Electronic Supplementary Information

Chemical recycling of poly(butylene terephthalate) into value-added biodegradable poly(butylene adipate-*co*-terephthalate)

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Materials

Adipic acid (AA) (99%, UTEPO technology Suzhou Co. Ltd.), butanediol (BDO) (99%, Suzhou Ketone biomedical technology Co. Ltd.), tetrabutyl titanate (98%, Sinopharm Chemical Reagent Co. Ltd.), lipase PS® (Burkholderia cepacia, ≥23,000 U/g, Aladdin Industrial Co. Ltd.), potassium phosphate buffer (pH 7.4, Aladdin Industrial Co. Ltd.) were used as received. Postconsumer PBT was provided by Suzhou Sunway Polymer Co. Ltd.

Instrumentation and analysis

The apparent number-average molar mass (M_n, GPC) and polydispersity ($Đ$) of various copolymers were measured by a Waters 1515 gel permeation chromatography (GPC) using three PL Mixed-C columns at 35 °C. Chloroform was used as an eluent at a flow rate of 1.0 mL/min, and the samples were calibrated with PS® standard samples. The samples were dissolved in $CHCl_3$ with a concentration of 2.0 mg/mL.

Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent Direct-Drive II 600 MHz NMR instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard, with the solution concentration of 10 mg/mL at 25 °C. The ^1H quantitative NMR spectra were collected with a 1.50 s acquisition time, 20 s relaxation delay, 9.6 kHz spectral window, 32 transients, and 8.4 μs 90° pulse width. The ^1H-^1H gCOSY (gradient correlation spectroscopy) experiments were performed with the standard Agilent sequence. This was conducted with a 9.6 kHz spectral width, 0.15 s acquisition time, 1 s relaxation delay, and 10.25 μs 90° pulse width; a total of 8 transients were averaged for 256 increments using the States method of Orthogonal detection in f1. Processing was done with shifted sine bell weighting functions in both dimensions and zero-filling to a 2048 × 2048 data matrix prior to Fourier transformation.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass characterization was performed on a Bruker UltrafleXtreme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd: YAG laser (355 nm). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Aldrich, > 99%) and Sodium trifluoroacetate (CF_3COONa) were served as matrix and cationizing agent, respectively. The matrix was dissolved in $CHCl_3$ at 20 mg mL^{-1} and the cationizing agent was dissolved in ethanol at 10 mg mL^{-1} and they were mixed in a ratio of 10/1 (v/v). The sample was dissolved in $CHCl_3$ at 10 mg mL^{-1}. Sample was prepared by depositing 0.5 μL of the mixture of matrix and cationizing agent on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 µL of the sample on a spot of dry matrix, and adding another 0.5 µL of the mixture of matrix and cationizing agent on top of the dry sample. The plate was inserted into the MALDI source after drying. The mass scale was calibrated externally using the peaks obtained from peptide standard at the molecular weight range under consideration. The sample was conducted in reflectron mode. And the data analysis was performed with Bruker's FlexAnalysis software.

Thermogravimetric analysis (TGA) was carried out on an SDT-2960TG/DTA TA Instruments at a heating rate of 10 °C min^{-1} from room temperature to 700 °C under nitrogen atmosphere.

Differential scanning calorimetry (DSC) was measured from -70 C to 250 °C on a TA Q100 instrument under a nitrogen atmosphere at a scanning rate of 10 °C /min for about 3-5 mg samples. The first cooling and second heating scans were used to determine the melting and crystallization peaks. T_m was taken from the peak temperature of the melting endotherm.

X-ray diffraction (XRD) data were acquired on X' Pert-Pro MPD diffractometer with a Cu Ka radiation source at room temperature (~ 25 °C). The spectra were recorded in the range from 10^o to 35^o.

