Supplementary Information

Biorenewable and Circular Polyolefin Thermoplastic Elastomers

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1. General Information

1.1 Materials

All reagents were purchased from the *Sigma-Aldrich*, *Alfa Aesar*, *J&K Chemicals*, *Energy Chemicals*, *Aladdin Reagents, Meryer Chemicals* or *Leyan Chemicals* and used without further purification unless otherwise stated. All the synthetic steps were carried

out under an inert argon atmosphere using standard Schlenk technique unless otherwise stated. All solvents were extra dry for reactions unless otherwise stated.

1.2 Characterizations

Nuclear magnetic resonance (NMR) experiments (^{1}H and ^{13}C) were recorded on a Bruker Avance NEO 400 instrument by using deuterated chloroform as a solvent. Chemical shifts were calibrated to the proton resonance of solvent (7.26 and 77.0 ppm for ^{1}H NMR and ^{13}C NMR spectroscopies, respectively).

High-resolution mass spectra (HRMS) were recorded by a Waters G2-XS QTof mass spectrometer which utilized an ESI ionization source.

Gel permeation chromatography (GPC) curves were measured with Malvern Viscotek 270 by using THF as the mobile phase at 40 °C. The flow rate was 1 mL/min, and the injection volume was 25 μL. A refractive index detector was employed to characterize the number average molecular weight (M_n) and molecular weight distribution ($Đ$) through conventional calibration by using narrow-distributed polystyrene as an internal standard.

High-Performance Liquid Chromatography (HPLC) curves were measured with Thermo Scientific U3000 using a solvent mixture (methanol: acetonitrile=50:50) as the eluent at 1 mL/min. The column used in the study is the gold C18 (150mm × 4.6mm, 5μm), with the temperature set at 25 ºC.The detection wavelength was set at 190 nm.

Samples for the XRD test were prepared by solution casting with film thickness of ~0.2 μm. The films were then cut into small 2 cm × 2 cm pieces for the XRD test. The tests were carried out using an X-ray diffractometer with 3 kW sealed X-ray tube, D/teX Ultra silicon strip detector and independent θ-θ geometry (XRD Ultima IV, Rigaku Americas Corporation, Japan). The X-ray source was Cu Kα. The 2θ testing range is from 10º to 50º, and the testing speed is 5º/min.

Calorimetric behavior of polymer samples was characterized with a Netzsch differential scanning calorimeter (DSC) or Mettler-Toledo DSC1 calibrated with an indium standard. The heating and cooling rates were fixed at 10 °C/min from -30 °C to 150 °C. The melting enthalpy was determined from the first heating scan unless otherwise stated.

The thermal degradation properties of the samples were probed through thermogravimetry by using a Netzsch TG 209 F1 system (Netzsch Instruments). The samples were heated from 30 °C to 800 °C at a rate of 20 °C/min under nitrogen protection.

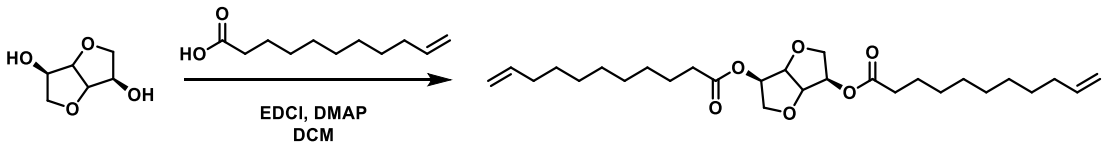
Rectangular polymer specimens were prepared with solution-casting polymer solutions (in toluene) onto mica substrates. After the specimens were vacuum dried at 110 °C overnight to reach a constant weight, the film could be easily peeled off from substrates and cut into several dog-bone specimens. Tensile tests were performed on MTS CMT8502 at a strain speed of 10 mm/min (unless otherwise stated) at ambient temperature (~25 ºC). The cyclic deformation with fixed tensile strain was performed to a tensile strain of 100% with the tensile strain rate of 100 mm/min and the relaxation strain rate of 100 mm/min, which was repeated ten times. Cyclic deformation with increased tensile strain was first carried out to the 100% tensile strain and then relaxed to the strain without residual stress; the specimen was then carried out to the 200% tensile strain and then relaxed to the strain without residual stress. In a similar fashion, the tensile strain was raised to 300%, 400%...1300%. The tensile deformation rate and the relaxation deformation rate were fixed to 100 mm/min.

Polarizing microscope image (POM) was recorded on Nikon eclipse LV100N polarizing microscope.

2. Synthesis

2.1 Synthesis of small molecules

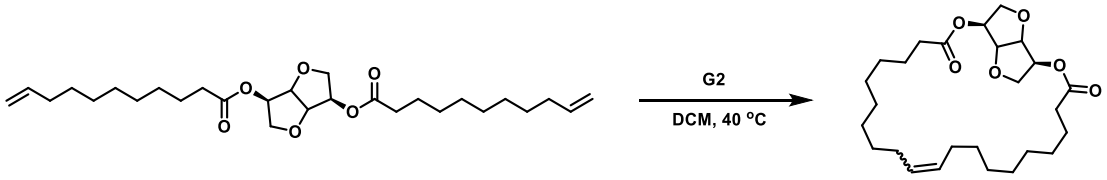
2.1.1 Synthesis of 1



1

Isomannide (1.00 g, 6.84 mmol), DMAP (0.84 g, 6.84 mmol), and undecenoic acid (2.52 g, 13.70 mmol) were dissolved in 50 mL DCM. Then EDCl (5.25 g, 27.34 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=5:1 as eluent). The product was obtained as a transparent liquid (3.22 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.80 (dq, *J*=11.4, 7.0, 2H), 5.09 (d, *J*=4.5, 2H), 4.96 (dd, *J*=24.1, 13.6, 4H), 4.69 (d, *J*=2.0, 2H), 4.03 (t, *J*=7.8, 2H), 3.79 (t, *J*=8.0, 2H), 2.37 (t, *J*=7.5, 4H), 2.03 (q, *J*=6.8, 4H), 1.70 – 1.60 (m, 4H), 1.42 – 1.21 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.26, 139.18, 114.17, 80.38, 73.53, 70.41, 33.91, 33.79, 29.28, 29.20, 29.05, 28.89, 24.86. HRMS m/z (ESI) calcd for $C_{28}O_6H_{46}Na$ $(M + Na)^+$ 501.3186, found 501.3195.

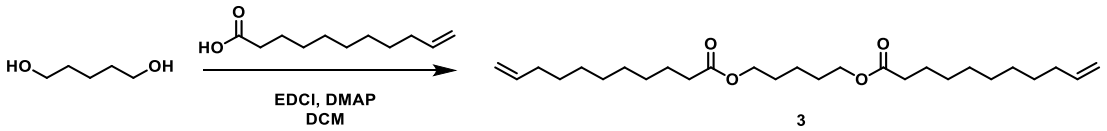
2.1.2 Synthesis of 2



1 2

1 (1.50 g, 3.13 mmol) was dissolved in 1.5 L DCM under N_2 protection. G2 catalyst (0.13 g, 0.15 mmol, 5 mol%) was added into the solution. The reaction mixture was heated to reflux and kept at this temperature for 2 h, then 0.55 mL DMSO was added to quench the reaction and stirred overnight. The mixture was cooled to room temperature, and was concentrated to obtain crude product. The residue was purified by silica flash chromatography (PE: EA=4:1 as eluent). The product was obtained as a colorless liquid (1.23 g, 97% yield, *trans*:*cis*=4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.35 (dd, *J*=4.5, 3.0, 2H), 5.18 – 5.05 (m, 2H), 4.69 (dd, *J*=4.2, 1.4, 2H), 3.99 (dd, *J*=9.7, 5.8, 2H), 3.86 (dd, *J*=9.6, 5.7, 2H), 2.38 (td, *J*=7.4, 3.8, 4H), 1.98 (m, 4H), 1.74 – 1.62 (m, 4H), 1.50 – 1.20 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.20, 130.55, 129.96, 80.71, 73.15, 73.03, 71.32, 71.27, 34.24, 34.19, 32.27, 29.09, 29.01, 28.93, 28.72, 28.68, 28.62, 28.32, 25.06, 24.99. HRMS m/z (ESI) calcd for $C_{26}O_6H_{42}Na$ $(M + Na)^+$ 473.2873, found 473.2884.

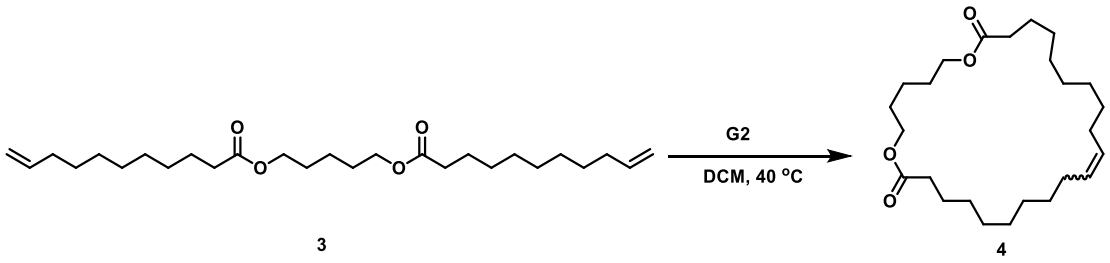
2.1.3 Synthesis of 3



3

Dipentanol (0.57 g, 5.43 mmol), DMAP (0.66 g, 5.43 mmol), and undecenoic acid (2.00 g, 10.85 mmol) were dissolved in 50 mL DCM. Then EDCl (4.16 g, 21.70 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=20:1 as eluent). The product was obtained as a colorless liquid (2.21 g, 93.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.82 (m, 2H), 4.96 (dd, *J*=24.6, 13.6, 4H), 4.07 (t, *J*=6.5, 4H), 2.29 (t, *J*=7.5, 4H), 2.03 (q, *J*=6.8, 4H), 1.73 – 1.50 (m, 8H), 1.48 – 1.21 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.91, 139.16, 114.15, 77.35, 77.03, 76.72, 64.00, 34.35, 33.78, 29.29, 29.21, 29.14, 29.06, 28.89, 28.31, 24.99, 22.48. HRMS m/z (ESI) calcd for $C_{27}O_4H_{48}Na$ $(M + Na)^+$ 459.3445, found 459.3452.

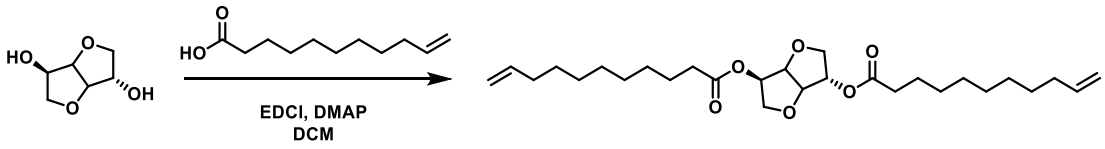
2.1.4 Synthesis of 4



3 4

3 (1.50 g, 3.44 mmol) was dissolved in 1.5 L DCM under N_2 protection. G2 catalyst (0.15 g, 0.17 mmol, 5 mol%) was added into the solution. The reaction mixture was heated to reflux for 2 h, then 0.55 mL DMSO was added to quench the reaction and stirred for additional overnight. The mixture was cooled to room temperature, and was concentrated to obtain crude product. The residue was purified by silica flash chromatography (PE: EA=5:1 as eluent). The product was obtained as a white solid (1.22 g, 88.1% yield, *trans*:*cis*=8:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.41 – 5.27 (m, 2H), 4.07 (m, 4H), 2.29 (t, *J*=6.1, 4H), 1.99 (s, 4H), 1.73 – 1.54 (m, 8H), 1.50 – 1.20 (m, 22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.95, 173.92, 130.62, 130.32, 64.00, 63.97, 34.47, 34.35, 32.60, 32.12, 29.18, 29.14, 29.08, 28.99, 28.89, 28.31, 28.13, 25.07, 25.00, 22.90, 22.47. HRMS m/z (ESI) calcd for $C_{25}O_4H_{44}Na$ $(M + Na)^+$ 431.3132, found 431.3138.

2.1.5 Synthesis of 5

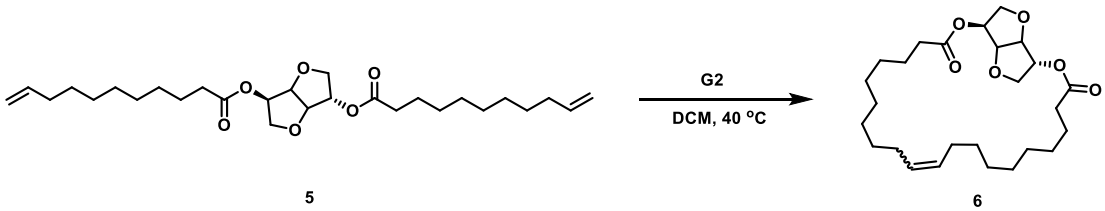


5

Isosorbide (1.00 g, 6.84 mmol), DMAP (0.84 g, 6.84 mmol), and undecenoic acid (2.52 g, 13.70 mmol) were dissolved in 50 mL DCM. Then EDCl (5.25 g, 27.34 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=6:1 as eluent). The product was obtained as a transparent liquid (2.31g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.71 (ddt, *J*=16.9, 10.2, 6.7, 2H), 5.12 – 5.03 (m, 2H), 4.95 – 4.80 (m, 4H), 4.74 (t, *J*=5.0, 1H), 4.38 (d, *J*=4.7, 1H), 3.94 – 3.78 (m, 3H), 3.71 (dd, *J*=9.8, 5.3, 1H), 2.33 – 2.14 (m, 4H), 1.95 (dd, *J*=14.3, 6.9, 4H), 1.62 – 1.45 (m, 4H), 1.35 – 1.13 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.70, 172.41, 138.74, 113.93, 85.70, 80.48,

77.60, 73.50, 73.14, 70.09, 33.82, 33.63, 33.50, 29.00, 28.99, 28.92, 28.89, 28.76, 28.60, 24.58, 24.54. HRMS m/z (ESI) calcd for $C_{28}O_6H_{46}Na$ $(M + Na)^+$ 501.3192, found 501.3197.

2.1.6 Synthesis of 6

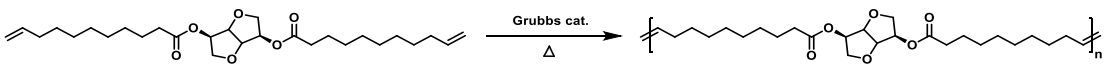


5 6

5 (1.50 g, 3.13 mmol) was dissolved in 1.5 L DCM under N_2 protection. G2 catalyst (0.13 g, 0.15 mmol, 5 mol%) was added into the solution. The reaction mixture was heated to reflux and kept at this temperature for 2 h, then 0.55 mL DMSO was added to quench the reaction and stirred overnight. The mixture was cooled to room temperature, and was concentrated to obtain crude product. The residue was purified by silica flash chromatography (PE: EA=4:1 as eluent). The product was obtained as a colorless liquid (1.11 g, 78% yield, *trans*:*cis*=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.43 – 5.31 (m, 2H),, 5.18 (ddd, *J*=14.4, 6.2, 3.1, 2H), 4.86 (dt, *J*=10.3, 5.1, 1H), 4.47 (d, *J*=4.6, 1H), 4.00 – 3.77 (m, 4H), 2.46 – 2.25 (m, 4H), 2.07 – 1.88 (m, 4H), 1.76 – 1.48 (m, 4H), 1.40 – 1.17 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.24, 173.20, 172.95, 172.86, 130.51, 130.25, 129.92, 129.84, 85.80, 85.72, 80.76, 80.74, 77.77, 77.66, 73.82, 73.70, 73.43, 70.70, 70.51, 34.16, 34.01, 32.17, 32.06, 29.74, 29.46, 29.35, 29.27, 29.08, 28.92, 28.87, 28.81, 28.80, 28.72, 28.61, 28.51, 28.46, 28.42, 28.37, 28.24, 27.96, 27.00, 26.79, 24.98, 24.93, 24.85, 24.70. HRMS m/z (ESI) calcd for $C_{26}O_6H_{42}Na$ $(M + Na)^+$ 473.2879, found 473.2884.

2.2 Synthesis of polymers

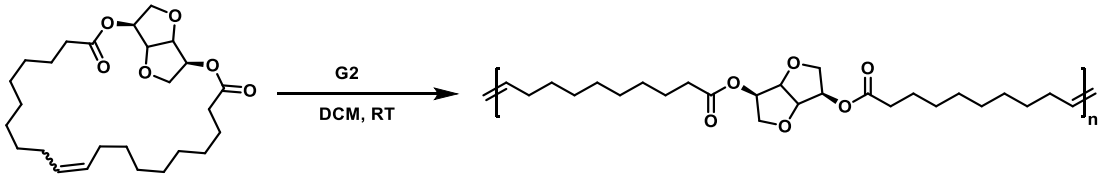
2.2.1 ADMET polymerization



Typical procedure to prepare **P1**: In an 8 mL via, **1** (0.50 g, 1.05 mmol, 100 eq.) was dissolved in toluene (2 mL). To the monomer solution, G2 (8.868 mg, 10.45 μmol, 1 eq.) was added and the reaction system was heated to specified temperature. After stirring for 12 h, G2 (4.43 mg, 5.23 μmol, 0.50 eq.) was added. After stirring for another 12 h, G2 (4.43 mg, 5.23 μmol, 0.50 eq.) was added. After stirring for another 24 h, the reaction was quenched by adding 100 μL ethyl vinyl ether (EVE). The filtrate was concentrated on a rotavapor. Precipitation in cold methanol thrice afforded 0.37 g

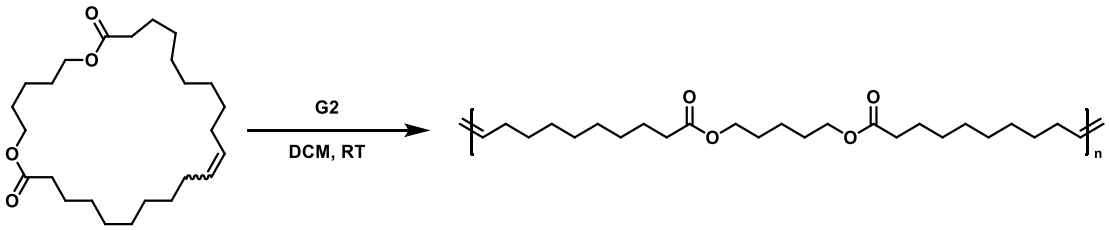
colorless **P1** as a viscous solid (74% yield). Other ADMET attempts were summarized in Table S1.

2.2.2 ROMP



Typical ROMP procedure: In a vial, **2** was dissolved in DCM. To the monomer solution, G2 was added to initiate the polymerization at room temperature. After stirring for a given time, the reaction was quenched by adding EVE. After stirring for another 15 min, Quadrapure TU macroporous particles and DCM were then added. The mixture was stirred overnight, filtered through a celite plug and concentrated on a rotavap. The solution was precipitated into cold methanol thrice to afford the white polymer products in solid state. Detailed polymerization conditions were summarized Table S2.

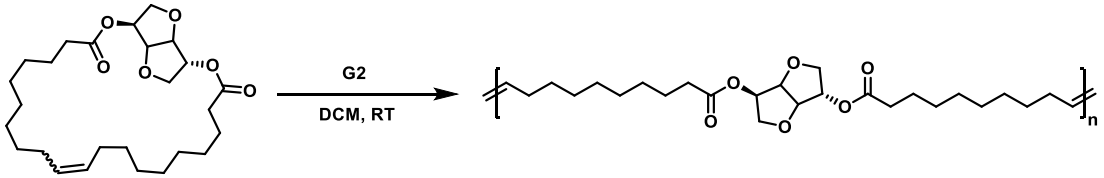
2.2.3 Synthesis of P10



4

In a 20 mL vial, **4** (0.50 g, 1.22 mmol, 500 eq.) was dissolved in DCM (4.9 mL). To the monomer solution, G2 (2.08 mg, 2.44 μmol, 1 eq.) was added to initiate the polymerization at room temperature. After stirring for 2 h, the reaction was quenched by adding 100 μL EVE. Precipitation in cold methanol thrice afforded 0.46 g colorless **P10** as a white solid (92.0% yield).

2.2.4 Synthesis of P11



6

In a 20 mL vial, **6** (0.50 g, 1.11 mmol, 500 eq.) was dissolved in DCM (1.11 mL). To the monomer solution, G2 (1.88 mg, 2.22 μmol, 1 eq.) was added to initiate the polymerization at room temperature. After stirring for 30 min, the reaction was quenched by adding 100 μL EVE. Precipitation in cold methanol thrice afforded 0.45 g

colorless **P11** as a white solid (90.0% yield).

3. Polymerization thermodynamics

3.1 Experiment

Thermodynamics studies were conducted for monomer **2**. The polymerization of **2** was conducted at various temperatures. The equilibrium monomer concentration $[M]_e$ for each temperature was measured via ^{1}H NMR. The thermodynamic parameters were obtained by plotting $\ln[M]_e$ against temperature 1/T (van't Hoff plot) according to equation:

$$\ln[M]_e = \Delta H/RT - \Delta S/R$$

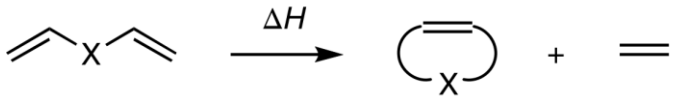
In equation, $[M]_e$ is the equilibrium monomer concentration in moles per liter, T is the reaction temperature in Kelvin (K), ΔH is the enthalpy of reaction in kilocalories per mole, ΔS is the entropy of reaction in calories per mole per Kelvin and R is the gas constant, 8.314 J mol^{-1} K^{-1}. The values for ΔH and ΔS can be obtained from the slope and the intercept of the van't Hoff plot, respectively. The following procedure is a representative example of the polymerization performed here.

2 (500 mg, 1.1 mmol, 1 equiv.) was dissolved in 0.55 mL xylene/toluene in a volumetric flask. Additional solvent was added to reach the 1 mL mark to form the 1 M monomer solution, which was transferred to a 1-dram vial. To the monomer solution was added G2 (9.30 mg, 0.011 mmol, 0.01 equiv.); 220 μL of the solution was added to four additional vials, and all five vials were then placed in preheated oil baths at the desired temperatures. Since time studies of the polymerization all show that the polymerization would have reached equilibrium within 1 h, the reactions were quenched at 1 h with EVE (20 μL) and the conversion was measured with ^{1}H NMR. The olefinic peaks in the ^{1}H NMR for the monomer and polymer were integrated to determine the residual monomer content at equilibrium. We also tried the ROMP at 0.15 M and 0.02 M following a similar process. All the data are summarized in Table S3.

3.2 DFT calculations of the ring strain energy

The computation of ring strain energy (RSE) of different monomers was conducted by calculating the enthalpy change of the ring-closing metathesis reaction shown below using density functional theory (DFT) at the B3LYP-D3(BJ)/6-31G(d,p) with G09 software.[2] After geometry optimization and frequency calculation, this equation was used directly to calculate the ΔH for the ring strain using the equation below:

$$\text{Ring strain energy} = \Delta H = (H_{\text{ring}} + H_{\text{ethylene}}) - H_{\text{diene}}$$



in which the H_{diene} represents the enthalpy for the ring-opened alkenes; H_{ring} represents the enthalpy for the cyclic monomer; and $H_{ethylene}$ represents the enthalpy for ethylene.

