Supporting Information for

Naphthalene Engineering of Chemically Recyclable Polyesters with Enhanced Thermal and Mechanical Properties

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(Table 1 entry 0)	-150 KDa, D - 1.40
(Table 1, entry 9)	$-47.6 k D_{0} P - 1.00$
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Materials and Methods

All synthesis and manipulations of air- and moisture-sensitive chemicals and materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar)-filled glovebox. High-performance liquid chromatography (HPLC)-grade anhydrous tetrahydrofuran (THF), toluene (TOL), and dichloromethane (DCM) were dried via a Vigor YJC-5 solvent purification system and stored over activated Davison 4 Å molecular sieves in glovebox. All monomers were recrystallized twice from DCM and petroleum ether (PE) to get the crystals of monomers. The crystals were dried in a vacuum oven at 60 °C for 1 day.

The initiator *p*-tolylmethanol was purchased from adamas and purified via sublimation at 55 °C under vacuum. The organic catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene **TBD** was purchased from adamas and purified via dissolution, filtration and sublimation at 110 °C under vacuum. The catalyst 2,6-diisopropylphenyl substituted β -diiminate zinc trimethylsilyl complex **Zn-1** was prepared according to literature procedures¹. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from adamas and used directly without treatment.



Molecular Weight Measurements

SEC Measurements of polymer number-average molecular weight (M_n) and molecular weight distributions or polydispersity indices ($\mathcal{D} = M_w/M_n$) were performed via size exclusion chromatography (SEC). The SEC instrument consisted of an Agilent LC system equipped with one guard column and two PL gel 5 µm mixed-C gel permeation columns and coupled with an Agilent G7162A 1260 Infinity II RI detector; The analysis was performed at 40 °C using THF as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated with 9 PS standards, and chromatograms were processed with Agilent OpenLab CDS Acquisition 2.5 molecular weight characterization software.

Spectroscopic Characterizations

NMR NMR spectra were recorded on an Agilent 400-MR DD2 or a Bruker AV II-400 MHz spectrometer. Chemical shifts for all spectra were referenced to internal solvent resonances and were reported as parts per million relate to SiMe₄. **HRMS** High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicroTOF-Q. **PXRD** X-ray powder patterns of the polymers

were obtained with a Bruker-D2 PHASER Powder X-Ray Diffractometer with Cu-K α radiation (λ = 1.5416 Å) at 30 kV and 10 mA (scan of 2θ = 2–30° with a step size of 0.2° and count time of 2 sec/step). Before analysis, specimens were cooled by liquid N₂ and grinded until a fine white powder was obtained.

Thermal Analysis

DSC Melting-transition temperature (T_m) and Glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on DSC25, TA Instrument. The heating rate was 10 °C/min and cooling rate was 10 °C/min. **TGA** Decomposition temperature (T_d) and maximum rate decomposition temperatures (T_{max}) of purified and thoroughly dried polymer samples were measured by thermogravimetric analyzer (TGA) on an TGA55, TA Instrument. Polymer samples were heated from ambient temperatures to 600 °C at a heating rate of 10 °C/min. Values of T_{max} were obtained from derivative (wt%/°C) vs. temperature (°C) plots and defined by the peak values, while T_d values were obtained from wt% vs. temperature (°C) plots and defined by the temperature of 5% weight loss.

Mechanical Analysis

Samples were made by melt press in a steel mold ($50 \times 40 \times 0.4 \text{ mm}^3$). Tensile stress/strain testing was performed by an Instron 5967 universal testing system using dog-bone-shaped test specimens (*ca.* 0.4 mm (thickness) × 4 mm (width) × 20 mm (grip width). Specimens were stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 5 times for each test, and the mechanical behavior reported are averaged from the measured data. The Young's modulus (*E'*) was calculated using the slope of the stress-strain curve from 0 to 1% strain.

General Monomer Preparations

General Procedure for M1–M4



M1–M4 were synthesized according to our previous literature², but the procedures were modified and thus described in detail below. Taking the synthesis of monomer M1 as an example, the synthesis processes of M2–M4 were similar, and the detailed processes were no longer described, the differences were pointed out separately.

