# Effects of Temperature and pH on the Degradation of Poly(lactic acid) Brushes

Lebo Xu, Kaitlyn Crawford, and Christopher B. Gorman*

Department of Chemistry, North Carolina State University, Box 8204, Raleigh, North Carolina 28795-8204, United States

ABSTRACT: Poly(lactic acid) (PLA) brushes were prepared through surface initiated ring-opening polymerization of L-lactide. Their degradation (depolymerization) was characterized by tracking their ellipsometric thickness as a function of time by repeated emersion from buffered, aqueous solutions. The pH and temperature both had a large effect on the rate of degradation. PLA brushes do not degrade in a manner similar to that of bulk PLA. Several experiments were performed, the results of which suggest that intramolecular transesterification (backbiting) was the pathway for the degradation of the PLA brush in basic, aqueous solution, similar to what has been observed for the depolymerization of PLA oligomers in basic solution. The PLA brushes degrade very slowly in acidic solution. This behavior is similar to the degradation of PLA oligomers in acidic solution.
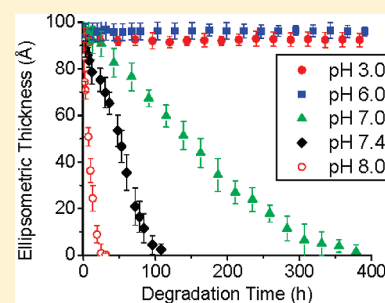
INTRODUCTION

Polymer brushes consist of a collection of polymer chains with one end attached to a surface, and their applications for surface modification have been explored extensively. Such modifications include the control of adhesion,[1] the formation of protective coatings,[2] the control of friction and wear,[3] and stabilization of nanoparticles.[4] Most attention has been focused on the growth of brushes. However, the opposite process—their degradation—could also be interesting and potentially useful. As a brush is removed from a surface, it exposes the underlying substrate. The rate at which the brush is removed dictates the temporal access of the underlying substrate. The substrate could then "turn on" as a sensor, reactive surface, etc. In this sense, the removal of the brush imparts a temporally dynamic property to the surface.

This broad idea of dynamic surfaces has had some investigation. By changing the pH of a solution above a polyampholyte brush, extension and collapse of the chains can be affected to tune the access to the surface.[5] Additionally, it has been shown that cleavage of chains from a surface can be used as another form of a dynamic surface.[6] We hypothesized that a simple way to remove the brush is through the disassembly of ester linkages in brushes. This route is used in bulk to degrade poly(esters). The sequential or random cleavage of the esters in the brush should offer very different temporal dynamics to those of the brush-based dynamic surfaces described above. The behavior of such brushes is not predictably obvious, however. The kinetics of the depolymerization process could be very different when a brush is compared to a bulk polymer sample. Indeed, bulk samples of poly(esters) take days to weeks (or longer) to degrade.[7] A brush is much smaller and thus will likely degrade substantially faster under similar conditions.

Bulk PLA can degrade via the acid- or base-catalyzed[8] hydrolysis of the ester bonds within it via random chain scission. Acid-catalyzed hydrolysis is regarded as the most facile mechanism for the degradation of bulk material,[7,9] and self-catalysis by the acidic, lactic acid resulting from the hydrolysis, has also been

illustrated.[7,9b,10] Furthermore, the hydrolysis rate of bulk material is affected by the material structure such as the degree of crystallinity and water vapor permeability.[11] Thus, the reported degradation rate could be quite different from sample to sample. For example, the reported, pseudo-first-order rate constants for degradation of bulk PLA samples with different morphologies varied from 0.13/hour[10b] to 0.41/day.[9b]

The degradation of PLA oligomers in solution has also been studied and exhibits different behavior from the bulk material.[12] At both acidic and basic pH the degradation was proposed to mainly occur by intramolecular transesterification (backbiting). A proposed mechanism for this process at elevated pH is shown in Scheme 1. Unlike in bulk PLA, the degradation of oligomeric PLA is fastest at elevated pH values. Furthermore, the terminal hydroxy groups were found to be critical for degradation. When the terminal groups were blocked by reacting them with succinic anhydride, the rate of degradation was significantly attenuated.[12a] Thus, an unanswered question is, with respect to degradation, would a PLA brush behave like a bulk sample or like oligomers in solution or differently than both?

