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Supporting Information for

Implementing Sulfur-Substitution Approach Toward a High-Performance Recyclable Polythioester

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Materials and Methods

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). An AXIMA Performance instrument was used in reflection mode with anthralin as the matrix. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by the solutions of matrix (0.4 μL, 5 mg/mL in tetrahydrofuran) and polymer (2 μL, 5 mg/mL in tetrahydrofuran) were mixed together. The mixed solution was spotted on the MALDI sample plate and air-dried. The raw data was processed in the Shimadzu Biotech MALDI-MS software.

Wide angle X-ray diffraction (WXRD)

Powder X-ray diffraction data were obtained using a Bruker D2 Phaser diffractometer with Cu-Kα radiation (λ = 1.5416 Å) at 30 kV and 10 mA (scan of 2θ = 1.5–60° with a speed of 1°/min).

WVTR and oxygen permeability

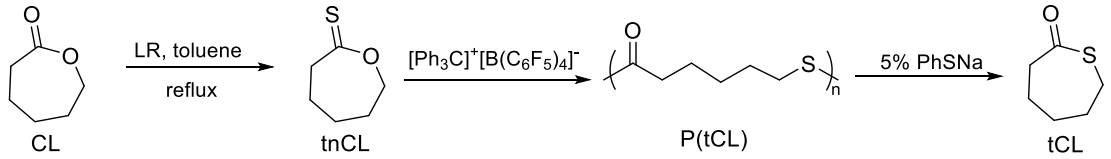
Individual sample thickness (~0.30 mm) was measured before testing using film thickness gauge TG-3130-A3. The WVTR was measured by a Labthink W3/062 equipment at 38 °C and 90% relative humidity. Oxygen permeability was measured by a Labthink Pressure Change Apparatus equipment G2/132 at 23 °C.

Mechanical Analysis

Tensile stress/strain testing was performed by an Instron 5967 universal testing system. Samples were made by melt press in a steel mold (50 × 4 × 0.4 mm^3) and were stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 4 times for each test, and the values reported are averaged from the measured data.

Monomer Preparations

Scheme S1. Synthesis of tCL



Step One: A mixture of caprolactone (20.6 g, 20 mL, 181 mmol) and Lawesson's reagent (43.8 g, 108 mmol) in toluene (400 mL) was stirred at reflux for 1 h. After 1 h, the full consumption of starting material was confirmed by TLC analysis. Upon cooling to room temperature (RT), the insoluble substance was filtered to remove. Then the removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 30/1), which afforded 2-oxepanethione as a yellow oil (13 g, yield = 55 %).[1] The obtained 2-oxepanethione (tnCL) was purified via vacuum distillation after drying over CaH_2 for 1 day, which was then stored at −35 °C inside the glovebox. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60−4.36 (m, 2H), 3.25−3.08 (m, 2H), 1.86 (ttt, *J* = 7.3, 5.0, 2.1 Hz, 2H), 1.81−1.66 (m, 4H).

Step Two: In this typical polymerization reaction, the solution of initiator $[Ph_3C]^+[B(C_6F_5)_4]^-$ (92.1 mg) in 2 mL toluene was added to the vigorously stirred prepared monomer (13 g) in 45.2 mL toluene. The polymerization reactions were performed in 250 mL glass bottle inside the glovebox at ambient temperature and [tnCL]/[I]=1000:1. After 1 h, the polymerization was quenched by addition of 10 mL $CDCl_3$ acidified with benzoic acid (2 wt%). The quenched mixture precipitated into 500 mL of cold methanol, filtered, and washed with cold methanol. This procedure was repeated twice to ensure any catalyst residue or unreacted monomer was removed. The polymer was dried in a vacuum oven at 60 °C to a constant weight. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, *J* = 7.3 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.73−1.51 (m, 6H), 1.45−1.33 (m, 2H).

Step Three: PEO-10000 and polymer (12.8 g) were mixed in a weight ratio of 2:1, and PhSNa (681 mg) was added. The mixture was subjected to vacuum distillation at 180 °C. After the reaction was stopped, the distillate was collected as the pure tCL (12 g, yield = 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08−2.99 (m, 2H), 2.91−2.82 (m, 2H), 2.12 (p, *J* = 5.9 Hz, 2H), 1.90−1.73 (m, 4H).

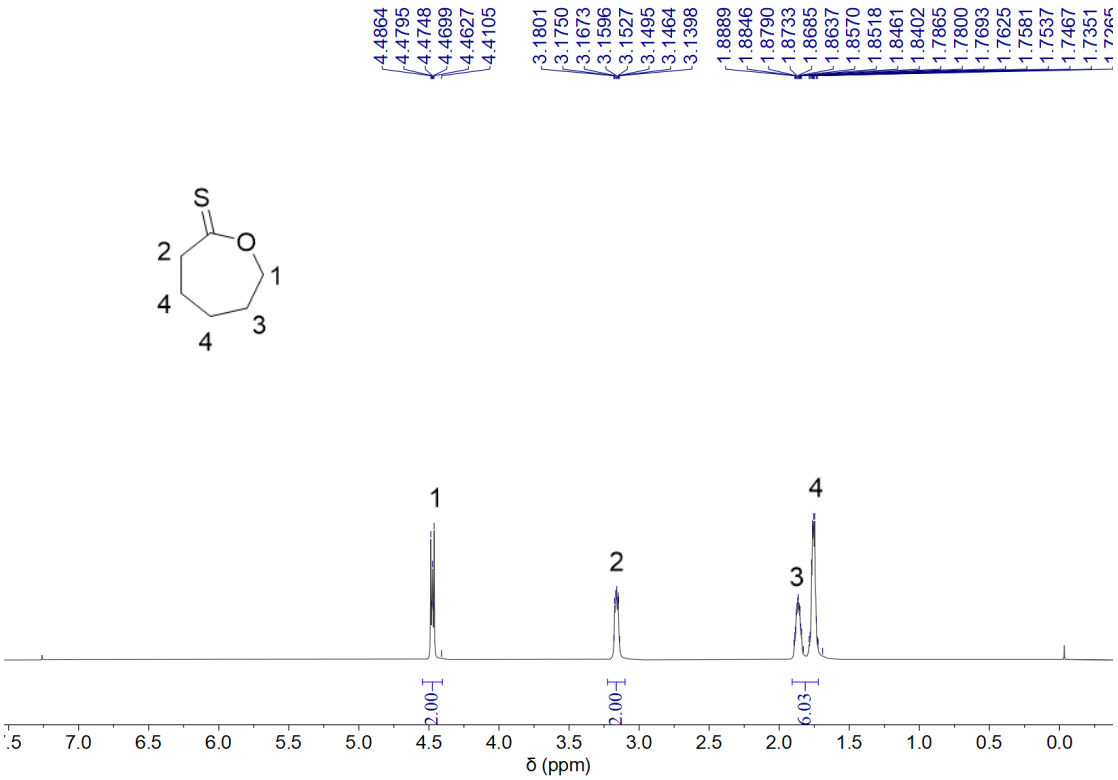


Fig. S1 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of tnCL.