Synthesis of **b**

3-methoxy salicylaldehyde **a1** (200 mmol, 1 equiv.) and ethyl 2-bromopropanoate **1** (1.1 equiv.) were added to a stirred suspension of anhydrous K_2CO_3 (1.5 equiv.) and KI (0.05 equiv.) in acetonitrile (500 mL). The mixture was stirred under reflux overnight. The cooled reaction mixture was filtrated and concentrated under reduced pressure to afford oily crude product. The crude product was dispersed in PE/EA solution (PE = 500 mL, EA = 50 mL), then the mixture was frozen for several hours at -20 °C. While the resulting solid was crushed, the supernatant was decanted. Then the residue was washed with PE for 2–3 times to afford a white solid product **b1** which was used directly for the next step. **b2–b4** were synthesized according to the synthesis method of **b1**, expect that corresponding starting materials 5-bromo salicylaldehyde **a2** 2 hydroxy-1-naphthaldehyde **a3** were used instead of **a1**. **b4** obtained a new alkyl long chain group by replacing ethyl 2-bromopropanoate **1** with methyl 2-bromooctanoate **2**.

Synthesis of c

Sodium borohydride (NaBH₄, 0.275 equiv.) was slowly added into a stirred solution of **b1** (1 equiv.) in ethanol and dichloromethane (EtOH : DCM = 250 mL : 250 mL) cooled to 0 °C with an ice water bath. The mixture was stirred at 0 °C for 30 min and quenched by a dilute hydrochloric acid solution (2 N, 100 mL) to pH \approx 5–7. The mixture was concentrated under reduced pressure to remove EtOH, and then the resulting mixture was extracted with DCM (100 mL \times 3). The combined organic layer was concentrated under reduced pressure to give the crude product **c1**, which was used directly in the subsequent reaction without further purification. **c2, c3** and **c4** were synthesized according to the synthesis method of **c1**. Methanol (MeOH) instead of ethanol (EtOH) was used for the synthesis of **c4**, while other conditions were same.

Synthesis of **d**

To the solution of crude product **c1** (1 equiv.) in tetrahydrofuran THF and H₂O (THF : H₂O = 300 mL : 300 mL) was added with NaOH (1.5 equiv.). The reaction mixture was extracted with DCM after stirring at RT for 1 h. The collected lower water phase was quenched with hydrochloric acid (6 N) solution to pH \approx 3–4 at 0 °C. Then the mixture was extracted with EtOAc (100 mL × 3). The combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure to give crude product **d1** as solid. The crude product was dispersed in PE/EA solution (PE = 500 mL, EA = 50 mL), then the mixture was frozen for several hours at –20 °C. The supernatant was decanted, while the resulting solid was crushed and washed with PE for 2–3 times to obtain white solid product **d1** (40.6 g, 90% total yield in three steps) which was used directly for the next step. **d2** (36.8 g, 67% total yield in three steps), **d3** (39.3 g, 53% total yield in three steps) and **d4** (33.5 g, 53% total yield in three steps) were synthesized according to the synthesis method of **d1**.

Synthesis of M

To a solution of crude carboxylic acid **c** (1 equiv.) in 600 mL of anhydrous DCM was added triethylamine (Et₃N) (1.5 equiv.) and hydroxybenzotriazole (HOBt) (1 equiv.). The resulting mixture was cooled to -5 °C, and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (1.2 equiv.) was added to the solution. After the addition, the solution was allowed to stir at -5 °C for 1 h. After that, the solution was warmed up to RT and continued to stir at RT overnight. The organic solution was washed with water and saturated brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc/DCM = 8/1/1) to afford **M1** (white solid, 26.1 g, 70% yield; 63% total yield in four steps). **M2** (white solid, 24.0 g, 70% yield; 47% total yield in four steps), **M3** (white solid, 21.0 g, 71% yield; 31% total yield in four steps) and **M4** (white solid, 12.5 g, 39% yield; 21% total yield in four steps) were synthesized according to the synthesis method of **M1**.

NMR spectra of d1-d4



¹H NMR (400 MHz, CDCl₃) δ 7.05 (t, *J* = 7.9 Hz, 1H), 6.96–6.87 (m, 2H), 5.03 (q, *J* = 6.9 Hz, 1H), 4.88 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 3.86 (s, 3H), 1.63 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 176.28, 151.21, 144.55, 133.41, 124.13, 122.16, 112.67, 75.96, 61.26, 55.89, 18.96.



Figure S1. ¹H NMR (CDCl₃, 25 °C) spectrum of d1.



Figure S2. ¹³C NMR (CDCl₃, 25 °C) spectrum of d1.



¹H NMR (400 MHz, CDCl₃) δ 7.49–7.30 (m, 2H), 6.82 (br, 2H), 6.71 (d, *J* = 8.6 Hz, 1H), 4.99–4.78 (m, 2H), 4.41 (d, *J* = 12.5 Hz, 1H), 1.67 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 174.70, 154.92, 132.78, 132.22, 131.72, 114.47, 114.37, 73.30, 61.57, 18.63.



Figure S3. ¹H NMR (CDCl₃, 25 °C) spectrum of d2.



