Kirk-Othmer Encyclopedia of Chemical Technology.

POLYMERS, ENVIRONMENTALLY DEGRADABLE

Interest in environmentally degradable plastics began in the early 1960s with the recognition that the common packaging plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET) were accumulating in the environment. Their designed and well-established resistance to environmental degradation was observed to be contributing to landfill depletion and litter problems resulting from careless disposal after use. At that time, the principal focus was on replacing these synthetic packaging plastics in all applications with environmentally degradable substitutes.

More recently, it has become increasingly apparent that in addition to the primary synthetic plastics, water-soluble and other specialty polymers and plastics such as poly(acrylic acid), polyacrylamide, poly(vinyl alcohol) and poly(alkylene oxides), and even some modified natural polymers, eg, cellulosics, also potentially contribute to environmental problems and thus become targets for environmentally degradable substitutes. These polymers are widely used as coatings additives, pigment dispersants, temporary coatings, and detergents, in mining, water treatment, etc. Therefore, this article covers polymers in a general sense rather than focusing on commodity plastics. The term polymer will refer to both water-soluble polymers and plastics, unless there is a need to differentiate the two principal polymer types that are the subject of most of the attention given to environmentally degradable polymers. The discussion covers all polymeric materials, natural, synthetic, and modified natural, designed to be degradable in the environment by any of the accepted degradation pathways: photodegradation, biodegradation, and chemical degradation which is hydrolytic or oxidative degradation. Of these pathways, biodegradation is recognized as by far the most important, insofar as it is the only one that can lead to complete removal from the environment, and accordingly it has received the greatest attention. The other degradation pathways are more appropriately described as biodeterioration or biodisintegration because their products are left in the environment unless they are biodegradable. There have been several excellent reviews on environmentally degradable polymers covering all aspects of the subject (1–18).

Concurrent with the movement toward a broadened focus of research to cover all polymeric materials, the initially high expectation for environmentally degradable polymers as a total solution to the polymer and plastic waste management issue was gradually accepted as being no longer tenable. Alternative technologies such as recycling of plastic materials, including recycling of plastics; recycling of plastics to monomers and subsequent repolymerization to the same or new polymers; recycling to olefinic feedstocks by pyrolysis; continued burial in landfill sites; and incineration are recognized as viable options, along with environmental degradation (see Recycling, plastics). Each disposal method has a part to play in polymer waste management; preference among them depends on many factors, including available processing facilities, collection of waste material, cost of new polymers, property requirements, etc. Therefore, research in 1996 on environmentally degradable polymeric materials is aimed at developing polymers for applications where they offer unique advantages over the competitive alternative: for example, in agricultural film where cost savings are possible with use of photo- or biodegradable polymers over collection and recycle of current products; compostable plastics for fast food wrappers which will eliminate the need for separation of food and plastic; difficult-to-recover water-soluble polymers and plastics; and personal and industrial hygiene products for diapers, feminine products, and hospital disposables. These products offer challenging synthesis opportunities for environmentally degradable polymers.

Environmentally degradable polymers face many issues and challenges not apparent or recognized in the early years of research. Their development requires a multidisciplinary approach, involving polymer synthesis chemists, analytical chemists, environmental scientists for establishing testing protocols for laboratory simulation of disposal environments, and microbiologists for evaluating the environmental fate and effects of the degradable polymers, their degradation products, and any residues left in the environment. In addition to the scientific issues, there are issues related to perceptions among the public in which strong emotions can play a part, and any new polymer developed as an environmentally degradable product will be scrutinized by consumers of the products it goes into and by national and international legislative bodies for confirmation that it is free from real or perceived adverse environmental effects, before global acceptance can become a reality. Thus, environmentally degradable polymers and plastics must meet very stringent guidelines for acceptance by a wide-ranging panel of reviewers. The importance of meeting this requirement is reflected in the search for acceptable definitions for environmentally degradable polymers and new, more meaningful laboratory testing protocols for quantitatively measuring degradation and environmental fate and effects, and correlating the results of these experiments with real-world exposures. Consequently, definitions and test methods are addressed early in this article, prior to describing the important synthetic approaches under evaluation for environmentally degradable plastics and polymers and identifying some current and potential commercial products.

1. Definitions

There have been numerous definitions proposed for environmentally degradable plastics and polymers. ASTM D1566 defines a polymer as “a macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition”; a plastic, as defined by ASTM D1695, is “a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow.” Definitions are important because they are indicative of expectations for the acceptance of environmentally degradable polymers and of the types of testing protocols that are needed to establish the acceptability of the polymers in the environment. The definitions developed by the American Society for Testing and Materials, ASTM D883-93, for degradable, biodegradable, hydrolytically degradable, and oxidatively degradable plastics and given here are probably the most widely accepted, either as written or in some slightly modified form. They are equally applicable to polymers, in general.

Degradable plastic is a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a particular period of time that determines its classification.

Biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae.

Hydrolytically degradable plastic is a degradable plastic in which the degradation results from hydrolysis.

Oxidatively degradable plastic is a degradable plastic in which the degradation results from oxidation.

Photodegradable plastic is a degradable plastic in which the degradation results from the action of natural daylight.

The definitions do not quantify the extent of degradation by any of the pathways and indicate only the mechanism that is operating to promote degradation. Although this is acceptable in a scientific sense in order to define the chemical process, it does not really go far enough to satisfy the requirements for environmentally acceptable polymers (19), which in the minds of legislators and lay people is the key issue. If environmentally

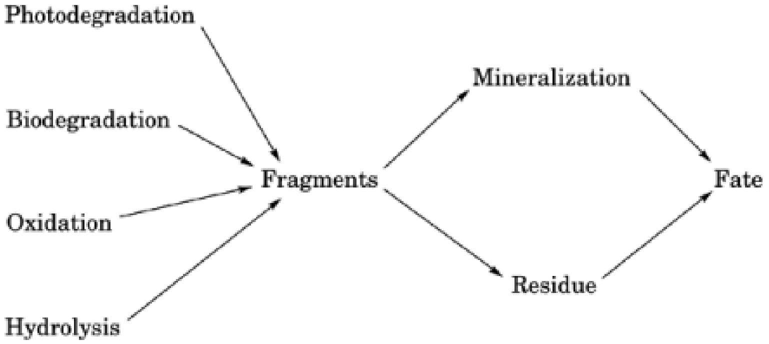


Fig. 1. Interrelationships of processes for environmentally degradable polymers.

degradable polymers and plastics are to be acceptable as a waste management option, definitions must be more practical and descriptive in conveying the assurance that no harmful residues are left in the environment after degradation has occurred. The ASTM definitions, therefore, require elaboration in order to address this deficiency (20). The environmental degradation processes are interrelated, as shown schematically in Figure 1.

All four degradation pathways, ie, biodegradation, oxidation, hydrolysis, and photodegradation, initially give intermediate products or fragments that may biodegrade further to some other residue, biodegrade completely and be removed from the environment entirely (being converted into biomass and carbon dioxide and/or methane, depending on whether it is an aerobic or anaerobic system) and ultimately mineralized, or remain unchanged in the environment. Mineralization, usually a slow process for polymeric materials and fragments, refers to complete conversion of a polymer (or any organic compound) to carbon dioxide or methane, water, and salts; it is used here loosely to indicate complete or total removal from the environment to carbon dioxide or methane, water, and biomass. In the cases where residues remain in the environment, they must be established as harmless by suitably rigorous fate and effect evaluations. Only biodegradation has the potential to remove plastic and polymers completely from the environment. Thus, when developing and designing polymers and plastics for degradation in the environment by other pathways, the final stage preferably should be complete biodegradation and removal from the environment, with ultimate mineralization. In this way, the polymers are essentially recycled through nature into microbial cells, plants, and higher animals (21), and thence back into chemical feedstocks. Therefore, an environmentally acceptable degradable plastic or polymer may be defined as one which degrades by any of the above-defined mechanisms, ie, biodegradation, photodegradation, oxidation, or hydrolysis, to leave no harmful residues in the environment (20). This definition has the advantage of not limiting the degree of degradation for a particular polymer but requiring sufficient testing for fragments and degradation products that are incompletely removed from the environment to ensure that no long-term damage or adverse effects to the ecological system remain a possibility. Polymers and plastics meeting this definition should be completely acceptable for disposal in the appropriate environment anywhere in the world.

2. Opportunities for Environmentally Degradable Plastics and Polymers

Opportunities play a significant part in driving research into the property requirements for environmentally degradable plastics and polymers and for the development of laboratory testing protocols. The conditions providing a significant stimulus for the development of environmentally degradable polymers and plastics are the same ones that govern waste management programs and the restriction of the uses for nondegradable

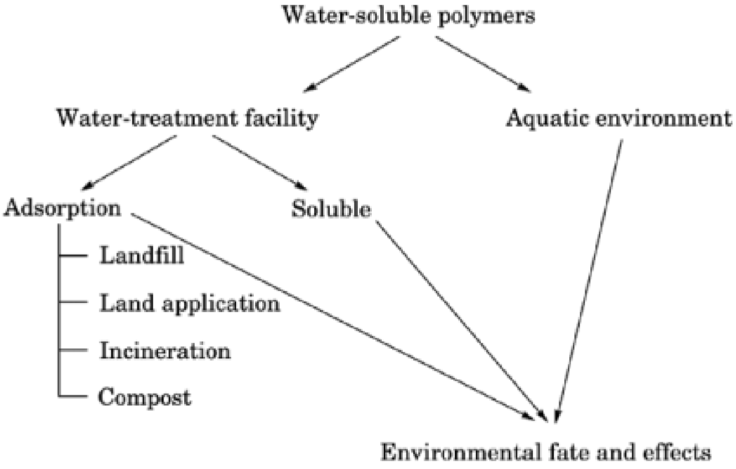


Fig. 2. Environmental disposal of water-soluble polymers.

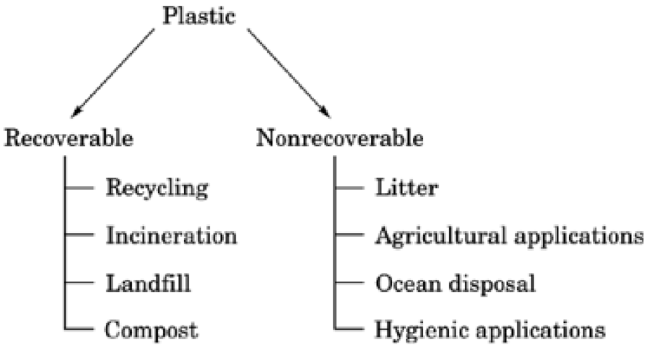


Fig. 3. Environmental disposal of plastics.

polymers and plastics in the environment. Figures 2 and 3 illustrate the disposal pathways of water-soluble polymers and plastics, respectively, two significant environmental waste-management problem areas.

