Electronic Supplementary Information for

Kinetics and Mechanism for Hydrothermal Conversion of Polyhydroxybutyrate (PHB) for Wastewater Valorization

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S1. Tube reactors

Tube reactors for PHB depolymerization were constructed with Swagelok® 316 stainless steel tubing and sealed at both ends with fitting caps (Figure S1, left). Dimensions of the reactor were 3/8" outer diameter × 3" length with 0.049" wall thickness. For reactions where gas products were collected and analyzed, dimensions of the tube were kept the same, but one end of the tube was sealed by a bleed valve with a connection adapter instead of an end cap (Figure S1, right). To determine the internal volume of the reactors for gas product analyses, a reactor was weighed before and after filling with room-temperature water, and the mass difference was converted to volume using water's density. Quadruplicate measurements yielded an internal volume of 3.4±0.1 mL. To collect gas samples, a small piece of plastic tube was used to attach the reactor valve outlet to a gas sample collection bag (Figure S1, right). Temperature-time profiles (Figure S2) of the tube reactors were measured with a thermocouple inserted inside a reactor filled with 2 mL of water.

Figure S1. Photo of tube reactors used for depolymerization (left) and dehydration and decarboxylation reactions (right). The latter was attached to a gas sampling bag via a small piece of plastic tube.

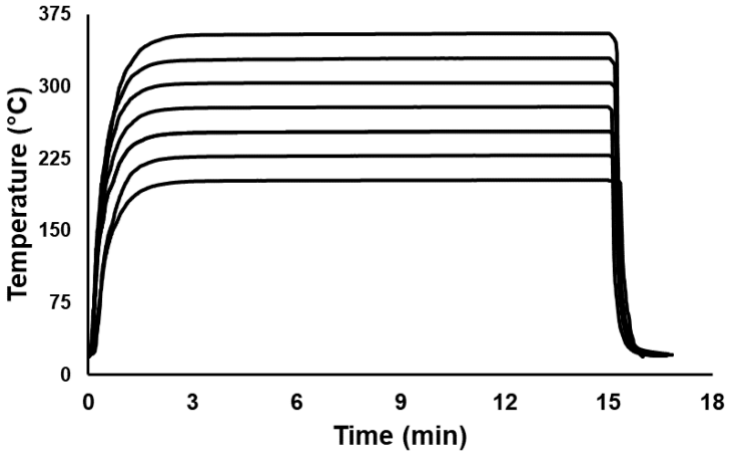

Figure S2. Temperature-time profiles of tube reactor used in hydrothermal experiments with PHB and its monomer acids. The reactor was filled with 2 mL of deionized water and heated (started at 0 min) by submersion in a fluidized sand bath (preheated to the setpoint temperatures corresponding to the plateau values observed). Cooling (started at 15 min) was accomplished by submersion of the reactor in room-temperature water.

S2. Analytic protocols

S2.1. Aqueous product analyses

Aqueous monomer acid products were analyzed by high-performance liquid chromatography (HPLC) coupled with a photodiode array ultraviolet-visible (UV-vis) detector (Shimadzu SPD-M20A). A reverse phase C_{18} column (Waters Spherisorb ODS2, 4.6 mm inter diameter × 150 mm length, 5 µm particle size, 80Å pore size) was used with 95% of pH = 2.4 H_2SO_4 solution and 5% of acetonitrile as eluents and pumped at 1 $mL \cdot min^{-1}$, the injection volume was 10 µL, wavelengths used for quantification were 210, 250, and 275 nm. Aqueous products were also analyzed for total organic carbon (TOC) by a Shimadzu TOC-L analyzer to determine yield of oligomers, which was calculated as the difference between the measured TOC value and organic carbon resulting from monomers determined by HPLC. Existence of oligomers was confirmed by hydrolyzing selected aqueous samples (initially with high oligomer contents) with an equivalent volume of 1 N NaOH and reanalyzing by HPLC. Increases in monomer concentrations in hydrolyzed samples were approximately equal to oligomer contents estimated by TOC analysis of the original samples.

S2.2. Gas products analyses

Gas products were analyzed by gas chromatography with thermal conductivity detector (GC-TCD) for air (sum of N_2 and O_2), CO, and CO_2, and flame ionization detector (GC-FID) for C_1–C_6 hydrocarbon gases (Thermo Scientific TRACE 1310). In all analyses, contents of CO or hydrocarbon gases other than propylene were <1% and were not reported here. A Supelco Carboxen 1010 column (30 m length × 0.53 mm inter diameter × 30 µm thickness) was used for GC-TCD and a Restek Alumina BOND column (50 m length × 0.53 mm inter diameter × 10 µm thickness) was used for GC-FID. For GC-TCD, the injection volume was 10 µL; the carrier gas was He, the column flow rate was 3 $mL \cdot min^{-1}$ with a split ratio of 2, the injector temperature was 100°C, the detector temperature was 250°C, the filament temperature was 300°C, the oven

temperature was 180°C, and the run time was 6 min. For GC-FID, the injection volume was 20 μL, the carrier gas was He, the column flow was kept at a constant column pressure of 4.3 psi, the split flow rate was 80 $mL \cdot min^{-1}$, the purge flow was 5 $mL \cdot min^{-1}$, the injector temperature was 130°C, the detector temperature was 200°C, the oven temperature was 135°C, and the run time was 8 min.

Yields of gas products were calculated as the sum of gas in headspace and gas dissolved in aqueous medium. Gas in headspace was calculated by the total volume of gas products and measured concentrations of individual gases. Total volume of gas was determined by volume of air and the concentration of air measured by GC-TCD. Volume of air was determined as the sum of air in reactor headspace (calculated by total reactor volume minus volume of added liquid) and air mixed into the sample during collection/storage/injection of gas samples. For each experiment, two blank samples were prepared with 40 mL (close to the total volume of gas generated during reaction) of pure CO_2 and stored and injected in the same manner as the gas samples. Volume of air was back-calculated using the measured air and CO_2 contents and volume of CO_2 (40 mL). For reactions where volume of the generated gas was not sufficient for analyses, 40 mL of H_2 was injected into the gas sampling bag. Gas dissolved in the aqueous phase of reactor solutions was calculated by assuming equilibrium with the measured gas phase concentrations at room temperature according to Henry's Law.[1]

Reference

1 W. M. Haynes, *CRC Handbook of Chemistry and Physics, 97th Edition*, CRC Press, 97th edn., 2016.