The preparation of PLA brushes has been described previously by us and others.[13] Most typically, they are prepared by surface initiated ring-opening polymerization of L-lactide. The thickest brushes (and the longest polymers in solution) are formed at relatively low temperature (25 °C). At this temperature, yields are very low, but this is not germane to the preparation of a brush where the percentage of conversion of monomer in solution to a brush on a surface is minimal.
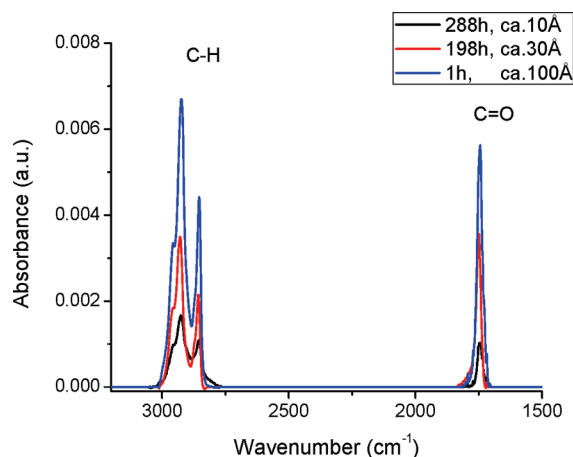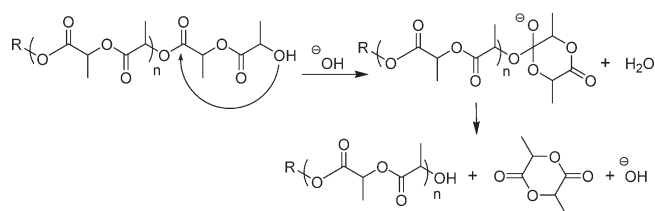
Although the synthesis of PLA brushes has been studied in some detail, we have not identified any work in which these brushes were removed. Thus, neither the conditions nor the rate

Scheme 1. Process of Backbiting To Depolymerize PLA, Forming Lactide As Proposed in Refs 12a and 12b

Figure 2. Plots of ellipsometric thicknesses versus degradation time at 37 °C with different pH values. Phosphate buffers of 10 mM ionic strength were used to control pH. Error bars represent the magnitude of the 90% confidence interval for five measurements on a sample.


Figure 1. ATR-FTIR spectra of PLA brushes grafted on silicon, initiated by surface silanol groups, after incubation in phosphate buffer, pH = 7.4, 10 mM ionic strength for 1, 198, and 288 h.

profiles for degradation have been determined. Here, the factors governing the rate of degradation of PLA brushes are investigated. The effect of pH and temperature are studied, and other experiments are presented to suggest the likely mechanism for this process.

■ RESULTS AND DISCUSSION

A. Preparation of PLA Brushes. PLA brushes of ca. 10 nm thickness were prepared via surface initiated ring-opening polymerization of L-lactide using silanol groups as initiators as described previously.[13d] Previously, we showed that the native silanol groups on silica were equally effective initiators as hydroxy groups presented by hydroxy-terminated self-assembled monolayers on gold.[13d] Thus, silanol groups on silica were used as initiators. The formation of PLA brushes were confirmed by attenuated total reflectance, Fourier transform infrared spectroscopy (ATR-FTIR), ellipsometry, and deionized water contact angle measurements, also as described previously.[13d]

The grafting density (σ) can be estimated from $\sigma = h\rho N_A/M$, where h is the thickness (ca. 10 nm), ρ is the density of PLA (1.21 g/cm^3), N_A is Avogadro's number, and M is the molecular weight of the polymer chains in the brush.[14] As it is not possible to measure the molecular weight of grafted PLA directly, the molecular weight is estimated based on PLA formed in solution alongside the PLA formed on the surface. Gel permeation chromatography gave a M_n of ca. 8000 Da, which provides an estimated grafting density of ca. 0.9/nm^2. Grafted polymers likely have lower molecular weights than those grown under similar
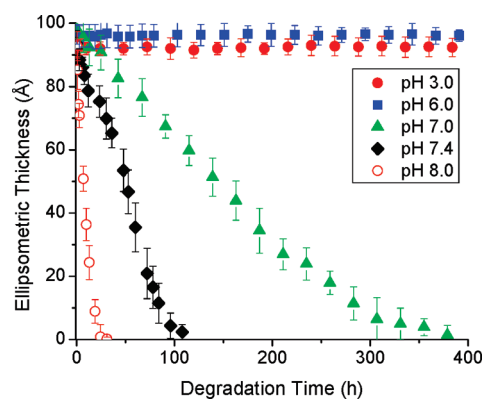
conditions from solution due to geometric confinement from the surface.[15] Thus, the actual grafting density likely is somewhat larger than estimated value. On the basis of these considerations, the PLA brushes prepared here have a relatively high grafting density and are brushlike in shape.[14,16]