Dynamic mechanical analysis (DMA) was carried out on a TA Instrument Q800. Rectangular samples with size of 30 mm × 5 mm were clamped in multi-frequency-strain mode using tension: film ramp. The frequency was 1 Hz, while the furnace heated at 3 °C/min from -100 °C to the temperature above which the storage modulus of the sample was too low to be measured by the instrument. T_g measurements were recorded using the maximum in tan δ peak. All DMA test strips were dried overnight at 50 °C under vacuum to remove residual water. The measurement was replicated up to 5 times for each sample.

The copolyesters were dried at 50 °C under vacuum for 24 h to remove residual water prior to compression molding. Films (0.2 mm thick) were pressed between two PTFE sheets at 160 °C and 10 MPa for 4 min before immediately quenching in a cold press at room temperature under a pressure of 10 MPa. Tensile tests were performed at an Instron model 5966 universal material testing system, which maintained under the same conditions and operated at an extension rate of 10 mm/min. Dumbbell-shaped tensile-test specimens (central portion, 2.96 mm width × 0.2 mm thick; gauge length 18 mm) were cut from the sheets and conditioned at room temperature for 24 h.

Copolyester films (disc-shape with d = 0.2 mm) were incubated in shaking table at 37 ± 0.1 °C, 120 rpm/min, in duplicate, in sample bottles containing potassium phosphate buffer (pH = 7.4, the ratio is 10 mg sample to 1 mL buffer), in the presence of lipase PS® (1 mg/mL). Reference samples were in similar sample bottles containing potassium phosphate buffer without lipase PS®. The solution was changed every 3 days. At each time point, samples were removed from the solution and washed with distilled water several times, and dried at 35 °C under vacuum for 12 h. Finally, the degradation products were weighted. The biodegradability was investigated by the weight ratio m/m_0, where m_0 and m were initial weight and the weight after degradation.

Experimental Section

Synthesis of PBA diol

The PBA diol was prepared via the traditional melt condensation polymerization strategy as shown in Scheme S1. A certain amount of butanediol (7.96 g) and adipic acid (10 g) were added into a flask and polymerized at 180 °C in nitrogen atmosphere. After 90 min, the temperature was raised to 230 °C and $Ti(n\text{-}C_4H_9O)_4$ (0.02 wt%) was added as catalyst. The condensation polymerization was conducted under vacuum condition for another 30 min to obtain PBA diol with ideal molecular weight. The chemical structure was determined by ^1H quantitative NMR, and the molecular weight and polydispersity $Đ$ were characterized by gel permeation chromatography (GPC) as 5.2 kg mol^{-1} and 1.8, respectively.

PBAT structure analysis by ^1H NMR

Peak f (δ = 3.69 ppm) in quantitative ^1H NMR spectra was used as a chain end proton for polymer structure estimation. The total repeating units of BT (N_{BT}) and BA (N_{BA}) in copolymers could be calculated by the integration ratio of chain end to corresponding repeating units, using the following equation:

$$\frac{I_a}{I_f} = \frac{4N_{BT}}{4} \qquad \text{(S1)}$$

$$\frac{I_g}{I_f} = \frac{4N_{BA}}{4} \qquad \text{(S2)}$$

$$M_n\left(g\,mol^{-1}\right) = 220 \times N_{BT} + 200 \times N_{BA} \qquad \text{(S3)}$$

where I_a, I_f and I_g are the integration values for the corresponding peak at positions a, f and g (Table S1), and N_{BA} and N_{BT} are the total repeating units of BA and BT, respectively.

For the degree of randomness (R) estimation, the molar fraction of terephthalate (P_T) and adipate (P_A) connected with butylene glycol (BG) units can be estimated from the integration value of three peaks (I_{TBA}, I_{ABA}, I_{TBT}), using the following equations:

$$P_T = \frac{P_{TBA}}{2} + P_{TBT} = \left(\frac{I_{TBA}}{2} + I_{TBT}\right) \Big/ (I_{TBA} + I_{TBT} + I_{ABA}) \qquad \text{(S4)}$$

$$P_A = \frac{P_{TBA}}{2} + P_{ABA} = \left(\frac{I_{TBA}}{2} + I_{ABA}\right) \Big/ (I_{TBA} + I_{TBT} + I_{ABA}) \qquad \text{(S5)}$$

where P_{TBA}, P_{TBT}, P_{ABA} are the proportions of TBA, TBT, ABA segments relative to the total intensity of butylene glycol units, respectively. The probabilities of an A unit next to T unit (P_{TA}) and a T unit next to an A unit (P_{AT}) are calculated using the following equations.