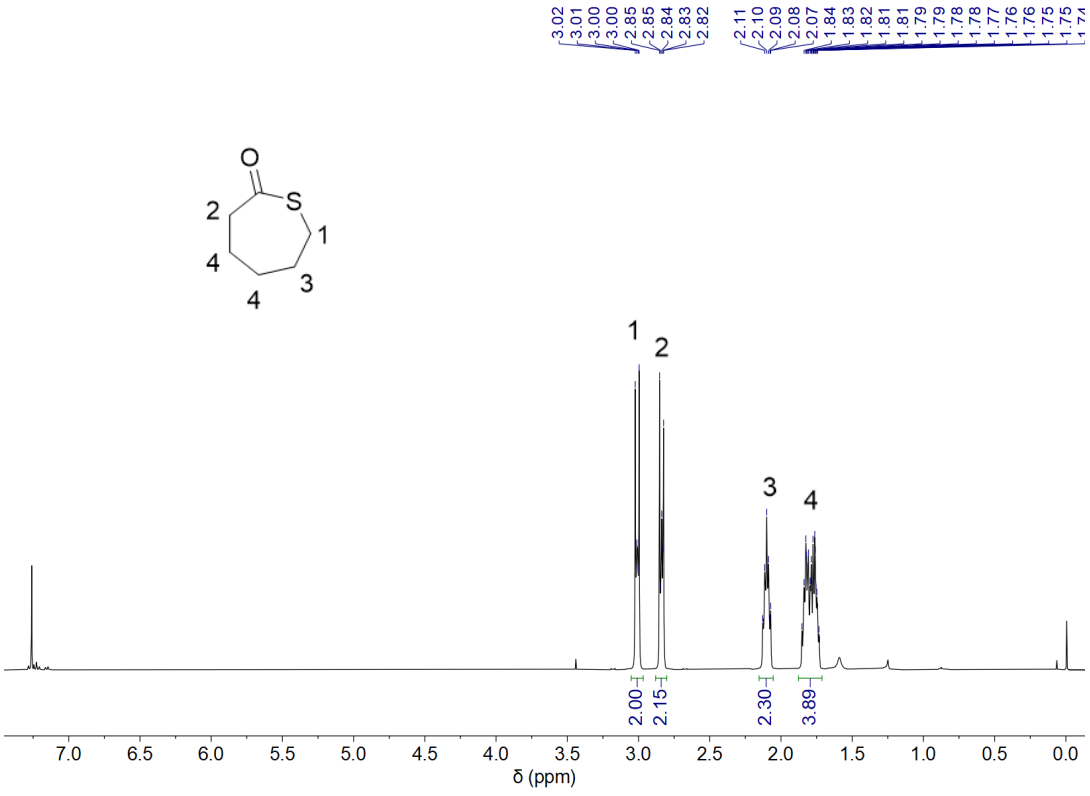


Fig. S2 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of tCL.

General Polymerization Procedures

Polymerization reactions were performed in 4 mL glass vials inside the glovebox for ambient temperature runs. In a typical polymerization reaction, the solution of catalyst in DCM or toluene was added to the vigorously stirred prepared monomer and initiator (benzyl mercaptan) solution in DCM or toluene. After a desired period of time, the polymerization was quenched by addition of 1 mL $CDCl_3$ with benzoic acid (1 wt.%). The quenched mixture precipitated into 50 mL of cold methanol, filtered, and washed with cold methanol. This procedure was repeated twice to ensure any catalyst residue or unreacted monomer was removed. The polymer was dried in a vacuum oven at 60 °C to a constant weight.

Table S1 Results of ROP of tCL. [a]

Entry	Cat.	[tCL]/[Cat.]/[I]	Time (h)	Conv.[b] (%)	$M_{n,Calcd}$ [c] (kDa)	$M_{n,SEC}$ [d] (kDa)	$Đ$ [d]
1	TBD	100:1:1	10 min	88	11.5	13.9	1.33
2	TBD	500:1:1	2	65	42.3	42.1	1.32
3	TBD	1000:1:1	4	60	78.1	43.3	1.31
4[e]	TBD	1500:1:1	5	74	144	39.2	1.33
5[e]	TBD	2000:1:1	7	82	214	31.3	1.35
6[f]	TBD	1000:1:0.33	20 min	83	108	15.0	1.70
7[f]	^{t}BuP$_4$	1000:1:1	4.5	91	118	54.8	1.92
8[f]	IMes	1000:1:1	1.3	47	61.2	36.9	1.68
9	**La**	1000:1:3	2 min	95	41.2	52.0	1.90
10	**La**	500:1:0	1.5 min	95	-	99.2	1.94
11	**La**	1000:1:0	4 min	94	-	103	1.67

[a] Condition: tCL = 50 mg, Concentration = 1.1 mol/L, initiator (I) = Benzyl Mercaptan, solvent = Tol, RT. [b] Monomer conversion measured by ^{1}H NMR of the quenched solution. [c] Calculated from $[M]_0/[BnSH]_0 \times Conv. \times MW_{\mathbf{M}} + MW_{BnSH}$. [d] Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$), determined by Size-Exclusion Chromatography (SEC) at 40 °C in THF. [e] Temp. = 60 °C. [f] Bulk polymerization, Temp. = 60 °C.

Polymer Characterization

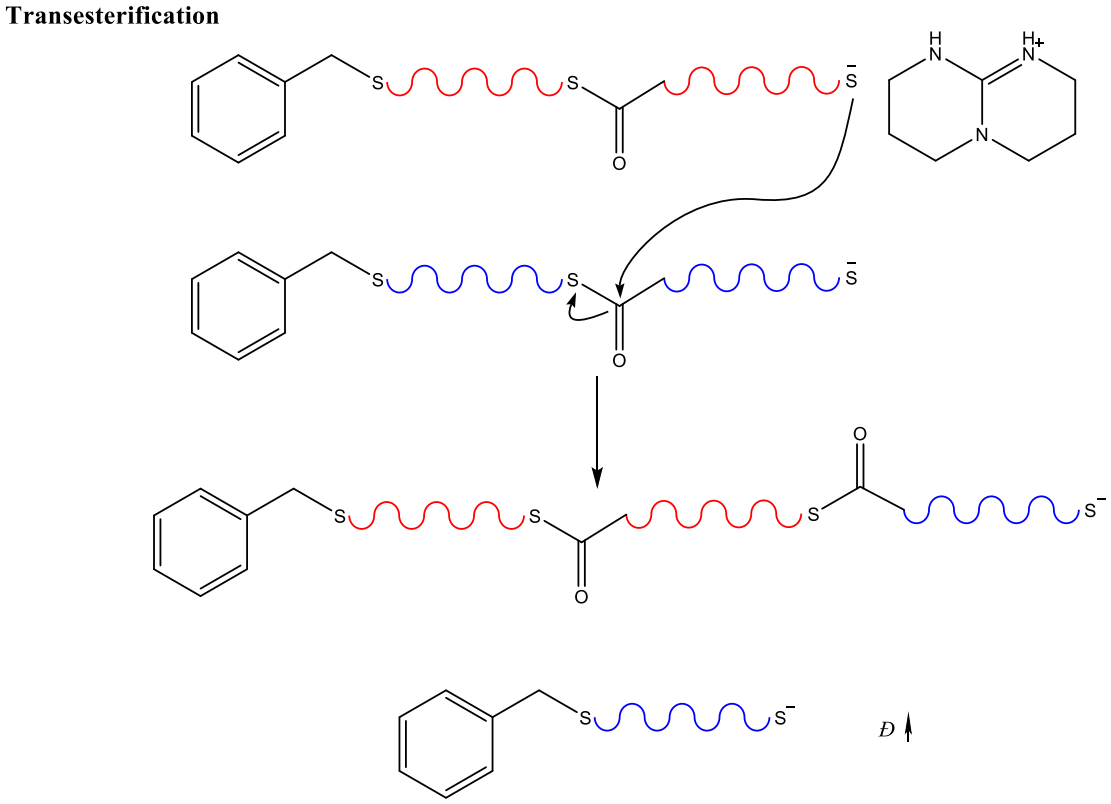
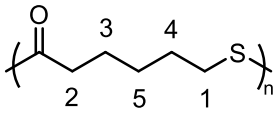


Fig. S3 Chain transesterification in this polymerization systems.

NMR spectra of polymer



P(tCL)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, *J* = 7.3 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.73−1.51 (m, 6H), 1.45−1.33 (m, 2H).

