POLY(LACTIC ACID) DEGRADABLE PLASTICS, COATINGS, AND BINDERS

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ABSTRACT

Biochemical processes to derive value from the management of high carbohydrate food wastes, such as potato starch, corn starch, and cheese whey permeate, have typically been limited to the production of either ethanol or methane. Argonne National Laboratory (ANL) believes that lactic acid presents an attractive option for an alternate fermentation end product, especially in light of lactic acids' being a viable candidate for conversion to environmentally safe poly(lactic acid) (PLA) degradable plastics, coatings, and binders.

Technology is being developed at ANL to permit a more cost effective route to modified high molecular weight PLA. Preliminary data on the degradation behavior of these modified PLAs shows the retention of the inherent hydrolytic degradability of the PLA modified, however, by introduced compositional variables.

A limited study was done on the hydrolytic stability of soluble oligomers of poly(L-lactic acid). Over a 34 day hold period, water-methanol solutions of PL-LA oligomers in the 2-10 DP range retained some 75% of their original molecular weight.

KEYWORDS
Binders
Biodegradable Polymers
Coatings
Degradable Polymers
Lactic Acid
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INTRODUCTION

The management of high carbohydrate food wastes, such as starch from the potato food processing industry, has become a serious economic and environmental burden. Argonne National Laboratory (ANL) is developing technology that:

- bioconverts existing food processing waste streams into lactic acid
- utilizes lactic acid for marking environmentally safe degradable plastics, coatings, and binders.

Lactic acid, being a simple hydroxy-carboxylic acid (α-hydroxypropionic acid), can be converted by self-condensation into poly(lactic acid) (PLA) plastics, coatings, and binders. Since PLA's ultimate degradation product, lactic acid, is biologically benign, PLA degradable plastics have already found wide acceptability and usage in medical applications[1] (e.g., for sutures, wound clips, and scaffolds, and drug delivery systems).

ANL is developing technology to capitalize on PLA's inherent hydrolytic susceptibility to address agricultural needs such as for mulch

films and controlled release coatings for fertilizer and pesticides. Preliminary studies suggest that PLAs also have an attractive balance of properties as coatings and binders for cellulosic substrates, the obvious advantage being PLA's ultimate 100% hydrolytic degradation into an environmentally friendly and biologically benign end product, lactic acid. This hydrolytic degradability of PLA is in marked contrast to the intransigence of alternate cellulosic binders and coatings such as polyvinyl acetate and ethylene -- acrylic acid copolymers.

1. DEGRADABILITY

In general, polymers can be placed in a ranking order of predicted susceptibility to in vivo degradation.[2,3]

a. hydrophobic, no hydrolyzable bonds (most stable) -- polyethylene, polypropylene, polystyrene, etc.

b. hydrophilic, no hydrolyzable bonds (may swell or dissolve but little or no degradation) -- polyethylene oxide, ethylene acrylic acid copolymers.

c. hydrophobic, hydrolyzable bonds (surface activity only or very slow degradation) -- polyethylene terephthalate (PET)

d. hydrophilic, hydrolyzable bonds (bulk degradation) -- poly(α-hydroxy acids) such as poly(lactic acid) (PLA) and poly(glycolic acid) (PGA).

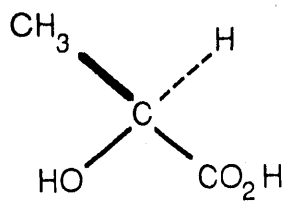
For poly(lactic acid) (PLA), the subject of this paper, bulk hydrolytic degradation seems to be the mechanism of breakdown (see Section 2.3.2). For the most part, it is generally agreed that enzymatic assistance of hydrolysis for rigid polyesters derived from lactic and glycolic acids is not operative.[4,5]

2. LACTIC ACID, POLYMERS, AND COPOLYMERS

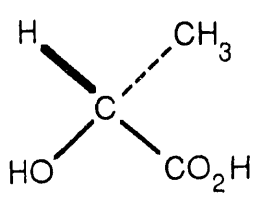
Three parameters regarding lactic acid and its conversion to poly(lactic acid) need be addressed prior to discussing properties and degradation behavior of PLA: (1) stereoisomeric purity; (2) degree of polymerization; (3) crystalline morphology.