$$P_{AT} = \frac{P_{TBA}}{2P_A} = I_{TBA} \,/\, (I_{TBA} + 2I_{ABA}) \qquad \text{(S6)}$$

$$P_{TA} = \frac{P_{TBA}}{2P_T} = I_{TBA} \,/\, (I_{TBA} + 2I_{TBT}) \qquad \text{(S7)}$$

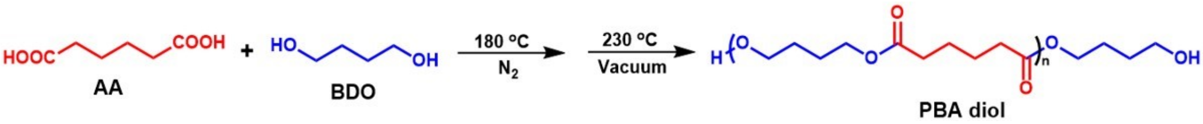
where I_{ABA}, I_{TBA}, I_{TBT} are the integration values from the corresponding ABA, TBA, TBT segments for ester-bonded methylene units, respectively.

The degree of randomness (R) is obtained by

$$R = P_{AT} + P_{TA} \qquad \text{(S8)}$$

Supplementary Scheme

Scheme S1. Synthetic route to PBA diol.



Supplementary Tables

Table S1. The peak integration value from ^{1}H NMR spectra of PBAT-*n* copolyesters with polymerization time of 180 min.

Sample	I_a	I_b	I_c	I_d	I_e	I_f	I_g
PBAT-2-1	52.2	16.2	32.9	32.7	68.3	1.00	110.9
PBAT-1-1	63.8	30.8	32.9	32.3	32.5	1.00	67.4
PBAT-1-2	67.0	42.6	23.4	22.0	12.9	1.00	35.9

Supplementary Figures

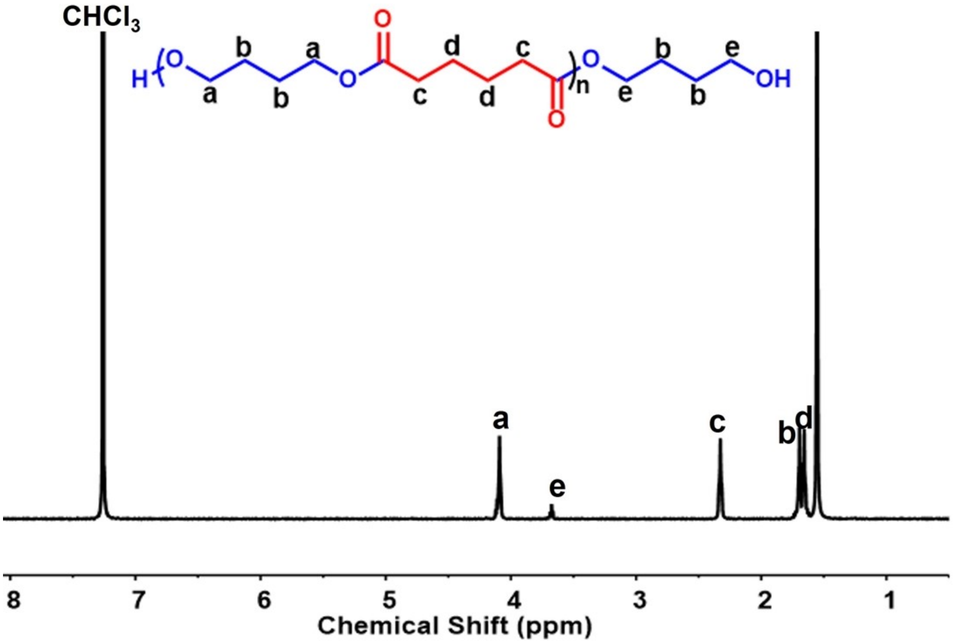


Fig. S1 ^{1}H quantitative NMR spectrum of PBA diol in $CDCl_3$. Concentration: 10 mg mL^{-1}.