Figure S4. ¹³C NMR (CDCl₃, 25 °C) spectrum of d2.



¹H NMR (400 MHz, CDCl₃: HFIP) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.88–7.80 (m, 2H), 7.63–7.51 (m, 1H), 7.47–7.39 (m, 1H), 7.17 (d, *J* = 9.1 Hz, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.11 (q, *J* = 6.9 Hz, 1H), 1.75 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃: HFIP) δ 176.69, 153.29, 132.56, 131.09, 130.00, 128.81, 127.74, 124.75, 122.68, 121.87, 114.21, 73.62, 55.84, 18.69.



Figure S5. ¹H NMR (CDCl₃ : HFIP, 25 °C) spectrum of d3.



Figure S6. 13 C NMR (CDCl₃ : HFIP, 25 °C) spectrum of d3.



¹H NMR (CDCl₃, 25 °C) δ 8.01 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 9.1 Hz, 1H), 5.17 (d, *J* = 11.8 Hz, 1H), 4.98 (d, *J* = 11.8 Hz, 1H), 4.74 (t, *J* = 6.0 Hz, 1H), 1.94–1.71 (m, 2H), 1.50–1.38 (m, 2H), 1.31–1.21 (m, 6H), 0.90–0.84 (m, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 176.32, 153.52, 132.80, 130.27, 129.59, 128.40, 127.12, 124.09, 123.19, 122.35, 114.35, 77.67, 55.00, 32.92, 31.69, 29.00, 25.38, 22.69, 14.16.



Figure S7. ¹H NMR (CDCl₃, 25 °C) spectrum of d4.



Figure S8. ¹³C NMR (CDCl₃, 25 °C) spectrum of d4.

NMR spectra of monomers M1-M4



M1

¹H NMR (CDCl₃, 25 °C) δ 7.06 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.97 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.36 (d, *J* = 12.7 Hz, 1H), 5.30 (d, *J* = 12.7 Hz, 1H), 5.00 (q, *J* = 6.8 Hz, 1H), 3.87 (s, 3H), 1.73 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 171.66, 151.19, 145.66, 128.65, 124.29, 120.60, 113.63, 76.94, 67.92, 56.12, 18.81. HRMS (LCMS-IT-TOF): m/z calculated for C₁₁H₁₃O₄ [M + H]⁺ 209.0809, found 209.0814.



Figure S9. ¹H NMR (CDCl₃, 25 °C) spectrum of M1.



Figure S10. ¹³C NMR (CDCl₃, 25 °C) spectrum of M1.



¹H NMR (CDCl₃, 25 °C) δ 7.41 (dd, J = 8.7, 2.4 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 5.51 (d, J = 14.0 Hz, 1H), 5.16 (q, J = 6.6 Hz, 1H), 5.07 (d, J = 14.0 Hz, 1H), 1.64 (d, J = 6.6 Hz, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 170.48, 155.62, 133.70, 131.84, 125.80, 121.79, 115.22, 73.99, 67.61, 18.16. HRMS (LCMS-IT-TOF): m/z calculated for C₁₀H₁₀BrO₃ [M + H]⁺ 256.9808, found 256.9813.



Figure S11. ¹H NMR (CDCl₃, 25 °C) spectrum of M2.



Figure S12. ¹³C NMR (CDCl₃, 25 °C) spectrum of M2.



M3

¹H NMR (CDCl₃, 25 °C) δ 7.88–7.79 (m, 3H), 7.62–7.51 (m, 1H), 7.50–7.38 (m, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 5.87 (d, *J* = 13.7 Hz, 1H), 5.77 (d, *J* = 13.7 Hz, 1H), 5.13 (q, *J* = 6.7 Hz, 1H), 1.72 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 171.64, 155.56, 131.36, 131.25, 130.59, 129.01, 127.63, 125.03, 121.83, 120.54, 119.19, 76.36, 63.42, 18.70. HRMS (LCMS-IT-TOF): m/z calculated for C₁₄H₁₃O₃ [M + H]⁺ 229.0860, found 229.0855.



Figure S13. ¹H NMR (CDCl₃, 25 °C) spectrum of M3.



Figure S14. ¹³C NMR (CDCl₃, 25 °C) spectrum of M3.



M4

¹H NMR (CDCl₃, 25 °C) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.87–7.78 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 5.90 (d, *J* = 13.5 Hz, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 4.89 (t, *J* = 6.1 Hz, 1H), 2.15–2.06 (m, 2H), 1.73–1.56 (m, 2H), 1.45–1.31 (m, 6H), 0.98–0.83 (m, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 171.53, 155.97, 131.43, 131.38, 130.75, 129.03, 127.64, 125.11, 121.91, 120.35, 120.31, 81.18, 63.25, 33.06, 31.80, 29.08, 25.45, 22.72, 14.19. HRMS (LCMS-IT-TOF): m/z calculated for C₁₉H₂₃O₃ [M + H]⁺ 299.1642, found 299.1638.