Water-soluble polymers (qv) after use are usually very dilute solutions and are preferably disposed of through wastewater treatment facilities or sometimes directly into the aquatic environment. On entering a wastewater treatment plant, a polymer may pass straight through it into streams, rivers, lakes, and other aquatic environments, or it may be adsorbed onto the suspended solids in the treatment plant. If it passes straight through, it is no different from direct disposal into those same aqueous environments, and the two disposal methods raise similar questions as to the fate and effects of the polymers. On the other hand, adsorption of a polymer onto sewage sludge results in the possibility of the polymer being landfilled, incinerated, composted, or land-applied as fertilizer or for soil amendment, depending on the local options available. However, here again, environmental fate and effects need to be addressed; it must be established how these polymers move in their new environmental compartments, and what are their incineration products. For water-soluble polymers, therefore, there is an obvious and distinct advantage for environmentally acceptable degradable polymers. There is a preference for biodegradable water-soluble polymers, as it is unlikely that the other degradation paths would be applicable in dilute aqueous solutions.

Water-soluble polymers should be designed to be completely biodegradable and removed in the disposal environment, generally the sewage treatment facility, because they may move rapidly and without difficulty throughout the environment. If biodegradation is not complete in the disposal environment, it must be assessed in subsequent environmental compartments that it enters. Once the biodegradation of a polymer has been confirmed, no uncertainty remains as to its fate and effects in any subsequent environmental compartments. The advantage of complete biodegradation is that it can be established with a high degree of certainty with the appropriate test methods, whereas the assessment of environmental fate and effect of any residue is always a risk assessment based on a limited study with a few aquatic species for all environments with which a water-soluble polymer may come into contact as it moves through the environment.

Plastic materials, as indicated, offer more disposal options than water-soluble polymers because they are usually solid, handleable materials and are recoverable in most cases after use for several disposal options, including landfilling, recycling, incineration, and composting. Composting, which is predominantly biodegradation with the possibility of oxidation and hydrolysis, is an opportunity for environmentally degradable plastics which are used in food applications, such as wrappers and utensils. In these uses, plastics are contaminated with food residues and the mix is ideally suitable for composting without separation. Where recovery of current plastics is not economically feasible, viable, controllable, or attractive, the plastics remain as litter; may be discarded at sea from naval vessels; may be used in farm and agricultural applications such as pre-emergence plant protection with sheets and mulch; or in hygienic applications such as diapers, sanitary napkins, and hospital garments and swabs, etc. These each constitute opportunities or a stimulus for the development of environmentally acceptable degradable plastics and polymers.

For water-soluble polymers, there is a well-established disposal infrastructure, with the widely available wastewater treatment plants, whereas plastics being developed for composting require large-scale implementation of a composting infrastructure. This fact will certainly influence the rate of their acceptance.

3. Test Methods for Environmentally Degradable Polymers

Among the degradation categories, by far the most significant research and development activity has been in biodegradation, followed by photodegradation, and very much less in oxidation and hydrolysis. However, it should be remembered that hydrolysis is frequently followed by biodegradation of the degradation products, and that oxidation and photodegradation often operate in tandem.

Test methods are usually laboratory evaluation of environmental degradation under the simulated real-world conditions to which a particular polymer or plastic will be exposed on disposal; however, it is sometimes desirable to do the testing under the most favorable conditions, to establish whether degradation is possible. Results of such tests only indicate the rate and extent of degradation under the test conditions and must be correlated with exposure in the real-world environment. The ultimate goal of laboratory test methods is predictability of environmental response to new polymers and plastics. This goal is probably more difficult for biodegradation than for photodegradation, because the environments for biodegradation differ widely in microbial composition, pH, temperature, moisture, etc, and are not readily reproduced in the laboratory. Once an environment has been sampled and placed within the confinements of a laboratory vessel, it can no longer interact with the greater environment in response to an added xenobiotic; thus results are frequently difficult to reproduce and may not always be representative of the response in real-world exposures. Photodegradation can be measured more readily.

Table 1. ASTM Standard Practices for Photodegradation

Test number	Standard test practice
D3826-91	degradation end points using a tensile test
D5071-91	operation of a xenon arc ARC-type exposure apparatus
D5208-91	operation of a fluorescent ultraviolet (uv) and condensation apparatus
D5272-92	outdoor exposure testing of photodegradable plastics

4. Test Methods

4.1. Photodegradation

Test methods for measuring photodegradation are usually a combination of an exposure to some form of radiation and subsequent property loss measurement in another test, for example a tensile strength loss (ASTM D882-83), impact resistance loss (ASTM D1709-85), tear strength loss (ASTM D1922-67), molecular weight loss, friability, disintegration, brittle point, etc. Several standard test practices have been developed within ASTM (22) for plastic exposure and are listed in Table 1. Subsequent property testing by the standard ASTM test methods, including those already named, may be done at various time intervals throughout the exposure to assess the rate of degradation. In ASTM terminology (ASTM D883-93), a test practice is a procedure which does not lead to a result in itself, that is, it is a conditioning for a standard test method which measures the change(s) that may have occurred.

4.2. Biodegradation

In the early years of biodegradation testing for polymers and plastics, the only tests conducted to establish biodegradability were related to microbial growth, weight loss, tensile changes, and other physical property losses. These are all indirect measurements of biodegradation and often led to results that were difficult to reproduce from laboratory to laboratory, giving rise to confusion on the susceptibility to biodegradation of a given polymer. The tests and their results have been reviewed in many articles (4, 22–24). More recent test methodology development has stressed the proper selection of environment to reflect probable disposal sites for a given polymer or plastic and the need for quantitative testing as the most important aspect of assessing acceptability for environmental disposal. Qualitative tests, however, are still recognized as important for indicating the rate of disintegration of plastics, which has a bearing on such disposal methods as composting for compaction and volume reduction of the compost.

Some of the early tests include Growth Ratings based on ASTM Tests G21-70 and ASTM G22-76, which actually were tests developed for assessing the resistance of plastics to fungal and bacterial growth, respectively. Fungal organisms such as *Aspergillus niger*, *Aspergillus flavus*, *Chaetomium globosum*, and *Penicillium funiculosum* and bacterial standards such as *Pseudomonas aeruginosa* are suggested in the test protocol, though it is not limited to these, and are evaluated for growth on suitable plastics. After a suitable time period, growth is assessed by a subjective numerical rating in which higher numbers are considered to correlate with the susceptibility of the plastic to biodegradation:

The advantage of this test is that it is quick and easy to do, and gives an indication of biodegradation potential. However, the test is not definitive, because any impurities in the plastic, such as plasticizers and solvents, may interfere with the test by promoting growth, and thus give false positive results. Other simple tests include the soil burial test used to demonstrate the biodegradability of polycaprolactone (25), following its disappearance as a function of time, and the clear zone method which indicates biodegradation by the formation of a clear zone in an agar medium of the test polymer or plastic as it is consumed (26). The burial

Rating	Growth
0	no visible growth
1	$<10\%$ of surface with growth
2	10–30% surface with growth
3	30–60% surface with growth
4	60–100% surface with growth

test is still used as a confirmatory test method in the real-world environment after quantitative laboratory methods indicate biodegradation.

The need to develop better tests, both qualitative and quantitative, has become apparent and is generating a great deal of activity in the areas of both plastics and water-soluble polymers. Many of the quantitative test protocols are based on the tests developed over the last 25 years in the detergent industry for water-soluble organic compounds, particularly surfactants, which have been scrutinized for biodegradability since the late 1960s. Many of these tests have been summarized (27) and are formalized in publications by the U.S. Environmental Protection Agency (EPA) (28) and the Organization for Economic and Cooperative Development (OECD) (29). This earlier work showed the value of choosing the environment applicable to the disposal method with detergents, the wastewater treatment plant, rivers, aquifiers, and soil; the conditions for running laboratory tests with temperature control; and addressing toxicity issues, acclimation potential, etc. Above all is recognition of the value of quantitative measurements of the products of biodegradation as the only reasonable means of assessing biodegradation (20).

Biodegradation in aerobic and anaerobic environments may be described by chemical equations, assuming a hydrocarbon polymer as is done in equations 1 (aerobic) and 2 (anaerobic). The equations are readily modified to include other elements that may be present in a particular polymer, and appear in the oxidized or reduced form, depending on the type of environment, aerobic or anaerobic, respectively. Most of the testing reported in the literature over the years has been with aerobic biodegradation conditions, probably because this is easier to do in the laboratory and because most disposal of polymers and plastics is into these environments. However, anaerobic degradation, which is particularly pertinent to water-soluble polymers that may enter anaerobic digestors in sewage treatment facilities, is the object of growing interest, and more information will undoubtedly be developed in the future on this condition. In this article, unless otherwise specified, biodegradation should be understood to be in an aerobic environment.

$$\text{polymer} + O_2 \longrightarrow CO_2 + H_2O + \text{biomass} + \text{residue} \qquad (1)$$

$$\text{polymer} \longrightarrow CO_2 + CH_4 + H_2O + \text{biomass} + \text{residue} \qquad (2)$$

To assess the degree of biodegradation quantitatively, analytical techniques are needed for any or all of the reactants and products; the polymer; oxygen uptake, known as biochemical oxygen demand (BOD); and the residue. The more rigorous the analysis, the more reliable the measurement of the extent of biodegradation and, of course, the greater the acceptability of the data and the conclusions drawn. For total biodegradation, there should be no residue remaining in the environment.

