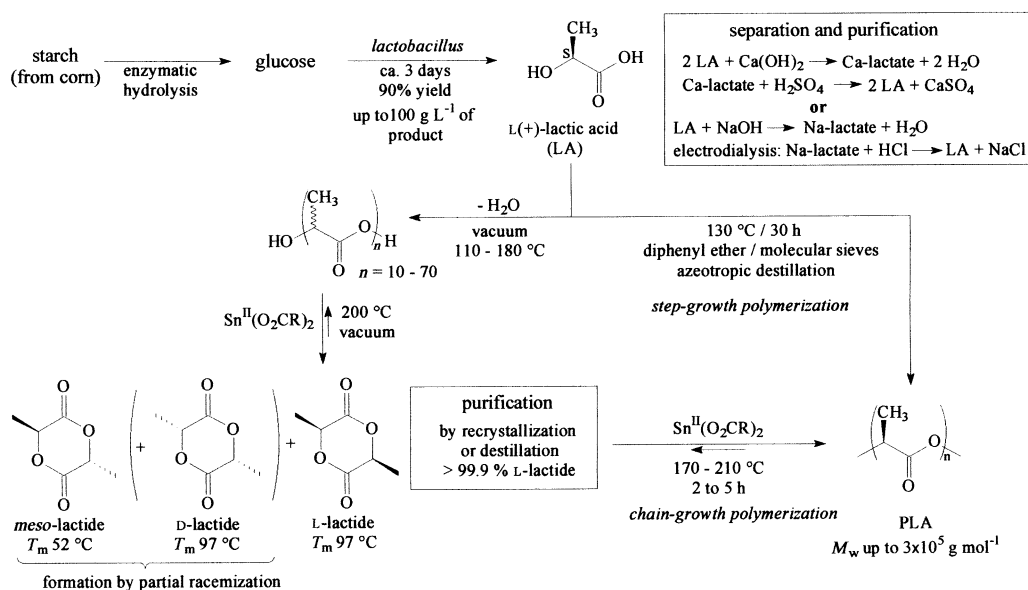
The biotechnological production of lactic acid by fermentation of carbohydrates, which can provide either enantiomer in high purity, dominates over chemical routes. In conventional processes, lactic acid is isolated by precipitation of the calcium salt with  $\text{Ca}(\text{OH})_2$ , followed by redissolution with  $\text{H}_2\text{SO}_4$ . For each kilogram of lactic acid produced, about one kilogram of gypsum is formed as a coproduct. Membrane-separation processes, such as electrodialysis, provide a more environmentally friendly alternative.<sup>[25]</sup>

The direct synthesis of PLA by polycondensation of lactic acid features the typical drawbacks of step-growth polymerizations:<sup>[26]</sup> owing to the correlation  $DP_n = 1/(1-p)$  between the degree of polymerization ( $DP_n$ ) and the conversion ( $p$ ) high molecular weights are only achieved at very high conversions (>99% conversion for a degree of polymerization of 100), and monofunctional impurities such as ethanol or acetic acid from fermentation limit the molecular weights attainable.<sup>[27]</sup> Nonetheless, high molecular weight

PLA ( $M_w 3 \times 10^5 \text{ g mol}^{-1}$ ) can be obtained by employing highly pure lactic acid and removing the water formed azeotropically during the polycondensation. The presence of solvents such as diphenyl ether is disadvantageous by comparison to solvent-free processes. Mitsui has developed this process to an industrial scale.<sup>[28]</sup>

By contrast, CargillDow, which was founded in 1997 by Dow Chemical and the agricultural company Cargill, produces PLA by ring-opening polymerization of the dimeric lactide. The latter is prepared from lactic acid via linear oligomers as intermediates in the presence of  $\text{Sn}^{\text{II}}$ -carboxylates or -alkoxides (Scheme 3). Small impurities of, for example, the *meso*-lactide, formed by racemization during the oligomerization and cyclization, can be removed from the L-lactide by distillation or crystallization. This is of importance, as the polymer properties are strongly dependent upon the stereostructure. By continuous distillation 99.9% pure L-lactide can be produced on a large scale. As a chain-growth polymerization, ring-opening polymerization affords high molecular weight polymer rapidly. For this equilibrium reaction the suitable temperature range is limited, as on the one hand the polymerization rate should be reasonably high and on the other hand the position of the equilibrium is required to be largely in favor of polymer formation. Therefore, small residues of lactide usually remain in the polymer. Polymerization can be performed anionically, cationically, or by a coordination mechanism. Coordination polymerization in the presence of  $\text{Sn}^{\text{II}}$ -octanoate occurs rapidly and with a low degree of racemization.<sup>[29]</sup> Toxicologically, traces of  $\text{Sn}^{\text{II}}$ -octanoate are regarded as uncritical for most plastics applications. Industrially, the polymerization is carried out in the melt or as a solid-state reaction.

