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Readily Degradable Aromatic Polyesters from Salicylic Acid

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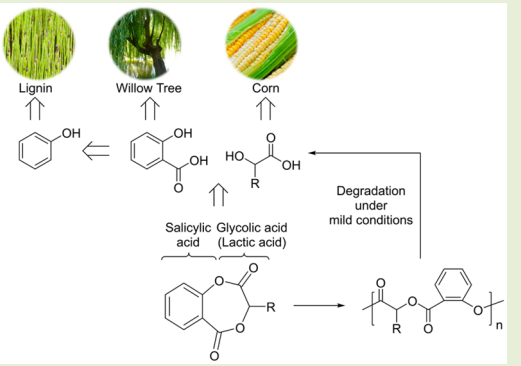
Supporting Information

ABSTRACT: Polyesters constitute around 10% of the global plastic market with aromatic polyesters, such as poly(ethylene terephthalate) (PET), being the most prevalent because of their attractive properties. As for most commercial plastics, polyesters are primarily derived from fossil resources and are not readily degradable, which raises a number of sustainability concerns. Designing polymers with competitive properties from sustainable feedstocks that rapidly degrade under mild conditions is an attractive strategy for addressing the current plastic waste problem. Here, the detailed synthesis and characterization of degradable, high molar mass aromatic polyesters derived from salicylic acid, poly(salicylic glycolide) (PSG), and poly(salicylic methyl glycolide) (PSMG) are described. The synthesis of polymers was investigated through mechanistic experiments and complementary computational studies. The glass transition temperature ($T_g \approx 85$ °C) and Young's modulus ($E \approx 2.3$ GPa) of these polyesters are comparable to those of PET. In contrast to the poor hydrolytic degradability of PET, both PSG and PSMG are readily degradable in neutral aqueous solutions (e.g., complete degradation in seawater at 50 °C in 60 days). These aromatic polyesters derived from salicylic acid have potential as future high-performance, sustainable, and degradable plastics.



Aromatic polyesters, such as poly(ethylene terephthalate) (PET), make up close to 10% of the global plastic market due to their useful thermal, mechanical, and gas barrier properties.[1,2] As with most commercial plastics, they are essentially nondegradable and largely found in single-use products, making them a major contributor to plastic waste. While about 30% of PET bottles are being recycled in the U.S.,[3,4] bottles only make up about half of the total PET resin produced, meaning roughly 85% of PET-based products are being incinerated, landfilled, or littered across our environment at their end-of-use. Importantly, estimates suggest that it takes hundreds of years for PET to decompose in natural environments.[5,6] Several attempts at accelerating the degradation of PET using glycolysis, aminolysis, and biocatalysis have been explored.[1,6]

Degradable polymers with commercially competitive properties are considered attractive alternatives because they could partly address plastic waste concerns.[7,8] Indeed, degradable polyesters including poly(lactic acid) (PLA),[9] poly(glycolic acid),[10] poly(caprolactone),[11] and polyhydroxybutyrate[12,13] have been developed successfully as sustainable and degradable polyesters. For example, PLA is being produced at about the billion-kilogram scale per year.[14−16] However, some polyesters labeled as degradable are not readily degradable in natural environments but rather require more aggressive conditions.[7,8] For example, PLA must be exposed to high temperature (e.g., 60 °C), above its glass transition temperature ($T_{g,PLA} \approx 60$ °C), and high humidity commonly encountered in industrial compositing facilities to induce hydrolytic degradation over reasonable time frames.[8,16] The incorporation of longer aliphatic chains into aromatic polyesters is a strategy used to enhance their degradation, often with an associated benefit of increasing their toughness. One example is poly(butylene adipate terephthalate) (PBAT, Ecoflex), which degrades within 3 months in soil.[15,17,18] However, incorporation of the aliphatic chains generally lowers T_g ($T_{g,PBAT} = -30$ °C),[15] which limits applications. In this regard, the development of polyesters with both high T_g and facile degradation characteristics under mild conditions is still a major challenge.

