Supplementary Information (SI) for Polymer Chemistry.

Electronic Supporting Information

Towards Degradable and Functionalizable Polymers: Alternating Ring-Opening Metathesis Copolymerization of Oxanorbornadiene Dicarboxylate and 2,3-Dihydrofuran

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1. Materials

Dimethyl 7-Oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (OND, >95%), n-butylamine (99%), benzylamine (98%), ethanolamine (99%), 1-thioglycerol (99%), ethyl vinyl ether (98%), dichloromethane (DCM, 99%), tetrahydrofuran (THF, 99%), benzyl mercaptan (99%), triethylamine (TEA, 99%), and methanol (99.9%) were purchased from Fisher Scientific and used without purification. 2,3-Dihydrofuran (DHF, 99%), polystyrene (M_n = 20,000 g/mol), Grubbs catalyst 3rd generation (M300), and Grubbs catalyst 2nd generation (M204) were purchased from Sigma Aldrich and used without purification.

2. Instrumentation

Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz) in $CDCl_3$ or DMSO-d_6. Chemical shifts are given in ppm downfield from tetramethylsilane (TMS).

Size Exclusion Chromatography (SEC): The molecular weight and polydispersity of synthetic polymers were determined by a size exclusion chromatography (SEC) system (TOSOH EcoSEC HLC-8320) equipped with a set of Phenomenex Phenogel 5μ, 1K-75K, 300 x 7.80 mm in series with a Phenomex Phenogel 5μ, 10K-1000K, 300 x 7.80 mm columns following a guard column and two detectors including a RI detector and a UV detector. The measurements were performed using HPLC-grade THF as the eluent at a flow rate of 0.5 mL/min at 35 °C and a series of polystyrene standards for the calibration of the columns.

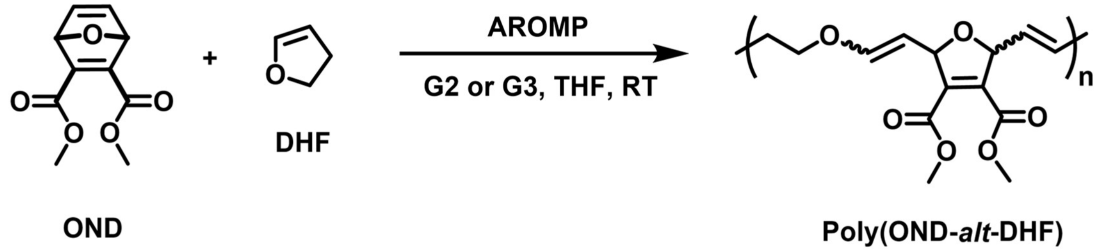
Differential Scanning Calorimetry (DSC): Differential scanning calorimetry (DSC) measurements were performed using a Guangdong Newgoer DSC-300C system under a nitrogen gas flow (100 mL/min). Two thermal cycles (-20 to 200 °C) with heating and cooling rates of 10 °C/min were performed. The glass transition temperatures were obtained from the second heating scans after removing the thermal history of polymers.

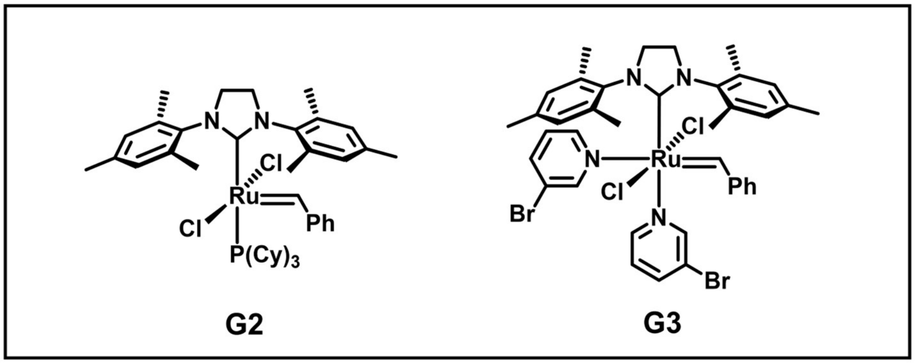
Thermogravimetric Analysis (TGA): Thermogravimetric analysis (TGA) was performed using a TA SDT Q600 system under a nitrogen gas flow (100 mL/min) with a heating rate of 10 °C/min. The temperature range for the analysis extended from ambient temperature to 650 °C.

Tensile Test: Tensile testing of polymers was performed using a Mark-10 F305-IMT system with a 200 N load at room temperature. A crosshead speed of 5 mm/min was used. P1 and polystyrene films were solvent-cast from a concentrated DCM solution in a covered Petri dish overnight, then dried under vacuum at 40 °C for two days. P5 was solvent-cast from a concentrated THF solution under the same conditions, followed by methanol soaking to remove residual THF, and subsequently dried under vacuum at 40 °C for two days. Rectangular samples (10 mm (L) × 5 mm (W)) were then cut from the polymer film using a razor blade.

3. Experimental Methods

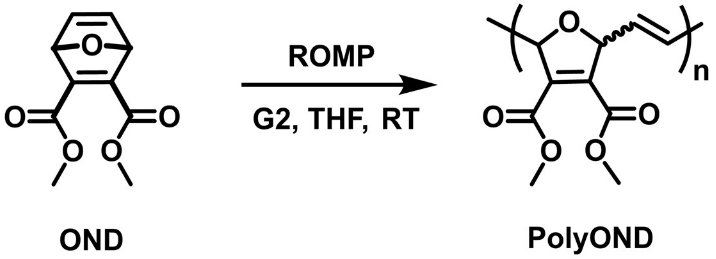
3.1. Synthesis of Poly(OND-*alt*-DHF) *via* AROMP





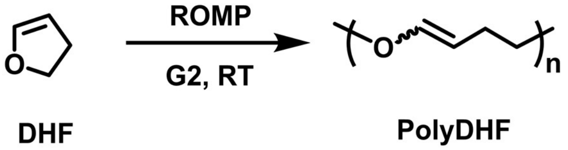
In a typical procedure for preparing Poly(OND-*alt*-DHF)$_{100}$, **OND** (200 mg, 0.95 mmol, 100 equiv.) and **DHF** (140 µL, 1.90 mmol, 200 equiv.) were dissolved in degassed THF (4 mL). Separately, a solution containing catalyst **G2** (8.0 mg, 0.0095 mmol, 1.0 equiv.) and degassed THF (2 mL) was prepared, and then quickly added to the monomer solution. The reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with excess ethyl vinyl ether (90 µL, 0.95 mmol, 100 equiv.) and precipitated into cold methanol to obtain the alternating copolymer.