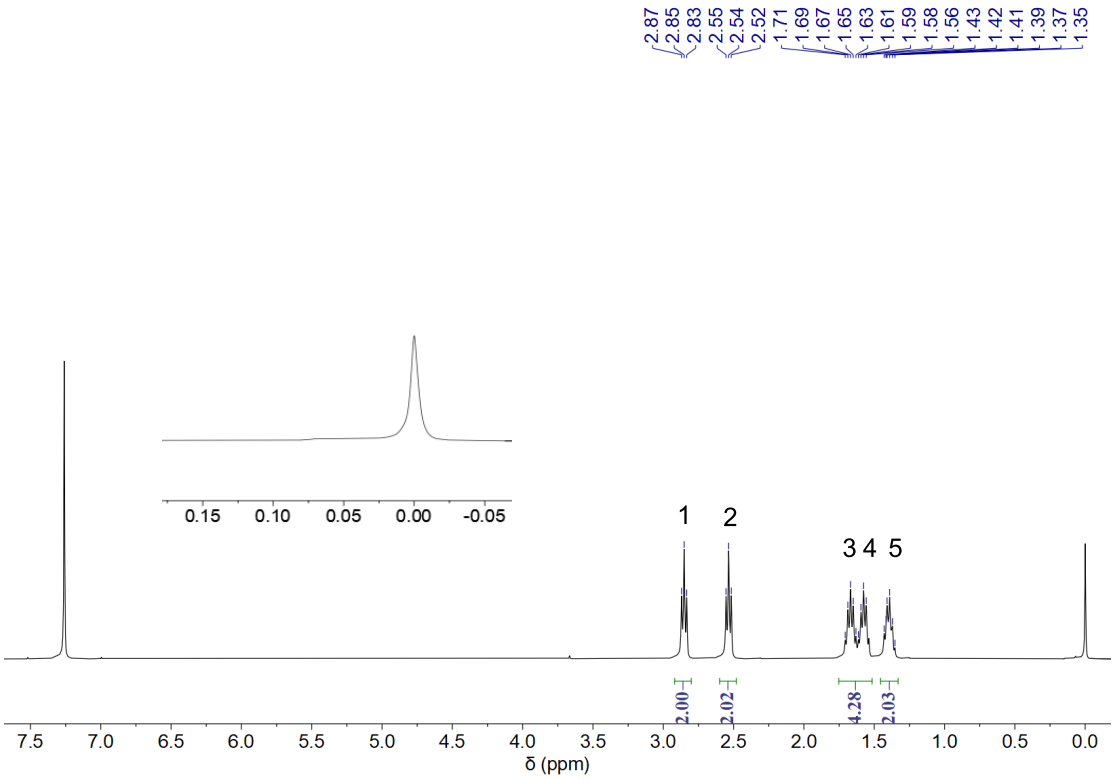


Fig. S4 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(tCL**)** obtained by [tCL]/[La] = 50/1.

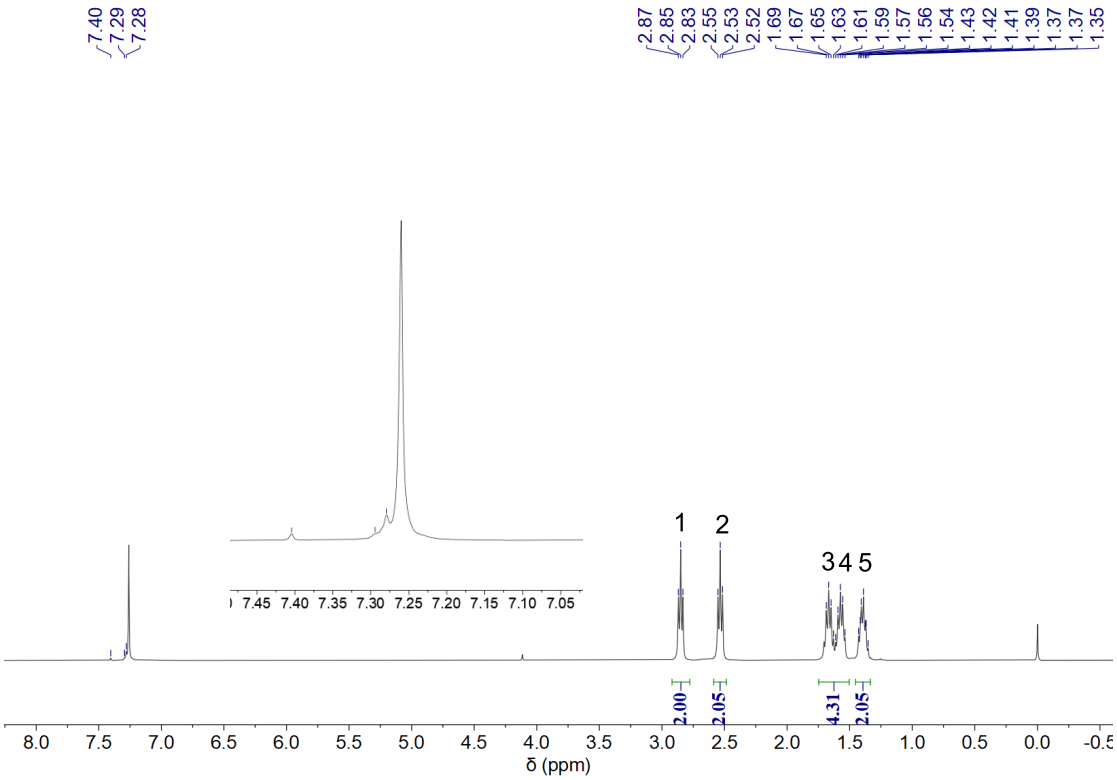


Fig. S5 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(tCL**)** obtained by [tCL]/[TBD]/ [BnSH] = 50/1/1.

The polymer was purified by dissolving in chloroform, and then precipitated into cold methanol, filtered, and washed with cold methanol. This procedure was repeated twice to ensure any catalyst residue or unreacted monomer was removed. The polymer was dried in a vacuum oven at 60 °C to a constant weight.

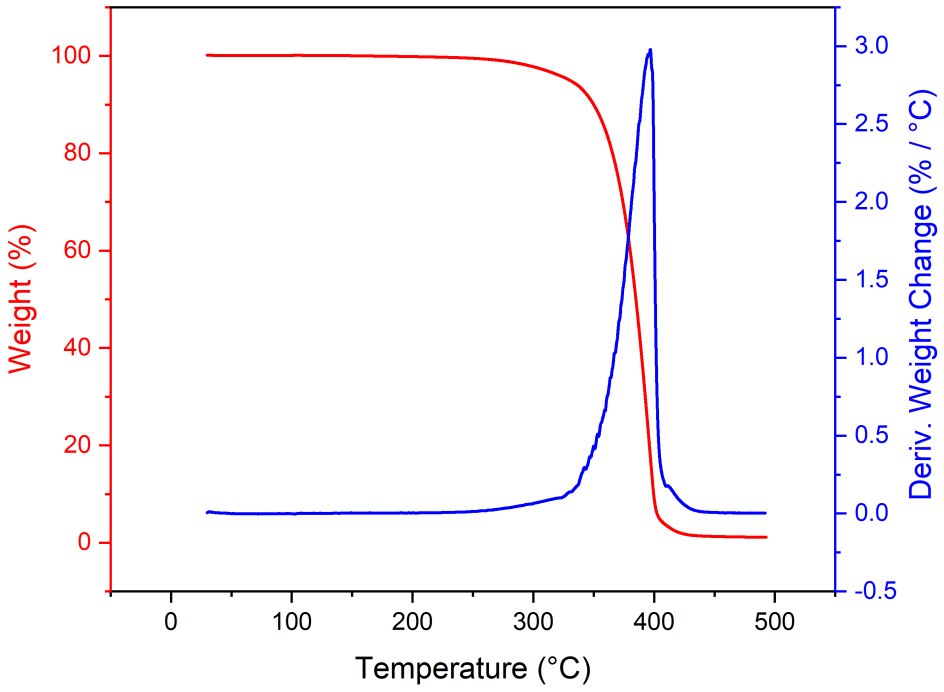


Fig. S6 TGA and DTG curves for P(tCL) obtained by [tCL]/[TBD]/[I] = 100/1/1, T_d = 330 °C, T_{max} = 397 °C.

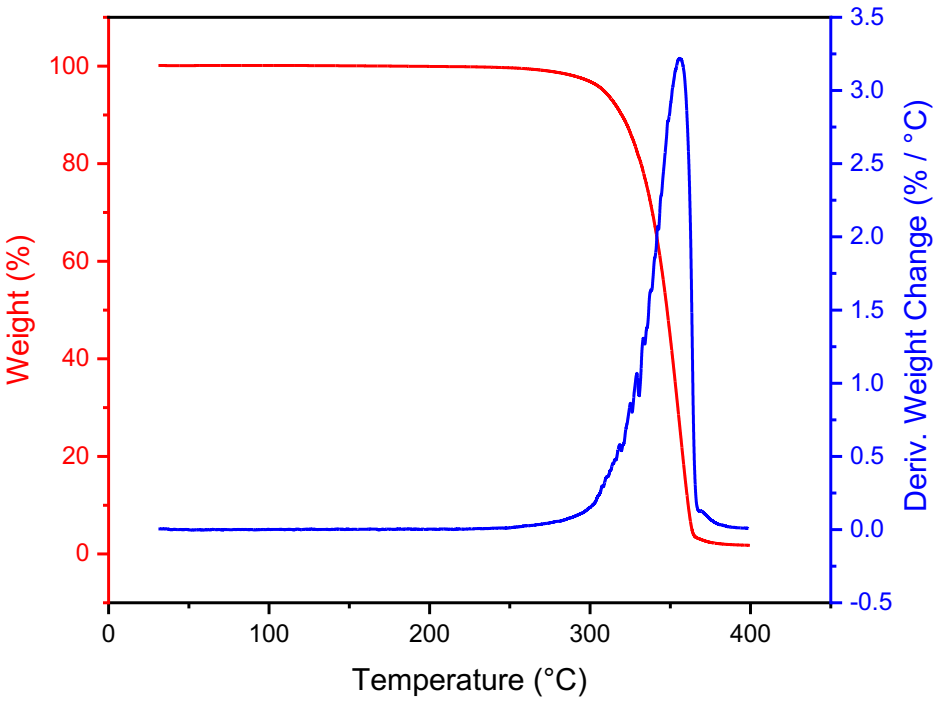


Fig. S7 TGA and DTG curves for P(tCL) obtained by [tCL]/[La] = 1000/1, T_d = 309 °C, T_{max} = 363 °C.

