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Marine-Degradable Polylactic Acid†

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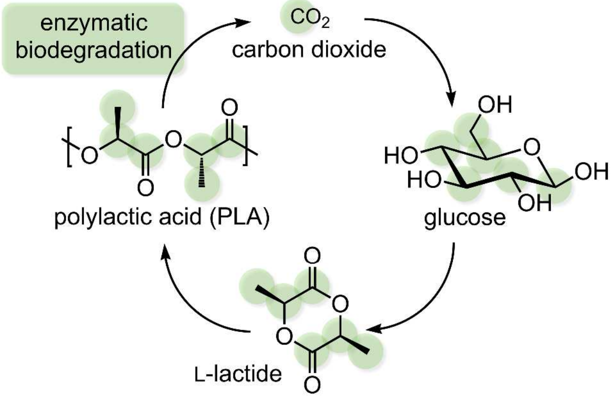
Polyesteracetal (PEA) copolymers of 1,3-dioxolan-4-one (DOX) with L-lactide (LA) were synthesized via ring-opening polymerization (ROP). Facile degradability in distilled water or seawater was observed—presumably via hydrolysis of the main-chain acetal functionality. Over 45 days, mass loss approached 2% and molecular weight loss (M_n) exceeded 15%; control experiments with polylactic acid (PLA) indicated no degradation.

Throughout the 20th century, commodity thermoplastics were almost exclusively derived from non-renewable fossil fuels and the industry has been driven by two main factors: cost and utility. In the 21st century, however, there is a strong push for a more responsible and holistic approach to plastics—an approach that includes a greater emphasis on the sources from which plastics are derived, as well as the ultimate fate of the materials after their useful lifetime is exhausted. In other words, modern sustainable plastics of the 21st century and beyond must be considered in terms of a *green birth*, a functional and effective life, and a *green death*.

Polylactic acid (PLA) has arguably enjoyed the most commercial success as a sustainable thermoplastic.[1] PLA has several drawbacks, however. It suffers from a low glass transition temperature (ranging from about 45° to 55° C) relative to petroleum-based counterparts (*e.g.*, 65–70 °C for polyethylene terephthalate and 95–100 °C for polystyrene).[2] For this reason, it is common to see disposable cups made of PLA marked “FOR COLD BEVERAGES ONLY”. Nevertheless, this disadvantage is outweighed by the facts that PLA can be made from sustainable resources, most commonly corn, and it is believed to possess the ability to degrade on a shorter timescale than traditional thermoplastics. While PLA is more amenable to degradation pathways than traditional hydrocarbon-based thermoplastics, the mechanisms by which it can degrade are limited, and are best done under very controlled circumstances, such as industrial composting, which requires enzymatic biodegradation (Scheme 1).[3] Left to degrade on its own in anaerobic landfill leachate or marine conditions, it is questionable whether PLA will degrade appreciably faster than traditional fossil fuel-based polymers, such as polyethylene.[4] Improvements to this limited degradation behaviour would transfigure PLA into a completely sustainable polymer with a green birth *and* a green death.



Scheme 1 The full lifecycle of polylactic acid (PLA) generally relies upon enzymatic biodegradation.

We sought to install an abiotically hydrolyzable functional group into the main-chain of PLA and targeted the acetal functional group because of our prior experience with polyacetals[5] and the ubiquity of the acetal group in nature. Indeed, it is the most prevalent monomer connecting group on earth since it links the glucose units of the most abundant polymer, cellulose. Intent on a ring-opening copolymerization with lactide strategy, we pursued the 5-membered heterocycle 1,3-dioxolan-4-one (DOX),[6] which bears both the ester and acetal functional groups. We synthesized this oxa-lactone from formaldehyde and glycolic acid which, in turn, can be made via hydrocarboxylation of formaldehyde with carbon monoxide,[7] both potentially renewable C1 feedstocks.[8] Alternatively, several catalysts have been described that produce 1,3-dioxolan-4-one directly from formaldehyde and carbon monoxide (Scheme 2).[9]

