

Post-polymerization functionalization strategy for the synthesis of sulfonyl (trifluoromethanesulfonyl)imide functionalized (co)polymers

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1. Materials

Acetonitrile, diethyl ether, dichloromethane (DCM), ethyl acetate, *n*-pentane, *N,N*-dimethylformamide (DMF), oxalyl chloride ((COCl)₂), sodium 3-bromosulfopropene, triethylamine (TEA), potassium carbonate (K₂CO₃), sodium azide (NaN₃), triphenyl phosphine (P(Ph)₃) poly(4-vinylphenol), poly(ethylene glycol) methyl ether acrylate (PEGA, *M*_n= 480 g.mol⁻¹), propargyl acrylate (PA), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP), 2,2'-azobis(2-methylpropionitrile) (AIBN), *L*-sodium ascorbate, *t*-butanol were purchased from Sigma-Aldrich. Trifluoromethanesulfonamide (CF₃SO₂NH₂) was purchased from TCI. PEGA (*M*_n= 480 g.mol⁻¹) and propargyl acrylate monomers were purified by passing through a basic aluminum oxide column. *N*-

succinimide acrylate (NHSA) was synthesized according to the method reported in the literature.¹

2. Characterizations

High resolution mass spectrometry (HRMS) experiments were performed with a Synapt G2 HDMS quadrupole/time-of-flight (Manchester, UK).

Samples were introduced at 10 $\mu\text{L min}^{-1}$ flow rate (positive mode: capillary voltage +2.8kV, sampling cone voltage: varied between +20V and +60V; negative mode: capillary voltage -2.27kV, sampling cone voltage: varied between -20V and -40V) under a desolvation gas (N_2) flow of 100 L h^{-1} heated at 35°C. Accurate mass experiments were performed using reference ions from PPG, PEG or CH_3COONa internal standard. All the samples were dissolved in methanol doped with 3mM ammonium acetate prior to analysis. Data analyses were conducted using MassLynx 4.1 programs provided by Waters.

Fourier-Transformation Infrared (FT-IR) spectra were recorded using a Perkin Elmer Spectrum Two FT-IR Spectrometer with an ATR accessory.

Nuclear magnetic resonance (NMR) spectra of ^1H , ^{13}C and ^{19}F nucleus were recorded using a Bruker AC 400 MHz.

Size exclusion chromatography (SEC) experiments were performed with a PL120 system (Polymer Laboratories, England), equipped with an injection valve (20 μL loop volume), a column oven and a Refractive Index detector thermostated at 70°C. Stationary phase was a set of a PL Resipore (50 x 8 mm) guard column and two PL Resipore (300 x 8 mm) columns (Polymer Laboratories, England). The eluent was DMF supplemented with 0.1 M LiBr and delivered at a 0.7 mL.min^{-1} flow rate. Samples were solubilized in a mixture of the eluent and toluene (flow marker) at 0.25 vol.%, at a concentration of 0.25 wt%. Polystyrene (PS) equivalent number-average and weight-average molar masses (M_n and M_w) and dispersities (D) were calculated by means of PS calibration curve using PS standards from 0.86 to 526.0 Kg.mol^{-1} (Agilent, USA).

¹ Pollak, A.; Blumenfeld, H.; Wax, M.; Baughn, R. L.; Whitesides, G. M. *Journal of the American Chemical Society* **1980**, 102, (20), 6324-6336.

Differential Scanning Calorimetry (DSC) experiments was carried out on a TA DSC Q20 using a heat/cool/heat cycle from 50°C to 200°C. The heating and cooling rates were 10°C min⁻¹. The glass-transition temperature, T_g, was determined from the second heating cycle of the DSC thermograms.

Thermogravimetric analysis (TGA) of STFSI functionalized (co)polymers was carried out on a Perkin Elmer thermogravimetric analyzer (TGA 800) with a heating rate of 10 °C/min from 40°C to 800 °C under a nitrogen atmosphere. The temperature was then raised to 1000°C at a heating rate of 20°C under oxygen atmosphere to pyrolyse all organic residues.

3. Synthesis of potassium 3-bromo, azido and amine-propylsulfonyl (trifluoromethanesulfonyl)imide

1.1. Synthesis of triethylammonium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide (1)

Oxalyl chloride (2.10 mL, 2.48 x10⁻² mol) and *N,N*-dimethylformamide (0.15 mL) were added dropwise under argon to a three-necked round bottom flask containing anhydrous acetonitrile (30.0 mL) at 0°C. The mixture was stirred 1h at room temperature. Then, the solution was chilled down to 0°C and sodium 3-bromosulfo propane (5.00 g, 2.22 x10⁻² mol) was added into the solution under argon. The resulting solution was continuously stirred at 0°C for 3h and 2h more at room temperature to achieve the formation of 3-bromo(chlorosulfonyl)propane. Then a solution of trifluoromethanesulfonamide (2.42 g, 1.62 x10⁻² mol) and triethylamine (6.80 mL, 4.91x10⁻² mol) dissolved in acetonitrile (10.0 mL) at 0°C under argon was added to the 3-bromo(chlorosulfonyl)propane solution. The reaction mixture was allowed to react at 0°C for 2h and then at room temperature for 16h under argon. The reaction mixture was filtered off and the recovered white solid was washed with acetonitrile. The filtrate was concentrated under vacuum then dissolved in dichloromethane and washed successively with a saturated NaHCO₃ solution, a solution of 1M chloride acid and a saturated NaCl solution, dried over MgSO₄, filtered and evaporated under reduced pressure. The product was obtained as amber oil (52% yield).

HRMS (C₁₀H₂₂BrF₃N₂O₄S₂): detected ion [M+(C₆H₁₆N)]⁺, *m/z*_{found} 536.1433; *m/z*_{calc} 536.1434

^1H NMR (DMSO d_6 , δ ppm): 3.63 ($-\text{CH}_2\text{Br}$, t, $J = 6.7$ Hz), 3.10 ($-\text{CH}_2\text{-SO}_2\text{NSO}_2\text{CF}_3$ and $-\text{CH}_2$) of TEA, m, 8H), 2.19 (CH_2 , dt, $J = 9.0, 6.8$ Hz, 2H), 1.18 ($-\text{CH}_3$ of TEA, t, $J = 7.3$ Hz, 9H).

