Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Bulk Depolymerization of Graft Polymers Based on *Trans*-Cyclobutane-Fused Cyclooctene

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Table of Contents

I. Materials and Methods

1. Materials

All reagents and solvents were purchased from commercial vendors and used without further purification unless noted otherwise. Triphenylphosphine (PPh_3) was recrystallized from toluene prior to use. Polyethylene Glycol Monomethyl Ether 4000 purchased from TCI America contains a significant amount of polyethylene glycol impurity which resulted in a concerining amount of difunctional crosslinker (confirmed by MALDI-ToF MS) and therefore Polyethylene Glycol Monomethyl Ether 5000 was used instead in this study. Silicycle F60 (230-400 mesh) silica gel was used to perform column (flash) chromatography. Dialysis was conducted using Spectra/Por® 4 Dialysis Tubing (12-14 kDa MWCO).

2. General ROMP procedures

In a nitrogen-filled MBraun Unilab glovebox, MM (100 equiv to G1) and PPh_3 (30 equiv to G1) were dissolved in degassed THF before initiation by adding a G1 stock solution, with the target MM concentration to be 25 mM. Polymerization was allowed to proceed at ambient temperature overnight before being terminated by the addition of ethyl vinyl ether (EVE). The resulting solution was precipitated in diethyl ether to remove PPh_3. The precipitate was dissolved in methanol and then dialyzed against DI water to remove any remaining small molecular weight PEG.

3. General bulk depolymerization procedures

In a 1 mL autosampler vial, 10 µL of G2 solution in DCM (5 mol% to the backbone olefin) was carefully added and let dry with the assistance of nitrogen flow to coat around the bottom of the vial. 10 mg of the graft polymer sample in the form of powder was transferred via a spatula to the bottom of the vial. The vial was brought to 100 °C and within a few minutes, the mixture of G2 and polymers turned into a clear and homogeneous melt with a reddish-orange hue (Fig. S12). A nitrogen stream was provided through the rubber septum from a needle throughout the reaction. Aliquots were taken by dipping a glass pipette into the melt and rinsing the pipette in an EVE/DCM (50/50 v/v) solution.

Fig. S1. A representive picture of a homogeneous melt mixture of ***g*-2k** and G2 after being heated to 100 °C for 1 min.

4. Ball milling assited depolymerization

Ball milling was conducted using a Retsch Mixer Mill CryoMill at 60 Hz frequency. 20 mg of graft polymer sample was charged with 5 mol% G2 and three stainless steel balls (D = 8 mm) in a 50 mL stainless steel grinding jar and subjected to a milling cycle of on-off-on-off-on with 10-min intervals. The resulting mixture was quenched with EVE/DCM (1 mL + 1 mL).

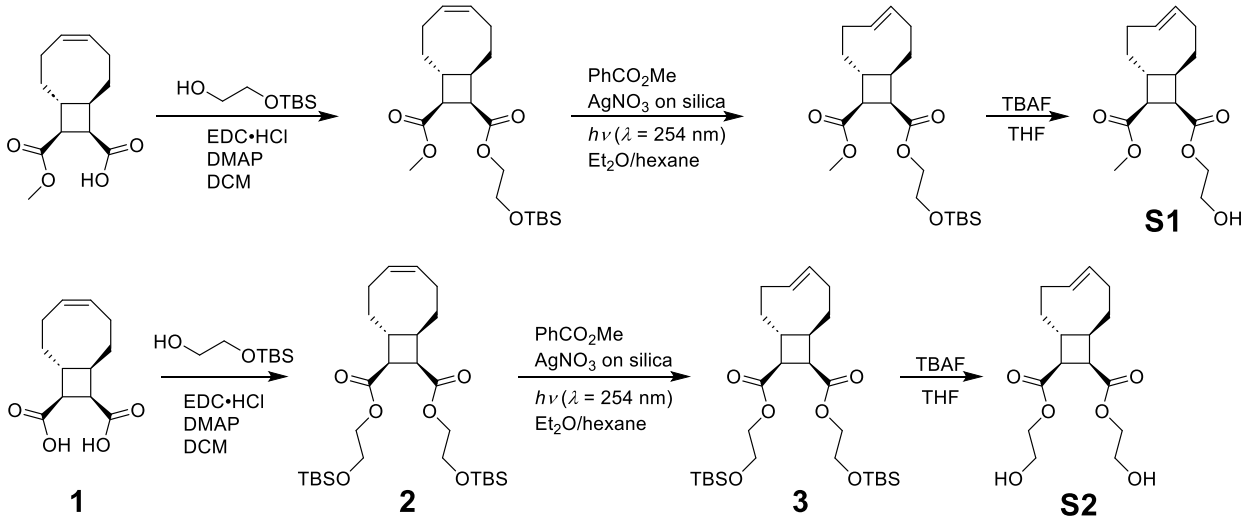
5. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H and ^{13}C NMR spectra were obtained at the University of Akron Magnetic Resonance Center using a Varian NMR 500MHz spectrometer. Chemical shifts (δ) were reported in part per million (ppm) referenced to the residual non-deuterated chloroform peak (δ = 7.26 [^{1}H] and 77.16 ppm [^{13}C]). The NMR spectra were obtained and analyzed using Agilent VnmrJ and MestReNova softwares, respectively.

6. Size-exclusion chromatography (SEC)

SEC was performed on a Tosoh EcoSEC HLC-8320GPC with two TSKgel GMHHR-M(S) analytical columns (7.8 mm ID × 30 cm, 13 μm) and one TSKgel guard column H_{HR}(S) (7.5 mm ID × 7.5 cm, 13 μm), connected in series with a built-in refractive index (RI) detector and a miniDAWN TREOS multi-angle light scattering (MALS) detector (Wyatt Technology). Experiments were run at 40 °C at a flow rate of 0.5 mL/min in $CHCl_3$ (0.25 vol% Et_3N) or in DMF (0.01 M LiBr) as the mobile phase.

II. Synthesis of Macromonomer Precursors



The macromonomer precursor **S1** was synthesized following our previous report.[1]

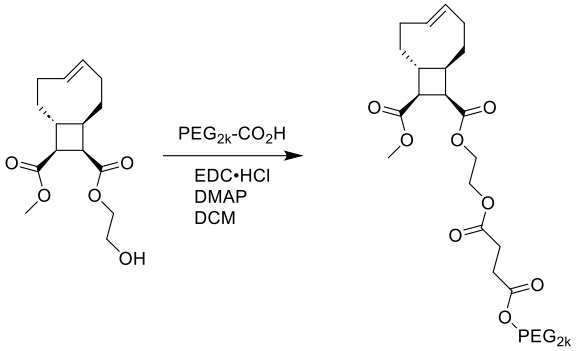
The synthesis of **S2** started from a dicaryboxylic acid **1** which was reported previously by our lab.[2] **1** (2,100 mg, 9.36 mmol, 1 equiv) was first dissolved by 100 mL anhydrous DCM in a 250 mL round-bottom flask, followed by the addition of 2-hydroxyethyl *tert*-butyldimethylsilyl ether[3] (3,632 mg, 20.6 mmol, 2.2 equiv), EDC•HCl (7,188 mg, 37.44 mmol, 4 equiv) and DMAP (114 mg, 0.936 mmol, 0.1 equiv). The mixture

was left to stir at room temperature overnight. The solution was concentrated by a rotary evaporator, taken up in ethyl acetate and washed with water and then saturated NH_4Cl solution. The organic phase was dried and eluted through a silica gel column using diethyl ether/hexane (1/4 v/v) as the eluent (R_f = 0.6). A light yellow viscous liquid **2** was obtained (2,908.8 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.72-5.50 (m, 2H), 4.21-4.04 (m, 4H), 3.84-3.72 (m, 4H), 3.40 (t, 1H), 2.88-2.78 (m, 1H), 2.70 (t, 1H), 2.46-2.36 (m, 1H), 2.30-2.19 (m, 1H), 2.18-2.10 (m, 2H), 2.10-1.99 (m, 2H), 1.66-1.57 (m, 1H), 1.33-1.24 (m, 1H), 1.24-1.17 (m, 1H), 0.91 (s, 9H), 0.90 (s, 9H) , 0.08 (s, 6H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.58, 167.10, 132.87, 129.56, 65.69, 65.38, 61.13, 52.05, 43.71, 42.86, 41.96, 39.21, 34.50, 31.56, 28.99, 25.83 25.82, 25.63, -3.60, -5.34. HRMS-ESI (m/z): calcd for $C_{28}H_{52}NaO_6Si_2^+$[M+Na]$^+$, 563.3200; found, 563.3210.

