

Supplementary Information

Epoxy Functionalized Cycloolefin Polymers by Ring-Opening Metathesis Polymerization

*Jongho So,^a Eun Seon Cho^b and Sang Youl Kim^{*a}*

^aDepartment of Chemistry, Korea Advanced Institute of Science and Technology Daejeon 34141, Republic of Korea

^bDepartment of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology Daejeon 34141, Republic of Korea

* Correspondence to S. Y. Kim (E-mail: kimsy@kaist.ac.kr)

Table of Contents

Experiment section	S2
NMR spectra	S5
Size Exclusion Chromatography (SEC) data	S13
Thermogravimetric analysis (TGA) data	S14
Differential scanning calorimetry (DSC) data	S15
Infrared (IR) spectra	S16
Solubility of polymers	S17

Experiment section

Materials. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a N₂ atmosphere. Dicyclopentadiene (DCPD), *meta*-chloroperoxybenzoic acid (*m*CPBA, ≤77%), dichloromethane (CH₂Cl₂, anhydrous, ≥99.8%), tetrachloroethane (TCE, anhydrous, ≥98.0%), palladium on activated carbon (Pd/C, 10 wt%), and ethyl vinyl ether (99%) were purchased from Sigma Aldrich. Acetic acid (AcOH, glacial, 99.5%) was purchased from Daejung. Solvents used in the glove box were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column. H₂ gas was purchased from SAMO Gas Co., LTD. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

General measurements. ¹H and ¹³C NMR spectra were recorded using a Bruker AVHD-400 spectrometer. The chemical shifts were quoted in parts per million (ppm) with reference to the residual peaks of CDCl₃ for ¹H (7.26 ppm) and ¹³C (77.16 ppm). Coupling constants, *J*, were reported in hertz unit (Hz). Splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; dd, doublet of doublet; dt, doublet of triplet; td, triplet of doublet; tt, triplet of triplet. Molecular weight and molecular weight distribution of the polymers were measured by gel permeation chromatography (GPC; Viscotek TDA302 instrument equipped with a packing column; PLgel 10 μm MIXED-B). GPC measurements were carried out with tetrahydrofuran (THF) as the eluent at a rate of 1 mL/min at 35°C, and the results were calibrated relative to linear polystyrene standards. The Fourier transform infrared (FT-IR) spectra of the compounds were recorded in films by Agilent 660 spectrophotometer and Nicolet iS50 spectrometer. The UV-visible spectra were obtained from a Shimadzu UV-2600 spectrometer in transmittance mode. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA Instruments TGA Q50 and a DSC Q20, respectively. TGA measurements were conducted at a heating rate of 10°C/min in N₂ and air. The glass transition temperature (*T*_g) values of the polymers were determined from the second heating scan of DSC thermograms at heating rate of 10°C/min in N₂.

Synthesis of 1. DCPD (6.78 g, 51.3 mmol) was dissolved in anhydrous CH₂Cl₂ (50 mL) at room temperature and ambient conditions. A solution of *m*CPBA (11.4 g, 50.9 mmol) in anhydrous CH₂Cl₂ (100 mL) was slowly added in three portions. After stirring for 3 hrs at room temperature, the white suspension was filtered through Celite. The filtrates were extracted successively with an aqueous solution of 10% NaHCO₃, dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (v/v = 1:9) as an eluent to yield a white solid (2.35 g, 31% yield). *R*_f = 0.33 (KMnO₄). ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.10 (dd, *J* = 8.7, 2.9 Hz, 2H, C=C-H), 3.33 (t, *J* = 2.5 Hz, 1H, CH), 3.17 (d, *J* = 2.5 Hz, 1H, CH), 2.93 (td, *J* = 3.0, 1.5 Hz, 1H, CH), 2.82 (m, 2H, CH₂), 2.55 (tt, *J* = 8.1, 3.9 Hz, 1H, CH), 1.91 (dd, *J* = 14.9, 9.0 Hz, 1H, CH), 1.51 (dt, *J* = 8.3, 1.9 Hz, 1H, CH), 1.39–1.31 (m, 2H, CH₂). ¹³C NMR (101 MHz, CDCl₃, ppm): δ 135.19 (s, C=C), 135.04 (s, C=C), 62.03 (s, C-O), 60.92 (s, C-O), 52.15 (s, CH), 51.15 (s, CH), 46.59 (s, CH₂), 44.79 (s, CH), 44.08 (s, CH), 31.22 (s, CH₂). Anal. Calcd. for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.22; H, 8.20.

Synthesis of poly(1). A solution of **1** (180 mg, 1.2 mmol) in CH₂Cl₂ (2.0 mL) was added rapidly by syringe to a 4 mL vial charged with the G1 catalyst (5.1 mg, 6.0 μmol) in CH₂Cl₂ (1.0 mL) under nitrogen atmosphere at room temperature. After 30 minutes, the reaction mixture was quenched with 0.5 mL ether vinyl ether. The solution was stirred for additional 15 min then precipitated in methanol. The resulting precipitate was collected and dried to afford poly(**1**) as a white solid in 96% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 5.53–5.29 (br, 2H), 3.55–3.42 (br, 1H), 3.40–3.27 (br, 1H), 3.10–2.51 (br, 3H), 2.47–2.30 (br, 1H), 2.02–1.84 (br, 1H), 1.80–1.64 (br, 1H), 1.52–1.21 (br, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm): δ 131.48, 130.56, 59.70, 59.52, 48.77, 44.83, 44.73, 44.61, 44.47, 43.11, 42.92, 36.44, 29.89. Anal. Calcd. for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 79.89; H, 8.21.

Synthesis of H-poly(1). The poly(**1**) (160 mg) was dissolved in 25 mL of anhydrous CH₂Cl₂. The mixture was transferred to an autoclave and 10 wt% of Pd/C (40 mg) was added. Under hydrogen pressure of 35 bar, the mixture was stirred vigorously at 65°C for 24 hr. After cooling to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. After pouring into methanol, the resulting precipitate was collected and dried to afford H-poly(**1**) as a

white solid in 95% yield. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 3.54–3.45 (br, 1H), 3.39–3.30 (br, 1H), 2.77–2.66 (br, 1H), 2.35–2.24 (br, 1H), 1.99–1.85 (br, 2H), 1.83–1.71 (br, 2H), 1.50–1.11 (br, 5H), 0.92–0.72 (br, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm): δ 59.68, 59.14, 47.03, 43.30, 43.15, 42.23, 40.12, 39.89, 37.66, 31.89, 29.94, 29.58, 28.45. Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.96; H, 9.39. Found: C, 78.10; H, 9.29.