Among others, polyesters from salicylic acid are promising given their aromatic structures and sustainable origins.[19] Uhrich and co-workers were pioneers in developing poly(anhydride-esters) from salicylic acid for potential medical applications.[20−23] Poly(salicylic glycolide) (PSG) and poly(salicylic methyl glycolide) (PSMG) are also promising sustainable polyesters, developed by the groups of Shalaby[24] and Baker.[25] Their research demonstrated the feasibility of synthesizing moderate molar mass polymers (~10 kg mol^{-1} for PSG and ~22 kg mol^{-1} for PSMG) and their potential degradability for biomedical applications. For example, a PSG

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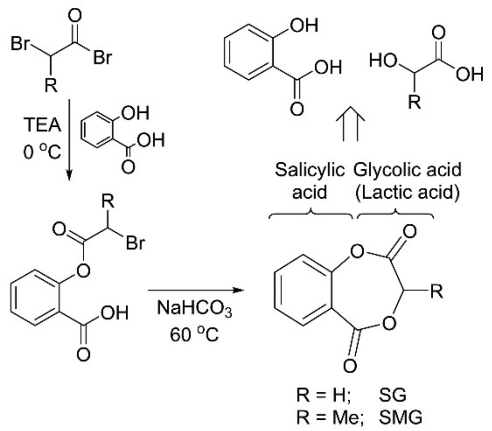
sample (≈10 kg mol^{-1}) showed 98% mass loss after 17 days in phosphate buffer solution (PBS, pH 7.3) at 50 °C.[24] In addition, these polymers exhibited good sterilization radiation stability in accelerated aging tests.[24,26,27] However, the polymerization, mechanical properties, and degradation kinetics have yet to be studied in full detail.

The present study includes (*i*) synthesis of high molar mass PSG and PSMG in a controlled manner, (*ii*) investigation of the detailed polymerization mechanism, (*iii*) evaluation of mechanical properties, (*iv*) characterization of structure−property relationships, (*v*) assessment of degradability under different aqueous conditions, and (*vi*) information on the degradation mechanism. We conclude that polyesters derived from salicylic acid exhibit great potential as future sustainable and degradable plastics.

Two types of salicylate cyclic ester compounds, salicylic glycolide (SG) and salicylic methyl glycolide (SMG), were prepared in high purity (Scheme 1).[24,25] Nuclear magnetic

Scheme 1. Synthesis of Salicylic Glycolide (SG) and Salicylic Methyl Glycolide (SMG)



resonance (NMR, ^{1}H and ^{13}C) spectroscopy and Fourier-transform infrared spectroscopy characterization data for both compounds were consistent with data reported in the literature (Figures S1−S6).[24−27] Additionally, X-ray crystallography results indicated they are seven-membered rings (Figure S7), which is consistent with electrospray ionization mass spectrometry results (Supporting Information).

The ring-opening transesterification polymerization (ROTEP) of SG and SMG was carried out in solution with benzene dimethanol (BDM) as an initiator while varying organic solvents and catalysts (Figure 1, Tables S1 and S2). For efficient synthesis of PSG, 1,1,2,2-tetrachloroethane (TCE) and Sn(Oct)$_2$ were used, and toluene and 4-dimethylaminopyridine (DMAP) were used for the efficient preparation of PSMG. The molar mass increased linearly with increasing $[M]_0/[I]_0$ at fixed conversion for both polymerizations (Figure 1). The molar mass at the equilibrium conversion determined by ^{1}H NMR spectroscopy correlated well with the theoretical molar mass at the equilibrium conversion, suggesting a controlled polymerization process. When the solution polymerizations of SG and SMG were monitored over time by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC) analyses (Figures S8−S11), first order kinetics in monomer and linear relationships between conversion and molar mass were observed in both

