Hydrolytic Degradation of Bio-based Polyesters: Effect of pH and Time

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ABSTRACT

A hydrolytic degradation study of two bio-based polyesters, poly(trimethylene malonate) (PTM) and poly(trimethylene itaconate) (PTI) with bimodal molecular weight distribution, was performed in aqueous solutions adjusted to pH values from ~5.5 to 11. Final weight loss varied from 20 to 37 wt% for PTM and from 7 to 21 wt% for PTI as a function of degradation time and initial solution pH. Fourier transform infrared (FTIR) spectroscopy was used to monitor ester bond concentration of these bioplastics, and the molecular weights and polydispersity index were obtained by gel-permeation chromatography (GPC). Solutions with lower initial pH values resulted in lower molecular weights for both PTM and PTI after one week of degradation. Degradation especially affected the amorphous region, leading to an increase in crystallinity of PTI samples.

KEYWORDS: Bioplastics, polyester, melt polycondensation, hydrolytic degradation.

1. Introduction

Biodegradation is limited to specific temperatures and moisture, oxygen, and nutrient contents where the responsible enzymes can function [1-5]. Polymers that are classified as being biologically degradable by fungal or bacterial enzymes, such as polylactic acid (PLA) and poly(ϵ -caprolactone) (PCL), may exhibit no degradation and appear biostable due to the lack of any biological activity in the environment. The incorporation of hydrolytically degradable bonds into the backbone of the polymer allow for an addition degradation route besides biologically degradation. Hydrolytically degradable materials require only the presence of (liquid) water.

Several types of hydrolytically degradable polymers, poly(anhydrides), poly(orthoesters), poly(depsipeptides), poly(ether esters), and poly(esters) are currently being researched as replacements for non-hydrolytically degradable petroleum-based polymers [6]. Poly(esters) have shown the most promise for commercialization and replacement of petroleum-based polymers with the development of poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and poly(ϵ -caprolactone) (PCL). In the 1960s and 1970s, PGA was the first bio-compatible and hydrolytically degradable synthetic polymers and was commercialized as dissolvable suture material [7]. This advance spurred research into other biocompatible polymers and into other applications for these polymers. However, performance issues encountered with PLA and PGA are poor thermal stability and brittleness [8, 9]. In our previous study, we synthesized novel bio-based polyesters, poly(trimethylene malonate) (PTM) and poly(trimethylene itaconate) (PTI), by following green chemistry principals, and these polyesters belong to the polyhydroxyalkanoates (PHAs) family [10].

In general, molecular weight (Mw) and crystallinity have been shown to have the largest impact on polyester degradation. With increasing crystallinity and Mw, the rate of PLA degradation decreases due to a hindrance in water being able to diffuse into the matrix; therefore, water is not in proximity to the polymer backbone and so hydrolysis is hindered [8, 9, 11-13]. Excess water forces ester hydrolysis to break ester bonds in acidic conditions that are found in polyesters, such as PLA [14-17]. If the system is basic, the driving force for hydrolytic degradation changes to the formation of stable carboxylate anions. Varying the solution pH in which aliphatic polyesters are laced can have a range of effects on degradation. It is generally agreed that pH affects the rate of degradation of bioplastics [18-20]. For polyesters like PLA and PGA, hydrolytic degradation is considered bulk degradation with two steps. The first step is the uptake of water into the polymer. The second step is the ester cleavage, and diffusion of low Mw products out of the polymer [6, 21-23]. If the polymer is sufficiently large that degradation product diffusion is slow, the increased number of end groups leads to auto-catalyzation conditions in which the interior of the polymer degrades at a faster rate than the surface of the polymer [23].

High degradation rates, complete degradation or substantial loss of mechanical properties, are desirable in only select applications, such as drug release, sensors, and specialty packaging. Polymers exhibiting a controlled degradation and complete degradation or substantial loss of mechanical properties (dependent on application) between 6 to 36 months could be used in a large number of disposable or short-term use product applications. The working assumption is that if the chemical structure of the polymer can be controlled, then the degradation (rate and total time) can be tailored for specific applications.

In this study, the hydrolytic degradation of these bioplastics with bimodal molecular weight distribution was examined under variable pH conditions for up to 10,000 min. Changes in

gravimetric weight, molecular weight, chemical functionality, and thermal properties were monitored by gel-permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC). The effects of Mw distribution on hydrolytic degradation were evaluated.

