Supporting Information for

Chemically Recyclable Poly(thioether-thioester)s via Ring-Opening Polymerization of Seven-Membered Thiolactones

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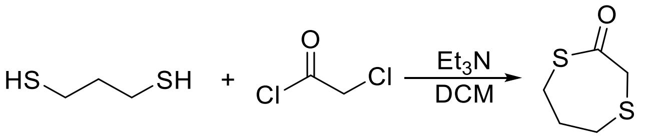
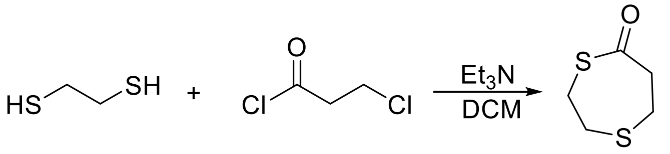
Monomer Preparations

Scheme S1. Synthesis of **M1**



To a solution of 1,3-dimercaptopropane (5.4 g, 50 mmol) and Et_3N (10.6 g, 105 mmol) in 200 mL of dried DCM was slowly added a solution of chloroacetyl chloride (4.2 g, 55 mmol) in 100 mL of DCM at −70 °C under Argon. The resulting solution was stirred for 8 h at 40 °C, and 40 mL ice water was added to quench the reaction. During the addition all the precipitated triethylamine hydrochloride was dissolved, and a two-phase system was formed. The organic phase was washed with water (4 ×100 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/DCM = 5/1) to give the final compound as white solid (2.1 g, 29% yield).[1] The pure product as colorless crystal was obtained by recrystallization from ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 2H), 3.12−3.05 (m, 2H), 2.97−2.90 (m, 2H), 2.46−2.38 (m, 2H).

Scheme S2. Synthesis of **M2**



To a solution of 1,2-ethanedithiol (4.7 g, 50 mmol) and Et_3N (10.6 g, 105 mmol) in 200 mL of dried DCM was slowly added a solution of 3-chloropropionyl chloride (7.0 g, 55 mmol) in 100 mL of DCM at −70 °C under Argon. The resulting solution was stirred for 2 h at 40 °C, and 40 mL ice water was added to quench the reaction. During the addition all the precipitated triethylamine hydrochloride was dissolved, and a two-phase system was formed. The organic phase was washed with water (4 × 100 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/DCM = 4/1) to give the final compound as white solid (0.4 g, 5% yield). The pure product as colorless crystal was obtained by recrystallization from ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47−3.39 (m, 2H), 3.34−3.27 (m, 2H), 3.21−3.14 (m, 2H), 2.86−2.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.19, 50.16, 34.20, 34.00, 24.65.

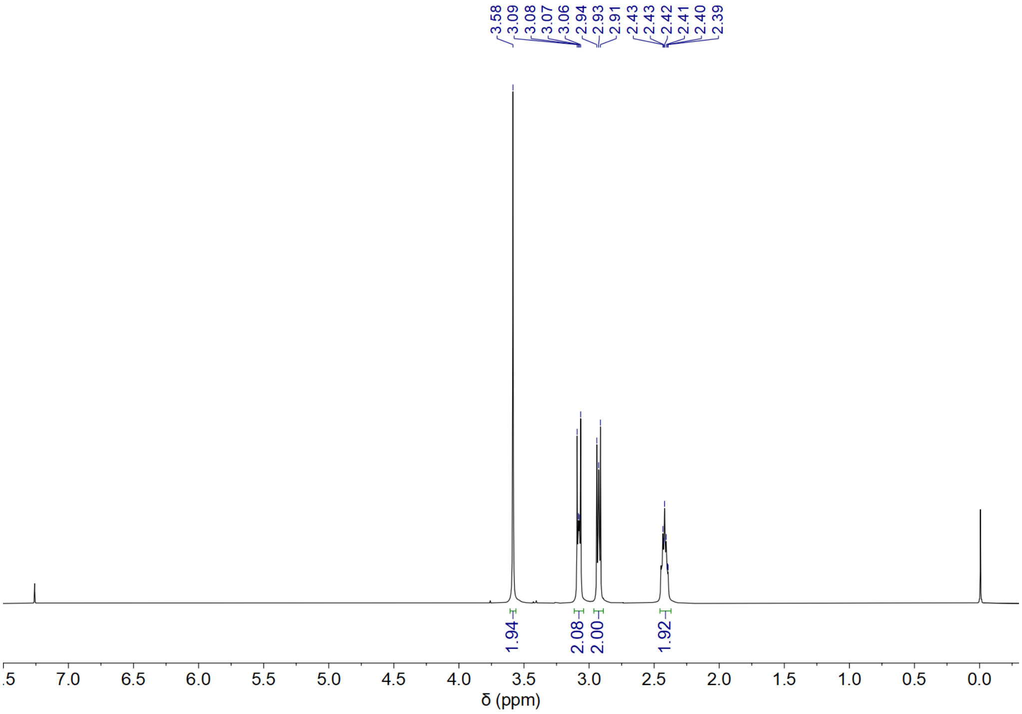


Fig. S1 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of **M1**.

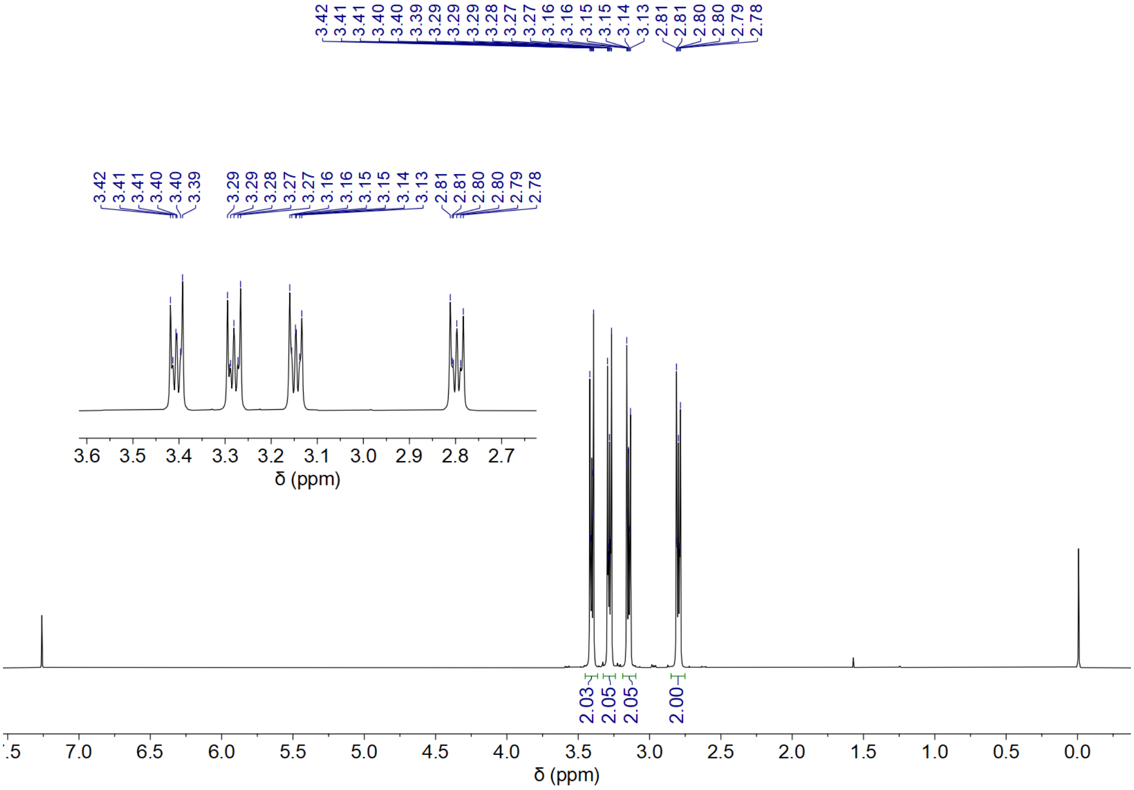


Fig. S2 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of **M2**.

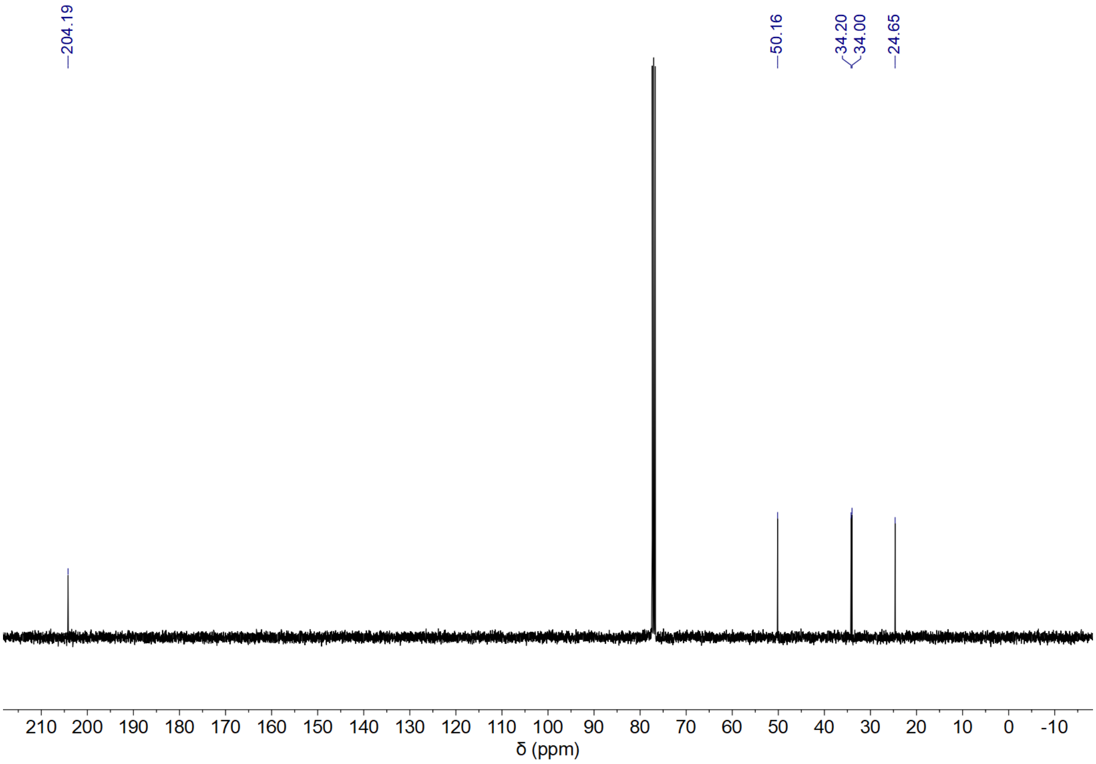


Fig. S3 ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of **M2**.

