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WATER-SOLUBLE BIODEGRADABLE POLYMERS: SYNTHETIC OR NATURAL-BASED RAW MATERIALS?

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ABSTRACT:

In this paper, we review some of the significant synthesis approaches that we and others have evaluated for producing commercially viable water-soluble biodegradable polymers. The goals set for these polymers, cost/performance equivalent with current non-biodegradable polymers and complete biodegradation or a high degree of certainty that they are free from potential adverse environmental impact, are realistic but very difficult to achieve. Hence, we believe that few new polymers are emerging or are likely to emerge in the near future because of the radical directional changes needed in the synthesis and environmental testing procedures for water-soluble biodegradable polymers. We consider polymers with structures and compositions that mimic nature most likely to eventually be successful in the market place regardless of raw material origin, provided that cost/performance comparable with current commercial polymers can be achieved. Poly(aspartic acid), recently developed, may be considered as a prototype of things to come

INTRODUCTION:

Products based on biodegradable polymers are expected to eventually become more widely accepted for two major reasons, broadening public awareness of their environmental advantages in certain applications areas, and the development and acceptance of reliable standard test methodology to confirm their biodegradability. However, significant barriers still remain to be overcome prior to their widespread acceptance. A major barrier is their cost/performance relative to non-biodegradable alternatives currently used and another, which is particularly relevant to plastics, is the availability of a composting facilities infrastructure for their disposal. A more subtle issue that crops up frequently relates to the conservation of resources and whether or not there are property, biodegradation, and environmental differentiations or advantages for biodegradable polymers based on natural or petrochemical raw materials. All issues are being addressed and are expected to ultimately be resolved leading to new commercial opportunities for biodegradable polymers in areas where they offer advantages.

Biodegradable water-soluble polymers, the subject of this paper, have a unique disposal advantage over biodegradable plastics in that wastewater treatment facilities represent a readily available infrastructure and they are globally widespread in all industrially advanced nations. Knowing the operational conditions and limitations of wastewater treatment facilities has had a significant impact on the design objectives of water-soluble biodegradable polymers. Whether there is an advantage for the use of natural over petrochemical based raw materials for the production of biodegradable water-soluble

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polymers is still debatable. We have spent considerable time wrestling with this issue for several years with particular respect to polymeric carboxylates and conclude, at this time, that mimicking natural polymer structures using synthetic chemistry is a good short-term compromise when designing biodegradable polymers. Ultimately, modification of naturally polymers may also prove viable. In this paper, we share some of the thoughts leading to this conclusion which are exemplified by the development of poly(aspartic acid) from L-aspartic acid. The polymer is a poly(amino acid) and is rapidly and completely biodegraded in a wastewater treatment facility. It represents a potential replacement for the widely used poly(acrylic acid), albeit with a cost/performance disadvantage.

WATER-SOLUBLE POLYMERS:

By definition, in this paper, water-soluble polymers include truly soluble polymers and hydrogels, or highly swollen, lightly crosslinked polymers, and water-soluble plastics, such as poly(vinyl alcohol). They are all widely used in specialty and commodity applications and may be prepared from synthetic, petroleum-based chemicals, or from raw materials of natural origin. This has lead to considerable discussion as to which is preferred from an environmental acceptability perspective, and may be related to recent widespread considerations to implement sustainable technology bases in the chemical industry.

Water-soluble polymers depending on their structure, molecular composition, functional groups, and molecular weight are used in a myriad of applications. These include:

- soluble polymers: polymeric surfactants, pigment dispersants, corrosion resistance, oil drilling chemicals, detergents, rheology modifiers, and thickeners.
- hydrogels: superabsorbent polymers, controlled release for fertilizers, and thickeners or gelling agents.
- plastics: agricultural films and superabsorbents for diapers and sanitary products.

The authors recognize that the problems facing water-soluble polymers in contact with terrestrial and aqueous environments are similar to those in biomedical applications. Interestingly, the two seemingly very different areas share many of the same problems relative to choice of raw materials for synthesis, biodegradability and environmental fate and effects. Therefore, although this current paper focuses only on water-soluble biodegradable polymers in terrestrial and aqueous environments, the reader is reminded that this close relationship has important synthesis and procedural implications for both fields.