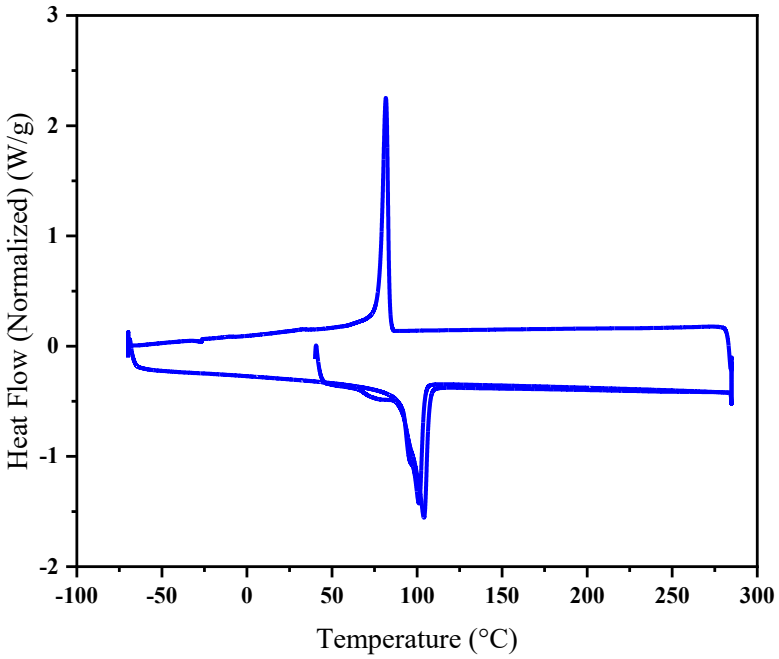


Fig. S8 DSC curves for P(tCL) obtained by [tCL]/[TBD]/[I] = 100/1/1, T_c = 82 °C, T_m = 101 °C.

MALDI-TOF MS Spectrum of The Low-Molecular-Weight P(tCL)

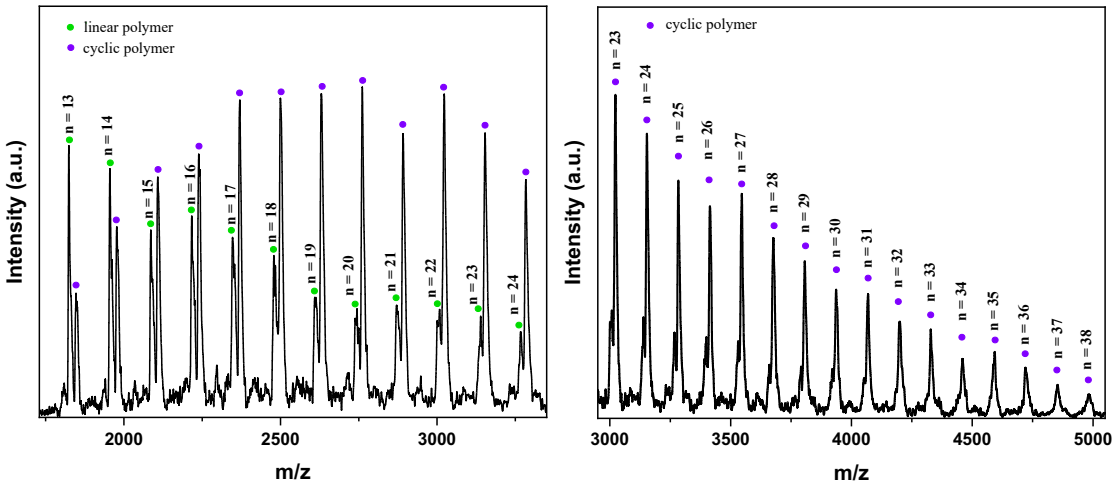


Fig. S9 MALDI-TOF MS spectrum of the low-molecular-weight P(tCL) produced by [tCL]/[TBD]/[BnSH] = 50/1/1.

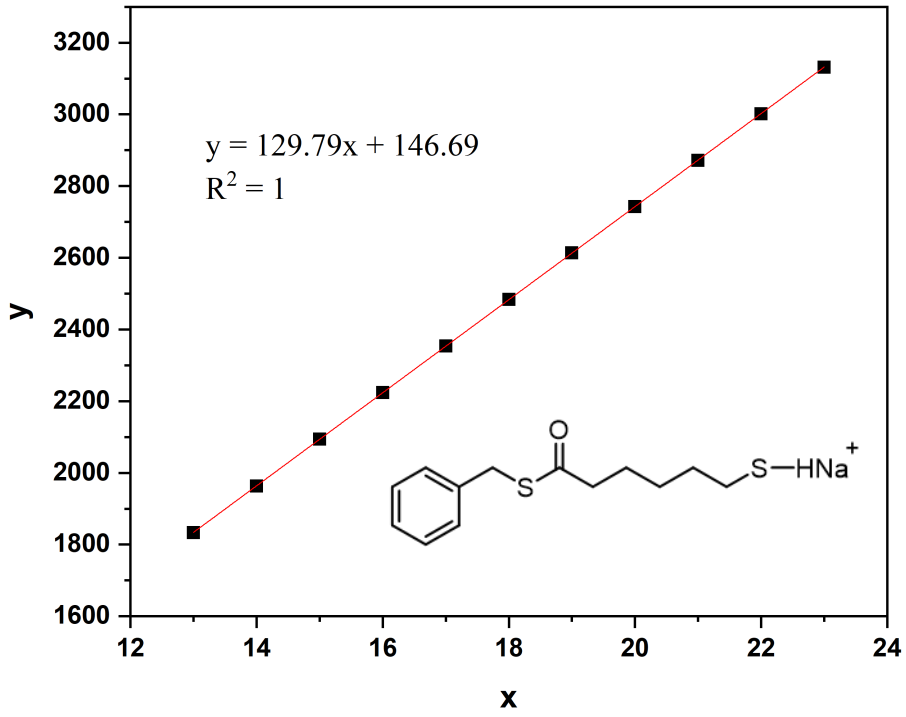


Fig. S10 linear plot of m/z values (y) vs the number of tCL repeat units (x).

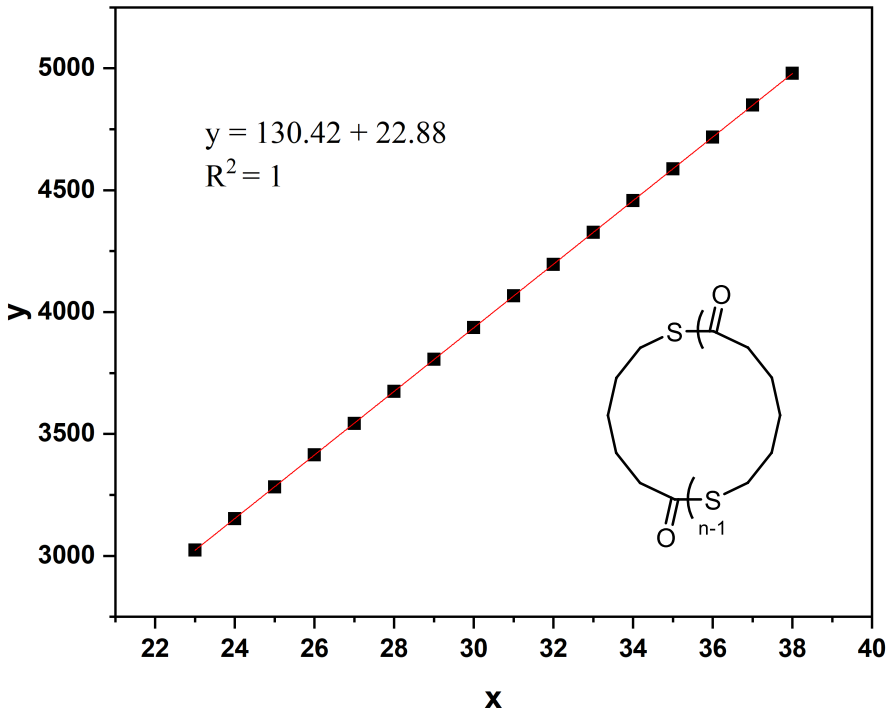


Fig. S11 cyclic plot of m/z values (y) vs the number of tCL repeat units (x).