^{13}C NMR (DMSO d_6 , δ ppm): 115.74-125.41 ($-\text{CF}_3$), 53.50 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), 46.25 ($\text{N}(\text{CH}_2\text{CH}_3)_3$), 33.43 ($-\text{CH}_2\text{Br}$), 28.00 ($-\text{CH}_2\text{CH}_2\text{Br}$), 9.09 ($\text{N}(\text{CH}_2\text{CH}_3)_3$).

^{19}F NMR (DMSO d_6 , δ ppm): -77.59.

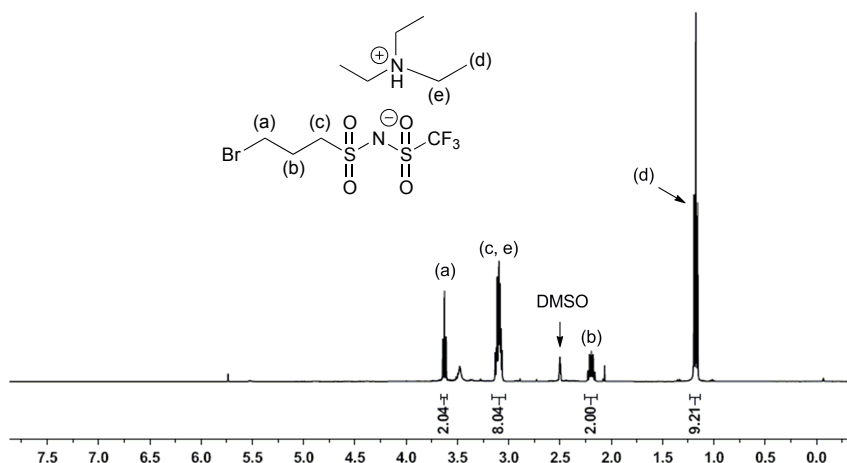


Figure S1: ^1H NMR spectrum of triethylamonium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide in DMSO- d_6 .

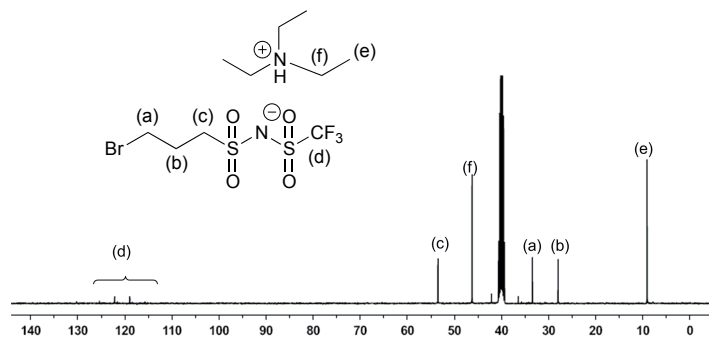


Figure S2: ^{13}C NMR of triethylamonium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide in DMSO- d_6 .

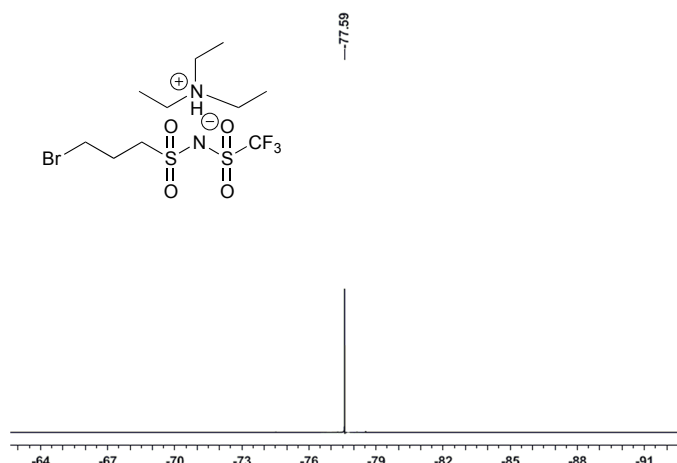


Figure S3: ^{19}F NMR of triethylamonium-3-bromopropylsulfonyl (trifluoromethane)sulfonimide in DMSO-d_6 .

1.2. Synthesis of potassium 3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide (**2**)

To the cold solution of triethylamonium-3-bromopropylsulfonyl (trifluoromethane-sulfonyl)imide (3.52 g, 8.11×10^{-3} mol) in acetonitrile (20.0 mL) was slowly added potassium carbonate (2.80 g, 2.03×10^{-2} mol). After the complete addition of K_2CO_3 , the mixture reaction was allowed to react at 0°C to room temperature for 24 hours. The solution was then filtered and the filtrate was concentrated under vacuum. The yellowish solid was recrystallized from hot dichloromethane. The mixture solution was then kept at -20°C for 24 h. The obtained solid was washed with cold *n*-pentane and dried under vacuum to obtain a white solid (73% yield).

HR-MS ($\text{C}_4\text{H}_6\text{BrF}_3\text{NO}_4\text{S}_2\text{K}$): detected ion $[\text{M-K}^+]^-$, m/z_{found} 333.8858; m/z_{calc} 333.8858 g.mol^{-1} .

^1H NMR (DMSO d_6 , δ ppm): 3.63 ($-\text{CH}_2\text{Br}$, t, $J = 6.7$ Hz, 2H), 3.10 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$, t, $J = 6.7$ Hz, 2H), 2.20 ($-\text{CH}_2\text{CH}_2\text{Br}$, m, 2H).

^{13}C NMR (DMSO d_6 , δ ppm): 115.72-125.44 ($-\text{CF}_3$), 53.51 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), 33.43 ($-\text{CH}_2\text{Br}$), 28.00 ($-\text{CH}_2\text{CH}_2\text{Br}$).

^{19}F NMR (DMSO d_6 , δ ppm): -77.56.