Figure S15. ¹H NMR (CDCl₃, 25 °C) spectrum of M4.



Figure S16. ¹³C NMR (CDCl₃, 25 °C) spectrum of M4.

General polymerization procedures

In glovebox, vigorously stirred prepared monomer and initiator (*p*-tolylmethanol) in solution were mixed with catalyst in solution in 4 mL glass vial for ambient temperature runs. (Note: the solution of catalyst was prepared freshly each time.) After an expected time, the mixture solution was quenched by chloroform solution with dissolved benzoic acid (1% w.t.). Then 10 μ L quenched mixture solution was taken out for ¹H NMR analysis to monitor the conversion of monomer. The remaining solution was dripped into 50 mL cold MeOH twice to precipitate polymer to remove unreacted monomer and catalyst residue. The white polymer was filtered, washed with cold methanol and dried in a vacuum oven at 60 °C overnight to a constant weight.

Copolymerization procedure was similar with the above procedure for homopolymerization of M1–M4. M3 and M5 were added into the 4 mL glass vial at the same time, and then initiator, solution, and catalyst in solution were also added. Copolymerization results were summarized in Table S1.

Copolymerization of monomers

MЗ



P[(**M3**)_n-co-(**M5**)_m]

Table S1. Copolymerization results of M3 and M5.^a

Μ5

Entry	[M3]/[M5]/[TBD]/[PMBA]	Time	Conv. ^{<i>b</i>} (%)	$M_{\rm n}{}^c$ (kDa)	D^{c}	$T_{g}^{d}(^{\circ}\mathrm{C})$
		30 s	79/45	N.D.	N.D	/
1 ^e	200/200/1/1	$2 \min$	97/83	47.8	1.12	/
		10 min	99/98	49.5	1.09	/
		30 min	99/99	63.2	1.28	39
2^e	160/240/1/1	10 min	96/77	61.2	1.06	/
	100/210/1/1	30 mim	99/99	67.7	1.10	25
3 ^e	80/220/1/1	10 min	94/61	46.9	1.12	/
	80/320/1/1	30 min	99/99	57.4	1.09	11
4 ^{<i>f</i>}	400/400/2/1	8 h	99/99	80.6	1.82	37
5 ^f	360/440/2/1	8 h	99/99	95.8	1.81	32
6 ^{<i>f</i>}	320/480/2/1	8 h	99/99	83.6	1.72	22

^{*a*}Conditions: [monomer] = 1.0 M, DCM as the solvent, TBD as the catalyst, *p*-tolylmethanol (PMBA) as the initiator, room temperature. ^{*b*}Monomer conversion measured by ¹H NMR of the quenched solution. ^{*c*}Number-average molecular weight (M_n) and dispersity index ($D = M_w/M_n$), determined by size exclusion chromatography (SEC) at 40 °C in THF. ^{*d*}Glass transition temperature T_g was measured by DSC with the cooling and heating rate of 10 °C min⁻¹ for all samples. ^{*e*}n(M3+M5) = 0.5 mmol. ^{*f*}n(M3+M5) = 10 mmol.

Characterization of polymers

NMR spectra of polymers

MeÓ

P(M1)

¹H NMR (CDCl₃, 25 °C) δ 7.00–6.90 (m, 1H), 6.88–6.77 (m, 2H), 5.41 (t, *J* = 12.8 Hz, 1H), 5.29–5.19 (m, 1H), 4.93–4.83 (m, 1H), 3.73–3.68 (m, 3H), 1.57–1.47 (m, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 172.36, 151.42, 144.96, 129.53, 123.78, 121.33 112.60, 76.70, 62.10, 55.80, 19.08.



Figure S17. ¹H NMR (CDCl₃, 25 °C) spectrum of P(M1).



Figure S18. ¹³C NMR (CDCl₃, 25 °C) spectrum of P(M1).



¹H NMR (CDCl₃, 25 °C) δ 7.36–7.18 (m, 2H), 6.67–6.52 (m, 1H), 5.30–5.15 (m, 2H), 4.83–4.71 (m, 1H), 1.60 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 171.18, 154.48, 132.36, 132.24, 126.52, 113.79, 113.72, 72.99, 61.94, 18.66.



Figure S19. ¹H NMR (CDCl₃, 25 °C) spectrum of P(M2).