Synthesis of H-poly(2). Under nitrogen atmosphere, H-poly(1) (50 mg) was dissolved in 1.5 mL of anhydrous TCE. To a TCE solution of H-poly(1), acetic acid (0.5 mL) was added. The reaction mixture was stirred at 100°C for 48 hrs, resulting in an orange-brown solution. After 48 hrs, the reaction mixture was poured into diethyl ether. The resulting precipitate was collected and dried to afford H-poly(2) as a yellowish solid in 95% yield. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 4.80–4.66 (br, 1H), 3.85–3.70 (br, 1H), 2.71 (br, 1H), 2.65–2.40 (br, 1H), 2.37–2.17 (br, 1H), 2.13–1.85 (br, 5H), 1.84–1.61 (br, 4H), 1.34–1.15 (br, 3H), 0.95–0.65 (br, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm): δ 172.50, 81.52, 77.36, 49.52, 42.45, 39.36, 36.21, 29.52, 28.56, 21.33. Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 68.55; H, 8.63. Found: C, 67.79; H, 8.78.

Preparation of Film. In a screw-capped vial, the corresponding polymers were dissolved in tetrachloroethane. The mixture was stirred and heated to 50°C. After complete dissolution, the resulting solution was cooled to room temperature. At a Teflon dish, the clear solution was spread through the syringe filter. All volatiles were carefully evaporated at room temperature for 24 h. The resulting film was further dried in a vacuum oven at 60°C for additional 24 h. After removing the volatiles, the thickness of the obtained film was measured by a thickness meter.

Polymerization of 1'. A solution of 1' (180 mg, 1.2 mmol) in CH_2Cl_2 (1.5 mL) was added rapidly by syringe to a 4 mL vial charged with the G1 catalyst (5.0 mg, 5.9 μmol) in CH_2Cl_2 (1.0 mL) under nitrogen atmosphere at room temperature. After 30 minutes, the reaction mixture was quenched with 0.5 mL ether vinyl ether. The reaction mixture was stirred for additional 15 min and then poured into methanol. *No precipitate was observed.* All volatiles were removed under vacuum and the resulting mixture was confirmed by the ^1H NMR spectroscopy, See Figure S13.

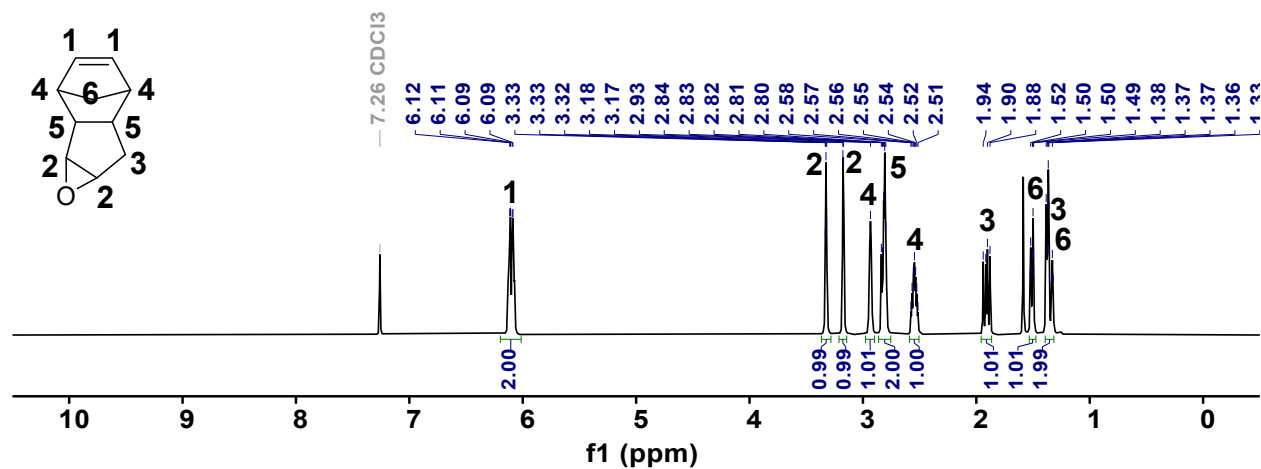


Figure S1. ^1H NMR spectrum of 1 in CDCl_3 .

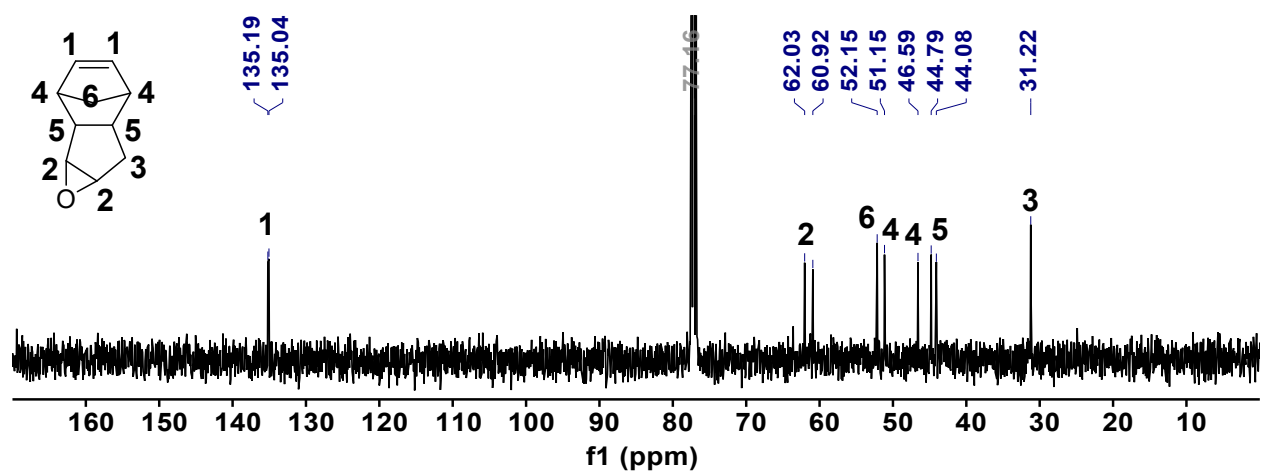


Figure S2. ^{13}C NMR spectrum of 1 in CDCl_3 .

