

Directions for Environmentally Biodegradable Polymer Research

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Received April 23, 1992

A major factor promoting interest in biodegradable polymers is the growing concern raised by the recalcitrance and unknown environmental fate of many of the currently used synthetic polymers. These polymers include both water-soluble and water-insoluble types. The former are generally specialty polymers with functional groups that effect water solubility such as carboxyl, hydroxyl, amido, etc.; the latter are usually nonfunctional polymers commonly referred to as commodity plastics. Both types of polymers are widely used in many applications. Water-soluble polymers are used, for example, in cosmetics, water treatment, dispersants, thickeners, detergents, and superabsorbents, and they include poly(acrylic acid), polyacrylamide, poly(vinyl alcohol), and poly(ethylene glycol). Plastics are used in packaging, disposable diaper backing, fishing nets, and agricultural film; they include polymers such as polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), and Nylon 6.6.

Synthetic polymers were originally developed for their durability and resistance to all forms of degradation, including biodegradation, and for special performance characteristics achieved through control of molecular weight and functionality. They are widely accepted because of these properties and because they are inexpensive and enhance the comfort and quality of life in our modern industrial society. However, these same properties that make the polymers so useful have contributed to a disposal problem. Plastics generally receive the brunt of media attention on this issue because of their visibility in the environment as litter and their obvious contribution to landfill depletion. Because of their low density, they occupy a high volume fraction of buried waste despite their relatively low weight fraction (10%).¹ Water-soluble polymers, on the other hand, enter the environment surreptitiously and unseen in waste-water streams and receive scant public attention. The water-soluble polymer industry, however, is well aware of the problem, and significant research has been done and is continuing to develop biodegradable polymers.² The detergent industry, for example, has completely switched from nonbiodegradable (branched alkyl)benzenesulfonate surfactants to biodegradable linear analogs. Consequently, the streams of foam previously visible in the effluent from wastewater treatment plants in the 1960s are no longer seen.

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Biodegradable polymers are only one of the available options for the waste management of polymers in the environment. They are in competition with alternative technologies such as incineration, recycling, and burial in landfill sites. No one option is likely to predominate, as each technology has its strong points and there are localities and product types that will be particularly well suited for a given option. Biodegradable plastics are likely to be favored in applications where recovery of conventional plastics for recycling or incineration is not cost effective or is difficult, e.g., agricultural films, fishing gear, fast-food wrappers, and diaper stock. In the case of water-soluble polymers, recovery is always difficult, though not impossible, and biodegradability is, therefore, a more cogent issue.

In discussing the future directions for biodegradable polymers, it is necessary to include the impact of the definition of a biodegradable polymer and testing protocol development. The following questions must be addressed:

Definition of a Biodegradable Polymer

What is a biodegradable polymer?

What is a biodegradable polymer expected to do in the environment?

Development of Testing Protocols

What tests are needed to establish the degree of biodegradability in a given environment?

What tests are needed to determine whether a biodegradable polymer is acceptable in the environment?

Future Directions for Biodegradable Polymers

How do the definitions and test protocols influence the future direction of research on biodegradable polymers?

Obviously, the definitions, test protocols, and future research objectives are interrelated, interdependent, and equally important. This has not always been recognized or accepted and has led to confusion in the literature and in research program goals: only when there is general agreement on testing protocols and terminology will it be possible to compare research results from different programs on biodegradable polymers. Recently, the international research effort, including organized societies such as the Japanese Biopolymer Society, American Society for Testing and Materials (ASTM), National Corn Growers Association, Institute for Scientific Research (ISR), and Lowell's Polymer Degradation Consortium on biodegradable polymers, appears to have recognized that these rela-

(1) Thayer, M. *Chem. Eng. News* 1989, April 5, 7.

(2) Hunter, M. L.; da Motta, M.; Lester, J. N. *Environ. Technol. Lett.* 1988, 9, 1-22.

