

La(III)-Catalysed degradation of polyesters to monomers via transesterifications

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Abbreviations used in this paper: acac: acetylacetonate, BD: 1,4-butanediol, DA: dimethyl adipate, cru: constitutional repeating unit, DS: dimethyl succinate, DP: dimethyl phthalate, EG: ethylene glycol, PBS: poly(butylene succinate), PEA: poly(ethylene adipate), PET: poly(ethylene terephthalate), rpm: rotations per minute.

DOI: 10.1039/c2cc.XXXXX

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Experimental Procedures

1. General

All procedures described in this paper were carried out under a nitrogen atmosphere by use of Schlenk and autoclave techniques. Unless otherwise noted, all reactants or reagents were obtained from commercial suppliers. Moisture-sensitive complexes such as [La(acac)₃] were stored and handled in a glovebox (VAC OMNI-LAB). MeOH was refluxed and distilled over magnesium dimethoxide under nitrogen and stored under nitrogen. [La(acac)₃], [Sc(OTf)₃], [Ti(acac)₄], [Mn(acac)₂], [Mn(acac)₃], [Fe(acac)₃], [Ru(acac)₃], [Co(acac)₂], [Co(acac)₃] and [Al(acac)₃] were purchased from commercial suppliers and used as received. [La(acac)₃] may exist as a hydrate, but in this study it was stored and treated in the glove box and the amount of material was calculated as anhydrous basis. Commercial polymers were provided by Mitsubishi chemical co. Gas-liquid chromatography was performed using a Shimadzu GC2014 equipped with an auto-injector using a Zebron ZB-WAXplus (0.25 mmf x 30 m), All samples were analysed and quantified by using dibenzyl as an internal standard. NMR Experiments were performed on a JEOL ECX-400P Spectrometer (400 MHz for ¹H). MALDI TOF-MS analysis was performed on a Bruker Daltonics autoflex speed using 3-(4-tert-butylphenyl)-2-methylprop-2-enylidenemalononitrile as the matrix. ICP-OES analysis was performed on Hitachi-hightech Spectro Arcos II.

2. Catalytic degradation of poly(butylene succinate)

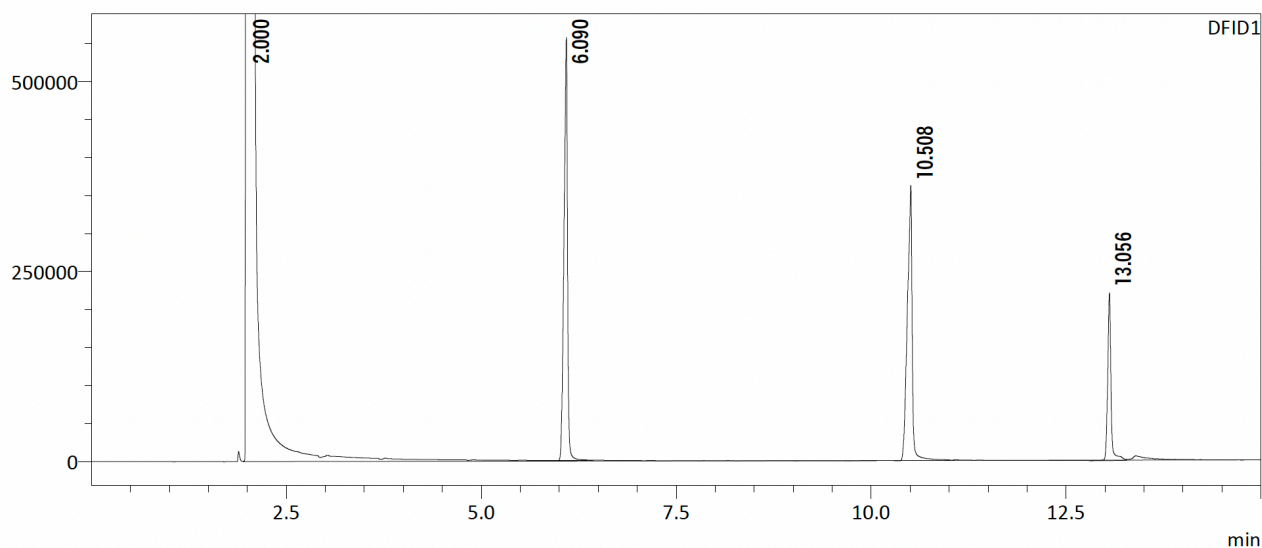
As a typical catalytic degradation, reaction procedure using PBS is described.

2.1. [La(acac)₃] (1 mol%) at 90 °C

In a glovebox, a magnetic stirring bar, poly(butylene succinate) (Mitsubishi Chemical Co. Bio-PBS, M_w = 90,700, M_n = 21,000) (116.8 mg, 0.001288 mmol as a whole chain, 0.680 mmol relative to the formula weight of constitutional repeating unit), [La(acac)₃] (3.0 mg, 0.0069 mmol, 1 mol% based on cru in an autoclave (Taiatsu techno Co., TVS-1-20, SUS316, 20 mL)). MeOH (5 ml) was added into the autoclave and the vessel was heated at 90 °C with 800 rpm for 4 h using an aluminum block bath with stirrer (EYELA, RCH-1000 BBS and SynFlex). The temperature control accuracy is ±1 °C. Dibenzyl (9.88 mg, 0.0542 mmol) was added in the reaction system as an internal standard for gas-liquid chromatography. Dimethyl succinate (0.697 mmol, >99%) and 1,4-butanediol (0.614 mmol, 90%) were obtained.

<Chrom atogram >

uV

**<Peak Report >**

Peak#	Retention Time	Area	Mark	Name
1	2.000	57450630	SV	
2	6.090	1766012	TV	
3	10.508	1573861	TV	
4	13.056	650965	T	
∓CEv		61441467		

Fig. S1. Gas-liquid chromatogram for degradation of PBS at 90 °C for 4 h catalysed by [La(acac)₃] (1 mol%). Methanol (Rt = 2.000), dimethyl succinate (Rt = 6.090 min), 1,4-butanediol (Rt = 10.508 min), dibenzyl as an internal standard (Rt = 13.058). Conditions: initial temp. = 110 °C, equilibrium time = 3.0 min, program time = 7.0 °C min⁻¹, final temp. = 220 °C, hold time = 9.0 min.

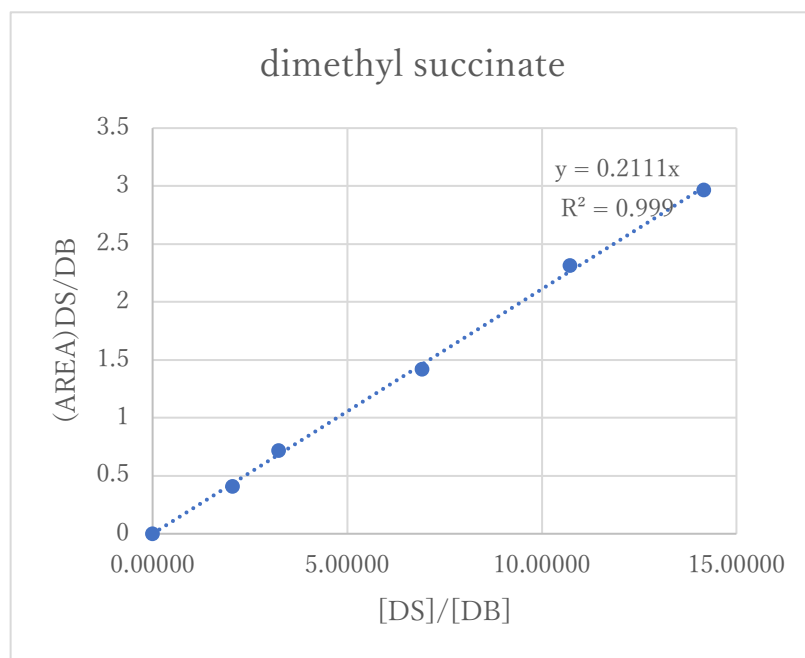


Fig. S2. Calibration curve for calculations of yields of dimethyl succinate. The horizontal axis indicates the relative concentration ratio of [dimethyl succinate]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on dimethyl succinate/dibenzyl. Dibenzyl was used for an internal standard.

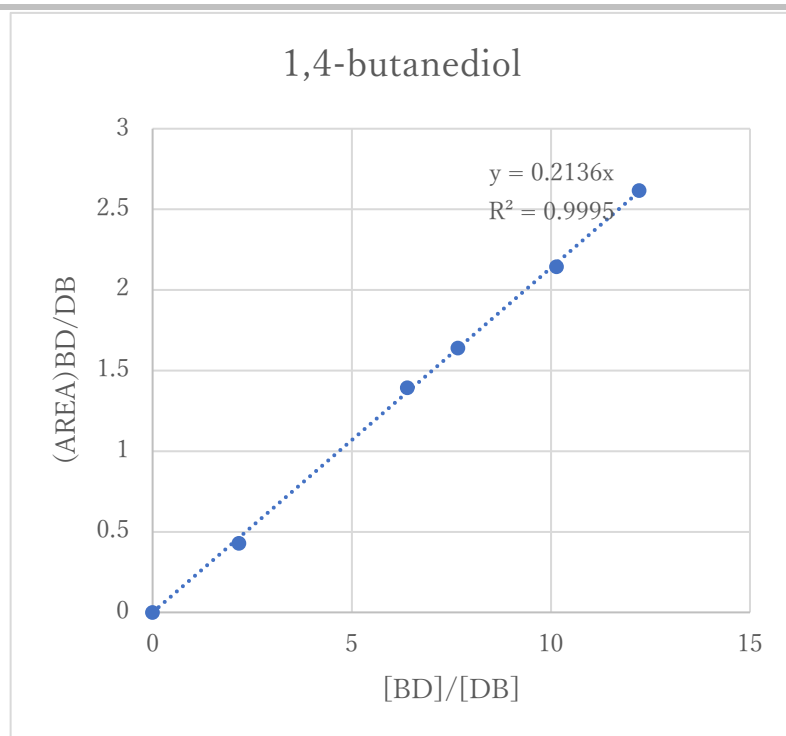


Fig. S3. Calibration curve for calculations of yields of 1,4-butanediol. The horizontal axis indicates the relative concentration ratio of [1,4-butanediol]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on 1,4-butanediol/dibenzyl. Dibenzyl was used for an internal standard.

2.2. [La(acac)₃] (1 mol%) at 90 °C using un-dried MeOH in the air

Poly(butylene succinate) (0.1164 g, 0.001283 mmol) and [La(acac)₃] (2.8 mg, 0.0064 mmol, 1 mol%) were stirred in as-received MeOH (5 ml) in the air at 90 °C for 4 h. Then, dibenzyl (9.68 mg, 0.0531 mmol) was added to the solution. Dimethyl succinate (0.7087 mmol, >99% yield) and 1,4-butanediol (0.6619 mmol, 98% yield).

2.3. [La(acac)₃] (1 mol%) at 70 °C

Poly(butylene succinate) (0.1154 g, 0.001272 mmol) and [La(acac)₃] (3.2 mg, 0.0073 mmol, 1 mol%) were stirred in MeOH (5 ml) at 70 °C for 4 h. Then, dibenzyl (10.02 mg, 0.0550 mmol) was added to the solution. Dimethyl succinate (0.2293 mmol, 34% yield) and 1,4-butanediol (0.2160 mmol, 32% yield).

2.4. [La(acac)₃] (1 mol%) at 80 °C

Poly(butylene succinate) (0.1163 g, 0.001282 mmol) and [La(acac)₃] (3.2 mg, 0.0073 mmol, 1 mol%) were stirred in MeOH (5 ml) at 80 °C for 4 h. Then, dibenzyl (9.99 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.388 mmol, 57% yield) and 1,4-butanediol (0.351 mmol, 52% yield).

