

Supporting Information For:

Liquid-Assisted Grinding Enables a Direct Mechanochemical Functionalization of Polystyrene Waste

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General Considerations:

Materials

All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Styrene was purchased from Acros and purified by passing through basic alumina immediately before use. 1,2-dichloroethane (DCE), purchased from ThermoFisher Scientific, and (trifluoromethyl)trimethylsilane (TMSCF₃), purchased from Tokyo Chemical Industry (TCI), were fractionally distilled, freeze-pump-thawed for three cycles, and stored over 3Å molecular sieves before use. Silver (I) triflate (AgOTf) was purchased from TCI. Anhydrous potassium fluoride (KF) and **Commercial PS** was purchased from Sigma-Aldrich. Plasticizers dioctyl terephthalate (DOTP) and tributyl citrate (TBC) were purchased from Sigma-Aldrich and were dried under high vacuum overnight at 100 °C before use. Post-consumer polystyrene (**PS**) waste was identified by the #6 recycling label. **EPS Foam** waste was sourced from the University of Washington Department of Chemistry waste collection and was either dissolved in dichloromethane (DCM), dried with sodium sulfate, and concentrated (**Native EPS Foam**) or precipitated into cold methanol (MeOH) once and dried under high vacuum (**Precipitated EPS Foam**) before use. Dyed **PS Lids** were obtained from a local café and either ground into flakes using a coffee grinder (**Native PS Lid**) or dissolved in DCM, treated with activated charcoal, filtered, and precipitated in cold MeOH once and dried under high vacuum (**Precipitated PS Lid**) before use. All air-sensitive atom transfer radical polymerization (ATRP) reactions were performed under inert atmosphere (nitrogen) using standard Schlenk technique. Ball milling experiments were performed using a Retsch Mixer Mill (MM 400) ball mill instrument in 5 mL stainless steel screw-top ball milling jars with two 8 mm stainless steel grinding balls (MSE Supplies LLC) unless otherwise noted. All ball milling experiments were charged with reagents (except for **PS**) and sealed under an inert atmosphere (nitrogen) in an Innovative Technologies Pure Lab glovebox. 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

^1H nuclear magnetic resonance (^1H NMR) spectra were taken on a Bruker AVANCE-300 at 300 MHz, a Bruker AVANCE-500 at 500 MHz, or a Bruker AVANCE NEO-500 at 500 MHz. ^{19}F nuclear magnetic resonance (^{19}F NMR) spectra were obtained on a Bruker AVANCE-500 at 470 MHz. ^1H NMR spectra were taken in chloroform-*d* with TMS (CDCl_3 , referenced to TMS, δ 0.00 ppm). ^{19}F NMR spectra were taken in chloroform-*d* doped with freon-11 (CDCl_3 , referenced to freon-11, δ 0.65 ppm) unless otherwise stated. Fluorobenzene (δ -112.96 ppm) or 4,4'-difluorobenzophenone (δ -105.65 ppm) were used as internal standards to quantify functionalization density. 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).

Gas chromatography–mass spectrometry (GCMS) data were collected on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 quadrupole mass spectrometer (electron impact ionization). The analyte was prepared at a concentration of ca. 0.1 mg/mL in dichloromethane.

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 (ca. 3 mg/mL) 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. The following *dn/dc* values were determined by the 100% mass recovery method using Wyatt ASTRA 7.3 software:

8.9 kDa PS: 0.1312, 9.3 kDa PS: 0.1301, 23.0 and 26.0 kDa PS: 0.1389

The following *dn/dc* value for post-consumer polystyrene (PS) was determined by the literature value for PS in CHCl_3 :¹

Commercial and Post-consumer PS: 0.1600

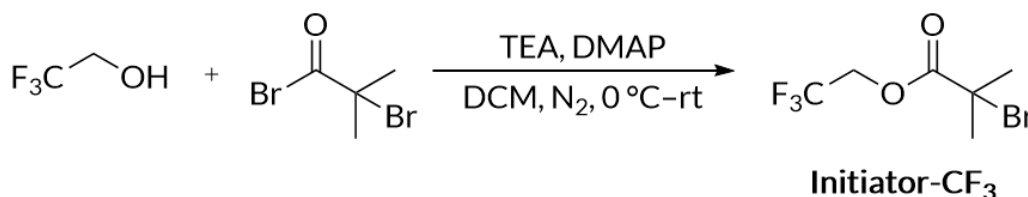
Note: Minimal changes to *dn/dc* values for TFM-PS were assumed. In other words, *dn/dc* value used for each TFM-PS sample is that of the initial polymer:

8.9 kDa TFM-PS: 0.1312, 9.3 kDa TFM-PS: 0.1301, 23.0 and 26.0 kDa TFM-PS: 0.1389, TFM-Commercial PS: 0.1600, TFM-EPS Foam: 0.1600, TFM-PS Lid: 0.1600

Differential scanning calorimetry (DSC) data were collected using a TA Discovery DSC 2500. Samples (ca. 5 mg) were placed in hermetically sealed aluminum Tzero pans, and samples were heated from 50 °C to 150 °C, cooled to 50 °C, and heated again to 150 °C at a ramp rate of 5 °C per minute. Data were collected during the second heating cycle. Glass transition temperature was determined at midpoint half height.

Synthetic and Experimental Procedures:

ATRP Initiator

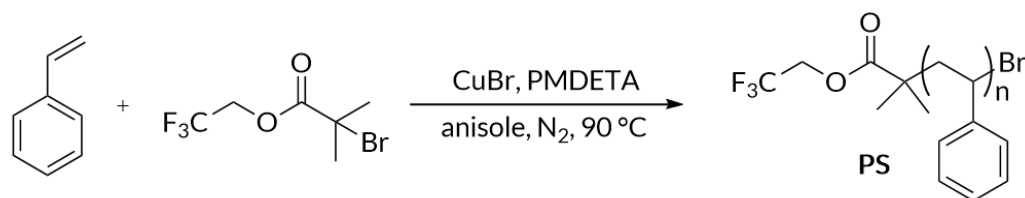


Synthesis of 2-Trifluoroethyl 2-bromoisobutyrate (Initiator-CF₃)

Following the literature procedure from Leibfarth,² 4-dimethylaminopyridine (DMAP) (45.5 mg, 0.370 mmol), triethylamine (TEA) (8.00 mmol, 1.11 mL), and dry dichloromethane (DCM) (8.55 mL) were added to a flame-dried 50 mL round bottom flask under N₂. The reaction mixture was then cooled to 0 °C while stirring. 2,2,2-trifluoroethanol (37.7 mmol, 5.00 mL) was degassed by sparging with N₂ for 15 minutes and subsequently added to the reaction flask. Then, α-bromoisobutyryl bromide (7.41 mmol, 0.920 mL) was added dropwise while still at 0 °C. The reaction mixture was then stirred at room temperature for 16 h. The mixture was washed with 1 M HCl five times. The organic layer was collected and dried over Na₂SO₄ and concentrated under reduced pressure to afford the product **Initiator-CF₃** as a colorless liquid (0.950 g, 51%) and used without further purification. The purity of the compound was determined by ¹H and ¹⁹F NMR and was in agreement with the literature.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.56 (q, $J = 8.30$ Hz, 2H), 1.97 (s, 6H). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -73.66 (s).

Polystyrene (PS) synthesis via ATRP



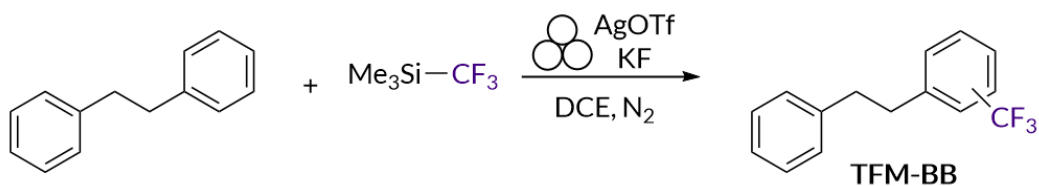
Representative Procedure: Polymerization of styrene (PS with CF_3 chain-end, target 10.6 kDa)

Following the literature procedure from Leibfarth,² CuBr (41.0 mg) was added to a flame-dried 50 mL Schlenk flask. After addition, the flask was degassed and backfilled with N_2 five times. **Initiator- CF_3** (140 mg, 0.580 mmol), styrene (59.0 mmol, 6.83 mL), and N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA) (0.300 mmol, 0.0620 mL) were dissolved in anisole (8.50 mL) and then added to the reaction flask. The reaction mixture was then degassed via three freeze-pump-thaw cycles and backfilled with N_2 . The solution was heated to $90\text{ }^\circ\text{C}$ and left to react overnight. The reaction was ended by removal from heat and dilution with acetone. The reaction mixture was passed through a neutral alumina plug to remove residual copper and concentrated under reduced pressure. The crude material was dissolved in DCM and precipitated into cold methanol (MeOH) three times for purification to afford **PS** as a white powder (2.75 g, 45%).

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.08 (br), 7.03 (br), 6.58 (br), 6.47 (br), 4.40 (br), 3.87 (br), 3.81 (br), 2.04 (br), 1.85 (br), 1.43 (br), 1.02 (br). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -73.56 (s). GPC-MALS: M_n , MALS = 8.9 kDa, $\text{D} = 1.01$, $dn/dc = 0.1391$.

Trifluoromethylation of Bibenzyl (BB)

Representative Procedure: Mechanochemical trifluoromethylation of small molecule



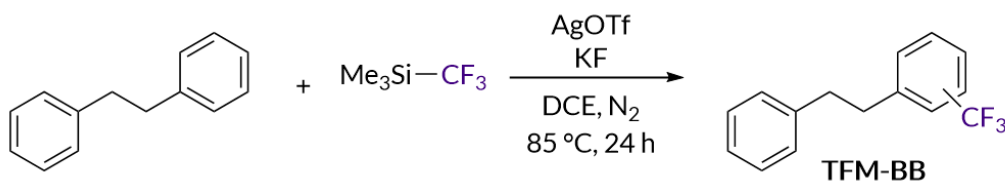
substrate (BB)

In a typical mechanochemical trifluoromethylation of **BB** experiment, to a 5 mL stainless steel milling jar charged with two 8 mm stainless steel milling ball was added bibenzyl **BB** (0.0730 g, 0.410 mmol). The jar was then brought inside the glovebox, where anhydrous KF (0.019 g, 0.32 mmol), AgOTf (0.0830 g, 0.320 mmol), and DCE (35.0 μL , 0.200 $\mu\text{L}/\text{mg}$ = volume of solvent relative to total mass of all other reaction components) for liquid-assisted grinding (LAG) were added. Then, TMSCF_3 (12.4 μL , 0.0800 mmol) was added and the jar

was sealed inside the glovebox before securing in the ball mill and shaken at 30 Hz for the desired amount of time. Once finished, fluorobenzene (7.60 μL , 0.0800 mmol) was added to the jar as an internal standard. Then, 1.00 mL of DCE was added and a 0.200 mL aliquot was extracted from the ball mill jar. The aliquot was then diluted with 0.400 mL CDCl_3 for ^{19}F NMR characterization. Meta and para isomers matched literature values for ^{19}F NMR shifts.³ The identity of the products was further confirmed by GCMS analysis (see **Figure S66** for **TFM-BB** and **Figure S67** for unreacted **BB**) of the crude reaction mixture.

^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -59.21 (s), -61.91 (s), -62.19 (s). GC retention time (min): 10.72. LRMS (EI): m/z calcd for $[\text{M}]^+$: 250.3; found: 250.1.

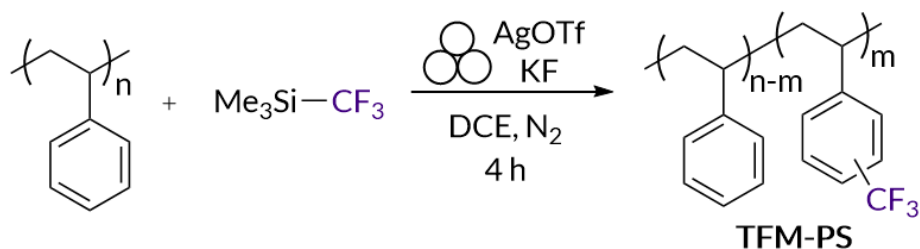
Representative Procedure: Solution-state trifluoromethylation of small molecule substrate



(BB)

Following the literature procedure from Sanford,⁴ in a typical solution-state trifluoromethylation of **BB** experiment, to a 4 mL oven-dried glass vial charged with a stir bar was added bibenzyl **BB** (0.148 g, 0.810 mmol). The vial was then brought inside the glovebox, where anhydrous KF (0.0190 g, 0.320 mmol), AgOTf (0.0830 g, 0.320 mmol), and DCE (0.200 mL) were added. Then, TMSCF_3 (12.4 μL , 0.0800 mmol) was added and the vial was sealed with a Teflon lined septa cap. The vial was then covered in foil to exclude light and heated to 85 $^\circ\text{C}$ for 24 h. Once finished, the reaction was cooled to room temperature and a solution of fluorobenzene (7.60 μL , 0.0800 mmol) in 1.00 mL DCE was added to the vial. A 0.200 mL aliquot was extracted from the crude mixture. The aliquot was then diluted with 0.400 mL CDCl_3 for ^{19}F NMR characterization of the crude reaction mixture.

Trifluoromethylation of Polystyrene (**PS**)



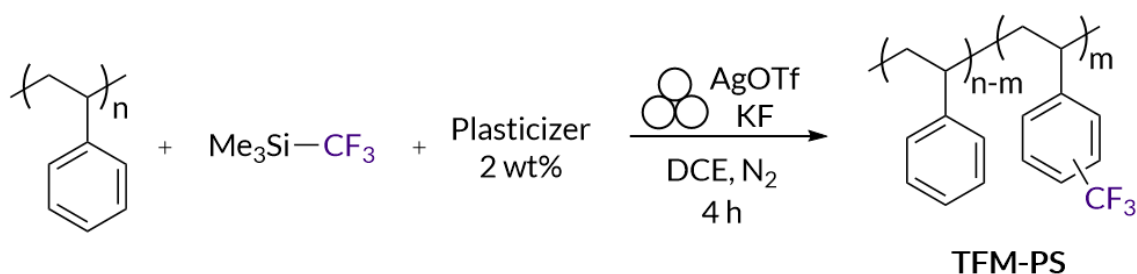
*Representative Procedure: Mechanochemical trifluoromethylation of polymer substrate (**PS**)*

In a typical mechanochemical trifluoromethylation of polystyrene experiment, to a 5 mL stainless steel milling jar charged with two 8 mm stainless steel milling balls was added

polystyrene (0.0840 g, 0.810 mmol relative to the repeat unit). The jar was then brought inside the glovebox, where AgOTf (0.0830 g, 0.320 mmol), anhydrous KF (0.0190 g, 0.320 mmol), and a stock solution of TMSCF₃ (12.4 μL, 0.0800 mmol) and DCE (39.6 μL, 0.200 μL/mg = volume of solvent relative to total mass of all other reaction components) for liquid-assisted grinding (LAG) were added. The jar was sealed inside the glovebox and then removed before securing in the ball mill and shaking at 30 Hz for the desired amount of time. Once finished, 2.00 mL of DCM was added to the jar, the jar was shaken by hand for 1 minute, and this process was repeated until all material was transferred to a vial. The vial was centrifuged (3000 rpm, 10 mins, ca. 23 °C) and passed through a basic alumina plug to remove solid and acidic byproducts and concentrated under reduced pressure.

¹H NMR (300 MHz, CDCl₃) δ(ppm): 7.08 (br), 7.03 (br), 6.58 (br), 6.47 (br), 4.40 (br), 3.87 (br), 3.81 (br), 2.04 (br), 1.85 (br), 1.43 (br), 1.02 (br). ¹⁹F NMR (470 MHz, CDCl₃) δ(ppm): -62.13 (br), -73.56 (br).

Representative Procedure: Mechanochemical trifluoromethylation of polymer substrate (PS) with 2 wt% plasticizer (DOTP)



In a typical mechanochemical trifluoromethylation of polystyrene experiment, to a 5 mL stainless steel milling jar charged with two 8 mm stainless steel milling balls was added polystyrene (0.0840 g, 0.810 mmol relative to the repeat unit). The jar was then brought inside the glovebox, where AgOTf (0.0830 g, 0.320 mmol), anhydrous KF (0.0190 g, 0.320 mmol), and a stock solution of TMSCF₃ (12.4 μL, 0.0800 mmol), 2 wt% DOTP (1.7 mg, 2 wt% relative to **PS** mass) and DCE (39.6 μL, 0.200 μL/mg = volume of solvent relative to total mass of all other reaction components) for liquid-assisted grinding (LAG) were added. The jar was sealed inside the glovebox and then removed before securing in the ball mill and shaking at 30 Hz for the desired amount of time. Once finished, 2.00 mL of DCM was added to the jar, the jar was shaken by hand for 1 minute, and this process was repeated until all material was transferred to a vial. The vial was centrifuged (3000 rpm, 10 mins, ca. 23 °C) and passed through a basic alumina plug to remove solid and acidic byproducts and concentrated under reduced pressure.

Representative Procedure: Purification of TFM-PS

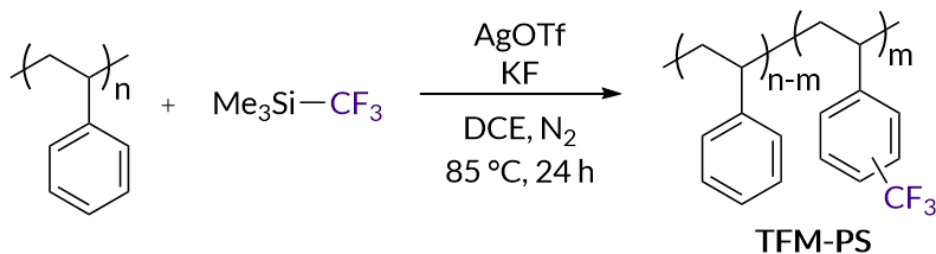
To remove any colored contaminants from ball milling, the crude reaction mixture was dissolved in DCM, stirred briefly with ca. 2 g of activated charcoal, and quickly filtered. Then, the filtrate was concentrated under reduced pressure.

For trituration, 20 mL of cold MeOH was then added to the dried, charcoal treated polymer and sonicated for 20 seconds before vacuum filtering to obtain the purified polymer. The purified sample was then dried in a vacuum oven at 60 °C overnight. To obtain functionalization density by ^{19}F NMR spectroscopy, a stock solution of 4,4-difluorobenzophenone in CDCl_3 doped with freon-11 was prepared and added to the purified polymer (See **Equation S4**).

To remove the high molecular weight shoulder in the **TFM-PS** product (**Figures 2 and S4**), preparative scale GPC was used. A **TFM-PS** sample was dissolved in HPLC grade chloroform (stabilized with 0.5 – 1% EtOH) at a concentration ca. 0.03 g/0.5 mL and filtered through a 0.45 μm syringe filter (hydrophobic PTFE, 25 mm), and purified via recycling pGPC (see **Figure S1** for a representative chromatogram). The collected fractions were then concentrated under reduced pressure and analyzed by analytical GPC and NMR spectroscopy.



Figure S1. Preparative GPC trace of **TFM-PS**. The product was collected on the fourth cycle to allow appropriate separation of polymer peaks.



Representative Procedure: Solution-state trifluoromethylation of polymer substrate (PS)

Following the literature procedure from Sanford,⁴ in a typical solution-state trifluoromethylation of **PS** experiment, to a 4 mL oven-dried glass vial charged with a stir bar was added **PS** (0.084 g, 0.810 mmol). The vial was then brought inside the glovebox, where AgOTf (0.0830 g, 0.320 mmol) and anhydrous KF (0.0190 g, 0.320 mmol) were added. Then, a stock solution of TMSCF₃ (12.4 μL, 0.0800 mmol) and DCE (0.200 mL) was added, and the vial was sealed with a Teflon lined septa cap. The vial was then covered in foil to exclude light and heated to 85 °C for 24 h. Once cooled to room temperature, 2.00 mL of DCM was added to the vial, the vial was shaken by hand for 1 minute, and this process was repeated until all material was transferred to a new vial. The vial was centrifuged (3000 rpm, 10 mins, ca. 23 °C) and passed through a basic alumina plug to remove solid and acidic byproducts and concentrated under reduced pressure. To obtain functionalization density by ¹⁹F NMR spectroscopy, a stock solution of 4,4-difluorobenzophenone in CDCl₃ doped with freon-11 was prepared and added to the purified polymer (See above purification procedure and **Equation S4**).

Supplementary Figures:

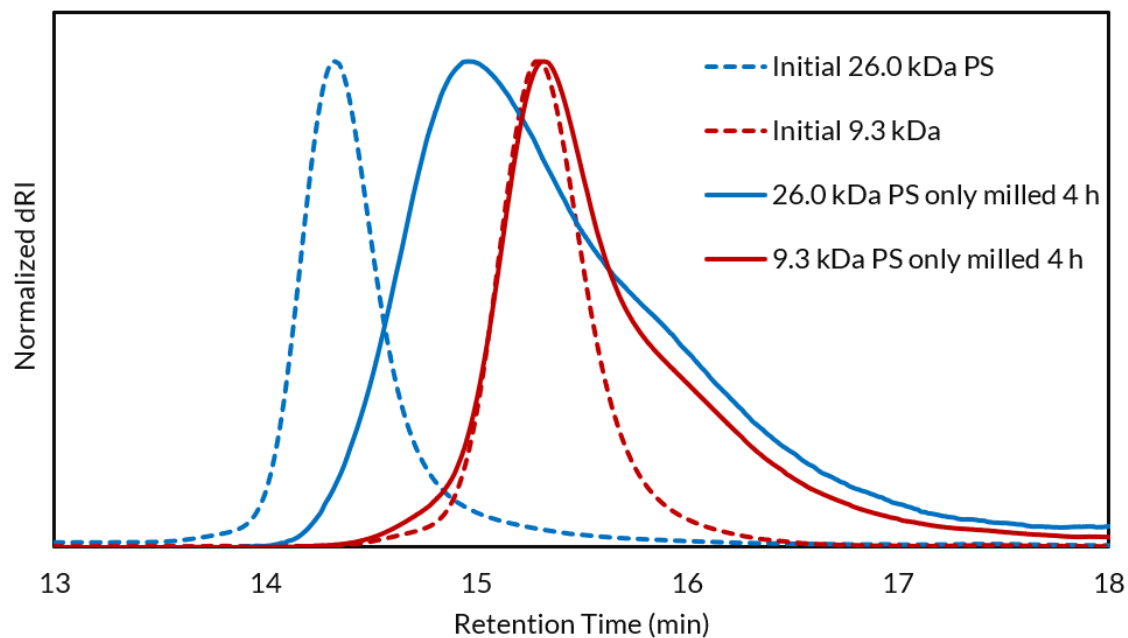


Figure S2. GPC-RI traces comparing the retention times of initial, well-defined **PS** and after 4 h milling alone (i.e., without any additional additives). Conditions: substrate = 0.81 mmol, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

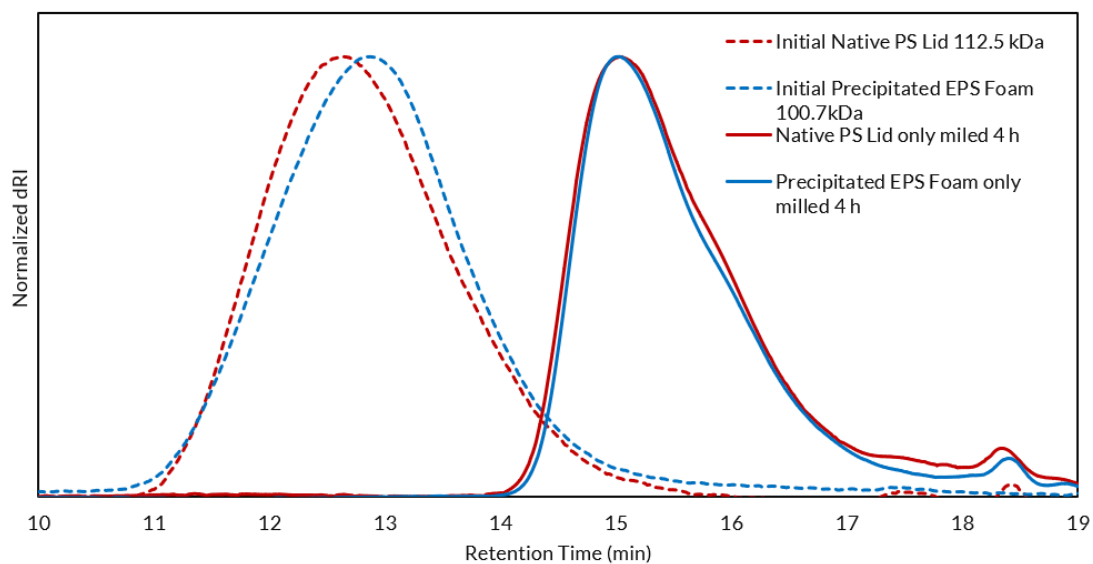


Figure S3. GPC-RI traces comparing the retention times of initial post-consumer **PS** and after 4 h milling alone (i.e., without any additional additives). Conditions: substrate = 0.81 mmol, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

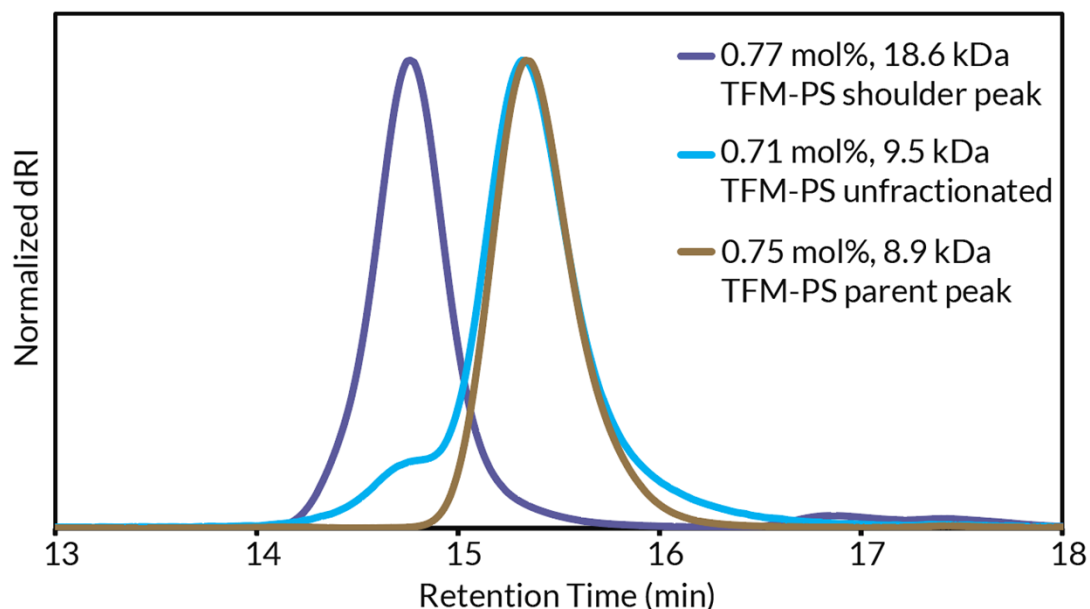


Figure S4. GPC-RI traces of 0.71 mol% **TFM-PS unfractionated** that was then purified by preparative GPC (pGPC) resulting in a 0.75 mol% **TFM-PS parent peak** and the purified higher molar mass 0.77 mol% **TFM-PS shoulder peak**. Functionalization density was determined by ^{19}F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard.

