

Synthesis of Polylactide with Varying Molecular Weight and Aliphatic Content: Effect on Moisture Sorption

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ABSTRACT: Polylactide (PLA) is a bio-based, biodegradable polymer, which is derived from lactic acid and has numerous potential applications, some of which are limited by its moisture barrier and thermal properties. Prior studies have been inconsistent about how moisture sorption in PLA varies with crystallinity and molecular weight. This research is a systematic study of how moisture sorption in PLA depends on molecular weight and aliphatic content via end-group modification. PLA with varying aliphatic content was synthesized by ring-opening polymerization of L-lactide initiated with different long-chain aliphatic alcohols. The terminating end groups were also modified from hydroxyl to acetoxy to eliminate hydrophilic end groups. Molecular weight was controlled

by varying the ratio of L-lactide monomer to alcohol initiator, and triethylaluminum was used as the catalyst for precise control over molecular weight. The molecular weight and end-group compositions were verified by gel permeation chromatography and nuclear magnetic resonance. Moisture sorption of the modified PLA samples was measured with a quartz crystal microbalance. Quartz crystal microbalance experiments revealed that both molecular weight and aliphatic content contributed to the sorption properties of PLA. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2543–2549, 2011

Key words: ring-opening polymerization; biopolymers; renewable resources; modification; thermal properties

INTRODUCTION

Most common polymeric materials are produced from nonrenewable fossil resources. Waste of polymeric material from incineration contributes to atmospheric carbon dioxide, and the United States Environmental Protection Agency estimates that nearly 25% of the municipal landfill space is occupied by plastics.¹ This concern is even more severe in Europe and Japan where landfill space is less available than in the United States. Many widely used plastic materials like polystyrene and poly(vinyl chloride) are made from toxic monomers. There is need to use eco-friendly methods in producing renewable commodity plastics that do not include harmful compounds in their manufacture.

Polylactide (PLA) is a bio-based biodegradable polymer, which can be produced from renewable sources such as corn and sugarcane, and has found numerous applications in the medical and pharmaceutical fields.² Some large-scale manufacturers are

beginning to favor PLA because it is renewable, conserves energy, and degrades easily.³

The properties of PLA such as melting point, crystallinity, and mechanical strength are affected by the polymer architecture and its molecular weight. PLA has glass-transition temperature (T_g) in the range of 50–80°C, whereas the melting temperature (T_m) ranges from 130°C to 180°C. Copolymerization of lactide with other monomers like glycolide or caprolactone can significantly enhance the properties and broaden the use of PLA.^{4–6}

PLA has numerous advantages over other polymers, including the following: (1) it is produced from renewable resources, (2) its production consumes less energy, (3) it can be recycled back to lactic acid, which is a nontoxic and naturally occurring metabolite, through hydrolysis or alcoholysis, (4) its manufacturing emits fewer greenhouse gas, (5) it is compostable, leading to reduced landfill volumes, (6) use of crops for polymer production improves farm economics, and (7) physical and mechanical properties of PLA can be tailored through the modification of its architecture.^{7,8}

The manufacturing of polymeric products from PLA has been hindered mainly by three factors: (1) high cost compared with other polymers because of its immature technology, (2) higher moisture sorption and faster moisture permeation, and (3) need for modified processing conditions. Most petroleum-based polymers are derived from alkenes or

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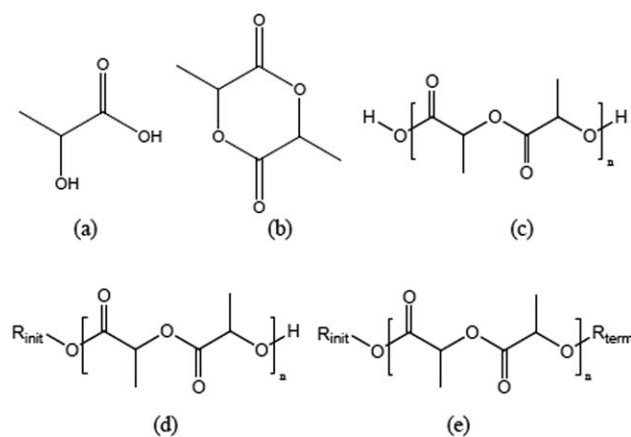


