

Synthesis of Midblock-sulfonated Triblock Copolymers

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Supporting Information

Experimental

Materials. Styrene (Aldrich, 99%), hexyl methacrylate (HMA, Aldrich, 98%) and 1H, 1H, 2H, 2H-perfluorooctyl methacrylate (FMA, SynQuest Laboratories, Inc., 97%) were passed through an activated alumina column to remove inhibitors prior to use. Copper(I) bromide (CuBr, Fluka, > 98.0%), 2,2'-bipyridyl (bpy, Alfa Aesar, 99%), α, α' -dibromo-*p*-xylene (Aldrich, 97%), toluene (Mallinckrodt Chemicals, ACS), α, α, α -trifluoro toluene (TFT, Aldrich, $\geq 99\%$), tetrahydrofuran (THF, Mallinckrodt Chemicals, ACS), dimethylformamide (DMF, Mallinckrodt Chemicals, ACS), dichloroethane (EMD Chemicals, Omi Solv), acetic anhydride (Alfa Aesar, 97+%) and sulfuric acid (J.T. Baker, ACS) were used as received.

Synthesis of Difunctional Polystyrene Macroinitiators. Difunctional polystyrene macroinitiators were prepared via bulk ATRP of styrene in the presence of CuBr and bpy. A one-neck round-bottom flask was filled with styrene, CuBr, bpy and α, α' -dibromo-*p*-xylene as a initiator at α, α' -dibromo-*p*-xylene:CuBr:bpy = 1:4:8. Freeze-thaw cycles were performed using vacuum and argon 5 times. The reaction flask was placed in an oil bath and heated at 110 °C for

7 h (**Scheme 1 (1)**). The resultant reaction mixture became viscous over the course of the reaction. The resulting reaction mixture was precipitated into methanol and then filtered. The separated polystyrene was redissolved in THF and was precipitated into methanol and then filtered. This precipitation process was repeated for three times to remove residual styrene monomer. Finally, the filtered polystyrene was dried in a reduced pressure at 70 °C over night. ^1H NMR (400 MHz, CDCl_3 , δ): 1.0 – 2.6 ppm (br, $-\text{CH}_2-$, $-\text{CH}_2\text{CH}-$), 4.3 – 4.6 ppm (br, $-\text{CH}_2\text{CHBr}$), 6.0 – 7.4 ppm (br, aromatic protons).

Synthesis of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA Triblock Copolymers.

PHMA-*b*-PS-*b*-PHMA triblock copolymer was synthesized via ATRP. As similar to Br-PS-Br synthesis, a one-neck round-bottom flask was filled with Br-PS-Br toluene solution, HMA, CuBr, bpy at Br-PS-Br:CuBr:bpy = 1:4:8 and freeze-thaw cycles were performed using vacuum and argon 5 times. The reaction proceeded at 105 °C for 24 h (**Scheme 1 (2)**). The resulted reaction mixture was precipitated into methanol, filtered and the precipitation process was repeated for three times to remove residual HMA monomer. The filtered PHMA-*b*-PS-*b*-PHMA triblock copolymer was dried in a reduced pressure at 50 °C for 24 h.

PFMA-*b*-PS-*b*-PFMA triblock copolymer synthesis followed the same procedure as PHMA-*b*-PS-*b*-PHMA triblock copolymer synthesis, except using FMA as monomer and toluene:TFT = 1:1 as solvent (**Scheme 1 (2)**). ^1H NMR of PHMA-*b*-PS-*b*-PHMA (400 MHz, CDCl_3 , δ): 0.8 – 2.5 ppm (br, $-\text{CH}_2-$, $-\text{CH}_2\text{CH}-$, $-\text{C}(\text{CH}_3)-$), 3.8 – 4.1 ppm (br, $-\text{CH}_2\text{OCO}-$), 6.0 – 7.4 ppm (br, aromatic protons). ^1H NMR of PFMA-*b*-PS-*b*-PFMA (400 MHz, CDCl_3 + an aliquot of hexafluorobenzene, δ): 0.8 – 2.5 ppm (br, $-\text{CH}_2-$, $-\text{CH}_2\text{CH}-$, $-\text{C}(\text{CH}_3)-$), 4.2 – 4.5 ppm (br, $-\text{CH}_2\text{OCO}-$), 6.0 – 7.4 ppm (br, aromatic protons).

Sulfonation of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA Triblock Copolymers.