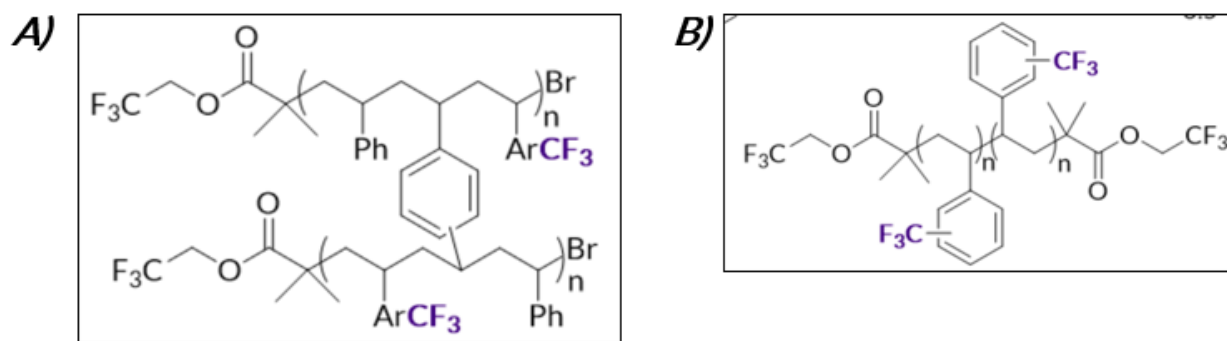


Figure S5. Possible dimer structures formed during mechanochemical TFM of PS: (A) Triflic acid-induced chain-coupling adapted from Lee et. al.⁵ and (B) proposed mechanochemical-induced event resulting in chain-coupling/branching.⁶

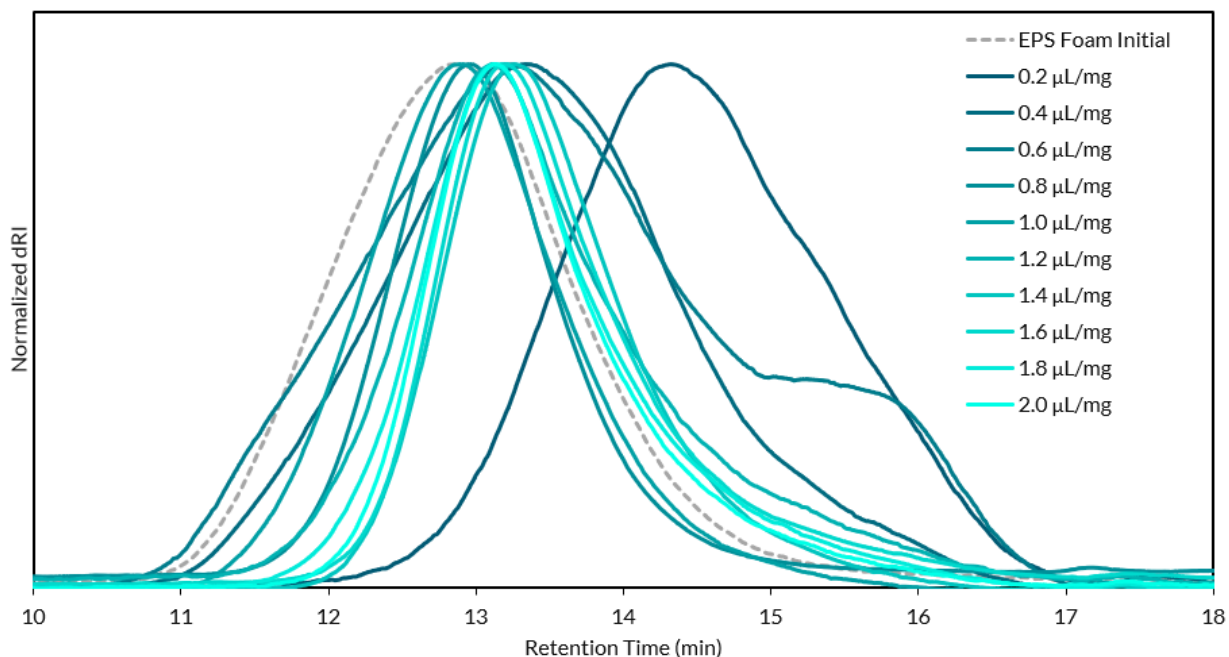


Figure S6. GPC-RI traces of **TFM-EPS Foam** following 4 h of ball milling with various amounts of LAG solvent. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF_3 = 0.08 mmol, LAG = x $\mu\text{L}/\text{mg}$, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C (See **Table 2**).

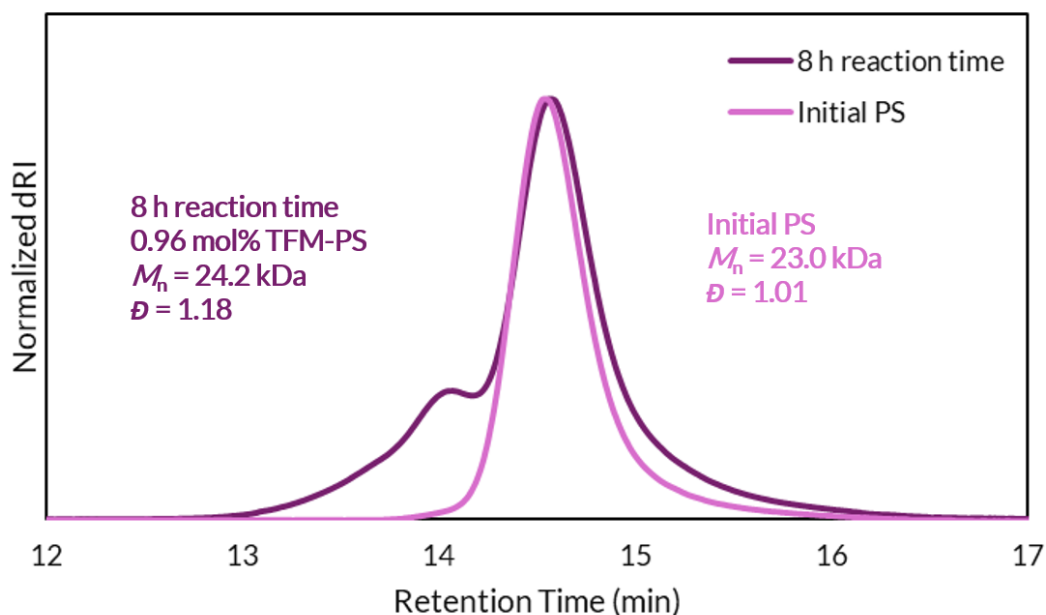


Figure S7. GPC-RI traces of Initial 23.0 kDa PS (pink) and TFM-PS (purple) following 8 h of ball milling under reaction conditions. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF_3 = 0.08 mmol, LAG = 0.4 $\mu\text{L}/\text{mg}$, 8 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

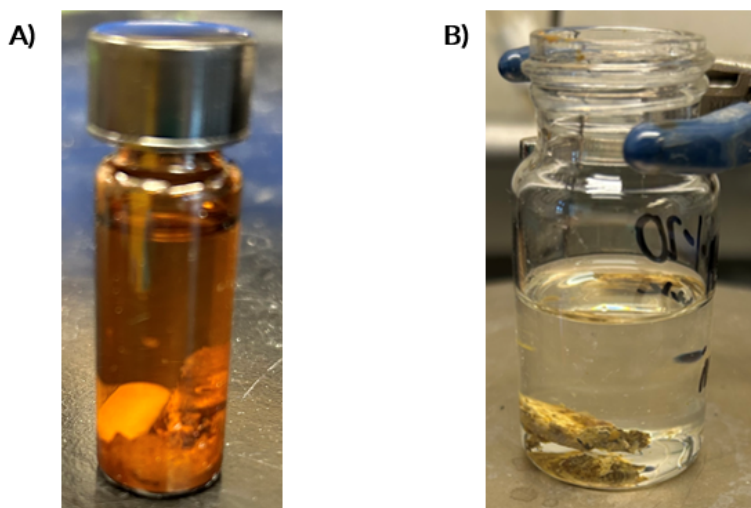


Figure S8. The above photographs were taken after attempted solution-state trifluoromethylation of **Precipitated EPS Foam**: (A) Insoluble polymeric material inside the reaction vial with DCM under ambient conditions and (B) recovered insoluble material in hot DCE (**Table S8, Entry 6**).

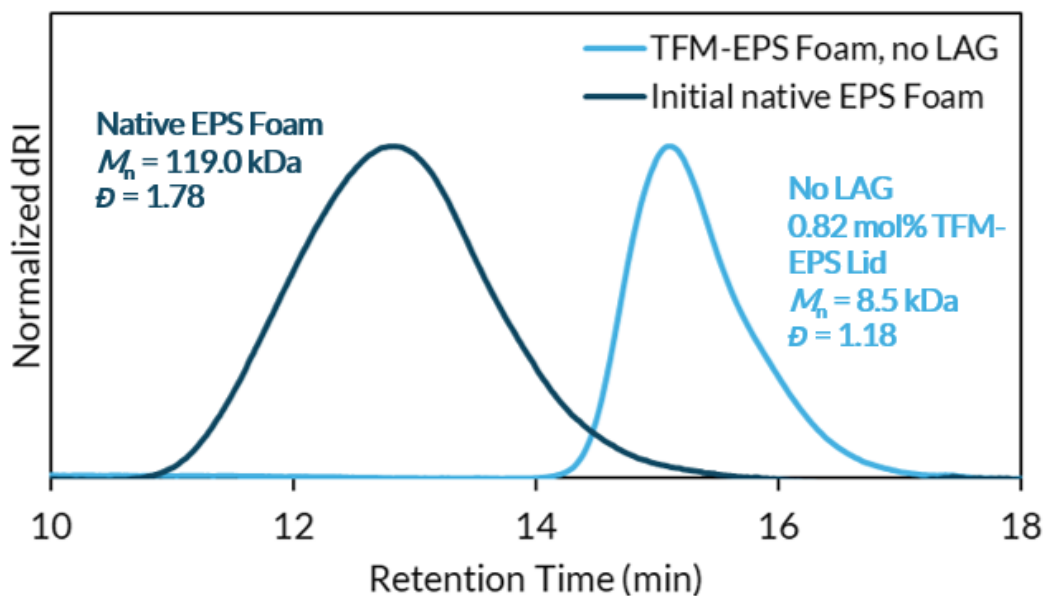


Figure S9. GPC-RI traces of initial **Native EPS Foam** (dark blue) and **TFM-EPS Foam** (light blue) following 4 h of ball milling under reaction conditions without LAG solvent added. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

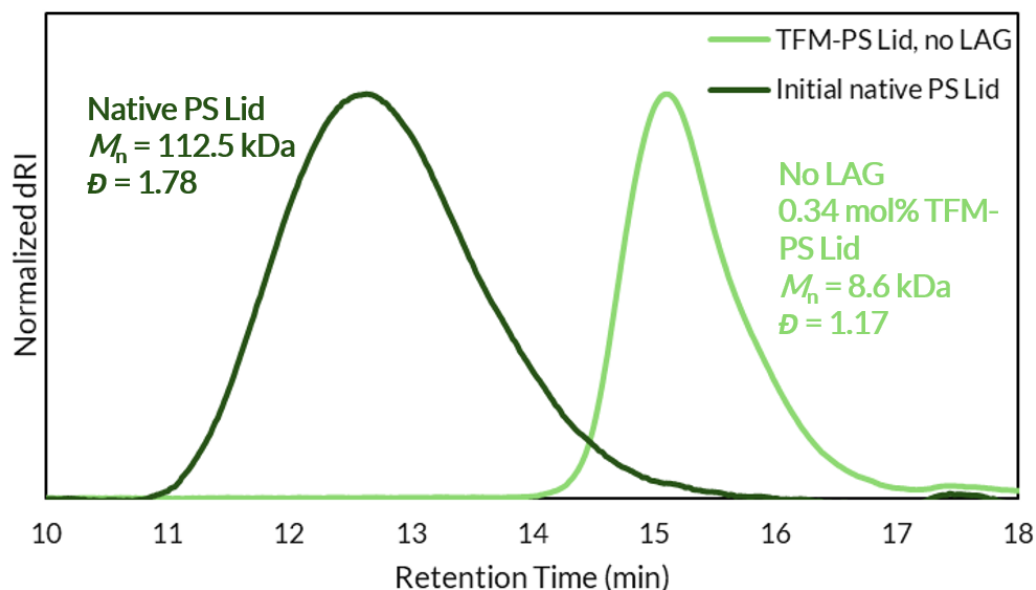


Figure S10. GPC-RI traces of initial **Native PS Lid** (dark green) and **TFM-PS Lid** (light green) following 4 h of ball milling under reaction conditions without LAG solvent added. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

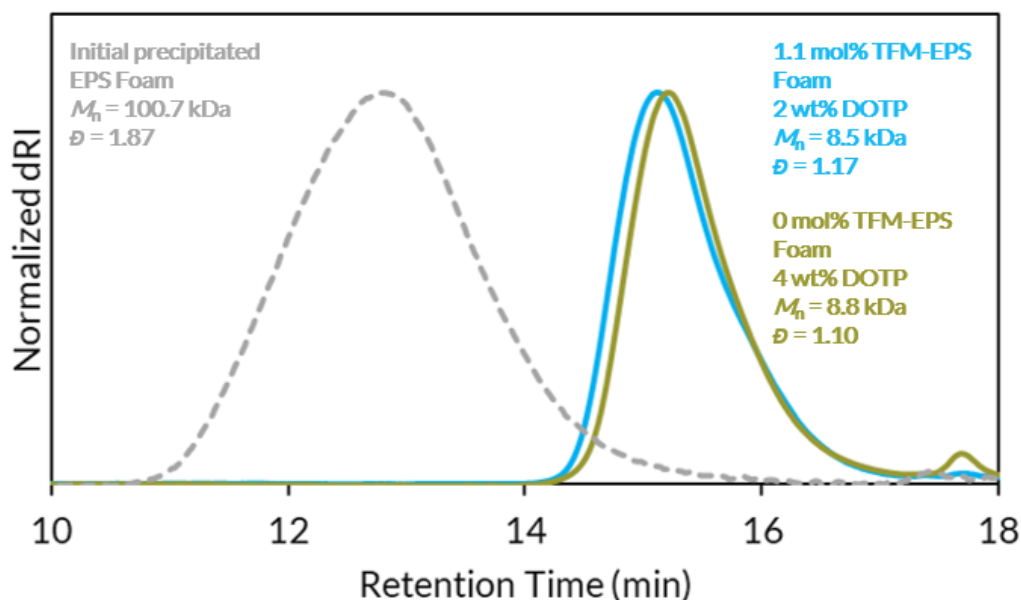


Figure S11. GPC-RI traces of initial **Precipitated EPS Foam** (gray dashes) and **TFM-EPS Foam** with 2 wt% DOTP (blue) and **TFM-EPS Foam** with 4 wt% DOTP (gold) following 4 h of ball milling under reaction conditions without LAG solvent added. Conditions: substrate =

0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, 2 wt% DOTP = 1.7 mg or 4 wt% DOTP = 5.4 mg, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

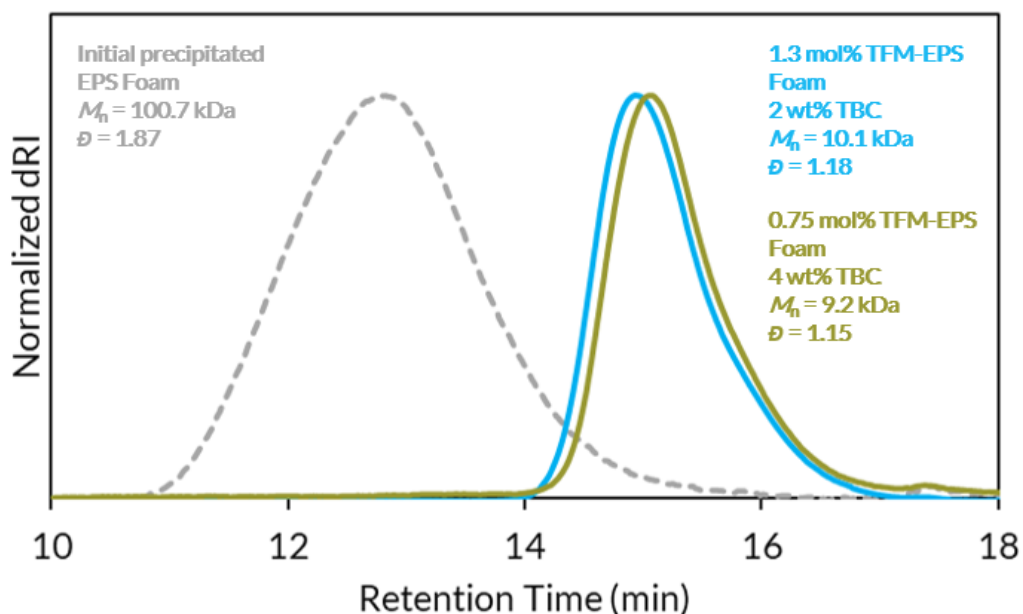


Figure S12. GPC-RI traces of initial **Precipitated EPS Foam** (gray dashes) and **TFM-EPS Foam** with 2 wt% TBC (blue) and **TFM-EPS Foam** with 4 wt% TBC (gold) following 4 h of ball milling under reaction conditions without LAG solvent added. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, 2 wt% TBC = 1.7 mg or 4 wt% TBC = 5.4 mg, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

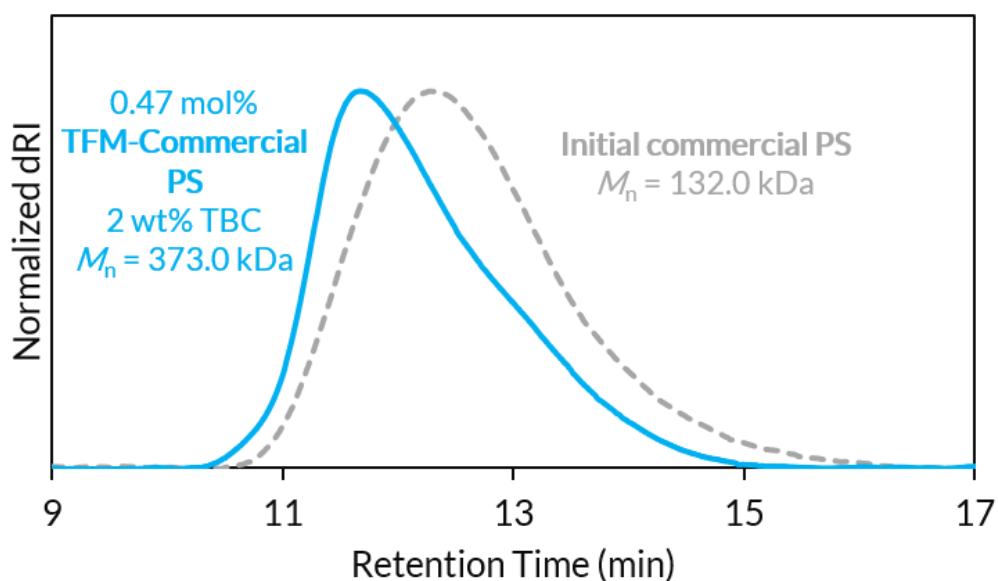
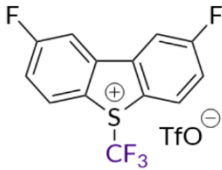
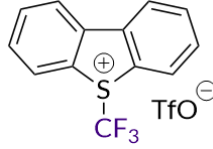
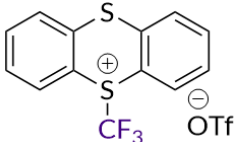


Figure S13. GPC-RI traces of initial **Commercial PS** (gray dashes) and **TFM-Commercial PS** with 2 wt% TBC (blue) following 4 h of ball milling under reaction conditions with 0.8 μL/mg

LAG solvent added. Conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, 2 wt% TBC = 1.7 mg, DCE (for LAG) = 0.8 μL/mg, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

Supplementary Tables:

Table S1. Unsuccessful mechanoredox trifluoromethylation of bibenzyl (**BB**) conditions^[a]

Entry	CF ₃ Source	Yield (%) ^[e]
1 ^[b]		<5
2 ^[c]		0
3 ^[d]		trace

[a] Mechanochemical parameters: 1.5 mL SS milling jar, 1x 8mm SS ball, 30 Hz, 3-4 h, jar temperature = 20 °C – 36 °C. [b] Reaction conditions: **BB** = 0.6 mmol, CF₃ source = 0.3 mmol, BaTiO₃ = 1.5 mmol, DMF (for LAG) = 0.2 μL/mg.⁷ [c] Reaction conditions: **BB** = 0.6 mmol, CF₃ source = 0.3 mmol, BaTiO₃ = 1.5 mmol, DMF (for LAG) = 0.2 μL/mg.⁷ [d] Reaction conditions: **BB** = 0.3 mmol, CF₃ source = 0.3 mmol, BaTiO₃ = 1.5 mmol, DMF (for LAG) = 0.2 μL/mg. [e] Yield was determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard (See **Equation S2**).

*Representative Procedure: Mechanoredox trifluoromethylation of small molecule substrate (**BB**)*

In a typical mechanoredox trifluoromethylation of **BB** experiment, to a 1.5 mL stainless steel milling jar charged with one 8 mm stainless steel milling ball was added bibenzyl **BB** (0.60 mmol), CF₃ source (0.30 mmol), BaTiO₃ (1.5 mmol), and DMF (0.2 μL/mg = volume of solvent relative to total mass of all other reaction components) for liquid-assisted grinding (LAG) were added. Then, the jar was sealed before securing in the ball mill and shaken at 30 Hz for the desired amount of time. Once finished, 1.00 mL of acetone was added to the jar, the jar

was shaken by hand for 1 minute, and this process was repeated until all material was transferred to a new vial. Then, fluorobenzene (0.30 mmol) was added to the vial as an internal standard. The vial was centrifuged (3000 rpm, 10 min, ca. 23 °C) and passed through a neutral alumina plug to remove nanoparticles. A 0.20 mL aliquot was extracted from the filtrate. The aliquot was then diluted with 0.40 mL CDCl₃ for ¹⁹F NMR characterization of the crude reaction mixture.

For **Table S1**, organic reagents and reaction byproducts were recovered (shown by ¹⁹F NMR spectroscopy) with small amounts of **TFM-BB** and unidentified side products due to unproductive reaction pathways resulting in complex mixtures and overlapping signals as shown in the ¹H NMR and ¹⁹F NMR spectra. See **Figures S14 and S15** for representative mechanoredox trifluoromethylation crude ¹H NMR spectra and ¹⁹F NMR spectra, respectively.

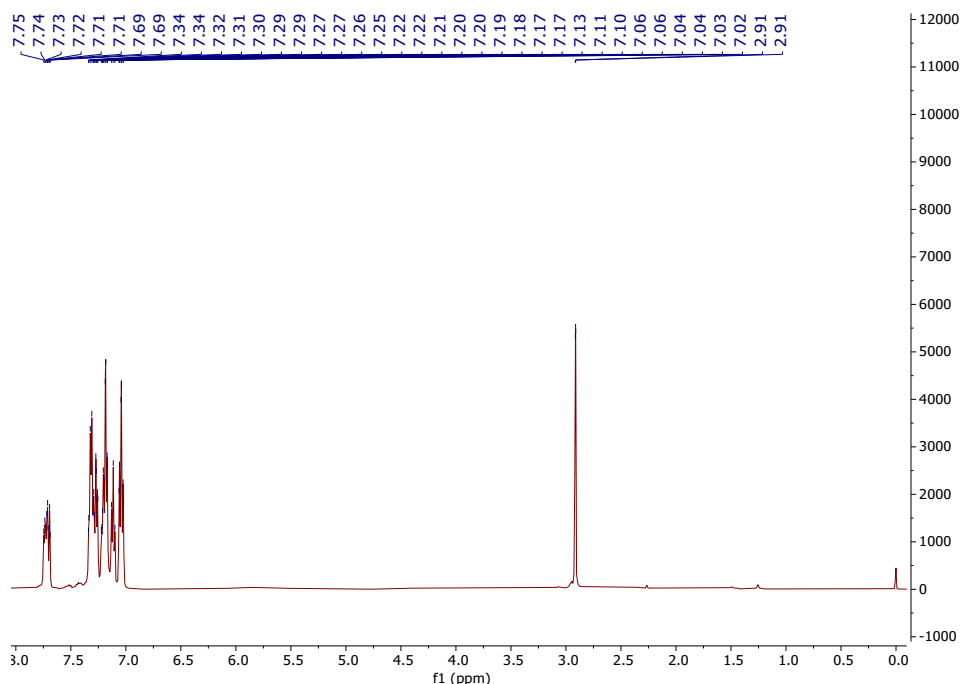


Figure S14. Representative ¹H NMR spectrum of optimized mechanoredox trifluoromethylation of **BB** (500 MHz, CDCl₃) (See **Table S1, Entry 1**).

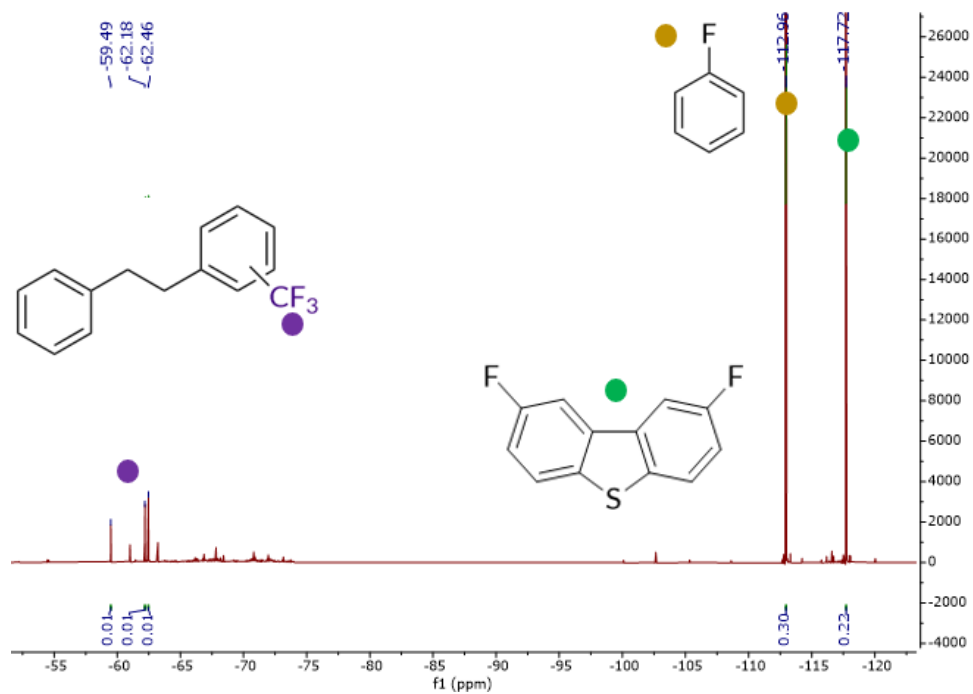


Figure S15. Representative ^{19}F NMR spectrum of optimized mechanoredox trifluoromethylation of **BB** (470 MHz, CDCl_3 with freon-11) (See **Table S1, Entry 1**). See **Equation S2** for determination of yield using fluorobenzene as an internal standard.