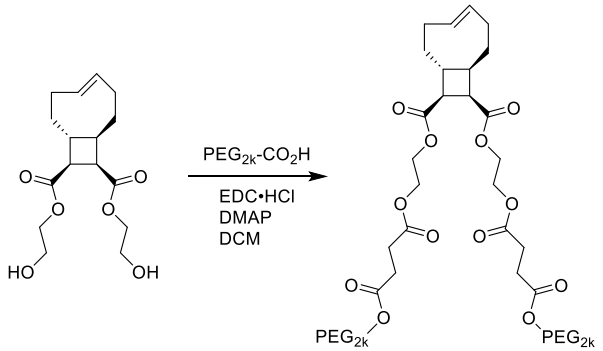
By using a flow photochemical reaction demonstrated in our previous work [1], **2** (2,908.8 mg, 5.38 mmol, 1 equiv) and methyl benzoate (1,464 mg, 10.76 mmol, 2 equiv) were dissolved in 100 mL of degassed Et_2O/hexane (4/6 v/v) in a quartz tube. A glass column (D = 2 cm, L = 9 cm) was first filled with 10 wt.% AgNO3-impregnated silica gel (18.3 g, 10.76 mmol of $AgNO_3$, 2 equiv), with the rest of the column (downstream side of it) filled with regular silica gel to prevent $AgNO_3$ leaching, with both ends of the column plugged with cotton balls. The reaction mixture was irradiated for 17 h in a Rayonet photoreactor chamber with 16 RPR2537A lamps (λ = 254 nm), while being circulated through the abovementioned column using a metering pump. The column was dried by air stream and emptied onto a separate column which was pre-packed with a layer of regular silica gel (10 g) at the bottom and a layer of fresh $AgNO_3$-impregnated silica gel (10 g) on the top. The remaining reaction mixture was eluted through the column by 200 mL of Et_2O/hexane (4/6 v/v) to recover the *cis*-isomer reactant and methyl benzoate. The column was further purged with 500 mL of acetone to elute the *trans*-isomer. The acetone solution was dried and added by 30% NH_4OH aqueous solution, which was extracted with diethyl ether (5 x 50 mL), dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The brown crude oil was purified via flash column chromatography (diethyl ether/hexane 1/4 v/v, R_f = 0.6) to yield an oily **3** (750 mg, 26%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.86-5.68 (m, 0.26H), 5.56-5.36 (m, 1.74H), 4.17-3.96 (m, 4H), 3.82-3.65 (m, 4H), 3.36 (t, 0.87H), 3.30 (t, 0.13H), 2.68 (q, 0.13H), 2.59 (t, 1H), 2.52 (q, 0.87H), 2.40-2.26 (m, 0.26H), 2.26-2.05 (m, 3.74H), 2.05-1.91 (m, 2H), 1.86-1.75 (m, 1H), 1.66-1.53 (tm, 1H), 1.49-1.44 (m, 1H), 0.86 (s, 9H), 0.85 (s, 9H), 0.03 (s, 6H), 0.02 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.70, 172.55, 134.46, 134.43, 65.73, 65.39, 61.15, 61.07, 45.27, 43.65, 42.77, 41.93, 41.16, 35.72, 33.19, 32.98, 25.83, 18.28, -5.34. HRMS-ESI (m/z): calcd for $C_{28}H_{52}NaO_6Si_2^+$[M+Na]$^+$, 563.3200; found, 563.3212.

To a solution of **3** (750 mg, 1.39 mmol, 1 equiv) in THF (3 mL) was added tetrabutylammonium fluoride (TBAF) (1 M solution in THF, 2.8 mL, 2 equiv). TLC suggested an instant complete consumption of **3** upon mixing of all components. The mixture was then diluted with ethyl acetate, washed with DI H_2O (x3) and brine, and filtered through Na_2SO_4 over a cotton ball. The solution was concentrated and directly loaded on a silica column and eluted with acetone/hexane (3/7 v/v) to yield a slightly yellow oil **S2** (430 mg, 100%). The product was kept as a 7.65 wt.% DCM solution preserved with 24 mg BHT. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.90-5.74 (m, 0.26H), 5.57-5.45 (m, 1.74H), 4.36-4.10 (m, 4H), 3.89-3.74 (m, 4H), 3.47 (t, 0.87H), 3.42 (t, 0.13H), 2.79 (q, 0.13H), 2.72 (t, 1H), 2.57 (q, 1H), 2.44-2.35 (m, 0.52H), 2.30-2.10 (m, 5.48H), 2.10-2.00 (m, 2H), 1.85-1.77 (m, 1H), 1.70-1.59 (m, 1H), 1.58-1.47 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.62, 173.19, 134.48, 134.38, 66.22, 66.19, 61.00, 45.46, 43.99, 42.76, 41.94, 41.11, 35.78, 33.17, 32.95, 30.32. HRMS-ESI (m/z): calcd for $C_{16}H_{24}NaO_6^+$ $[M+Na]^+$, 335.1471; found, 335.1456.

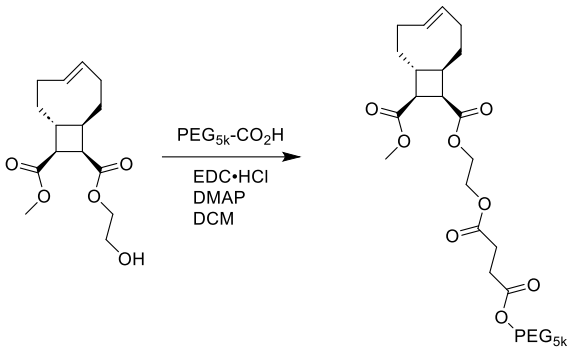
III. Synthesis of Macromonomers



MM-2k was prepared according to our previous report [1].



MM-2-2k was prepared similarly. Briefly, PEG2k-CO_2H (1,514 mg, 0.72 mmol, 3.33 equiv) was dissolved in 5 mL DCM, followed by the addition of **S2** (67.5 mg, 0.216 mmol, 1 equiv), EDC•HCl (166 mg, 0.864 mmol, 4 equiv) and DMAP (26 mg, 0.216 mmol, 1 equiv). The next day, the solution was washed with saturated NH_4Cl solution and brine sequentially. The DCM phase was concentrated on a rotary evaporator and precipitated into cold diethyl ether to collect a white solid (750 mg, 48%).



MM-5k was prepared silimiarly to **MM-2k**. A white solid was obtained at 75% yield.