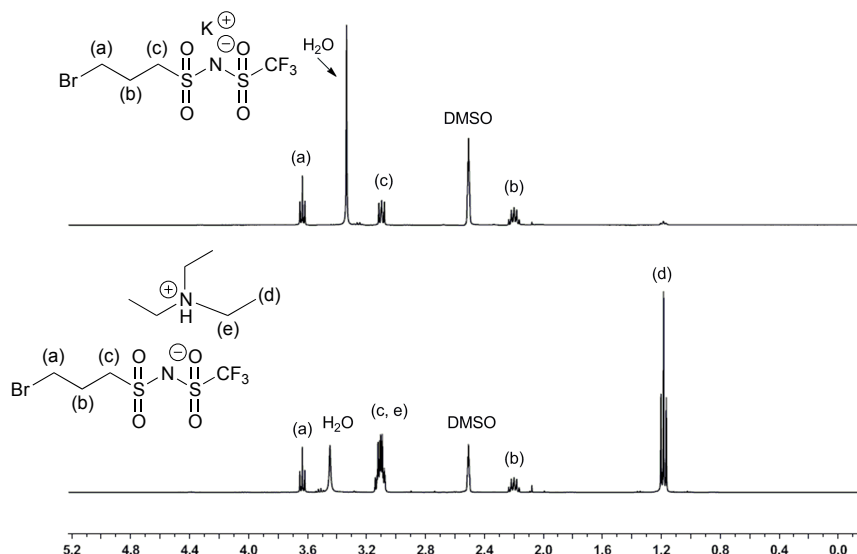


Figure S4: ^1H NMR spectra of triethylamonium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide (bottom) and potassium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide (top) in DMSO-d_6 .

1.3. Synthesis of potassium 3-azidopropylsulfonyl (trifluoromethanesulfonyl)imide (**3**)

To the cold solution of potassium-3-bromopropylsulfonyl (trifluoromethanesulfonyl)imide (1.00 g, 2.70×10^{-3} mol) in DMF (3.0 mL) was slowly added sodium azide (0.50 g, 7.69×10^{-2} mol). After the complete addition of NaN_3 , the mixture was allowed to react at 0°C to room temperature for 24 hours under argon. The solid was filtered out and washed with ethyl acetate. The solvents were then evaporated under vacuum. The recovered solid was dissolved in ethyl acetate; the solution was filtered and concentrated under vacuum. This operation was repeated twice to get the final product (75% yield).

HR-MS ($\text{C}_4\text{H}_6\text{F}_3\text{N}_4\text{O}_4\text{S}_2\text{K}$): detected ion $[\text{M-K}^+]^-$ m/z_{found} 294.9789; m/z_{calc} 294.9788 g.mol^{-1} .

^1H NMR (DMSO d_6 , δ ppm): 3.47 ($-\text{CH}_2\text{N}_3$, t, $J = 6.9$ Hz, 2H), 3.03 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$, t, $J = 6.9$ Hz, 2H), 1.91 ($-\text{CH}_2\text{CH}_2\text{N}_3$, m, 2H).

^{13}C NMR (DMSO d_6 , δ ppm): 115.73-125.40 ($-\text{CF}_3$), 52.16 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), 49.67 ($-\text{CH}_2\text{N}_3$), 24.13 ($-\text{CH}_2\text{CH}_2\text{N}_3$).

^{19}F NMR (DMSO d_6 , δ ppm): -77.54.

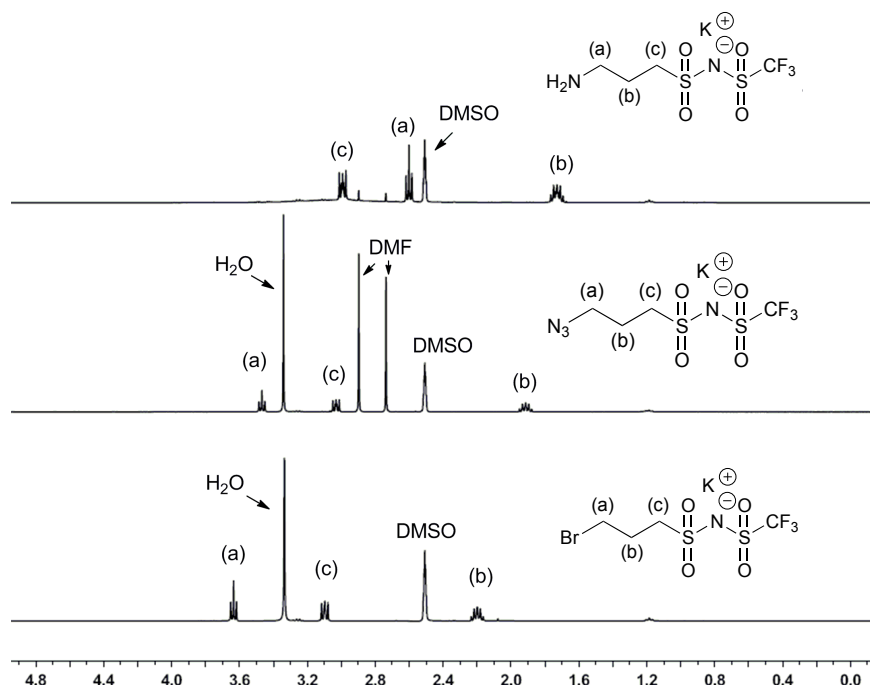


Figure S5: ^1H NMR spectra of potassium 3-bromo-(**2**) (bottom), azido-(**3**) (middle) and amino-(**4**) (top) C_3 -STFSI derivatives in DMSO-d_6

1.4. Synthesis of potassium 3-aminopropylsulfonyl (trifluoromethanesulfonyl)imide (**4**)

To the cold solution of potassium-3-azidopropylsulfonyl (trifluoromethanesulfonyl)imide (0.60 g, 1.80×10^{-3} mol) in THF (10.0 mL) was slowly added the solution of triphenyl phosphine (0.70 g, 2.67×10^{-3} mol) dissolved in 4 mL of THF. After the complete addition of $\text{P}(\text{Ph})_3$, the mixture was allowed to react at 0°C to room temperature for 40 hours under argon. After this time, 2.0 mL of demineralized water was added to the mixture and the solution was vigorously stirred for 5 h. The solvents were evaporated under vacuum. The crude solid was dissolved in demineralized water, filtered and extracted three times with dichloromethane. The aqueous phase was evaporated and the product was dried under vacuum (74% yield).

HR-MS ($\text{C}_4\text{H}_8\text{F}_3\text{N}_2\text{O}_4\text{S}_2\text{K}$): detected ion $[\text{M-K}]^+$ m/z_{found} 268.9884; m/z_{calc} 268.9883.