2. Experimental Section

2.1. Materials

The PTM sample used for the degradation study was bulk polymerized from 1,3-propane diol (PDO, 98%, Sigma Aldrich) and malonic acid (MA, 99%, VWR) using AlCl_3 catalyst (98%, Sigma Aldrich) with a 100:1 monomer to catalyst ratio at 155 °C for 4 h. With a similar way, the PTI sample was bulk polymerized from 1,3-propanediol (PDO, 98%, Sigma Aldrich) and itaconic acid (IA, 99%, VWR) using AlCl_3 catalyst (98%, Sigma Aldrich) with a 100: 1 monomer to catalyst ratio at 155 °C for 16 h. Additional details on the PTM and PTI synthesis and characterization was provided previously [10]. KOH (99%) and Optima tetrahydrofuran (+99.9%) were purchased from Fisher Scientific. All chemicals purchased were used as received without further purification.

2.2. Hydrolytic Degradation

PTM was compression molded into a 12 cm x 12 cm x 0.159 cm sheet using a Carver 15 ton floor stand press at 6.9 MPa for 10 min at 30 °C. The sheet was cut into 1 cm x 0.318 cm x 0.318 cm samples, and each sample was placed into individual vials. PTI was ground by hand into a powder using a mortar and pestle until all particles could easily sift through 18 x 18 mesh stainless steel wire cloth. Hydrolysis was performed in DI water and in basic aqueous solutions

formed by adjusting the pH of DI water (pH 5.4) to pH 7, 9, and 11 using a concentrated DI-KOH solution. DI water was chosen as a control, and pH 7, 9, and 11 were chosen since bioplastics had faster hydrolysis rates at basic pHs. For the PTM hydrolysis experiment, the samples were initially placed under vacuum at room temperature for 24 h to remove excess water. Vials were then prepared containing one compression molded PTM coupon or 0.75 g of PTI powder along with 10 mL of the aqueous solutions. One set of vials had no liquid added as an ‘air’ control, to attempt to take into account any changes due to aging alone. All of the sealed sample vials were then placed into a 25 °C water bath for 10, 100, 1000, and 10000 min. At each pre-designated time, the samples were removed from solution and gently blotted with a KimWipe®. They were then vacuum dried (25 torr) at room temperature for 24 h. All degradation samples were run in triplicate.

The weight change was calculated according to the following equation:

$$\text{weight change (\%)} = \frac{w_0 - w_t}{w_0} * 100 \quad (1)$$

where w_0 and w_t represent the initial weight and the weight at time t , respectively.

2.3. Characterization

The PTM polymer samples were characterized by attenuated total reflectance (ATR) FTIR spectroscopy at discrete times during the degradation study using a Thermo Electron 6700 instrument (DTGS detector, room temperature, dry air purge, ZnSe crystal with a 60° angle of incidence). The PTI polymer samples were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Thermo Electron 6700 instrument with a He-Ne laser, liquid nitrogen-cooled MCT-A* detector, and EasyDiff accessory (Pike Technologies) at room

temperature using a dry air purge. Samples were mixed with KBr powder at 5 wt.% PTI and 100% KBr was used for the sample spectra background. The peaks were fitted with PeakSolve in Thermo Scientific Omnic 8.1.10. Gaussian peaks were fitted at specific wavenumbers to minimize standard error. A peak height ratio (PHR) calculation was used in the quantitative analysis of FTIR spectra. PHR uses the height of the C-C rocking at 1465 cm^{-1} as the denominator and the height of the peak of interest as the numerator to form a ratio. Gel permeation chromatography (GPC) data was collected with a Waters GPC with RI detector, 4E and 5E (polystyrene-divinylbenzene, 4.6 x 300 mm) Styragel® columns, Optima THF as the effluent at 0.3 mL/min, and a ten-point polystyrene calibration. A TA Instruments Q-2000 modulated DSC (mDSC) with a nitrogen purge was used for thermal analysis with the TA Universal Analysis 2000 software (v4.7A). mDSC samples were analyzed from -90 to 250 °C (at 5 °C/min) under 50 mL/min of nitrogen.