Sulfonation of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA was conducted using acetyl sulfate in 1,2-dichloroethane (**Scheme 1 (3)**). Acetyl sulfate solution was generated via the sequential addition of sulfuric acid and acetic anhydride in 1,2-dichloroethane at 0 °C.⁵ The amount of acetyl sulfate as well as reaction time was varied to achieve different degree of sulfonation (**Table S1, Table S2**). The reaction mixtures were precipitated in water, filtered, re-dissolved in THF, and then precipitated into water. The separated sulfonated triblock copolymers were dried in a reduced pressure at 50 °C for 48 h.

Polymer Characterization. ¹H NMR spectra of the polymers were obtained on a Bruker DRX-400 spectrometer using *d*-chloroform, *d*8-tetrahydrofuran or *d*6-dimethylsulfoxide (Cambridge Isotope) as a solvent. Size Exclusion Chromatography (SEC) was performed in a DMF with lithium bromide mobile phase equipped with a Waters 1515 isocratic HPLC pump. Glass transition temperatures (*T*_g) were determined using a differential scanning calorimeter (DSC) Q200 (TA Instruments) at a heating rate of 10 °C/min under nitrogen in the range of - 80 °C – 210 °C. Glass transition temperatures are reported as the onset and the transition midpoint during the second or third heat.

Small Angle X-Ray Scattering. SAXS measurements were made on a Rigaku (formerly Molecular Metrology) instrument equipped with a pinhole camera with Osmic microfocus source and parallel beam optic. The instrument is equipped with a Cu target ($\lambda = 1.542 \text{ \AA}$) and a multiwire area detector. Measurements were taken under vacuum at ambient temperature. Typical collection time was around 10 min.

Proton Conductivity. Proton conductivity measurements were performed using AC impedance spectroscopy on a Solartron SI 1260 Impedance/Gain-Phase Analyzer. The

conductivity of free-standing films was measured using a two-point, in-plane geometry at frequencies between 100 kHz and 100 Hz. Humidity and temperature were controlled using an Espec SH-241 humidity chamber. Temperature was held at 30 °C while relative humidity was varied from 20 % to 90 %. The impedance plot was linear at high frequencies and was extrapolated to the real axis to determine the membrane resistance. Proton conductivity (σ) was calculated using,

$$\sigma = \frac{l}{RA} \quad (1)$$

where l is the length between electrodes, R is the resistance of the membrane, and A is the cross-sectional area of the membrane available for ionic current. Membrane samples for conductivity ranged in thickness between 50 and 100 μm .

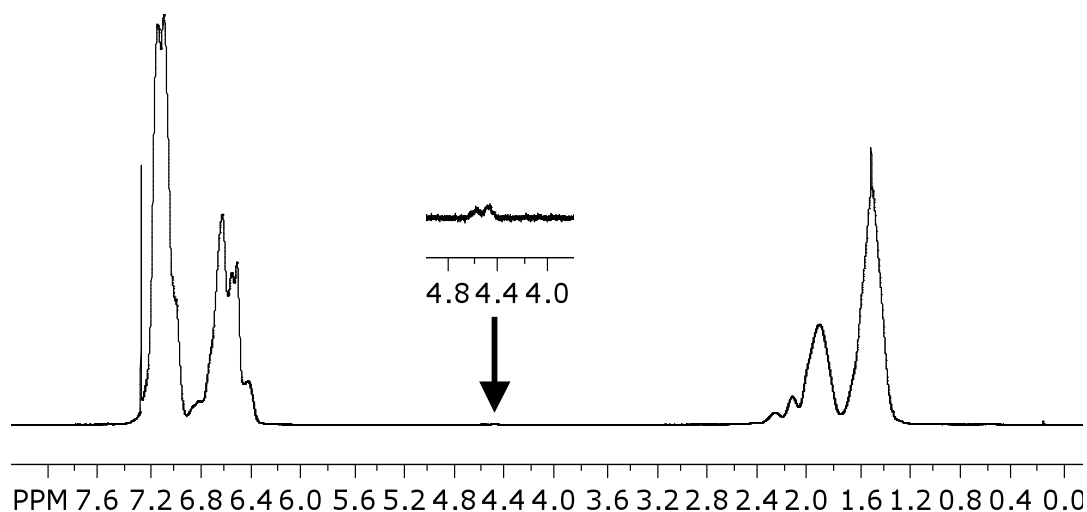


Figure S1. ¹H NMR Spectrum of Br-PS-Br.