^1H NMR (DMSO d_6 , δ ppm): 2.99 ($-\text{CH}_2-\text{SO}_2\text{NSO}_2\text{CF}_3$, 2H), 2.60 ($-\text{CH}_2\text{NH}_2$, t, $J = 6.8$ Hz, 2H), 1.73 ($-\text{CH}_2\text{CH}_2\text{NH}_2$, m, 2H).

^{13}C NMR (DMSO d_6 , δ ppm): 115.73-125.40 ($-\text{CF}_3$), 53.09 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), 40.36 ($-\text{CH}_2\text{NH}_2$), 28.13 ($-\text{CH}_2\text{CH}_2\text{NH}_2$).

^{19}F NMR (DMSO d_6 , δ ppm): -77.47.

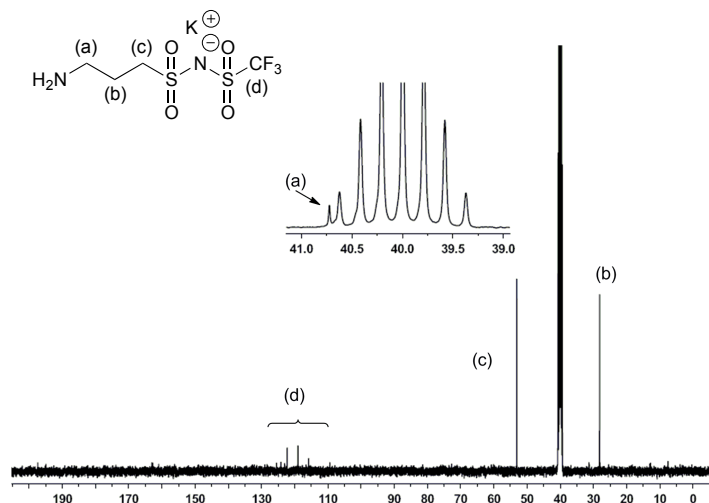


Figure S6: ^{13}C NMR spectrum of potassium 3-aminopropylsulfonyl (trifluoromethanesulfonyl)imide in DMSO-d_6 .

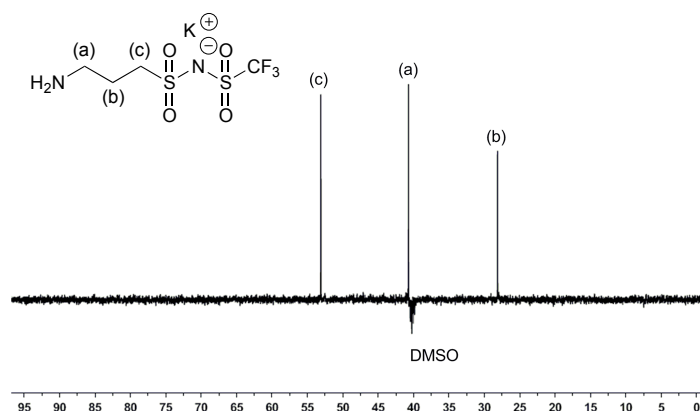
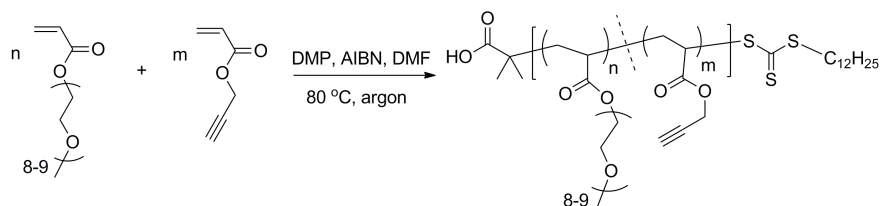


Figure S7: DEPT 135 ^{13}C NMR spectrum of potassium 3-aminopropylsulfonyl (trifluoromethanesulfonyl)imide in DMSO-d_6 .

4. Synthesis of well-defined alkyne-functionalized copolymers based on propargyl acrylate and poly(ethylene glycol) methyl ether acrylate



Scheme S1: RAFT polymerization of PEGA and propargyl acrylate in DMF at 80°C with $[\text{PEGA}]_0 : [\text{PA}]_0 : [\text{DMP}]_0 : [\text{AIBN}]_0 = 31 : 40 : 1 : 0.15$.

In the general procedure for RAFT polymerization, PEGA ($M_n = 480 \text{ g.mol}^{-1}$, 2.50 g, $5.21 \times 10^{-3} \text{ mol}$), propargyl acrylate (0.75 g, $6.82 \times 10^{-3} \text{ mol}$), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP, 62.0 mg, $1.70 \times 10^{-4} \text{ mol}$), AIBN (3.7 mg, $2.26 \times 10^{-5} \text{ mol}$) and DMF (7.5 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was deoxygenated by bubbling argon for 30 min. The solution was then immersed in an oil bath thermostated at 80°C to allow the polymerization to occur. The polymerization was stopped after 5 h by rapid cooling and exposing the polymerization solution to air. The DMF was removed under reduced pressure. The resulting product was then dissolved in DCM and precipitated in cold diethyl ether. The final product obtained as a yellow gummy product. $M_{n,\text{SEC}} = 12300 \text{ (g.mol}^{-1}\text{)}$; $D=1.20$. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 0.81 (t, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 1.19 ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 2.56 ($\text{HC}\equiv\text{C-}$), 3.31 ($\text{CH}_3\text{O-}$), 3.38-3.76 ($(-\text{OCH}_2\text{CH}_2-)_{7-8}$), 4.13 ($-\text{COOCH}_2\text{CH}_2\text{O-}$), 4.61 ($-\text{COOCH}_2\text{C}\equiv\text{CH}$). $M_{n,\text{NMR}} = 8365 \text{ (g.mol}^{-1}\text{)}$ with $DP_{n,\text{PEGA}} = 13$ and $DP_{n,\text{PA}} = 16$.