IV. G2 Stability

To test and simplify characterizing the decomposition of G2 through NMR analysis of the benzylidene proton peak, we mimicked the depolymerization conditions by subjecting a mixture of G2 in PEG 2k (2 wt.%) to 100 °C for 7 days. The NMR comparison before and after the heat treatment showed that one third of G2 remained intact.

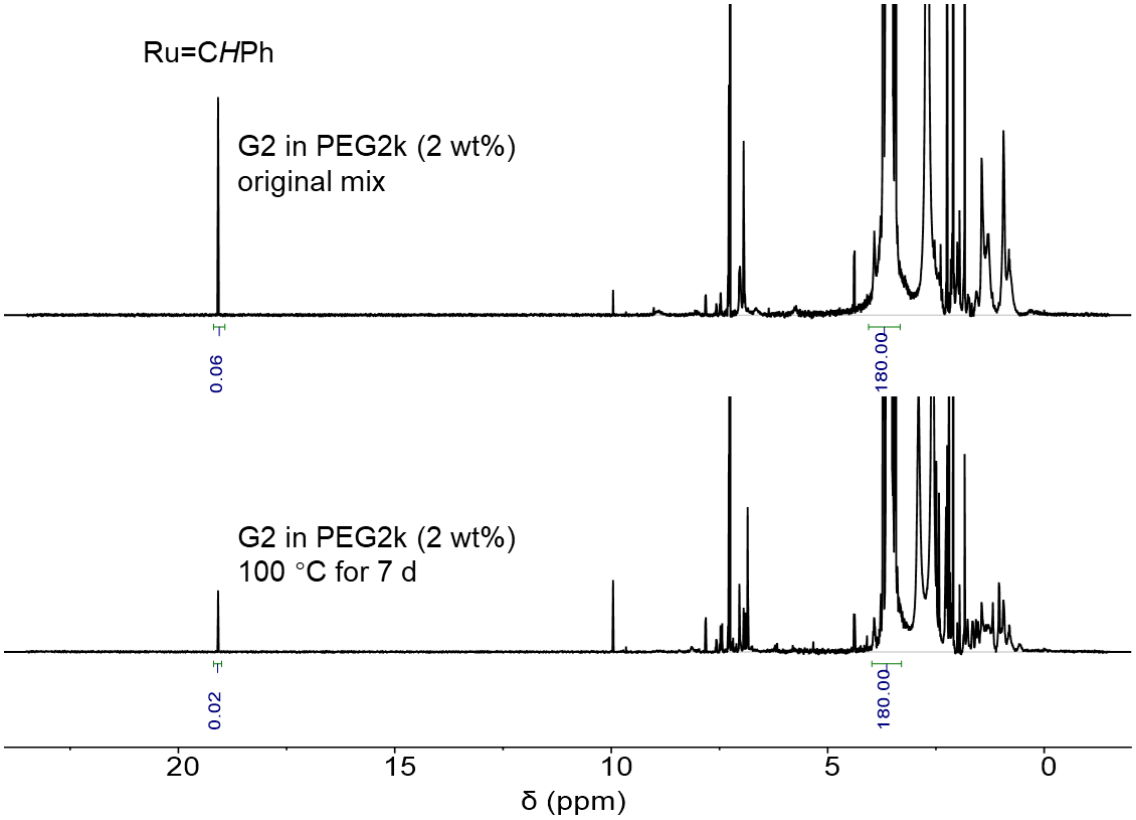


Fig. S2. Decomposition of G2 in PEG at 100 °C for 7 days.

V. Confirmation of Depolymerization Equililibrium

To confirm the equilibrium state, we subjected ***g*-2-2k** to 5 mol% G2 at 100 °C for 7 days and added another 5 mol% G2. NMR and SEC analyses were conducted on the samples before the second addition of G2 on day 8 and after the addition on day 15. The results showed nearly identical components and suggested that the depolymerization equilibrium had been established before the second addition of G2.

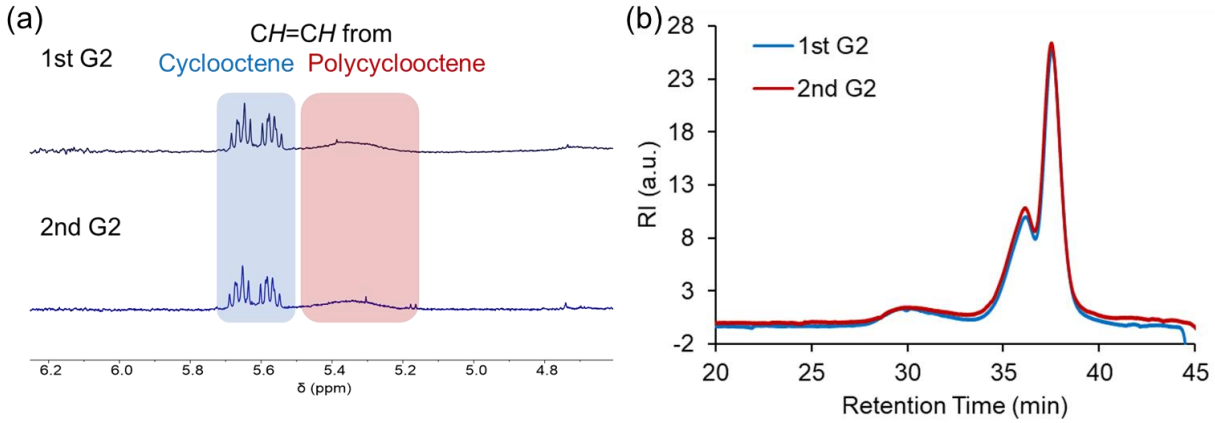


Fig. S3. (a) NMR and (b) SEC analyses of depolymerization of ***g*-2-2k** before and after a second addition of G2.

VI. Supplimentary Figures

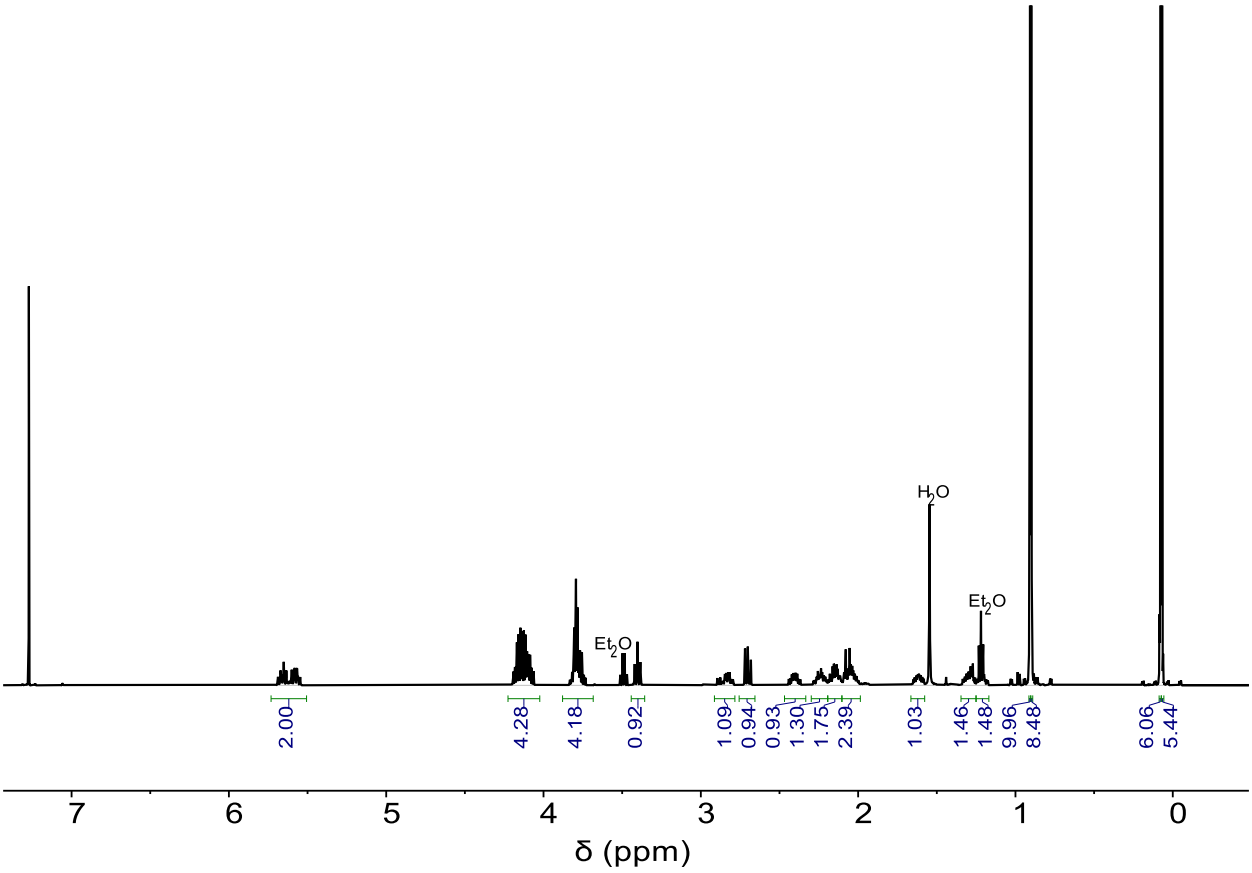


Fig. S4. ^{1}H NMR spectrum of **2**.

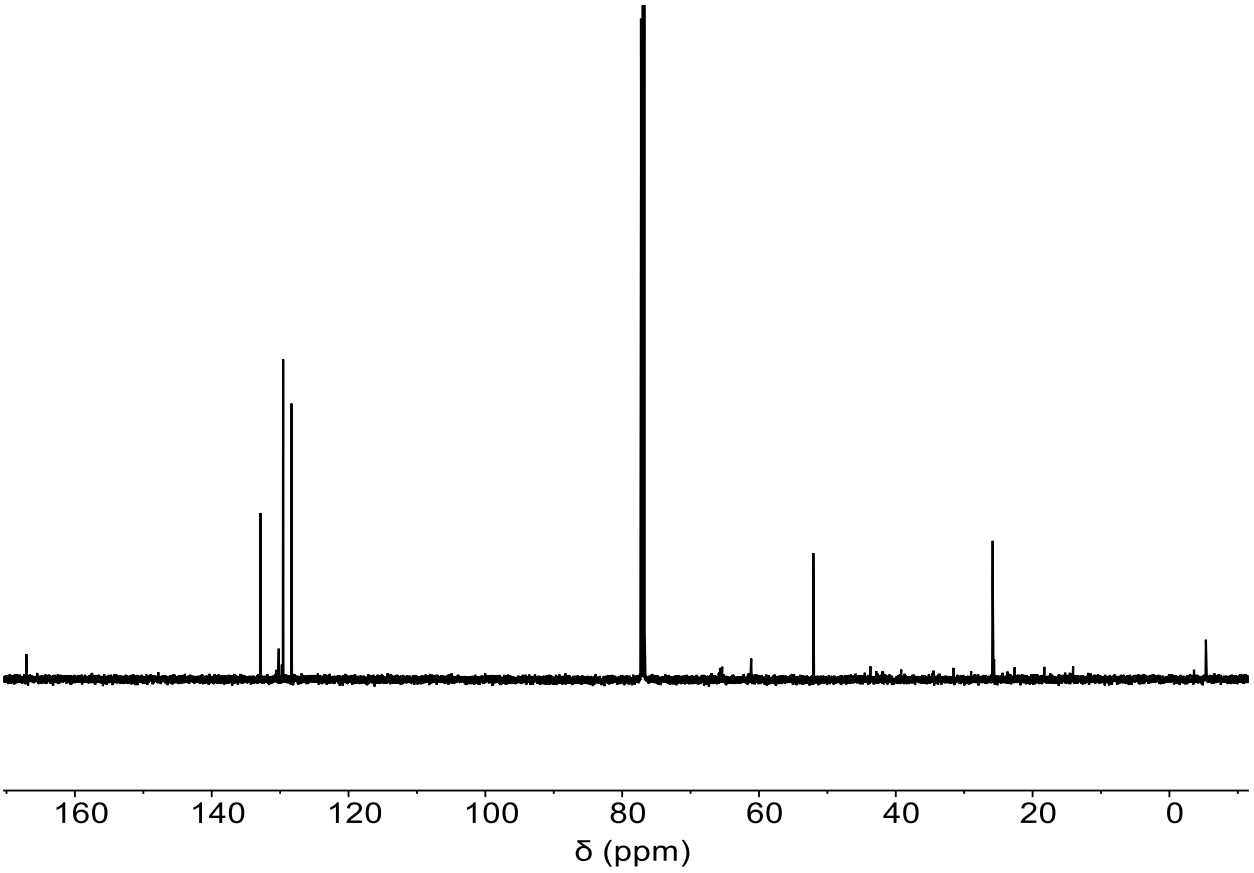


Fig. S5. ^{13}C NMR spectrum of **2**.

