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VIEWPOINT

Biodegradable Polymers for the Environment

Richard A. Gross and Bhanu Kalra

Biodegradable polymers are designed to degrade upon disposal by the action of living organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, and lactic acid. The need to create alternative biodegradable water-soluble polymers for down-the-drain products such as detergents and cosmetics has taken on increasing importance. Consumers have, however, thus far attached little or no added value to the property of biodegradability, forcing industry to compete head-to-head on a cost-performance basis with existing familiar products. In addition, no suitable infrastructure for the disposal of biodegradable materials exists as yet.

Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for the long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers (BPs) disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae. Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. BPs are often derived from plant processing of atmospheric CO_2. Biodegradation converts them to CO_2, CH_4, water, biomass, humic matter, and other natural substances. BPs are thus naturally recycled by biological processes (Fig. 1).

The worldwide consumption of biodegradable polymers has increased from 14 million kg in 1996 to an estimated 68 million kg in 2001. Target markets for BPs include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters). BP commercialization is, however, hampered by competition with commodity plastics that are inexpensive and familiar to the customer. Also, an infrastructure for the disposal of BPs in bioactive environments must be developed and will require capital investments. Without an extensive network of efficient composting and other bioconversion facilities that, in addition to compost, yield other valuable chemical intermediates, BPs and other biodisposables (food, yard-waste, nonrecycled paper) are destined to be entombed in dry landfill environments designed to retard biodegradation.

In this Viewpoint we report on progress, technical and social challenges, and environmental benefits of BPs. We describe what we view as highly promising biodegradable polymers that are either in development or already marketed (Fig. 2). For comprehensive reviews that include more detailed descriptions of research on biodegradable polymers for environmental applications, see (*1–3*).

Biodegradable Plastics from Starch and Cellulose

Starch is an inexpensive, annually renewable material derived from corn and other crops. The biodegradation of starch products recycles atmospheric CO_2 trapped by starch-producing plants. All starches contain amylose and amylopectin, at ratios that vary with the starch source. This variation provides a natural mechanism for regulating starch material properties.

Starch-based BPs can be produced by blending or mixing them with synthetic polymers. By varying the synthetic blend component and its miscibility with starch, the morphology and hence the properties can be regulated easily and efficiently. This approach has been successfully implemented by Novamont under the Mater-Bi trademark (Tables 1 and 2) (*4*). Blends containing thermoplastic starch (destructurized starch that is noncrystalline, produced by the application of heat and work) may be blended or grafted with biodegradable polyesters [such as polycaprolactone (PCL)] to increase flexibility and resistance to moisture. These materials are mainly formed into films and sheets. Blends with more than 85% starch are used for foaming and injection molding. The foams can be used as loose-fill in place of polystyrene; the starch-based loose fills have an average density of 6 to 8 kg/m³, compared with 4 kg/m³ for expanded polystyrene loose fill (*5*). Loose-fill materials from starch are

Polytechnic University, National Science Foundation Center for Biocatalysis and Bioprocessing of Macromolecules, Six Metrotech Center, Brooklyn, NY 11201, USA. E-mail: rgross@duke.poly.edu
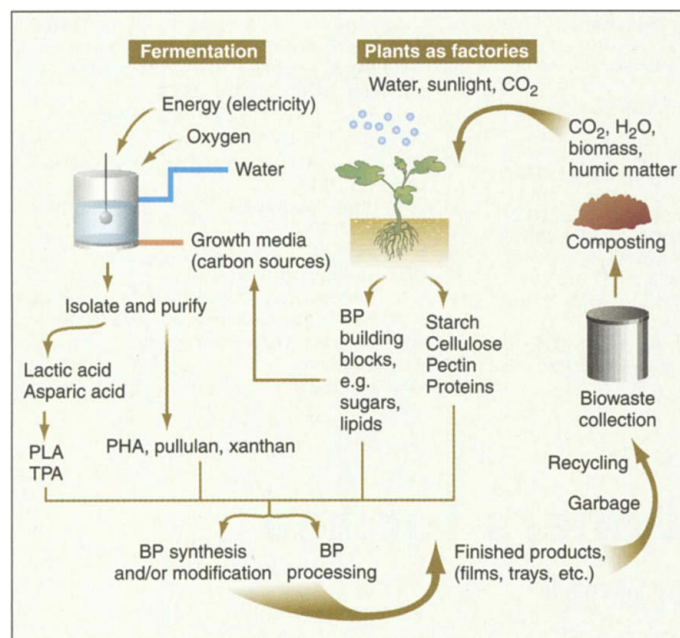
Fig. 1. Cyclic process by which agricultural products and fermentative routes can yield biodegradable polymers. Upon disposal in bio-bins and exposure to a bioactive environment, BPs will biodegrade to natural substances such as CO_2, water, humic matter, and biomass. New agricultural crops, using nutrients from compost and fixing CO_2, will produce new polymer building blocks, monomers, and polymers.