PLA is a transparent stiff thermoplast with a glass transition temperature ( $T_g$ ) around 60 °C and a melt temperature ( $T_m$ ) of 170 to 180 °C. Its high modulus compares to that of PET or cellophane. Controlled incorporation of *meso*-lactide can reduce the stereoregularity, yielding a softer



Scheme 3. Synthesis of poly(lactic acid) (PLA).

material. Melt viscosity can be varied across a broad range, enabling processing by, for example, injection molding, melt spinning of fibers, film casting, and thermoforming. Amongst numerous potential applications stiff containers and fibers are pursued in particular (Figure 2). Clothing made from PLA is claimed to provide the same wearing comfort as PET or cotton at a better dimensional stability.<sup>[30,32]</sup>



**Figure 2.** Examples for applications of poly(lactic acid). Left: food containers; right: pillow liners. Photographs: CargillDow.

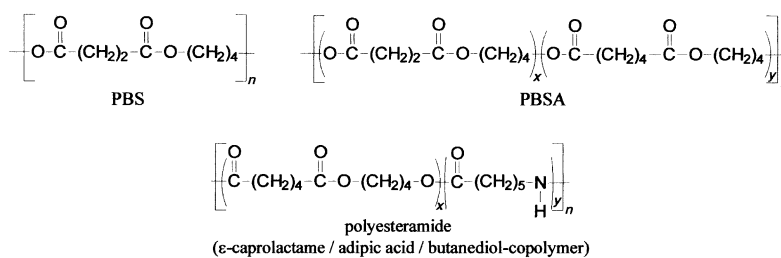
In April 2002 CargillDow started operation of a PLA plant with a capacity of 140000 t per year in Blair, Nebraska (tradename “NatureWorks”) with <sup>[31]</sup> Starch isolated from corn serves as a raw material, which is hydrolyzed to glucose.<sup>[32]</sup> In Japan PLA is marketed by Mitsui under the tradename LACEA.<sup>[28,33]</sup>

### Aliphatic Polyesters and Polyesteramides

Polyesters prepared from petroleum-based terephthalic acid and ethylene glycol (PET) or 1,4-butanediol (PBT) are commodity polymers used for a broad range of applications.<sup>[34]</sup> They are not biologically degradable. By contrast, aliphatic polyesters have been known since the 1960s to be biodegradable.<sup>[35]</sup>

Regarding the choice of dicarboxylic acids and diols (or lactones) suited for the synthesis of such entirely aliphatic polyesters, in addition to their availability the melting temperature of the polyesters which is required to be significantly above room temperature for most applications (> ca. 80°C), as well as the crystallization temperature impose restrictions. Poly(butylene succinate) (PBS) has a melting temperature of 114°C and crystallizes at about 75°C. Blown films have mechanical properties similar to the ubiquitous low density polyethylene (LDPE) films. Incorporation of adipic acid in poly(butenesuccinate-*co*-butylene adipate) (PBSA) increases the degradation rate by lowering the crystallinity; however, the lower crystallization temperatures can be disadvantageous. PBS and PBSA are marketed by Showa Denko under the tradename Bionolle.

Polyamides such as Nylon-6 or Nylon-6,6 are produced on a large scale. Like PET these semicrystalline polyamides are biodegraded only extremely slowly. By contrast, aliphatic



polyesteramides with a sufficient ester content and a random distribution of amide and ester moieties are biologically degradable. Copolymers of  $\epsilon$ -caprolactam (ca. 60 wt %), adipic acid, and butanediol possess mechanical properties and a melting temperature similar to those of LDPE, and they are suited for film applications. Copolymers of hexamethylenediamine, adipic acid, butanediol, and diethylene glycol (amide content ca. 40 wt %) are more rigid, making them suited for injection molded parts such as flower pots and disposable cutlery as well as for fibers. Like PBS and PBSA, the synthesis of aliphatic polyesters is based on petrochemicals. The polymers are biodegradable, fulfilling the requirements of the aforementioned standard test method DIN V 54900.

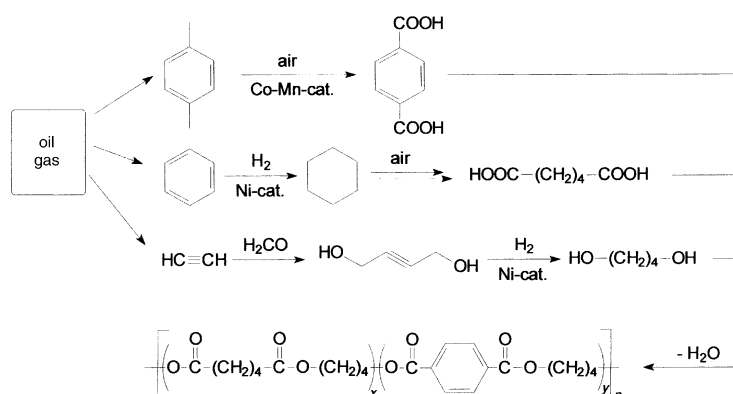
Polyesteramides were sold commercially by Bayer from 1997 to 2001 under the tradename BAK.<sup>[36]</sup> A combination of the high costs associated with establishing any new plastic in the market with the disadvantages imposed on biodegradable polymers based on petroleum versus materials based on renewable resources by current legislation in Germany (vide infra) was given as a reason for abandoning this business.<sup>[37]</sup>