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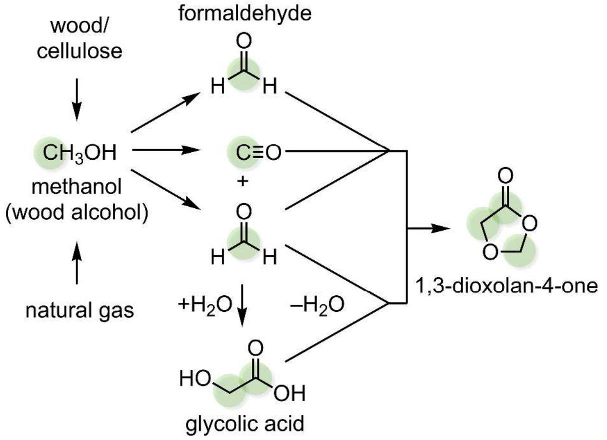
Table 1. Polymerization and Characterization Data for Polyesteracetals from 1,3-Dioxolan-4-one (DOX) and L-Lactide (LA).[a]

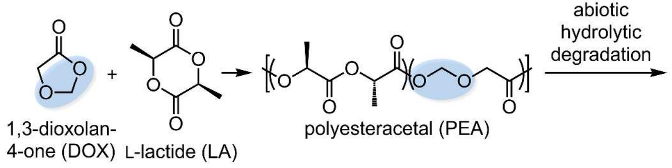
Entry	DOX:LA feed	DOX:LA incorporation	[M]:[I]	Yield (%)	M_n[b]	M_w[b]	PDI	T_m(ºC)[c]	T_g(ºC)[c]
1	0:100	0:100	500:1	93	26,300	53,500	2.04	174	44
2	10:90	4:96	500:1	91	64,100	100,200	1.56	157	51
3	20:80	10:90	500:1	85	36,300	53,700	1.47	152	52
4	30:70	19:81	500:1	76	27,400	41,400	1.51	139	49
5	40:60	25:75	500:1	68	20,800	32,000	1.54	120	42
6	50:50	36:64	500:1	51	10,000	14,100	1.40	116	42
7	60:40	n.d.	500:1	49	n.d.	n.d.	n.d.	104	41
8	100:0	100:0	500:1	10	n.d.	n.d.	n.d.	217	--
9	100:0	100:0	50:1	37	n.d.	n.d.	n.d.	189	7
10	100:0	100:0	10:1	70	n.d.	n.d.	n.d.	186	3

[a] Polymerization conditions: 24 hrs at 100°C in toluene using the stated [monomer]:[initiator] ratio with tin(II)ethyl hexanoate/benzyl alcohol as the initiating system. [b]Molecular weights determined by GPC using polystyrene standards. DOX homopolymers were not soluble in the GPC solvent (THF) and thus molecular weight data was not determined (n.d.). [c]Thermal data determined by DSC.



Scheme 2 Cyclic esteracetal 1,3-dioxolan-4-one made from sustainable or non-sustainable C1 feedstocks.

Standard[10] and proprietary[11] ring-opening polymerization (ROP) initiators are effective for the copolymerization of 1,3-dioxolan-4-one with lactide, installing the esteracetal functional group that is essentially absent from the polymer literature (Scheme 3).[12] Table 1 tabulates our series of polyesteracetals with variable amounts of incorporated DOX comonomer.[13] The persistence of the acetal functional group—which can conceivably be lost via formaldehyde extrusion during polymerization—is readily verified and quantified by ^{1}H NMR (see the Electronic Supplementary Information). The DOX incorporation/feed quotient increases somewhat from 40% to 70% with increasing feed (Table 1, entries 2–6), but never reaches unity, indicating some relative reluctance of DOX toward ring-opening polymerization.



Scheme 3 Copolymerization strategy for synthesizing the polyesteracetal (PEA) copoly(lactide/1,3-dioxolan-4-one).