2.1 Stereoisomeric Purity

The central carbon atom of lactic acid has four different atoms or groups attached to it and therefore exists in two stereoisomeric forms, L or D



L(+) Lactic Acid

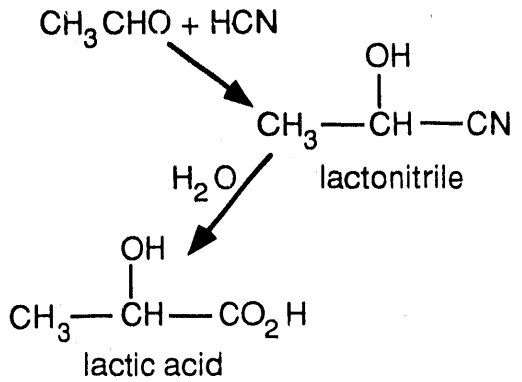


D(-) Lactic Acid

In the two formulas above, the central carbon atom (asymmetric center), the hydroxyl (OH), and carboxyl groups (CO_2H) are in the plane of the paper. For L(+) lactic acid, the methyl group (CH_3) is above the plane of the paper, and the hydrogen atom (H) is below. For D(-) lactic acid, the reverse is true: the hydrogen atom (H) is above and the methyl group (CH_3) below the plane of the paper.

"Natural" lactic acid, obtained by bacterial fermentation processes, e.g., as manufactured and sold by CCA-NV (Netherlands) -- PURAC being their USA subsidiary -- has a minimum stereoisomeric purity of 97% as the L(+) form.

Synthetic lactic acid, manufactured by a chemical route

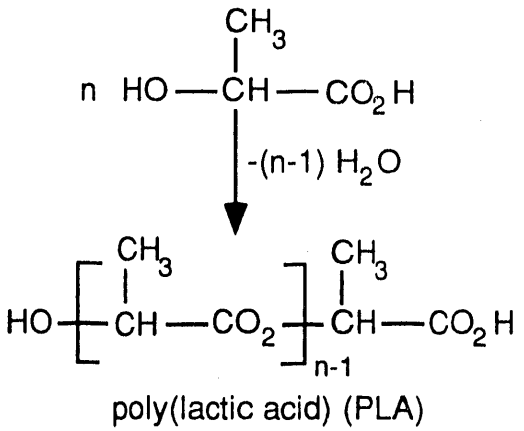


of necessity gives racemic lactic acid, i.e., both L(+) and D(-) stereoisomers in equimolar amounts.

2.2 Degree of Polymerization, DP (Molecular Weight)

Degree of polymerization (DP) is a measure of how many units of lactic acid are combined to form larger molecules. If 2 molecules of lactic acid combine with splitting out of 1 molecule of water, a dimer results, i.e., a DP of 2.

Usually the direct self esterification condensation to form polymer is represented generically by the equation:



Note that, as in the first example, if n = 2 the resulting product is the dimer. If 5 molecules of lactic acid were to condense, i.e., n = 5, the resultant molecule would be a pentamer (penta = 5).

Whether the subscript n or (n-1) is used for the bracket of the above equation is usually inconsequential if the molecular weight of the PLA is sufficiently high, i.e., DPs greater than ca. 20.

It should be appreciated that throughout a self-condensation esterification, no unique oligomer results as the condensation reaction proceeds but rather a statistical average degree of polymerization, $\overline{DP}_n$.(6) Thus, if p = extent of reaction, then $\overline{DP}_n = 1/(1-p)$. If 50% of the OH and CO_2H groups react (p = 0.50) then $\overline{DP}_n = 2$ (dimer). If 80% (4/5) react (p = 0.80), then the resultant $\overline{DP}_n$ is 5. To realize a relatively high number average of about 25,000, i.e., an average $\overline{DP}_n$ of ca 350, the extent of reaction (p) would need be greater than 99.7%.