B. Degradation of PLA Brushes in Aqueous Solution. To investigate whether PLA brushes can be removed from a substrate by some type of polymer breakdown, PLA brush samples with ca. 10 nm thicknesses were soaked in phosphate buffer solution of pH 7.4 (10 mM ionic strength). After a given reaction time, samples were removed and characterized by ellipsometry and ATR-FTIR. The ATR-FTIR spectra of PLA brushes with different incubation times are shown in Figure 1. The measured ellipsometric thicknesses of each sample are also marked in the figure caption. After 198 h of soaking in aqueous solution, the ellipsometric thickness of the brush decreased to ca. 3 nm. Compared to the original value, the brush thickness decreased about 70%. The thickness of the brush soaked for 288 h was reduced to ca. 1 nm. These results indicate that grafting thicknesses of PLA brushes decrease with increased incubation time. The decreased thickness indicates the removal of brushes from substrate. The changes in the ATR-FTIR spectra show a similar trend. With increased soaking time, the IR intensities decreased accordingly. The ellipsometry measurements and ATR-FTIR spectra support that PLA brushes are able to be removed from the substrate by being placed in aqueous solution.

C. Effect of pH. To study the effect of pH on the degradation, PLA brushes were incubated in phosphate buffer at different pH values at 37 °C. Periodically, the samples were removed, rinsed with distilled water, and dried under nitrogen. The dry thicknesses of the brushes were measured by ellipsometry. The decrease of ellipsometric thickness was plotted versus degradation time, as shown in Figure 2.

The degradation was rapid at pH 8.0. The brush with a thickness of ca. 10 nm was totally removed in ca. 25 h. When the pH was decreased to 7.4, about 100 h was needed to remove the brush with a thickness of ca. 10 nm. Under neutral conditions, pH = 7.0, the degradation was slow. It took about 450 h to remove a brush with a similar thickness. When acidic buffers were used (pH = 6.0 and pH = 3.0), no obvious degradation was observed in this time period. Thus, the pH value has a large effect on the rate of degradation. To demonstrate this point further, brushes were incubated successively in buffer with pH = 6.0 and
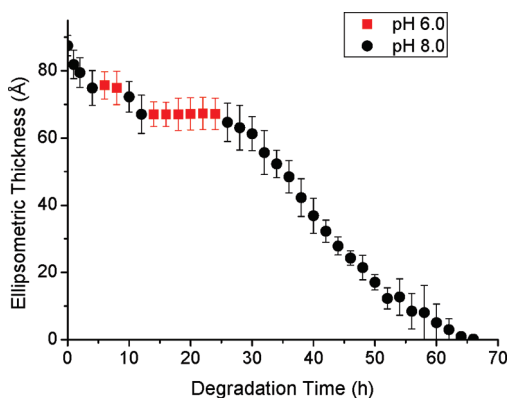
Figure 3. Plots of ellipsometric thickness versus degradation time at alternating pH values (pH 6.0 and pH 8.0) at 37 °C. Phosphate buffers of 10 mM ionic strength were used to control pH. Error bars represent the magnitude of the 90% confidence interval for five measurements on a sample.
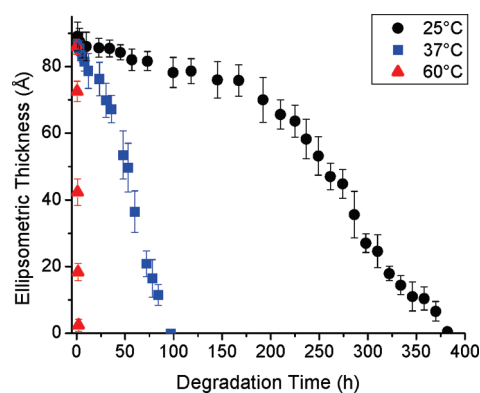

Figure 4. Plots of ellipsometric thicknesses versus degradation time at different temperatures. Phosphate buffer, pH = 7.4, 10 mM ionic strength was used to control pH. Error bars represent the magnitude of the 90% confidence interval for five measurements on a sample.

pH = 8.0. The ellipsometric thicknesses were monitored and plotted versus degradation time as shown in Figure 3.