4. Depolymerization studies by ruthenium catalysts

4.1 Depolymerization procedure

General procedure: The polymers were dissolved in chloroform or deuterated chloroform ($CDCl_3$) at a concentration of 20 mM ([olefin]=20 mM) and heated at 50 °C in the presence of 1 mol% G2 catalyst for 1 h.

After depolymerization, the reaction system was directly use for proton NMR test to determine the monomer recover ratio. After NMR test, the solvent was evaporated for GPC test.

4.2 Repolymerization of the recycled macrocyclic oligomers

Taking **P4** as an example, the depolymerized system of **P4** using the typical depolymerzation condition (G2, 1% mol, 50 ºC, 1 h) includes a family of homologous macrocyclic oligomers, i.e., monomers, dimers, and other macrocycles. The oligomeric mixture was mixed with Quadrapure TU macroporous particles in dichloromethane and stirred overnight. The mixture was then filtered through a celite plug and concentrated on a rotavap. The residual catalyst in the polymer can be entirely eliminated through adsorption with Quadrapure TU macroporous particles, ensuring the purity suitable for repolymerization.

These mixtures were then used for repolymerization to prepare recycled polymer with adjustable molecular weights simply by adjusting the catalyst loading ratio. The detailed repolymerization conditions were summarized in Table S5. Taking ***r*P4** as an example, in a 100 mL vial, 10.00 g depolymerized mixture of **P4** (22.19 mmol, 100 eq.) was dissolved in 45 mL dichloromethane. To the monomer solution, G2 (188.39 mg, 0.22 mmol, 1 eq.) was added. After stirring for 30 min, the reaction was quenched by adding 1 mL EVE. The filtrate was concentrated on a rotavap, which was directly used for ^{1}H NMR and GPC tests. The conversion was determined to be 92%. Crude ***r*P4** can be further purified by precipitation into ether.

4.3 Depolymerization kinetics

P4 was dissolved in deuterated chloroform ($CDCl_3$) at a concentration of 20 mM ([olefin]=20 mM) and heated to 50 °C in the presence of 1 mol% G2. Aliquot was taken

out at a few time intervals and quenced by adding EVE. Then the solvent was removed for GPC measurement to determine each fraction ratio.

4.4 Temperature effect

Depolymerization of **P4** at different temperatures of 20 ºC, 35 ºC, 50 ºC and 65 ºC was studied at 20 mM. The following procedure is a representative example of depolymerization experiments performed here:

In a small vial with a stir bar, **P4** (60 mg, 0.13 mmol, 100 eq.) was dissolved in 6.4 mL $CHCl_3$. To the solution was added 100 μL of a stock solution of G2 (1.13 mg, 1.33 μmol, 1 eq.), such that desired concentration of 20 mM olefin was reached. Different vials were placed in a preheated oil bath at 20 ºC, 35 ºC, 50 ºC and 65 ºC, then allowed to react for 1 h, after which 10 μL EVE was added to quench the depolymerization. Volatiles were removed using a rotavap and the residue was used for GPC tests to determine the monomer recovery ratio.

4.5 Catalyst type effect

Depolymerization of polymer **P4** using different Ru carbene catalysts (G1, G2, G3, HG2) was studied at 20 mM, 50 ºC. The following procedure is a representative example of depolymerization experiments performed here:

In a small vial with a stir bar, **P4** (60 mg, 0.13 mmol, 100 eq.) was dissolved in 6.4 mL $CHCl_3$. To the solution was added 100 μL of a stock solution of catalyst (1.33 μmol, 1 eq.), such that desired concentration of 20 mM olefin was reached. Different vials were placed in a preheated oil bath at 50 ºC, then allowed to react for 1 h, after which 10 μL EVE was added to quench the depolymerization. Volatiles were removed using a rotavap and the residue was used for GPC tests to determine the monomer recovery ratio.

4.6 Catalyst loading effect

Depolymerization of polymer **P4** using G2 catalyst with different loading ratios (0.1 mol%, 0.5 mol%, 1 mol%, 2 mol%, 5 mol%) was studied at 20 mM, 50 ºC. The following procedure is a representative example of depolymerization experiments performed here:

In a small vial with a stir bar, **P4** (60 mg, 0.13 mmol, 100 eq.) was dissolved in 6.4 mL $CHCl_3$. To the solution was added 100 μL of a stock solution of catalyst (1.33 μmol, 1 eq.), such that desired concentration of 20 mM olefin was reached. Different vials were placed in a preheated oil bath at 50 ºC, then allowed to react for 1 h, after which 10 μL EVE was added to quench the depolymerization. Volatiles were removed using

a rotavap and the residue was used for GPC tests to determine the monomer recovery ratio.

4.7 Concentration effect

Depolymerization of polymer **P4** was conducted at concentrations of [olefin] = 1 mM, 5 mM, 10 mM, 20 mM, 100 mM and 150 mM at 50 ºC. The following procedure is a representative example of depolymerization experiments performed here:

In a small vial with a stir bar, **P4** (60 mg, 0.13 mmol, 100 eq.) was dissolved in $CHCl_3$. To the solution was added 100 μL G2 (1.13 mg, 1.33 μmol, 1 eq.), such that desired concentration of polymer olefin groups was reached. The vials were placed in a preheated oil bath at 50 ºC and allowed to react for 1 h, after which 10 μL EVE was added to quench the depolymerization. The solvent was evaporated and directly used for GPC tests to determine the monomer recovery ratio.

4.8 Molecular weight effect

Depolymerization of polymers at M_n of 23300 Da, 46000 Da, 103600 Da, 158300 Da, 303000 Da, 648100 Da and 722000 Da were studied at 50 ºC. The following procedure is a representative example of depolymerization experiments performed here:

In a small vial with a stir bar, polymer (60 mg, 0.13 mmol, 100 eq.) was dissolved 6.4 mL in $CHCl_3$. To the solution was added 100 μL G2 (1.13 mg, 1.33 μmol, 1 eq.), such that desired concentration of 20 mM olefin was reached. The vials were placed in a preheated oil bath at 50 ºC and allowed to react for 1 h, after which 10 μL EVE was added to quench the polymerization. Volatiles were removed using a rotavap and the residue was used for GPC tests to determine the monomer recovery ratio.

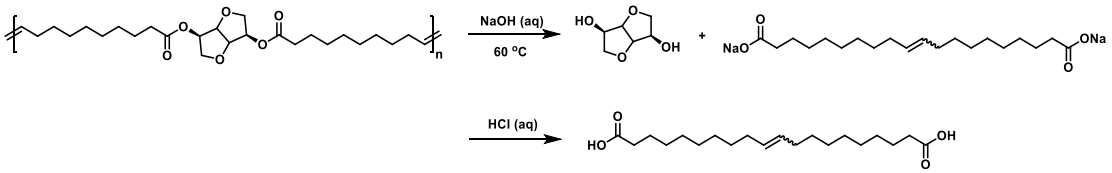
4.9 Scaled up monomer recycling experiment

In order to balance the monomer recovery ratio and solvent cost, typical depolymerization procedure is selected (G2, 1 mol%, 50 ºC, 1 h). 10.2 g **P2**-**P9** elastomer specimens (with different molecular weights) were mixed together to dissolve in 1110 mL chloroform, which was degassed and immersed in 50 ºC oil bath. Then 188.40 mg G2 catalyst was added, the reaction was stirred for 1 h, then 767.6 μL DMSO was added. The reaction was stirred overnight. The solvent was removed by rotavap and collected. The residue was dispersed with 15 g silica gel. Then the silica gel mixture was added to a buchner funnel with a short silica plug. Then 300 mL recovered $CHCl_3$ was added to elute the sample at reduced pressure. The first yellowish component was discarded. Then 700 mL recovered $CHCl_3$ was added to elute the monomer at reduced pressure, where the residual catalyst, dimers and other oligomers

will be truncated in the silica plug. The filtrate was concentrated on a rotavap, 5.70 g colorless liquid was collected with high purity (HPLC >99%) as the pristine monomer, and can be used for repolymerization.

5. Degradation studies and polycondensation of hydrolyzed products

5.1 Degradation studies by alkaline solution

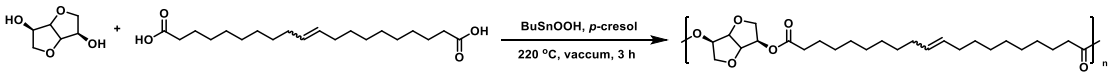


100 mg **P4** was charged with 10 mL of 10 wt% NaOH (aq) at 60 ºC without protection. The polymeric specimen gradually became crushed and dispersed in the solution. The solution was heated and stirred for 24 h. The aqueous solution was extracted by 15 mL ethyl acetate. The organic phase and aqueous phase were separated with different processing method to recover the monomers.

The organic phase was washed by water and dried over Na_2SO_4. After passing through a short silica plug, 30 mg white solid was obtained after solvent evaporation. ^{1}H NMR spectrum indicates that the recovered product corresponds to isomannide with high purity as its raw material.

After acidification with 0.25 M HCl, the aqueous phase reached a pH of 3, leading to the formation of a white, fluffy precipitate during the titration process. Subsequently, the precipitate was extracted by adding 15 mL ethyl acetate to the solution. The organic layer was then separated and dried over Na_2SO_4. Upon solvent evaporation, a white powder was obtained without further purification. Analysis of the ^{1}H NMR spectrum revealed a cleanly integrated spectrum for the olefin-coupled diacid resulting from metathesis polymerization.

5.2 Polycondensation of hydrolyzed products



Isomannide (500.0 mg, 3.421 mmol), olefin-coupled diacid (1.165 g, 3.421 mmol), *p*-cresol (0.5549 g, 5.132 mmol), and BuSnOOH (1.429 mg, 6.842 μmol) were weighed into a three-neck flask. The flask was equipped with a nitrogen gas inlet, a top stirrer, and a distillation head with a thermometer and a receiving flask attached to it. The reactor was heated to 240 °C under a constant nitrogen flow and slightly sitrred for 8 h. The oil was then cooled to 220 °C. Afterward, polycondensation was carried out at the same temperature under high vacuum for 3 h. After the system was cooled to room

temperature, the product was dissolved in chloroform. Precipitation in methanol thrice afforded 1.12 g polymer (72.7% yield, M_n=51300, $Đ$=2.52).

6. Tables

6.1 ADMET polymerization

Table S1. ADMET polymerization attempts for the preparation of **P1**.

[M]: Cat.	Cat.	Solvent	Time (h)	Conc.	T (°C)	Yield (%)	M_n (Da)	$Đ$	*Trans* ratio[a]
1000: 1	G2	Toluene	12	0.33 M	80	64%	9100	1.94	78%
200:1	G2	Toluene	12	0.5 M	70	68%	10600	2.44	80%
100: 1	G2	Toluene	12	0.5 M	70	66%	12400	1.87	82%
100: 1 After 12 h add 0.5 eq	G2	Toluene	24	0.5 M	70	70%	12600	1.96	83%
100: 1	G3	Toluene	24	0.5 M	70	50%	5500	1.93	67%
100: 1	G1	Toluene	24	0.5 M	70	51%	5500	1.75	83%
100 :1 After 12 h add 0.5 eq	G2	Toluene	24	0.5 M	70	68%	13000	1.98	83%
100: 1 After 12 h add 0.5 eq After 24 h add 0.5 eq	G2	Toluene	48	0.5 M	70	74%	23300	1.93	84%

[a]Ratio of *trans* configuration of C=C bond along the polymer backbone.

6.2 ROMP

Table S2. ROMP polymerization conditions.

	Conc.	[M]: G2	Time	Solvent	Conv. (%)	M_n (Da)	$Đ$	*Trans* ratio[a]
P2	0.20 M	100:1	10 h	DCM	98%	46000	1.88	75%
P3	1.00 M	100:1	30 min	DCM	97%	103600	2.16	81%
P4	1.00 M	150:1	30 min	DCM	95%	158300	2.10	81%
P5	1.00 M	250:1	30 min	DCM	96%	227800	2.28	81%
P6	1.00 M	500:1	30 min	DCM	97%	303000	2.40	82%
P7	1.00 M	1000:1	30 min	DCM	91%	648100	2.97	83%
P8	1.00 M	1000:1	15 min	DCM	86%	722000	2.85	86%
P9	1.00 M	1000:1	5 min	DCM	75%	794200	2.55	73%
P10	0.25 M	500:1	2 h	DCM	95%	106100	1.80	79%
P11	1.00 M	500:1	30 min	DCM	96%	310500	2.53	83%

[a]Ratio of *trans* configuration of C=C bond along the polymer backbone.

6.3 ROMP thermodynamics

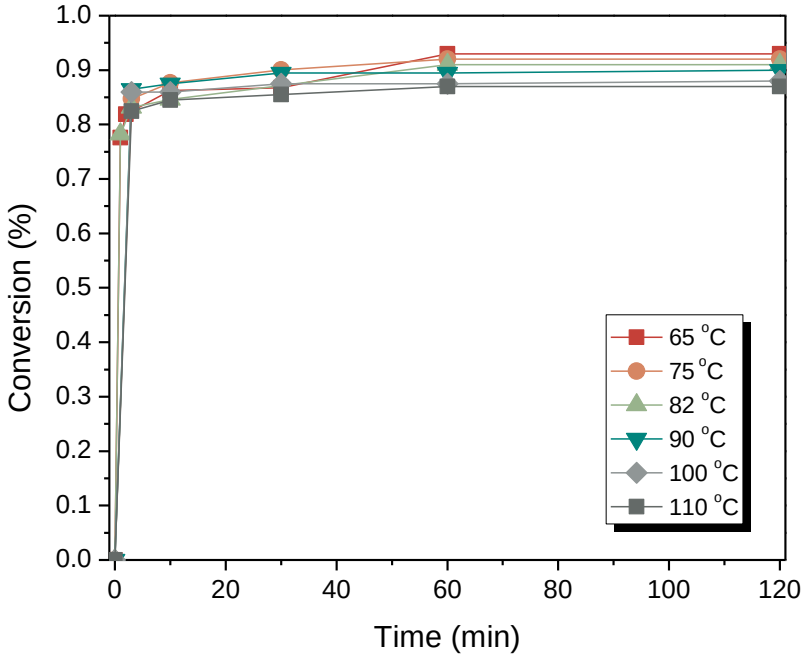


Figure S1. Monomer conversion *vs* time for polymerization of monomer **2** at different temperatures ($[M]_0$=0.15 M, in xylene, **2**: G2=100: 1).

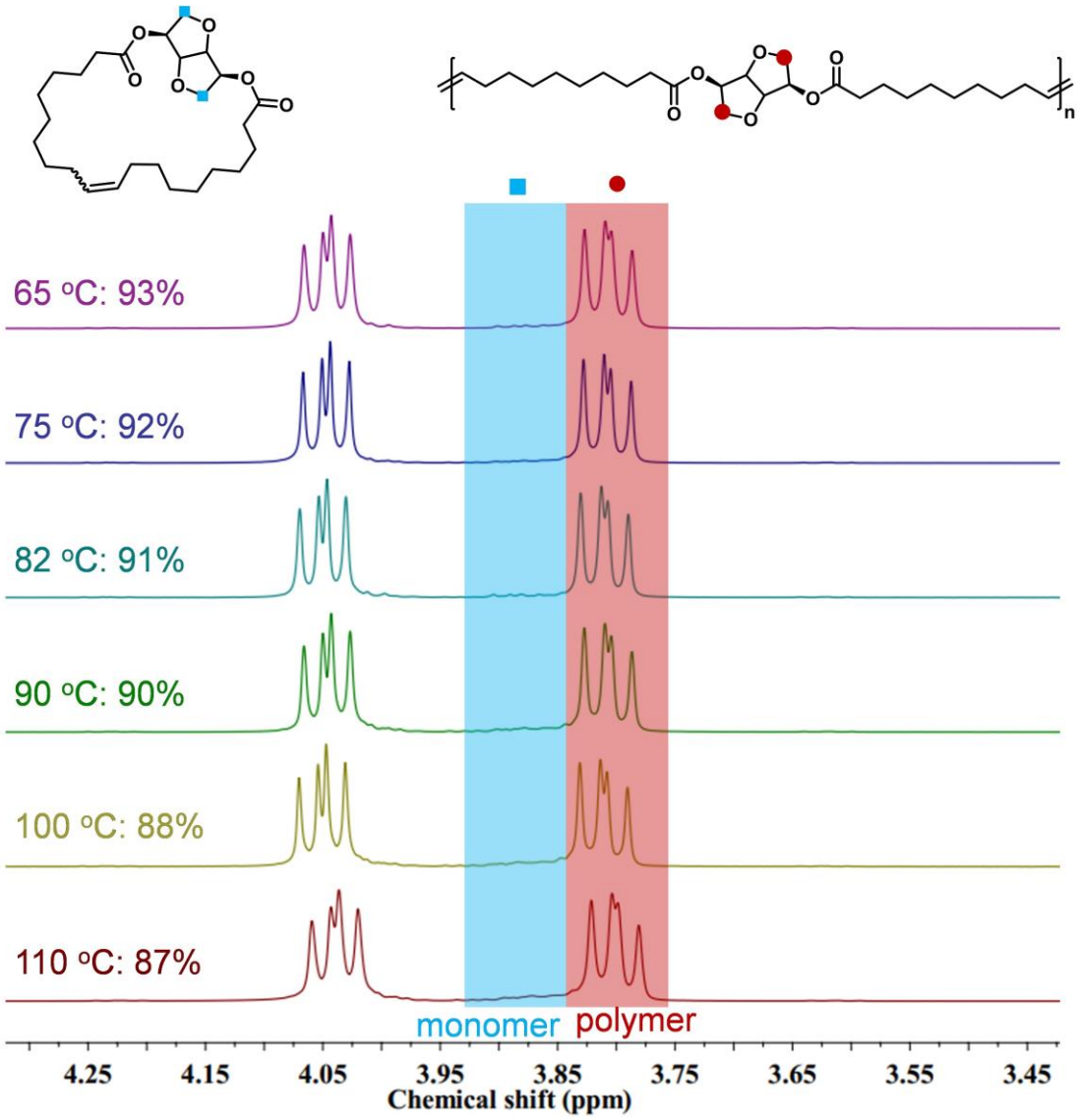


Figure S2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) on thermodynamic studies of **2** ($[M]_0$=0.15 M, in xylene, **2**: G2=100: 1).

Table S3. Equilibrium monomer concentration for polymerization at various temperatures (with 0.01 eq. of G2 catalyst).

Conc. (M)	T (°C)	Solvent	Conv.	$[M]_e$
1.0	20	Xylene	>95%	<0.05
1.0	35	Xylene	>95%	<0.05
1.0	45	Xylene	>95%	<0.05
1.0	55	Xylene	>95%	<0.05
1.0	65	Xylene	>95%	<0.05
1.0	40	Toluene	>95%	<0.05
1.0	20	Toluene	>95%	<0.05

1.0	5	Toluene	>95%	<0.05
1.0	-10	Toluene	>95%	<0.05
1.0	-25	Toluene	>95%	<0.05
1.0	-40	Toluene	>95%	<0.05
1.0	-55	Toluene	>95%	<0.05
0.15	65	Xylene	93%	0.0105
0.15	75	Xylene	92%	0.012
0.15	82	Xylene	91%	0.0135
0.15	90	Xylene	90%	0.015
0.15	100	Xylene	88%	0.018
0.15	110	Xylene	87%	0.0195
0.02	10	Toluene	75%	0.0050
0.02	18	Toluene	70%	0.0060
0.02	23	Toluene	66%	0.0068
0.02	35	Toluene	58%	0.0084
0.02	42	Toluene	51%	0.0098

Based on the results of Table S3, all the polymerization (at 1.0 M) proceeds near quantitatively (>95% conversion) at different temperatures. We therefore utilized the data of 0.15 M to plot van't Hoff relationship for **2**, a slope of -1857 and an intercept of 0.9268 were obtained. The enthalpy change and entropy change of the reaction were calculated as follows:

$$\Delta H/R = -1857$$

$$-\Delta S/R = 0.9268$$

The calculation resulted in ΔH =-3.69 kcal mol^{-1}, ΔS =-1.84 cal mol^{-1} K^{-1}, and T_c=1731 ºC for the polymerization of **2** in xylene at 0.15 M.

In a similar manner, the calculation resulted in ΔH =-3.67 kcal mol^{-1}, ΔS =-2.44 cal mol^{-1} K^{-1}, and T_c=1228 ºC for the polymerization of **2** in toluene at 20 mM.

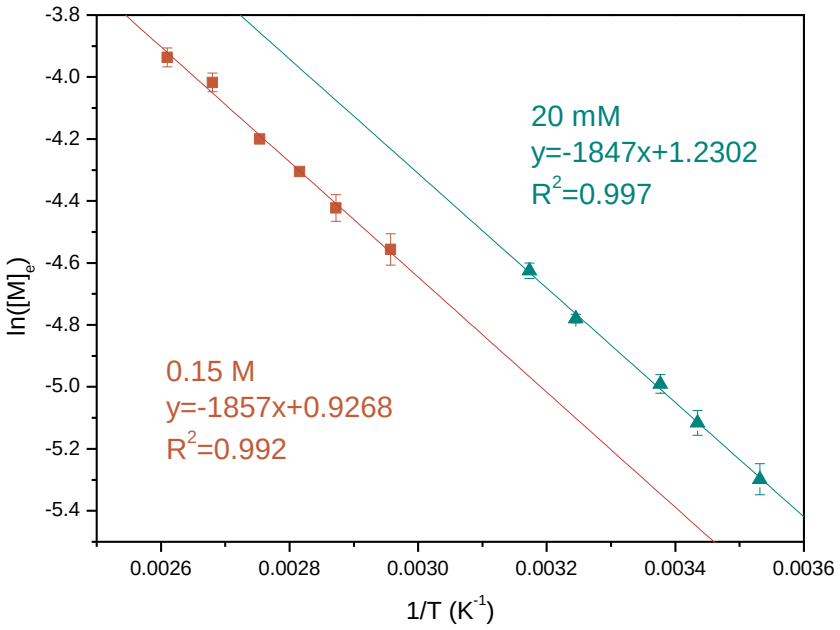


Figure S3. van't Hoff plot for monomer **2** polymerized at 0.15 M and 20 mM.

6.4 Ring strain energy (RSE)

Table S4. Calculated RSE values

Compound	Sum of electronic and thermal enthalpies (a.u.)	RSE (kcal/mol)
Diene	-1545.467342	/
trans-Monomer **2**	-1466.918800	3.71
cis-Monomer **2**	-1466.916083	5.42
Ethylene	-78.542623	/

6.5 Repolymerization of the recycled macrocyclic oligomers

Table S5. Ring-opening metathesis repolymerization conditions

Entry	Polymer	[M]: G2	Time	Solvent	Conv. (%)	M_n (Da)	$Đ$
1	/	50:1	30 min	DCM	90%	105000	2.22
2	***r*P4**	100:1	30 min	DCM	92%	141900	2.08
3	/	150:1	30 min	DCM	91%	191800	2.30
4	/	250:1	30 min	DCM	93%	283300	2.35
5	/	500:1	30 min	DCM	92%	396700	2.82

7. Figures

7.1 Figures for the properties of P1

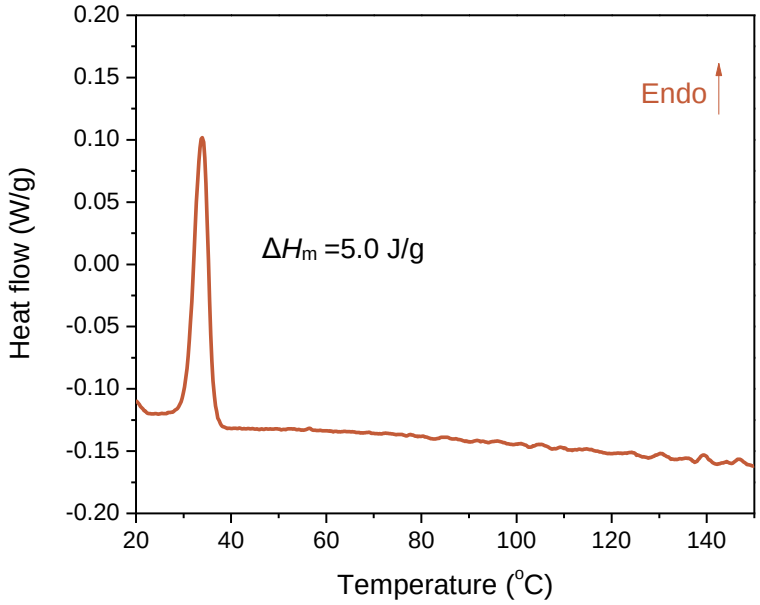


Figure S4. DSC heating scans of **P1**.