Another concomitant feature of this self-condensation polymerization(6) is the necessary broadening out of the distribution of individual size molecules that make up the statistical $\overline{DP}_n$ as the extent of reaction (p) increases. Some consequences of this broadening will be discussed in Section 4 "Hydrolytic Stability of PLA Oligomers."

It is interesting to note that oligomers of poly(L(+)-lactic acid) in the range of 2 to 10 units have been shown to have plant growth regulator (PGR).(7) These PGR properties for oligomeric poly(L(+)-lactic acid) enhance the attractiveness of PLA for agricultural applications such as for controlled release coatings for fertilizers and pesticides, and for agricultural mulch films.

2.2.1 Molecular weight and physical properties. According to an early paper by USDA Laboratory in Philadelphia,[8] racemic PLA becomes solid at room temperature at a MW of about 3,000, i.e., $\overline{DP}_n$ of ca 40: "The polymers of moderate molecular weight are viscous oils whereas those having molecular weights of approximately 3,000 and above are brittle glass-like masses."[8] This early work, with direct self condensation of racemic lactic acid in which molecular weights were distressingly low (ca 3,000), reinforces the difficulties associated with the reversible esterification reaction, i.e., as the $\overline{DP}_n$ builds up the viscosity of the melt becomes so high that further water of reaction can not escape before causing the reverse hydrolysis of previously formed higher molecular weight PLA.

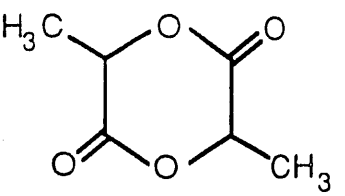
In contrast to racemic PLA, poly(L(+)-Lactic Acid), which can more easily associate into packed crystalline structures (see Section 2.3, Crystalline Morphology); even at a low molecular weight of 2,000 PL(+)LA, appears to be a non-tacky granular power.

Direct self-condensation of lactic acid to PLA appears to be limited to an upper molecular weight of about 20,000, but even this range of molecular weight is only accessible after long reaction times (48-72 hours), high temperatures (185-190°C), and high levels of sulfonic acid ion exchange resin catalysts.[9]

Actually, it appears that for self-supporting structures of PLA, i.e., films, fibers, and microcapsules, a minimum molecular weight of about 25,000 is needed: "It is generally recognized now that polyesters do not approach good, representative physical properties until the molecular weight is at least 25,000."[10]

Poly(L(+)-lactic acid) of sufficiently high molecular weight shows a crystalline melting point (Tm) of about 173-177°C and a relatively high glass transition temperature (Tg)* of 56-58°C. Amorphous (racemic) PLA obviously shows no crystalline melting point, while having a comparable Tg (56-58°C).[10,11] Despite the high crystalline melting point, both crystalline P(L(+)-LA) as well as racemic PLA, above their glass transition temperature (Tg)* of 56-58°C show a broad tacky, softening behavior.

2.2.2 Ring opening polymerization.
The only practical approach, to date, for achieving high molecular weight PLA has been by the ring opening polymerization of lactide with tin catalysts such as stannous chloride and stannous octoate.[12,13,14] The lactide itself (the cyclic dimeric anhydride of lactic acid) (I) is prepared by the high temperature "cracking" of low molecular weight PLA.[12]

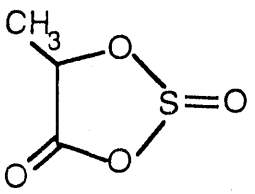


I Lactide

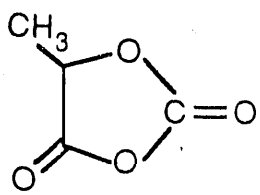
Ring opening polymerization of lactide of high purity (absence of chain terminators, such as water, and lactic acid), in the presence of tin catalysts can easily result in PLA polymers of usefully high molecular weight, e.g., 50,000 to 200,000. Such high molecular weight PLAs are of interest in medicinal applications.[1] Unfortunately, because of the low volume for these medicinal applications and the high purity needed, the price of these medical grade PLAs at the present time is very high, ca $2,500/kg.