3.2. Synthesis of PolyOND Homopolymer *via* ROMP



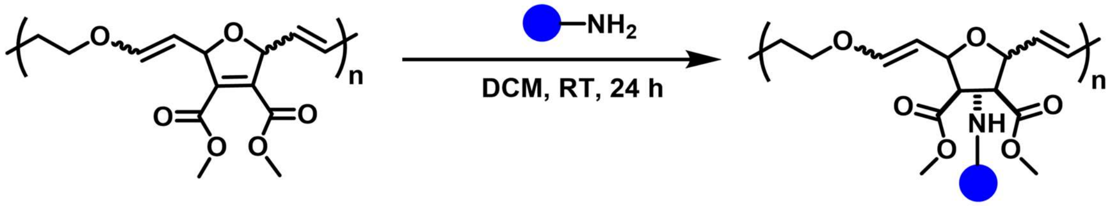
In a typical procedure for the synthesis of PolyOND, **OND** (200 mg, 0.95 mmol, 100 equiv.) was dissolved in degassed THF (4 mL). Separately, a solution containing catalyst **G2** (8.0 mg, 0.0095 mmol, 1.0 equiv.) and degassed THF (2 mL) was prepared, and then quickly added to the monomer solution. The reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with excess ethyl vinyl ether (90 µL, 0.95 mmol, 100 equiv.) and precipitated into cold methanol to obtain the homopolymer. Monomer conversion of OND was determined to be 14% by ^{1}H NMR spectroscopy.

3.3. Synthesis of PolyDHF Homopolymer



The synthesis of polyDHF was performed using a protocol from a previous work.[1] In a typical procedure for the synthesis of PolyDHF, olefin metathesis catalyst **G2** (64 mg, 0.076 mmol, 1.0 equiv.) was quickly added to the degassed **DHF** (0.56 mL, 7.6 mmol, 100 equiv.) The reaction mixture was stirred for 2 h at room temperature until a quantitative conversion of DHF was observed. The resulting homopolymer was further analyzed by NMR analysis.

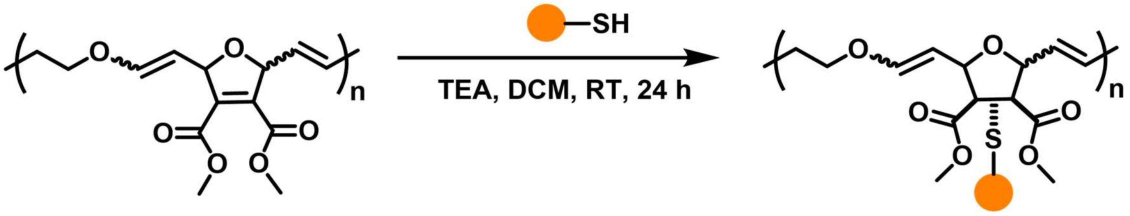
3.4. Post-Polymerization Modification via Aza-Michael Addition



Poly(OND-*alt*-DHF) **P2-P4**

In a general protocol for aza-Michael addition, a solution of Poly(OND-*alt*-DHF) (280 mg, 1.0 mmol of repeating units, 1.0 equiv.) in DCM (5 mL) was added an amine (20 mmol, 20 equiv.). After stirring for 24 h, the reaction solution was concentrated and then added with cold methanol to precipitate the polymer products.

3.5. Post-Polymerization Modification via Thia-Michael Addition



Poly(OND-*alt*-DHF) **P5-P6**

In a general protocol for **thia-Michael addition**, a solution of Poly(OND-*alt*-DHF) (280 mg, 1.0 mmol of repeating units, 1.0 equiv.) in DCM (5 mL) was added a thiol (20 mmol, 20 equiv.), followed by triethylamine (280 μL, 2.0 mmol, 2.0 equiv.). After stirring for 24 h, the reaction solution was concentrated and then added with cold methanol to precipitate the polymer products

3.6. Acid-Promoted Degradation of Polymers

In a typical procedure for polymer degradation study, 40 μL of 1 M HCl aqueous solution was added into 1960 μL of polymer solution (10 mg/mL in THF). The resulting solution was analyzed by THF-SEC at predetermined time points.

4. Supporting Table and Figures

Table S1. Polymer information for the alternating copolymers developed in this study.

Entry[a]	**$[OND]_0$:$[DHF]_0$:$[Cat.]_0$**	**Catalyst**	**Polymerization Time (h)**	**Monomer Conversion (%)**[b]	**Alternating Dyads (%)**[b]	**$M_{n,SEC}$ (kDa)**[c]	**$Đ$**[c]
1	30:60:1	G3	24	>99	99	10.9	1.6
2	50:100:1	G3	24	>99	98	16.8	1.9
3	100:200:1	G3	24	75	99	25.1	2.4
4	30:60:1	G2	24	>99	99	12.5	1.7
5	50:100:1	G2	24	>99	99	19.0	1.6
6	100:200:1	G2	24	>99	99	36.4	1.6

[a]All the polymerizations were performed at room temperature (20 °C). The initial monomer concentration (OND) was 0.15 M. [b]Monomer conversions and alternating dyads were determined by ^{1}H NMR spectroscopy. [c]Number-average molecular weights ($M_{n,SEC}$) and their distributions ($Đ$) were determined by SEC.

