Supplementary Information

Efficient Chemical Recycling of Poly(3-hydroxybutyrate) to Crotonic Acid via a Sodium Crotonate/Stearyl Alcohol Catalytic System

Yankai Zhang, Chenxi Zhu, Haoyi Wang, Yunbiao Qi, Ping Sun, Quanxing Zhang and Wei Jiang*

State Key Laboratory of Water Pollution Control and Green Resource Recycling & National Engineering Research Center for Organic Pollution Control and Resource Reuse & School of the Environment Nanjing University, Nanjing 210023, China

* Corresponding author: jiangwei@nju.edu.cn, Tel: +86-25-8968-0399

1. Characterization

1.1 Gas chromatography (GC)

The quantitative determination of the synthesized CA was conducted by GC on an Agilent 7890B gas chromatograph using nitrogen as the carrier gas. The analysis was performed with an Agilent CP-cyclodextrin-β-236M-19 capillary column (50 m × 0.25 mm i.d., film thickness 0.25 μm) and a flame ionization detector (FID). The column temperature was increased from 70 to 250 ℃ at a rate of 15 ℃/min. The injector and FID temperatures were maintained at 250 ℃.

1.2 Gel Permeation Chromatography (GPC)

GPC was carried out on an Agilent 1260 Infinity II GPC/SEC System using two PL HFIPgel (7.5×300 mm, 9 μm; 7.5×50 mm, 9 μm) columns in series, with a HFIP eluent. Measurements were conducted at 40 ℃ with a flow rate of 1 mL/min. Samples were detected with a differential refractive index (RI) detector. Number-average molar mass (M_n) and dispersities (PDI, M_w/M_n) were calculated against a PMMA calibration (molar mass range 1250 Da – 1677000 Da). The polymer samples were dissolved in HPLC-grade HFIP at a concentration of 5 mg/mL and filtered through a 0.2 μm microfilter prior to analysis.

1.3 Differential scanning calorimetry (DSC)

The melting and crystallization properties of the polymer were analyzed by DSC Q2000 produced by TA Instruments. Experiments were performed under N_2 flow (50 mL/min) using aluminium pans. Samples (2-5 mg) were equilibrated at 0 ℃ then heated at a rate of 10 ℃/min to 220 ℃ and held at 220 ℃ for 3 minutes. The sample was then cooled at a rate of 20 ℃/min to 0 ℃ and held at 0 ℃ for 3 minutes. The sample was then heated at a rate of 10 ℃/min to 220 ℃ and held at 220 ℃ for 3 minutes.

1.4 Differential scanning calorimetry (NMR)

NMR spectra were obtained using a Bruker Avance II 600 MHz NMR spectrometer. The chemical shift (δ, ppm) was calibrated using the residual proton signal of the solvent.

2. Supplemental tables

Table S1. Comparison of catalytic degradation of PHB to CA[a]

Entry	Alcohol	[Catalyst] : [Alcohol] : [PHB][b]	Yield/%	Purity [c]/%	M_w [d]/kDa	
					Start	End
1	StOH	0.05 : 1 : 5	80.8	99.6	483.5	1.0
2	1-dodecanol	0.05 : 1 : 5	85.7	91.3	483.5	0.9
3	1-docosanol	0.05 : 1 : 5	80.1	99.5	483.5	1.0
4	1-hexacosanol	0.05 : 1 : 5	81.2	99.6	483.5	1.1

[a] The degradation reactions were performed at 150 °C under 3 Torr for 3 h. [b] Molar ratios are reported with respect to the PHB repeating unit; 20 g of PHB was used in each experiment. [c] Determined by GC. [d] Determined by GPC.

Table S2. Cost analysis for the bench-scale process in this study[a]

Input	Quantity	Unit	Cost (CNY)
Post-consumer PHB	20	g	0
StOH	12.58	g	1.68
NaCA	0.25	g	0.98
Electricity for process[b]	8.225	kW⓿h	3.70

[a] All calculations are based on the degradation of 20 g of PHB waste. [b] Electricity consumption was estimated based on the rated power of the equipment, including the stirred heating reactor, vacuum oil pump, and condenser circulation system.

Table S3. Typical technologies for chemical degradation of PHB to low-molecular weight chemicals.