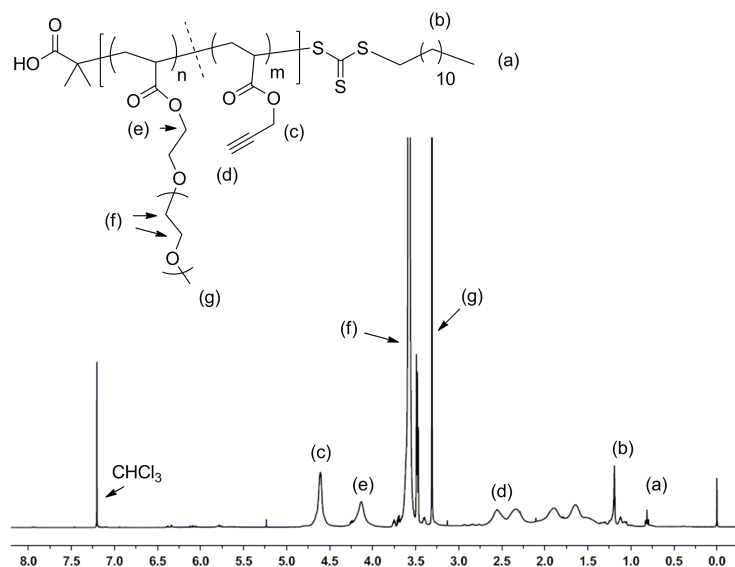
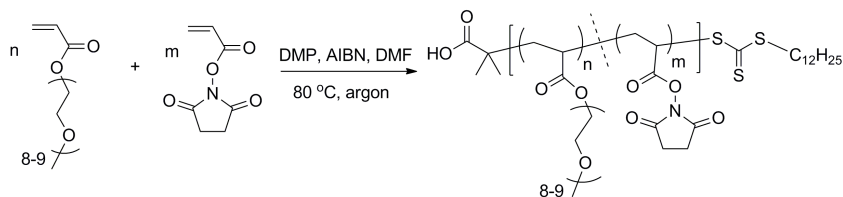


Figure S8: $^1\text{H NMR}$ spectrum of poly(poly(ethylene glycol)acrylate-*co*-propargyl acrylate) P(PEGA₁₃-*co*-PA₁₆) (**7**) in CDCl_3 .

5. Synthesis of well-defined poly(*N*-succinimide acrylate -co- poly(ethylene glycol) methyl ether acrylate) copolymer



Scheme S2: RAFT copolymerization of PEGA and NHSA monomer in DMF at 80 °C with $[PEGA]_0 : [NHSA]_0 : [DMP]_0 : [AIBN]_0 = 31 : 40 : 1 : 0.15$.

In the general procedure for RAFT polymerization, PEGA ($M_n = 480 \text{ g.mol}^{-1}$, 2.50 g, $5.21 \times 10^{-3} \text{ mol}$), *N*-succinimide acrylate (NHSA, 1.15 g, $6.80 \times 10^{-3} \text{ mol}$), DMP agent (0.062 g, $1.70 \times 10^{-4} \text{ mol}$), AIBN (3.7 mg, $2.26 \times 10^{-5} \text{ mol}$) and DMF (7.50 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was deoxygenated by bubbling argon for 40 min. The solution was then immersed in an oil bath thermostated at 80 °C to allow the polymerization to occur. The polymerization was stopped after 5h30min by rapid cooling and exposing the polymerization solution to air. The DMF was removed under reduced pressure. The resulting product was then dissolved in DCM and precipitated in cold diethyl ether. The final product obtained as a yellow gummy product. $M_{n,SEC} = 21000 \text{ (g.mol}^{-1}\text{)}$; $D = 1.24$, and $M_{n,NMR} = 20876 \text{ g.mol}^{-1}$ with $DP_{n,PEGA} = 29$ and $DP_{n,NHSA} = 39$. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 0.81 (t, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 1.19 ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 2.74 ($-\text{CH}_2\text{CH}_2-$ of *N*-succinimide), 3.31 ($\text{CH}_3\text{O-}$), 3.38-3.76 ($-\text{OCH}_2\text{CH}_2-$)₇₋₈, 4.13 ($-\text{COOCH}_2\text{CH}_2\text{O-}$).

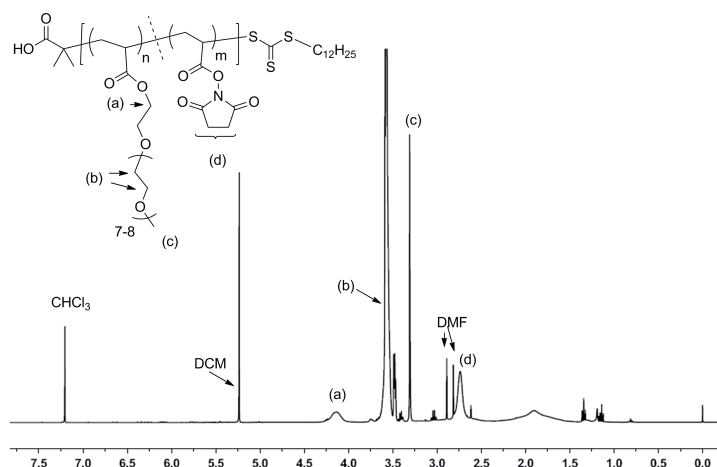
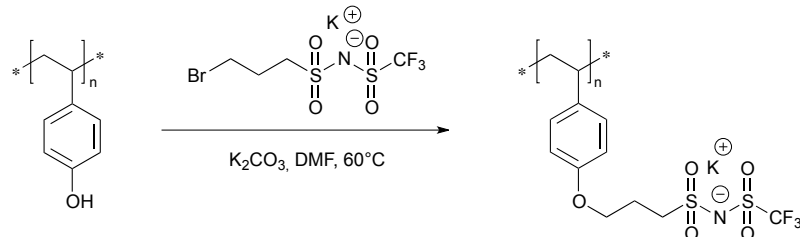


Figure S9: $^1\text{H NMR}$ spectrum of poly(poly(ethylene glycol)acrylate-*co*-*N*-succinimide acrylate) P(PEGA₂₉-*co*-NHSA₃₉) (**9**) in CDCl_3 .

6. Grafting of potassium 3-bromopropylsulfonyl (trifluoromethanesulfonyl)-imide onto the poly(4-vinylphenol)



Scheme S3: Synthesis of STFSI-functionalized poly(4-vinylphenol).