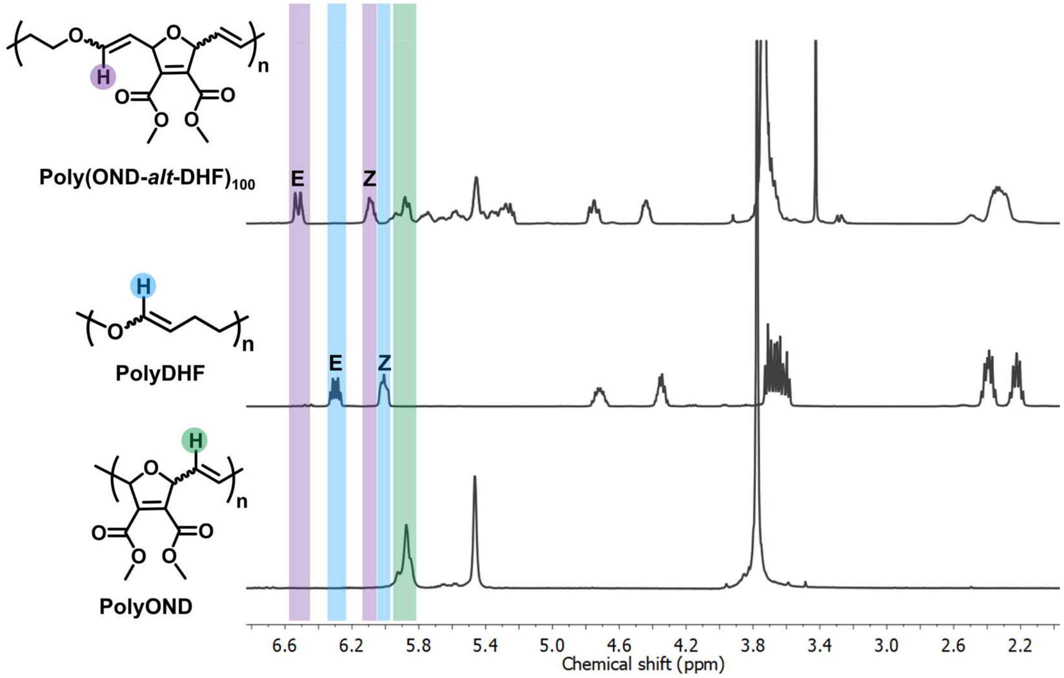


Figure S1. ^{1}H NMR full spectra of poly(OND-*alt*-DHF)$_{100}$, polyDHF, and polyOND in CDCl$_3$ at 25 °C. The signals attributed to vinylic protons (highlighted in blue) in polyDHF homopolymer are absent in the NMR spectrum of Poly(OND-*alt*-DHF)$_{100}$, suggesting that DHF only copolymerized with OND.

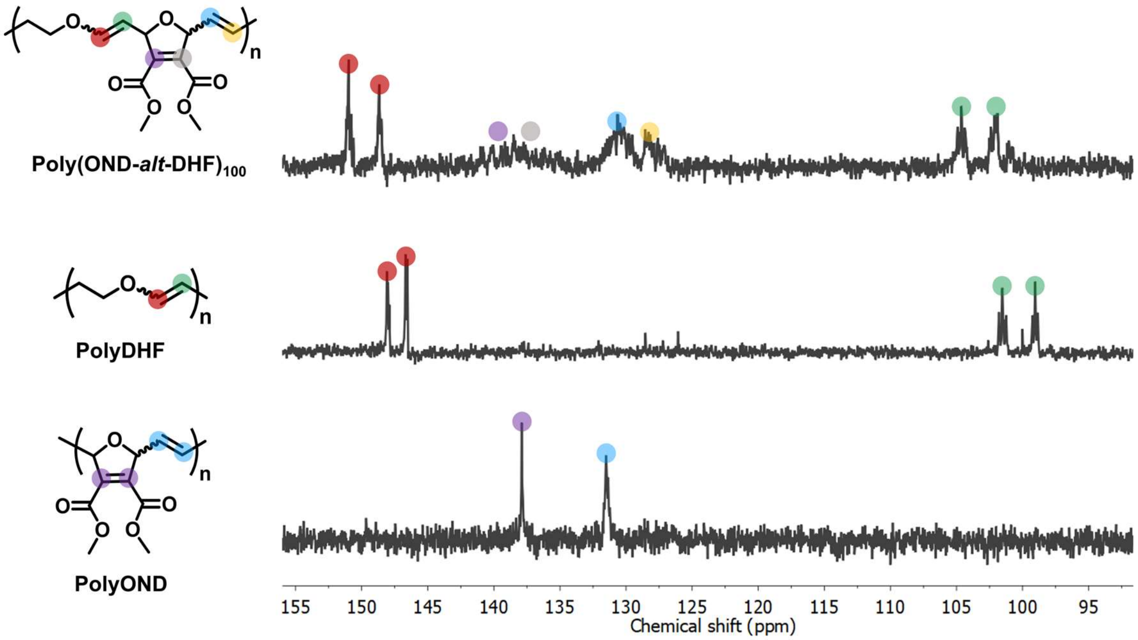
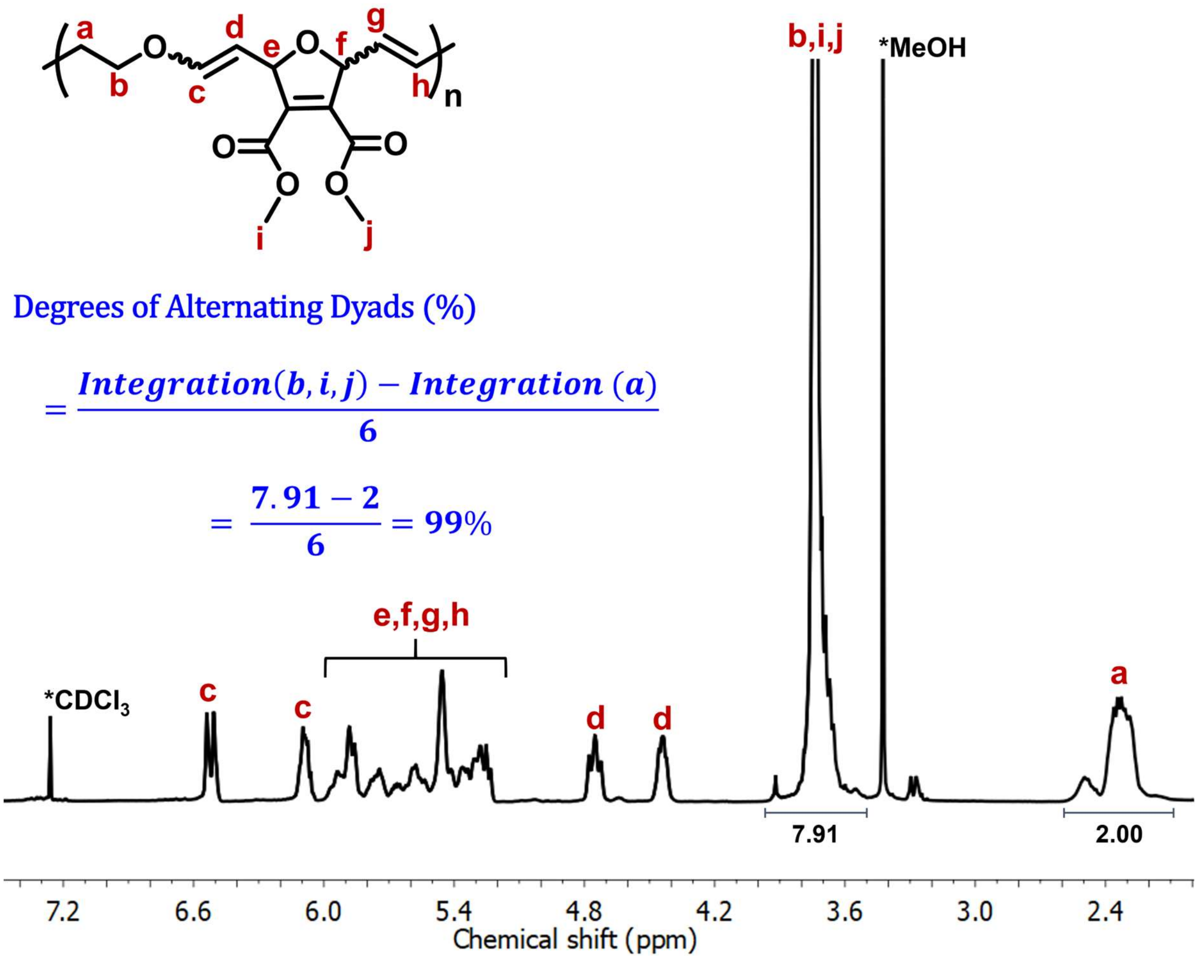