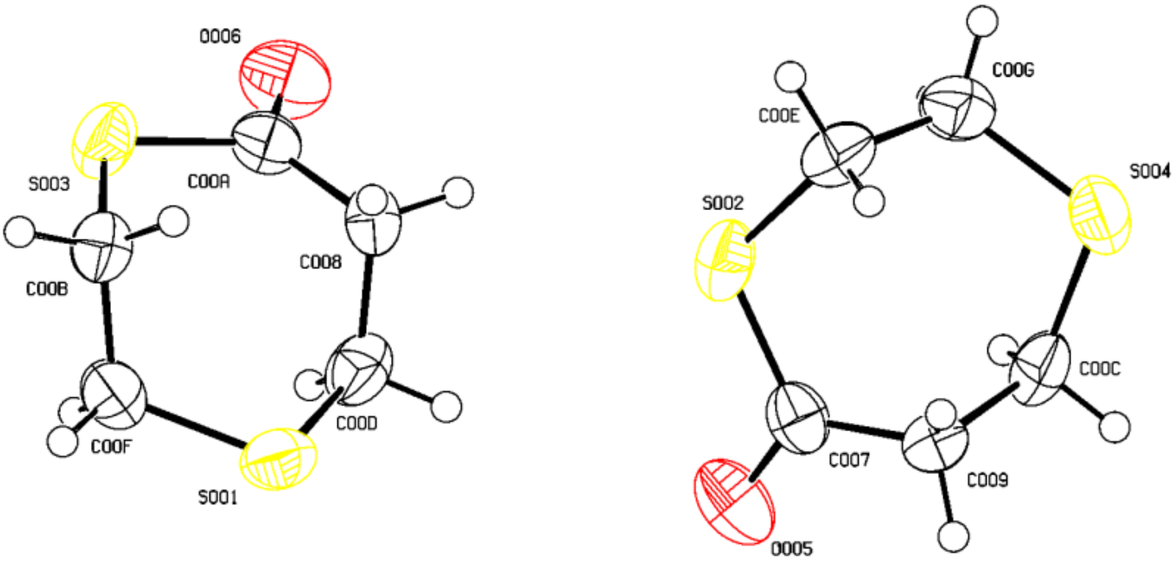


Fig. S4 X-ray structure of **M2**.

Table S1 Crystallographic table for **M2**.

	M2
CCDC number	2354510
Empirical formula	C5H8OS2
Formula weight	148.23
Temperature/K	285.0
Crystal system	triclinic
Space group	P-1
a/Å	8.2387(12)
b/Å	8.2964(13)
c/Å	10.4688(17)
α/°	93.346(6)
β/°	92.138(5)
γ/°	109.112(5)
Volume/Å3	673.76(18)
Z	4
ρcalcg/cM2	1.461
μ/mm-1	0.688
F(000)	312.0
Crystal size/mM2	0.42 × 0.22 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.904 to 55.182
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	13114
Independent reflections	3089 [Rint = 0.0497, Rsigma = 0.0410]
Data/restraints/parameters	3089/0/145
Goodness-of-fit on F2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0453, wR2 = 0.1110
Final R indexes [all data]	R1 = 0.0657, wR2 = 0.1200
Largest diff. peak/hole / e Å-3	0.32/-0.32

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 S2 Results of ROP of **M1**. [a]

Entry	Cat.	[**M1**]:[Cat.]:[I]	Time (min)	Conv.[b] (%)	$M_{n,Calcd}$ [c] (kDa)	$M_{n,SEC}$[d] (kDa)	$Đ$ [d]
1	TBD	100:1:1	1	93	13.8	8.8	1.40
2	TBD	200:1:1	1	93	27.5	13.7	1.41
3	TBD	500:1:1	5	94	69.6	45.9	1.54
4	TBD	1000:1:1	10	95	141	62.1	1.65
5	TBD	2000:1:1	60	21	62.2	26.9	2.04
6	TBD	2000:1:2	60	44	130	40.6	1.71
7	DBU	500:1:1	1	10	7.40	7.54	1.19
8	DBU	500:1:1	10	31	22.9	20.0	1.30
9	DBU	500:1:1	60	73	54.0	33.9	1.92
10	**La**	1000:1:0	180	17	-	18.7	1.84
11	**La**	1000:1:3	180	12	5.9	24.7	1.51

[a] Condition: **M** = 50 mg, [M] = 1.1 mol/L, initiator (I) = Benzyl Mercaptan, solvent = DCM, RT. [b] Monomer conversion measured by ^{1}H NMR of the quenched solution. [c] Calculated from $[\mathbf{M}]_0/[\mathrm{BnSH}]_0$ × Conv. × $\mathrm{MW}_{\mathbf{M}}$ + $\mathrm{MW}_{\mathrm{BnSH}}$. [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.

Table S3 Results of ROP of **M2**.[a]

Entry	Cat.	[**M2**]:[Cat.]:[I]	Time (min)	Conv.[a] (%)	$M_{n,\mathrm{Calcd}}$[c] (kDa)	$M_{n,\mathrm{SEC}}$[d] (kDa)	$Đ$[d]
1	TBD	100:1:1	1	97	14.4	28.1	1.58
2	TBD	200:1:1	1	97	28.7	47.2	1.51
3	TBD	500:1:1	5	88	65.1	182	1.57
4	TBD	500:1:1	10	98	72.5	101	1.55
5	TBD	1000:1:1	20	80	118	247	1.67
6	TBD	1000:1:1	60	97	144	220	1.56
7	TBD	2000:1:1	120	77	228	256	1.62

[a] Condition: **M** = 50 mg, [M] = 1.1 mol/L, initiator (I) = benzyl mercaptan, solvent = DCM, RT. [b] Monomer conversion measured by ^{1}H NMR of the quenched solution. [c] Calculated from [**M**]$_0$/[BnSH]$_0$ × Conv. × MW$_{\mathbf{M}}$ + MW$_{\mathrm{BnSH}}$. [d] Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$), determined by size-exclusion chromatography (SEC) at 27 °C in DCM.

Polymer Characterization

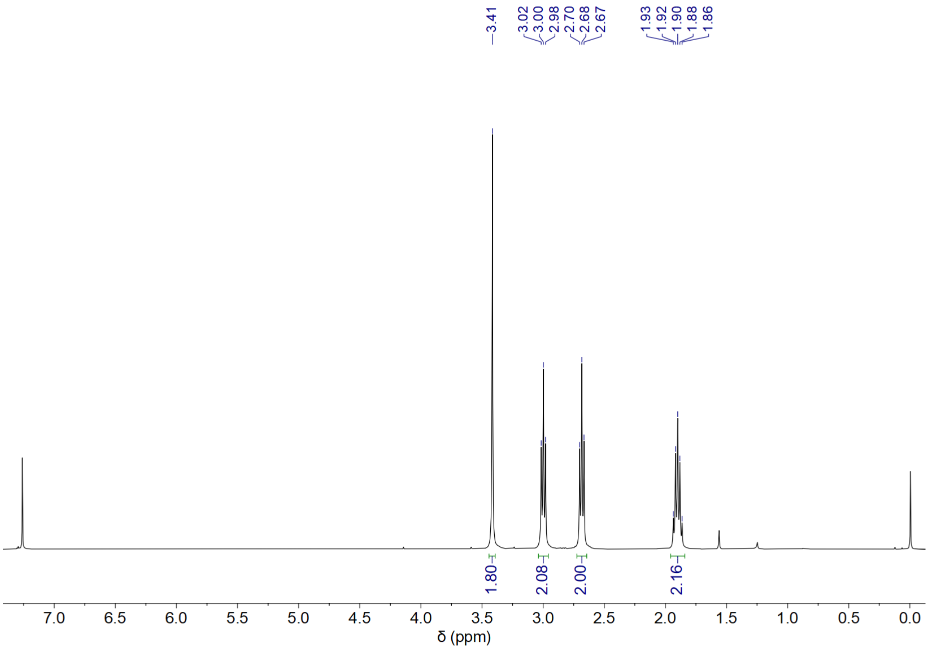


Fig. S5 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(**M1**) obtained by [**M1**]/ [TBD]/[I] = 500/1/1.

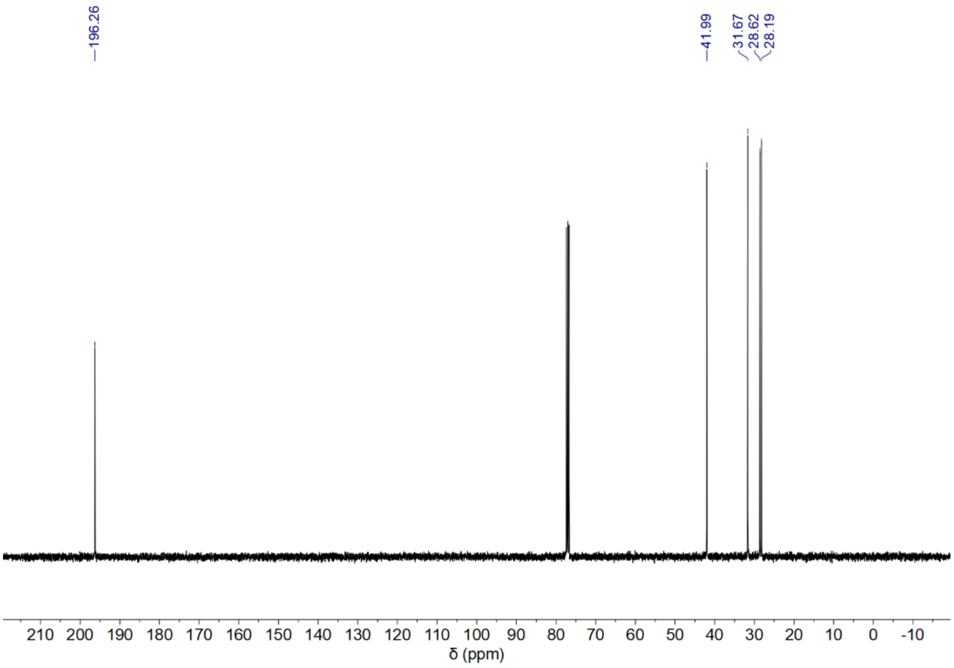


Fig. S6 ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(**M1**) obtained by [**M1**]/ [TBD]/[I] = 500/1/1.