generally water sensitive. This is a problem if the packaging material is exposed to water, but an advantage when down-the-drain disposal is desired. By mixing thermoplastic starch with cellulose derivatives, rigid and

dimensionally stable injection-molded articles result.

Chemically modified plant cellulose is used in a remarkably diverse set of applications. For example, cellulose acetate is used in many common applications, including toothbrush handles and adhesive tape backing. Until the mid-1990s, plastic-grade celluloseacetates were believed to be nonbiodegradable because of their high degree of modification (or substitution). Between two and three of the glucose repeat unit hydroxyl groups are normally acetylated. However, studies in simulated compost environments revealed that cellulose acetates with degrees of substitution of up to 2.5 are biodegradable (*6*). A decrease in the degree of substitution of cellulose acetate from 2.5 to 1.7 results in a large increase in the rate of their biodegradation. Eastman Chemical

Company has developed fully biodegradable cellulose acetates that are promising but not yet commercially available (*7*, *8*).

Biodegradable Plastics from Polyesters

As early as 1973, it was shown that the polyester poly(ε-caprolactone) degrades when disposed in bioactive environments such as soil (*9–11*). This and related polyesters are water resistant and may be melt-extruded into sheets, bottles, and various shaped articles, marking these plastics as primary targets for use as BPs. Several biodegradable polyesters are now in the market or at an advanced stage of development.

Polyhydroxylalkanoates (PHAs) are produced directly from renewable resources by microbes. They can be accumulated to high levels in bacteria (~95% of the cellular dry weight), and their structures can be manipulated by genetic or physiological strategies (*12*, *13*). The physical properties and biodegradability of PHAs can be regulated by blending with synthetic or natural polymers. The widespread synthesis of PHAs by microbes is matched by a corresponding abundance of microbes that produce PHA-degrading enzymes. PHAs with short side chains behave similarly to polypropylene, whereas PHAs with longer side chains are elastomeric.

In the late 1980s, ICI Zeneca commercialized PHAs produced by microbial fermentation under the trade name Biopol. Wella AG used the polymer to make shampoo bottles. Biopol was expensive (Table 2), but customers accepted the price as part of an all-natural high-end cosmetic product. Such consumer behavior is unusual; in most cases, consumers are not willing to pay more for a product that is natural and/or biodegradable.

In 1994, Sommerville and co-workers developed genetically altered plants that contained the necessary metabolic pathway to accumulate PHAs (*14*). In an attempt to bring this technology to market, Monsanto spliced the plastic-producing gene sequence into canola plants. They created a plant that was not only 14% plastic, but also could be used to produce canola oil. However, Monsanto believed that PHA-producing plants would not be commercially viable unless 20% or more of the plant was plastic. In 1998, the company abandoned further development of PHAs. Metabolix (Cambridge, MA) continues to pursue the commercialization of PHAs both in plant crops and by fermentation processes (*15*). Recent efforts to express the copolymer in *Escherichia coli* also hold promise for reducing production cost and simplifying purification.