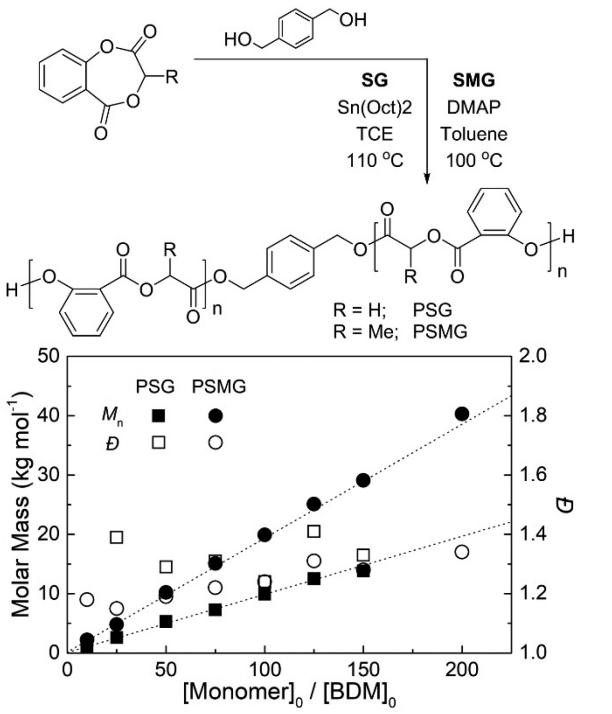


Figure 1. Solution polymerizations of SG and SMG. Solution polymerization of SG in TCE at 110 °C with $[SG]_0$ = 1.0 M, $[Sn(Oct)_2]_0$ = 0.005 M, and SMG in toluene at 100 °C with $[SMG]_0$ = 1.0 M, $[DMAP]_0$ = 0.02 M. Each polymerization was performed to the equilibrium conversion and the dashed lines indicate the theoretical molar mass at the equilibrium conversion. Molar mass and dispersity (*Đ*) were determined by ^{1}H NMR spectroscopy and SEC, respectively.

polymerizations, providing additional evidence for controlled polymerizations (Figures S12 and S13). The relatively low equilibrium conversion of SG (56%) is presumably due to less ring strain (Figure S14), which was corroborated by computational studies (see Computational Mechanistic Studies section in the Supporting Information).

A higher equilibrium conversion of SG (∼74%) was achieved in bulk conditions, as expected ($[SG]_0/[I]_0$ = 100) due to the high initial monomer concentration ($[SG]_0$ ≈ 4.8 M; Table S3). The molar mass increased upon increasing the $[M]_0/[I]_0$ ratio, resulting in molar masses up to 17.1 kg mol^{-1} (PSG) and 58.0 kg mol^{-1} (PSMG). Polymers with higher molar mass (e.g., 100 kg mol^{-1}) could not be obtained in a one-step bulk polymerization presumably due to low level impurities (e.g., water). However, the polymers could be extended by using the synthesized hydroxyl-telechelic polymers as macroinitiators. Both high molar mass PSG ($M_{n,NMR}$ = 86.8 kg mol^{-1}) and PSMG ($M_{n,NMR}$ = 91.2 kg mol^{-1}) were obtained by repeated extensions (1−3 additional monomer additions); these samples were used for the measurements of the mechanical properties and entanglement molar mass (M_e).

To provide insight into the mechanism of the ROTEP of SG, stoichiometric ring-opening was accomplished under similar conditions as for the solution polymerizations described earlier (Figure 2a). A high degree of region-selectivity was observed; based on the ^{1}H NMR spectrum, only the pathway A product was observed with no products from pathway B (Figures S15−S16 for NMR spectra). This is due to the difference in electrophilicity between the two carbonyl groups and steric effects, consistent with a previous report.[25] This also