Figure S20. ¹³C NMR (CDCl₃, 25 °C) spectrum of P(M2).



P(M3)

¹H NMR (CDCl₃: HFIP, 25 °C) δ 7.75–7.39 (m, 3H), 7.34–7.06 (m, 2H), 6.97–6.78 (m, 1H), 5.90– 5.57 (m, 1H), 5.55–5.30 (m, 1H), 4.86–4.50 (m, 1H), 1.63–1.32 (m, 3H). ¹³C NMR (CDCl₃: HFIP, 25 °C) δ 174.35, 153.92, 133.18, 131.74, 129.60, 128.66, 127.64, 124.60, 122.78, 116.53, 114.06, 74.21, 59.14, 18.17.



Figure S21. ¹H NMR (CDCl₃ : HFIP, 25 °C) spectrum of P(M3).



Figure S22. ¹³C NMR (CDCl₃ : HFIP, 25 °C) spectrum of P(M3).



P(M4)

¹H NMR (CDCl₃, 25 °C) δ 7.73–7.39 (m, 3H), 7.30–7.25 (m, 1H), 7.24–7.02 (m, 1H), 7.00–6.85 (m, 1H), 5.87–5.32 (m, 2H), 4.79–4.50 (m, 1H), 2.00–1.75 (m, 2H), 1.50–1.30 (m, 2H), 1.28–1.09 (m, 6H), 0.89–0.72 (m, 3H). ¹³C NMR (CDCl₃, 25 °C) δ 171.65, 154.46, 133.34, 131.19, 129.28, 128.46, 127.09, 123.97, 123.02, 116.63, 114.18, 77.64, 58.23, 32.96, 31.67, 29.04, 25.17, 22.66, 14.15.



Figure S23. ¹H NMR (CDCl₃, 25 °C) spectrum of P(M4).



Figure S24. ¹³C NMR (CDCl₃, 25 °C) spectrum of P(M4).



5.5 2.0 4.5 4.0 2.5 1.5 8.5 7.5 7.0 6.5 6.0 5.0 3.5 3.0 1.0 0.5 8.0 0.0 -0. f1 (ppm)

Figure S25. ¹H NMR (CDCl₃, 25 °C) spectrum of $P[(M3)_{10}-co-(M5)_{10}]$ produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1.



Figure S26. ¹H NMR (CDCl₃, 25 °C) spectral analysis of $P[(M3)_{10}-co-(M5)_{10}]$ produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1.

a) P(M3), top; b) P(M5), middle; c) P[(M3)₁₀-co-(M5)₁₀], bottom.

$$\frac{[\mathbf{M3}]}{[\mathbf{M5}]} = \frac{x - y}{y} = \frac{4.2 - 2}{2} = 1.1$$


Figure S27. ¹³C NMR (CDCl₃, 25 °C) spectrum of $P[(M3)_{10}-co-(M5)_{10}]$ produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1.



Figure S28. ¹H NMR (CDCl₃, 25 °C) spectrum of $P[(M3)_9-co-(M5)_{11}]$ produced by [M3]/[M5]/[TBD]/[I] = 360/440/2/1.

$$\frac{[\mathbf{M3}]}{[\mathbf{M5}]} = \frac{x - y}{y} = \frac{3.7 - 2}{2} = 0.85$$



Figure S29. ¹H NMR (CDCl₃, 25 °C) spectrum of $P[(M3)_8$ -*co*-(M5)₁₂] produced by [M3]/[M5]/[TBD]/[I] = 320/480/2/1.

$$\frac{[\mathbf{M3}]}{[\mathbf{M5}]} = \frac{x - y}{y} = \frac{3.4 - 2}{2} = 0.7$$

Thermal properties of polymers



Figure S30. DSC curves of P(M1) produced by [M1]/[TBD]/[I] = 1000/1/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table 1, entry 5)



Figure S31. DSC curves of P(M2) produced by [M2]/[TBD]/[I] = 1000/1/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table 1, entry 9)



Figure S32. DSC curves of P(M3) produced by [M3]/[TBD]/[I] = 200/1/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table 1, entry 10) a) Ramp 10 °C/min to 200 °C. b) Ramp 10 °C/min to 240 °C. c) TGA curve of the weight change of P(M3) at 240 °C for 1 h



Figure S33. DSC curves of P(M4) produced by [M4]/[TBD]/[I] = 1000/1/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table 1, entry 13)



Figure S34. TGA curves of P(M1) produced by [M1]/[TBD]/[I] = 1000/1/1 in DCM at a heating rate of 10 °C/min. (Table 1, entry 5)