Materials	Technologies	Reaction conditions	Products	Ref.
PHB	Catalytic pyrolysis	240°C, 30 min, with $Mg(OH)_2$ catalyst	~100% selectivity of CA	1
PHB	Pyrolysis	In cyclohexane solution, 210°C, 5 h	89 wt% yield of CA	2
PHB	Thermolytic distillation	170°C, 60 min, 150 mbar	92% yield and 98% selectivity of CA	3, 4
PHB	Hydrolytic degradation	200°C, 240–360 min	~80% recovery of BHBA	5
PHB	Catalytic pyrolysis	240°C, 6 h, with triruthenium dodecacarbonyl catalyst	22.9 wt% yield of propylene	6
PHB	Catalytic reforming	240°C, 9 h, with CeO_2 catalyst	35 wt% yield of bio-oil and 17 wt% yield of propylene	7
PHB	Acid degradation	220°C, 3 h, in phosphoric acid solution	38.2 wt% yield of hydrocarbon oils	8
PHB	Catalytic pyrolysis	240°C, 6 h, with solid phosphoric acid catalyst	30 wt% yield of hydrocarbon oils	9
PHB	Catalytic hydrogenlysis	200°C, 24 h, with Pd/C catalyst	45.6 wt% yield of butyrates, 24.4 wt% yield of butanol	10
PHB	Thermolysis and esterification	200°C, 6 h and 18 bar	60% selectivity of MC	11
PHB	Catalytic methanolysis	Refluxed at 67°C for 60 h, in methanol–chloroform solution, with sulfuric acid catalysis	68% recovery of HBME	12
PHB	Catalytic methanolysis	140°C, 2 h, with ferric chloride catalysis	88.3% yield of HBME	13

3. Supplemental figures

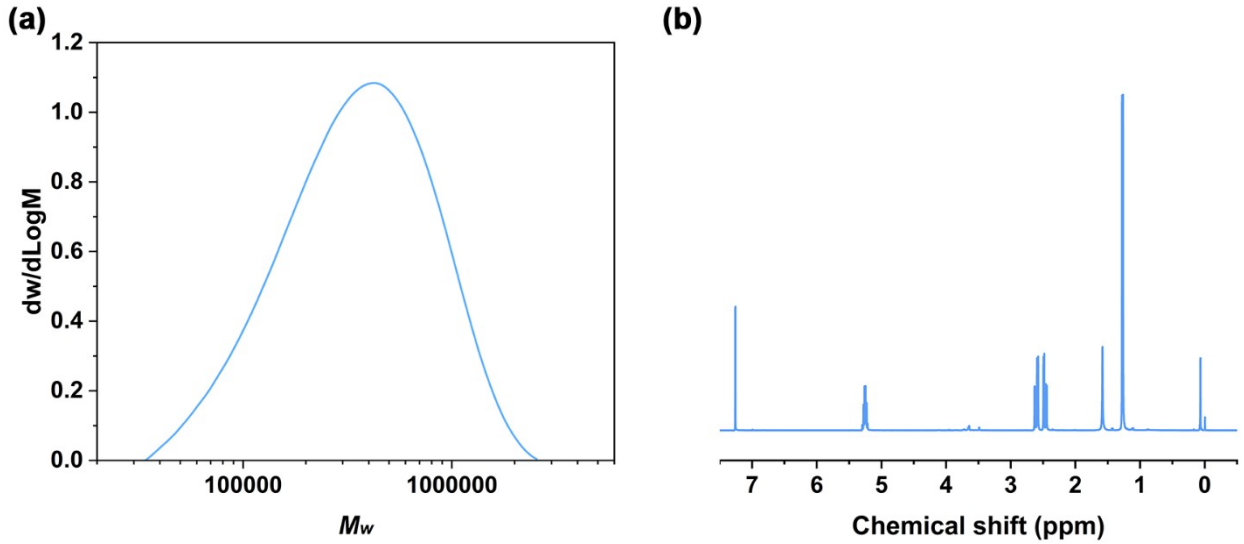


Figure S1. (1) Molecular weight distribution of commercial PHB determined by GPC. (2) ^{1}H NMR spectrum of the PHB feedstock.