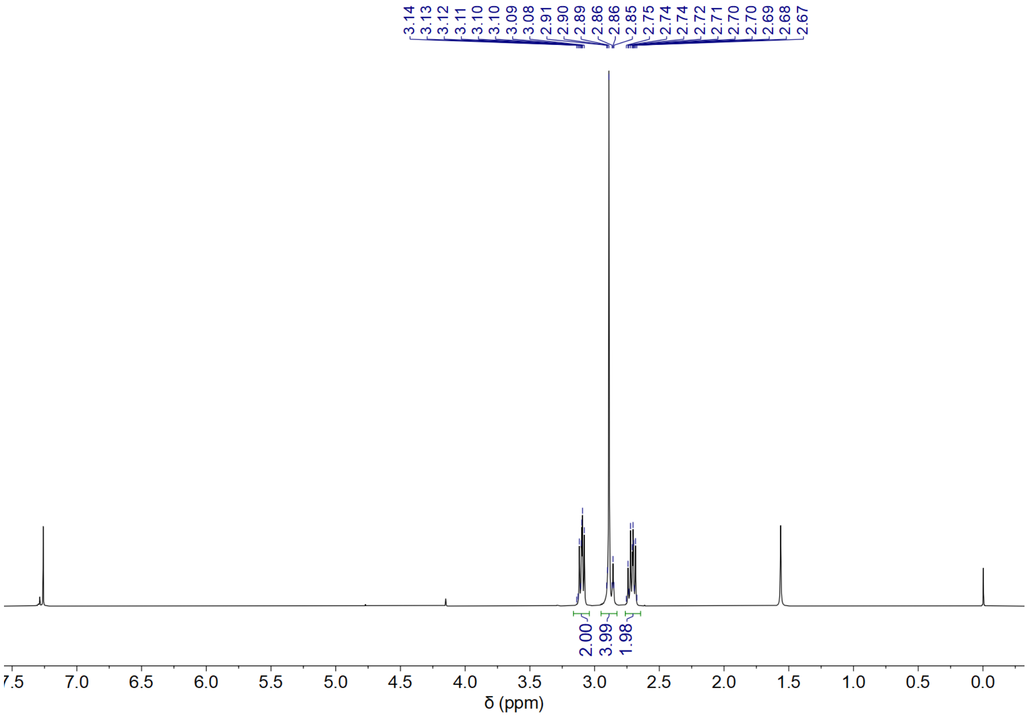


Fig. S7 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(**M2**) obtained by [**M2**]/ [TBD]/[I] = 500/1/1.

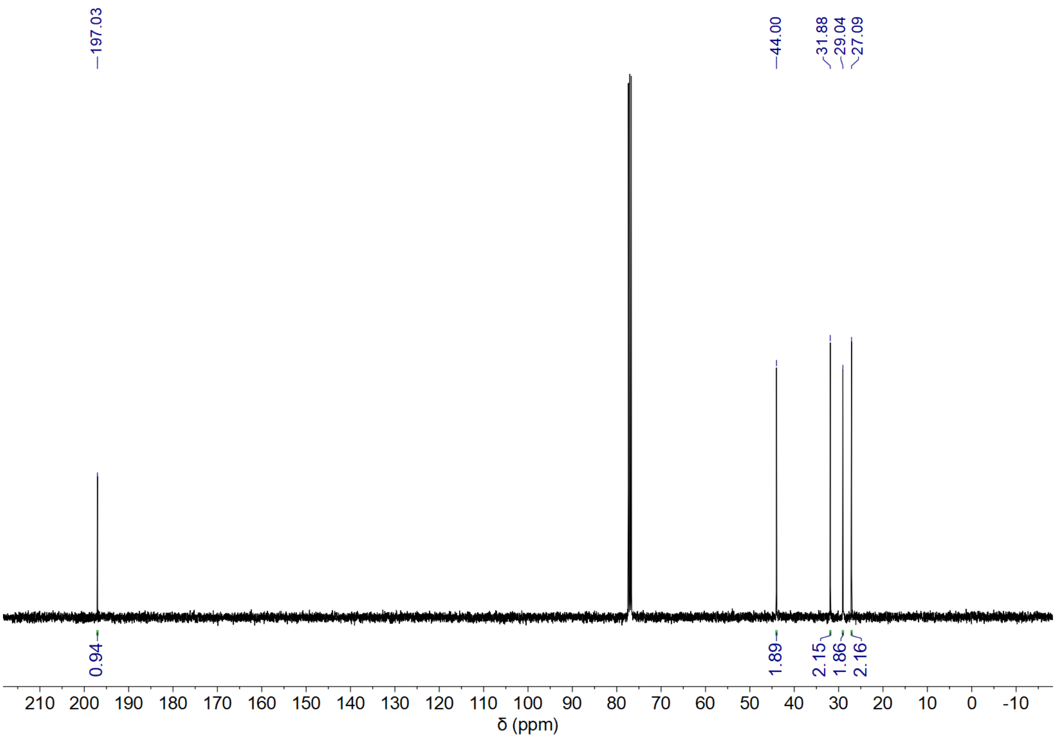


Fig. S8 ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(**M2**) obtained by [**M2**]/ [TBD]/[I] = 500/1/1.

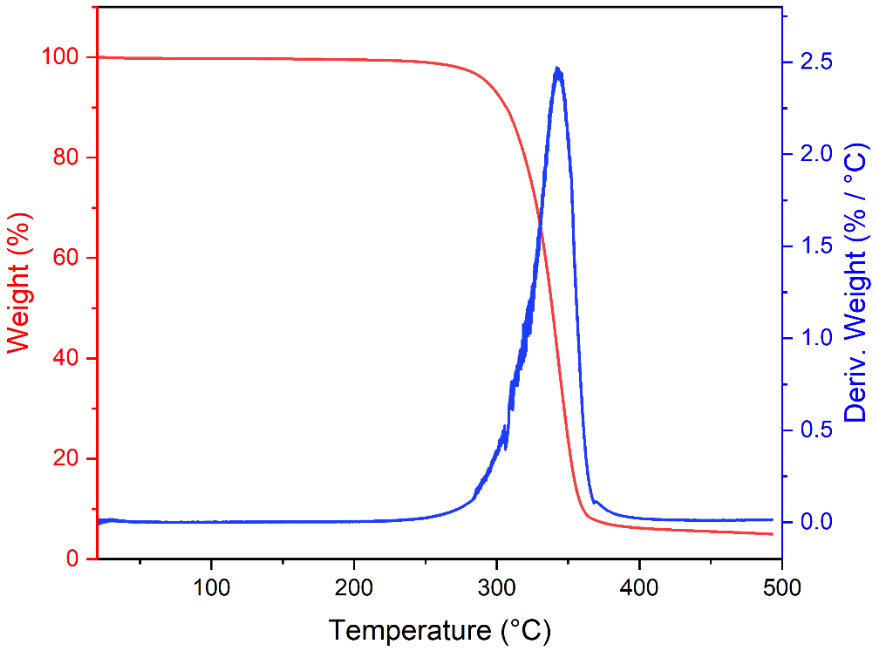


Fig. S9 TGA and DTG curves for P(**M1**) obtained by [**M1**]/[TBD]/[I] = 500/1/1, T_d = 293 °C, T_{max} = 343 °C.

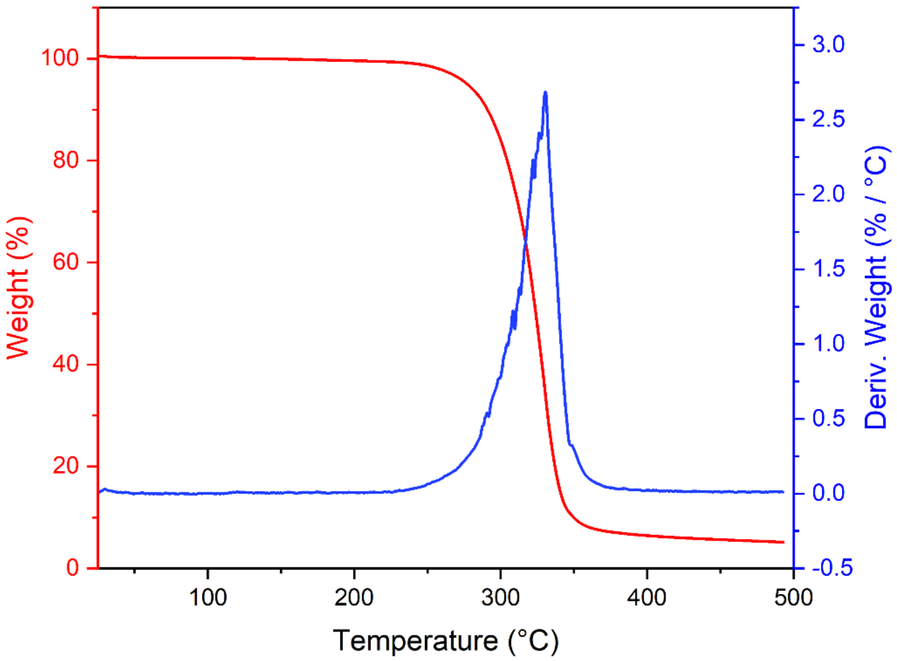


Fig. S10 TGA and DTG curves for P(**M2**) obtained by [**M2**]/[TBD]/[I] = 500/1/1, T_d = 275 °C, T_{max} = 320 °C.

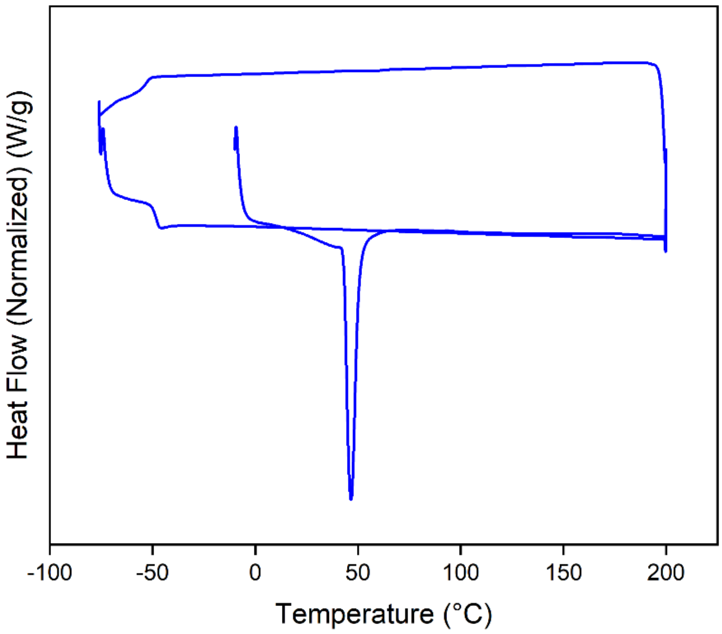


Fig. S11 DSC curves for P(**M1**) obtained by [**M1**]/[TBD]/[I] = 500/1/1, T_g = −49 °C, T_m = 47 °C.