Poly(lactic acid) (PLA). The manufacture of polyester from lactic acid was pioneered by Carothers in 1932 (*16*) and further developed by Dupont (*17*) and Ethicon. Prohibitive production costs restricted the applicability of these
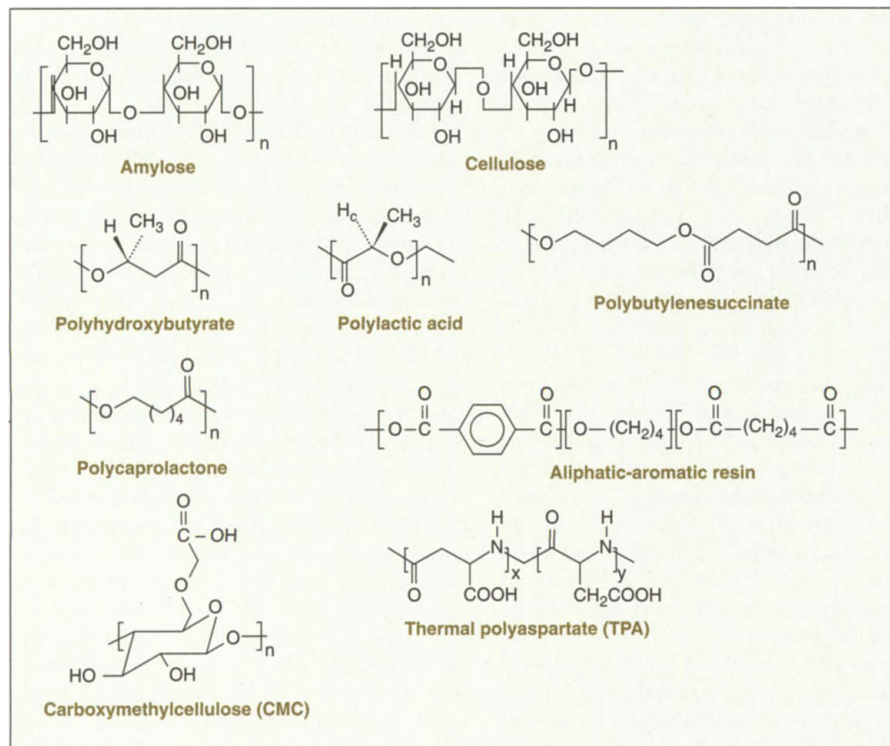

Fig. 2. Structures of selected biodegradable polymers.

Table 1. Physical properties of Mater-Bi materials, polyesters, and reference polyolefins.

Property	PHB (Biopol)	PHB-V (Biopol)	PCL (Tone 787)	PLA (Ecopia)	PAS (Bionolle 1000)	PAS Bionolle 1000	PEA (BAK 1095)	Ecoflex	Eastar Bio	Mater-Bi Y101U	Mater-Bi ZF 03U/A	Mater-Bi NF01U	PS	LDPE
Melting point (°C)	177	135	60	177–180	96	114	125	110–115	108	–	64	110	–	–
Tensile stress at break (Mpa)	40	25	4	45	40	60	25	36	22	26	31	25	–	8–10
Elongation at break (%)	6	25	800–1000	3	600	800	400	820	700	27	900	600	1–2.5	15–600
Tensile modulus (Mpa)	4000	1000	386	2800	300	500	180	80	100	1700	180	120	2800–3500	–
Density (g/cm³)	1.25	1.25	1.145	1.21	1.3	1.2	1.07	1.25	1.22	1.35	1.23	1.3	1.04–1.09	–

polymers outside the medical field until the late 1980s. Since then, major breakthroughs in process technology, coupled with decreased costs of biologically produced lactic acid, have led to the commercial-scale production of BPs from lactic acid for nonmedical applications. This integration of biotechnology and chemistry is an important strategy that will be critical to improvements in many other chemical processes in future years.

Two chemical routes have been developed to convert lactic acid to high molecular weight PLA. Cargill Dow LLC uses a solvent-free continuous process and a novel distillation method (*18*). In contrast, Mitsui Toatsu (*18*) converts lactic acid directly to high molecular weight PLA by a solvent-based process with the azeotropic (where vapor and liquid have the same composition at some point in distillation) removal of water by distillation. Lactic acid also has nonpolymer applications, including the conversion of lactic acid to its ethyl ester (ethyl lactate) for use as a naturally derived solvent. As new markets for lactic acid become available, the cost of PLA will decrease further (*18*).

PLA crystallinity, crystallization rate, transparency, and degradation rate of finished products are conveniently controlled by the copolymerization of selected L- to D-isomer ratios of lactide or lactic acid. Upon disposal, PLA degrades primarily by hydrolysis, not microbial attack. Hence, even at high humidity, it is uncommon to encounter contamination of high molecular weight PLA by fungi, mold, or other microbes. This unusual characteristic of a BP is attractive for applications in which they are in direct contact with foods for extended time periods. PLA can be converted into compost in municipal compost facilities. It can be thermally processed with minimal changes to standard machinery.

PLA is currently used in packaging (film, thermoformed containers, and short–shelf-life bottles). Cargill Dow LLC uses conventional melt-spinning processes to form fibers for clothing and other uses (*19*). Fabrics produced from PLA provide a silky feel, durability, and moisture-management properties (moisture is quickly wicked away from the body, keeping the wearer dry and comfortable).