Entries 1–7 of Table 1 confirm the anticipated result that comonomer incorporation diminishes the polymer melting temperature (T_m), which ranges from 174 °C for the PLA homopolymer to 116 °C for the polyesteracetal with 36 mol% acetal incorporation. The comonomer is apparently functioning as a defect in this trend. Less anticipated is the result that small amounts of acetal incorporation—4 mol% (Table 1, entry 2), 10 mol% (Table 1, entry 3), or 19 mol% (Table 1, entry 4)—effect an *increase* in the polymer glass transition temperature (T_g) compared to that of the homopolymer. For 4 mol%, 10 mol%, and 19 mol%, the T_g values were measured as 51 °C, 52 °C, and 49°C, respectively, compared to that similarly measured for our homopolymer of PLA, 44 °C. Such an increase in T_g is rare,[14] but would be expected for comonomers with substantial conformational rigidity.[2,15] Indeed the acetal functional group imposes such rigidity via anomeric interactions. In this case, the esteracetal functional group can engage two specific anomeric interactions with oxygen lone pair donations into the σ* of an adjacent C–O bond and into the σ* of an adjacent C–C(O) bond. Similar anomeric interactions are responsible for the observed preference of the *gauche* conformation over the *trans* conformation by 2.5 kcal/mol in polyoxymethylene[5b,16]—far surpassing the ground state difference of 0.08 kcal/mol for the two lowest energy conformations in ordinary PLA.[17]

The comparative reluctance of 1,3-dioxolan-4-one (DOX) to copolymerize was probed computationally and ring-strain appears to play an important role. Figure 1 depicts the gas-phase thermodynamics for the ROP of DOX and γ-butyrolactone (BL), the simple lactone analogue of DOX. The enthalpy of polymerization is approximated by insertion of the heterocycle into the carbonyl-oxygen bond of methyl acetate and comparing the corresponding heats of formation, as determined by the G3(MP2) computational method. The five-membered rings are relatively stable and when including the entropic penalty of polymerization (*circa* 9 kcal/mol) exhibit a positive (endergonic, unfavourable) free energy of polymerization at room temperature.[18] The unfavourable polymerization enthalpy of BL can be offset by the favourable polymerization enthalpy of LA and 50:50 copolymers of BL and LA are readily achieved.[18] A similar phenomenon appears operative for DOX and allows for DOX:LA copolymers with substantial (36%) DOX incorporation (Table 1, entry 7).

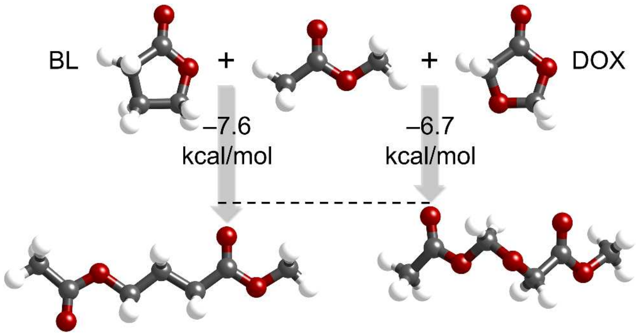


Figure 1 Computational studies (G3(MP2)) imply that the ring-strain of 1,3-dioxolan-4-one (DOX, ΔH = –6.7 kcal/lmol) is slightly less than that of γ-butyrolactone (BL, ΔH = –7.6 kcal/mol).

Anomalously, homopolymerization of DOX seems to succeed (Table 1, entries 8–10), despite the apparent unfavourable thermodynamics and the fact that the slightly more strained analogue BL has never been homopolymerized. Our posited explanation for this mirrors that given for the facile ROP of seemingly stable trioxane with ΔH_{poly} = –0.4 kcal/mol.[19] In polyoxymethylene (POM), the acetal functional group enforces conformational regularity and compels chain–chain interactions via its strong local dipole.[19,5b] These effects promote *crystallization polymerization*,[20] in which *overall* favourable thermodynamics are achieved by exothermic polymer precipitation, a phenomenon not observed for poly(γ-butyrolactone) because of its relatively weak chain-chain interactions and low crystallinity.[21] Homopolymers of 1,3-dioxolan-4-one are highly crystalline, high melting (T_m up to 217 °C), but insoluble in common organic solvents, making them particularly challenging to characterize. Thus we focused our degradation studies on the polyesteracetal copolymers.