The commercial poly(4-vinyl phenol) ($M_{n,SEC} = 17400 \text{ g.mol}^{-1}$, $D = 1.65$, 0.06 g , $3.45 \times 10^{-6} \text{ mol}$), K_2CO_3 (0.30 g , $2.17 \times 10^{-3} \text{ mol}$) and DMF (4.0 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was stirred at room temperature for 1 h and then the solution of potassium 3-bromopropylsulfonyl (trifluoromethane)sulfonimide (0.21 g , $5.64 \times 10^{-4} \text{ mol}$) dissolved in 1.0 mL of DMF was added to the bottom flask. The reaction was reacted at room temperature for 1 h and then at 60°C for 24 h under argon. The product was purified by dialysis against demineralized water for three days using cellulose membrane with $M_{wCO} = 3500 \text{ g.mol}^{-1}$. The functional polymer was obtained by lyophilization. $M_{n,SEC} = 34200 \text{ g.mol}^{-1}$; $D = 1.40$. ^1H NMR (DMSO d_6 , δ ppm): $0.54\text{--}2.28$ ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$ and $(\text{CH}_2\text{--CH-})_n$), $2.90\text{--}4.10$ ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), $6.02\text{--}7.34$ ($-\text{C}_6\text{H}_4$). ^{19}F NMR (DMSO d_6 , δ ppm): -77.36 , -77.54 .

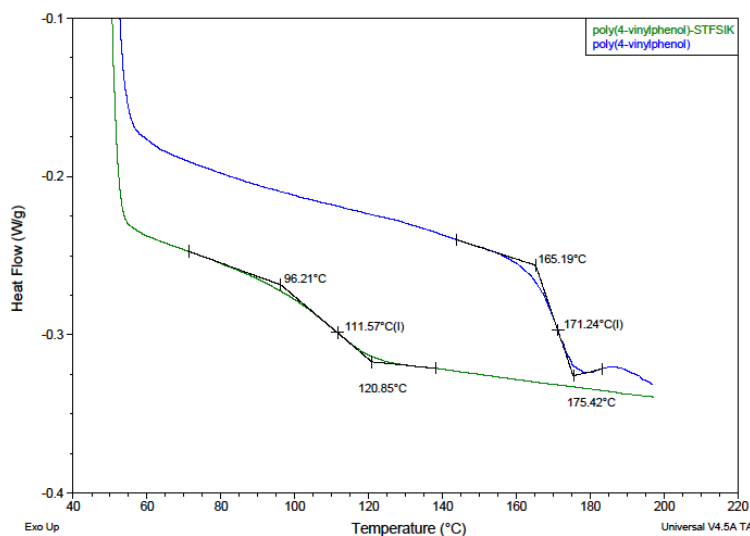


Figure S10: Superposition of DSC thermograms of poly(4-vinylphenol) and functional poly(4-vinylphenol)-STFSIK

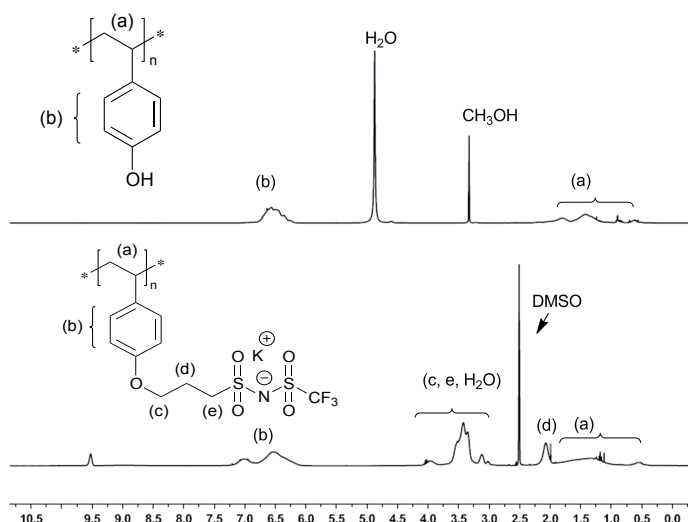
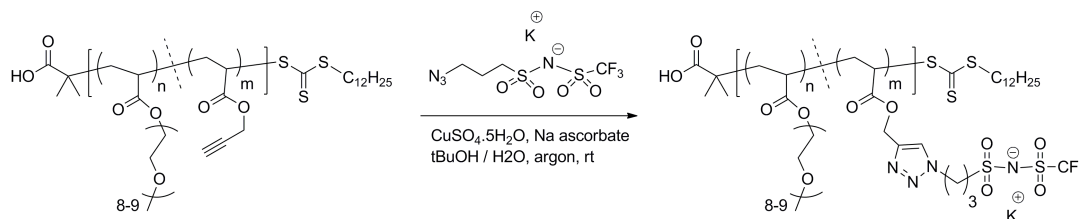


Figure S11: ^1H NMR spectra of (top) poly(4-vinylphenol) and (bottom) poly(4-vinylphenol) functionalized with $\text{C}_3\text{-STFSIK}$ in $\text{DMSO } d_6$.

7. Grafting of potassium 3-azidopropylsulfonyl (trifluoromethanesulfonyl)-imide onto the $\text{P}(\text{PEGA}_{13}\text{-co-PA}_{16})$ copolymer



Scheme S4: Synthesis of TFSI-functionalized $\text{P}(\text{PEGA-co-PA})$ copolymer.

$\text{P}(\text{PEGA}_{13}\text{-co-PA}_{16})$ copolymer ($M_{n,\text{NMR}} = 8365 \text{ g.mol}^{-1}$, $D = 1.20$, 0.10 g , $1.20 \times 10^{-5} \text{ mol}$) and $\text{N}_3\text{-C}_3\text{-STFSI}$ (4) (0.062 g , $1.86 \times 10^{-4} \text{ mol}$), *t*-butanol (2.50 mL) and copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 6.0 mg , $2.4 \times 10^{-5} \text{ mol}$) in ultra pure water (2.0 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was deoxygenated by bubbling argon for 30 min. To this solution, the deoxygenated solution of *L*-sodium ascorbate (10 mg , $5.05 \times 10^{-6} \text{ mol}$) in water (0.5 mL) was added to the bottom flask. The reaction was carried out at room temperature for 20 h under argon. The functional copolymer was purified using the same procedure as described above. $M_{n,\text{SEC}} = 23600 \text{ g.mol}^{-1}$; $D = 1.13$. ^1H NMR ($\text{DMSO } d_6$, δ ppm): 0.84 (t, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 1.22 ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S-}$), 2.99 ($-\text{CH}_2\text{SO}_2\text{NSO}_2\text{CF}_3$), 3.24 ($\text{CH}_3\text{O-}$), 3.35-3.76 ($(-\text{OCH}_2\text{CH}_2-)_8$).

9), 4.11 (-COOCH₂CH₂O-), 4.37-4.82 (-COOCH₂- and -CH₂CH₂CH₂SO₂NSO₂CF₃), 8.31 (-CH_{triazole}). ¹⁹F NMR (DMSO d₆, δ ppm): -77.52 ppm.

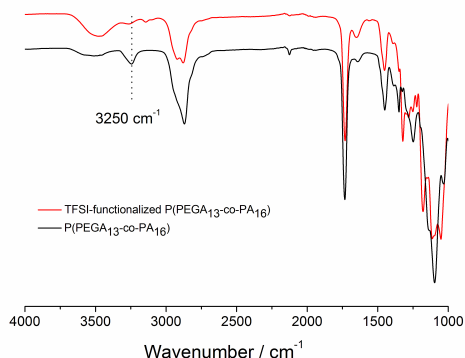
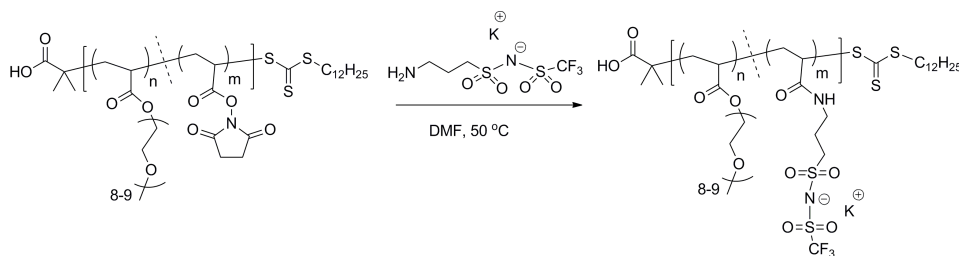


Figure S12: FT-IR spectra of P(PEGA-*co*-PA) copolymer before (black line) and after (red line) reaction with (3).

8. Grafting of 3-aminopropylsulfonyl (trifluoromethanesulfonyl)imide onto the P(PEGA₂₉-*co*-NHSA₃₉) copolymer



Scheme S5: Synthesis of STFSI-functionalized P(PEGA-*co*-STFSIA) copolymer.

P(PEGA₂₉-*co*-NHSA₃₉) copolymer ($M_{n,NMR}$ = 20876 g.mol⁻¹, \bar{D} = 1.24, 0.25 g, 1.20 x 10⁻⁵ mol) and DMF (2.0 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was deoxygenated by bubbling argon for 10 min. To this solution, the deoxygenated solution of (4) (0.12 g, 3.90 x 10⁻⁴ mol) in DMF (1.0 mL) was added in to the bottom flask. The reaction was then carried out at 50 °C under argon for 24 h. The functional copolymer was purified using the same procedure as described above. ¹H NMR (DMSO d₆, δ ppm): 1.78 (-CH₂CH₂SO₂NSO₂CF₃) 2.82-3.17 (-NHCH₂CH₂CH₂SO₂NSO₂CF₃), 3.24 (CH₃O-), 3.35-3.76 ((-OCH₂CH₂-)₇₋₈), 4.11 (-COOCH₂CH₂O-). ¹⁹F NMR (DMSO d₆, δ ppm): -77.52 ppm.

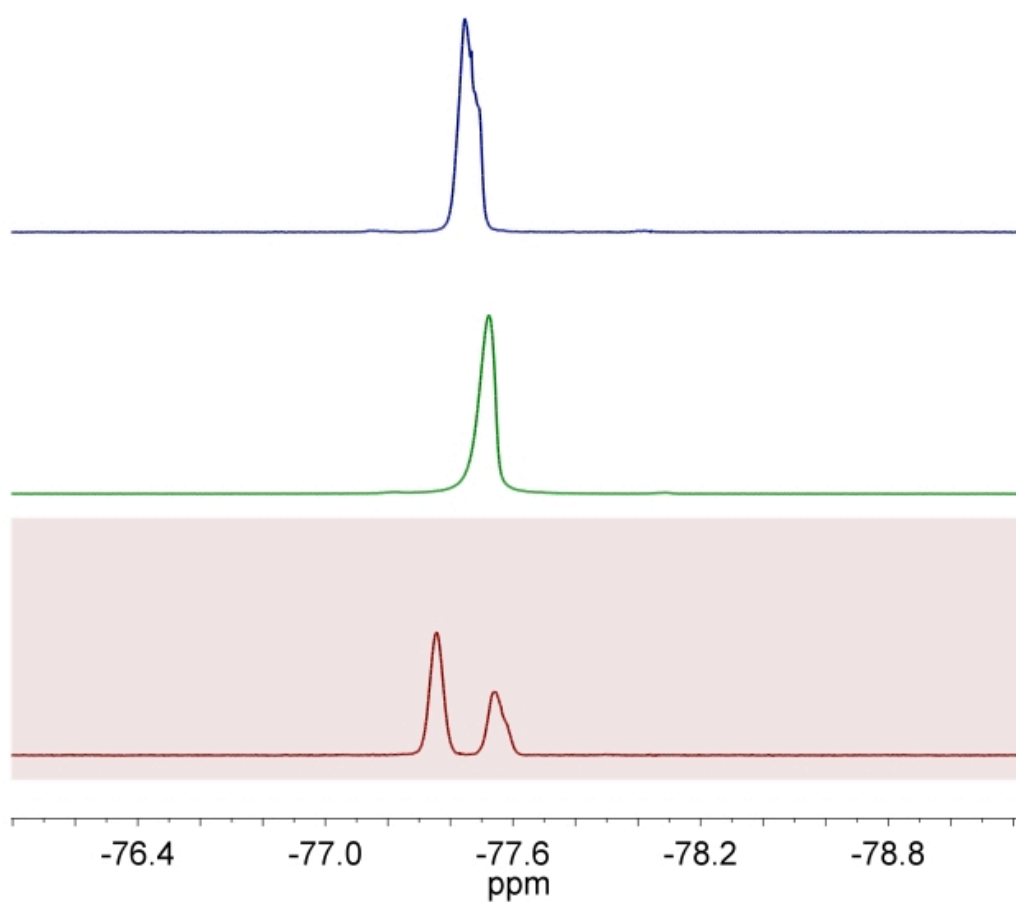


Figure S13: ^{19}F NMR spectra of (bottom) functional poly(4-vinylphenol)-STFSIK (**6**), (middle) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI triazol)methyl acrylate (**8**) and (top) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI)acrylamide (**10**)