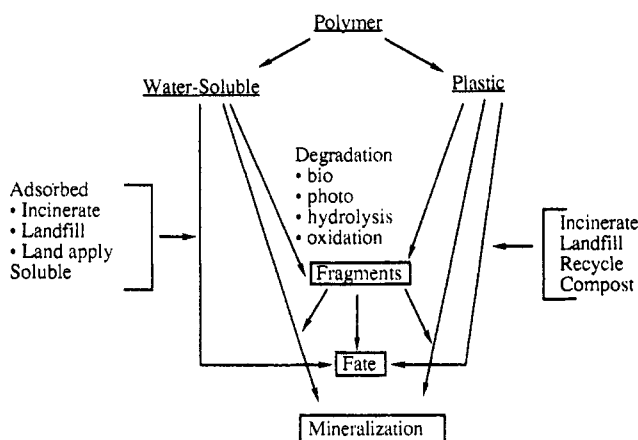


Figure 1. Environmental disposal of polymers.

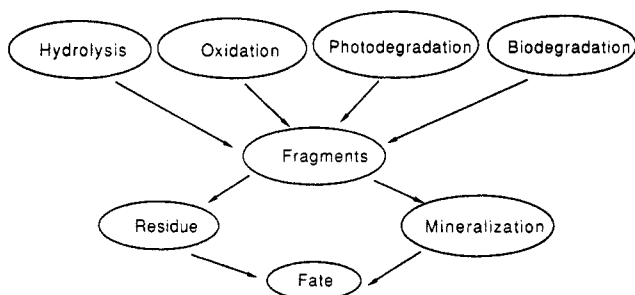


Figure 2. Environmental degradation pathways.

tionships are important, and this should accelerate agreement on the issues and, consequently, research progress.

In this Account, I will present a personal perspective on definitions and test protocols for biodegradable polymers as well as how they will influence the future direction and developments in the field. However, before doing so, I will digress briefly to present a commentary on the role of biodegradable polymers in environmental waste management. This should be useful for those readers unfamiliar with the subject, and it will set the stage for the rest of the discussion.

Environmental Waste Management of Polymers

Four end results are possible from the exposure of polymers in the environment (Figure 1): they may partially degrade by nonbiologically mediated processes, leading to fragmentation due to weight loss or erosion; they may partially degrade or fragment by biologically mediated processes, i.e., biodegrade; they may mineralize, i.e., totally biodegrade to gaseous products, water, salts, and biomass; and they may remain without significant change in the environment. It is notable that the uncertain fate and environmental effects of polymers lost in the environment, as described above, are common to recoverable polymers that are landfilled, incinerated, recycled, and composted. There are several environmental degradation pathways for both water-soluble and water-insoluble polymers, including photodegradation, oxidation, hydrolysis, and biodegradation, as seen in Figure 2. Mineralization or complete biodegradation leads to a natural biological recycling of polymers, making them utilizable for important processes such as plant growth, thus entering into the food chain of higher animals. However, as indicated, biodegradation may also be incomplete and produce

fragments (this is observed in blends of biodegradable and nonbiodegradable products, such as starch-olefin blends³ that had some popularity and achieved notoriety when claimed without substantiation to be biodegradable⁴), as all the other degradation pathways do. Without continued biodegradation, these fragments and those produced by other degradation mechanisms remain in the environment. Their fate and effect on the environment may be recalcitrant without harmful side effects, toxicity to animals and soil microbes, impoverishment of soil fertility, transportation of heavy metals through the environment, etc. This uncertainty clearly poses a huge problem which must be addressed and resolved for each polymer and disposal route. All the degradation pathways mentioned are often referred to collectively as biodegradation in spite of their obvious and significant differences, which emphasizes the importance of definitions and test protocols to be discussed in this Account.