3. Results and Discussion

3.1. Synthesis and Characterization

PTM was produced by the melt polycondensation of PDO with MA. The maximum yield ($\sim 78 \pm 5$ wt.%) was obtained at the reaction conditions of 155 °C and 4 h with the product having a bimodal weight average molecular weight of ~ 63 kDa (with 1.82 PDI and 1.6 wt.%) and ~ 1.8 kDa (with 1.83 PDI and 98.4 wt.%). PTM with a glass transition, -57 °C is a linear polymer composed of ester and ether backbone bonds. However, PTI is a branched copolymer that is a rigid semi-crystalline material with possible load bearing application. The maximum yield (78 ± 8 wt.%) and ester concentration were obtained at 155 °C and 16 h reaction conditions. For the THF-soluble PTI material, the measured weight average molecular weight was ~ 51 kDa (with

1.71 PDI and 1.5 wt.%) and ~1.4 kDa (with 1.78 PDI and 98.5 wt.%), and a cold crystallization temperature was found at ~160 °C.

3.2. Hydrolytic Degradation

Degradation of PTM and PTI was carried out in aqueous solutions adjusted by KOH to pH 7, 9, and 11, DI water with an initial pH of 5.4, and a control with no fluid referred to as air at 25 °C for 10, 100, 1000, and 10000 min. All samples do not show significant weight loss during the first 10 min of degradation, **Fig. 1**. Even though there is a significant weight loss rate initially, it appears that there is an induction period before degradation products can diffuse out of the polymer and cause a significant change in DI and pH 7's dry weight.

Fig. 1. PTM and PTI percent weight change as a function of degradation time (◇: air; □: DI water; △: pH 7; --: pH 9; ○: pH 11). Error bars represent 95% confidence intervals for 3 replicates.

In the first 100 min as water diffuses into the DI and pH 7, the A_{AC2} and A_{AL1} reaction rates are increasing as there is an increased excess of water to shift the reactions equilibrium to products, Fig. 2. There is a correlation between starting pH and final weight loss that can be explained considering whether the hydrolysis is base-mediated or acid-catalyzed. Acid-catalyzed ester hydrolyses predominately follow the A_{AC2} and A_{AL1} mechanisms (Fig. 3). During the ‘bimolecular’ A_{AC2} mechanism, the bond at the ‘acyl’ carbon is broken by two molecules of water whereas the bond at the ‘alkyl’ carbon breaks in the A_{AL1} mechanism. In the base-mediated ester hydrolyses, the B_{AC2} mechanism is the dominate mechanism that requires a basic aqueous solution. The reaction mechanisms for A_{AC2} and A_{AL1} require an excess of water to drive the reactions to completion [14-17]. DI and pH 7 dry weights decrease and become significantly different at 10,000 min. DI is significantly more acidic initially, pH 5.4, than pH 7, which had its pH adjusted by the addition of KOH. DI is assumed to only follow A_{AC2} and A_{AL1} due to the lack of the addition of a base, such as KOH, to the solution, which does not allow DI’s degradation mechanisms to following B_{AC2} kinetics [14-17]. It is assumed that the KOH is affecting pH 7 degradation rate by interfering with the A_{AC2} and A_{AL1} mechanisms. KOH could be stabilizing the carboxylate anion in pH 7 and hinder the protonation of carbonyl carbon in the A_{AC2} and A_{AL1} mechanisms, which is assumed to be happening in all solutions with KOH added.

Fig. 2. Weight loss rate as a function of aging time for **PTM and PTI** ($\diamond$: air; $\square$: DI water; $\triangle$: pH 7; $\blacksquare$: pH 9; $\circ$: pH 11).

(a)

(b)

(c)

Fig. 3. The A_{AC2} (a), A_{AL1} (b), and B_{AC2} (c) ester hydrolysis reaction mechanisms.