Figure 3 shows that the degradation occurred under basic conditions and essentially stopped under acidic conditions. Thus, degradation is a process which is able to be controlled by tuning the pH value. Furthermore, the pH dependence of degradation of PLA brushes is not the same as that of bulk PLA or PLA oligomers in solution. Bulk PLA degrades well at both increased and decreased pH values.[7,9,10] PLA oligomers degrade faster at high pH but also degrade at low pH.[12a] No degradation was observed on PLA brushes under acidic pH conditions on this time scale.[17]

D. Effect of Temperature. The effect of temperature was also examined by degrading brushes in buffer (10 mM ionic strength, pH = 7.4) at different temperatures. The thicknesses were monitored as a function of degradation time and plotted in Figure 4. Higher temperature lead to more rapid degradation. The rate is quite sensitive to temperature. Raising the temperature just 12 °C accelerated the complete removal of the brush by a factor of 4.

E. Probing the Mechanism of Degradation. The first concern with regards to the mechanism of degradation of PLA is to determine whether this behavior is merely the result of hydrolysis of the Si—OR bonds anchoring the polymer chains to
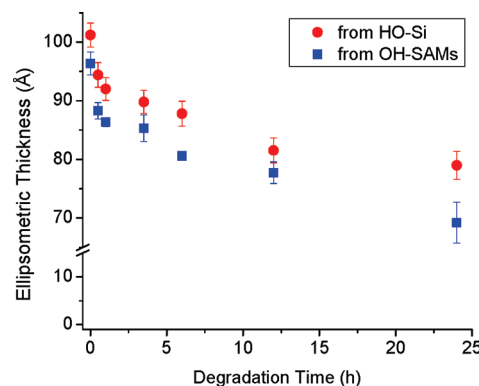
Figure 5. Plots comparing the effect of linkage group on the degradation of PLA brushes. Samples was grown from the native hydroxy groups on silicon/silica or 11-mercapto-1-undecanol SAMs on gold. Phosphate buffer, pH = 8.0, with 10 mM ionic strength were used to control pH at 25 °C. Error bars represent the magnitude of the 90% confidence interval for five measurements on a single sample.

the surface. Hydrolysis of a silyl ether can be catalyzed by either acid or base.[18] The rate of brush removal here is only increased at elevated pH, however. Nevertheless, to further rule out the hydrolysis of the Si—OR bond, the degradation of brushes with different linkage groups was compared. Degradation of PLA brushes anchored to silica was compared to that of brushes anchored to gold via 11-mercapto-1-undecanol. Hydroxyl-terminated thiol self-assembled monolayers have been reported to be hydrolytically stable for a week at pH < 13.[19] Brushes on silicon and gold substrates were incubated in buffer solution, pH 8.0, at 25 °C for 24 h. The thicknesses were tracked and are plotted in Figure 5. Little difference was observed due to different linkage, indicating that hydrolysis of the Si—OR bonds did not play a role in the overall degradation/removal of the brush. Indeed, the brushes on silica were, if anything, slightly more stable toward degradation than those on gold.

As previously discussed above, on short-chained PLA oligomers in solution,[12] degradation is faster at elevated pH but does also occur under acidic pH conditions. This has been attributed to the relative rates of backbiting at different pH values.[12] As described above, the pH dependence of the degradation process for the PLA brushes is not the same as that of PLA oligomers in solution. However, the acceleration under basic conditions is similar and thus suggests the backbiting mechanism. Several experiments were performed to support this mechanistic hypothesis.

For backbiting to be effective, the terminal hydroxy groups must be accessible to the aqueous solution. Deionized water contact angle measurements were taken to determine how water wet the brushes. The ellipsometric thickness and contact angle were measured at four time points: immediately after preparation, after samples stood in air for 12 h, after samples were subsequently soaked for 0.5 h in deionized water at 37 °C, and after subsequently standing again in air for 7 days. The results are shown in Table 1.