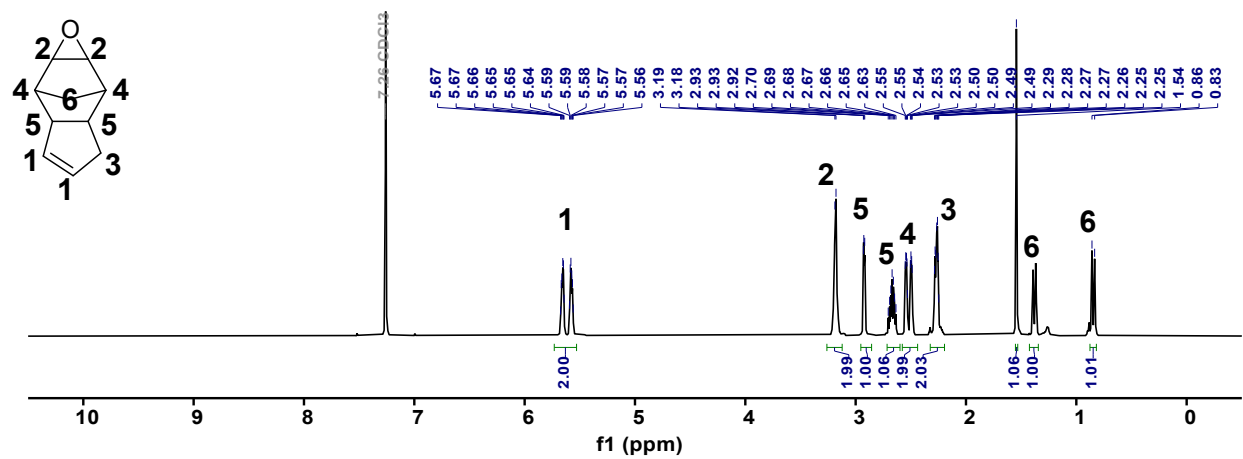


Figure S3. ¹H NMR spectrum of **1'** in CDCl₃.

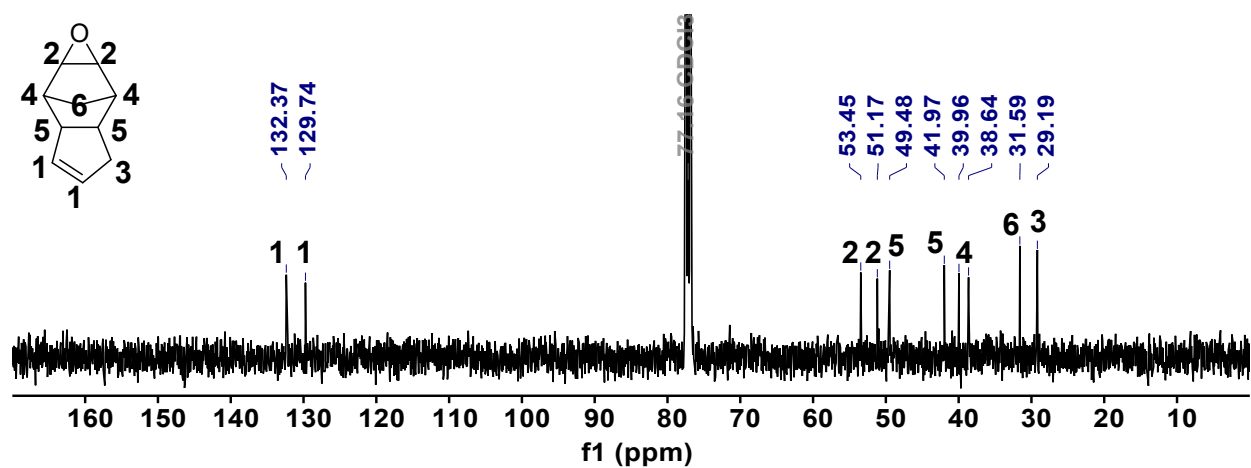


Figure S4. ¹³C NMR spectrum of **1'** in CDCl₃.

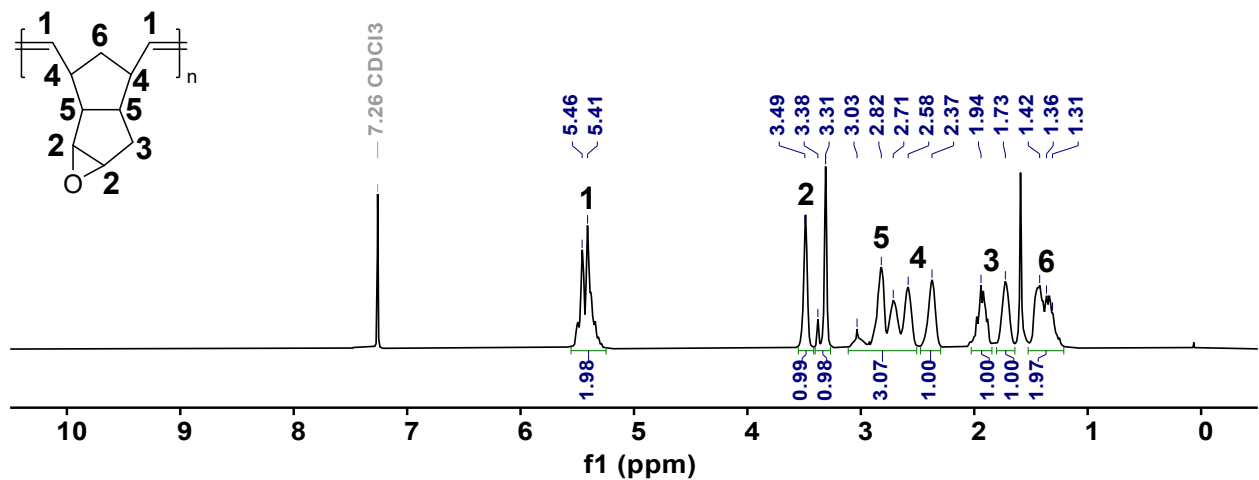


Figure S5. ^1H NMR spectrum of poly(1) in CDCl_3 .