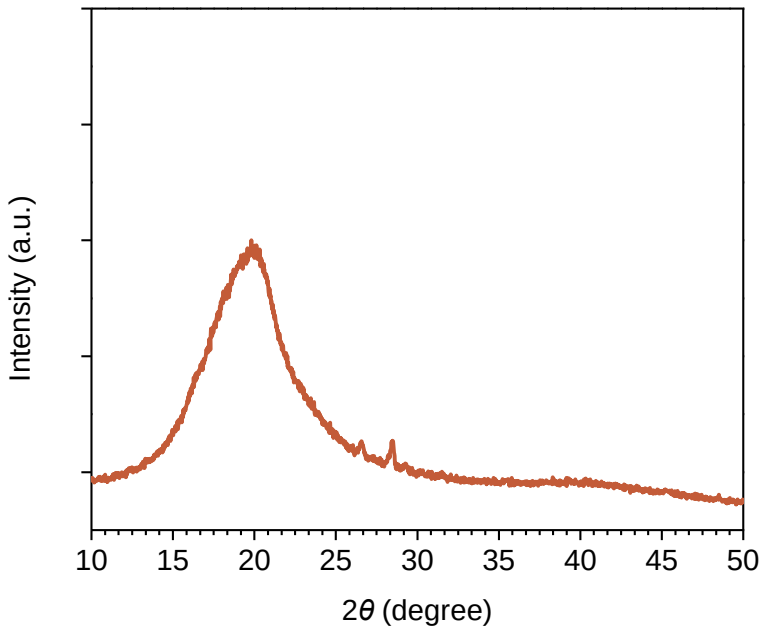


Figure S5. XRD curve of **P1**.

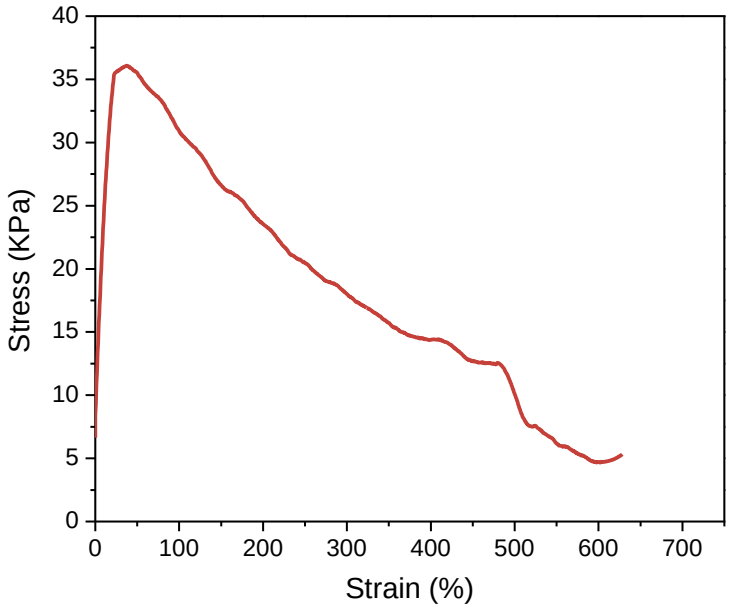


Figure S6. Stress-strain curve of **P1**.

7.2 Figures for monomer structure

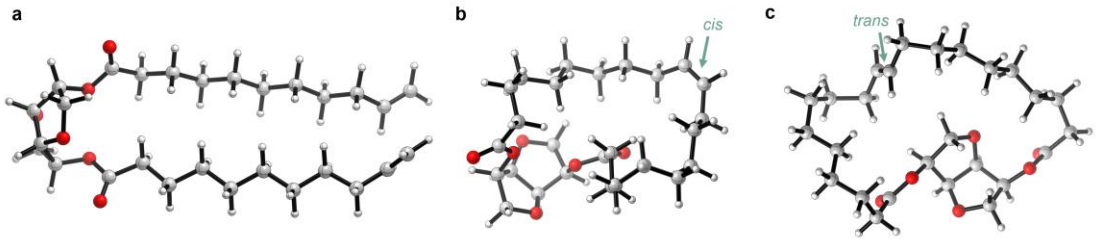


Figure S7. Optimized conformation of (a) **1,** (b) *cis* isomer of **2**, and (c) *trans* isomer of **2**.

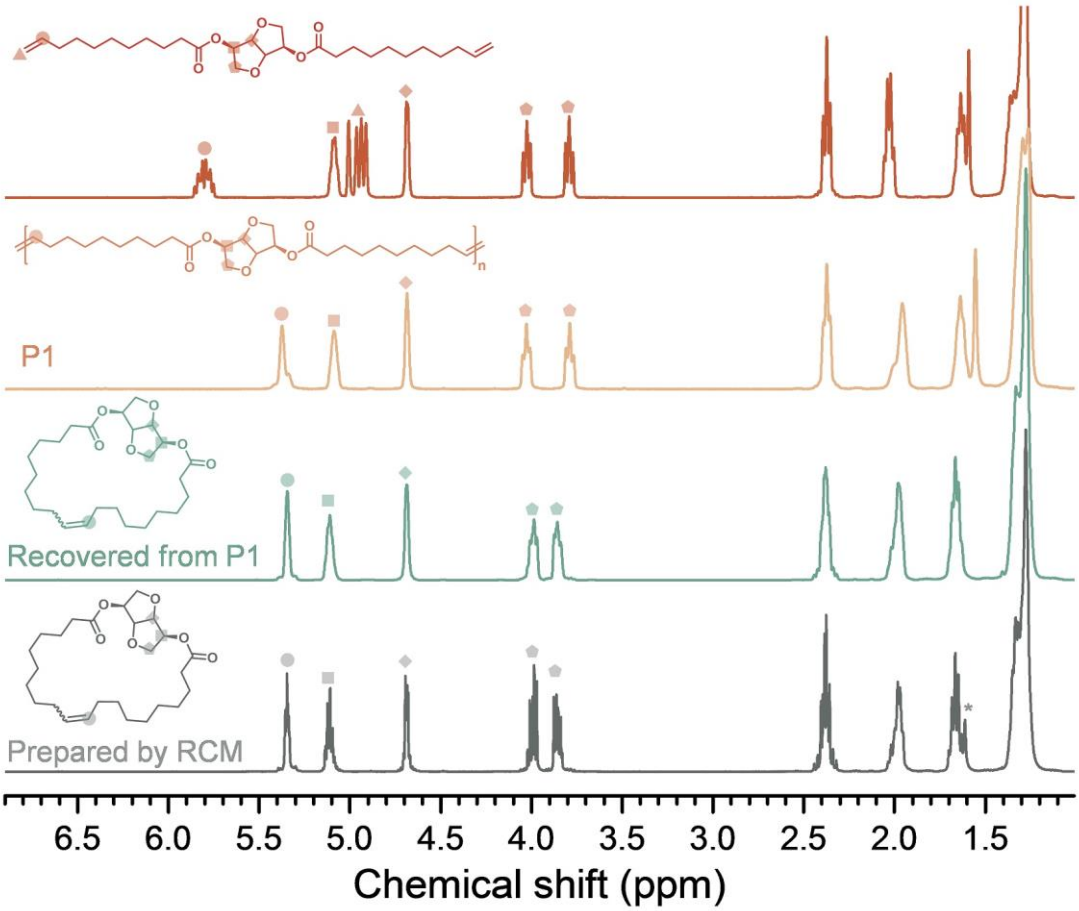


Figure S8. ^{1}H NMR spectra (400 M, $CDCl_3$) of **1**, **P1**, recovered monomer from the depolymerization of **P1** and and ring-closing metathesis prepared **2**.

7.3 Figure for polymer molecular weight characterizations

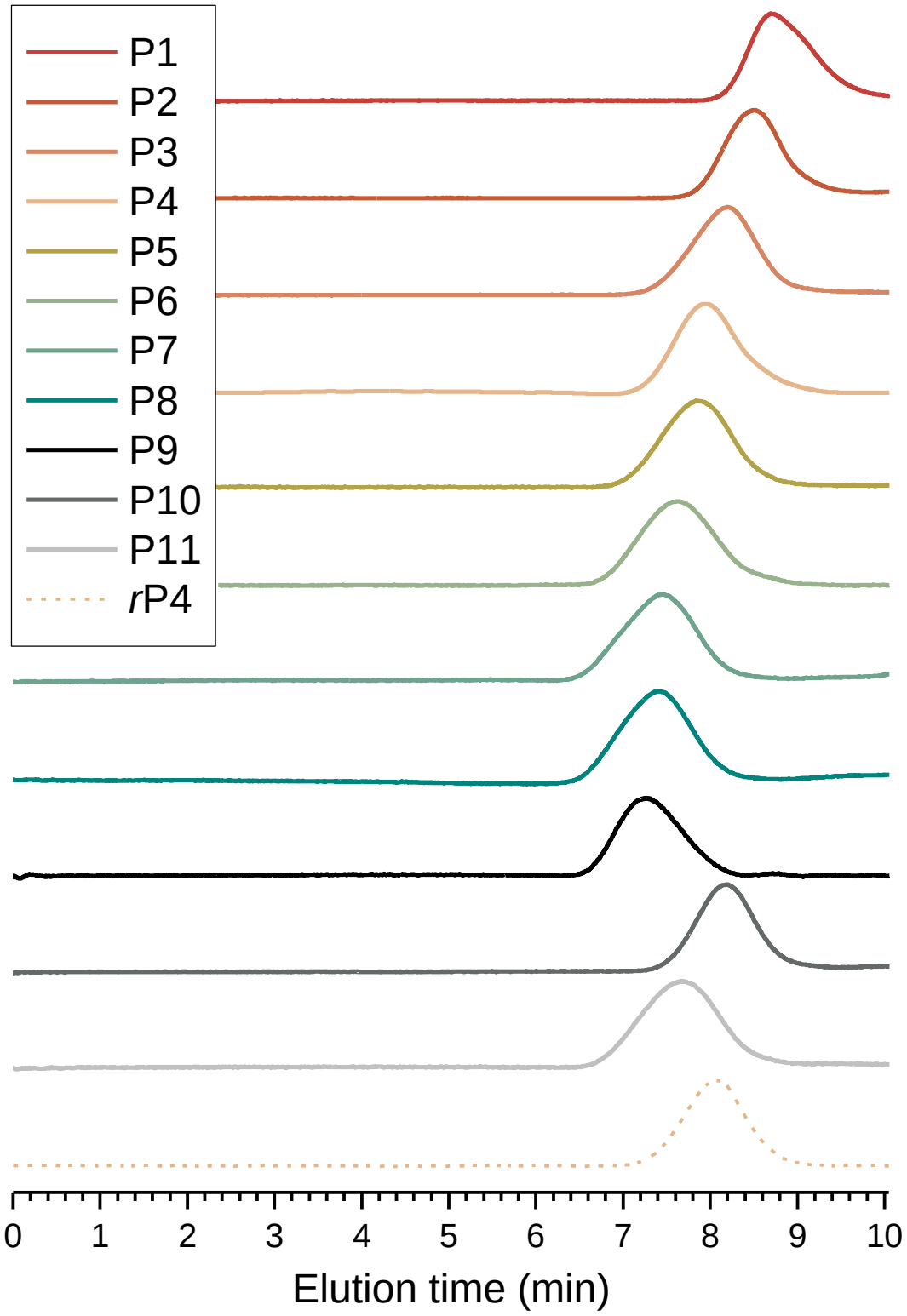


Figure S9. GPC elution traces of polymers.

7.4 Figure for the determination of crystallinity of P4

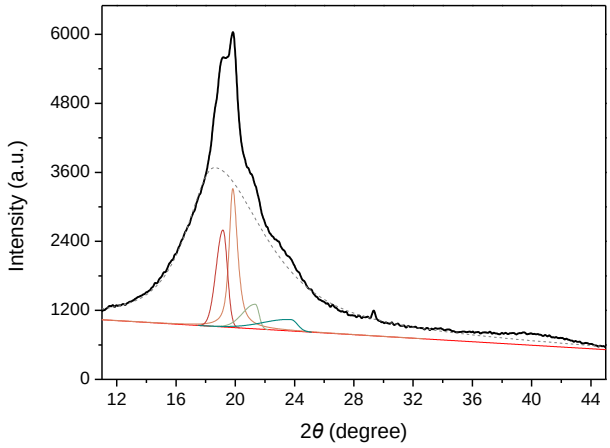


Figure S10. Deconvolution of XRD spectrum of **P4**.

7.5 Figures for the thermal properties of polymers

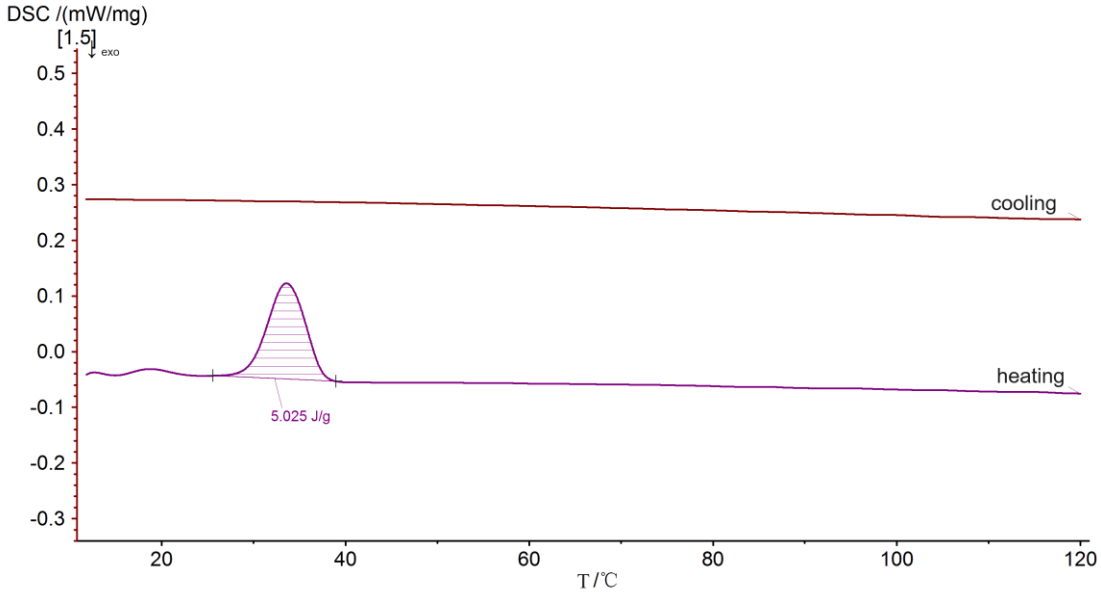


Figure S11. DSC scans of **P1**.

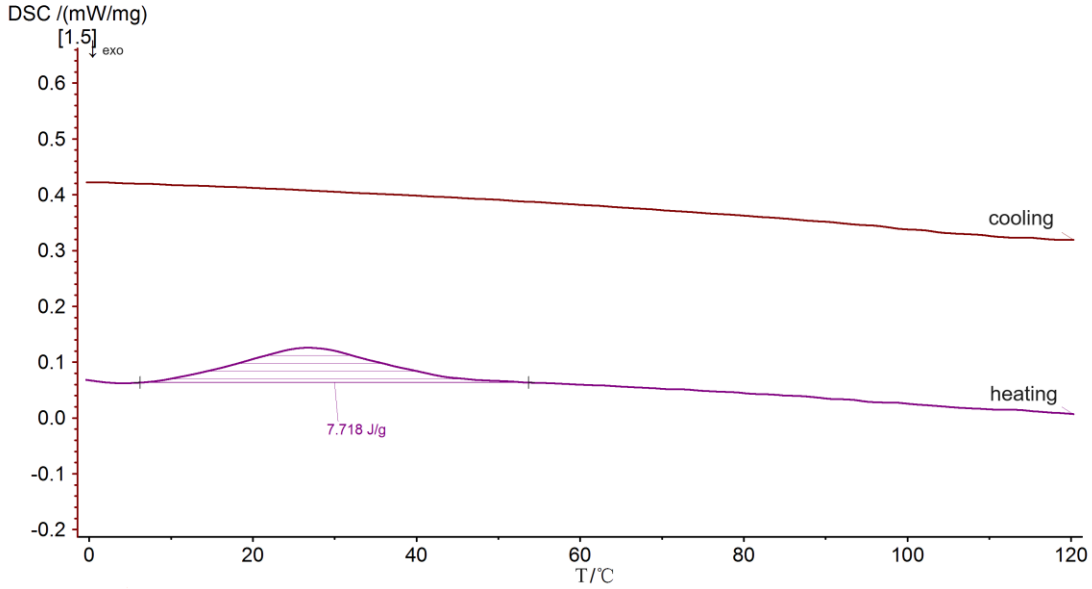


Figure S12. DSC scans of **P2**.

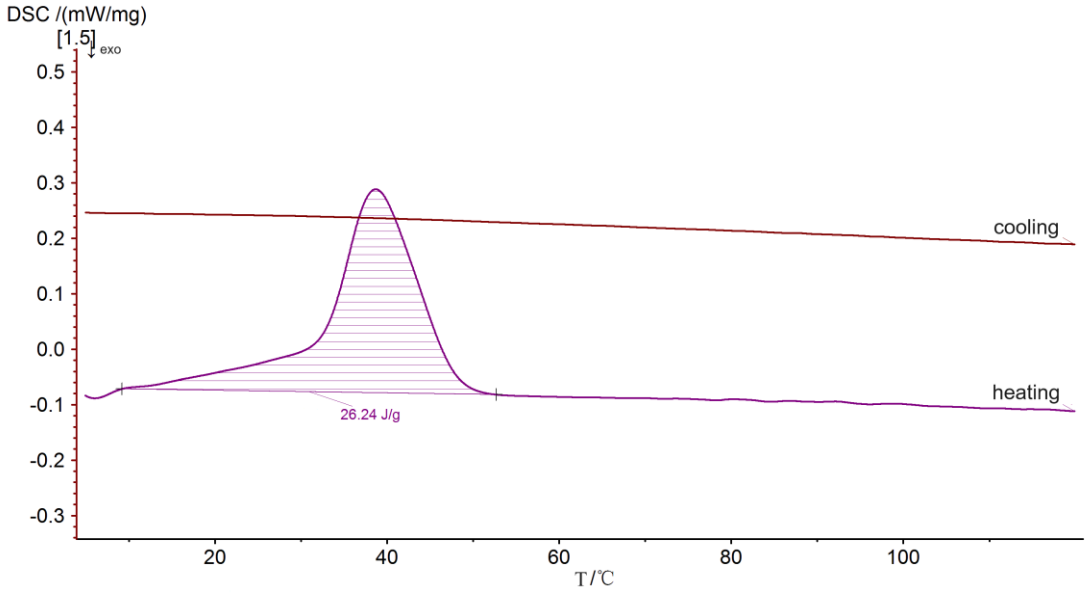


Figure S13. DSC scans of **P3**.

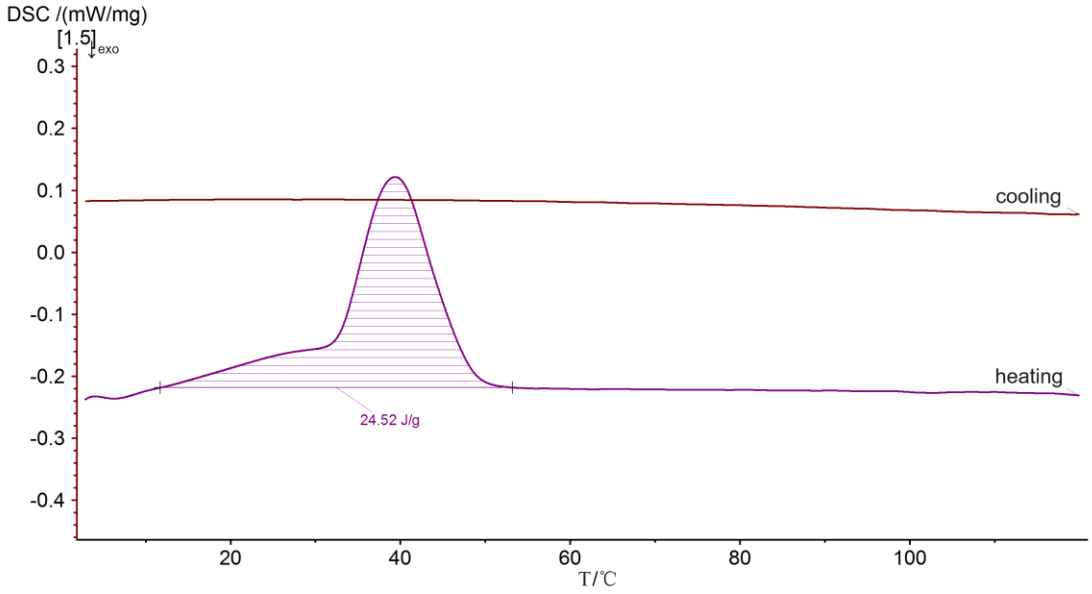


Figure S14. DSC scans of **P4**.

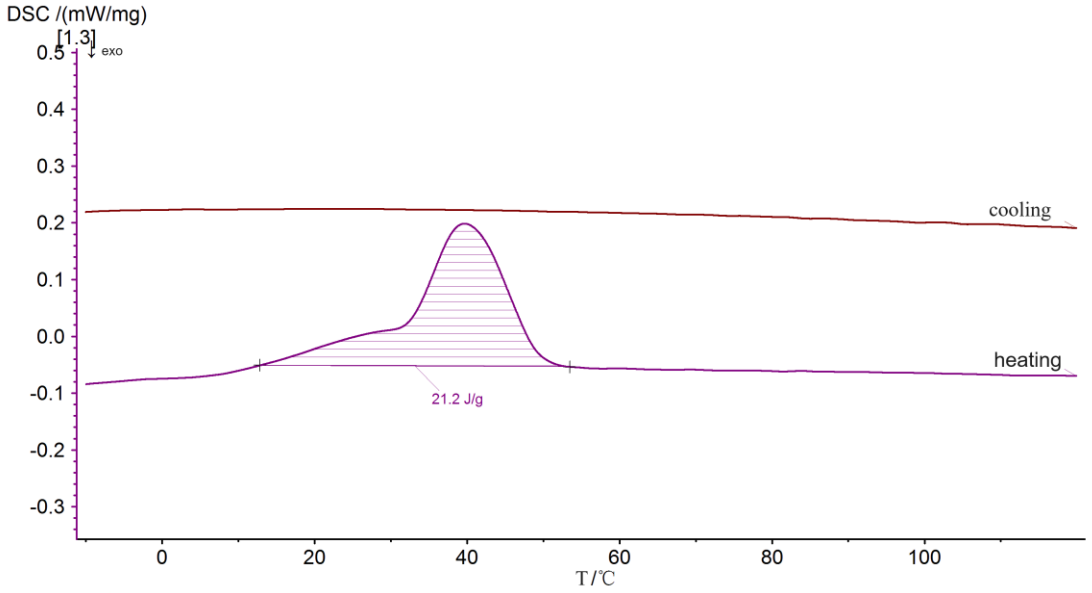


Figure S15. DSC scans of **P5**.