2.5. [La(acac)₃] (1 mol%) at 100 °C

Poly(butylene succinate) (0.1168 g, 0.001288 mmol) and [La(acac)₃] (3.1 mg, 0.0071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.54 mg, 0.05791 mmol) was added to the solution. Dimethyl succinate (0.6987 mmol, >99% yield) and 1,4-butanediol (0.6079 mmol, 90% yield).

2.6. [La(acac)₃] (1 mol%) at 110 °C

Poly(butylene succinate) (0.1182 g, 0.001303 mmol) and [La(acac)₃] (2.9 mg, 0.0067 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to the solution. Dimethyl succinate (0.6946 mmol, >99% yield) and 1,4-butanediol (0.6599 mmol, 96% yield).

2.7. [La(acac)₃] (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1177 g, 0.001298 mmol) and [La(acac)₃] (0.30 mg, 0.00069 mmol, 0.1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.13 mg, 0.05566 mmol) was

added to the solution. Dimethyl succinate (0.0289 mmol, 4% yield) and 1,4-butanediol (0.0322 mmol, 5% yield).

2.8. [La(acac)₃] (1 mol%) at 120 °C

Poly(butylene succinate) (0.1167 g, 0.001287 mmol) and [La(acac)₃] (3.0 mg, 0.0069 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.648 mmol, 96% yield) and 1,4-butanediol (0.599 mmol, 88% yield).

2.9. [La(acac)₃] (1 mol%) at 130 °C

Poly(butylene succinate) (0.1163 g, 0.001282 mmol) and [La(acac)₃] (2.9 mg, 0.0067 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (10.04 mg, 0.05516 mmol) was added to the solution. Dimethyl succinate (0.6496 mmol, 96% yield) and 1,4-butanediol (0.6164 mmol, 91% yield).

2.10. [La(acac)₃] (1 mol%) at 135 °C

Poly(butylene succinate) (0.1162 g, 0.001281 mmol) and [La(acac)₃] (3.0 mg, 0.0070 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.90 mg, 0.0543 mmol) was added to the solution. Dimethyl succinate (0.696 mmol, >99% yield) and 1,4-butanediol (0.630 mmol, 93% yield).

2.11. [La(acac)₃] (1 mol%) at 150 °C

Poly(butylene succinate) (0.1156 g, 0.001275 mmol) and [La(acac)₃] (2.9 mg, 0.0068 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to the solution. Dimethyl succinate (0.6719 mmol, >99% yield) and 1,4-butanediol (0.6307 mmol, 94% yield).

2.12. [La(OTf)₃] (1 mol%) at 90 °C

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and [La(OTf)₃] (3.8 mg, 0.0065 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (10.13 mg, 0.05566 mmol) was added to the solution. Dimethyl succinate (0.0899 mmol, 13% yield) and 1,4-butanediol (0.0902 mmol, 13% yield).

2.13. [Sc(OTf)₃] (1 mol%) at 100 °C

Poly(butylene succinate) (0.1162 g, 0.001281 mmol) and [Sc(OTf)₃] (3.4 mg, 0.0069 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.26 mg, 0.05637 mmol) was added to the solution. Dimethyl succinate (0.0495 mmol, 7% yield) and 1,4-butanediol (0.0553 mmol, 8% yield).

2.14. [Sc(OTf)₃] (1 mol%) at 110 °C

Poly(butylene succinate) (0.1153 g, 0.001271 mmol) and [Sc(OTf)₃] (3.4 mg, 0.0069 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.00 mg, 0.05495 mmol) was added to the solution. Dimethyl succinate (0.0983 mmol, 15% yield) and 1,4-butanediol (0.1014 mmol, 15% yield).

2.15. [Sc(OTf)₃] (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1155 g, 0.001273 mmol) and [Sc(OTf)₃] (0.35 mg, 0.00071 mmol, 0.1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.0055 mmol, 1% yield) and 1,4-butanediol (0.0079 mmol, 1% yield).

2.16. [Ti(acac)₄] (1 mol%) at 120 °C

Poly(butylene succinate) (0.1166 g, 0.001286 mmol) and [Ti(acac)₄] (5.0 mg of 63% solution in isopropyl alcohol, 0.0071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.158 mmol, 23% yield) and 1,4-butanediol (0.159 mmol, 23% yield).

2.17. [Ti(acac)₄] (1 mol%) at 130 °C

Poly(butylene succinate) (0.1165 g, 0.001285 mmol) and [Ti(acac)₄] (5.1 mg of 63% solution in isopropyl alcohol, 0.0072 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.574 mmol, 85% yield) and 1,4-butanediol (0.538 mmol, 80% yield).

2.18. [Ti(acac)₄] (1 mol%) at 135 °C

Poly(butylene succinate) (0.1166 g, 0.001286 mmol) and [Ti(acac)₄] (5.4 mg of 63% solution in isopropyl alcohol, 0.0077 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.92 mg, 0.0544 mmol) was added to the solution. Dimethyl succinate (0.700 mmol, >99% yield) and 1,4-butanediol (0.632 mmol, 93% yield).

2.19. [Ti(acac)₄] (1 mol%) at 150 °C

Poly(butylene succinate) (0.1181 g, 0.001302 mmol) and [Ti(acac)₄] (5.2 mg of 63% solution in isopropyl alcohol, 0.0074 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.09 mg, 0.0544 mmol) was added to the solution. Dimethyl succinate (0.6915 mmol, >99% yield) and 1,4-butanediol (0.6567 mmol, 96% yield).

2.20. [Mn(acac)₂] (1 mol%) at 90 °C

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and [Mn(acac)₂] (1.69 mg, 0.00668 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (9.87 mg, 0.0542 mmol) was added to the solution. Dimethyl succinate (0.0344 mmol, 5% yield) and 1,4-butanediol (0.0355 mmol, 5% yield).

2.21. [Mn(acac)₂] (1 mol%) at 100 °C

Poly(butylene succinate) (0.1161 g, 0.001280 mmol) and [Mn(acac)₂] (1.75 mg, 0.00691 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.03 mg, 0.05511 mmol) was added to the solution. Dimethyl succinate (0.4273 mmol, 63% yield) and 1,4-butanediol (0.4003 mmol, 59% yield).

2.22. [Mn(acac)₂] (1 mol%) at 110 °C

Poly(butylene succinate) (0.1151 g, 0.001269 mmol) and [Mn(acac)₂] (1.67 mg, 0.00660 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.04 mg, 0.05516 mmol) was added to the solution. Dimethyl succinate (0.5514 mmol, 82% yield) and 1,4-butanediol (0.5462 mmol, 82% yield).

2.23. [Mn(acac)₂] (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1151 g, 0.001269 mmol) and [Mn(acac)₂] (0.18 mg, 0.00071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.19 mg, 0.05599 mmol) was added to the solution. Dimethyl succinate (0.0060 mmol, 1% yield) and 1,4-butanediol (0.0100 mmol, 2% yield).

2.24. [Mn(acac)₂] (1 mol%) at 120 °C

Poly(butylene succinate) (0.1179 g, 0.001300 mmol) and [Mn(acac)₂] (1.68 mg, 0.00664 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.99 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.646 mmol, 94% yield) and 1,4-butanediol (0.606 mmol, 89% yield).

2.25. [Mn(acac)₂] (1 mol%) at 130 °C

Poly(butylene succinate) (0.1154 g, 0.001272 mmol) and [Mn(acac)₂] (1.70 mg, 0.00672 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (10.02 mg, 0.05505 mmol) was added to the solution. Dimethyl succinate (0.6549 mmol, 98% yield) and 1,4-butanediol (0.6351 mmol, 95% yield).

2.26. [Mn(acac)₂] (1 mol%) at 130 °C in the air

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and [Mn(acac)₂] (1.70 mg, 0.00672 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h under air. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.603 mmol, 89% yield) and 1,4-butanediol (0.575 mmol, 84% yield).

2.27. [Mn(acac)₂] (1 mol%) at 130 °C using un-dried MeOH

Poly(butylene succinate) (0.1177 g, 0.001298 mmol) and [Mn(acac)₂] (1.74 mg, 0.00687 mmol, 1 mol%) were stirred in un-dried MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (9.92 mg, 0.0544 mmol) was added to the solution. Dimethyl succinate (0.632 mmol, 92% yield) and 1,4-butanediol (0.593 mmol, 87% yield).

2.28. [Mn(acac)₂] (1 mol%) at 130 °C using un-dried MeOH in the air

Poly(butylene succinate) (0.1155 g, 0.001273 mmol) and [Mn(acac)₂] (1.69 mg, 0.00668 mmol, 1 mol%) were stirred in un-dried MeOH (5 ml) at 130 °C for 4 h under air. Then, dibenzyl (10.03 mg, 0.05511 mmol) was added to the solution. Dimethyl succinate (0.4424 mmol, 66% yield) and 1,4-butanediol (0.4274 mmol, 64% yield).

2.29. [Mn(acac)₂] (1 mol%) at 135 °C

Poly(butylene succinate) (0.1182 g, 0.001303 mmol) and [Mn(acac)₂] (1.72 mg, 0.00679 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.89 mg, 0.0543 mmol) was added to the solution. Dimethyl succinate (0.699 mmol, >99% yield) and 1,4-butanediol (0.619 mmol, 90% yield).

2.30. [Mn(acac)₂] (1 mol%) at 140 °C

Poly(butylene succinate) (0.1163 g, 0.001283 mmol) and [Mn(acac)₂] (1.72 mg, 0.00679 mmol, 1 mol%) were stirred in MeOH (5 ml) at 140 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to the solution. Dimethyl succinate (0.6547 mmol, 97% yield) and 1,4-butanediol (0.5846 mmol, 87% yield).

2.31. [Mn(acac)₂] (1 mol%) at 150 °C

Poly(butylene succinate) (0.1183 g, 0.001304 mmol) and [Mn(acac)₂] (1.73 mg, 0.00683 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.712 mmol, >99% yield) and 1,4-butanediol (0.679 mmol, 99% yield).

2.32. [Mn(acac)₃] (1 mol%) at 90 °C

Poly(butylene succinate) (0.1170 g, 0.001290 mmol) and [Mn(acac)₃] (2.35 mg, 0.00661 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (9.88 mg, 0.0542 mmol) was added to the solution. Dimethyl succinate (0.0036 mmol, 1% yield) and 1,4-butanediol (0.0055 mmol, 1% yield).

2.33. [Mn(acac)₃] (1 mol%) at 100 °C

Poly(butylene succinate) (0.1153 g, 0.001278 mmol) and [Mn(acac)₃] (2.39 mg, 0.00673 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.46 mg, 0.05747 mmol) was added to the solution. Dimethyl succinate (0.2912 mmol, 43% yield) and 1,4-butanediol (0.2915 mmol, 43% yield).

2.34. [Mn(acac)₃] (1 mol%) at 100 °C in the air

Poly(butylene succinate) (0.1163 g, 0.001282 mmol) and [Mn(acac)₃] (2.39 mg, 0.00673 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h in the air. Then, dibenzyl (10.16 mg, 0.05582 mmol) was added to the solution. Dimethyl succinate (0.2036 mmol, 30% yield) and 1,4-butanediol (0.2205 mmol, 33% yield).

2.35. [Mn(acac)₃] (1 mol%) at 100 °C using un-dried MeOH

Poly(butylene succinate) (0.1161 g, 0.001280 mmol) and [Mn(acac)₃] (2.51 mg, 0.00707 mmol, 1 mol%) were stirred in un-dried MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.155 mmol, 23% yield) and 1,4-butanediol (0.143 mmol, 21% yield).