Preliminary degradation studies were performed on the 10:90 polyesteracetal copolymer, which analyzed to 4% DOX incorporation (Table 1, entry 2). A direct comparison was sought between this novel polyesteracetal and commercial Ingeo™ polylactic acid, sold by Natureworks, both of which are fairly amorphous. Ingeo™ is approximated here as poly(DL-lactide) (PDLLA) and is quite different from isotactic PLLA samples, which are highly crystalline and would be an unfair comparison to PEA because the high crystallinity would likely thwart degradation. Thin films (0.25 mm thickness) of these polymers were stirred in aqueous acid, buffered to pH = 1.0. The films were monitored over time by mass (after rinsing the films with deionized water and drying) and by molecular

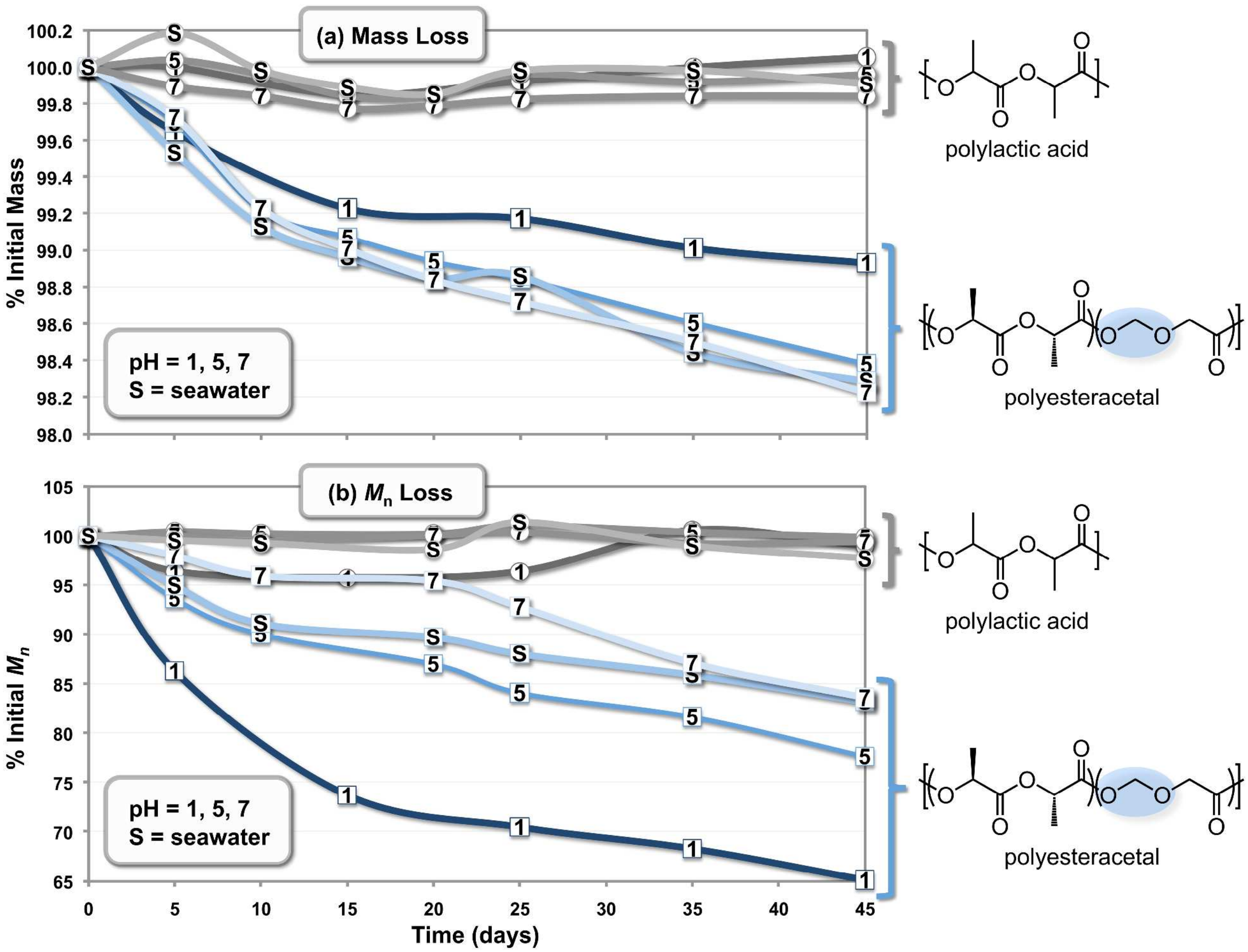


Figure 2 Whereas poly(DL-lactide) (PDLLA) is not affected, the polyesteracetal (4% DOX) shows considerable molecular weight loss (a) and mass loss (b) upon exposure to aqueous environments of pH 1, pH 5, pH 7 (distilled water), and seawater, over 45 days.

weight (GPC, also after rinsing and drying). Analysis revealed that the polyesteracetal copolymer decomposed appreciably with more than 1% mass loss occurring over 45 days (Figure 2a), and 35% molecular weight loss (M_n) over the same time period (Figure 2b). In contrast, films of PDLLA showed no appreciable degradation over the 45-day study. The Ingeo™ essentially behaved as an inert control in our comparative experiment.