Water-soluble polymers may be classified in a number of different ways, molecular weight, hydrophilic/hydrophobic compositional balance, functional groups (anionic, cationic, and nonionic), structure(linear, branched, crosslinked, etc.), and synthetic or natural origin which often reflect their applications. For example, several relationships between molecular weight and applications for water-soluble polymeric carboxylic acids are shown in Table 1.

Table 1. Molecular Weight and Uses for Water-Soluble Carboxylated Polymers

Molecular weight Range	Use
< 10, 000	Dispersants
10,000 to 100,000	Rheology Modifiers
> 100,000	Thickeners and Flocculants
Infinite(gels)	Adsorbents/Controlled release

Some examples of naturally-occurring polymers used as isolated or in modified form are included in Table 2. Modification to achieve desirable properties, it should be noted, may or may not interfere with biodegradability, which must be established, but it certainly will require processing and additional cost. The balance between these two will determine the viability of these products as biodegradable water-soluble polymers(1,2).

Table 2. Natural-Based Water-Soluble Polymers

Polymer	Functional Groups
starch	hydroxyl
starch-oxidized	aldehyde and carboxyl
cellulose	hydroxyl
cellulose-alkoxylated	hydroxyalkyl
cellulose-carboxyalkylated	carboxyalkyl
chitin	amide
chitosan	amine
pectins	carboxyl
hyaluronic acid	carboxyl
proteins	amine/carboxyl/etc.
lignin	sulfonate

Synthetic raw materials from the petrochemical-based industry have been cheap and available in great diversity for a number of years and have lead to a plethora of new water-soluble polymers with uniquely good cost/performance benefits in many applications. Condensation, addition, and ring-opening polymerization technologies are all widely employed in the synthesis of water-soluble polymers. The environmental response to these polymers has only recently, the last ten years or so, come to be a consideration in their continued use(1,2). There is little evidence to suggest that there is need for concern with many of these polymers, but testing must be done to establish confidence that they either biodegrade or are harmless in the environment and remain so as their concentration builds with time and continued use. Selected examples of synthetic water-soluble polymers are shown in Table 3.

Table 3. Water-Soluble Polymers from Synthetic Raw Materials

Polymerization	Polymer
addition/vinyl	poly(acrylic acid) poly(methacrylic acid) poly(vinyl alcohol) poly(hydroxyalky acrylates) poly(styrenesulfonic acid) polyvinylpyrrolidone
condensation	polyesters polyamides polyacetals polyethers
ring-opening	poly(alkylene oxides) copoly(alkylene oxides-lactones) polycarbonates

BIODEGRADATION OF WATER-SOLUBLE POLYMERS:

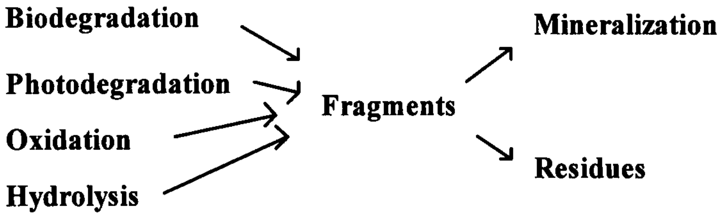
The degradation of polymers in the environment may be by several pathways, all of which are sometimes collectively, but erroneously, called biodegradation. These different pathways or mechanisms have been defined in various ways, those used here for water-soluble polymers are based on the ASTM definitions(3,4) which are generally consistent with all the others.

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

- *a biodegradable polymer* is one in which degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi, and algae.
- *a hydrolytically degradable polymer* is one which degrades by hydrolysis
- *an oxidatively degradable polymer* is one which degrades by oxidation.
- *a photodegradable polymer* is one which degrades by the action of natural daylight.