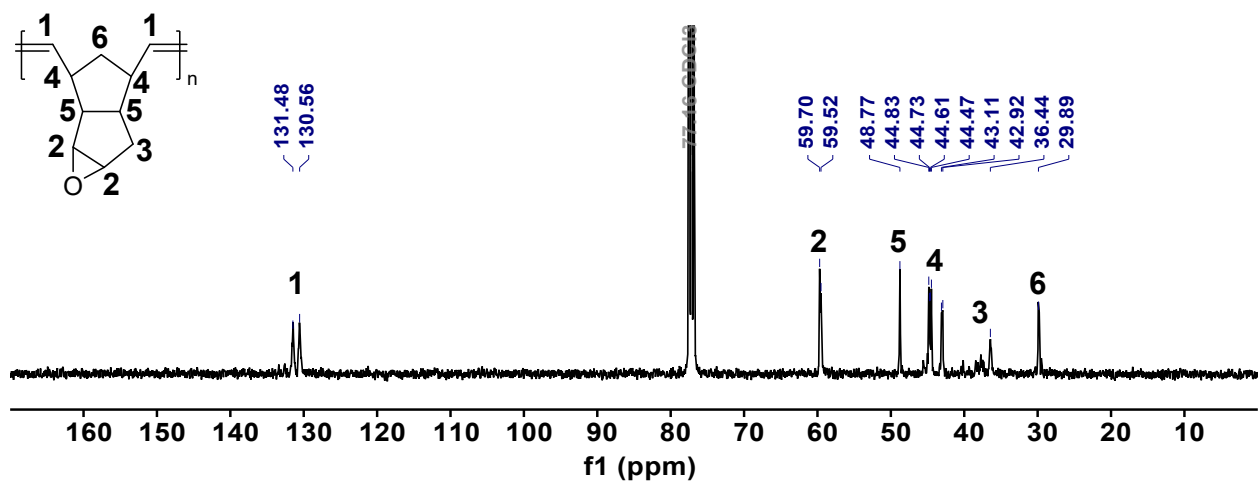


Figure S6. ^{13}C NMR spectrum of poly(1) in CDCl_3 .

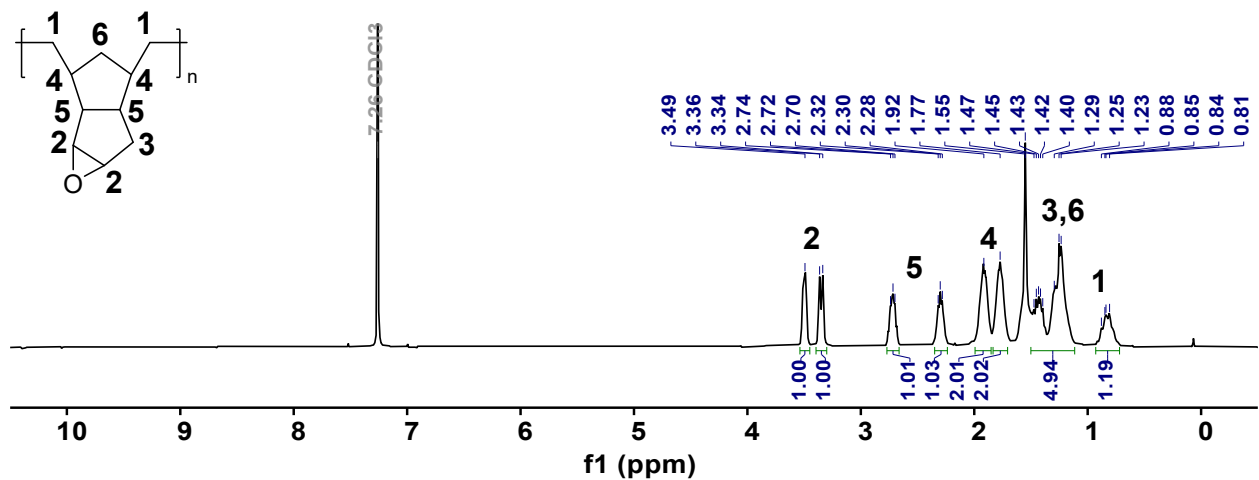


Figure S7. ^1H NMR spectrum of H-poly(1) in CDCl_3 .

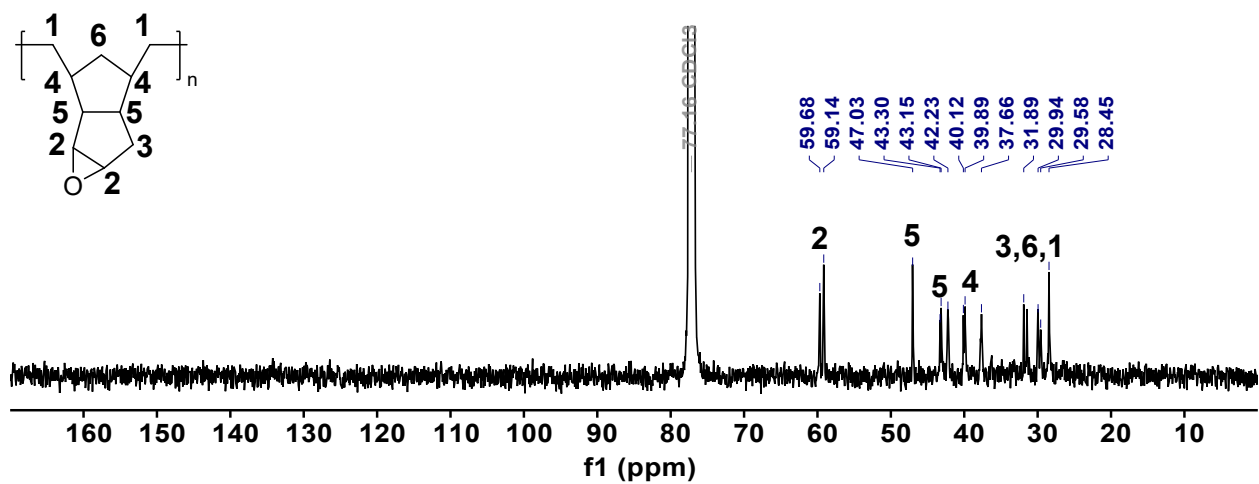


Figure S8. ^{13}C NMR spectrum of H-poly(1) in CDCl_3 .