2.36. [Mn(acac)₃] (1 mol%) at 100 °C using un-dried MeOH in the air

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and [Mn(acac)₃] (2.52 mg, 0.00709 mmol, 1 mol%) were stirred in un-dried MeOH (5 ml) at 100 °C for 4 h in the air. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.127 mmol, 19% yield) and 1,4-butanediol (0.120 mmol, 18% yield).

2.37. [Mn(acac)₃] (1 mol%) at 110 °C

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and [Mn(acac)₃] (2.38 mg, 0.00670 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.02 mg, 0.05505 mmol) was added to the solution. Dimethyl succinate (0.6537 mmol, 96% yield) and 1,4-butanediol (0.6234 mmol, 92% yield).

2.38. [Mn(acac)₃] (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1163 g, 0.001282 mmol) and $[\text{Mn}(\text{acac})_3]$ (0.26 mg, 0.00073 mmol, 0.1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.15 mg, 0.05577 mmol) was added to the solution. Dimethyl succinate (0.0055 mmol, 1% yield) and 1,4-butanediol (0.0095 mmol, 1% yield).

2.39. $[\text{Mn}(\text{acac})_3]$ (1 mol%) at 120 °C

Poly(butylene succinate) (0.1150 g, 0.001268 mmol) and $[\text{Mn}(\text{acac})_3]$ (2.36 mg, 0.00664 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (10.10 mg, 0.05549 mmol) was added to the solution. Dimethyl succinate (0.6746 mmol, >99% yield) and 1,4-butanediol (0.6495 mmol, 97% yield).

2.40. $[\text{Mn}(\text{acac})_3]$ (1 mol%) at 130 °C

Poly(butylene succinate) (0.1160 g, 0.001279 mmol) and $[\text{Mn}(\text{acac})_3]$ (2.36 mg, 0.00664 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (9.94 mg, 0.0545 mmol) was added to the solution. Dimethyl succinate (0.639 mmol, 95% yield) and 1,4-butanediol (0.586 mmol, 87% yield).

2.41. $[\text{Mn}(\text{acac})_3]$ (1 mol%) at 135 °C

Poly(butylene succinate) (0.1167 g, 0.001287 mmol) and $[\text{Mn}(\text{acac})_3]$ (2.39 mg, 0.00673 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.7103 mmol, >99% yield) and 1,4-butanediol (0.6507 mmol, 96% yield).

2.42. $[\text{Mn}(\text{acac})_3]$ (1 mol%) at 150 °C

Poly(butylene succinate) (0.1167 g, 0.001287 mmol) and $[\text{Mn}(\text{acac})_3]$ (2.39 mg, 0.00673 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.03 mg, 0.05511 mmol) was added to the solution. Dimethyl succinate (0.6738 mmol, 99% yield) and 1,4-butanediol (0.6480 mmol, 96% yield).

2.43. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 90 °C

Poly(butylene succinate) (0.1175 g, 0.001296 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.36 mg, 0.00680 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to the solution. Dimethyl succinate (0.0194 mmol, 3% yield) and 1,4-butanediol (0.0265 mmol, 4% yield).

2.44. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 100 °C

Poly(butylene succinate) (0.1214 g, 0.001339 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.49 mg, 0.00705 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.26 mg, 0.05637 mmol) was added to the solution. Dimethyl succinate (0.2072 mmol, 29% yield) and 1,4-butanediol (0.1893 mmol, 27% yield).

2.45. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 110 °C

Poly(butylene succinate) (0.1163 g, 0.001282 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.40 mg, 0.00680 mmol, 1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to the solution. Dimethyl succinate (0.5896 mmol, 87% yield) and 1,4-butanediol (0.5768 mmol, 85% yield).

2.46. $[\text{Fe}(\text{acac})_3]$ (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1157 g, 0.001276 mmol) and $[\text{Fe}(\text{acac})_3]$ (0.23 mg, 0.00065 mmol, 0.1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.0136 mmol, 2% yield) and 1,4-butanediol (0.0198 mmol, 3% yield).

2.47. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 120 °C

Poly(butylene succinate) (0.1173 g, 0.001293 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.40 mg, 0.00680 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (10.17 mg, 0.05588 mmol) was added to the solution. Dimethyl succinate (0.6525 mmol, 96% yield) and 1,4-butanediol (0.5985 mmol, 88% yield).

2.48. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 130 °C

Poly(butylene succinate) (0.1156 g, 0.001275 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.35 mg, 0.00665 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (9.97 mg, 0.0547 mmol) was added to the solution. Dimethyl succinate (0.631 mmol, 94% yield) and 1,4-butanediol (0.592 mmol, 88% yield).

2.49. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 135 °C

Poly(butylene succinate) (0.1170 g, 0.001290 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.26 mg, 0.00639 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.672 mmol, 99% yield) and 1,4-butanediol (0.647 mmol, 95% yield).

2.50. $[\text{Fe}(\text{acac})_3]$ (1 mol%) at 150 °C

Poly(butylene succinate) (0.1158 g, 0.001277 mmol) and $[\text{Fe}(\text{acac})_3]$ (2.39 mg, 0.00677 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.660 mmol, 98% yield) and 1,4-butanediol (0.648 mmol, 96% yield).

2.51. $[\text{Ru}(\text{acac})_3]$ (1 mol%) at 135 °C

Poly(butylene succinate) (0.1160 g, 0.001279 mmol) and $[\text{Ru}(\text{acac})_3]$ (2.57 mg, 0.00644 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (10.05 mg, 0.05522 mmol) was added to the solution. Dimethyl succinate (0.0240 mmol, 4% yield) and 1,4-butanediol (0.0301 mmol, 4% yield).

2.52. $[\text{Co}(\text{acac})_2]$ (1 mol%) at 100 °C

Poly(butylene succinate) (0.1197 g, 0.001320 mmol) and $[\text{Co}(\text{acac})_2]$ (1.82 mg, 0.00708 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (10.21 mg, 0.05610 mmol) was added to the solution. Dimethyl succinate (0.0055 mmol, 1% yield) and 1,4-butanediol (0.0107 mmol, 2% yield).

2.53. $[\text{Co}(\text{acac})_2]$ (0.1 mol%) at 110 °C

Poly(butylene succinate) (0.1171 g, 0.001291 mmol) and $[\text{Co}(\text{acac})_2]$ (0.16 mg, 0.000622 mmol, 0.1 mol%) were stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.0203 mmol, 3% yield) and 1,4-butanediol (0.0252 mmol, 4% yield).

2.54. $[\text{Co}(\text{acac})_2]$ (1 mol%) at 120 °C

Poly(butylene succinate) (0.1160 g, 0.001279 mmol) and $[\text{Co}(\text{acac})_2]$ (1.73 mg, 0.00673 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.99 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.4189 mmol, 62% yield) and 1,4-butanediol (0.400 mmol, 59% yield).

2.55. $[\text{Co}(\text{acac})_2]$ (1 mol%) at 130 °C

Poly(butylene succinate) (0.1182 g, 0.001303 mmol) and $[\text{Co}(\text{acac})_2]$ (1.70 mg, 0.00661 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (9.97 mg, 0.0547 mmol) was added to the solution. Dimethyl succinate (0.601 mmol, 87% yield) and 1,4-butanediol (0.676 mmol, 84% yield).

2.56. $[\text{Co}(\text{acac})_2]$ (1 mol%) at 135 °C

Poly(butylene succinate) (0.1175 g, 0.001296 mmol) and $[\text{Co}(\text{acac})_2]$ (1.73 mg, 0.00671 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.6436 mmol, 94% yield) and 1,4-butanediol (0.5750 mmol, 84% yield).

2.57. $[\text{Co}(\text{acac})_2]$ (1 mol%) at 150 °C

Poly(butylene succinate) (0.1175 g, 0.001296 mmol) and $[\text{Co}(\text{acac})_2]$ (1.75 mg, 0.00681 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (9.99 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.6575 mmol, 96% yield) and 1,4-butanediol (0.6595 mmol, 97% yield).

2.58. $[\text{Co}(\text{acac})_3]$ (1 mol%) at 100 °C

Poly(butylene succinate) (0.1181 g, 0.001302 mmol) and $[\text{Co}(\text{acac})_3]$ (2.62 mg, 0.00735 mmol, 1 mol%) were stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (9.87 mg, 0.0542 mmol) was added to the solution. Dimethyl succinate (0.0012 mmol, 0% yield) and 1,4-butanediol (0.0039 mmol, 1% yield).

2.59. $[\text{Co}(\text{acac})_3]$ (1 mol%) at 120 °C

Poly(butylene succinate) (0.1160 g, 0.001279 mmol) and $[\text{Co}(\text{acac})_3]$ (2.35 mg, 0.00660 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (10.06 mg, 0.05527 mmol) was added to

the solution. Dimethyl succinate (0.3523 mmol, 52% yield) and 1,4-butanediol (0.3509 mmol, 52% yield).

2.60. [Co(acac)₃] (1 mol%) at 130 °C

Poly(butylene succinate) (0.1167 g, 0.001287 mmol) and [Co(acac)₃] (2.41 mg, 0.00676 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (10.02 mg, 0.05505 mmol) was added to the solution. Dimethyl succinate (0.5808 mmol, 86% yield) and 1,4-butanediol (0.5368 mmol, 79% yield).

2.61. [Co(acac)₃] (1 mol%) at 135 °C

Poly(butylene succinate) (0.1162 g, 0.001281 mmol) and [Co(acac)₃] (2.36 mg, 0.00662 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (10.13 mg, 0.05566 mmol) was added to the solution. Dimethyl succinate (0.6243 mmol, 93% yield) and 1,4-butanediol (0.5622 mmol, 83% yield).

2.62. [Co(acac)₃] (1 mol%) at 150 °C

Poly(butylene succinate) (0.1180 g, 0.001301 mmol) and [Co(acac)₃] (2.41 mg, 0.00676 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.02 mg, 0.05505 mmol) was added to the solution. Dimethyl succinate (0.6986 mmol, >99% yield) and 1,4-butanediol (0.7039 mmol, >99% yield).

2.63. [Al(acac)₃] (1 mol%) at 130 °C

Poly(butylene succinate) (0.1175 g, 0.001296 mmol) and [Al(acac)₃] (2.19 mg, 0.00675 mmol, 1 mol%) were stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (10.01 mg, 0.05500 mmol) was added to the solution. Dimethyl succinate (0.1755 mmol, 26% yield) and 1,4-butanediol (0.1775 mmol, 26% yield).

2.64. [Al(acac)₃] (1 mol%) at 135 °C

Poly(butylene succinate) (0.1187 g, 0.001309 mmol) and [Al(acac)₃] (2.20 mg, 0.00678 mmol, 1 mol%) were stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (10.05 mg, 0.05522 mmol) was added to the solution. Dimethyl succinate (0.1733 mmol, 25% yield) and 1,4-butanediol (0.1827 mmol, 27% yield).

2.65. [Al(acac)₃] (1 mol%) at 150 °C

Poly(butylene succinate) (0.1155 g, 0.001273 mmol) and [Al(acac)₃] (2.17 mg, 0.00669 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.09 mg, 0.05544 mmol) was added to the solution. Dimethyl succinate (0.6724 mmol, >99% yield) and 1,4-butanediol (0.6534 mmol, 97% yield).

2.66. Without catalyst at 100 °C

Poly(butylene succinate) (0.1199 g, 0.001322 mmol) was stirred in MeOH (5 ml) at 100 °C for 4 h. Then, dibenzyl (9.82 mg, 0.0539 mmol) was added to the solution. Dimethyl succinate (0.0012 mmol, 0% yield) and 1,4-butanediol (0.0018 mmol, 0% yield).