pH 9 and pH 11 initially started as base-mediated degradation through B_{AC2} hydrolysis mechanisms, and as aging time proceeds, the pH of the surrounding solutions decrease to acidic conditions, seen in Figs. S1 and S2, where A_{AC2} and A_{AL1} mechanisms dominate the hydrolysis of pH 9 and pH 11, and B_{AC2} mechanism does not occur. pH 9 and pH 11 had significant amounts of KOH initially added to adjust the pH, and the K^+ ion had a significant effect on the degradation of pH 9 and pH 11. With increasing K^+ ion content from pH 7 to pH 11 samples, there is a decrease in weight change as the K^+ ion inhibits A_{AC2} and A_{AL1} mechanisms even under acidic conditions at longer aging times. During the degradation, the degradation rates for pH 9 and pH 11, Fig. 2, do not have an increase from 10 to 100 min in an opposite trend to the degradation rates of DI and pH 7. Even though pH 9 and pH 11 are under acidic conditions from 10 to 100 min, the A_{AC2} and A_{CL1} mechanisms are not as effective at degrading PTM. The increased concentration of K^+ ions with increasing initial solution basicity reduces pH 9 and pH 11 weight change and weight change rate over 10,000 min aging time. The major influence on weight change and weight change rate is the concentration of ions in the initial solution for the degradation of PTM through carboxylate anion stabilization by K^+ acid-base interaction. Final weight loss varied from 20 to 37 wt% for PTM and from 7 to 21 wt% for PTI as a function of degradation time.

In a good comparison study, Yoshioka et al. tested the degradation behaviors of three different aliphatic biodegradable polymers, poly(L-lactic acid) (PLLA), poly(lactic-co-glycolic acid) (PLGA), and poly(ϵ -caprolactone) (PCL) [24]. All degradations were performed in pH 7.4 phosphate-buffer solution (PBS) at 37 °C. It was reported that the PLGA samples lost 80% of

their original weight after 24 weeks. The weight loss of the PLLA samples was slower at a 16% reduction over 26 weeks, and PCL samples lost only 1% of their original weight after 26 weeks.

3.3. FTIR Spectroscopy

The degraded PTM materials from pH 7, 9, and 11, DI, and Air were examined using ATR-FTIR to monitor changes in functional group concentration as a function of aging time. A representative spectrum can be seen in Fig. S3. The area of interest on all spectra was the carbonyl stretch region from 1500 to 1900 cm^{-1} , and the peak fitting was performed on the region of 1500 to 1870 cm^{-1} , Fig. S4. Seven peaks were identified in this region as 1587 cm^{-1} carboxylate anion carbonyl stretch(1), 1633 cm^{-1} cis-alkene stretch (2), 1672 cm^{-1} trans-alkene, vinylidene, tri or tetra-substituted alkene stretch (3), 1702 cm^{-1} dimerized carboxylic acid carbonyl stretch (4), 1726 cm^{-1} ester carbonyl stretch (5), 1749 cm^{-1} ester carbonyl stretch (6), and 1777 cm^{-1} cyclic ester carbonyl stretch (7). There are two ester carbonyl peaks identified in the region of 1725 to 1750 cm^{-1} where ester carbonyls are present. It is theorized that there are two different types of esters present in PTM. The first type of ester at 1726 cm^{-1} is a higher Mw ester carbonyl, and the second type of ester at 1749 cm^{-1} is either a large cyclic ester or low Mw ester carbonyl.

The ester carbonyl degradation could be monitored by peak fitting the carbonyl stretch and monitoring the change in peak height ratio (PHR). Peak height ratio (PHR) is a semi-quantitative measure of relative changes in concentration for a particular peak of interest. PHR uses the height of the C-C rocking at 1465 cm^{-1} as the denominator and the height of the peak of interest as the numerator to form a ratio. PHR for the ester carbonyl peak at 1749 cm^{-1} decreased by a maximum of ~2 units during degradation as hydrolysis reduced the concentration of ester groups

in PTM for all samples in solution (Fig. 4). The ‘Air’ sample PHR was maintained ~8.8 over the 10,000 min study duration demonstrating that in air PTM does not show any appreciable degradation at 25 °C. DI and pH 7 had the largest decrease in PHR, ~2 units, after 10,000 min.

Fig. 4. PHR of the ester carbonyl peak (1749 cm^{-1}) in PTM as a function of degradation time (◇: air; □: DI water; △: pH 7; ---: pH 9; ○: pH 11). Initial PHR: 9.8.

A representative PTI DRIFT spectrum can be seen in Fig. S5. Similar to PTM, the area of interest is the carbonyl stretch region from 1900 to 1500 cm^{-1} . Changes in carbonyl peak location and size qualitatively indicates the formation of carboxylic acid and the ester degradation. Seven peaks were identified in the 1900 to 1500 cm^{-1} wavenumber range (Fig. S6): 1586 cm^{-1} carboxylate anion carbonyl stretch (1), 1639 cm^{-1} vinylidene stretch (2), 1673 cm^{-1} trans-substituted alkenes or tri-/quad-substituted alkenes stretch (3), 1704 cm^{-1} dimerized carboxylic acid carbonyl stretch (4), 1744 cm^{-1} ester carbonyl stretch (5), 1786 cm^{-1} cyclic anhydride carbonyl symmetric stretch (6), and 1822 cm^{-1} cyclic anhydride carbonyl asymmetric stretch (7).