The degradation pathways are related, as shown in Figure 1 in that they may all occur in the environment and all lead in the first instance to fragmentation; however, they are strongly differentiated in that only biodegradation may result in complete elimination of the original polymer from the environment. This is termed complete biodegradation when the original organic material, polymer in this case, is converted into carbon dioxide, water, and biomass. Mineralization is the process of ultimate complete conversion of the original organic material, including that originally incorporated into biomass into carbon dioxide, water, and salts. It should be noted that any or all of the degradation pathways are acceptable in the initial stages of environmental degradation, but for environmental acceptance, biodegradation must be complete, as described above.

Figure 1. Environmental Degradation Pathways



ANALYTICAL REQUIREMENTS:

The analytical requirements for establishing the degree of biodegradation are based on the chemistry of biodegradation in either an aerobic, presence of oxygen, or anaerobic, absence of oxygen, environments of choice which are represented by equations 1 and 2, respectively, below. These equations pertain specifically to carbon, hydrogen, and oxygen- containing polymers but are readily adaptable to polymers for polymers containing other elements where the additional elements appear in oxidized or reduced form depending on aerobicity or anaerobicity of the environment, respectively. The term polymer may be exchanged for fragments, if the degradation is by several environmental pathways as indicated above in Figure 1..

Aerobic biodegradation:

polymer + O_2 -----> CO_2 + H2O + Biomass + Residue(s) (1)

Anaerobic biodegradation:

polymer -----> CO_2 + CH_4 + H_2O + Biomass + Residue(s) (2)

The level of biodegradation may be assessed by accurately establishing concentration changes of the polymer, oxygen uptake, evolution of CO_2 and/or CH_4, polymer incorporation into biomass, and residue(s). Oxygen uptake is an indirect method and, therefore, the least preferred. Biomass change due to polymer assimilation requires radiolabelled polymers for detection, and residue analysis may be complicated by fragment analysis and estimation. In most cases, where a polymer is significantly biodegradable, at least 20-30%, gas evolution analysis is a good indicator of degradation, especially when coupled with a decrease in water soluble carbon.

As the degree of biodegradation reaches levels of acceptability with commercial potential, testing becomes very critical and radiolabels are often required to completely substantiate results and identify exactly polymer degradation products and there removal from the environment.

DISPOSAL OF WATER-SOLUBLE POLYMERS:

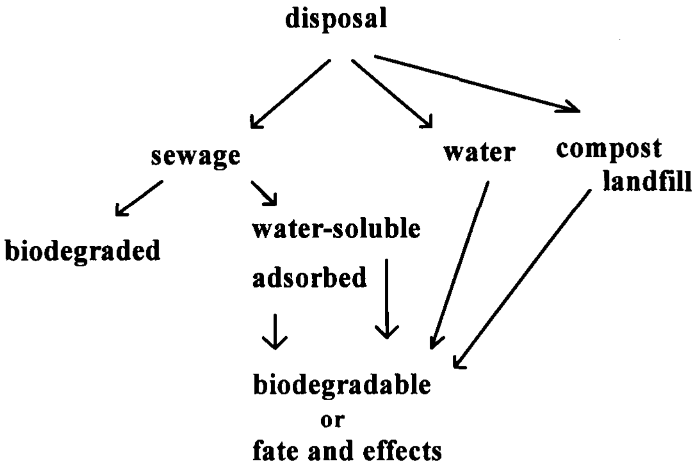
There are several pathways for the disposal of water-soluble polymers after their useful life is complete. Figure 2 captures the most important of these. Truly water-soluble polymers tend to be either discarded into a public or private sewage or wastewater treatment system or directly into the aqueous environment. Water-soluble packaging materials and hydrogels, on the otherhand, offer the additional options of landfilling or composting.

Water-soluble polymers that enter sewage treatment facilities may remain in solution or partially or completely adsorb on the sludge/biomass solid component. Those that remain in solution pass through the treatment plant into the waterways and eventually into almost any environmental compartment imaginable due to their solubility/mobility with the potential to adsorb on other substrates in those environment. Water-soluble polymers discarded directly into waterways have a similar fate. Adsorbed polymers, on the otherhand, are eventually transferred to a subsequent environmental compartment wherever the sludge is disposed of, which may include land application, landfill, compost, incineration, etc. Incineration may impact air quality, while leakage from the other repositories may eventually lead to unwanted terrestrial or aqueous environmental exposure.