*Tg is the temperature at which significant internal segmental mobility of individual polymer chains begins to occur.

Considerable effort has been made toward achieving high molecular weight PLA by an alternate technology. Two such approaches were the ring opening polymerization of cyclic anhydrosulfite of lactic acid (II)[15] and the cyclic anhydrocarboxylate of lactic acid (III).[16]



II Lactic Acid-Anhydrosulfite



III Lactic Acid-Anhydrocarboxylate

Neither cyclic anhydride polymerized cleanly (with liberation of SO_2 from II or CO_2 from III) to give PLA of molecular weight greater than about 3,000. Thus, the cyclic lactide polymerization (and copolymerization) at the present time remains the only route to high molecular weight PLA.

2.3 Crystalline Morphology

All assemblages of high polymers consist of a tangled mass of long linear chains. If there is a symmetry and regularity to the repeating unit of the polymer chain, there is a statistical probability that some domains of parallel chains will approach close enough so that attractive forces between chains (Van der Waal, dipolar, and hydrogen bonding) will be strong enough to cause "bundles" of parallel chains to form crystalline domains, i.e. crystallites,[17] see Figure 1.

Since it is statistically impossible for all chains to associate, there will be amorphous domains consisting of chain ends and polymer "tie" chains, i.e., those that cross over from one crystallite to another. The bulk random assemblage of polymer chains between and around these crystallites do not allow them to lock against each other. Notice the wide open loops of polymer in these amorphous domains (Figure 1).

The action of chemical agents, including water, on polymers proceeds more readily by orders of magnitude, at the accessible linkages within the structure, i.e. within the amorphous domains rather than at the surface, or within the crystallites.[18,19]

2.3.1 How easily does poly(lactic acid) crystallize?

A comprehensive study of poly(lactic acid) and poly(glycolic acid)(PGA) and copolymers of the two (PGLA) was reported by Reed and Gilding.[20] As expected, a PGA, with a very tight linear molecular structure

$$HO\,[CH_2\,CO_2]_n\,CH_2\,CO_2\,H$$

(no methyl groups jutting off the backbone as for PLA) showed the highest degree of crystallinity, ca 50%. For poly(L(+)-lactic acid), i.e. PLA comprised exclusively of L(+) lactic acid units, the maximum crystallinity observed was 37%. The crystallinity of copolymers of L(+) lactic acid and glycolic acid decreased from either extreme of acid, showing no crystallinity, i.e., complete amorphousness, in the mid-range of 25-65% L(+)-lactic acid in the copolymer.

PLA, from racemic lactic acid with methyl groups jutting off randomly from the polyester backbone chain, showed no crystallinity whatever.

2.3.2 How does crystallinity affect degradation behavior?

The extensive literature concerning the degradation of polyesters has been reviewed by Holland et al.[21] After penetration of water into the polymer matrix, degradation starts through a bulk hydrolysis of ester bonds and the molecular weight decreases, although there is very little mass loss over a variable period of time (related to molecular weight, molecular structure, and

crystallinity). When the molecular weight of the bulk plastic drops down to about 10-15% of its original value, to a remaining molecular weight of about 2,000 to 5,000 then observable weight loss resulting from the solubilization of polyester segments sets in.[18-20, 22-24] Some considerations relating to the molecular weight of soluble P(L(+)-LA) oligomers will be discussed in Section 4. Hydrolytic Stability of P(L(+)-LA) oligomers.

As mentioned earlier, in crystalline polymers like poly(glycolic acid) (PGA), poly(L(+)-LA) and poly(epsilon-caprolactone) (PCL) degradation first occurs in the amorphous regions and later in the crystalline domains.[18-19, 23, 25-26]

3. ALTERNATE APPROACH TO (MODIFIED) HIGH MOLECULAR WEIGHT PLA

3.1 Coupling Approach

Since only low molecular weight PLA seems to be accessible by the direct self condensation of lactic acid with a reasonable expenditure of time and energy, i.e., molecular weights of 2,000-5,000, $\overline{DP}_n$ 28 to 70, it seemed prudent to investigate traditional approaches to extending molecular weight by chain coupling of suitability terminated low molecular weight PLA segments. Unfortunately, because of the restrictions of patentability considerations, significant experimental details can not be given at this time.