Table S2. Optimization of mechanochemical trifluoromethylation of **BB**^[a]

Entry	BB Equiv.	Arene Equiv.	LAG ($\mu\text{L}/\text{mg}$)	Jar Size (mL) ^[b]	Time (h)	Yield (%) ^[c]	Functionalization (mol%) ^[c]
1	10	20	0.2	1.5	3	21	1.1
2	5	10	0.2	1.5	3	10	1.0
3	1	2	0.2	1.5	3	0	0
4	10	20	0.8	1.5	3	8	0.40
5	10	20	0.2	5	3	38	1.9
6	5	10	0.2	5	3	33	3.3
7	10	20	0.2	5	4	38	1.9
8	5	10	0.6	5	4	7	0.68
9	5	10	1.1 ^[d]	5	4	<5	<0.20
10	5	10	0.2	5	4	55	5.5

[a] Reaction conditions: **BB** = 0.41 mmol (5 equiv. substrate, 10 equiv. arene), AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE (for LAG) = 37.4 μL (0.2 $\mu\text{L}/\text{mg}$), 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C–36 °C. [b] 1x 8 mm SS ball was used for 1.5 mL jars and 2x 8 mm SS balls were used for 5 mL jars. [c] Yield and functionalization density were determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard (See **Equation S2** and **Equation S1**, respectively). [d] LAG amount is equal to solvent volume under solution-state conditions.

Table S3. Infrared thermometer temperature readings of the ball mill jar's surface^[a]

Time (h)	Temperature (°C)
1	27.3
2	29.8
3	31.2
4	36.1

[a] Reaction conditions: **BB** = 0.41 mmol (5 equiv. substrate, 10 equiv. arene), AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE (for LAG) = 37.4 μL (0.2 $\mu\text{L}/\text{mg}$), 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C.

Table S4. Mechanochemical trifluoromethylation of **BB** controls

Entry	Conditions	Yield (%) ^[d]	Functionalization (mol%) ^[d]
1 ^[a]	Standard reaction	55	5.5
2	No LAG	5	0.50
3	Under air	<5	<0.50
4	1 equiv. K ₂ HPO ₄	5	0.50
5	3 equiv. K ₂ HPO ₄	<5	<0.50
6	No milling	0	0
7 ^[b]	37.4 μ L, 36 °C	<5	<0.50
8 ^[c]	0.2 mL DCE, 36 °C	<5	<0.50

[a] Standard mechanochemical reaction conditions: **BB** = 0.41 mmol (5 equiv. substrate, 10 equiv. arene), AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE (for LAG) = 37.4 μ L (0.2 μ L/mg), 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C. [b] Solution-state reaction conditions at maximum recorded ball mill temperature (**See Table S3**) with LAG solvent amounts: **BB** = 0.41 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 37.4 μ L/mg, 4 h, 36 °C. [c] Solution-state reaction conditions at maximum recorded ball mill temperature (**See Table S3**): **BB** = 0.41 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 0.2 M (relative to **BB**), 4 h, 36 °C. [d] Yield and functionalization density were determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard (See **Equation S2** and **Equation S1**, respectively).

Table S5. Functionalization calculation comparison for model **PS** substrates

Entry	Substrate	Chain-end <i>m</i> (mol%) ^[a]	Internal standard <i>m</i> (mol%) ^[b]
1	8.9 kDa PS	0.91	1.1
2	9.3 kDa PS	0.92	1.3
3	26.0 kDa PS	1.0	1.1

[a] Functionalization density was determined by ¹⁹F NMR spectroscopy using the polymer chain-end as an internal standard (See **Equation S3**). [b] Functionalization density was

determined by ^{19}F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard (See **Equation S4**).

Table S6. Mechanochemical TFM of ca. 25 kDa **PS** LAG solvent screening^[a]

Entry	LAG Solvent	m (mol%) ^[b]	Initial M_n (kDa) ^[c]	Initial \bar{D} ^[c]	Final M_n (kDa) ^[c]	Final \bar{D} ^[c]
1	DCE	1.1	26.0	1.01	31.6	1.43
2	MeCN	0.25	26.0	1.01	20.8	1.29
3	THF	1.7	23.0	1.01	26.8	1.23
4	DMF	<0.10	26.0	1.01	23.9	1.14
5	EtOAc	1.9	23.0	1.01	37.8	4.92

[a] Reaction conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF_3 = 0.08 mmol, LAG = 0.4 $\mu\text{L}/\text{mg}$, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C. [b] Functionalization density was determined by ^{19}F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard (See **Equation S4**). [c] M_n and \bar{D} were determined by GPC-MALS-RI.

Table S7. Mechanochemical TFM of **Precipitated EPS Foam** LAG solvent screening^[a]

Entry	LAG Solvent	m (mol%) ^[b]	Initial M_n (kDa) ^[c]	Initial \bar{D} ^[c]	Final M_n (kDa) ^[c]	Final \bar{D} ^[c]
1	DCE	1.1	101	1.87	71.0	1.45
2 ^[d]	EtOAc	0	101	1.87	-	-
3 ^[d]	THF	0.68	101	1.87	668	1.70

[a] Reaction conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF_3 = 0.08 mmol, LAG = 0.8 $\mu\text{L}/\text{mg}$, 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C. [b] Functionalization density was determined by ^{19}F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard (See **Equation S4**). [c] M_n and \bar{D} were determined by GPC-MALS-RI. [d] Mostly insoluble polymeric material was recovered. See **Figure S8** for representative photographs of insoluble fraction.

Table S8. Solution-state trifluoromethylation of various substrates^[a]

Entry	Substrate	Substrate Equiv.	Arene Equiv.	Yield (%) ^[b]	<i>m</i> (mol%) ^[b]	Initial <i>M_n</i> (kDa) ^[c]	Initial <i>Đ</i> ^[c]	Final <i>M_n</i> (kDa) ^[c]	Final <i>Đ</i> ^[c]
1	BB	10	20	61 ^[d]	6.7 ^[d]	-	-	-	-
2	BB ^[e]	5	10	81 ^[d]	8.1 ^[d]	-	-	-	-
3	8.9 kDa PS	10	10	31	3.1	8.9	1.01	12.3	1.46
4	26.0 kDa PS	10	10	6.4	0.64	26.0	1.01	35.2	1.51
5 ^[f]	Native EPS Foam	10	10	-	-	119	1.78	- ^[g]	-
6	Precipitated EPS Foam	10	10	0	0	101	1.87	24.0 ^[g]	1.58
7 ^[h]	Precipitated EPS Foam	10	10	0	0	101	1.87	164 ^[g]	3.51
8	Native PS Lid	10	10	<5	<0.50	113	1.78	236	1.99
9	Commercial PS	10	10	0	0	132	2.19	158 ^[g]	2.02

[a] Reaction conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 0.2 mL, 24 h, 85 °C. [b] Yield and functionalization density were determined by ¹⁹F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard, with yield defined as [*m*]/[TMSCF₃] (See **Equation S4** for calculation of functionalization density). [c] *M_n* and *Đ* were determined by GPC-MALS-RI. [d] Yield and functionalization density were determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard (See **Equations S2 and S1**, respectively). [e] Reaction conditions: substrate = 0.41 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 0.2 mL, 24 h, 85 °C. [f] No soluble PS was obtained, confirmed by GPC-RI analysis. [g] Determined by GPC-MALS-RI for soluble fraction only. See Figure S8 for photograph of insoluble fractions. [h] Reaction conditions: substrate = 0.41 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 158.4 μL (0.8 μL/mg), 24 h, 85 °C.

Table S9. Mechanochemical trifluoromethylation of **Precipitated EPS Foam** with 8 wt% plasticizer^[a]

Entry	Substrate	Plasticizer	m (mol%) ^[b]	Initial M_n (kDa) ^[c]	Initial \bar{D} ^[c]	Final M_n (kDa) ^[c]	Final \bar{D} ^[c]
1	Precipitated EPS Foam	8 wt% DOTP	1.2	101	1.87	84.4	1.33
2 ^[d]	Precipitated EPS Foam	8 wt% TBC	<0.50	101	1.87	27.9	3.37

[a] Reaction conditions: substrate = 0.81 mmol, AgOTf = 0.32 mmol, KF = 0.32 mmol, TMSCF₃ = 0.08 mmol, DCE = 0.8 μ L/mg, DOTP or TBC = 8 wt% (relative to PS mass), 4 h, 2x 8 mm SS balls, 5 mL jar, jar temperature = 20 °C – 36 °C. [b] Functionalization density was determined by ¹⁹F NMR spectroscopy using 4,4'-difluorobenzophenone as an internal standard (See **Equation S4** for calculation of functionalization density). [c] M_n and \bar{D} were determined by GPC-MALS-RI. [d] Insoluble polymeric material was recovered. See **Figure S8** for representative photo of insoluble fraction.

Analytical Gel Permeation Chromatography:

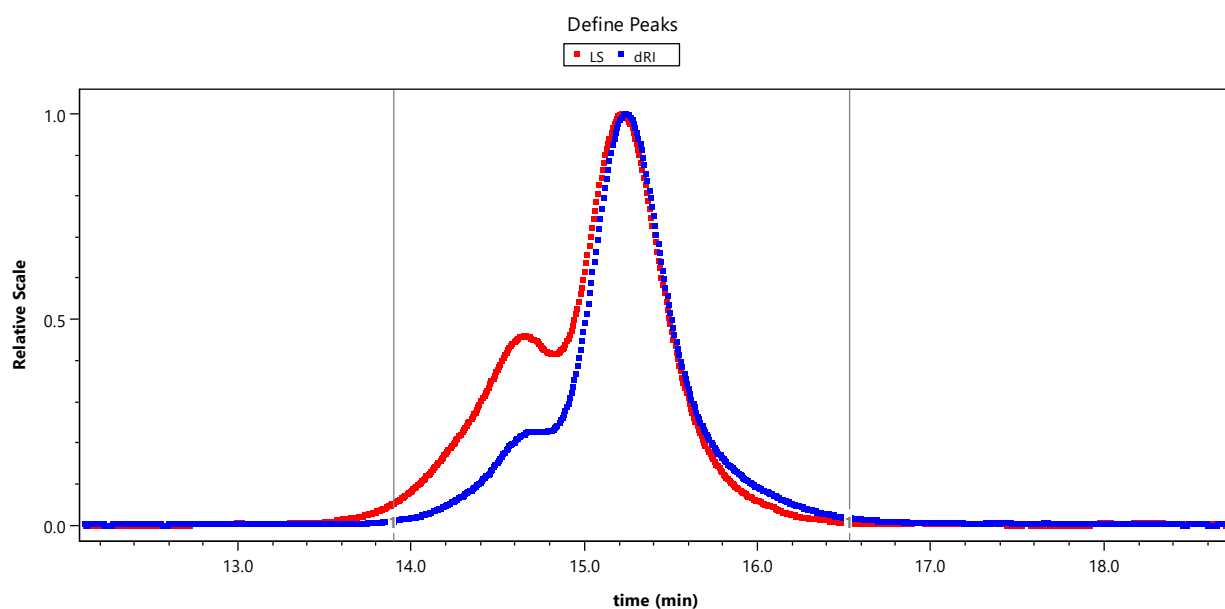


Figure S16. Representative GPC-RI (blue) and GPC-LS (red) traces of mechanochemically functionalized 9.6 kDa **TFM-PS** (1.3 mol%) in native ASTRA software (See **Table 1, Entry 2**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

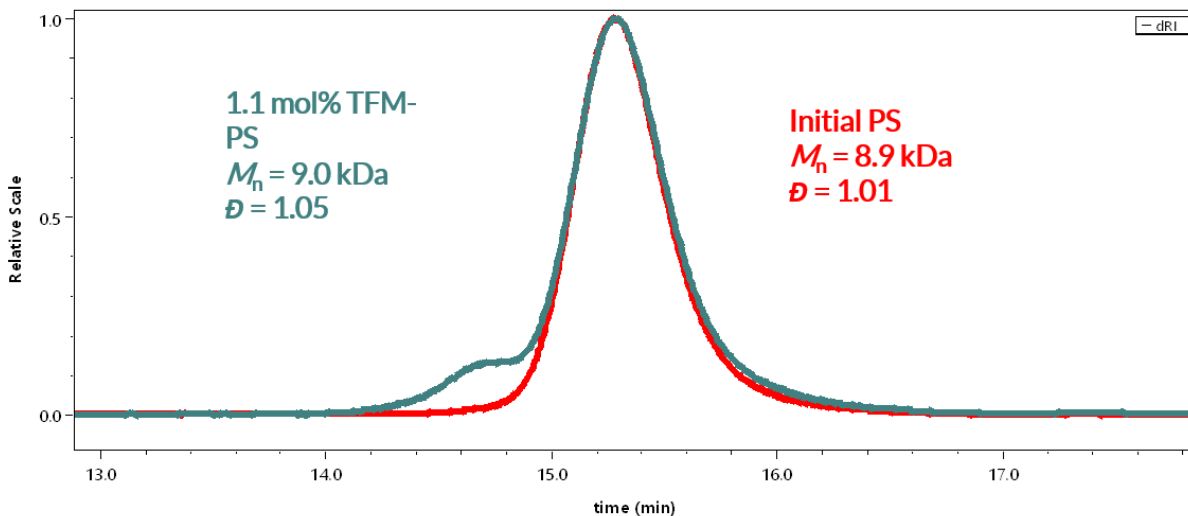


Figure S17. GPC-RI trace (teal) of mechanochemically functionalized 9.0 kDa **TFM-PS** (1.1 mol%) and GPC-RI trace (red) of the initial 8.9 kDa **PS** (See **Table 1, Entry 1**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

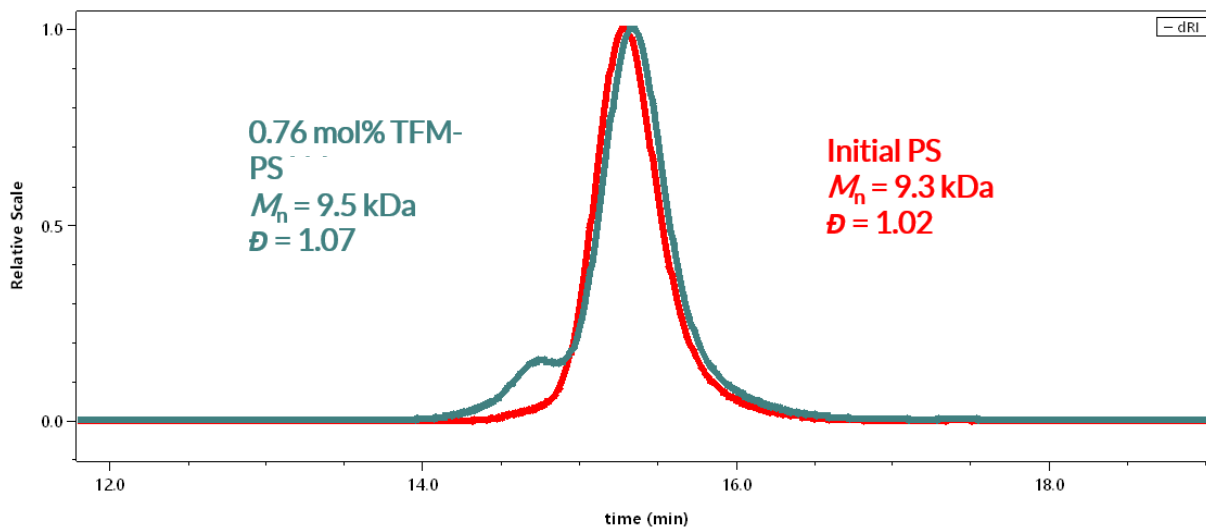


Figure S18. GPC-RI trace (teal) of mechanochemically functionalized 9.5 kDa **TFM-PS** (0.76 mol%) and GPC-RI trace (red) of the initial 9.3 kDa **PS** (See **Table 1, Entry 3**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

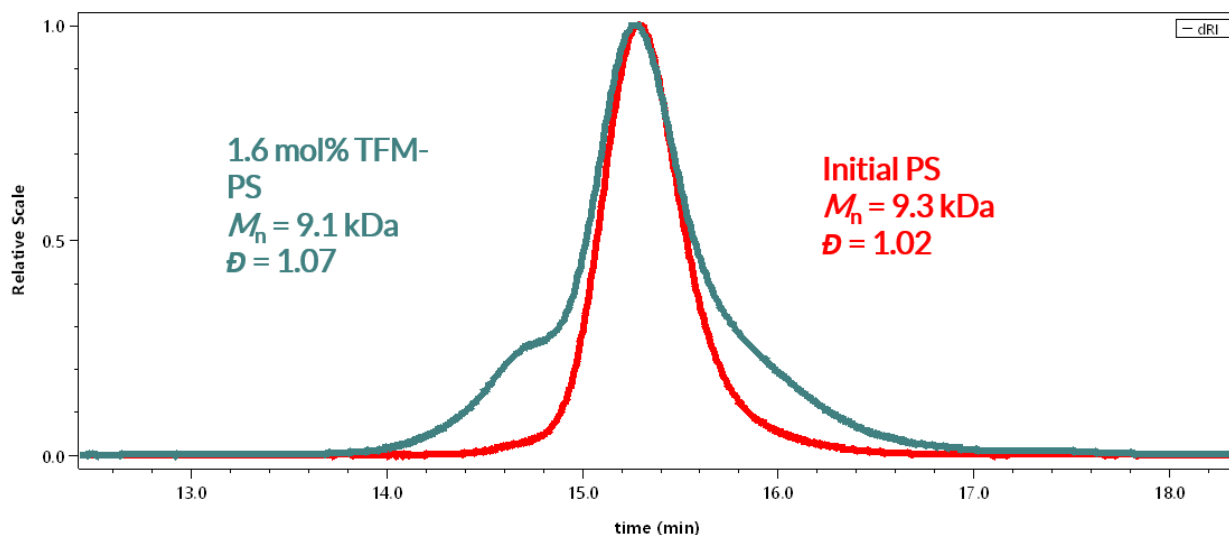


Figure S19. GPC-RI trace (teal) of mechanochemically functionalized 9.1 kDa **TFM-PS** (1.6 mol%) and GPC-RI trace (red) of the initial 9.3 kDa **PS** (See **Table 1, Entry 4**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L/mg}$, 4 h milling w/ 2x 8 mm SS balls.

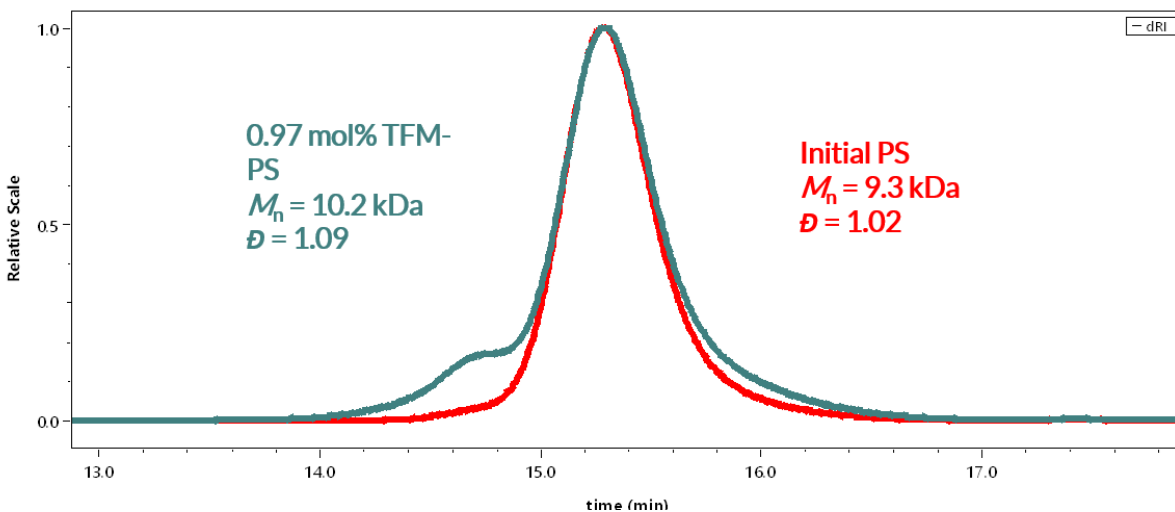


Figure S20. GPC-RI trace (teal) of mechanochemically functionalized 10.2 kDa **TFM-PS** (0.97 mol%) and GPC-RI trace (red) of the initial 9.3 kDa **PS** (See **Table 1, Entry 5**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L/mg}$, 4 h milling w/ 2x 8 mm SS balls.

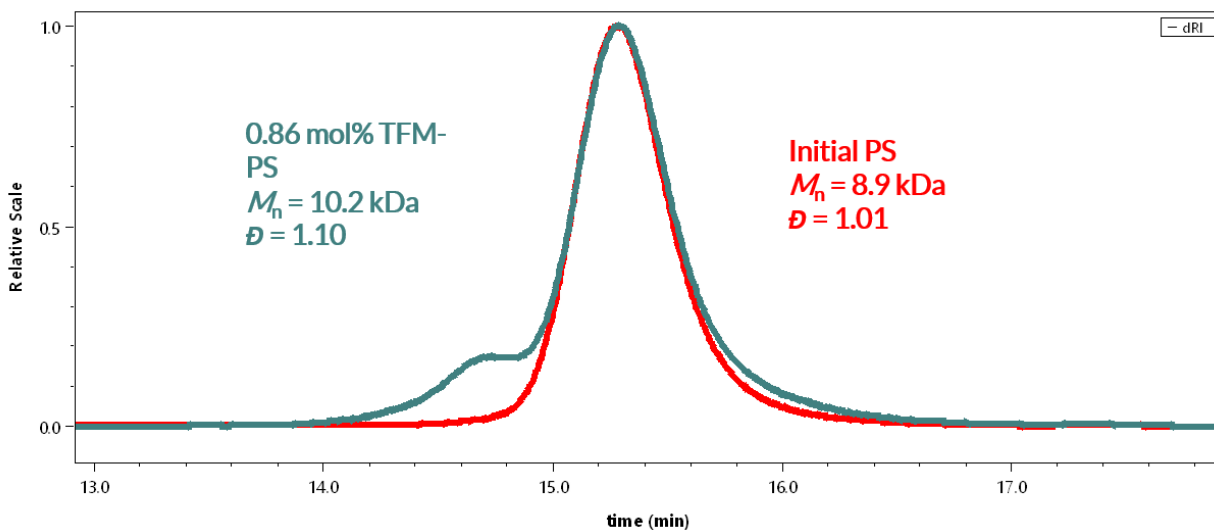


Figure S21. GPC-RI trace (teal) of mechanochemically functionalized 10.2 kDa **TFM-PS** (0.86 mol%) and GPC-RI trace (red) of the initial 8.9 kDa **PS** (See **Table 1, Entry 6**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.2 \mu\text{L/mg}$, 4 h milling w/ 2x 8 mm SS balls.

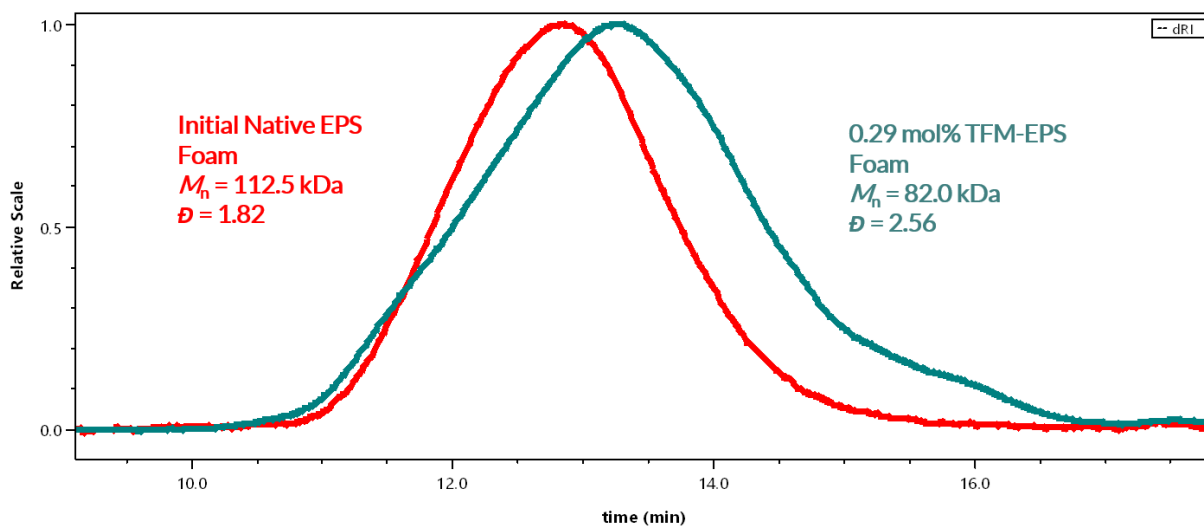


Figure S22. GPC-RI trace (teal) of mechanochemically functionalized 82.0 kDa **TFM-EPS Foam** (0.29 mol%) and GPC-RI trace (red) of the initial 119 kDa **Native EPS Foam** (See **Table 3, Entry 1**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , $\text{DCE} = 0.8 \mu\text{L/mg}$, 4 h milling w/ 2x 8 mm SS balls.