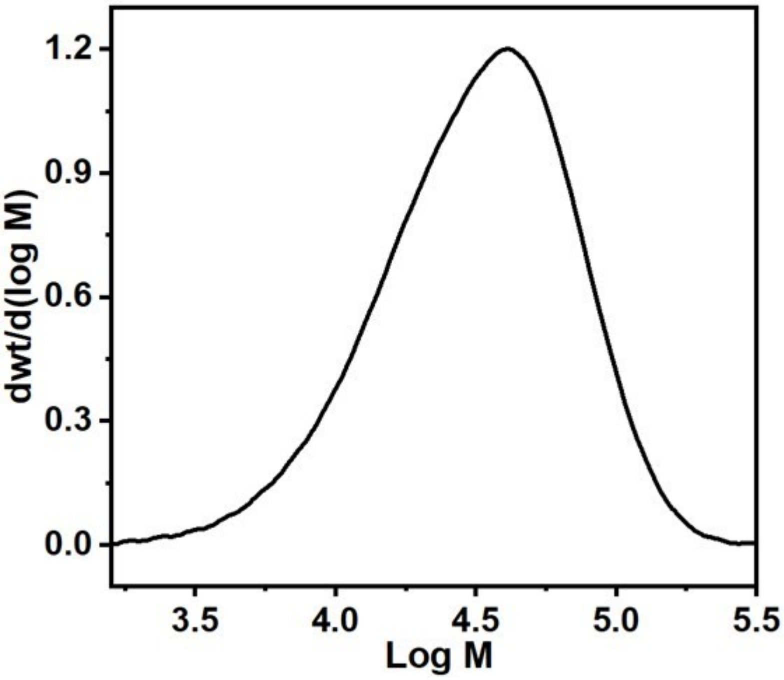


Fig. S2 GPC curve of PBA diol.

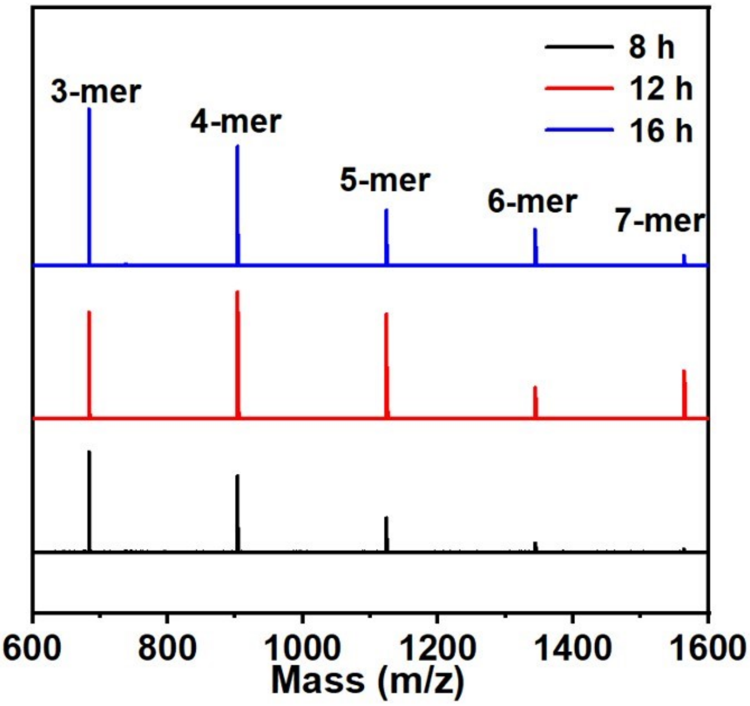


Fig. S3 MALDI-TOF mass spectra of crude COBTs before column purification with different cyclodepolymerization time (8 h, 12 h and 16 h).