Figure S2. ^{13}C NMR spectra of poly(OND-*alt*-DHF)$_{100}$, polyDHF, and polyOND in CDCl$_3$ at 25 °C. The signals attributed to vinylic carbons (highlighted in green and red) in polyDHF homopolymer are absent in the NMR spectrum of Poly(OND-*alt*-DHF)$_{100}$, suggesting that DHF only copolymerized with OND.



Degrees of Alternating Dyads (%)

$$= \frac{\boldsymbol{Integration(b,i,j) - Integration\ (a)}}{\mathbf{6}}$$

$$= \frac{\mathbf{7.91 - 2}}{\mathbf{6}} = \mathbf{99\%}$$

Figure S3. ^{1}H NMR spectrum of alternating copolymer poly(OND-*alt*-DHF)$_{100}$ (Entry 6 in Table S1) in CDCl$_3$ at 25 °C. Based on the integrations of methylene protons (a) and methylene protons (b) from DHF repeating units, and the methyl protons (i,j) from OND repeating unit, the copolymer contains over 99% of alternating dyads (OND-DHF).

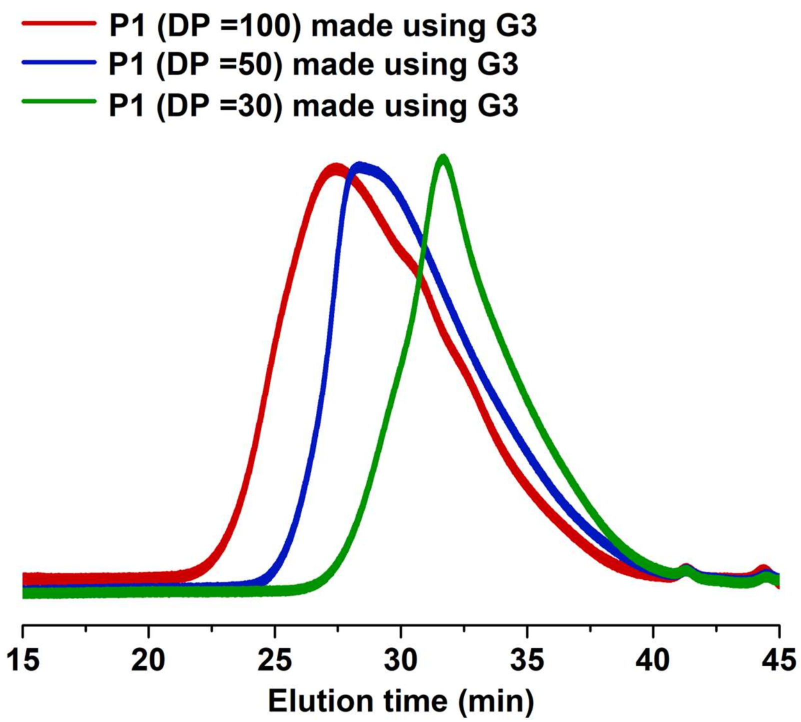


Figure S4. SEC traces of poly(OND-*alt*-DHF) with different targeted degrees of polymerization (DP). These polymers were prepared using G3 (Entries 1-3 in Table S1).

