Supporting Information for "A Divergent Synthetic Route to Functional Copolymer Libraries via Modular Polymers"

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Materials and Characterization:

Benzylamine, n-hexylamine, triethylamine, tribasic potassium phosphate (K_3PO_4), carbon disulfide (CS_2), and 4,4'-difluorobenzophenone were purchased from Oakwood Chemical. Dichloromethane (DCM), 12.1N HCl, hexanes, acetone, tetrahydrofuran (THF), methanol (MeOH), and *N*,*N*-dimethylformamide (DMF) were purchased from Fisher Scientific. Dodecanethiol, 2-bromo-2-methylpropionic acid, azobisisobutyronitrile (AIBN), 1,4-dioxane, Thionyl chloride, and 1,3,5-trioxane were purchased from Sigma Aldrich. 2,3,4,5-Tetrafluorophenol was purchased from Synquest. Sodium 4-vinylbenzenesulfonate was purchased from Ambeed. Acryloyl chloride was purchased from Alfa Aesar. Furfurylamine was purchased from Aldrich Chemical. Allylamine was purchased from Acros Organics. Deuterated solvents were purchased from Cambridge Isotope Labs. SnakeSkin™ dialysis tubing (16mm I.D., 3.5 kDa MWCO) was purchased from ThermoFisher. AIBN was recrystallized from MeOH prior to use. SnakeSkin™ dialysis tubing was soaked in DI H_2O for 15 minutes prior to use. All other chemicals were used as received.

^{1}H NMR spectra were acquired on an Agilent MR4 400 MHz or Neo 600 MHz (equipped with Prodigy Cryoprobe) spectrometer. Chemical shifts in the ^{1}H NMR spectra were referenced to the residual solvent resonance signals. ^{13}C NMR spectra were acquired on an Agilent MR4 400 MHz spectrometer. ^{19}F NMR spectra were acquired on a 400 MHz JEOL system.

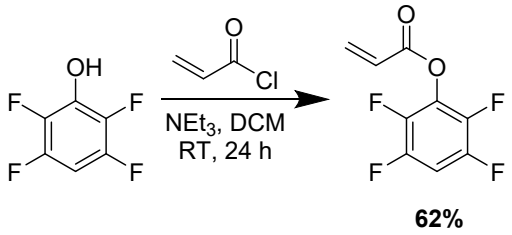
Quantitative ^{19}F NMR (QFNMR) was performed by taking a 50 µL aliquot of reaction solution and adding it to an NMR tube with DMSO-d_6 or acetone-d_6 and 4,4'-difluorobenzophenone as an internal standard. The samples were run in the spectrometer using 256 scans and a 3s relaxation delay. Spectra were analyzed using MestReNova by applying an automatic phase correction, ablative baseline (5 points, 10 passes), and line broadening (2 Hz

exponential). The 4,4'-difluorobenzophenone peak at -106 ppm was always integrated to 1.00 while the polymeric peaks (-139 ppm, -153 ppm) and phenoxide leaving group peaks (~-144 ppm, ~-164ppm) were integrated. The conversion was calculated by dividing the average integration of the leaving group peaks by the sum of the average integration of leaving group plus polymer peaks. The error in conversion was calculated by propagating the standard deviation between the two sets of fluorines (ortho and meta to the oxygen) through the conversion calculation. Conversion data for each step is tabulated in the corresponding synthesis sections.

Size exclusion chromatography (SEC-MALS) was performed using a mobile phase consisting of N,N-dimethylacetamide (DMAc) with 50 mM LiCl at a rate of 1.0 mL/min at 40 °C on two Agilent Technologies PLgel 10 μm MIXED-B LS 300 x 7.5 mm columns connected in series with Wyatt Technologies TRIOS II light scattering and Optilab T-REX differential refractive index (dRI) detectors. While DMAc is somewhat nucleophilic and therefore could displace reactive TFP groups during analysis, we see agreement in molecular weight between SEC-MALS and NMR end-group analysis done in non-nucleophilic solvents, suggesting that such displacement did not occur to a significant extent. Data analysis was performed using Astra version 7.2.2.10 software (Wyatt Technologies). The dn/dc value of poly(tetrafluorophenylacrylate) in DMAc was measured as 0.0477. The dn/dc value of poly(tetrafluorophenyl styrene sulfonate) in DMAc was measured as 0.0623.

Synthetic Methods

Synthesis of 2,3,5,6-tetrafluorophenyl acrylate (TFPA):



62%

2,3,5,6-Tetrafluorophenol (40.6302g, 244.7 mmol, 1.0 equiv.) was placed in a 250-mL 3-neck round bottom flask that was fitted with a magnetic stir bar and attached to an addition funnel via the central neck. The tetrafluorophenol was then dissolved in approximately 50 mL of DCM and placed under a N_2 atmosphere. Triethylamine (50 mL, 358.5 mmol, 1.46 equiv.) was added by syringe in one portion via one of the side necks and the solution was stirred in an ice bath for 20 minutes. Acryloyl chloride (21.5 mL, 265.8 mmol, 1.09 equiv.) was added dropwise through the addition funnel over the course of approximately 30 minutes and the reaction was stirred at room temperature overnight. The crude reaction was filtered into a separatory funnel and washed with three, 50 mL portions of 3M HCl and three, 50 mL portions of saturated sodium chloride solution. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed by a rotary evaporator. The crude product was then purified by automated flash column chromatography using silica gel and a hexanes/acetone gradient and dried *in vacuo* to isolate the product as a colorless oil (33.4 g, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.0 (m, 1H), 6.7 (dd, 1H), 6.4 (dd, 1H), 6.1 (dd, 1H)

^{19}F NMR (375 MHz, $CDCl_3$, δ): -139, -153

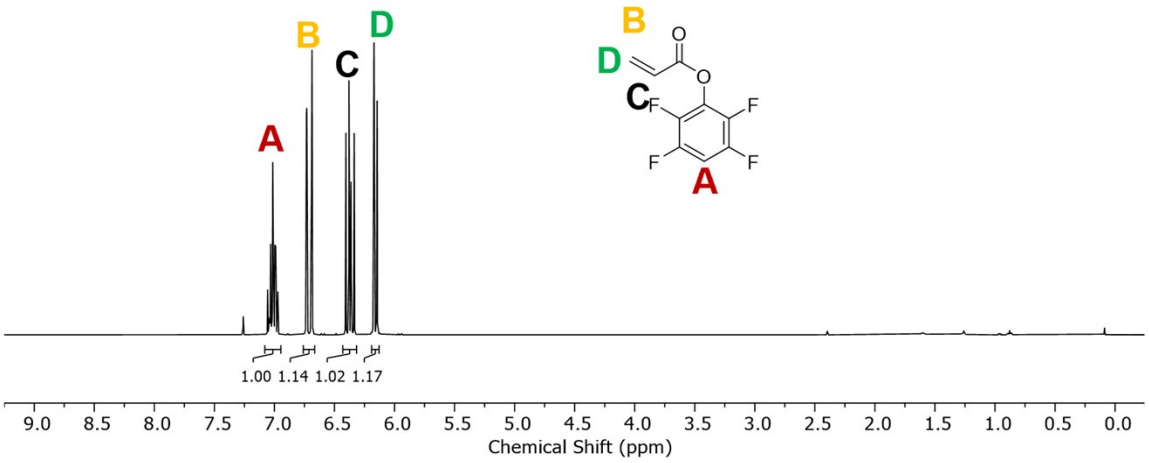


Figure S1. *^{1}H NMR (400 MHz) spectrum of tetrafluorophenyl acrylate (TFPA) in $CDCl_3$.*

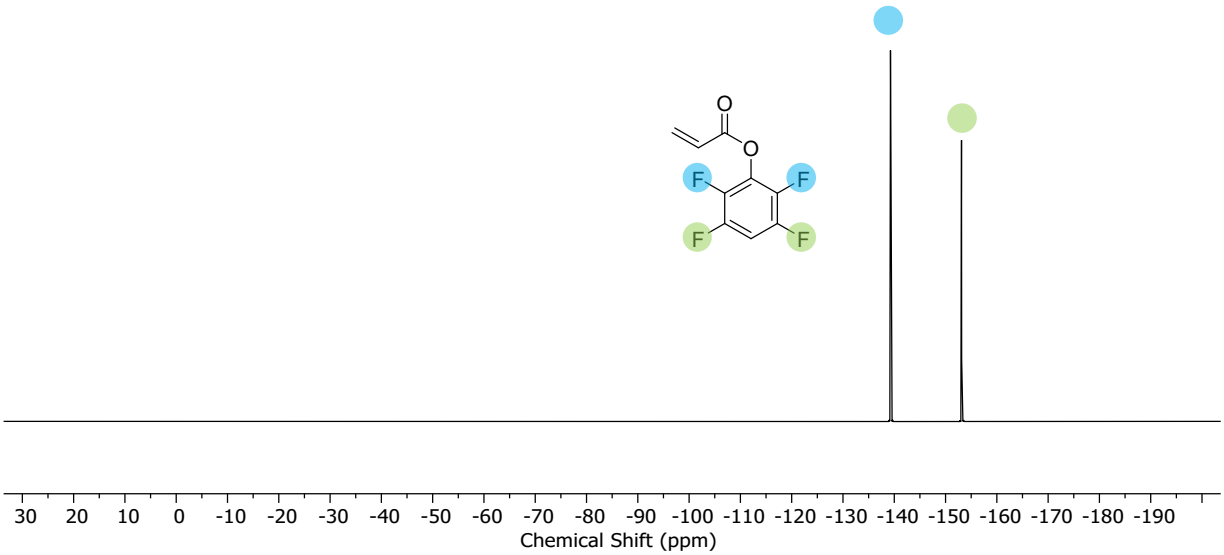
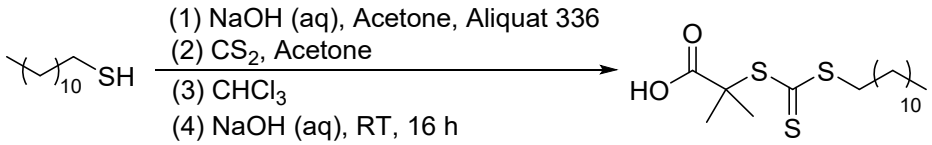


Figure S2. *^{19}F NMR (375 MHz) spectrum of tetrafluorophenyl acrylate (TFPA) in $CDCl_3$.*

Synthesis of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT):



Caution! Carbon disulfide (CS_2) should be handled in a fume hood because it is highly volatile, flammable, and toxic. After CS_2 addition, all subsequent reagents were added in one portion to minimize exposure.

DDMAT was prepared as previously reported.[28] Dodecanethiol (49 mL, 0.2 mol) , Aliquat 336 (3.26 g), and 125 mL acetone were combined in a 3-neck 1L round bottom, cooled on an ice bath, and sparged with N_2. Using an addition funnel, NaOH (8.4 g) in 15 mL water was added dropwise, producing a white solid precipitate immediately. After 15 min of stirring, a solution of carbon disulfide (12 mL) in 26 mL acetone was added dropwise to the reaction. During this dropwise addition, the white solid gradually dissolved and the solution became orange. Once all the solid precipitants had dissolved, 25 mL chloroform was added to the reaction in one portion, followed by a dropwise addition of NaOH (40 g) in 40 mL water. The sparging and ice bath were removed, and the solution was stirred overnight at room temperature. After 24 h a thick layer of orange-yellow precipitate formed. The reaction was diluted with 300 mL water, then concentrated HCl (50 mL) was added. The solution was stirred at room temperature for several minutes and the solid residue was broken up with a spatula. The solid was collected via vacuum filtration, then stirred overnight in 700 mL isopropanol. The remaining aqueous-organic filtrate which contained dark red oil was evaporated and the resulting orange precipitate was collected by filtration and added to the stirring isopropanol solution.