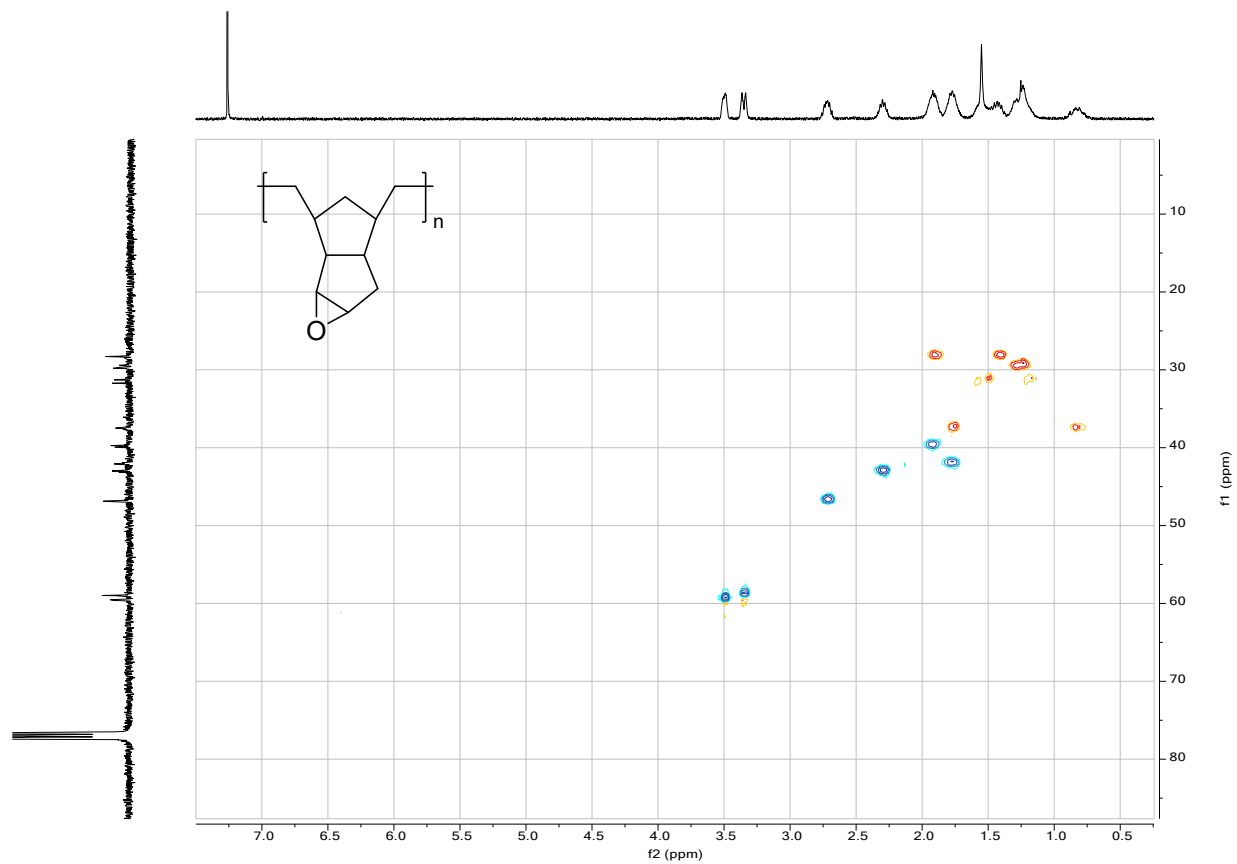


Figure S9. ^1H - ^{13}C HSQC NMR spectrum of H-poly(**1**) in CDCl_3 .

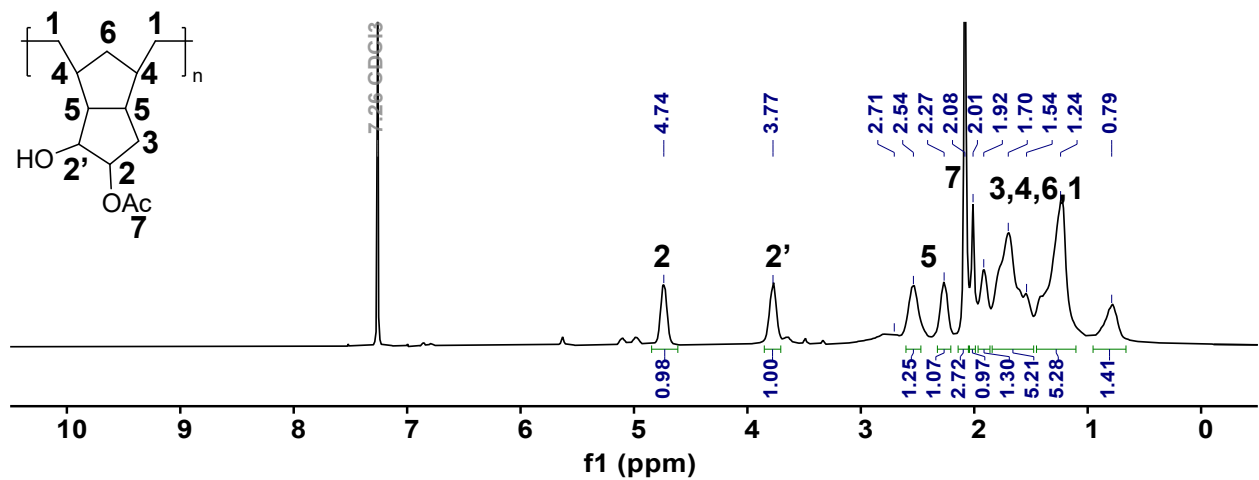


Figure S10. ^1H NMR spectrum of H-poly(2) in CDCl_3 .

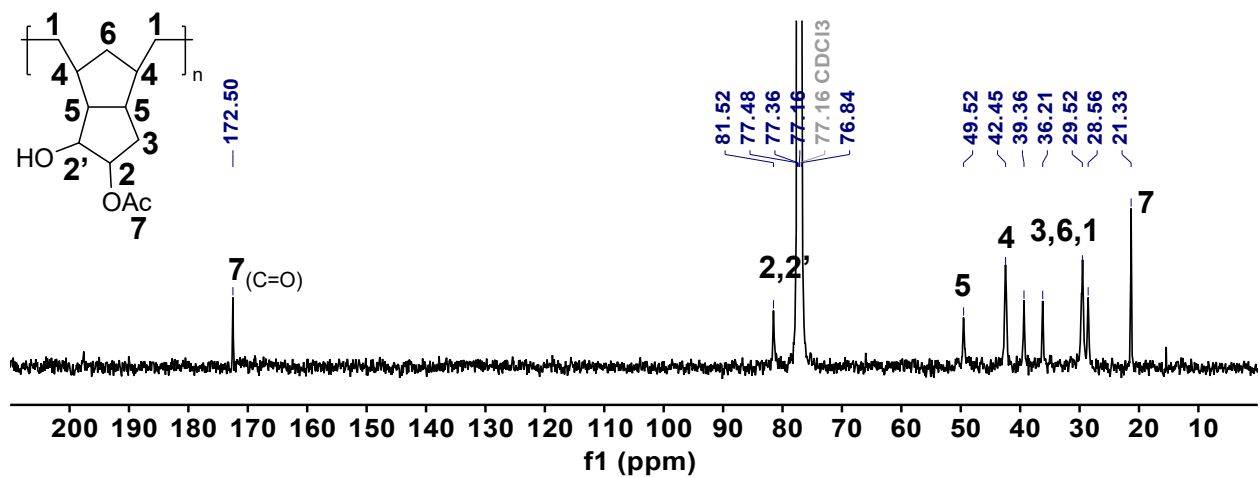


Figure S11. ^{13}C NMR spectrum of H-poly(2) in CDCl_3 .