Figure 1 Molecular structure of (a) lactic acid, (b) lactide, (c) standard PLA (HO-PLA-OH), and the modified PLAs: (d) R_{init} -PLA-OH and (e) R_{init} -PLA- R_{term} .

aromatic monomers and are nonpolar, whereas the high ester content of PLA has higher polarity, which increases degradability but also reduces the water barrier properties. In practical applications, PLA products have higher moisture permeability. For example, PLA water bottles exhibit noticeable water loss over the course of several months.^{8–10}

The properties of non-end-capped PLAs (HO-PLA-OH) and one end-capped PLA (HO-PLA-R) have been reported.^{11,12} However, this article presents a systematic study of how moisture sorption in PLA depends on molecular weight and aliphatic content via modification of both end groups. Figure 1 shows the molecular structures of lactic acid, lactide, and several forms of PLA. Standard PLA has two hydrophilic end groups: an alcohol initiating end group and a carboxylic acid terminating end group. The modified PLA samples in this study were prepared with alcohol initiators leading to an aliphatic initiating end group R_{init} . Termination of the polymerization with appropriate chemicals can lead to either a hydroxyl end group or an aliphatic terminal end group, R_{term} . PLA with varying aliphatic content was achieved by initiating with different long-chain aliphatic fatty alcohols from butyl (C4) to palmityl (C16). Also, PLAs with benzyl initiating end were synthesized to investigate how changes in end group affect moisture sorption properties. Molecular weight was controlled by varying the molar ratio of L-lactide monomer to alcohol initiator (C16 palmityl, C10 decyl, C4 butyl, and benzyl). Triethylaluminum was used as the catalyst because of the better control over molecular weight.^{5,13–15} Samples of modified PLA were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR). Moisture sorption in the

modified PLA was measured with quartz crystal microbalance (QCM).^{16–20}

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich (St. Louis, MO). (3S)-*cis*-3,6-Dimethyl-1,4-dioxane-2,5-dione or L-lactide (98%) was the monomer and was purified by recrystallization from anhydrous ethyl acetate (99.8%). Palmityl alcohol, decyl alcohol, butyl alcohol (anhydrous, 99.8%), and benzyl alcohol (anhydrous, 99.8%) were used as initiators. Triethylaluminum in toluene (1.9M) was used as the catalyst because of improved control over molecular weight compared with other catalysts. Anhydrous toluene (99.8%) was used as the solvent. All the monomers, initiators, solvents, and catalysts were stored under a dry nitrogen atmosphere in a Glove box (Vacuum Atmospheres Company, Hawthorne, CA). Chloroform and methanol were used to purify the modified PLA samples by precipitation. For termination with acetoxy group, acetic anhydride obtained from Aldrich was used without further purification.

Synthesis of PLA

Preparation of the reaction mixture was conducted inside the glove box with moisture level below 20 ppm; early experiments with higher moisture levels led to lower molecular weights, broader polydispersity, and lower yields. Lactide was recrystallized with ethyl acetate before it was synthesized. The recrystallized lactide was mixed in a reaction vessel with triethylaluminum in toluene (1.9M), anhydrous toluene (99.8%), and the desired initiator.²¹ The mole ratio of alcohol initiator to catalyst is 1 : 1 because they form living macroinitiator as shown in Figure 2. Then, the reaction vessel was sealed with a stopper under nitrogen atmosphere to prevent exposure to moisture. The reaction flask was immersed in an oil bath at 70°C for 40 h to complete the reaction. Subsequently, the reaction mixture was a viscous solution. To terminate the polymerization, two pathways were used; (1) For a hydroxyl terminating end group, the reaction mixture was removed from the oil bath and dissolved in chloroform. Then, the polymer solution was precipitated in cold methanol. The resultant white spongy precipitate was vacuum-filtered and dried in an oven at 100°C overnight under reduced pressure (about 0.5 mmHg). (2) To prepare acetoxy terminated PLA, an additional reaction was conducted in the oil bath at 70°C during polymerization. Acetic anhydride was injected into the reaction vessel through a septum stopper and allowed to