Suffice it to say, that by judicious choices of coupling agents, preliminary indications are that "pseudo" high molecular weight PLA can be prepared by coupling of low molecular weight PLA segments.

The coupling approach also leads to significant modificiability of PLA by block copolymerization with reactive segments of "tailor-designed" (and desired) characteristics.

3.2 Degradation Behavior of Coupled PLA Polymers and Copolymers

A limited study was done on assessing the relative degradability of coupled PLA (PLAX) vs. PLA prepared by lactide polymerization (PLA), molecular weight ca 22,000. Also included in this study was a modified PLA composed of PLA blocks copolymerized with 35 weight per cent of a non-degradable hydrophobic extending block (Y), (PLAX-CO-Y). The environment for this study was a water-saturated composting mud composed of 1/5 household compost residue and 4/5 potting soil. Four sample films, 5.08 cm x 5.08 cm, of each type were immersed in the soil and weight change and film properties were evaluated after different time periods. The results are shown graphically in Figure 2.

Some observations on the results of this limited study follow:

1. PLA [68 L(+), 32 D(-)], MW 22,000, surprisingly showed an immediate and significant weight gain. The PLA, originally glass clear and transparent, became milk glass opaque, within just 24 hours in that composting soil. Weight gain continued uninterrupted with an apparent maximum being reached at 68 days for a total weight pick up of about 77%. It is apparent from the high level of weight gain that chemical hydrolysis alone was not responsible, but rather that imbibing of water was also occurring. This was confirmed by oven drying a sample at 32 days. A net loss of weight of 14% was recorded.

PLA film, over the total time period of 314 days, seemed to be getting progressively stiffer and more brittle. Negligible adherent surface deposit was seen for PLA.

2. PLAX -- this hydrophobic-bridged PLA showed a significantly delayed weight gain (water pick-up) as compared to PLA. Once weight gain began (after about 6 days) opacity developed in the film and weight gain closely

paralleled that of PLA. A peak of weight gain occurred at about 92 days with a maximum weight pick up of about 82%. Again, at 32 days oven drying of a sample showed an actual mass loss of 11.2%.

For PLAX, also significant stiffening and embrittlement occurred throughout the immersion period.

3. PLAX -- CO-Y. This block copolymer with a relatively hydrophobic domain as expected, showed significantly decreased weight gain propensity as compared to PLA and PLAX. Over the extended immersion period, surface texture became shrivelled and corrugated. In contrast to PLA and PLAX, this film developed a strong brown coloration and a heavy skatole odor as well. Somewhat surprising, physical properties starting with its initial though rubbery elasticity seemed to hold up remarkably well for this type of film.

Although not shown in Figure 2, films samples of both PET (polyethylene terephthalate) and PE (polyethylene) were also immersed over that 314 day study period. Neither PET nor PE showed any signs of change. Within experimental error, weight change for both PET and PE was negligible (<1%).

4. HYDROLYTIC STABILITY OF P(L(+)-LA) OLIGOMERS

As mentioned in Section 2.3.2, bulk degradation of PLA typically shows little or no mass loss until the molecular weight of the PLA drops to the range of 2,000 to 5,000. At this molecular weight range for the bulk PLA fragmentation into soluble oligomers of PLA begins to occur. There seems to have been very little study done concerning the hydrolytic stability of soluble oligomeric PLA fragments, which in their own right seem to have some interesting and useful properties, e.g., as plant growth regulators (PGR).(7)

As discussed in this section, the hydrolytic stability of soluble oligomers of P(L(+)(-LA) was followed by titration of carboxylic acid functionality over a 34 day period in a methanol/water solution.