Poly(ε-caprolactone), PCL, and poly(alkyene succinate)s. PCL is a thermoplastic biodegradable polyester synthesized by chemical conversion of crude oil, followed by ring-opening polymerization. PCL has good water, oil, solvent, and chlorine resistance, a low melting point, and low viscosity, and is easily processed thermally. To reduce manufacturing costs, PCL may be blended with starch—for example, to make trash bags. By blending PCL with fiber-forming polymers (such as cellulose), hydroentangled nonwovens (in which bonding of a fiber web into a sheet is accomplished by entangling the fibers by water jets), scrub-suits, incontinence products, and bandage holders have been produced (*19*). The rate of hydrolysis and biodegradation of PCL depends on its molecular weight and degree of crystallinity. However, many microbes in nature produce enzymes capable of complete PCL biodegradation.

In contrast to PCL, PLA from lactide, and PHAs, a series of biodegradable aliphatic polyesters have been developed on the basis of traditional polycondensation reactions. Most notable are the poly(alkyene succinate)s manufactured by Showa Denko, trademarked Bionolle. Undoubtedly, their development was inspired by the lessons learned in working with PCL. These polyesters have properties that mimic those of traditional plastics such as low-density poly(ethylene) (LDPE). Their physical properties and biodegradation kinetics depend on the choice and composition of the diol/diacid building blocks. Current uses of Bionolle are in fibers, films, bottles, and cutlery. Bionolle plastics have been found to biodegrade in compost, moist soil, fresh water, activated sludge, and sea water.

Increasing the strength of biodegradable polyesters. The strength of aliphatic polymers may be increased by substituting a fraction of the ester links by amide groups, which increase interchain hydrogen bonding and, therefore, material strength. Bayer has introduced an injection-moldable grade of poly(ester amide), BAK 2195, built from hexamethylene diamine, adipic acid, butanediol, and diethylene glycol (*20*). The company recently withdrew from the production and sale of this product (*21*). The strength of polyester BPs can also be increased by substituting some aliphatic diacid building blocks with more rigid aromatic diacids. Eastman Chemical Company (*22*) and BASF (*23*) have developed such aliphatic/aromatic

Table 2. Installed capacity of some starch-based materials and polyesters.

Material	Company	Installed capacity (tons/year)
Mater-Bi starch	Novamont	20,000
Ecofoam	National Starch	20,000
Poly(hydroxy butyrate-co-hydroxy valerate)	Metabolix	?
Poly(lactic acid)	Cargill Dow LLC	140,000
Poly(ε-caprolacton)	Union Carbide	>5,000
Poly(butanediyl succinate)s	Showa Denko	3,000
Poly(ester amide)	Bayer	?
Poly(ethylene terephthalate, adipate)	Eastman Chemical	15,000
Poly(ethylene terephthalate, adipate)	BASF	8,000

resins that retain their biodegradability. BASF projects a double-digit growth figure for its aliphatic/aromatic resin, Ecoflex (21), which is used mainly as an additive to plastics from renewable resources (for example, blended with thermoplastic starch) and as a primary component of films and laminates. Some of the physical properties of these polyesters, as well as their installed capacity and the company producing them, are listed in Tables 1 and 2.

Water-Soluble Biodegradable Polymers

Water-soluble polymers are used as detergent builders, scale inhibitors, flocculants, thickeners, emulsifiers, and paper-sizing agents. They are found in cleaning products, foods, toothpaste, shampoo, conditioners, skin lotions, and textiles. The largest volumes of water-soluble polymers are prepared from acrylic acid, maleic anhydride, methacrylic acid, and various combinations of these monomers. With the exception of their oligomers, these polymers are not biodegradable. Conventional water-soluble polymers therefore persist in oceans, lakes, and other water depositories. Consumers do not see these polymers washed up on beaches; their effects are harder to see, making the problem more dangerous. To avoid further accumulation of recalcitrant substances in waterways, the commercial development of water-soluble BPs is urgently needed.