The recoverable waste-management options, incineration, landfill (which has limited value unless managed), composting, and recycling, are most useful for plastics that have form and substance and can be handled easily. However, water-soluble polymers that enter sewage-treatment plants may adsorb on sewage sludge and be removed for incineration, landfill, or land application as fertilizer. If adsorption does not occur and the polymers are not biodegradable, water-soluble polymers will remain in that environment with uncertain fate and environmental impact.

Plastics may be collected after use and returned for incineration to produce energy, for landfill, for composting, or for recycling back to the marketplace. Landfill disposal is the least preferred option because of space limitations and the high volume requirement for plastics. It is possible because of these space limitations that landfill will only accept the residues from incineration and composting in the future. Composting is controlled degradation of polymers involving primarily biodegradation, with oxidation and hydrolysis in a lesser role, and it is potentially a valuable waste-management option for recovered polymers. It will, however, be subject to all the limitations placed on environmentally degradable polymers, and the discussion here addressing directions in environmentally biodegradable polymer research is applicable to polymers designed for recovery and composting. Recycling of polymers usually is a spiral down to one of the other disposal methods, as plastics are expected to suffer property attrition during the repetition of this process. Recycling of plastics through recovery of the component monomers and synthesizing virgin plastic is possible in some cases, e.g., poly(ethylene terephthalate) (PET) and poly(methyl methacrylate), and disposal is, therefore, not an issue.

Considering all the disposal options raised above, biodegradable polymers that completely mineralize to carbon dioxide, methane, etc. offer an attractive approach to environmental waste management. Partial biodegradation or fragmentation may be an acceptable option, provided that the fragments are demonstrably not harmful to the environment.

(3) Otey, F. *Org. Coat. Plast. Chem.* 1977, 37 (2), 297.

(4) Rothgeb, T. M.; Pittinger, C. A.; Kuta, C. C. *HAPPI, Household Pers. Prod. Ind.* 1991, March, 64-69. Krupp, L. R.; Jewell, W. J. *Environ. Sci. Technol.* 1992, 26, 193-198.

Definition of Biodegradable Polymers

Biodegradation is a term that everyone understands to be enzymatically promoted degradation, yet no definition has been coined that is universally acceptable for biodegradable polymers. There are probably several reasons for this, but one of the major ones, in my opinion, is the wide range of disciplines, represented by, e.g., biologists, biochemists, polymer chemists, engineers, lawyers, legislators, environmentalists, manufacturers, and lay people, involved directly in biodegradable polymer research or with an opinion on requirements. All of these groups have their own perspective and agendas on what they expect a polymer to do in the environment in order to be called or defined as biodegradable. The definition appears to be confused with classification as to the extent of biodegradation that occurs and what is deemed acceptable for disposal in the environment.

To resolve this problem, I propose that the biodegradability of a given polymer be expressed as shown in eqs 1 and 2 for aerobic and anaerobic environments, respectively. For simplicity, I have chosen a polymer composed of carbon and hydrogen as the example, but the equations and arguments extend to any polymeric composition by simple modification of the equations to reflect other elements present. A solution for the equations will lead us to an acceptable definition of what is expected of a biodegradable polymer in the environment.

aerobic environment

$$C_t = CO_2 + H_2O + C_r + C_b \quad (1)$$

anaerobic environment

$$C_t = CO_2 + CH_4 + H_2O + C_r + C_b \quad (2)$$

For a given polymer with a total carbon content C_t exposed to a biotic aerobic environment, the degree of biodegradation can be accounted for by carbon dioxide evolved, carbon residual in the environment, C_r , and carbon converted into biomass, C_b . Complete biodegradation (i.e., mineralization), partial biodegradation, and no biodegradation (i.e., recalcitrance) are defined by $C_r = 0$, $0 < C_r < C_t$, and $C_r = C_t$, respectively.

These solutions serve to define a biodegradable polymer in any environment. The extent of biodegradation is determined by measuring carbon dioxide (and methane for an anaerobic environment), residual carbon, and carbon converted into biomass. Whether an incompletely biodegradable polymer, that is, one that does not mineralize, is acceptable for disposal in the environment will depend on fate and environmental impact studies of the residual material.