The freshly prepared brush had a small contact angle, showing that it is a relatively hydrophilic surface. This contact angle increased when the sample was incubated in air and decreased when the sample was placed under water. Under these conditions, no appreciable change in thickness was observed. These behaviors are consistent with a brush that can reconstruct via reorientation of the terminal groups of the individual polymer

Table 1. Deionized Water Contact Angle and Ellipsometric Thickness of PLA Brushes at Different Times

	freshly prepared	12 h in air	H₂O soaked	7 days in air
DI water contact angle (deg)	20 ± 1	46 ± 1	$<5^a$	62 ± 1
ellipsometric thickness (Å)	89 ± 2	84 ± 3	82 ± 2	82 ± 2

[a] The contact angle was too small to be accurately measured.
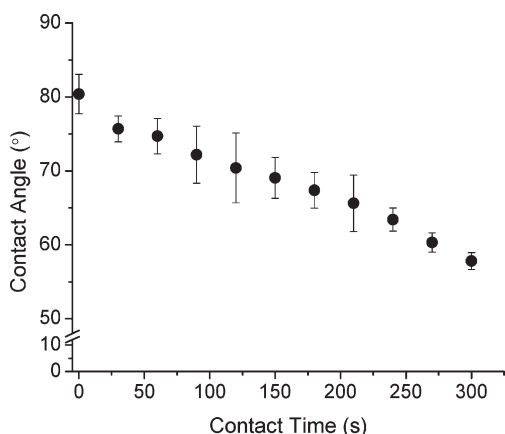
Figure 6. Plot of DI water contact angle of water on a PLA brush versus contact time. The sample was stored in air for 1 month after preparation. Error bars represent the magnitude of the 90% confidence interval for six measurements on a single sample. The change in volume of the droplet over this period due to evaporation was negligible.
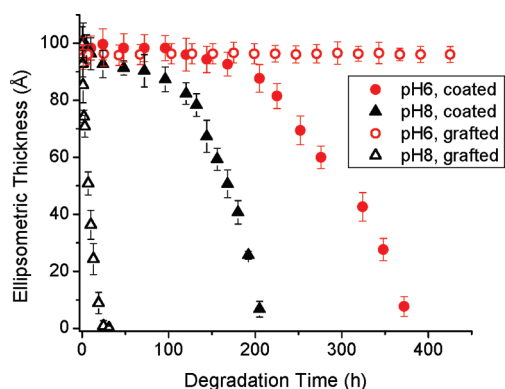
Figure 7. Change in ellipsometric thickness with time for spin-coated and grafted PLA samples of similar thicknesses. Samples were incubated in 10 mM phosphate buffer at the indicated pH values and at 37 °C.

chains.[20] Immediately after preparation, the surface presents a large fraction of hydroxyl terminal groups, which is consistent with the growth mechanism in which hydroxyl groups are accessible to catalyst to form reactive centers for propagation. After sitting in air, these terminal groups bury themselves within the brush, lowering the brush/air interfacial free energy. This process reverses when the sample is soaked in water and reverses again when placed back into the air. This process has been observed for other polymers such as oxidized, low-density

polyethylene film.[21] Thus, the hydroxyl groups are accessible to aqueous solution. This process was characterized more quantitatively by measuring the water contact angle of a droplet of water on a PLA brush as a function of time (Figure 6). The contact angle decreased monotonically.

To illustrate the difference between PLA brushes and bulk PLA, spin-coated layers of PLA were prepared on the same types of substrates and with similar thicknesses to PLA brushes. Samples were degraded in phosphate buffer solution at pH 6.0 and 8.0 at 37 °C (Figure 7). The ellipsometric thicknesses were tracked to evaluate the degradation. Note that the spin-coated samples degraded under both basic and acidic conditions, but the brush only degraded under basic conditions. Further, the brush degraded rapidly under basic conditions compared to the spin-coated samples.

We propose that the different organization of PLA chains between the grafted and spin-coated samples is the most likely cause of these different behaviors. In grafted samples, chain ends are left near the brush/solution interface after synthesis. Here, they are more able to orient/reorient so that the hydroxyl end groups can protrude into the solution. In the spin-coated samples, PLA chain ends are distributed uniformly throughout the sample. As a result, they are, on average, less able to orient/reorient so that the hydroxyl end groups can protrude into the solution. This explanation is consistent with more facile backbiting in the degradation of the brushes than in bulk (or spin-coated samples).

To support this hypothesis, water contact angles of spin-coated and grafted samples were obtained for samples stored in air and samples immersed for 1 h in water. The contact angle of spin-coated samples changed from ca. 75° (stored in air) to ca. 65° (immersed for 1 h in water). However, the contact angle of grafted samples changed from ca. 60° (stored in air) to ca. 5° (immersed for 1 h in water). This large change in the latter contact angles is consistent with reorientation of the chain ends in the brushes (and facile backbiting) but much less reorientation of the chain ends in the spin-coated samples.