Figure S35. TGA curves of P(M2) produced by [M2]/[TBD]/[I] = 1000/1/1 in DCM at a heating rate of 10 °C/min. (Table 1, entry 9)



Figure S36. TGA curves of P(M3) produced by [M3]/[TBD]/[I] = 200/1/1 in DCM at a heating rate of 10 °C/min. (Table 1, entry 10)



Figure S37. TGA curves of P(M4) produced by [M4]/[TBD]/[I] = 1000/1/1 in DCM at a heating rate of 10 °C/min. (Table 1, entry 13)

Thermal properties of P[(M3)_n-co-(M5)_m]



Figure S38. DSC curves of $P[(M3)_{10}-co-(M5)_{10}]$ produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table S1, entry 4)



Figure S39. DSC curves of $P[(M3)_9$ -*co*-(M5)_{11}] produced by [M3]/[M5]/[TBD]/[I] = 360/440/2/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table S1, entry 5)



Figure S40. DSC curves of $P[(M3)_8$ -*co*-(M5)₁₂] produced by [M3]/[M5]/[TBD]/[I] = 320/480/2/1 in DCM at a heating and cooling scanning rate of 10 °C/min. (Table S1, entry 6)

SEC traces of polymers



Figure S41. SEC trace of P(M1) produced by [M1]/[TBD]/[I] = 1000/1/1 in DCM. $M_n = 122$ kDa, D = 1.19. (Table 1, entry 5)



Figure S42. SEC trace of P(M2) produced by [M2]/[TBD]/[I] = 1000/1/1 in DCM. $M_n = 158$ kDa, D = 1.48. (Table 1, entry 9)



Figure S43. SEC trace of P(M4) produced by [M4]/[TBD]/[I] = 200/1/1 in DCM. $M_n = 47.6$ kDa, D = 1.09. (Table 1, entry 12)

SEC traces of P[(M3)_n-co-(M5)_m]



Figure S44. SEC trace of $P[(M3)_{10}-co-(M5)_{10}]$ produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1 in DCM. $M_n = 80.6$ kDa, D = 1.82. (Table S1, entry 4)



Tensile testings and mechanical properties of polymers

Figure S45. Molded polymer images of P(M1)–P(M4).



Figure S46. Tensile testing of P(M1) ($M_n = 97.5$ kDa, D = 1.81) produced by [M1]/[TBD]/[I] = 500/2/1 at a strain rate of 10 mm/min.

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Sample number	Yield strength ^b	Tensile strength ^c	Strain ^d	$E^{\prime e}$		
1	(MPa)	(MPa)	(%)	(GPa)		
1	44.8	40.5	10.8	2.53		
2	/	34.2	4.37	2.22		
3	/	31.3	9.39	2.16		
4	/	29.4	4.47	2.33		
5	/	35.7	8.80	2.29		
Average	/	34.2	7.57	2.31		
Standard deviation	/	4.28	2.96	0.14		

Table S2. Mechanical properties of P(M1).^{*a*}

^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at yield. ^{*c*}Stress at break. ^{*d*}Strain at break. ^{*e*}Young's modulus (*E*') calculated as the slope from 0 to 1% strain.



Figure S47. Tensile testing of P(M4) ($M_n = 65.7 \text{ kDa}$, D = 1.16) produced by [M4]/[TBD]/[I] = 500/2/1 at a strain rate of 10 mm/min.

1 1			
Sample number	Tensile strength ^b (MPa)	Strain ^c (%)	E'd (GPa)
1	7.68	1.05	0.80
2	4.72	0.62	0.81
3	4.46	0.6	0.82
4	4.08	0.54	0.77
5	4.10	0.54	0.75
Average	5.01	0.67	0.79
Standard deviation	1.51	0.22	0.03

	Table S	5 3. M	echanical	properties	of P	(M 4)). ^a
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^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at break. ^{*c*}Strain at break. ^{*d*}Young's modulus (E') calculated as the slope from 0 to 1% strain.





Figure S48. Molded and stretched copolymer images of $P[(M3)_n$ -*co*- $(M5)_m]$. Molded copolymers produced by a) [M3]/[M5]/[TBD]/[I] = 400/400/2/1, left; b) [M3]/[M5]/[TBD]/[I] = 360/440/2/1, middle; c) [M3]/[M5]/[TBD]/[I] = 320/480/2/1, right.



Figure S49. Tensile testing of $P[(M3)_{10}$ -*co*-(M5)_{10}] (Table S1, entry 4, $M_n = 80.6$ kDa, D = 1.82) produced by [M3]/[M5]/[TBD]/[I] = 400/400/2/1 repeated with five replicates at a strain rate of 10 mm/min.