Qualitative assessment of biodegradation where changes such as weight loss, tensile strength loss, disintegration, etc, are measured is useful in that it indicates the loss of properties as a guideline to the physical breakdown of the plastic and its decomposition in various environments such as compost, landfill, etc, and particularly in the intended disposal environment. To differentiate biodegradation and abiotic degradation such

Table 2. Biodegradation Test Protocols

Test number	Environment	Measurement
ASTM D5209-92	aerobic sewage sludge	CO_2
ASTM D5210-92	anaerobic sewage sludge	CO_2 and CH_4
ASTM D5247-92	aerobic specific microorganisms	molecular weight
ASTM D5271-93	aerobic activated sewage sludge	O_2 and CO_2
ASTM D5338-92	aerobic controlled composting	CO_2
ASTM D5437-93	marine floating conditions	physical properties
MITI Test	mixed microbial	O_2

as oxidation and hydrolysis, it is usually necessary to do a simultaneous control test with a killed inoculum (cyanide or mercury salts are acceptable) in which no degradation should be observed if only biodegradation is involved in the plastic degradation. This test would also serve as a test method for hydrolytic or oxidative degradation, should degradation occur in the abiotic environment.

There have been numerous communications on the subject of biodegradation test methods, including aerobic compost (30), anaerobic bioreactor (31), general methodology and future directions (32–34), and a fine review article (24). ASTM (22) and MITI (35) have also set forth standard testing protocols for plastics, as shown in Table 2, whereas OECD test methods (29) are more suited to water-soluble polymers.

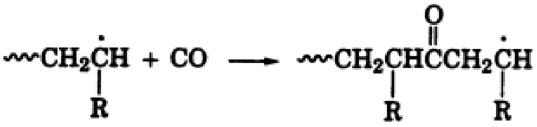
The current state of testing (ca 1996) is greatly improved over that which prevailed during the early days of research. However, it should be recognized that the biodegradation test protocols discussed here are only screening tests for readily biodegradable polymers and plastics. Failure in these tests does not exclude the possibility of biodegradation; it merely indicates that under the environmental conditions evaluated there is no biodegradation. Repeated tests, particularly in other environments, are recommended before acceptance of nonbiodegradability. The possibility of toxicity of the polymer and the need for lower concentration testing should also be explored. In the latter case it may be necessary to resort to isotopic labeling in order to measure biodegradation by monitoring low concentrations of carbon dioxide evolution. In many cases with synthetic polymers, it may also be important to allow acclimation to occur so that enzymes may be induced that will biodegrade them. In addition to attention to improved biodegradation test method development, there is a need to establish the fate and effect of residues and degradation fragments in the environment where biodegradation is incomplete, whether it stems from biodegradable polymers and plastics or from any of the other environmental degradation pathways. Some efforts are being made in this area, eg, work on water-soluble polymers (36) and ASTM Standard Practice D5152-91 (22) for extracting aqueous solubles from the solid fragments produced by the environmental degradation of plastics for testing in standard aquatic toxicity protocols. Biodegradation has no value in itself; it is a part of fate and effects to be utilized in the important Environmental Safety Assessment (34).

4.3. Degradation Mechanisms

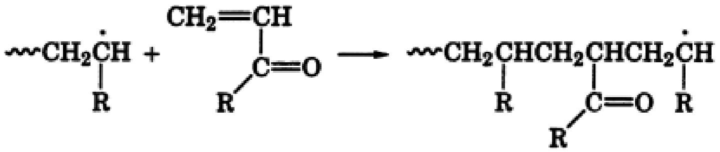
5. Photodegradation

Photodegradable polymers degrade in the environment by chain scission promoted by natural daylight and usually oxygen to yield low molecular weight fragments that are more susceptible to biodegradation than the original high molecular weight polymer. The polymers are generally structurally similar to currently used environmentally stable polymers but have been modified during synthesis or post-treatment to insert photochemically active groups. The addition of carbonyl functionality (37–40) into the polymer main or side chain, or of external photosensitizers and pro-oxidants such as metal salts (41, 42), benzophenone (43), ketones (44), ethers (44), mercaptans (44), and polyunsaturated compounds (45) are representative examples. The concept and mechanism of fragmentation is well established and there are commercial products based on ethylene–carbon monoxide copolymers for use in six-pack holders and agricultural film. The ultimate fate of the fragments produced is not yet fully established; in most cases the argument is put forward that if the molecular weight of the degradation products is low enough, then they will biodegrade.

The synthesis of copolymers of olefins with carbon monoxide (eq. **3**) or ketones (eq. **4**) leads to backbone or side-chain carbonyl functionality, respectively. When $R = C_6H_5$, the monomer is styrene, and when $R = H$, the monomer is ethylene (46–48).

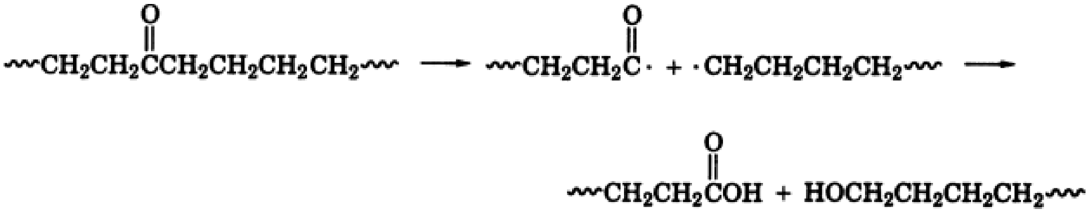


$$\sim CH_2\underset{\substack{|\\ R}}{\dot{C}}H + CO \longrightarrow \sim CH_2\underset{\substack{|\\ R}}{C}H\overset{\substack{O\\ \|}}{C}CH_2\underset{\substack{|\\ R}}{\dot{C}}H \tag{3}$$

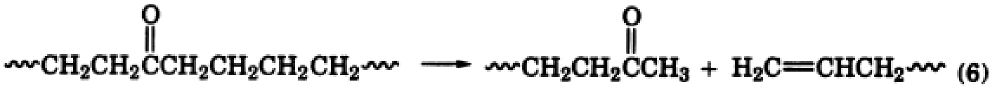


(4)

When the polymers are exposed to ultraviolet radiation, the activated ketone functionalities can fragment by two different mechanisms, known as Norrish types I and II. The degradation of polymers with the carbonyl functionality in the backbone of the polymer results in chain cleavage by both mechanisms, but when the carbonyl is in the polymer side chain, only Norrish type II degradation produces main-chain scission (37, 49). A Norrish type I reaction for backbone carbonyl functionality is shown by equation **5**, and a Norrish type II reaction for backbone carbonyl functionality is equation **6**.

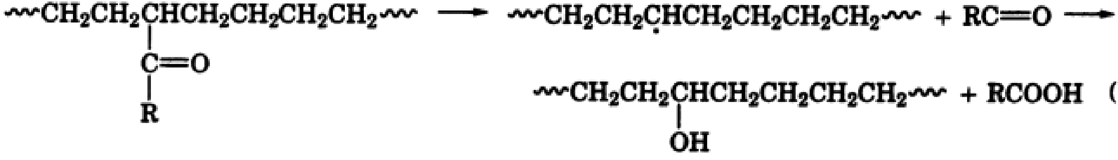


$$\sim CH_2CH_2\overset{\substack{O\\ \|}}{C}CH_2CH_2CH_2CH_2\sim \longrightarrow \sim CH_2CH_2\overset{\substack{O\\ \|}}{C}\cdot + \cdot CH_2CH_2CH_2CH_2\sim \longrightarrow \sim CH_2CH_2\overset{\substack{O\\ \|}}{C}OH + HOCH_2CH_2CH_2CH_2\sim \tag{5}$$

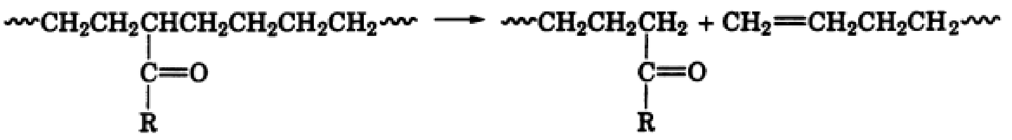


$$\sim CH_2CH_2\overset{\substack{O\\ \|}}{C}CH_2CH_2CH_2CH_2\sim \longrightarrow \sim CH_2CH_2\overset{\substack{O\\ \|}}{C}CH_3 + H_2C{=}CHCH_2\sim \tag{6}$$

A Norrish type I reaction for side-chain carbonyl functionality is equation **7**, and a Norrish type II reaction for side-chain carbonyl functionality is equation **8**.



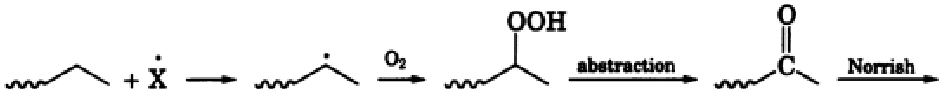
$$\sim CH_2CH_2\underset{\substack{|\\ C=O\\ |\\ R}}{C}HCH_2CH_2CH_2CH_2\sim \longrightarrow \sim CH_2CH_2\underset{\bullet}{C}HCH_2CH_2CH_2CH_2\sim + R\dot{C}{=}O \longrightarrow \sim CH_2CH_2\underset{\substack{|\\ OH}}{C}HCH_2CH_2CH_2CH_2\sim + RCOOH \tag{7}$$



$$\sim CH_2CH_2\underset{\substack{|\\ C=O\\ |\\ R}}{C}HCH_2CH_2CH_2CH_2\sim \longrightarrow \sim CH_2CH_2\underset{\substack{|\\ C=O\\ |\\ R}}{C}H_2 + CH_2{=}CH_2CH_2CH_2\sim \qquad (8)$$

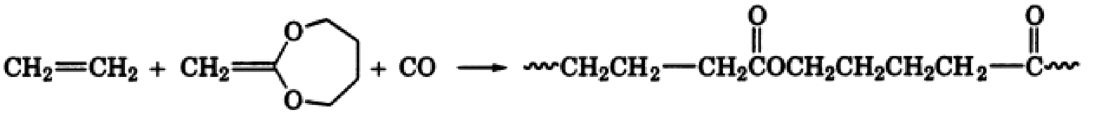
Norrish type I chemistry is claimed to be responsible for about 15% of the chain scission of ethylene–carbon monoxide polymers at room temperature, whereas at 120°C it promotes 59% of the degradation. Norrish I reactions are independent of temperature and oxygen concentration at temperatures above the T_g of the polymer (50).