Once the solution had a uniform yellow-orange appearance (i.e., no solid, dark orange pieces visibly stirring in the solution), the solution was filtered to remove a light-yellow solid. The

organic layer was concentrated with rotary evaporation to yield a dark red oil that immediately began to crystallize. The dark red solid was recrystallized using hot hexanes. Without cooling, the recrystallization solution was quickly filtered to remove a white solid, then stored overnight at –20 °C to induce crystallization of orange crystals. These crystals were recrystallized a second time with hot hexanes to yield pure product as bright yellow crystals (17.60 g, 24% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.3 (t, 2H), 1.7 (m, 8H), 1.4 (m, 2H), 1.3 (s, 16H), 0.9 (t, 3H)

^{13}C NMR (100 MHz, $CDCl_3$, δ): 220.7, 179.4, 55.6, 37.2, 32.0, 29.7, 29.6, 29.5, 29.4, 29.1, 29.0, 27.8, 25.3, 22.7, 14.1

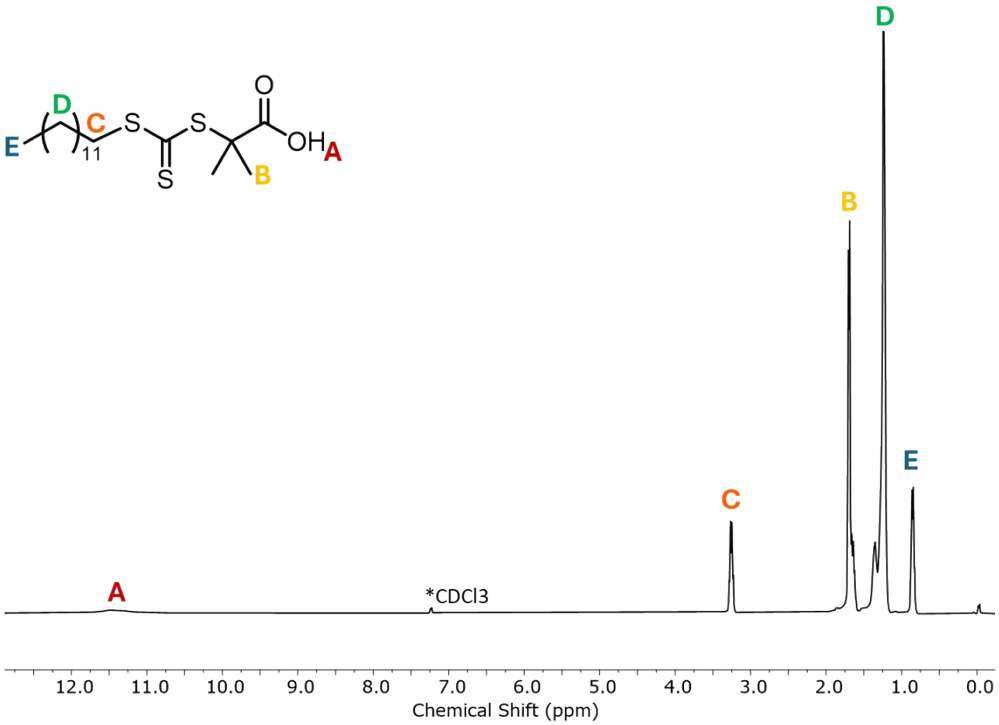


Figure S3. *^{1}H NMR (400 MHz) spectrum of DDMAT in $CDCl_3$.*

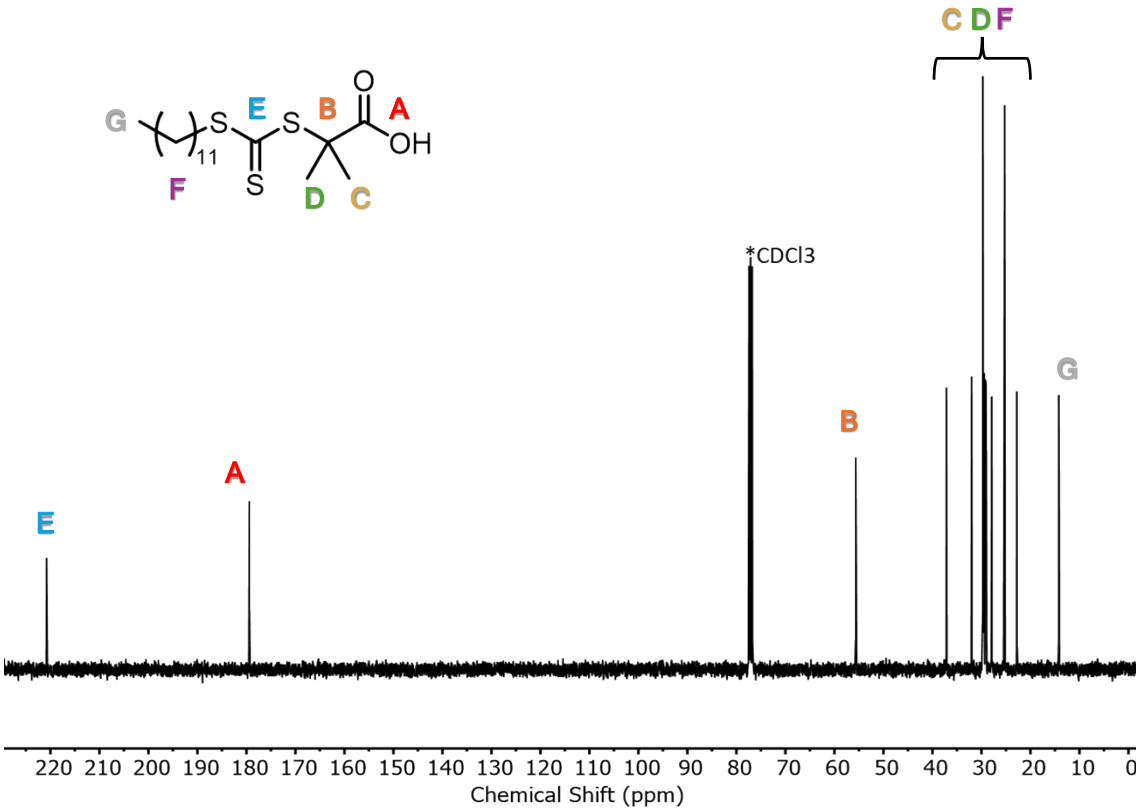
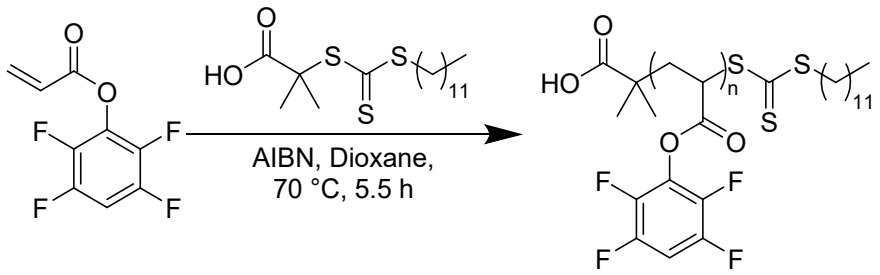


Figure S4. *^{13}C NMR (100 MHz) spectrum of DDMAT in $CDCl_3$.*

RAFT Polymerization of TFPA:



DDMAT (0 1325g, 0.363 mmol, 1 equiv.), TFPA (10.0g, 45.4 mmol, 125 equiv.), and AIBN (5.9 mg, 0.036 mmol, 0.1 equiv.) were combined in a glass vial with 7 mL of 1,4-dioxane. A small crystal of 1,3,5-trioxane was added as an internal NMR standard and an initial NMR aliquot was taken. The vial was sealed, then sparged with N_2 for 30 minutes before being added to a heating block equilibrated at 70 °C and allowed to react for 5.5 hours. The viscous reaction solution was then exposed to air and a crude NMR sample was taken. ^1H NMR of the crude sample

indicated a 97% conversion. The solvent was removed *in vacuo,* then the sample was redissolved in THF (~7 mL) and precipitated into chilled methanol (~200 mL). The precipitate was filtered then the polymer re-precipitated twice more before being dried at room temperature on a Schlenk line vacuum overnight. ^{1}H NMR spectrometric end group analysis and size exclusion chromatography (SEC) were used to characterize the polymer molecular weight (**Figure S5.–S7**).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.9 (br s), 3.2 (br s), 2.6-1.9 (br m), 0.9 (t, 3H); M_n = 22.9 kDa (end-group analysis)

^{19}F NMR (375 MHz, $CDCl_3$, δ): -139 (br s), -153 (br s).

SEC (MALS, DMAc w/ 50 mM LiCl, *dn/dc*=0.0477 mL/g): M_n = 24.3 kDa, $Đ$ = 1.58

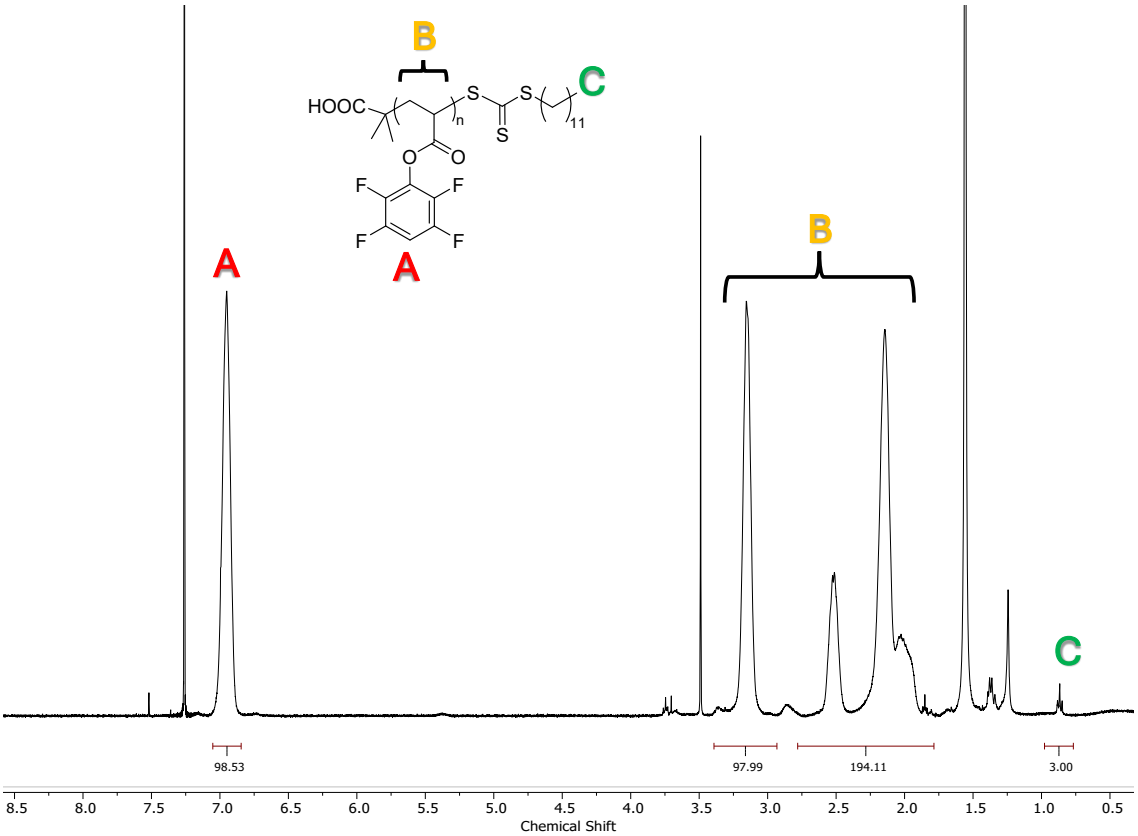


Figure S5. *^{1}H NMR (400 MHz) spectrum of PTFPA in $CDCl_3$.*

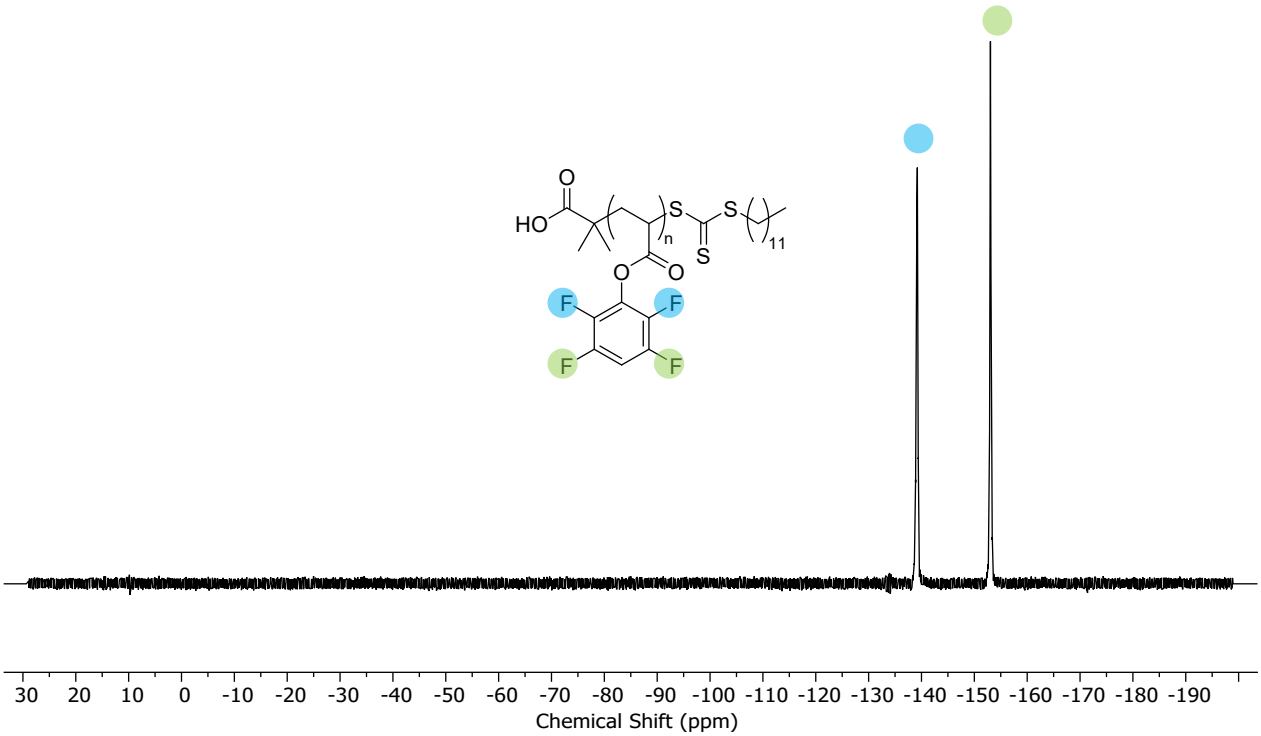


Figure S6. *^{19}F NMR (375 MHz) spectrum of PTFPA in $CDCl_3$.*

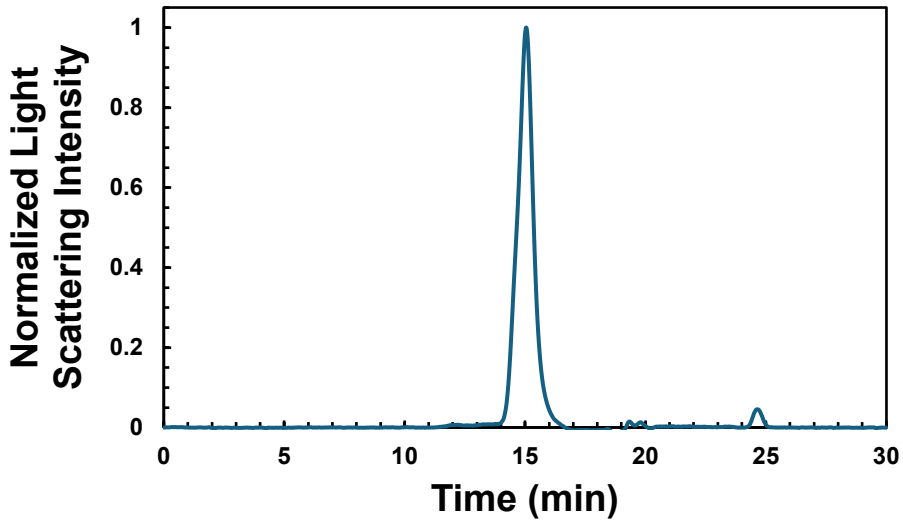


Figure S7. *SEC light scattering trace of PTPFA in DMAc with 50 mM LiCl.*

Representative Post-Polymerization Modification Procedure (50:50 poly(benzylacrylamide-co-hexylacrylamide) copolymer:

PTFPA (0.0506g, 0.23 mmol, 1.0 equiv.) was placed in a 6-dram glass vial with a magnetic stir bar and dissolved in 1 mL of EtOAc. Triethylamine (16 µL, 0.11 mmol, 0.5 equiv.) was added followed by benzylamine (12 µL, 0.11 mmol, 0.5 equiv.). The reaction was added to a heating block pre-heated to 60 °C and stirred for 2 hours. The vial was removed from heat and a 50 µL aliquot was taken for ^{19}F NMR analysis. Additional triethylamine (16 µL, 0.11 mmol, 0.5 equiv.) and hexylamine (15 µL, 0.11 mmol, 0.5 equiv.) were added to the reaction solution and it was stirred at 60 °C for an additional 2 hours. A second 50 µL aliquot was taken for ^{19}F NMR. The solvent was removed *in vacuo* and the sample was redissolved in DMF before being placed in a dialysis bag and dialyzed against DMF for 3 days. ^{19}F NMR confirmed full removal of the tetrafluorophenoxide leaving group while ^{1}H NMR was used to characterize the final polymer structure.

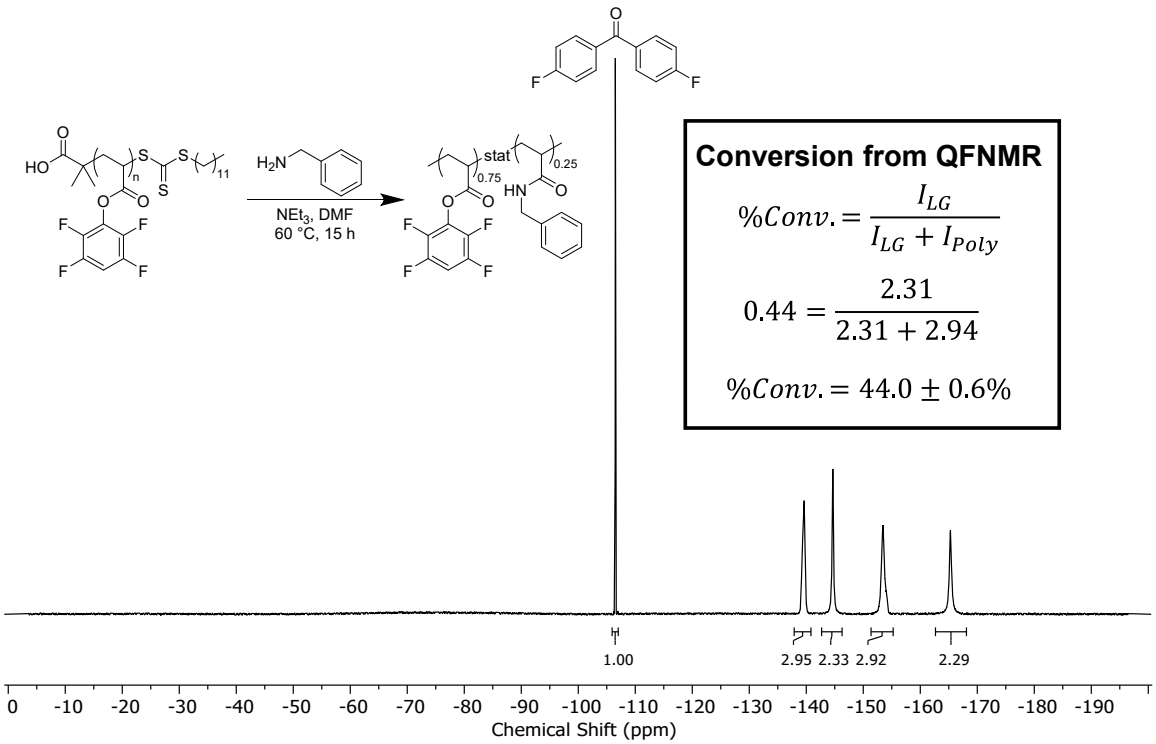


Figure S8. *Functionalization of PTFPA with 0.25 equiv. of benzylamine in DMF and characterization by quantitative ^{19}F NMR (375 MHz, DMSO-d_6) with an internal standard.*

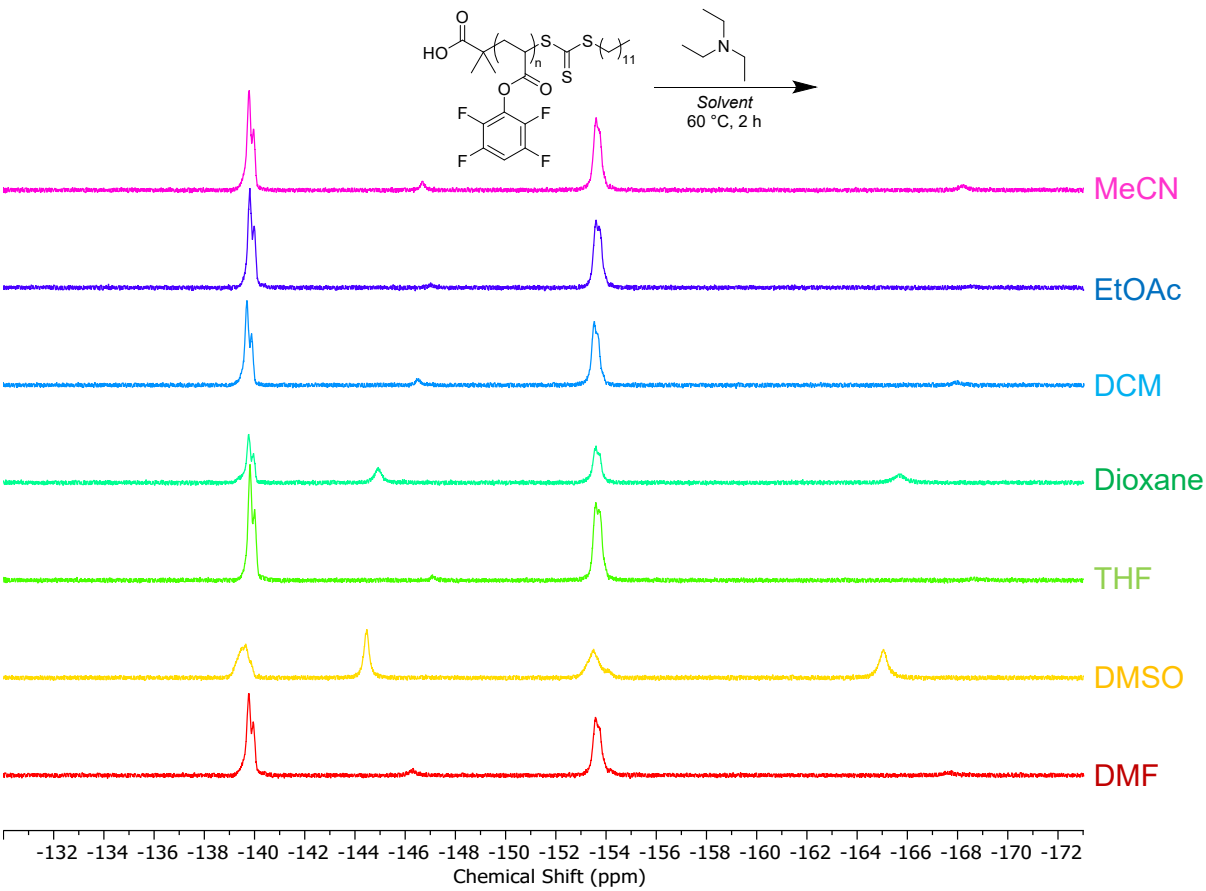


Figure S9. *^{19}F NMR (375 MHz, DMSO-d_6) solvent screen of PTFPA in the presence of triethylamine and various solvents. NMR measurements were taken after a reaction period of two hours at 60 °C.*

Table S1. *Conversion calculated from QFNMR solvent screen of PTFPA in the presence of triethylamine and various solvents.*

Solvent	$I_{Poly\ 1}$ (-139 ppm)	$I_{LG\ 1}$ (-144 ppm)	$I_{Poly\ 2}$ (-153 ppm)	$I_{LG\ 2}$ (-164 ppm)	Approximate Conversion (%)
MeCN	5.52	0.48	5.42	0.42	7.6
EtOAc	5.7	0	5.48	0	0
DCM	4.6	0.38	4.49	0.37	7.62
Dioxane	3.76	1.54	3.66	1.36	28
THF	7.06	0.27	6.8	0.29	3.9
DMSO	3.88	3.2	3.74	2.91	44
DMF	5.88	0.60	5.67	0.54	9.0

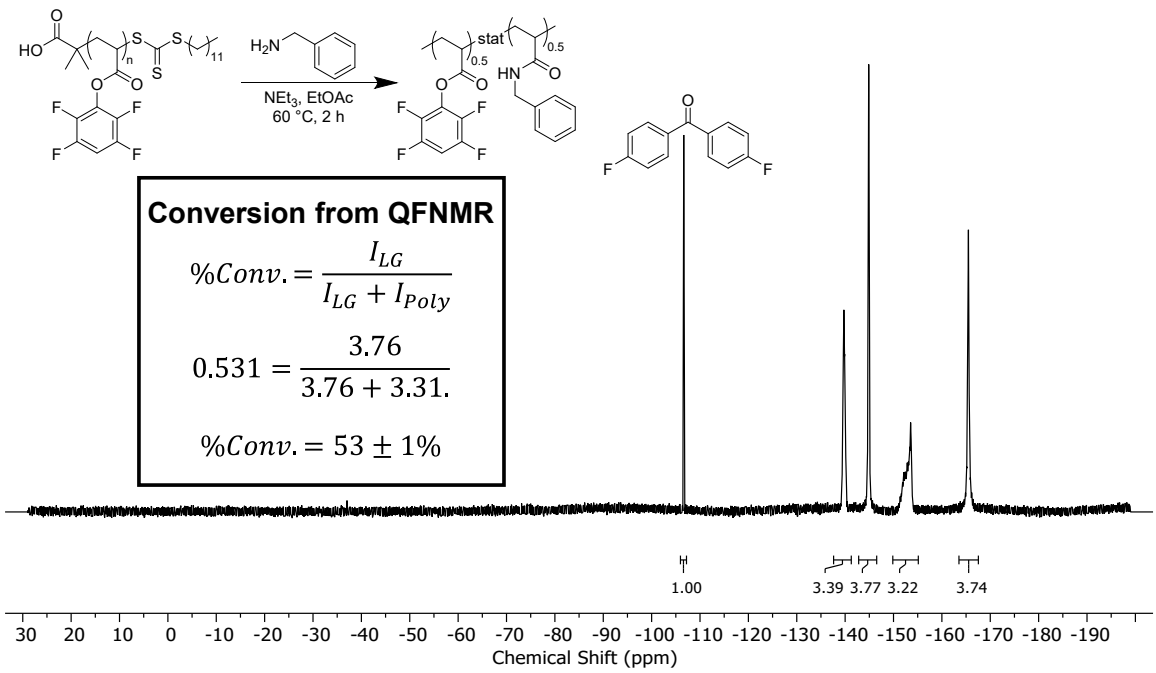
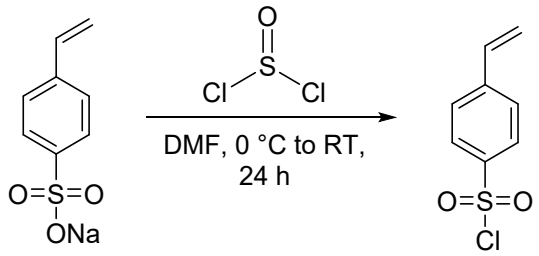


Figure S10. *Functionalization of PTFPA with 0.5 equivalents benzylamine in EtOAc and characterization by quantitative ^{19}F NMR (375 MHz, DMSO-d_6) with an internal standard.*

Synthesis of p-Styrenesulfonyl chloride:



84%

Sodium 4-vinylbenzenesulfonate (25 g, 121.2 mmol, 1 equiv.) was dried in an oven overnight in a round bottom flask and cooled under N_2 gas. To the round bottom flask, 80 mL of DMF was added and the suspension was stirred for 30 min under N_2 in an ice bath. Thionyl chloride (35 mL,294 mmol, 4 equiv.) was added in three portions via syringe over 10 min. The reaction was kept on ice for 3 h before it was left overnight and allowed to warm to room temperature. The reaction solution was poured slowly into 300 mL of iced DI water while stirring

to quench the excess thionyl chloride. This solution was stirred for five minutes before transferring to a separatory funnel and extracting with diethyl ether (3 x 80 mL). The organic layer was dried with magnesium sulfate, filtered, and concentrated on the rotary evaporator. The product was isolated as a light-yellow liquid and used immediately without further purification. If not used immediately, the sulfonyl chloride intermediate was stored at –20 °C until use.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.9 (d, 2H), 7.6 (d, 2H), 6.7 (dd, 2H), 5.9 (d, 1H), 5.5 (d, 1H)

^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.4, 142.8, 134.8, 127.4, 127.16, 119.4

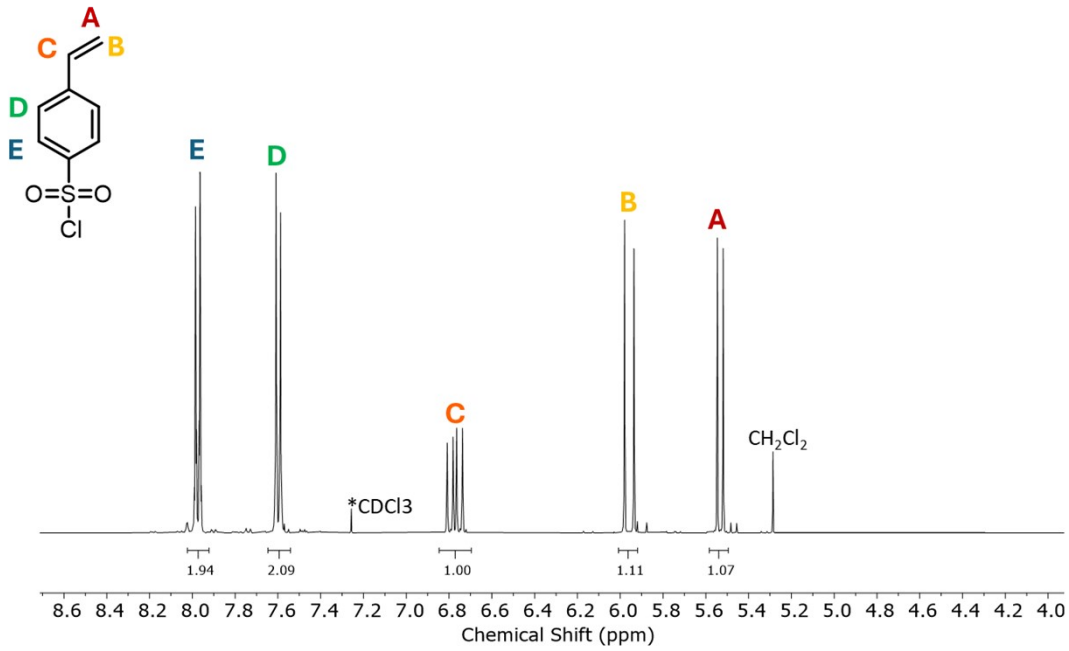


Figure S11. *^{1}H NMR (400 MHz) spectrum of tetrafluorophenyl styrene sulfonate (TFPSS) in $CDCl_3$.*

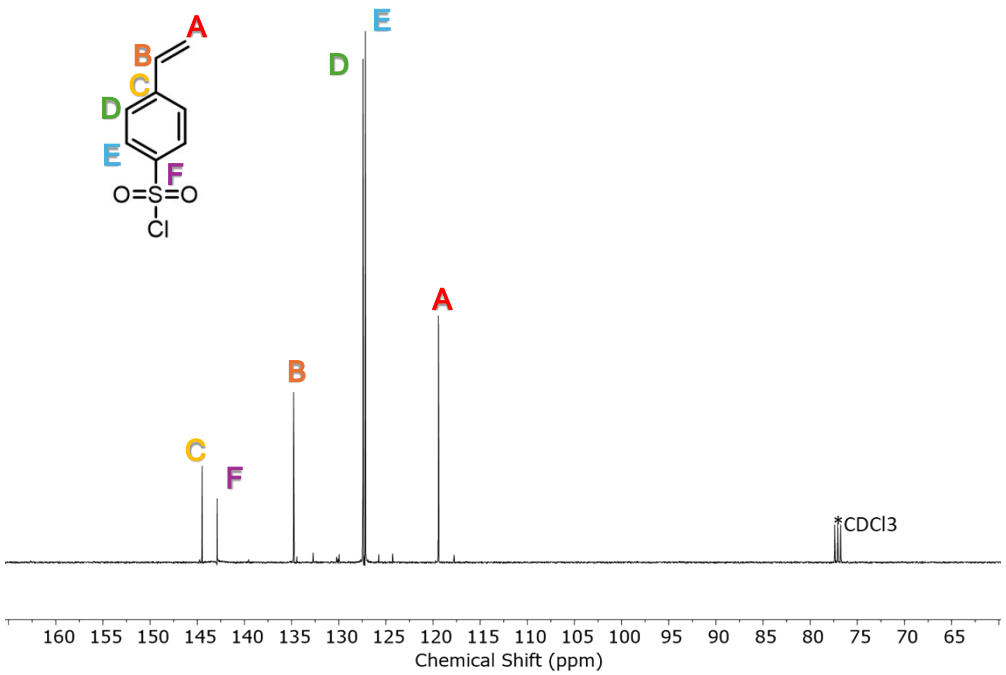
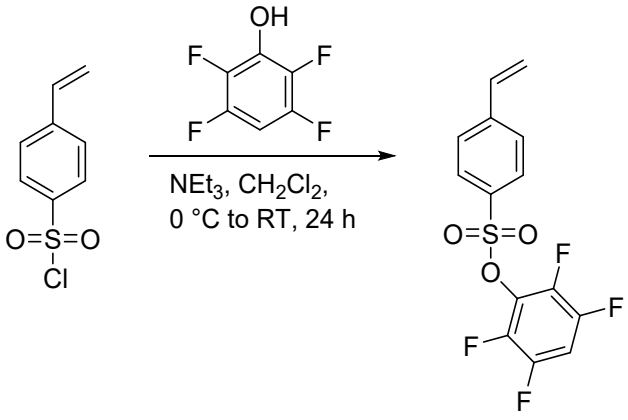


Figure S12. *^{13}C NMR (100 MHz) spectrum of tetrafluorophenyl styrene sulfonate (TFPSS) in $CDCl_3$.*

Synthesis of 2,3,5,6-tetrafluorophenyl styrene sulfonate (TFPSS):



74%

Tetrafluorophenol (19.45 g, 117.1 mmol, 1.2 equiv.) was dissolved in 325 mL of dichloromethane and stirred in an ice bath for 15 min before adding triethylamine (27 mL, 266 mmol, 2 equiv.) and stirring another 15 min. p-Styrenesulfonyl chloride (19.7 g, 97.2 mmol, 1 equiv.) was dissolved in 25 mL of dichloromethane and added dropwise via an addition funnel

over 30 min. The reaction was kept on ice and slowly warmed to room temperature overnight. After 24 h, the reaction was washed with 3 M hydrochloric acid solution, saturated sodium bicarbonate solution, and water. The organic layer was dried with magnesium sulfate and filtered before concentrating on the rotary evaporator. The crude product was purified via flash column chromatography using a 30:70–60:40 hexane:DCM gradient. The final product was dried overnight on the vacuum line and isolated as a white crystalline solid (27.8 g, 74%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.9 (d, 2H), 7.6 (d, 2H), 7.06 (m, 1H), 6.8 (dd, 1H), 5.9 (d, 1H), 5.5 (d, 1H)

^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.2, 135.0, 133.4, 128.9, 127.0, 119.0, 104.7, 104.5, 104.4

^{19}F NMR (375 MHz, $CDCl_3$, δ): -137, -150

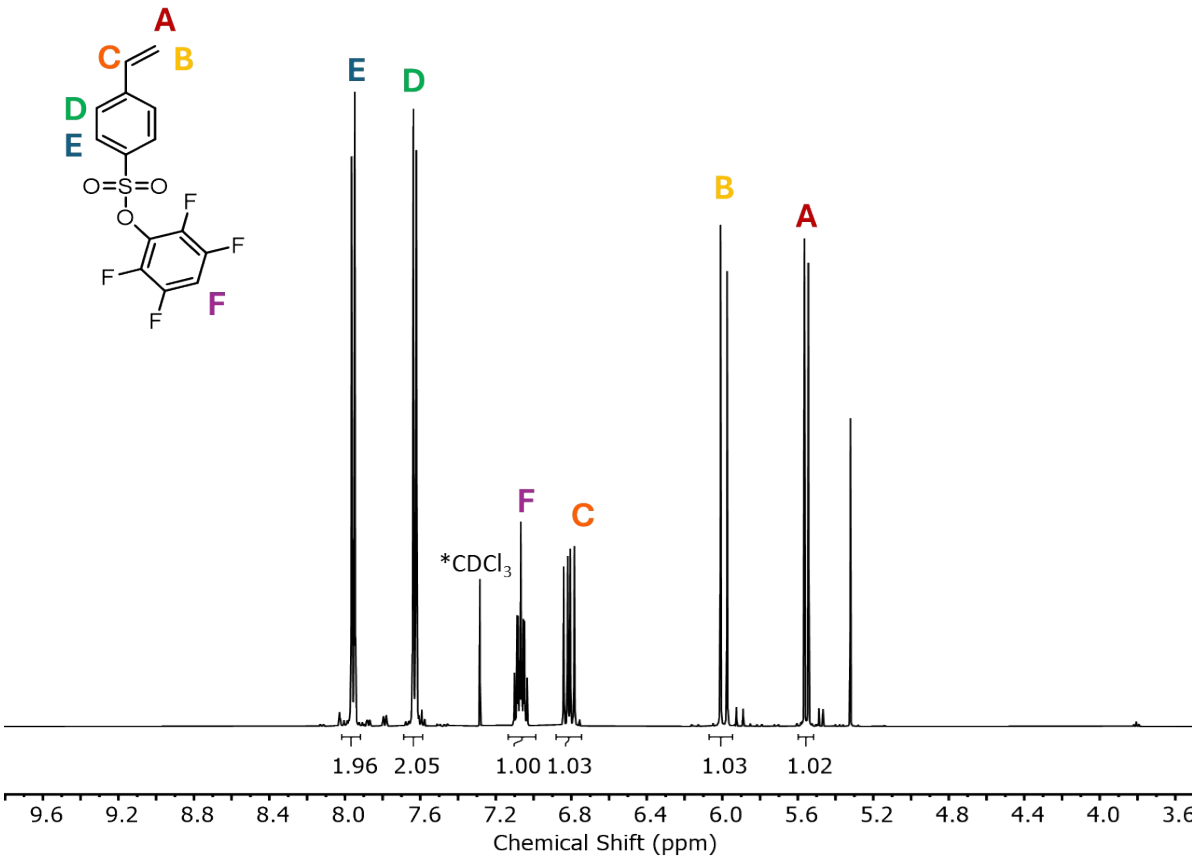


Figure S13. *[1]H NMR (400 MHz) spectrum of tetrafluorophenyl styrene sulfonate (TFPSS) in $CDCl_3$.*

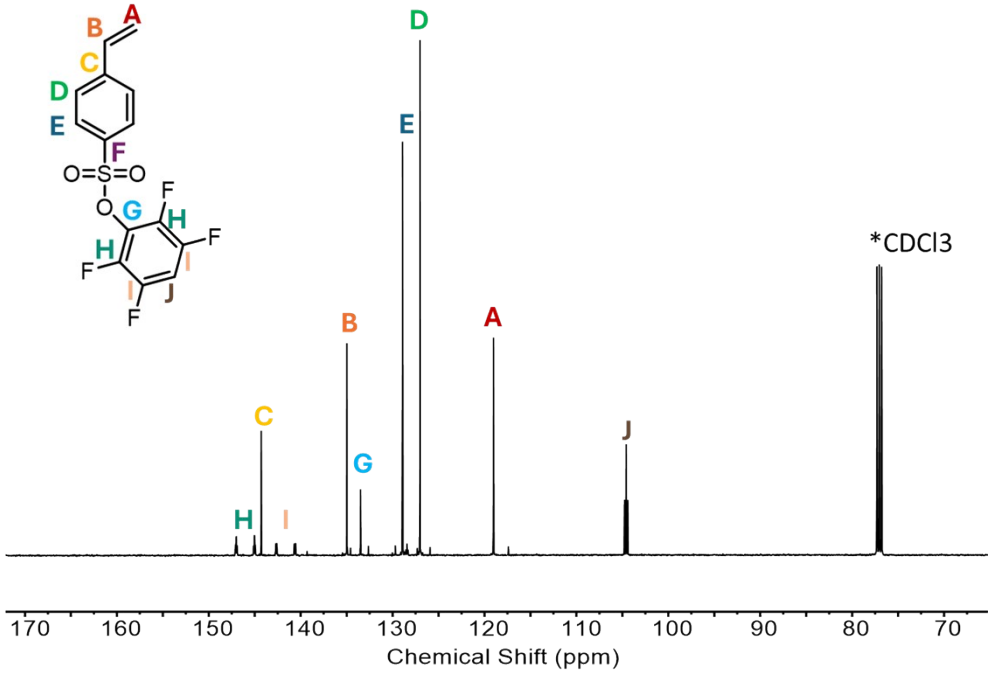


Figure S14. *[13]C NMR (100 MHz) spectrum of tetrafluorophenyl styrene sulfonate (TFPSS) in $CDCl_3$.*