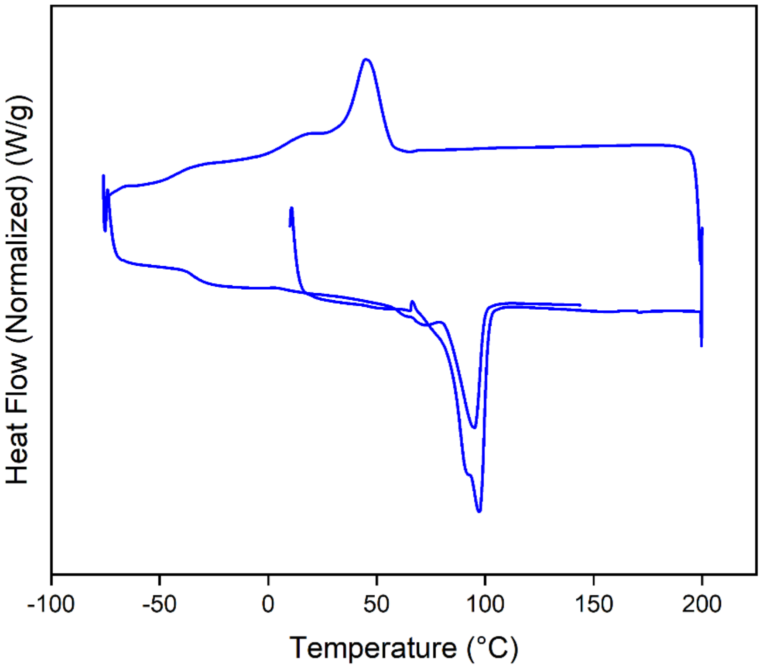


Fig. S12 DSC curves for P(**M2**) obtained by [**M2**]/[TBD]/[I] = 500/1/1, T_g = −33 °C, T_c = 46 °C, T_m = 95 °C and 97 °C.

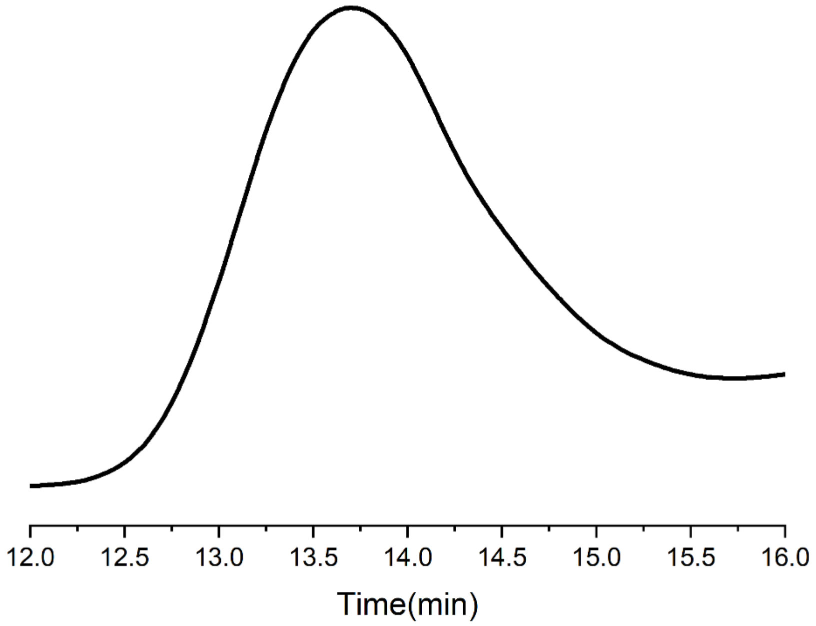


Fig. S13 SEC trace of P(**M1**) obtained by [**M1**]/[TBD]/[I] = 200/1/1, M_n = 44.0 kDa, *Đ* = 1.43

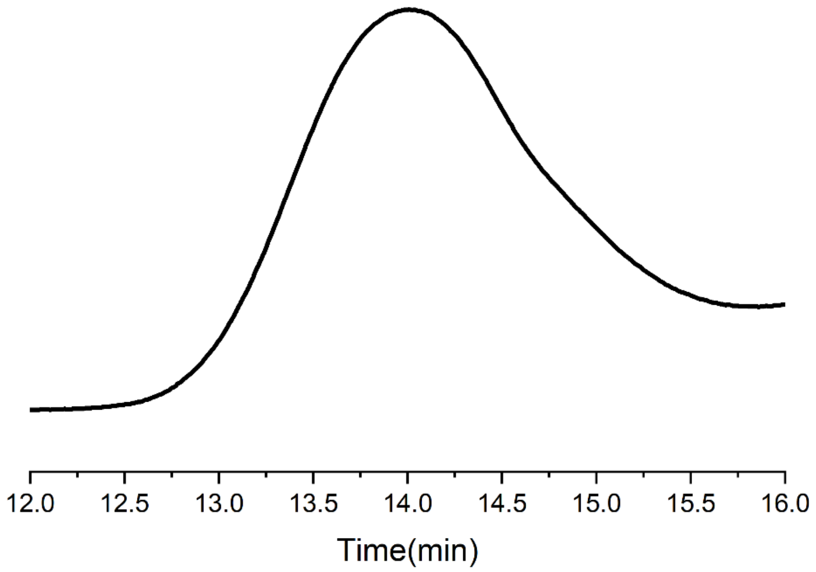


Fig. S14 SEC trace of P(**M1**) obtained by [**M1**]/[TBD]/[I] = 1000/1/1, M_n = 46.1 kDa, *Đ* = 1.43

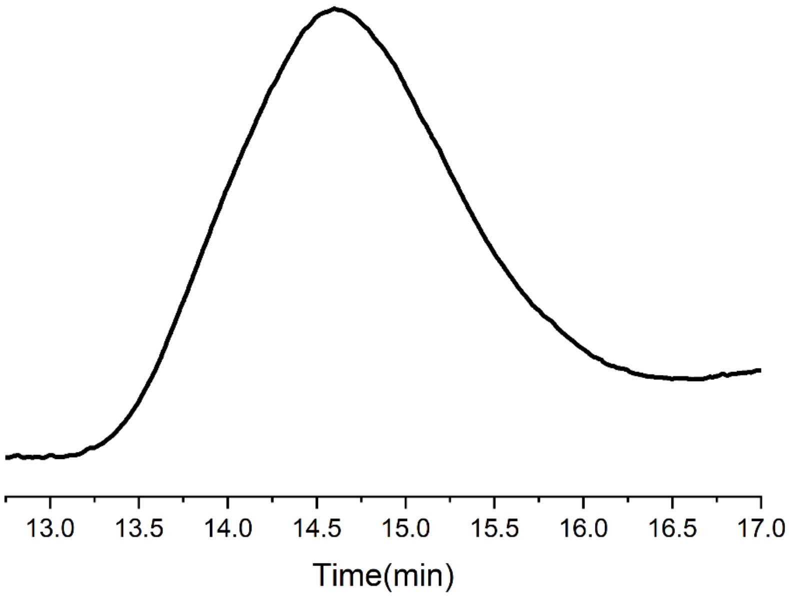


Fig. S15 SEC trace of P(**M2**) obtained by [**M2**]/[TBD]/[I] = 500/1/1, M_n = 47.2 kDa, $Đ$ = 1.51

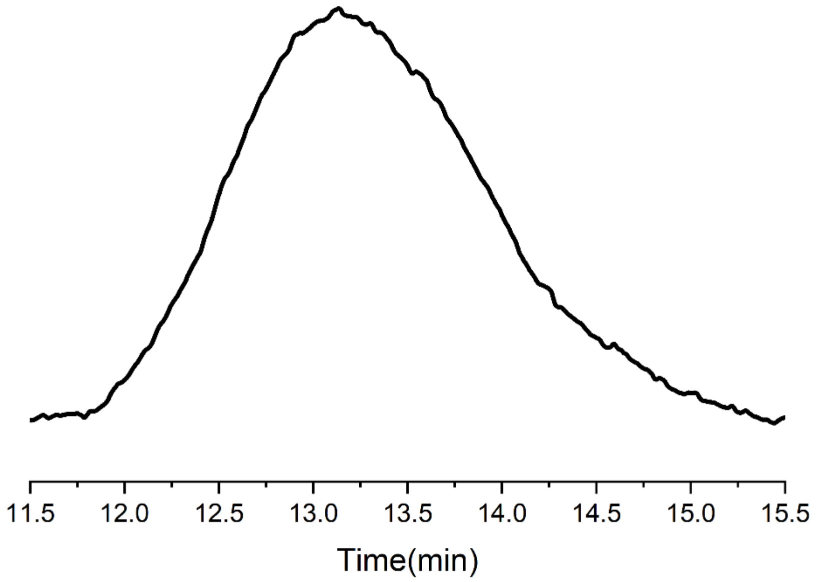


Fig. S16 SEC trace of P(**M2**) obtained by [**M2**]/[TBD]/[I] = 1000/1/1, M_n = 220 kDa, $Đ$ = 1.56

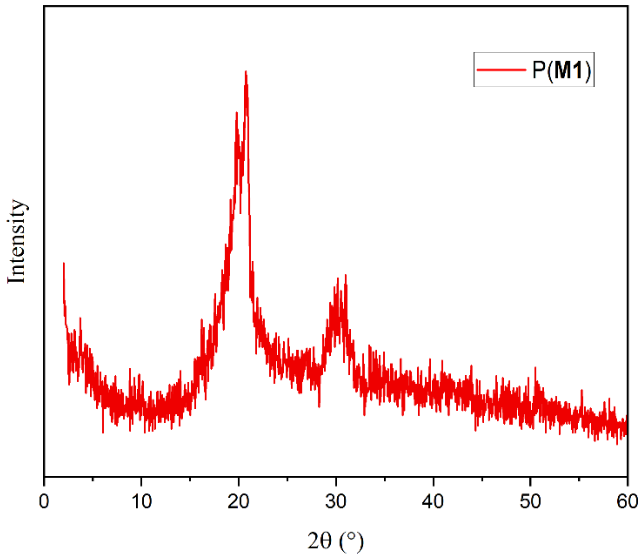


Fig. S17 Powder XRD profiles of P(**M1**).

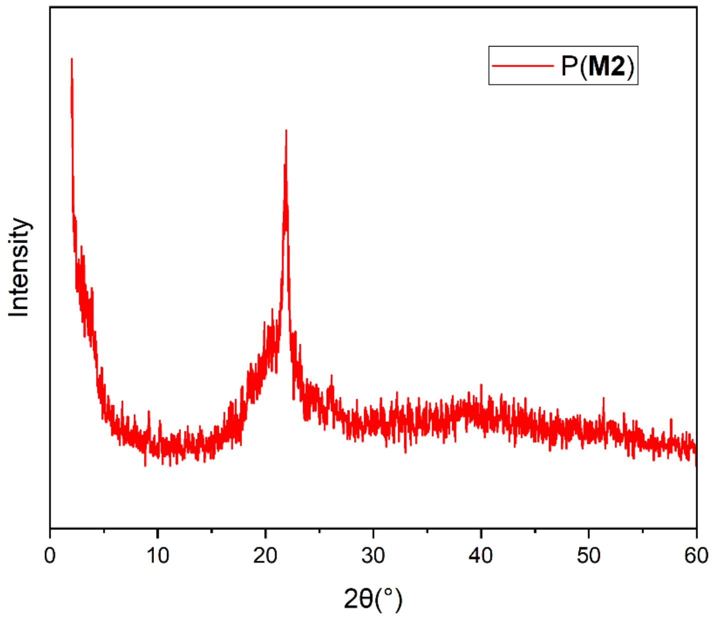


Fig. S18 Powder XRD profiles of P(**M2**).