Table S4. Mechanical properties of $P[(MS)_{10}-co-(MS)_{10}]$."						
Sample number	Tensile strength ^b (MPa)	Strain ^c (%)	E'd (GPa)			
1	40.8	4.86	1.56			
2	37.8	3.95	1.84			
3	41.7	5.29	1.61			
4	37.1	3.54	1.68			
5	37.1	3.54	1.73			
Average	38.9	4.24	1.68			
Standard deviation	2.19	0.80	0.11			

Table S4. Mechanical properties of P[(M3)₁₀-co-(M5)₁₀].^a

^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at break. ^{*c*}Strain at break. ^{*d*}Young's modulus (*E*') calculated as the slope from 0 to 1% strain.



Figure S50. Tensile testing of $P[(M3)_9$ -co- $(M5)_{11}]$ (Table S1, entry 5, $M_n = 95.8$ kDa, D = 1.89) produced by [M3]/[M5]/[TBD]/[I] = 360/440/2/1 repeated with five replicates at a strain rate of 10 mm/min.

Sampla number	Yield strength ^b	Tensile strength ^c	Strain ^d	E 'e
Sample number	(MPa)	(MPa)	(%)	(GPa)
1	12.9	11.4	54.4	0.63
2	14.9	12.2	62.7	0.67
3	18.0	14.7	142	0.88
4	15.4	12.4	78.8	0.81
5	20.7	13.6	61.4	0.96
Average	16.4	12.9	79.9	0.79
Standard deviation	3.02	1.30	35.9	0.14

Table S5. Mechanical properties of P[(M3)9-co-(M5)11].^a

^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at yield. ^{*c*}Stress at break. ^{*d*}Strain at break. ^{*e*}Young's modulus (*E*') calculated as the slope from 0 to 1% strain.



Figure S51. Tensile testing of $P[(M3)_8$ -co-(M5)₁₂] (Table S1, entry 6, $M_n = 83.6$ kDa, D = 1.72) produced by [M3]/[M5]/[TBD]/[I] = 320/480/2/1 repeated with five replicates at a strain rate of 10 mm/min.

Samula mumban	Yield strength ^b	Tensile strength ^c	Strain ^d	E 'e
Sample number	(MPa)	(MPa)	(%)	(GPa)
1	4.32	9.28	500	0.32
2	4.76	9.52	503	0.37
3	4.87	9.79	545	0.29
4	5.94	9.89	492	0.35
5	5.59	9.34	509	0.32
Average	5.10	9.56	510	0.33
Standard deviation	0.66	0.27	20.6	0.03

Table S6. Mechanical properties of P[(M3)₈-co-(M5)₁₂].^a

^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at yield. ^{*c*}Stress at break. ^{*d*}Strain at break. ^{*e*}Young's modulus (*E'*) calculated as the slope from 0 to 1% strain.

Polymer materials	Tensile strength (MPa)	Straind (%)	E'(GPa)
$P[(M3)_8$ -co-(M5) ₁₂] ^a	9.6^{b}	510 ^c	0.33^{d}
LDPE ³	9.9	312	-
HDPE ³	30.2	900	-
P3HB ⁴	32	2.1	2.8
$PLLA^4$	28–50	2–6	1.2-3.0
<i>i</i> PP ⁵	26	420	1.2

Table S7. A summary of mechanical properties of $P[(M3)_8$ -*co*- $(M5)_{12}]$ and commercial polymer materials.

^{*a*}Condition: Tested by uniaxial tensile tests at a strain rate of 10 mm/min. ^{*b*}Stress at break. ^{*c*}Strain at break. ^{*d*}Young's modulus (*E'*) calculated as the slope from 0 to 1% strain. The mechanical properties of the other polymers listed in the Table S7 were from the literatures^{3–5}.

Chemical Recycling to Monomer (CRM)

General procedure for the CRM of polymers under bulk thermal.

PEO and polymer were mixed in a ratio of 10:1, and a catalytic amount of $Sn(AcO)_2$ was added. The mixture was kept at 110 °C–140 °C with stirring under vacuo for a certain time. After the reaction was stopped, the sublimate was collected, weighted, and characterized by ¹H NMR spectroscopy.

Entry	Polymers	Sn(AcO) ₂ (mol%)	Time (h)	T (°C)	Monomer Yield ^b (%)
1	P(M1)	3	24	110	99
2	P(M2)	3	40	110	98
3	P(M3)	10	54	140	86
4	P(M4)	10	54	140	88

Table S8. Results of bulk thermal chemical recycling of M1–M4.^a

^{*a*}Condition: all polymers were purified twice, catalyst: Sn(AcO)₂, cooling temperature: 5 °C with ethyl alcohol. m[PEO] : m[\mathbf{M}] = 10 : 1. ^{*b*}The monomer yield determined by the amount of the sublimate and the purity of recycled monomer determined by ¹H NMR spectroscopy.