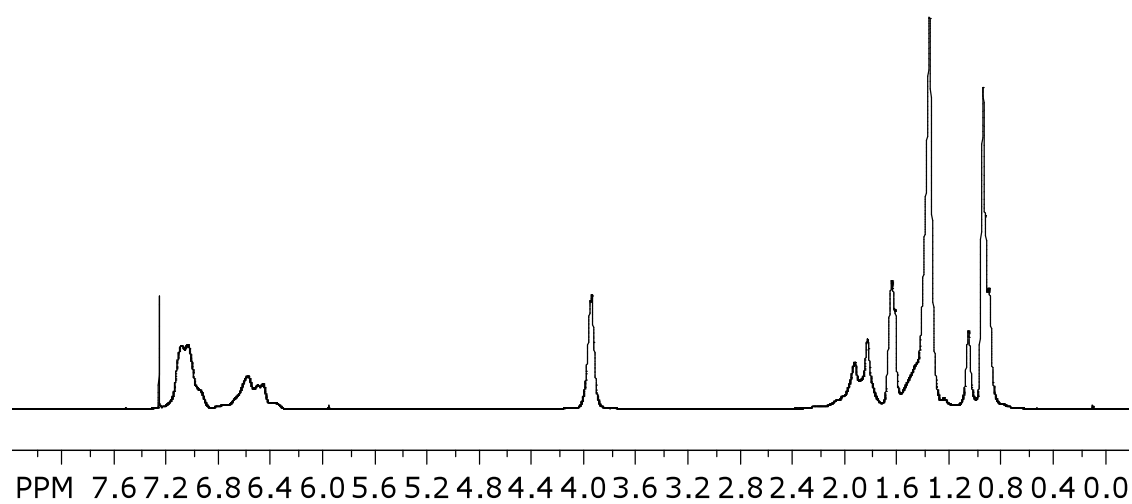


Figure S2. ^1H NMR spectrum of PHMA-*b*-PS-*b*-PHMA.

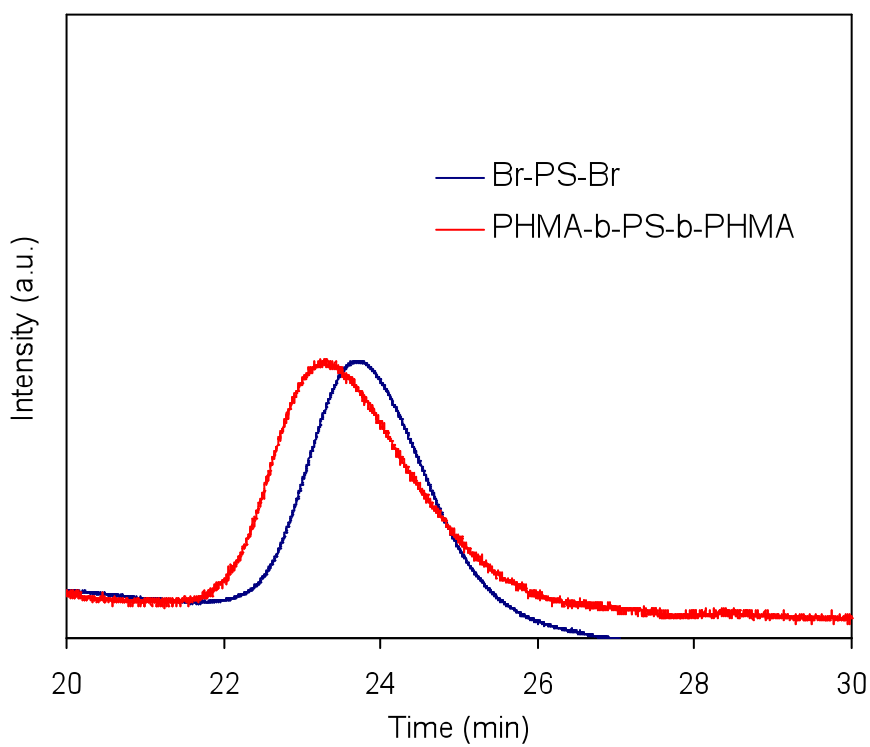


Figure S3. SEC curves of Br-PS-Br and PHMA-*b*-PS-*b*-PHMA.