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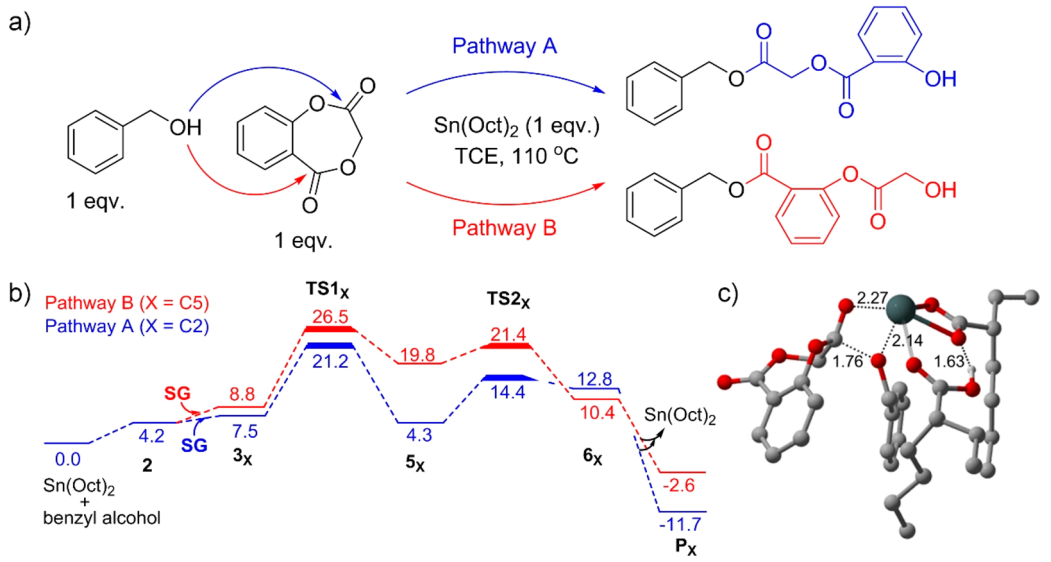

Figure 2. (a) Stoichiometric ring-opening reaction of SG. (b) Gibbs free energy (kcal mol^{-1}) profiles for pathways A and B involved in the ROTEP of SG catalyzed by $Sn(Oct)_2$. (c) Optimized transition state geometries involved in the nucleophilic addition step ($\mathbf{TS1}_X$) through pathway A. The bond distances are in Å. Computational calculations were at the $SMD_{(DCM)}$/M06/6-311+G(d,p),SDD(Sn)//ωB97X-D/6-31G(d,p),LANL2DZ-(Sn) level of theory.