Degradation of polyolefins such as polyethylene, polypropylene, polybutylene, and polybutadiene promoted by metals and other oxidants occurs via an oxidation and a photo-oxidative mechanism, the two being difficult to separate in environmental degradation. The general mechanism common to all these reactions is that shown in equation **9**. The reactant radical may be produced by any suitable mechanism from the interaction of air or oxygen with polyolefins (42) to form peroxides, which are subsequently decomposed by ultraviolet radiation. These reaction intermediates abstract more hydrogen atoms from the polymer backbone, which is ultimately converted into a polymer with ketone functionalities and degraded by the Norrish mechanisms (eq. **5–8**).



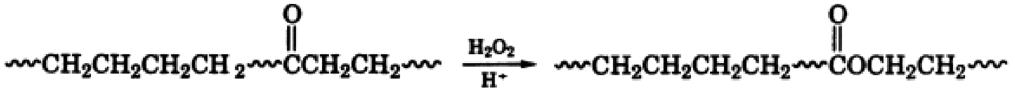
(9)

Research on photodegradable polymers is still very active as an end in itself and for their use as additives for biodegradable polymers to encourage more rapid biodegradation by decreasing molecular weight. Exxon (51) and Quantum (52) have received patents for polyolefin–polyester–carbon monoxide compositions. The Exxon route is by copolymerization of ethylene, carbon monoxide, and 2-methylene-1,3-dioxapane. The use of dioxapane is based on a clever invention by W. J. Bailey to introduce an ester linkage into polyolefins during free-radical polymerization such that they become susceptible to biodegradation. Thus Exxon scientists combine Bailey's idea with a known photodegradable product to enhance biodegradation of the fragments. The polymer has the structural elements shown in equation **10** in concentrations related to the degradation response required and controlled by the synthesis variables.



(10)

Quantum, by contrast, converted an ethylene–carbon monoxide polymer into a polyester-containing terpolymer by treatment with acidic hydrogen peroxide, the Baeyer-Villiger reaction (eq. **11**). Depending on the degree of conversion to polyester, the polymer is totally or partially degraded by a biological mechanism.



$$\sim CH_2CH_2CH_2CH_2\sim\overset{\substack{O\\ \|}}{C}CH_2CH_2\sim \xrightarrow[H^+]{H_2O_2} \sim CH_2CH_2CH_2CH_2\sim\overset{\substack{O\\ \|}}{C}OCH_2CH_2\sim \qquad (11)$$

Other patents include copolymers of vinyl ketones with acrylates, methacrylates, and styrene (53); an ethylene–carbon monoxide (1–7 wt %) blend as a photo-initiator in polycaprolactone–polyethylene blends (54); ethylene–carbon monoxide for degradable golf tees (55); a vinyl ketone analogue of Exxon's carbon monoxide–dioxapane–ethylene (56); a photodegradable food wrapper based on blends of a polyolefin–starch and photoactivators for polyolefin degradation (57); and a carboxylated polyethylene–carbon monoxide–norbornene-2,3-dicarboxylic acid (58).

Photodegradation chemistry has evolved to a highly practical state; commercial products are in existence and others are being evaluated. The degradation mechanisms are understood to the point of property loss for the polymers. Complete environmental acceptability is still lacking. It is not sufficient to expect low molecular weight fragments to be biodegradable; this must be demonstrated.

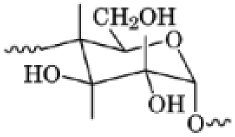
6. Biodegradation

Biodegradable polymers and plastics are readily divided into three broad classifications: (*1*) natural, (*2*) synthetic, and (*3*) modified natural. These classes may be further subdivided for ease of discussion, as follows: (*1*) natural polymers; (*2*) synthetic polymers may have carbon chain backbones or heteroatom chain backbones; and (*3*) modified natural may be blends and grafts or involve chemical modifications, oxidation, esterification, etc.

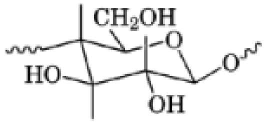
6.1. Natural Polymers

Natural polymers, or biopolymers, are produced in nature by all living organisms. As a class they represent truly renewable resources since they are biodegradable, even if slowly in some cases. Because they are produced in nature there is no concern about this slow rate of biodegradation, contrary to concerns about synthetic polymers. Biopolymers are considered environmentally acceptable degradable polymers. The most widespread natural polymers are the polysaccharides, such as cellulose and starch. Other important classes include polyesters such as polyhydroxyalkanoates, proteins like silk and poly(γ-glutamic acid), and hydrocarbons such as natural rubber. Usually the natural polymers exist in an optically active form, biopolymers with asymmetric centers being always isotactic. An excellent description of many biopolymers has been given in an edited book (59) with chapters on silk proteins, collagen, polyhydroxyalkanoates, microbial polysaccharides, microbial cellulose, hyaluronic acid, alginates, and other miscellaneous biomaterials. Other sources include a review on biodegradable polymers (17) and the proceedings of the NATO Advanced Research Workshop on New Biodegradable Microbial Polymers (60). With few exceptions, natural polymers are not suitable polymers for practical applications as of 1996, either because they lack the property requirements or because they are too expensive for other than specialty, high value-niche markets such as biomedical applications. There are opportunities in blends and for less costly chemically modified polymers such as starch and celluloses.

Polysaccharides are largely limited to starch and cellulose derivatives for practical applications either in plastics or as water-soluble polymers. Both these polymers are composed of D-glycopyranoside repeating units to very high molecular weight, thousands of units. They differ in that starch is poly(1,4- α-D-glucopyranoside) **(1)** and cellulose is poly(1,4- β-D-glucopyranoside) **(2)**. This difference in structure controls biodegradation rates and properties of the polymers.



(1)

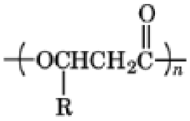


(2)

Complex carbohydrates (qv) such as microbially produced xanthan, curdlan, pullulan, hyaluronic acid, alginates, carageenan, and guar are accepted as biodegradable and are finding uses where cost is not an impediment. Xanthan is the predominant microbial polysaccharide on the market, ca 10,000 t worldwide (59), and finds use in the food industry and as a thickener in many industrial applications (see Gums). It is foreseeable that other polysaccharides will gain acceptance in specialty areas where biodegradability is essential.

Proteins (qv) have not found widespread use as plastic materials because they are not soluble or fusible without decomposition; hence, they must be used as found in nature. They are of course widely used as fibers. Examples are wool, silk, and gelatin (collagen), which is used as an encapsulant in the pharmaceutical and food industries. The structure of proteins is an extended chain of amino acids joined through amide linkages which are readily degraded by enzymes, particularly proteases. Recent activity in poly(γ-glutamic acid) (60) with control of stereochemistry by the inclusion of manganese ions may be important for future developments in biodegradable water-soluble polymers with carboxyl functionality, which is an intensely researched and desirable goal for detergent applications.

Polyesters are known to be produced by many bacteria as intracellular reserve materials for use as a food source during periods of environmental stress. They have received a great deal of attention since the 1970s because they are biodegradable, can be processed as plastic materials, are produced from renewable resources, and can be produced by many bacteria in a range of compositions. The thermoplastic polymers have properties that vary from soft elastomers to rigid brittle plastics in accordance with the structure of the pendent side-chain of the polyester. The general structure of this class of compounds is shown by **(3)**, where $\mathrm{R} = \left(\mathrm{CH_2} \right)_m \mathrm{CH_3}$, $n = >100$, and $m = 0 - 8$.



$$\left(\mathrm{O}\underset{\mathrm{R}}{\mathrm{CH}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \right)_n$$

(3)

These polyesters have been comprehensively reviewed (61–63). All the polyesters are 100% optically pure and are 100% isotactic. When R is $\mathrm{CH_3}$, ie, poly(β-hydroxybutyrate) (PHB) the polymer is highly crystalline, with a melting point of 180°C and a glass-transition temperature, T_g, of 5°C (64). This combination of high T_g and high crystallinity makes polymer films and plastics very brittle and plasticization is preferred to improve the properties. This is accomplished in the commercially available BIOPOL from Zeneca (formerly ICI) by using bacteria to produce a copolymer containing β-hydroxyvalerate ($\mathrm{R} = \mathrm{C_2H_5}$). By feeding the bacteria, *Alcaligenes eutrophus*, a mixed feed of propionic acid and glucose (65) a random copolymer is produced with some control over the composition. These polymers have better mechanical properties and are produced on a relatively large scale for this new polymer fermentation technology (a few hundred tons per year). Their acceptance would be more widespread if the price were closer to the synthetic commodities with which they compete, since they are produced from renewable resources and are of natural origin and thus environmentally appealing. Attempts to reduce costs are underway in a number of laboratories: the cost of processing with the current polymers is excessive due to the isolation steps which include clean-up of bacterial debris. If these polymers could be produced by isolated enzymatic processes this would be avoided. Another intriguing possibility is to produce these natural polymers in plants rather than bacteria by transferring the bacterial genes to suitable plants. Some work (66) in mustard plants has succeeded in the production of minute quantities. The day when poly(hydroxyalkanoate)s are produced in the volumes and at the price of starch may herald a new age for plastics and polymers, but it is not yet here. Some of the opportunities for these materials have been discussed (67).

The longer side-chain polyesters **(3)**, where m is 3–6, are produced by a variety of bacteria, usually as copolymers and with low crystallinity, low melting points, and low glass-transition temperatures. These polyesters are elastomeric and have excellent toughness and strength (63). They are inherently biodegradable but as the chain length is increased the biodegradation rate is greatly reduced, indicating that the hydrophilic–hydrophobic balance of the polymer plays a large role in biodegradation (68). Other biodegradation studies are under way to evaluate mechanisms (69) using ^{13}C-labeled poly(hydroxybutyrate) and effect of environment (70) on the rate of biodegradation in lake Lugano, Switzerland.

All these polyesters are produced by bacteria in some stressed conditions in which they are deprived of some essential component for their normal metabolic processes. Under normal conditions of balanced growth the bacteria utilizes any substrate for energy and growth, whereas under stressed conditions bacteria utilize any suitable substrate to produce polyesters as reserve material. When the bacteria can no longer subsist on the organic substrate as a result of depletion, they consume the reserve for energy and food for survival; or upon removal of the stress, the reserve is consumed and normal activities resumed. This cycle is utilized to produce the polymers which are harvested at maximum cell yield. This process has been treated in more detail in a paper (71) on the mechanism of biosynthesis of poly(hydroxyalkanoate)s.