Plastics that are water-soluble are easier to recover than polymers in solution and have the option of landfill or composting for their disposal. As they slowly dissolve they also have potential for exposure in other environmental compartments.

It is clear, therefore, from the current disposal methods, that biodegradable polymers would offer a large measure of protection in avoiding potentially widespread environmental contamination with polymers of uncertain fate and effects.

Figure 2. Disposal of Water-Soluble Polymers



BIODEGRADABLE WATER-SOLUBLE POLYMER DEFINED:

It should be obvious from the foregoing section on the disposal of water-soluble polymers that polymers which biodegrade completely in a disposal compartment offer a significant environmental advantage over their recalcitrant analogues. There is no requirement for the consideration of fate and effects in subsequent environmental compartments into which non-biodegradable or slowly biodegradable polymers migrate.

In designing biodegradable water-soluble polymers for practical applications, then, a time scale for complete biodegradation is preferrably chosen based on the disposal method and the disposal environment. For water-soluble polymers these are sewage treatment facilities or composting facilities. Both are well understood with respect to residence times, but only sewage treatment facilities offer a viable disposal site at this time, since no infra structure exists for composting of polymers. Sewage treatment facilities are fairly standard throughout the world with a few hours residence time for the aqueous media and about two weeks for the sludge turnover. Composting facilities, on the otherhand have a residence time of several weeks. The interpretation for designing biodegradable water-soluble polymers is that the polymer should be adsorptive and complete biodegradation should occur in two weeks in a sewage treatment facility. For compostables, the polymers should also be adsorptive, but biodegradation may be considerably slower.

Goals for defining and developing water-soluble biodegradable polymers are thus easily delineated as shown below. In the case of incomplete biodegradation, if a risk assessment indicates confidence that no adverse environmental impact is probable, the polymers should be accepted. This will cover current products where no evidence exists, over a number of years of exposure, for problems, at least until biodegradable replacements are available; and also the use of natural polymers which may also be slow in biodegradation.

- preferably complete biodegradation, i.e. removal from the environment of the original polymer, within the residence time of the disposal site.

- if not complete in the disposal site, good evidence and a careful risk assessment that no toxic or harmful degradation products are produced at any time in subsequent environmental compartments.

- acceptable cost/performance relative to current and future options

SYNTHETIC APPROACHES:

There have been many synthetic approaches to water-soluble biodegradable polymers based on both natural renewable resources and on synthetic intermediates(1,2). This paper focuses primarily on polymeric carboxylic acids but the methodology is representative of all water-soluble polymers. The options available are shown below for renewable resources and synthetic raw materials:

- polymers from renewable resources:
    - use as isolated
    - chemically modify by oxidation, esterification, etc.
    - graft with synthetic addition and condensation polymers

- synthetic raw materials:
    - addition polymers
    - condensation polymers

Figure 3 summarizes the major approaches to modifying starch to produce biodegradable carboxylated polymers. There are serious drawbacks to all the reactions which have been discussed elsewhere(2). Oxidative cleavage of the 2,3 bond in the anhydroglucose ring is achievable by several methods such as periodate to produce the dialdehyde which may be subsequently oxidized with chlorate to the dicarboxylic acid. Direct oxidation with hyperchlorite has also been demonstrated. Both methods allow controlled introduction of carboxyl acidity, however, there is an established inverse relationship between biodegradability and performance, low oxidation produces biodegradable polymers while high oxidation delivers properties to the poly(carboxylic acids) but prevents biodegradation in the time frame of the disposal residence discussed above. Likewise, specific oxidation at the 6-position delivers biodegradability at low oxidation, while at high oxidation specificity is lost with oxidation at the 2,3 positions also occurring and the poly(carboxylic acid) produced is not biodegradable. Grafting of vinyl monomers, acrylic acid, for example, is possible, but the biodegradability of chains beyond oligomers is lacking(4), and, consequently, this is not a viable option to produce biodegradable poly(carboxylic acids). Functionalization by alkoxylation is achievable with subsequent oxidation of the alcohol to carboxylic acid. However, cost performance and biodegradation have never been demonstrated. Esterification and etherification of the 6 carbon primary hydroxyl is also well known, but not enough work has been done to verify whether acceptable cost/performance and biodegradability can be achieved by these approaches.