Thus, we see the subtle difference between the definition of a biodegradable polymer and an environmentally acceptable biodegradable polymer: A biodegradable polymer *may* be partially or totally degraded by enzymatic processes whereas an environmentally acceptable biodegradable polymer *must* be mineralized or produce no environmentally harmful residues, if only partially biodegradable. In other words, fate and effect in the environment, as with any other organic material, are the issues to be considered when designing envi-

ronmentally biodegradable polymers. Therefore, it is essential to develop test protocols that not only quantitatively measure biodegradation but also address the issue of fate and environmental effects, if mineralization is not achieved.

Test Protocol Development

Many of the early workers⁵ in biodegradable plastics used either burial or microbial growth tests^{6,7} to indicate susceptibility to biodegradation. In spite of the obvious nonquantitative nature of these tests, they were and remain useful screening tests. Microbial growth tests are rated 0–4, depending on density of growth, 0 being none, and 4 being heavy; they are subjective and can be misleading in the case of polymer blends, especially where one component may be biodegradable; e.g., a simple plasticizer in plasticized poly(vinyl chloride) may result in a heavy growth from the minor component, though poly(vinyl chloride) is established as not biodegradable.

More recently, it has become apparent that several major factors need to be considered in developing test protocols for polymers. These are shown below:

Measurement

- Physicomechanical changes
- Chemical changes and products formed
- Weight loss

Environment

- Natural
- Simulated
- Accelerated
- Disposal
- Use

Polymer

- Concentration
- Form

Fate

- Environmental effects

Measurement. Measurement of physicomechanical changes and weight loss in a given environment is possible and useful only for plastics. It has value for following property attrition as biodegradation proceeds and may be of importance where a plastic is used in an environment where it is desired that the properties erode with time of exposure, e.g., biodegradable fishing gear and agricultural plastic sheeting. Plastic properties, such as tensile strength,⁸ impact resistance,⁹ and tear strength,¹⁰ are good indicators of property loss, which is an indirect measurement of biodegradation. In addition, loss in weight of biodegradable polymers, as a function of time, when carried out with the proper biologically active and abiotic controls, is also useful as an indirect method. The extent of biodegradation and rates claimed from these tests must be confirmed by direct quantitative methods to be discussed below.

Following chemical changes during biodegradation is a well-established procedure for water-soluble polymeric surfactants and organic compounds used in

(5) Potts, J. E.; et al. *Polymers and Ecological Problems*; Plenum Press: New York, 1973.

(6) ASTM Standard G22-76 (bacterial growth).

(7) ASTM Standard G21-76 (fungal growth).

(8) ASTM Standard D882-83.

(9) ASTM Standard D1709-85.

(10) ASTM Standard D1922-67.

detergents.^{11,12} These tests are generally applicable to water-soluble polymers in an aqueous environment of choice. Tests of importance, in this regard, include biochemical oxygen demand (BOD), carbon dioxide (aerobic) evolution, carbon dioxide and methane (anaerobic) evolution, and residual carbon or soluble organic carbon (SOC) after the test is complete.

Biochemical oxidation demand is usually reported as a percentage of the theoretical or determined oxygen demand required for complete chemical oxidation of the substrate polymer and is a good preliminary measure of biodegradation. However, the values obtained may become less reliable if the polymers are easily susceptible to chemical oxidation. Carbon dioxide evolution and residual soluble organic carbon (SOC) measurements are done simultaneously; they give a better indication of biodegradation, because by insertion of these values in eq 1, biomass carbon can be obtained by difference and a carbon accountability established. A further refinement of the carbon dioxide and combined SOC test uses ¹⁴C-labeled polymers, permitting tests to be run at very low concentrations, which are more consistent with environmental exposure levels. Furthermore, the carbon incorporation into biomass can be obtained by separation and combustion to ¹⁴CO₂.