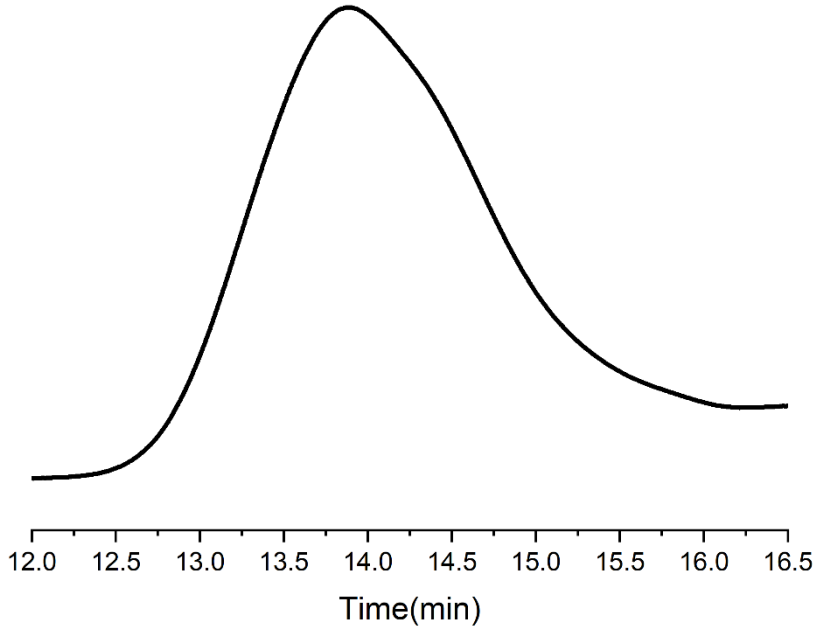


Fig. S12 SEC trace of P(tCL) obtained by [tCL]/[TBD]/[I] = 100/1/1, M_n = 13.9 kDa, $Đ$ = 1.33 (Table S1, entry 1).

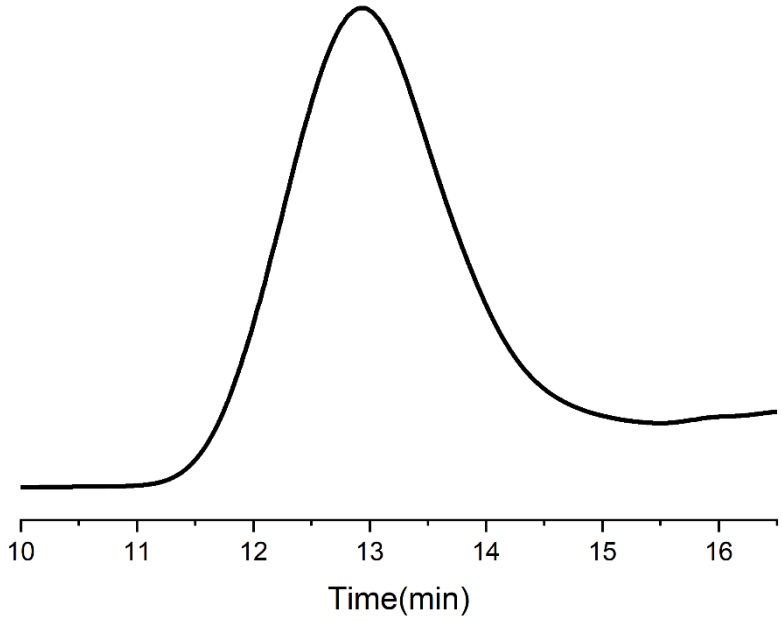


Fig. S13 SEC trace of P(tCL) obtained by [tCL]/La[N(SiMe$_3$)$_2$]$_3$ = 1000/1, M_n = 103 kDa, $Đ$ = 1.67 (Table S1, entry 10).

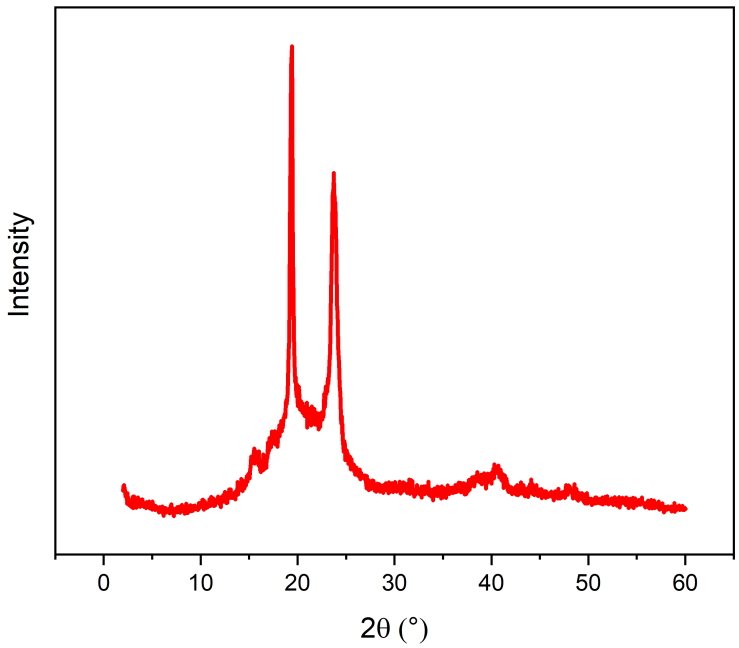


Fig. S14 Powder XRD profiles of P(tCL).

Mechanical Property

Low-density polyethylene (Particle size = 80 mesh; product code LDPE™ 2426K) was purchased from SINOPEC. Samples were made by melt pressing at 120 °C in a steel mold (50 × 40 × 0.4 mm3). Tensile stress/strain testing was performed by an Instron 5967 universal testing system. Samples were made by hot pressure in a steel mold (50 × 60 × 0.6 mm^3) and were stretched at a strain rate of 10 mm/min at ambient temperature until break.

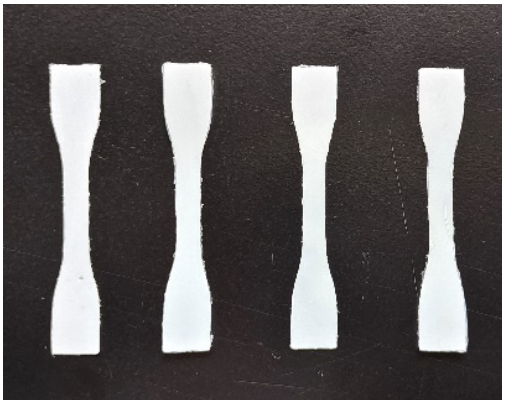


Fig. S15 Polymer samples for mechanical test.

Table S2 Melt pressing temperature and M_n and $Đ$ before and after melt pressing.

Sample	Pressing temperature (°C)	before pressing		after pressing	
		M_n (kDa)	$Đ$	M_n (kDa)	$Đ$
P(tCL)	102	63.7	1.68	62.4	1.71
Low-M_n P(tCL)	102	28.9	1.50	29.6	1.57

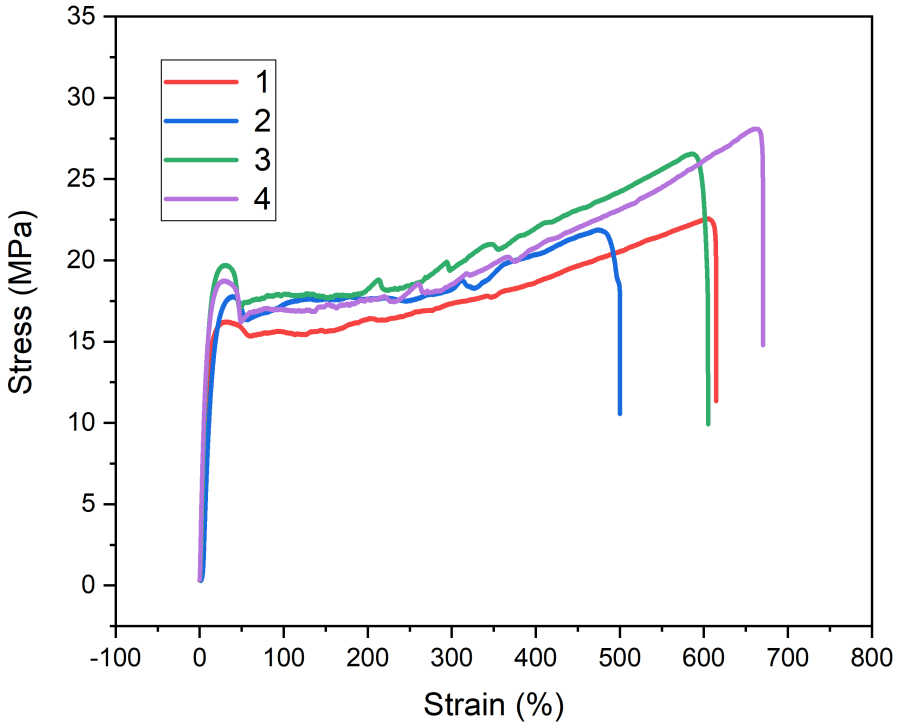


Fig. S16 Stress-strain curves of P(tCL)s.