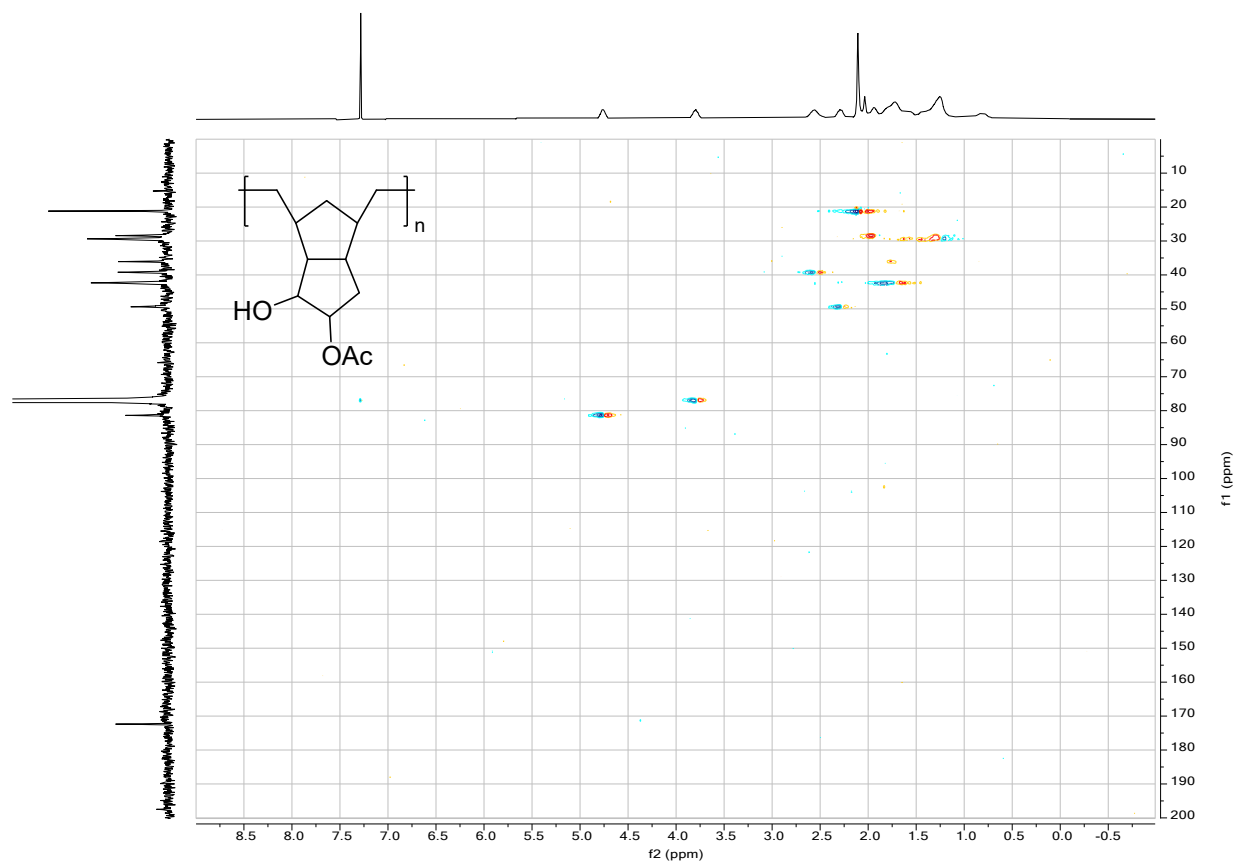


Figure S12. ^1H - ^{13}C HSQC NMR spectrum of H-poly(2) in CDCl_3 .

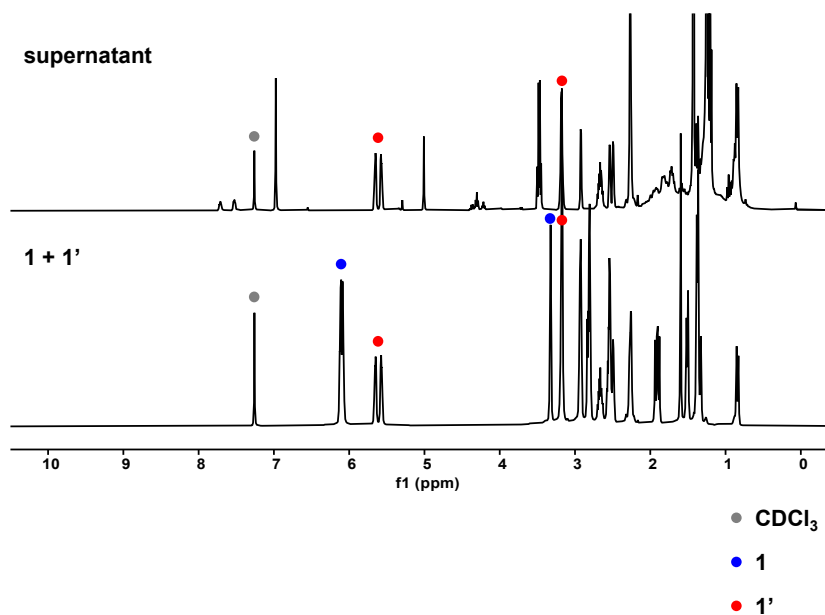


Figure S13. ^1H NMR spectra of the supernatant after polymerization (above) and the mixture of monomer **1** and **1'** (below) in CDCl_3 .