Table S9. Result of re-polymerization of recycled M4 produced by bulk thermal chemical recycling.^a

Entry	Monomer	[M]/[Cat]/[I]	Time (h)	Conv. ^{<i>b</i>} (%)	$M_{\rm n}{}^c$ (kg/mol)	$D^{c}\left(M_{\mathrm{w}}/M_{\mathrm{n}}\right)$
1	M4	50/1/1	1	99%	12.2	1.46

^{*a*}Condition [**M**] = 1 M, DCM as the solvent, TBD as the catalyst, *p*-tolylmethanol as the initiator, room temperature. ^{*b*}Monomer conversion was measured by ¹H NMR of quenched solution. ^{*c*}Number average eight (M_n) and dispersity ($D = M_w/M_n$), determined by size exclusion chromatography at 40 °C in THF.



Figure S52. ¹H NMR spectra of recycled M1 by bulk thermal depolymerization of P(M1). a) P(M1) obtained by [M1]/[TBD]/[I] = 200/1/1, top; b) recycled M1 by the thermal depolymerization, middle; c) starting M1 for comparison, bottom.



Figure S53. ¹H NMR spectra of recycled M2 by bulk thermal depolymerization of P(M2). a) P(M2) obtained by [M2]/[TBD]/[I] = 200/1/1, top; b) recycled M2 by the thermal depolymerization, middle; c) starting M2 for comparison, bottom.



Figure S54. ¹H NMR spectra of recycled M3 by bulk thermal depolymerization of P(M3). a) P(M3) obtained by [M3]/[TBD]/[I] = 200/1/1, top; b) recycled M3 by the thermal depolymerization, middle; c) starting M3 for comparison, bottom.



Figure S55. ¹H NMR spectra of recycled M4 by bulk thermal depolymerization of P(M4). a) P(M4) obtained by [M4]/[TBD]/[I] = 200/1/1, top; b) recycled M4 by the thermal depolymerization, middle; c) starting M4 for comparison, bottom.

General procedure for the CRM of polymers in dilute solutions

A tube containing the purified polymer sample with 3 mol% **Zn-1** in toluene (0.02 M) was sealed and heated to 140 °C for 21 h and 58 h under an argon atmosphere. After cooling back to room temperature, the reaction mixture was concentrated to give a solid, which was used for ¹H NMR analysis to determine the recycled monomer yield.



Zn-1

Table S10. Results of chemical recycling of M3–M4 in dilute solution.^a

Polymers ^b	T (°C)	Time (h)	Monomer Yield ^c (%)
D(M2)	140	21	92
$P(\mathbf{N13})$	140	58	98
$\mathbf{D}(\mathbf{M}\mathbf{A})$	140	21	93
P(114)		58	96

^{*a*}Condition: All reactions were in toluene (0.02 M) and glovebox, catalyst: **Zn-1** 3 mol%. ^{*b*}P(**M3**) obtained by [**M3**]/[**Zn-1**]/[I] = 200/1/1; P(**M4**) obtained by [**M4**]/[**Zn-1**]/[I] = 200/1/1. ^{*c*}The monomer yield determined by ¹H NMR analysis.



Figure S56. ¹H NMR spectra of recycled M3 by solution depolymerization of P(M3) at 21 h. a) P(M3) obtained by [M3]/[TBD]/[I] = 200/1/1, top; b) recycled M3 by the solution depolymerization, middle; c) starting M3 for comparison, bottom.



Figure S57. ¹H NMR spectra of recycled M3 by solution depolymerization of P(M3) at 58 h. a) P(M3) obtained by [M3]/[TBD]/[I] = 200/1/1, top; b) recycled M3 by the solution depolymerization, middle; c) starting M3 for comparison, bottom.



Figure S58. ¹H NMR spectra of recycled M4 by solution depolymerization of P(M4) at 21 h. a) P(M4) obtained by [M4]/[TBD]/[I] = 200/1/1, top; b) recycled M4 by the solution depolymerization, middle; c) starting M4 for comparison, bottom.



Figure S59. ¹H NMR spectra of recycled M4 by solution depolymerization of P(M4) at 58 h. a) P(M4) obtained by [M4]/[TBD]/[I] = 200/1/1, top; b) recycled M4 by the solution depolymerization, middle; c) starting M4 for comparison, bottom.

Chain transesterification



Figure S60. Chain transesterification in this polymerization systems.
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