To further test the backbiting hypothesis, brushes were treated with succinic anhydride. This process has been shown previously[12a] to convert the hydroxyl terminal groups into carboxylic acid terminal groups (Scheme 2), which do not undergo backbiting.

After exposing brushes to 1 M succinic anhydride/anhydrous THF solution at 37 °C overnight, the DI water contact angle, measured right after preparation, increased from ca. 5° to ca. 30°. This value matches that reported for SAMs partially functionalized with nitrilotriacetic acid,[22] supporting the conversion shown. Then the treated samples were put in buffer with pH = 8.0 at 37 °C, and the decrease in thickness over time was compared to untreated samples (Figure 8).

Treatment with succinic anhydride slowed the degradation of the brush, especially at the beginning of the trial. The results suggest the terminal hydroxy groups have a function in the degradation, supporting the backbiting mechanism. However, the treatment did not prevent degradation. We think it is likely because, over these long times, slow hydrolysis of the ester bonds removes these blocking groups. The resulting brushes can then undergo backbiting. Also, the reaction of the terminal hydroxy groups with succinic anhydride may not be complete. Considering that the terminal hydroxy groups reorganize within the brush as discussed above, some may be buried in the brush in the organic solvent (THF) used to introduce the succinic anhydride.

Scheme 2. Reaction between PLA Brush and Succinic Anhydride
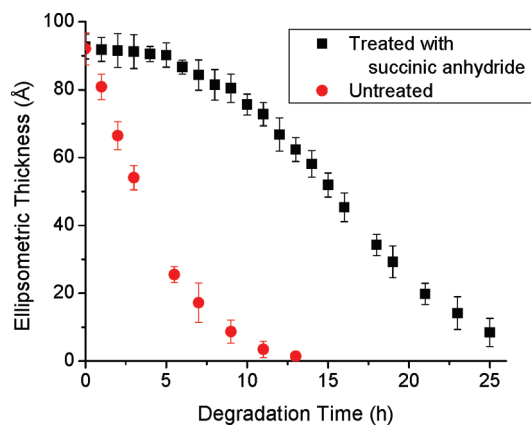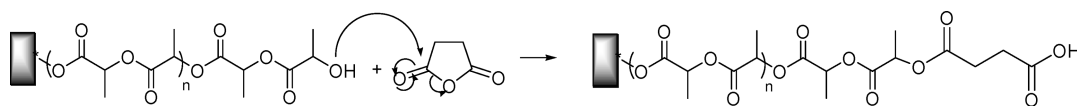
Figure 8. Plots of ellipsometric thickness of treated and untreated PLA brushes versus degradation time at 37 °C. A phosphate buffer, pH = 8.0, 10 mM ionic strength was used to control pH. Error bars represent the magnitude of the 90% confidence interval for five measurements on a sample.

CONCLUSIONS

The results shown here indicate that the thickness of PLA brushes decrease with time when exposed to aqueous solutions. The rate of this decrease is highly dependent on pH and temperature. This high sensitivity might be exploited in applications where variability in the temporal dynamics of hydrolysis is useful. Further, the principal mechanism for this decrease appears to be depolymerization due to backbiting—the same mechanism observed for depolymerization of PLA oligomers in basic solution. Yet, PLA oligomers also degrade in acidic solution, but the PLA brushes studied here do not over the time scales studied. Thus, degradation of PLA brushes is distinguished from both isolated chains and bulk material.

EXPERIMENTAL SECTION

Si/SiO$_x$ substrates with PLA brushes grown upon them were prepared as described previously.[13d] Briefly, silicon wafers were cleaned and treated by ultraviolet-generated ozone, (UVO) to prepare silanol groups on surface. The hydroxyl-terminated SAM on gold (Evaporated Metal Films TA134) was prepared by deposition of a 1 mM solution of 11-mercapto-1-undecanol (Aldrich, 97%) in ethanol for 24 h at room temperature. These substrates were reacted with an anhydrous tetrahydrofuran (THF) solution containing 100 mM L-lactide and 1 mM tin bis(2-ethyl hexanoate) in flame-dried vials for 24 h. The sealed vials were gently agitated using a multipurpose rotator (Barnstead International, Dubuque, IA).