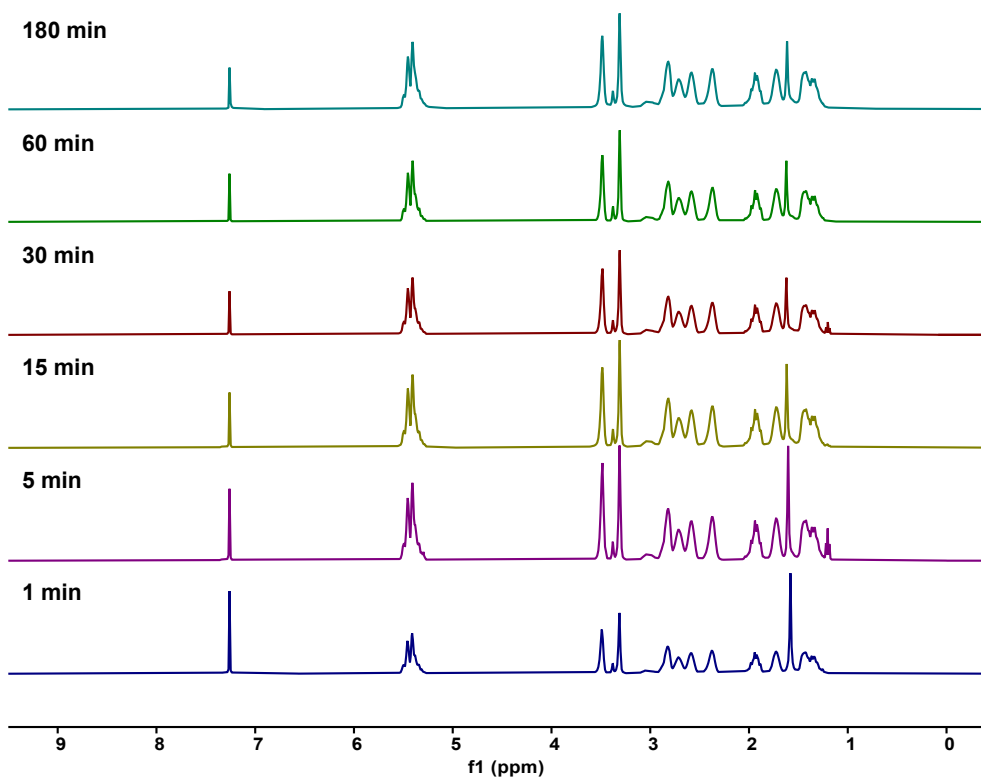


Figure S14. ^1H NMR spectra of poly(**1**) in CDCl_3 at the various polymerization time.

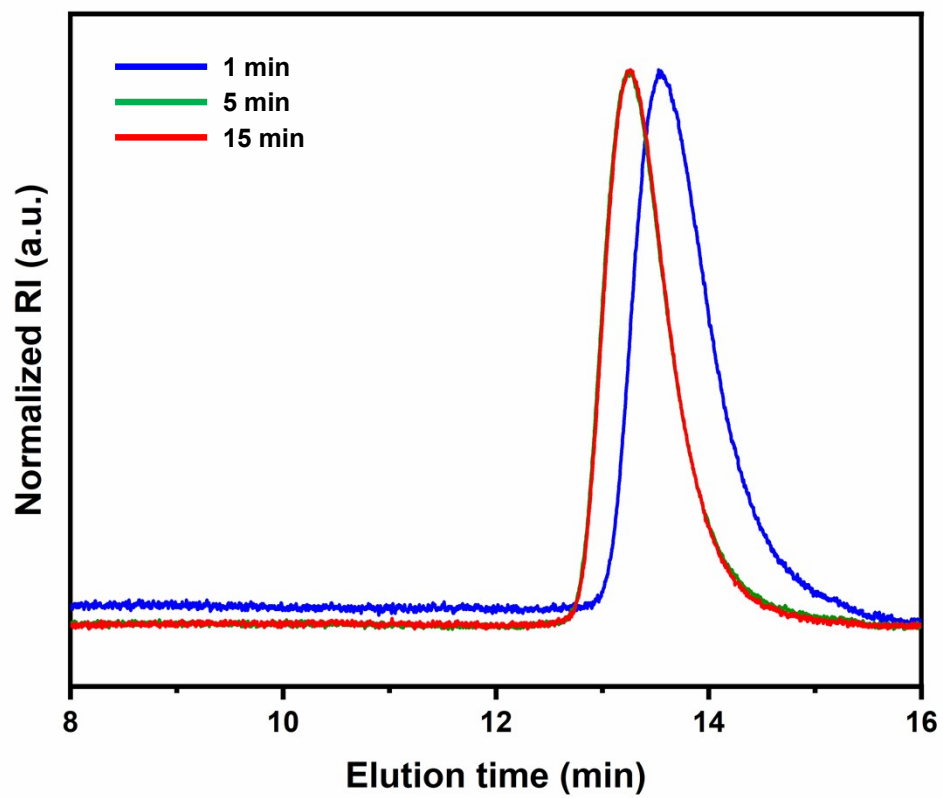


Figure S15. GPC traces of poly(1) depending on the polymerization time.

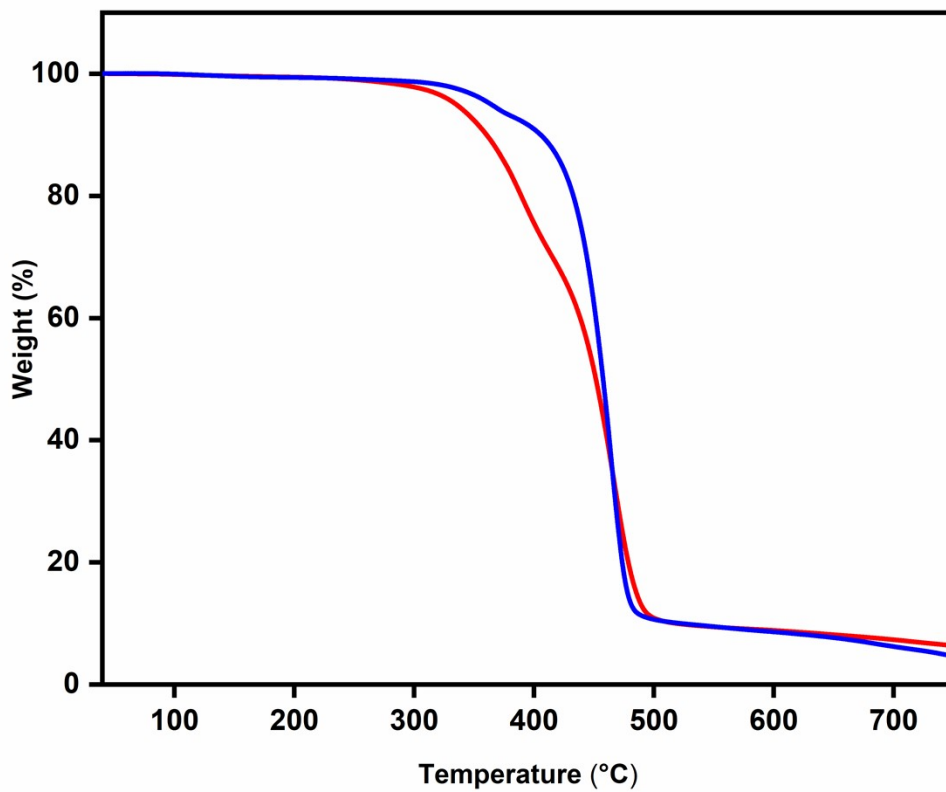


Figure S16. TGA curves of H-poly(1) (blue) and H-poly(2) (red) in N₂.