2.67. Without catalyst at 110 °C

Poly(butylene succinate) (0.1166 g, 0.001286 mmol) was stirred in MeOH (5 ml) at 110 °C for 4 h. Then, dibenzyl (10.16 mg, 0.05582 mmol) was added to the solution. Dimethyl succinate (0.0033 mmol, 0% yield) and 1,4-butanediol (0.0051 mmol, 1% yield).

2.68. Without catalyst at 120 °C

Poly(butylene succinate) (0.1164 g, 0.001283 mmol) was stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.0199 mmol, 3% yield) and 1,4-butanediol (0.0466 mmol, 7% yield).

2.69. Without catalyst at 130 °C

Poly(butylene succinate) (0.1150 g, 0.001268 mmol) was stirred in MeOH (5 ml) at 130 °C for 4 h. Then, dibenzyl (10.04 mg, 0.0551 mmol) was added to the solution. Dimethyl succinate (0.0742 mmol, 11% yield) and 1,4-butanediol (0.0959 mmol, 14% yield).

2.70. Without catalyst at 135 °C

Poly(butylene succinate) (0.1164 g, 0.001283 mmol) was stirred in MeOH (5 ml) at 135 °C for 4 h. Then, dibenzyl (10.04 mg, 0.05516 mmol) was added to the solution. Dimethyl succinate (0.0817 mmol, 12% yield) and 1,4-butanediol (0.0757 mmol, 11% yield).

2.71. Without catalyst at 140 °C

Poly(butylene succinate) (0.1156 g, 0.001275 mmol) was stirred in MeOH (5 ml) at 140 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl succinate (0.124 mmol, 18% yield) and 1,4-butanediol (0.120 mmol, 18% yield).

2.72. Without catalyst at 150 °C

Poly(butylene succinate) (0.1150 g, 0.001268 mmol) was stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.03 mg, 0.05511 mmol) was added to the solution. Dimethyl succinate (0.3685 mmol, 55% yield) and 1,4-butanediol (0.3527 mmol, 53% yield).

3. Large scale catalytic degradation of poly(butylene succinate)**3.1. Degradation**

In a glovebox, a magnetic stirring bar, poly(butylene succinate) (Mitsubishi Chemical Co. Bio-PBS, $M_w = 90,700$, $M_n = 21,000$) (10.3929 g, 0.1139 mmol as a whole chain, 60.02 mmol relative to the formula weight of constitutional repeating unit), $[La(acac)_3]$ (291.1 mg, 0.6673 mmol, 1 mol% based on cru in a autoclave (Taiatsu techno co., TVS-1-300, SUS316, 20 mL 300 ml). MeOH (250 ml) was added into the autoclave and the vessel was heated at 90 °C for 4 h using a thermostatted oil bath (Toray-Dow Corning Silicone co., SRX310). Dibenzyl (1.0069 g, 5.525 mmol) was added in the reaction system as an internal standard for gas-liquid chromatography. Dimethyl succinate (64.18 mmol, >99%) and 1,4-butanediol (59.17 mmol, 98%) were obtained. After removal of MeOH by a rotary evaporator, a pale-yellow oil was obtained (15.270 g). According to the internal standard (dibenzyl) in the 1H NMR spectrum, this oil contained dimethyl succinate (56.4 mmol, 93%) and 1,4-butanediol (51.1 mmol, 85%).

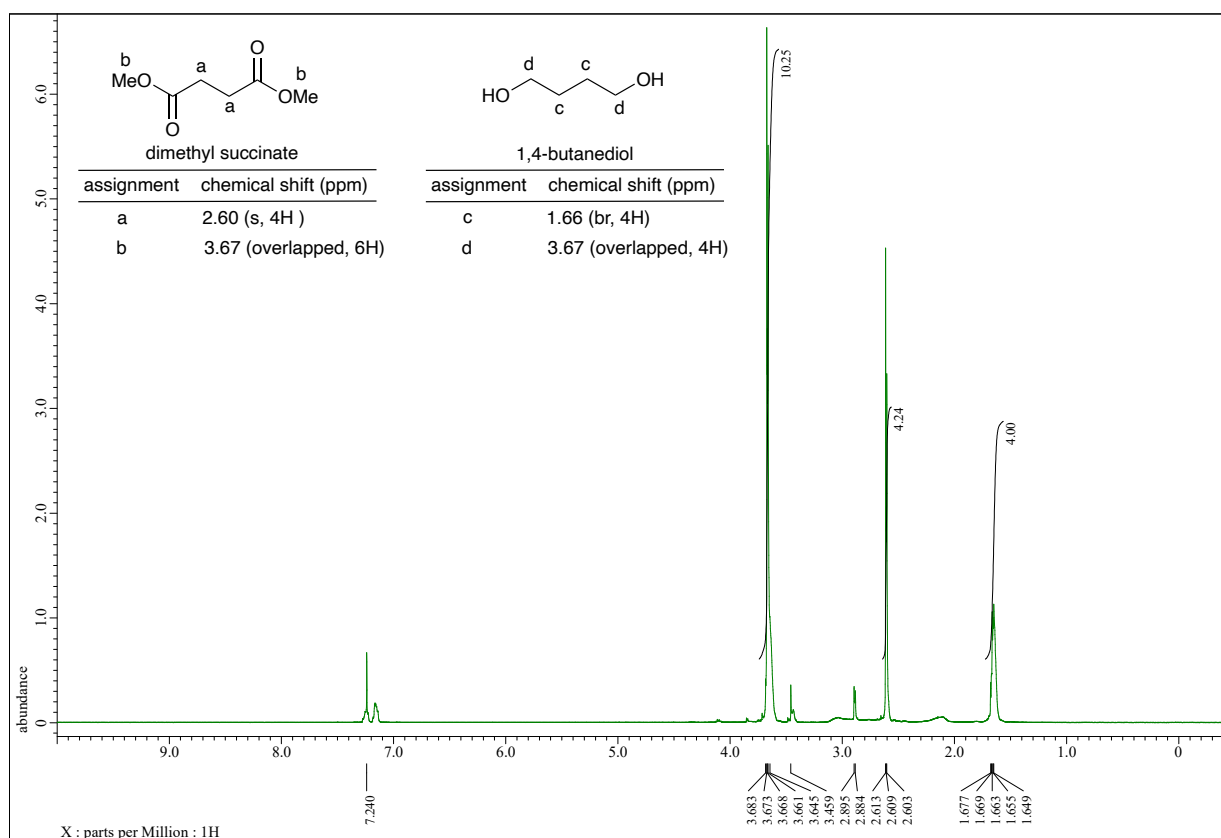


Fig. S4. ^1H NMR Spectrum of the obtained monomers in CDCl_3 (400 MHz). The hydroxo resonances were obscured. Resonances at 2.29 ppm (m) and 7.1-7.2 (br) are assignable to dibenzyl as an internal standard for GLC analysis. The relative ratio of dimethyl succinate and 1,4-butanediol based on this ^1H NMR is 1.06:1.00.

3.2. Separation of dimethyl succinate and 1,4-butanediol from degraded oil

Similar to the degradation described in section 3.1., degradation of poly(butylene succinate) (Mitsubishi Chemical Co. Bio-PBS, $M_w = 90,700$, $M_n = 21,000$) (10.4555 g, 0.1153 mmol) was degraded at $100\text{ }^\circ\text{C}$ for 4 h in the presence of $[\text{La}(\text{acac})_3]$ (1 mol%). Dibenzyl (0.95148 mg, 5.221 mmol) was added into the MeOH solution as an internal standard. Dimethyl succinate (63.88 mmol, >99%) and 1,4-butanediol (58.27 mmol, 96%). After removal of MeOH by a rotary evaporator, a pale yellow oil (14.9682 g) was obtained. Extraction of the degraded oil with Et_2O followed by removal of Et_2O with a rotary evaporator gave a pale-yellow oil (11.6182 g). This oil was separated into two layers, with pure dimethyl succinate from the lower layer and a mixture of dimethyl succinate and 1,4-butanediol from the upper layer. Then, the remaining degraded oil was extracted with EtOH. Removal of EtOH from the extracted solution gave 1,4-butanediol with an incorporated EtOH (3.0182 g).

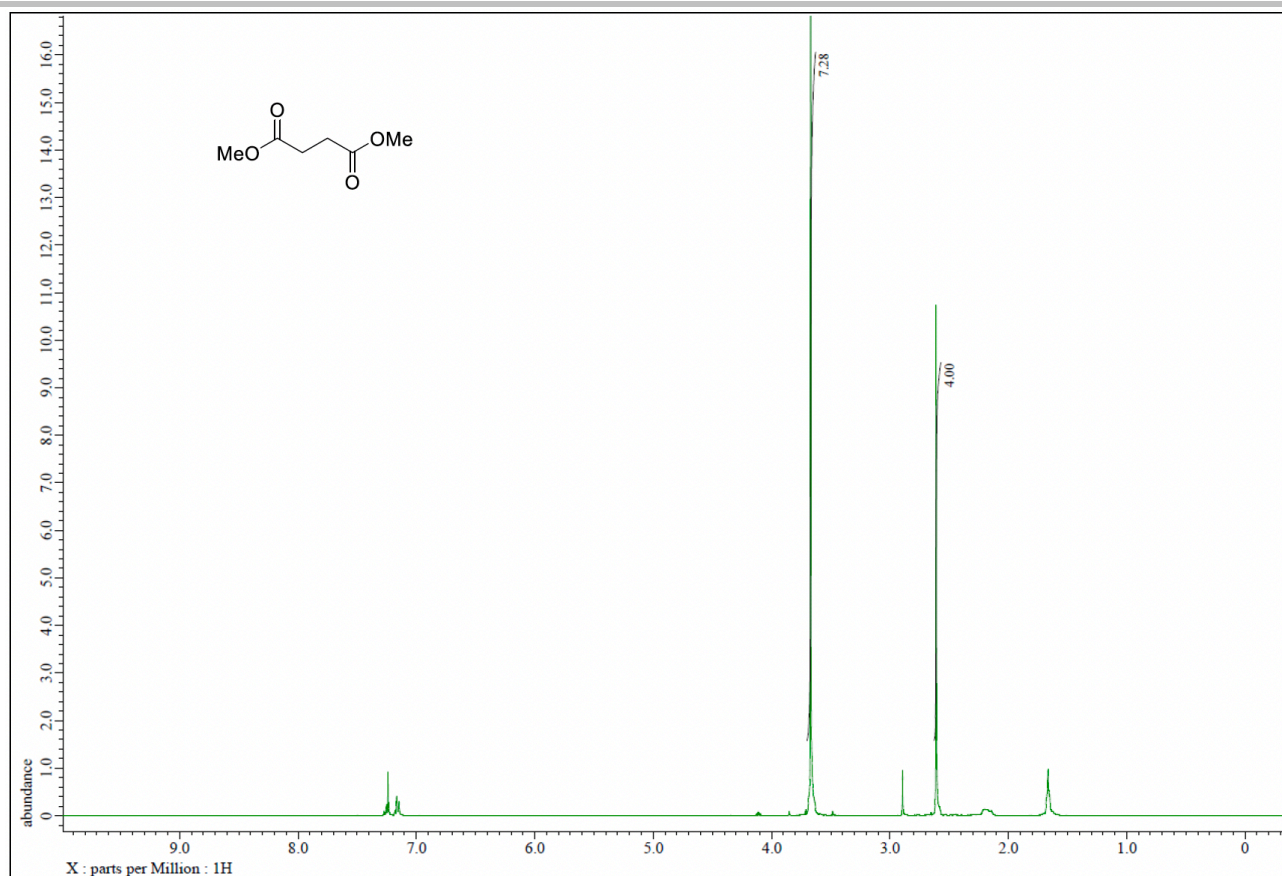


Fig. S5. ^1H NMR (CDCl_3) of the lower layer of oil obtained by extraction with Et_2O .