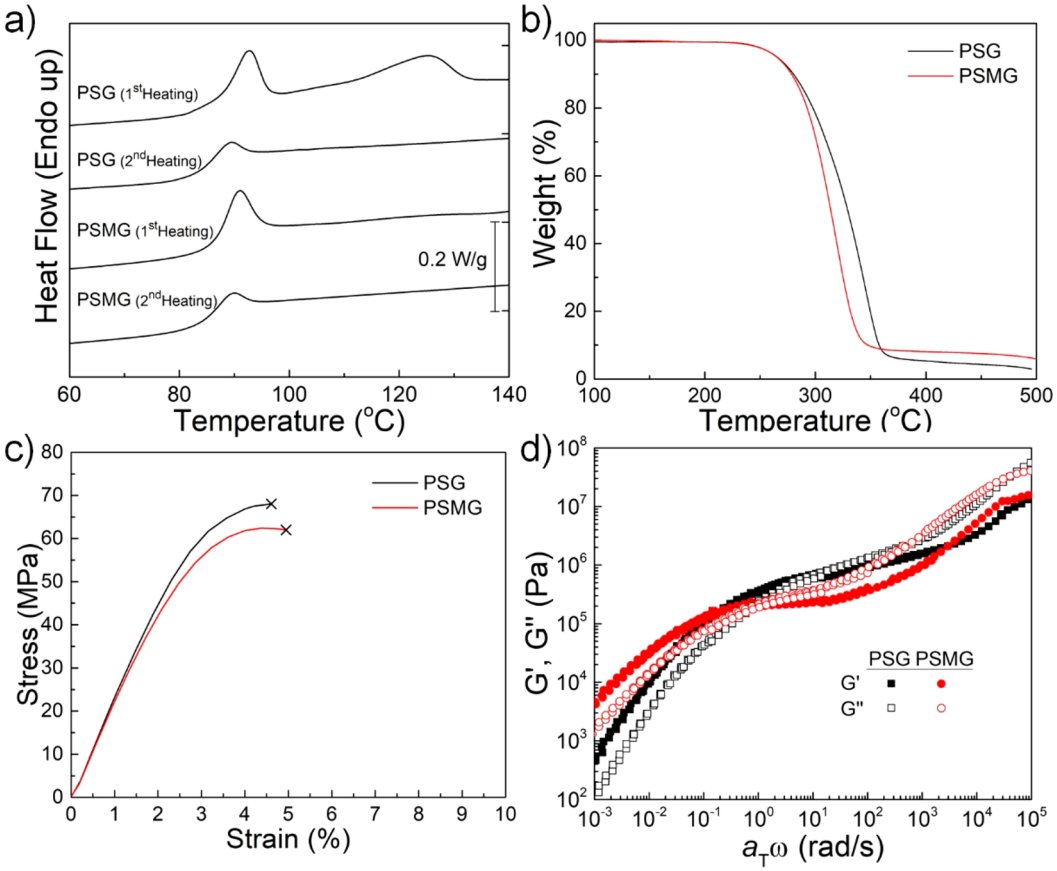

Figure 3. Thermal and mechanical properties of PSG and PSMG. (a) DSC curves (first heating, 10 °C min^{-1}; second heating, 5 °C min^{-1}), (b) TGA traces (in air, 10 °C min^{-1}), (c) strain−stress curves, and (d) master curves (reference temperature = 110 °C).

suggests that the propagating chain end is likely a phenol species instead of an aliphatic alcohol. In an analogous small molecule study using 4-methoxy phenol, only the pathway to product A was observed (Figures S17 and S18), demonstrating that propagation also occurs with high regio-selectivity via pathway A. The microstructure of PSG was investigated by ^{13}C NMR spectroscopy (Figure S19); a sharp peak in the ^{13}C spectral region corresponding to the α-carbon (61.6 ppm) suggests that the regio-specific ring-opening occurs throughout the polymerization, resulting in an almost perfectly alternating