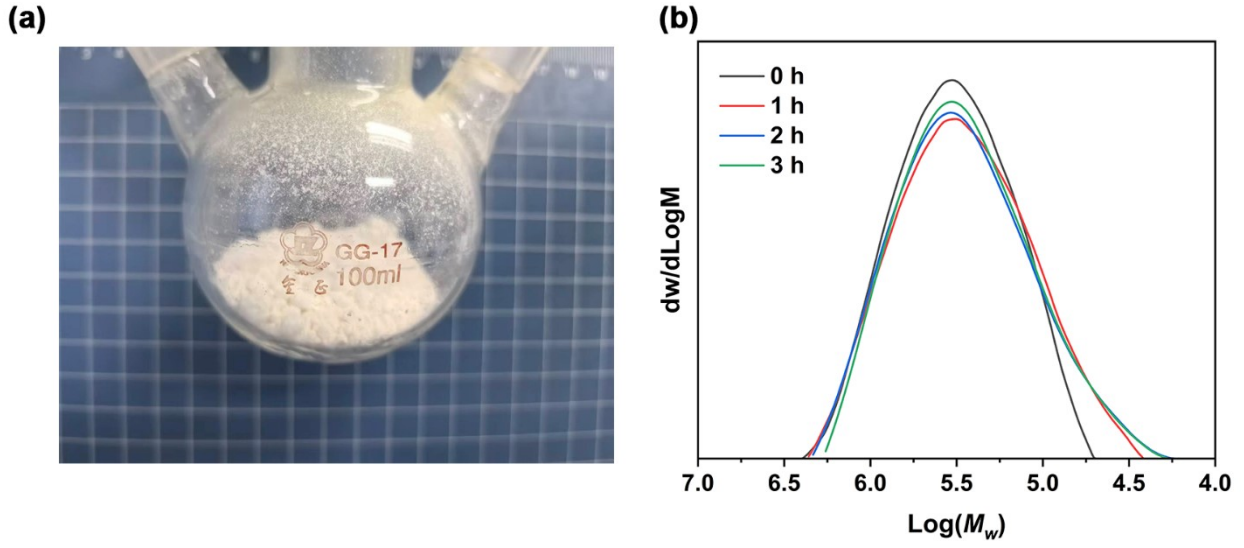


Figure S2. (a) Physical state of PHB upon heating in the absence of catalyst. (b) Molecular weight evolution of PHB without catalyst.

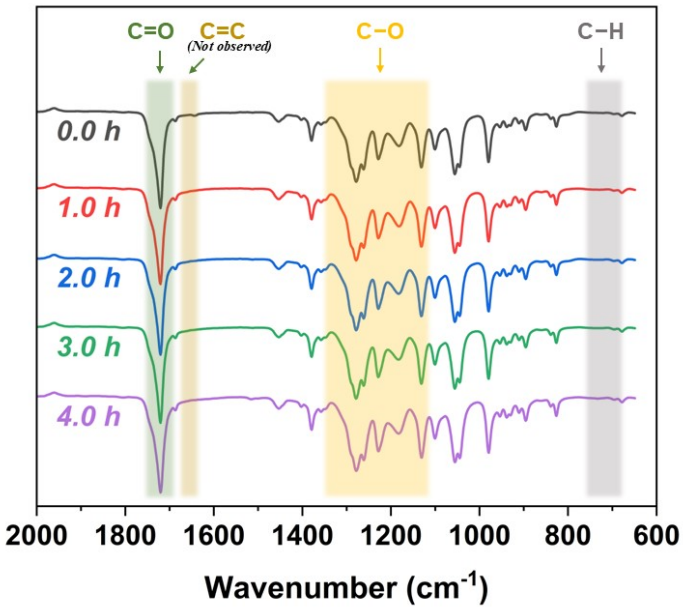
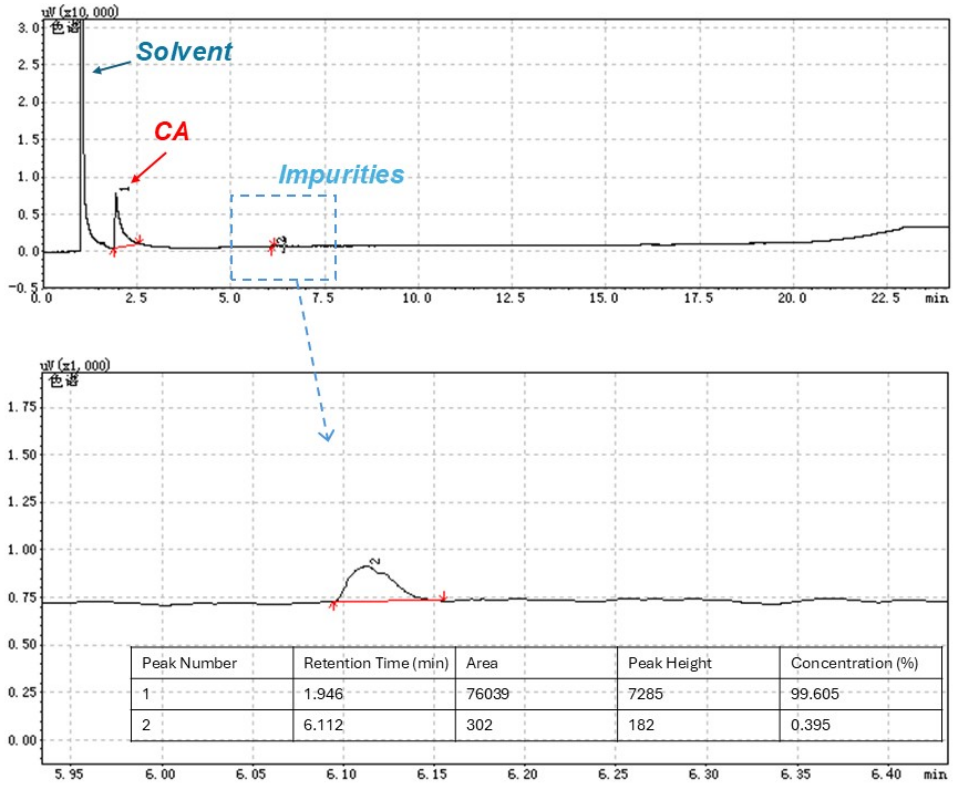


Figure S3. FTIR spectra of PHB in the absence of a catalyst.