6.2. Synthetic Polymers

Synthetic polymers are well established in many applications where their environmental resistance properties are highly valued. Evolving environmental awareness and waste-disposal problems have led to increasing activity to develop biodegradable synthetic analogues of these polymers, particularly water-soluble polymers and plastics, which are used in packaging and other areas of opportunity. Natural polymers are ultimately degraded and consumed in nature in a continuous recycling of resources, but since synthetic polymers did not evolve naturally, the plethora of enzymes available in nature for degrading natural polymers are not in the main useful for synthetic polymers. The search for synthetic polymeric structures that can be biodegraded has progressed from minor modification of the nondegradables in use to structures that mimic nature, for which more success has been achieved.

Despite the fact that biodegradation testing until the late 1980s has been very unreliable and the interpretation of many reported data in the literature is questionable, some guidelines based on polymer structure, polymer physical properties, and environmental conditions at the exposure site have emerged for predicting the biodegradability of synthetic polymers (9, 72, 73). In considering polymer structure, the following generalizations can be made:

A higher hydrophilic/hydrophobic ratio is better for biodegradation.
Carbon chain polymers are unlikely to biodegrade.
Chain branching is deleterious to biodegradation.
Condensation polymers are more likely to biodegrade.
Lower molecular weight polymers are more susceptible to biodegradation.
Crystallinity slows biodegradation.

Table 3. Hydrocarbon Branching and Molecular Weight Effects on Biodegradability

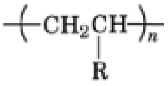
Compound	Mol wt	Number of branches	Growth test[a]
dodecane	170	0	4
2,6,11-trimethyldodecane	212	3	0
hexadecane	226	0	4
2,6,11,15-hexadecane	282	4	0
tetracosane	338	0	4
squalene	422	6	0
dotriacontane	450	0	4
hexatriacontane	506	0	0
tetracontane	562	0	0
tetratetracontane	618	0	0

[a] ASTM tests G21-70 and G22-76. Higher numbers are considered to correlate with the susceptibility of the plastic to biodegradation.

Favorable polymer physical properties include water solubility and sample purity. Environmental conditions to consider in evaluating biodegradability are temperature, pH, moisture, oxygen, nutrients, suitable microbial population (fungal, algae, bacterial), concentration, and test duration.

6.2.1. Carbon Chain Backbone Polymers

These polymers may be represented by **(4)** and considered derivatives of polyethylene, where n is the degree of polymerization and R is (an alkyl group or) a functional group: hydrogen (polyethylene), methyl (polypropylene), carboxyl (poly(acrylic acid)), chlorine (poly(vinyl chloride)), phenyl (polystyrene) hydroxyl (poly(vinyl alcohol)), ester (poly(vinyl acetate)), nitrile (polyacrylonitrile), vinyl (polybutadiene), etc. The functional groups and the molecular weight of the polymers, control their properties which vary in hydrophobicity, solubility characteristics, glass-transition temperature, and crystallinity.



$$-\!\left(\mathrm{CH_2}\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}\right)_n\!-$$

(4)

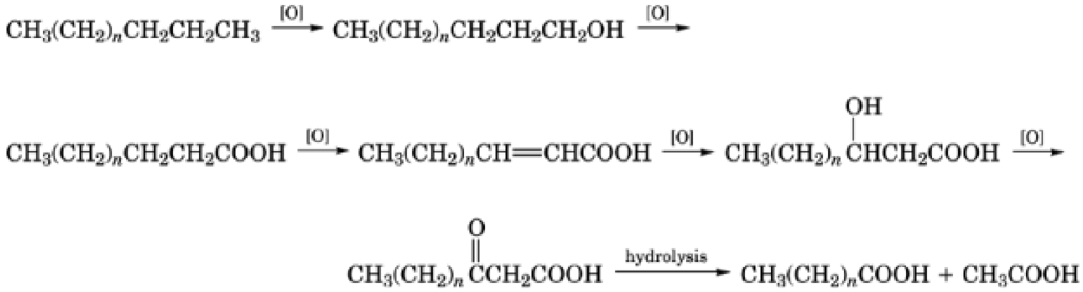
Polyethylene with molecular weights into the oligomer or hydrocarbon range have been studied very extensively (4, 23, 25) and also at the higher range (74–82). The latter experiments are long term with radiolabeled polymer running for many years. The earlier work was based on fungal and bacterial growth tests and indicated that polyethylene and other high molecular weight carbon chain polymers did not support growth. A few anomalous results were attributed to plasticizer or low molecular weight impurities which had already been shown to be biodegradable in similar tests with pyrolyzed polyethylene and simple hydrocarbons. In the same work (4, 23, 25) it was also found that branching of hydrocarbon chains limits biodegradation and the molecular weight cut-off for linear molecules appears to be in the 500 dalton range, but more rigorous testing is needed for confirmation. Some of these data are shown in Tables 3 and 4.

The increase in degradation with lower molecular weight may be a result of many factors. For example, transportation of polymer across cell walls is more likely at lower molecular weight, or it may be the mechanism of biodegradation or because of random or chain-end cleavage prior to entering the cell. Chain-end *exo*-biodegradation by β-oxidation is indicated schematically in Figure 4 for a simple hydrocarbon. The individual oxidation steps are enzyme-catalyzed with a final hydrolysis to a two-carbon diminished chain and acetic acid, which is then presumably biodegraded. Such a mechanism would explain the occurrence of slower

Table 4. Biodegradability of Low Mol Wt Pyrolysis Products of HDPE and LDPE

Pyrolysis temperature, °C	Mol wt	Growth rating[a]
control (HDPE)	123,000	0
400	16,000	1
450	8,000	1
500	3,200	3
535	1,000	3
control (LDPE)	56,000	0
400	19,000	1
450	12,000	1
500	2,100	2
535	1,000	3

[a] ASTM tests G21-70 and G22-76. Higher numbers are considered to correlate with the susceptibility of the plastic to biodegradation.



$$\mathrm{CH_3(CH_2)_{\mathit{n}}CH_2CH_2CH_3} \xrightarrow{[\mathrm{O}]} \mathrm{CH_3(CH_2)_{\mathit{n}}CH_2CH_2CH_2OH} \xrightarrow{[\mathrm{O}]}$$

$$\mathrm{CH_3(CH_2)_{\mathit{n}}CH_2CH_2COOH} \xrightarrow{[\mathrm{O}]} \mathrm{CH_3(CH_2)_{\mathit{n}}CH{=}CHCOOH} \xrightarrow{[\mathrm{O}]} \mathrm{CH_3(CH_2)_{\mathit{n}}}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2COOH} \xrightarrow{[\mathrm{O}]}$$

$$\mathrm{CH_3(CH_2)_{\mathit{n}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2COOH} \xrightarrow{\text{hydrolysis}} \mathrm{CH_3(CH_2)_{\mathit{n}}COOH + CH_3COOH}$$

Fig. 4. β-Oxidative degradation of hydrocarbons.

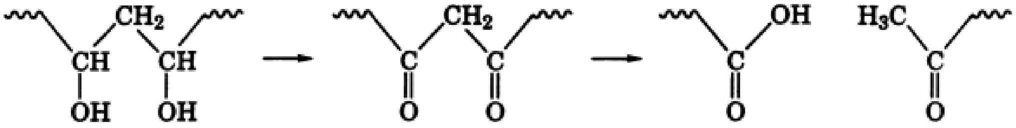
biodegradation at higher molecular weight, where there would be fewer chain ends. The terminal groups found in oxidized and photodegraded polyethylene are oxygen-containing and these should expedite biodegradation via a β-oxidation mechanism, but proof of this is preferable to prediction.

Results of experiments (74–82) that are, as of 1996, several years along and continuing suggest that polyethylene is slowly biodegraded and is slightly accelerated by pretreatment with surfactants or an oxidation process. This meticulous work is identifying some of the myriad degradation products, many of which are oxygen-containing, as is expected if the degradation process for polyethylene is, as projected, initially oxidation and then enzymatic.

Other high molecular weight hydrocarbon polymers are not biodegradable, but oligomers of *cis*-1,4-isoprene (83), butadiene (84), and styrene (85), are degradable. And there has been further confirmation of biodegradation of oligomeric ethylene (86).

Functional derivatives of polyethylene, particularly poly(vinyl alcohol) and poly(acrylic acid) and derivatives, have received attention because of their water-solubility and disposal into the aqueous environment. Poly(vinyl alcohol) is used in a wide variety of applications, including textiles, paper, plastic films, etc, and poly(acrylic acid) is widely used in detergents as a builder, a super-absorbent for diapers and feminine hygiene products, for water treatment, in thickeners, as pigment dispersant, etc (see Vinyl polymers, vinyl alcohol polymers).

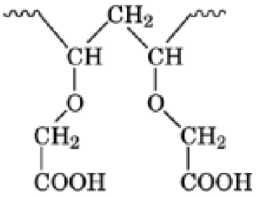
Poly(vinyl alcohol), obtained by the hydrolysis of poly(vinyl acetate) is probably the only carbon chain polymer to be fully biodegradable. The biodegradation is a random chain cleavage of 1,3-diketones formed by an enzyme-catalyzed oxidation of the secondary alcohol functional groups in the polymer backbone. The biodegradation was first observed as a reduction in aqueous viscosity of the polymer in the presence of soil bacteria (87). Subsequently, a *Pseudomonas* species was identified as the soil bacterium responsible for the degradation over a degree of polymerization range of 500–2000 (88). Utilizing the polymer as a sole carbon source in an aqueous polymer solution at a concentration of 2700 ppm, it was reduced to 250–300 ppm concentration in 7–10 d at pH 7.5–8.5 and 35–45°C. An oxidative endo mechanism was proposed and later substantiated (89) by quantifying the oxygen uptake at 1 mole for every mole of hydrogen peroxide produced and identifying the degradation products as ketones and carboxylic acids, as shown in the following (eq. **12**). An alternative mechanism (90, 91), in which the products were identified as an alcohol and a carboxylic acid was subsequently proved to be in error, and the mechanism shown is widely accepted. It is also supported by the rapid biodegradation of chemically oxidized poly(vinyl alcohol) (92–94).

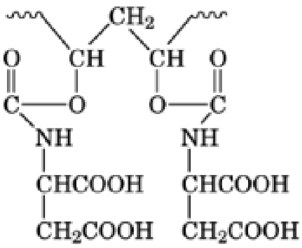

(12)

Other bacterial strains identified as biodegrading poly(vinyl alcohol) include *Flavobacterium* (95) and *Acinetobacter* (96) and many others, as well as fungi, molds, and yeasts (97). Industrial evaluations at Du Pont (98) and Air Products (99) indicate that over 90% of poly(vinyl alcohol) entering wastewater treatment plants is removed, and hence no environmental pollution is likely.