Mechanical Property

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 mM2) and were stretched at a strain rate of 10 mm/min at ambient temperature until break.

Table S4 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(**M1**)	50	72.4	1.72	94.9	1.56
P(**M2**)	110	199	1.84	131.5	2.08

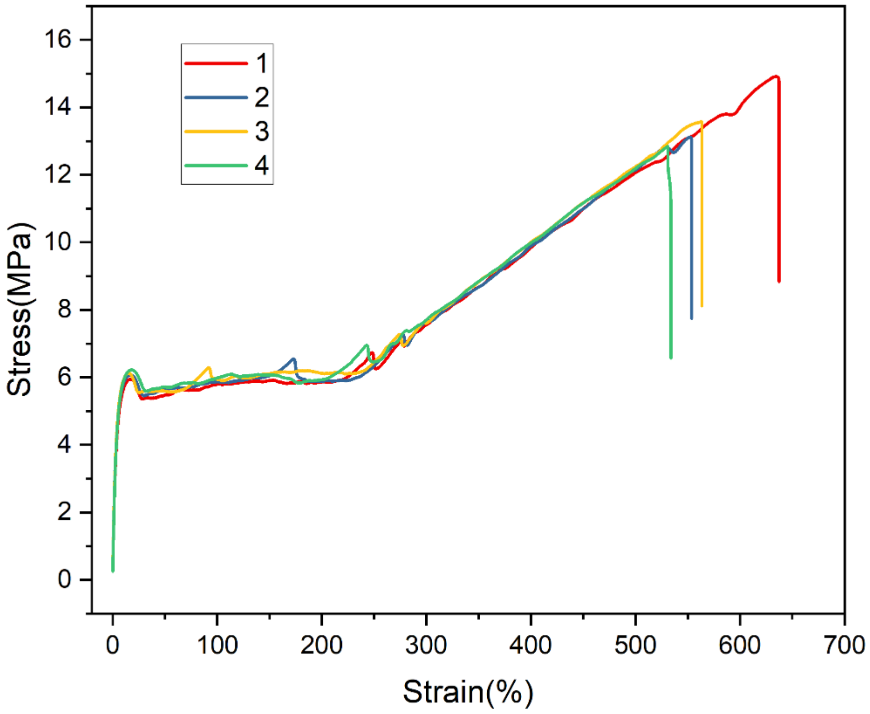


Fig. S19 Stress-strain curves of P(**M1**)s.

Table S5 Summary of mechanical properties of P(**M1**)s.[a]

Entry	σ_Y (MPa)	σ_B (MPa)	E (MPa)	Elongation (%)
1	5.96	14.82	160	637
2	6.55	13.06	171	554
3	6.14	13.56	172	563
4	6.22	11.31	156	534
Average	6.22 ± 0.25	13.19± 1.45	165 ± 7.97	572 ± 44.99

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

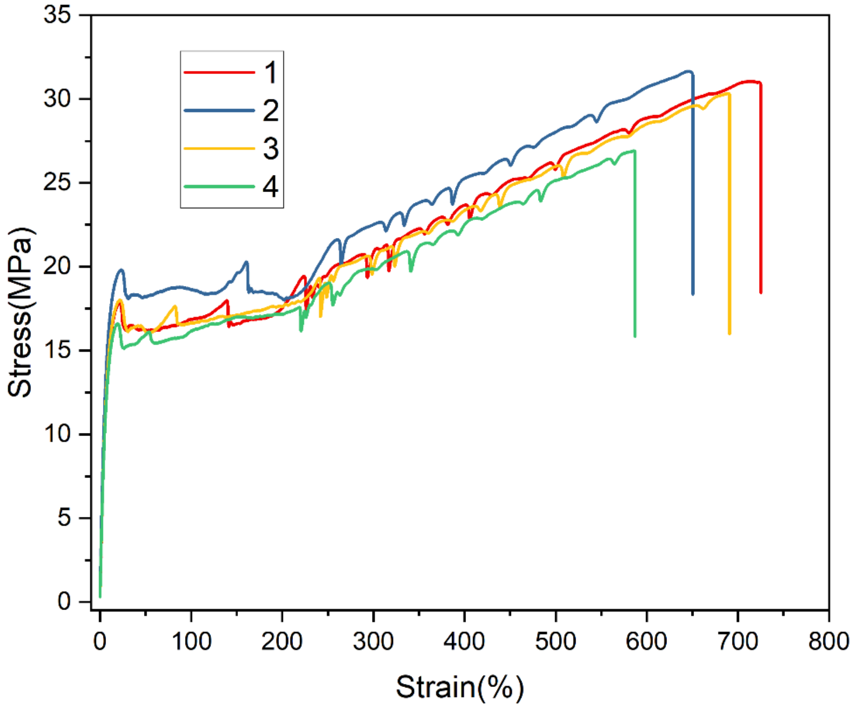


Fig. S20 Stress-strain curves of P(**M2)**s.

Table S6 Summary of mechanical properties of P(**M2**)s.[a]

Entry	σ_Y (MPa)	σ_B (MPa)	E (MPa)	Elongation (%)
1	17.81	30.82	238	725
2	19.82	31.43	289	650
3	17.99	30.27	229	690
4	16.56	26.90	233	586
Average	18.05 ± 1.34	29.86 ± 2.02	247 ± 28.05	663 ± 59.64

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

The Hydrolytic Stability Study

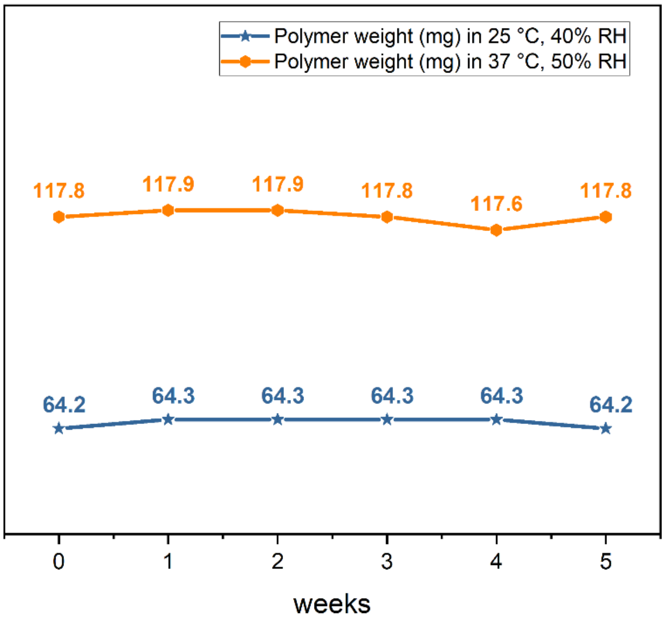


Fig. S21 The polymer weight change curves of P(**M1**).

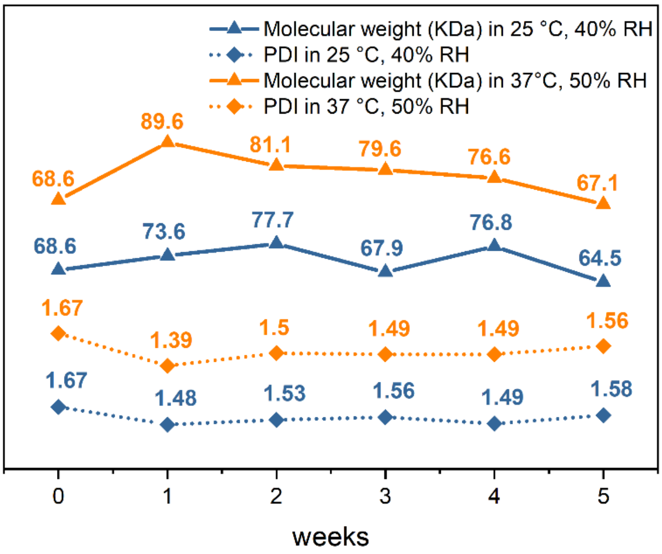


Fig. S22 The polymer weight change curves of P(**M1**).

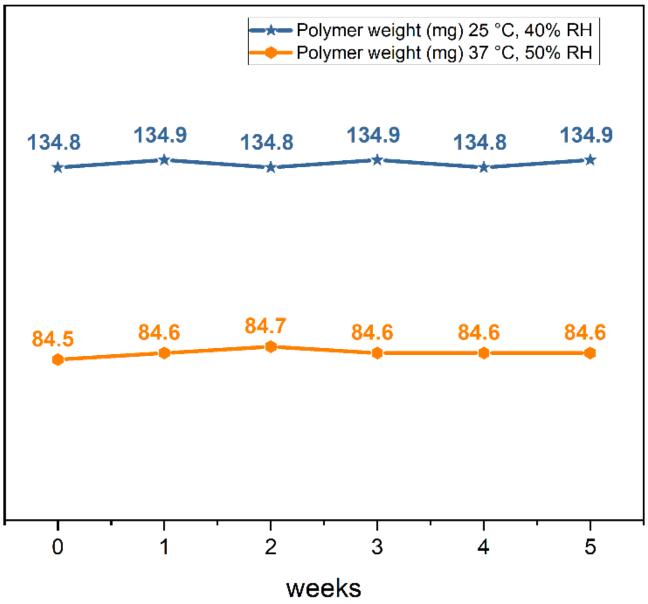


Fig. S23 The polymer weight change curves of P(**M2**).