As with PTM, degradation of PTI samples is expected due to ester hydrolysis, and so the ester carbonyl PHR should correspondingly decrease. As shown in Fig. 5, the PHR for the ester carbonyl did decrease as a function of degradation time for all samples, except the air control. DI had the largest decrease in ester carbonyl PHR from ~2.7 to 2.0 over 100 to 10,000 min. pH 7 also had a significant decrease in ester carbonyl PHR (~0.5 units) from 100 to 10,000 min. Ester degradation at pH 7 may have been slightly hindered by the K⁺ ions in solution stabilizing the carboxylate anions. However, the amount of KOH necessary to adjust the pH was very small and, within statistical variability, does not appear to have impacted degradation. pH 9 and pH 11 maintained ester carbonyl concentrations the best at 10,000 min. These results are as expected, because under more acidic conditions, greater ester hydrolysis takes place.

Fig. 5. PHR of the ester carbonyl peak (1744 cm^{-1}) as a function of aging time for PTI (◇: air; □: DI water; △: pH 7; —: pH 9; ○: pH 11). Initial PHR: 2.6.

3.4. Gel Permeation Chromatography (GPC)

PTM experienced significant decreases in Mw as a function of time, Fig. 6. In the first 10 min, no significant decrease in Mw and in 1749 cm^{-1} PHR for DI and pH 7 indicates that the low Mw material diffused out of PTM. If the low Mw PTM was diffusing out of DI and pH 7, the PDI should have decrease, Fig. 6, which does occur. By 100 min for DI and pH 7, there is a significant increase in PDI as the A_{AC2} and A_{AL1} mechanisms degrade ester bonds and decrease 1749 cm^{-1} PHR with a lack of degradation product diffusion out of the samples. At 1,000 and 10,000 min for DI and pH 7, the Mw significantly decreases from ~2100 to less than 1800 Da and 1400 Da, respectively. The DI and pH 7's PDI decrease at 1,000 and 10,000 min as diffusion is able to remove degradation products and decrease the PDI. pH 11 and pH 9 have no significant changes in dry weight, 1749 cm^{-1} , or Mw during the first 100 min, Figs. 2, 4 and 6. The PDI initially decrease from the control, Air, during the first 10 min as low Mw material diffuses out of the material, and at 100 min, the PDI increases by ~0.1 degradation does occur without significant impact on any other parameter, Fig. 6. Starting at 1,000 min, the Mw for each sample becomes distinct from any other sample, Fig. 6. It becomes apparent at 1,000 min that the ester hydrolysis is proceeding at different rates based on the initial pH of the solutions as the change in 1749 cm^{-1} PHR and Mw are decreasing uniquely for each condition. All solution become acidic in the initial 10 min as low Mw material diffuses into the solution, and the acidic solution facilitates the acid catalyzed ester hydrolyses through the A_{AC2} and A_{AL1} mechanisms. The pH 11 and pH 9 transition from a base mediated ester hydrolyses medium to an acid catalyzed ester hydrolyses medium as the pH shifts from a basic solution to an acidic solution.

Fig. 6. Molecular weight and PDI as a function of aging time for PTM ($\diamond$: air; $\square$: DI water; $\triangle$: pH 7; $--$: pH 9; $\circ$: pH 11). Initial Mw: 1791 Da. Initial PDI: 1.82.

