Does Crystallinity Affect Polymer Degradation Rates?
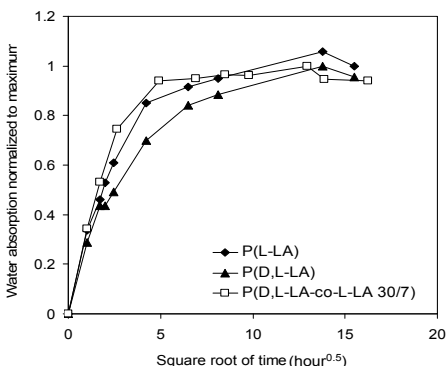
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Statement of Purpose: Crystalline structures are thought to be responsible for slow degradation of polymers such as that of poly(L-lactide) (PLLA). A well accepted explanation is that molecular mobility is lower in crystalline polymers than that in amorphous materials. However, after careful reviewing the literature, we have not found much direct experimental evidence supporting this explanation. Most degradation tests did use polymers with different crystallinity. However, those polymers also had different chain configurations (e.g. PLLA having L-L bonds while PLDLA having L-D bonds). Configuration differences could play a significant role in degradation but were not examined. In the present study, we selected polymers with varying crystallinity and configurations, and simultaneously measured water diffusivity and solubility and polymer degradation rates. The results demonstrated that there was no significant correlation between the molecular mobility and the degradation rates.
Methods: Polylactide samples, both crystalline and amorphous, were used in the present test. Disc samples (12 mm in diameter and 1 mm in thickness) were made via melt-pressing. Degradation testing was done by immersing the discs in PBS buffered solution (pH7). Molecular weights, water uptake, and mass loss were measured after various immersing times. Water diffusivity was obtained by fitting the data of water uptake as a function of time. Water solubility in these polymers was determined from the saturated water contents. Degradation reaction constants were estimated with the methods used in reference [1]. All the tests were repeated for three times.
Results: Water uptake as a function of soaking time in PBS for crystalline (PLLA) and amorphous (PDLLA) polymers (crystallinity 31% versus 0) are shown in Figure 1. The initial increase of water uptake as a function of time is due to water diffusing into samples (swelling). Diffusion coefficients were estimated based on diffusion equation (1D). The results were shown in Table 1.

Fig. 1. Water uptake during samples being soaked in PBS.

The difference in diffusion coefficients of samples of different crystallinity is rather small (40%). After a few days, water uptake reached saturation; the saturated
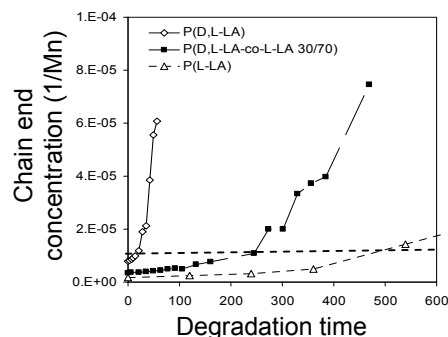
values measure the solubility of water in these polymers (Table 1). Again, the difference due to crystallinity is very small (1.0% versus 1.1%) (Degradation within this time frame was insignificant. See Figure 2).

Table 1. Diffusion coefficients and solubility of water and degradation kinetics (k_2) of the samples used in the study.

Polymer	Crystallinity (%) (DSC estimation)	Water solubility (wt%)	D (cm^2/s) X 10^8	k_2 ($M^{-1}s^{-1}$) X 10^{10}
PDLLA-co-LLA (30/70wt)	0	1.0	6.3	0.4
PDLLA	0	1.0	3.9	2.2
PLLA	31	1.1	4.7	0.09

The degradation results of these polymers are plotted in Figure 2. Degradation of PLLA was significantly slower than that of PDLLA. The degradation reaction rate constants were fitted using a 2nd order degradation mechanism [1] and listed in Table 1. The amorphous sample degraded almost 20 times faster than the crystalline PLLA. If water diffusion controls degradation, reaction rate should be proportional to the diffusion coefficients (Smoluchowski theory). The difference in the degradation rates here is much more significant than could be if water diffusivity (40%) controls the rates. These results suggest that water diffusion cannot be a major factor affecting degradation. The difference in degradation rates could be due to the difference in polymer chain configuration. PLLA has L-L bonds while PDLLA has L-D bonds. L-D bonds have more open structures than L-L bonds and allow water molecules to approach the reaction centers much more easily. This can lead to much faster degradation rates in PDLLA.

Figure 2. End group concentration of polymers (1/Mn) as a function of degradation testing time of the polymers.

Conclusions: PDLLA degrades much faster than PLLA. This difference is not due to the difference in water diffusion and solubility in samples. It could be due to the difference in steric effects between L-L and L-D bonds.
References: Lyu SP et al. Biomacromolecules. 2007, 8:2301-2310.