Water-soluble BPs may be synthesized by modifying starch and cellulose. For example, carboxymethyl cellulose (CMC) having different degrees of carboxymethyl substitution is a family of marketed water-soluble polymers. Hydroxyethyl cellulose (HEC) is used as thickeners in drilling fluids and as fluid-loss agents in cementing. For such polysaccharide-derived polymers, the rate or extent of product biodegradability decreases when higher levels of modification of cellulose (more than one substituent per sugar ring) are required to achieve desired performance characteristics (24). Furthermore, many of these polymers have not yet been studied by standardized testing methods to determine their biodegradability (24, 25). Water-soluble polysaccharides are also produced by microbial fermentation. Xanthan is the most widely used microbial polysaccharide. Industrial uses of xanthan include oil recovery (viscosity control), paper manufacturing, agriculture (stimulation of plant growth), and cosmetics. Pullulan has shown a plethora of potential applications. For example, its good moisture retention and low oxygen permeability has led to its use as edible films for food packaging.

Poly(amino acids) with free carboxylic groups, such as poly(aspartic acid) and poly(glutamic acid), are excellent candidates for use as water-soluble BPs. Thus far, polymers based on aspartic acid have attained the greatest commercial success. Poly(aspartic acid)s

(thermal polyaspartate, TPAs) may be produced by two different routes (26, 27). They are functionally equivalent to poly(acrylic acid) and, when highly linear, are fully biodegradable. TPAs are being targeted for three global markets: performance chemicals, diapers, and agriculture. According to the Donlar Corporation (28), these aggregate markets represent a global market potential of $20 billion. In agriculture, TPAs have been found to stimulate crop growth by enhancing root development (28). Poly(malic acid)s, the polyester equivalent of poly(aspartic acid)s, may be useful polymers for detergents that biodegrade. However, these polymers are hydrolytically unstable.

To date, poly(vinyl alcohol) is the only polymer with exclusively carbon atoms in the main chain that is regarded as biodegradable. It is currently used in textiles, paper and packaging industries as paper coatings, adhesives, and films.

Perspectives and Conclusions

The development of BPs is best viewed in the wider context of the "greening" of industrial chemistry. In future years, it will be largely driven by three factors: the need to derive more carbon for chemical processes from renewable substances instead of oil reserves, to develop cleaner chemical processes, and to avoid perturbing the ecosystem.

Key opportunities exist to build BPs from annually renewable crops and agro-industrial waste-streams (29). The production of monomers and polymers with enzymes (30), microbes, or plants represents a cleaner and safer way of doing chemistry. Breakthroughs in the genetic engineering of metabolic pathways have yielded microbes that more efficiently convert inexpensive feedstocks (such as molasses, starch, and waste lipids) to BP building blocks (such as lactic acid) (18). Cloning and expression of genes in plants has created new possibilities for using photosynthesis to directly synthesize polymers in plants (14). These powerful technologies will allow the continued development of cost-effective biological routes to a wide range of chemicals, including monomers and polymers. By using genetic methods to manufacture safe chemicals in specific plant compartments, the separation of plant-derived polymers from foods during harvesting will be facilitated.

An important benefit of renewable feedstocks, as compared with petroleum, is a reduction in the emission of fossil fuel–derived CO_2. For example, on the basis of one estimate, the volume of PLA production in 2020 will be 3.6 billion kg/year. If these polymers displace an equivalent amount of fossil fuel–based polymers, then 192 trillion Btus of fossil-derived fuel will be saved per year, resulting in a reduction in the emission of CO_2 by 10 million tons.

To avoid perturbing the ecosystem, processes must be cyclic, without creating chemical or biological imbalances. BPs from annually renewable materials allow cyclic processes that can be renewed over short time intervals (less than 1 year). The chemicals taken from nature will be returned to nature without perturbing the environment. This is a large departure from current practices. At present there is little or no current value to the manufacturer who develops such an environmentally friendly product, and BPs must therefore compete head-to-head in cost and performance with existing familiar and inexpensive products (e. g., plastic resins such as polyethylene cost about 50 cents per pound). This is extremely difficult because new processes require intensive research and large capital expenses and must be scaled-up to be economically competitive. BPs are often designed to mimic the "feel" of existing materials. It will be important when developing and marketing BPs to identify and exploit the unique attributes of the materials.

Biodegradable polymers are only beneficial when they can actually biodegrade. Water-soluble polymers normally enter a wastewater treatment facility; the infrastructure of such facilities is readily available in all industrially advanced nations. Such facilities provide high levels of bioactivity that rapidly degrade water-soluble BPs. In contrast, the infrastructure of bioactive systems for the disposal of non–water-soluble BPs is seriously lagging. Without such an infrastructure, valuable biodisposables such as food and yard waste (25 to 30% of total municipal solid waste) are often buried in dry landfill environments (31). The logical solution is to convert biowastes to valuable compost, chemical intermediates, and energy through aerobic and anaerobic processes. A wide network of sophisticated composting and other bioconversion facilities for the reprocessing of BPs and other biowastes is essential for the future health of our ecosystem.