In spite of their insolubility in water, plastics have been shown to biodegrade in tests similar to the carbon dioxide/SOC test for water-soluble polymers. Recent ASTM standards have been established for aerobic¹³ and anaerobic¹⁴ sewage-sludge exposure with carbon accountability, a key result, as indicated earlier, for establishing the degree of plastic biodegradability. Carbon accountability in the case of plastics includes gaseous carbon, soluble carbon, insoluble carbon, and biomass incorporation, all of which are measurable. Because plastics are not usually disposed of in sewage sludge, the test results are considered an indicator of biodegradability and are run under controlled laboratory test conditions. The predictive nature of these tests on the biodegradability of plastics in actual disposal sites has not yet been established.

Environment. The choice of environment for testing a polymer is extremely important and should be governed by the anticipated disposal method, use environment, or whether accelerated testing is desired. These environments may be natural or simulated. Environments for water-soluble polymers will be generally limited to sewage sludge, ground water, and river water, whereas plastics will use environments such as soil, seawater, freshwater, landfill, and compost. A sewage-sludge environment for plastics may be considered an accelerated test, since it is a richer microbial environment than the plastic is likely to see in use or disposal. The recent development of biologically active aerobic compost¹⁵ and an anaerobic bioreactor¹⁶ simulation to test plastic degradation also may be classified as accelerated degradation testing methodologies.

(11) Swisher, R. D. *Surfactant Biodegradation*; Marcel Dekker, Inc.: New York, 1987.

(12) *OECD Guidelines for Testing Methods, Degradation and Accumulation Section*; OECD: Washington, DC, 1981; Nos. 301A-E, 302A-C, 303A, 304A.

(13) ASTM Standard D5209-92.

(14) ASTM Standard D5210-92.

(15) Tanna, R. J.; Gross, R.; McCarthy, S. P. *Polym. Mater. Sci. Eng.* 1992, 67, 294-295.

(16) Gu, J. D.; McCarthy, P. P.; Smith, G. P.; Elseriel, D.; Gross, R. *Polym. Mater. Sci. Eng.* 1992, 67, 230-231.

There are many difficulties in projecting laboratory results to real world exposures, but better control is achieved in the laboratory and the results will indicate trends, if not an accurate time scale for biodegradation. Since microbial populations vary widely, a poor selection of inoculum may result in no biodegradation, and several replicate tests are required before biodegradation is precluded. Sometimes acclimation is required to allow the buildup of bacterial populations capable of degrading a particular polymer, and this should be considered and evaluated if negative results are obtained in initial screening.

Polymer. The polymer concentration may influence biodegradation. High concentrations, especially for water-soluble polymers, may be toxic to a particular microbial population in a given environment, yet low concentration may not permit quantitative measurements. To balance these extremes, it is necessary to test different concentrations and determine suitable limits. It may be necessary to resort to using radio-labeled polymers, as mentioned earlier for water-soluble polymers, which permits realistic environmental concentration levels to be tested.

Plastic form may also influence the biodegradation tests. Surface pretreatment, surface defects, surface area, porosity, crystallinity, etc. can change degradation characteristics from sample to sample of the same polymer.

Fate and Environmental Effects. Tests for environmental fate are necessary to establish that the residues of partially biodegradable polymers do not have a harmful effect on the environment. The concept is to take the residues from biodegradation tests run in any environment and by suitable transfer put them into a standard toxicity test. This difficult task has not yet been reduced to practice for plastics, though a recent publication¹⁷ indicates that such tests are in development for water-soluble polymers.

Considering the importance of fate and effect of biodegradable polymers on the environment with respect to their acceptance, these tests are urgently needed and ought to receive a high priority. No partially biodegradable polymer should be accepted for environmental disposal unless it has been demonstrated that it leaves harmless residues.