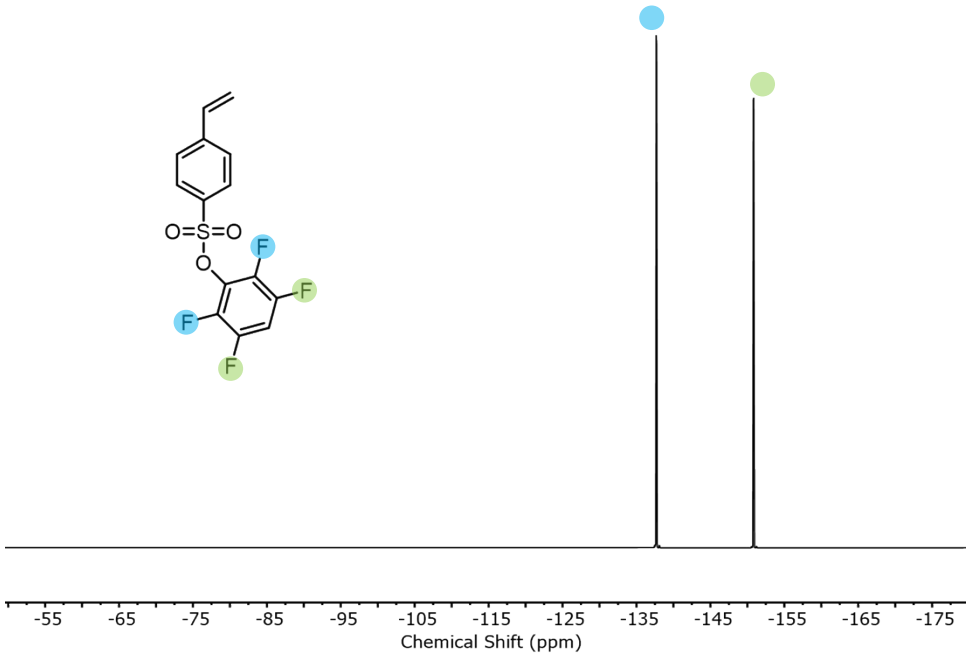
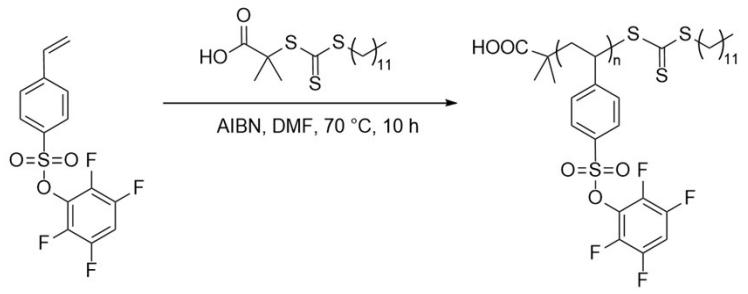


Figure S15. *[19]F NMR (375 MHz) spectrum of tetrafluorophenyl styrene sulfonate (TFPSS) in $CDCl_3$.*

RAFT polymerization of TFPSS:



Tetrafluorophenyl styrene sulfonate (TFPSS, 10 g, 100 eq.), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (164 mg, 1 eq), and azobisisobutyrnitrile (AIBN) (5.93 mg, 0.1 eq) were dissolved in dimethylformamide (20 mL, ~2 M). 1,3,5-trioxane (~70 mg) was dissolved in the solution as an internal standard. The vial was sealed, then sparged with N_2 for 30 minutes before being added to an oil bath equilibrated at 70 °C and allowed to react for 6 hours. The viscous reaction solution was then exposed to air and ^{1}H NMR of the crude sample indicated a 97% conversion. The reaction solution was diluted with THF (~10 mL) and precipitated into methanol (~300 mL). The precipitate was filtered then the polymer re-precipitated twice more before being dried at room temperature on a Schlenk line vacuum overnight. ^{1}H NMR end group analysis and size exclusion chromatography (SEC) were used to characterize the polymer molecular weight (**Figure S16.–S18.**).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.0 (br s), 7.6 (br s), 6.6-7.4 (br s), 1.6 (br s), 0.8 (t, 3H); M_n = 22.9 kDa (end-group analysis)

^{19}F NMR (375 MHz, $CDCl_3$, δ): -137 (br), -152 (br)

SEC (MALS, DMAc w/ 50 mM LiCl, *dn/dc*=0.0623 mL/g): M_n = 33 kDa, $Đ$ = 1.40

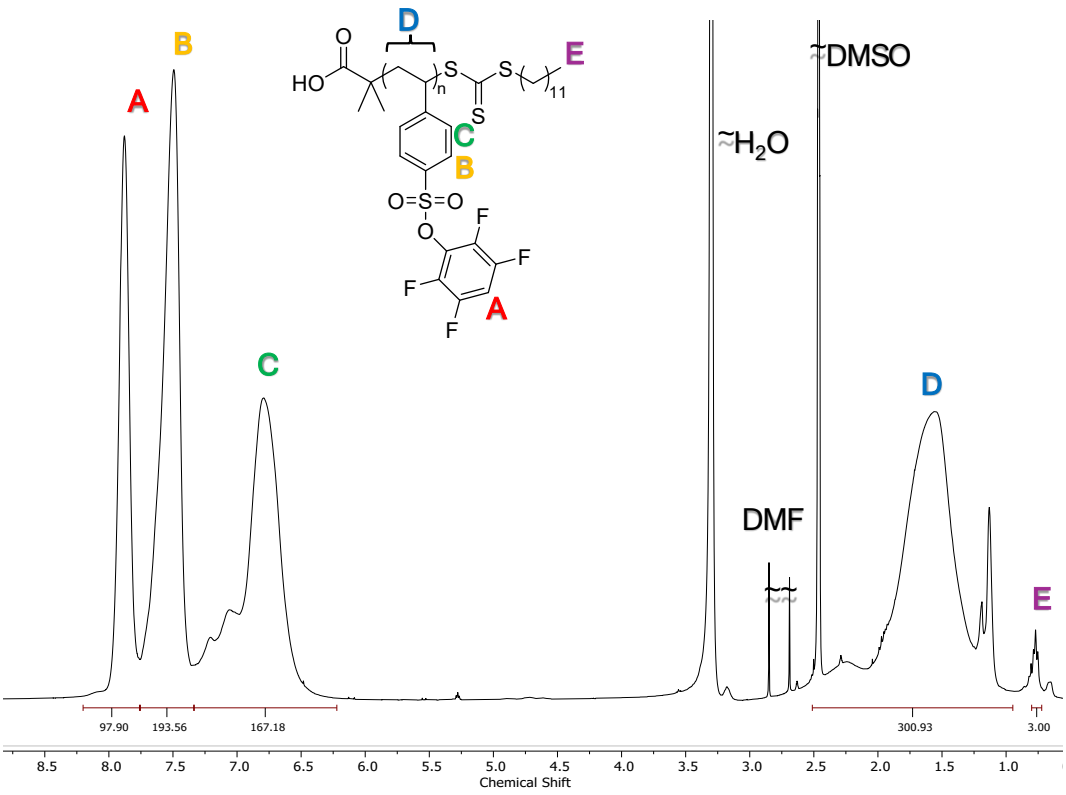


Figure S16. *^{1}H NMR (400 MHz) spectrum of PTFPSS in DMSO-d_6*

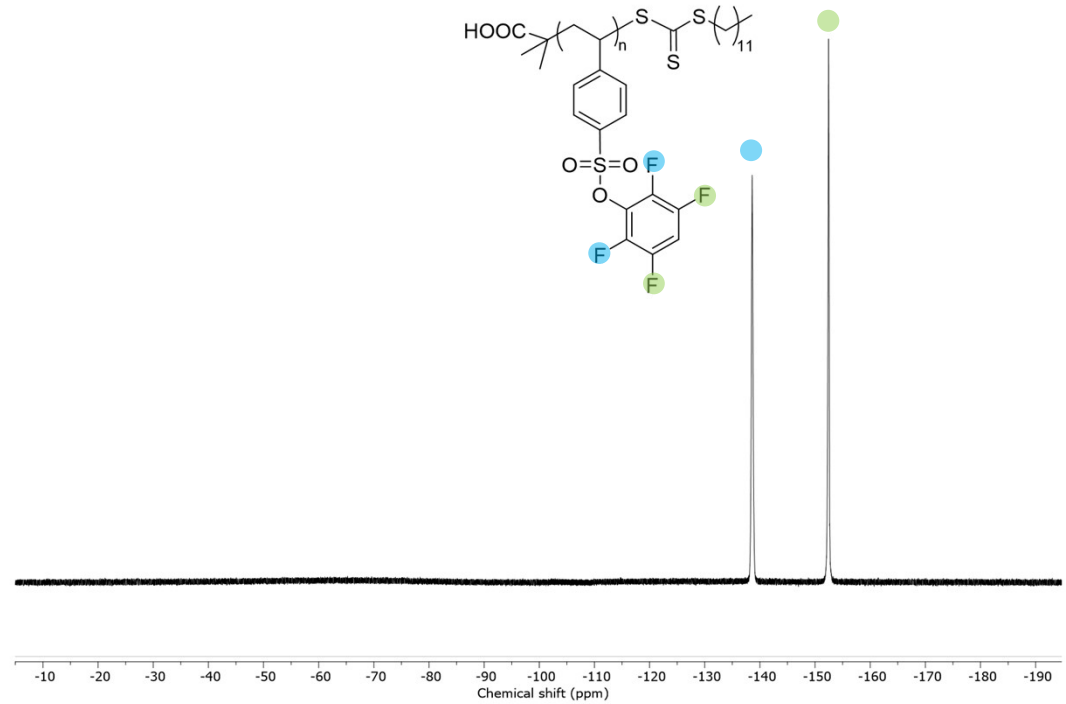


Figure S17. *^{19}F NMR (375 MHz) spectrum of PTFPSS in DMSO-d_6.*

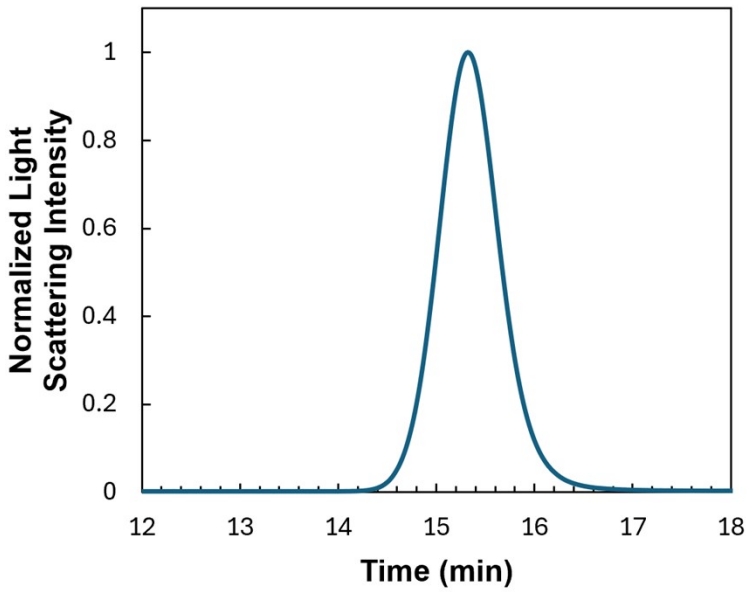


Figure S18. *SEC light scattering trace of PTFPSS parent polymer in DMAc with 50 mM LiCl.*

Representative Post-Polymerization Modification (50:50 poly(benzylstyrene sulfonyl-co-hexylstyrene sulfonyl) copolymer):

Activated ester parent polymer (TFPSS) (300 mg, 0.90 mmol, 1 equiv.) was dissolved in 5 mL of DMF. Benyzlamine (49 µL, 0.45 mmol, 0.5 equiv.) and triethylamine (63 µL, 0.45 mmol, 0.5 equiv.) were added to the reaction solution. The reaction was heated for 2 h at 65 °C. After the vial was removed from heat and a 50 µL aliquot was taken for ^{19}F NMR analysis. To the reaction solution, hexylamine (59 µL, 0.45 mmol, 0.5 equiv.) and triethylamine (0.55 mol equiv.) were added and allowed to stir for 2 h. A second 50 µL aliquot was taken for ^{19}F NMR analysis. The reaction solution was concentrated and dialyzed against tetrahydrofuran. The final polymer was characterized by ^{1}H NMR and SEC.

Post-Polymerization Modification with 10 additions of 0.1 Equivalents

Activated ester parent polymer (PTFPA or SSTFP) (1.14 mmol, 1 equiv.) was dissolved in solvent (EtOAc or DMF) with 4,4'-diflourobenzophenone (0.568 mmol, 0.5 equiv.) as an internal

standard. Benzylamine (0.114 mmol, 0.1 equiv.) and triethylamine (0.114 mmol, 0.1 equiv.) were added then the reaction solution was added to heat and allowed to react. A 50 µL aliquot was taken for ^{19}F NMR analysis, then a second portion of benzylamine and triethylamine were added and allowed to react. This was repeated for 10 total additions.