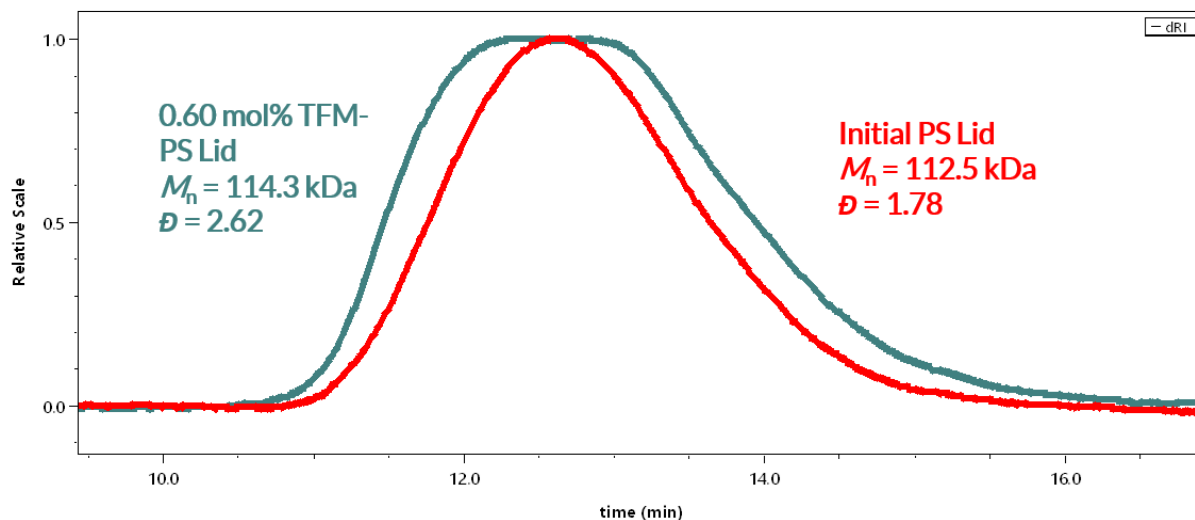


Figure S23. GPC-RI trace (teal) of mechanochemically functionalized 114.3 kDa **TFM-PS Lid** (0.60 mol%) and GPC-RI trace (red) of the initial 113 kDa **Native PS Lid** (See **Table 3, Entry 2**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 1.0 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

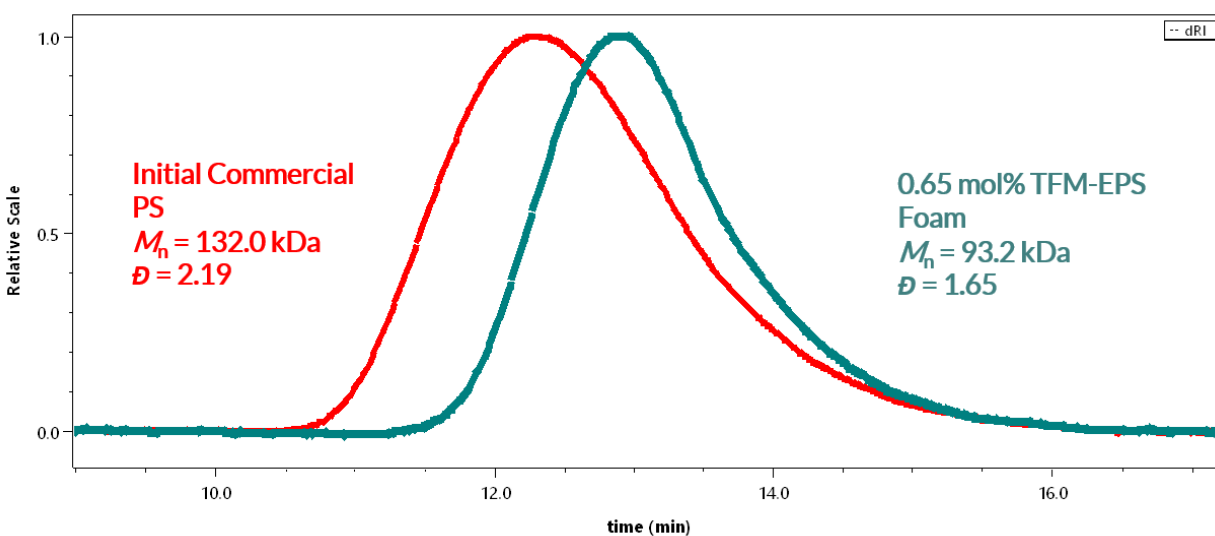


Figure S24. GPC-RI trace (teal) of mechanochemically functionalized 93.2 kDa **TFM-Commercial PS** (0.65 mol%) and GPC-RI trace (red) of the initial 132 kDa **Commercial PS** (See **Table 3, Entry 3**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 1.0 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

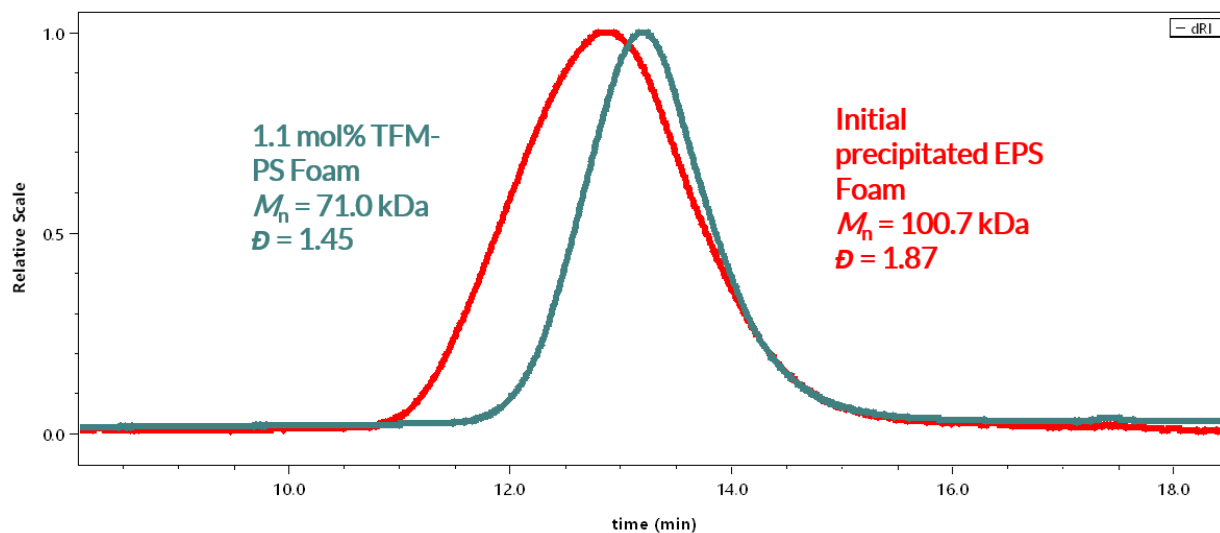


Figure S25. GPC-RI trace (teal) of mechanochemically functionalized 71.0 kDa **TFM-EPS Foam** (1.1 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table 3, Entry 4**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 0.8 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

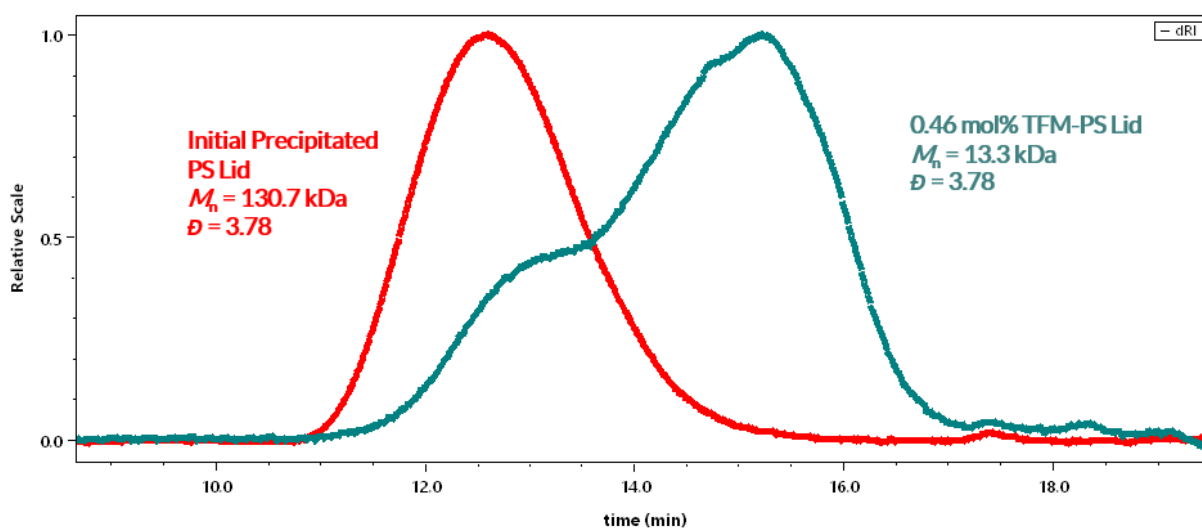


Figure S26. GPC-RI trace (teal) of mechanochemically functionalized 13.3 kDa **TFM-PS Lid** (0.46 mol%) and GPC-RI trace (red) of the initial 131 kDa **Precipitated PS Lid** (See **Table 3, Entry 5**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 1.0 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

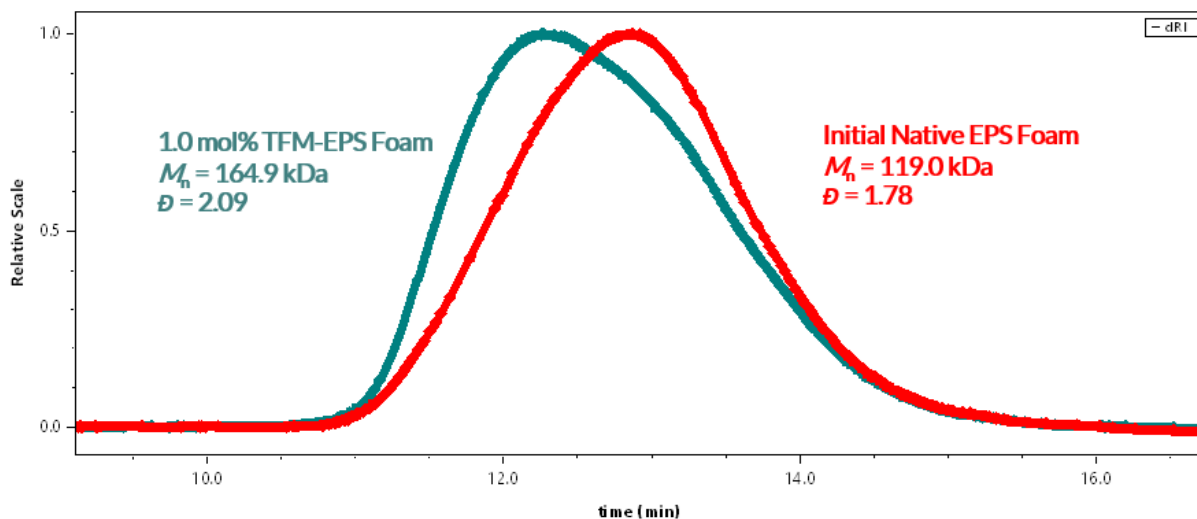


Figure S27. GPC-RI trace (teal) of a mechanochemical functionalization with 2 wt% DOTP resulting in 165 kDa **TFM-PS** (1.0 mol%) and GPC-RI trace (red) of the initial 119 kDa **Native EPS Foam** (See **Figure 5**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 1.0 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

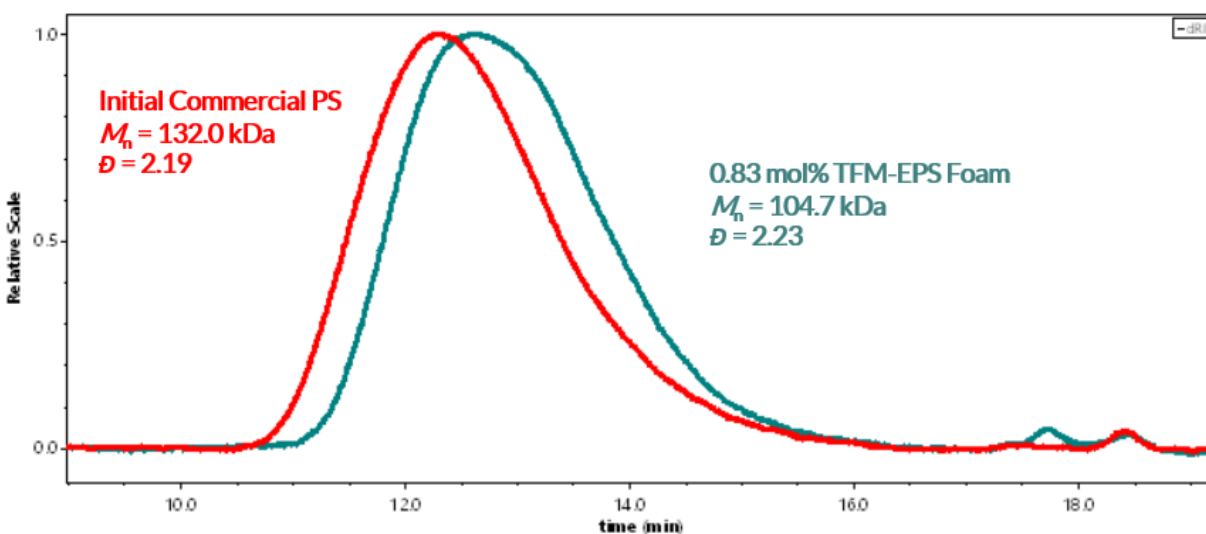


Figure S28. GPC-RI trace (teal) of a mechanochemical functionalization with 2 wt% DOTP resulting in 105 kDa **TFM-Commercial PS** (0.83 mol%) and GPC-RI trace (red) of the initial 132 kDa **Commercial PS** (See **Figure 5**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 1.0 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

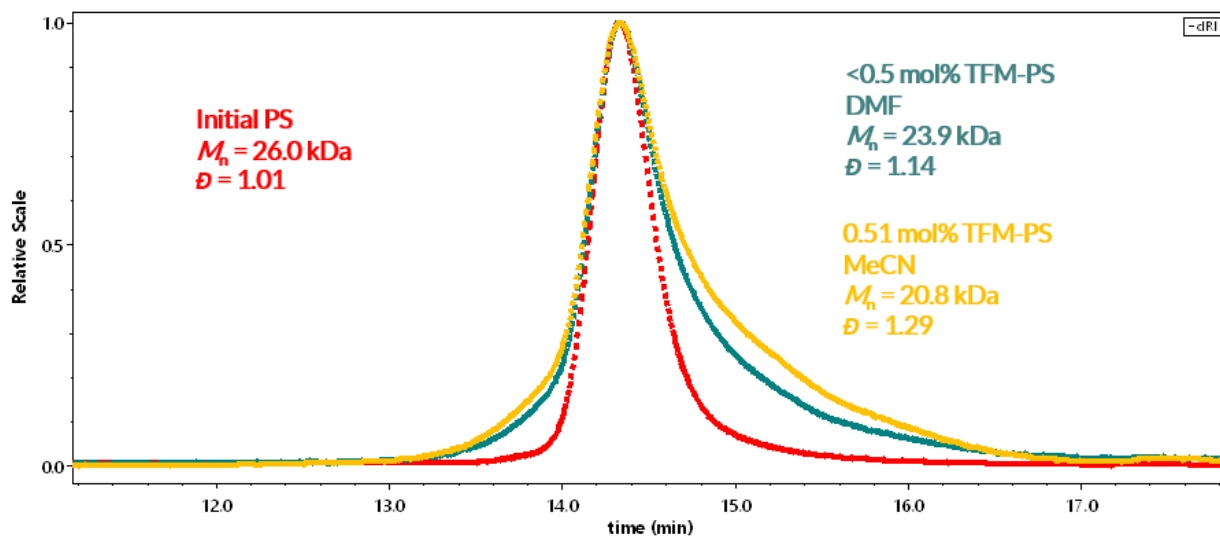


Figure S29. GPC-RI trace (yellow) of mechanochemical functionalization in MeCN (LAG) resulting in 20.8 kDa **TFM-PS** (0.25 mol%), GPC-RI trace (teal) of mechanochemical functionalization in DMF (LAG) resulting in 23.9 kDa **TFM-PS** (<0.10 mol%), and GPC-RI trace (red) of the initial 26.0 kDa **PS** (See **Table S6, Entries 2 and 4**, respectively). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , LAG = 0.4 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

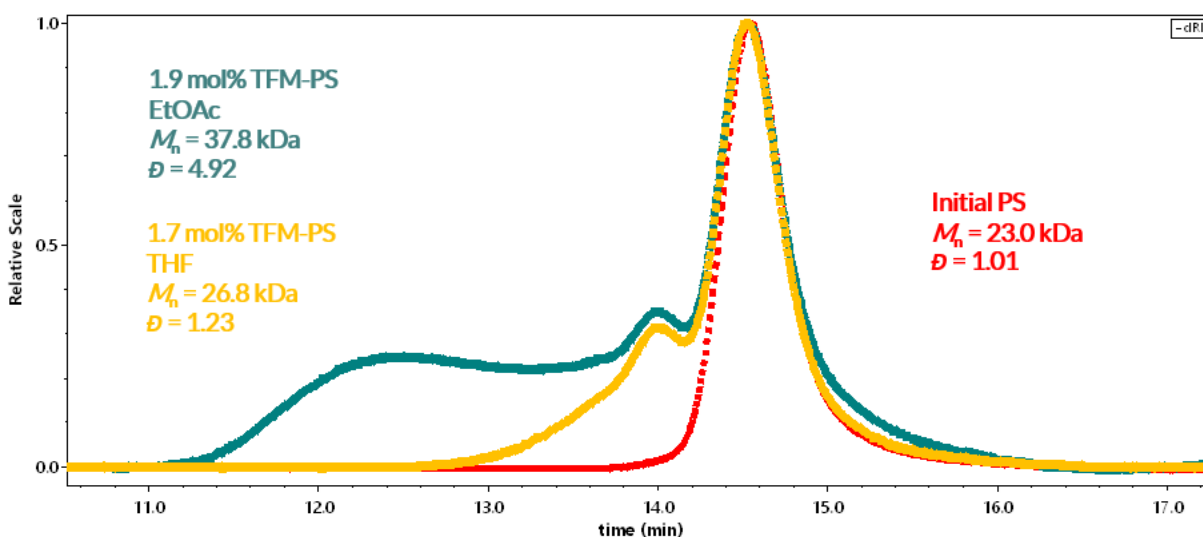


Figure S30. GPC-RI trace (yellow) of mechanochemical functionalization in THF (LAG) resulting in 26.8 kDa **TFM-PS** (1.7 mol%), GPC-RI trace (teal) of mechanochemical functionalization in EtOAc (LAG) resulting in 37.8 kDa **TFM-PS** (1.9 mol%), and GPC-RI trace (red) of the initial 23.0 kDa **PS** (See **Table S6, Entries 3 and 5**, respectively). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , LAG = 0.4 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

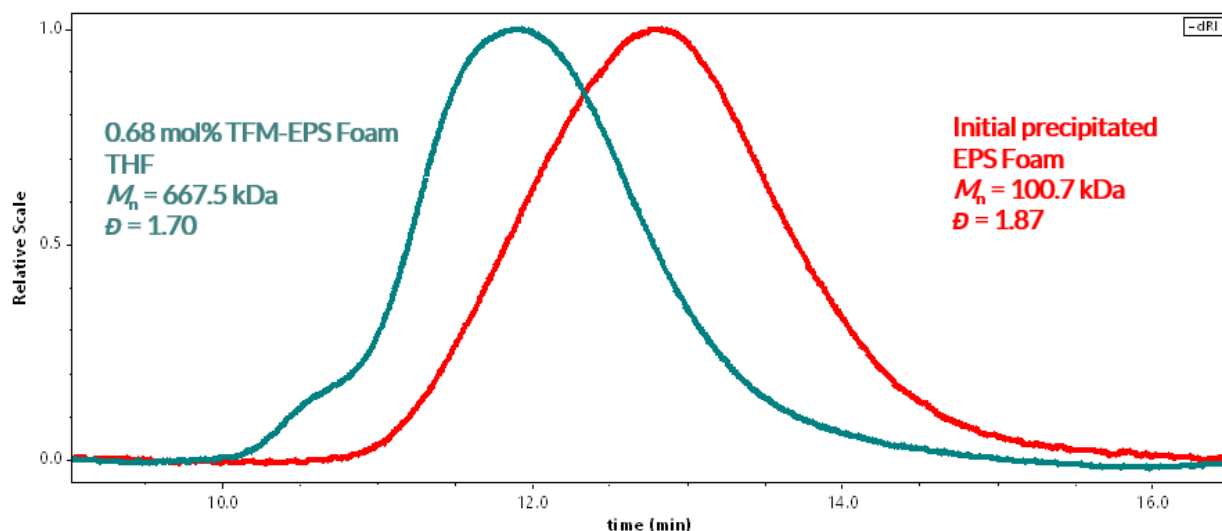


Figure S31. GPC-RI trace (teal) of mechanochemical functionalization in THF (LAG) resulting in 668 kDa **TFM-PS** (0.68 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table S7, Entry 3**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf , 40 mol% KF , LAG = 0.8 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

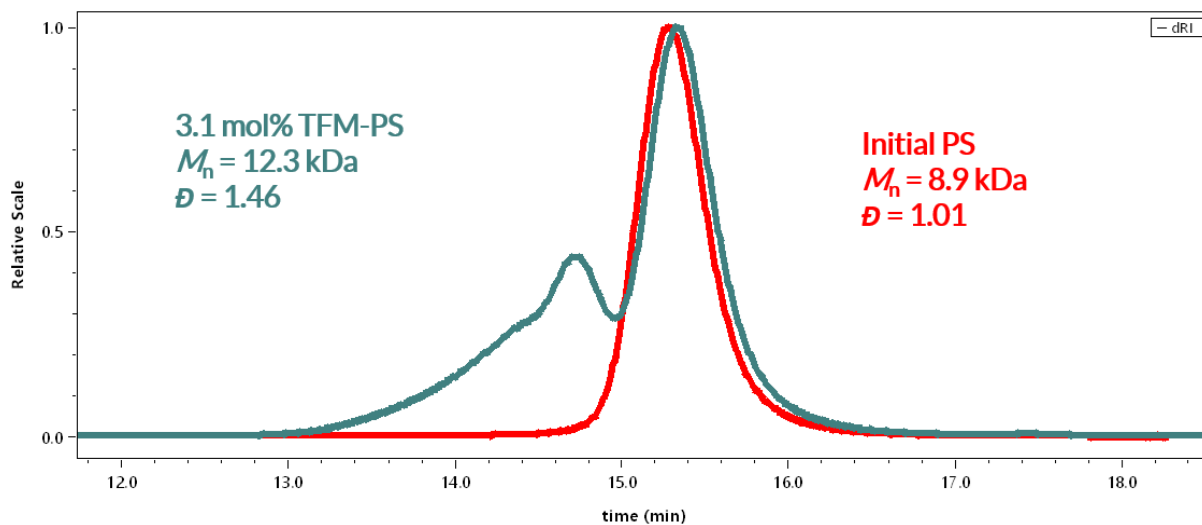


Figure S32. GPC-RI trace (teal) of a solution-state functionalization resulting in 12.3 kDa **TFM-PS** (3.1 mol%) and GPC-RI trace (red) of the initial 8.9 kDa **PS** (See **Table S8, Entry 3**). Conditions: $\text{DCE} = 0.2$ mL, 24 h, 85 $^\circ\text{C}$.

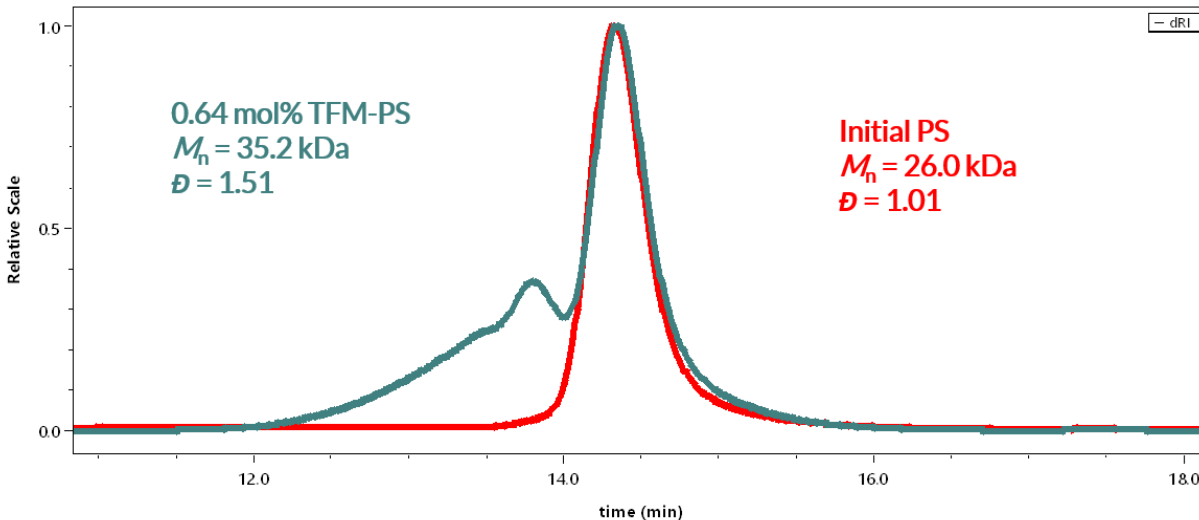


Figure S33. GPC-RI trace (teal) of solution-state functionalization resulting in 35.2 kDa **TFM-PS** (0.64 mol%) and GPC-RI trace (red) of the initial 26.0 kDa **PS** (See **Table S8, Entry 4**). Conditions: DCE = 0.2 mL, 24 h, 85 °C.

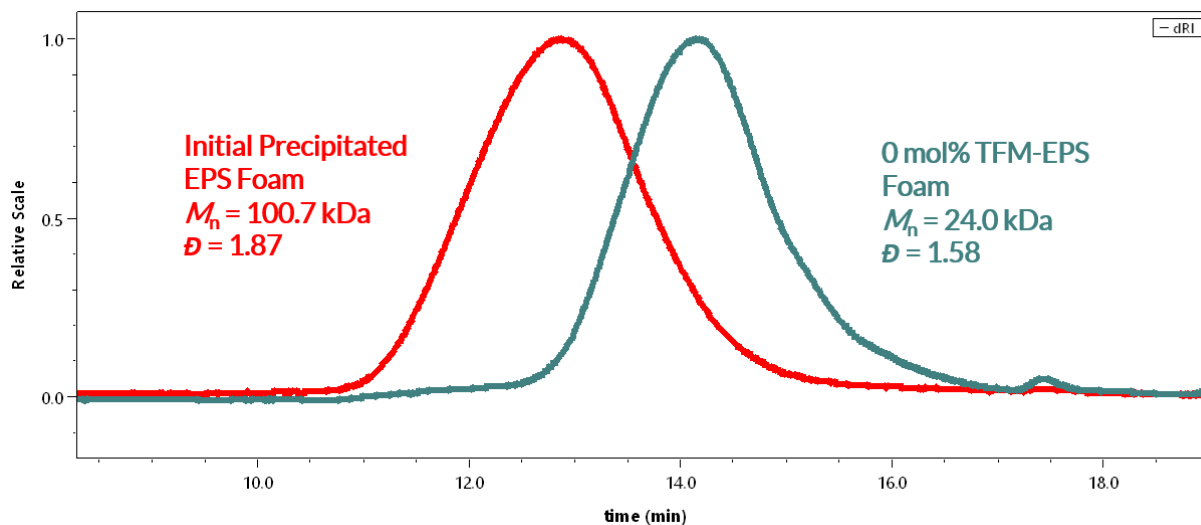


Figure S34. GPC-RI trace (teal) of an attempted solution-state functionalization resulting in 24.0 kDa **PS** in which no trifluoromethylation was observed (0 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table S8, Entry 6**). Conditions: DCE = 0.2 mL, 24 h, 85 °C.

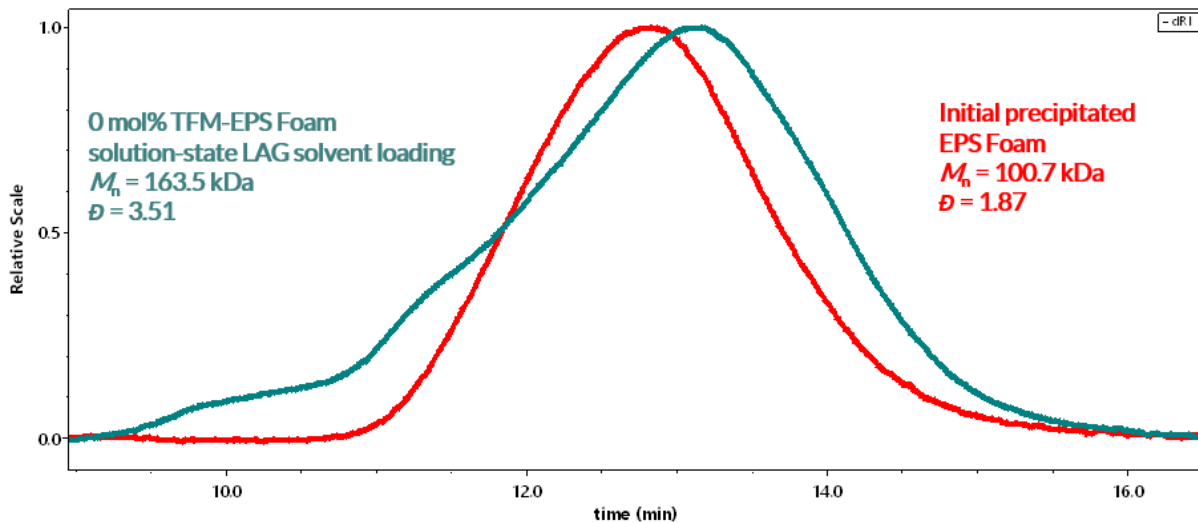


Figure S35. GPC-RI trace (teal) of an attempted solution-state functionalization resulting in 164 kDa **PS** in which no trifluoromethylation was observed (0 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table S8, Entry 7**). Conditions: DCE = 0.2 mL, 24 h, 85 °C.

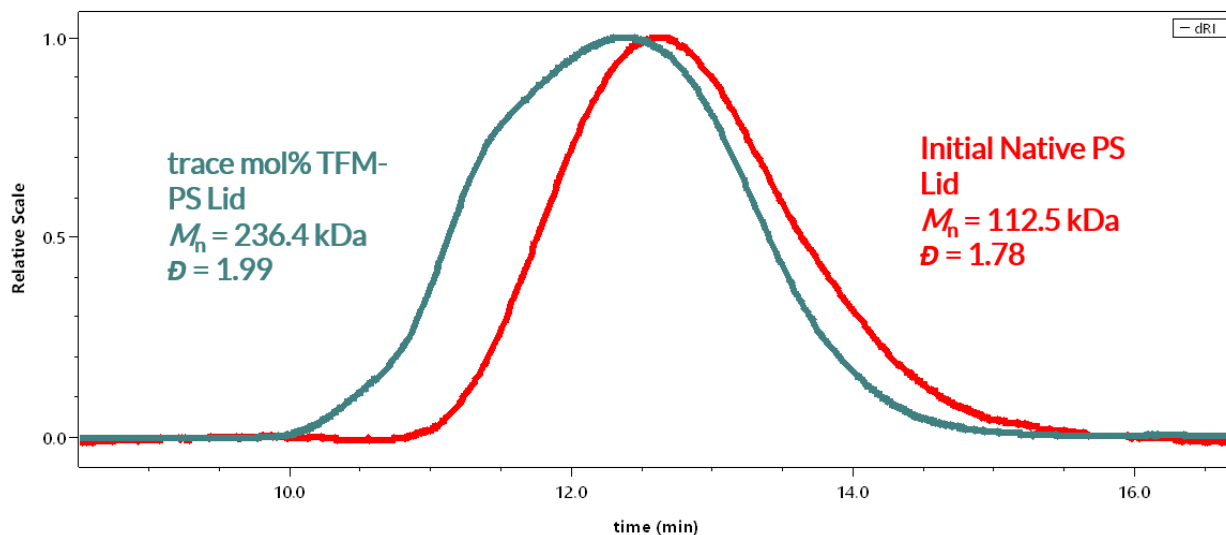


Figure S36. GPC-RI trace (teal) of an attempted solution-state functionalization resulting in 236 kDa **PS** in which only trace amounts of trifluoromethylation was observed (i.e., trifluoromethyl peak at -62.13 ppm could not be integrated) and GPC-RI trace (red) of the initial 112.5 kDa **Native PS Lid** (See **Table S8, Entry 8**). Conditions: DCE = 0.2 mL, 24 h, 85 °C.

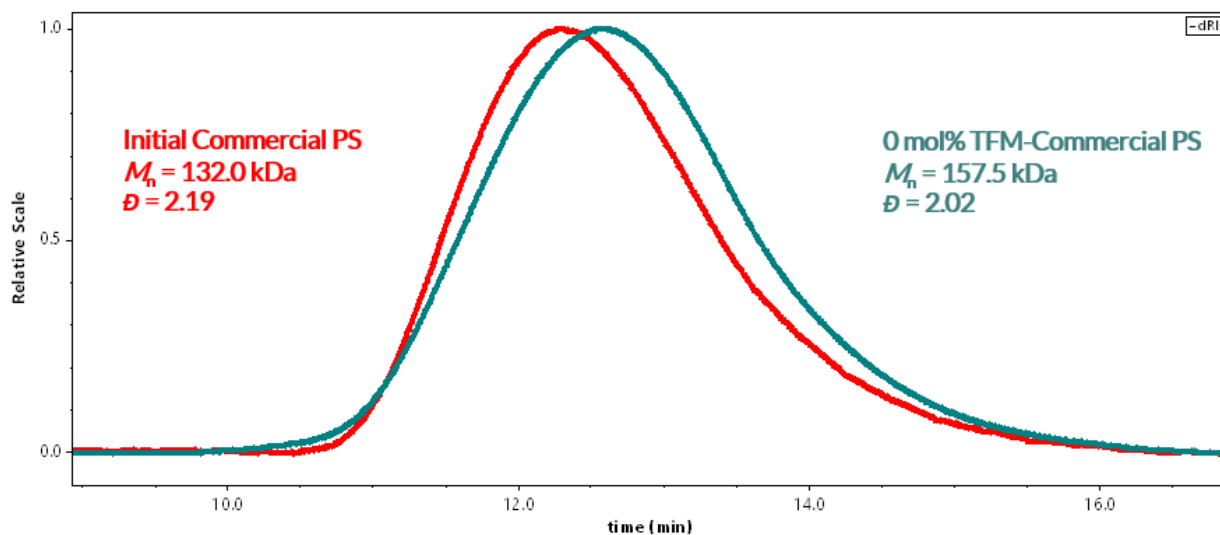


Figure S37. GPC-RI trace (teal) of an attempted solution-state functionalization resulting in 158 kDa **TFM-Commercial PS** in which no trifluoromethylation was observed (0 mol%) and GPC-RI trace (red) of the initial 132 kDa **Commercial PS** (See **Table S8, Entry 9**). Conditions: DCE = 0.2 mL, 24 h, 85 °C.

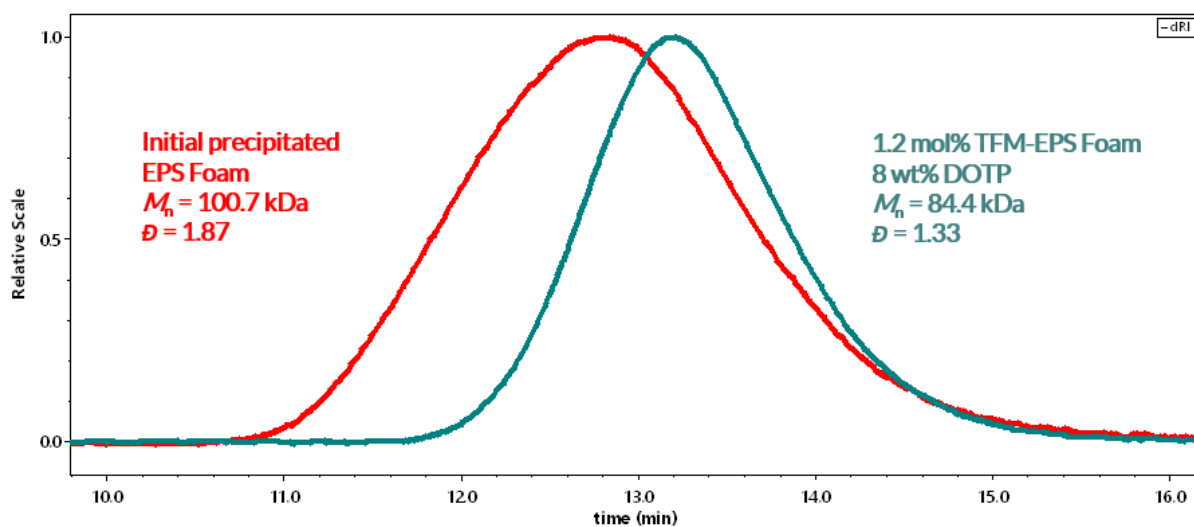


Figure S38. GPC-RI trace (teal) of a mechanochemical functionalization with 8 wt% DOTP resulting in 84.4 kDa **TFM- PS** (1.2 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table S9, Entry 1**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 0.8 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

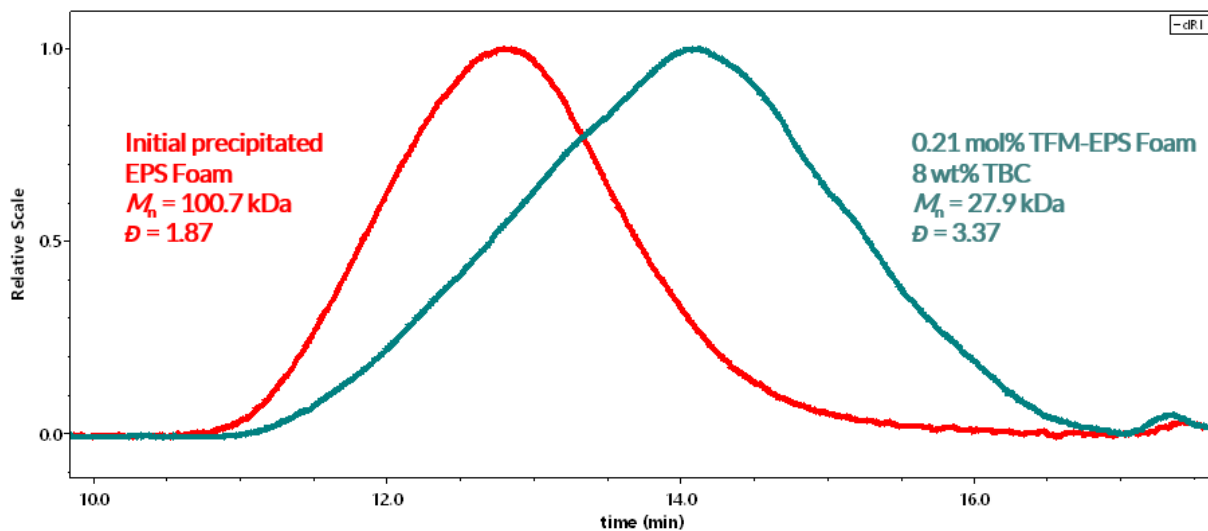


Figure S39. GPC-RI trace (teal) of a mechanochemical functionalization with 8 wt% TBC resulting in 27.9 kDa **TFM- PS** (<0.50 mol%) and GPC-RI trace (red) of the initial 101 kDa **Precipitated EPS Foam** (See **Table S9, Entry 2**). Conditions: 10 mol% TMSCF_3 , 40 mol% AgOTf, 40 mol% KF, DCE = 0.8 $\mu\text{L}/\text{mg}$, 4 h milling w/ 2x 8 mm SS balls.

NMR Spectroscopy:

^1H NMR Spectroscopy

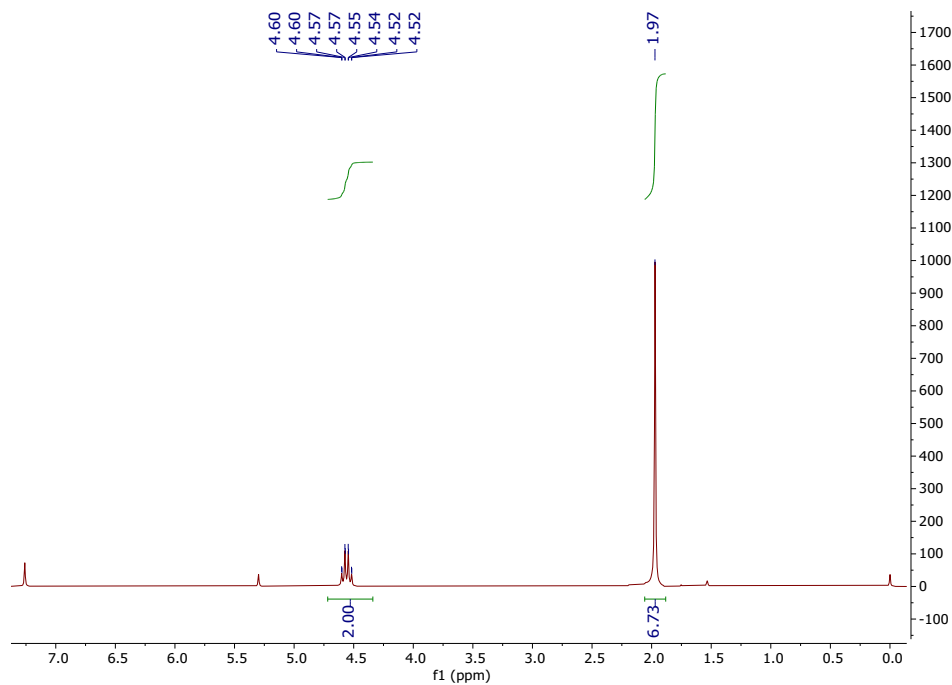


Figure S40. ^1H NMR spectrum of Initiator- CF_3 (300 MHz, CDCl_3).

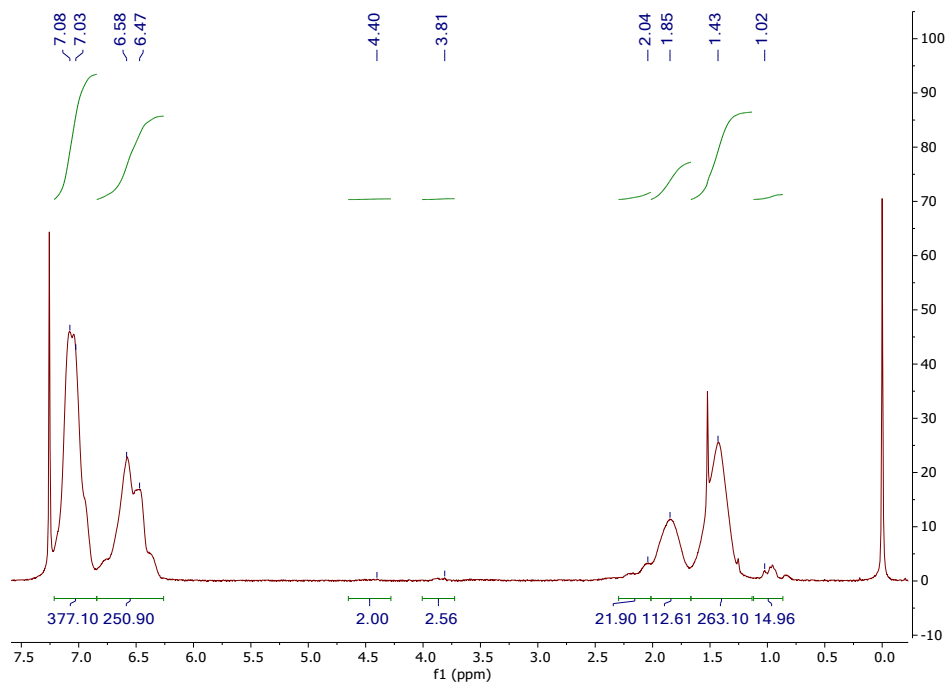


Figure S41. Representative ^1H NMR spectrum of in-house PS (8.9 kDa with CF_3 chain-end shown) (500 MHz, CDCl_3).

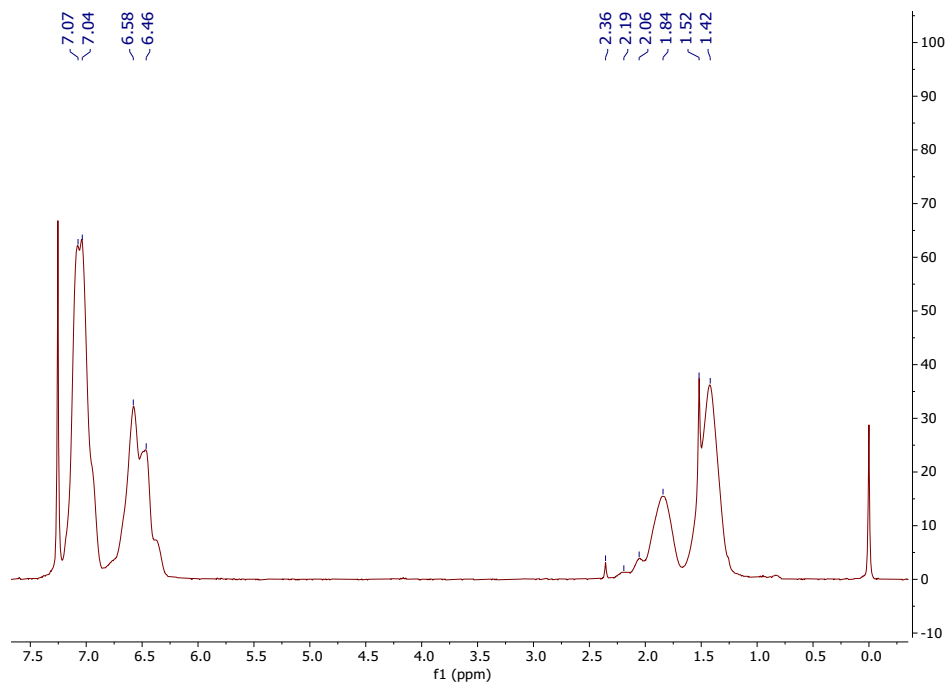


Figure S42. ^1H NMR spectrum of **Precipitated EPS Foam** (300 MHz, CDCl_3).

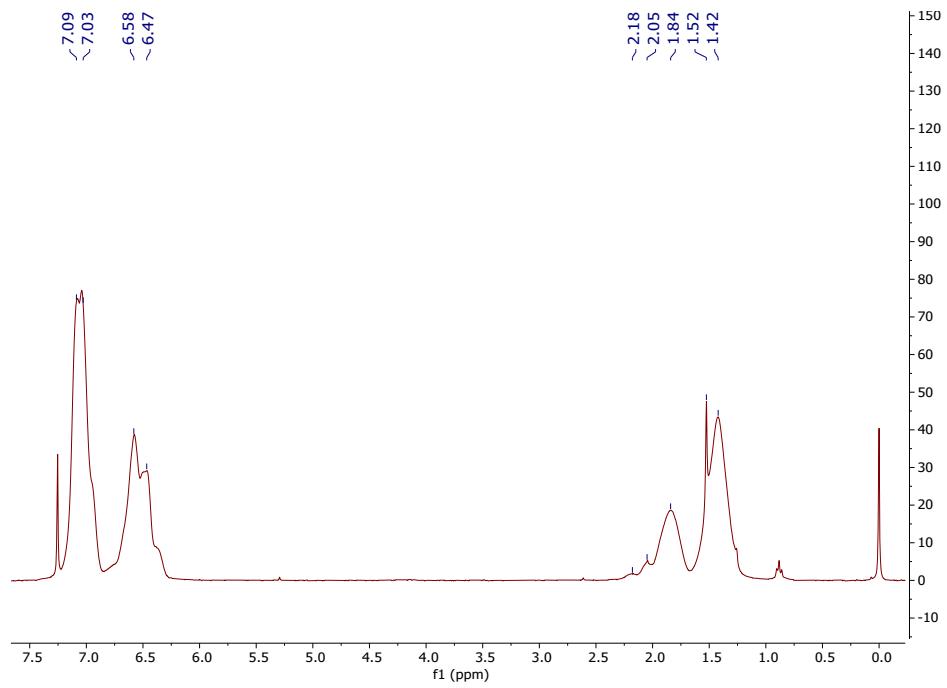


Figure S43. ^1H NMR spectrum of **Native EPS Foam** (300 MHz, CDCl_3).

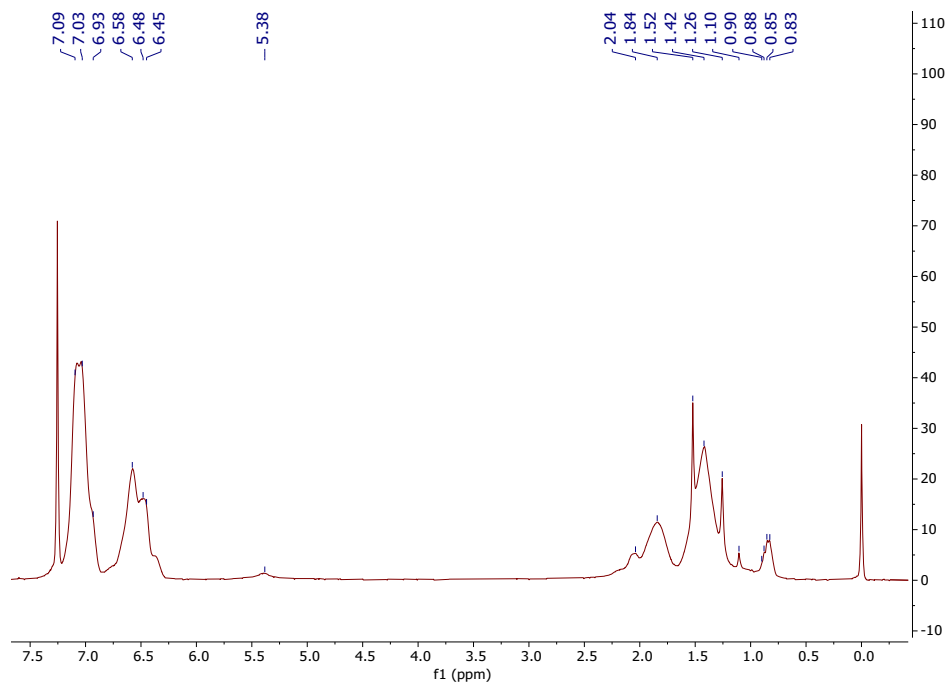


Figure S44. ^1H NMR spectrum of dyed **Native PS Lid** (300 MHz, CDCl_3).

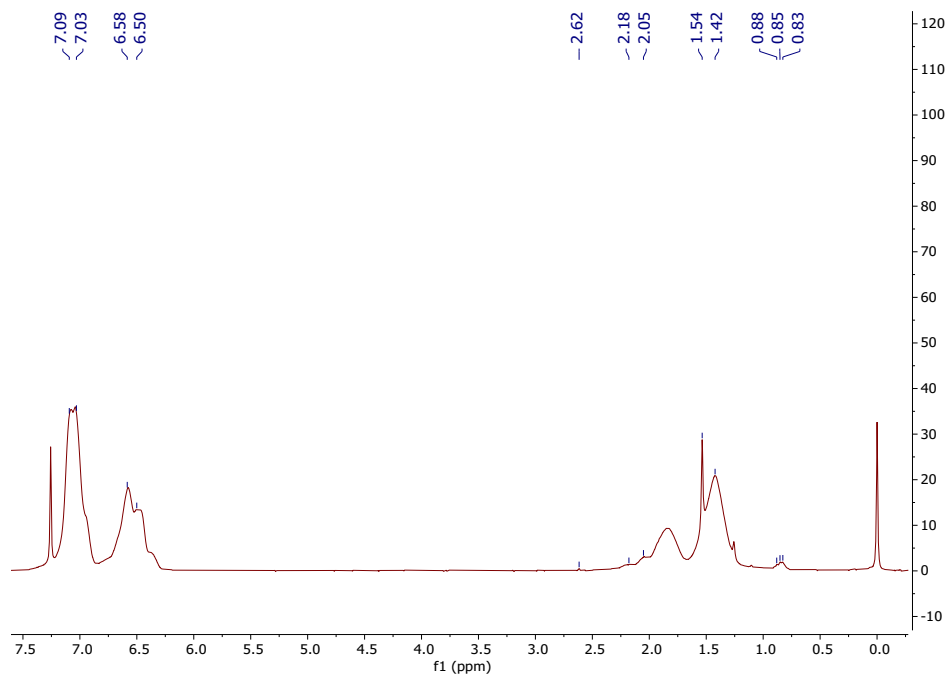


Figure S45. ^1H NMR spectrum of **Precipitated PS Lid** (300 MHz, CDCl_3).

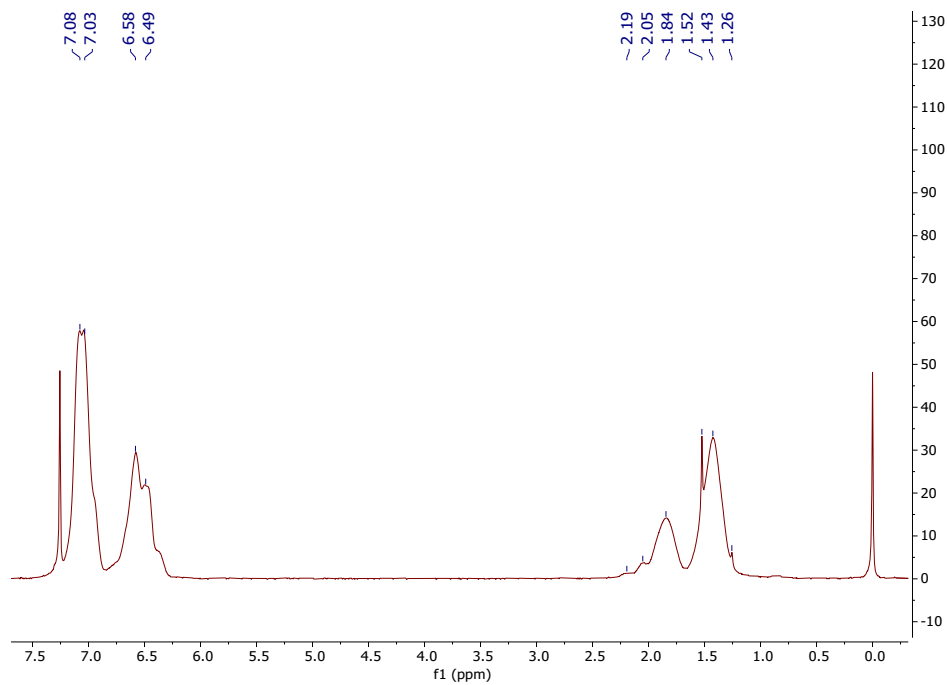


Figure S46. ^1H NMR spectrum of **Commercial PS** (300 MHz, CDCl_3).

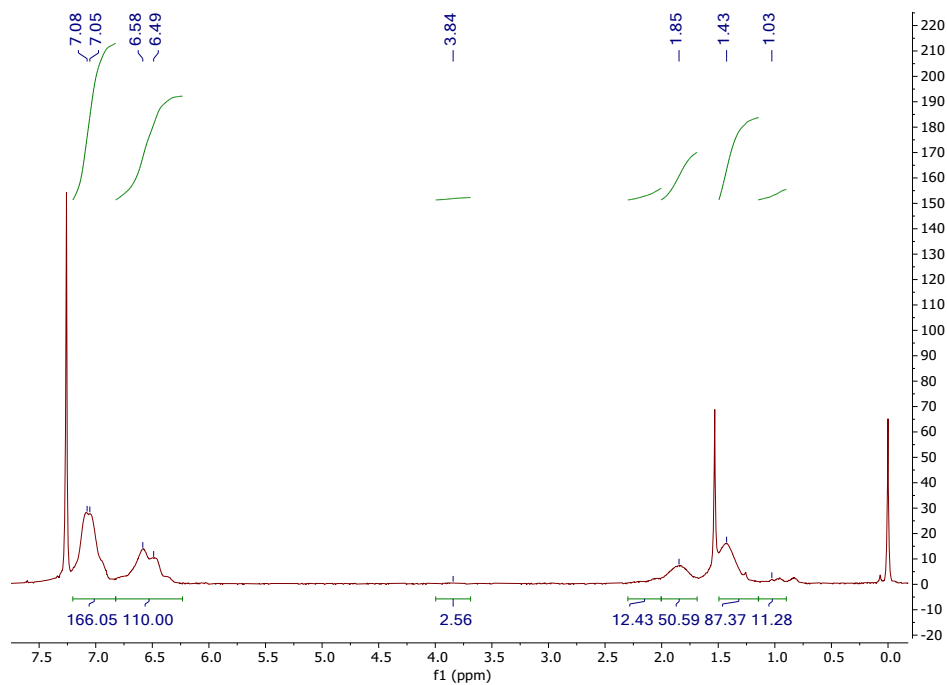


Figure S47. Representative ^1H NMR spectrum of **TFM-PS** (1.1 mol% shown) from 8.9 kDa **PS** (300 MHz, CDCl_3) (See **Table 1, Entry 1**).