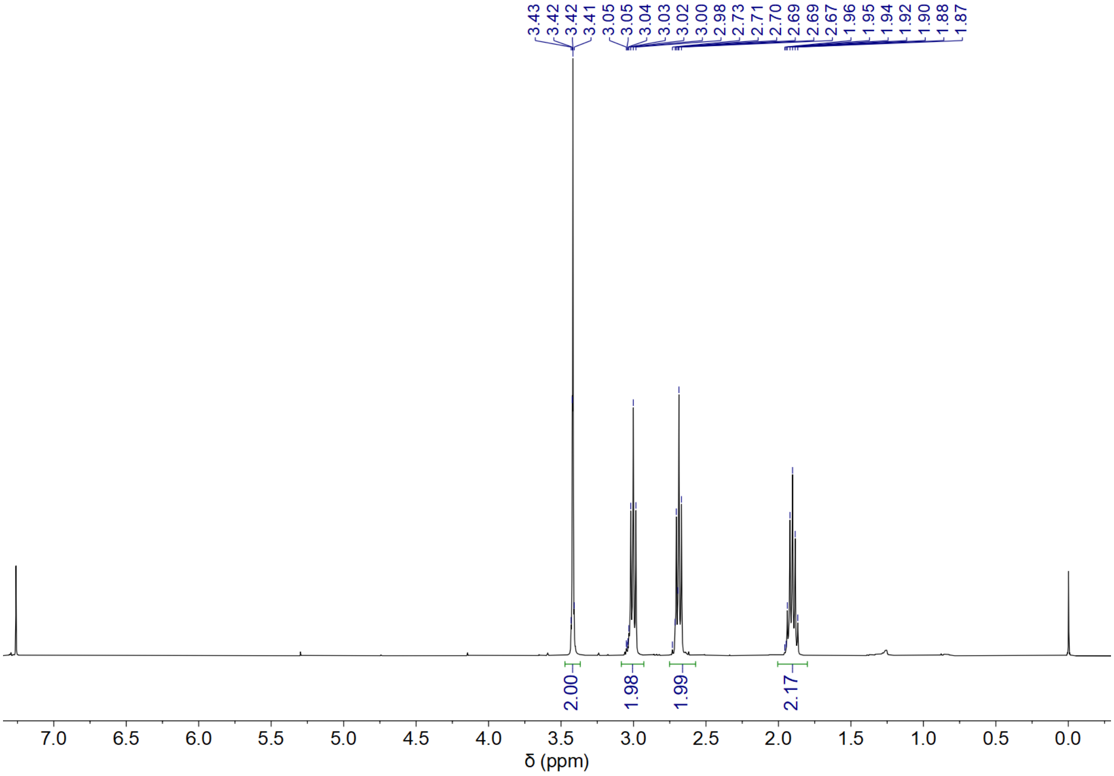


Fig. S24 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of **M1** after 5 weeks.

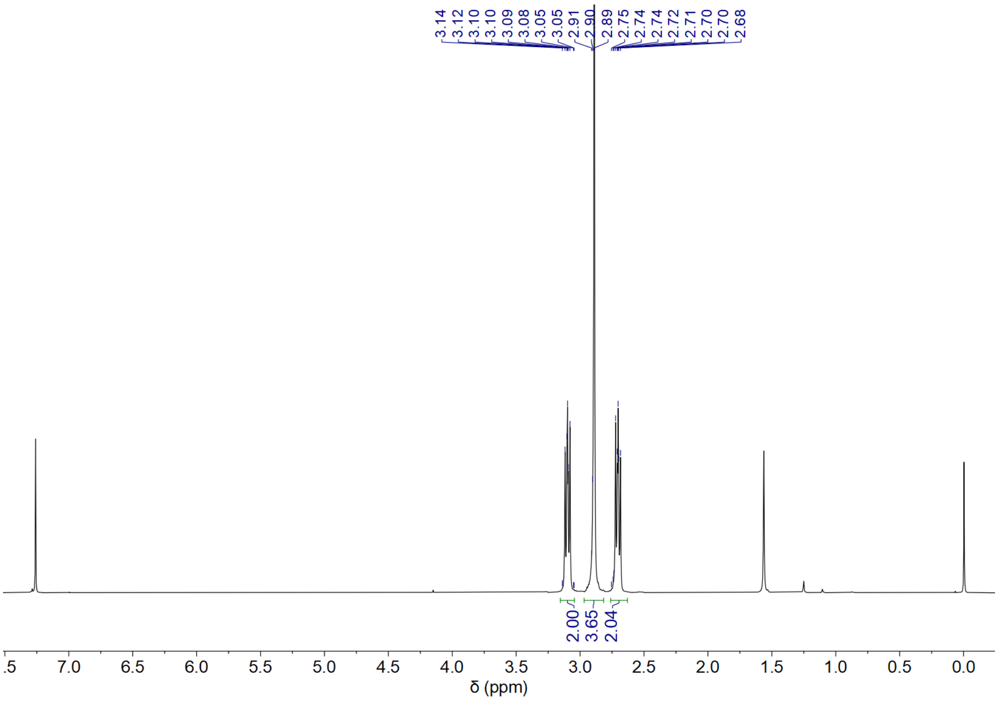


Fig. S25 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of **M2** after 5 weeks.

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 S7 Raw data over equilibrium conversion at various temperatures for **M1**.

Entry	T(K)	Con. (%)	$[M]_0$(mol/L)	$T^{-1}(K^{-1})$	$[M]_{eq}$ mol/L	$\ln[M]_{eq}$ mol/L
1	313.15	85.421	1	0.00319	0.14579	-1.925
2	338.15	80.441	1	0.00295	0.19559	-1.6317
3	363.15	77.061	1	0.00275	0.22939	-1.4723
4	388.15	72.826	1	0.00257	0.27174	-1.3029

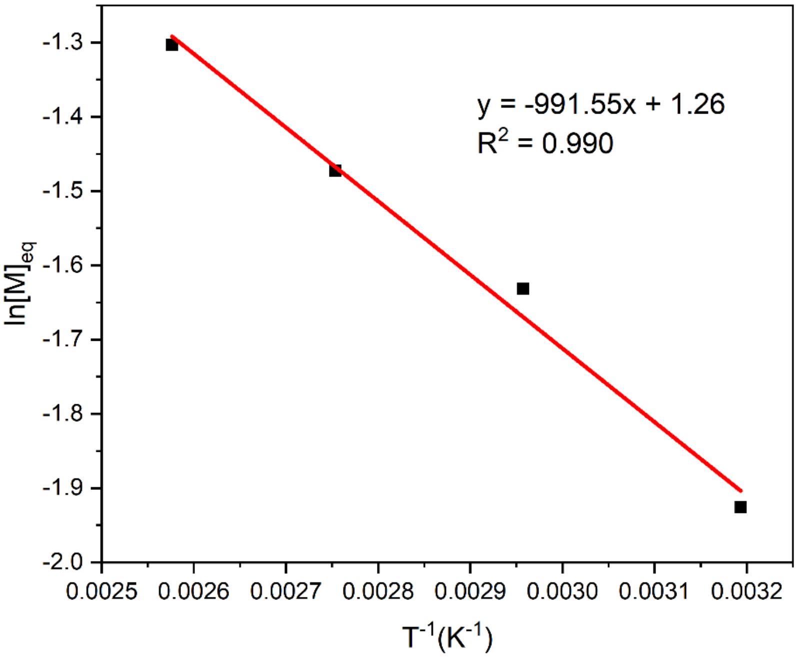


Fig. S26 Van't Hoff plot of ln[**M1**]$_{eq}$ vs. reciprocal of the absolute temperature (T^{-1}).

The Van't Hoff plot of ln[**M1**]$_{eq}$ versus T^{-1} gave a linear fitting with a slope of −991.55 and an intercept of +1.26, from which the thermodynamic parameters were calculated to be $\Delta H_p° = -8.24$ kJ mol^{-1} and $\Delta S_p° = -10.49$ J mol^{-1} K^{-1}, based on the equation ln[**M1**]$_{eq}$ $=\Delta H_p°/RT - \Delta S_p°/R$, where R is the molar gas constant. T_c was calculated to be 785 K (512 °C) at [**M1**]$_0$ = 1 mol/L, based on the equation $T_c = \Delta H_p°/ (\Delta S_p° + R\ln$ [**M1**]$_0$).

Table S8 Raw data over equilibrium conversion at various temperatures for **M2**.

Entry	T(K)	Con. (%)	$[M]_0$(mol/L)	$T^{-1}(K^{-1})$	$[M]_{eq}$ mol/L	$\ln[M]_{eq}$ mol/L
1	323.15	93.78	0.1	0.003094	0.006221	-5.079
2	363.15	84.36	0.1	0.002753	0.01564	-4.157
3	383.15	77.97	0.1	0.002609	0.022028	-3.815
4	403.15	71.69	0.1	0.002480	0.028306	-3.564

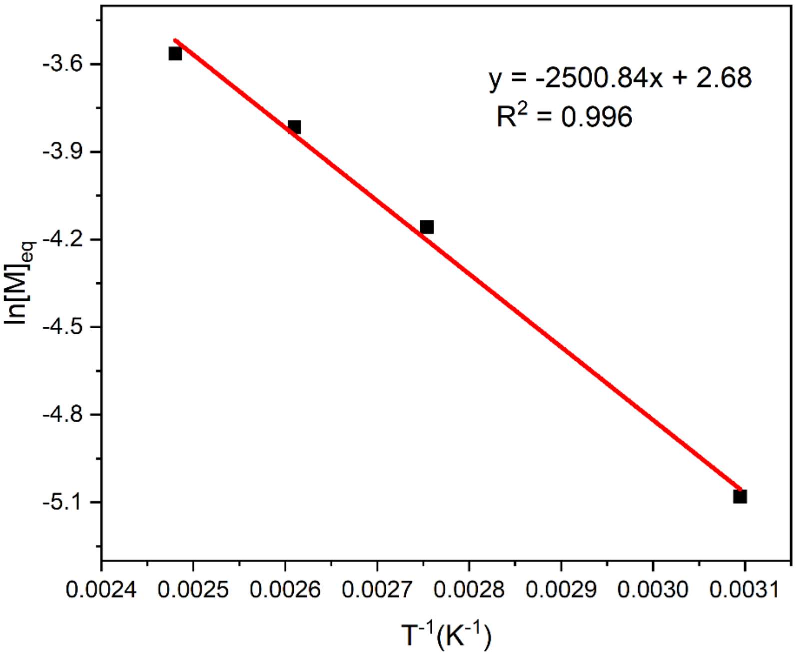


Fig. S27 Van't Hoff plot of ln[**M2**]$_{eq}$ vs. reciprocal of the absolute temperature (T^{-1}).

The Van't Hoff plot of ln[**M2**]$_{eq}$ versus T^{-1} gave a linear fitting with a slope of −2500.84 and an intercept of +2.68, from which the thermodynamic parameters were calculated to be $\Delta H_p°$ = −20.79 kJ mol^{-1} and $\Delta S_p°$ = −22.32 J mol^{-1} K^{-1}, based on the equation ln[**M2**]$_{eq}$ =$\Delta H_p°/RT - \Delta S_p°/R$, where R is the molar gas constant. T_c was calculated to be 931 K (658 °C) at [**M2**]$_0$ = 1 mol/L, based on the equation $T_c = \Delta H_p°/ (\Delta S_p° + R\ln [\mathbf{M2}]_0)$.