### Aliphatic–Aromatic Polyesters

Various companies are currently marketing copolyesters of adipic acid and terephthalic acid with butanediol (BASF: trade name Ecoflex; DuPont: Biomax; Eastman Chemical: Eastar Bio).<sup>[38]</sup> By contrast to traditional terephthalic acid copolymers (PET and PBT) such aliphatic–aromatic copolyesters are biologically degradable, however the chain stiffness is increased compared to that of the entirely aliphatic polyesters discussed in the previous section.<sup>[39]</sup> The monomers are made petrochemically (Scheme 4).<sup>[40]</sup>

Ecoflex is a random copolymer containing approximately equal amounts of adipic acid and of terephthalic acid. The glass transition occurs at  $-30^\circ\text{C}$ , the melting temperature is 110–115°C. The physical and mechanical properties of this soft thermoplastic are similar to those of LDPE, and it can be processed on conventional equipment for LDPE (Figure 3).

The material is marketed as a compostable packaging film, for agricultural films, as a hydrophobic protective coating for food containers made from foamed starch of from paper, and as a blend component (Figure 4).<sup>[41]</sup> Copolyesters with a higher terephthalic acid content have been reported to be suited for fiber applications.<sup>[38c]</sup> Ecoflex is currently produced by BASF in a pilot plant with an annual capacity of 8000 t. This aliphatic–aromatic polyester also fulfills the requirements of the standard test method DIN V 54900 for



**Scheme 4.** Synthesis of aliphatic–aromatic polyesters from fossil resources.

biological degradability. Complete hydrolysis to the monomers is observed, which are metabolized further to carbon dioxide and water.<sup>[42]</sup>

In 2002 Rieger et al. reported on the synthesis of the biodegradable poly(hydroxybutyrate) (PHB) by cobalt-catalyzed alternating copolymerization of carbon monoxide with propylene oxide.<sup>[43a]</sup> The currently attainable molecular weights of  $5 \times 10^4 \text{ g mol}^{-1}$ <sup>[43b]</sup> are still limited, and by comparison to the other polymer syntheses reviewed, the reaction remains to be transferred to an industrial scale. Nonetheless this new reaction certainly represents an attractive alternative based on classical petrochemicals to the aforementioned microbial synthesis of PHB.

### Nature or Petrochemistry?

Regarding the source of raw materials, biologically degradable polymers can be produced based on renewable resources, as well as on a petrochemical basis. For the commercial success the price is decisive primarily. While consumers may be willing to pay a slightly higher price for, for example, a biodegradable package, this willingness has its limits. Today an indefinite variety of consumer goods claims to be ecologically beneficial—whether justified or not—reducing willingness to pay an obvious premium in an individual case. Although the price of a polymer resin is always a snapshot due to variable raw materials cost, economy of production scale, and marketing strategy etc., the contemporary pricing is nonetheless instructive. Ecoflex, produced by BASF in a pilot plant with 8000 t annual capacity, is currently sold for € 3.10 per kg, placing it in the price range of engineering plastics.<sup>[44]</sup> PLA, produced by CargillDow on a large scale, is currently available for less than € 2.20 per kg.<sup>[45]</sup> For comparison, the price of PET has been fluctuating between € 1 and 1.50 per kg in the past few years, and polyethylene is priced at about € 0.80 per kg currently.<sup>[52]</sup> Thus, a biologically degradable polyester based on renewable resources is approaching prices of commodity plastics for the first time. As an example of the impact of legislation, in Germany lower mandatory costs for a disposal by means of biodegradable compostable waste (which is collected separately in many German cities) could represent an advantage for biodegradable materials over conventional plastics.<sup>[46]</sup> A field test in the city of Kassel, Germany, conducted from May 2001 to the end of 2002 probed the reliability of separation of biodegradable plastics from conventional plastics by consumers.<sup>[47]</sup> It is also worth mentioning that currently in Germany one is only allowed to dispose of biodegradable plastics by the compostable waste collection if these were produced from renewable resources—although the ecological merits of the latter are debatable as the following paragraph reveals.