Poly(vinyl acetate), the precursor of poly(vinyl alcohol), hydrolyzed to less than 70%, is claimed to be nonbiodegradable under conditions similar to those that biodegrade the fully hydrolyzed polymer (100) (see Vinyl polymers poly (vinyl acetate polymers).

Carboxylate derivatives of poly(vinyl alcohol) are biodegradable and function in detergents as cobuilders, although they are too costly to be practical as of 1996. Vinyloxyacetic acid has been polymerized **(5)** (101, 102), and Lever has patented polymers, eg, poly(vinyloxyaspartic acid) **(6)**, based on vinyl carbamates obtained from the reaction of vinyl chloroformates and amino acids such as aspartic and glutamic acids (103). Both hydrolyze to poly(vinyl alcohol) and then biodegrade.


(5)

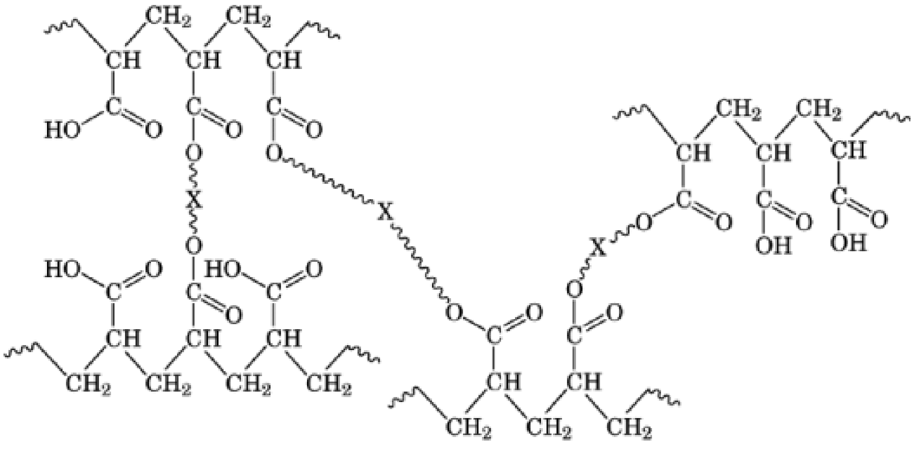

(6)

Copolymers of vinyl alcohol with acrylic or maleic acid have been evaluated in detergents as potentially biodegradable cobuilders by a number of laboratories (104–106), but the results were not encouraging for balancing biodegradation and performance. Higher than 80 mol % of vinyl alcohol is required for high levels of biodegradation, and less than 20 mol % for acceptable performance.

The use of poly(carboxylic acids) in detergents is well established and has been well reviewed (107). Their lack of biodegradability at preferred performance molecular weights, ca 70 (5,000 dalton) for poly(acrylic acid) and 1,000 (70,000 dalton) for copoly(acrylic–maleic acids), even though there are ample data to indicate no harmful environmental effects, has resulted in a massive search for degradable replacements. After many efforts to copolymerize, by a free-radical mechanism, acrylic and maleic acids to biodegradable polymers with a whole range of vinyl monomers (108–113) and graft substrates, including polysaccharides (114), it is recognized that earlier work (115) with functional polymers and oligomeric hydrocarbons (4, 23, 25) is correct and only low molecular weight oligomeric carbon chain polymers are likely to be biodegradable, regardless of functionality. More recent confirmation has come from Japan (116, 117).

High molecular weight poly(acrylic acid), polyacrylamide, and poly(vinylpyrrolidinone) ozonized to oligomers with molecular weights less than 14 (1000 daltons) showed a marked increase in their biodegradability, with the exception of polyacrylamide (115). Later work (116, 117) was based on oligomers of acrylic acid obtained by chromatographic separation from low molecular weight polymers. The results all indicate that poly(acrylic acids) are not completely biodegradable above about a degree of polymerization of 6–8 (400–600 daltons).

Other efforts to use radical polymerization to synthesize biodegradable carboxylated polymers have been based on combining low molecular weight oligomers through degradable linkages and by introducing weak links into the polymer backbone. BASF (118) and NSKK (119) have patented acrylic oligomers chain-branched with degradable linkages designated X in **(7)**. Grillo Werke has patented copolymers of acrylic acid and enol sugars (120). The degradability of these polymers has not been clearly established, but the branching is likely to be a problem.



(7)

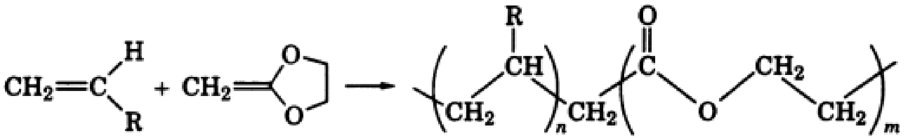
Several miscellaneous carbon chain backbone polymers have been claimed as biodegradable without clear evidence, including copolymers of methyl methacrylate and vinyl pyridinium salts (121), where the pyridinium salt is hypothesized to act as a magnet for bacteria which then cleave the chain into small fragments that biodegrade completely. An ethylene–vinyl alcohol copolymer has been converted into a terpolymer ester by a Baeyer Villiger reaction (122). Also, polymers of α-hydroxyacrylic acid have been made (123). The terpolymer ester is probably biodegradable, but the polyacid fails to differentiate adsorption on solids in a sewage sludge test from biodegradation.

6.2.2. Heteroatom Chain Backbone Polymers

This class of polymers includes polyesters, which have been widely studied from the initial period of research on biodegradable polymers, polyamides, polyethers, polyacetals, and other condensation polymers. Their linkages are quite frequently found in nature and these polymers are more likely to biodegrade than hydrocarbon-based polymers.

Low melting, low molecular weight aliphatic polyesters were shown to be readily biodegradable using soil burial tests (4) and ASTM bacterial and fungal growth methods (ASTM G21-70 and G22-76). From this work, polycaprolactone was recognized as one of a select few commercially available synthetic polymers that is beyond a doubt biodegradable. Since that time many other workers have confirmed the biodegradability of aliphatic polyesters using other test protocols (124–126) such as lipase hydrolysis with measurement of the rate of production of water-soluble oligomers. Results also indicate that as the aliphatic polyesters become more hydrophobic, either from acid or alcohol chain length extension, the biodegradation rate is slowed. Amorphous regions of polyesters are more readily biodegradable than crystalline regions (127).

During this early period, a very ingenious free-radical route to polyesters was used to introduce weak linkages into the backbones of hydrocarbon polymers and render them susceptible to biodegradability (128–131). Copolymerization of ketene acetals with vinyl monomers incorporates an ester linkage into the polymer backbone by rearrangement of the ketene acetal radical as illustrated in equation **13**. The ester is a potential site for biological attack. The chemistry has been demonstrated with ethylene (128–131), acrylic acid (132), and styrene (133).



(13)

Interest in biodegradable polyesters has been predominantly focussed on aliphatic polyester structures and includes ring opening of 1,5-dioxepan-2-one (134), polyesters of aliphatic acids with glycols, but also some terephthalic acid and sulfoterephthalic acid as a compostable diaper (135). Perhaps the biggest advances in the synthetic polyester area are the close match for BIOPOL, the expensive bacterial polyester (136) which has the chirality but lacks the molecular weight of the natural polymer; and the new product BIONOLLE from Showa High Polymer (137–139) that is supposedly a biodegradable polyester. Patents (137) suggest that BIONOLLE is an aliphatic ester coupled with a polyisocyanate and that ease of biodegradation and properties are inversely related. Both these inventions indicate that progress is being made on meeting the property requirements for biodegradable polymers.

Aliphatic polyesters are also available by the chemical reaction of carbon monoxide and formaldehyde (140), carbon dioxide and epoxy compounds (141), and bisepoxies and biscarboxylic acids (142).

Poly(lactic acid) [50-21-5] has until very recently been known only in the medical field as an expensive polymer for the manufacture of sutures (qv) and other biomaterials. With cheap lactic acid becoming available from the fermentation of waste agricultural products, there has been a surge of activity to develop new polymerization methods and to find commercial outlets for the products. Though still more expensive than common commodity polymers, the introduction of products for niche markets such as agricultural films and mulch and the fast-food industry is anticipated to occur by the mid- to late 1990s. There are many patents issuing in the homo- and copolymer synthesis and process areas, principally from just a few sources, ie, Cargill

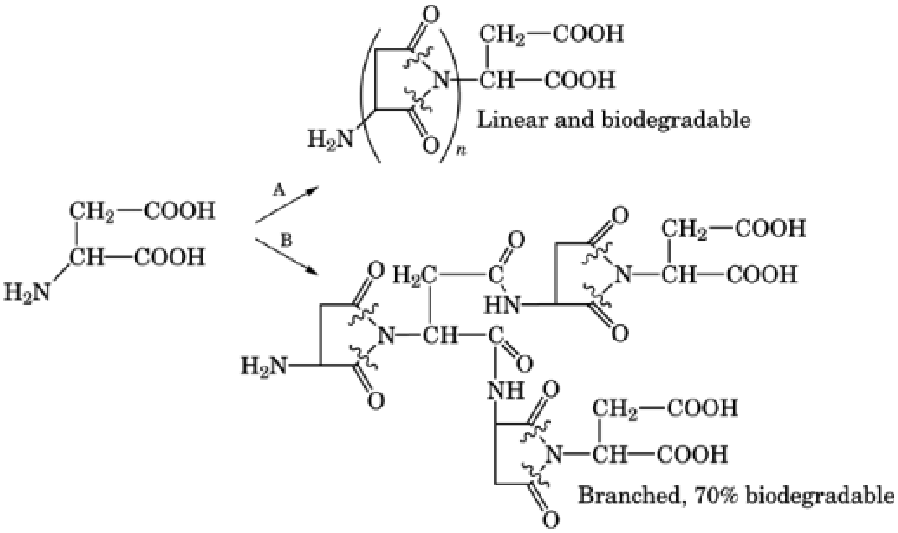


Fig. 5. Condensation polymers of aspartic acid.

(143), Du Pont (144), Mitsui Toatsu (145), and Battelle Memorial Laboratories (146). Others active in this area include Shimadzu and Argonne National Laboratories.