Similar experiments conducted in pH 5 water, pH 7 water (distilled water), and seawater (Atlantic Ocean, pH = 7.5) showed that the polyesteracetal copolymer decomposed under slightly acidic, neutral, and slightly basic conditions (Figure 2). In pH 7 water, the polyesteracetal copolymer degraded with nearly 2% mass loss and more than 15% molecular weight loss (M_n) over 45 days. Films of PDLLA showed no appreciable degradation over the 45-day study under these conditions. Interestingly, the polyesteracetal copolymer showed the most rapid degradation by mass under neutral conditions, yet molecular weights decreased most precipitously under highly acidic conditions. The mechanism for this phenomenon is a topic for additional study.

The SEM images of Figure 3 further illustrate the water-degradability conferred by the acetal functional group. Figures 3a and 3d depict the relatively smooth surfaces of poly(DL-lactide) (PDLLA) and the polyesteracetal (DOX = 4 mol%), respectively, immediately following sample preparation. Figures 3b and 3c depict the fate of PDLLA after exposure to aqueous pH = 7 and pH = 1 conditions, respectively, for 45 days. Note that very little change in the surface roughness can be discerned under these conditions. Figures 3e and 3f depict the appearance of the polyesteracetal after being subjected to aqueous pH = 7 and pH = 1 conditions, respectively, for 45 days. While little surface change is found for the pH = 7 conditions, the surface erosion at pH = 1 for the polyesteracetal is substantial and sharply contrasts with the unperturbed outcome for PDLLA under identical conditions (Figure 3c). Indeed, the presence of the esteracetal functional group in the main-chain facilitates surface degradation, often a critical first step in polymer decomposition.[22]

Presumably, the hydrolytic degradation occurs at the acetal group or possibly at the glycolic ester group, which is sterically less hindered than the native lactic ester groups. It seems likely that formaldehyde is an eventual by-product of degradation. While there are concerns about adverse health effects of this molecule,[23] it should be considered that the human body makes about 50 grams of formaldehyde per day[24] allowing for the presence of formaldehyde in every human cell, in human blood at 2.5 ppm, and in human breath from 4.3 to 73 ppb.[25] Moreover, the half-life of blood plasma formaldehyde is 1.5 minutes[23] and that of atmospheric formaldehyde in daylight is 50 minutes.[26] Formaldehyde is already ubiquitous at low concentrations and the degradation rates of these PEA polymers, measured in months and years, should not lead to significantly increased exposure to formaldehyde. Put another way, a 10 gram bottle made of 4 mol% DOX PEA could emit 85 mg of formaldehyde, the equivalent amount found in nine pears.[27] Thus, the incorporation of the acetal functional group into PLA should have net environmental benefits because the enhanced rate of degradation can prevent long-term accumulation of this plastic in the environment.