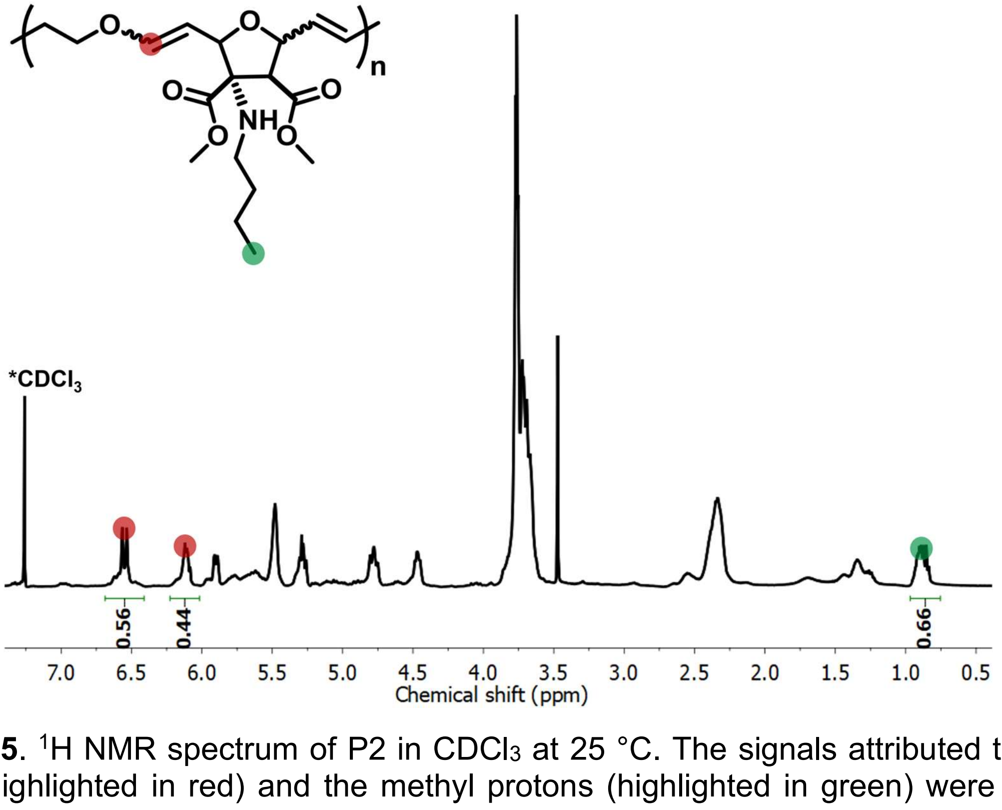


Figure S5. ^{1}H NMR spectrum of P2 in CDCl$_3$ at 25 °C. The signals attributed to vinylic proton (highlighted in red) and the methyl protons (highlighted in green) were used to estimate the degree of functionalization (22%) upon aza-Michael addition.

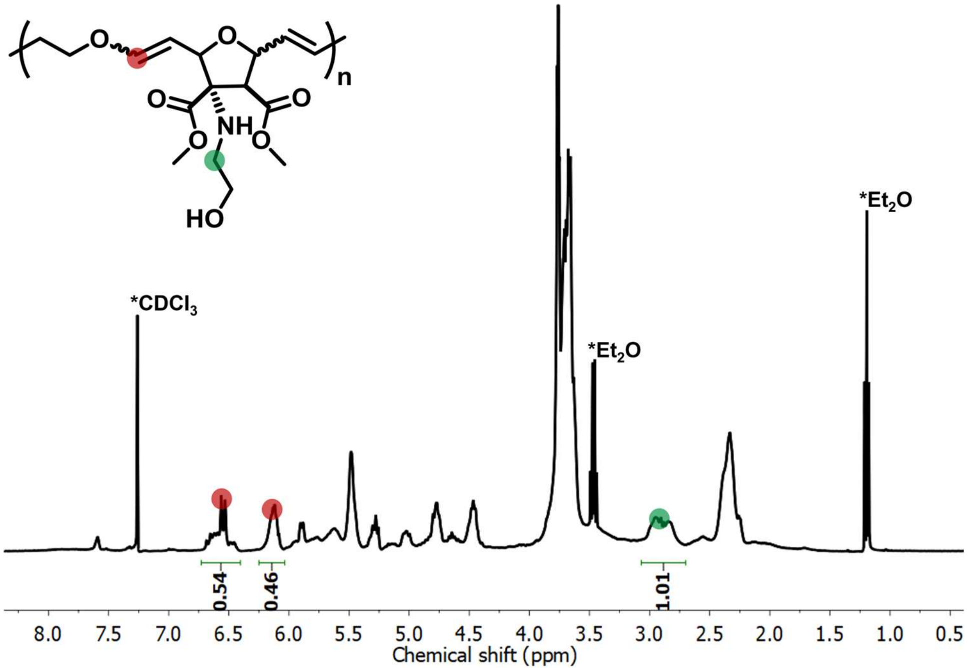


Figure S6. ^{1}H NMR spectrum of P3 in $CDCl_3$ at 25 °C. The signals attributed to vinylic proton (highlighted in red) and the methylene protons (highlighted in green) were used to estimate the degree of functionalization (50%) upon aza-Michael addition.

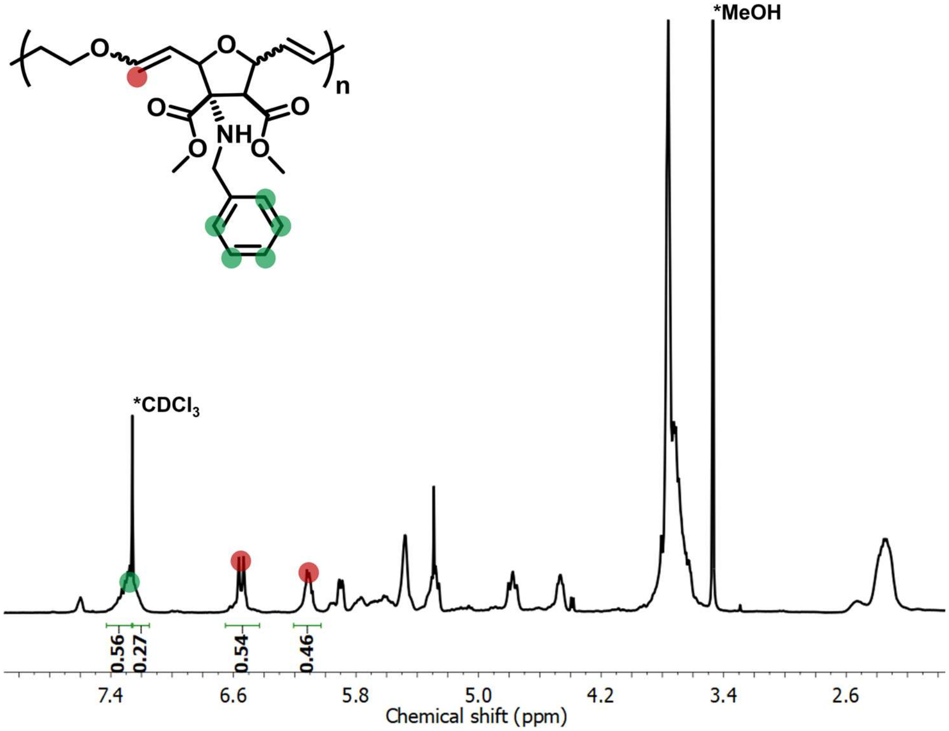


Figure S7. ^{1}H NMR spectrum of P4 in $CDCl_3$ at 25 °C. The signals attributed to vinylic proton (highlighted in red) and the aromatic protons (highlighted in green) were used to estimate the degree of functionalization (16%) upon aza-Michael addition.