4.1 Molecular Weight Distribution of Self Condensed Lactic Acid

If lactic acid is subjected to self-condensation by heat and vacuum to form ester linkages with release of water, the degree of polymerization (DP) continually increases (see Section 2.2). The universally accepted mathematical treatment of this condensation reaction by Paul J. Flory(6) notes that at any extent of reaction (p), a number average DP can be designated, $\overline{DP}_{\overline{n}}$, for which $\overline{DP}_{\overline{n}} = 1/(1-p)$. This $\overline{DP}_{\overline{n}}$, however, is made up of a spectrum of individual molecular weight components, also determined by a simple mathematical expression, $N_X = p^{(x-1)}(1-p)$, where N_X is the probability of a condensed molecule having x units at the given extent of reaction (p). Table 1 gives a breakdown of that distribution for the very early stages of that condensation reaction.

At a $\overline{DP}_{\overline{n}}$ of 3, extension of the mathematical treatment would show that less than 1% of the assemblage of oligomers has 10 or more units. For a $\overline{DP}_{\overline{n}}$ of 6, 13.5% of the oligomers would have a DP of 10 or more.

Because of the bracketing of oligomers within the 2 to 10 range for $\overline{DP}_{\overline{n}}$= 3 (the range of interest for PGR properties), the hydrolytic stability of P(L(+)-LA)oligomers at $\overline{DP}_{\overline{n}}$= 3 was studied in more detail.

4.2 Solvent Precipitation of P(L(+)-LA) Oligomers

L(+)-Lactic acid was subjected to self condensation (no additional acid catalyst) and the gross molecular weight of the esterification mix

was followed by acid-base titration of residual carboxylic acid end groups (methanol solution, phenolphthalein end point). This titration gives directly the number average molecular weight, $\overline{MW}_{\overline{n}}$, of the polymerizing mix. From a plot of $\overline{MW}_{\overline{n}}$ vs $\overline{DP}_{\overline{n}}$, the corresponding $\overline{DP}_{\overline{n}}$ can readily be determined. At these low degrees of polymerization, i.e., DP less than 10, the molecular weight contribution of chain ends can not be ignored. Note also that $\overline{DP}_{\overline{n}}$ need not be a whole integer since it represents a statistical average of the molecular weight for each molecule of the total assemblage of molecules. The esterification was stopped at a determined $\overline{DP}_{\overline{n}}$ of 3.11, i.e., essentially 99% of the assemblage of molecules in the 1-10 units range.

Water precipitation of higher molecular weight ends for this 3.11 $\overline{DP}_{\overline{n}}$ P(L(+)-LA) from various solvents was evaluated as a means of further narrowing the distribution of oligomers while transferring them to a hydrolytically active (water rich) environment.

Both acetone and acetonitrile proved to have too good solvating power for P(L(+)-LA) since addition of water caused delayed precipitation of higher molecular weight oligomers. Those oligomers which did separate "oiled out" as gummy masses with apparently heavy occlusion of associated solvent.

Methanol, a solvent ordinarily known for its low solvent power for PLA (frequently used as a "non-solvent" precipitant for PLA from good solvent solutions, such as acetone, toluene, chloroform), does completely dissolve low molecular weight digomers of PLA. Increasing additions of water to methanol solutions of this 3.11 $\overline{DP}_{\overline{n}}$ P(L(+)-LA) did result in increasing separation of "dry" flocs of higher molecular weight oligomers of PLA. Remember, however, that a $\overline{DP}_{\overline{n}}$ of 3.11, the upper limit for oligomers, <2%, is only of the order of 10-12 units). The hydrolytic stability of $\overline{DP}_{\overline{n}}$ 3.11 P(L(+)-LA) was therefore studied in methanol-water mixes.