Future Test Developments. If biodegradable polymers are to be used widely, it will ultimately be necessary to identify the microorganisms that biodegrade them and the enzymatic mechanisms involved. This will permit identification of disposal sites consistent with the polymer's mode of biodegradation, assuring its removal from the environment. Obviously, this may take several years, but in developing new polymers, this should be incorporated into the respective programs.

Directions for Biodegradable Polymer Development

Future directions for the development of biodegradable polymers will be based on the broad experience base we have for many synthetic and natural polymers and on what we have now established that biodegradable polymers are required to do in the environment. Over

(17) Scholz, N. *Tenside, Surfactants, Deterg.* 1991, 28, 277-281.

the last two decades, many synthetic and natural polymers have been tested for biodegradation in a variety of tests. Though these tests are not always totally satisfactory, they do permit the development of general guidelines for the relationship between structure and biodegradation, which have been summarized in a recent publication¹⁸ and are expanded on herein:

Naturally occurring polymers biodegrade.

Chemically modified natural polymers may biodegrade, depending on the extent of modification.

Synthetic addition polymers with carbon-chain backbones do not biodegrade at molecular weights greater than about 500.

Synthetic addition polymers with heteroatoms in their backbones may biodegrade.

Synthetic step-growth or condensation polymers are generally biodegradable to a greater or lesser extent, depending on

chain coupling (ester > ether > amide > urethane);

molecular weight (lower is faster than higher);

morphology (amorphous is faster than crystalline); and

hydrophilicity vs hydrophobicity (hydrophilic is faster than hydrophobic).

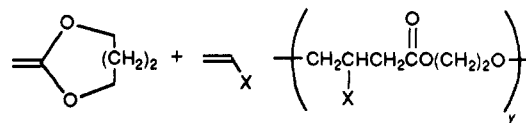
Water solubility does not guarantee biodegradability.

The synthetic polymers that do biodegrade tend to have structures similar to those found in naturally occurring polymers, suggesting that microbial populations produce enzymes that may not discriminate between polymers of similar structure. This is a good indicator for future research directions. Examples of synthetic polymers that biodegrade include poly(vinyl alcohol),¹⁹ which is the only carbon-chain polymer to biodegrade; poly(ethylene oxide);²⁰ poly(lactic acid);²¹ and polycaprolactone.²² Tokiwa²³ has shown that polyesters of aliphatic poly(carboxylic acids) and polyfunctional alcohols are generally biodegradable.

If we accept the definitions submitted in this Account for biodegradable polymers and environmentally acceptable biodegradable polymers, the future course of developments in this field becomes clearer to predict. Establishing that biodegradable polymers pose no environmental threat is likely to prove more difficult, costly, and time consuming than discovering, developing, and testing for environmentally acceptable biodegradable polymers. The options we have are then primarily limited to (1) development of new synthetic polymers based on chemistries known to promote environmentally acceptable biodegradability, essentially mimicking nature, e.g., polyesters, peptides, etc.; (2) use of available environmentally acceptable biodegradable synthetic polymers, alone and modified by blending or some other method of combination with natural polymers; and (3) use of natural polymers either as obtained or by careful, selected modification.

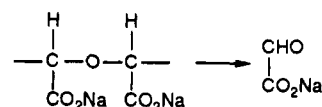
Developing new synthetic polymers is not easy, but not impossible as exemplified by the inspirational and creative work of Bailey²⁴ and Monsanto scientists.²⁵

Bailey's research is based on the introduction of ester linkages as trigger sites into carbon-chain polymers which promote biodegradability. He developed ketene acetal monomers that readily copolymerize free radically with unsaturated monomers, including ethylene and acrylic acid to introduce the ester "trigger" sites.



X = hydrogen or functional group

In Monsanto's chemistry, the trigger is pH control in poly(carboxylic acids) based on polyacetals from glyoxylic acid. These polymers, which are base stable, readily hydrolyze in neutral or acidic water to a biodegradable monomer.



Both examples indicate that clever synthesis can lead to new biodegradable synthetic polymers through judiciously placed trigger points that are unstable or known to be biodegradable in a given environment.