Bulk Thermal Chemical Recycle to Monomer

P(**M1**) and P(**M2**):

In a sublimation equipment, P(**M1**) or P(**M2**) and the catalyst were mixed and kept at 120−160 °C with stirring under vacuo for a certain time. After the reaction was stopped, the sublimate was collected, weighted, and characterized by ^{1}H NMR spectroscopy.

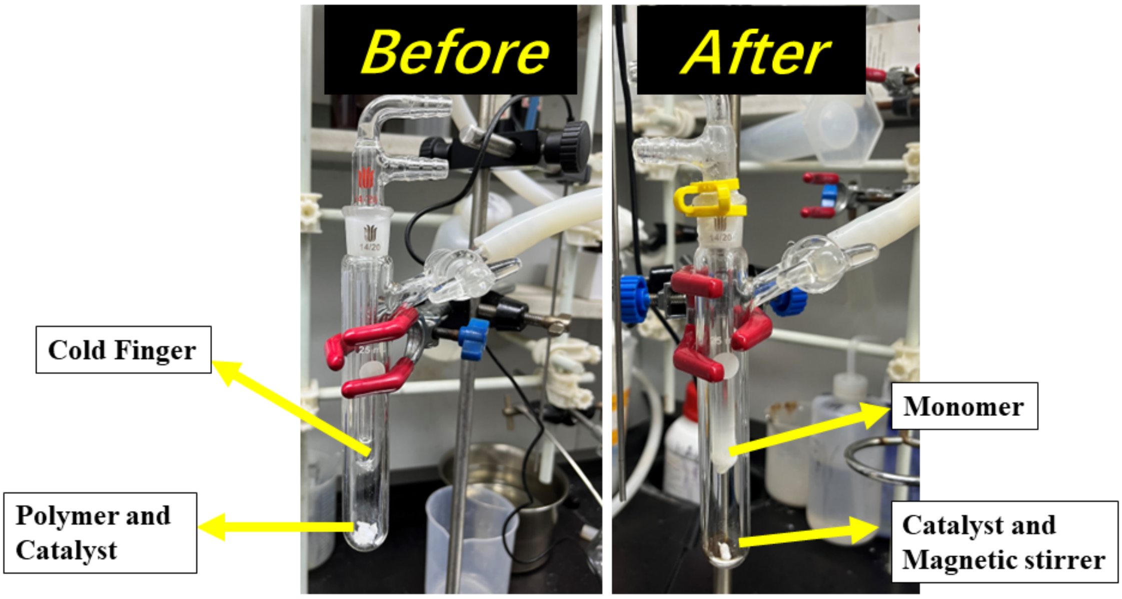


Fig. S28 Thermal depolymerization of polymers to monomers via sublimation.

Table S9 Results of bulk thermal depolymerization of **P**(**M1**).

Entry	Catalyst	Catalyst loading(mol%)	Temperature(°C)	Time(h)	Monomer yield[a] (%)
1	$Sn(Oct)_2$+PEO	10	150	11	93
2	$Sn(Oct)_2$	0.025	120	11	4
3	$Sn(Oct)_2$	0.1	150	10	-
4	$Sn(Oct)_2$	0.2	150	10	7
5	$Sn(Oct)_2$	0.5	160	11	40
6	$Sn(Oct)_2$	1	150	11	93
7	$Sn(AcO)_2$	2	135	5	56
8	$Sn(AcO)_2$	2	135	11	90
9	$Sn(AcO)_2$	2	150	5	87

[a] the monomer yield determined by the amount of the sublimate and the purity of recycled monomer determined by ^{1}H NMR spectroscopy.

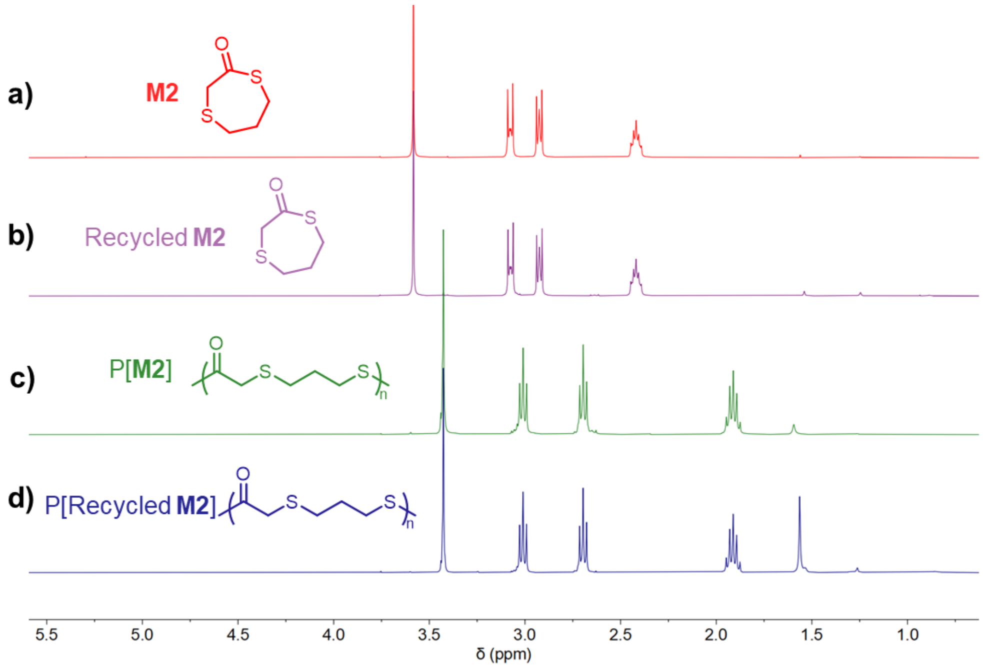


Fig. S29 ^{1}H NMR spectra of the recycled **M1** by the thermal depolymerization of P(**M1**).

a) Starting **M1** for comparison; b) Recycled **M1** by the thermal depolymerization; c) P(**M1**) obtained by [**M1**]/[TBD]/[I] = 500/1/1; d) P(**M1**) (repolymerization) obtained by [recycled **M1**]/[TBD]/[I] = 500/1/1.

Table S10 Results of bulk thermal depolymerization of **P**(**M2**).

Entry	Catalyst	Catalyst loading(mol%)	Temperature(°C)	Time(h)	Monomer yield (%) [a]
1	^tBuOK	5	175	10	50
2	^tBuOK	10	175	10	54
3	PhSNa	10	170	11	60
4	$Sn(Oct)_2$+PEO	1	150	11	32
5	$Sn(Oct)_2$+PEO	5	150	11	54
6	$Sn(Oct)_2$	5	100	11	27
7	$Sn(OAc)_2$	5	100	11	23
8	Sb_2O_3	10	175	10	-
9	$La[N(SiMe_3)_2]_3$	10	170	10	-

[a] the monomer yield determined by the amount of the sublimate and the purity of recycled monomer determined by ^1H NMR spectroscopy.

Table S11 Results for depolymerization of P(**M2**) in dilute solution.[a]

Entry	Catalyst	Catalyst loading(mol%)	Temperature (°C)	Time (h)	Conv. (%) [b]
1	^{t}BuOK	5	130	10	-
2	TBD	5	130	10	-
3	TBD	5	100	12	-
4	$Sn(Oct)_2$	5	160	10	57
5	$Sn(OAc)_2$	5	160	11	62
9	$Sn(OAc)_2$	5	160	48	62

[a] Reaction conditions: [M] = 0.01 M. [b] Polymer conversion measured by ^{1}H NMR of the solution.

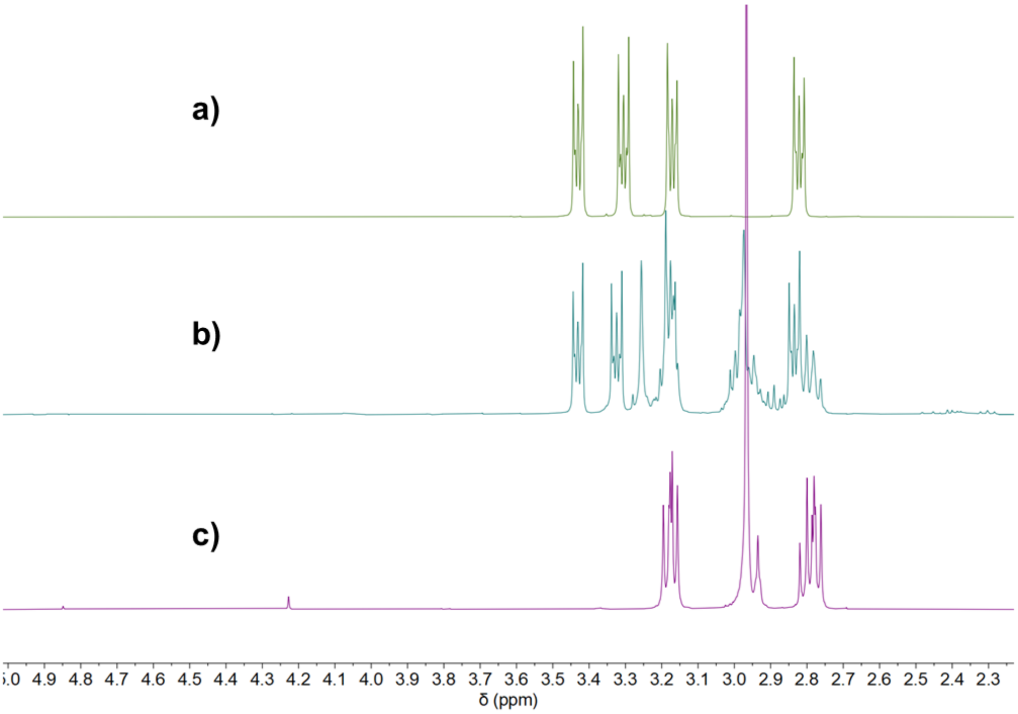


Fig. S30 ^{1}H NMR spectra of the recycled **M2** by the dilute solution depolymerization of P(**M2**).

a) Starting **M2** for comparison; b) Depolymerization product of P(**M2**); c) P(**M2**) obtained by [**M2**]/[TBD]/[I] = 500/1/1.

Table S12 Results of repolymerization of recycled **M1**.

Entry	[**M**]/[Cat.]/[I]	Time (min)	Conv.[a] (%)	$M_{n,Calcd}$ [b] (kDa)	$M_{n,\ SEC}$ [c] (kDa)	$Đ$ [c]
1	100:1:1	10 min	95	14.1	5.58	1.24
2	500:1:1	10 min	92	68.2	9.88	1.26

[a] Monomer conversion measured by ^{1}H NMR of the quenched solution. [b] Calculated from [**M**]$_0$/[BnSH]$_0$ × Conv. × $MW_{\mathbf{M}}$ + 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.

Metal ion adsorption study with P(M1)

General procedure for the preparation of 60 ppm metal ion solution.