4.3 Methanol/Water Solubility and Hydrolytic Stability of PLA Oligomers

To study the hydrolytic stability of P(L(+)-LA) oligomers, the following procedure was followed:

A master solution of 3.11 $\overline{DP}_{\overline{n}}$ P(L(+)-LA) was made up in anhydrous methanol, 50.0 g per 250 mls of solution. To five containers, each holding 25 mls of the PLA solution was added with vigorous stirring increasing 50 mls increments of deionized water. All solutions precipitated a fine floc of insoluble higher end PLA oligomers. Sample A was composed of 25 mls of water; B, 25 mls PLA solution with 100 mls of water; C, 25 with 150; D, 25 with 200; and E, 25 with 250. Within one hour, a completely clear homogeneous methanol/water solution of oligomers resulted (at the bottom of each container remained a small but undetermined amount of settled insoluble "higher" molecular weight PLA oligomers). The nominal methanol content of each sample was A, 33% MeOH; B, 20% MeOH; C, 14.3% MeOH; D, 11.1% MeOH; and E, 9.1% MeOH.

The average degree of polymerization, $\overline{DP}_{\overline{n}}$, of the soluble range of oligomers in each sample was determined as a function of time by titrating free and combined carboxylic acid functionality. An aliquot of the clear supernatant liquor was titrated for free carboxylic acid functionality and then for total combined carboxylic acid content after complete saponification with excess alkali for the same sample. The ratio of total [CO_2 H] to free [CO_2 H] for each sample is, of necessity,

defined as the average $\overline{DP_n}$ for that soluble oligomer sample.

Samples were analyzed over a 34 day period (room temperature). The results are given in Table 2 and shown graphically in Figure 3.

Some observations concerning the results of Table 3 (and Figure 3):

1. As expected, the DPn of soluble oligomers of P(L(+)-LA) decreases with increasing per cent of water in a methanol water solvent mix (remember that the original 3.11 $\overline{DP_n}$ was completely soluble in 100% methanol).

2. The rate of hydrolysis (decrease in $\overline{DP_n}$) increases with increasing water component of the methanol/water solvent mix. A comparison of $\overline{DP_n}$ at 34 days vs. 5 days shows a decrease of 4.5% for A, 15.2% for B, 18.3% for C, 20.2% for D, and 22.3% for E.

3. Implicit in observation 2 above is its corrolary that even after 34 days P(L(+)LA) oligomers in the $\overline{DP_n}$ range up to 10 units still retain some 75% of their original molecular weight. That 10 units of combined lactic acid is the upper limit for a $\overline{DP_n}$ of 3 follows from the mathematical treatment of the condensation reaction.(6) Work is underway to confirm these implied distribution results by preparative scale chromotography of the actual distribution.

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CONCLUSIONS

Lactic acid, as an end product from the fermentation of high carbohydrate food wastes, offers an attractive resource material for preparing poly(lactic acid) degradable plastics, coatings, and binders. Preliminary work at Argonne National Laboratory shows promise for the development of a more cost effective route to converting lactic acid to modified high molecular weight PLA. Of special interest for PLA is its complete degradability into an environmentally friendly end product, lactic acid. An added advantage for PLAs use in agricultural applications, is that at intermediate degradation levels, oligomeric fragments in the 2-10 unit range, show plant growth regulator (PGR) properties (L(+)-isomer).

ACKNOWLEDGMENT

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Table 1 Molecular Weight Distribution for Self-Condensed PLA

Extent of Reaction p	Average $\overline{DP}_n$	% Lactic Acid monomer	% DP=2 dimer	% DP=3 trimer	% DP=4 tetramer	% DP=5 pentamer	% DP≥6
0.50	2	50	25	12.5	6.3	3.1	3.1
0.667	3	33.3	22.2	14.8	9.9	6.6	13.2
0.833	6	16.7	11.6	9.7	8.0	6.7	47.4

Table 2 Solution Stability of Soluble Oligomers of P(L(+)-LA) in Methanol/Water Solutions

Sample	% MeOH	Average Degree of Polymerication[a] $\overline{DP}_n$ Days of Hydrolysis at 25°C 1	5	12	34
A	33	-	2.66	2.62	2.54
B	20	-	2.44	2.31	2.07
C	14.3	-	2.41	2.27	1.97
D	11.1	2.49	2.43	ND	1.94
E	9.1	-	2.42	2.29	1.88

[a]Average degree of polymerization, $\overline{DP}_n$, determined by the ratio of free CO2H to total combined CO2H for each sample as determined by acid-base titration.)