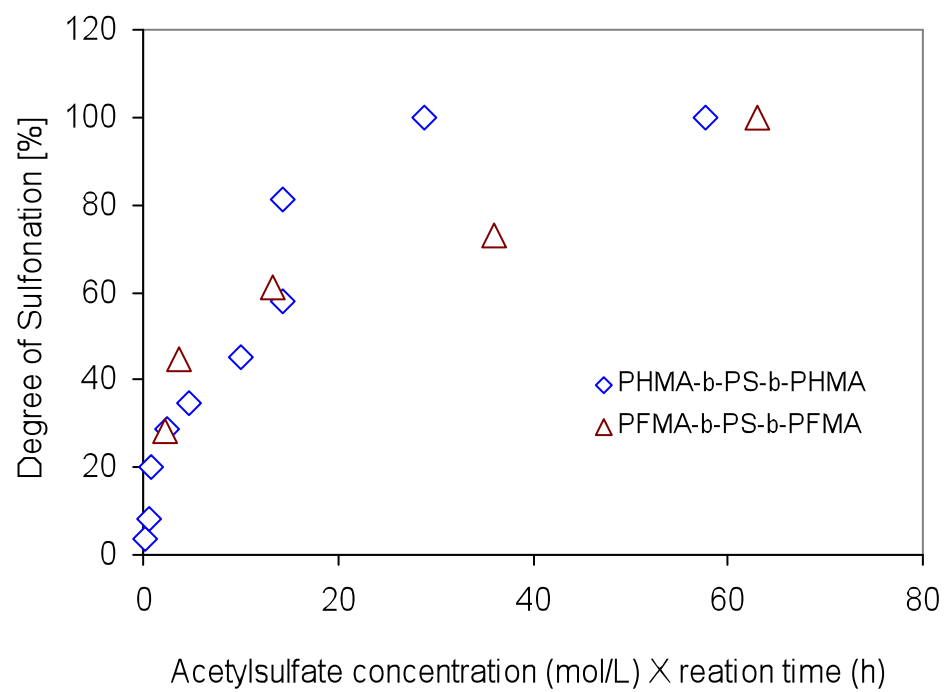


Figure S4. Degree of sulfonation controlled by acetylsulfate concentration and reaction time.

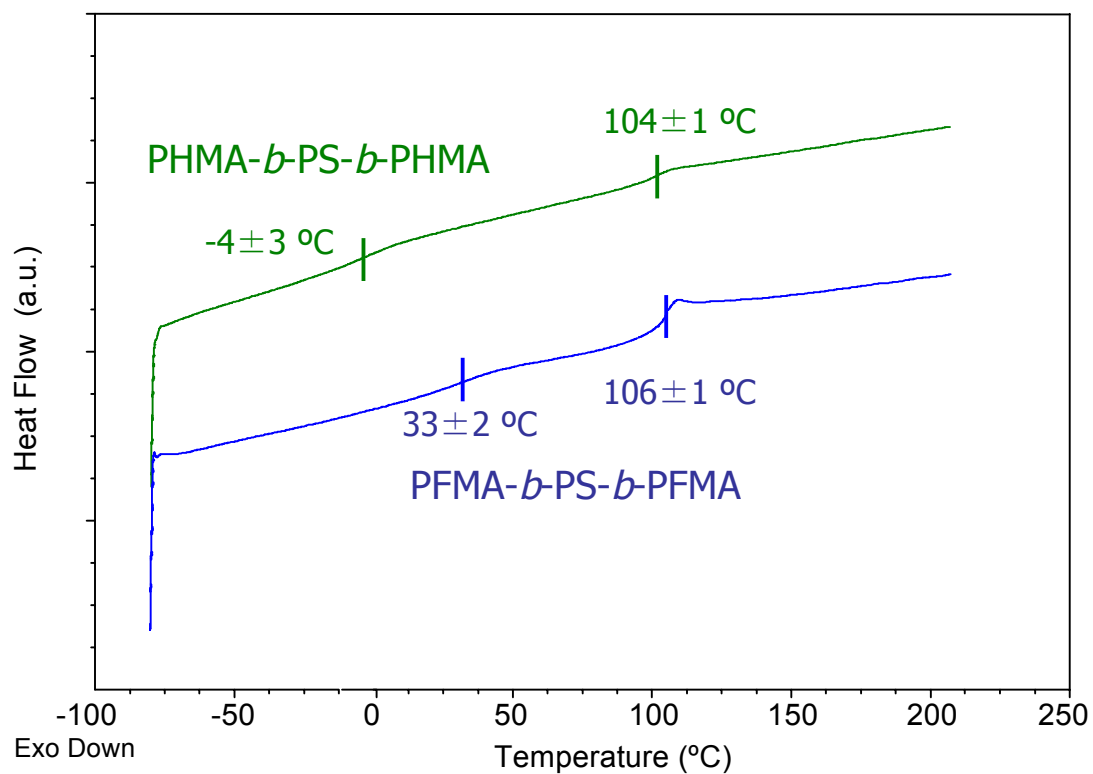


Figure S5. DSC thermograms of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA.