Table S3 Summary of mechanical properties of P(tCL)s. [a]

Entry	σ_Y (MPa)	σ_B (MPa)	*E* (MPa)	Elongation (%)
1	16.23	19.67	199.16	614.55
2	17.79	18.22	144.39	499.84
3	19.71	17.04	214.87	604.85
4	18.75	25.04	239.28	670.23
Average	18.12 ± 1.48	19.99 ± 3.53	199.43 ± 40.23	597.37 ± 71.11

[a] Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, σ_Y: yield strength, σ_B: break strength, *E*: Tensile modulus.

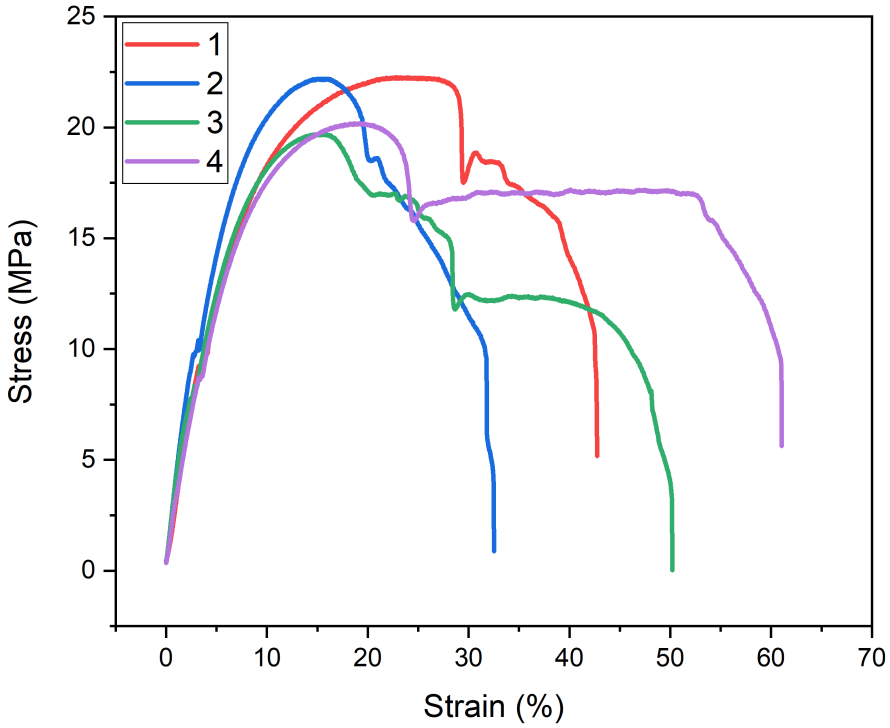


Fig. S17 Stress-strain curves of Low-M_n P(tCL) samples.

Table S4 Summary of mechanical properties of Low-M_n P(tCL). [a]

Entry	σ_Y (MPa)	σ_B (MPa)	E (MPa)	Elongation (%)
1	20.19	9.44	308	61.0
2	22.26	8.50	296	42.7
3	22.19	9.57	411	36.5
4	19.71	8.49	402	51.2
Average	21.09 ± 1.33	9.00 ± 0.59	354.14 ± 60.62	47.8 ± 10.65

[a] Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, σ_Y: yield strength, σ_B: break strength, E: Tensile modulus.

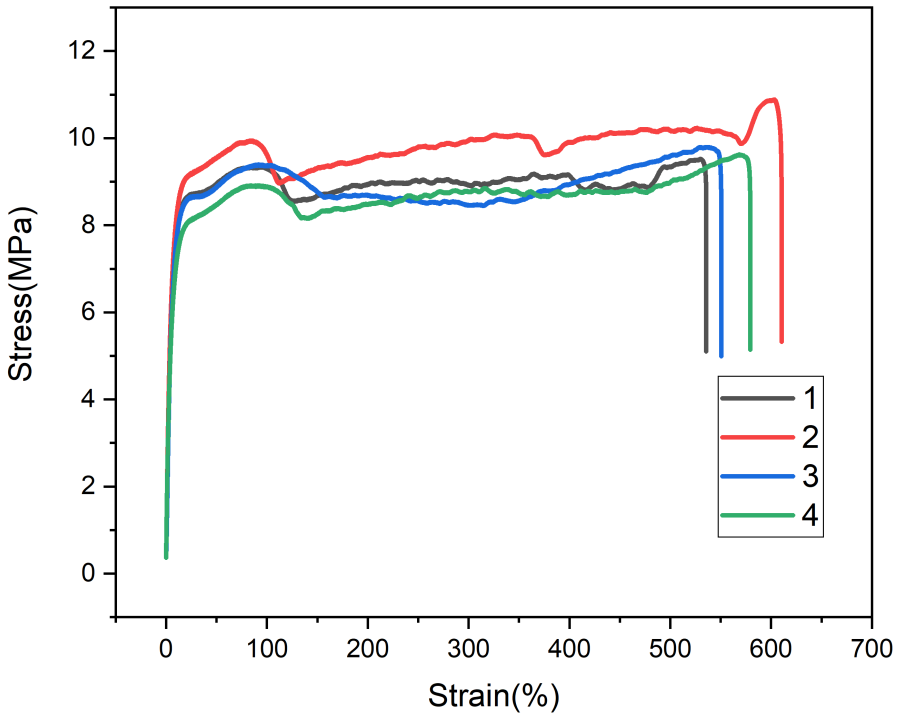


Fig. S18 Stress-strain curves of LDPE.

Table S5 Summary of mechanical properties of LDPE.[a]

Entry	σ_Y (MPa)	σ_B (MPa)	E (MPa)	Elongation (%)
1	9.35	8.67	169	536
2	9.95	9.03	171	610
3	9.39	8.49	134	551
4	8.91	8.66	174	579
Average	9.40 ± 0.43	8.71 ± 0.23	162 ± 18.63	569 ± 32.99

[a] Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, σ_Y: yield strength, σ_B: break strength, E: Tensile modulus.

Transport Property

Table S6 Oxygen permeability values of LDPE and P(tCL).

Samples	Average thickness(mm)	Oxygen transmissibility (cm^{-3}/m^2 d pa)	*P* O_2 (Barrer)
LDPE	0.397	$2.87*10^{-3}$	1.76
P(tCL)	0.310	$77.87*10^{-4}$	0.38

Table S7 Water vapor transmission rate of LDPE and P(tCL).

Samples	Average thickness(mm)	*WVT* (g/m^2 day)	*WVTR* (g mm m^{-2} day^{-1})
LDPE	0.296	0.814	0.24
P(tCL)	0.309	7.32	2.26

The Hydrolytic Stability Study

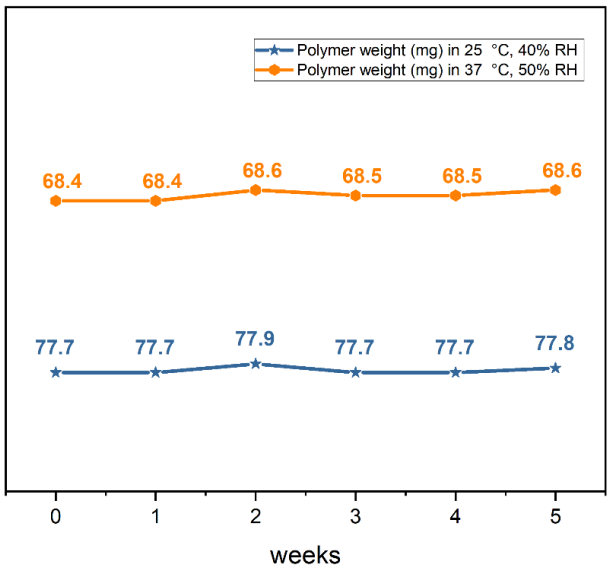


Fig. S19 The polymer weight change curves of P(tCL).