Peak Number	Retention Time (min)	Area	Peak Height	Concentration (%)
1	1.946	76039	7285	99.605
2	6.112	302	182	0.395

Figure S4. Representative GC chromatogram of the product mixture.

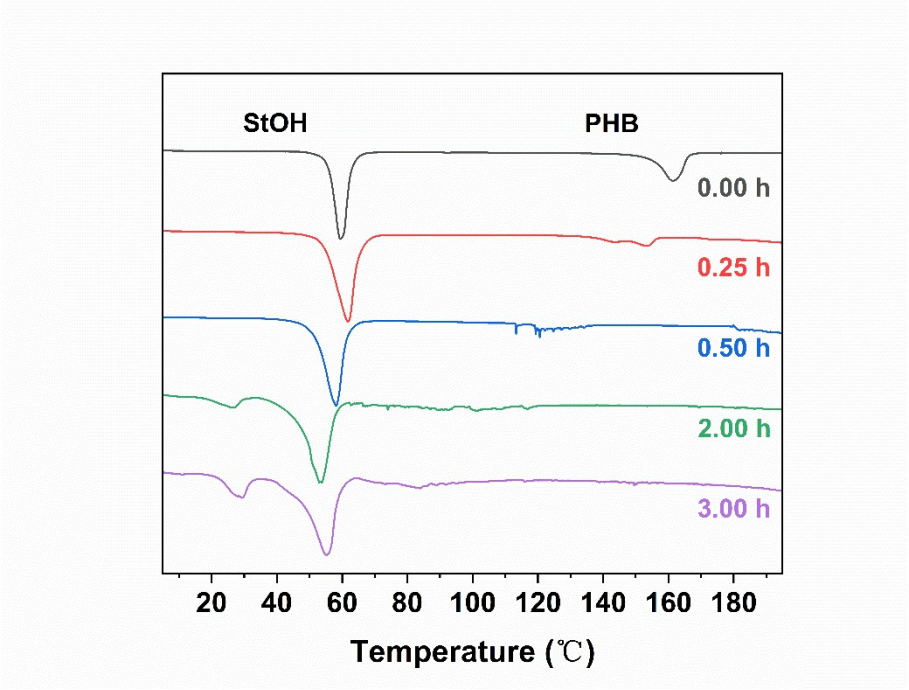


Figure S5. DSC analysis of the PHB degradation process.

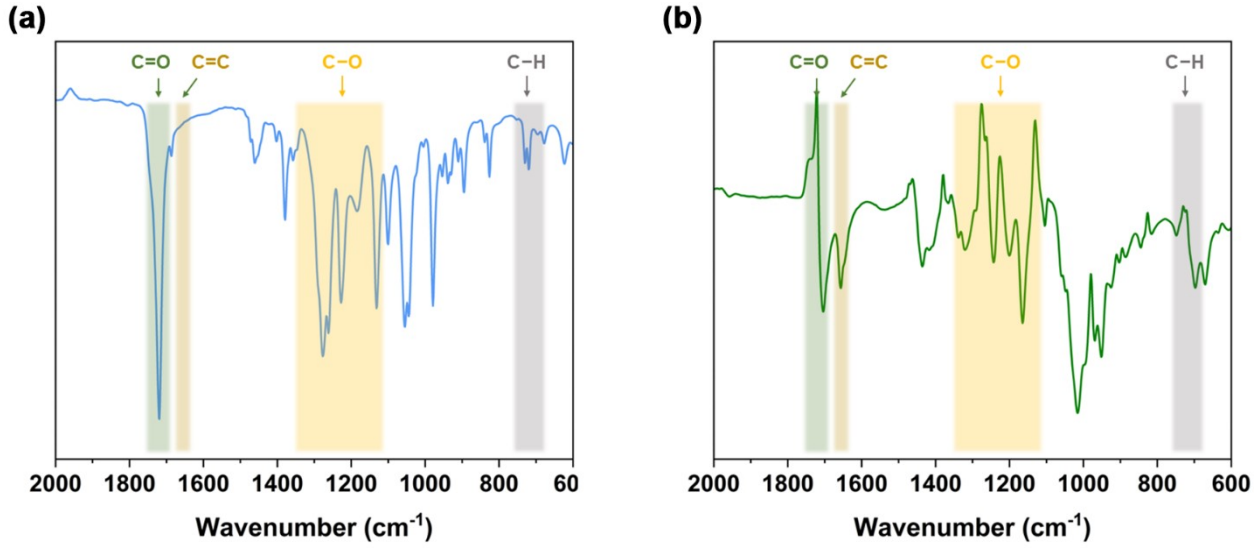


Figure S6. (a) FTIR analysis of PHB treated with StOH only (no C=C formation observed). (b) FTIR analysis of PHB degradation catalyzed by NaCA in DMSO (showing C=C bond formation).

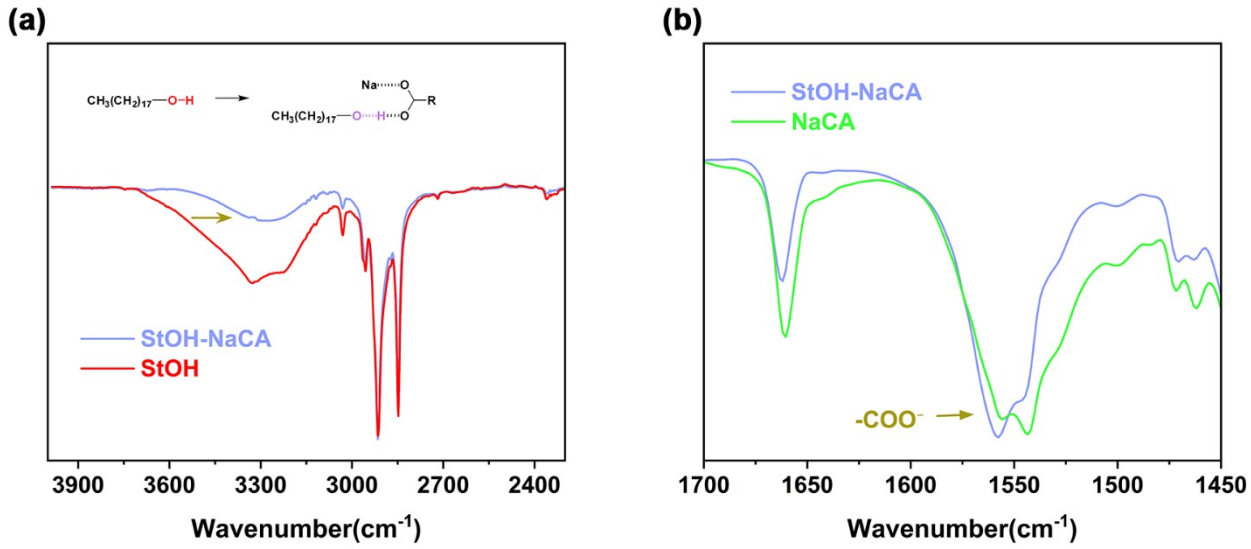


Figure S7. FTIR analysis of the interaction between StOH and NaCA.

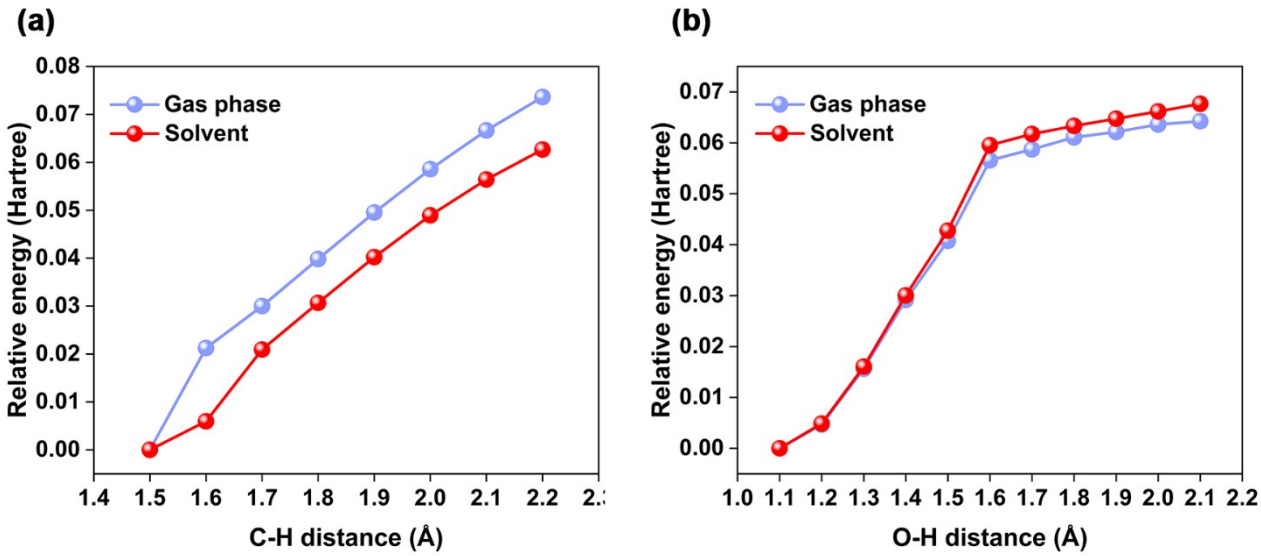


Figure S8. (a) Potential energy profile for C-H bond cleavage. (b) Potential energy profile for C-C bond cleavage.

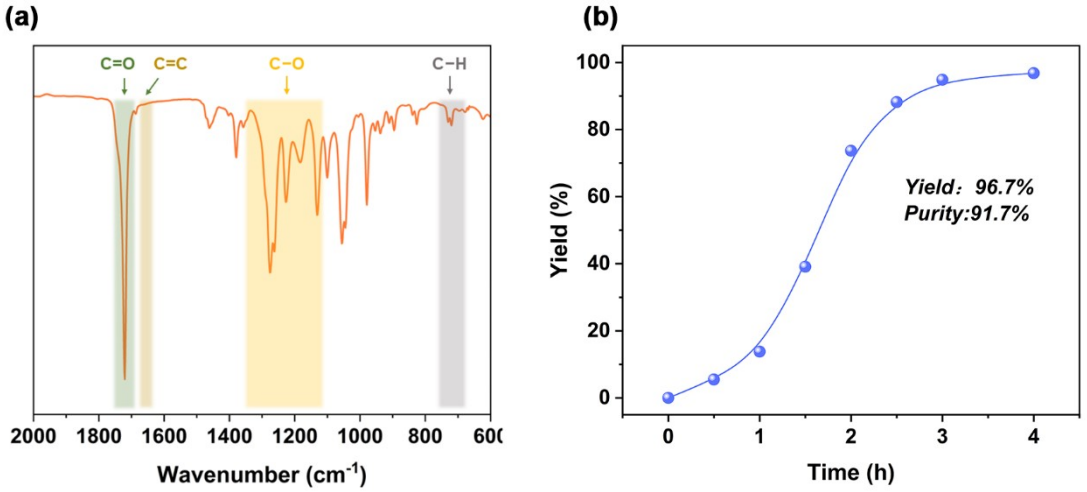


Figure S9. (a) FTIR spectrum of PHB in the $Sn(Oct)_2$/StOH system. (b) Crude CA yield from PHB degradation catalyzed by StO-CA/NaCA (main impurity: lactide derived from stearyl lactate).

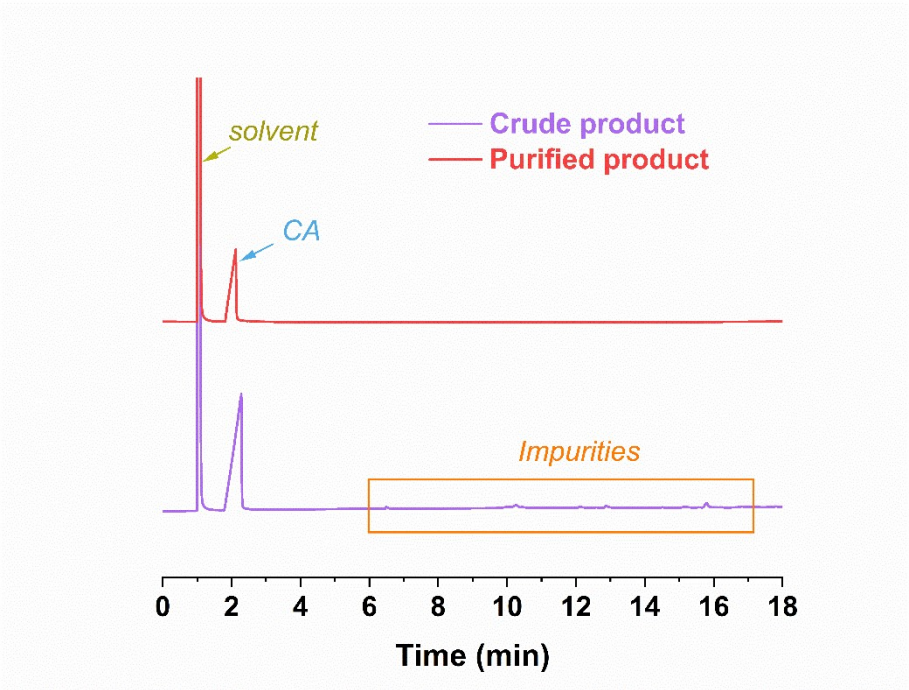


Figure S10. GC analysis of crude and purified CA products.

