Supporting Information For:

Crosslinking 1,4-Polybutadiene via Allylic Amination: A New Strategy for Deconstructable Rubbers

Mercie N. Hodges, Ana Paula Kitos Vasconcelos, Laura Reed, and Matthew R. Golder*

Department of Chemistry and Molecular Engineering & Science Institute,
University of Washington, Seattle, WA 98195, United States

Corresponding author: goldermr@uw.edu

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General Considerations

Materials

All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Curing was conducted in a Cole-Parmer OVV-400-24-120 Programmable Vacuum Oven, 24 L at 62 °C. Preparative-scale gel permeation chromatography (prep-GPC) was performed using a Japan Analytical Industries LaboACE recycling preparative HPLC system equipped with JAIGEL-2.5HR and JAIGEL-3HR columns in series using chloroform (stabilized with 0.5% - 1.0% ethanol) as the mobile phase.

Characterization

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Bruker AVANCE-500 at 500 MHz or a Bruker AVANCE-300 at 300 MHz. ^{19}F nuclear magnetic resonance (^{19}F NMR) spectra were obtained on a Bruker AVANCE-500 at 470 MHz. ^{13}C 1D nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AVANCE -500 at 126 MHz or a Bruker AVANCE-800 at 200 MHz. ^{1}H NMR spectra were taken in chloroform-*d* with TMS ($CDCl_3$, referenced to TMS, δ 0.00 ppm) and DMSO-*d6* $(CD_3)_2SO$, referenced to the peak of the residual $(CH_3)_2SO$ peak, δ 2.54 ppm). ^{19}F NMR spectra were taken in chloroform-*d* doped with freon-11 ($CDCl_3$, referenced to freon-11, δ 0.65 ppm). ^{13}C NMR spectra were taken in chloroform-*d* ($CDCl_3$, referenced to residual $CHCl_3$, δ 77.36 ppm). Spectra were analyzed on MestreNova software. Chemical shifts are represented in parts per million (ppm); splitting patterns are assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), m (multiplet), and br (broad); coupling constants, *J*, are reported in hertz (Hz).

Gel permeation chromatography (GPC) data were collected on Agilent 1260 HPLC equipped with a Wyatt 8-angle DAWN NEON light-scattering detector, ViscoStar NEON viscometer, and Optilab NEON refractive index detector. GPC samples were analyzed at a flow rate of 1 mL/min in chloroform (stabilized with 0.5 – 1.0% ethanol) through two Agilent PLgel MIXED-C columns at 35 °C. *dn/dc* values were determined by the 100% mass recovery method using Wyatt ASTRA 7.3 software.

Mass spectrometry data were collected on an Agilent 5973 GC-MS (EI) with negative ionization or a Bruker Esquire LC Ion Trap (ESI) using negative ionization and gentle spray.

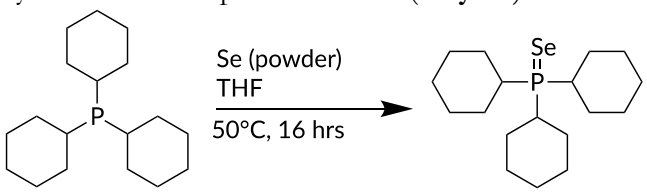
Thermogravimetric analysis (TGA) data were collected using a TA Discovery Q5000 thermogravimetric analyzer. Samples were heated in aluminum Tzero pans at a rate of 10 °C per minute from 23 °C to 500 °C under an N_2 atmosphere.

Rheological measurements were conducted on an TA Instruments Discovery Hybrid Rheometer-2 at 23 °C. Using an 8 mm parallel plate (Peltier plate Stainless steel) and a gap height of 1000 μm, the storage and loss moduli were recorded at frequencies ranging from 0.1-100 Hz at 0.5% or 0.25% strain (within the linear viscoelastic range based on initial strain sweeps at 1 Hz).

Compression tests were performed using a Universal Test Machine (Test Resources, 100-25-12) with either a 1 kN or 43N load cell.

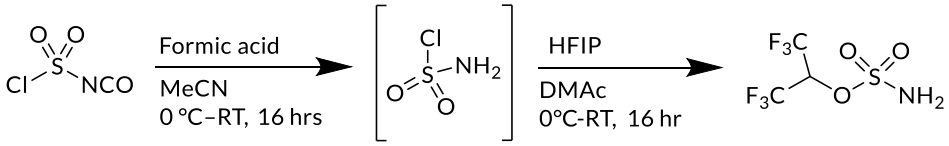
Synthetic and Experimental Procedures

Synthesis of Phosphine Selenide (**PCy_3Se**):



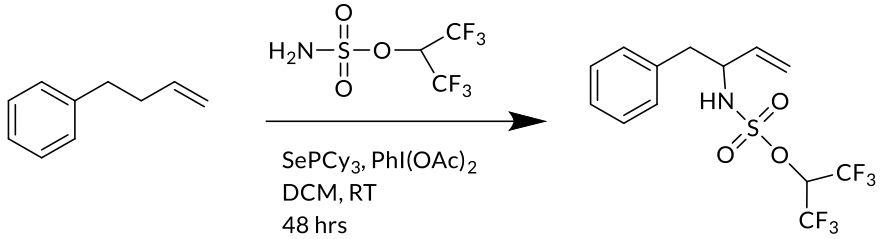
In a nitrogen-filled glovebox, tricyclohexylphosphine (2.0 g, 7.1 mmol, 1.0 eq) and Se powder (1.7 g, 21 mmol, 3.0 eq) were added to a 100 mL RBF. The contents were sealed with a rubber septum, removed from the glovebox, placed under a nitrogen atmosphere, and suspended in dry THF (20 mL). A reflux condenser was added, and the reaction was stirred at 45 °C under N_2 for 14 hours. The reaction mixture was then cooled to room temperature and passed through a plug of Celite (DCM, 30 mL). The crude product was concentrated under reduced pressure, recrystallized from hot acetone (25 mL), and cooled to –20 °C for 20 hours. The resulting white crystals were filtered and dried to afford pure PCy_3Se (1.6 g, 61%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ(ppm): 2.03 (overlap, 12H), 1.99 (m, 3H), 1.47 (m, 6H), 1.30 (overlap, 12H). Analytical data is in accordance with values reported in the literature.[1]

Synthesis of 1,1,1,3,3,3-hexafluoroisopropyl sulfamate (**HFIPS**):



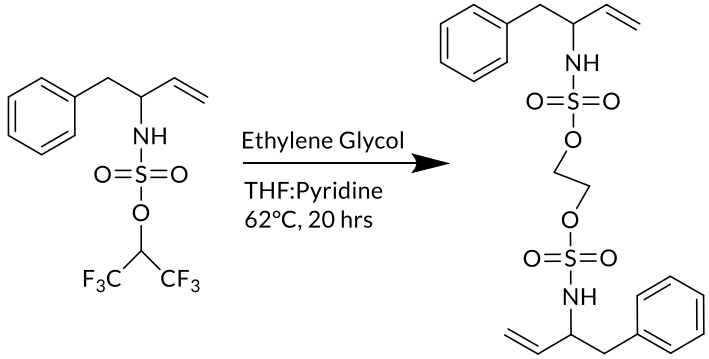
A 200-mL round bottom flask was cooled to 0.0 °C and acetonitrile (8.0 mL) and chlorosulfonyl isocyanate (13 g, 91 mmol, 1.3 eq) were added. To this mixture formic acid (3.8 g, 88 mmol, 1.3 eq) was added dropwise. The reaction stirred at 0.0 °C for 10 minutes, then warmed to room temperature and stirred for 14 hours. The reaction was then cooled to 0 °C again, and a mixture of 1,1,1,3,3,3-hexafluoroisopropanol (12 g, 70 mmol, 1.0 eq) in dimethylacetamide (8.0 mL) was added dropwise. The solution was warmed to room temperature and stirred for 16 hours. The reaction was quenched by the addition of water (40 mL). The aqueous layer was extracted three times with 50 mL of diethyl ether. The organic layer was then washed five times with 50 mL of water, once with 50 mL of brine, and twice with 40 mL of a 5% lithium chloride solution. The organic layer was then dried over sodium sulfate and concentrated under reduced pressure. Material was then solubilized in dichloromethane and insoluble impurities removed by gravity filtration. Drying the material under reduced pressure yielded a fluffy white solid (11 g, 63%). **^{1}H NMR** (500 MHz, DMSO-*d_6*) δ(ppm): 8.53 (s, 2H), 6.23 (p, 1H). **^{19}F NMR** (470 MHz, DMSO-*d_6*, referenced to freon-11) δ(ppm): -72.23 (s, 6F). Analytical data is in accordance with values reported in the literature.[2]

Synthesis of **4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (2)**:



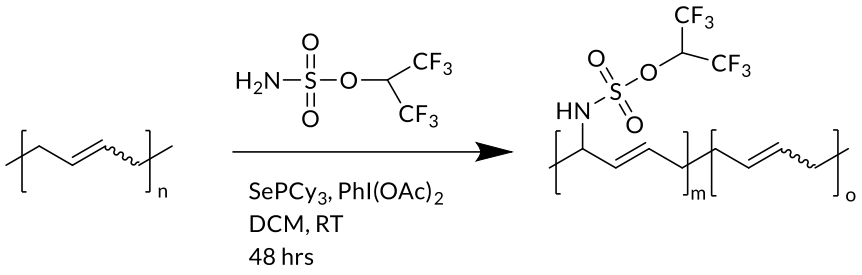
A septa-capped 20 mL vial was charged with selenium phosphide (0.14 g, 0.4 mmol, 20 mol%) followed by the addition of HFIPS (0.99 g, 4.0 mmol, 2.0 eq) and 4-phenyl-1-butene (0.26 g, 2.0 mmol, 1.0 eq) and stirred with DCM (10 mL). Diacetoxyiodobenzene (1.3 g, 4.0 mmol, 2.0 eq) was added to this mixture, followed by sparging with nitrogen gas for 10 minutes. The reaction then stirred for 48 hours and was monitored by TLC. The reaction was quenched by addition of a gross excess of dimethyl sulfamide. Selenium salts were filtered out, and the reaction was concentrated under reduced pressure, then purified by column chromatography through silica (80:20 hexanes:ethyl acetate). Fractions with pure product were combined and concentrated under reduced pressure to yield a yellow oil (1.4 g, 74%). **GC-MS** (*m*/*z* 377.2 g/mol, RT 11.5 min.), **^{1}H NMR** (500 MHz, $CDCl_3$), δ(ppm): 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 (m, 1H), 7.18 (d, *J* = 6.9 Hz, 2H), 5.77 (m, 1H), 5.24 (s, 1H), 5.22 (d, *J* = 5.2 Hz, 2H), 5.09 (sep, *J* = 5.8 Hz, 1H), 4.83 (q, *J* = 8.9 Hz, 1H), 4.30 (qu, *J* = 7.2 Hz, 1H), 2.96 (m, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$, referenced to freon-11), δ(ppm): -72.82 (q, *J* = 8.2 Hz, 3F), -72.93 (q, *J* = 8.2 Hz, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$, referenced to solvent residual peak), δ(ppm): 135.52 (d, *J* = 3.2 Hz), 129.72 (s), 128.87 (s), 127.39 (s), 117.82 (s), 72.88 (m), 58.69 (s), 41.50 (s).

Dimerization of 4-phenyl-1-butene with ethylene glycol **(3)**:



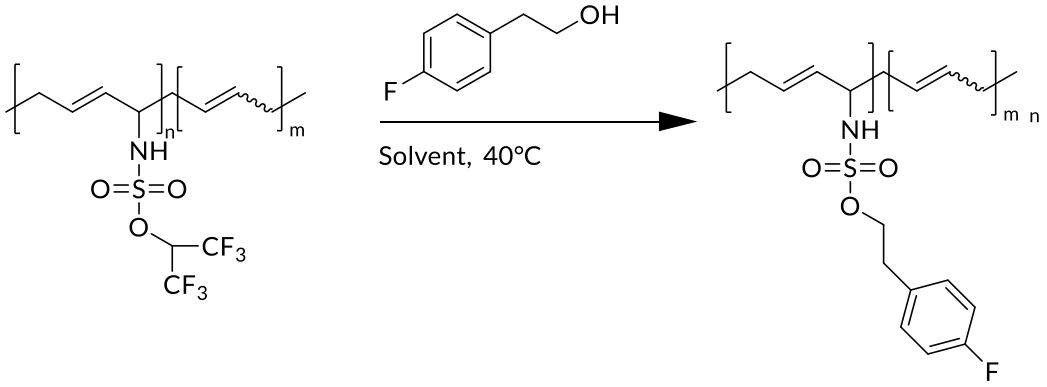
4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (0.10 g, 0.26 mmol, 2.0 eq) was added to a 4 mL vial with ethylene glycol (0.0082 g, 0.13 mmol, 1.0 eq) and 1.5 weight times 4-phenyl-2-hexafluoroisopropylsulfamate-1-butene solvent (tetrahydrofuran and pyridine in a 1:1 weight ratio). Material was stirred at 62 °C for 20 hours then concentrated under reduced pressure and purified by preparatory gel permeation chromatography (GPC) to yield a dark yellow oil (0.029 g, 45%). (**ESI-MS** (*m*/*z* 478.8 g/mol). **^{1}H NMR** (500 MHz, $CDCl_3$), δ(ppm): 7.33 (m, 4H), 7.26 (t, *J* = 3.5 Hz, 2H), 7.20 (t, *J* = 8.8 Hz, 4H), 5.82 (m, 2H), 5.22 (m, 4H), 4.57 (overlap, 2H), 4.20 (sep, *J* = 7.5, 6.9 Hz, 2H), 4.04 (m, 2H), 4.00 (m, 1H), 3.85 (m, 1H), 2.95 (m, 2H), 2.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, referenced to solvent residual peak), δ(ppm): 137.65 (d, *J*= 8.8 Hz), 136.86 (s), 136.56 (s), 136.44 (d, *J* = 1.9 Hz), 129.88 (s), 129.80 (s), 128.79 (s), 128.68 (s), 127.75 (s), 127.02 (s), 67.16 (s), 58.26 (s), 57.33 (d, *J* = 8.8 Hz), 41.88 (s), 41.55 (s).

Functionalization of 1,4-polybutadiene with 1,1,1,3,3,3-hexafluoroisopropyl sulfamate (**PBD-HFIPS**):



A 500 mL round bottom flask was charged with selenium phosphide (1.33 g, 3.70 mmol, 5 mol%) and HFIPS (1.83 g, 7.40 mmol, 0.10 eq), then 1,4-polybutadiene (~7 kDa, 4.00 g, 74.0 mmol, 1 eq) was added and the reagents dissolved in dichloromethane (0.2 M, 370 mL). Once the reagents were dissolved Diacetoxyiodobenzene was added (2.38 g, 7.40 mmol, 0.10 eq) and the reaction was sparged with nitrogen gas for 10 minutes. The reaction stirred at room temperature under a nitrogen atmosphere for 48 hours, followed by quenching with a gross excess of dimethyl sulfate and stirred for an additional 12 hours. Selenium salts were removed by gravity filtration, and the material was concentrated under reduced pressure. The crude material was washed 3 times with cold methanol, then dialyzed against 95:5 acetone:water for 24 hours with 3.5 kDa MWCO cellulose dialysis tubing with a small amount of triethylamine added to disrupt hydrogen bonding. After dialysis the material was dried over sodium sulfate and concentrated under reduced pressure. Percent functionalization was determined by using 4,4-difluorobenzophenone as an internal standard. Material was a thick, sticky brown solid (4.090 g, 90%) **GPC** (Figure S1: M_n 7.02 kDa, Đ = 1.022). **^{1}H NMR** (500 MHz, $CDCl_3$, doped with 4,4-difluorobenzophenone), δ(ppm): 5.56 (m, 22H), 5.41 (dd, J = 21.4, 4.5 Hz, 224H), 4.97 (m, 32H), 2.08 (d, J = 22.2 Hz, 465H). **^{19}F NMR** (470 MHz, $CDCl_3$, referenced to freon-11, doped with 4,4-difluorobenzophenone), δ(ppm): -73.00 (s, 6F). **^{13}C NMR** (126 MHz, $CDCl_3$, referenced to solvent residual peak), δ(ppm): 130.23 (dd, J = 7.3, 3.2 Hz), 129.76 (s), 129.58 (t, J = 3.0 Hz), 32.87 (s), 27.54 (s).

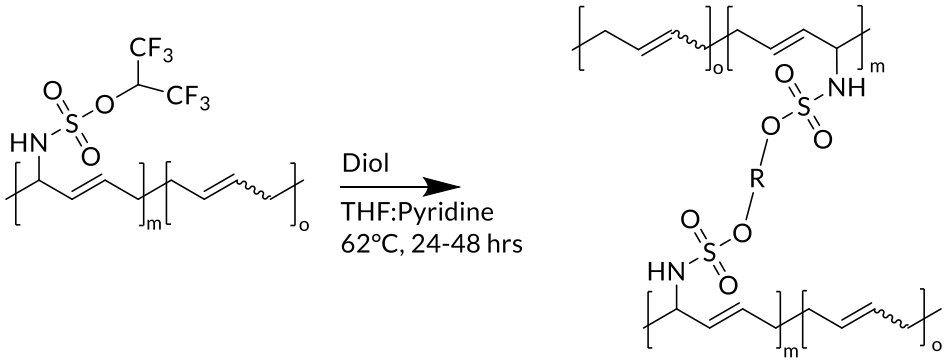
Synthesis of **1,4-polybutadiene-4-fluorophenethyl sulfamate (4)**:



PBD-HFIP-6 (0.050 g, 0.68 mmol, 1.0 eq) was added to a 4 mL vial with 4-fluorophenethyl alcohol (0.095 g, 0.68 mmol, 1.0 eq) with pyridine and dichloroethane or tetrahydrofuran (see table S1). The reaction stirred at 40°C for 20 hours. The solution was concentrated under reduced pressure and purified by washing 3x with cold methanol and 1x with acetonitrile. Material was a pale brown, viscous solid (0.042 g, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$,), δ(ppm): 7.19 (m, 5H), 7.00 (m, 5H), 5.56 (m, 18H), 5.41 (overlap, 224H), 4.97 (m, 33H), 2.08 (overlap, 465H). **^{19}F NMR** (470 MHz, $CDCl_3$,

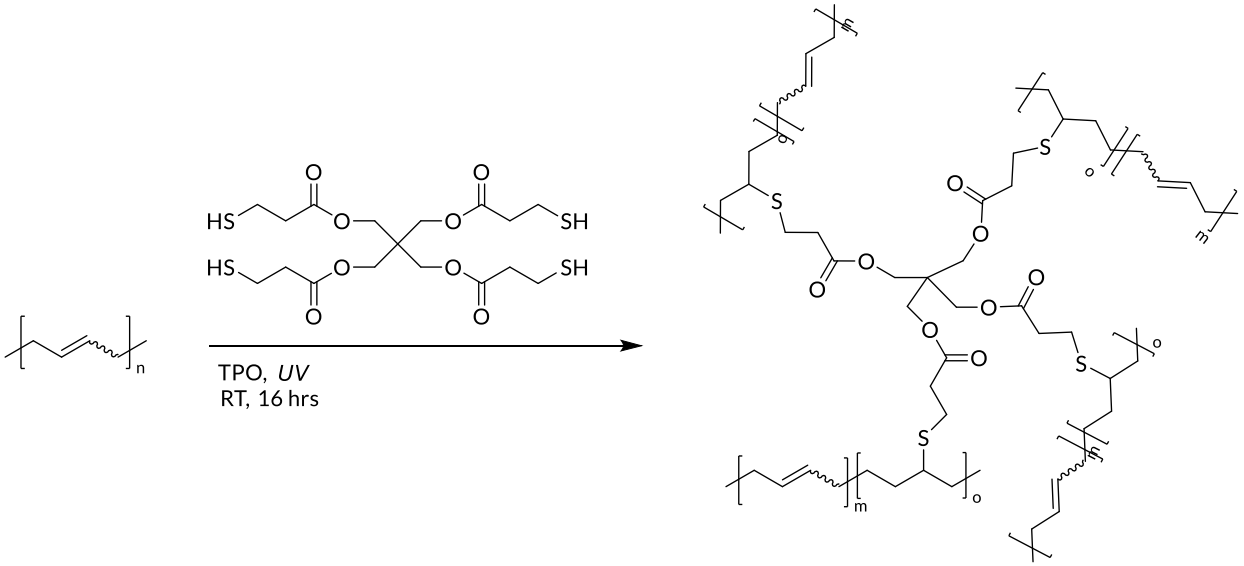
referenced to freon-11), δ(ppm): -116.70 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$, referenced to solvent residual peak), δ(ppm): 130.31 (d, J = 130.2 Hz), 129.78 (s), 118.79 (s), 116.11 (s), 32.89 (s), 27.56 (s).

Representative Procedure for crosslinking 1,4-polybutadiene with glycols:



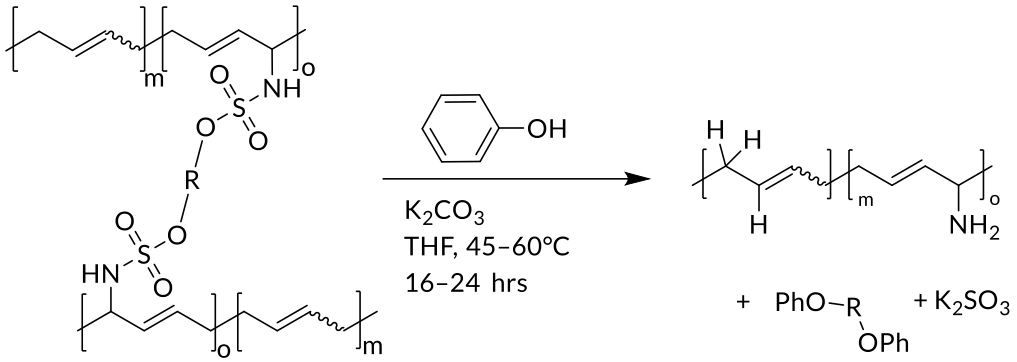
Diethylene glycol (0.36 g, 3.4 mmol, 0.50 eq) was added to a 1:1 mixture of pyridine and tetrahydrofuran (1.5x weight of PBD-HFIPS) and vortexed to mix. This solution was then added to PBD-HFIPS-3 (0.50 g, 6.8 mmol, 1 eq) and vortexed for 15 minutes at 3000 RPM to mix. The resulting mixture was then cured at 62 °C for 24-48 hours (dependent on crosslinking density). After curing, the material was removed by destruction of the reaction vessel, then dried at 62 °C for a further 48 hours to yield a dark brown puck. Material was characterized by swelling (Table S4), rheology (Figures S35–36), and compression testing (Figures S39–44).

Crosslinking 1,4-polybutadiene with pentaerythritol tetrakis(3-mercaptopropionate):



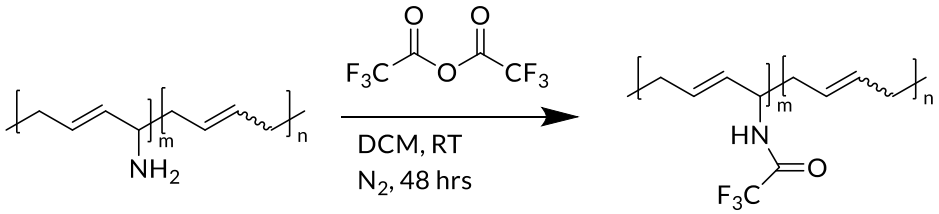
Tetrakis(3-mercaptopropionate (0.18 g, 0.37 mmol, 0.020 eq) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (0.020 g, 0.057 mmol, 0.0031 eq) were added to a 7 mL vial, followed by 1,4-polybutadiene (1.0 g, 19 mmol, 1.0 eq). The mixture was centrifuged at 3000 RPM for 10 minutes, then sonicated for 12 hours. Following sonication the material was exposed to UV light for 16 hours. After curing, the material was removed by destruction of the reaction vessel and characterized without further purification. Material was characterized by swelling (Table S4), rheology (Figures S33–34) and compression testing (Figures S37–38).

Representative procedure for deconstruction of **PBD-R-X**:



PBD-R-X (0.075 g, 1.2 mmol, 1.0 eq) was added to tetrahdrofuran (2.1 w/v%, 35 mL) followed by the addition of phenol (1.1 g, 12 mmol, 10 eq) and potassium carbonate (1.6 g, 12 mmol, 10 eq). The reaction stirred at 45 or 60 °C (see table S3) for 16-48 hours (see table S3). Reaction was quenched with 40 mL of deionized water. The organic layer was collected and material re-solubilized with dichloromethane and dried over sodium sulfate. After concentrating under reduced pressure the product was washed with cold methanol to remove excess phenol and diphenyl glycol. Material was a light brown, viscous solid (0.050 g, 76%). **GPC** (Figure S1). **^{1}H NMR** (500 MHz, $CDCl_3$), δ(ppm): 5.56 (m, 18H), 5.41 (overlap, 224H), 4.97 (m, 32H), 2.08 (overlap, 465H).

Fluorination of deconstructed **PBD-NH$_2$-3**:



PBD-3-NH$_2$ (0.150 g, 2.8 mmol, 1.0 eq) was dissolved in dichloromethane (11 mL, 0.25 M) and stirred under a nitrogen atmosphere. Trifluoroacetic anhydride (0.707 g, 3.7 mmol, 1.2 eq) was added dropwise and the reaction stirred under a nitrogen atmosphere for 48 hours. The crude product was concentrated under reduced pressure then washed 3x with cold methanol. Material was a brown, viscous solid (0.145 g, 90%). Percent amidation was determined by ^{1}H and ^{19}F NMR comparison to an internal standard following the same procedure as determining percent amination of PBD-HFIPS (**equations S1-S3**). **^{1}H NMR** (500 MHz, $CDCl_3$,), δ(ppm): 5.56 (m, 19H), 5.41 (overlap, 224H), 4.97 (m, 31H), 2.08 (overlap, 464H). **^{19}F NMR** (470 MHz, $CDCl_3$, referenced to freon-11), δ(ppm): -74.72 (b, 3F).

Tables of Compiled Data:

Table S1: Thermoplastic Substitution Conditions:

Temperature (°C)	Solvent	Isolated %Yield
40	Pyridine:THF	90
40	Pyridine:DCE	86

Table S2: Compiled **PBD-EG-X** Controls:

PBD-HFIPS	Ethylene Glycol	Solvent	Concentration (wt%)	Temperature (°C)	Crosslinked Material
Yes	Yes	THF:Pyridine	1.5	62	Yes
Yes	**No**	THF:Pyridine	1.5	62	No
No	Yes	THF:Pyridine	1.5	62	No

Table S3: Decrosslinking Conditions:

Specimen	Temperature (°C)	Reaction Time (h)	%Yield (Recovered)
PBD-EG-3	45	24	57
PBD-DEG-3	45	16	54
PBD-DEG-6	60	48	76
PBD-TEG-3	45	20	36

Analytical Gel Permeation Chromatography (GPC) Data:

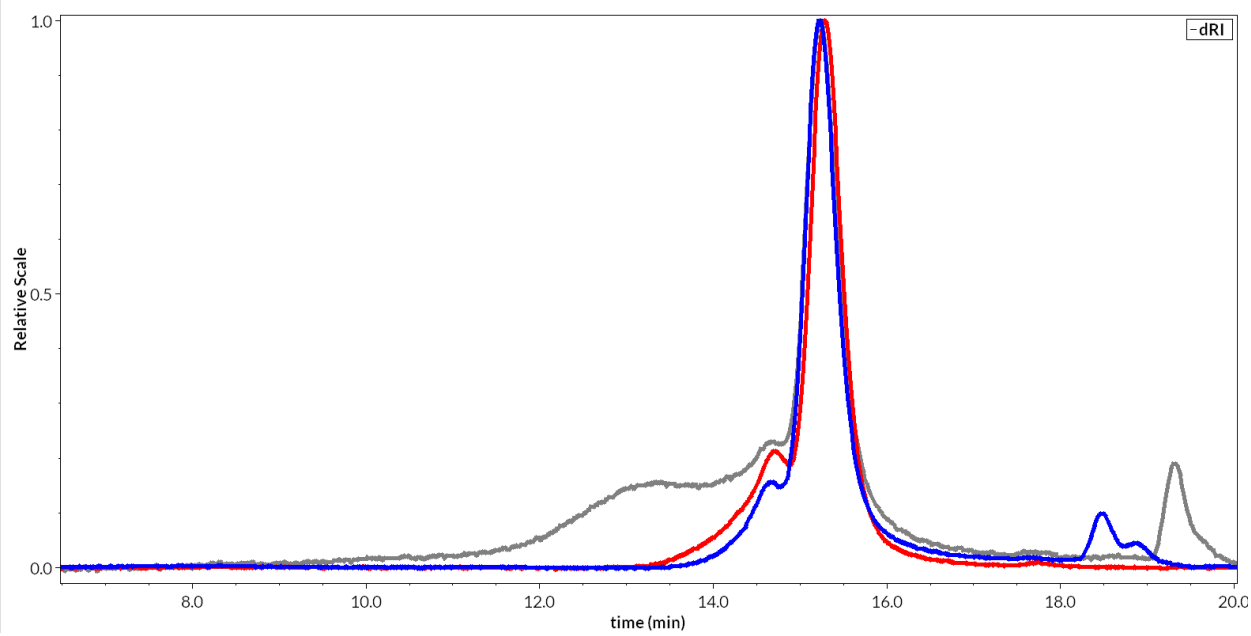


Figure S1: GPC-RI trace of **PBD** (Sigma-Aldrich, M_n = 6.9 kDa, Đ = 1.1) in red, **PBD-HFIPS-3** in blue, and soluble product after deconstruction of **PBD-DEG-3** in gray.

Mass Spectrometry

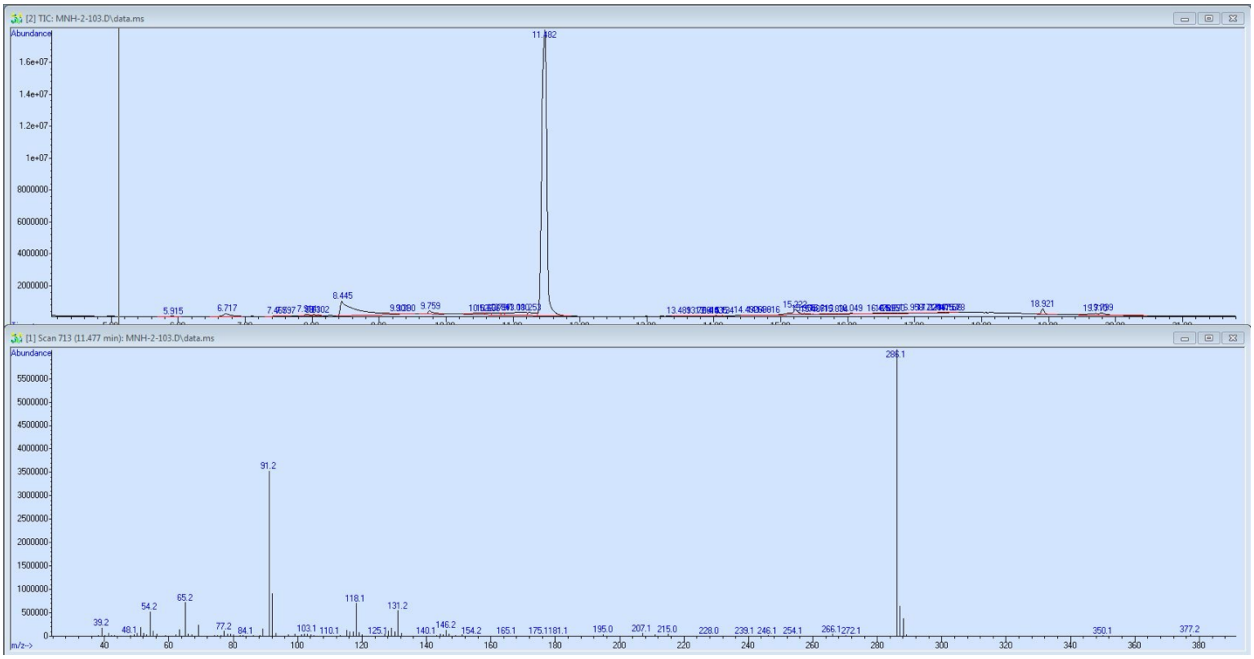


Figure S2: GC-MS (EI) of **4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (2)**. $[M]^-$ = $C_{13}H_{13}O_3F_6NS$ (theor: m/z = 377.3, found: m/z = 377.3), $[M - C_7H_7]^-$ = $C_6H_6O_3F_6NS$ (theor: m/z = 286.2, found: m/z = 286.1), $[C_7H_7]^-$ (theor: m/z = 91.1, found: m/z = 91.2).

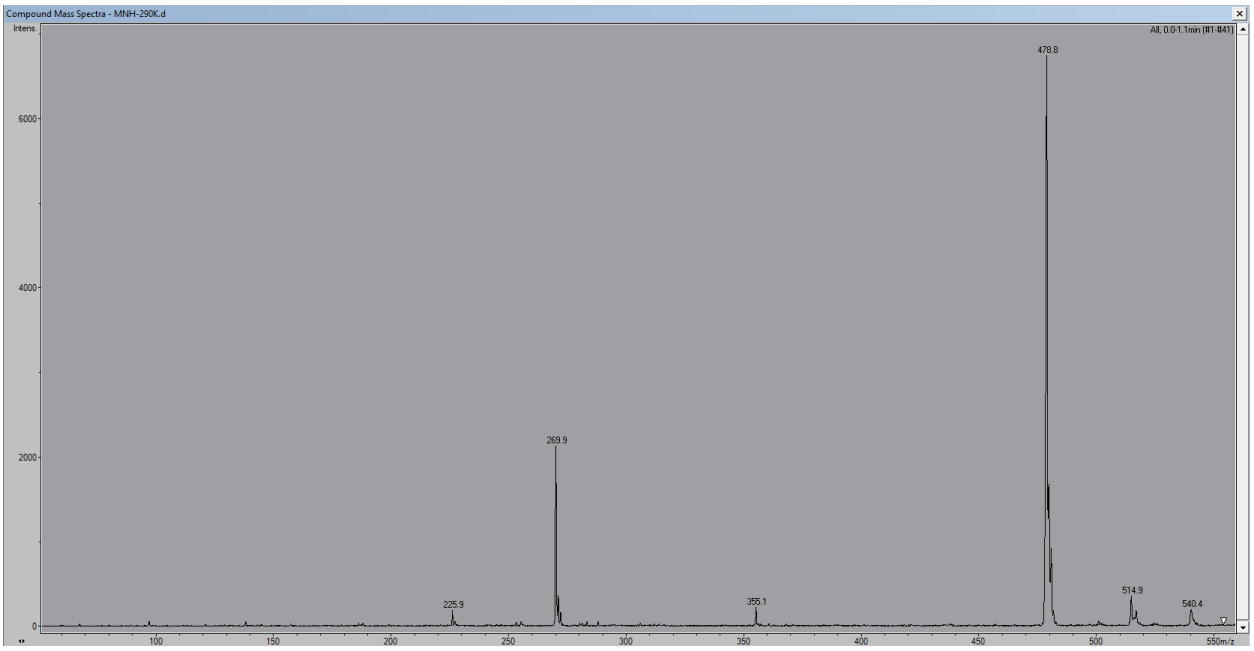


Figure S3: ESI-MS (negative ionization) of **4-phenyl-1-butene dimerized with ethylene glycol (3)**. $[M - H]^-$ = $C_{22}H_{27}O_6N_2S_2$ (theor: m/z 479.1, found: m/z 478.8).

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

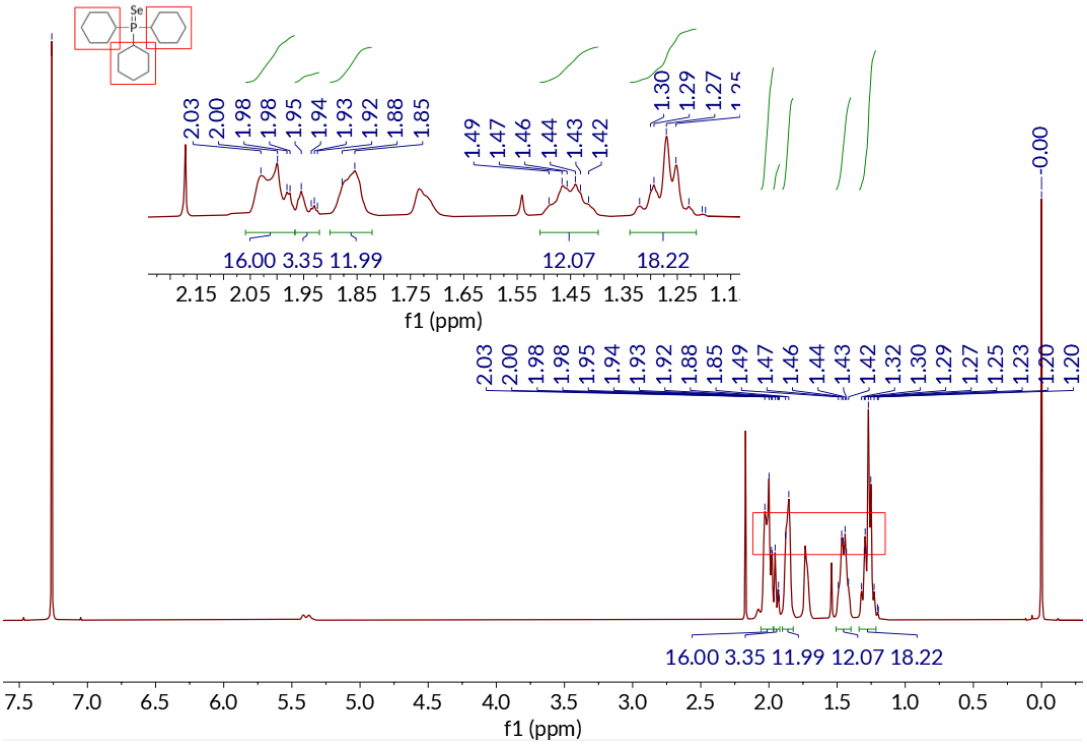


Figure S4: ^{1}H NMR spectrum of phosphine selenide **(PCy_3Se)** catalyst (500 MHz, $CDCl_3$).

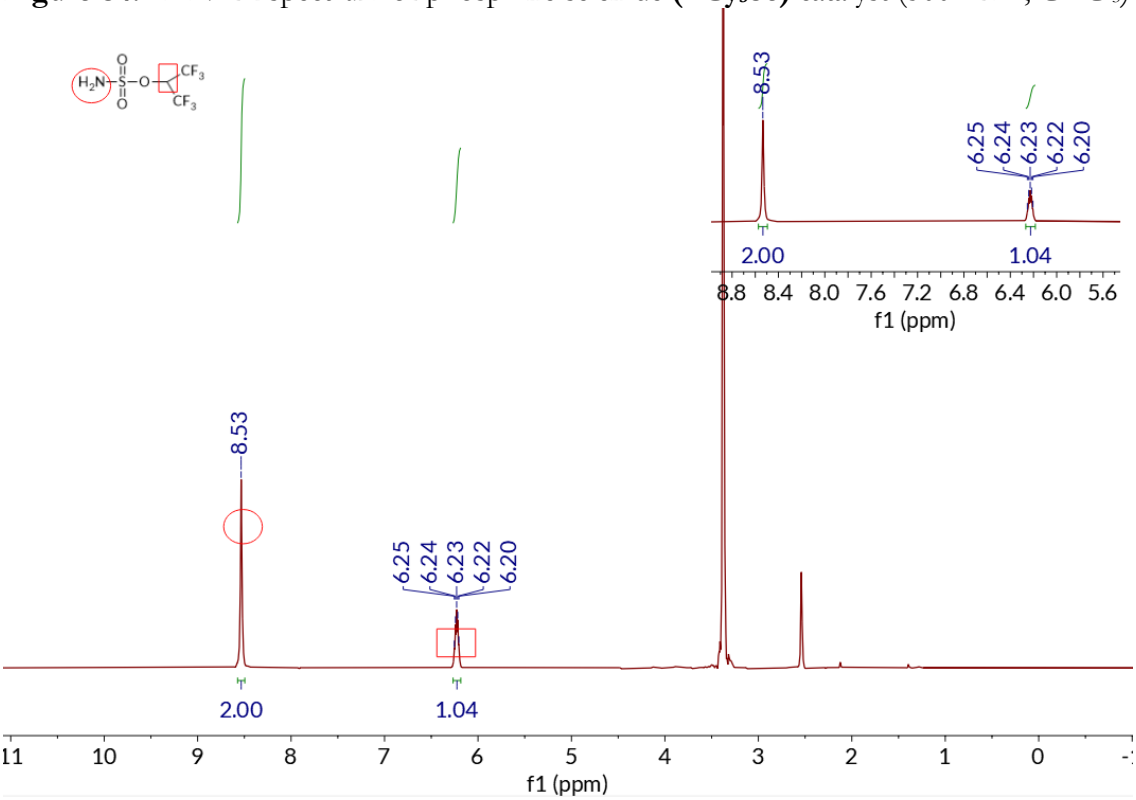


Figure S5: ^{1}H NMR spectrum of 1,1,1,3,3,3-hexafluoroisopropyl sulfamate **(HFIPS)** (500 MHz, DMSO-d_6, referenced to solvent residual peak).

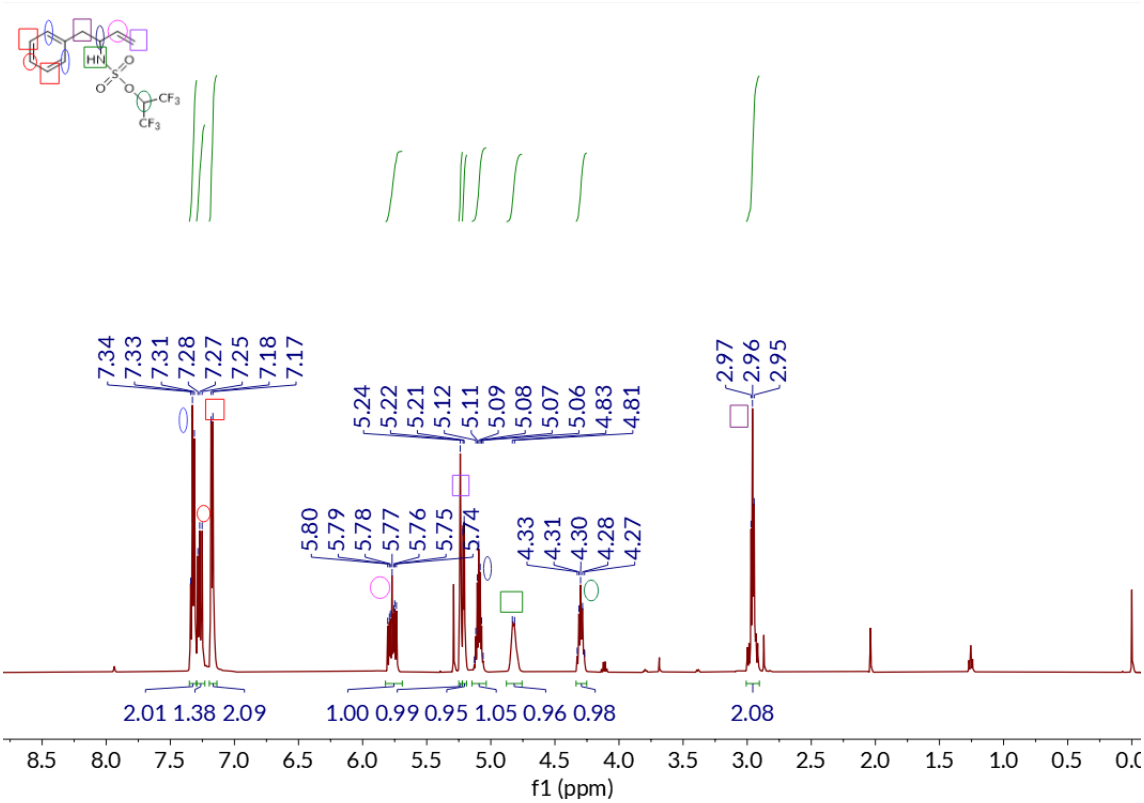


Figure S6: ^{1}H NMR spectrum of **4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (2)** (500 MHz, $CDCl_3$).

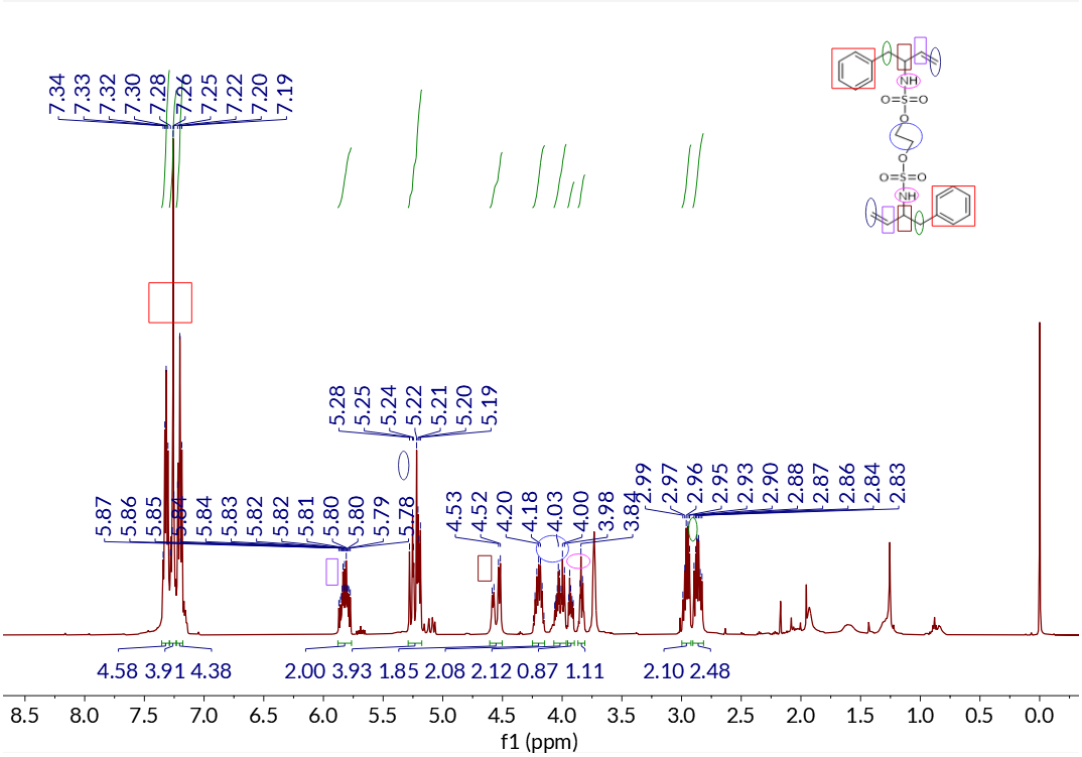


Figure S7: ^{1}H NMR spectrum of **4-phenyl-1-butene dimerized with ethylene glycol (3)** (500 MHz, $CDCl_3$).

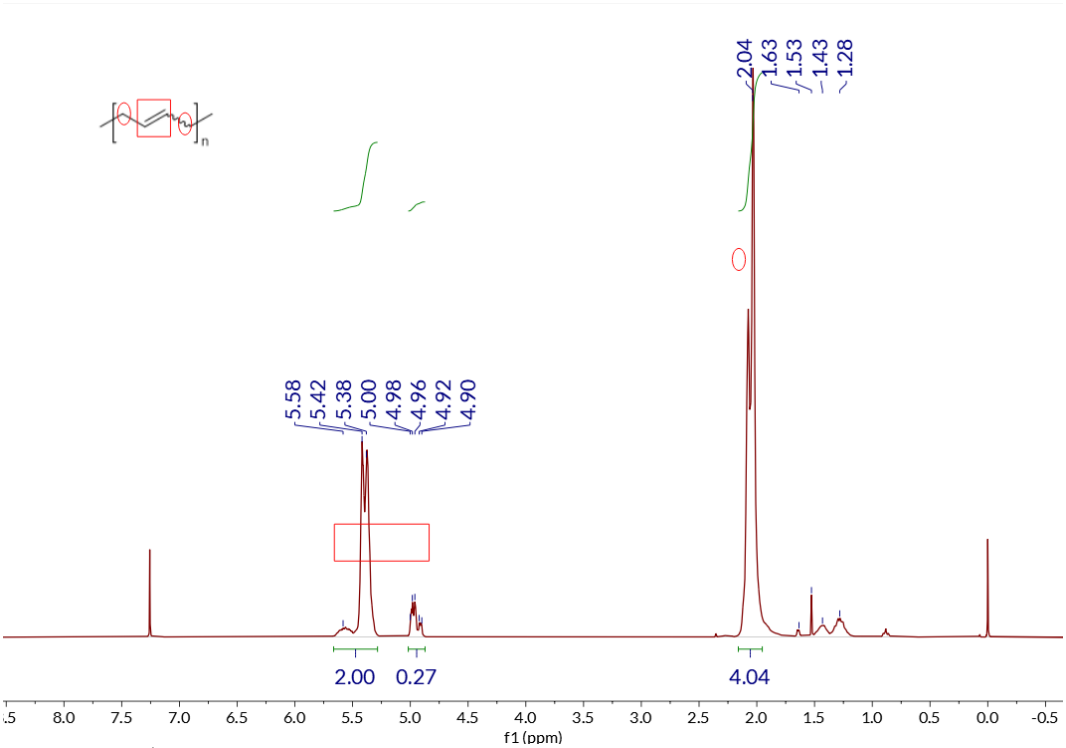


Figure S8: ^{1}H NMR spectrum of **PBD** (87% *cis-trans,* 13% vinyl) (300 MHz, $CDCl_3$).

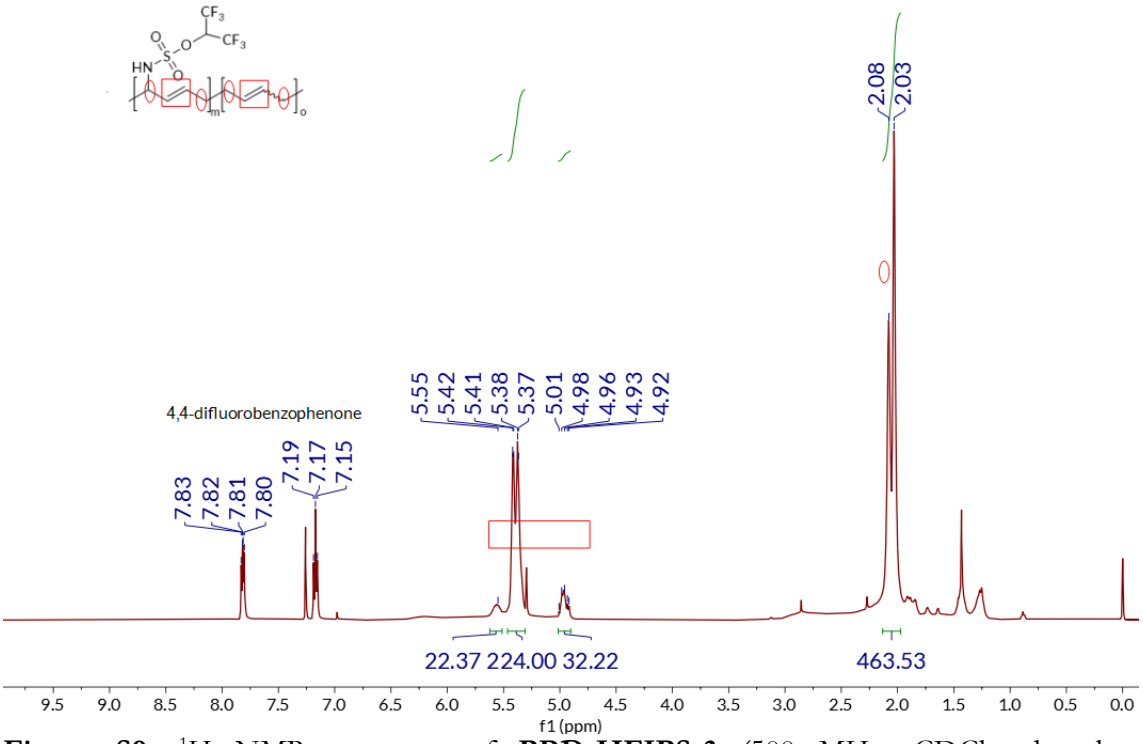


Figure S9: ^{1}H NMR spectrum of **PBD-HFIPS-3** (500 MHz, $CDCl_3$, doped with 4,4-difluorobenzophenone).

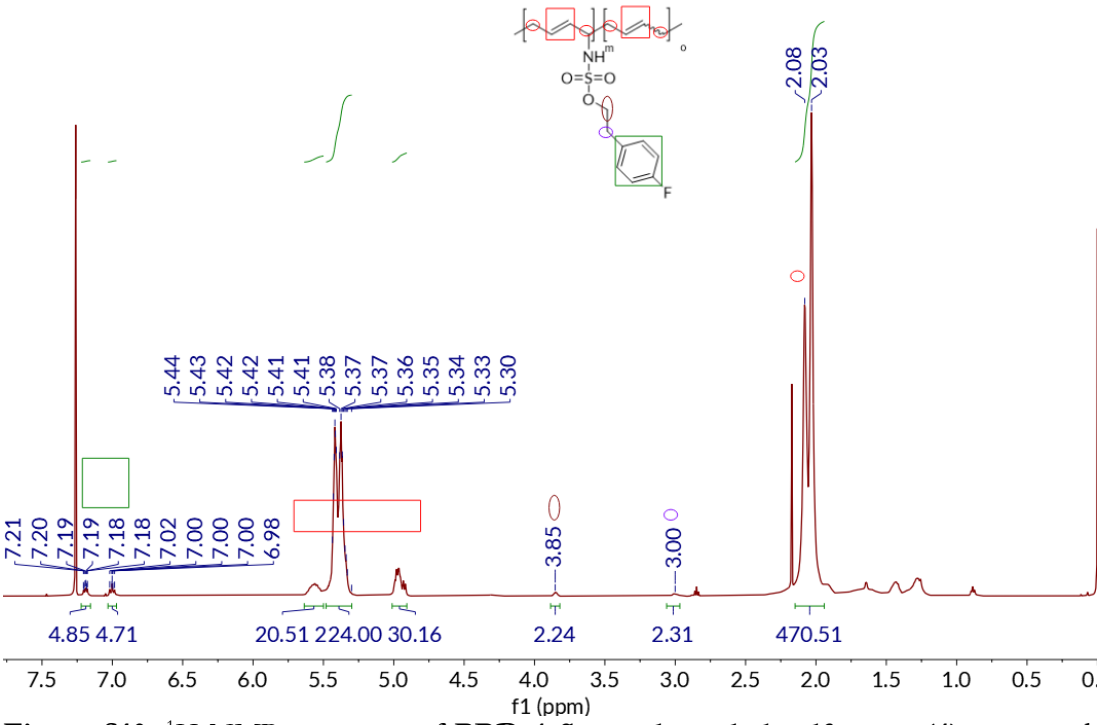


Figure S10: ^{1}H NMR spectrum of **PBD-4-fluorophenethyl sulfamate (4)** generated from **PBD-HFIPS-6** (500 MHz, $CDCl_3$).

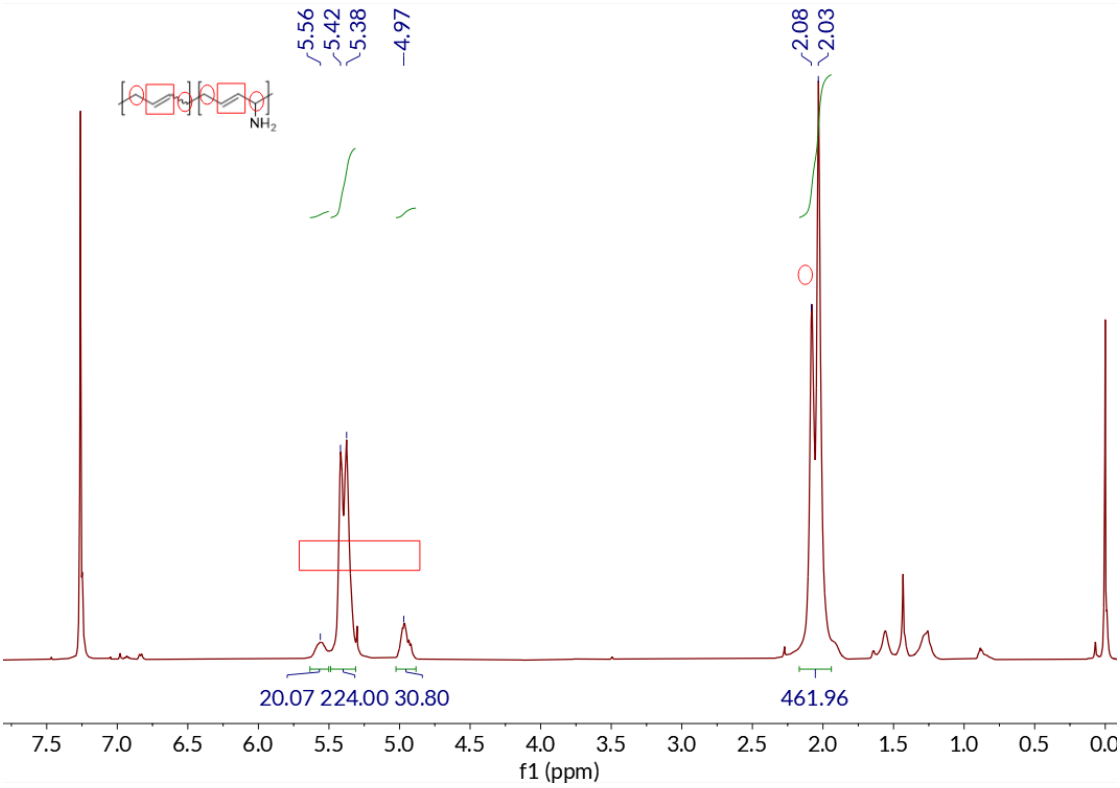


Figure S11: ^{1}H NMR spectrum of deconstructed **PBD-DEG-3** (i.e., **PBD-NH$_2$-3**) (500 MHz, $CDCl_3$).

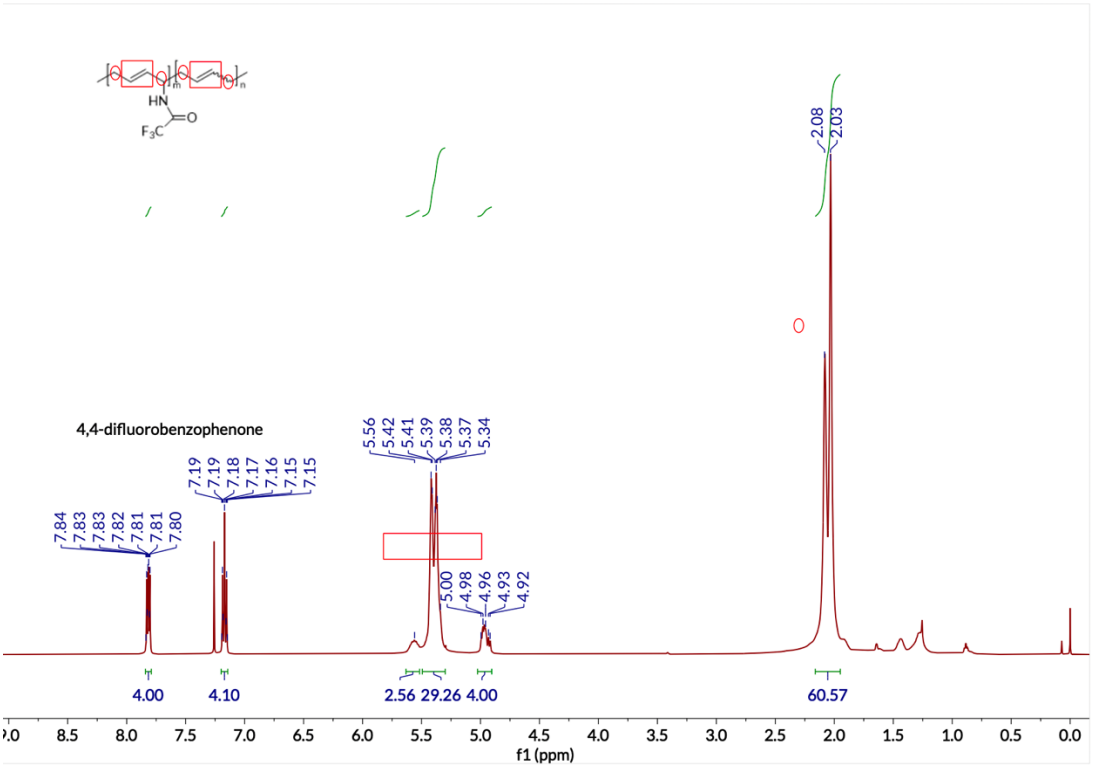


Figure S12: ^{1}H NMR spectrum of **PBD-NH$_2$-3** amidated with trifluoroacetic anhydride (500 MHz, $CDCl_3$, doped with 4,4-difluorobenzophenone [0.020 mmol]).

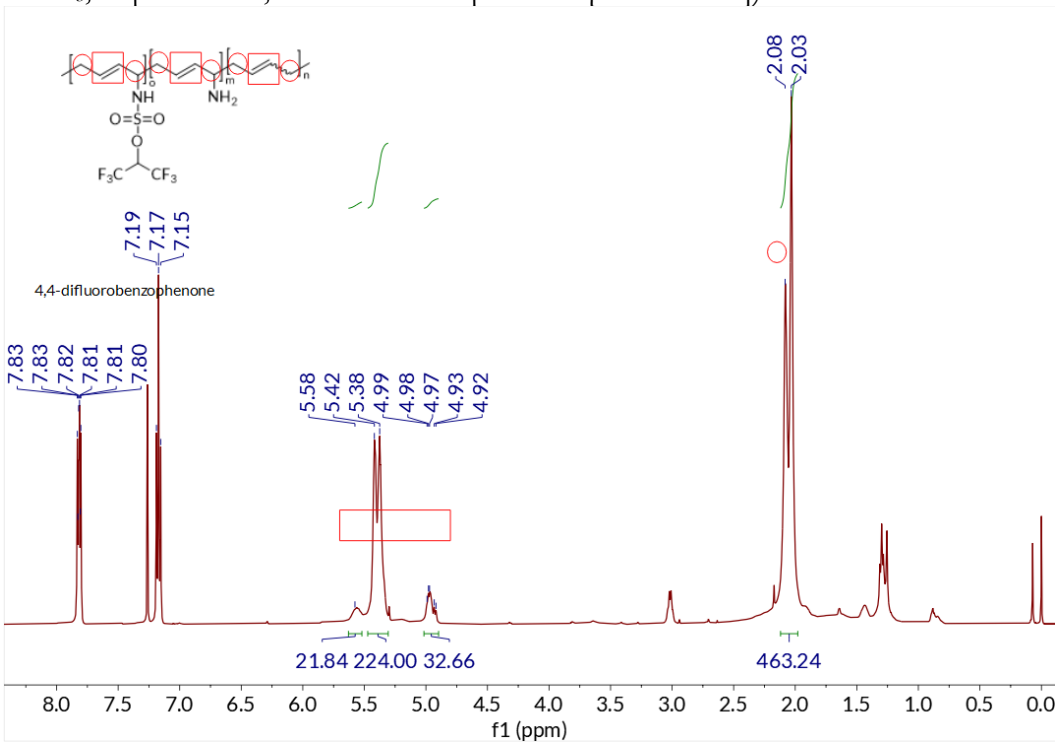


Figure S13: ^{1}H NMR spectrum of **PBD-TEG-3** decrosslinked and reaminated to form **(PBD-NH$_2$-3)-HFIPS-6** (500 MHz, $CDCl_3$, doped with 4,4-difluorobenzophenone).

Fluorine nuclear magnetic resonance (^{19}F NMR) spectroscopy:

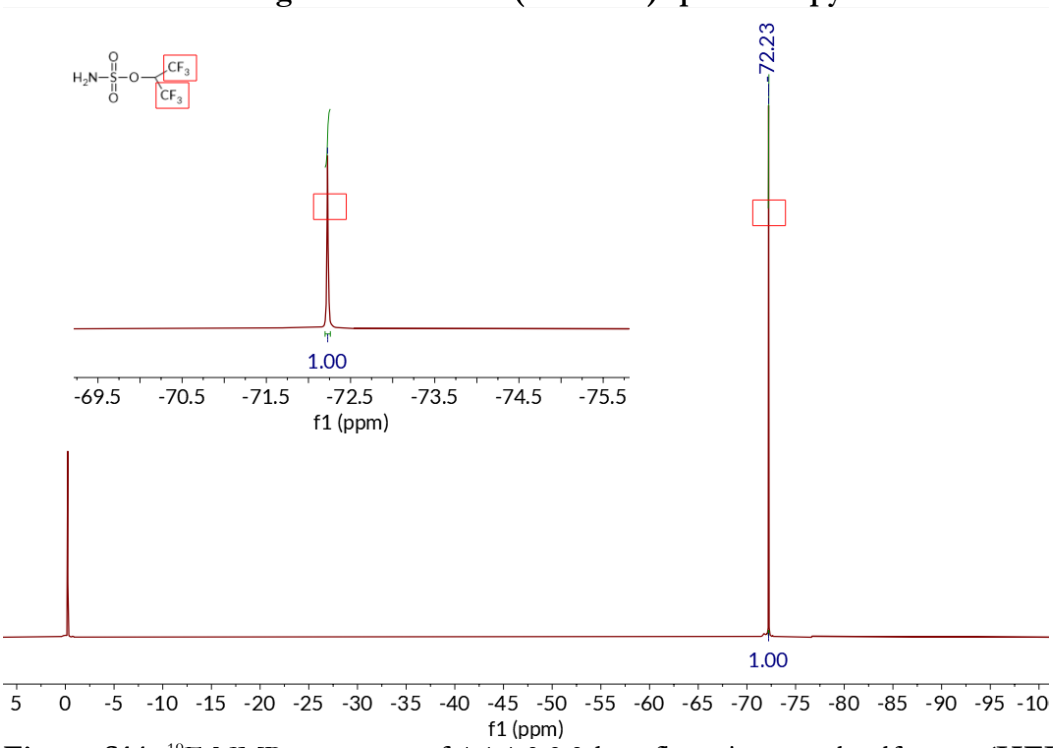


Figure S14: ^{19}F NMR spectrum of 1,1,1,3,3,3-hexafluoroisopropyl sulfamate **(HFIPS)** (470 MHz, DMSO-d_6, referenced to freon-11).

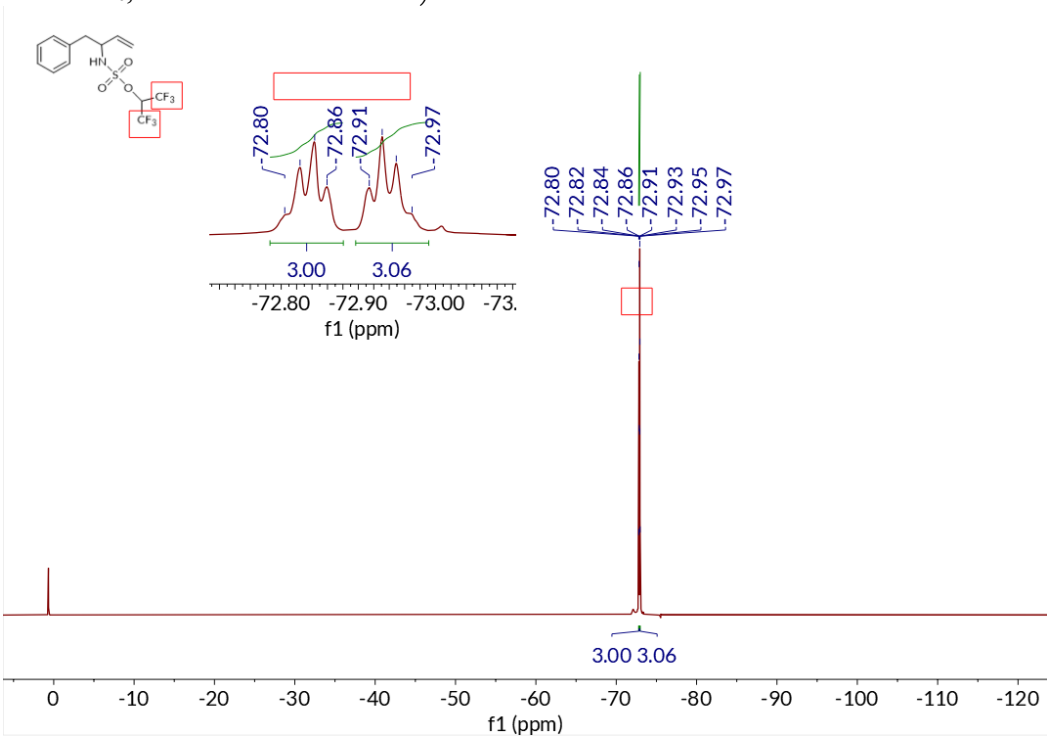


Figure S15: ^{19}F NMR spectrum of **4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (2)** (470 MHz, $CDCl_3$, referenced to freon-11).

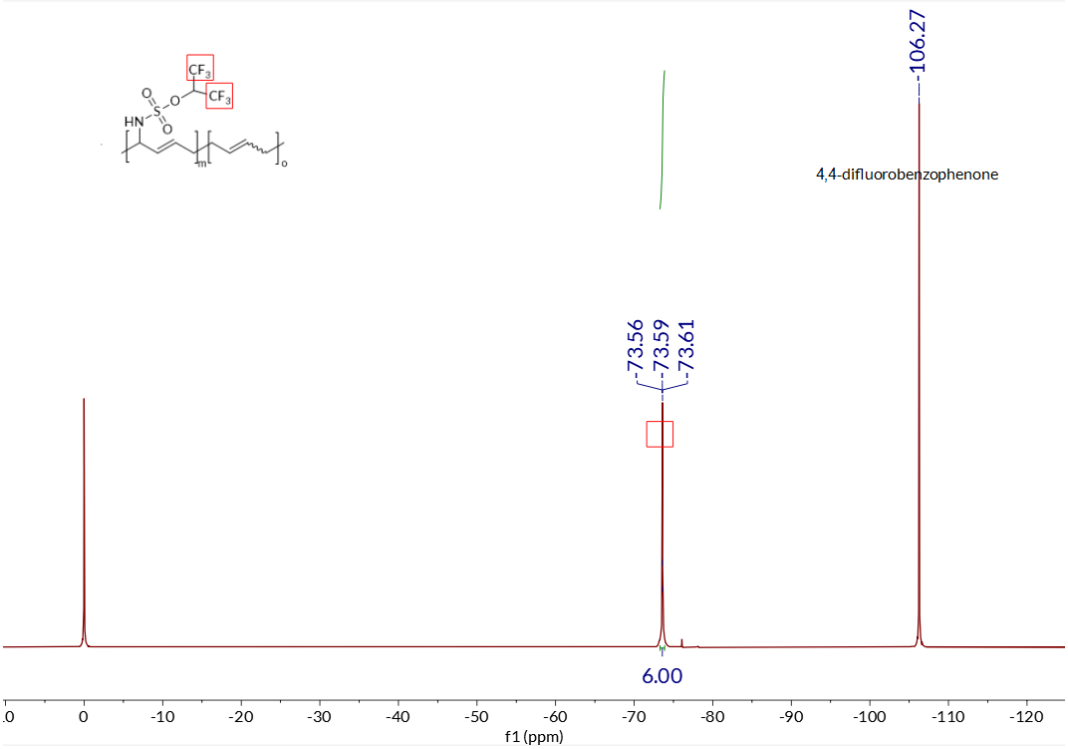


Figure S16: ^{19}F NMR spectrum of **PBD-HFIPS-3** (470 MHz, $CDCl_3$, referenced to freon-11, doped with 4,4-difluorobenzophenone).

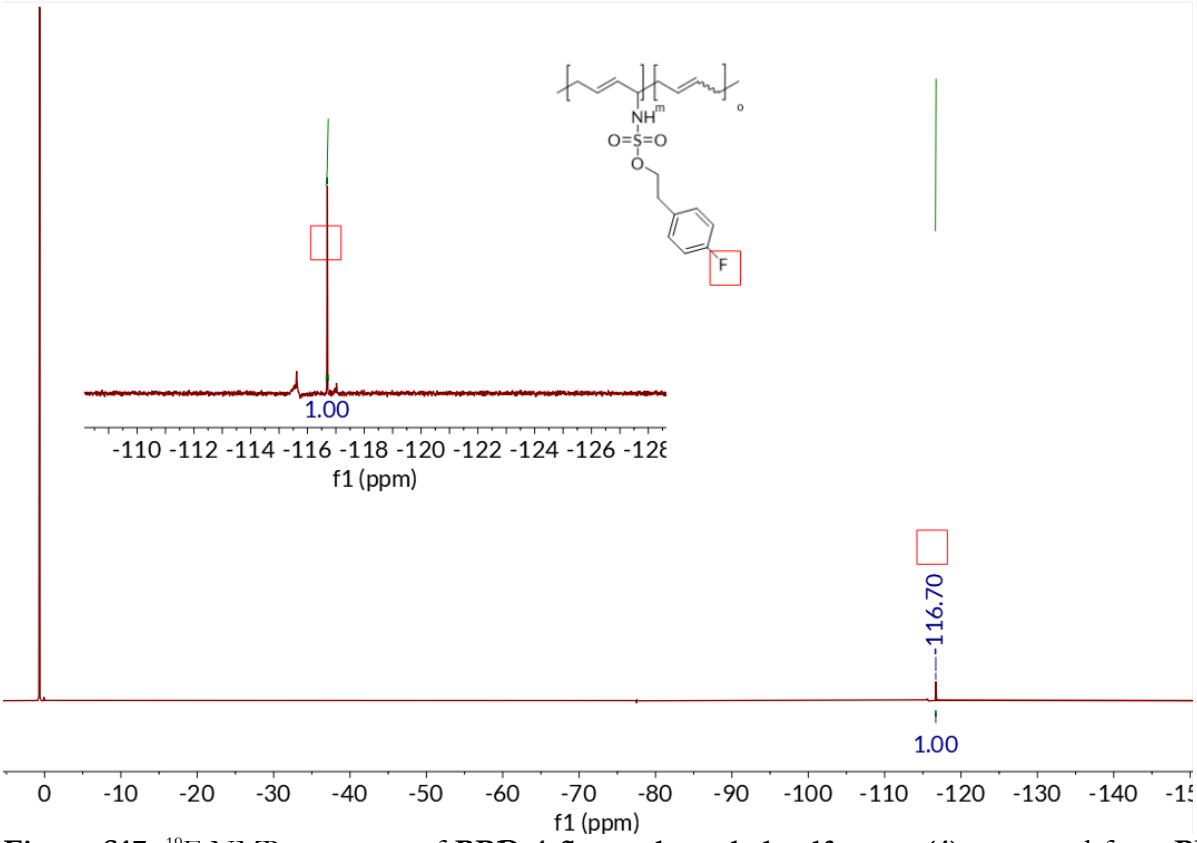


Figure S17: ^{19}F NMR spectrum of **PBD-4-fluorophenethyl sulfamate (4)** generated from **PBD-HFIPS-6** (470 MHz, $CDCl_3$).

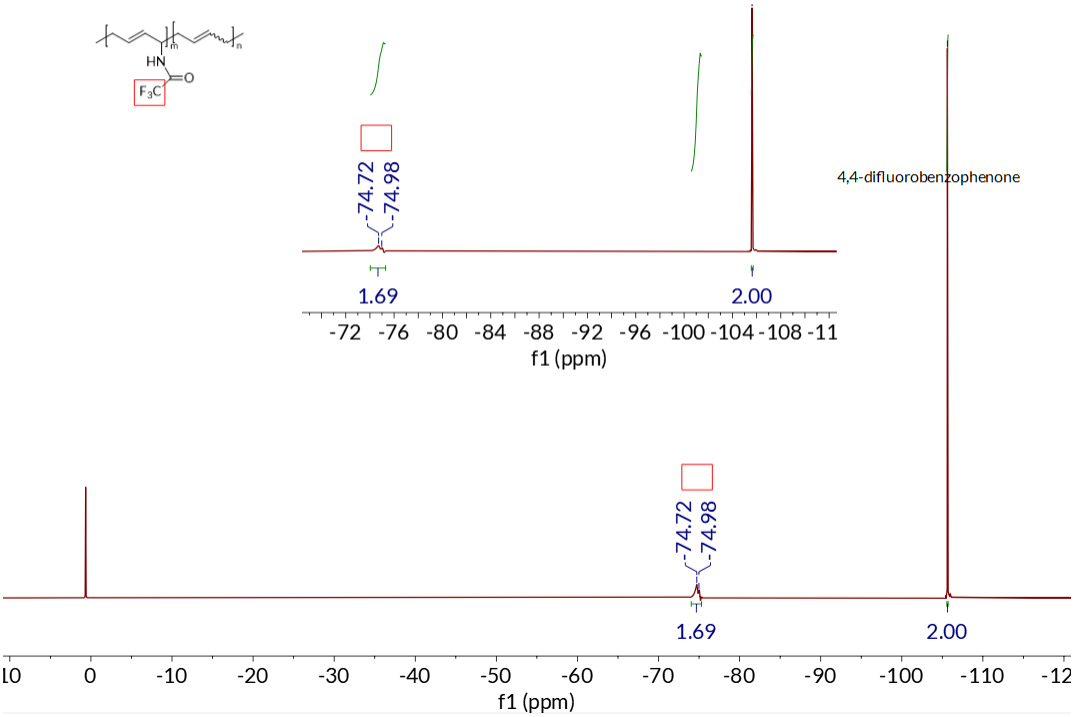


Figure S18: ^{19}F NMR spectrum of **PBD-NH$_2$-3** amidated with trifluoroacetic anhydride (470 MHz, $CDCl_3$, referenced to freon-11, doped with 4,4-difluorobenzophenone [0.020 mmol])

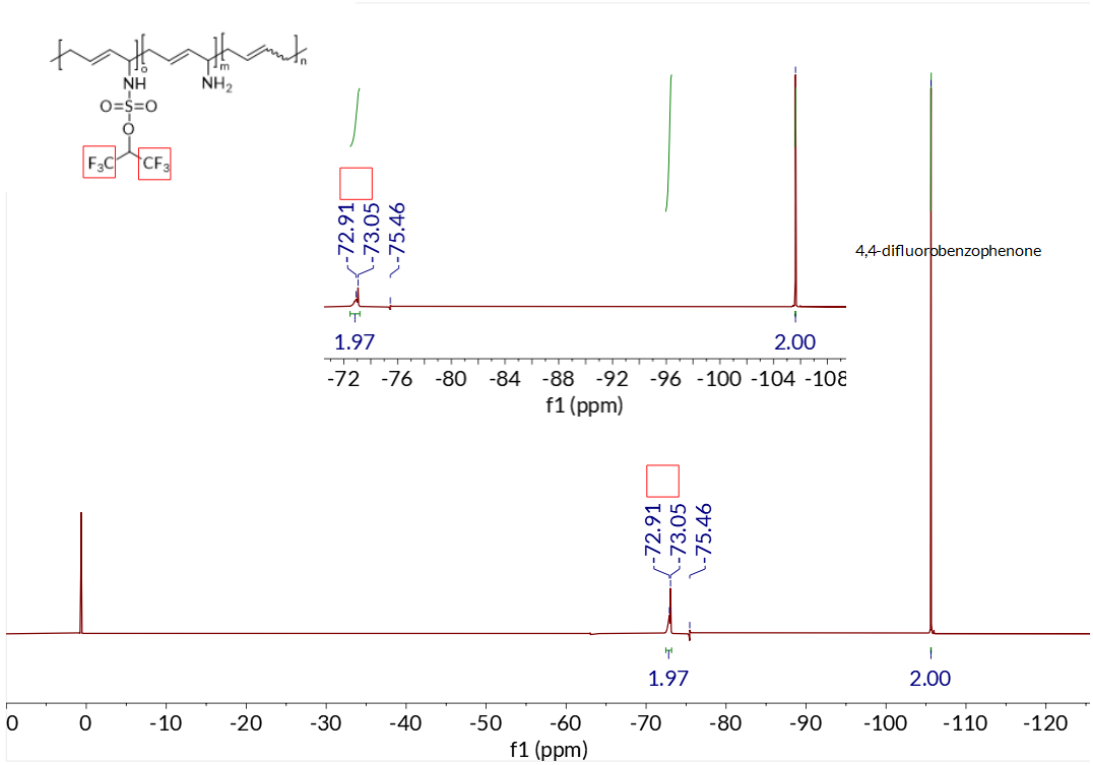


Figure S19: ^{19}F NMR spectrum of **PBD-TEG-3** decrosslinked and reaminated to form **(PBD-NH$_2$-3)-HFIPS-6** (470 MHz, $CDCl_3$, referenced to freon-11, doped with 4,4-difluorobenzophenone).

Carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy:

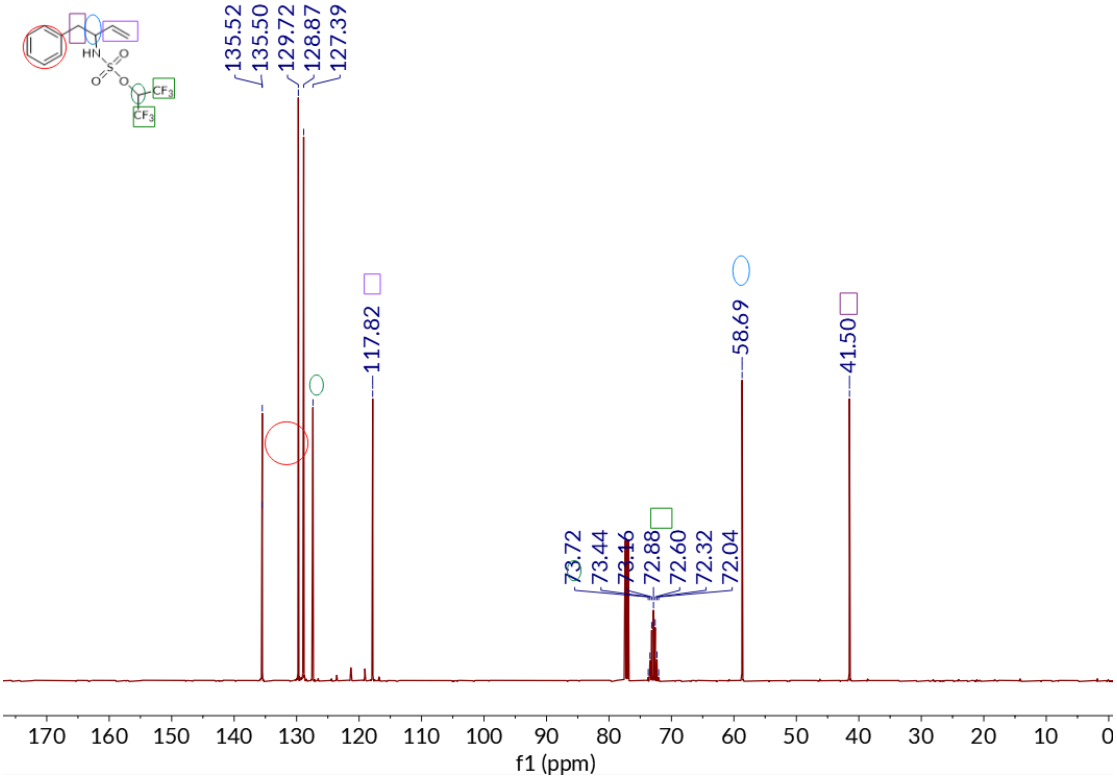


Figure S20: ^{13}C NMR spectrum of **4-phenyl-2-hexafluoroisopropylsulfamate-1-butene (2)** (126 MHz, $CDCl_3$).

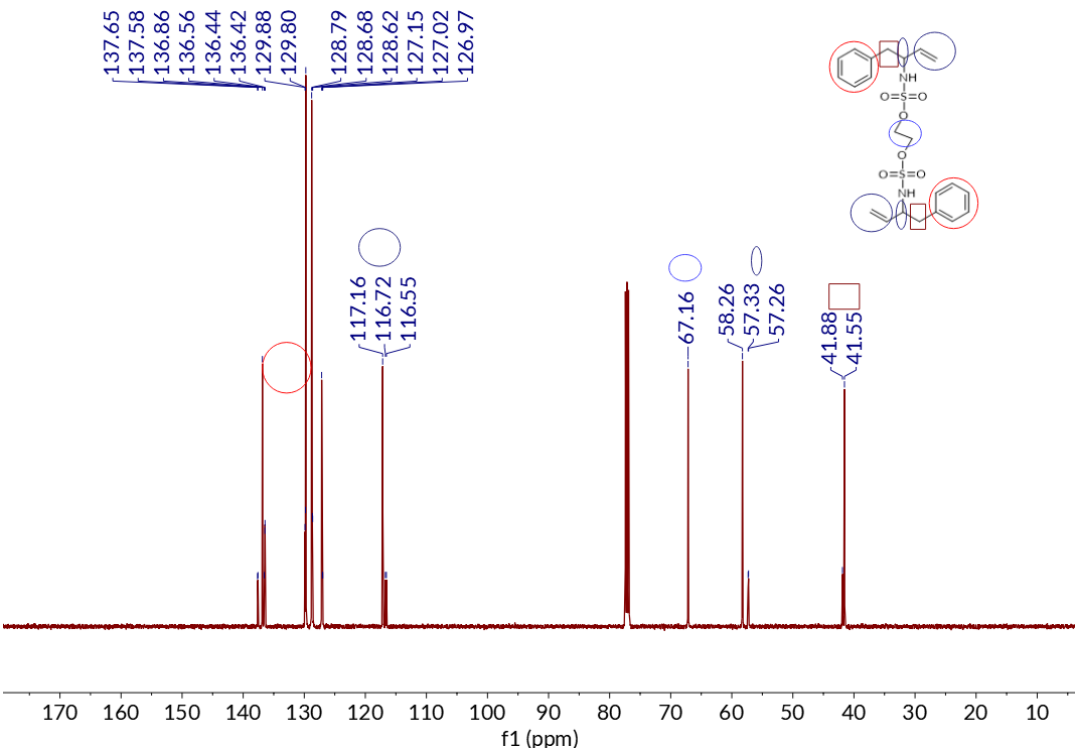


Figure S21: ^{13}C NMR spectrum of **4-phenyl-1-butene dimerized with ethylene glycol (3)** (126 MHz, $CDCl_3$).

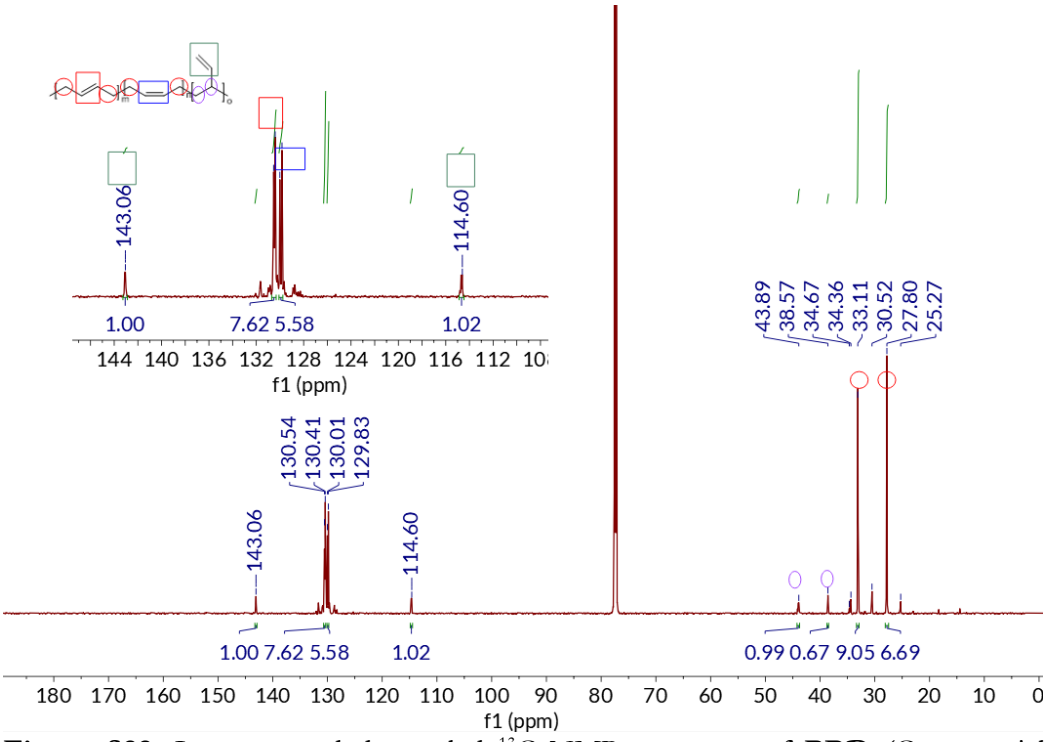


Figure S22: Inverse-gated decoupled ^{13}C NMR spectrum of **PBD** (Commercial sample, Sigma-Aldrich) (200 MHz, $CDCl_3$ w/o TMS). Integration of diagnostic signals at 115 ppm and 143 ppm relative to other olefinic signals (ca. 130 ppm) reveals *13%* vinyl content in this sample.

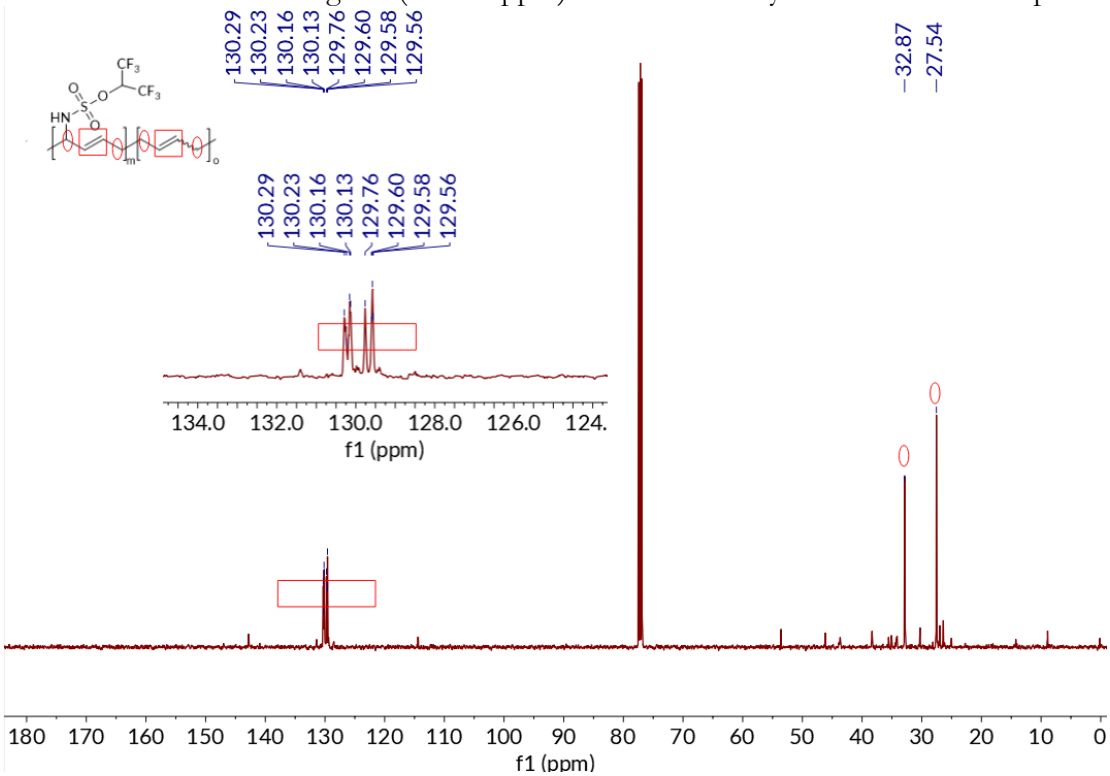


Figure S23: ^{13}C NMR spectrum of **PBD-HFIPS-3** (126 MHz, $CDCl_3$).

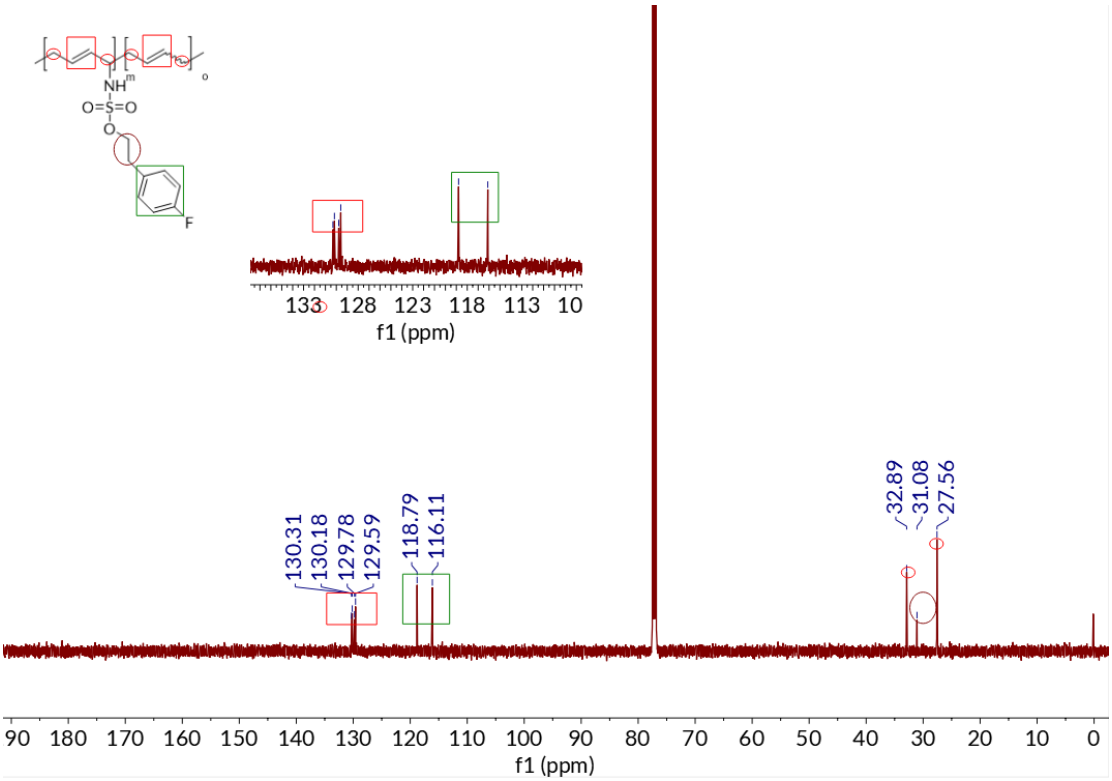


Figure S24: ^{13}C NMR spectrum of **PBD-4-fluorophenethyl sulfamate (4)** (126 MHz, $CDCl_3$).

Thermogravimetric Analysis (TGA)

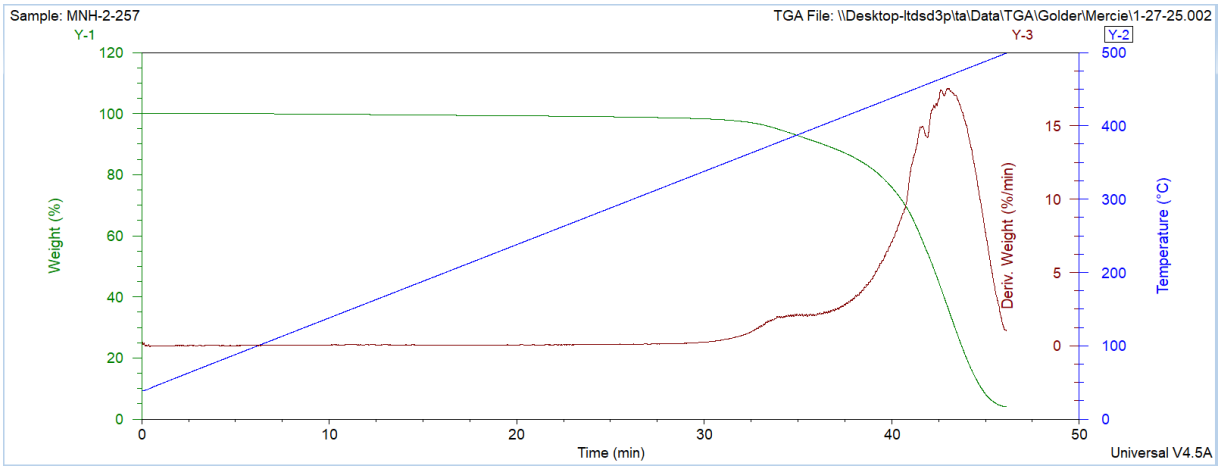


Figure S25: Thermogravimetric analysis of **PBD-Thiol-3** (9.991 mg) $T_{d,10\%}$ 401 °C

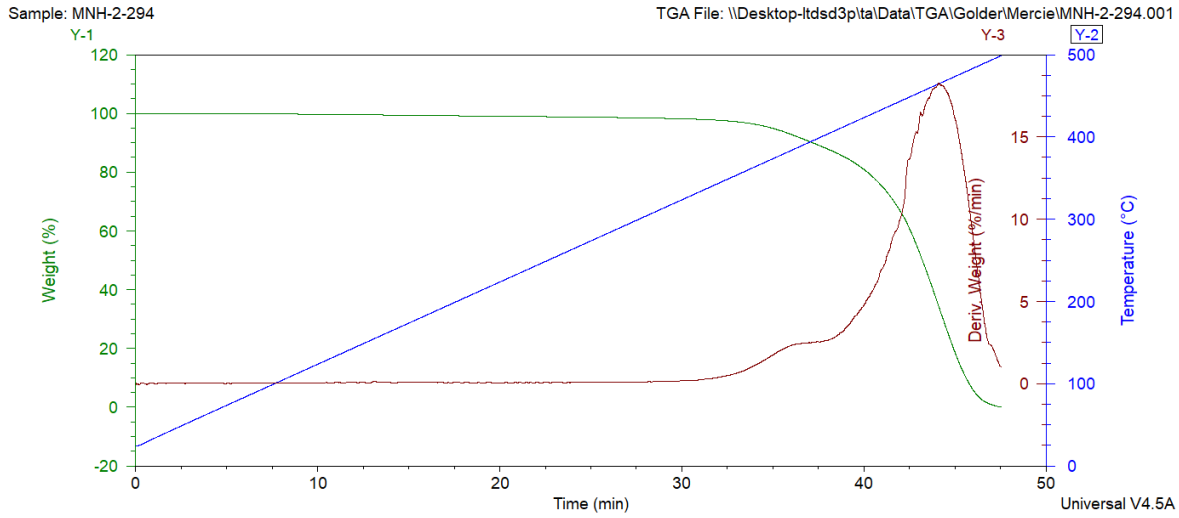


Figure S26: Thermogravimetric analysis of **PBD-Thiol-8** (3.931 mg) $T_{d,10\%}$ 395 °C

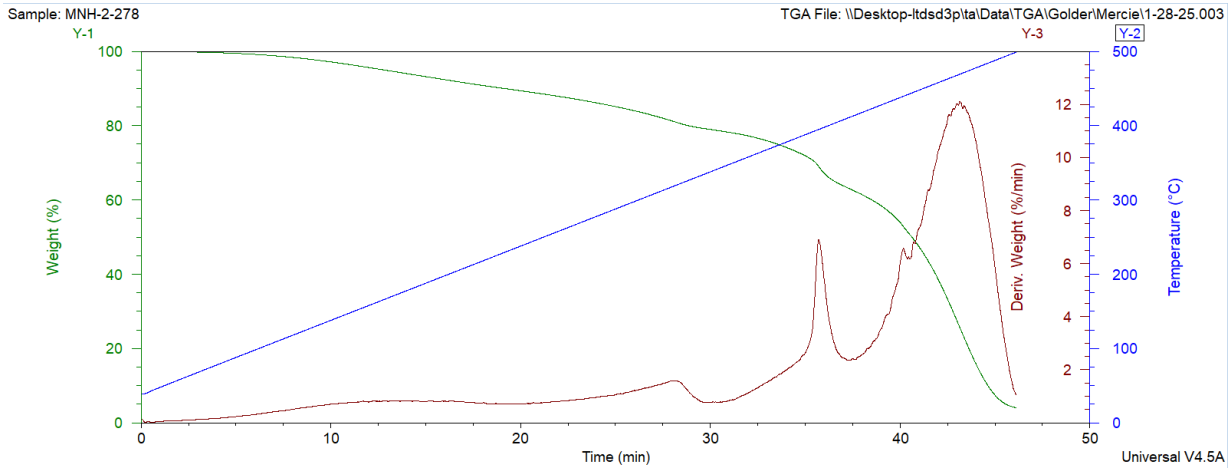


Figure S27: Thermogravimetric analysis of **PBD-EG-3** (14.192 mg) $T_{d,10\%}$ 229 °C

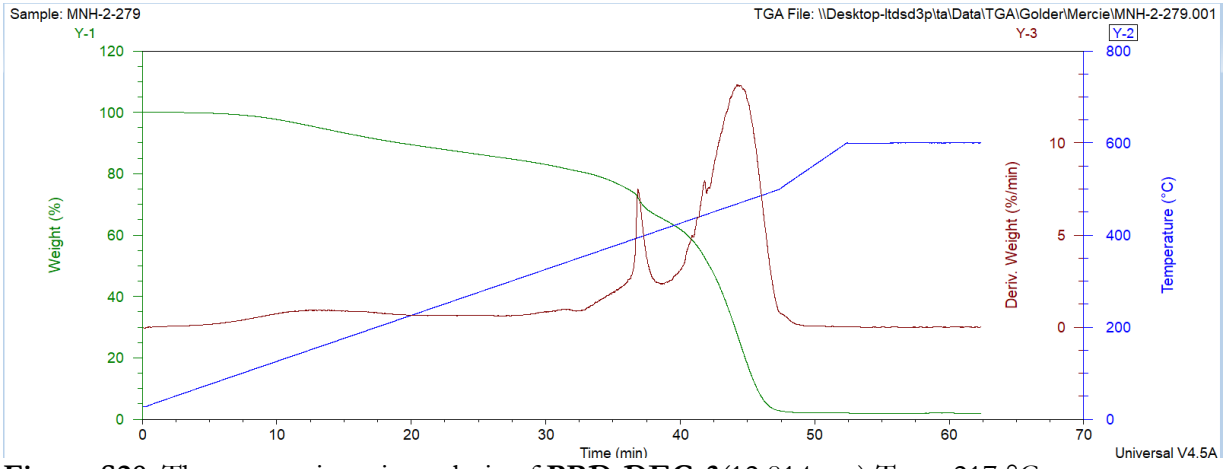


Figure S28: Thermogravimetric analysis of **PBD-DEG-3**(12.814 mg) $T_{d,10\%}$ 217 °C

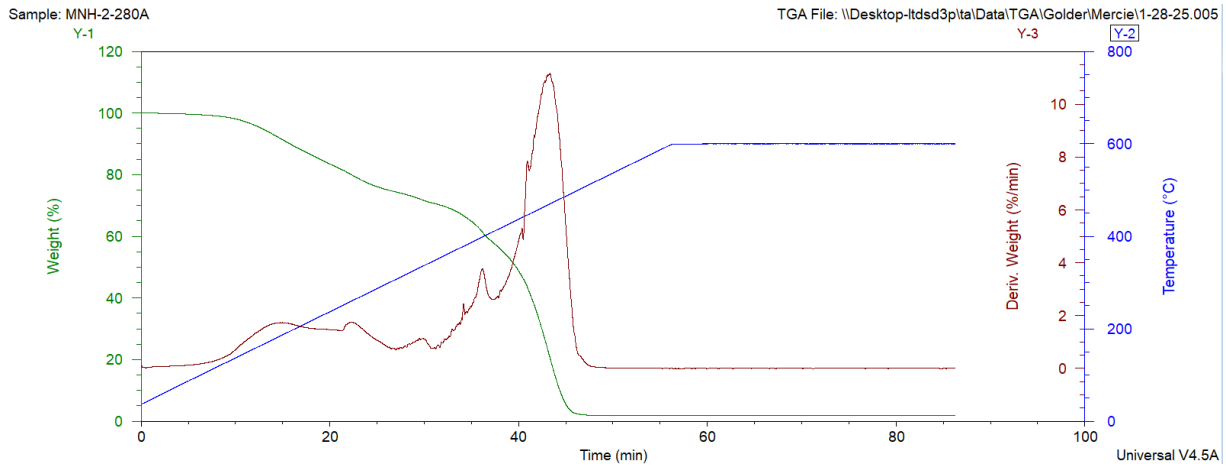


Figure S29: Thermogravimetric analysis of **PBD-TEG-3** (18.082 mg) $T_{d,10\%}$ 194 °C

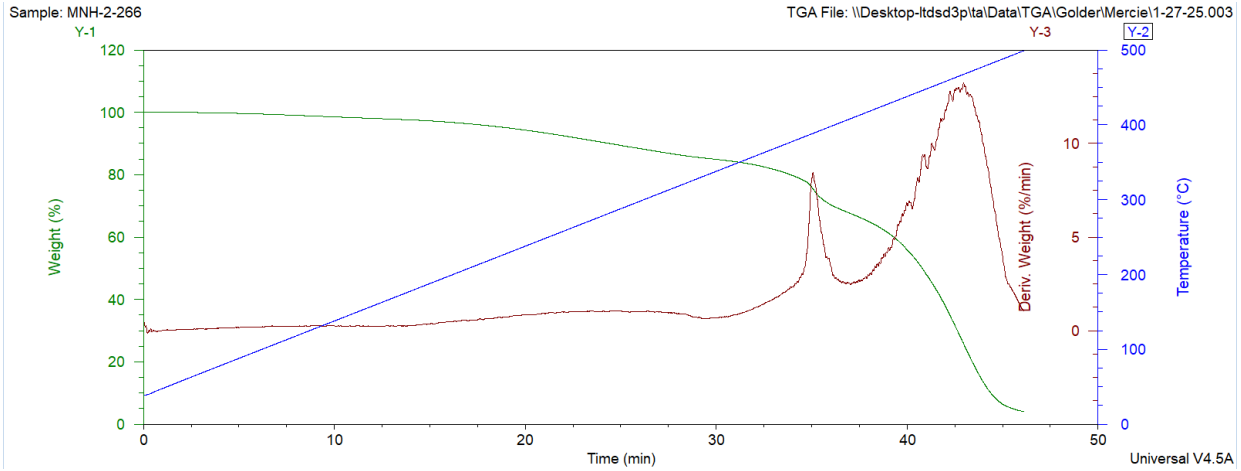


Figure S30: Thermogravimetric analysis of **PBD-EG-6** (4.225 mg) $T_{d,10\%}$ 282 °C

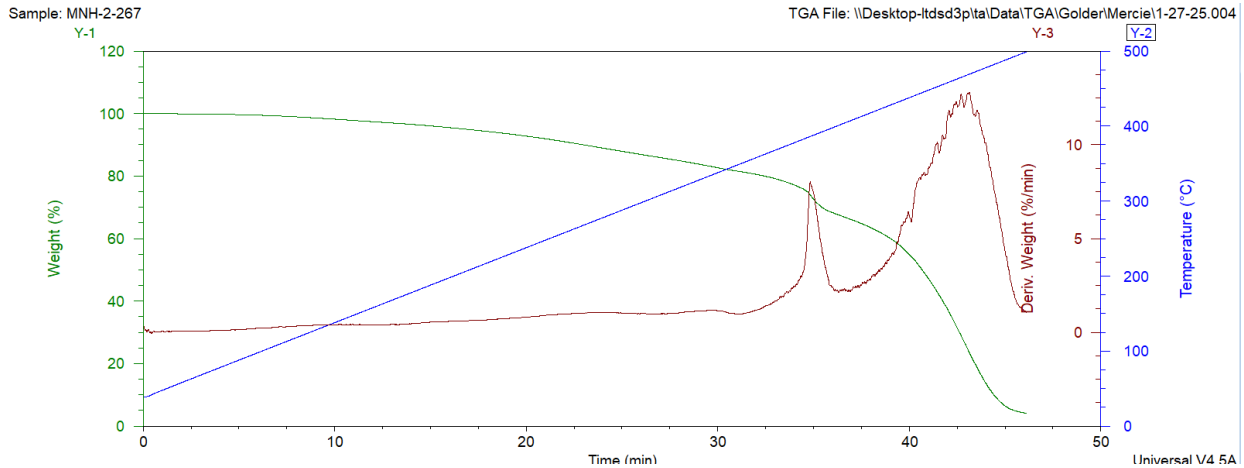


Figure S31: Thermogravimetric analysis of **PBD-DEG-6** (6.817 mg) $T_{d,10\%}$ 266 °C

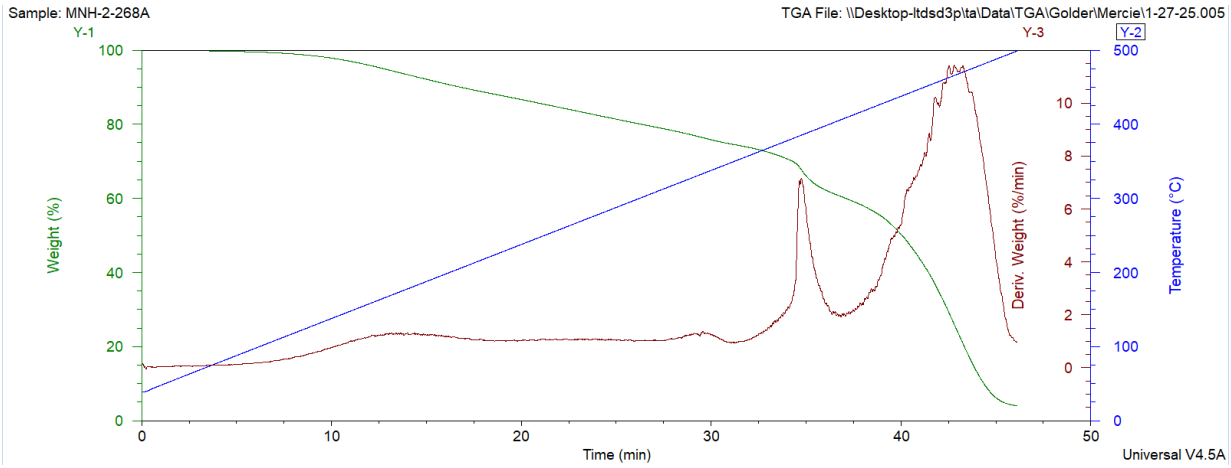


Figure S32: Thermogravimetric analysis of **PBD-TEG-6** (8.661 mg) $T_{d,10\%}$ 206 °C

Rheological data:
Rheological testing was carried out on 8 mm diameter, 1 mm thick discs.

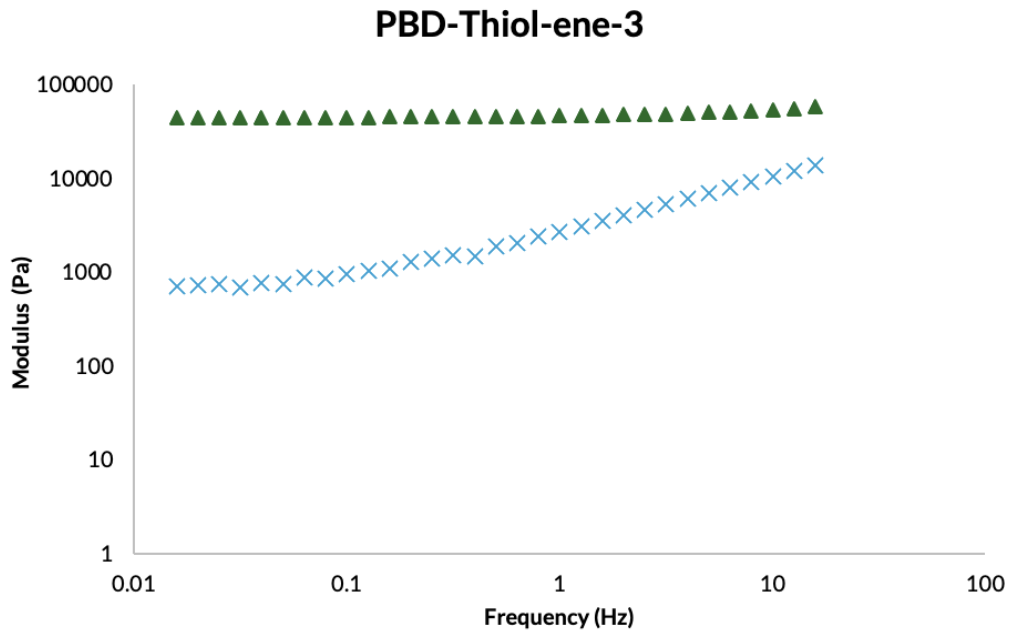


Figure S33: Frequency sweep of **PBD-Thiol-3** at 0.25% strain.

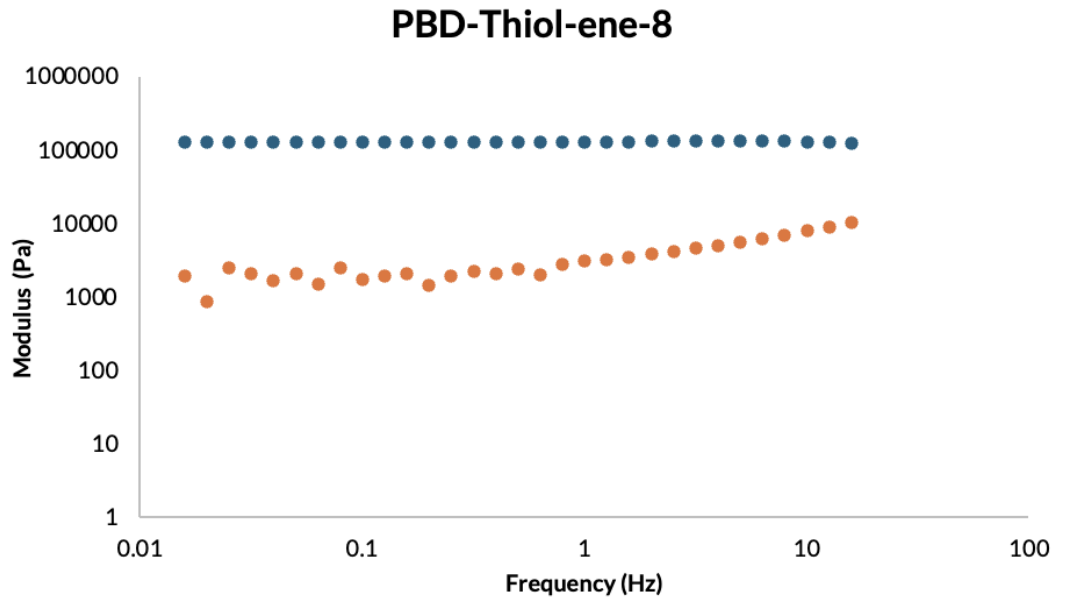


Figure S34: Frequency sweep of **PBD-Thiol-8** at 0.50% strain.

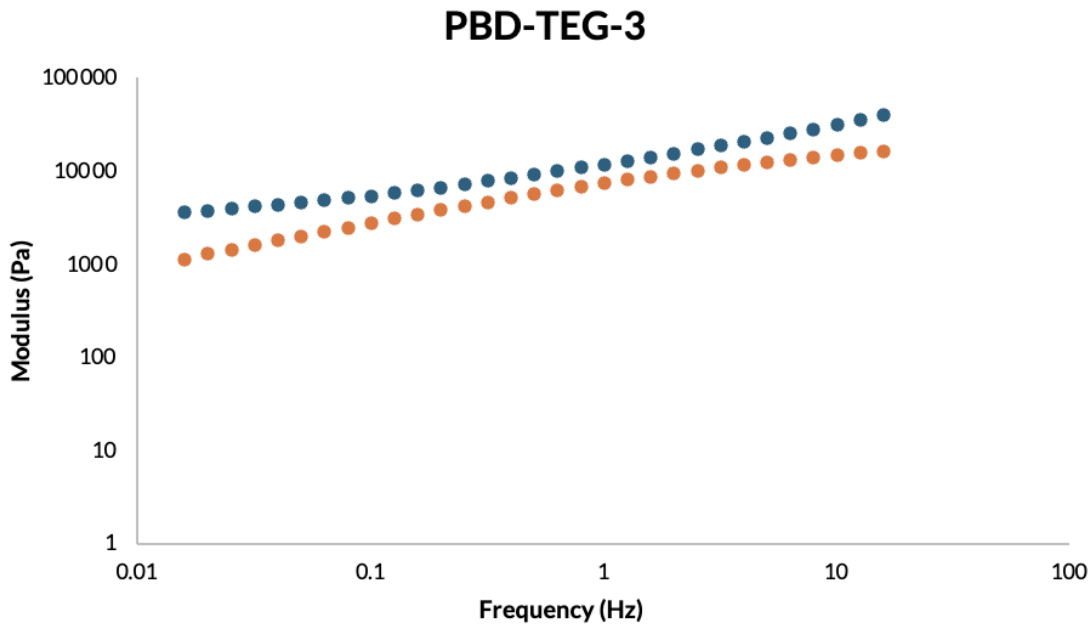


Figure S35: Frequency sweep of **PBD-TEG-3** at 0.50% strain.

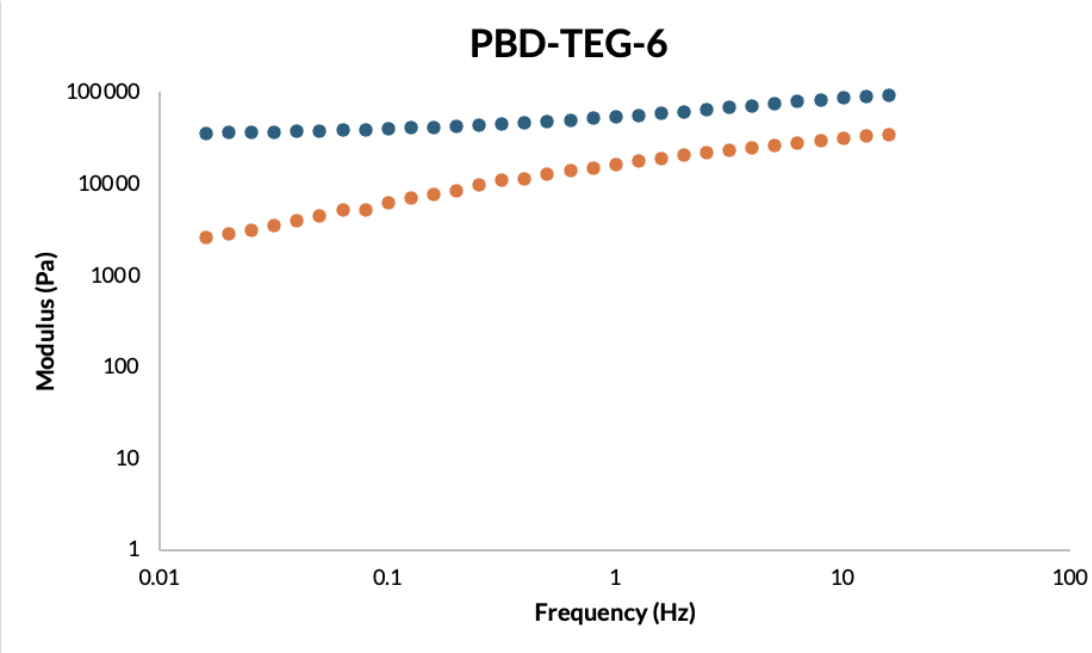


Figure S36: Frequency sweep of **PBD-TEG-6** at 0.50% strain.

Compression Data:
All compression analysis was carried out on 5 mm diameter, 3 mm thick discs.

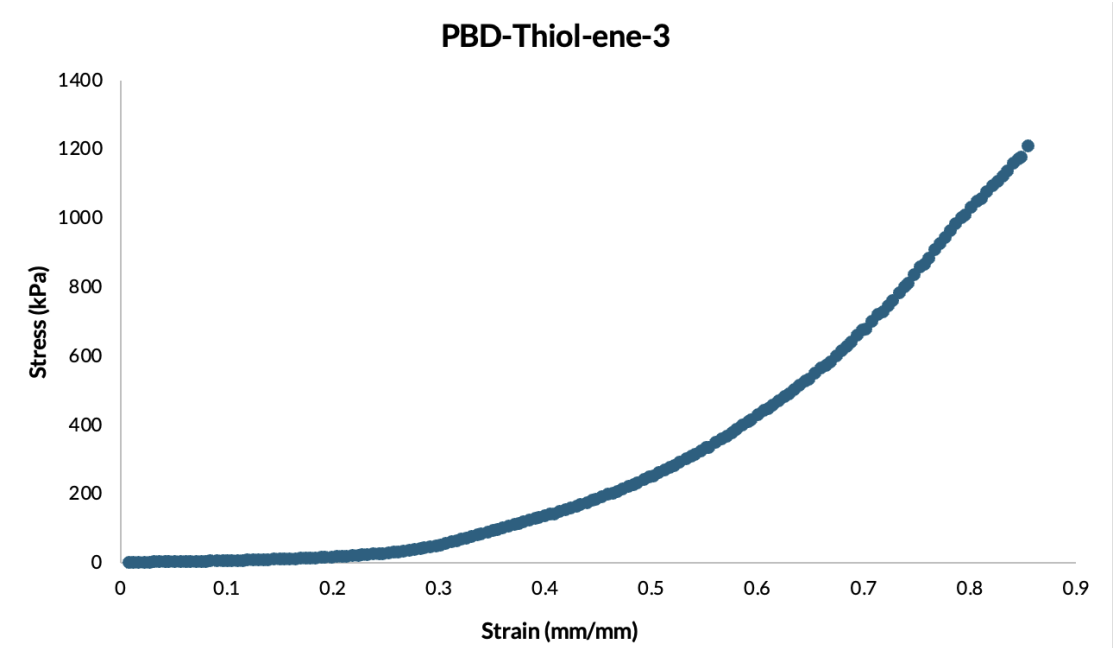


Figure S37: Compression of representative **PBD-Thiol-3** specimen with 1 kN load frame cell, measured to strain at break.

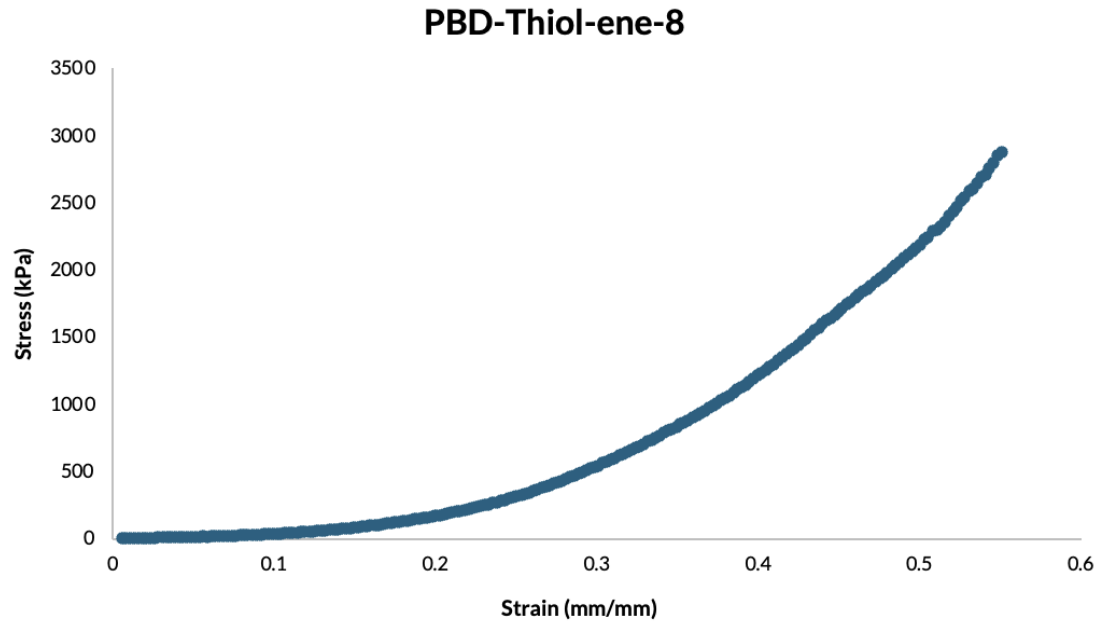


Figure S38: Compression of representative **PBD-Thiol-8** specimen with 1 kN load frame cell, measured to strain at break.

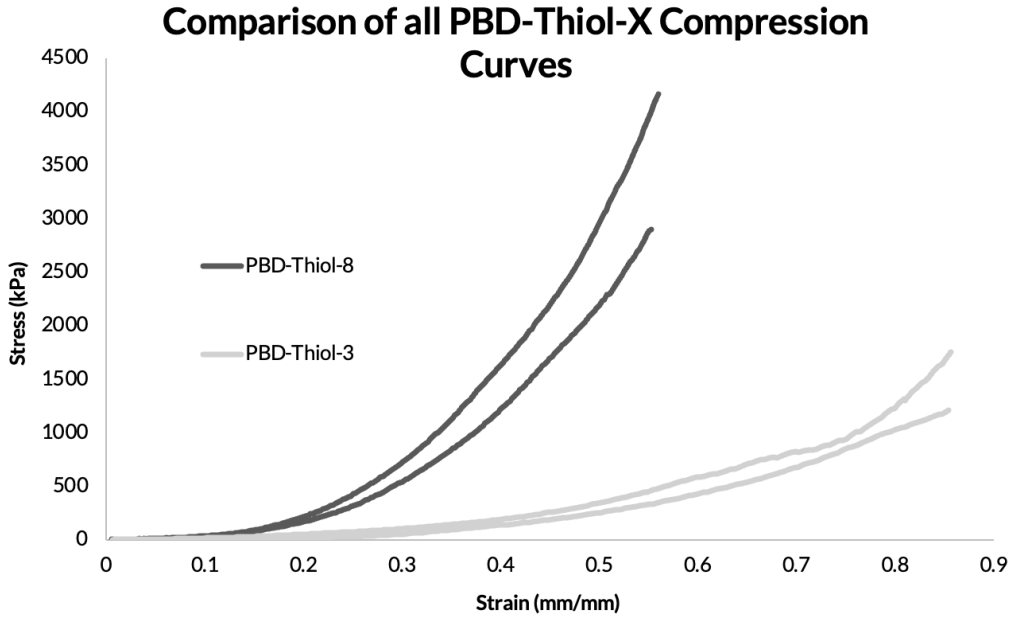


Figure S39: Overlay of duplicate compression analysis of both **PBD-Thiol-X** specimens (n = 2 each).

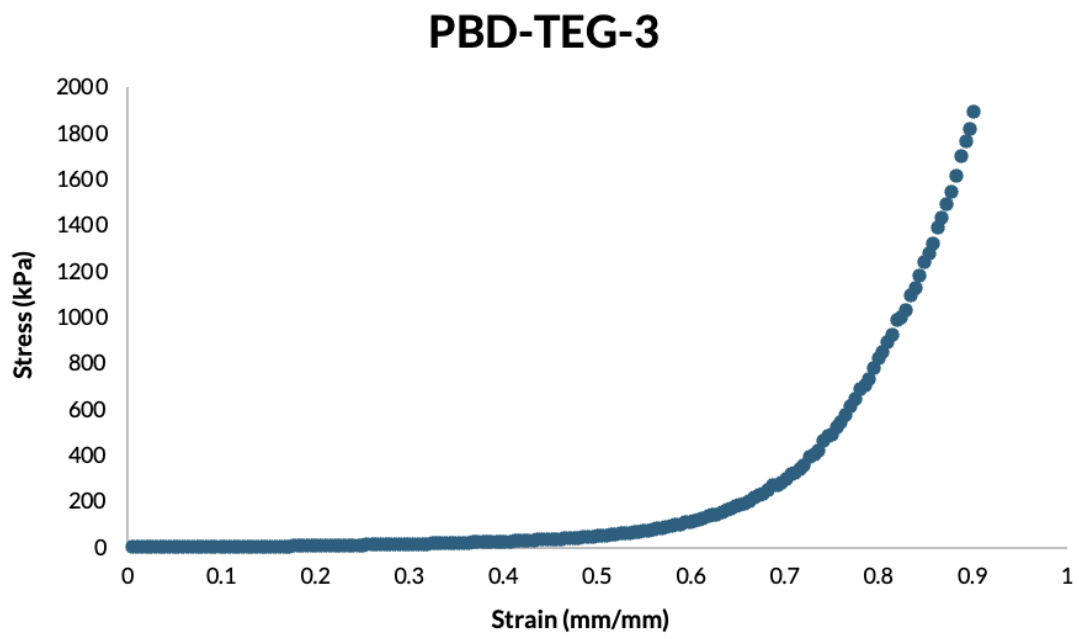


Figure S40: Compression of representative **PBD-TEG-3** specimen with 43N load frame cell, measured to strain at break.

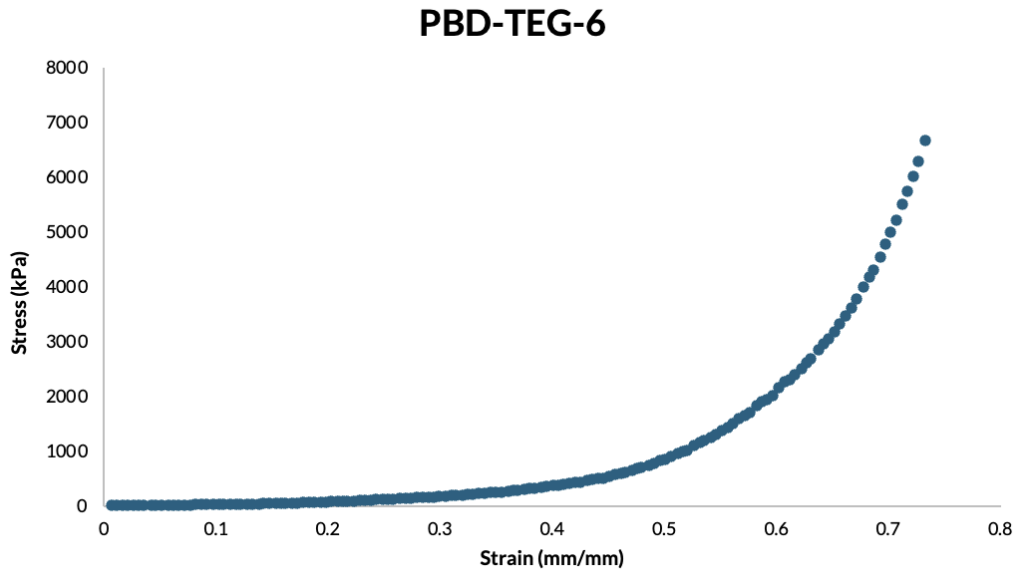


Figure S41: Compression of representative **PBD-TEG-6** specimen with 1 kN load frame cell, measured to strain at break.

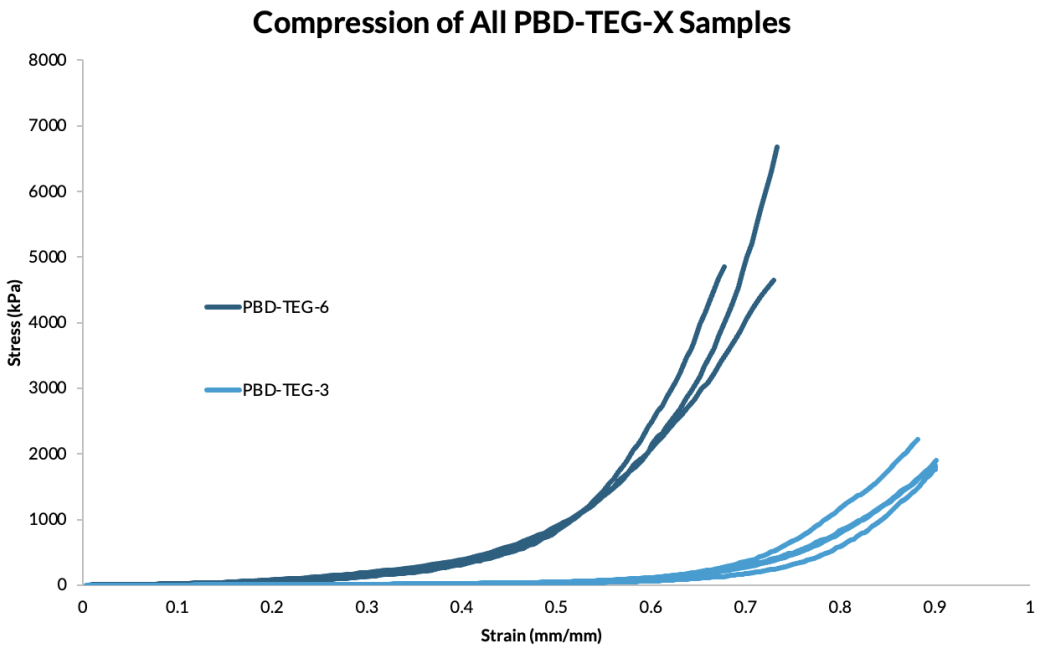


Figure S42: Overlay of replicate compression analysis of **PBD-TEG-3** (n = 4) and **PBD-TEG-6** (n = 3) specimens.

Swelling Data:
Specimens were trimmed to the same size in triplicate and weighed, then soaked in 5 mL of tetrahydrofuran (THF) for 40 hours. Immediately upon removal from THF samples were again weighed and the difference in weights was calculated. The percent increase determined by dividing the difference by the starting measurement. Specimens were compared by one-tailed T-test to determine statistically significant differences in percent increase in weight.

Table S4: Weights and Volumes of Specimens before and after swelling in THF

Sample	Wo (mg)	Wf (mg)	Diff (mg)	%Inc (mg)
PBD-EG-6A	10.5	73.2	62.7	597.1
PBD-EG-6B	8.2	54.5	46.3	564.6
PBD-EG-6C	12.4	77.4	65.0	524.2
Ave PBD-EG-6	**10.4**	**68.4**	**58.0**	**562.0**
Std Dev	**2.1**	**12.2**	**10.2**	**36.5**
PBD-DEG-6A	9.1	61.0	51.9	570.3
PBD-DEG-6B	12.4	66.8	54.4	438.7
PBD-DEG-6C	9.5	59.5	50.0	526.3
Ave PBD-DEG-6	**10.3**	**62.4**	**52.1**	**511.8**
Std Dev	**1.8**	**3.9**	**2.2**	**67.0**
PBD-TEG-6A	12.3	68.2	55.9	454.5
PBD-TEG-6B	12.9	65.9	53.0	410.9
PBD-TEG-6C	12.8	74.8	62.0	484.4
Ave PBD-TEG-6	**12.7**	**69.6**	**57.0**	**449.9**
Std Dev	**0.3**	**4.6**	**4.6**	**37.0**
PBD-EG-3A	9.9	110.4	100.5	1015.2
PBD-EG-3B	10.9	110.3	99.4	911.9
PBD-EG-3C	13.0	127.5	114.5	880.8
Ave PBD-EG-3	**11.3**	**116.1**	**104.8**	**935.9**
Std Dev	**1.6**	**9.9**	**8.4**	**70.3**
PBD-DEG-3A	14.3	155.1	140.8	984.6
PBD-DEG-3B	10.1	113.2	103.1	1020.8
PBD-DEG-3C	14.2	150.0	135.8	956.3
Ave PBD-DEG-3	**12.9**	**139.4**	**126.6**	**987.2**
Std Dev	**2.4**	**22.9**	**20.5**	**32.3**
PBD-TEG-3A	15.2	135.5	120.3	791.4
PBD-TEG-3B	19.3	174.0	154.7	801.6
PBD-TEG-3C	16.1	137.6	121.5	754.7
Ave PBD-TEG-3	**16.9**	**149.0**	**132.2**	**782.6**
Std Dev	**2.2**	**21.6**	**19.5**	**24.7**
PBD-Thiol-3A	27.3	222.3	195.0	714.3
PBD-Thiol-3B	24.4	202.2	177.8	728.7
PBD-Thiol-3C	30.1	243.7	213.6	709.6
Ave PBD-Thiol-3	**27.3**	**222.7**	**195.5**	**717.5**
Std Dev	**2.9**	**20.8**	**17.9**	**9.9**
PBD-Thiol-8A	19.2	82.2	63.0	328.1
PBD-Thiol-8B	24.1	83.2	59.1	245.2
PBD-Thiol-8C	31.6	116.6	85.0	269.0
Ave PBD-Thiol-8	**25.0**	**94.0**	**69.0**	**280.8**
Std Dev	**6.2**	**19.6**	**14.0**	**42.7**

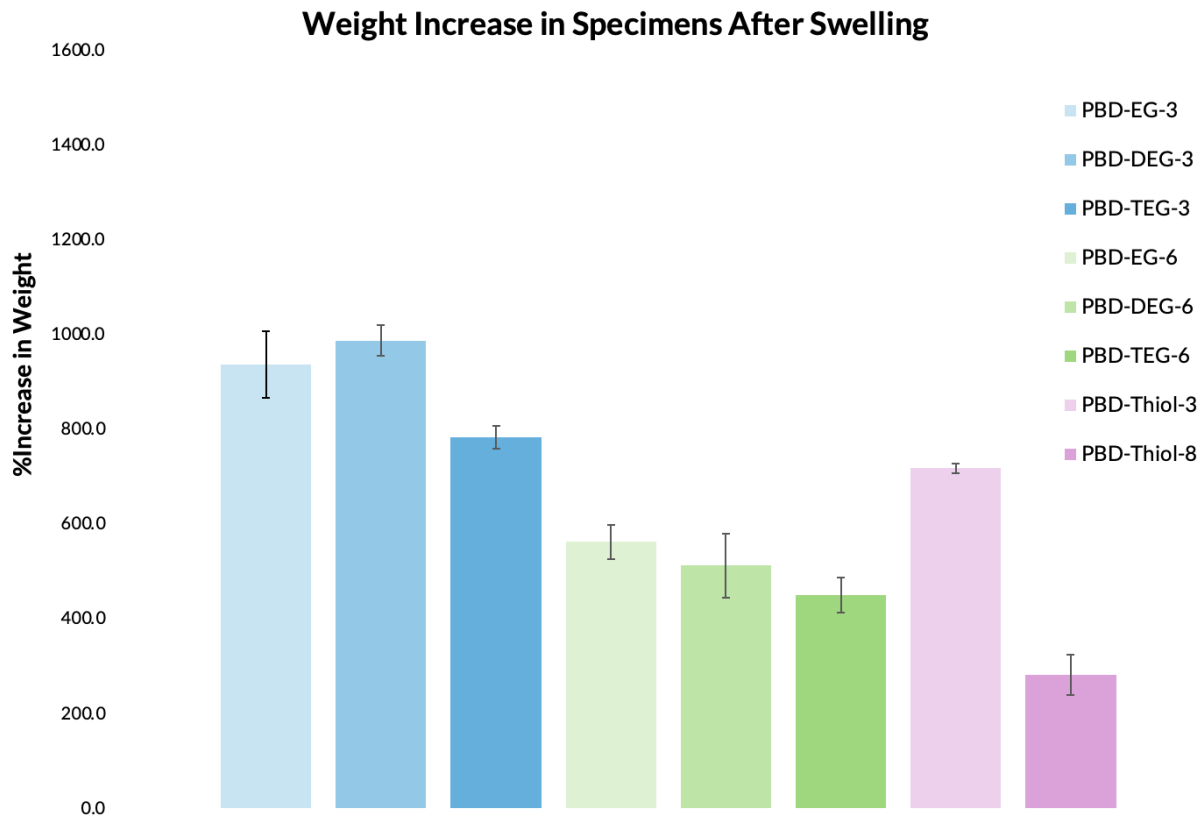


Figure S43: Graphical representation of mass increase (%) after swelling specimens.

Table S5: Results of one-tailed T-tests comparing the average percent increase in weight after swelling of specimens. P values < 0.05 are considered statistically significant, * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$

Specimens Being Compared	P-Value
PBD-EG-3 v. **PBD-DEG-3**	0.1673
PBD-DEG-3 v. **PBD-TEG-3**	0.0004769 (***)
PBD-EG-3 v. **PBD-TEG-3**	0.03526 (*)
PBD-EG-6 v. **PBD-DEG-6**	0.1686
PBD-DEG-6 v. **PBD-TEG-6**	0.1280
PBD-EG-6 v. **PBD-TEG-6**	0.01011 (*)
PBD-EG-3 v. **PBD-EG-6**	0.001917 (**)
PBD-DEG-3 v. **PBD-DEG-6**	0.0007893 (***)
PBD-TEG-3 v. **PBD-TEG-6**	0.0004953 (***)
PBD-Thiol-3 v. **PBD-Thiol-8**	0.001670 (**)

Analytical Calculations:

Representative calculation of using of 4,4-difluorobenzophenone as an internal standard for determining sulfamate density:

0.033 mmol of 4,4-difluorobenzophenone was added to 0.60 mL of $CDCl_3$ and used as a solvent in ^{1}H and ^{19}F NMR. The aromatic peaks were integrated to 4H (**Figure S44**), and the PBD peaks integrated relative to this.

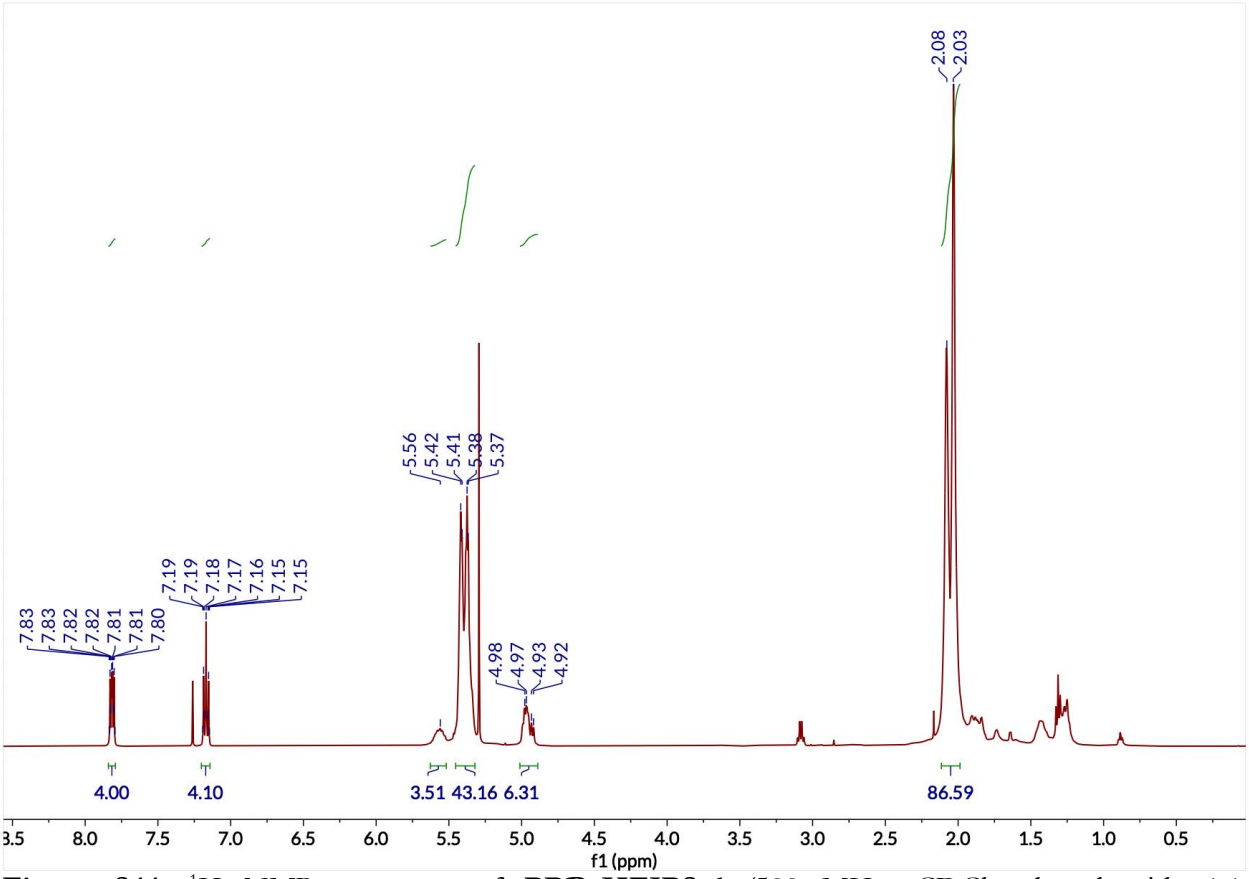


Figure S44: ^{1}H NMR spectrum of **PBD-HFIPS-6** (500 MHz, $CDCl_3$, doped with 4,4-difluorobenzophenone).

The mole amount of the PBD backbone was determined by dividing the relative inegration of the *cis-trans-* alkene peaks by 2H and multiplying by 0.87, as the backbone is 87% *cis- trans-*. Multiplying this by the mmols of 4,4-difluorobenzophenone yields the mmols of PBD present.

$$mole\ amount\ PBD = \frac{43.16}{2} x0.87x0.033\ mmol = 0.62\ mmol\ PBD$$

Equation S1: Determining the mole amount of the PBD backbone.

Similar analysis is then performed on a ^{19}F NMR spectrum of the same compound:

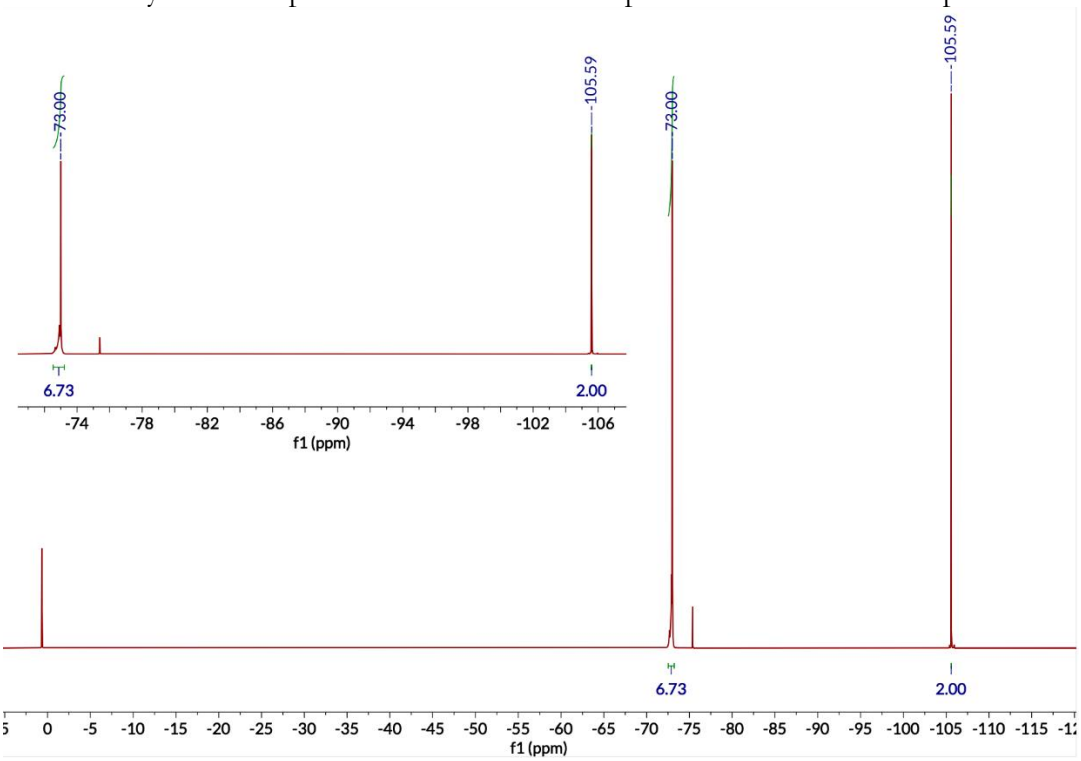


Figure S45: ^{19}F NMR spectrum of **PBD-HFIPS-6** (470 MHz, $CDCl_3$, referenced to freon-11, doped with 4,4-difluorobenzophenone).

The mole amount of grafted HFIPS was determined by dividing the relative integration of the PBD-HFIPS fluorine peak by 6F and multiplying this by the mmols of 4,4-difluorobenzophenone yields the mmols of PBD present.

$$mole\ amount\ PBD = \frac{6.73}{6} x 0.033\ mmol = 0.037\ mmol\ HFIPS$$

Equation S2: Determining the mole amount of grafted HFIPS.

The mmols of grafted HFIPS can then be divided by the mmols of PBD backbone and multiplied by 100 to yield the percent of sulfamate functionalization.

$$\%Sulfamate\ Functionalization = \frac{0.037\ mmol\ HFIPS}{0.62\ mmol\ PBD} x 100 = 6.0\%$$

Equation S3: Determining the percent functionalization of **PBD-HFIPS-X**.

Images of Materials

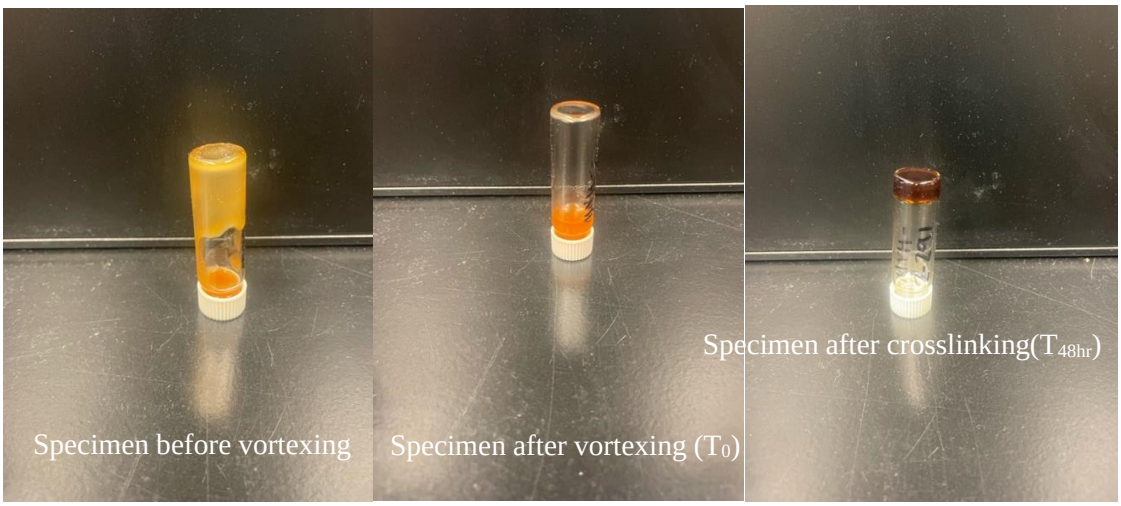


Figure S46: Representative sol-gel image of **PBD-EG-3** before and after crosslinking

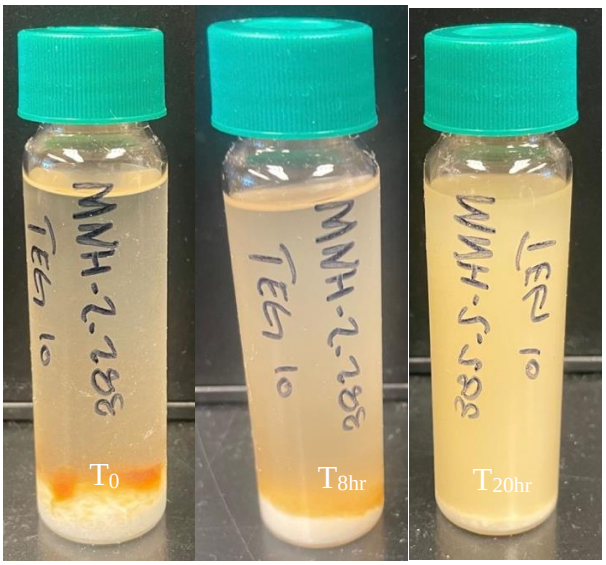


Figure S47: Representative images of the progression of decrosslinking **PBD-TEG-3**

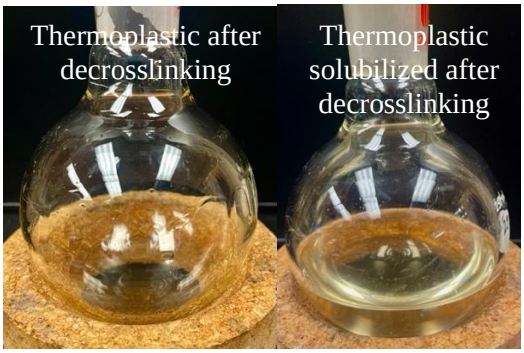


Figure S48: Final product of decrosslinking **PBD-TEG-3**

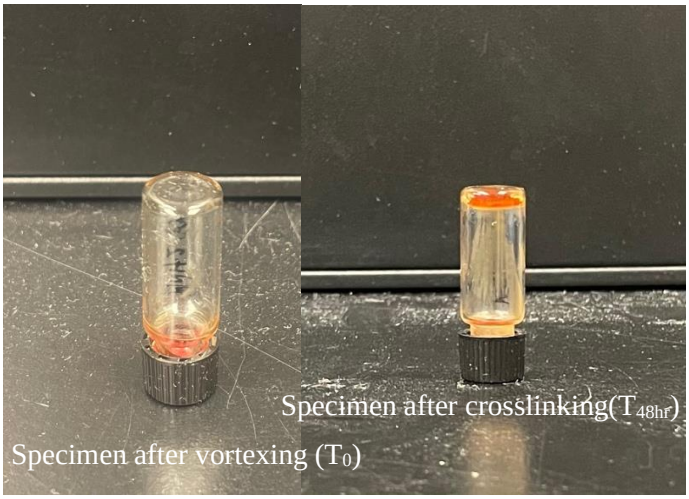


Figure S49: Representative sol image of **(PBD-NH_2-3)-HFIPS-6** (generated from decrosslinked then reaminated **PBD-R-3**) prior to re-crosslinking [left] and gel image of **(PBD-NH_2-3)-TEG-6** after re-crosslinking with TEG [right].

References

(1) Teh, W. P.; Obenschain, D. C.; Black, B. M.; Michael, F. E. Catalytic Metal-Free Allylic C−H Amination of Terpenoids. *J Am Chem Soc* 2020, *142* (39), 16716–16722. https://doi.org/10.1021/jacs.0c06997.

(2) Sguazzin, M. A.; Johnson, J. W.; Magolan, J. Hexafluoroisopropyl Sulfamate: A Useful Reagent for the Synthesis of Sulfamates and Sulfamides. *Org Lett* 2021, *23* (9), 3373–3378. https://doi.org/10.1021/acs.orglett.1c00855.