Polyamides have received some attention and the results indicate that the stereochemistry of the groups close to the amide linkages and the hydrophilic nature control biodegradability (147, 148). A more general study on polyesters, polyureas, polyurethanes, and polyamides is a good fundamental early study (151) guiding the later work in this general area. It has been demonstrated that polyesteramides are difficult to hydrolyze chemically yet can be biodegraded rapidly at ambient conditions in the right environment (150). Support for this observation comes from Japan (151, 152). Although polymers of nylon-6 are considered nonbiodegradable, oligomers and low molecular weight polymers of less than 157 (11,000 daltons) will biodegrade (153).

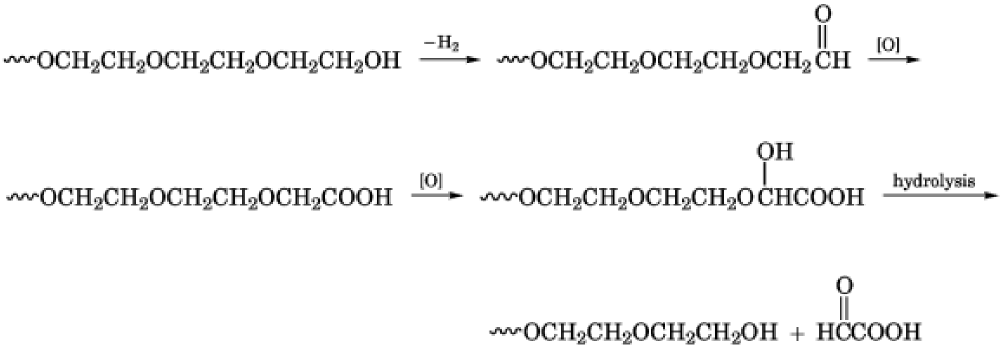
Water-soluble polyesters and polyamides containing carboxyl functionality are reported to be biodegradable detergent polymers by BASF and may be obtained by condensation polymerization of monomeric poly(carboxylic acid)s such as citric acid, butane-1,2,3,4-tetracarboxylic acid, tartaric acid, and malic acid with polyols (154); with amino compounds, including amino acids (155); and with polysaccharides (156). Early work (157, 158) demonstrated the self-condensation of malic acid to biodegradable polyesters regardless of the ester, α- or β-linkage formed. Procter and Gamble has patented succinylated poly(vinyl alcohol) (159).

Polyanionics are available also from poly(amino acid)s based on poly(carboxyamino acid)s such as glutamic acid and aspartic acid. Though both are known and claimed as biodegradable homopolymers, aspartic acid is more amenable to a practical industrial synthesis by thermal polymerization, since it has no tendency to form an internal *N*-anhydride. An alternative synthesis is from ammonia and maleic acid. Only the acid-catalyzed condensation of L-aspartic acid yields an authenticated biodegradable polymer (160). The noncatalyzed process and the ammonia–maleic acid processes give partially (ca 30 wt % residue remains in the Sturm test for CO_2 evolution, ASTM D5209-92) biodegradable polymers, owing to the molecules being branched and resistant to enzymatic attack. The structures are shown in Figure 5. Starting from aspartic acid, pathway A is acid-catalyzed thermal condensation, and B is noncatalyzed thermal condensation. The polysuccinimides shown hydrolyze at the point indicated to give mixtures of α- and β-poly(aspartic acid) salts. Regardless of the stereochemistry of the starting aspartic acid, L or D, the final product is the DL racemate.

Many synthesis patents and publications from aspartic acid (161–166) and ammonia–maleic (167, 168) processes have issued and the product is expected to find use in many applications, including dispersants (169,

170) and detergents (171, 172). BASF has an aspartic acid copolymer patent with carbohydrates and polyols (173), and Procter and Gamble (174) has a patent for poly(glutamic acid) [25513-46-6], both for biodegradable detergent cobuilders. There is one patent for poly(methyl γ-glutamate) as a transparent plastic with excellent strength and biodegradability (175).

Polyethers have been investigated since about 1962, especially poly(ethylene glycol), which is water soluble and is widely used in detergents and as a synthesis intermediate in polyurethanes. It has been established that the nature of the degradation of poly(ethylene glycols) with molecular weights higher than 6000 daltons is symbiotic, but below a molecular weight of 1000 daltons the polymer is biodegraded by many individual bacteria (176). The enzymatic *exo*-degradation pathway described in Reference 176 is shown schematically as equation **14**. The first stage is dehydrogenation (oxidation), the second stage is oxidation, the third stage is an oxidation that is followed by a hydrolysis to remove a two-carbon fragment as glyoxylic acid. Degradation of poly(ethylene glycols) with molecular weights of 20,000 daltons has been reported.



$$\sim\mathrm{OCH_2CH_2OCH_2CH_2OCH_2CH_2OH} \xrightarrow{-H_2} \sim\mathrm{OCH_2CH_2OCH_2CH_2OCH_2}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{H} \xrightarrow{[O]}$$

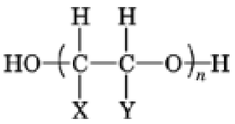
$$\sim\mathrm{OCH_2CH_2OCH_2CH_2OCH_2COOH} \xrightarrow{[O]} \sim\mathrm{OCH_2CH_2OCH_2CH_2O}\overset{\overset{OH}{|}}{\mathrm{C}}\mathrm{HCOOH} \xrightarrow{\text{hydrolysis}}$$

$$\sim\mathrm{OCH_2CH_2OCH_2CH_2OH} + \mathrm{H}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{COOH} \qquad (14)$$

Anaerobically, poly(ethylene glycol) degrades slowly, although molecular weights up to 2000 daltons have been reported (177, 178) to biodegrade.

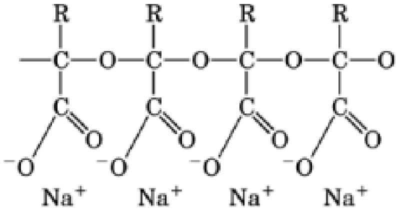
The biodegradation of poly(alkylene glycols) is hindered by their lack of water solubility, and only the low oligomers of poly(propylene glycol) are biodegradable with any certainty (179–181), as are those of poly(tetramethylene glycol) (182). A similar *exo*-oxidation mechanism to that reported for poly(ethylene glycol) has been proposed.

Polyether carboxylates have been evaluated as biodegradable detergent polymers (183–185). They all fit the general structure of the series made in an extensive evaluation of anionic and cationic polymerized epoxy compounds in the molecular weight range of several hundred to a few thousand, where X or Y may be carboxyl functionality and X or Y may be hydrogen or a substituent bearing a carboxyl functionality (185). Biodegradability, based on biochemical oxygen demand (BOD), is structure dependent.



$$\mathrm{HO}\!\left(\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{\mathrm{C}}}-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{\mathrm{C}}}-\mathrm{O}\right)_{n}\!\mathrm{H}$$

Water-soluble biodegradable polycarboxylates with an acetal or ketal weak link were inventions of Monsanto scientists in the course of their search for biodegradable detergent polymers. However, the polymers were prevented by economics from reaching commercial status. The polymers are based on the anionic or cationic polymerization of glyoxylic esters at low temperature (molecular weight is inversely proportional to the polymerization temperature) and subsequent hydrolysis to the salt form of the polyacid, which is a hemiacetal ($R = H$) or ketal ($R = CH_3$) if methylglyoxylic acid is used, and stable under basic conditions.



Biodegradation results from the pH drop such a detergent polymer experiences as it leaves the alkaline laundry environment (pH ca 10) and enters the sewage or ground water environment (pH close to neutral); the polymer (now a polyacid rather than a salt) is unstable and hydrolyzes to monomer which rapidly biodegrades. The chemistry has been reported in many patents (186) and several publications (187, 188).

Similar polyacetals were prepared by BASF scientists from ω-aldehydic aliphatic carboxylic acids (189, 190) and by the addition of poly(hydroxycarboxylic acid)s such as tartaric acid to divinyl ethers (191) as biodegradable detergent polymers.

6.3. Modified Natural Polymers

Modifying natural polymers offers a way of capitalizing on their well-accepted biodegradability in the development of polymers that might be environmentally acceptable. The modification must not interfere with the biodegradation process and the product must meet guidelines for environmental acceptability, ie, they must be either demonstrated to be totally biodegraded and removed from the environment, or be biodegradable to the extent that no environmentally harmful residues remain. With this requirement in mind, the approaches that have received the most attention include blends with other natural and synthetic polymers, grafting of another polymeric composition, and chemical modification to introduce some desirable functional group by oxidation or some other simple chemical reaction, such as esterification or etherification.

Starch is made thermoplastic at elevated temperatures in the presence of water as a plasticizer, allowing melt processing alone or in blends with other thermoplastics (192–194). Good solvents such as water lower the melt-transition temperature of amylose, the crystalline component of starch, so that processing can be done well below the decomposition–degradation temperature.

The most important commercial application has been the blending of polyethylene with starch in the presence or absence of other additives to promote compatibility. The interest in this approach goes back to the 1970s (195), and there is continuing activity with commercial products from several companies. There are a great many other contributors to this field. One pioneer developed starch–polyethylene compatibilized with ethylene–acrylic acid copolymers (196) and ethylene–vinyl alcohol polymers (197). Later work with polyethylene capitalizing on this early research includes Novamont (also known as Butterfly in some of its patents) with starch blends containing hydroxy acids, urethanes, polyamides, and polyvinyls (198), Warner-Lambert (Novon) (199, 200), the U.S. Army with cellulose acetate (201), Henkel with alkyds (202), Iowa State University with proteins and oxidized polyethylene (203, 204), ADM (205), Solvay with polycaprolactone (206), and Agritech with a starch minimum of 30 wt % (207).

Biodegradation studies of starch blends have not been conclusive where a nondegradable synthetic polymer has been the blend component; probably biodisintegration would be a better term to describe these polymers. The principal deficiencies of products based on this chemistry, aside from the incomplete biodegradation, are water-sensitivity of manufactured articles, and the balance of this and biodegradation with the starch level in the product.

Other blends such as polyhydroxyalkanoates (PHA) with cellulose acetate (208), PHA with polycaprolactone (209), poly(lactic acid) with poly(ethylene glycol) (210), chitosan and cellulose (211), poly(lactic acid) with inorganic fillers (212), and PHA and aliphatic polyesters with inorganics (213) are receiving attention.