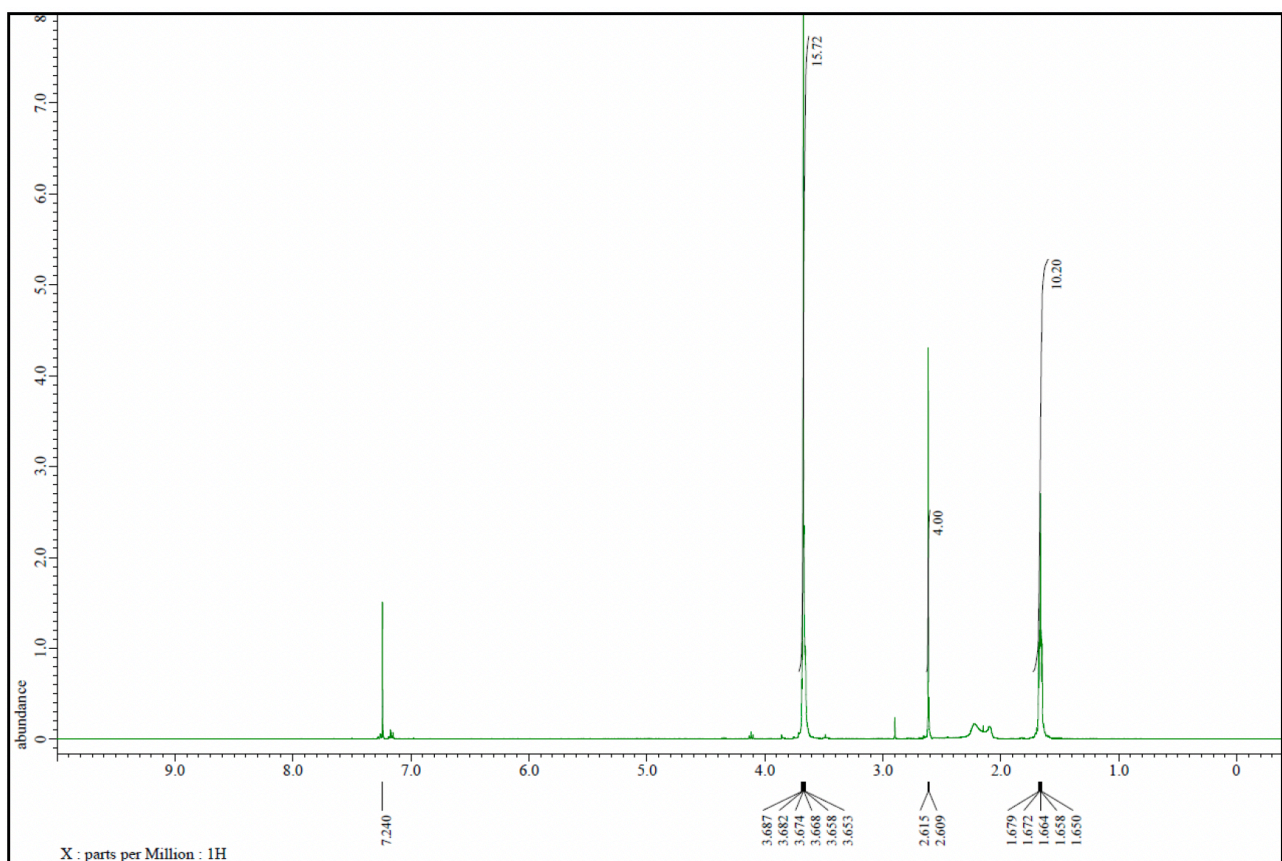


Fig. S6. ^1H NMR (CDCl_3) of the upper layer of oil obtained by extraction with Et_2O . This sample contains dimethyl succinate and 1,4-butanediol in 4:10 ratio.

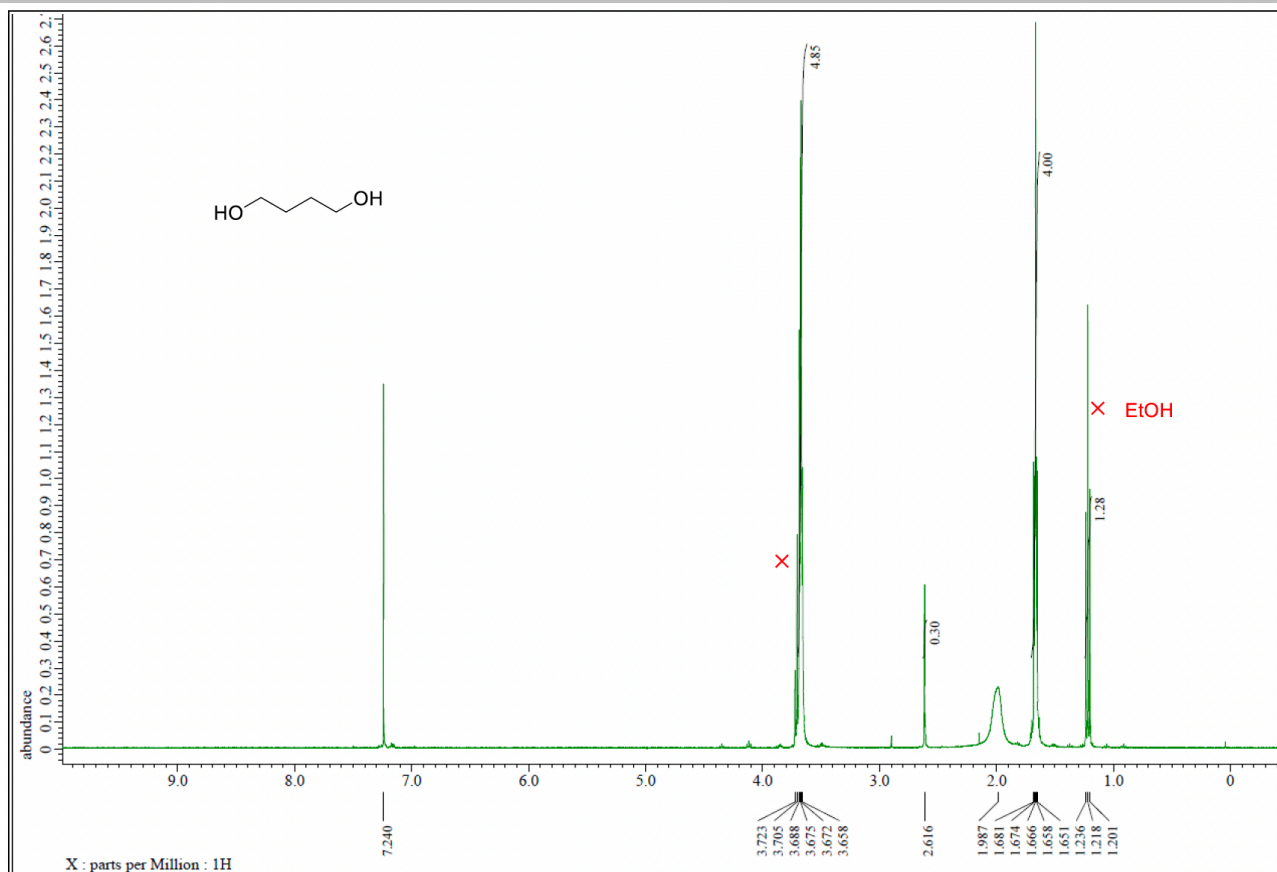


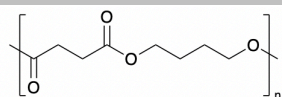
Fig. S7. ^1H NMR (CDCl_3) of the oil obtained by extraction with EtOH. This sample contains EtOH and small amount of dimethyl succinate. The ratio of dimethyl succinate and 1,4-butanediol is in 0.3:4.

3.3. Effect of MeOH volume on degradation

Poly(butylene succinate) (Mitsubishi Chemical Co. Bio-PBS, $M_w = 90,700$, $M_n = 21,000$) (10.9252 g, 0.1205 mmol) and $[\text{La}(\text{acac})_3]$ (297.4 mg, 0.6818 mmol, 1 mol%) were stirred in MeOH (125 ml) at $90\text{ }^\circ\text{C}$ for 4 h. Then, dibenzyl (1.0027 g, 5.5015 mmol) was added to the solution. Dimethyl succinate (66.4538 mmol, >99% yield) and 1,4-butanediol (59.9927 mmol, 95% yield).

4. Polymerisation of degraded poly(butylene succinate)

The obtained mixture of dimethyl succinate (56.4 mmol) and 1,4-butanediol (51.1 mmol) was pre-treated at $100\text{--}110\text{ }^\circ\text{C}$ for 1 h at 0.6–1.0 kPa to give a pale yellow oil, which turned a sticky solid at room temperature. Then, $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (15.0 μl , 0.0512 mmol, 0.1 mol%) was added into the oligomer and the reaction system was heated at $215\text{ }^\circ\text{C}$ for additional 2 h at 3–4 Pa. The resulting polymer was dissolved in chloroform at room temperature and was purified by reprecipitation for 3 times in MeOH. The polymer was filtrated using a grass-fiver sheet and dried under reduced pressure to give poly(butylene succinate) as a colourless powder. Yield 5.7913 g. (55.7% yield based on the starting poly(butylene succinate)).



colourless powder
5.7913 g (56% total yield)

Fig. S8. Obtained polymer by polymerisation of degraded oil.

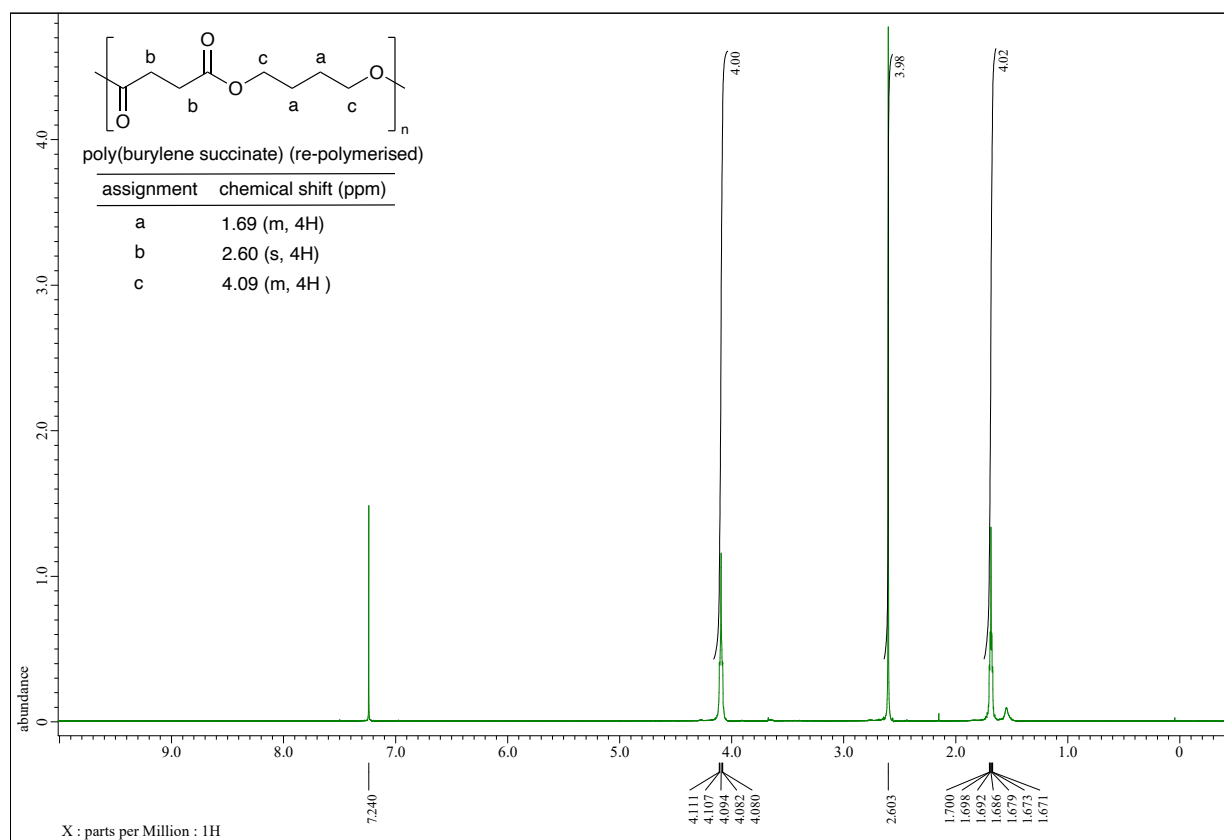


Fig. S9. ^1H NMR Spectrum of the obtained poly(butylene succinate) in CDCl_3 (400 MHz). ^1H NMR data in literature¹: ^1H NMR (400 MHz, CDCl_3): δ 1.689 (m, 4H), 2.605 (s, 4H), 4.099 (t, 4H).

from with EtOH from the remained oil. The inductively coupled plasma optical emission spectroscopy (ICP-EOS) analysis of lanthanum in these crude monomers showed 13 ppm in dimethyl succinate and 0.36% in 1,4-butanediol.