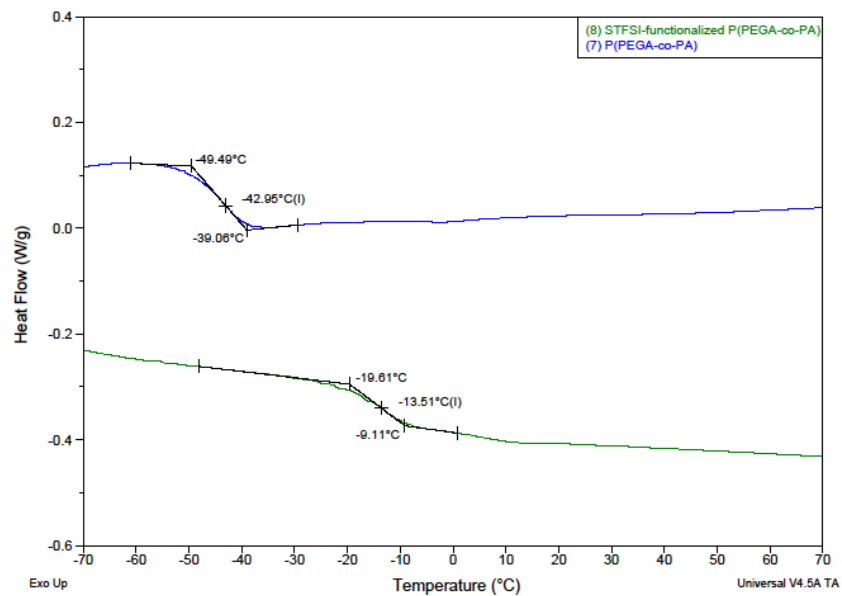


Figure S14: Superposition of DSC thermograms of (blue) poly(poly(ethylene glycol)acrylate-*co*-propargyl acrylate) (**7**) and (green) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI triazol)methyl acrylate (**8**).

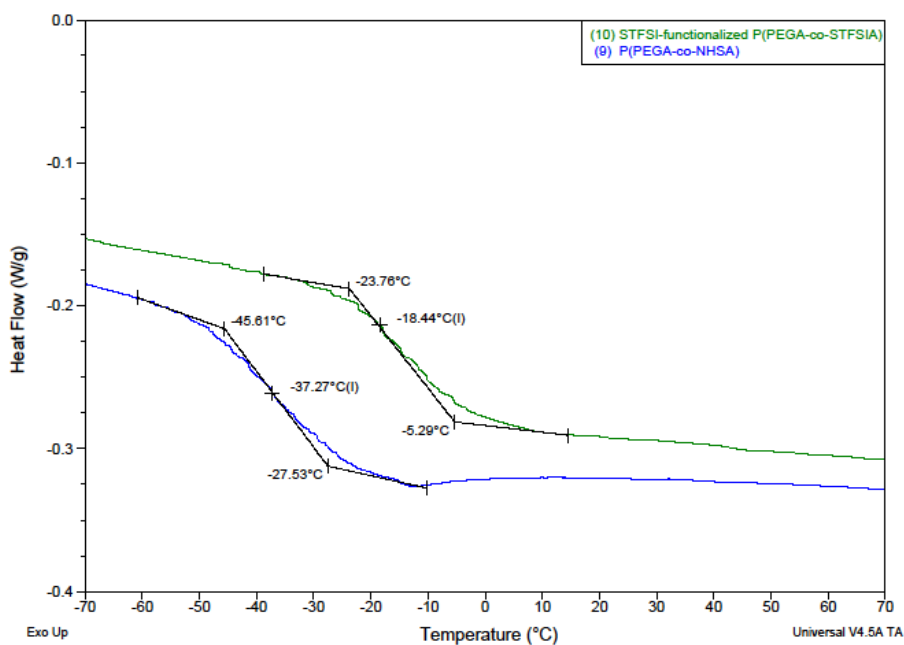


Figure S15: Superposition of DSC thermograms of (blue) poly(poly(ethylene glycol)acrylate-*co*-*N*-succinimide acrylate) (**9**) and (green) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI)acrylamide (**10**).

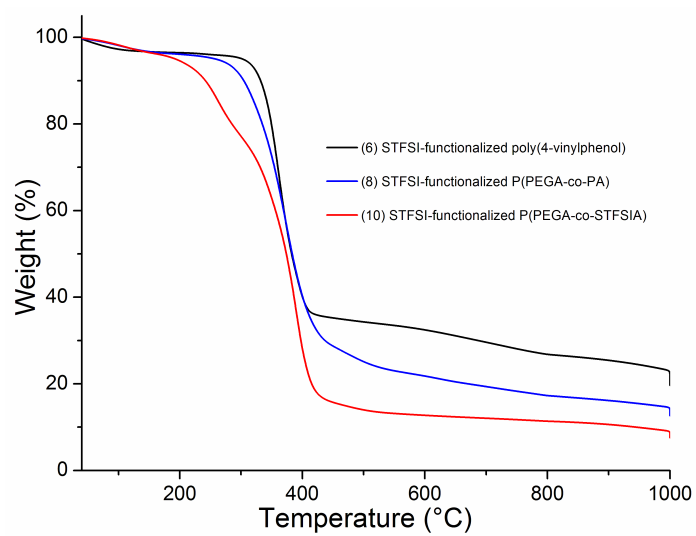


Figure S16: TGA thermograms of (black) STFSI functionalized poly(4-vinylphenol) **(6)**, (blue) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI triazol)methyl acrylate **(8)** and (red) functional poly(poly(ethylene glycol)acrylate-*co*-propyl STFSI)acrylamide **(10)**.