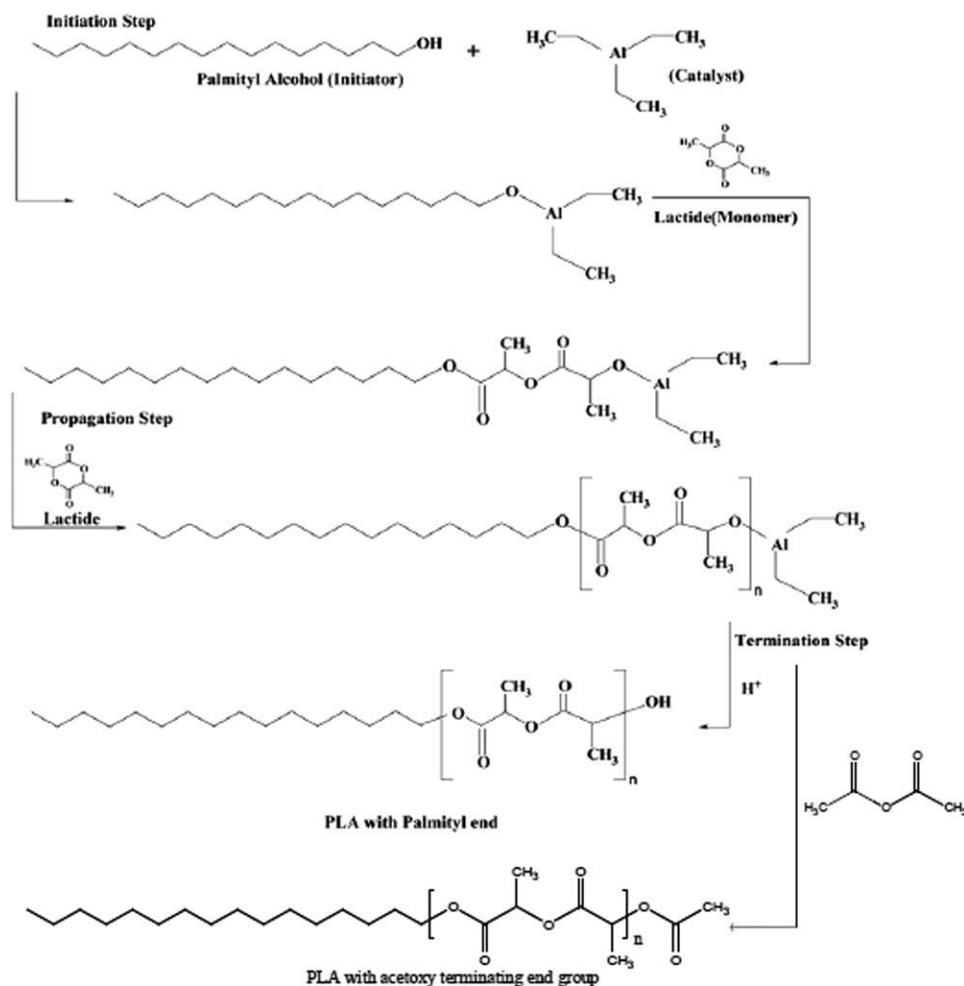


Figure 2 Reaction mechanism of synthesis of PLA with palmityl initiating end group having hydroxyl or acetoxy terminating end group.

react in oil bath at 70°C for an additional 24 h. The concentration of acetic anhydride was the same as that of alcohol initiator as shown Figure 2.

D10K

1H -NMR (500 MHz, $CDCl_3$): $H_3C-(CH_2)_{13}-CH_2-CH_2-$ (0.9 ppm), $H_3C-(CH_2)_{13}-CH_2-CH_2-$ (1.3 ppm), $H_3C-(CH_2)_{13}-CH_2-CH_2-$ (4.18 ppm), $-CH_3$ of PLA (1.6 ppm), and $-H$ of PLA (5.2 ppm).