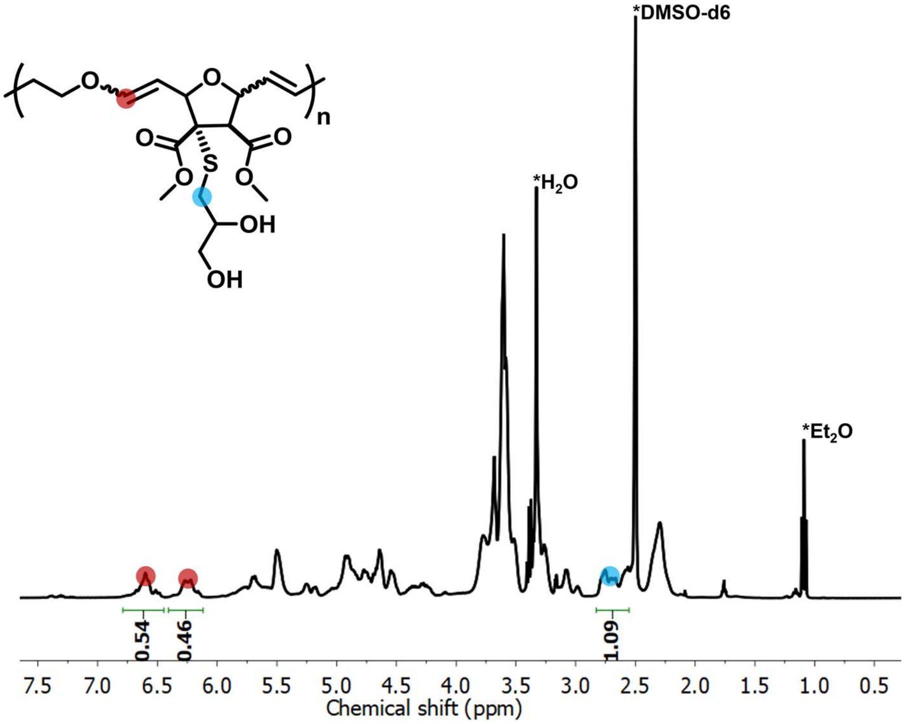


Figure S8. ^{1}H NMR spectrum of P5 in DMSO-d$_6$ at 25 °C. The signals attributed to vinylic proton (highlighted in red) and the methylene protons (highlighted in blue) were used to estimate the degree of functionalization (54%) upon thia-Michael addition.

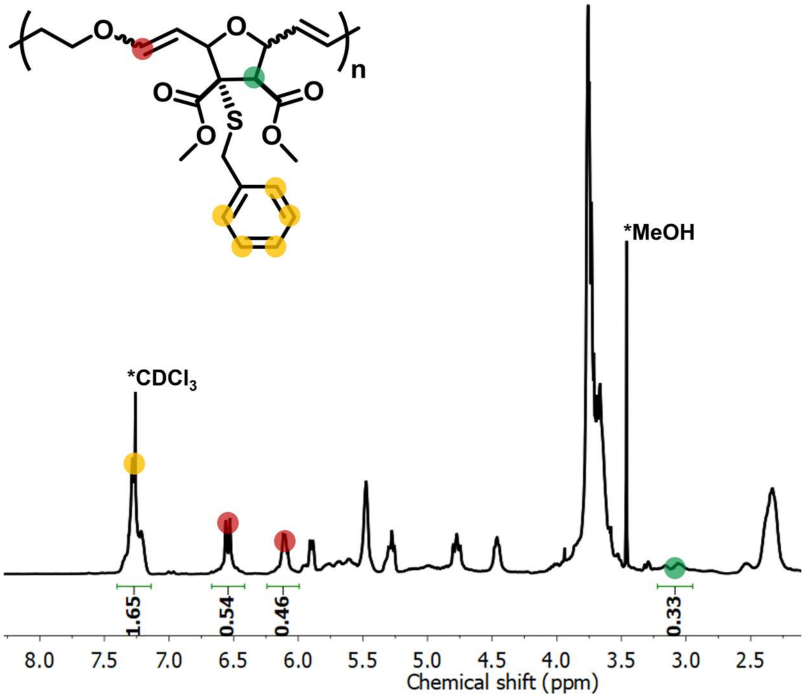


Figure S9. ^{1}H NMR spectrum of P6 in CDCl$_3$ at 25 °C. The signals attributed to vinylic proton (highlighted in red) and the methine proton (highlighted in green) were used to estimate the degree of functionalization (33%) upon thia-Michael addition.