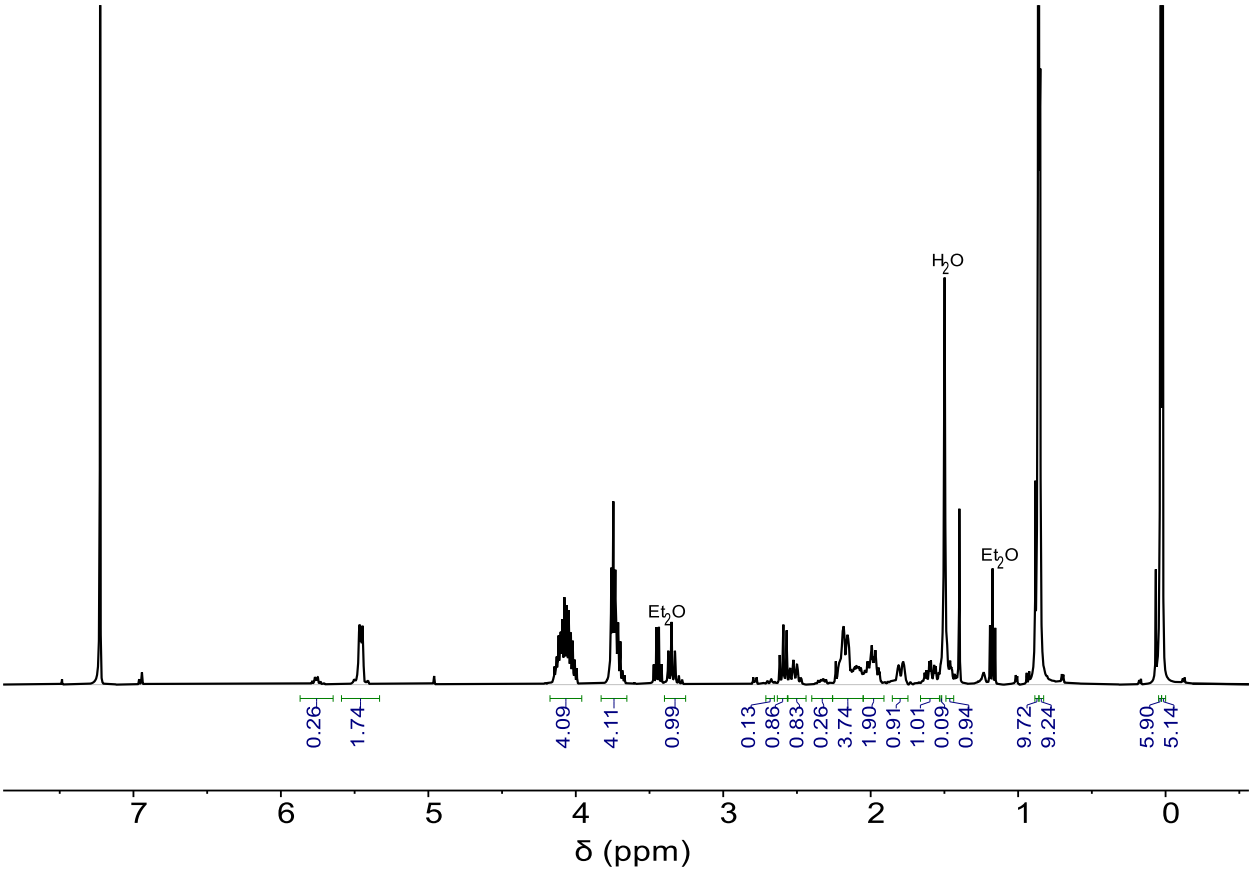


Fig. S6. ^{1}H NMR spectrum of **3**.

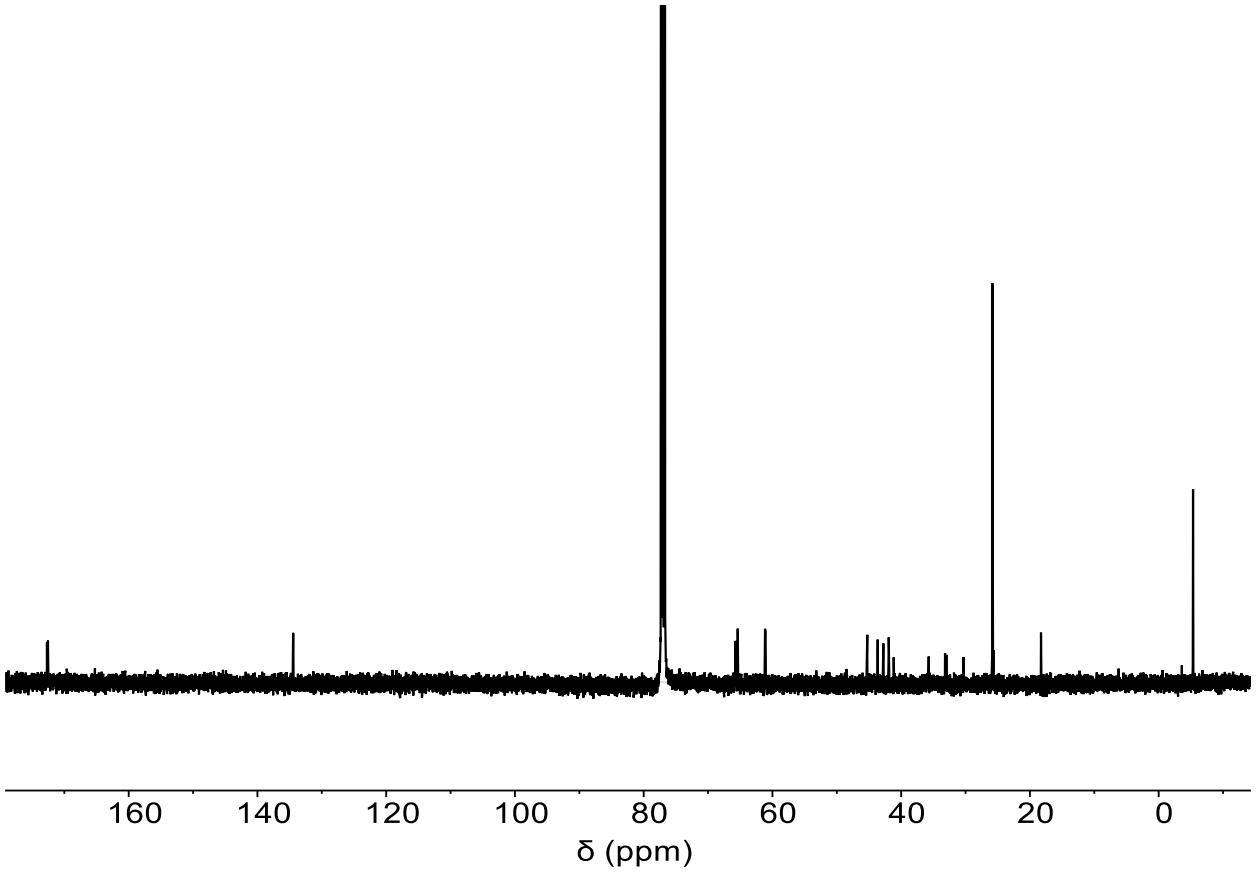


Fig. S7. ^{13}C NMR spectrum of **3**.

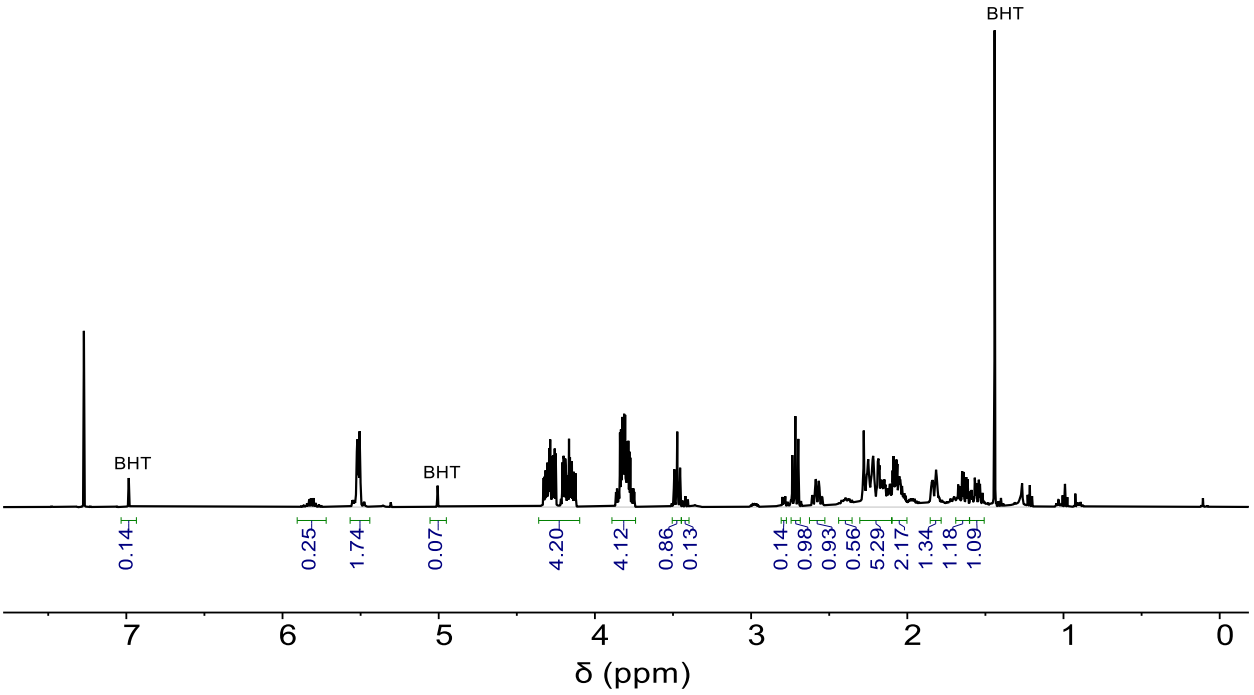


Fig. S8. ^{1}H NMR spectrum of **S2**.