The production of poly(lactic acid) as an example can be roughly considered as a complete closed cycle with regard to the raw materials (Scheme 1). However, this picture neglects the energy required for the production of fertilizers, pesticides, transport of raw materials and of intermediates, and

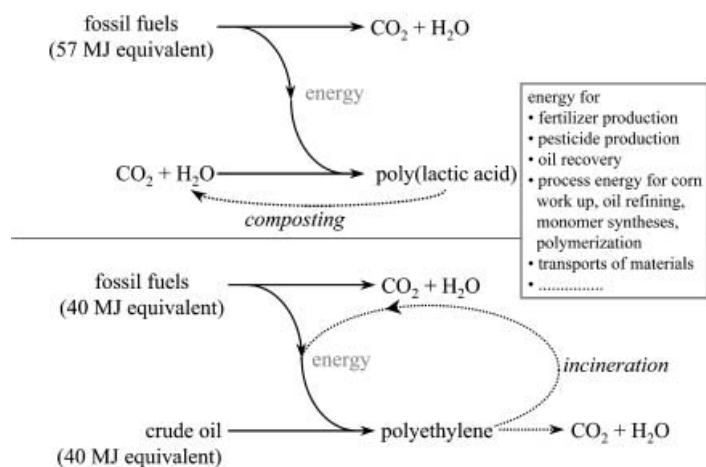


**Figure 3.** Film blowing with an aliphatic–aromatic copolyester (Ecoflex). Photograph: BASF AG.



**Figure 4.** Examples of applications of aliphatic–aromatic copolyesters. a) Packaging film made from Ecoflex. b) Coated paper cup. c) Shopping bag suited for subsequent use as a compost bag made from Mater-Bi (a blend with starch). Photographs: BASF AG (a,b) and Novamont (c).

process energy for polymer production, which is generated from fossil fuels primarily today. According to Cargill-Dow<sup>[32,48]</sup> production of 1 kg of PLA resin (Scheme 5; steps



**Scheme 5.** Current raw materials and CO<sub>2</sub> balance for poly(lactic acid) and polyethylene for disposal of poly(lactic acid) by composting and of polyethylene by incineration with energy generation.

from CO<sub>2</sub> to polymer in Scheme 1) currently consumes 57 MJ energy equivalents of fossil fuels. For comparison, production of 1 kg of PET or of 1 kg of LDPE requires 80 MJ energy equivalents.<sup>[49]</sup> The latter corresponds to 2 kg of crude oil, half of which is not burnt for energy generation but serves as a raw material for the polymer. The *higher* amount of CO<sub>2</sub> formed from fossil fuels during PLA synthesis than during PET or LDPE synthesis is approximately matched by the amount of CO<sub>2</sub> consumed during photosynthesis of the biomass used as a raw material.<sup>[48,49]</sup> The overall balance for PHB as an example of a polymer produced microbially is no better with the currently available technology.<sup>[50]</sup>

Considering the further life cycle of the polymer, composting as a frequently propagated solution is not necessarily the most useful scenario: incineration provides additional energy at a similar CO<sub>2</sub>-balance, and even upon disposal in landfills at least no CO<sub>2</sub> is released (fermentation of organic waste to methane, which can be used as an energy source, has a better energy balance by comparison to composting, however it is performed only sporadically today). The provocative suggestion to improve the global CO<sub>2</sub>-balance by depositing materials based on renewable resources in landfills, where they will degrade very slowly despite their principle degradability, is worth mentioning.<sup>[51]</sup>

Biologically degradable materials based on renewable resources are certainly not per se as “green” as they might appear at first sight. Notwithstanding, they can certainly offer ecological advantages. However, the fuel source employed for energy generation is more decisive than the raw materials source for polymer synthesis. If the overall energy demand were satisfied for the largest part from non-fossil sources such as wind energy, solar power, or water power (or also nuclear power, which is however obviously subject to debate for other reasons), polymers based on renewable resources could

possess a significantly better balance by comparison to petrochemical polymers. CargillDow has announced that it intends to use wind energy for PLA production in the future, and to improve the ecological and economical balance by using waste plant parts such as stems and leaves instead of corn. The contained cellulose and hemicelluloses will serve as a raw material, and the lignin will be incinerated for energy generation.<sup>[48]</sup>

Ultimately, society must balance such different factors as the emission of greenhouse gases, environmental pollution by pesticides and also by oil production, leakage of pollutants from compost or landfills, land consumption for farming, and the willingness to pay slightly higher prices against one another in a rational discussion. It should be noted that in some countries a complex system of regulations already provides a strict framework, for example, in the EU.

Independent of these considerations the biodegradable materials developed over the past decade enable new niche applications, which strictly require biodegradability. Examples previously outlined comprise compost bags or agricultural films. In addition, beyond the issue of degradability and the raw materials source, newly available polymers such as poly(lactic acid) and aliphatic–aromatic copolyesters are also attractive materials due to their property profile.

Received: April 9, 2003 [M1655]

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