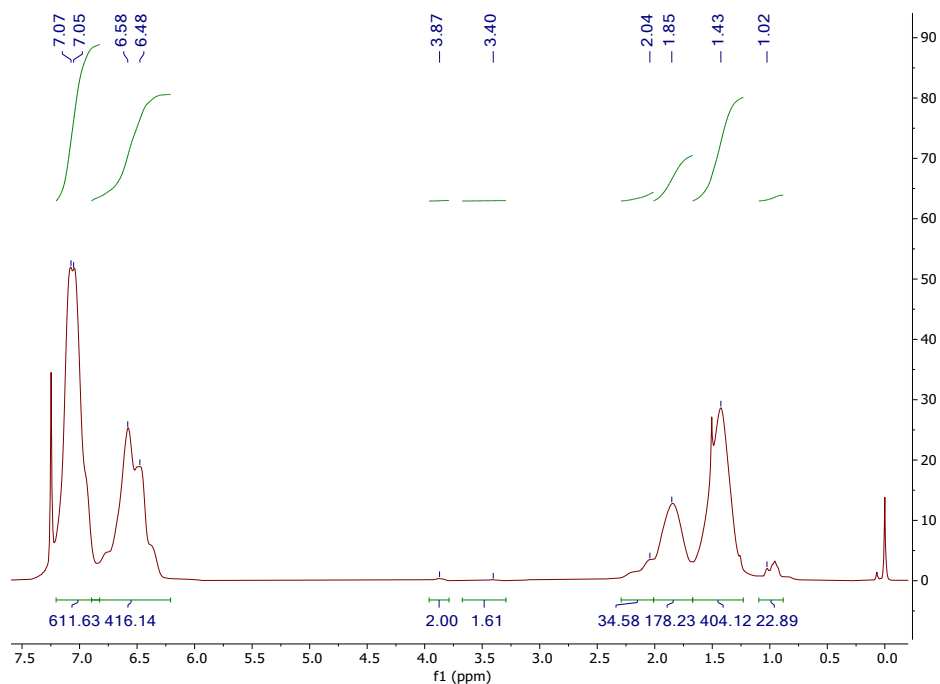


Figure S48. Representative ^1H NMR spectrum of **TFM-PS** (1.3 mol% shown) from 9.3 kDa **PS** (300 MHz, CDCl_3) (See **Table 1, Entry 2**).

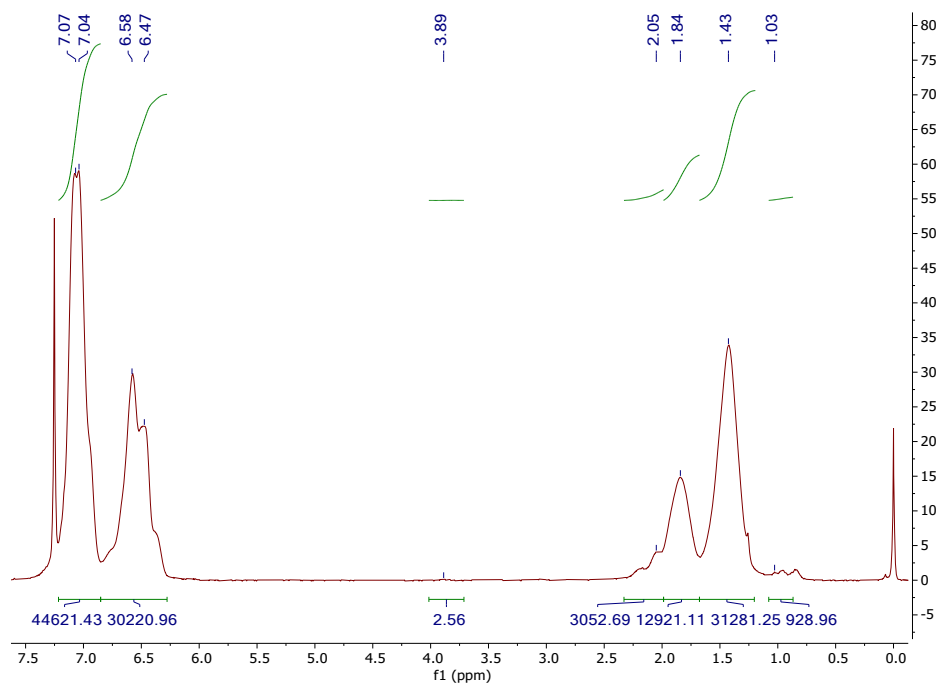


Figure S49. Representative ^1H NMR spectrum of **TFM-PS** (1.1 mol% shown) from 26.0 kDa **PS** (300 MHz, CDCl_3) (See **Figure 3A, Entry 0.4 $\mu\text{L}/\text{mg}$ LAG**).

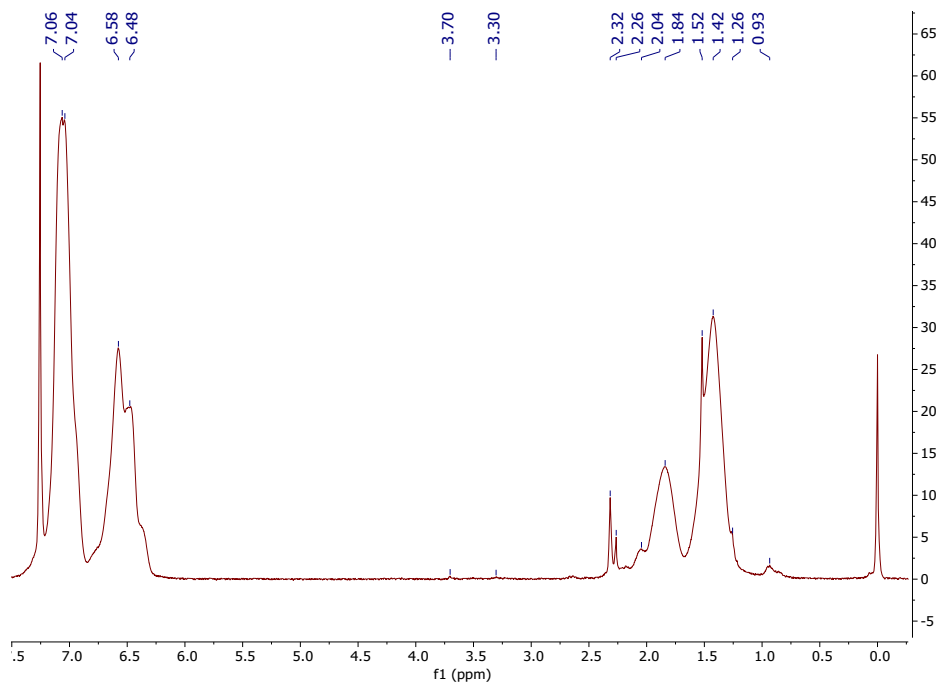


Figure S50. Representative ^1H NMR spectrum of **TFM-EPS Foam** (1.1 mol% shown) from 101 kDa **precipitated EPS Foam** waste (300 MHz, CDCl_3) (See **Table 2, Entry 4**).

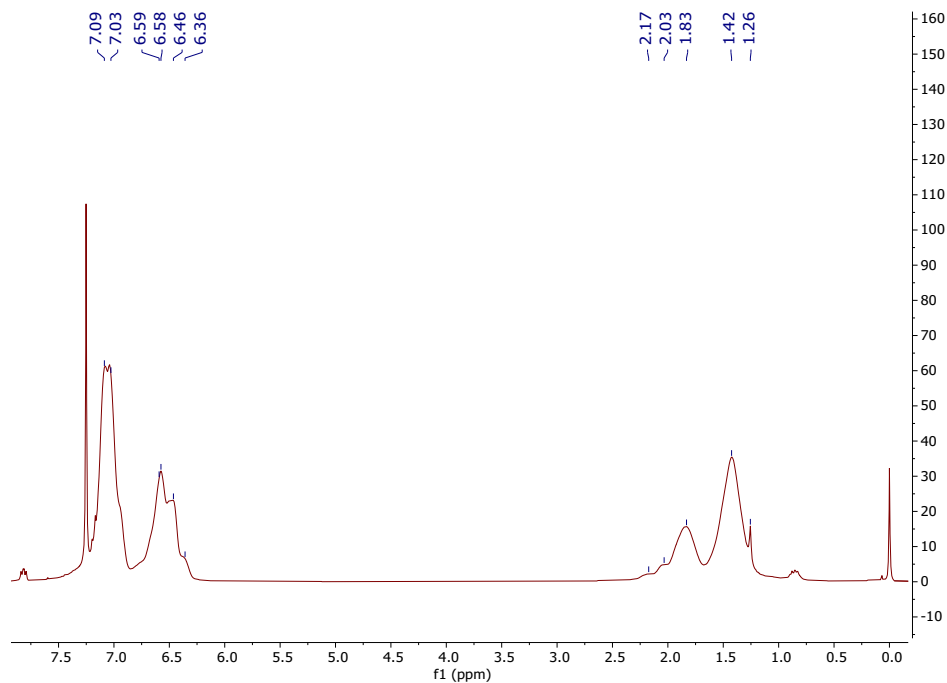


Figure S51. Representative ^1H NMR spectrum of **TFM-EPS Foam** (0.29 mol% shown) from 119 kDa **Native EPS Foam** waste (300 MHz, CDCl_3 with 4,4'-difluorobenzophenone as an internal standard for ^{19}F NMR) (See **Table 3, Entry 1**).

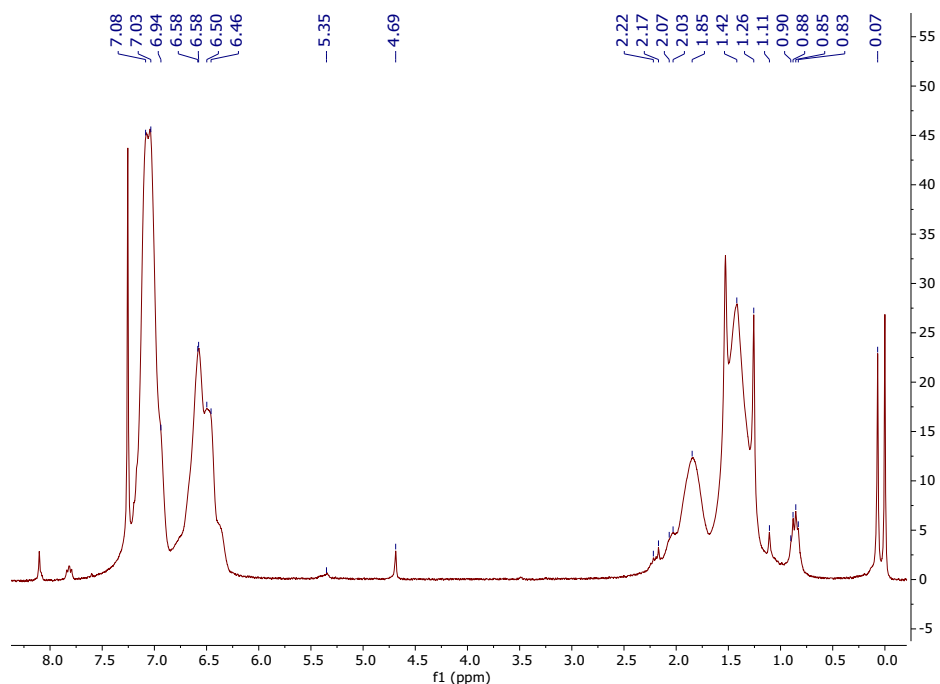


Figure S52. ^1H NMR spectrum of **TFM-PS Lid** (0.60 mol% shown) from 113 kDa **Native PS Lid** (300 MHz, CDCl_3 with 4,4'-difluorobenzophenone as an internal standard for ^{19}F NMR) (See **Table 3, Entry 2**).

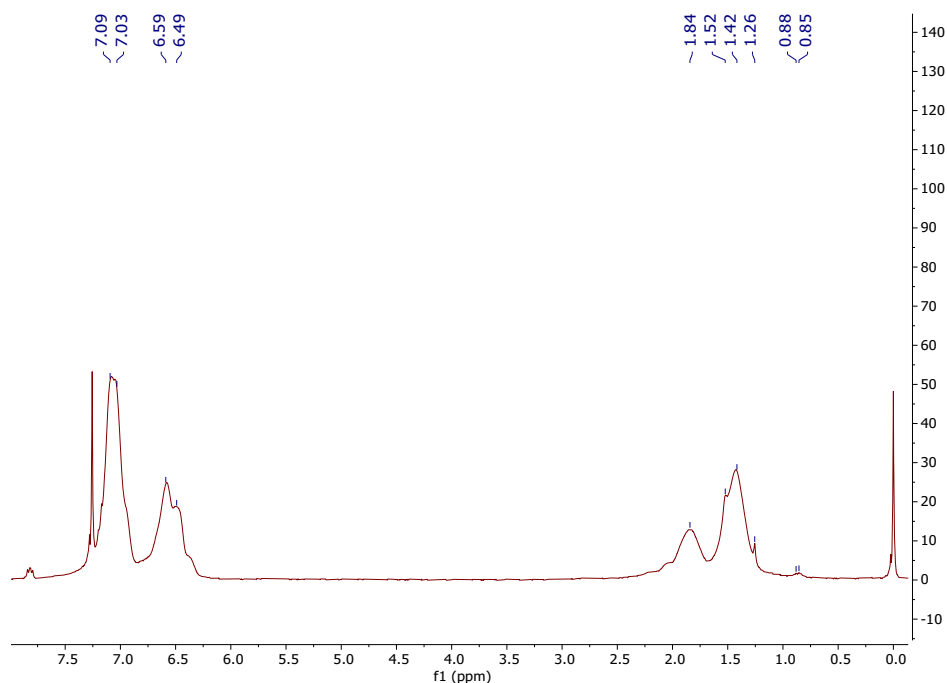


Figure S53. Representative ^1H NMR spectrum of **TFM-PS Lid** (0.46 mol% shown) from 131 kDa **Precipitated PS Lid** waste (300 MHz, CDCl_3 with 4,4'-difluorobenzophenone as an internal standard for ^{19}F NMR) (See **Table 3, Entry 5**).

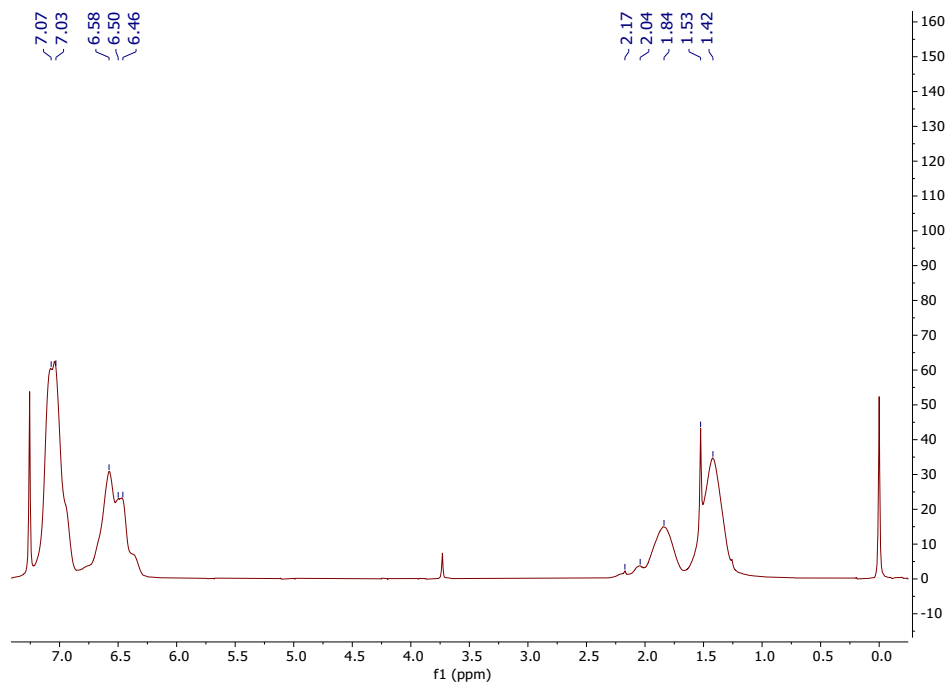


Figure S54. Representative ¹H NMR spectrum of **TFM-Commercial PS** (0.65 mol% shown) from 132 kDa **Commercial PS** (300 MHz, CDCl₃) (See **Table 3, Entry 3**).

¹⁹F NMR Spectroscopy

MS-I-106 crude post wash 19F.10.fid
19F

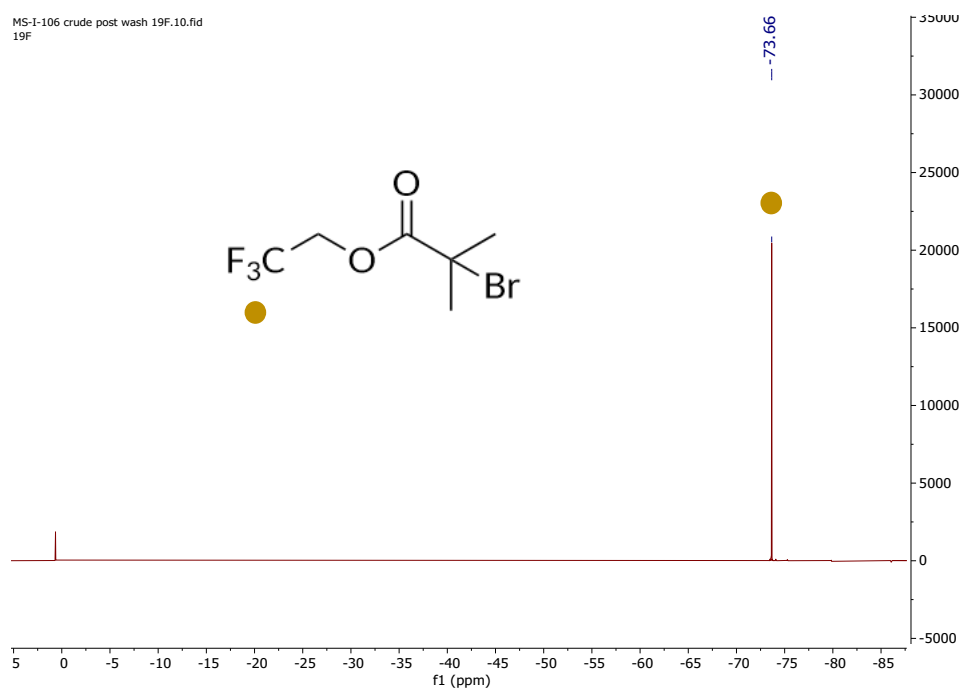


Figure S55. ¹⁹F NMR spectrum of **Initiator-CF₃** (470 MHz, CDCl₃ with freon-11).

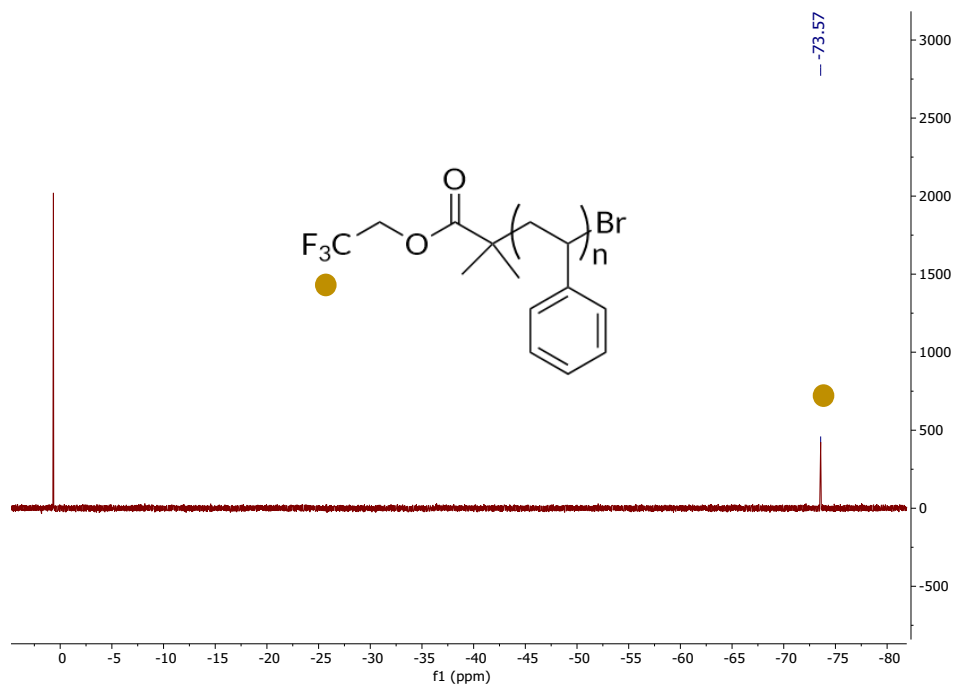


Figure S56. Representative ¹⁹F NMR spectrum of 8.9 kDa **PS** (with CF₃ chain-end) (470 MHz, CDCl₃ with freon-11).

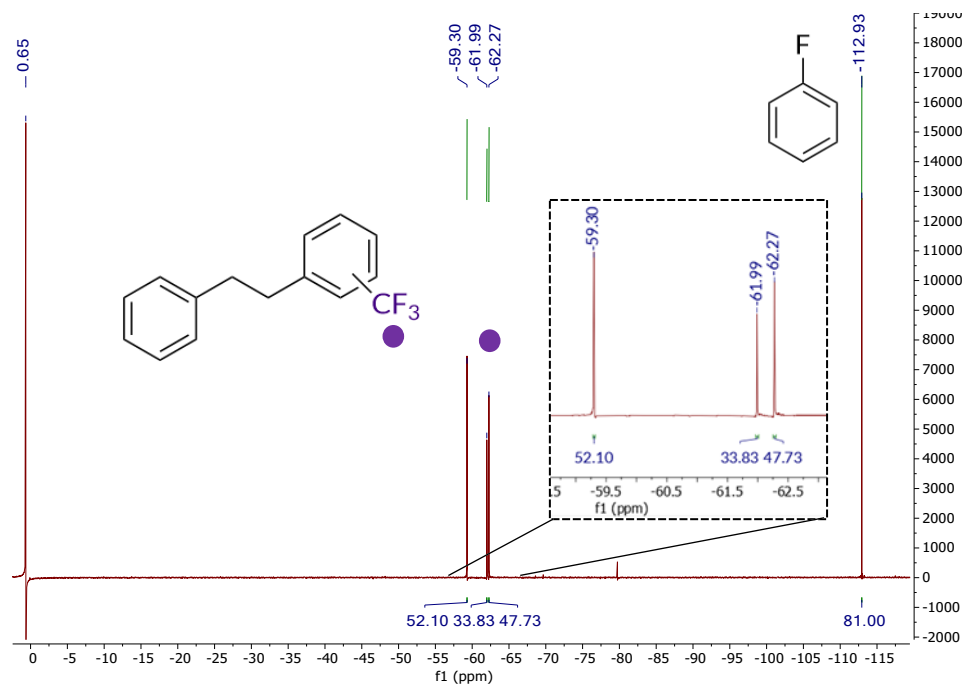


Figure S57. Representative ^{19}F NMR spectrum of a crude reaction mixture containing **TFM-BB** (5.5 mol% shown, see **Table S4, Entry 1**) (470 MHz, CDCl_3 with freon-11 and fluorobenzene). See **Equation S1** for integral normalization and functionalization density calculation example.

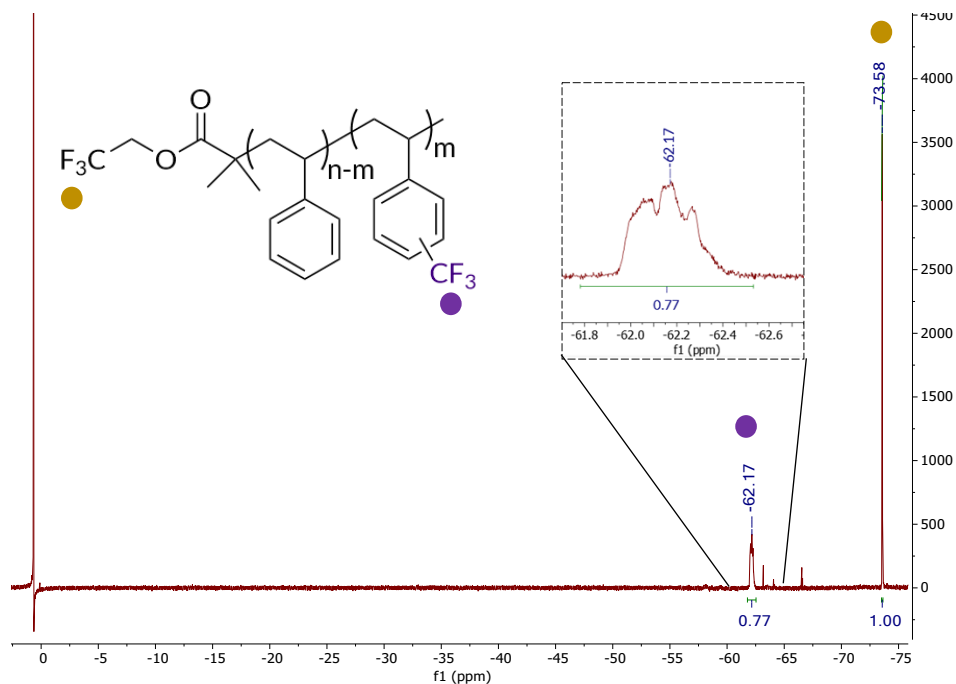


Figure S58A. Representative ^{19}F NMR spectrum of crude **TFM-PS** (0.91 mol% shown, see **Table S5, Entry 1**) from 8.9 kDa **PS** (470 MHz, CDCl_3 with freon-11). See **Equation S3** for representative functionalization density calculated from the CF_3 chain-end.

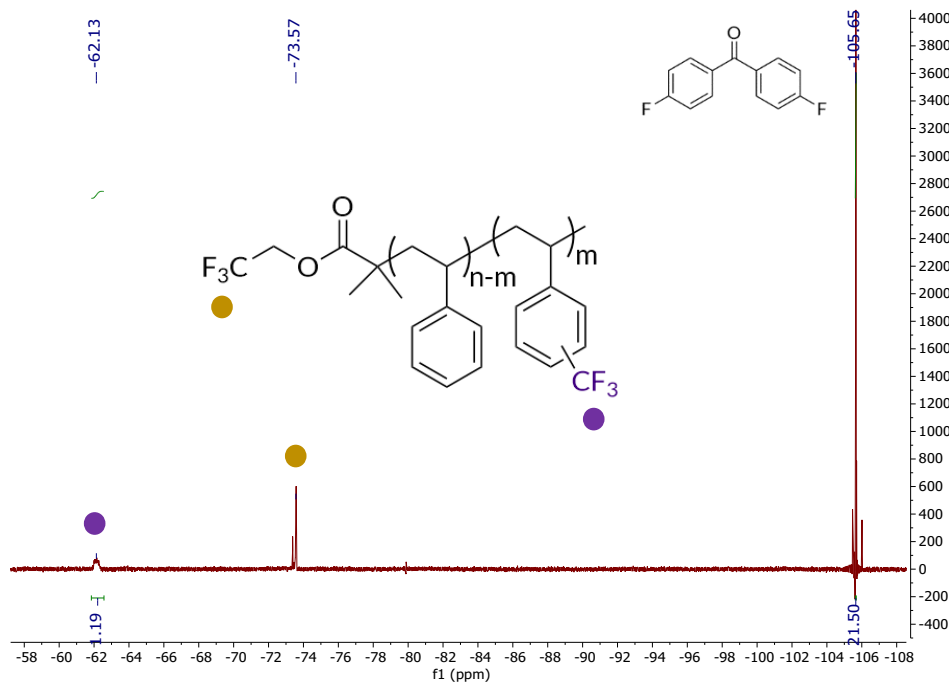


Figure S58B. Representative ^{19}F NMR spectrum of purified **TFM-PS** (1.1 mol% shown, see **Table 1, Entry 1**) from 8.9 kDa **PS** (470 MHz, CDCl_3 referenced to 4,4'-

difluorobenzophenone). See **Equation S4** for representative functionalization density calculated from the internal standard.