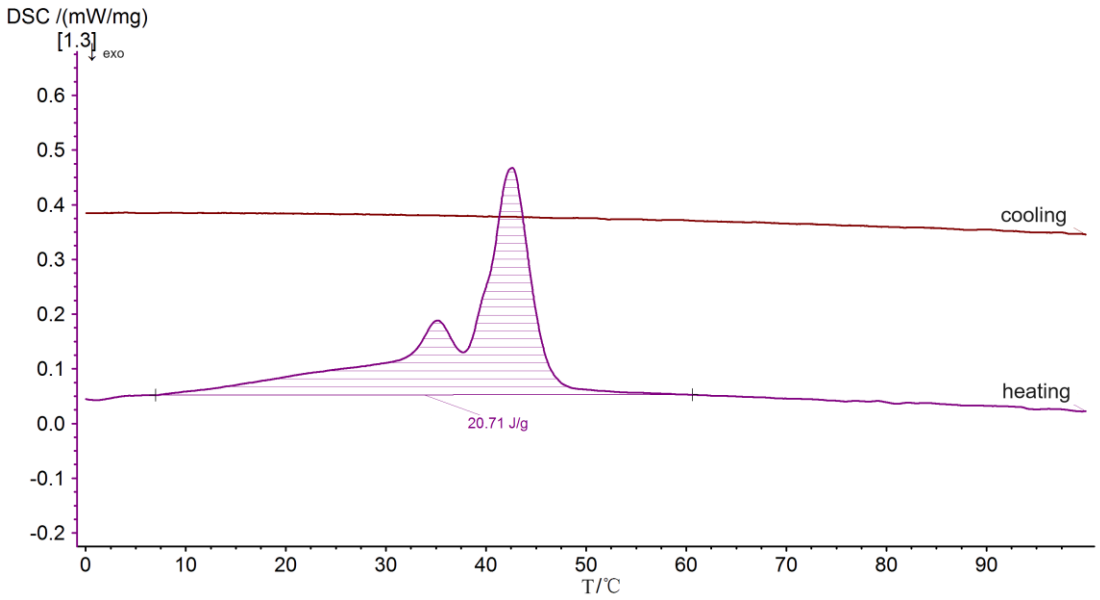


Figure S16. DSC scans of **P6**.

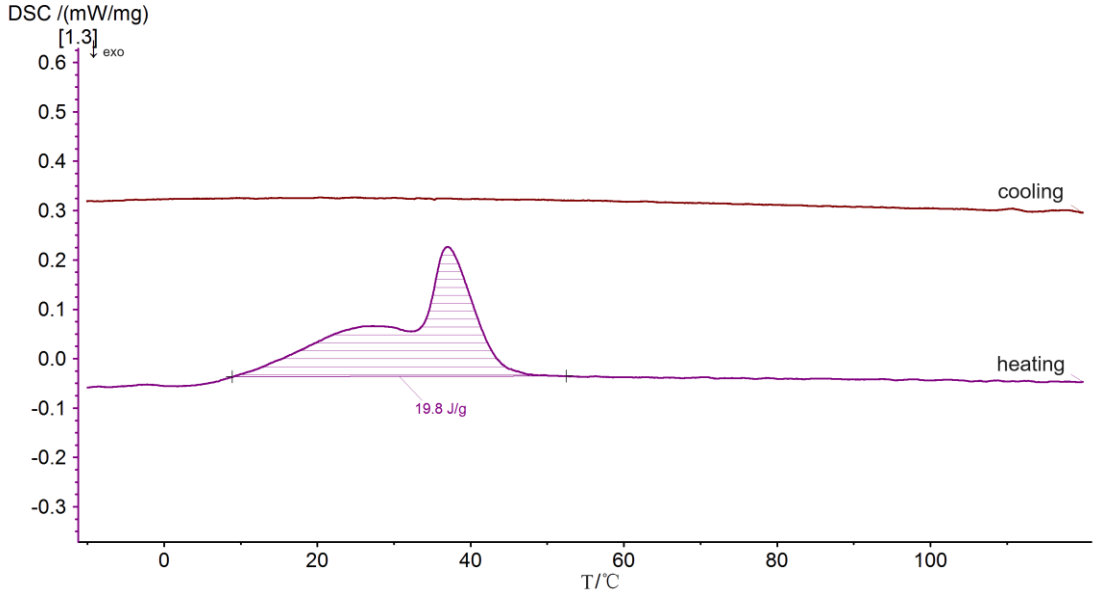


Figure S17. DSC scans of **P7**.

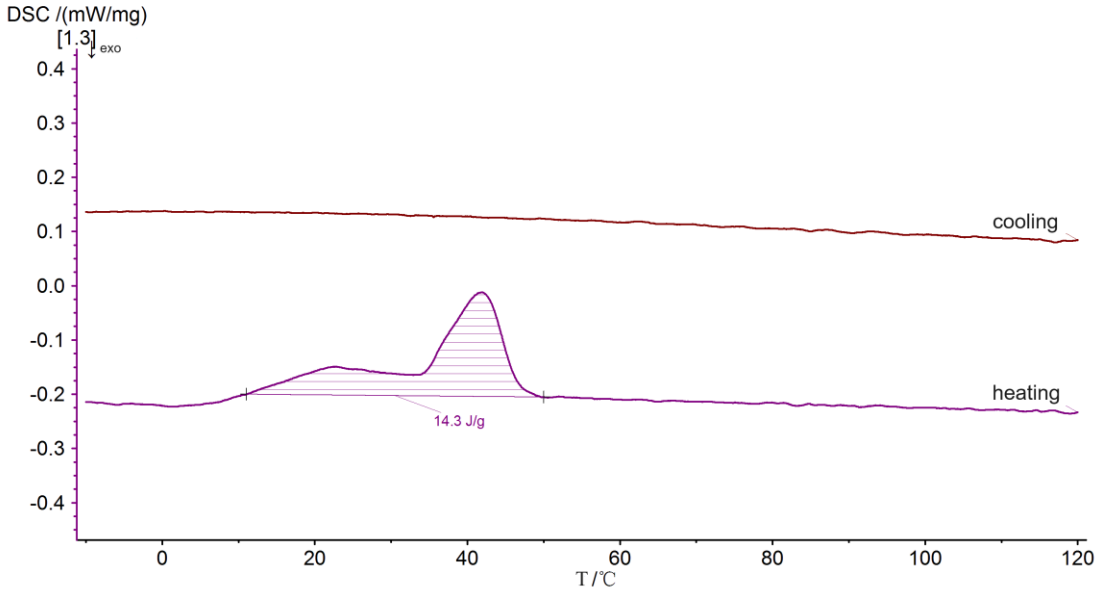


Figure S18. DSC scans of **P8**.

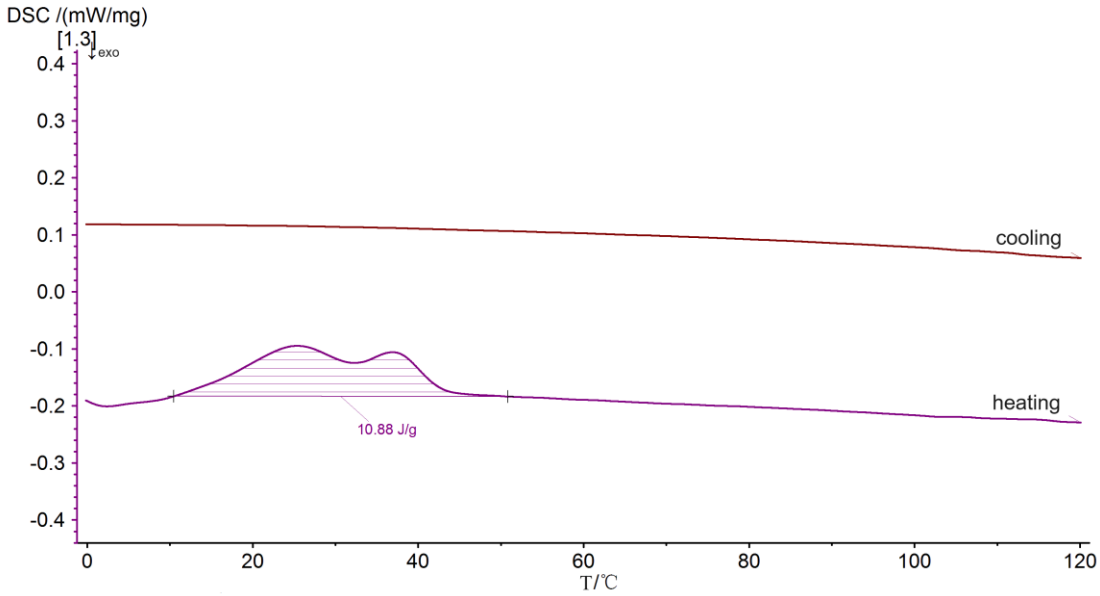


Figure S19 DSC scans of **P9**.

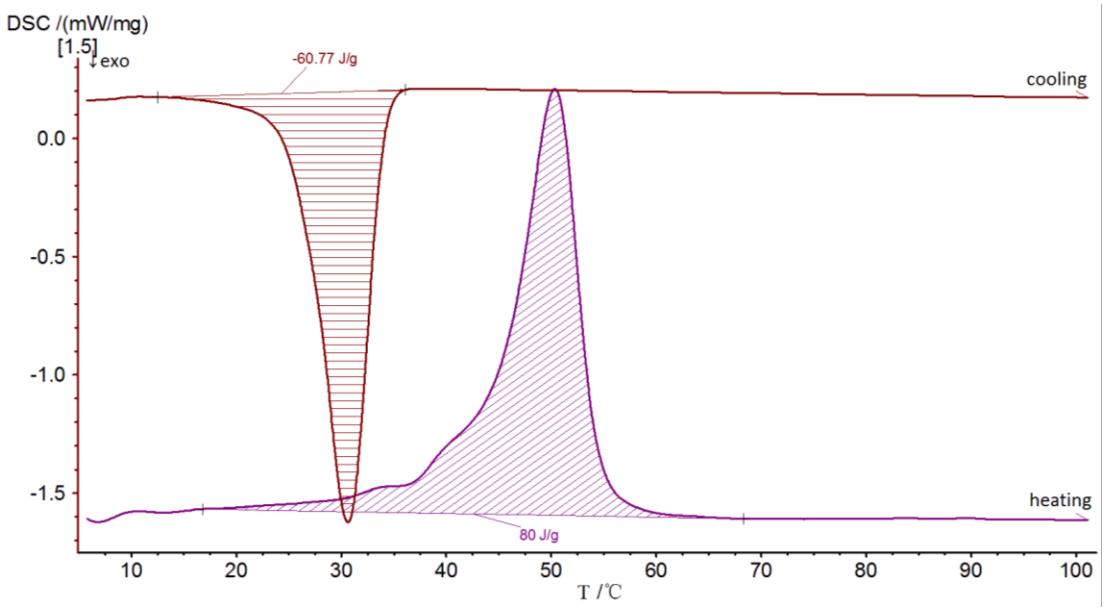


Figure S20. DSC scans of **P10**.

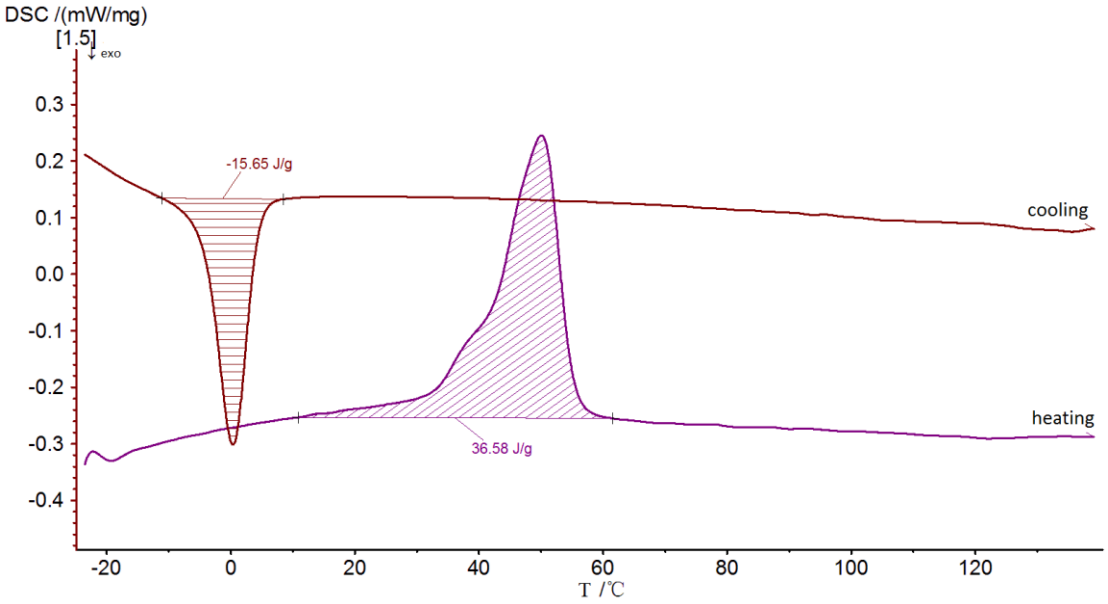


Figure S21. DSC scans of **P11**.

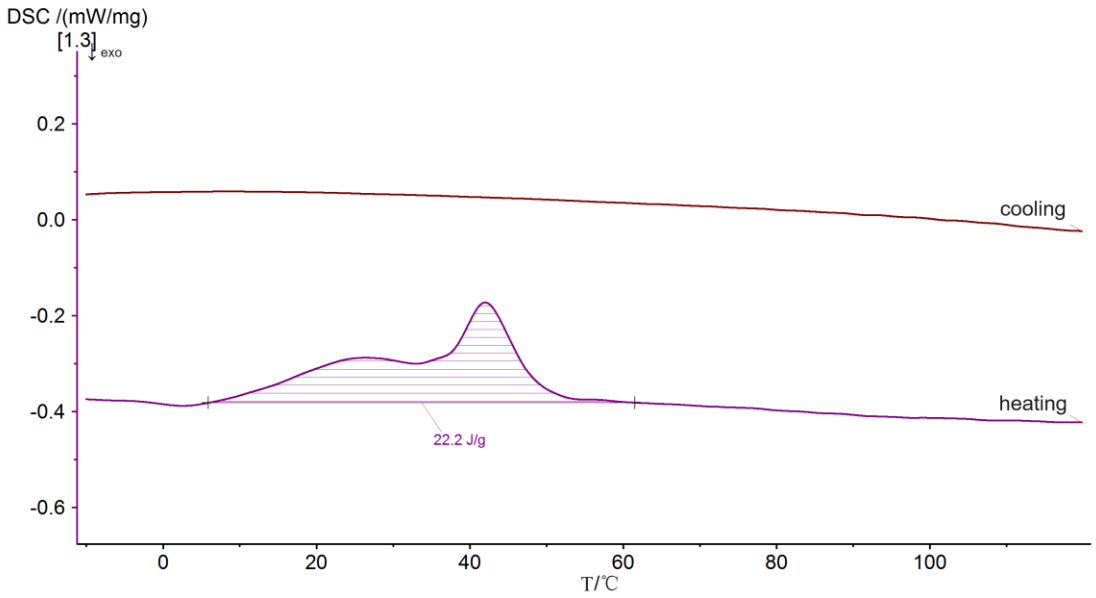


Figure S22. DSC scans of ***r*P4**.

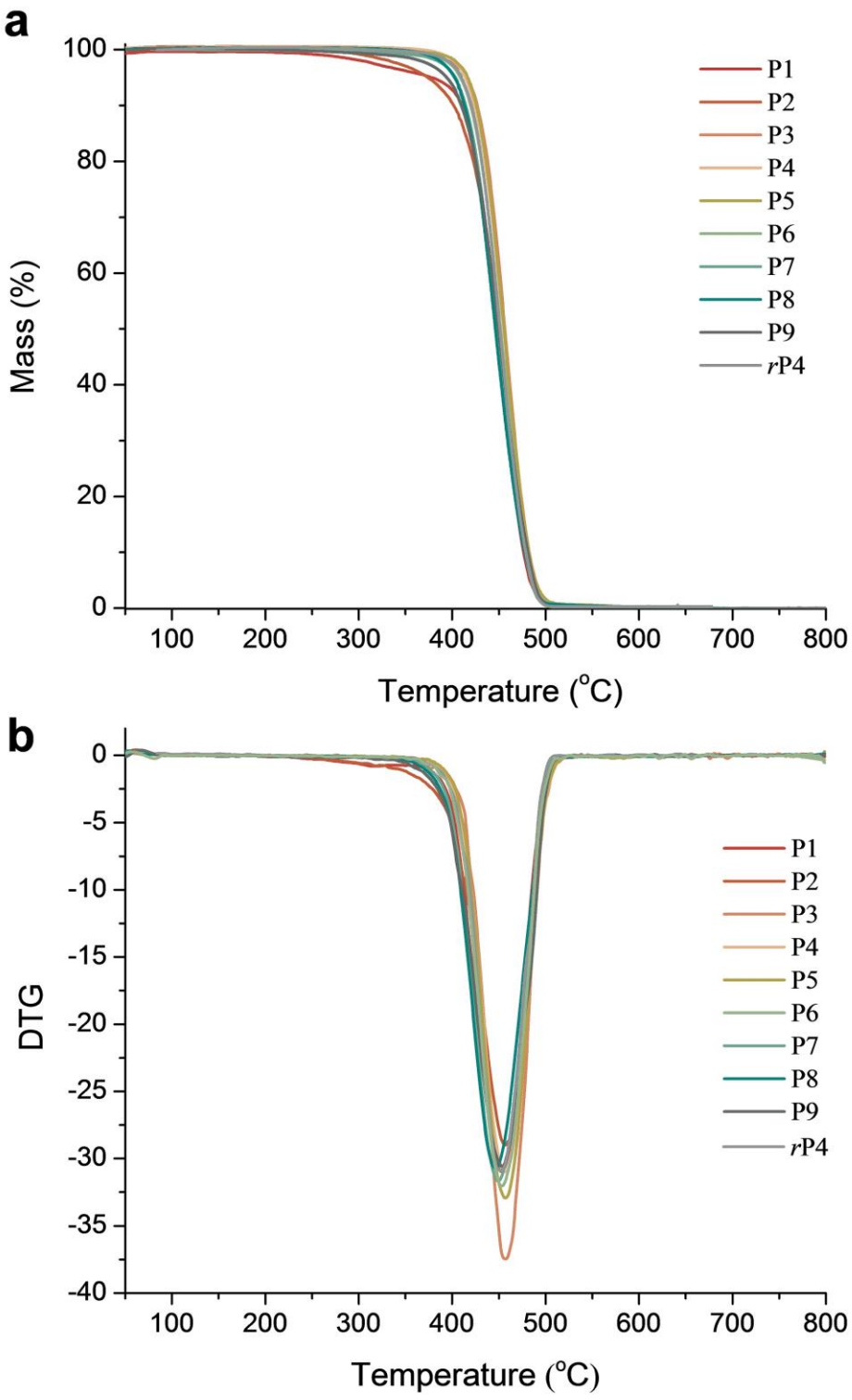


Figure S23. (a) TGA of polymers. (b) DTG of polymers.

7.6 Figures for the comparision of P11 and P6

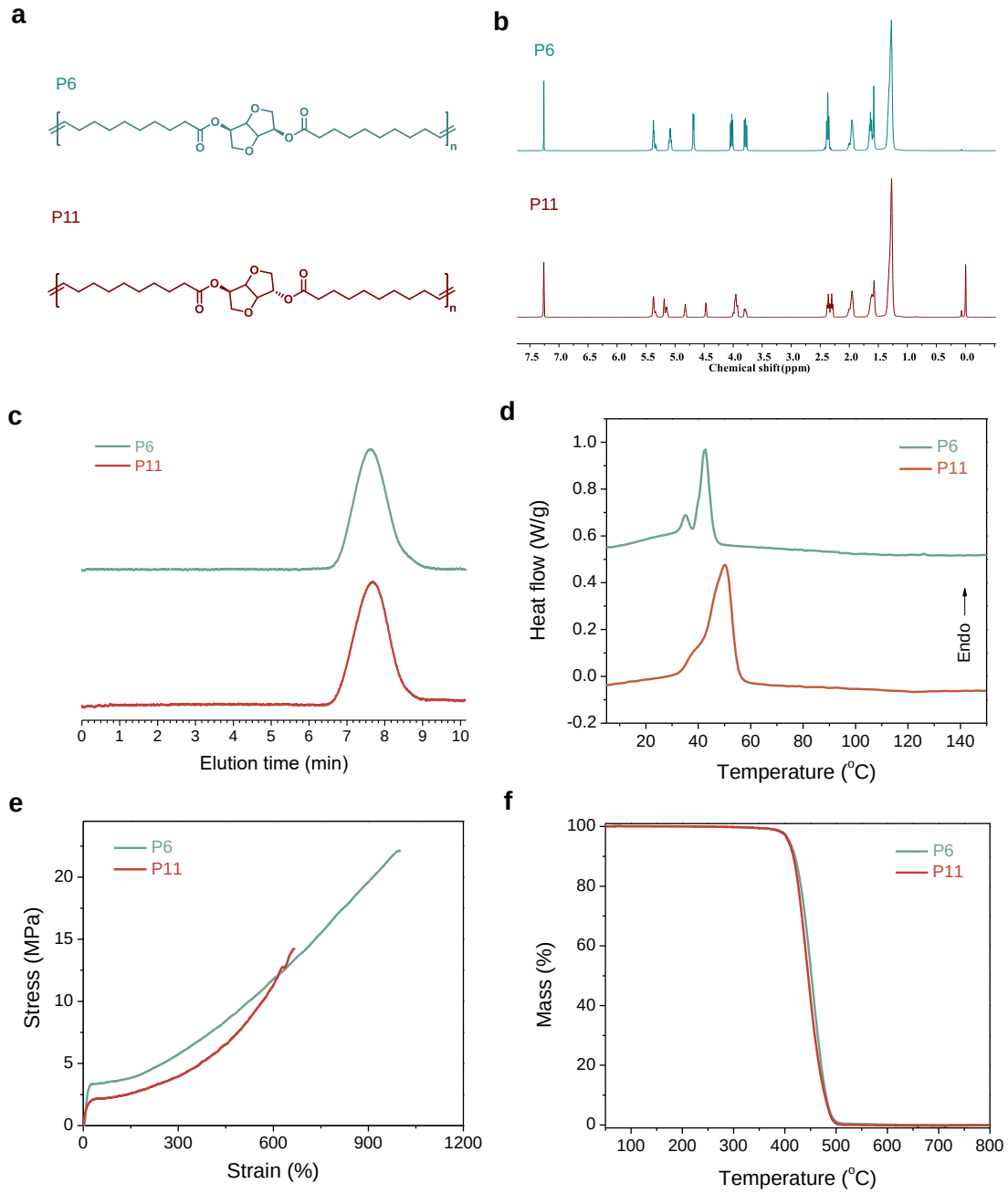


Figure S24. (a) Chemical structure of **P6** and **P11**. (b) ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **P6** and **P11**. (c) GPC elution curves of **P6** and **P11**. (d) DSC heating scan of **P6** and **P11**. (e) Mechanical properties of **P6** and **P11**. (f) TGA curves of **P6** and **P11.**

7.7 Figures for the mechanical properties of P4

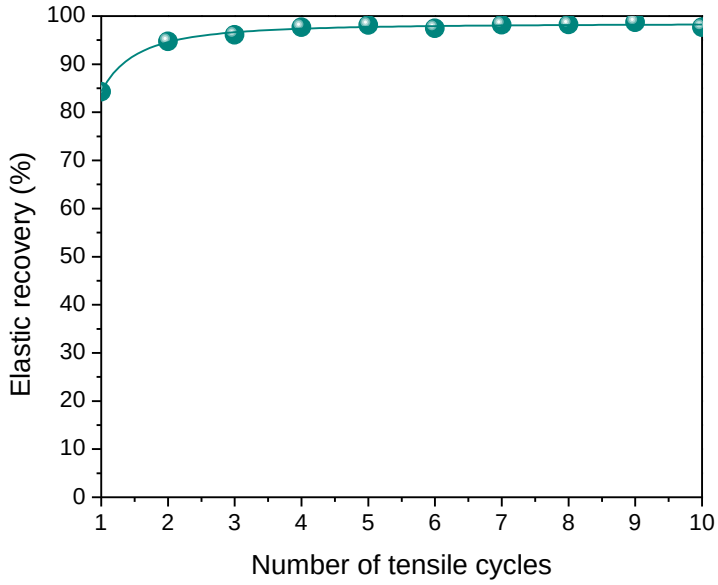


Figure S25. Changes of elastic recovery resilience as a function of the number of tensile cycles for **P4**.