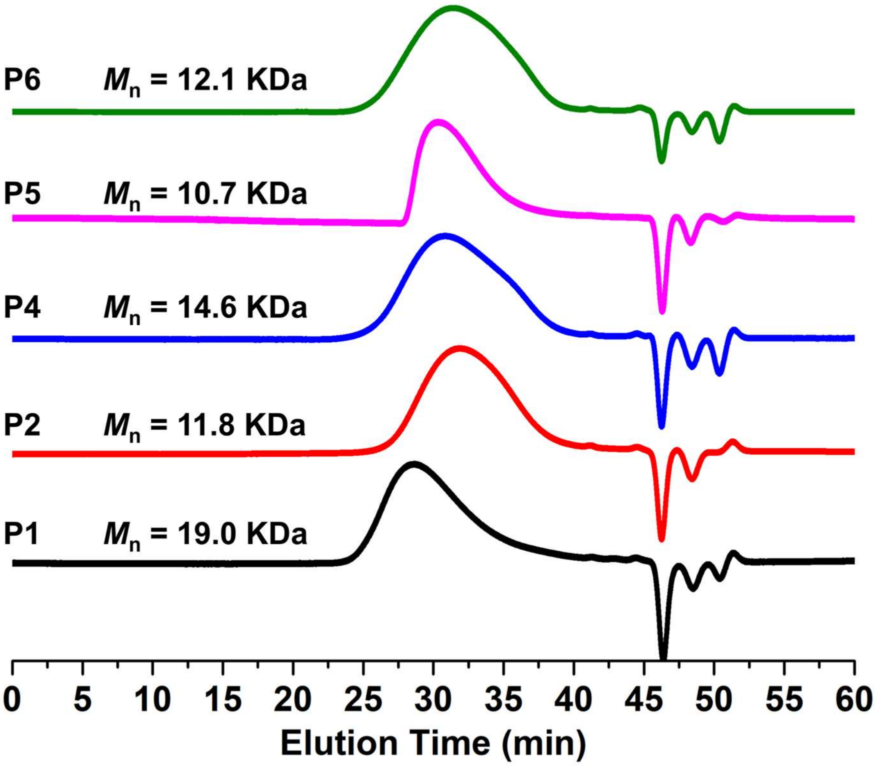


Figure S10. SEC traces of P1 (Entry 5 in Table S1), P2, P4, P5, and P6.

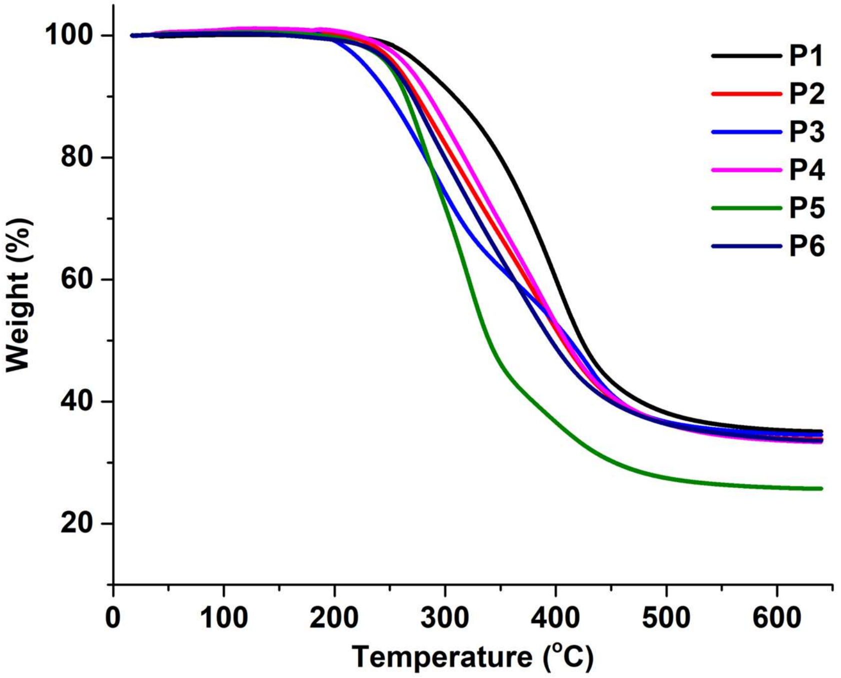


Figure S11. TGA thermograms of P1-P6.

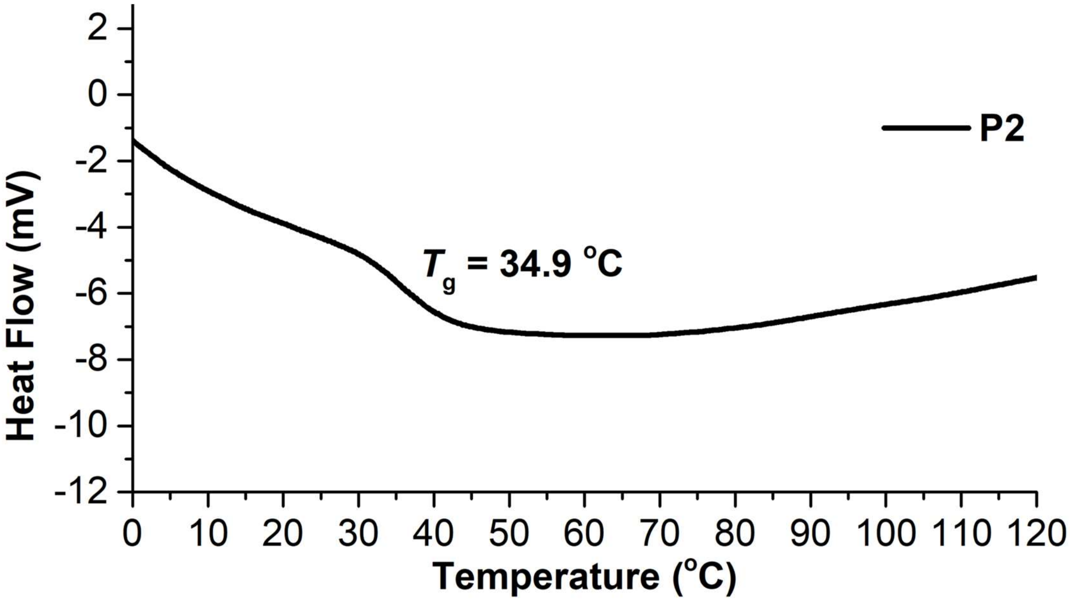


Figure S12. DSC thermogram of P2. T_g value was determined by the midpoint of the sigmoidal change in the heat capacity.