B10K

1H -NMR (500 MHz, $CDCl_3$): $H_3C-(CH_2)_2-CH_2-$ (1 ppm), $H_3C-(CH_2)_2-CH_2-$ (1.3 ppm), $H_3C-(CH_2)_2-CH_2-$ (4.2 ppm), $-CH_3$ of PLA (1.6 ppm), and $-H$ of PLA (5.2 ppm).

Φ 10K

1H -NMR (500 MHz, $CDCl_3$): $C_6H_5-CH_2-$ (7.2 ppm), $C_6H_5-CH_2-$ (4.4 ppm), $-CH_3$ of PLA (1.6 ppm), and $-H$ of PLA (5.2 ppm).

P10K

1H -NMR (500 MHz, $CDCl_3$): $H_3C-(CH_2)_{14}-CH_2-$ (0.8 ppm), $H_3C-(CH_2)_{14}-CH_2-$ (1.2 ppm), $-CH_3$ of PLA (1.6 ppm), and $-H$ of PLA (5.2 ppm).

P10KA

1H -NMR (500 MHz, $CDCl_3$): $H_3C-(CH_2)_{14}-CH_2-$ (0.8 ppm), $H_3C-(CH_2)_{14}-CH_2-$ (1.2 ppm), $-C(O)-CH_3$ (2.08 ppm), $-CH_3$ of PLA (1.6 ppm), and $-H$ of PLA (5.2 ppm).

Reaction mechanism

The reaction mechanism as shown in Figure 2 was followed by all the initiators used. In Figure 2, selected alcohol was reacted with triethyl aluminum to form an initiator through an anionic coordination mechanism.²² Propagation of L-lactide with the anionic coordination initiator (aluminum alkoxide) was carried out at 70°C for 40 h. The terminating end group was determined by termination step. A

TABLE I
GPC Analysis of Modified Poly(lactide) Samples Prepared for This Project

Sample	Initiator	Terminator	Aliphatic content (% mass)	Ant. wt.	Exp. wt.	PDI	Degree of poly.	Sorption slope ($\times 10^4$)	Sorption variance	Mole ratio of water and PLA
P4K	Palmityl alcohol	Hydroxyl	5.7	3,000	$\sim 4,000$	1.22	27.3	79.3	2.3	1.76
P6K	Palmityl alcohol	Hydroxyl	4.0	5,000	$\sim 6,000$	1.20	40.5	59	3.0	1.97
P10K	Palmityl alcohol	Hydroxyl	2.3	10,000	$\sim 10,000$	1.31	70.8	63.7	2.3	3.54
P10KA	Palmityl alcohol	Acetoxy	2.3	10,000	$\sim 10,000$	1.18	68	25.3	0.25	1.41
P30KA	Palmityl alcohol	Acetoxy	0.74	30,000	$\sim 30,000$	1.22	210.9	52.3	2.35	8.72
P90KA	Palmityl alcohol	Acetoxy	0.25	90,000	$\sim 90,000$	1.29	624.1	58.3	0.33	29.15
D6K	Decyl alcohol	Hydroxyl	2.5	6,000	$\sim 6,000$	1.20	42.3	69.3	0.3	2.31
D10K	Decyl alcohol	Hydroxyl	1.5	10,000	$\sim 10,000$	1.32	70.5	71	1	3.92
B4K	Butyl alcohol	Hydroxyl	1.8	5,000	$\sim 4,000$	1.18	27.3	120.3	0.3	2.67
B10K	Butyl alcohol	Hydroxyl	0.7	10,000	$\sim 10,000$	1.30	68.4	74.3	0.3	4.13
Φ 6K	Benzyl alcohol	Hydroxyl	1.7	5,000	$\sim 6,000$	1.20	42.5	77.7	0.3	2.59
Φ 10K	Benzyl alcohol	Hydroxyl	1.1	10,000	$\sim 10,000$	1.33	70.9	81.7	0.3	4.54
Φ 20K	Benzyl alcohol	Hydroxyl	0.5	20,000	$\sim 20,000$	1.51	140.8	81.3	2.3	9.03