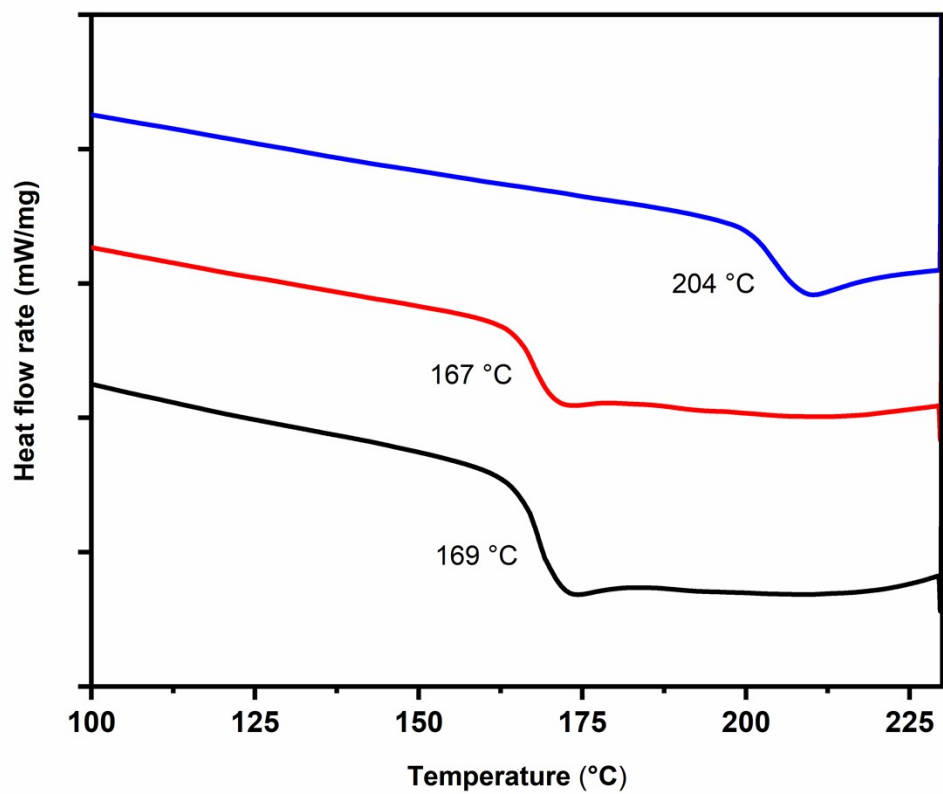


Figure S17. DSC curves of poly(1) (blue), H-poly(1) (red) and H-poly(2) (black) in nitrogen atmosphere.

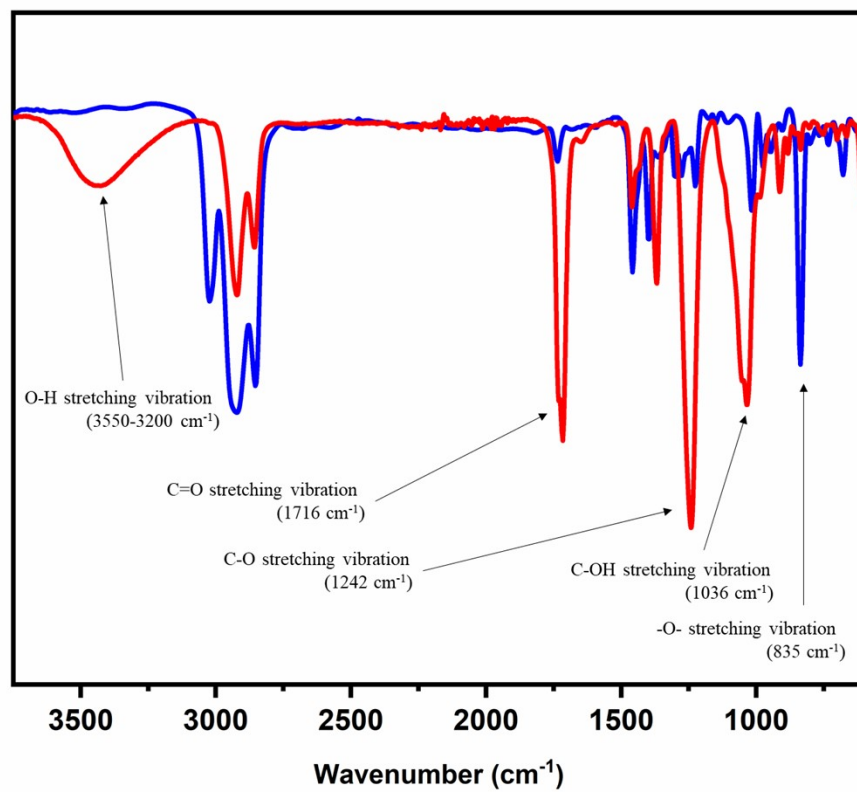


Figure S18. IR spectra of H-poly(1) (blue) and H-poly(2) (red).

Table S1. Solubility of the poly(1), H-poly(1) and H-poly(2).^a

Solvents ^b	poly(1)	H-poly(1)	H-poly(2)
Hexane	–	–	–
CyHx	–	–	–
Decalin	–	–	–
CCl ₄	–	–	–
Toluene	–	–	–
Xylene	–	–	–
Benzene	–	–	–
CB	++	–	–
DCB	++	–	–
Ether	–	–	–
DCM	++	+	+
DCE	++	+	+
2-propanol	–	–	–
THF	++	–	+
CHCl ₃	++	+	+
EA	–	–	–
Dioxane	–	–	+
Acetone	–	–	–
CH ₃ CN	–	–	–
DMF	–	–	+
DMAc	–	–	+
NMP	++	–	+
DMSO	–	–	+
Water	–	–	–

^a Solubility was determined with 2 mg of polymer in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; –, insoluble. ^b Abbreviations: CyHx, cyclohexane; CCl₄, carbon tetrachloride; CB, chlorobenzene; DCB, dichlorobenzene; DCM, dichloromethane; DCE, 1,2-dichloroethane; THF, tetrahydrofuran; CHCl₃, chloroform; EA, ethyl acetate; CH₃CN, acetonitrile; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide