Supporting Information for:

Poly(ethyl glyoxylate)-derived self-immolative elastomers

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General Methods and Materials

General Materials. Ethyl vinyl ether, 4,7,10-trioxa-1,13-tridecanediamine, trifluoroacetic acid, trichloroacetic acid, trifluoroacetic anhydride, CH_2Cl_2 and NEt_3 were obtained from Millipore Sigma (Mississauga, Canada). Ethyl glyoxylate in toluene solution (50% w/w) and hydrochloric acid (6N in water) was obtained from Fisher Scientific (Ottawa, Canada). 4,5-Dimethoxy-2-nitrobenzyl alcohol was obtained from AK scientific (CA, United States). Triphenylmethanol was obtained from TCI (Tokyo, Japan). CH_2Cl_2 and NEt_3 were distilled over CaH_2 under a nitrogen atmosphere before use. Ethyl glyoxylate was purified over P_2O_5 as previously reported.[1] All other chemicals were of reagent grade and were used without further purification.

General Methods. ^{1}H NMR spectra for PEtG were obtained using a 400 MHz Bruker AvIII HD instrument. NMR chemical shifts were reported in parts per million (ppm) and were calibrated against the residual solvent signal of $CDCl_3$ (7.26 ppm). ^{1}H NMR spectra for PEtG degradation studies were obtained using a 500 MHz Agilent DD2 NMR Spectrometer. NMR chemical shifts were reported in parts per million (ppm) and were calibrated against the residual solvent signal of CD_2Cl_2 (5.32 ppm). FTIR spectra were obtained with a Thermo Scientific iS50 with a Perkin Elmer UATR Single Bounce with Diamond Crystal Pike Technologies VeeMax II variable angle ATR. SEM images were taken with a FEL Quanta FEG 250 with a BF/DF STEM detector at 10kV and in low vacuum (130 Pa) and water vapor. DART-MS spectra were taken with a JEOL AccuTOF Plus 4G spectrometer. THF Size exclusion chromatography (SEC) analyses were performed using a Viscotek GPCmax VE2001 solvent module (Agilent Tech.), a Viscotek VE3580 RI detector operating at 30 °C, two sequential Agilent Polypore (300 × 7.5 mm; molar mass range 200−2,000,000 g/mol) columns, and a Polypore guard column (50 × 7.5 mm). THF (glass distilled grade) was used as the eluent and the flow rate was set to 1 mL/min. Samples were dissolved in THF at a concentration of ~5 mg/mL. Each sample was filtered through a 0.2 μm polytetrafluoroethylene syringe filter prior to injection using a 50 μL loop. Samples were run at a flow rate of 1 mL/min for 30 min at 20 °C. Molar masses as well as dispersities ($Đ$) were determined by conventional calibrations using poly(methyl methacrylate) (PMMA) standards purchased from Viscotek.

Synthesis of PEtGs

All PEtGs were synthesized using the same procedure as **8k PEtG** *(representative PEtG*

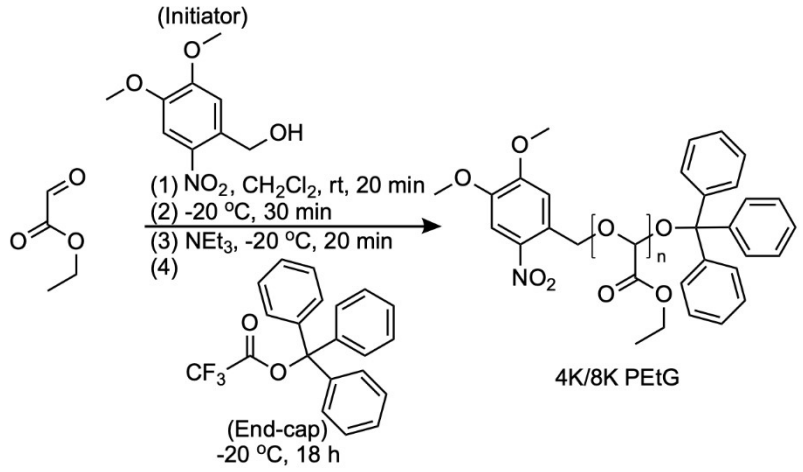

Figure S1 Synthesis of PEtG

synthesis)

Synthesis of 8k PEtG (representative PEtG synthesis). The end-capping agent trityl trifluoroacetate was first prepared as follows: to triphenylmethanol (7.65 g, 29.4 mmol, 12.0 equiv.) in a Schlenk flask under N_2 were added trifluoroacetic acid (4.49 mL, 58.8 mmol, 24.0 equiv.) and trifluoroacetic anhydride (9.90 mL, 58.8 mmol, 24.0 equiv.). The resulting yellow mixture was stirred at room temperature for 30 min, and then the volatile components were removed in vacuo using a cold trap charged with solid NaOH to consume acidic gas. The yellow solid residue was then dissolved in 5 mL of dry CH_2Cl_2. This end-cap solution was set aside. To a 250 mL flame-dried Schlenk flask under an N_2 atmosphere, 4,5-dimethoxy-2-nitrobenzyl alcohol (0.521 g, 2.45 mmol, 1.00 equiv.) was added as initiator and dissolved in 35 mL of dry CH_2Cl_2. Then, purified ethyl glyoxylate (18.3 mL, 196 mmol, 80 equiv.) was added to this flask, and the resulting solution was stirred for 20 min at room temperature. The solution was subsequently cooled to -20 °C and stirred for 20 min. Freshly distilled NEt_3 (2.73 mL, 19.6 mol, 8.00 equiv.) was then added to the polymerization flask, and the solution was stirred for another 20 min. The end-cap solution was cooled to -20 °C before being added to the reaction flask. The reaction stirred for 5 min and then was stoppered under N_2 and put in a -20 °C freezer for 24 h. Concentration of the crude polymerization mixture under vacuum was followed by precipitation in 500 mL of methanol:water (10:1), yielding 15.3 g of pure polymer residue as a tacky solid, which was collected by decanting off the supernatant and concentrating under vacuum. Yield = 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 – 1.37 (m, 302H), 4.11 – 4.38 (m, 192H), 5.52 – 5.69 (m, 89H), 7.21 – 7.52 (m, 16H), 7.73 – 7.74 (m 1H). SEC: M_n = 7.9 kg/mol, M_w = 11.7 kg/mol, $Đ$ = 1.49.

Synthesis of 5k PEtG. This polymer was synthesized by the same method as 8k PEtG with the following reagent quantities: 4,5-dimethoxy-2-nitrobenzyl alcohol (0.104 g, 4.90 mmol, 1.00

equiv), purified ethyl glyoxylate (18.3 mL, 196 mmol, 40 equiv.), triphenylmethanol (15.31 g, 58.8 mmol, 12.0 equiv.), trifluoroacetic acid (8.98 mL, 118 mmol, 24.0 equiv.) and trifluoroacetic anhydride (19.8 mL, 118 mmol, 24.0 equiv). Yield = 13.5 g, 67.5%. %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 – 1.40 (m, 167H), 4.11 – 4.39 (m, 107H), 5.52 – 5.69 (m, 53H), 7.21 – 7.52 (m, 16H), 7.73 – 7.74 (m 1H). SEC: M_n = 4.7 kg/mol, M_w = 7.6 kg/mol, $Đ$ = 1.63.

Synthesis of crosslinked network. 5k poly(ethyl glyoxylate) (1.54 g, 0.151 mmol) was dissolved in minimal anhydrous dioxane (0.77 mL) on a shaker in a 1 dram vial for 2 hours or until fully dissolved. Then 10 mole percent of 4,7,10-trioxa-1,13-tridecanediamine (0.136 g, 0.299 mL, 0.619 mmol) relative to ethyl ester moieties as determined by M_n of the SEC was added. The solution was immediately mixed using a 1 mL syringe for ~60 s and 0.7 mL of the resulting solution was added to each of the Teflon molds. The mold was left in the hood under ambient conditions to cure overnight. The cured network was then dried in a vacuum oven for 4 h at 50 °C. The PEtG was covered with aluminum foil throughout to avoid degradation though UV light exposure.

Calculation for 10 mol percent diamine to ethyl ester

Molar mass of PEtG from SEC = 4650 g/mol

Subtract weight of endcaps: 4650 g/mol - 455.29 g/mol = 4194.71g/mol

Divide by the weight of the repeat unit to get ethyl esters per polymer strand:

$$\frac{4194.71 g/mol}{102.03\ g/mol} = 41.11$$

Multiply the number of moles of polymer by the number of ethyl esters:

0.151 mmol * 41.11= 6.19 mmol ethyl ester

Multiply by 0.1 to get 10%: 6.189 * 0.1= 0.619 mmol of diamine added

Mechanical testing methods

Material preparation for tensile testing. To create a sample for tensile testing the material was removed from the mold (3 identical wells each with a width of 14 mm, length of 37 mm, and depth of 3 mm) and cut into strips (figure S2F) using our 3D printed jig and razor blades. The ends were also trimmed to remove the thicker portion created by surface tension drawing the

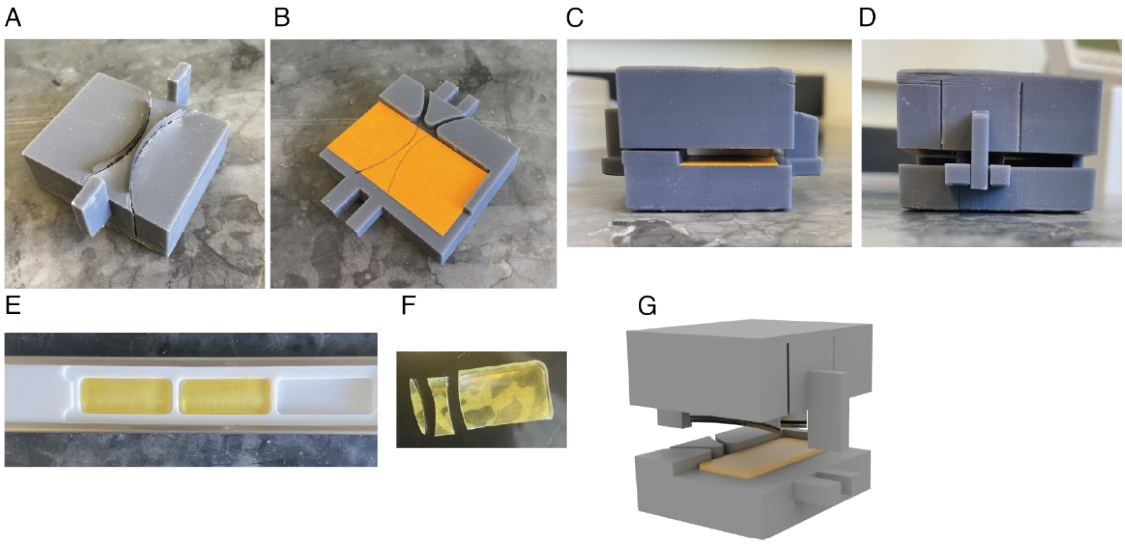

Figure S2 Picture of the (A) top of the jig with razor blades (B) bottom of the jig, top and bottom together from the (C) side and (D) front. Picture of the gels (E) in the mold and (F) after being cut. (G) 3D rendering of the jig with a sample (orange) ready to be cut

polymer solution higher in the edge of the mold.

Mechanical studies. Once the sample was prepped and its dimensions double checked, it was mounted on the Cell Scale Univert mechanical tester, using lightweight spring clamps. The top was mounted first then the instrument was adjusted to create a gap of 4.5 mm. For pull to break tests, the instrument was set to move at 0.2 mm/s. For cycling tests, the instrument was set to preload at 0.04 N and then strain to 20% over 4.5 s and then recover over 20 s and rest for another 20 s before repeating 10 times. For stress relaxation tests, the instrument was set to strain to 10% hold for 100 s and then strain to 20% and hold for another 100 s.

UV degradation studies. The crosslinked or monoamine reacted material was held with a glass microscope slide between two Kessil KSPR160L-370-G2 UV lamps at 100 percent power and an average intensity of 137mW/cm^2.

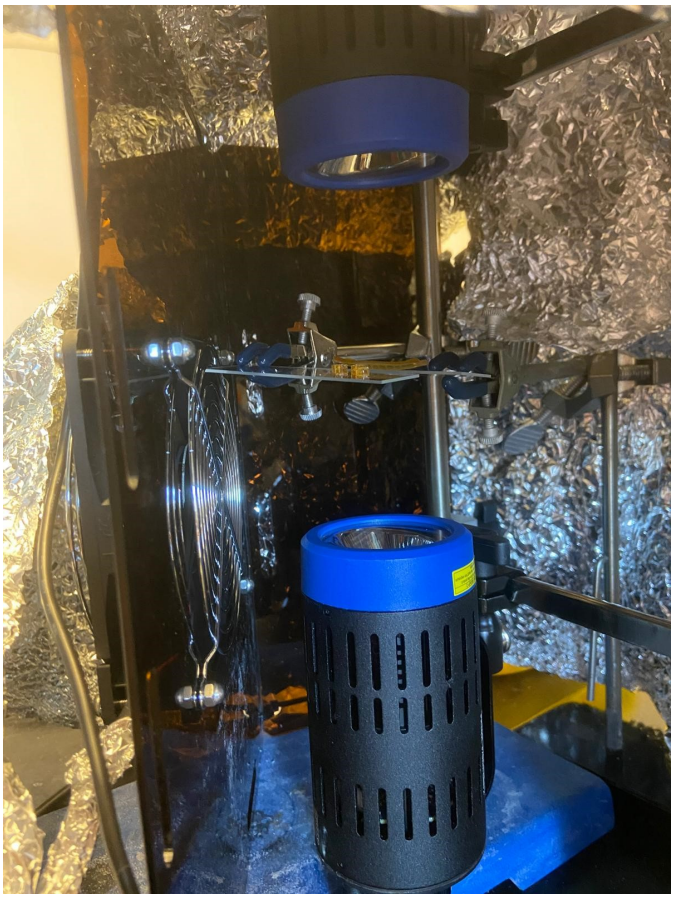

Figure S3. PEtG material held between two UV lamps

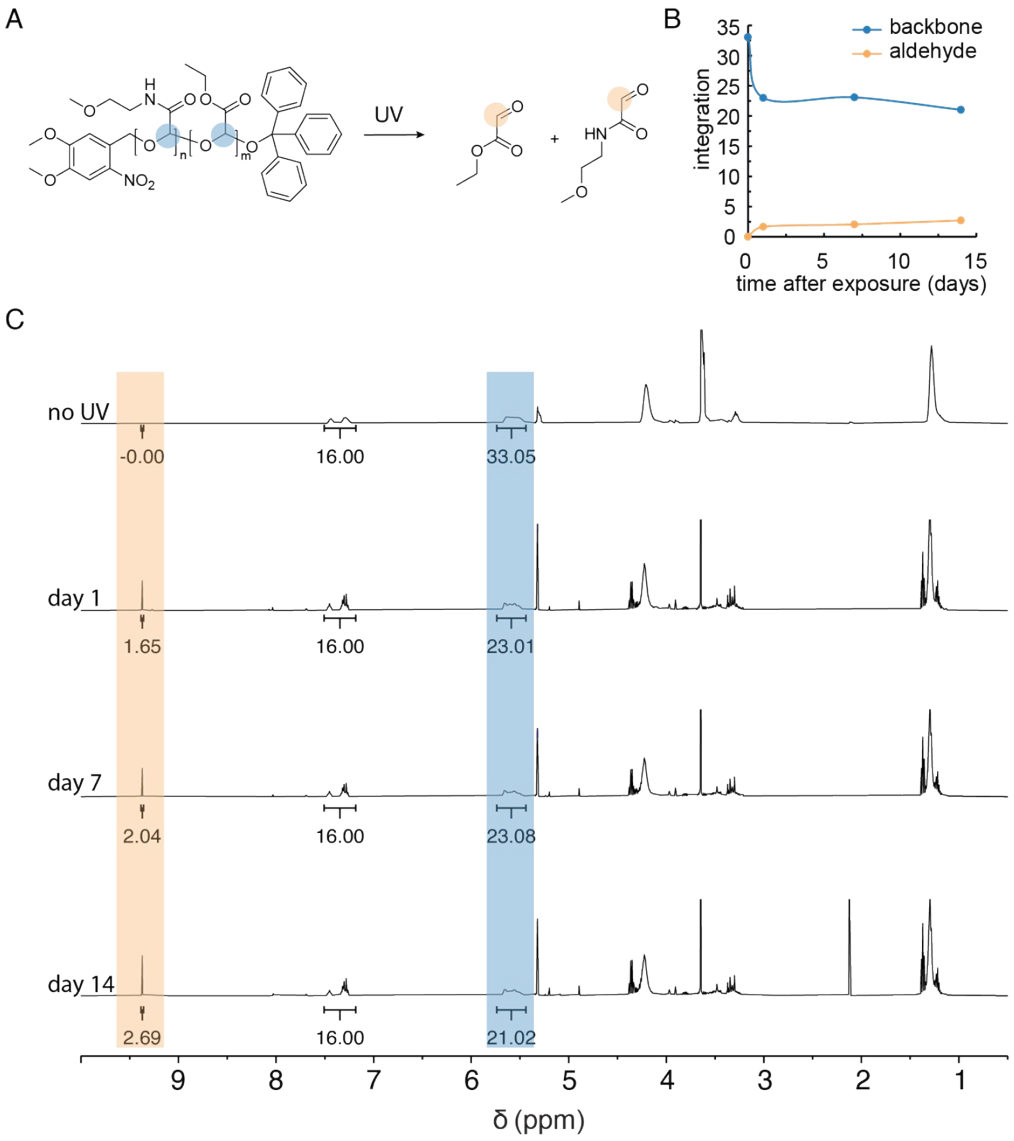

Figure S4. (A) Depolymerization of PEtG with appended monoamine. (B) Integration of aldehyde and back bone peaks over the course of 14 days and (C) full qNMR spectra (CD_2Cl_2, 500 MHz) showing the appearance of the aldehyde peak

Acid degradation studies. A small piece of the crosslinked material was submerged into acetone and acid was added to give a total volume of 1 mL. For example, for 10% TFA the PEtG was submerged in 0.9 ml of acetone and 0.1 mL of TFA was added. For the 1 M HCl, I started with the crosslinked PEtG in 0.83 mL of acetone and 0.17 mL of 6 M HCl was added.

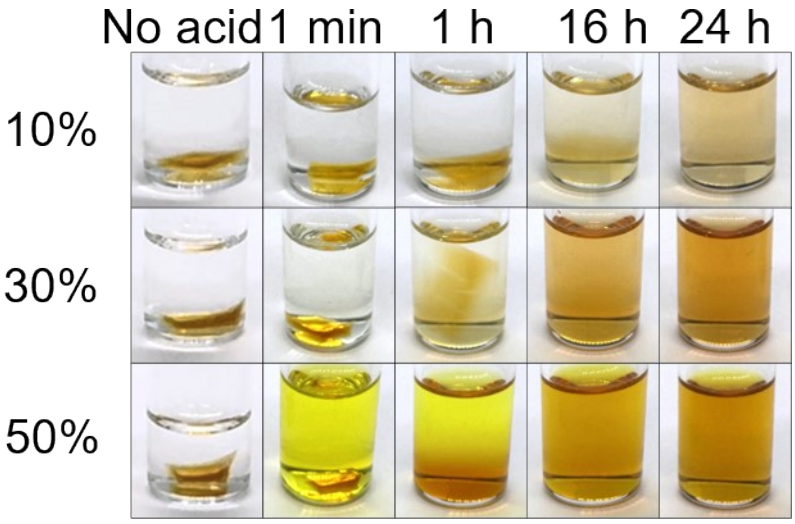

Figure S5. Pictures of 5k PEtG network with 10 mole percent crosslinker submerged in 10%, 30% or 50% trifluoracetic acid up to 24 hours

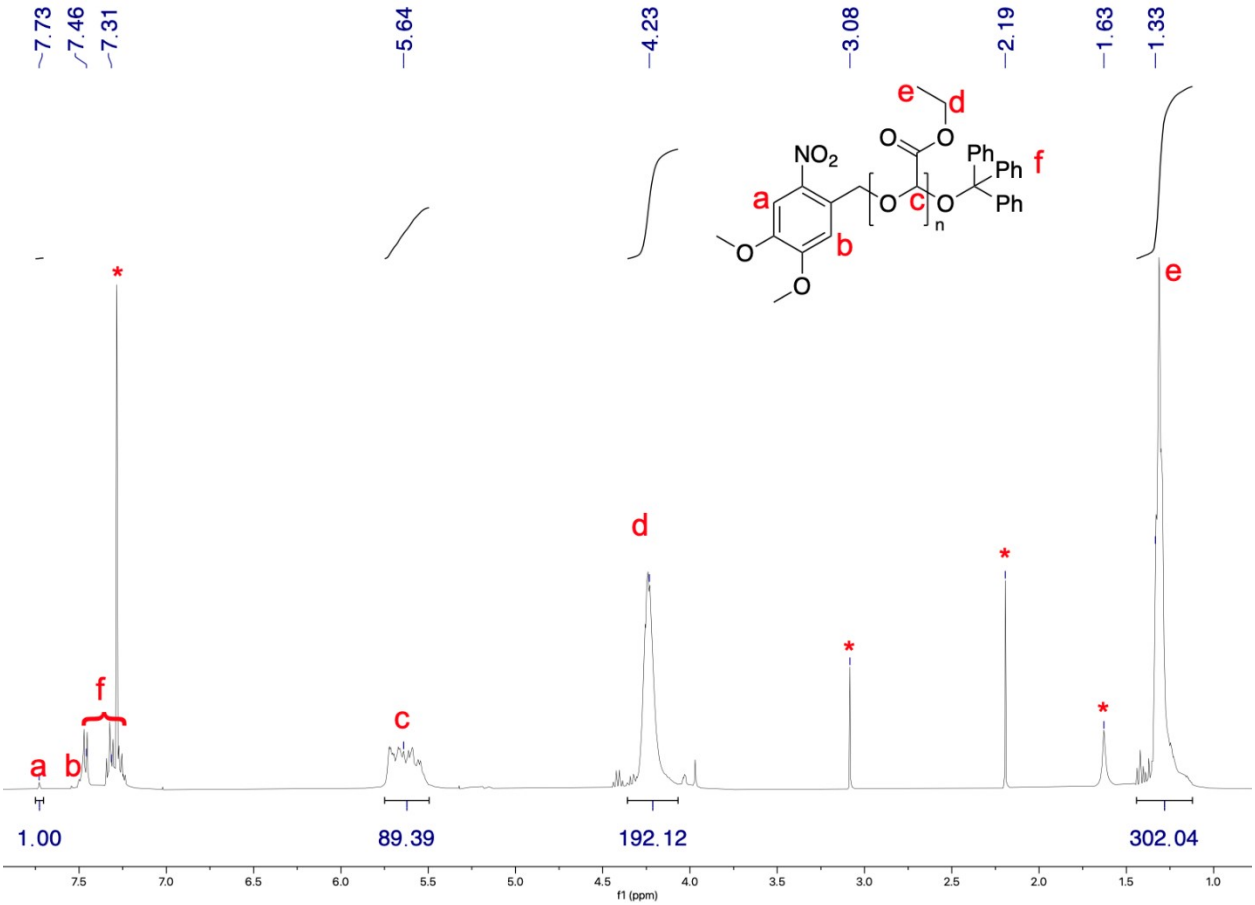

Figure S6. ^{1}H NMR spectrum of **8k PEtG** ($CDCl_3$, 400 MHz), * indicates peaks corresponding to chloroform, methanol, acetone, and water (from left to right).