Sample, sample number based on the initiator used and experimental molecular weight; Ant. wt., anticipated molecular weight (g/mol, number-average molecular weight); Exp. wt., experimental molecular weight (g/mol, number-average molecular weight); PDI, polydispersity index; Degree of poly., experimental average degree of polymerization.

hydroxyl group (-OH) was produced by obtaining a proton from cold methanol, whereas an acetoxy group (-OC(O)CH₃) was obtained by an esterification reaction between aluminum alkoxide and acetic anhydride as shown in Figure 2.

Characterization and measurements

GPC was used to determine the molecular weight and molecular weight distribution. A Waters®515 GPC was used with two 30-cm-long, 7.5-mm-diameter, 5- μ m styrene-divinyl benzene columns in series (PL gel; Polymer Laboratories, Amherst, MA; 50 Å pore-size and mixed-C as the first and second columns, respectively). The columns were equilibrated and run at 30°C using tetrahydrofuran as the elution solvent at a flow rate of 1 mL/min. A refractive index detector was used to analyze the data based on polystyrene standards. The glass-transition temperature, T_g , and the melting temperature, T_m , of the polymers synthesized were obtained by DSC (TA Instruments Q2000) based on the second heating scan of 5°C/min. Samples ranged in weight from 5 to 12 mg and were placed in sealed aluminum pans; at least three scans were taken for each sample. A Varian 500 MHz ¹H-NMR in the Chemistry Department (Drexel University) was used to confirm the structure of the polymer prepared. The solvent used for NMR was *d*-chloroform, and the temperature was 25°C. The number of scans taken was between 8 and 64, with a recycle delay of 5 sec.

A SCS1G3P-12 (Cookson Electronics Equipment) spin coater was used for coating the polymer film onto a QCM quartz crystal. Coating was performed at 3000 rpm for 60 sec. Excess solution was placed on the top of the crystal, which was then rotated at

high speed to spread the solution by centrifugal force. Spin coating effectively achieves uniform thin films. As soon as spin coating was carried out, heat treatment was conducted at 70°C for 12 h to evaporate the solvent completely.

A Masscal G1 QCM was used to determine the effect of relative humidity on sorption phenomena within polymer films at 22°C. QCM is a device that measures changes in mass through variations in the oscillation frequency of a quartz crystal from its resonance frequency. QCM is a highly mass-sensitive measuring device, which can determine mass changes as small as 1 ng/cm².^{23,24}

RESULTS AND DISCUSSION

PLA was synthesized by ring-opening polymerization of L-lactide with various alcohols as initiator. An experimental overview of experiments is shown in Table I. Samples were labeled according to the initiating alcohol (palmityl [P], decyl [D], butyl [B], and benzyl [Φ]) and the approximate molecular weight in thousands (e.g., 10K for $\sim 10,000$ molecular weight). For example, a 10,000 molecular weight sample initiated with decyl alcohol and terminated with a hydroxyl is D10K. Also, samples terminated with an acetoxy group are indicated by "A"; thus, P30KA has a palmityl initiating end group, an acetoxy terminating end group, and a molecular weight of $\sim 30,000$.

Table I and Figure 3 show the molecular weight, degree of polymerization, and polydispersity of modified PLA samples synthesized in the project measured by GPC. The polydispersity index (PDI) is the ratio of weight-average molecular weight to the number-average molecular weight. DP is the average

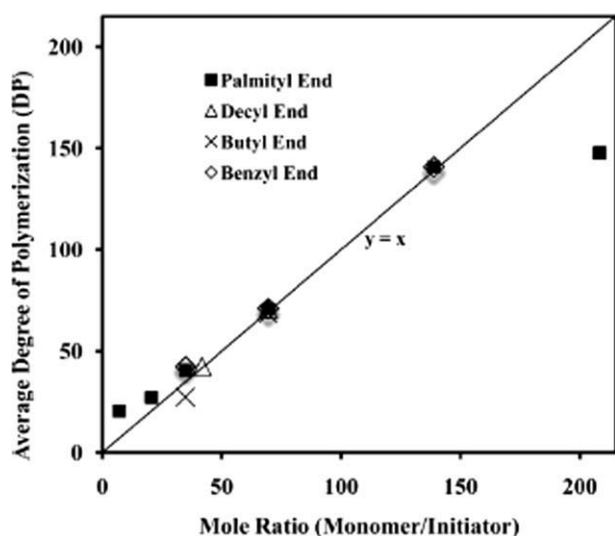


Figure 3 Comparison of theoretical ($y = x$) and experimental degree of polymerization.

degree of polymerization of the PLA. The PDI is typically in the range of 1.2–1.3, which is typical for the triethyl aluminum catalyst.^{5,21} The measured values of molecular weights and degrees of polymerization are similar to anticipated values based on the monomer : initiator ratio. As shown in Figure 3, the measured and anticipated degree of polymerization agrees quite well for intermediate molecular weights. These results indicate that alcohols used were true initiators for lactide polymerization, and triethylaluminum acted as the catalyst. The low PDI (<1.5) represented minimal transesterification.

DSC analysis

DSC measurements show that the PLA samples with different degrees of polymerization (N) have different glass-transition temperatures (T_g). The variation of T_g with degree of polymerization agrees well with the Fox and Flory²⁵ equation:

$$T_g(N) = T_g(\infty) - C/N \quad (1)$$

Here, $T_g(\infty)$ is the glass-transition temperature for infinite molecular weight and C is a constant.

In Figure 4, the glass-transition temperature is plotted versus reciprocal of degree of polymerization of all the samples. The glass-transition temperature data were fitted to eq. (1) by linear regression with $T_g(\infty) = 338.8$ K (65.8°C) and $C = 741.1$.

Sorption experiments

Sorption of water into modified PLA samples was measured by QCM. Generally, the sorption isotherms for PLA are nearly linear for relative humid-

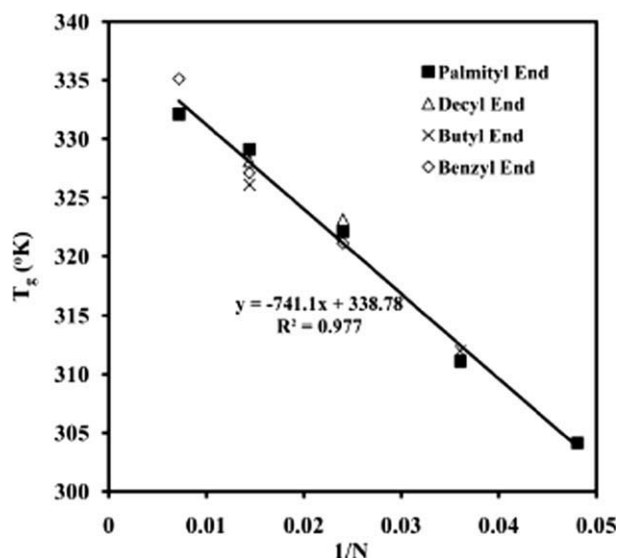


Figure 4 The glass-transition temperature versus reciprocal N .

ity below 50%; thus, in this article, only the slope of the sorption isotherm is reported. For each sample, at least three different films were prepared and at least three cycles of humidity changes were performed to determine the slope. Figure 5 displays a bar chart of the slopes of sorption isotherms for all the modified PLA samples; the error bars represent the 95% confidence intervals for slope based on multiple measurements. The unit of slope is $\text{gH}_2\text{O}/(\text{gPLA} \times \text{relative humidity})$, with the relative humidity as a fractional value; thus, the value of the slope represents the amount of water ($\text{gH}_2\text{O}/\text{gPLA}$) that would be absorbed at 100% relative humidity if the linear portion of the sorption isotherm were extrapolated to 100% relative humidity. Samples with