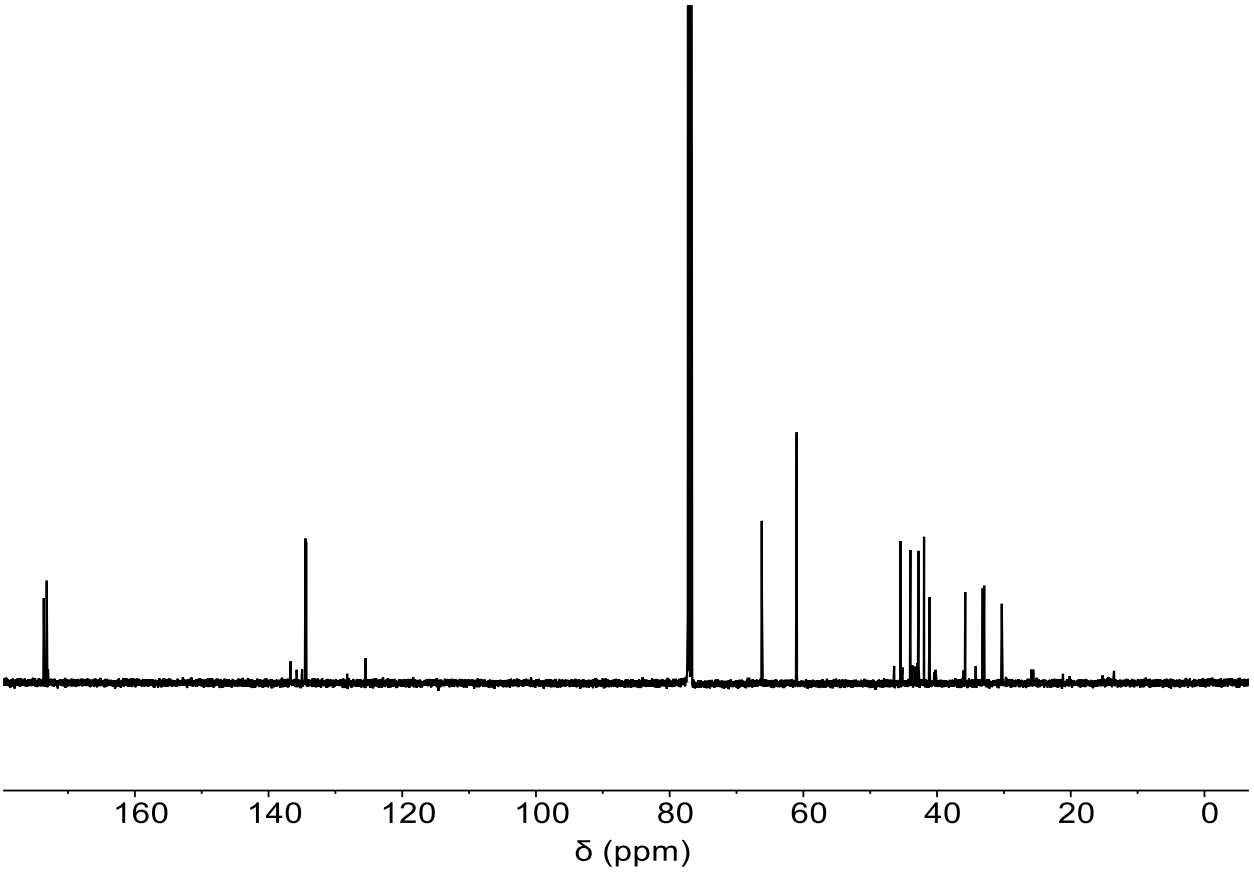


Fig. S9. ^{13}C NMR spectrum of **S2**.

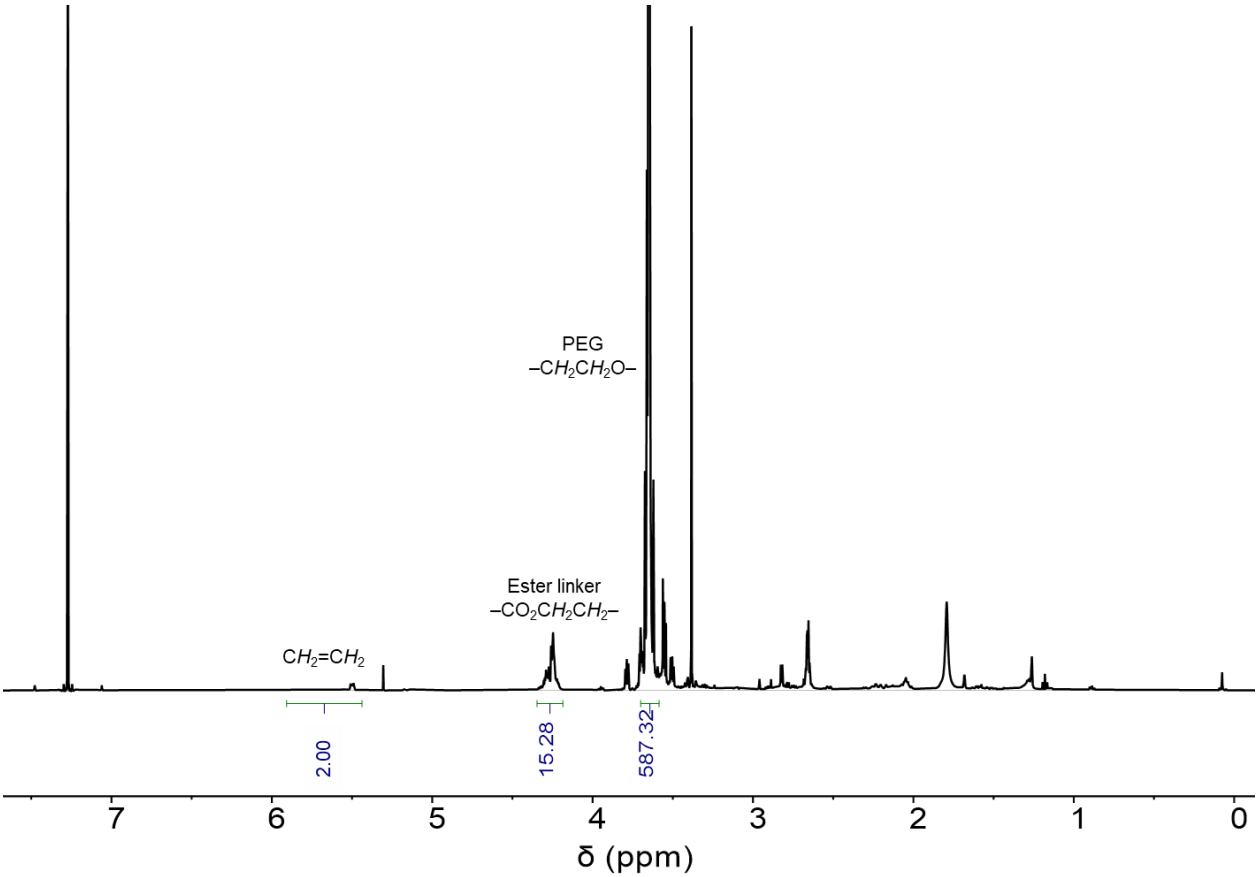


Fig. S10. ^{1}H NMR spectrum of **MM-2-2k**.