The currently available biodegradable synthetic polymers that have their established uses as water-soluble polymers include poly(vinyl alcohol) and poly(ethylene oxide). In the case of biodegradable plastics, they are poly(vinyl alcohol) and polyesters, such as polycaprolactone. In all cases, they are specialized in functionality for water-soluble polymer needs or limited in their respective mechanical properties as plastics. The plastics and water-soluble polymers are used in blends with natural polymers such as starch²⁶⁻²⁸ to permit better processing of the starch component and improve the mechanical properties. These polymer blends show promise in several areas of use such as temporary packaging, agricultural film, and biomedical applications.

Natural polymers or polymers based on naturally derived monomers offer the biggest incentive for future development. They are products from renewable resources that totally biodegrade in their natural form, given the choice of environment. They may be used as isolated, as water-soluble polymers or plastics, alone or suitably blended (vide supra) with other biodegradable polymers to meet performance needs. They may be chemically modified to produce functional water-soluble and insoluble polymers and plastics, but if so, they must then be tested for biodegradability since modification may inhibit enzymatic processes that promote biodegradation of the natural polymer. An excellent example of modified natural polymer biodegradability is chemically modified cellulose acetate (substitution values of 1.7 and 2.5), which has recently been reported.²⁹

(18) Swift, G. *ACS Symp. Ser.* 1990, 443, 1-12.

(19) Suzuki, T.; et al. *Agric. Biol. Chem.* 1978, 42 (6), 1217.

(20) Kawai, F. *Crit. Rev. Biotechnol.* 1987, 6, 273.

(21) Keeler, R. *Res. Dev.* 1991, Feb 52-57.

(22) Potts, J. E.; et al. *Aspects of Degradation and Stabilization of Polymers*; Elsevier: Amsterdam, 1978; p 617.

(23) Tokiwa, Y.; et al. *Biodegradable Materials*; CRC Press: Boca Raton, 1990; pp 545-553.

(24) Bailey, W. J. *Proc. Int. Biodegrad. Symp.*, 3rd, 1975 1976.

(25) Monsanto. U.S. Patents 4144226, 4146495, 4204052, 4233422.

(26) Warner-Lambert. Eur. Pat. Appl. 409783-A, 1991.

(27) National Starch. Eur. Pat. Appl. 375831-A, 1989.

(28) Butterfly SRL. W.O. Pat. 91 022025A, 1991.

(29) Gu, J. D.; McCarthy, S. P.; Smith, G. P.; Eberiel, D.; Gross, R. J. *Polym. Mater. Sci. Eng.* 1992, 67, 351-352.

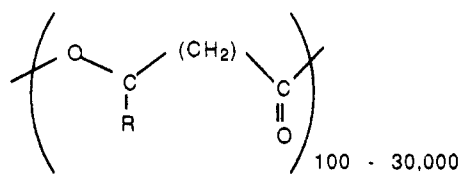


Figure 3. Structure of poly(hydroxyalkanoic acids): R = alkyl, haloalkyl, nitrile-substituted alkyl, aryl.

One of the most exciting developments in this area of natural polymers is the development of polymers based on bacterially produced poly(hydroxyalkanoic acids) shown in Figure 3. Certain bacteria produce these polymers as storage materials during periods of nutrient stress. The range of structures available is very wide,³⁰ depending on the bacteria and carbon source on which they are grown. Their chemistry, enzymology, and properties, which may range from elastomers to fibers to films, has been reviewed by several people.^{31,32} The polymers are presently expensive, and the question of commercial viability has not yet been answered. It took almost 60 years from their discovery by Lemoigne³³ in 1925 to small-scale production by Imperial Chemical Industries in Great Britain³⁴ of a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, known commercially as BIOPOL. This polymer has physical properties similar to those polypropylene.

