Supplementary Information

1. Polymerization Mechanism

PLH copolymers could be prepared using co-catalyst of *p*-TSA and SnCl₂·2H₂O (the molar ratio of *p*-TSA/ SnCl₂·2H₂O was 1/1) by polycondensation. The terminal groups of LA and HDA are firstly coordinated with the catalyst center of Sn(II), which should exist on tin(II)-oxide cluster 2 formed by the hydrolysis of tin chloride. The dehydration is drived among the carboxylate and hydroxyl ligands with formation of Sn-OH(3), as shown in Scheme S1. The proton acid TSA added to the catalyst can work as a ligand of the catalyst site. It can fill the open coordination sites of the catalyst to prevent the side reaction. Moreover, addition of TSA can also stimulate the dehydration of intermediate product, increasing the rate of reaction.



Scheme S1. Hypothetical condensation mechanism by the action of the Sn(II)–TSA systems.

2. Structure Characterization

The chemical structure of PLH was characterized by FTIR. FTIR spectrum of PLH (LA/HAD = 10/1 as an example) is shown in Figure S1. The strong peak at 1758 cm⁻¹ assigned to the absorption of the ester group in PLH. The absorption of terminal hydroxyl groups around 3480 cm⁻¹ is very weak, indicating formation of the PLH copolymer with high molecular weights.



Figure S1. FTIR spectrum of PLH.

3. Wettability

Since the interaction between water and the materials for the biological and agriculture fields is very important. The contact angle measurements were performed to estimate the surface wettability of the polymer. The sessile drop method was used to measure the angle between the solid and liquid interface. Ultra-pure water was dropped on the surface of the polymer, and the averaged contact angle was recorded at ten different places at room temperature using a goniometer (Dataphysics, Germany).

Figure S2 shows the contact angles of the copolymers with different HDA compositions. The water contact angles of the PLH sheets were found to be $89^{\circ} \pm 1^{\circ}$, $91^{\circ} \pm 1^{\circ}$, $95^{\circ} \pm 1^{\circ}$, $97^{\circ} \pm 1^{\circ}$, $99^{\circ} \pm 1^{\circ}$, and $107^{\circ} \pm 1^{\circ}$, respectively, increasing with an increase in HDA content, possibly due to the high hydrophobicity of the PHDA ($135^{\circ} \pm 1^{\circ}$), Thus, it was concluded that its hydrophobicity increased by the insertion of HDA in PLA. Therefore, the surface wettabilities of the PLH sheets are hydrophobicity and could be controlled by adjusting the chemical compositions.



Figure S2. Contact angle images of the PLH copolymers with various compositions, PLA and PHDA homopolymers. PLA (a), PLH9.3 (b), PLH7.8 (c), PLH7.0 (d), PLH6.3 (e), PLH6.1 (f), PLH5.0 (g), and PHDA (h).

4. Mechanical Measurement

The tensile modulus (E), strength at break (σ_b), and elongation at break (ε_b) of the PLH copolymers were conducted by using Kaiqiang WDT-10 testing machine in triplicate at an elongation speed of 10 mm/min. The results are shown in Figure S3.



Figure S3. Tensile stress-strain curves of PLH copolymers (PLH7.8, PLH7.0, PLH6.3, PLH6.1, and PLH5.0).

5. Hydrolytic Degradation

FTIR spectra of PLH7.0 before (a) and after (b) degradation in pH 7.4 buffer solution are shown in Figure S4. The peak at 1757 cm⁻¹ of PLH7.0 was belong to the typical signals originated from stretching vibration of carbonyl groups. After degradation for 40 days, a new peak at 1614 cm⁻¹ appeared, which assigned to the carboxylic acid group. Moreover, a broad band at 2500–3600 cm⁻¹ was observed after degradation, which could be ascribed to the hydroxyl and carboxyl groups. These results indicated the PLH degraded and formed the hydroxyl and carboxyl groups in the chain end.



Figure S4. FTIR spectra of PLH7.0 before (a) and after (b) degradation in pH 7.4 buffer solution.

The change in LA/HDA ratio during the degradation inside the polymer matrix was monitored by ¹H NMR (Figure S5). LA has its characteristic peaks at δ 5.18 (OC–CH), 1.58 (CHCH₃) and HDA has its characteristic peaks at δ 4.13 (OCH₂), 2.37 (OCCH₂), 1.57 (OCCH₂CH₂), 1.30 (CH₂CH₂CH₂CH₂CH₂). The spectra recorded from the residue of the two cases displayed, in addition to the signals characteristic of the polymer, another one arising from CH₂OH end groups. This signal is indicative of the presence of reduced molecular weight fragments in full agreement with data provided by the GPC analysis.



Figure S5. ¹H NMR spectra of PLH7.0 in CDCl₃ before (**a**) and after (**b**) incubation at pH 7.4 for 40 days.