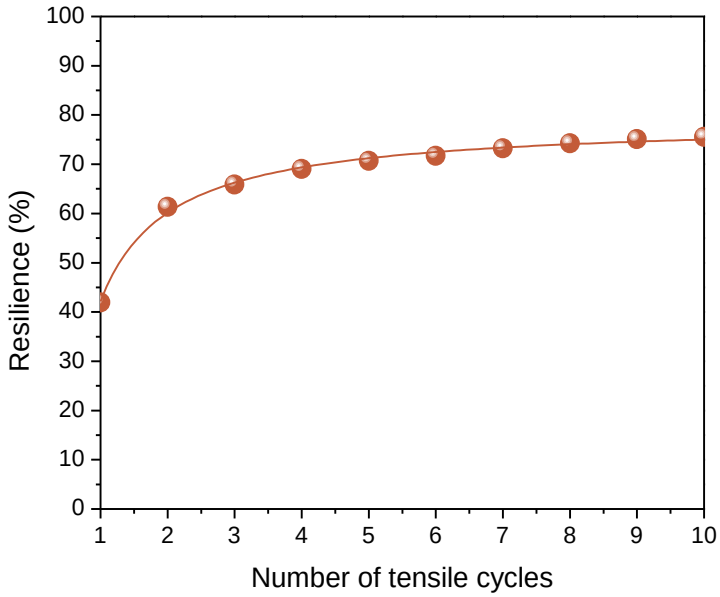


Figure S26. Changes of resilience as a function of the number of tensile cycles for **P4**.

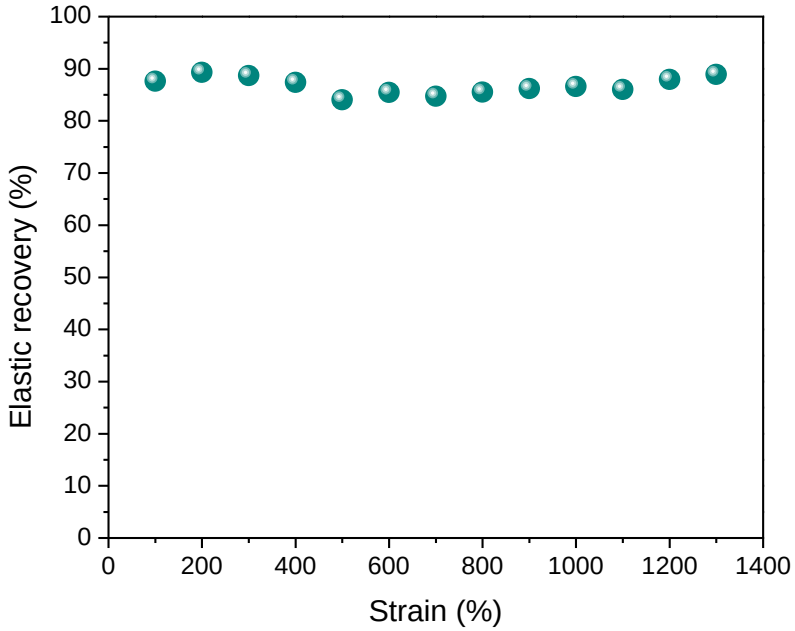


Figure S27. Changes of elastic recovery resilience as a function of the strain of step-cycle tensile tests for **P4**.

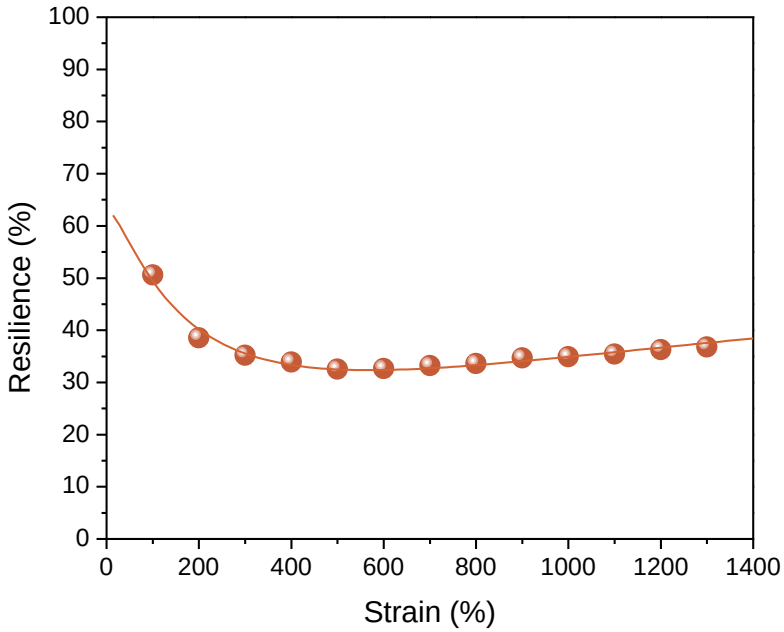


Figure S28. Changes of resilience as a function of the strain of step-cycle tensile tests for **P4**.

7.8 Figures for the strain-induced crystallization of P4

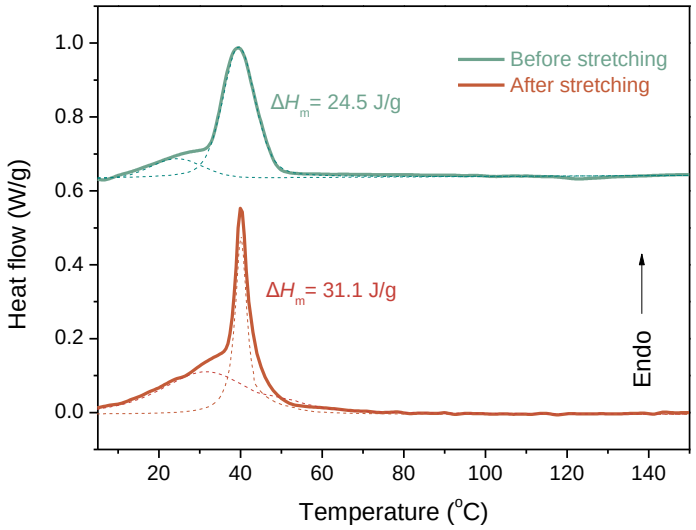


Figure S29. First DSC heating scan of **P4** before stretching and after stretching. After stretching, samples are taken near the failure point from tensile tested sample.

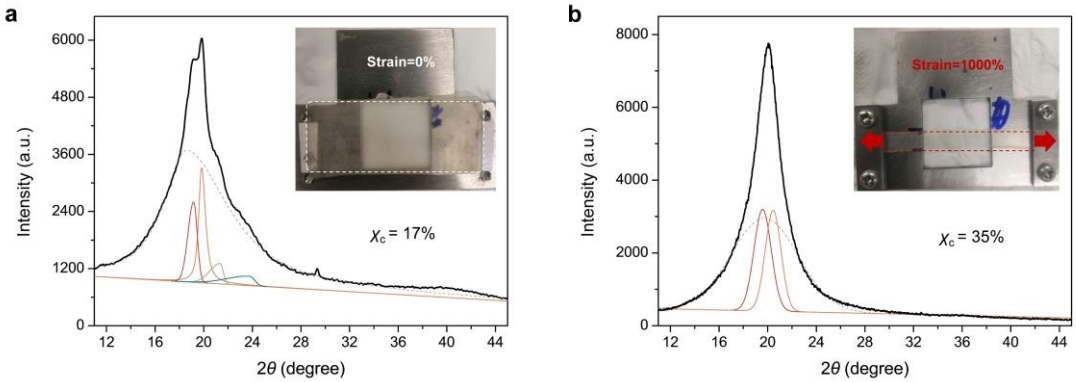


Figure S30. XRD spectra of **P4** (a) before stretching and (b) after stretching.

7.9 Figures for the characterization of recovered macrocyles

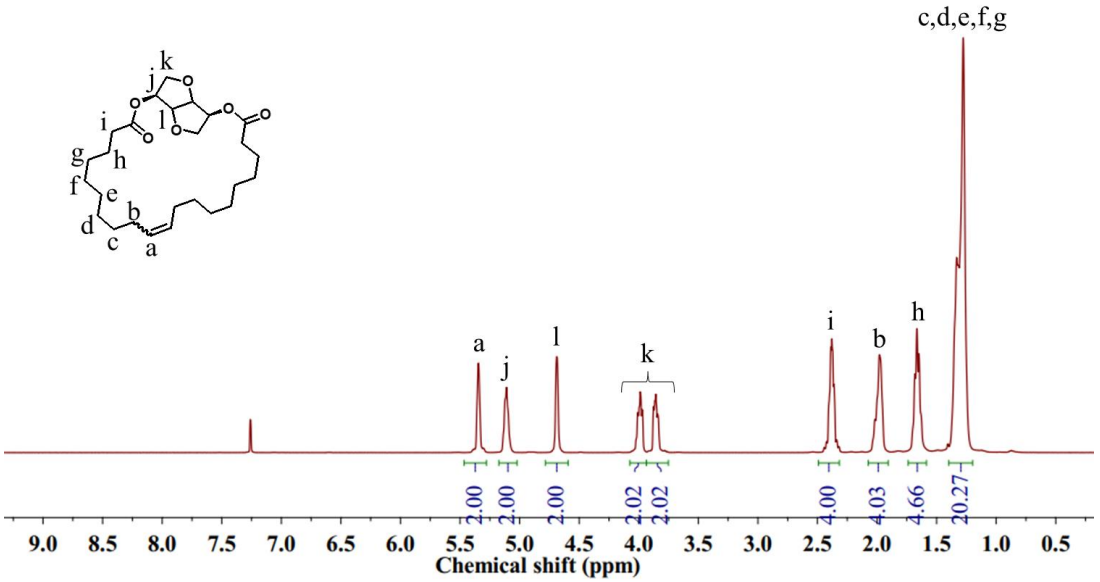


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of recovered monomer.

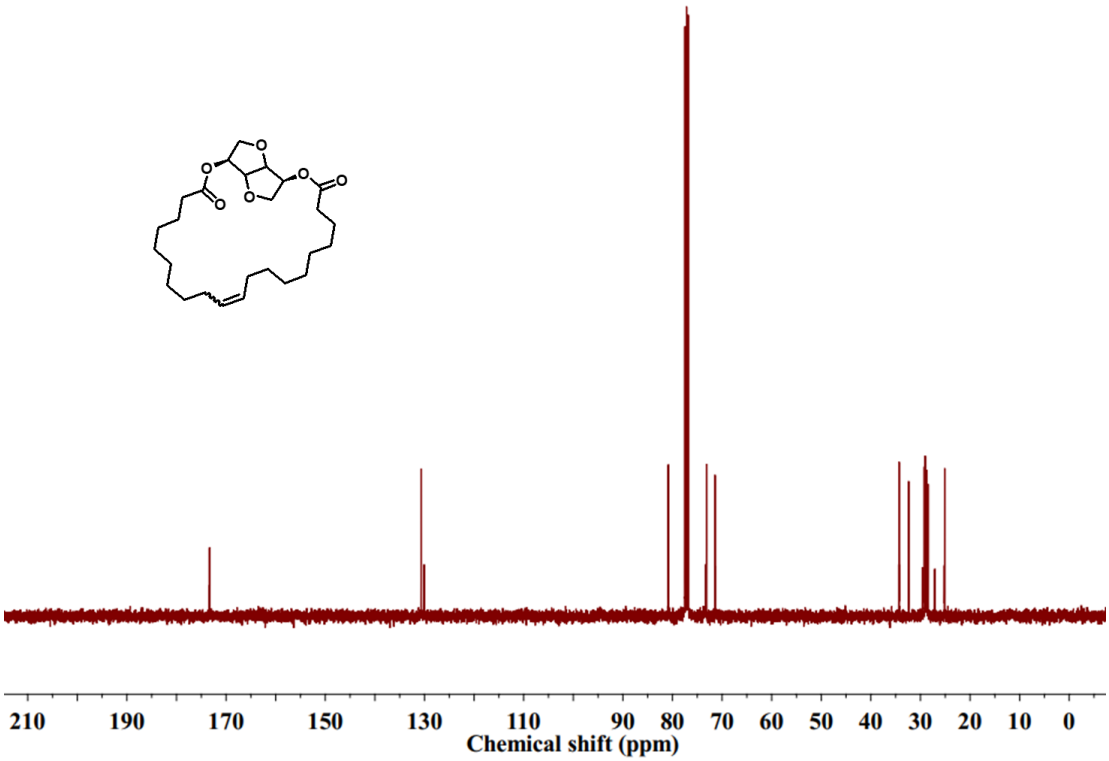


Figure S32. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of recovered monomer.

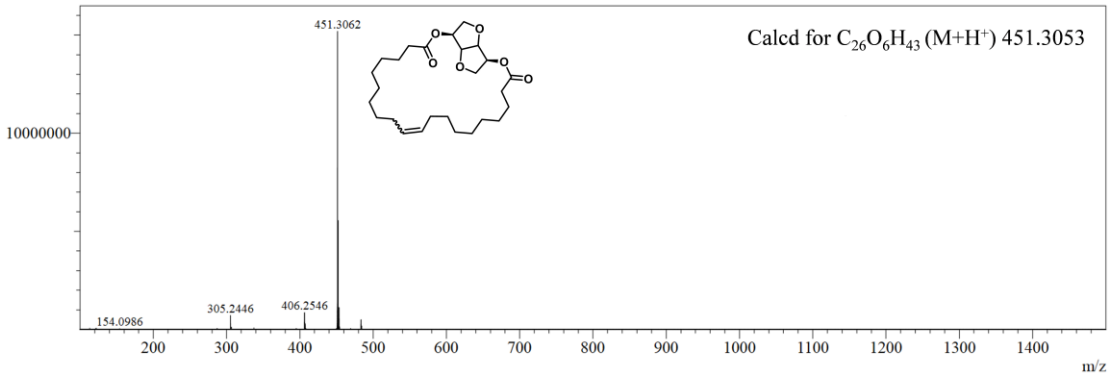


Figure S33. ESI-HRMS of recovered monomer.

7.10 Figures for depolymerization kinetics study

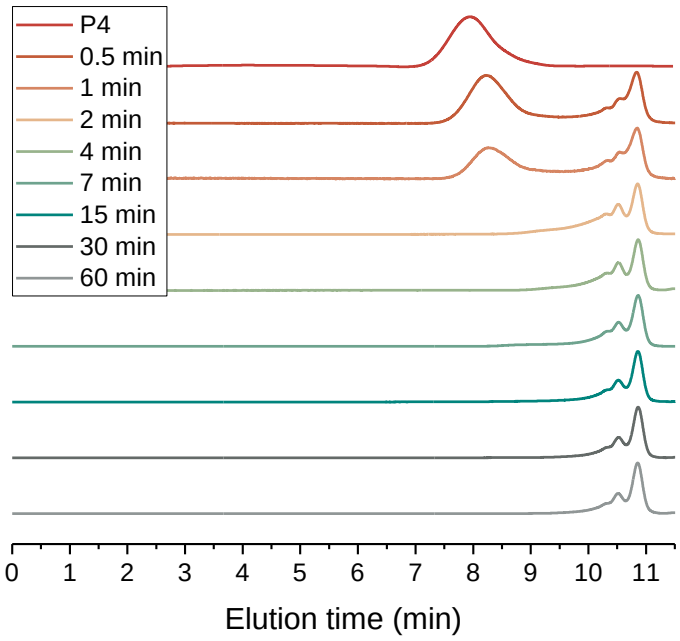


Figure S34. GPC elution curves for the depolymerization of **P4** with evolved time.

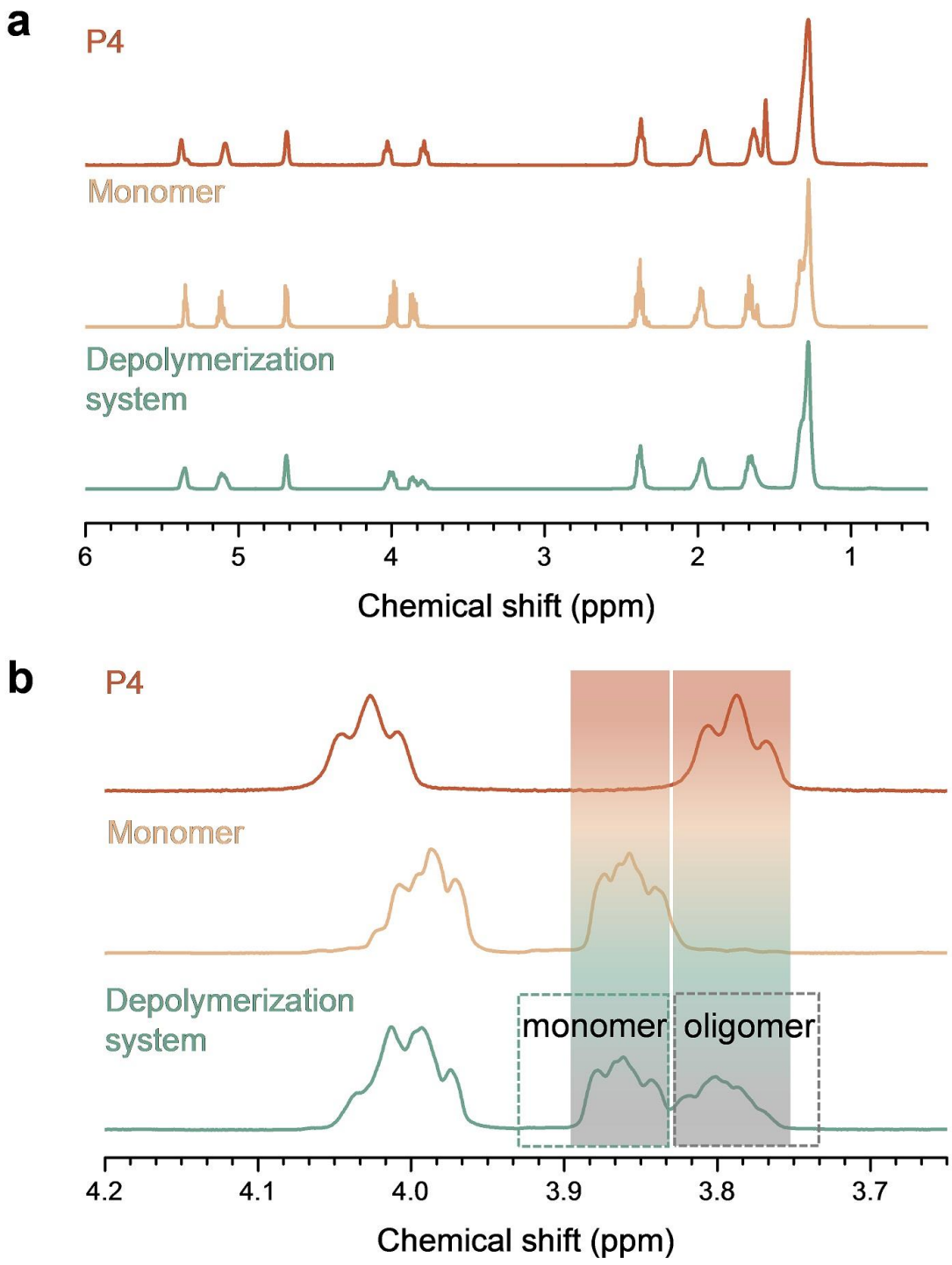


Figure S35. (a) ^{1}H NMR spectra of monomer, **P4**, and depolymerized system of **P4**. (b) Enlarged area of Figure S35a.

7.11 Figures for repolymerization of the recycled macrocyclic oligomers

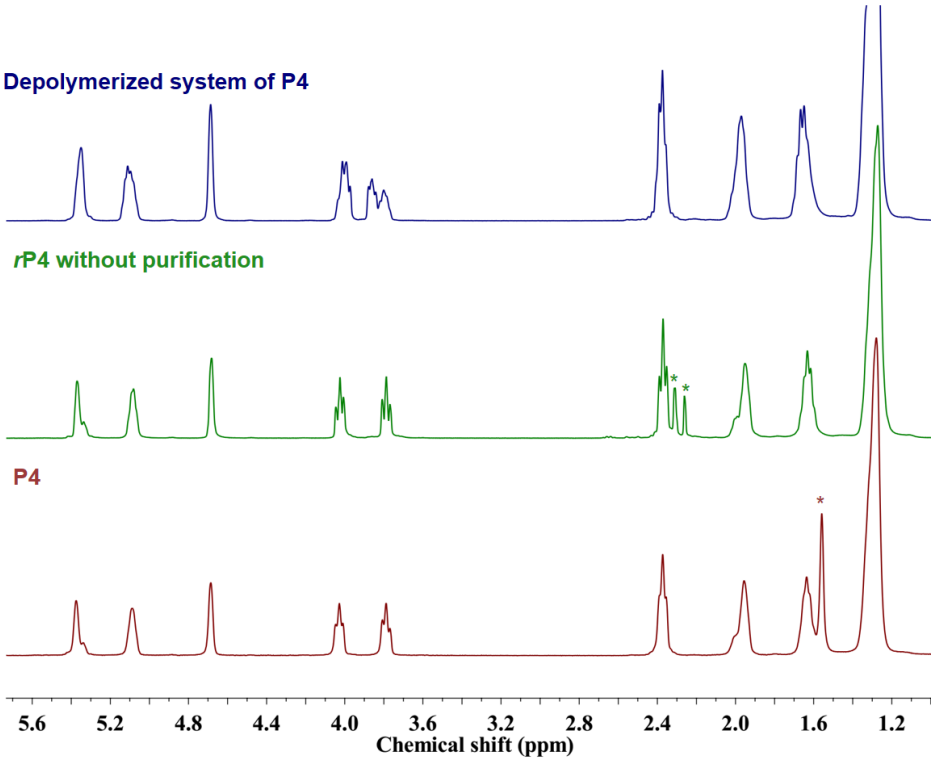


Figure S36. ^{1}H NMR spectra (400 M, $CDCl_3$) for the comparison of depolymerized system of **P4**, ***r*P4** without purification and pristine **P4**.