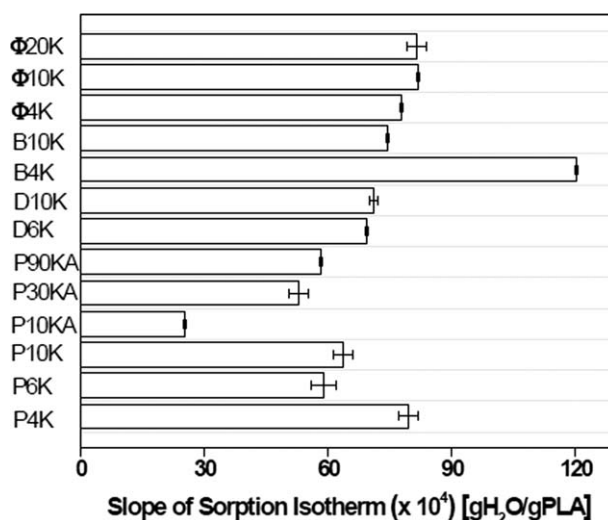


Figure 5 Summary of sorption results with 95% confidence interval.

larger slopes indicate that more water is absorbed into these samples than samples with lower slopes.

Comparison of PLA with palmityl end groups

All of the samples labeled P(number)K correspond to modified PLA initiated with palmityl alcohol and terminated with a hydroxyl. As molecular weight decreases, aliphatic content of the polymer (i.e., the mass fraction of the polymer that is composed of the palmityl end group) increases from $\sim 2.3\%$ (P10K) to $\sim 5.7\%$ (P4K) by mass, and the moisture sorption is lower at a molecular weight of 6000 than at either 4000 or 10,000 (as shown in Fig. 5). One-way analysis of variance statistical analysis indicated that the differences in moisture sorption of P4K, P6K, and P10K were statistically significant at 95% confidence level; the confidence intervals are shown as error bars in Figure 5. For P10K and P6K, there is a decrease in sorption with an increase in aliphatic content, but, for P6K and P4K, the sorption increases significantly despite the increase in aliphatic content. This indicates that both molecular weight and aliphatic content contribute toward sorption properties. At low molecular weight, the hydrophilicity of the hydroxyl end group or increases in free volume created by higher concentration of end groups leads to higher water sorption.

The effect of the hydroxyl end group on sorption was addressed by preparing the samples P10K and P10KA; both of these samples have a palmityl end group on the initiating end and molecular weight of approximately 10,000 g/mol. The P10K sample has a hydroxyl (-OH) end group on the terminating end, and the P10KA sample has an acetoxy (-C(O)CH₃) end group on the terminating end. The aliphatic contents of both P10K and P10KA are approximately 2.3%. However, moisture sorption in P10KA is much smaller than in P10K; the sorption isotherm slope for P10K is 0.00637 gH₂O/gPLA/RH, and, for P10KA, it is 0.00253 gH₂O/gPLA/RH; P10KA absorbs approximately 40% as much water as P10K. Replacement of the hydrophilic hydroxyl group with an acetoxy group can either lead to a reduction in hydrophilic binding sites for water sorption or lead to a reduction in available free volume for water sorption. Based on 10,000 g/mol of molecular weight, this change in sorption corresponds to approximately two molecules of water binding to each hydroxyl group.

Acetoxy end-capped PLA polymers were prepared at higher molecular weights and correspondingly lower aliphatic contents. P10KA, P30KA, and P90KA are 2.3%, 0.74%, and 0.25% aliphatic, respectively. At higher molecular weights (and lower aliphatic contents), the slope of the sorption isotherm increases and seems to approach a limiting value of close to

0.006 gH₂O/gPLA/RH because of the aliphatic content decreasing and approaching zero. This suggests that sorption is more effectively modified by varying aliphatic content than by varying molecular weight.