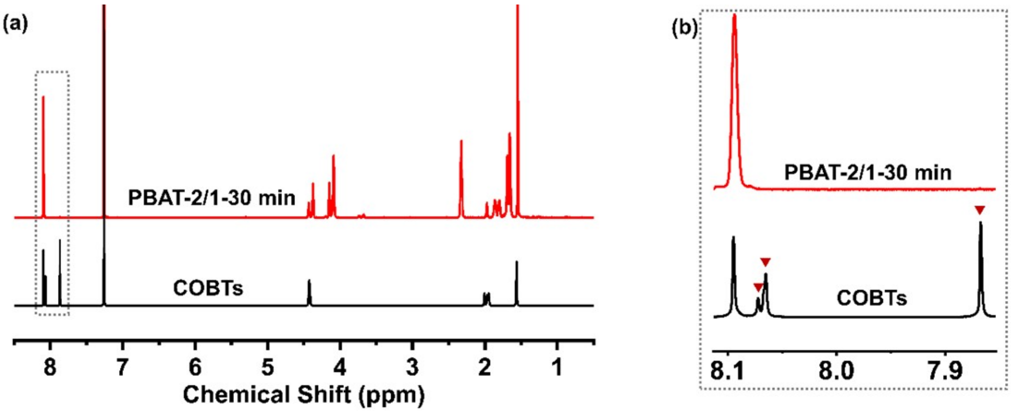


Fig. S4 ^{1}H NMR spectra (a) and partial amplification (b) of PBAT-2/1-30 min and COBTs in $CDCl_3$**.**

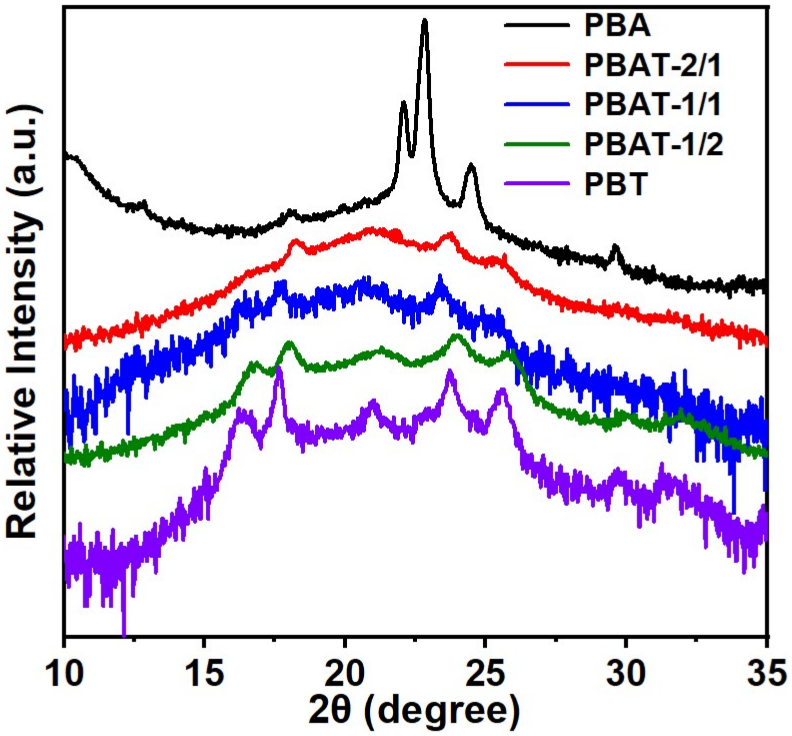


Fig. S5 WAXD profiles of PBAT copolyesters.

Supplementary References

S1. D. J. Brunelle, T. Takekoshi, *U.S. Patent 5407984* **1995**.

S2. D. J. Brunelle, G. Kailasam,J. A. Serth-Guzzo, P. R. Wilson, *U. S. Patent 5668186* **1997**.

S3. S. C. Hamilton, J. A. Semlyoen, D. M. Haddleton, *Polymer* **1998,** *39*, 3241-3252.