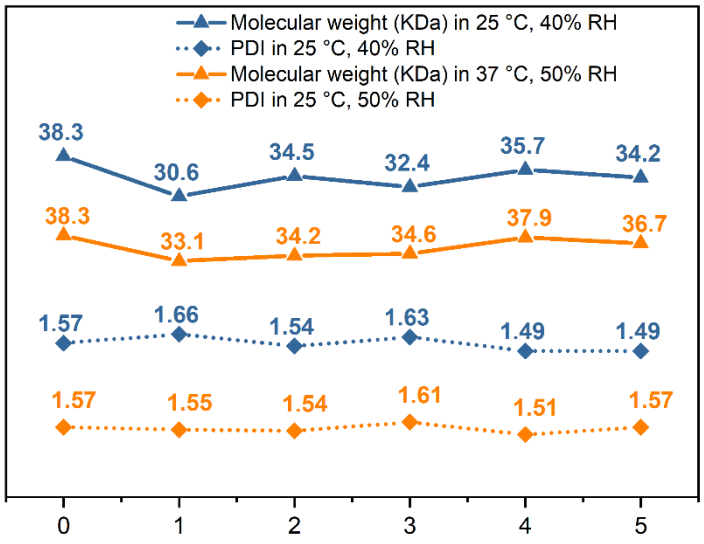


Fig. S20 The molecular weight and dispersity change curves of P(tCL).

Thermodynamic Study

In an argon-filled glovebox, a DMSO-d_6 stock solution of monomer (0.5 mmol), TBD (0.01 mmol), and BnSH (0.01 mmol, [M]/[TBD]/[I] = 50/1/1) was prepared in a 5 mL volumetric flask. The mixture was stirred for 10 min, and the resulting solution was divided into 4 NMR tubes, with each tube containing 0.35 mL reaction solution. These four tubes were placed in four pre-heated oil baths at different temperature. The above procedure was repeated twice so that three parallel samples were studied at each temperature. After the reaction reached the equilibrium, each polymerization for the thermodynamic studies was quenched with 0.25 mL DMSO-d_6 with benzoic acid (2 wt.%). The monomer concentration at the equilibrium was determined by ^{1}H NMR spectroscopy.

Table S8 Raw data over equilibrium conversion at various temperatures for tCL.

Entry	T(K)	Con. (%)	$[M]_0$(mol/L)	$T^{-1}(K^{-1})$	$[M]_{eq}$ mol/L	ln$[M]_{eq}$ mol/L
1	333.15	55.45	0.1	0.00300	0.04455	-3.1111
2	353.15	45.66	0.1	0.00283	0.05434	-2.9125
3	373.15	36.42	0.1	0.00268	0.06358	-2.7555
4	393.15	26.14	0.1	0.00254	0.07386	-2.6056

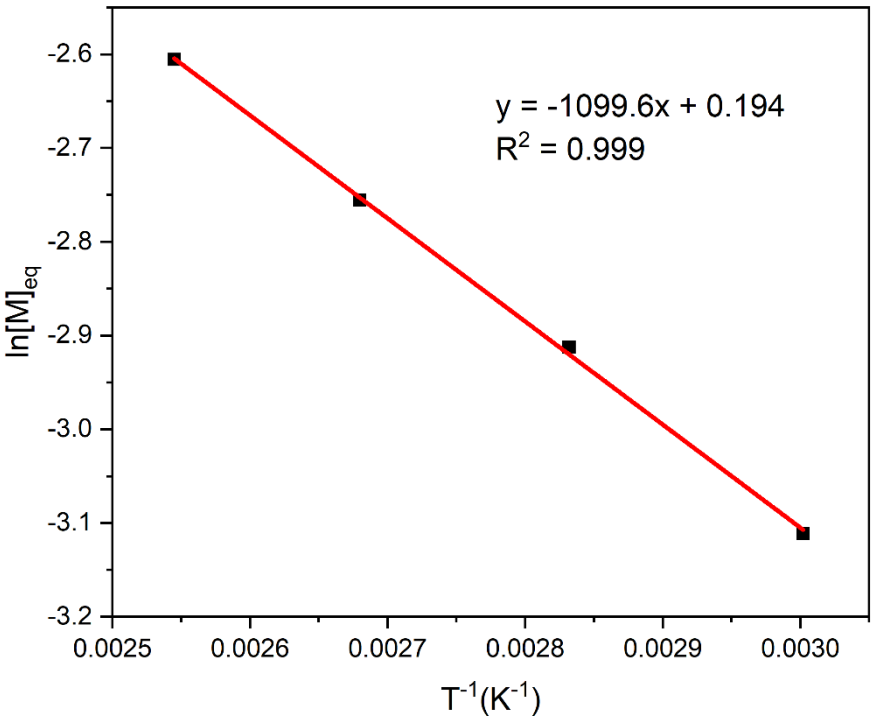
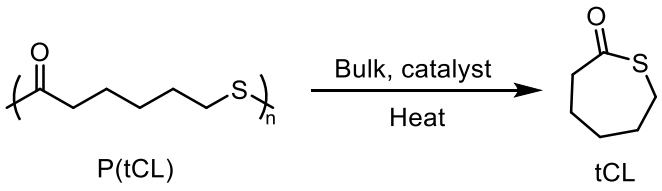


Fig. S21 Van't Hoff plot of $\ln[tCL]_{eq}$ vs. reciprocal of the absolute temperature (T^{-1}).

The Van't Hoff plot of $\ln[tCL]_{eq}$ versus T^{-1} gave a linear fitting with a slope of -1099.6 and an intercept of +0.194, from which the thermodynamic parameters were calculated to be ΔH_p° = −9.1 kJ mol^{-1} and ΔS_p° = −1.61 J mol^{-1} K^{-1}, based on the equation $\ln[tCL]_{eq} = \Delta H_p^\circ/RT - \Delta S_p^\circ/R$, where R is the molar gas constant. T_c was calculated to be 5652 K (5379 °C) at $[tCL]_0$ = 1.0 mol/L, based on the equation $T_c = \Delta H_p^\circ / (\Delta S_p^\circ + R\ln [tCL]_0)$.

Chemical Recycling to Monomer (CRM)



General procedures for the CRM of polymers under thermal bulk condition.

P(tCL):

Polymer P(tCL) and PEO-10000 were mixed in a weight ratio of 2:1, then the catalyst was added. The mixture was subjected to vacuum distillation at 180 °C. After the reaction was stopped, the sublimate was weighted and characterized by ^{1}H NMR spectroscopy.

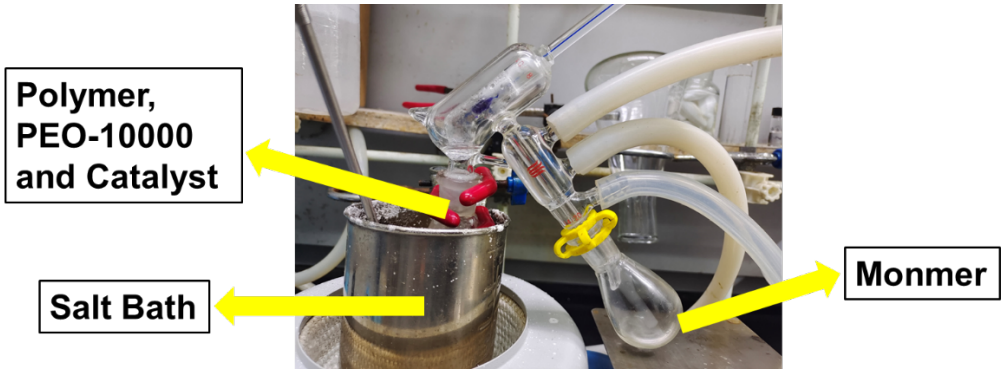


Fig. S22 Thermal depolymerization of polymer to monomer via vacuum distillation.