Spin-coated PLA samples were prepared by coating PLA solutions on silanized silicon substrates. The PLA used for spin-coating was collected from the solution in which the PLA brushes were prepared. The collected PLA was dissolved in anhydrous THF to make solution with concentration of 1 mg/mL. The silicon substrates, cleaned in ethanol with sonication, were etched in 5% HF in ethanol solution and then oxidized in UVO cleaner. The treated substrates were silanized by placing them in 1% (v/v) N-hexadecyltrichlorosilane (Gelest) in anhydrous toluene for 1 h. The spin-coating was conducted on a home-built spin-coater with a rotation speed of ca. 3000 rpm. The PLA solution was dropped on the rotating substrate. The wet sample was rotated for 3 min allow solvent to evaporate. The sample was then further dried under vacuum for 1 h.

Hydrolysis/depolymerization studies were conducted in 20 mL glass vials. PLA brush samples were soaked in ca. 10 mL phosphate buffer at a given pH value. The vials were placed in an oil bath at the designated temperature. At various time points, the sample was removed from the buffer solution, rinsed with a large amount of DI water, and dried with a stream of nitrogen before ellipsometric thickness measurements.

The thicknesses of brushes were measured by a single-wavelength ellipsometer at a 70° angle (AutoEL-III, Rudolph Research, Flanders, NJ). The sample was rinsed with DI water and dried under nitrogen before measurements. Five measurements, four at the corners and one at the center, were taken on each rectangular sample with dimensions of ca. 5 mm × 10 mm. The average of those five measurements was used to calculate the thickness of each brush.

The ATR-FTIR spectra were collected on the Excalibus Series bench (Varian) with the MIRacle Single Reflection ATR kits (PIKE). The ATR crystal was a germanium crystal. The pressure to hold the sample was 530 lb. The background scans were collected in air.

Gel permeation chromatography (GPC) was performed on a Varian PL-GPC 50 PLUS system with an Alltech Jordi-Gel DVB 500 Å column. The column was calibrated using polystyrene standard samples (Easivial PS-M standards, Varian). The solvent was THF (J.T. Baker HPLC). The polymer in solution was precipitated out and washed with ethanol, dried under vacuum overnight, and dissolved in THF to make a sample with concentration of 1 mg/mL.

DI water contact angles were measured on a homemade setup. A 5 μL droplet of DI water was placed on the sample using a microsyringe. The image of DI water droplet was collected by video camera (Panasonic GP-KR222). Then the image was analyzed by ImageJ software (Image J 1.32j, Wayne Rasband, National Institutes of Health) to determine the contact angle value. A humidifier was employed to increase the humidity level to minimize the evaporation of water during the experiments.

AUTHOR INFORMATION

Corresponding Author
*E-mail: cbgorman@ncsu.edu.

ACKNOWLEDGMENT

REFERENCES

(1) (a) Raynor, J. E.; Petrie, T. A.; García, A. J.; Collard, D. M. *Adv. Mater.* **2007**, *19* (13), 1724–1728. (b) Harris, B. P.; Kutty, J. K.; Fritz, E. W.; Webb, C. K.; Burg, K. J. L.; Metters, A. T. *Langmuir* **2006**, *22* (10), 4467–4471. (c) Mei, Y.; Wu, T.; Xu, C.; Langenbach, K. J.; Elliott, J. T.; Vogt, B. D.; Beers, K. L.; Amis, E. J.; Washburn, N. R. *Langmuir* **2005**, *21* (26), 12309–12314.

(2) (a) Tugulu, S.; Klok, H. A. *Biomacromolecules* **2008**, *9* (3), 906–912. (b) Howarter, J. A.; Youngblood, J. P. *Adv. Mater.* **2007**, *19* (22), 3838–3843.

(3) Vyas, M. K.; Schneider, K.; Nandan, B.; Stamm, M. *Soft Matter* **2008**, *4* (5), 1024–1032.

(4) (a) Leermakers, F. A. M.; Zhulina, E. B.; van Male, J.; Mercurieva, A. A.; Fleer, G. J.; Birshtein, T. M. *Langmuir* **2001**, *17* (14), 4459–4466. (b) Lu, Y.; Mei, Y.; Walker, R.; Ballauff, M.; Drechsler, M. *Polymer* **2006**, *47* (14), 4985–4995. (c) Vivek, A. V.; Pradipta, S. M.; Dhamodharan, R. *Macromol. Rapid Commun.* **2008**, *29* (9), 737–742.

(5) Sanjuan, S.; Tran, Y. *Macromolecules* **2008**, *41* (22), 8721–8728.

(6) Koylu, D.; Carter, K. R. *Macromolecules* **2009**, *42* (22), 8655–8660.

(7) Siparsky, G. L. In *Polymers from Renewable Resources Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; American Chemical Society: Washington, DC, 2000; pp 230−251.