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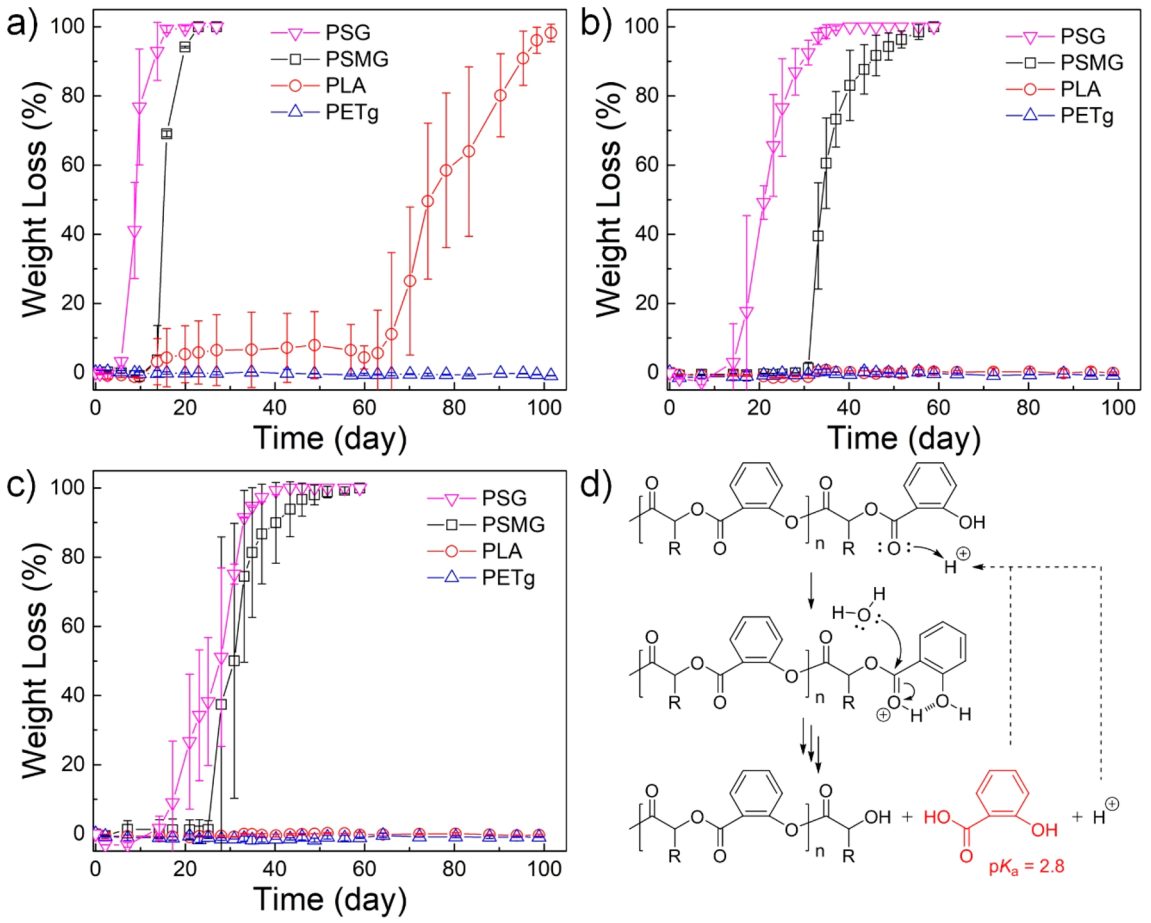

Figure 4. Weight loss profiles of polymers under the hydrolytic degradation at (a) 50 °C in 1 M PBS (pH 7.4), (b) 50 °C in seawater (pH 8.0), and (c) 50 °C in DI water (pH 7.1). (d) Plausible degradation mechanism of PSG and PSMG. Acidic nature of salicylic acid moiety facilitates degradation.

structure.[28−30] Furthermore, the ROTEP of SMG also occurs only through pathway A (Figures S20−S24). This regioselective ring opening procedure was corroborated by computational studies. For both ring-opening pathways, the nucleophilic addition of benzyloxide to the carbonyl carbon of the SG monomer ($\mathbf{TS1}_X$) was found to be rate-determining step (Figure 2b). Pathway A is computed to be preferred over pathway B by 5.3 kcal mol^{-1} due to the formation of the thermodynamically stable intermediate ($\mathbf{5}_X$) (Figure 2c), consistent with experimental observations (see Supporting Information for detailed information).

The thermal and mechanical properties of PSG and PSMG were examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile testing. Both PSG and PSMG showed $T_g \approx 85$ °C (Figure 3a), consistent with previous reports (65−92 °C).[24−27] The T_gs of PSG and PSMG are notably higher than those of other polyesters with an aromatic ring in the ortho position.[31,32] This may be due to the two planar ester linkages around the aromatic ring and a short aliphatic chain. PSG, as precipitated, displayed a melting peak at $T_m = 125$ °C during the first heating cycle but no melting endotherm during the second heating cycle, likely due to slow crystallization kinetics.[32,33] In contrast, no melting peak was observed in PSMG as expected due to its atactic structure. Both PSG and PSMG displayed $T_d \approx 265$ °C (T_d, defined by the temperature of 5% mass loss in air), demonstrating that they are thermally robust (Figures 3b and S25 for isothermal experiments at 100 °C).