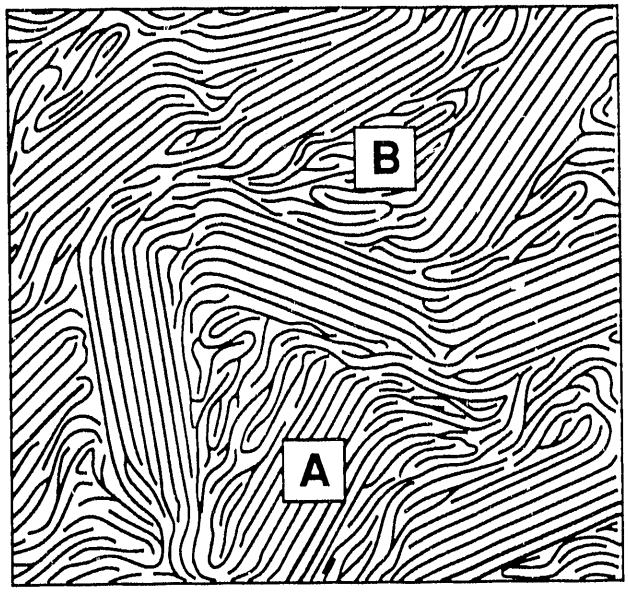

Figure 1. Morphology of a Semi-Crystalline Polymer
(A - crystalline, B - amorphous areas)

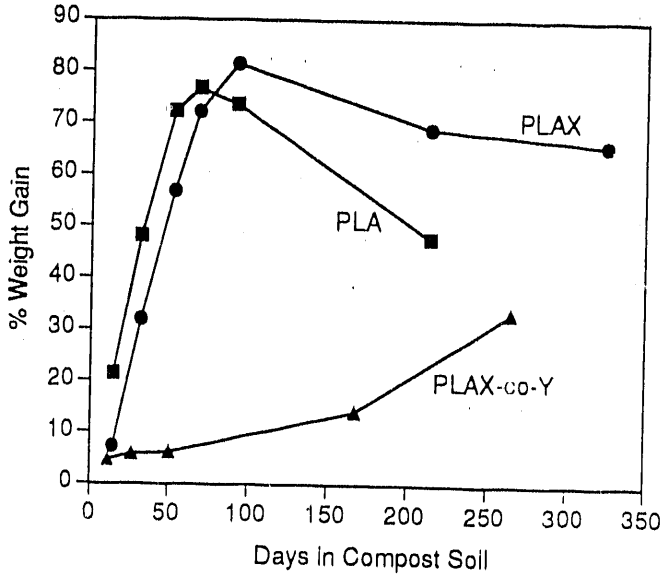

Figure 2. Weight Gain for (modified) PLA Films
in Wet Compost Soil

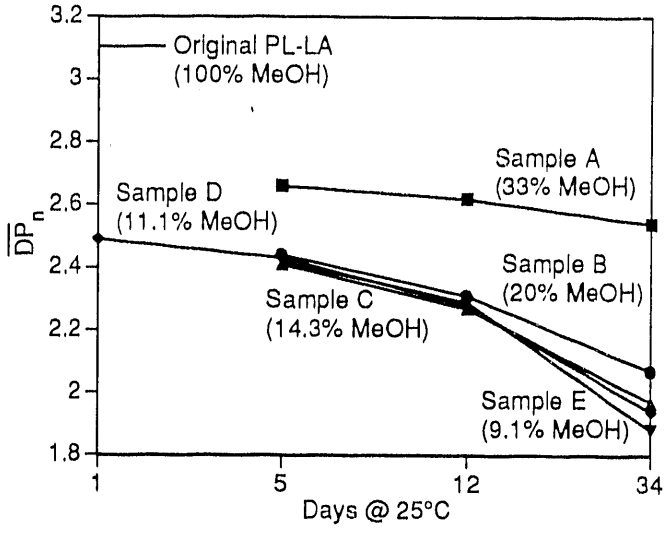

Figure 3. Solution Stability of Oligomers of
Poly (L-Lactic Acid) in MeOH/H_2O

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