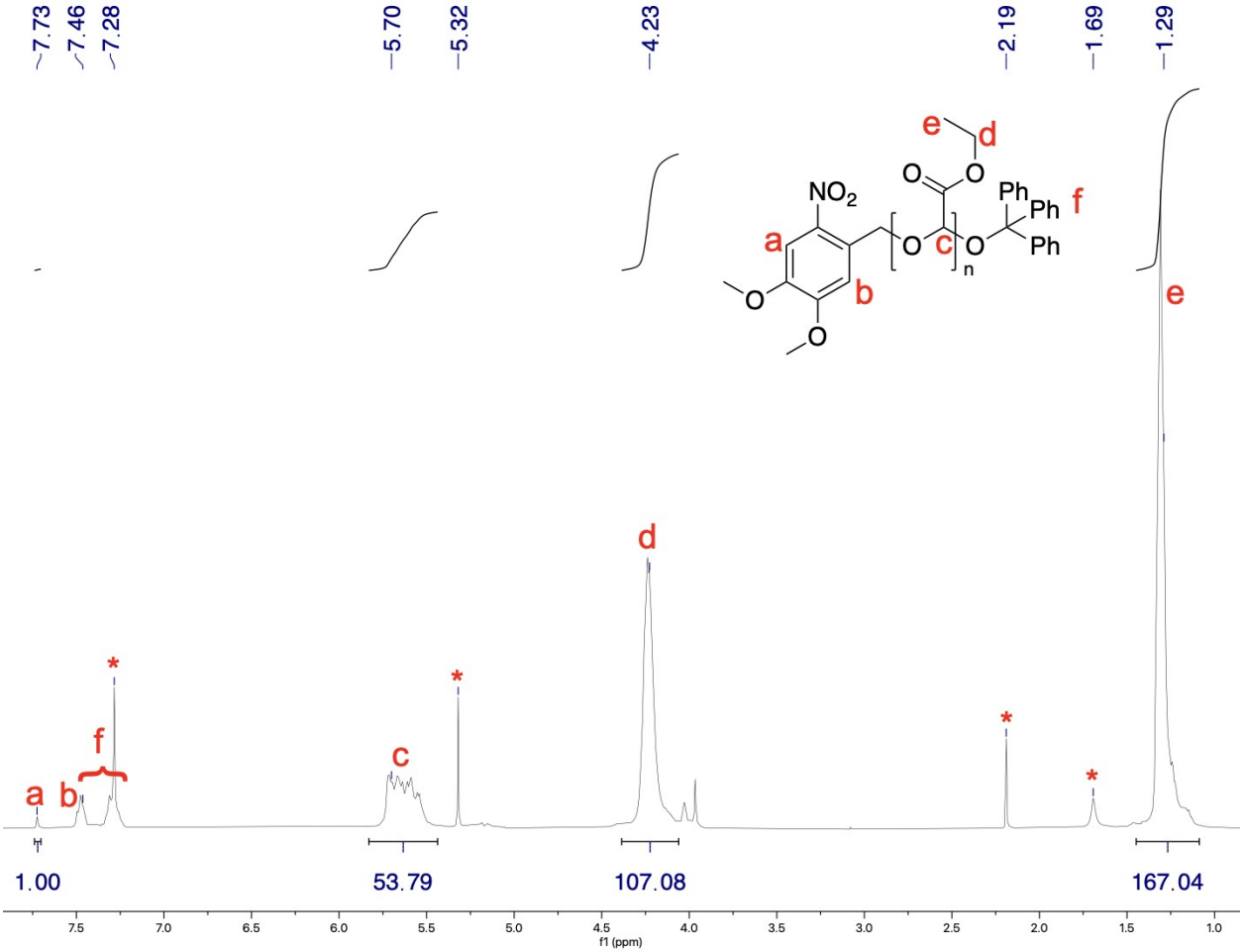

Figure S7. ^{1}H NMR spectrum of **5k PEtG** (CDCl3, 400 MHz), * indicates peaks corresponding to chloroform, dichoromethane, methanol, acetone, and water (from left to right).