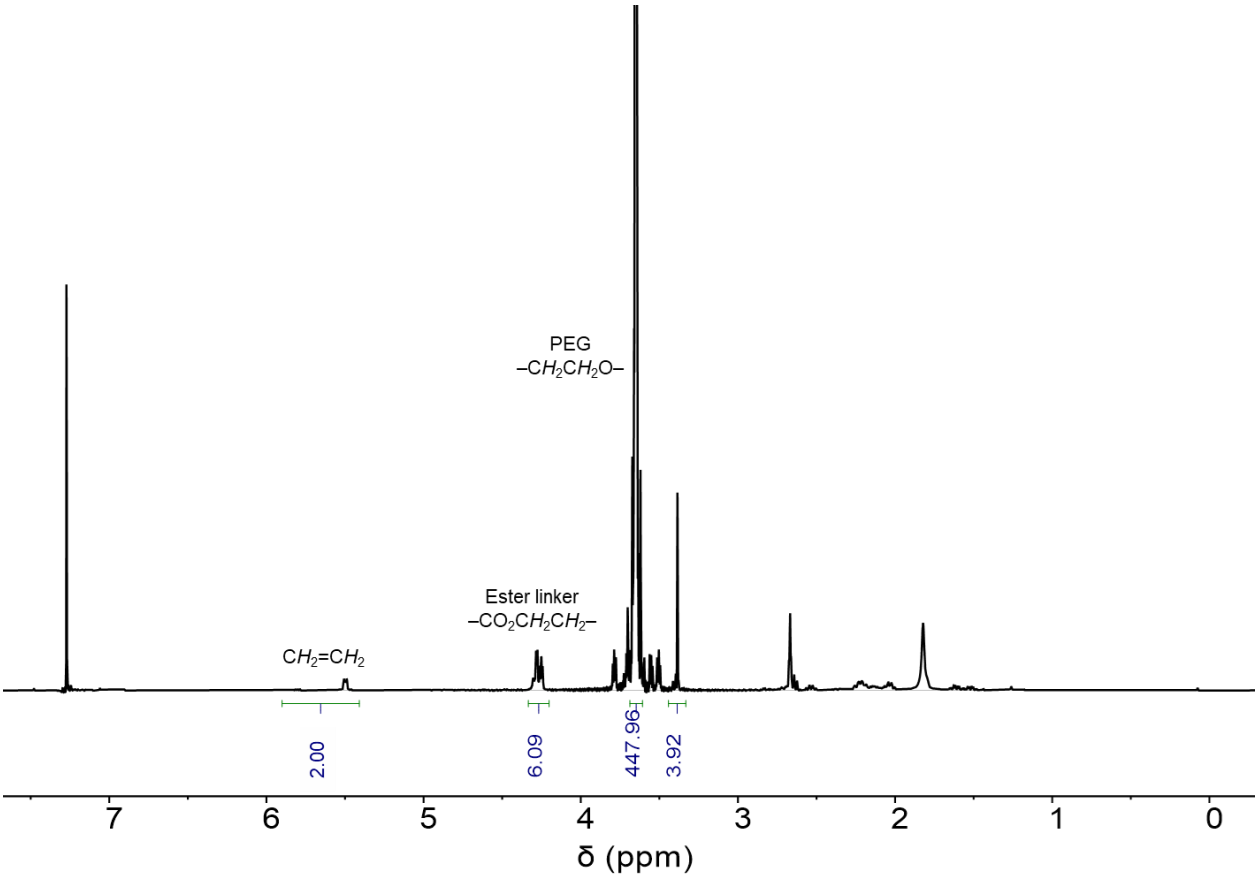


Fig. S11. ^{1}H NMR spectrum of **MM-5k**.

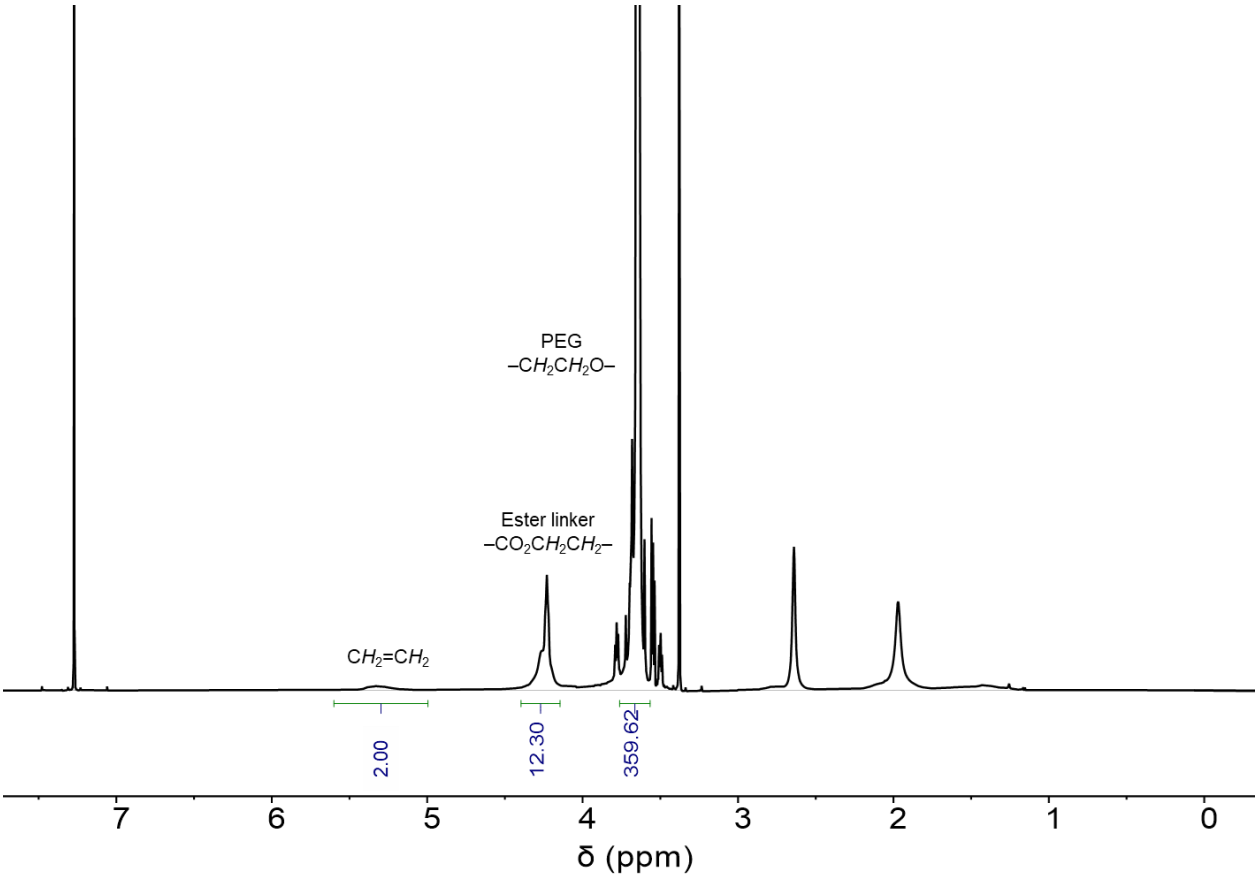


Fig. S12. ^{1}H NMR spectrum of ***g*-2-2k**.