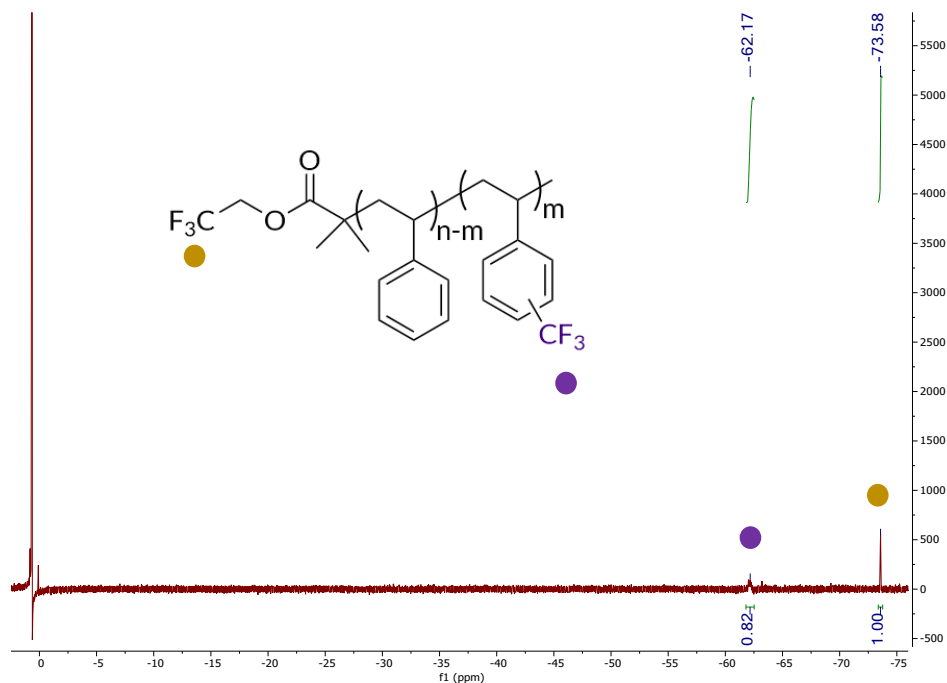


Figure S59A. Representative ¹⁹F NMR spectrum of crude **TFM-PS** (0.92 mol% shown, see **Table S5, Entry 2**) from 9.3 kDa **PS** (470 MHz, CDCl₃ with freon-11). See **Equation S3** for functionalization density calculated from the CF₃ chain-end.

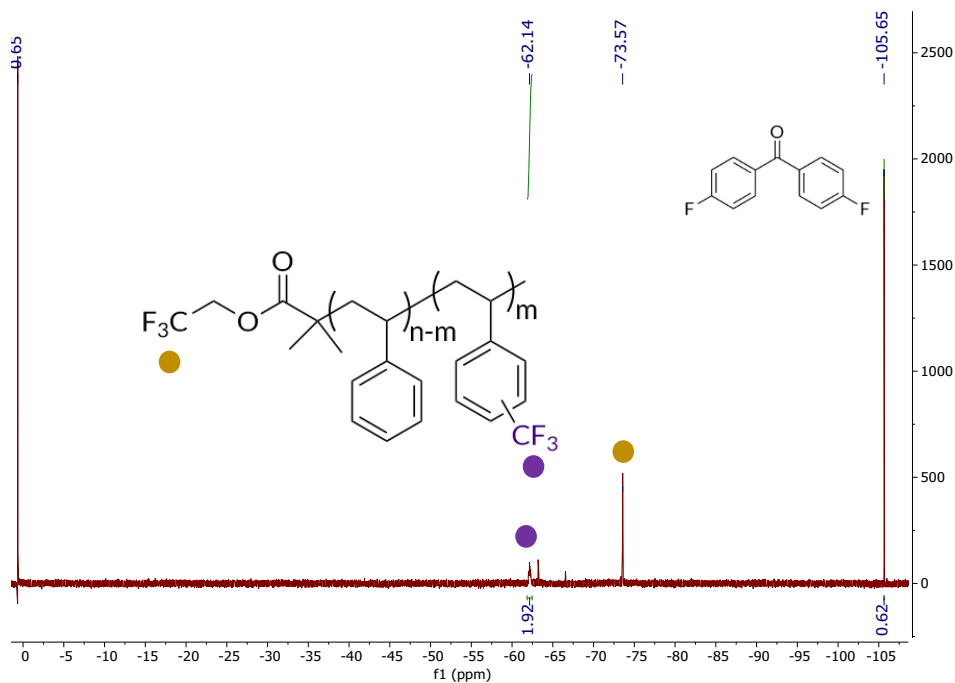


Figure S60B. Representative ^{19}F NMR spectrum of purified **TFM-PS** (1.1 mol% shown, see **Figure 3A, Entry 0.4 $\mu\text{L}/\text{mg}$ LAG**) from 26.0 kDa **PS** (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

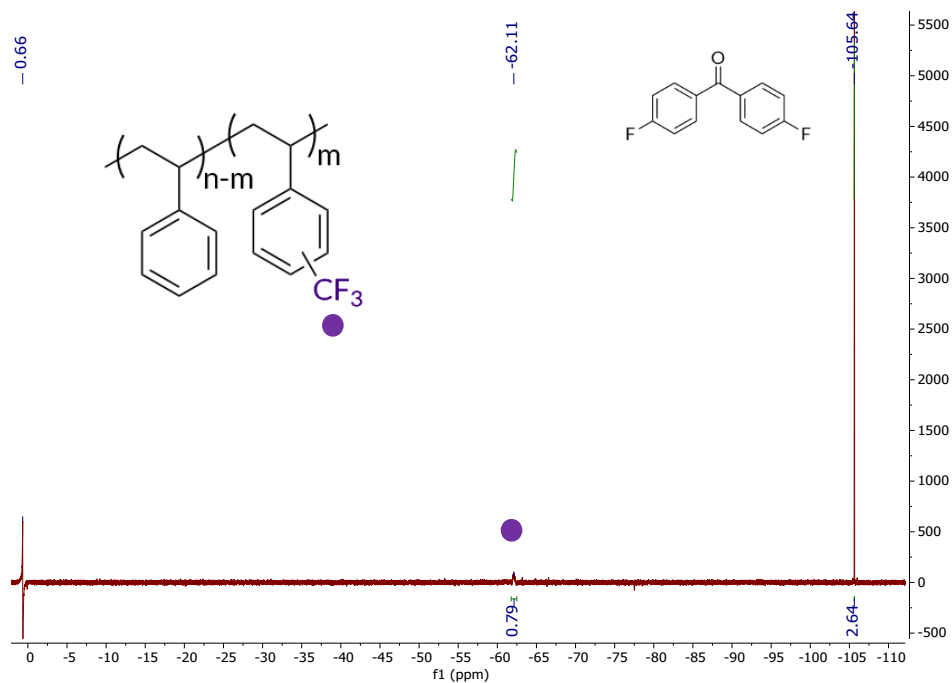


Figure S61. Representative ^{19}F NMR spectrum of purified **TFM-EPS Foam** (0.29 mol% shown, see **Table 3, Entry 1**) from 119 kDa **Native EPS Foam** waste (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

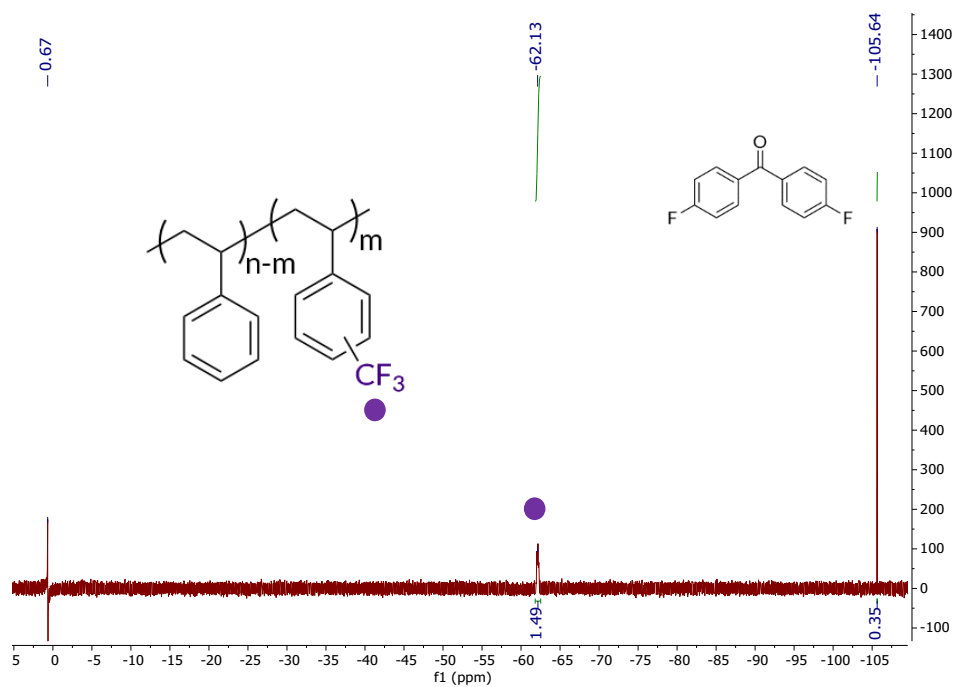


Figure S62. Representative ^{19}F NMR spectrum of purified **TFM-EPS Foam** (1.1 mol% shown, see **Table 3, Entry 4**) from 101 kDa **Precipitated EPS Foam** waste (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

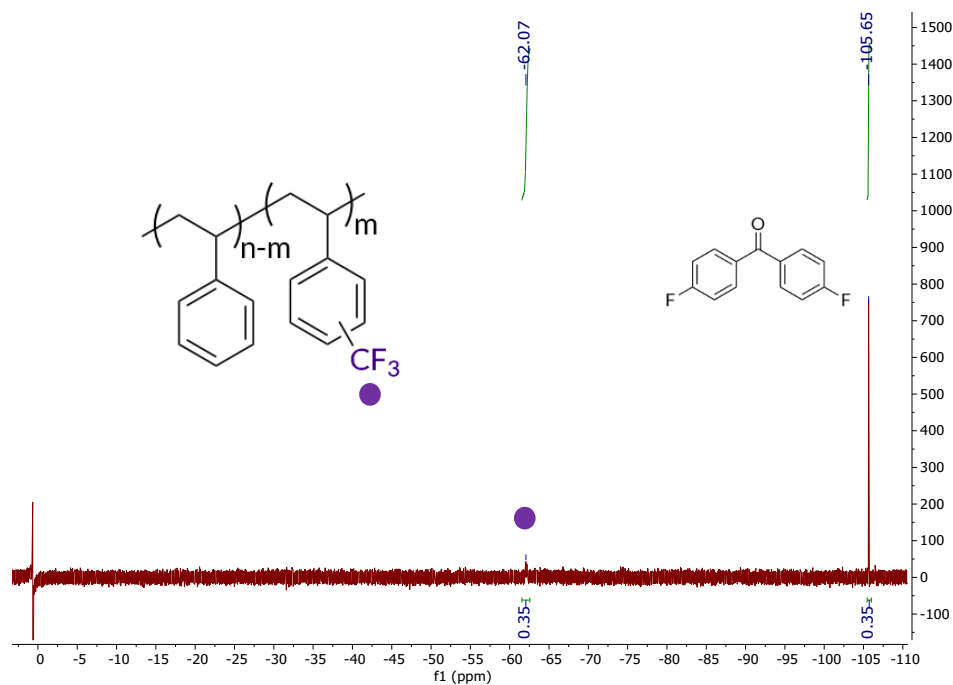


Figure S63. ^{19}F NMR spectrum of purified **TFM-PS Lid** (0.60 mol% shown, see **Table 3, Entry 2**) from 113 kDa **Native PS Lid** (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

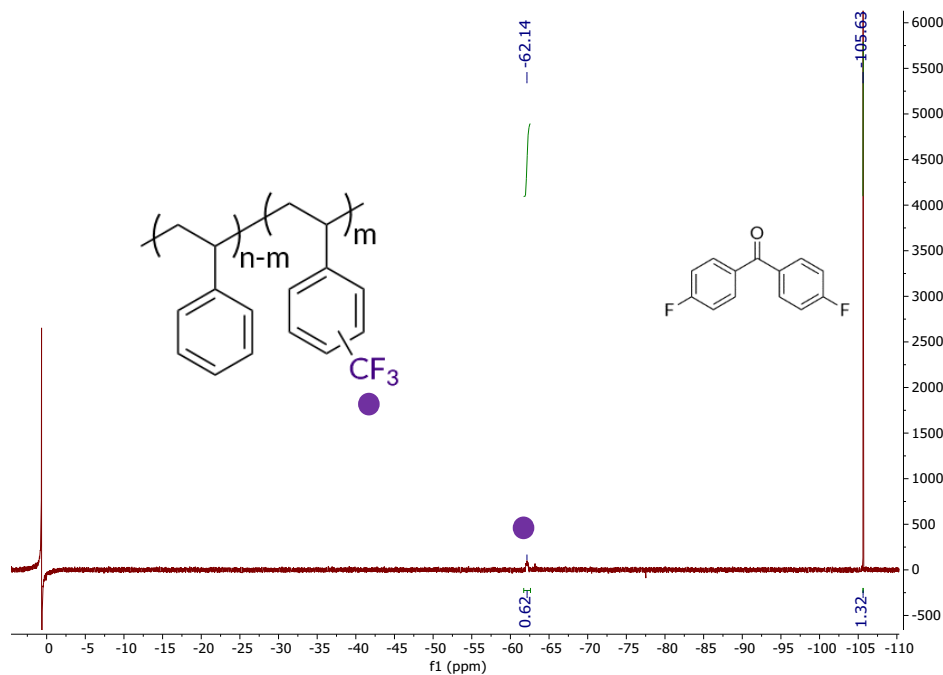


Figure S64. Representative ^{19}F NMR spectrum of purified **TFM-PS Lid** (0.46 mol% shown, see **Table 3, Entry 5**) from 131 kDa **Precipitated PS Lid** (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

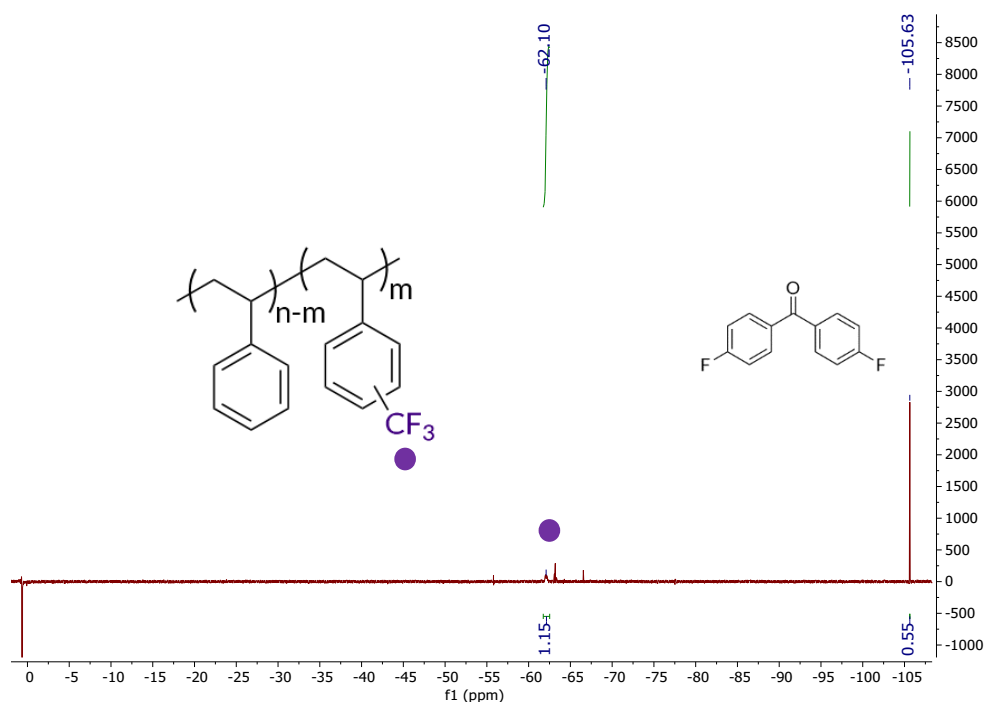


Figure S65. Representative ^{19}F NMR spectrum of purified **TFM-Commercial PS** (0.65 mol% shown, see **Table 3, Entry 3**) from 132 kDa **Commercial PS** (470 MHz, CDCl_3 with freon-11). See **Equation S4** for representative functionalization density calculated from the internal standard.

Gas Chromatography-Mass Spectrometry (GCMS)

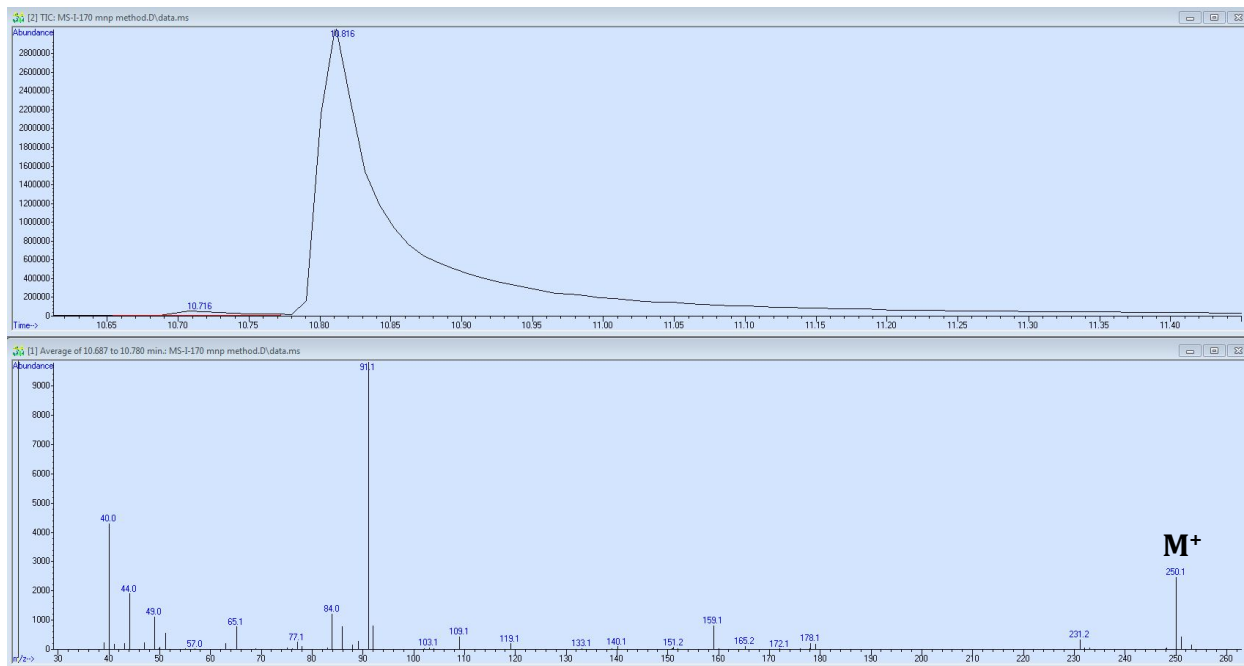


Figure S66. GCMS spectra of a crude reaction mixture containing **TFM-BB** (1.6 mol%). GC retention time of **TFM-BB** is 10.72 min. LRMS (EI): m/z calcd for $[M]^+$: 250.3; found: 250.1.

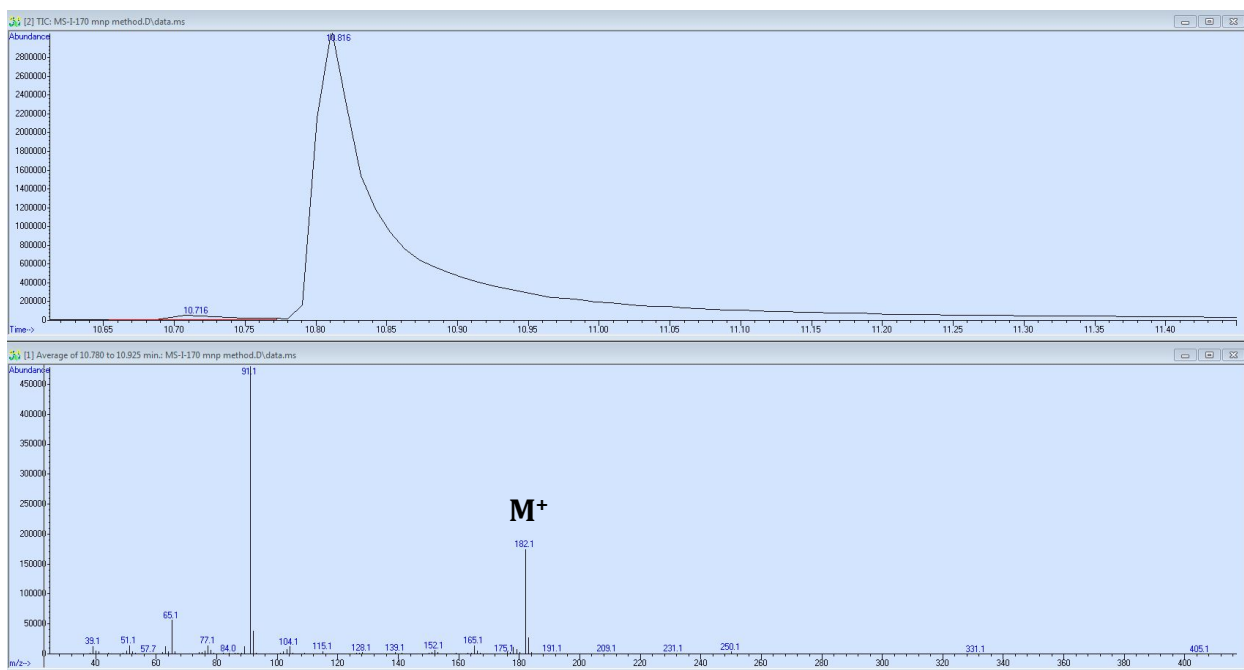


Figure S67. GCMS spectra of a crude reaction mixture containing **BB**. GC retention time of **BB** is 10.82 min. LRMS (EI): m/z calcd for $[M]^+$: 182.3; found: 182.1.

Differential Scanning Calorimetry (DSC):

Traces of the DSC data analyzed in TRIOS software as shown below, indicating the glass transition temperature (T_g) calculated at the midpoint half height of the inflection of the second heat.

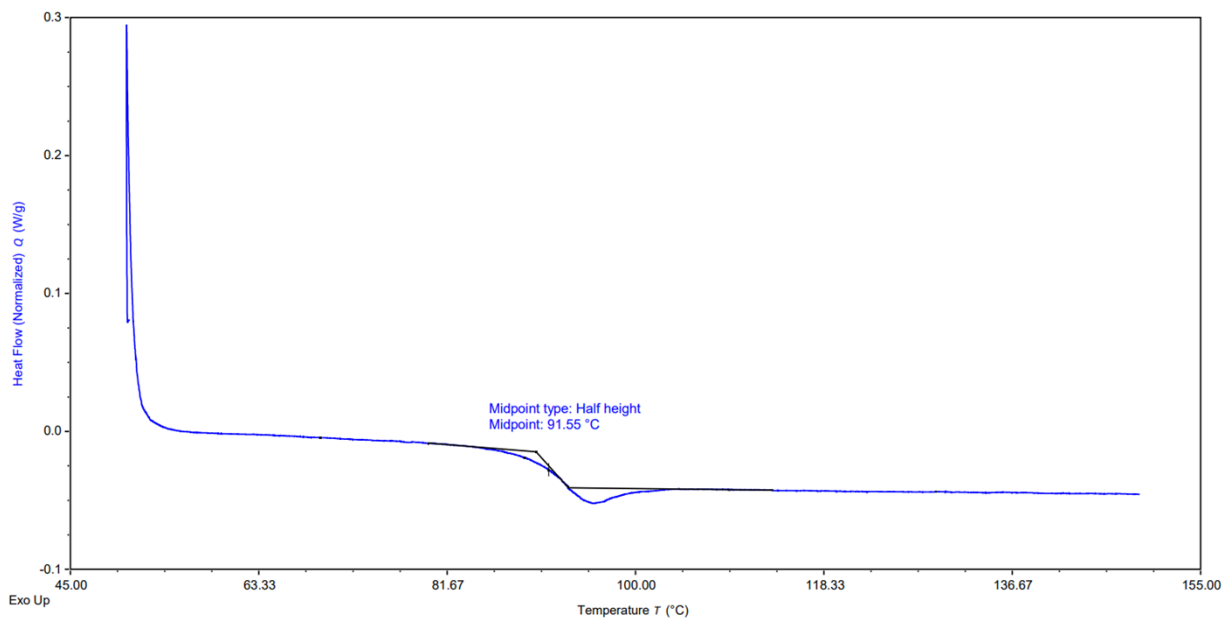


Figure S68. DSC trace of 8.9 kDa PS (4.3 mg), $T_g = 91.6$ $^{\circ}$ C.

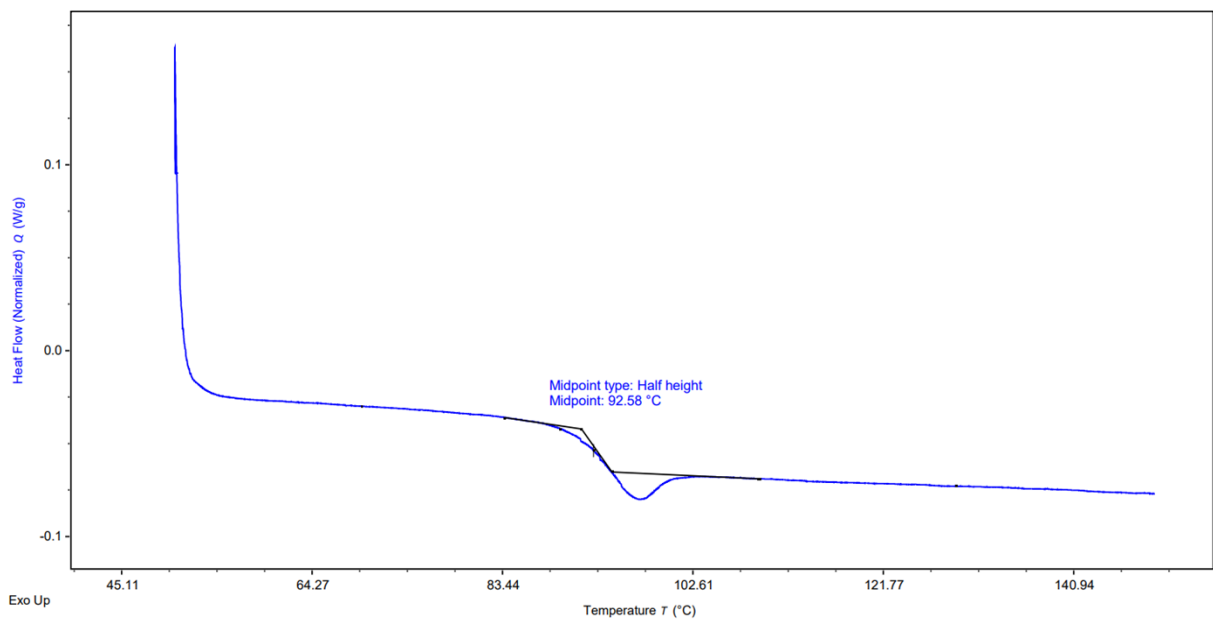


Figure S69. DSC trace of 9.3 kDa PS (4.4 mg), $T_g = 92.6$ $^{\circ}$ C.