Synthesis approaches to biodegradable polymeric carboxylates base on synthetic intermediates have been widely investigated by many researches with few instances of success(2). The well known biodegradable synthetic polymers poly(vinyl alcohol) and poly(ethylene oxide) may both be modified to produce biodegradable poly(carboxylic acids) but at an enormous cost penalty involving new monomer synthesis and polymerization chemistry.

Synthetically produced condensation polymers have proven far more reasonable in their potential to biodegrade, as might be expected as they resemble many natural polymers in structure. Poly(malic acid) has been demonstrated to be biodegradable and a useful detergent polymer if somewhat hydrolytically unstable, and poly(glyoxylic acid) has long been accepted as a technical equivalent for poly(acrylic acid). However, cost considerations and synthesis difficulties preclude both of these polymers.

A recent major breakthrough in the development of biodegradable polymeric carboxylic acids is the discovery that poly(aspartic acid), by condensation of L-aspartic acid, is a functional equivalent of poly(acrylic acid) and meets all the biodegradation requirements set forth in this paper. The polymer has the distinction in being modeled on a natural protein structure, yet is produced synthetically from starting materials that may be produced by fermentation or from purely synthetic starting materials, ammonia and maleic anhydride. These reaction sequences are shown in the reaction schematic Figure 4. Maleic anhydride is the common synthetic starting material.

Interestingly, only the product from the L-aspartic acid route is biodegradable to the extent required for complete biodegradation in a sewage treatment facility, and this is the preferred method of synthesis(5) for polymers disposed of in this manner. It is worth noting that the similar product obtained by the alternative route may be acceptable in other disposal sites, but no definitive data on this has yet been obtained in our laboratories, or seen in the literature. The differences in performance and biodegradation of the two polymers has been attributed to chain branching and probably polymer backbone structural differences. These differences are strongly indicative of the need to thoroughly understand structure performance relationships not only for polymer properties but also for predictability of biodegradation in a given environment.