Table S9 Results of bulk thermal depolymerization of P(tCL).[a]

Entry	Catalyst	Catalyst loading(mol%)	Temperature(°C)	Time(h)	Monomer yield (%) [b]
1	$Sn(Oct)_2$	5	120	5	-
2	$Sn(AcO)_2$	5	120	8	-
3	PhSNa	5	180	2	92
4	PhSNa	2	180	5	33

[a] Condition: The mass of polymer sample was 3 g, $M_{n\,(PEO)}$=10000, m_{PEO}:$m_{polymer}$ = 2:1. [b] the monomer yield determined by the amount of the sublimate and the purity of recycled monomer determined by ^{1}H NMR spectroscopy.

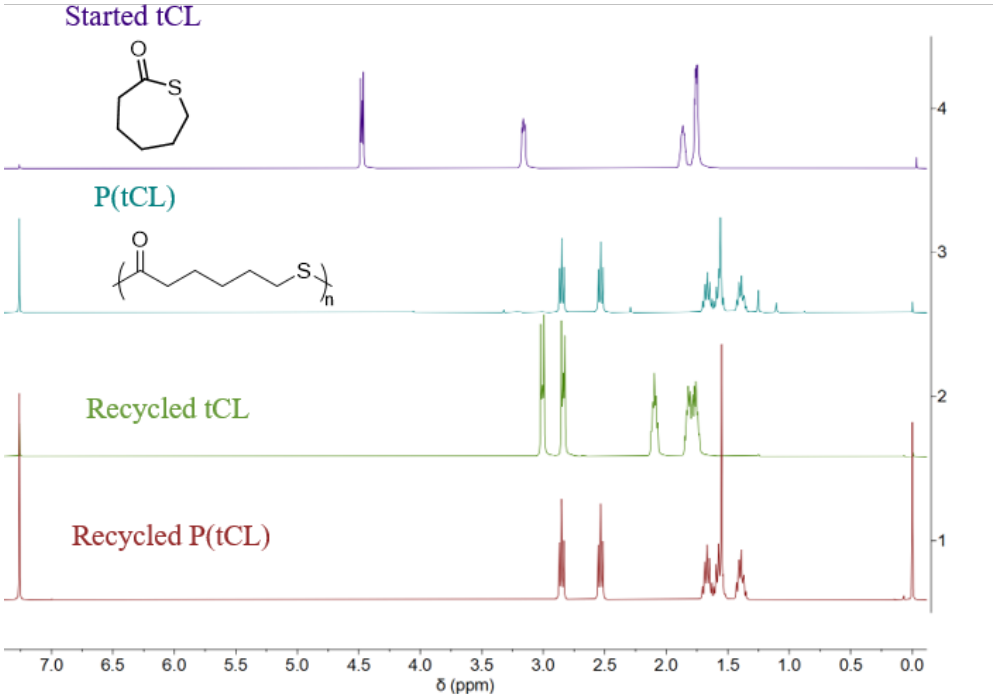


Fig. S23 ^{1}H NMR spectra of the recycled tCL by the thermal depolymerization of P(tCL).

a) Starting tCL for comparison; b) Recycled tCL by the thermal depolymerization; c) P(tCL) obtained by [tCL]/[TBD]/[I] = 100/1/1; d) P(tCL) (repolymerization) obtained by [recycled tCL]/[TBD]/[I] = 100/1/1.

Table S10 Results of repolymerization of recycled tCL.

Entry	**M**	[**M**]/[Cat.]/[I]	Time (min)	Conv.[a] (%)	$M_{n,Calcd}$ [b] (kDa)	$M_{n,SEC}$ [c] (kDa)	$Đ$ [c]
1	tCL	100:1:1	10 min	85	11.1	12.6	1.39

[a] Monomer conversion measured by ^{1}H NMR of the quenched solution. [b] Calculated from $[\mathbf{M}]_0/[BnSH]_0 \times Conv. \times MW_{\mathbf{M}} + MW_{BnSH}$. [c] Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$), determined by Size-Exclusion Chromatography (SEC) at 40 °C in THF.

General procedure for the CRM of P(tCL) from a mixture of commodity plastics.

Commodity polymer samples obtained from various sources were mixed with P(tCL) (3.0 g) and loaded into a 50 mL round-bottom flask, then PEO-10000(14.0g) and 5% PhSNa (158 mg) were added. The flask was connected to a vacuum distillation equipment. The mixture was then placed in a hot salt bath and heated to 180−190 °C under vacuo for 3 hours. Clear distillate was collected, weighted (2.7 g, 90% yield), and characterized by ^{1}H NMR spectroscopy. The collected monomer was directly polymerized without further purification.

Table S11 Composition of polymer mixture used in depolymerization study from mixed feedstocks.

Component	Abbreviation	Source	Initial Mass (g)	Weight (%)
Poly(thiocaprolactone)	P(tCL)	Synthesized	3.0	42.9
Polyethylene	HDPE	Post-use bag	1.0	14.3
Isotactic Polypropylene	PP	Post-use Box	1.0	14.3
Polyethylene terephthalate	PET	Post-use Bottle	1.0	14.3
Polystyrene	PS	Post-use dental floss pick	0.50	7.1
Acrylonitrile-butadiene rubber	NBR	Post-use gloves	0.50	7.1

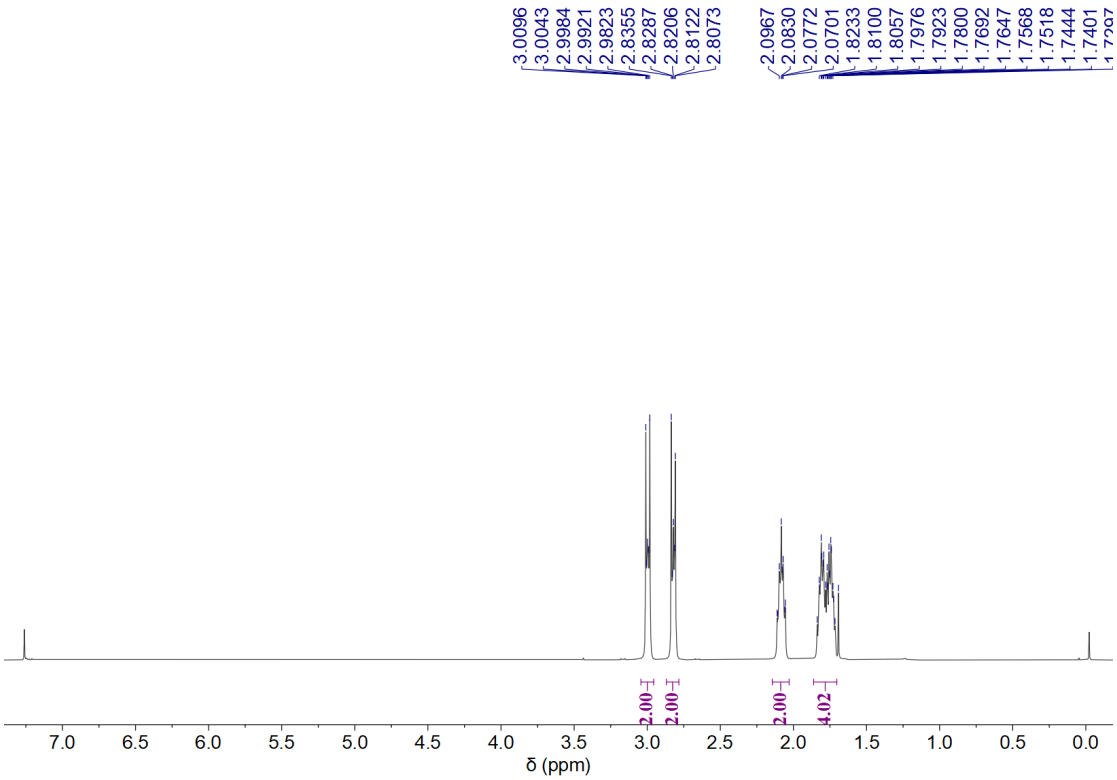


Fig. S24 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of recycled tCL after depolymerization.

Table S12 Results of repolymerization recycled tCL.

Entry	**M**	[**M**]/[Cat.]/[I]	Time (min)	Conv.[a] (%)	$M_{n,Calcd}$ [b] (kDa)	$M_{n,SEC}$ [c] (kDa)	$Đ$ [c]
1	tCL	100:1:1	12 min	>99	12.9	11.8	1.33

[a] Monomer conversion measured by ^{1}H NMR of the quenched solution. [b] Calculated from $[\mathbf{M}]_0/[BnSH]_0 \times Conv. \times MW_{\mathbf{M}} + MW_{BnSH}$. [c] Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$), determined by Size-Exclusion Chromatography (SEC) at 40 °C in THF.

Reference

[1] *J. Am. Chem. Soc.* **1990**, *112*, 6263-6276.