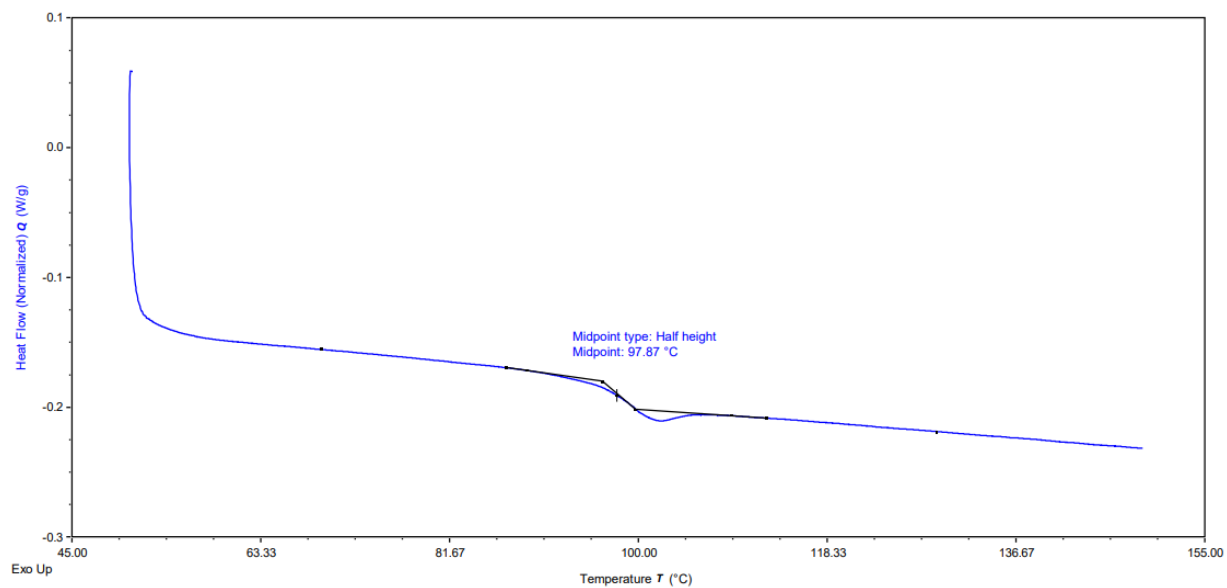


Figure S70. DSC trace of 23.0 kDa PS (5.5 mg), $T_g = 97.9$ °C.

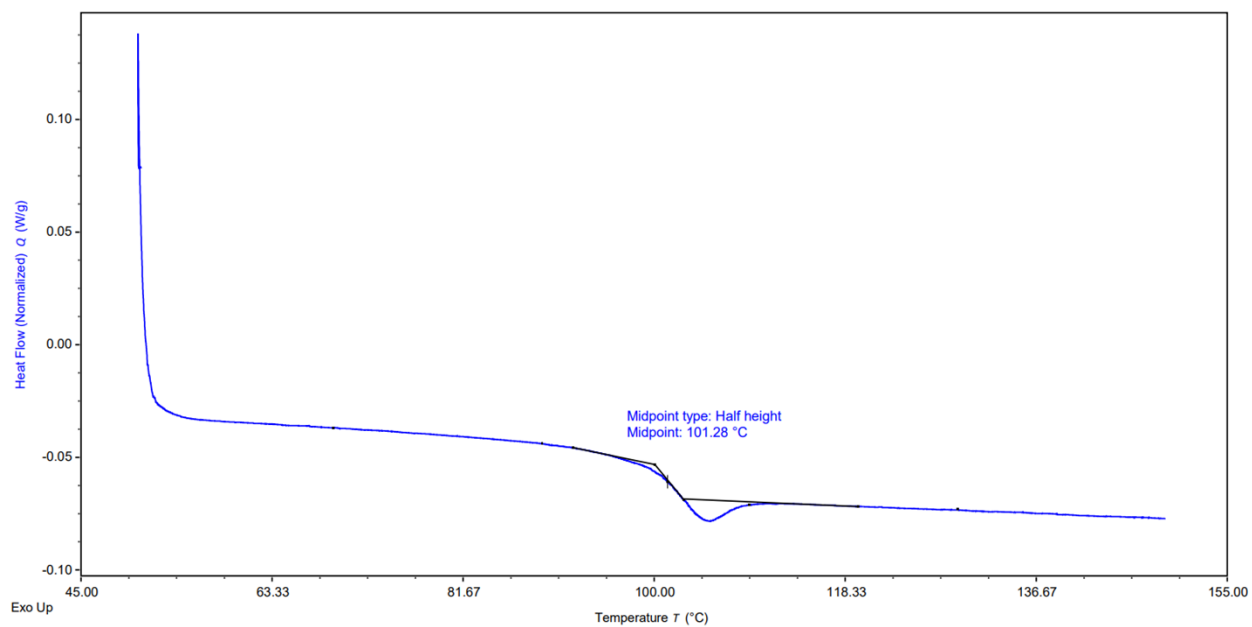


Figure S71. DSC trace of 26.0 kDa PS (5.7 mg), $T_g = 101.3$ °C.

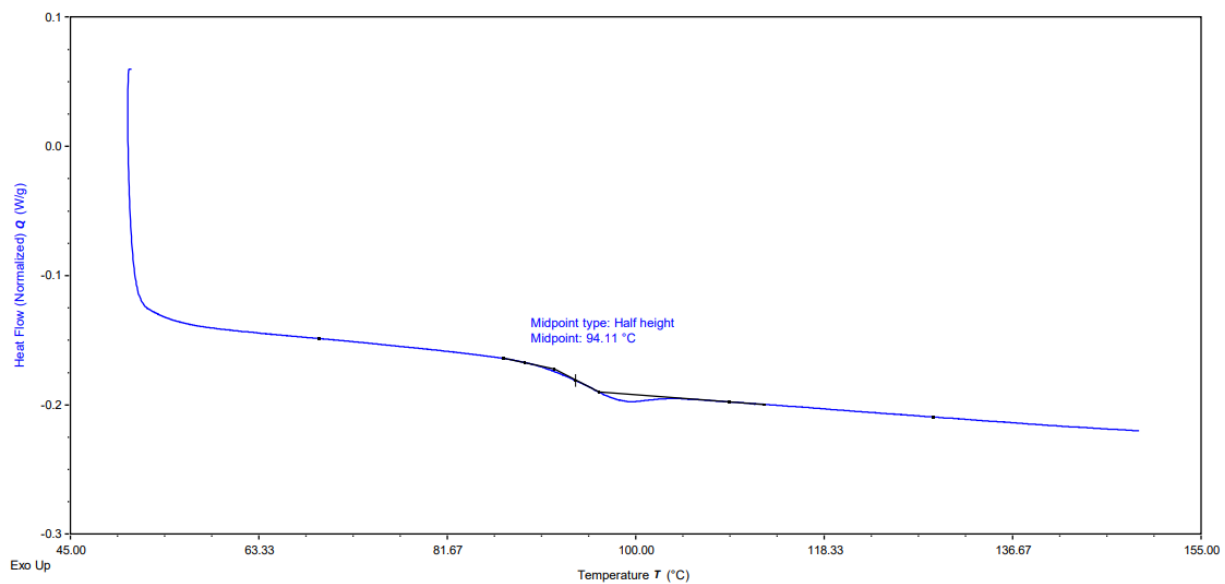


Figure S72. DSC trace of **Native EPS Foam** (6.0 mg), $T_g = 94.1$ °C.

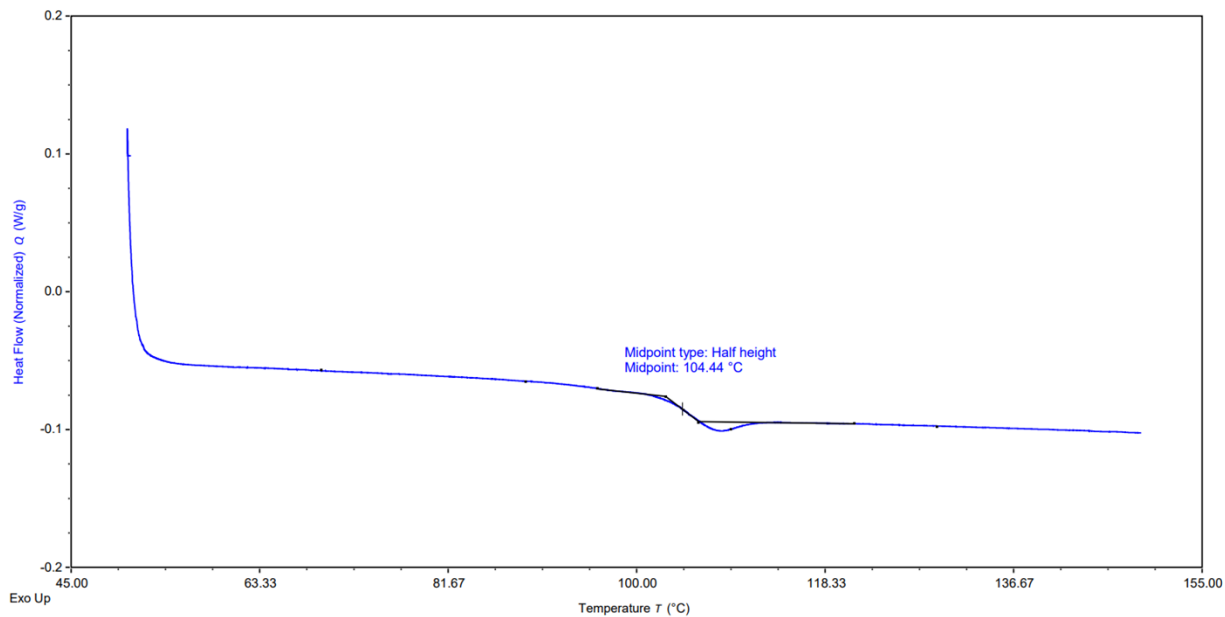


Figure S73. DSC trace of **Precipitated EPS Foam** (5.4 mg), $T_g = 104.4$ °C.

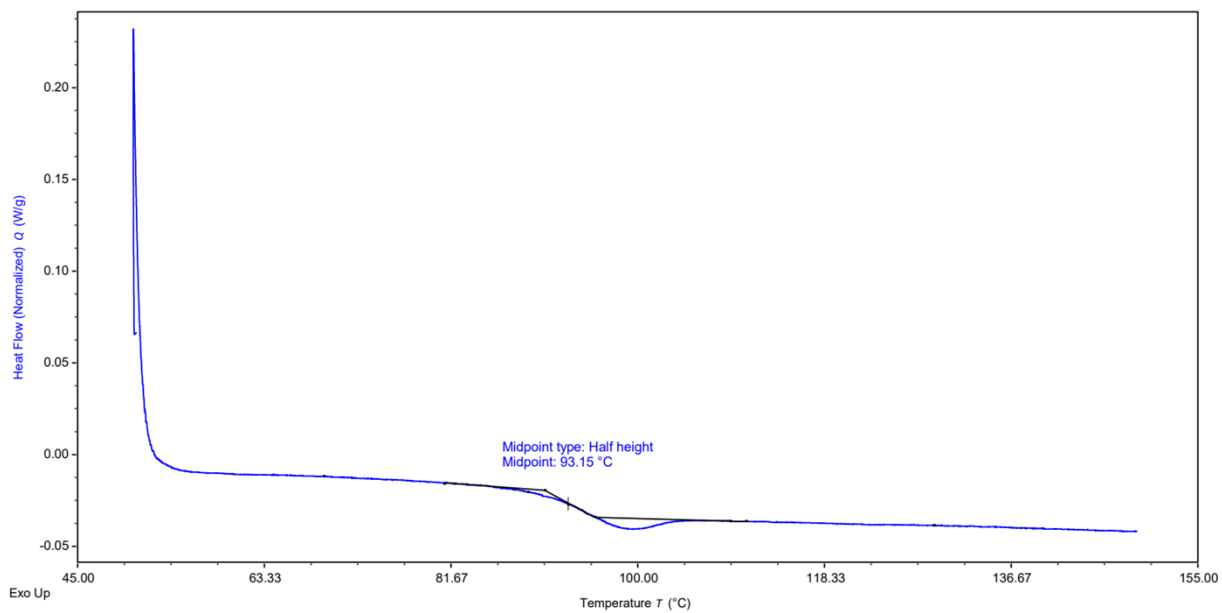


Figure S74. DSC trace of **Native PS Lid** (6.0 mg), $T_g = 93.2$ °C.

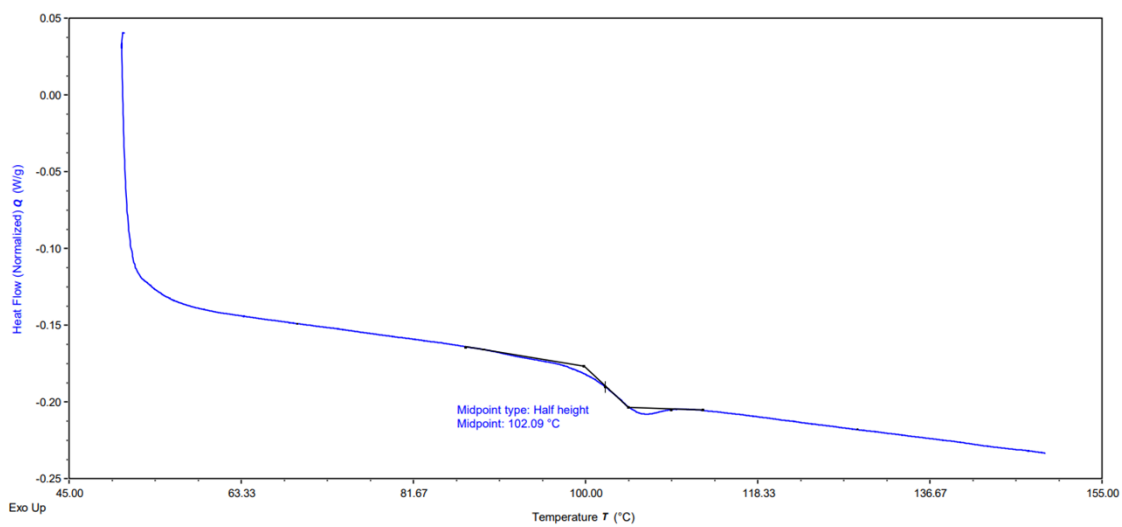


Figure S75. DSC trace of **Precipitated PS Lid** (5.2 mg), $T_g = 102.1$ °C.

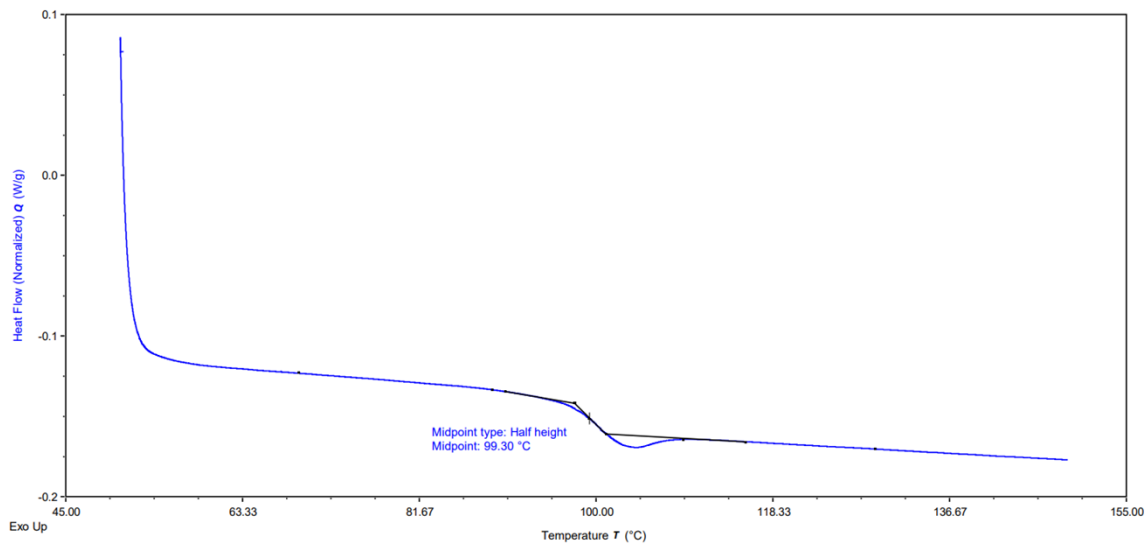


Figure S76. DSC trace of **Commercial PS** (14.5 mg), $T_g = 99.3$ °C.

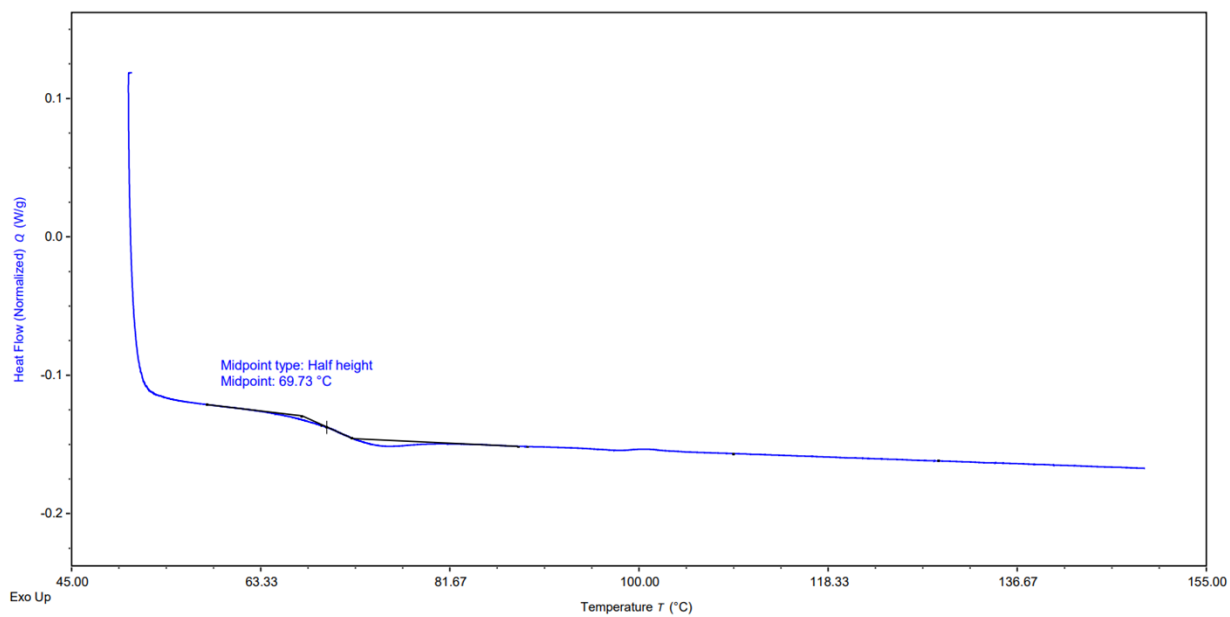


Figure S77. DSC trace of 26.0 kDa **PS** that was milled 4 h with 0.4 $\mu\text{L}/\text{mg}$ DCE and 12.4 μL TMSCF_3 (8.5 mg), $T_g = 69.7$ °C (See **Figure 3C**).

Example Analytical Calculations:

Functionalization density and yield via ^{19}F NMR spectroscopy

Percent functionalization of **BB** was determined by analyzing ^{19}F NMR spectra (**Figure S57**). The number of trifluoromethyl groups added to the substrate was found by integrating the fluorobenzene shift in the ^{19}F NMR spectrum to 81 μmol (1 equiv. fluorobenzene, 1F) (-112.96 ppm). Integrating the three peaks corresponding to trifluoromethylation of the aromatic unit (I_{CF_3}), summing, and dividing by 3 (to account for 3F) gives the total μmol of CF_3 functional groups added. The number of CF_3 groups added was then divided by the total μmol of **BB** added to the reaction multiplied by 2 to account for the 2 arenes, allowing for a direct functionalization comparison to **PS**. This was then multiplied by 100 to give the functionalization density per arene.

$$\mu\text{mol of CF}_3 = \frac{\sum I_{\text{CF}_3}}{3}$$

$$\% \text{ Functionalization of BB} = \frac{\mu\text{mol of CF}_3}{(\mu\text{mol BB} * 2)} * 100$$

Equation S1. Representative calculation for small molecule functionalization quantification via fluorobenzene internal standard for **TFM-BB**

For example, **TFM-BB** with 5.5 mol% functionalization:

$$\mu\text{mol of CF}_3 = \frac{(52.1 + 33.8 + 47.7)}{3} = 44.5 \mu\text{mol CF}_3$$

$$\% \text{ Functionalization of BB} = \frac{44.5 \mu\text{mol CF}_3}{(810 \mu\text{mol arene})} * 100 = 5.5 \text{ mol}\%$$

Small molecule yield was determined by analyzing the ^{19}F NMR spectrum (**Figure S57**). The number of trifluoromethyl groups added to the substrate was found by integrating the fluorobenzene shift in the ^{19}F NMR spectra to 81 μmol (1 equiv. fluorobenzene, 1F) (-112.96 ppm). Integrating the three peaks corresponding to trifluoromethylation of the aromatic unit, summing, and dividing by 3 gives the total μmol s of CF_3 functional groups added (see **Equation S1**). The number of CF_3 groups added was then divided by the total μmol of TMSCF_3 added to the reaction times 100 to give percent yield.

$$\text{Yield} = \frac{\mu\text{mol CF}_3}{\mu\text{mol TMSCF}_3} * 100$$

Equation S2. Representative calculation for small molecule yield via fluorobenzene internal standard for **TFM-BB**

For example, **TFM-BB** with 5.5 mol% functionalization:

$$\text{Yield} = \frac{44.5 \mu\text{mol } CF_3}{81 \mu\text{mol } TMSCF_3} * 100 = 55 \%$$

Percent functionalization of **TFM-PS** was determined by analyzing GPC-MALS-RI data and the ^{19}F NMR spectrum (**Figure S59A**). M_n was determined from GPC-MALS-RI in Astra (dn/dc = that of the initial polymer). The number of trifluoromethyl groups added to the polymer was found by integrating the chain-end peak in the ^{19}F NMR spectra to 1F (-73.4 ppm). Integrating the peak corresponding to trifluoromethylation of the aromatic repeat unit (I_{CF_3}) gives the total number of functional groups added per polymer chain. The number of CF_3 groups added was then divided by the total number of repeat units, based on the M_n , and multiplied by 100 to give the percent functionalization.

$$\% \text{ Functionalization } (m) = \frac{I_{CF_3}}{\text{number of arene units}} * 100$$

Equation S3. Representative calculation for functionalization quantification with chain-end analysis for **TFM-PS**

For example, for 9.3 kDa **TFM-PS**:

$$\% \text{ Functionalization } (m) = \frac{0.82 \text{ } CF_3}{89 \text{ arene units}} * 100 = 0.92 \text{ mol}\%$$

Percent functionalization of **TFM-PS** was determined by analyzing ^{19}F NMR spectra (**Figure S59B**). The number of trifluoromethyl groups added to the polymer was found by integrating the 4,4'-difluorobenzophenone shift in the ^{19}F NMR spectrum to the μmol added (ca. 0.62 μmol , 2F) (-105.65 ppm). Integrating the peak corresponding to trifluoromethylation of the aromatic repeat unit (I_{CF_3}) and multiplying by 2/3 to account for the different number of F nuclei, gives the total μmol of CF_3 groups added to the polymer in the sample. The number of CF_3 groups added was then divided by the total μmol of repeat units, based on the mass of the purified polymer in the NMR sample, and multiplied by 100 to give the percent functionalization.

$$\mu\text{mol of } CF_3 = I_{CF_3} \left(\frac{2}{3} \right)$$

$$\% \text{ Functionalization } (m) = \frac{\mu\text{mol of } CF_3}{\left(\frac{\text{mass}_{\text{polymer}}}{\text{MW repeat unit}} \right) * 1000} * 100$$

Equation S4. Representative calculation for functionalization quantification via 4,4'-difluorobenzophenone internal standard for **TFM-PS**

For example, for 9.3 kDa **TFM-PS** with $I_{IS} = 0.62 \mu\text{mol}$:

$$\mu\text{mol of } CF_3 = 1.92 \left(\frac{2}{3} \right) = 1.28 \mu\text{mol of } CF_3$$

$$\% \text{ Functionalization (m)} = \frac{1.28 \mu\text{mol of } CF_3}{\left(\frac{10.28 \text{ mg}}{104.15 \text{ g/mol}} \right) * 1000} * 100 = 1.3 \text{ mol}\%$$

Quantification of Additives Mass in Native PS Lid

To determine a conservative mass balance of **PS** and additives in the **Native PS Lid**, we carefully dissolved the **Native PS Lid** (3.3169 g) in ca. 50 mL of DCM. The solution was precipitated into 350 mL cold MeOH and filtered. The powder was washed with ca. 50 mL cold MeOH three times and subsequently dried under vacuum overnight at 60 °C. The supernatant was concentrated under reduced pressure and transferred into a tared vial with ca. 10 mL MeOH three times. After concentrating under reduced pressure, the sample was dried under high vacuum overnight.

Based on this result, we estimate the **Native PS Lid** contains ca. 1–2 wt% of additives (0.0294 g of MeOH soluble material from the supernatant) and ca. 98–99 wt% **PS** (3.1757 g).

We attempted to identify possible additives and/or plasticizers using ^1H NMR spectroscopy (**Figure S78**) and GCMS (**Figure S79**). The resulting analytical data from the supernatant sample were too complex to identify specific additives and/or plasticizers in the **Native PS Lid**.

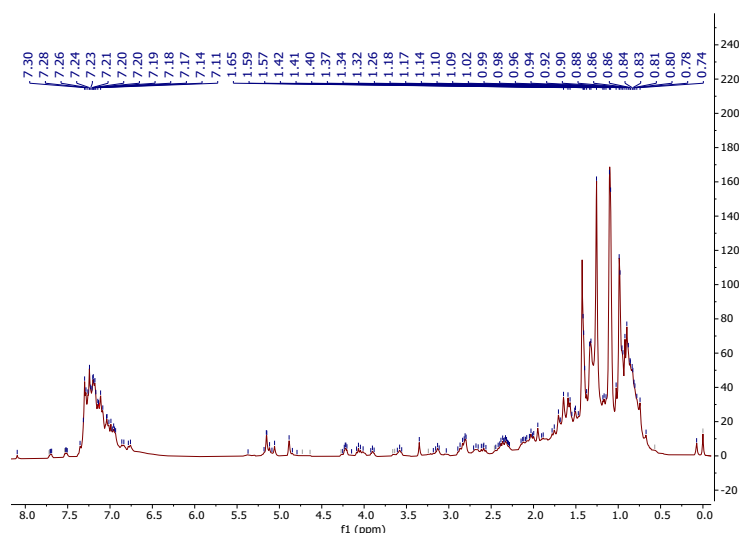


Figure S78. ^1H NMR spectrum of the MeOH soluble compounds (0.0294 g) in the supernatant from the precipitation of **Native PS Lid** (300 MHz, CDCl_3).

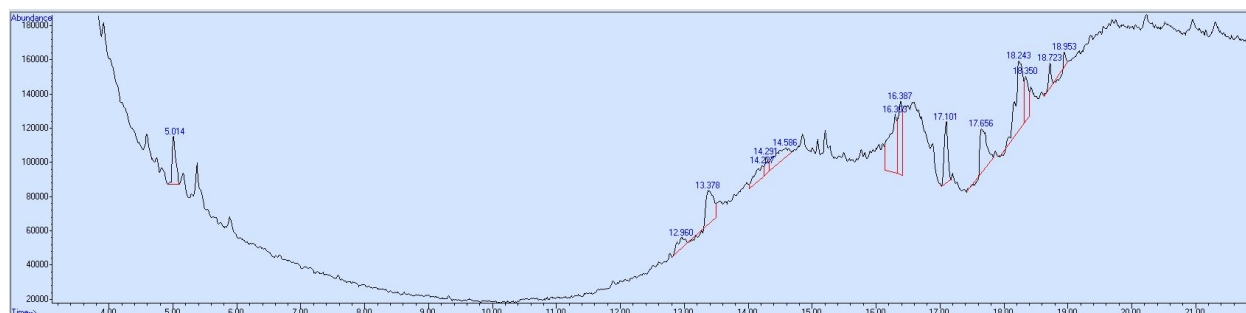


Figure S79. GCMS spectra of a crude reaction mixture containing the MeOH soluble compounds (0.0294 g) in the supernatant from the precipitation of **Native PS Lid**.

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