Figure 3. Polymeric Carboxylic Acids from Polysaccharides

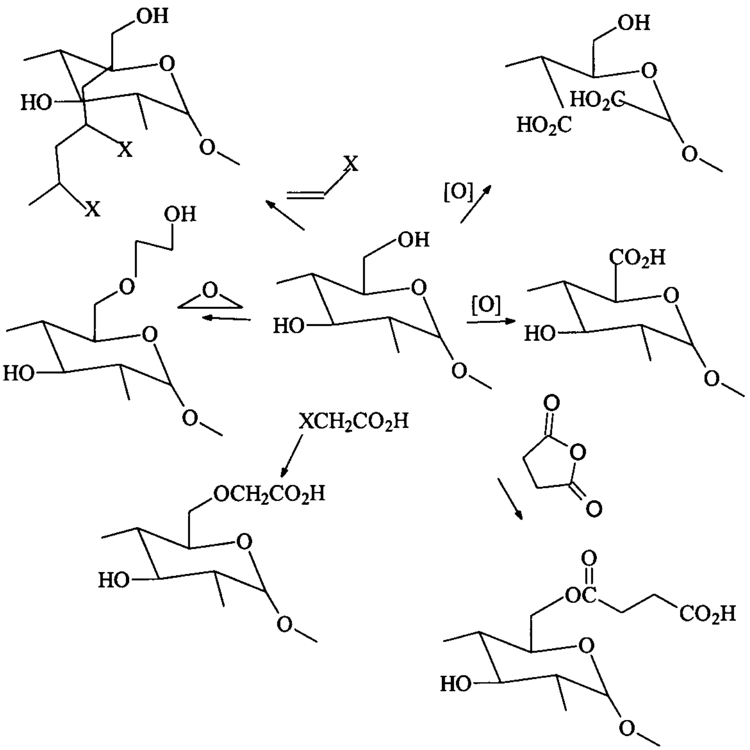
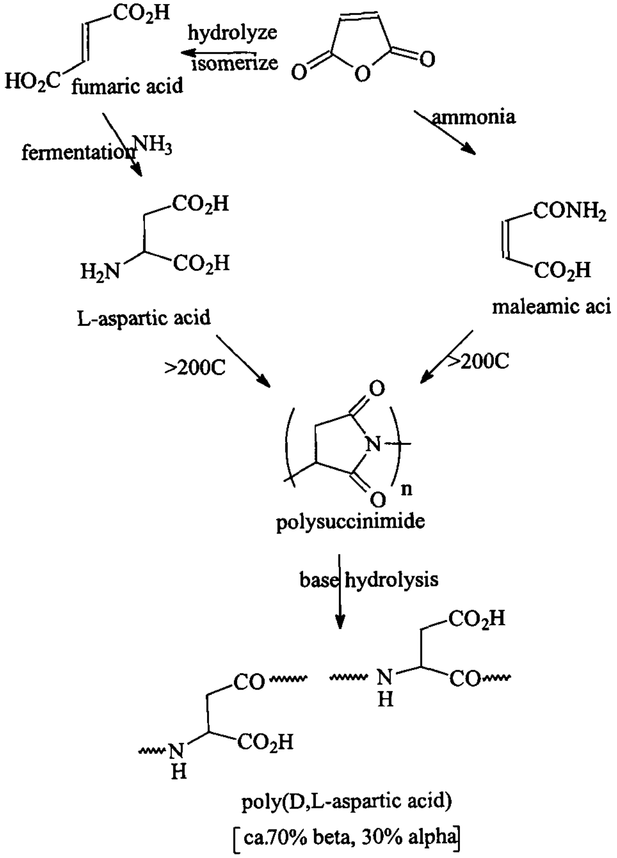


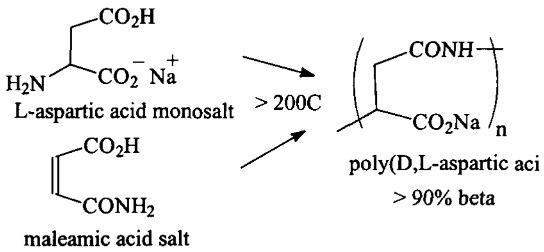
Figure 4. The Synthesis of Poly(Aspartic Acid)



Efforts to change the alpha/beta ratio by modifying the above hydrolysis reaction of polysuccinimide have proven unsuccessful. It is possible, however, to obtain near quantitatively the beta isomer by thermally polymerizing the monosodium salt of L-aspartic acid as indicated in Figure 5.

Molecular weight control is under evaluation, currently the upper limits are in the range 2000 to 3000 daltons. Performance is slightly poorer than poly(acrylic acid) in most applications and biodegradability has not been established yet.

Figure 5. Synthesis of Sodium Poly(beta-D,L-Aspartic Acid)



CONCLUSIONS:

With so much information on the biodegradability of water-soluble polymers in the literature, there are still gross misconceptions on this subject. Currently, few useful functional water-soluble biodegradable polymers that degrade in an acceptable time scale, as defined in this paper, are known. The only major exceptions are poly(aspartic acid), when prepared by appropriate procedures, poly(ethylene oxide), and poly(vinyl alcohol). Several generalizations may be made for directing future research on the development of biodegradable water-soluble polymers:

- carbon chain polymers generally do not biodegrade, with the noted exception of poly(vinyl alcohol).
- condensation polymers with suitable functionality are easy to prepare by the condensation of AB_2 monomers, and are usually biodegradable but may not be economically viable.
- modification of natural resources may, but not necessarily, yield biodegradable water-soluble polymers.
- water-solubility is not an indication of biodegradability.
- *polymers with structures similar to those found in nature may offer the best option for designing biodegradable water-soluble polymers(this is likely to be true also for plastics, also), regardless of the origin of the raw material used in the synthesis.*

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