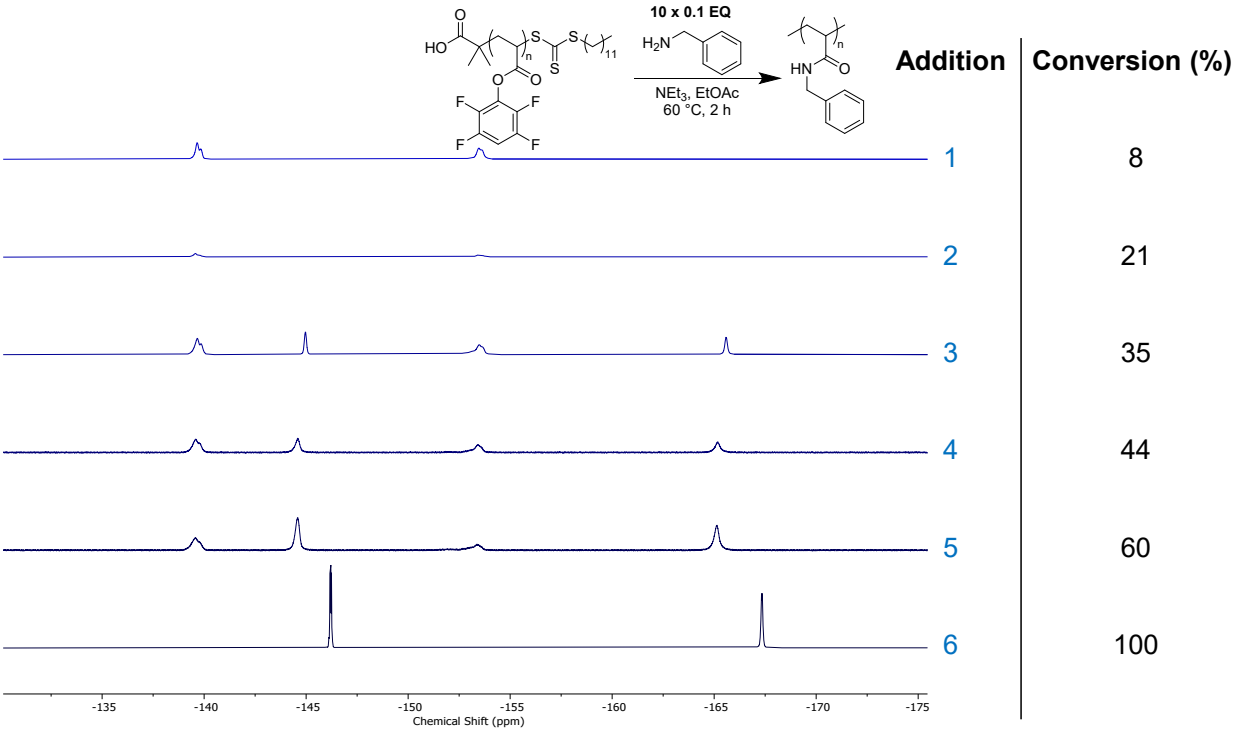


Figure S19. *Functionalization of PTFPA 6 times with 0.1 equivalents benzylamine and characterization by quantitative ^{19}F NMR (375 MHz, DMSO-d_6) with an internal standard.*

NMR Kinetic Experiment Procedure:

PTFPA (0.05 g, 0.227 mmol, 1 equiv.) was dissolved in 250 µL of acetone-d_6. Separately, benzylamine (12.5 µL, 0.11 mmol, 0.5 equiv.), triethylamine (16.0 µL, 0.11 mmol, 0.5 equiv.), and 4,4'-diflourobenzophenone (0.0251 g, 0.114 mmol, 0.5 equiv.) were dissolved in 250 µL of acetone-d_6. The two solutions were mixed in a scintillation vial and immediately pipetted into an NMR tube. The NMR tube was introduced into the instrument with the variable temperature probe

set to 45 °C. ^{19}F NMR scans (64 scans, 3s delay) were taken approximately every 8.5 minutes for a period of 2 hours after mixing.

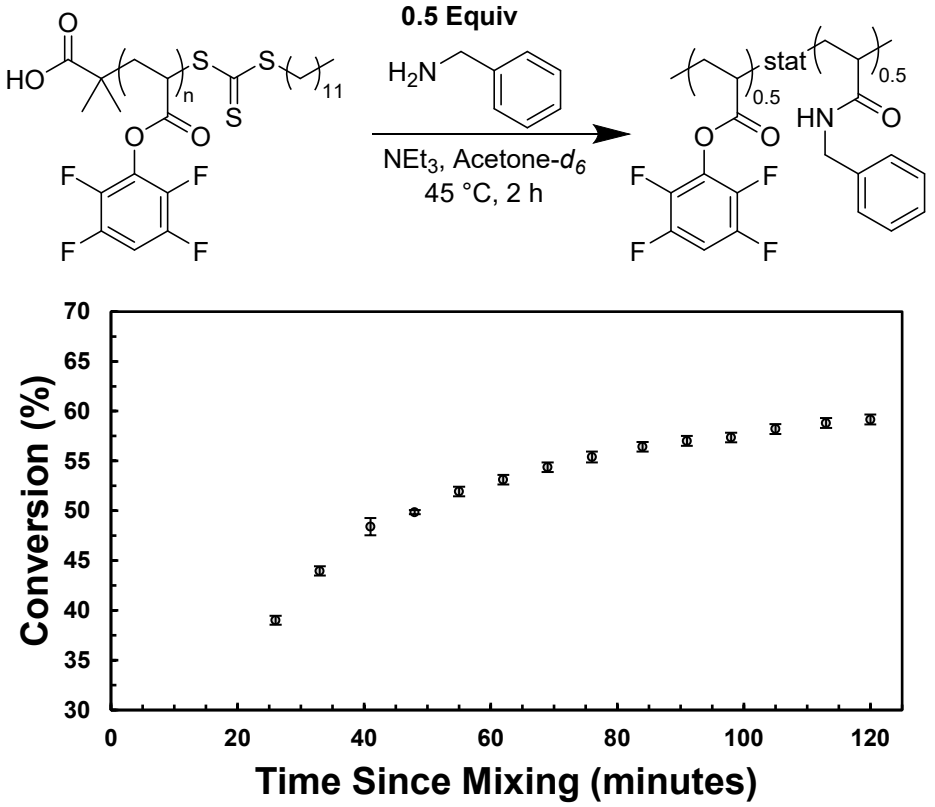


Figure S20. *Conversion vs time as measured by QFNMR (375 MHz, acetone-d_6) for the functionalization of PTFPA with benzylamine.*

Table S2. *Conversion calculated from QFNMR (375 MHz, acetone-d_6) for functionalization of PTFPA with benzylamine versus time after mixing.*

Time After Mixing (minutes)	$I_{Poly\ 1}$ -139 ppm	$I_{LG\ 1}$ -144 ppm	$I_{Poly\ 2}$ -153 ppm	$I_{LG\ 2}$ -164 ppm	Average % Conversion
26	1.04	0.66	1.04	0.67	39.0 ± 0.4
33	0.95	0.74	0.95	0.75	44.0 ± 0.5
41	0.83	0.76	0.79	0.76	48.4 ± 0.9
48	0.85	0.84	0.84	0.84	49.9 ± 0.2
55	0.81	0.87	0.81	0.88	51.9 ± 0.5
62	0.79	0.89	0.79	0.90	53.1 ± 0.5
69	0.76	0.90	0.76	0.91	54.4 ± 0.5
76	0.75	0.92	0.74	0.93	55.4 ± 0.5
84	0.73	0.94	0.73	0.95	56.4 ± 0.5
91	0.72	0.95	0.72	0.96	57.0 ± 0.5
98	0.71	0.95	0.71	0.96	57.4 ± 0.5
105	0.70	0.97	0.70	0.98	58.2 ± 0.5
113	0.69	0.98	0.69	0.99	58.8 ± 0.5
120	0.68	0.98	0.68	0.99	59.2 ± 0.2

Divergent Post-Polymerization Modification:

Activated ester parent polymer (PTFPSS or PTFPA) (1.8 mmol, 1 equiv.) was dissolved in 6 mL of DMF containing 4, 4'-Difluorobenzophenone (15 mg) as an internal standard in a 6-dram vial. Benzylamine (49 μL, 0.45 mmol, 0.25 equiv.) and triethylamine (63 μL, 0.45 mmol, 0.25 equiv.) were added, and the reaction mixture was heated for 2 h at 65 °C. After the vial was removed from heat, a 50 μL aliquot was taken for ^{19}F NMR analysis. For the second-generation modification, two 2.5 mL aliquots of the original 6 mL reaction solution were transferred into separate 6-dram vials. To one vial, hexylamine (50 μL, 0.38 mmol, 0.5 equiv.) and triethylamine (0.5 mol equiv.) were added and stirred for 2 h. To the other, furfurylamine (33 μL, 0.38 mmol, 0.5 equiv.) and triethylamine (0.5 mol equiv.) were added under the same condition. A 50 μL aliquot was taken from each of the reaction solutions for ^{19}F NMR analysis. For the third-generation modification, two 1 mL aliquots were taken from each of the two 2.5 mL second-generation solutions and transferred into four separate 6-dram vials (two from the

benzylamine/hexylamine solution and two from the benzylamine/furfurylamine solution). To one of the 1 mL benzylamine/hexylamine solutions, furfurylamine (6.6 µL, 0.075 mmol, 0.25 equiv.) and triethylamine (0.25 mol equiv.) were added and allowed to stir overnight. To the other 1 mL benzylamine/hexylamine solution, allylamine (5.6 µL, 0.075 mmol, 0.25 equiv.) and triethylamine (0.25 mol equiv.) were added and stirred overnight. To one of the benzylamine/furfurylamine solutions, hexylamine (10 µL, 0.075 mmol, 0.25 equiv.) and triethylamine (0.25 mol equiv.) were added and allowed to stir overnight. To the other 1 mL benzylamine/furfurylamine solution, allylamine (6 µL, 0.075 mmol, 0.25 equiv.) and triethylamine (0.25 mol equiv.) were added and allowed to stir overnight. A 50 µL aliquot was taken from each of the reaction solutions for ^{19}F NMR analysis. The 4 final reaction solutions were then dialyzed against DMF for 3 days. The dialyzed solutions were then concentrated and further characterized by ^{1}H NMR and SEC.

Table S3. *Conversion calculated from QFNMR (375 MHz, acetone-d_6) for divergent synthesis of acrylamide copolymers.*

Generation	Addition	$I_{Poly\ 1}$ -139ppm	$I_{LG\ 1}$ -144ppm	$I_{Poly\ 2}$ -153ppm	$I_{LG\ 2}$ -164ppm	Total % Conversion
1	+0.25 BA	1.59	0.47	1.57	0.47	22.9 ± 0.2
2	0.25 BA +0.5 HA	0.58	1.46	0.55	1.48	72 ± 1
	0.25 BA +0.5 FA	0.67	1.42	0.67	1.40	67.8 ± 0.8
3	0.25 BA 0.5 HA +0.25 FA	0.13	1.88	0.10	1.87	94 ± 1
	0.25 BA 0.5 HA +0.25 AA	0.08	1.92	0.07	1.93	96.3 ± 0.6
	0.25 BA 0.5 FA +0.25 HA	0.15	1.86	0.12	1.86	93 ± 1
	0.25 BA 0.5 FA +0.25 AA	0.11	1.87	0.10	1.88	94.7 ± 0.6

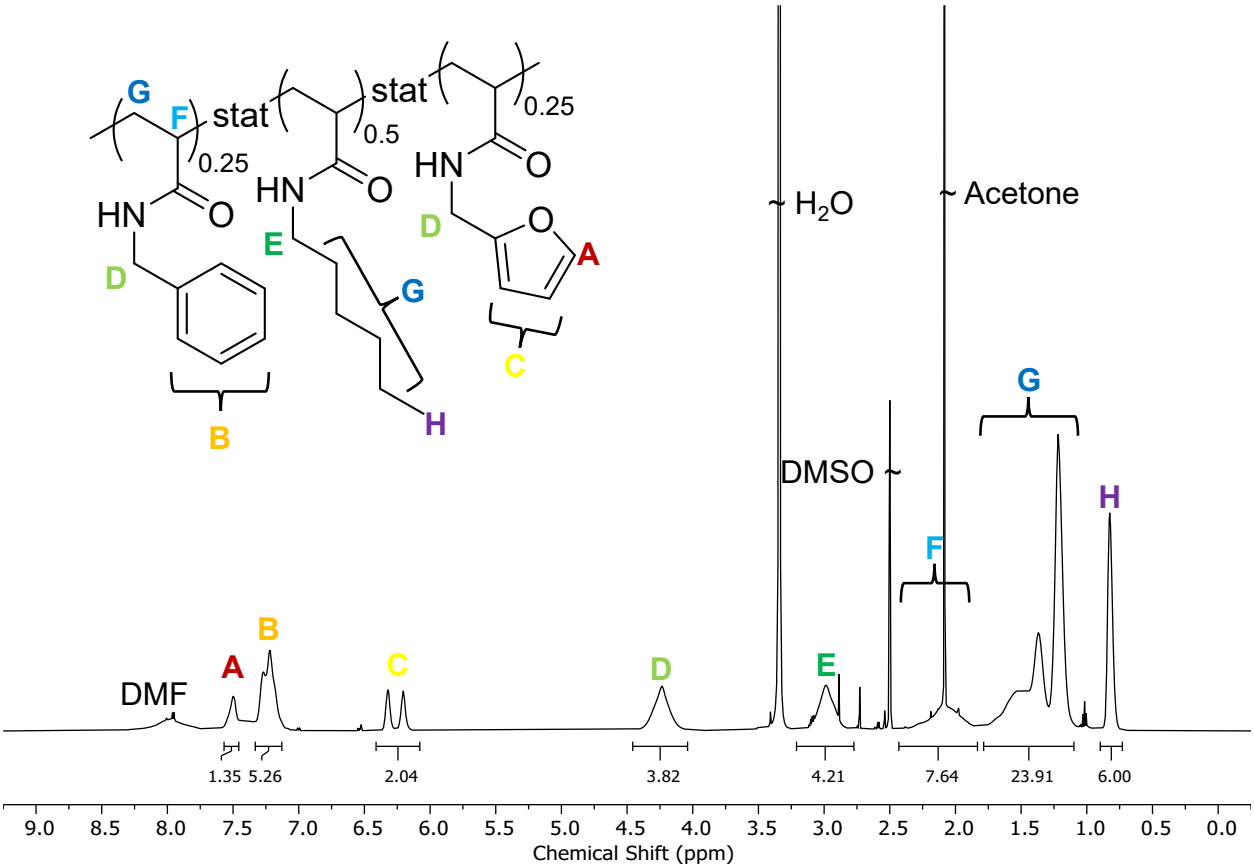


Figure S21. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly(benzylacrylamide-stat-hexylacrylamide-stat-furfurylacrylamide) copolymer in acetone-d_6.*