The effect of varying length of initiating end group

Comparing samples with the same molecular weight and varying aliphatic content improves insight about the effect of end groups on sorption properties (as shown in Fig. 5). For polymer samples with approximately 10,000 g/mol molecular weight (B10K, D10K, and P10K), increasing the aliphatic content from 0.7% (in B10K) to 2.3% (in P10K) causes a consistent decrease in water sorption with an overall decrease of about 14%. Similarly for 6000 molecular weight samples, when aliphatic content increases from 2.5% (D6K) to 4.0% (P6K), the water sorption decreases by almost 15%. In both these cases, higher hydrophobic content results in reduced sorption properties of the samples.

Sorption in low-molecular-weight PLA

Mass uptakes of water in the two 4000 molecular weight samples (B4K and P4K) were higher than all the other samples despite having higher aliphatic content. Sample B4K absorbed approximately twice the amount of water than that of P6K and was more than 50% higher than any of the 10,000 molecular weight samples. As discussed earlier, low-molecular-weight samples have a higher content of hydroxyl end groups and also may have higher free volume because of having a higher fraction of end groups; both of these factors can lead to higher sorption. The sorption of B4K (120.3 gH₂O/gPLA/RH) is much higher than P4K (79.3 gH₂O/gPLA/RH), which is likely because of the significantly higher aliphatic content of P4K. However, the glass-transition temperatures (T_g) of both B4K ($T_g = 37^\circ\text{C}$) and P4K ($T_g = 38^\circ\text{C}$) are closer to the experimental temperature (approximately 22°C) than the T_g of the other polymer samples. The properties of the polymer change near T_g , which may result in unusual behavior of the mass uptake of B4K and P4K.

CONCLUSIONS

Modified PLA samples were prepared with alcohol initiators of varying molecular weights. GPC measurements show that the experimental degree of polymerization coincides well with the theoretical degree of polymerization. These results indicate that alcohols used are true initiators for lactide polymerization and triethylaluminum acts as catalyst. DSC analysis shows that when molecular weight

increases, both T_g and T_m of PLA increased simultaneously in accordance with the Flory–Fox theory. DSC results for samples of equal molecular weight but with different end groups show that there was no significant variation in T_g and T_m because of the end groups. This is likely because of weight fraction of end groups being low enough that the thermal properties depend only on molecular weight. However, the sorption properties are significantly affected by both molecular weight and end group composition.

Moisture sorption measurements on the modified PLA samples indicate that the aliphatic content of the polymer because of the end groups contributes significantly toward sorption properties. With an increase in mass percentage of aliphatic content from 0.6% (B10K) to 2.3% (P10K), the moisture sorption decreases by about 14%. The trend in sorption with molecular weight is also affected by the terminating end group. When the terminating end group is a hydroxyl, sorption increases significantly for molecular weights below 5000. To further understand the effect of the terminating end group, acetoxy end group was introduced by esterification with acetic anhydride. When the terminating end group is hydrophobic (an acetoxy group), the water sorption decreases by about 56 wt %. Based on the mole ratio of water and PLA shown in Table I, approximately two water molecules were eliminated because of the substitution of an acetoxy for a hydroxyl terminating end group. Furthermore, double end-capped PLA such as P10kA, P30kA, and P90kA with palmityl and acetoxy end groups showed that, at high molecular weights, water sorption increases monotonically with decreasing aliphatic content.

Generally, moisture sorption in the modified PLA samples is affected by polymer composition, i.e., the fraction of the polymer that has the hydrophobic end groups (butyl, decyl, palmityl, and acetyl), the fraction that has the hydrophilic end groups (hydroxyl), and the fraction that is the polyester backbone, and by the free volume of the polymer. In this article, the polymer composition was varied systematically to observe the changes in sorption properties. In samples of high molecular weight (>30,000) where the end group compositions are close to zero, water sorption is independent of molecular weight. At moderate molecular weights (4000–10,000), the contributions of both aliphatic and hydrophilic end groups can affect sorption in logical ways. The lowest water sorption value is observed in the P10KA samples, which have hydrophobic end groups on both ends of the polymer, and the highest

water sorption value is observed in B4K, which has a short aliphatic group on the initiating end and a hydrophilic hydroxyl group on the terminating end.

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