The high molar mass PSG and PSMG samples were used for tensile testing and dynamic mechanical analysis (DMA). The PSG and PSMG displayed tensile strength of $\sigma_B = 64.4 \pm 3.2$ MPa, elastic modulus of $E = 2.3 \pm 0.1$ GPa, and elongation at break of $\varepsilon_b = 4.7 \pm 0.3\%$ (measured by following the ASTM D1708 protocol, Figures 3c and S26). Their tensile strengths and elastic moduli are comparable to PLA ($\sigma_B \approx 32$ MPa, $E \approx 2.2$ GPa)[34] and PET ($\sigma_B \approx 58$ MPa, $E \approx 1.7$−2.7 GPa),[35,36] while their elongation at breaks are comparable to PLA ($\varepsilon_b \approx 6\%$)[34] but lower than PET ($\varepsilon_b \approx 50$−300%).[35,36] The brittle nature for PSG and PSMG is due to the relatively large M_e; the M_e values of PSG (5.7 kg mol^{-1}) and PSMG (4.8 kg mol^{-1}) were evaluated by the plateau modulus (at minimum tan δ) in DMA (Figures 3d and S27 for dynamic strain sweep) and are similar to that of PLA ($M_e \approx 4.0$−8.7 kg mol^{-1}),[37,38] but higher than PET ($M_e \approx 1.2$−1.5 kg mol^{-1}).[35,39] The large M_e means that there are fewer entanglements at equivalent chain length available to resist deformation, which can promote brittle fracture.[53] However, we expect that the brittle nature of PSG and PSMG could be remedied to produce soft, ductile, and tough materials by employing one of the many established strategies for toughening PLA.[40]

Hydrolytic degradation experiments were performed by immersing PSG and PSMG into various aqueous media such as phosphate buffer solution (PBS, pH 7.4), artificial seawater

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(pH 8.0), deionized (DI) water (pH 7.1), and 0.1 M NaOH solution (Figures 4a−c and S28 and S29). As model systems, these conditions provide strong evidence of degradability in natural environments (e.g., ocean), in vivo, and industrial composting systems. The degradation experiments at 50 °C allowed us to observe the completion of the degradation over experimentally accessible time frames. The degradation experiments of PLA and poly(ethylene terephthalate-*co*-isophthalate) (PETg) under the same conditions were simultaneously evaluated for comparison. PLA was selected as a representative degradable polyester and PETg was selected as another control sample because of its similar chemical and physical characteristics (e.g., modulus, chemical structure, T_g, and amorphous nature) to PSG and PSMG.

Upon immersion in all aqueous media at 50 °C, both PSG and PSMG showed significant weight loss after a short induction time (within 30 days; Figure 4a−c). In contrast, PLA showed slower weight loss; PLA degraded over longer induction time (≈60 days) in PBS and did not show any weight loss in seawater and DI water for 100 days. PETg under the same condition did not show any weight loss over 100 days. This accelerative degradation of PSG and PSMG occurred in PBS at a lower temperature (37 °C) after a longer induction period (≈110 days; Figure S28). This suggests that complete degradation of PSG and PSMG may occur in other aqueous media with a longer induction time at a lower temperature, which would be even more attractive for applications. In addition, PSG and PSMG showed faster weight loss profiles in alkaline aqueous solution (0.1 M NaOH) than PLA (Figure S29). The degradation products from PSG and PSMG are salicylic acid and glycolic acid or lactic acid, respectively (Figures S30 and S31).