(8) Jung, J. H.; Ree, M.; Kim, H. *Catal. Today* **2006**, *115* (1−4), 283–287.

(9) (a) Vert, M.; Li, S. M.; Garreau, H. *J. Biomater. Sci., Polym. Ed.* **1995**, *6* (7), 639–649. (b) Zhang, X. C.; Wyss, U. P.; Pichora, D.; Goosen, M. F. A. *J. Bioact. Compat. Polym.* **1994**, *9* (1), 80–100.

(10) (a) Siparsky, G. L.; Voorhees, K. J.; Miao, F. D. *J. Environ. Polym. Degrad.* **1998**, *6* (1), 31–41. (b) Shih, C. *J. Controlled Release* **1995**, *34*, 9–15. (c) Schmitt, E. A.; Flanagan, D. R.; Linhardt, R. J. *Macromolecules* **1994**, *27* (3), 743–748.

(11) (a) Feng, X. D.; Song, C. X.; Chen, W. Y. *J. Polym. Sci., Part C: Polym. Lett.* **1983**, *21* (8), 593–600. (b) Grizzi, I.; Garreau, H.; Li, S.; Vert, M. *Biomaterials* **1995**, *16* (4), 305–311. (c) Cai, H.; Davé, V.; Gross, R. A.; McCarthy, S. P. *Polym. Prepr.* **1995**, *36* (1), 422–423.

(12) (a) de Jong, S. J.; Arias, E. R.; Rijkers, D. T. S.; van Nostrum, C. F.; Kettenes-van den Bosch, J. J.; Hennink, W. E. *Polymer* **2001**, *42* (7), 2795–2802. (b) van Nostrum, C. F.; Veldhuis, T. F. J.; Bos, G. W.; Hennink, W. E. *Polymer* **2004**, *45* (20), 6779–6787.

(13) (a) Choi, I. S.; Langer, R. *Macromolecules* **2001**, *34* (16), 5361–5363. (b) Möller, M.; Nederberg, F.; Lim, L. S.; Kånge, R.; Hawker, C. J.; Hedrick, J. L.; Gu, Y. D.; Shah, R.; Abbott, N. L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39* (20), 3529–3538. (c) Tretinnikov, O. N.; Kato, K.; Iwata, H. *Langmuir* **2004**, *20* (16), 6748–6753. (d) Xu, L.; Gorman, C. B. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (15), 3362–3367.

(14) Wu, T.; Efimenko, K.; Genzer, J. *J. Am. Chem. Soc.* **2002**, *124* (32), 9394–9395.

(15) Gorman, C. B.; Petrie, R. J.; Genzer, J. *Macromolecules* **2008**, *41* (13), 4856–4865.

(16) (a) Wu, T.; Efimenko, K.; Vlcek, P.; Subr, V.; Genzer, J. *Macromolecules* **2003**, *36* (7), 2448–2453. (b) Wu, T.; Gong, P.; Szleifer, I.; Vlcek, P.; Subr, V.; Genzer, J. *Macromolecules* **2007**, *40* (24), 8756–8764.

(17) The samples in acidic buffer were monitored for a longer time than that shown in the figure. The brush in buffer at pH 6.0 fully degraded in 2 months. However, the thickness of sample in buffer with pH 3.0 was unchanged after 2 months.

(18) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley: New York, 1979.

(19) Kong, B.; Kim, Y.; Choi, I. S. *Bull. Korean Chem. Soc.* **2008**, *29* (9), 1843–1846.

(20) (a) We acknowledge that this experiment does not conclusively rule out contamination via nonpolar materials from air that are then washed off when the sample was incubated in water. This contamination, however, would be slight since thickness does not change appreciably. This experiment also does not probe changes in surface morphology (which are related to change in polymer conformation) which take place over longer length scales. (b) Wallace, W. E.; Fischer, D. A.; Efimenko, K.; Wu, W.-L.; Genzer, J. *Macromolecules* **2001**, *34* (15), 5081–5082. (c) This paper shows that the solvent in contact with the oxidized polyethylene surface has a large effect on the reorientation of these oxidized groups: Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3* (5), 799–815.

(21) (a) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725–740. (b) Rassmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736–4745. (c) Wilson, M. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 8718–8719.

(22) Lee, J. K.; Kim, Y. G.; Chi, Y. S.; Yun, W. S.; Choi, I. S. *J. Phys. Chem. B* **2004**, *108* (23), 7665–7673.