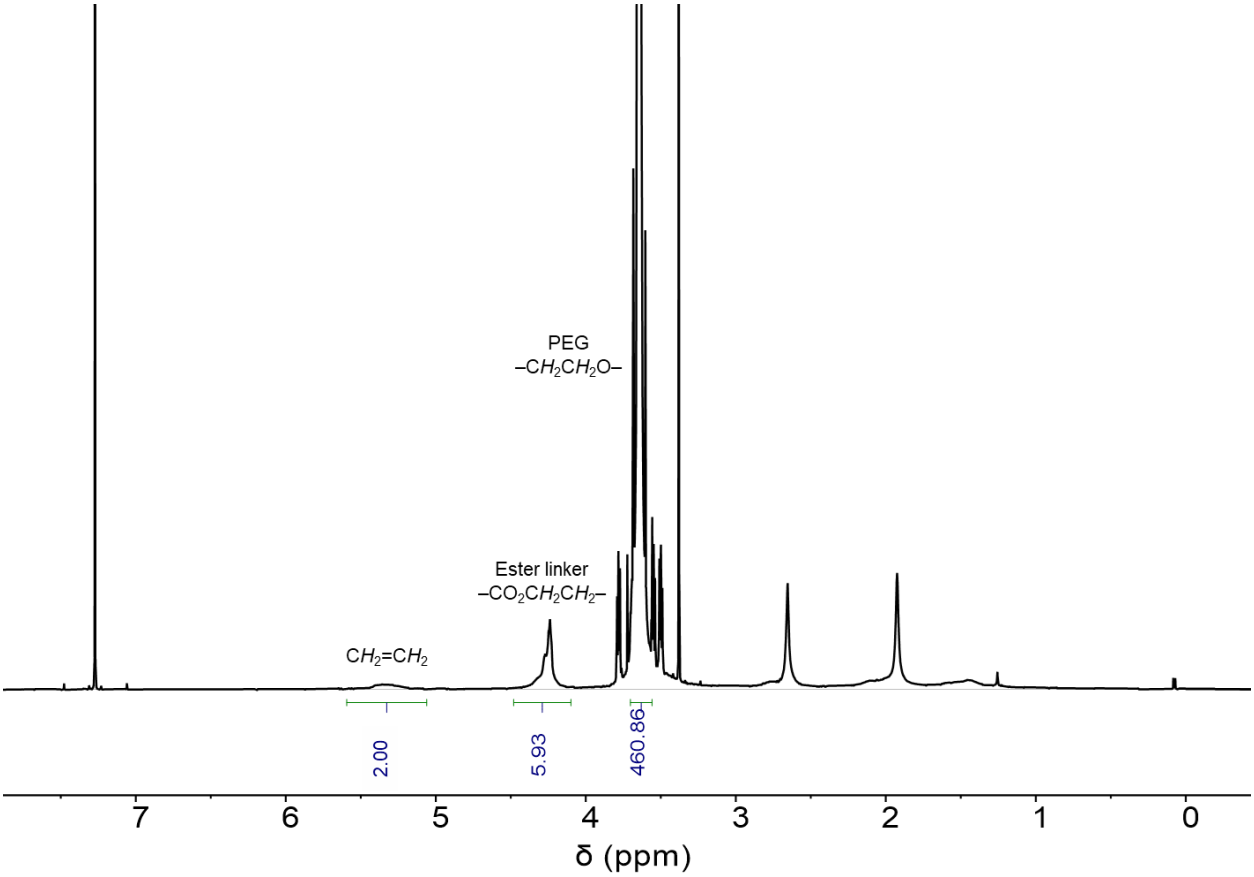


Fig. S13. ^{1}H NMR spectrum of ***g*-5k**.

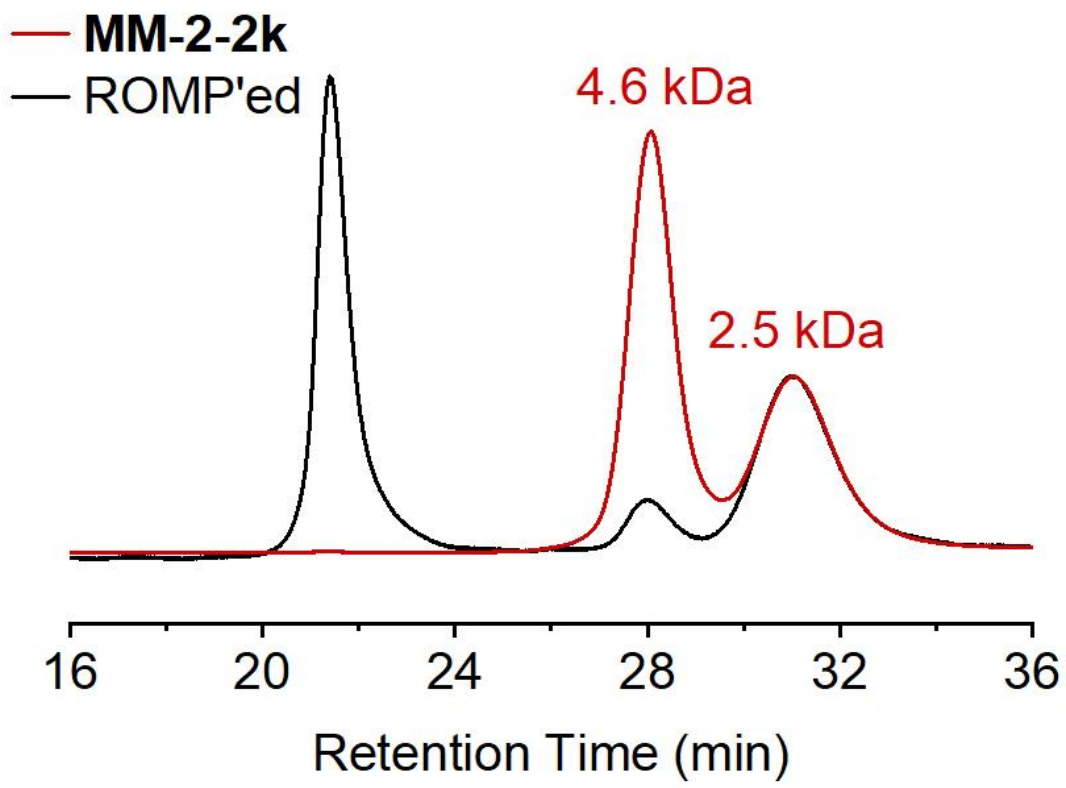


Fig. S14. **MM-2-2k** and crude mixture after ROMP for 13 h.

References

1. Z. Wang, S. Yoon and J. Wang, *Macromolecules*, 2022, **55**, 9249-9256.
2. D. Sathe, J. Zhou, H. Chen, H.-W. Su, W. Xie, T.-G. Hsu, B. R. Schrage, T. Smith, C. J. Ziegler and J. Wang, *Nat. Chem.*, 2021, **13**, 743-750.
3. J. D. Lewicky, M. Ulanova and Z. H. Jiang, *Carbohydr. Res.*, 2011, **346**, 1705-1713.