Even though the solution switches from a basic to an acid medium, the concentration of K^+ ions does not change. The K^+ ion will stabilize the carboxylate anions and hinder the carbonyl carbon protonation in the A_{AC2} and A_{AL1} mechanisms. pH 11, with the highest concentration of K^+ ions, only has a Mw decrease of 200 Da and compared to DI decrease of 800 Da at relatively the same final pH, the K^+ ions are significantly impacting the A_{AC2} and A_{AL1} mechanisms during acid catalyzed ester hydrolyses. The pH 11 PDI increases over the aging time and pH 9 PDI does not change from 100 to 10,000 min with a significant decrease in Mw. For pH 11, ester hydrolyses is occurring and producing degradation products that are too large to diffuse out leading to an increasing in PDI with a decreasing Mw from 10 to 10,000 min. pH 9 maintains a constant PDI with a decreasing Mw and dry weight, Fig. 1, from 100 to 1,000 min. pH 9 has ester hydrolyses as shown by the decreasing Mw and 1749 cm^{-1} PHR, and considering the constant PDI and decreasing dry weight together, pH 9 degradation products are diffusing out of PTM at a rate that causes the PDI to be maintained as pH 9 decreases in Mw. Two major factors affecting PTM's

Mw and PDI during degradation are concentration of K^+ ions and diffusion of low Mw material into solution, which was characterized by GPC.

PTI exhibited significant degradation from 100 to 10,000 min as shown by the weight change, FTIR spectroscopy analysis, and aqueous phase pH discussed before. Though the THF soluble material had a low concentration in the GPC results, the polymer produced was elastic to stiff and brittle due to cross-linking and branching of the polymer. Partially soluble PTI did initially have a bi-modal Mw distribution. The higher Mw polymer was above 10,000 Da and will be referred to as HMw. The lower Mw polymer was below 10,000 Da and will be referred to as LMw. The PTI air control LMw and PDI did not deviate from the starting materials LMw and PDI, 1379 ± 9 Da and 1.61 ± 0.17 (Fig. 7). During the initial 100 min, DI water and pH 7, 9, and 11 LMw increased by ~100 Da when compared to the air control. The increase in LMw is due to the diffusion of polymer into the solution, and this diffusion causes the pH of all solution to become acidic (Fig. S2). There was no change in PTI's LMw from 100 to 1000 min for all solutions. From 1,000 min to 10,000 min, the molecular weights of DI water, and pH 7, 9, and 11 solutions Mw decreased by 50 to 200 Da as hydrolytic degradation occurs and LMw material diffuse into the aqueous phase. The degradation for pH 9 and pH 11 starts off as B_{AC}2 in the first 100 min and converts to A_{AC}2 and A_{AL}1 as the surrounding solution becomes acidic (Fig. S2). pH 11 and pH 9 hydrolyses were inhibited by the presence of K^+ ions that stabilized the carboxylate anions. With increasing initial solution acidity and reduction in K^+ ion, the reduction in LMw increases.

Fig. 7. LMw and PDI as a function of aging time for PTI ($\diamond$: air; $\square$: DI water; $\triangle$: pH 7; $\blacksquare$: pH 9; $\circ$: pH 11). Initial Mw: 1379 Da. Initial PDI: 1.78.

The PDI for DI water and pH 7, 9, and 11 trends were not as systematic as the Mw trends (Fig. 7). Air does appear to decrease from ~ 1.77 to ~ 1.6 at 1,000 to 10,000 min, but it is still with the confidence interval of the neat material, 1.71 ± 0.17 PDI. It is not believed that this is degradation of air control because it was not accompanied by a decrease in sample weight, change in the FTIR, or a change in the Mw. For DI and pH 9 from 100 to 1,000 min, the PDIs appear to increase from ~ 1.73 to ~ 1.8 and ~ 1.73 to ~ 1.76 . The increase in PDI with no change in Mw from 100 to 1,000 min shows that degradation is occurring, and the degradation products have not diffused out of the polymer leading to an increase in PDI. From 1,000 to 10,000, DI and pH 9 PDI reduce from ~ 1.8 and ~ 1.76 to ~ 1.65 and ~ 1.6 , respectively. pH 7 did not experience an increase in PDI as a function of aging time. From 100 to 10,000 min, pH 7 PDI decreases from 1.75 to 1.62, whereas pH 11 had no apparent dependence on PDI.

In the initial 100 min, Fig. 8, the high molecular weight material, HMw, is lower than the control, but only statically significantly for pH 9. At 1,000 min, all samples in solution are

significantly different than the Air control and have reduced in Mw. The lower Mw material did not show any significant change in Mw at 1,000 min. After 1,000 min, the HMw was not detected, and it is assumed that the HMw has degraded to a point at which it is indistinguishable from the lower Mw material. Examining the PDI during the first 1,000 min, Fig. 8, the PDI did not change. This gives evidence that the HMw is not experiencing random chain scission and is experiencing end chain scission. If the HMw was experiencing random chain scission, a broadening of the PDI would have occurred. Hydrolytic degradation is preferentially degrading the HMw with end chain scission.