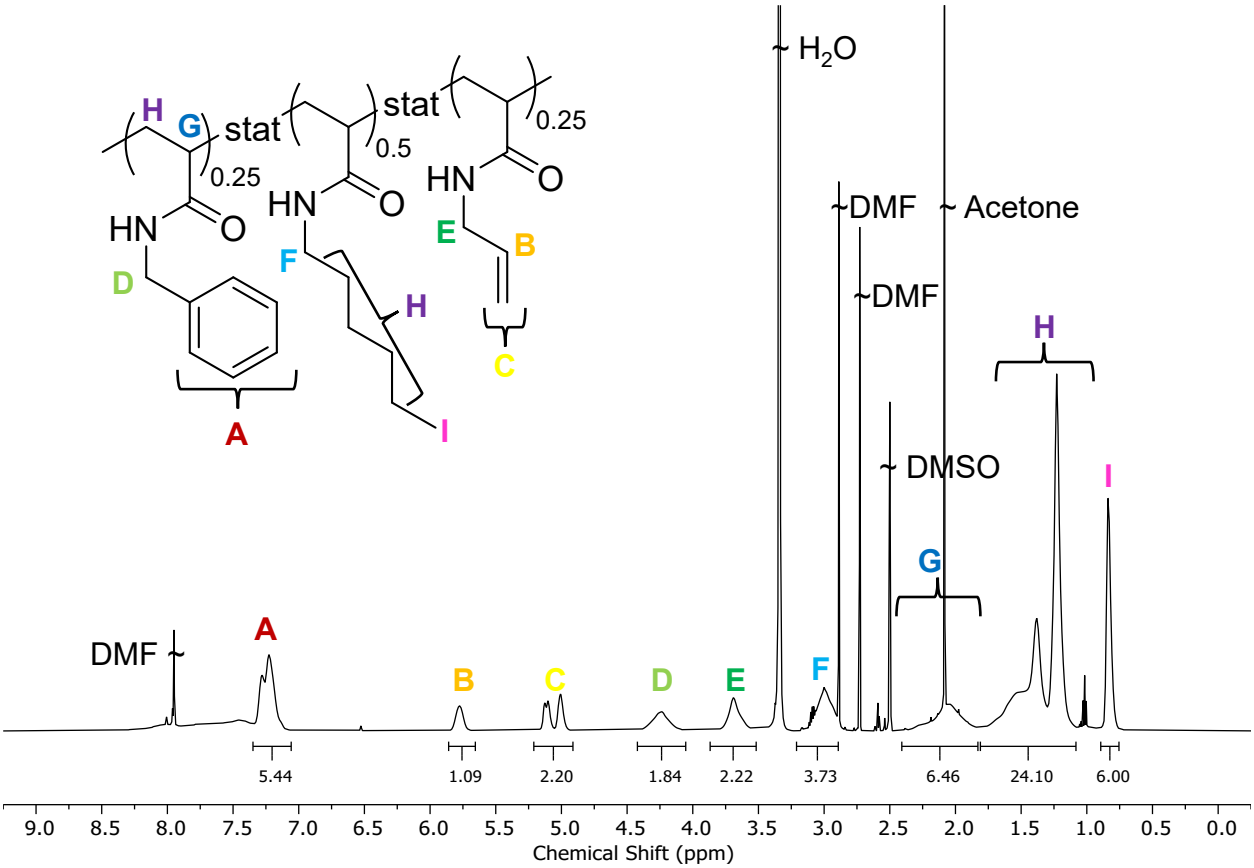


Figure S22. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly(benzylacrylamide-stat-hexylacrylamide-stat-allylacrylamide) copolymer in acetone-d_6.*

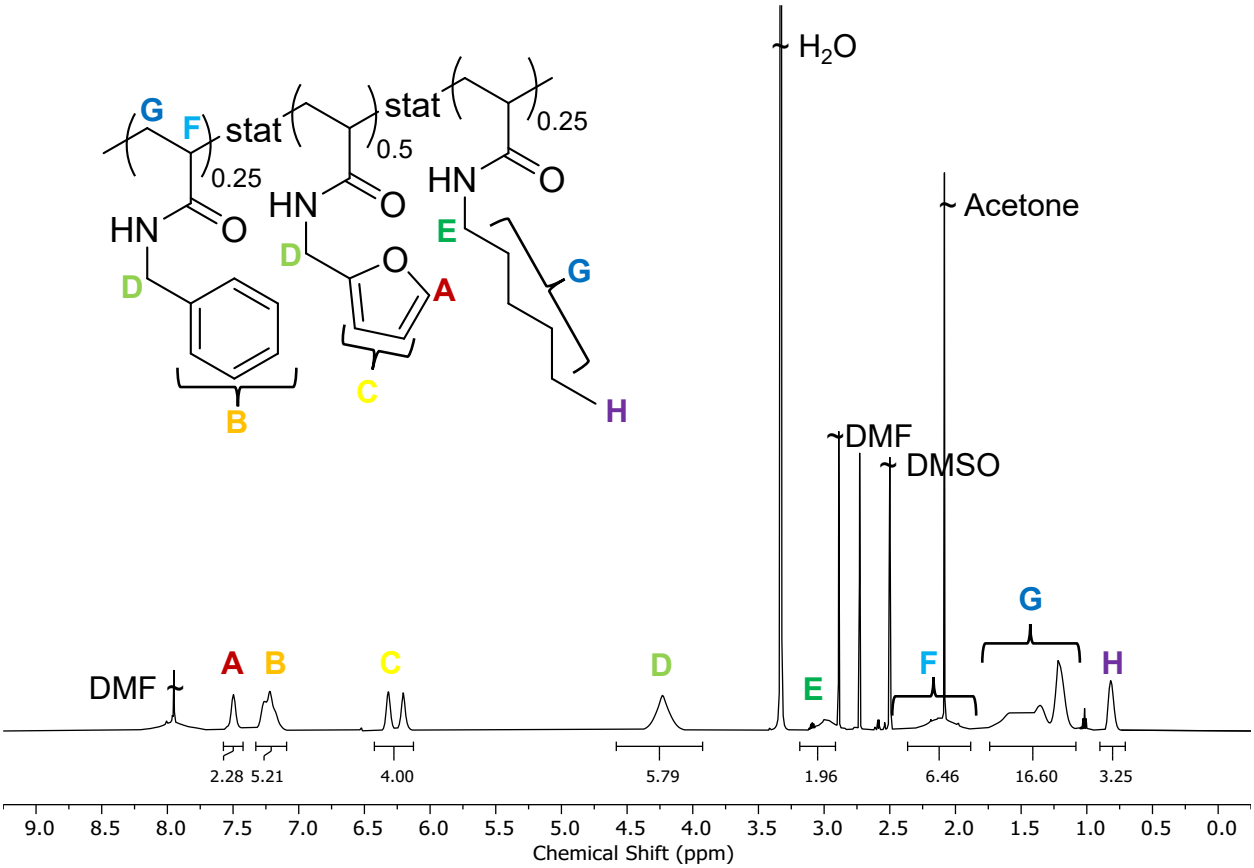


Figure S23. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly(benzylacrylamide-stat-furfurylacrylamide-stat-hexylacrylamide) copolymer in acetone-d_6.*

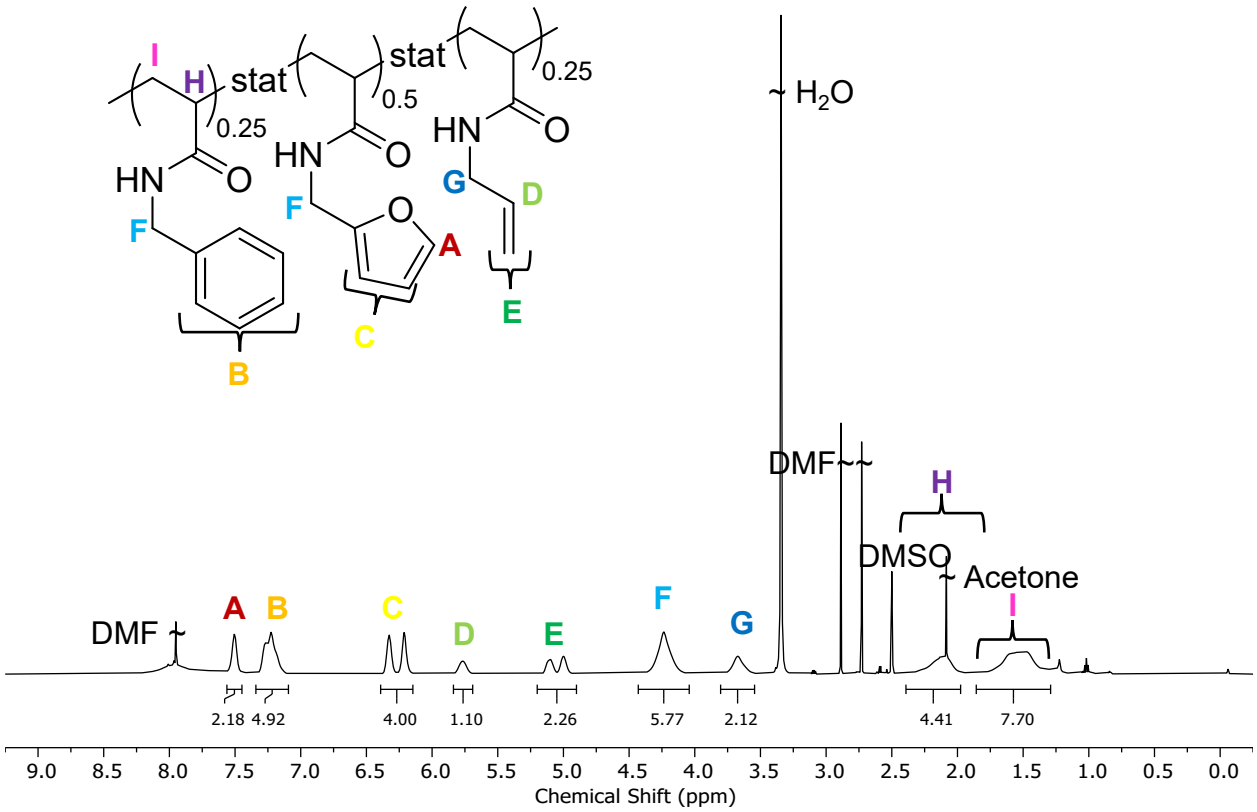


Figure S24. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly(benzylacrylamide-stat-furfurylacrylamide-stat-allylacrylamide) copolymer in acetone-d_6.*

Table S4. *Conversion calculated from QFNMR (375 MHz, DMSO-d_6) for divergent synthesis of styrene sulfonate copolymers.*

Generation	Addition	$I_{Poly\ 1}$ -139 ppm	$I_{LG\ 1}$ -145 ppm	$I_{Poly\ 2}$ -152 ppm	$I_{LG\ 2}$ -165 ppm	Total % Conversion
1	0.25 BA	20.57	6.09	20.39	5.93	22.69 ± 0.16
2a	0.25 BA +0.5 HA	6.13	20.28	6.06	20.14	76.3 ± 0.04
2b	0.25 BA +0.5 FA	5.45	20.29	5.39	20.14	78.86 ± 0.03
3a	0.25 BA 0.5 HA +0.25 FA	0.11	24.32	0.04	24.11	99.69 ± 0.14
3b	0.25 BA 0.5 HA +0.25 AA	0.08	27.48	0.01	27.49	99.84 ± 0.13
3c	0.25 BA 0.5 FA +0.25 HA	0.12	25.78	0.07	25.54	99.63 ± 0.09
3d	0.25 BA 0.5 FA +0.25 AA	0.05	28.21	0.01	28.29	99.89 ± 0.07