The different blending compositions seem to be limited only by the number of polymers available and the compatibility of the components. The latter blends, with all natural or biodegradable components, appear to afford the best approach for future research as property balance and biodegradability is attempted. Starch and additives have been evaluated in detail from the perspective of structure and compatibility with starch (214).

Starch has also been a substrate of choice for biodegradable polymers, by grafting with synthetic polymers to achieve property improvement and new properties such as carboxyl functionality, not available in starch, with retention of as much biodegradability as possible. Obtaining thermoplastic polymers from the ionic grafting of styrene to starch has been demonstrated (215), and radical grafting of acrylate esters (216) has also been reported. The latter was recommended as a mulch, as it rapidly decomposed in the presence of fungi. The extent of biodegradation of both these materials must be questioned as the acrylic and styrene components are known for their resistance to biodegradation.

Other grafts to natural materials are exemplified by work in which polyesters are produced from sugars and polycarboxylates by enzyme catalysis (217). These polymers and the method of synthesis may well be one of the future directions of renewable resource chemistry. This method is similar to some very early research on cellulose condensation with polyfunctional isocyanates and optionally propylene glycol (218); some degradation was claimed. The utility and potential for lignin grafted with styrene has been shown (219), and it is claimed that the product is totally biodegradable, owing to the potency of white rot *Basidiomycetes*, a lignin degrader. Further proof is required, but this is a promising lead.

Natural polymers have also received attention as graft sites for carboxylic monomers to produce detergent polymers (DP), though without great success. The synthetic portion of the graft is not usually biodegradable, although in some cases attempts were made to meet molecular weight limitations (less than DP of ca 6–8). Acrylic grafts onto polysaccharides in the presence of alcohol chain-transfer agents (220) were not completely biodegradable, nor were the ones based on initiation with Ce^{4+} (221) and mercaptan (222, 223). Protein substrates (224) are expected to be similar to the starch grafts; the fundamental problem is the need to control acrylic acid polymerization to the oligomer range, as indicated earlier, in order to have complete biodegradability.

Simple chemical reactions on natural polymers are widely known to produce polymers such as hydroxyethylcellulose, hydroxypropylcellulose, carboxymethyl cellulose, cellulose acetates and propionates, and many others that have been in commerce for many years (see Cellulose ethers; Cellulose esters organic). Their biodegradability is not at all well established. Carboxymethylcellulose, for example, has been claimed to be biodegradable below a degree of substitution of about 2, which is similar to that of cellulose acetate. More recently, there have been attempts to more rigorously quantify biodegradation of the cellulose acetates (218, 225) and to establish a property–biodegradation relationship. Rhône-Poulenc also indicates that cellulose acetate with a degree of substitution of about 2 is biodegradable, in agreement with the earlier references (226). Cellulose has been discussed as a renewable resource (227). The ampholytic product of the reaction of chitosan with citric acid is claimed to be biodegradable (228).

Carboxylated natural polymers have been known for many years, with the introduction of carboxymethylcellulose. This product has wide use in detergents and household cleaning formulations, although it is of questionable biodegradability at the level of substitution on cellulose required for performance. Nevertheless, carboxylated polysaccharides are a desirable choice for many applications, and the balance of biodegradation with performance that is achievable has been recognized as an attractive possible goal met in this case with a high probability of success. Three approaches have been employed: esterification, oxidation, or Michael addition of the hydroxyl groups to unsaturated carboxylic acids such as maleic and acrylic, with some attempts to react specifically at the primary or secondary sites.

Esterification with poly(carboxylic anhydride)s can be controlled to minimize diesterification and crosslinking to produce carboxylated cellulosic esters. An Eastman Kodak patent claimed the succinylation of cellulose to different degrees, 1 per 3 anhydroglucose rings (229) and 1 per 2 rings (230). Henkel (231) also

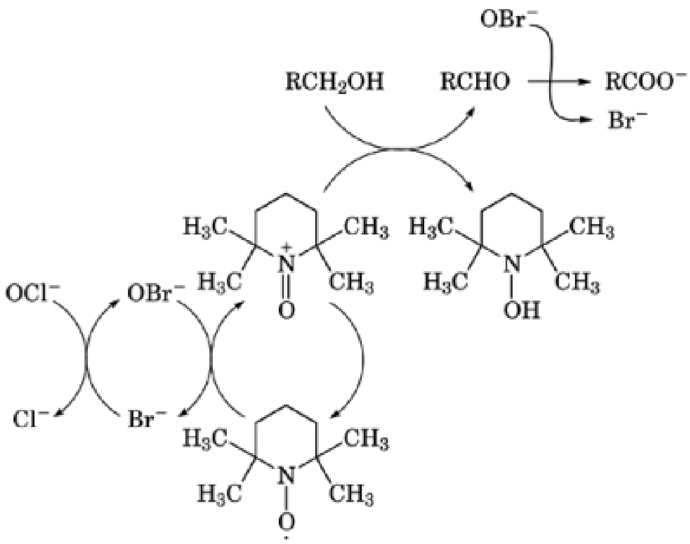


Fig. 6. Specific oxidation of the 6-hydroxyl of starch using bromide–hypochlorite and tetramethylpiperidine oxide (TEMPO).

has a patent for a surfactant by the esterification of cellulose with alkenylsuccinic anhydride; presumably, substitution governs the hydrophile–hydrophobe balance of the product.

Oxidation of polysaccharides is a far more attractive route to polycarboxylates, potentially cleaner and less costly than esterification. Selectivity at the 2,3-secondary hydroxyls and the 6-primary is possible. Total biodegradation with acceptable property balance has not yet been achieved. For the most part, oxidations have been with hypochlorite–periodate under alkaline conditions. In the 1990s, catalytic oxidation has appeared as a possibility, and chemical oxidations have also been developed that are specific for the 6-hydroxyl oxidation.

A wide range of polysaccharides, starch, xyloses, amyloses, pectins, etc, with hypochlorite–periodate have been oxidized (232–235). The products are either biodegradable at low oxidation levels or functional at high oxidation levels; the balance has not yet been established. From Delft University have come contributions in the search to control the hypochlorite–periodate liquid-phase oxidations of starches (236, 237) and research for finding catalytic processes to speed up the oxidation with hypochlorite. Hypobromite offers one solution and is generated *in situ* from the inexpensive hypochlorite and bromide ion (238, 239). At the same time, a method has been published for oxidizing specifically the 6-hydroxyl group (primary) of starch by using TEMPO and bromide–hypochlorite (240), as shown in Figure 6.

Chemical oxidation with strong acid is reportedly selective at the 6-hydroxyl, either with nitric acid–sulfuric acid–vanadium salts (241) which is claimed as specific for the 6-hydroxyl up to 40% conversion, or with dinitrogen tetroxide in carbon tetrachloride, with similar specificity up to 25% conversion (242).

Catalytic oxidation in the presence of metals is claimed as both nonspecific and specific for the 6-hydoxyl depending on the metals used and the conditions employed for the oxidation. Nonspecific oxidation is achieved with silver or copper and oxygen (243), and noble metals with bismuth and oxygen (244). Specific oxidation is claimed with platinum at pH 6–10 in water in the presence of oxygen (245). Related patents to water-soluble carboxylated derivatives of starch are Hoechst's on the oxidation of ethoxylated starch and another on the oxidation of sucrose to a tricarboxylic acid. All the oxidations are specific to primary hydroxyls and are with a platinum catalyst at pH near neutrality in the presence of oxygen (246, 247). Polysaccharides as raw materials in the detergent industry have been reviewed (248).

Table 5. Environmentally Degradable Polymers

Polymer	Developer	Degradation
poly(lactic acid)	Cargill, Ecochem, Biopak, Mitsui Toatsu	hydrolysis and biodegradation
cellophane	Flexel	biodegradation
PHBV	Zeneca	biodegradation
starch-based	Novamont	biodegradation
polycaprolactone	Union Carbide, Solvay	biodegradation
starch-activator	Ecostar	photo- or biodegradation
starch foam	National Starch	biodegradation
polyolefin-activator	Plastigone	photodegradation
polyester	Showa High Polymer	biodegradable
poly(ethylene–CO)	Dow	photodegradation
poly(vinyl alcohol)	Rhône-Poulenc, Air Products Kuraray, Hoechst	biodegradation
poly(ethylene glycol)	Union Carbide, Dow	biodegradation
cellulosics	Rhône-Poulenc, Eastman	biodegradation
poly(aspartic acid)	Rohm and Haas	biodegradable

7. Production of Environmentally Degradable Polymers

There are signs that the use of environmentally degradable polymers and plastics is expanding. As the market begins to become aware of the availability of these new materials, it is expected that they will move into niche opportunities. When this occurs, production will increase, and costs, the biggest barrier to acceptance, should begin to come down. Some of the polymers in production at some scale larger than laboratory are shown in Table 5.

The only product with substantial sales in 1996 is a photodegradable, environmentally degradable ethylene–carbon monoxide polymer used for six-pack holders, which are often carelessly thrown away so as to litter the environment. This litter will slowly disappear as it degrades into fine fragments. The U.S. EPA has let it be known that although this is acceptable for now, future products should degrade by a combination of photodegradation and biodegradation to ensure complete removal from the environment.

International agreement is close as of 1996 on what an acceptable environmentally degradable polymer should do in the environment; succinctly put, it must not harm the environment. There has been much progress in the early 1990s on this issue; standard protocols are available to determine degradation in the environment of disposal, and definitions are understood and accepted in a broad sense, if not in detail. Fate and effects issues for these new polymers are being addressed, and these will be resolved and appropriate tests developed.

Perhaps the most significant remaining issue is the cost of these polymers; most are at least three to five times that of the current products that must be displaced. There must be a recognition that a clean environment has a price. Regardless of cost, the interested parties in this area realize that environmentally degradable polymers are unlikely to be a significant force in the waste management of polymers. They will be used where they are best suited and offer advantages over the competing technologies, such as recycle, landfilling, and incineration. Some obvious areas of opportunity are in fast food, agriculture, sanitary articles for plastics, and water-soluble polymers which are not recoverable after use. A significant advantage for environmentally degradable water-soluble polymers is the ready availability of a disposal infrastructure in municipal wastewater treatment plants. Composting, a promising disposal avenue for plastics, on the other hand, is in need of development, and no plans are in place to do this, a fact that is hindering the growth of these plastics.

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