Fig. 8. High Mw and PDI as a function of aging time for PTI ($\diamond$: air; $\square$: DI water; $\triangle$: pH 7; $--$: pH 9; $\circ$: pH 11). Initial Mw: 50650 Da. Initial PDI: 1.71.

The HMw concentration increased in the first 1,000 min before it was degraded to where it was indistinguishable from the lower Mw material. The HMw area on the GPC trace increased for all samples except Air from 100 to 1,000 min, Fig. S7. During the same time period, there was a significant decrease in the dry weight of the samples, Fig. 1. The low Mw material is diffusing

out of PTI, which was postulated earlier, while the HMw is too large to diffuse out of PTI. The diffusion of low Mw into solution increases HMw concentration in first 1,000 min.

3.5. Thermal Properties

PTM and PTI samples were examined with DSC during the degradation. The data for the thermal behavior of the neat (nondegraded, 0 min) and degraded PTM and PTI samples in only DI water are presented in Table 1. The neat PTM was an amorphous copolymer with a glass transition temperature (T_g) of approximately -58 °C. It is well known that the molecular weight of polymer is a significant factor on T_g . That is, a decrease in T_g can be related to a decrease in the molecular weight due to higher chain mobility. PTM exhibited a glass transition temperature (T_g) that trended upwards as a function of increasing degradation time for all samples. This could be associated with the diffusion of low molecular weight PTM into water.

Table 1. Thermal analysis data of degraded PTM and PTI samples in only DI water as a function of degradation time.

Polymer	Degradation Time (min)	T_g (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
PTM	0	-58	-	-	-	-
	10	-58	-	-	-	-
	100	-57	-	-	-	-
	1000	-52	-	-	-	-
PTI	0	-	159	159	214	20.6
	100	-	160	161	228	28.0
	1000	-	162	163	231	26.7
	10000	-	162	163	232	25.6

T_g glass transition temperature, T_{m1} first melting temperature, T_{m2} second melting temperature, T_{cc} cold crystallization peak temperature, ΔH_m melting enthalpy.

Neat PTI is a semi-crystalline polymer with a cold crystallization temperature of 159 °C and a double melting temperature of 159 °C and 214 °C. The bimodal molecular weight distribution can result in this bimodal melting behavior. The cold crystallization temperature and melting temperatures of the PTI both increased as a function of the degradation time. The increase in the melting points can be attributed to the scission of the ester bonds in the polymer chain. The initial degradation in the amorphous phase could happen quickly since water attacks the weakly packed segments more easily. This resulted in increased chain mobility, and thus new, more organized crystalline regions occurred. As a result, this behavior could increase the melting point of semi-crystalline PTI during the degradation. Since the melting enthalpy for 100% crystalline PTI was unknown, the degree of crystallinity (X_m) was not calculated. Therefore, the total melting enthalpies were used to monitor PTI's crystallinity. In general, the crystallinity of PTI tended to increase with the degradation. This could be explained by the behavior of semi-crystalline polymers, such as PTI, undergoing partial degradation of the amorphous phase, as was previously described. Even though the crystallinity decreased gradually from 100 min until 10000 min, it was still higher than that of neat PTI.

4. Conclusions

As part of our efforts to develop degradable, bio-based polyesters, a hydrolytic degradation of PTM and PTI samples with bimodal molecular weight distribution was investigated at 25 °C using pH 7, 9, and 11 KOH/DI water solutions and also DI water (pH 5.4) for up to 10,000 min. Weight loss was observed for all of the aqueous solutions tested with weight loss inversely proportional to the initial solution pH. PTM was susceptible for a weight loss of almost 40 wt% over a wide range of pH values in only one week, and PTI showed a maximum weight loss of approximately 20 wt.% during that same time frame. It is notable that although the aqueous

solution had different initial pH values, the degradation of the polymers results in a pH of ~3.4 for all of the solutions after 100 min of degradation. DSC studies showed that hydrolytic degradation induced crystallinity for PTI. Both of these new materials are green (renewably bio-based) and hydrolytically degradable, making them environmentally sensitive.

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Associated Content

Supporting Information. Representative FTIR spectra of PTM and PTI in the degradation solution.

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