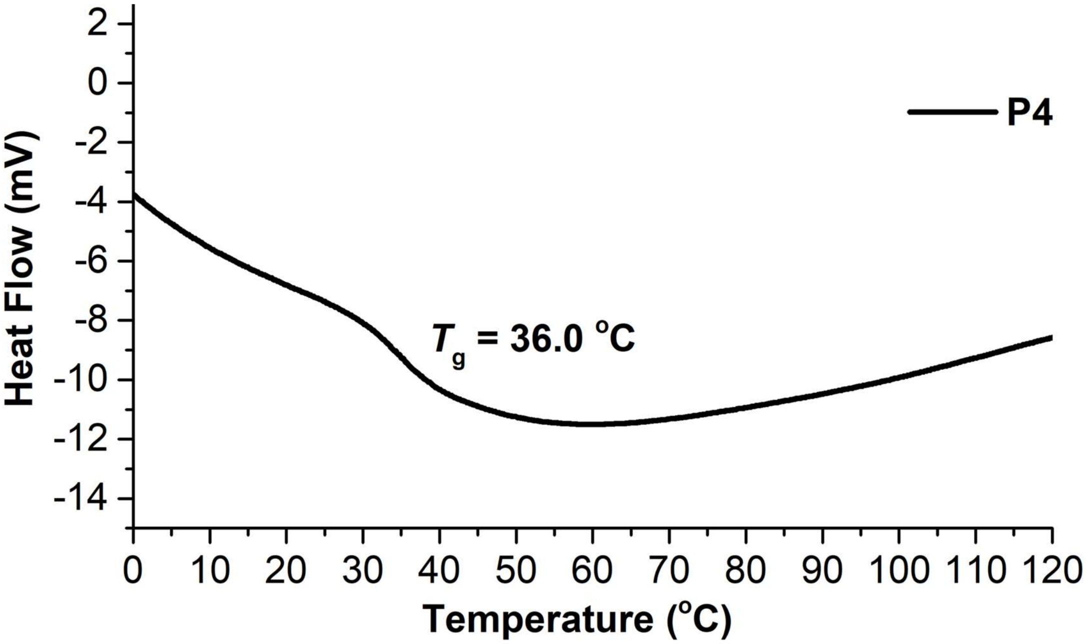


Figure S13. DSC thermogram of P4. T_g value was determined by the midpoint of the sigmoidal change in the heat capacity.

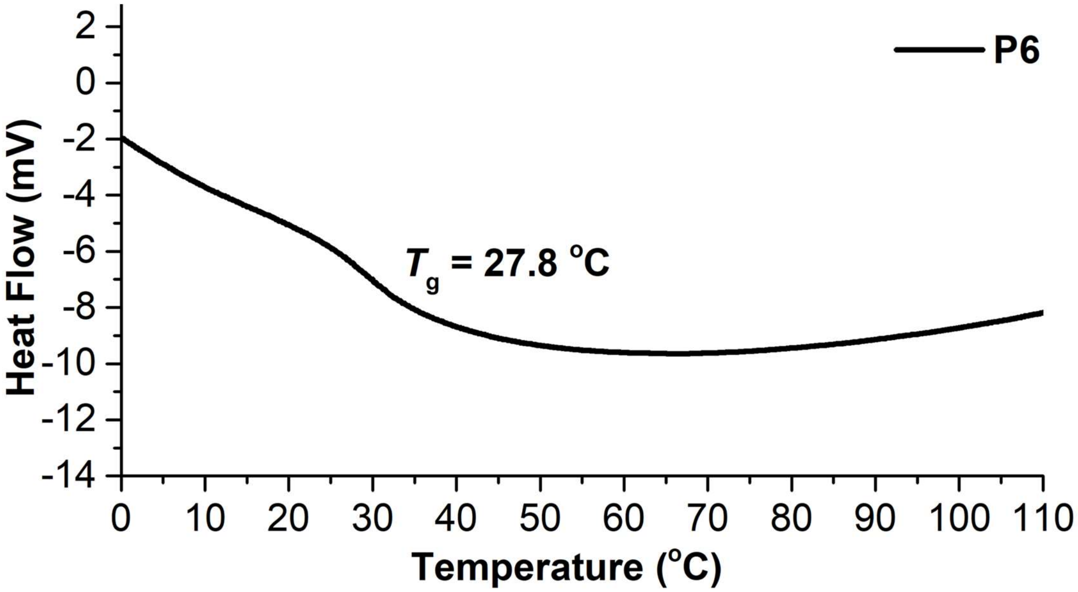


Figure S14. DSC thermogram of P6. T_g value was determined by the midpoint of the sigmoidal change in the heat capacity.

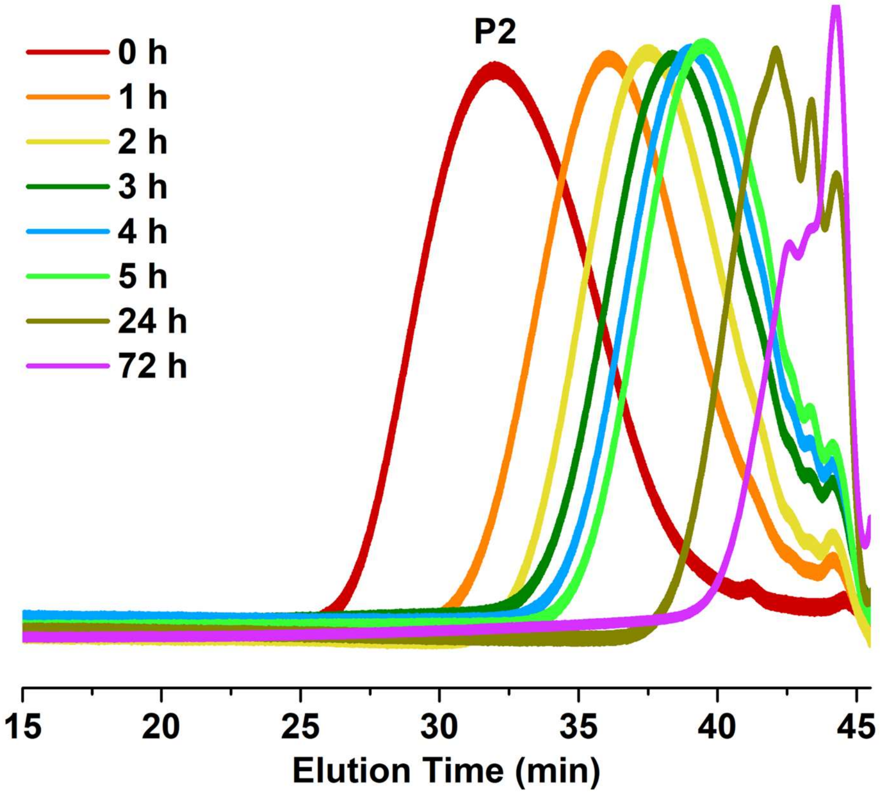


Figure S15. SEC traces of P2 as a function of the degradation time. The concentrations of HCl and water in THF are 0.02 and 1.1 M, respectively.

5. References

1. J. D. Feist and Y. Xia, *J. Am. Chem. Soc.*, 2020, **142**, 1186-1189.