6. Degradation of poly(butylene succinate) (Mw: 125,000)

6.1. [La(acac)₃] (1 mol%) at 70 °C

Poly(butylene succinate) (0.1245 g, 0.0009960 mmol) and [La(acac)₃] (3.3 mg, 0.0076 mmol, 1 mol%) were stirred in MeOH (5 ml) at 70 °C for 4 h. Then, dibenzyl (10.14 mg, 0.05571 mmol) was added to the solution. Dimethyl succinate (0.3454 mmol, 48% yield) and 1,4-butanediol (0.3094 mmol, 43% yield).

6.2. [La(acac)₃] (1 mol%) at 80 °C

Poly(butylene succinate) (0.1253 g, 0.001002 mmol) and [La(acac)₃] (3.3 mg, 0.0076 mmol, 1 mol%) were stirred in MeOH (5 ml) at 80 °C for 4 h. Then, dibenzyl (10.05 mg, 0.05522 mmol) was added to the solution. Dimethyl succinate (0.5306 mmol, 73% yield) and 1,4-butanediol (0.4672 mmol, 64% yield).

6.3. [La(acac)₃] (1 mol%) at 90 °C

Poly(butylene succinate) (0.1256 g, 0.001005 mmol) and [La(acac)₃] (3.2 mg, 0.0073 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (10.08 mg, 0.05538 mmol) was added to the solution. Dimethyl succinate (0.7531 mmol, >99% yield) and 1,4-butanediol (0.6932 mmol, 95% yield).

6.4. Without catalyst at 90 °C

Poly(butylene succinate) (0.1252 g, 0.001002 mmol) was stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (10.07 mg, 0.05533 mmol) was added to the solution. Dimethyl succinate (0% yield) and 1,4-butanediol (0% yield).

7. Effect of particle size on degradation rate of poly(butylene succinate) (Mw: 136,000)

7.1. Preparation of poly(butylene succinate) powder

Poly(butylene succinate) pellets (2.0 x 2.0 x 5.0 mm³) were pulverised in a blade-and -mesh grinder. The typical size of the polymer particles was about 100 μm.

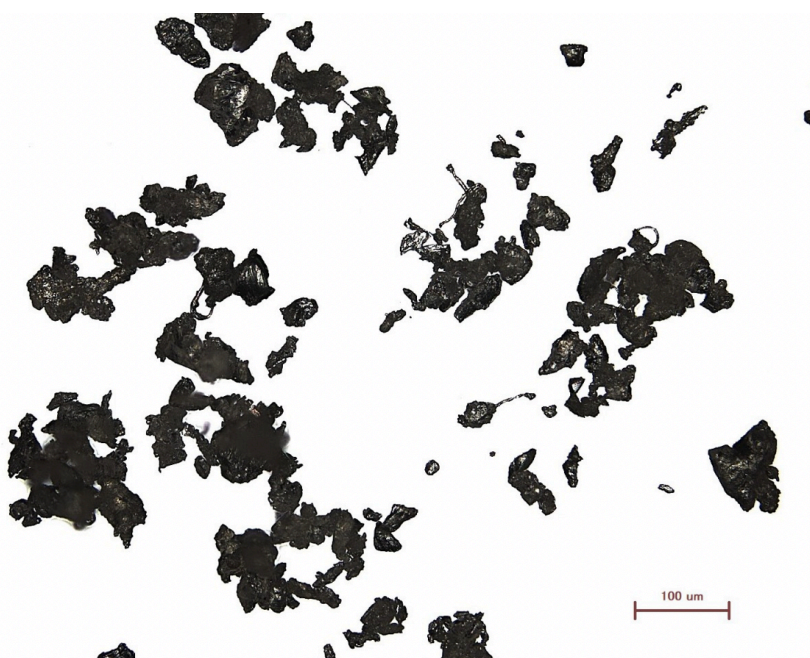


Fig S11. Size of poly(butylene succinate) powder.

7.2. Degradation of pellets for 0.5 h

Poly(butylene succinate) pellets (0.1170 g, 0.0008610 mmol) and [La(acac)₃] (3.0 mg, 0.0069 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 0.5 h. Then, dibenzyl (10.10 mg, 0.05542 mmol) was added to the solution. Dimethyl succinate (0.3018 mmol, 44% yield) and 1,4-butanediol (0.3029 mmol, 45% yield).

7.3. Degradation of pellets for 1.0 h

Poly(butylene succinate) pellets (0.1185 g, 0.0008720 mmol) and [La(acac)₃] (3.1 mg, 0.0071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 1.0 h. Then, dibenzyl (9.88 mg, 0.0542 mmol) was added to the solution. Dimethyl succinate (0.5224 mmol, 76% yield) and 1,4-butanediol (0.5351 mmol, 78% yield).

7.4. Degradation of powder for 0.5 h

Poly(butylene succinate) powder (0.1184 g, 0.0008713 mmol) and [La(acac)₃] (3.3 mg, 0.0076 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 0.5 h. Then, dibenzyl (9.98 mg, 0.0548 mmol) was added to the solution. Dimethyl succinate (0.3403 mmol, 49% yield) and 1,4-butanediol (0.3461 mmol, 50% yield).

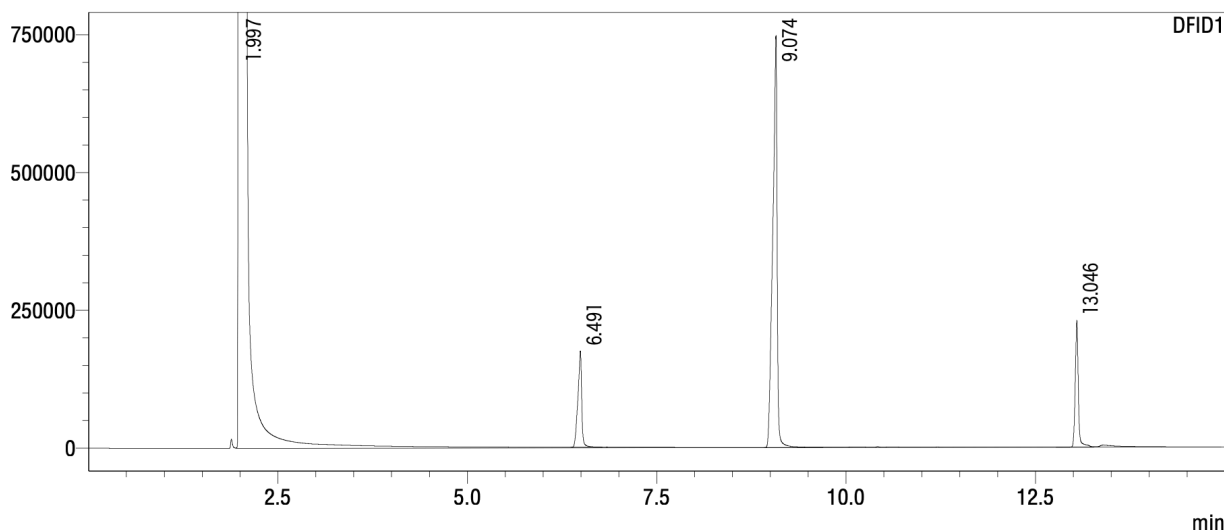
7.5. Degradation of powder for 1.0 h

Poly(butylene succinate) powder (0.1183 g, 0.0008706 mmol) and [La(acac)₃] (3.0 mg, 0.0069 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 0.5 h. Then, dibenzyl (10.01 mg, 0.05492 mmol) was added to the solution. Dimethyl succinate (0.4861 mmol, 71% yield) and 1,4-butanediol (0.5128 mmol, 75% yield).

8. Degradation of poly(ethylene adipate) (Mw: 10,000)

<Chrom atogram >

uV



<Peak Report>

Peak#	Retention Time	Area	Mark	Name
1	1.997	59053832	SV	
2	6.491	613931	T	
3	9.074	3010255	T	
4	13.046	661059	T	
‡CEV		63339076		

Fig. S12. Gas-liquid chromatogram for degradation of PEA at 90 °C for 4 h catalysed by [La(acac)₃] (1 mol%). Methanol (Rt = 1.997 min), ethylene glycol (Rt = 6.491 min), dimethyl adipate (Rt = 9.074 min),

dibenzyl as an internal standard ($R_t = 13.046$). Conditions: initial temp. = 110 °C, equilibrium time = 3.0 min, program time = 7.0 °C min⁻¹, final temp. = 220 °C, hold time = 9.0 min.

8.1. [La(acac)₃] (1 mol%) at 90 °C

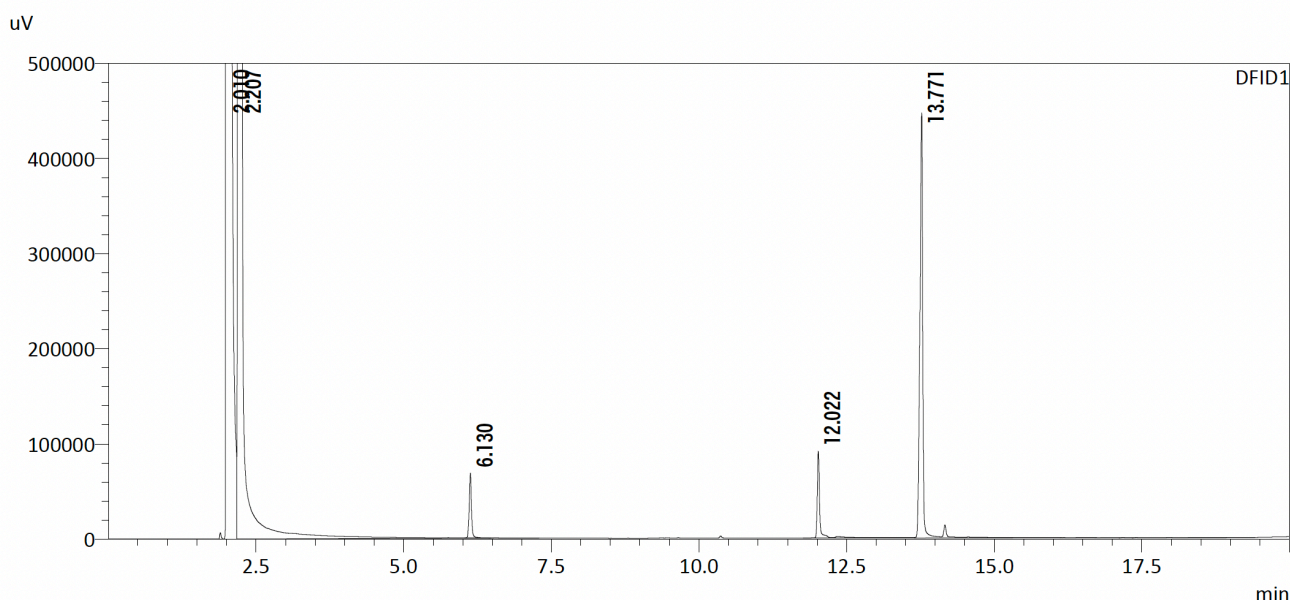
Poly(ethylene adipate) (0.1195 g, 0.001195 mmol) and [La(acac)₃] (2.9 mg, 0.0067 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (9.99 mg, 0.0548 mmol) was added to the solution. Dimethyl adipate (0.690 mmol, 99% yield) and ethylene glycol (0.755 mmol, >99% yield).

8.2. Without catalyst at 90 °C

Poly(ethylene adipate) (0.1174 g, 0.001174 mmol) was stirred in MeOH (5 ml) at 90 °C, for 4 h. Then, dibenzyl (9.97 mg, 0.0547 mmol) was added to the solution. Dimethyl adipate (0.0116 mmol, 2% yield) and ethylene glycol (0.0381 mmol, 6% yield).

9. Degradation of poly(ethylene terephthalate) (Mw: 38,500)

<Chrom atogram >



<Peak Report >

Peak#	Retention Time	Area	Mark	Name
1	2.010	41932083	V	
2	2.207	11885140	SV	
3	6.130	183993	TV	
4	12.022	290926	S	
5	13.771	1472878	SV	
±CEv		55765020		

Fig. S13. Gas-liquid chromatogram for degradation of PET at 150 °C for 4 h catalysed by [La(acac)₃] (1 mol%). Methanol (5 ml, $R_t = 2.010$ min), chloroform (4 ml) as a co-solvent for GLC analysis ($R_t = 2.207$ min) ethylene glycol ($R_t = 6.130$ min), dibenzyl as an internal standard ($R_t = 12.022$ min), dimethyl terephthalate ($R_t = 13.771$ min). Conditions: initial temp. = 110 °C, equilibrium time = 3.0 min, program time = 8.0 °C min⁻¹, final temp. = 220 °C, hold time = 8.0 min.

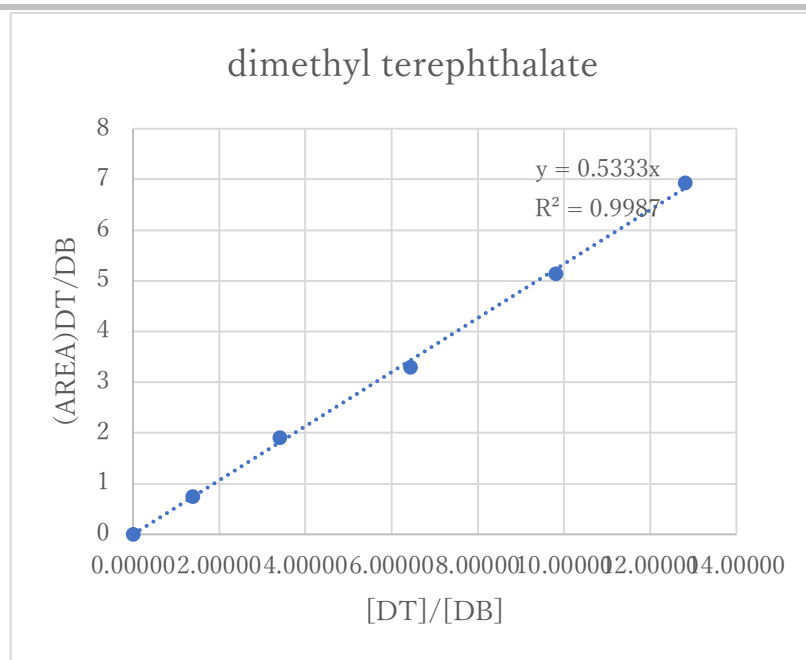


Fig. S14. Calibration curve for calculations of yields of dimethyl terephthalate. The horizontal axis indicates the relative concentration ratio of [dimethyl terephthalate]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on dimethyl terephthalate/dibenzyl. Dibenzyl was used for an internal standard.

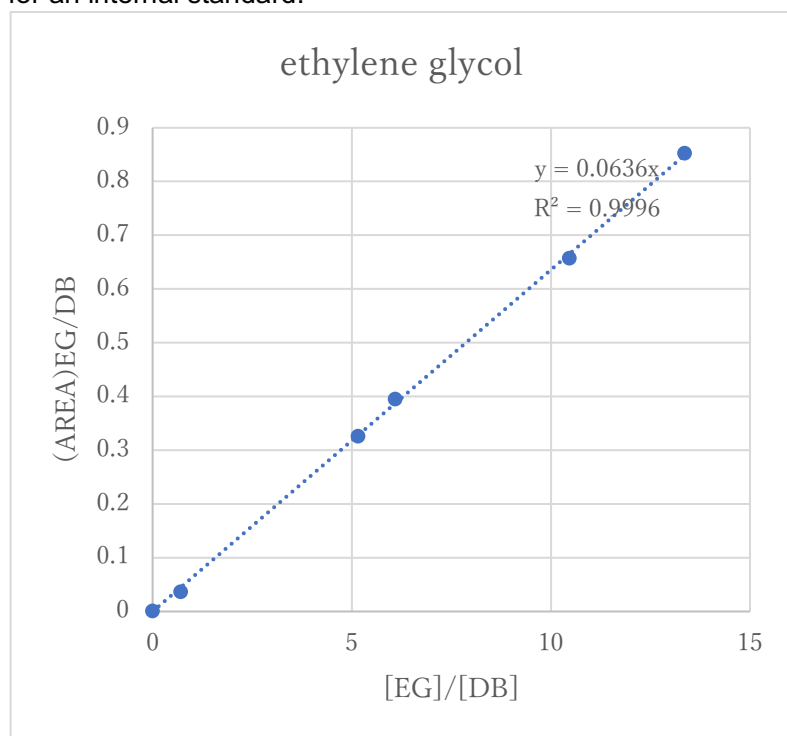


Fig. S15. Calibration curve for calculations of yields of ethylene glycol. The horizontal axis indicates the relative concentration ratio of [ethylene glycol]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on ethylene glycol/dibenzyl. Dibenzyl was used for an internal standard.

9.1. [La(acac)₃] (1 mol%) at 90 °C

Poly(ethylene terephthalate) (0.1378 g, 0.003579 mmol) and [La(acac)₃] (3.1 mg, 0.0071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (10.13 mg, 0.05566 mmol) was added to

the solution. Dimethyl terephthalate (0.0042 mmol, 1% yield) and ethylene glycol (0.0106 mmol, 1% yield).

9.2. [La(acac)₃] (1 mol%) at 120 °C

Poly(ethylene terephthalate) (0.1293 g, 0.003358 mmol) and [La(acac)₃] (3.3 mg, 0.0076 mmol, 1 mol%) were stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.89 mg, 0.0543 mmol) was added to the solution. Dimethyl terephthalate (0.0785 mmol, 12% yield) and ethylene glycol (0.0648 mmol, 10% yield).

9.3. [La(acac)₃] (1 mol%) at 150 °C

Poly(ethylene terephthalate) (0.1329 g, 0.003452 mmol) and [La(acac)₃] (3.1 mg, 0.0071 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.35 mg, 0.05687 mmol) was added to the solution. Dimethyl terephthalate (0.6469 mmol, 94% yield) and ethylene glycol (0.6736 mmol, 97% yield).

9.4. Without catalyst at 90 °C

Poly(ethylene terephthalate) (0.1298 g, 0.003371 mmol) was stirred in MeOH (5 ml) at 90 °C for 4 h. Then, dibenzyl (9.92 mg, 0.0544 mmol) was added to the solution. Dimethyl terephthalate (0% yield) and ethylene glycol (0% yield).

9.5. Without catalyst at 120 °C

Poly(ethylene terephthalate) (0.1303 g, 0.003384 mmol) was stirred in MeOH (5 ml) at 120 °C for 4 h. Then, dibenzyl (9.95 mg, 0.0546 mmol) was added to the solution. Dimethyl terephthalate (0.0050 mmol, 1% yield) and ethylene glycol (0.0035 mmol, 1% yield).

9.6. Without catalyst at 150 °C

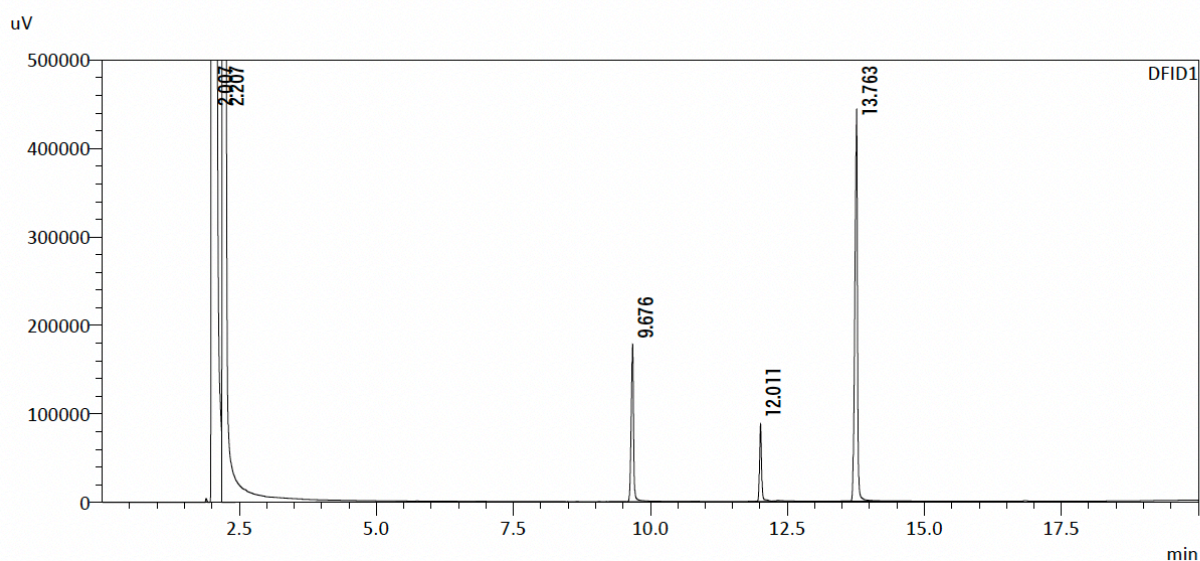
Poly(ethylene terephthalate) (0.1392 g, 0.003616 mmol) was stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.10 mg, 0.05549 mmol) was added to the solution. Dimethyl terephthalate (0.1303 mmol, 18% yield) and ethylene glycol (0.1171 mmol, 16% yield).

10. Degradation of commercially available poly(ethylene terephthalate) bottle of natural water

A commercially available poly(ethylene terephthalate) bottle (the molecular weight unknown) was cut by scissors and small plate of the plastic (0.1415 g) and [La(acac)₃] (3.2 mg, 0.0073 mmol, 1 mol%) stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (10.05 mg, 0.05514 mmol) was added to the solution. Dimethyl terephthalate (0.7290 mmol, 99% yield) and ethylene glycol (0.7605 mmol, >99% yield).

11. Degradation of poly(butylene terephthalate)

<Chrom atogram >



<Peak Report >

Peak#	Retention Time	Area	Mark	Name
1	2.007	44381705	V	
2	2.207	9709820	SV	
3	9.676	551316	S	
4	12.011	253867	S	
5	13.763	1478926	SV	
#CEv		56375633		

Fig. S16. Gas-liquid chromatogram for degradation of PBT at 150 °C for 4 h catalysed by [La(acac)₃] (1 mol%). Methanol (Rt = 2.007 min), chloroform as a co-solvent for GLC analysis (Rt = 2.207 min) 1,4-butanediol (Rt = 9.676 min), dibenzyl as an internal standard (Rt = 12.011 min), dimethyl terephthalate (Rt = 13.763 min). Conditions: initial temp. = 110 °C, equilibrium time = 3.0 min, program time = 8.0 °C min⁻¹, final temp. = 220 °C, hold time = 8.0 min.

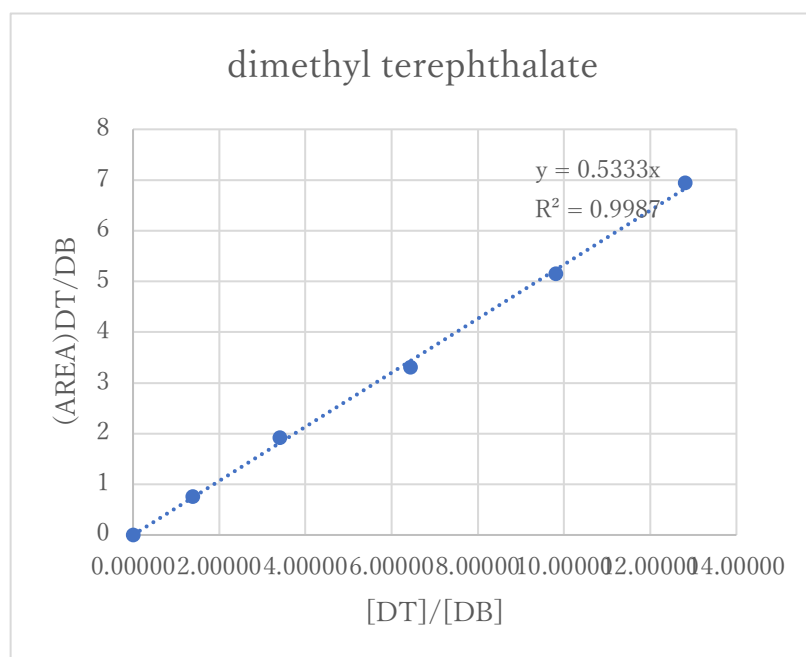


Fig. S17. Calibration curve for calculations of yields of dimethyl terephthalate. The horizontal axis indicates the relative concentration ratio of [dimethyl terephthalate]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on dimethyl terephthalate/dibenzyl. Dibenzyl was used for an internal standard.

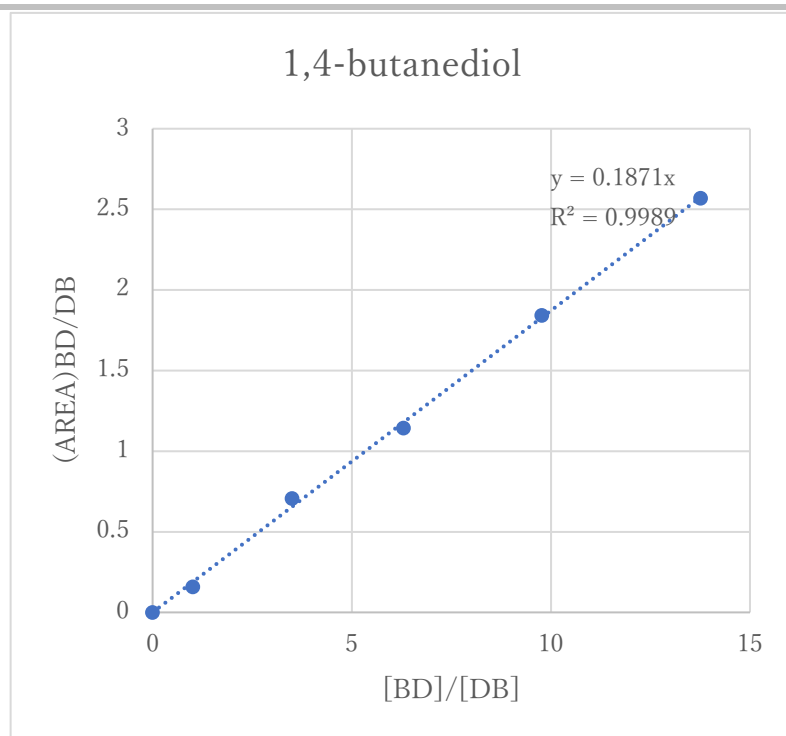


Fig. S18. Calibration curve for calculations of yields of dimethyl terephthalate. The horizontal axis indicates the relative concentration ratio of [dimethyl terephthalate]/[dibenzyl]. The vertical axis indicates the ratio of peak area on chromatogram based on dimethyl terephthalate/dibenzyl. Dibenzyl was used for an internal standard.

11.1. [La(acac)₃] (1 mol%) at 150 °C (Mn = 32,000)

Poly(butylene terephthalate) (0.1512 g, 0.004725 mmol) and [La(acac)₃] (3.3 mg, 0.0076 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (9.97 mg, 0.0547 mmol) was added to the solution. Dimethyl terephthalate (0.5975 mmol, 87% yield) and ethylene glycol (0.6439 mmol, 92% yield).

11.2. [La(acac)₃] (1 mol%) at 150 °C (Mn = 20,000)

Poly(butylene terephthalate) (0.1484 g, 0.007420 mmol) and [La(acac)₃] (3.2 mg, 0.0073 mmol, 1 mol%) were stirred in MeOH (5 ml) at 150 °C for 4 h. Then, dibenzyl (9.90 mg, 0.0543 mmol) was added to the solution. Dimethyl terephthalate (0.5859 mmol, 87% yield) and ethylene glycol (0.6280 mmol, 93% yield).

11.3. Without catalyst at 150 °C (Mn = 32,000)

Poly(butylene terephthalate) (0.1497 g, 0.004678 mmol) was stirred in MeOH (5 ml) at 150 °C, for 4 h. Then, dibenzyl (9.91 mg, 0.0554 mmol) was added to the solution. Dimethyl terephthalate (0.0188 mmol, 3% yield) and ethylene glycol (0.0186 mmol, 3% yield).

11.4. Without catalyst at 150 °C (Mn = 20,000)

Poly(butylene terephthalate) (0.1458 g, 0.007290 mmol) was stirred in MeOH (5 ml) at 150 °C, for 4 h. Then, dibenzyl (10.04 mg, 0.05409 mmol) was added to the solution. Dimethyl terephthalate (0.0439 mmol, 7% yield) and ethylene glycol (0.0381 mmol, 6% yield).

12. Photos of experiments

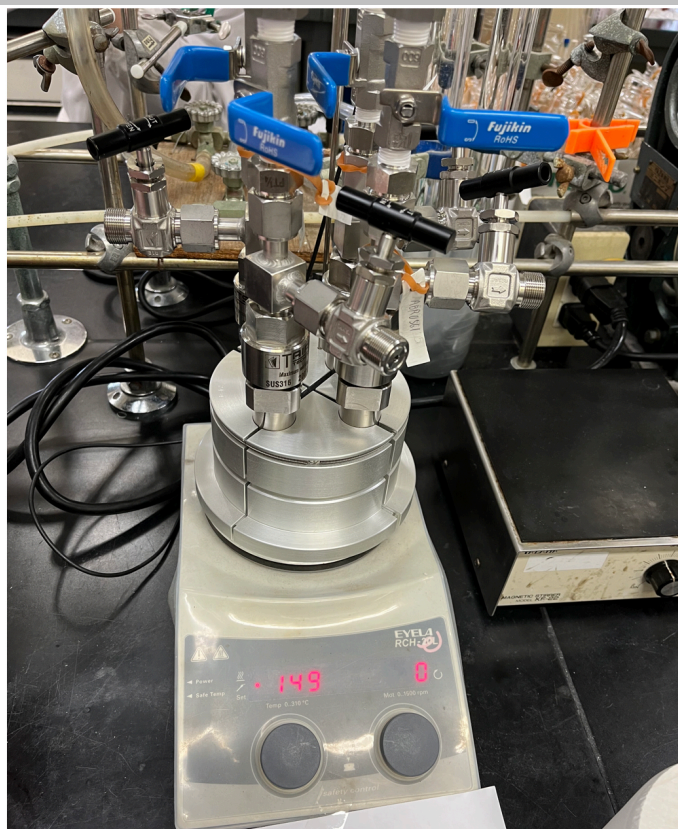


Fig. 19. Typical reaction vessels and the heating and stirring equipment. The aluminum block heater with 4 holes for autoclaves is a custom-order equipment. The reaction temperature could be controlled in the range of ± 1 °C and the magnetic stirrer was set at 800 rpm (EYELA, RCH-1000 BBS and SynFlex). The volume of each autoclave is 20 ml (Taiatsu techno co., TVS-1-20, SUS316).

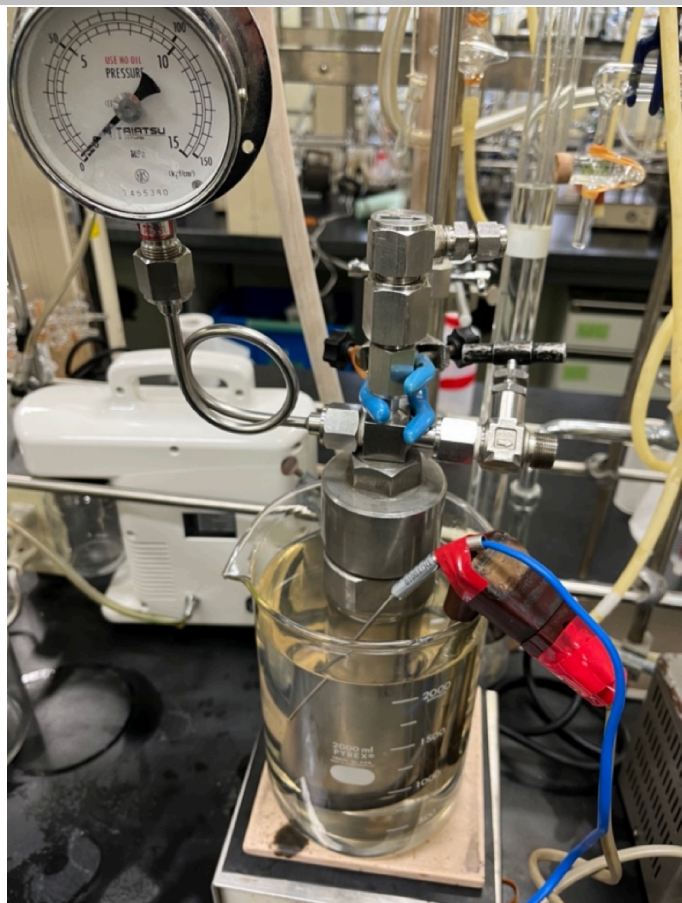


Fig. 20. A 10-gram scale catalytic degradation of **PBS**. The volume of autoclave is 300 ml (Taiatsu techno co., TVS-1-300, SUS316).

14. Reference

- (1) M. Gigli, N. Lotti, M. Gazzano, L. Finelli and A. Munari, *Polym. Eng. Sci.*, 2013, **53**, 491.