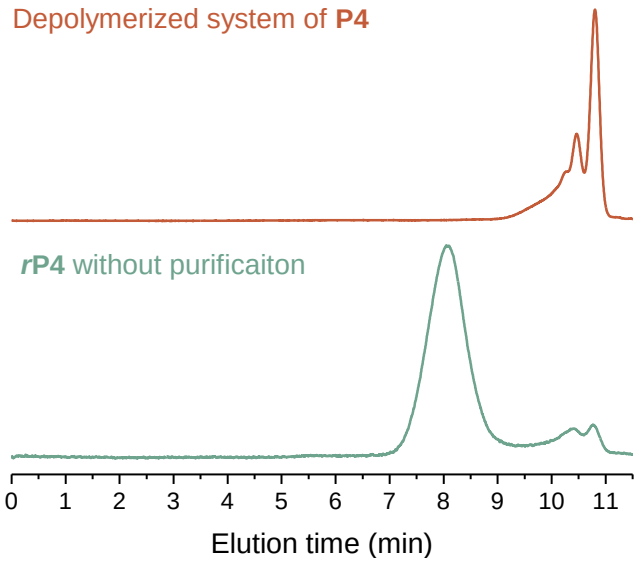


Figure S37. GPC elution curve for the depolymerized system of **P4** and ***r*P4** without purification.

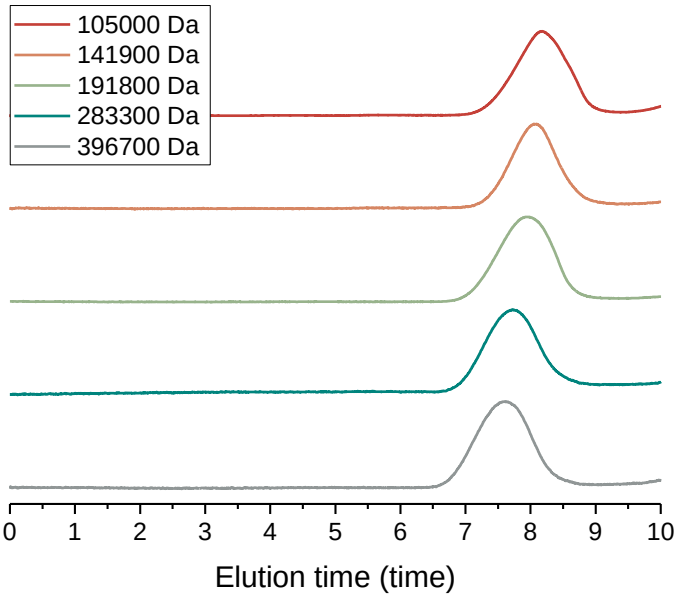


Figure S38. GPC elution curve for the repolymerization of recycled macrocyclic oligomers.

7.12 Figures for monomer recycling

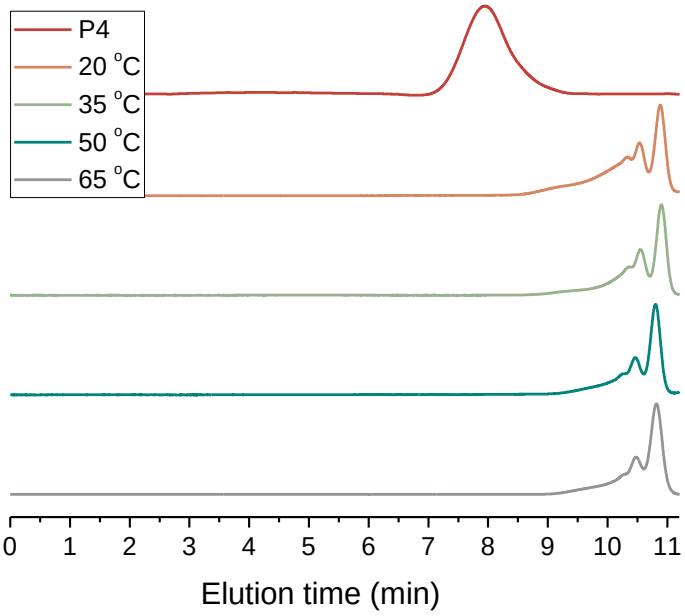


Figure S39. GPC elution curves for the depolymerization of **P4** at different temperatures.

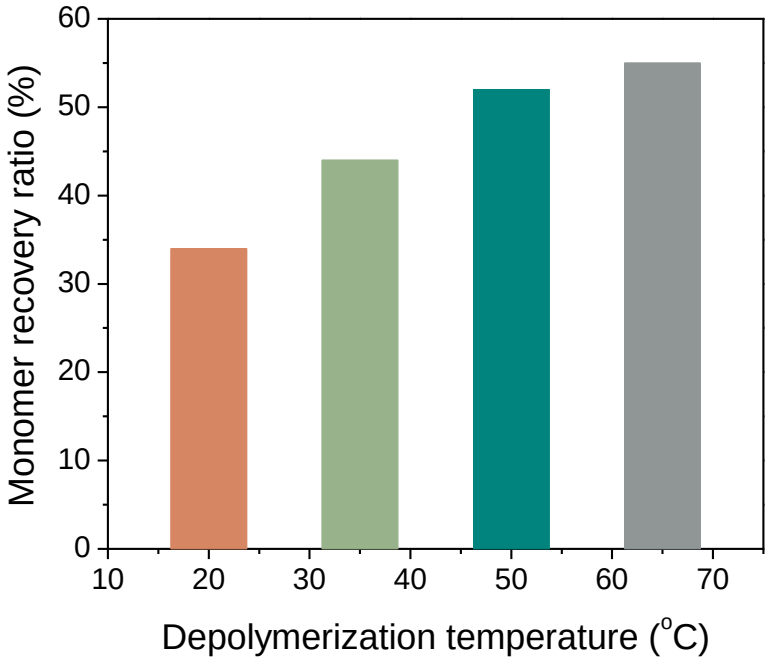


Figure S40. Monomer recovery ratio for the depolymerization of **P4** at different temperatures.

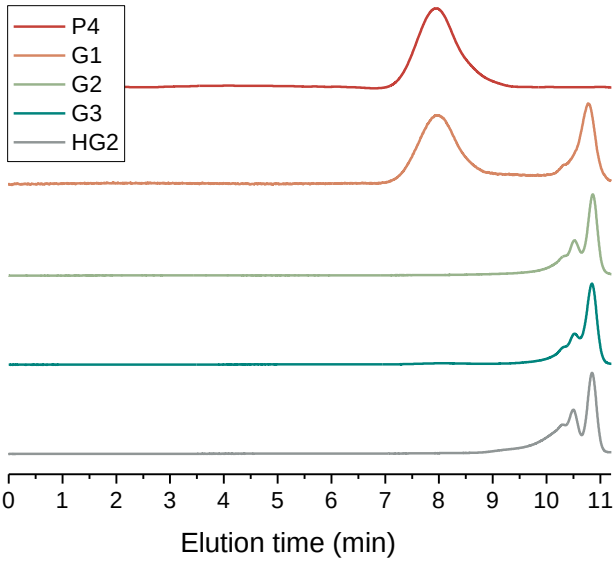


Figure S41. GPC elution curves for the depolymerization of **P4** using different catalysts.

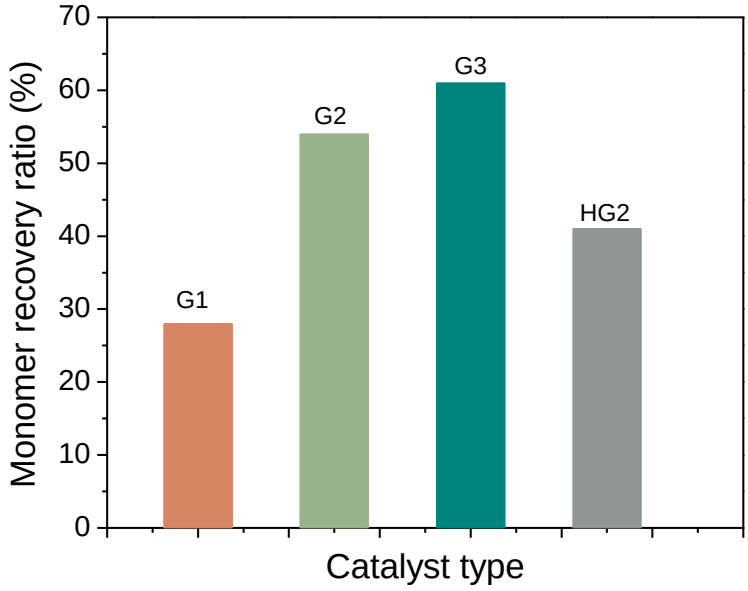


Figure S42. Monomer recovery ratio of for the depolymerization of **P4** using different catalysts.

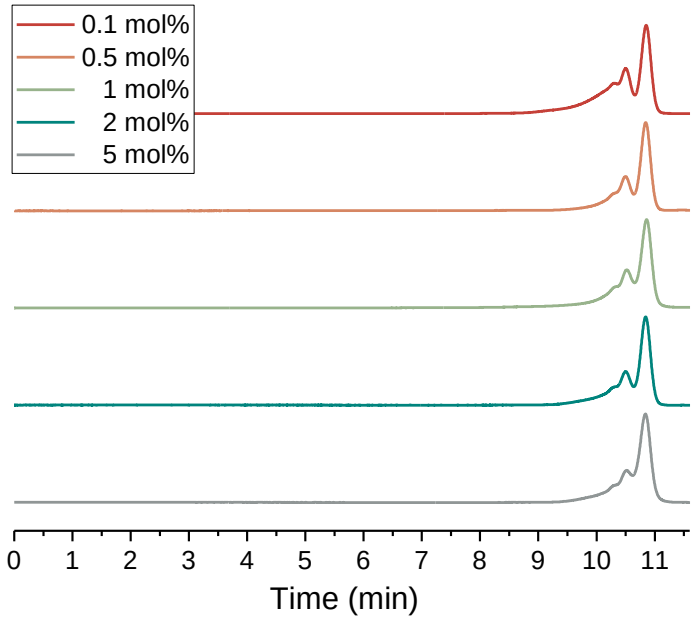


Figure S43. GPC elution curves for the depolymerization of **P4** using G2 with different loading ratio.

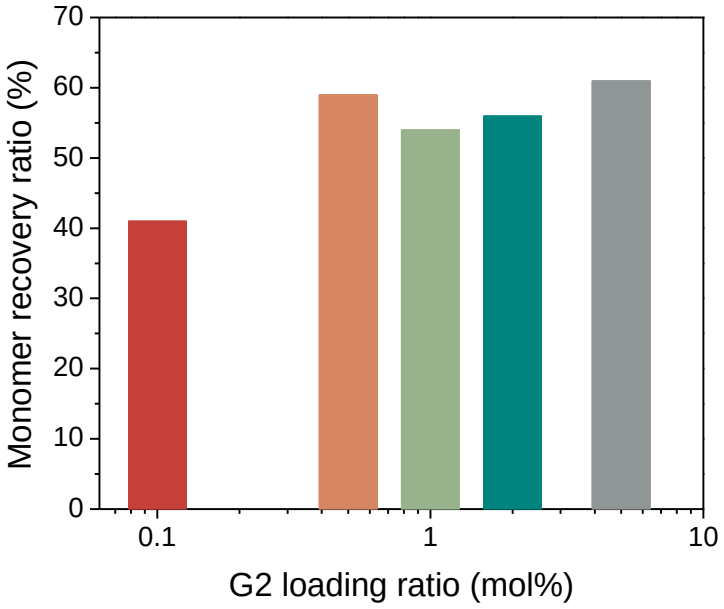


Figure S44. Monomer recovery ratio for the depolymerization of **P4** using G2 with different loading ratio.

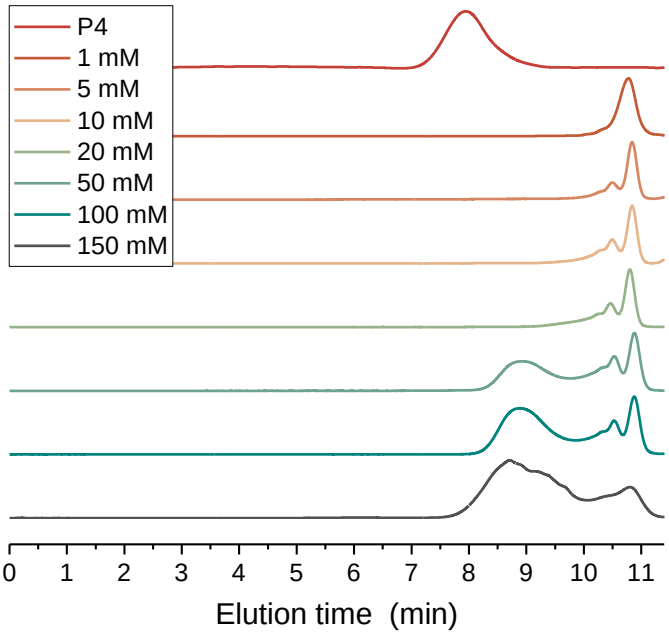


Figure S45. GPC elution curves for the depolymerization of **P4** at different olefin concentrations.

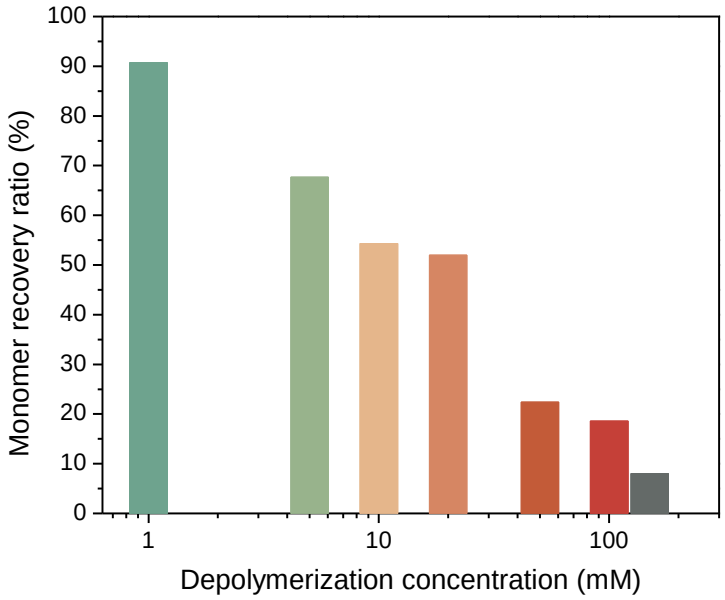


Figure S46. Monomer recovery ratio for the depolymerization of **P4** at different olefin concentrations.

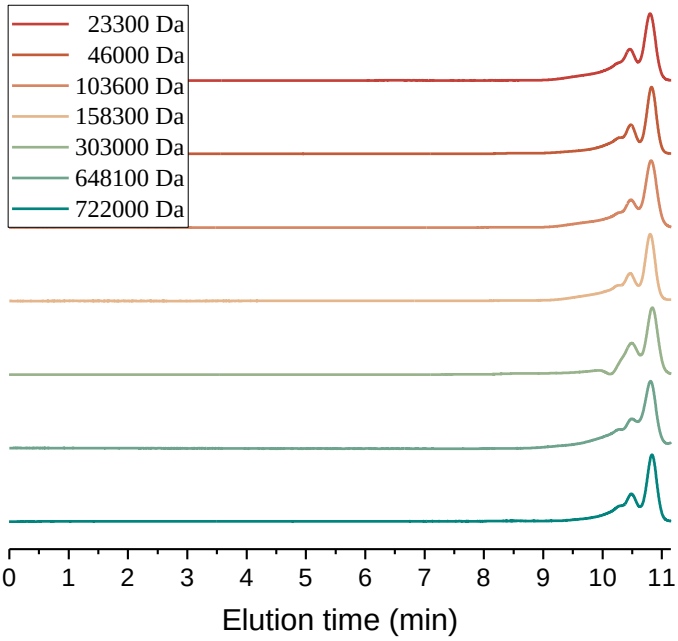


Figure S47. GPC elution curves for the depolymerization of polymer with different molecular weights.

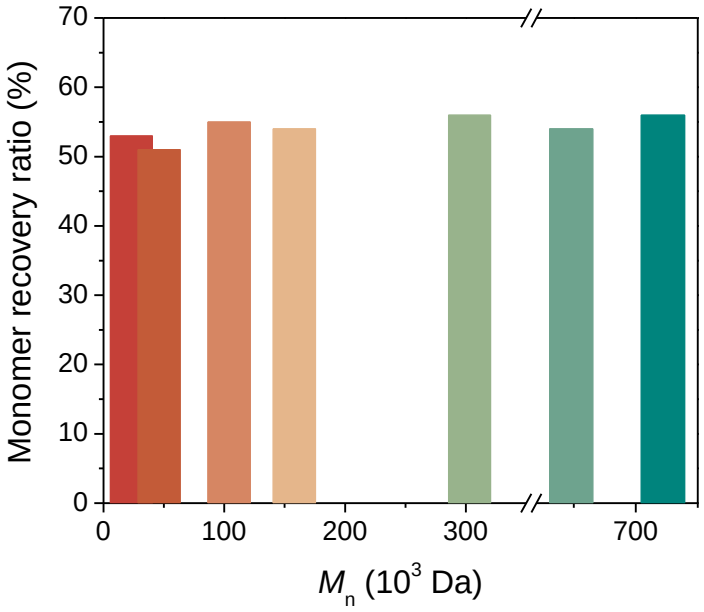


Figure S48. Monomer recovery ratio for the depolymerization of polymer with different molecular weights.

7.13 Figures for scaled up depolymerization

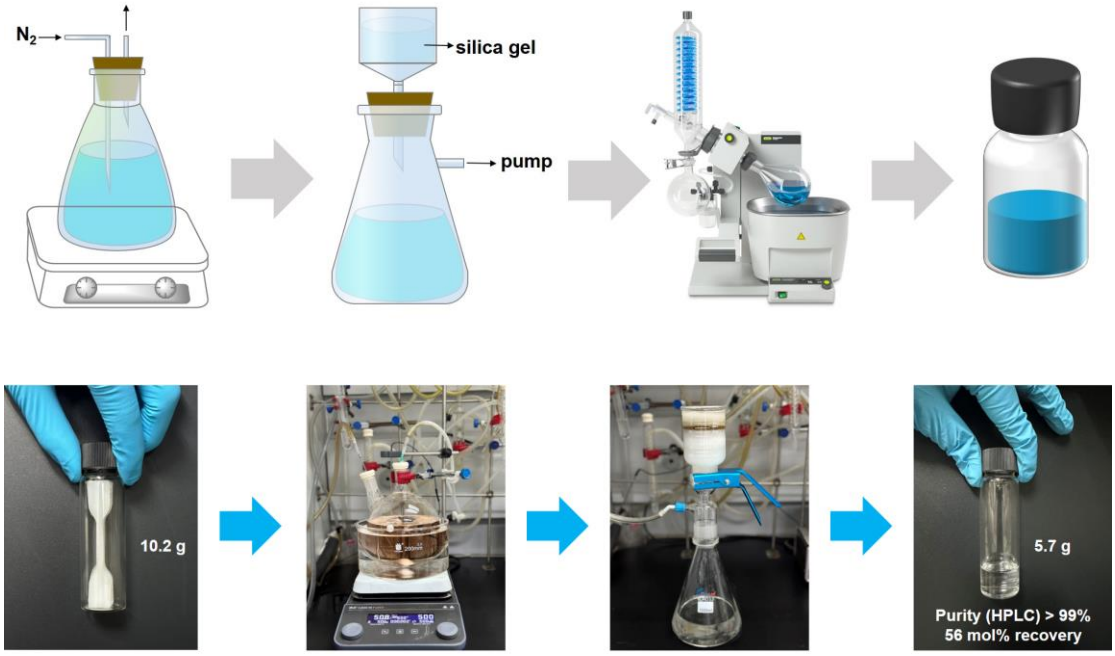


Figure S49. Monomer recycling protocol by ring-closing metathesis depolymerization.

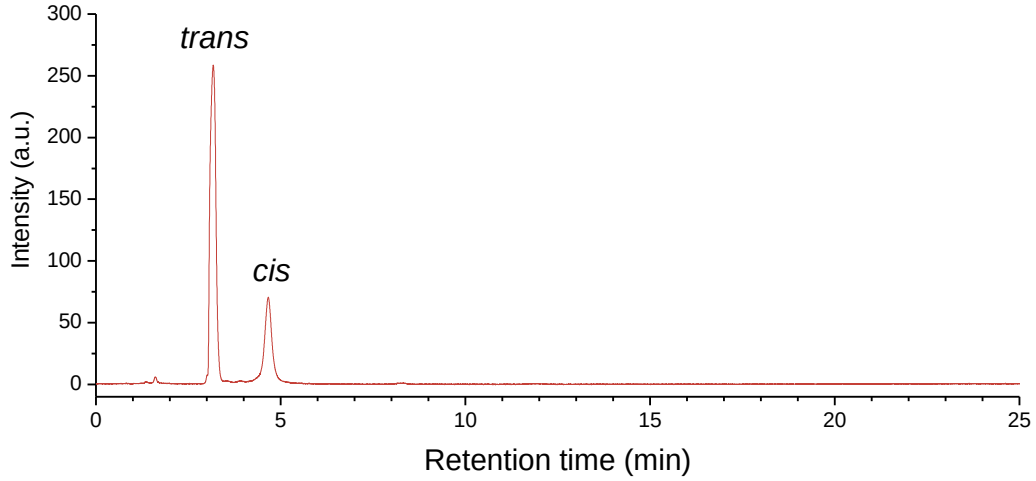


Figure S50. HPLC elution curves of recovered monomer **2**.

7.14 Figures for alkaline degradation

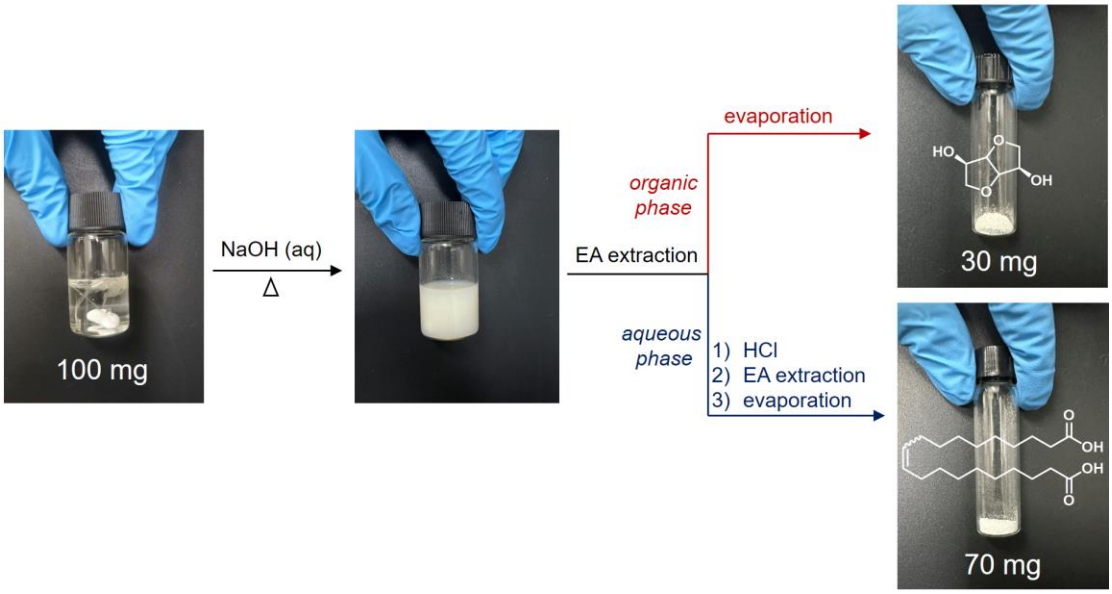


Figure S51. Alkaline degradation protocol of polymers.