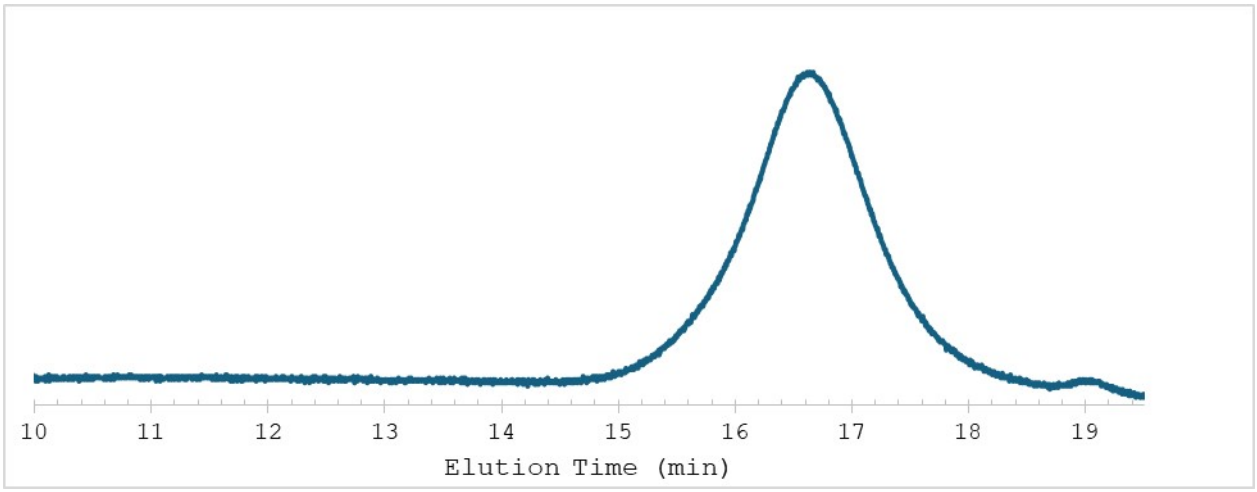

Figure S8 Size-exclusion chromatogram of **8k PEtG** in THF (refractive index detection).

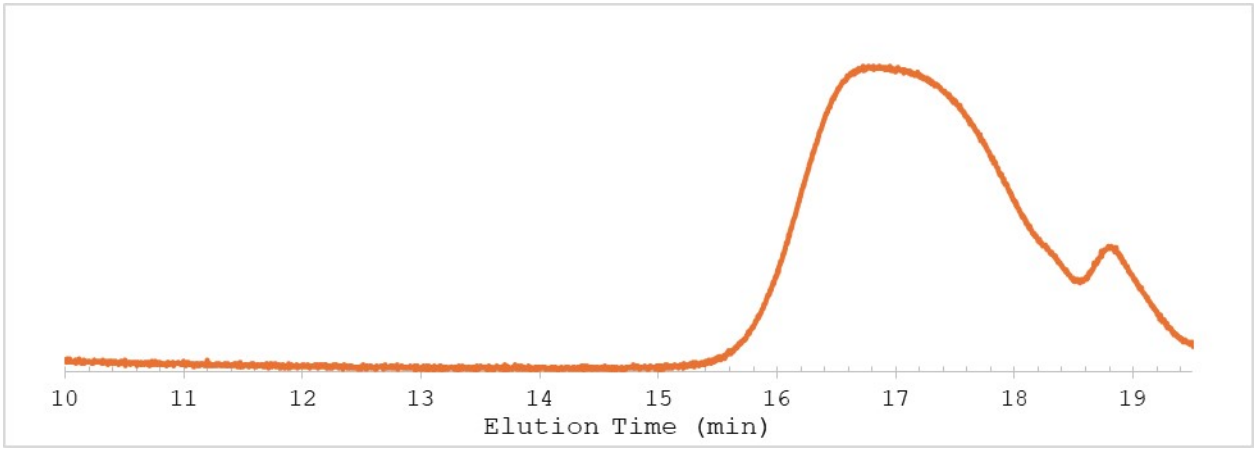

Figure S9 Size-exclusion chromatograms of **5k PEtG** in THF (refractive index detection).

References:

1. A. Rabiee Kenaree and E. R. Gillies, *Macromolecules*, 2018, **51**, 5501–5510.