On the basis of on economic and environmental considerations, the commercialization of BPs will continue to increase in markets where products have a relatively short-use lifetime. It is important to remember, however, that biodegradable polymers can be sufficiently sturdy to withstand standard wash-cycle treatments in textile garments. Misconceptions that biodegradable polymers cannot be stable for multiple-use articles over lifetimes of years will need to be addressed.

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VIEWPOINT

Green Chemistry: Science and Politics of Change

Martyn Poliakoff,[1]* J. Michael Fitzpatrick,[2] Trevor R. Farren,[1] Paul T. Anastas[1]

The chemical industry plays a key role in sustaining the world economy and underpinning future technologies, yet is under unprecedented pressure from the effects of globalization and change in many of its traditional markets. Against this background, what will be needed for the industry to embrace efforts to make it "greener"? We explore some of the issues raised by the development of "green chemistry" techniques and identify potential barriers to their implementation by industry.

Most processes that involve the use of chemicals have the potential to cause a negative impact on the environment. It is therefore essential that the risks involved be eliminated or at least reduced to an acceptable level. In its most simple form, risk can be expressed as

$$\text{Risk} = \text{Hazard} \times \text{Exposure} \qquad (1)$$

Traditionally, the risks posed by chemical processes have been minimized by limiting exposure by controlling so-called circumstantial factors, such as the use, handling, treatment, and disposal of chemicals. The existing legislative and regulatory framework that governs these processes focuses almost exclusively on this issue. By contrast, green chemistry (Table 1) (1–3) seeks to minimize risk by minimizing hazard. It thereby shifts control from circumstantial to intrinsic factors, such as the design or selection of chemicals with reduced toxicity and of reaction pathways that eliminate by-products or ensure that they are benign. Such design reduces the ability to manifest hazard (and therefore

risk), providing inherent safety from accidents or acts of terrorism.

Legislation has been effective in improving environmental conditions, but toxic materials are still discharged in considerable amounts—7 billion pounds (3.2 × 10⁸ kg) in 2000 in the United States alone (4). Regulation clearly has a major and continuing role to play in lessening the environmental impact of the chemical industry (5). Green chemistry can potentially generate an even greater environmental benefit by removing the intrinsic hazard of particular products or processes, thereby moving them outside the scope of many environmental regulations.

Involvement of Academia and Industry

Green chemistry is a major component of the science underlying the "responsible care" program of the chemical industry (6) and of "sustainable development" (7). Making reduced hazard an important criterion for judging the performance of a product or process provides a new challenge for traditional academic research. Academic interest in green chemistry is reinforced by the increasing requirement by funding agencies that academic research should address quality-of-life issues and should be commercially more exploitable, and by increased "outsourcing" of industrial research to universities. As a result,

worldwide research aimed at cleaner processing has increased sharply (8).

Already in the 19th century, environmental regulation resulted in the cleanup of the LeBlanc soda process and other similarly polluting processes (9). More recently, the Montreal Protocol has led to the successful replacement of chlorofluorocarbons by compounds that do not affect the ozone layer appreciably. However, given society's demand for chemical products, most of these improvements could not have taken place in the absence of viable methods for reducing the environmental impact of the processes or introducing less harmful replacement products. Today, there is an increasing awareness that sophisticated technologies and radical new processes will be needed for the full potential for environmental improvement to be realized. Major advances in understanding the relation between the molecular structure of chemical products and their toxicity mean that we can begin to design "safer" chemicals.

The term "green chemistry" was coined only 10 years ago (10). Given that the development time for a new chemical process is often more than a decade, there has been insufficient time for green chemistry principles (Table 1) to be translated systematically into industrial processes. Nevertheless, many recently developed processes and products fulfill most of these principles. For example, the waste greenhouse gas, N_2O, from the manufacture of adipic acid (a component of nylon) is being reused as the oxidant in a greener route to phenol (11). Tetrakis(hydroxymethyl)phosphonium phosphate is used as a low-dose, low-toxicity control agent for

[1]School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK. [2]Rohm & Haas Co., 100 Independence Mall West, Philadelphia, PA 19106, USA.

*To whom correspondence should be addressed. E-mail: martyn.poliakoff@nottingham.ac.uk