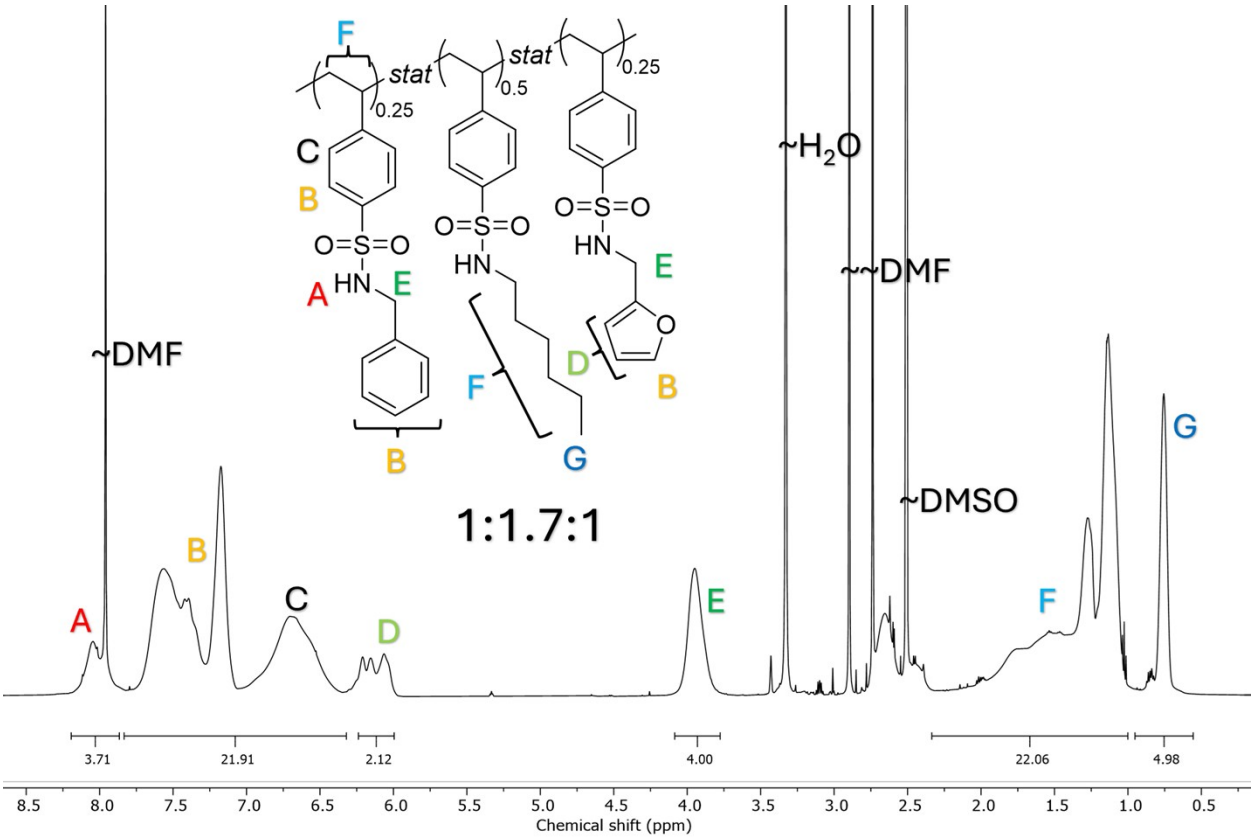


Figure S25. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly((benzylsulfonamido)styrene-stat-(hexylsulfonamido)styrene-stat-(furfurylsulfonamido)styrene) copolymer in DMSO-d_6.*

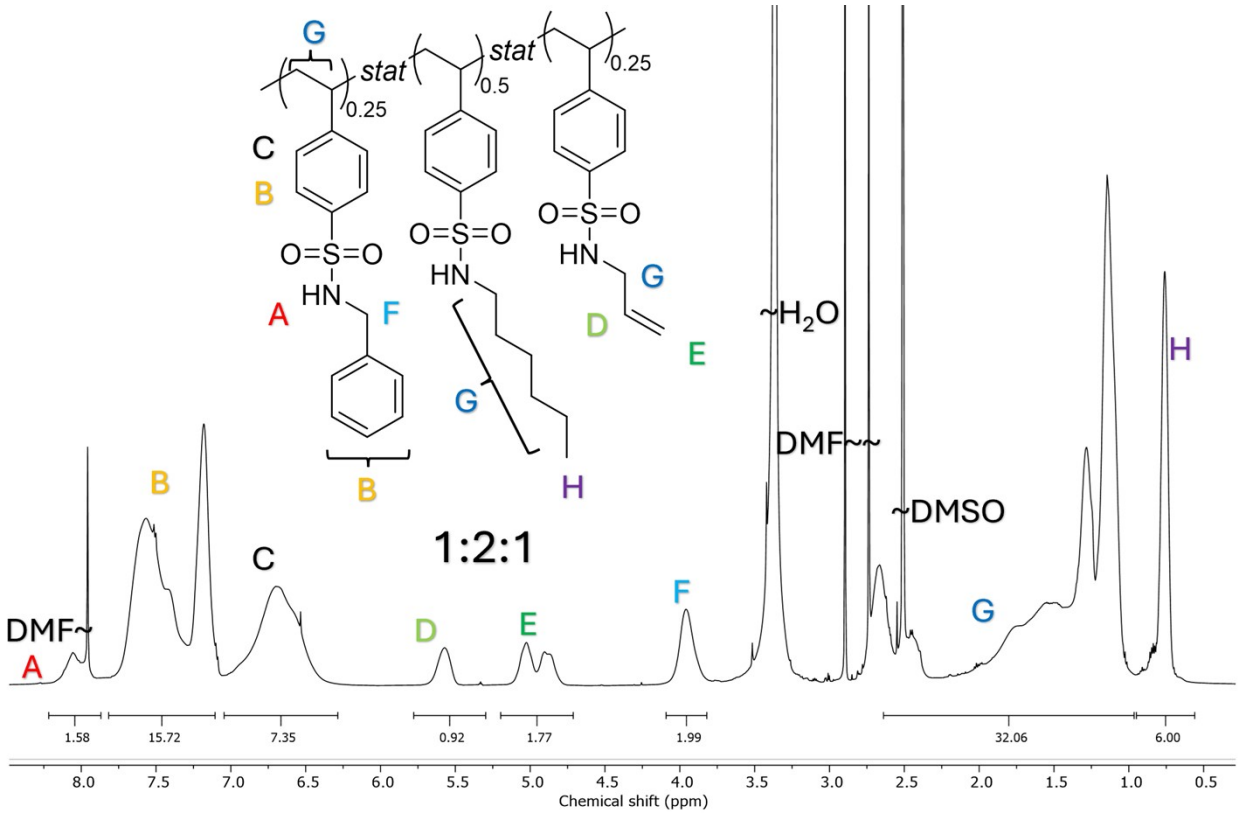


Figure S26. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly((benzylsulfonamido)styrene-stat-((hexylsulfonamido)styrene-stat-(allylsulfonamido)styrene) copolymer in DMSO-d_6.*

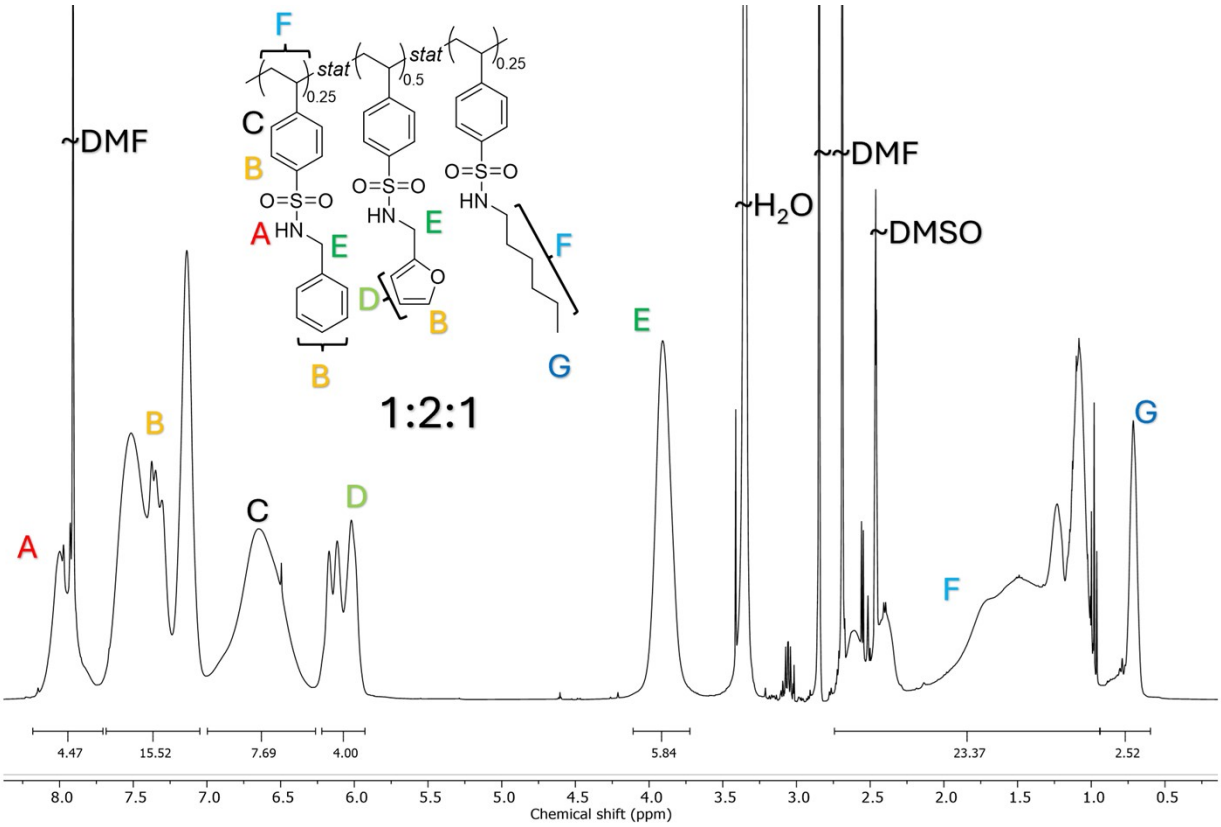


Figure S27. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly((benzylsulfonamido)styrene-stat-(furfurylsulfonamido)styrene-stat-hexylsulfonamido)styrene) copolymer in DMSO-d_6.*

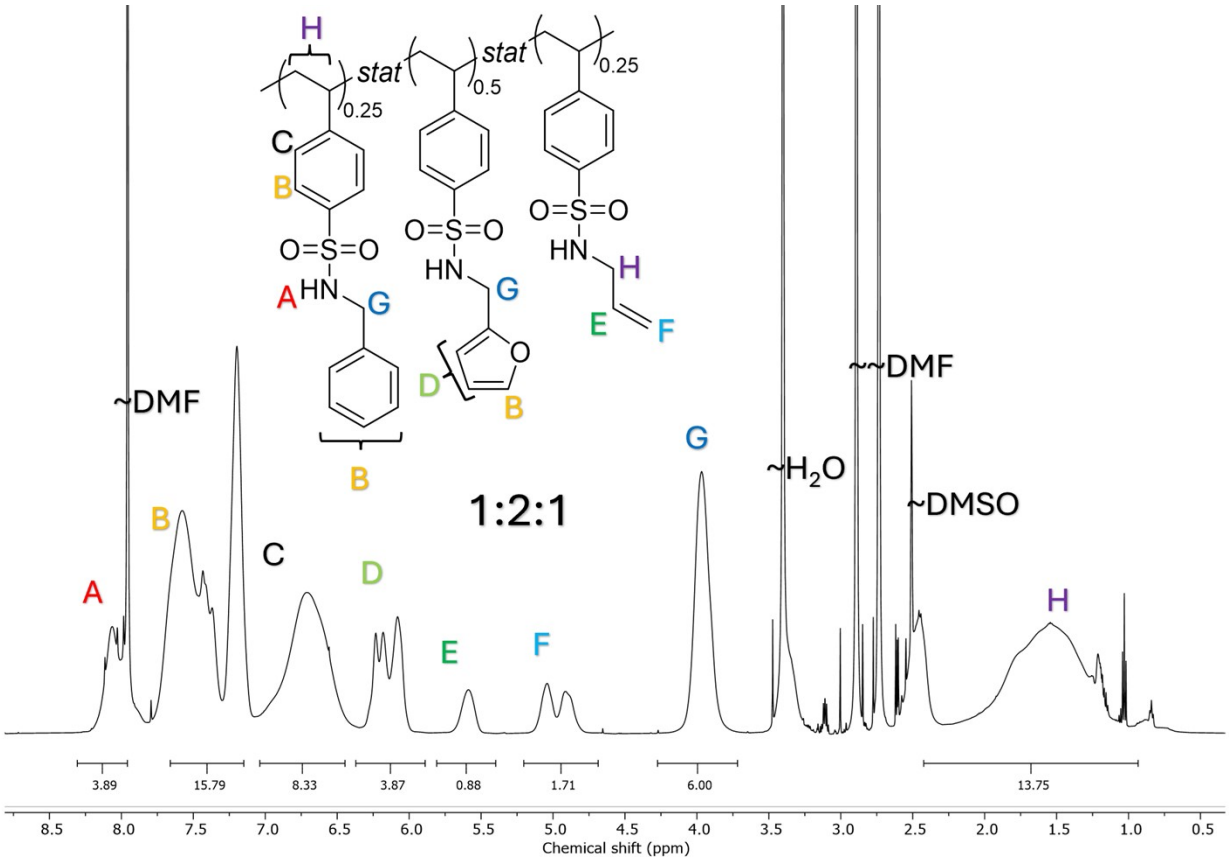


Figure S28. *^{1}H NMR (600 MHz) spectrum of 25:50:25 poly((benzylsulfonamido)styrene-stat-(furfurylsulfonamido)styrene-stat-(allylsulfonamido)styrene) copolymer in DMSO-d_6.*