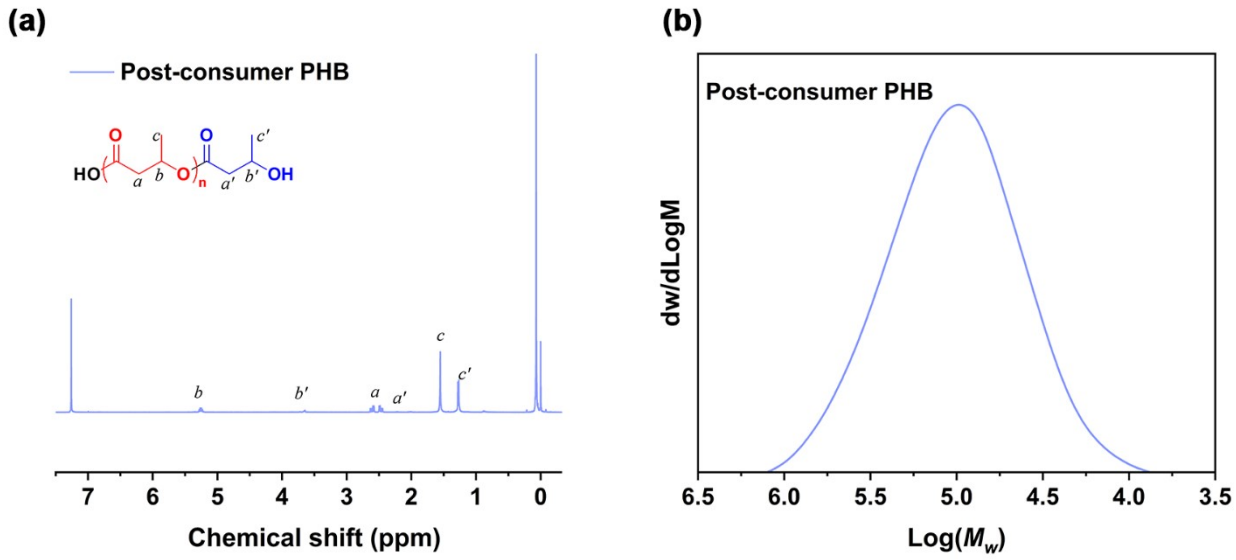


Figure S11. Characterization of post-Consumer PHB: (1) ^{1}H NMR spectrum. (2) GPC analysis

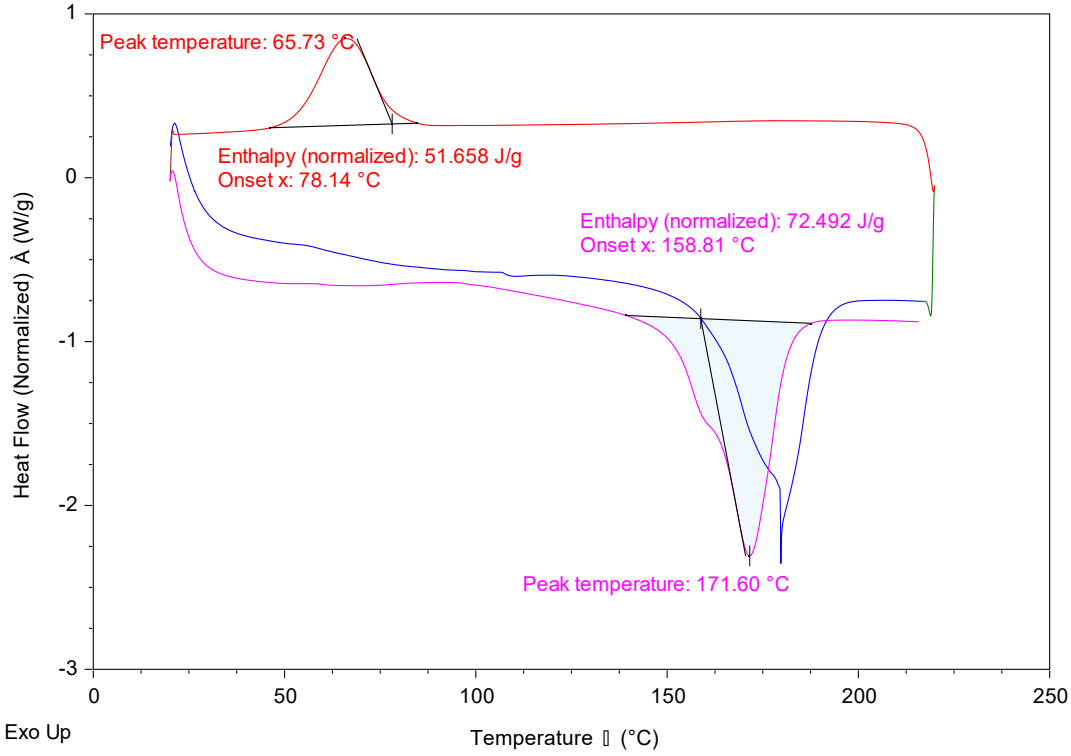


Figure S12. DSC analysis of post-consumer PHB.