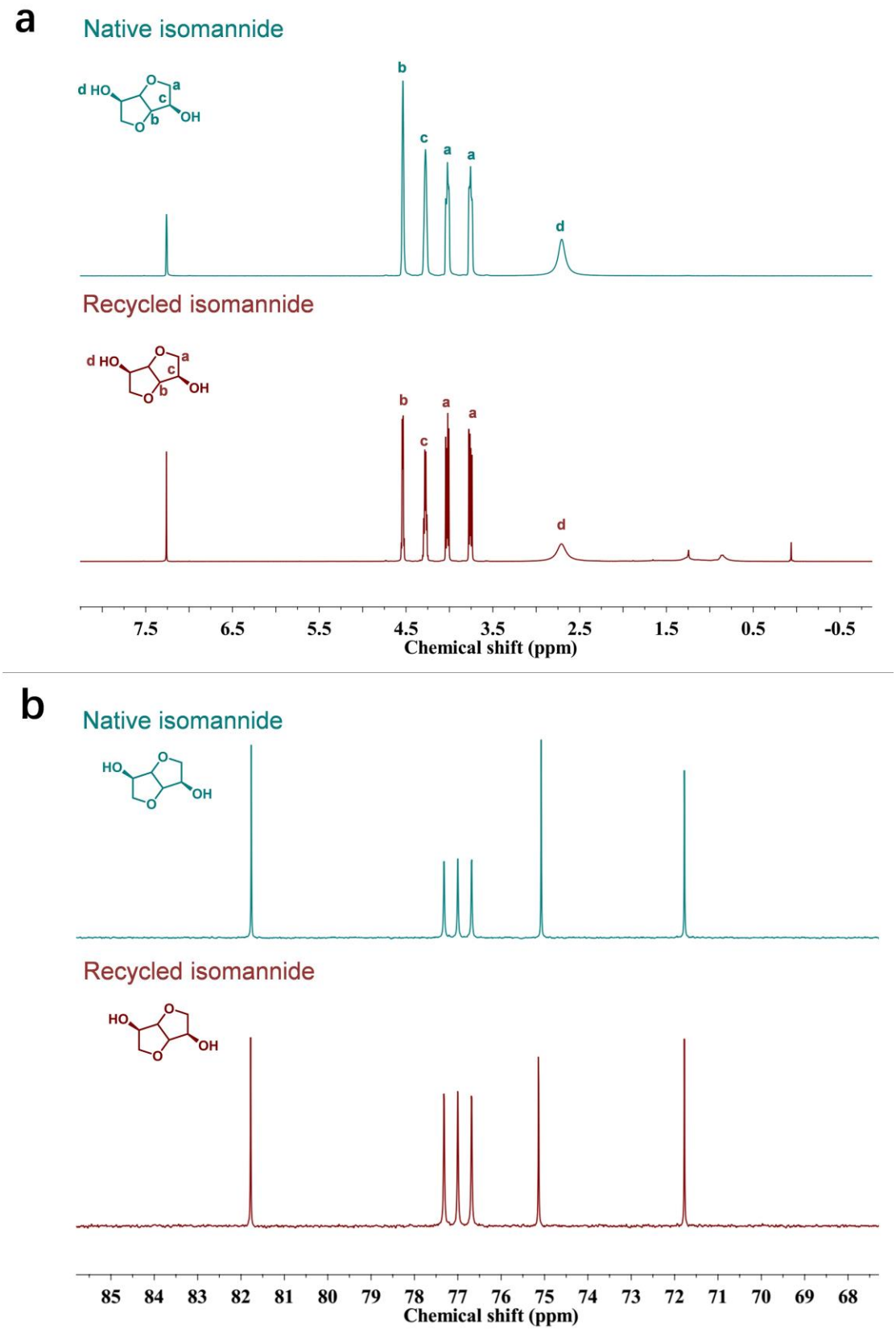


Figure S52. (a) ^{1}H NMR spectra (400 M, $CDCl_3$) of isomannide recovered from alkaline degradation. (b) ^{13}C NMR spectra (101 M, $CDCl_3$) of isomannide recovered from alkaline degradation.

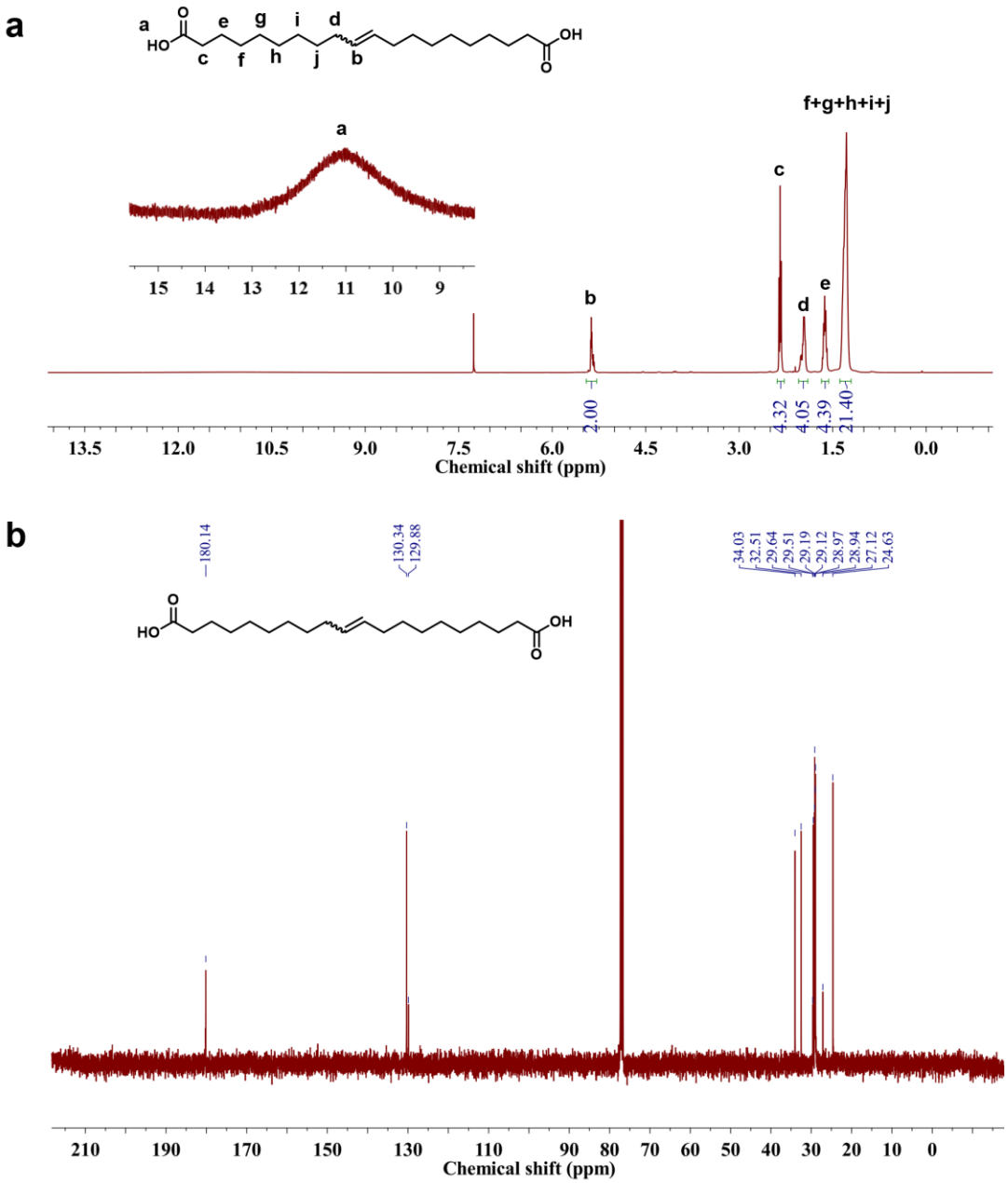


Figure S53. (a) ^{1}H NMR spectrum (400 M, $CDCl_3$) of unsaturated α,ω-dicarboxylic acids recovered from alkaline degradation. (b) ^{13}C NMR spectrum (101 M, $CDCl_3$) of unsaturated α,ω-dicarboxylic acids recovered from alkaline degradation.

7.15 Figures for the polycondensation of hydrolyzed products

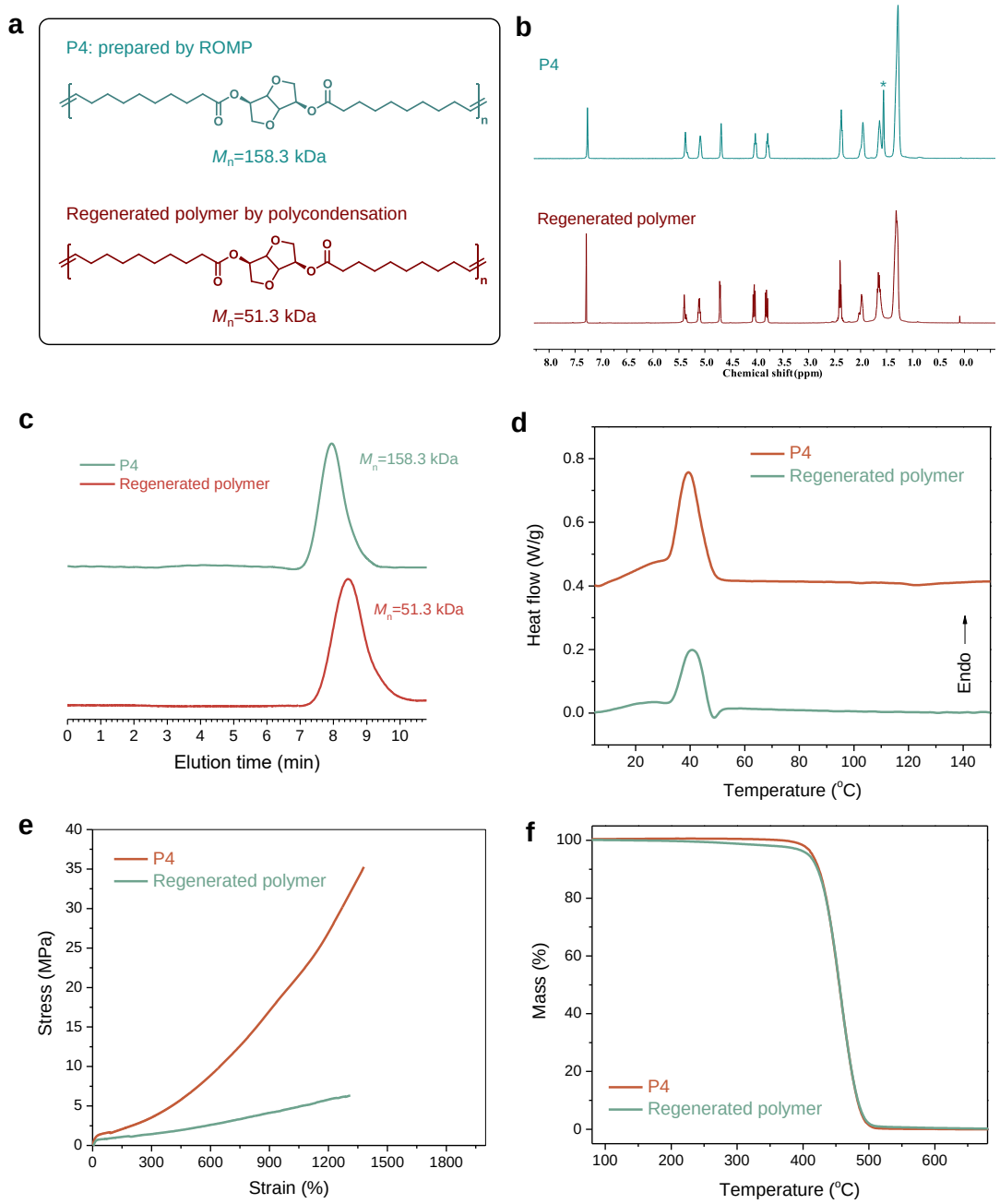


Figure S54. (a) Chemical structure of **P4** and regenerated polymer by polycondensation. (b) ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **P4** and regenerated polymer. (c) GPC elution curves of **P4** and regenerated polymer. (d) DSC heating scan of **P4** and regenerated polymer. (e) Mechanical properties of **P4** and regenerated polymer. (f) TGA curves of **P4** and regenerated polymer**.**

7.16 NMR spectra of small organic molecules

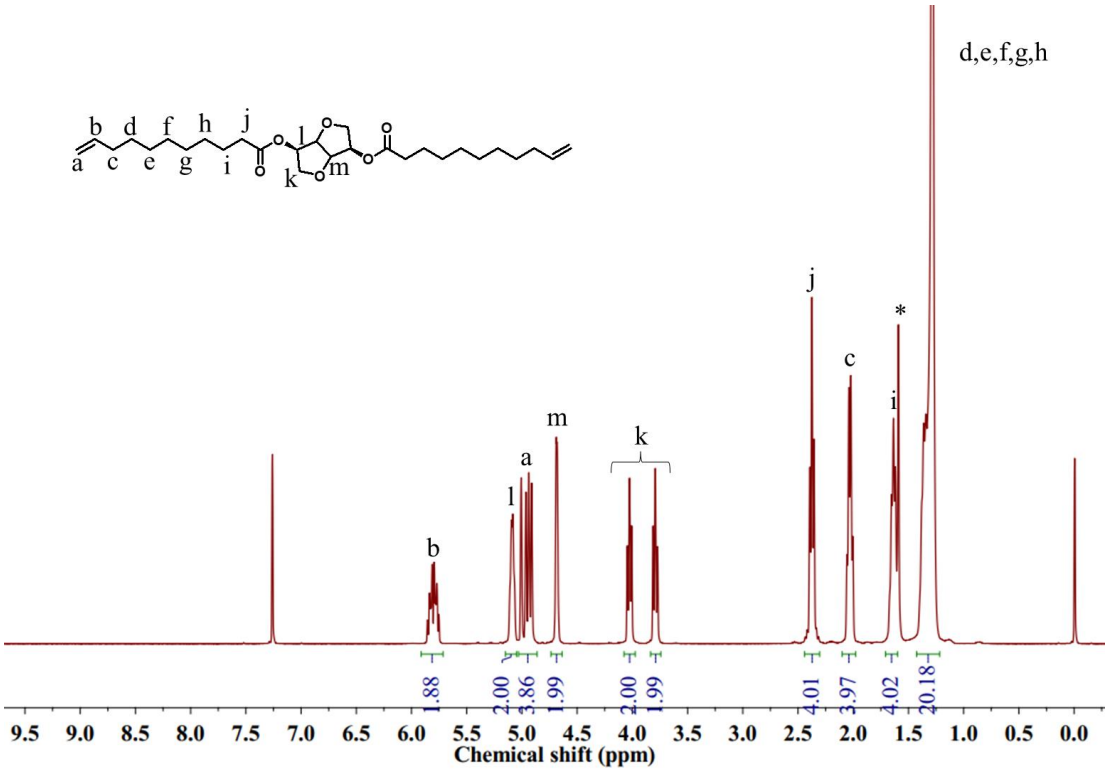


Figure S55. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **1**.

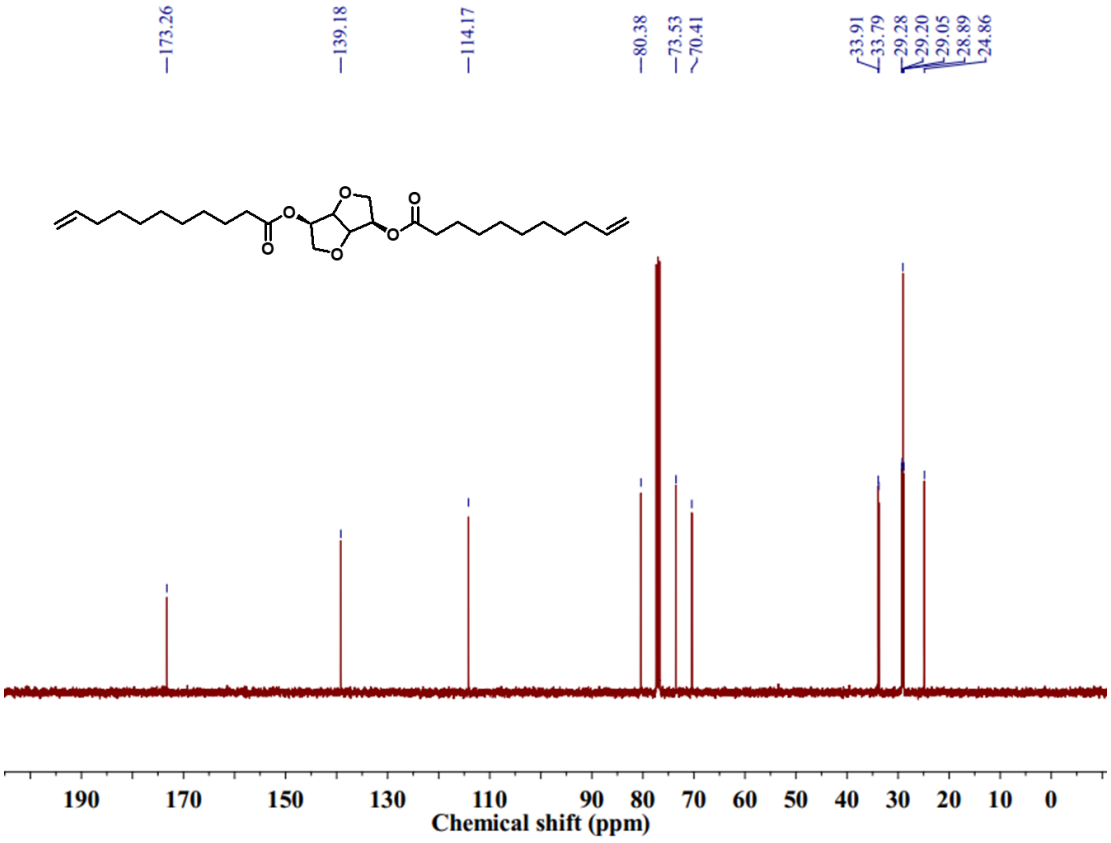


Figure S56. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **1**.

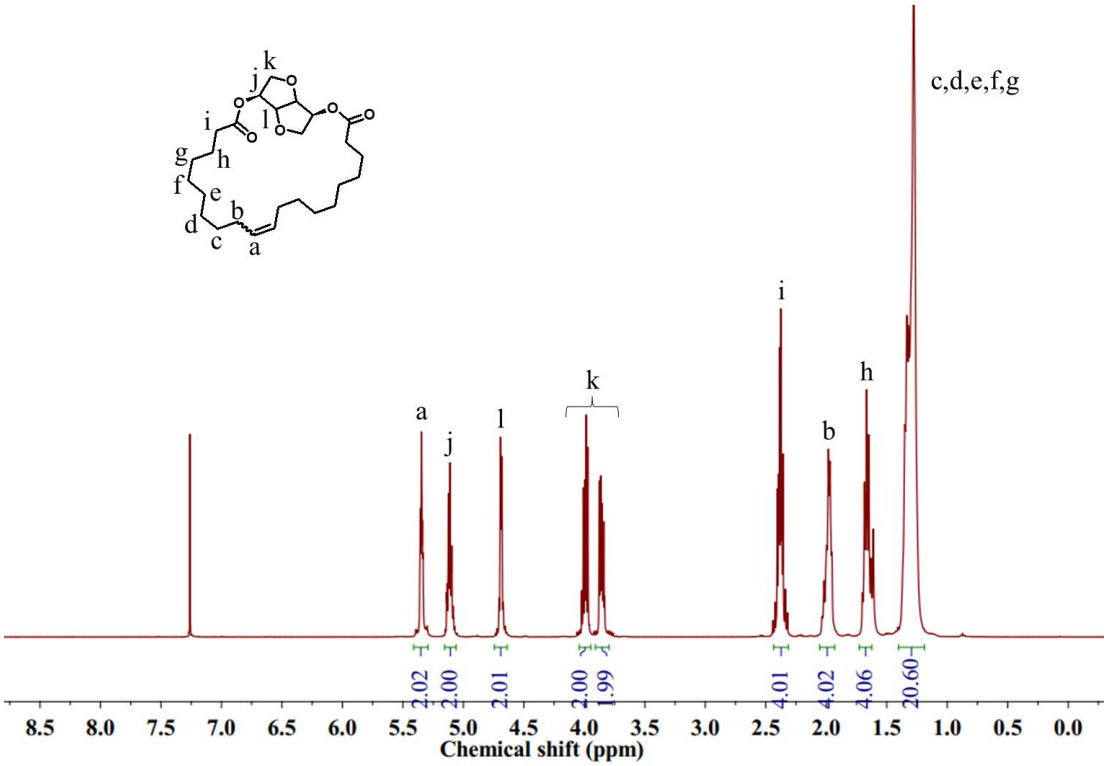


Figure S57. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **2**.

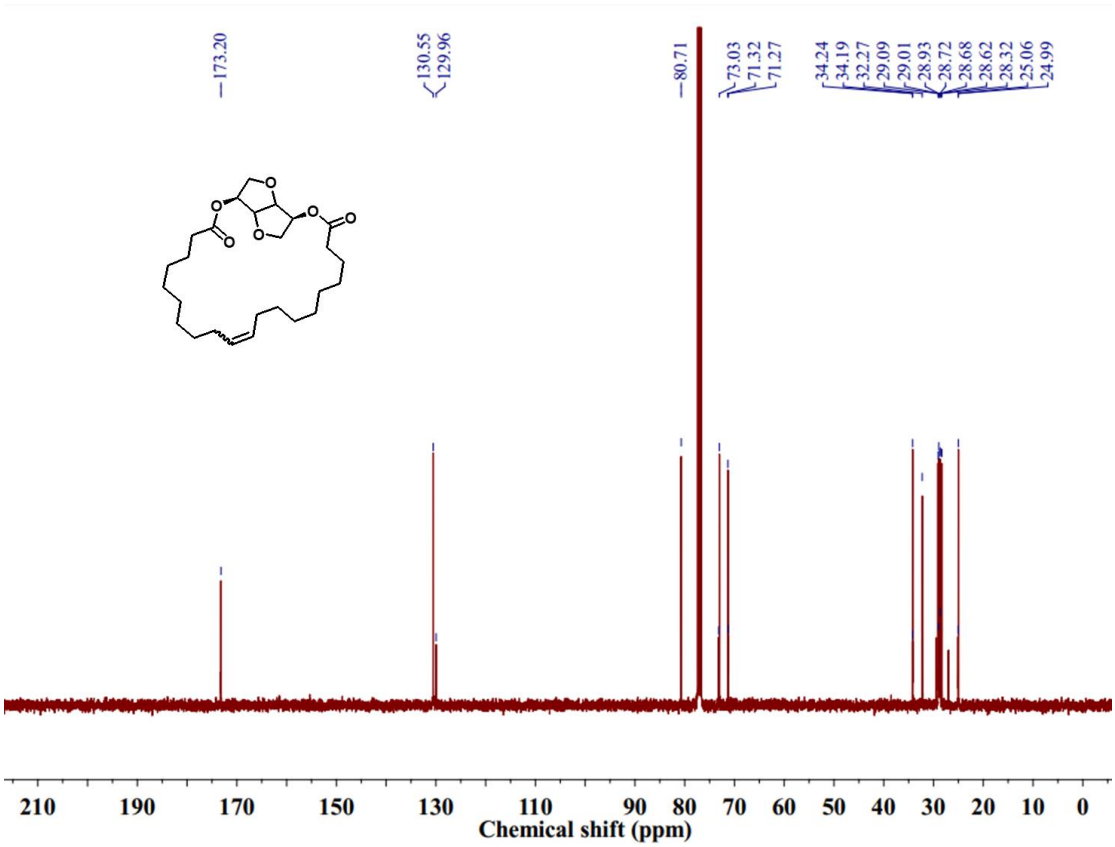


Figure S58. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **2**.