Because poly(hydroxyalkanoic acids) are produced by new technology, they are forerunners of a new approach to natural polymers from fermentation processes, which, because of the need for biodegradable polymers, will find increasing applications as progress is made to bring down their manufacturing costs and to understand how to control the enzymatic processes that control molecular weight, functionality, and consequently, properties.

Just as bacterially produced poly(hydroxyalkanoic acids) appear to be the best route to new biodegradable plastics, bacterial celluloses and polysaccharides may be routes to new water-soluble polymers. A recent book edited by Byrom³⁵ points out the value of bacterial polymers which include, in addition to the poly(hydroxyalkanoic acids), cellulose, hyaluronic acid, and alginates. Many will always be expensive, but through a combined effort of biochemistry and polymer science, new polymers will be developed through biological synthesis and chemical modification of these natural-origin polymers that meet the demands for environmentally biodegradable polymers as well as practical applications. In my view, this area will become a major focus for research and development activities over the next decade.

(30) Brandl, H.; Gross, R. A.; Lenz, R. W.; Fuller, R. C. *Appl. Environ. Microbiol.* 1988, 521.

(31) Doi, Y. *Microbial Polyesters*; VCH: New York, 1990.

(32) Steinbuechel, A. *Biomaterials*; Byrom, D., Ed.; Macmillan: New York, 1991; pp 125-213.

(33) Lemoigne, M. *Ann. Inst. Pasteur (Paris)* 1925, 39, 144-173.

(34) Imperial Chemical Industries. Eur. Pat. Appl. 0052459, 1981; 0069497, 1983.

(35) Byrom, D., Ed. *Biomaterials*; Macmillan: New York, 1991.

(36) Seeley, R. S. *Chem. Bus.* 1992, Feb, 28-30.

Finally, monomers such as lactic acid produced from natural resources³⁶ represent another opportunity to be exploited in the search for biodegradable polymers. Already, several major manufacturers are contemplating production of poly(lactic acid) from cheaply available monomer produced by fermentation for use in packing film and other industrial applications, in addition to its current use in medical applications, such as sutures.

Obviously, a major part of the future for biodegradable polymers is from nature's own factory, as would be predicted from our experience base mentioned earlier and from everyone's expectations that polymers that are now labeled biodegradable should be environmentally acceptable.

Concluding Remarks

It is my opinion that we are close to reaching agreement on what is acceptable as a biodegradable polymer in the environment, and these requirements can be met by both synthetic and natural polymers. Natural polymers assure biodegradability and environmental compatibility or acceptance without harmful effects and will be favored, if economics can be controlled, for application in both plastics and water-soluble polymers. These developments may take several years, and in the interim, the few available biodegradable synthetic polymers will continue to be used, alone and in blends with cheap natural products such as starch, especially if they can be shown to leave no harmful residues in the environment. It should be stressed that no polymer should be considered acceptable unless demonstrated to meet the requirements outlined and presented in this Account.

Biodegradable polymers, in general, may never replace the major commodity plastics, but they will offer a viable waste-management option for polymers that are not readily or economically recoverable for recycling and incineration. In essence, this implies that both biodegradable water-soluble polymers and plastics will continue as major targets for research and development efforts in the polymer industry and academia. Success will be measured by balancing properties and biodegradability to meet all demands. It is important to state that the need for water-soluble biodegradable polymers is at present more apparent due to the nonrecoverable nature of these polymers, relative to biodegradable water-insoluble polymeric materials.

I am indebted to many people who, over the last few years, have freely exchanged ideas with me on this very interesting subject; in essence, forging my current position. To name a few, but exclude none, Professors Huang (University of Connecticut); Lenz and Fuller (University of Massachusetts, Amherst); Gross and McCarthy (University of Massachusetts, Lowell); Wool (University of Illinois); Doi (Tokyo Institute of Technology); Kawai (Kobe University); Matsumura (Keio University); Dr. Narayan and colleagues at ASTM; and finally, colleagues at Rohm and Haas.