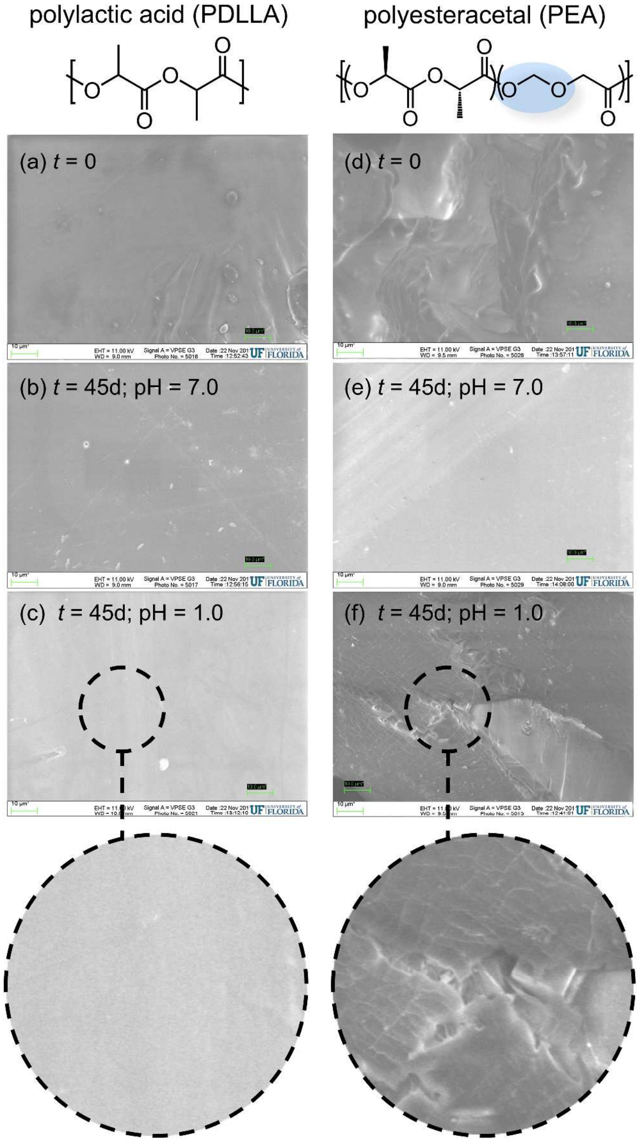


Figure 3 Under various aqueous conditions, surface erosion over 45 days is insignificant for poly(DL-lactide) (PDLLA) but is quite conspicuous for the polyesteracetal (4% DOX) when pH =1.

Conclusions

The acetal functional group has been incorporated into the main chain of polylactic acid (PLA) via ring-opening copolymerization of lactide and the oxa-lactone, 1,3-dioxolan-4-one. This comonomer was prepared by condensation of glycolic acid and formaldehyde, the final step along a conceptual pathway employing C1 feedstocks from biomass: methanol, formaldehyde, and carbon monoxide. The presence of the acetal functional group, even at just 4 mol% abundance, substantially altered the properties and behaviour of the PLA. For example, it increased the glass transition temperature of PLA for acetal incorporations in the range of 4 mol% to 19 mol%. Facile degradation of the polyesteracetal was observed in aqueous media over 45 days, including pH = 1, pH = 5, pH = 7 (distilled water), and seawater (pH = 7.5). Mass loss, molecular weight loss, in addition to surface erosion (by SEM, for pH = 1), were observed for the polyesteracetal (DOX = 4 mol%), whereas PLA showed no measurable change under these conditions.

The polyesteracetals described herein are designed to have thermal properties similar to those of PLA homopolymer, yet undergo more facile main-chain hydrolysis via simple water degradation under abiotic conditions. Thus, enzymatic hydrolysis is likely still feasible, but not necessary for the initial degradation steps that convert high molecular weight polymer to oligomers. With an extrapolated 5–10 year degradation profile in seawater and constituent building blocks derived from biomass, these polyesteracetals constitute excellent sustainable alternatives to traditional thermoplastics originating from non-renewable resources.

Acknowledgements

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Table of Contents Graphic:

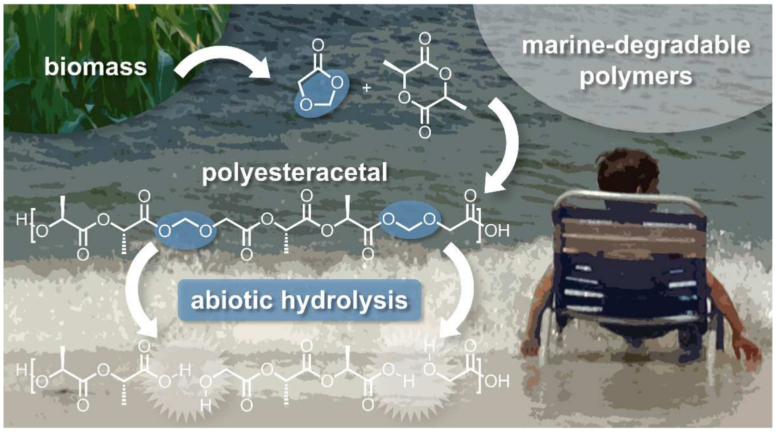

Table of Contents Text: Incorporation of the acetal functional group into the main-chain of polylactic acid affords polyesteracetals that degrade readily in seawater.