Trivalent chromium standard solution (1000 μg/mL in 5.0 wt% HCl) was purchased from Beijing North Weiye Institute of Measuring and Testing Technology. It was diluted with deionized water to prepare a Cr^{3+} stock solution with a concentration of ~ 60.0 ppm.

$CoCl_2$ (55.1 mg) was dissolved in 25 mL of 1.0 mol/L HNO_3 to prepare Co^{2+} solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Co^{2+} stock solution with a concentration of ~60.0 ppm.

LiCl (152.7 mg) was dissolved in 25 mL of 1.0 mol/L HNO_3 to prepare Li+ solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Li+ stock solution with a concentration of ~60.0 ppm.

$MnCl_2$ (57.3 mg) was dissolved in 25 mL of 1.0 mol/L HNO_3 to prepare Mn^{2+} solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Mn^{2+} stock solution with a concentration of ~60.0 ppm.

$CuSO_4{\cdot}5H_2O$ (98.2 mg) was dissolved in 25 mL of 1.0 mol/L HCl to prepare Cu^{2+} solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Cu^{2+} stock solution with a concentration of ~60.0 ppm.

$CdCO_3$ (38.4 mg) was dissolved in 25 mL of 1.0 mol/L HCl to prepare Cd^{2+} solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Cd^{2+} stock solution with a concentration of ~60.0 ppm.

$HAuCl_4$ (43.12 mg) was dissolved in 25 mL of 1.0 mol/L HCl to prepare Au^{3+} solution with concentration of ~1000 μg/mL. It was diluted with deionized water to prepare a Au^{3+} stock solution with a concentration of ~60.0 ppm.

Cobaltous chloride, Lithium chloride, Lead chloride, Copper sulfate pentahydrate, Chloroauric acid and Cadmium carbonate were purchased from Energy Chemical.

General procedure of metal ion removal analysis.

4 mg P(M1) was dissolved in 100 μL DCM with a stir bar, then add a 4.0 mL of metal ion solution (about 60 ppm). After the solution was stirred at room temperature for 2 h, the solvent was filtered through a 0.2 μm syringe filter, and the metal ion concentration in the remained solution was determined by atomic absorption spectroscopy (AAS).

Table S13 Adsorption of metal ions with P(**M1**).[a]

Entry	Metal ions	$m_{[PM1]}$ (mg)	Time (h)	C_0 (ppm) 1st/2nd/3rd	C_f (ppm) 1st/2nd/3rd	Average Removal Efficiency[b] (%)	Standard Deviation
1	Li^+	4	2	58.6/56.6/56.6	58.0/56.5/55.0	1.47	1.45
2	Co^{2+}	4	2	59.5/58.1/58.1	59.4/53.9/54.8	4.35	3.70
3	Cr^{3+}	4	2	60.2/57.1/57.1	59.7/57.0/56.3	0.80	0.61
4	Cu^{2+}	4	2	27.3/28.7/28.7	27.0/26.7/26.8	5.20	3.55
5	Mn^{2+}	4	2	54.4/57.1/57.1	53.9/56.6/54.6	2.13	2.05
6	Cd^{3+}	4	2	56.4/58.1/58.1	55.9/55.7/55.8	2.96	1.80
7	Au^{3+}	4	2	46.7/46.7/46.7	0.19/0.20/0.14	99.6	0.0577

[a]Carried out in aqueous solutions of metal ion compounds, the solutions were prepared with concentration of ~60 mg/L, and C_0 is the real concentration measured by AAS. 4.0 mL of metal ion solution was directly added into DCM solution of P(**M1**). C_f is the concentration of the clear liquid after filtration. [b]Removal efficiency = $(C_0 - C_f)/C_0 \times 100\%$.

Table S14 Adsorption of metal ions with P(**M1**) in mixed metal ions.[a]

Entry	Metal ions	C_0 (ppm)	C_f (ppm)	Removal Efficiency[b] (%)
1	Li^+	57.1	56.8	0.52
2	Co^{2+}	56.8	56.1	1.23
3	Cr^{3+}	58.6	57.5	1.87
4	Cu^{2+}	58.9	58.8	0.17
5	Mn^{2+}	54.1	53.3	0.90
6	Cd^{3+}	56.1	55.6	0.89
7	Au^{3+}	42.9	1.93	95.5

[a]Carried out in aqueous solutions of metal ion compounds, the solutions were prepared with concentration of ~60 mg/L, and C_0 is the real concentration measured by AAS. 4.0 mL of metal ion solution was directly added into DCM solution of P(**M1**). C_f is the concentration of the clear liquid after filtration. [b]Removal efficiency = $(C_0 - C_f)/C_0 \times 100\%$.

Table S15 Au^{3+}Adsorption with P(**M1**).[a]

Entry	$m_{[PM1]}$ (mg)	Time (h)	C_0 (ppm)	C_f (ppm)	Removal Efficiency[b] (%)
1	4	2	46.69	0.19	99.6
2	4	6	46.69	0.14	99.7
3	4	6	1250	521	58.3

[a]Carried out in aqueous solutions of Au^{3+} compounds, the solutions were prepared with different concentration, and C_0 is the real concentration measured by AAS. 4.0 mL of Au^{3+} solution was directly added into DCM solution of P(**M1**). C_f is the concentration of the clear liquid after filtration. [b]Removal efficiency = $(C_0 - C_f)/ C_0 \times 100\%$.

General procedure for the CRM of polymers under bulk thermal in vacuum.

The P(**M1**) adsorbent after the adsorption of Au(III) ions was dried in a vacuum oven at 60 °C for 24 h and then brought inside an argon-filled glovebox. It was transferred into a 25 mL sublimation. Then, the catalyst was added into it. After that, the equipment was sealed, brought outside of the glovebox, and heated in vacuum. The sublimate was collected, weighted, and characterized by ^{1}H NMR spectroscopy.

Table S16 Results of bulk thermal chemical recycling of P(**M1**) - Au^{3+}.

Entry	Catalyst	Catalyst loading(mol%)	Temperature(°C)	Time(h)	Monomer yield (%) [a]
1	Sn(Oct)$_2$	2	170	10	-
2	Sn(AcO)$_2$	2	170	10	-
3	Sn(AcO)$_2$	5	140	12	70
4	Sn(AcO)$_2$	5	140	12	73

[a] the monomer yield determined by the amount of the sublimate and the purity of recycled monomer determined by ^{1}H NMR spectroscopy.

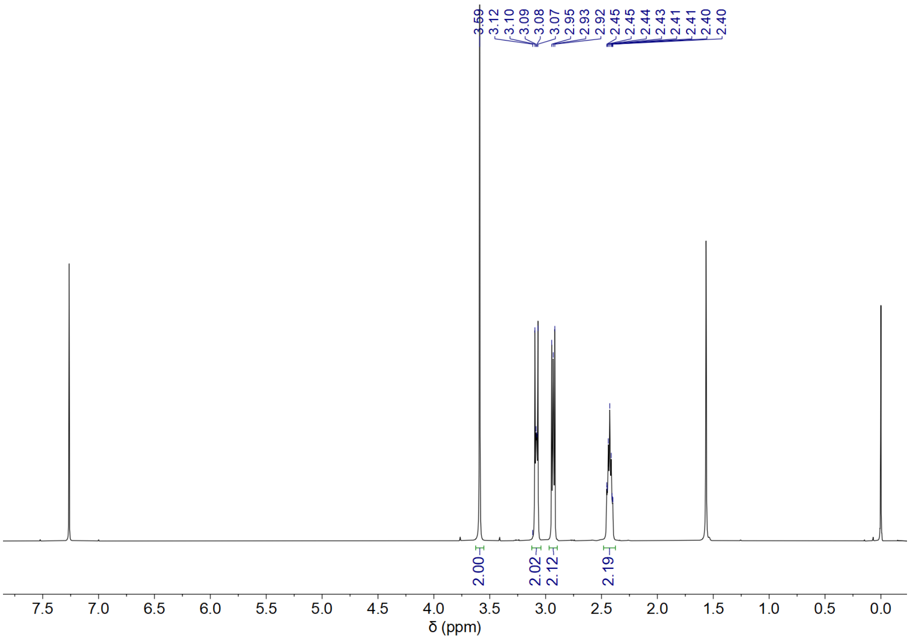


Fig. S31 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of recycled **M1** after depolymerization.

MALDI-TOF MS of P(M1)

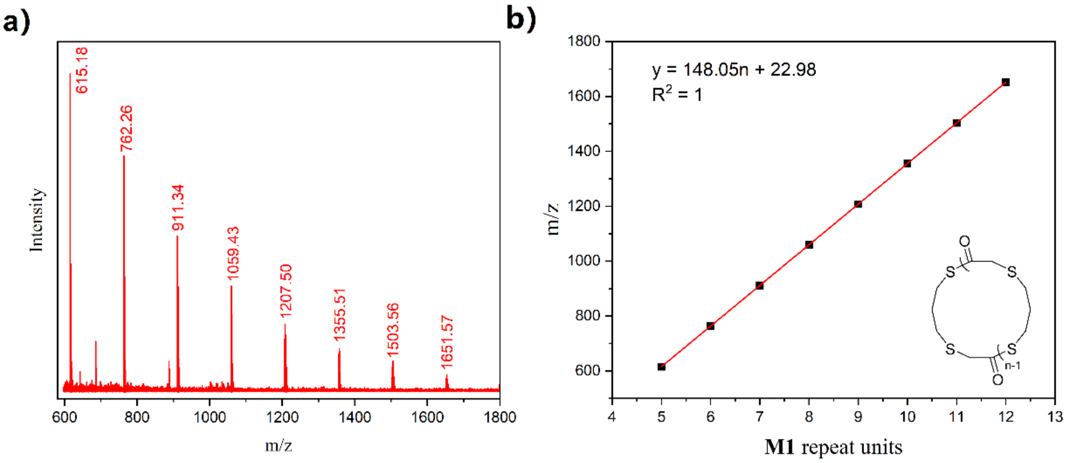


Fig. S32 MALDI-TOF MS spectrum of the low-molecular-weight P(**M1**).

a) MALDI-TOF MS spectrum of the low-molecular-weight P(**M1**) produced by [**M1**]/[TBD]/[I] = 50/1/1.
b) linear plot of m/z values vs the number of **M1** repeat units.

The spacing between the two neighboring molecular ion peaks corresponding to the exact molar mass of the repeat unit, **M1** [mass/charge ratio (m/z) = 148.00], as shown by the slope of the linear plot of m/z values (y axis) versus the number of **M1** repeat units (x axis). The intercept of the plot, 22.98, corresponding to circular structure of the polymer.

Reference

1. C. M. Archer, J. R. Dilworth, J. D. Kelly, M. J. Rosser, Y. Zheng, *J. Chem. Soc., Dalton Trans.*, **1997**, 1403-1410.