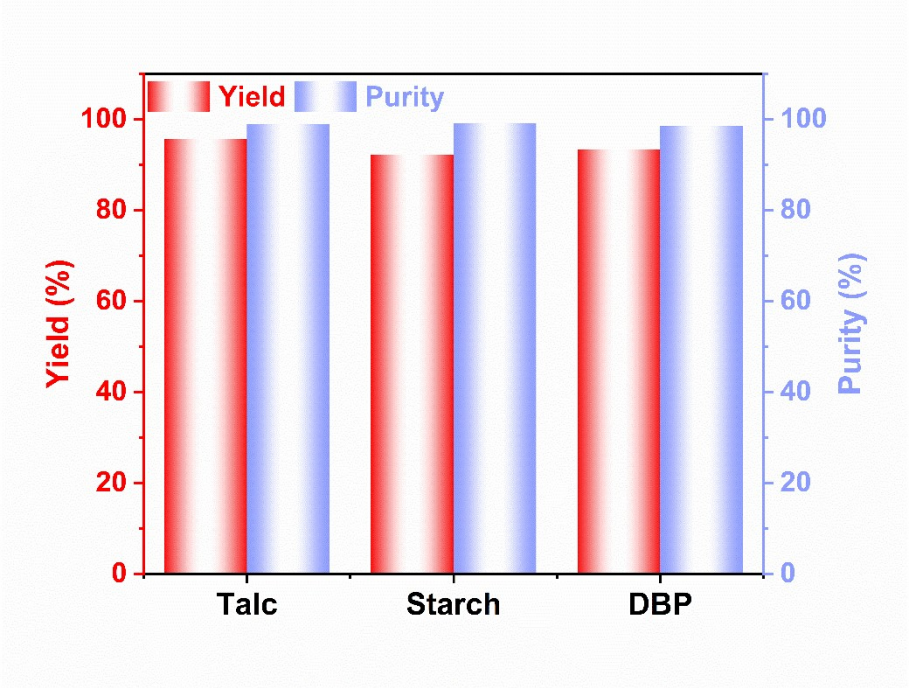


Figure S13. PHB degradation using StO–CA/NaCA in the presence of additives or plasticizers (5 wt%, 150 °C, 3 Torr, 3 h).

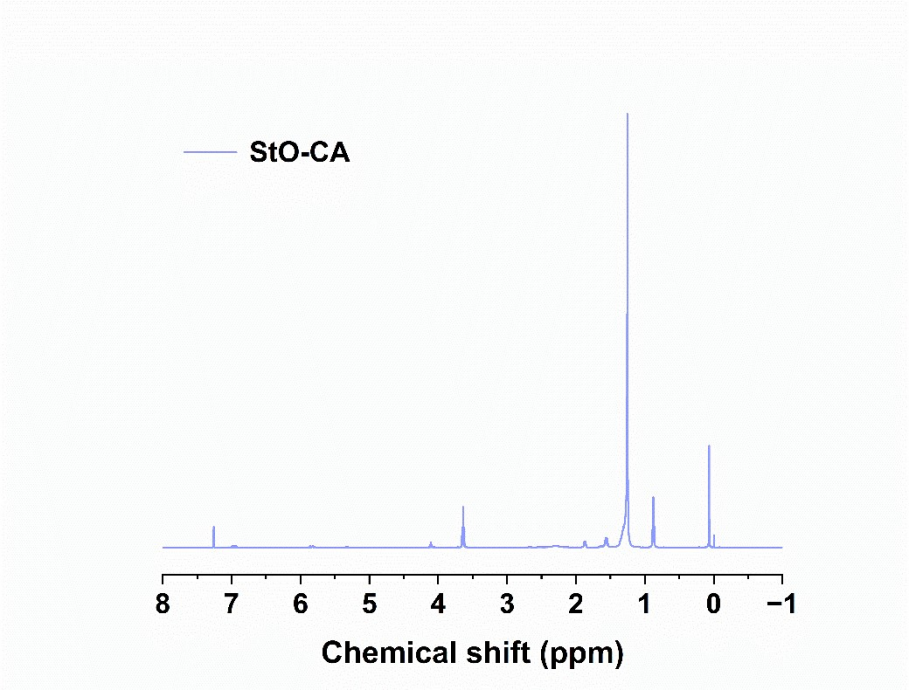


Figure S14. ^{1}H NMR characterization of the post-reaction residue following seven cycles of operation.

References

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