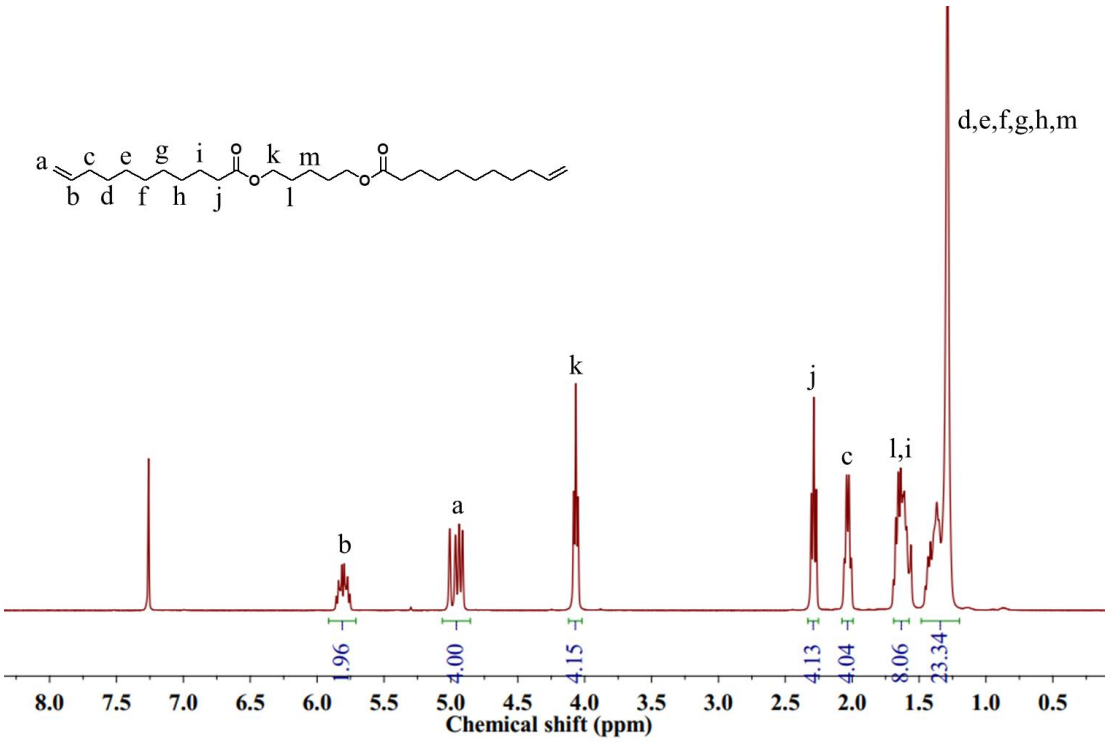


Figure S59. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **3**.

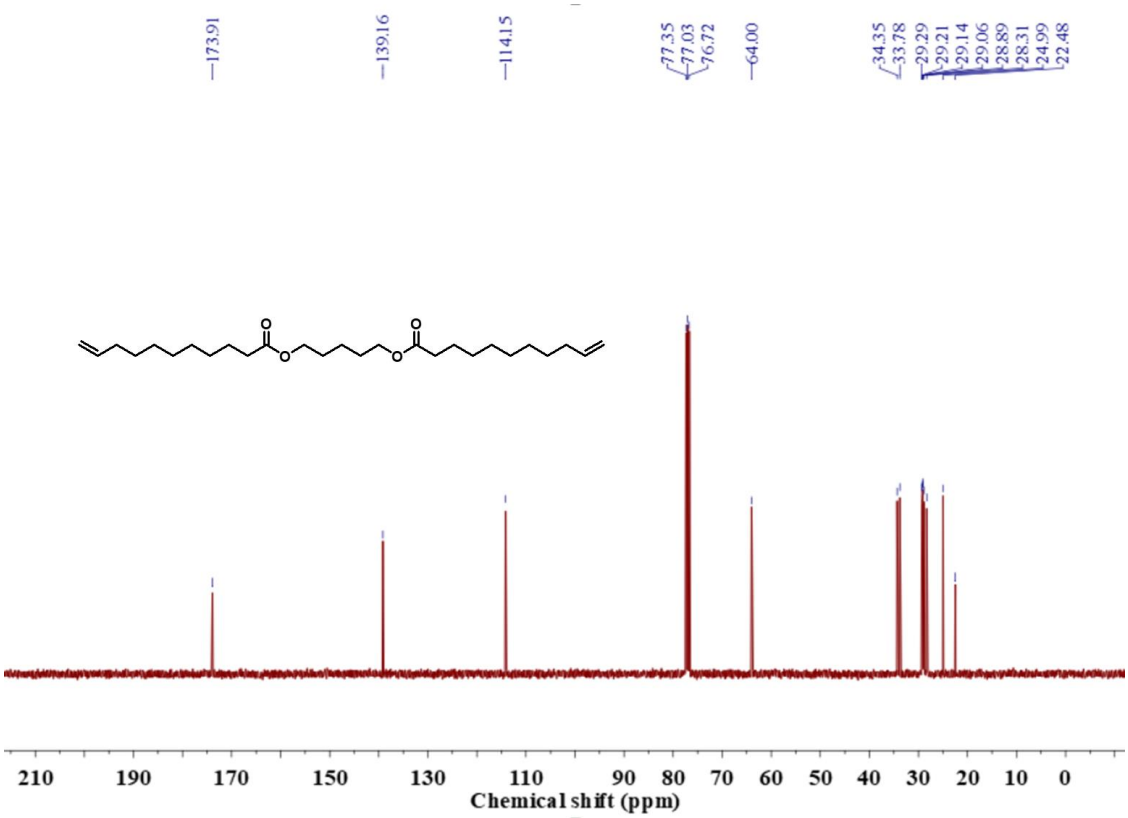


Figure S60. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **3**.

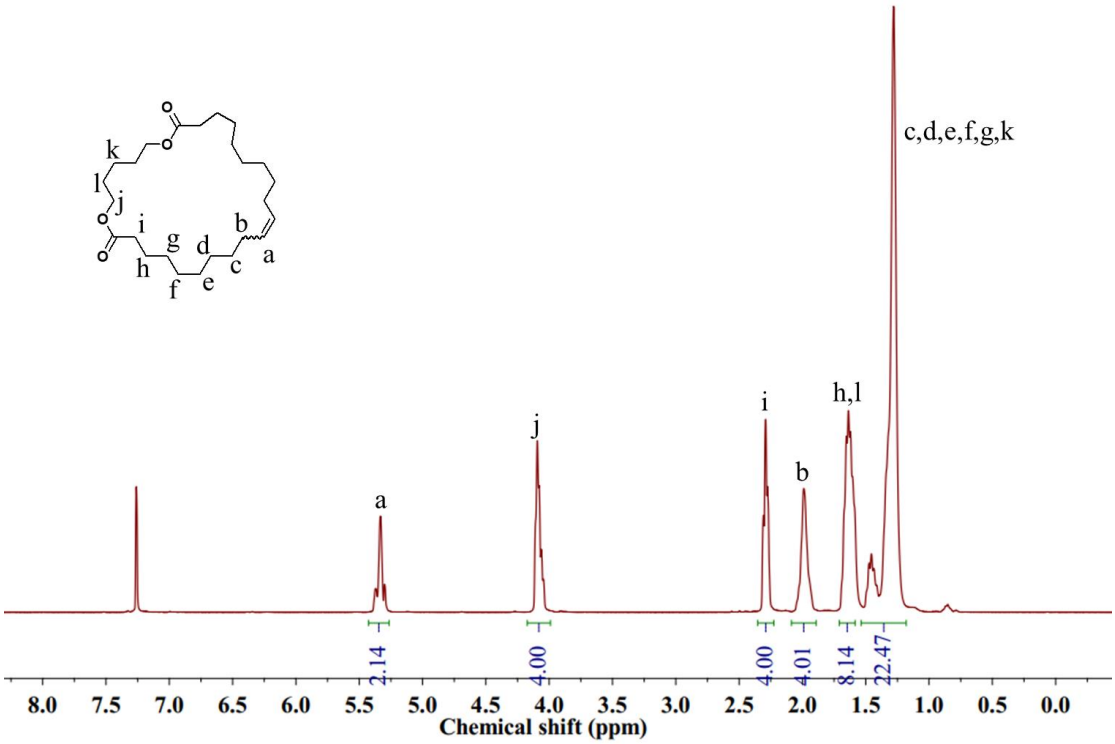


Figure S61. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **4**.

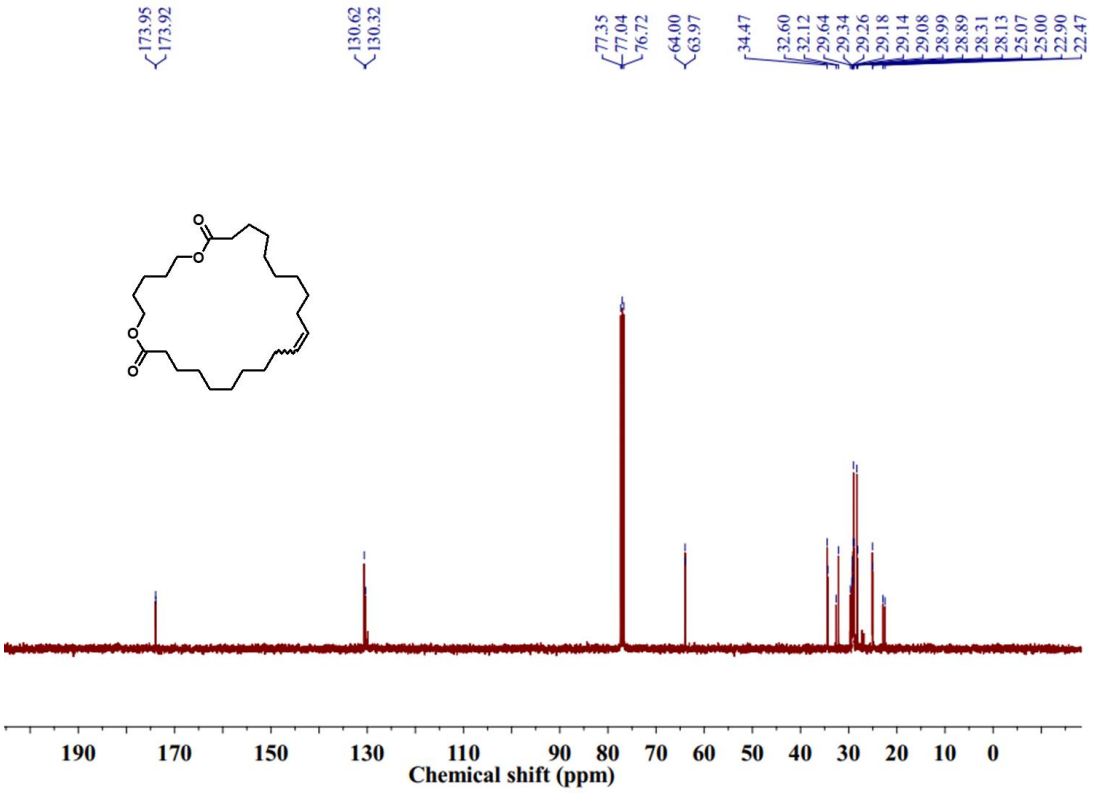


Figure S62. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **4**.

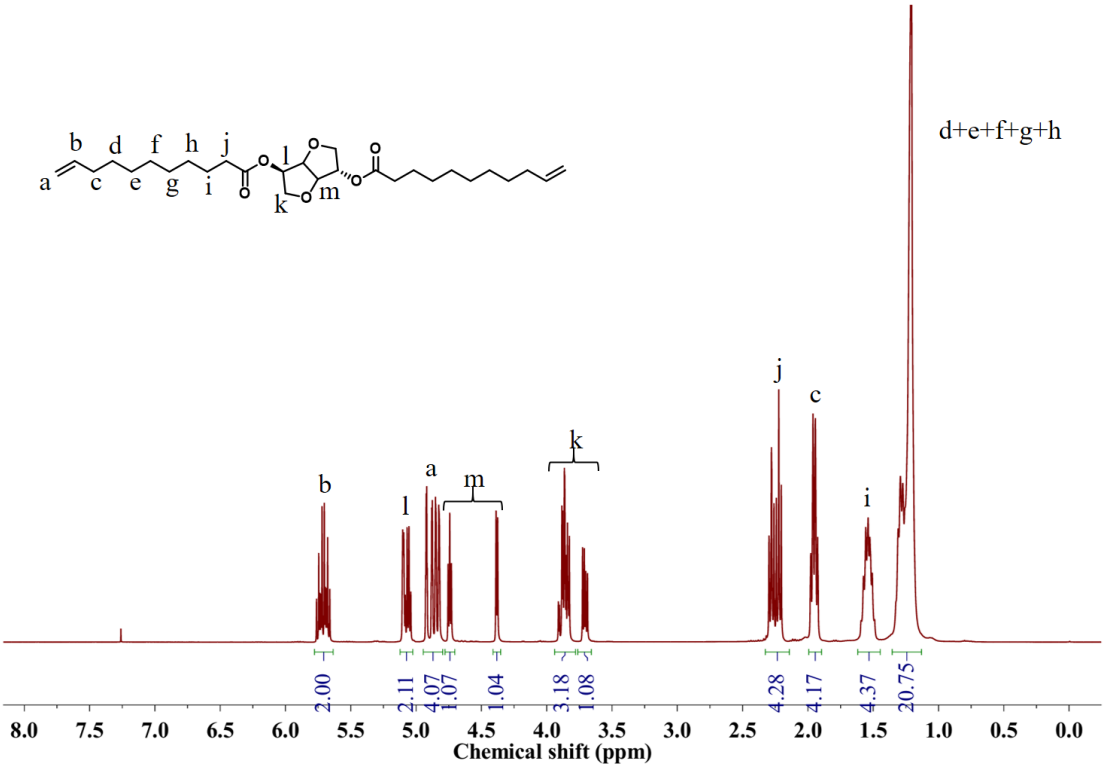


Figure S63. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **5**.

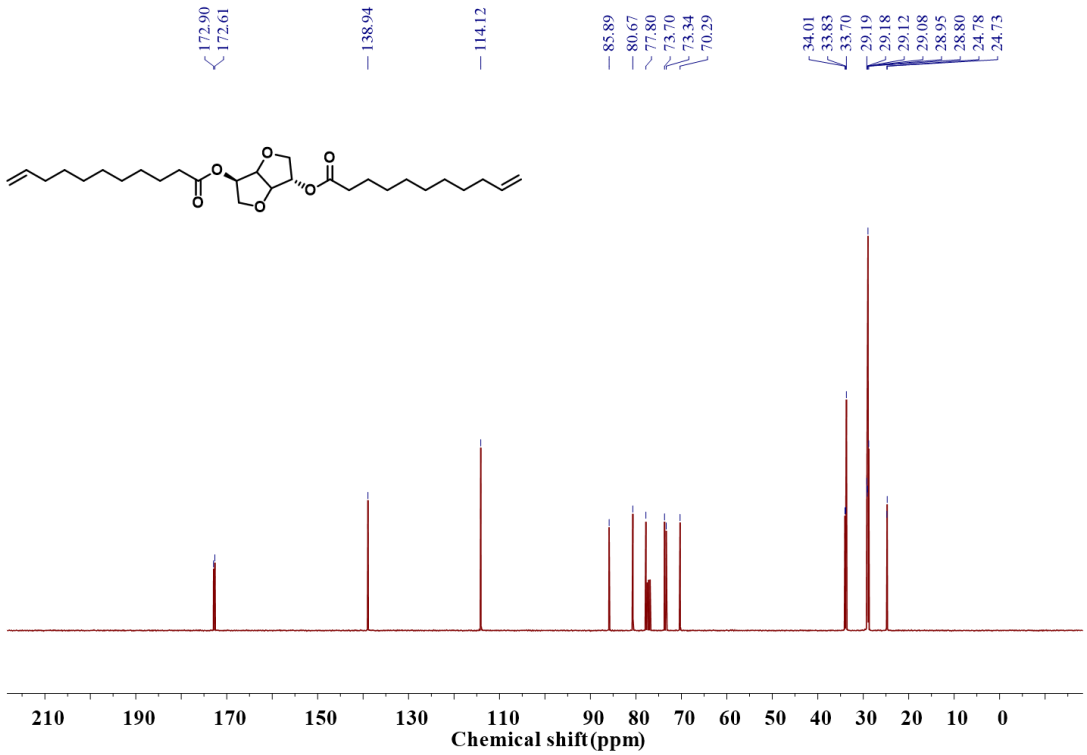


Figure S64. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **5**.

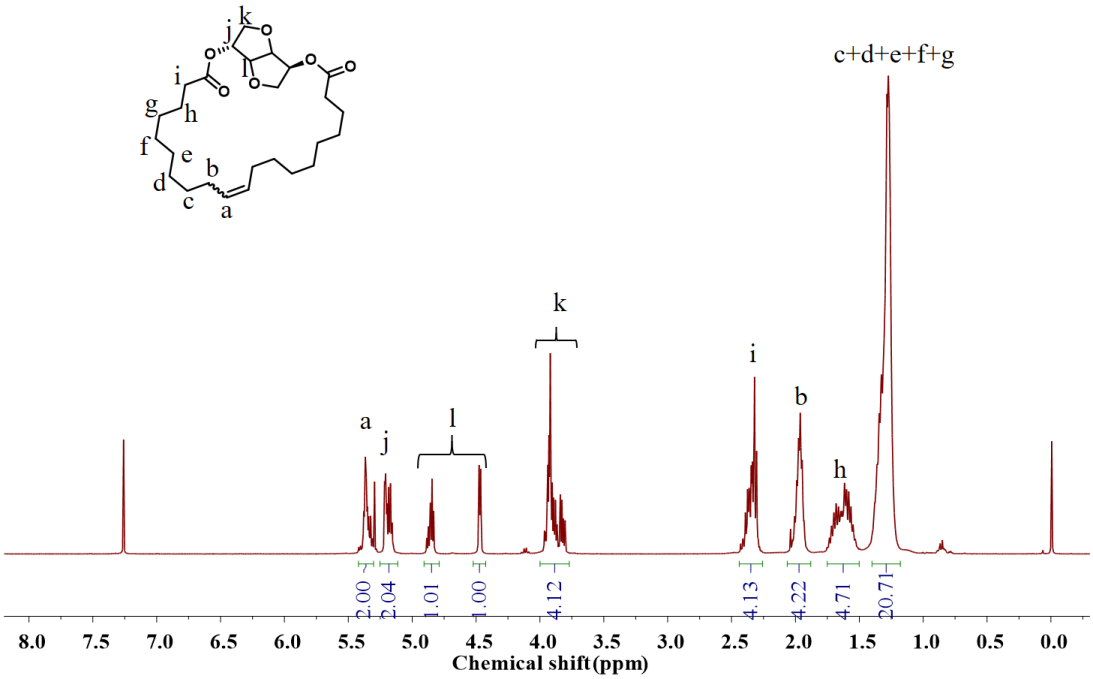


Figure S65. ^{1}H NMR spectrum (400 M, $CDCl_3$) of **6**.

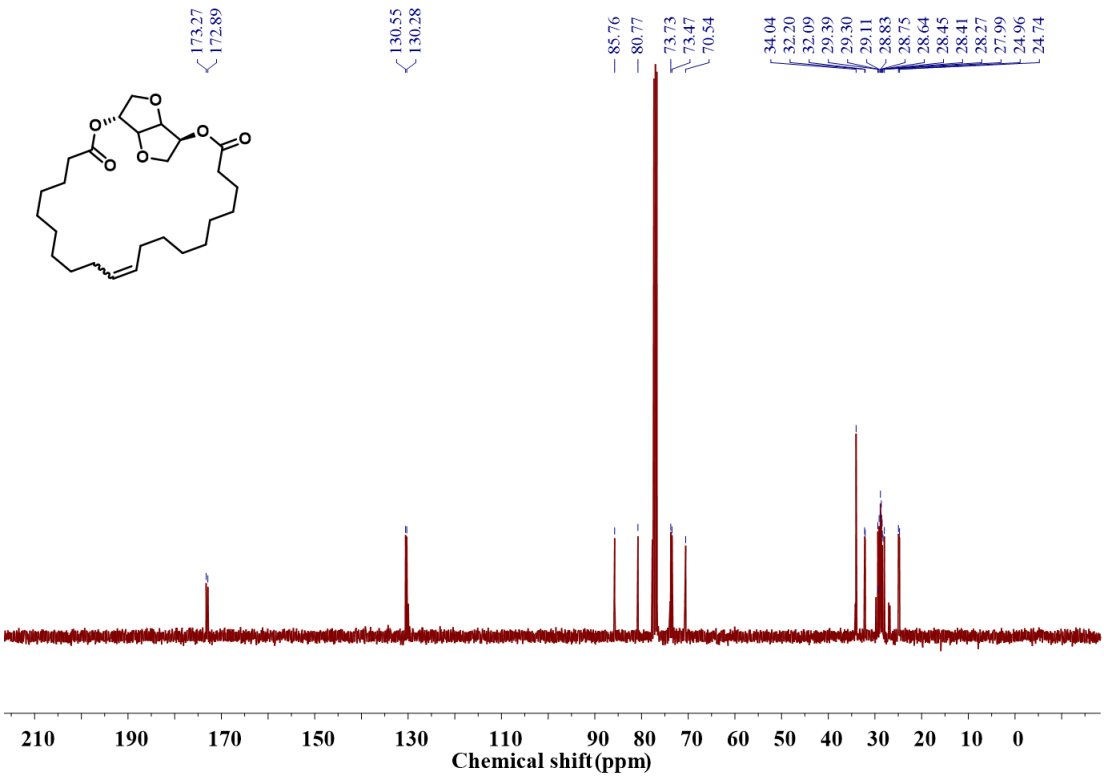


Figure S66. ^{13}C NMR spectrum (101 M, $CDCl_3$) of **6**.

Reference

(1) Zhang, H.; Zhou, Z.; Chen, X.; Yu, B.; Luo, Z.; Li, X.; Rahman, M. A.; Sha, Y. Sequence-Controlled Metallopolymers: Synthesis and Properties. *Macromolecules*

2021, *54* (19), 9174-9184.

(2) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.