Degradation of PSG and PSMG in all the neutral aqueous media followed the bulk erosion model; the polymer samples became opaque and swollen during the induction period followed by a significant weight loss (Figure 4a−c).[8,41−45] In contrast, degradations in alkaline solution follow the surface erosion model; the polymer samples became smaller with concomitant continuous weight loss, consistent with the behavior of other polyesters under similar conditions (Figure S29).[41,54−56] When the bulk erosion occurs at a temperature lower than the T_g of the polymer, hydrolyzed products cannot readily diffuse out, resulting in accumulation of acidic degradation products inside. The localized acid can catalyze the hydrolysis of polymer chains inside, thereby accelerating the degradation (autocatalysis).[46] A variety of parameters such as hydrophilicity, crystallinity, and T_g were considered to account for the rapid degradation of PSG and PSMG.[47−49] However, those conventional factors should not be key factors, because all the polymers are amorphous and possess similar hydrophilicity (Table S4 for contact angle values). This suggests that other critical factors play a dominant role for the facile degradation behavior of PSG and PSMG.

One hypothesis for the rapid degradation of PSG and PSMG is that the salicylic acid moiety plays a critical role in acid- or base-mediated hydrolysis of polyesters (Figure 4d and Figure S32). The autocatalysis upon the degradation of PSG and PSMG is more efficient than that of PLA because the salicylic acid (pK_a 2.8)[50] generated from PSG or PSMG degradation is more acidic than lactic acid (pK_a 3.9)[51] generated from PLA degradation. This acid-amplified degradation of PSG and PSMG is consistent with the steeper slope in weight loss than PLA (Figure 4a). The electrophilicity of the carbon atom in the carbonyl group is another important parameter under basic degradations because nucleophilic attack to the carbonyl is often the rate-limiting step for ester hydrolysis in neutral/alkaline conditions.[52] The carbonyl group near the phenoxy (∼PhO-CO-CHR) is more reactive than the carbonyl that near the alkoxy (∼Ph-CO-O-CHR or CH_2-CO-O-CH_2) given that pK_a of phenol (∼10) is lower than that of aliphatic alcohols (∼16). This phenoxide is a better leaving group (weaker base). This is also consistent with the aforementioned polymerization mechanism. This suggests that the ester linkage in PSG and PSMG is more hydrolyzable under basic conditions than that in PLA (Figure S32), and is supported by the hydrolysis of monomers under basic conditions (Figures S33 and S34). In addition, under base-catalyzed hydrolysis of PSG and PSMG, the polymer chain end is phenoxide, which is more stable than aliphatic alkoxides (e.g., chain end of PLA degradation). This indicates the base-catalyzed degradations of PSG and PSMG are more thermodynamically favorable. This facilitated degradation under basic conditions is consistent with both earlier weight loss occurrence (earlier acid generation) in PBS than PLA (Figure 4a) and faster weight loss under 0.1 M NaOH than PLA (Figure S29).

To summarize the degradation mechanism, the salicylic acid moiety plays a critical role in both acid- and base-mediated degradations. The steps of rapid degradation are (*i*) polymer swells with water, (*ii*) degradation occurs inside the material in a facile fashion, (*iii*) salicylic acid is generated, and (*iv*) degradation inside is amplified by the salicylic acid (autocatalysis). The high ionic strength of 1 M PBS contributed to faster and continuous swelling, resulting in earlier weight loss occurrence than seawater or DI water.[10] In general, PSG showed slightly faster degradation than PSMG possibly due to its somewhat more hydrophilic surface (Table S4), more acidic product generation, and less steric hindrance.

In conclusion, high molar mass PSG and PSMG were successfully synthesized, and detailed polymerization kinetics and mechanisms were investigated. Both high molar mass PSG and PSMG showed relatively high T_g (≈85 °C), good thermal stability (T_d ≈ 265 °C), and high modulus. These polyesters degraded faster than PET and PLA in all aqueous media tested, including simulated seawater. The facile degradation properties were attributed to the nature of the salicylic acid moiety. These findings provide insight into the development of high T_g and readily degradable aromatic polyesters that could substitute for nondegradable PET derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.9b00890.

Experimental methods, supplementary characterization data (^{1}H and ^{13}C NMR spectroscopy, crystallography, SEC, polymerization kinetics, tensile testing, rheology experiments, degradation profiles, contact angle), computational method, and discussion on computational results (PDF)

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Notes

The authors declare no competing financial interest.

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