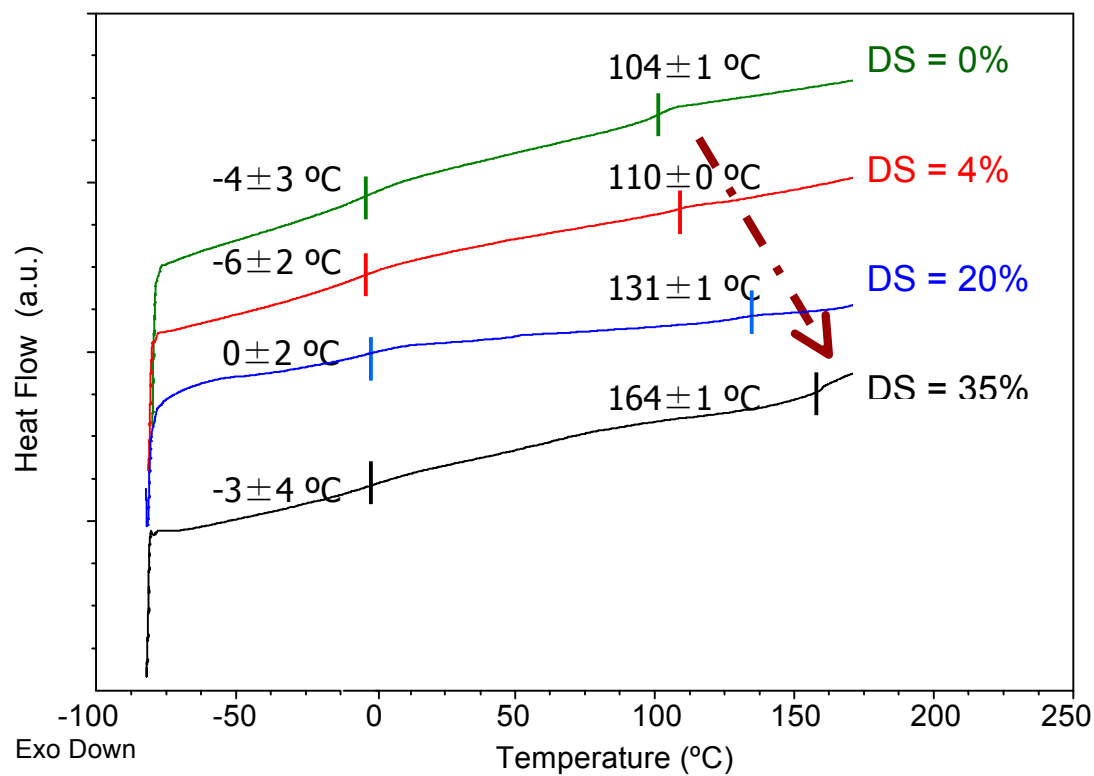


Figure S6. DSC thermograms of sulfonated PHMA-*b*-PS-*b*-PHMA.**Table S1.** Reaction conditions and properties of sulfonated PHMA-*b*-PS-*b*-PHMA.

Acetyl sulfate/PS [mol/mol]	Reaction time [h]	Degree of sulfonation [%]	IEC ^{NMR}	T _g ¹ [°C]	T _g ² [°C]	Casting Solvent
0	0	0	0	-4±3	104±1	1,4-Dioxane
0.25	6	3.8	0.13	-6±2	110±0	1,4-Dioxane
0.50	6	8.1	0.28	0±2	120±1	1,4-Dioxane
0.75	6	19.9	0.67	-3±2	131±3	1,4-Dioxane
0.50	24	28.7	0.94	-2±1	166±3	1,4-Dioxane
1.00	24	34.9	1.13	-3±4	164±1	1,4-Dioxane
1.40	36	45.1	1.42	0±4	N/A	1,4-Dioxane
1.00	72	57.9	1.76	-6±1	N/A	DMF
2.00	36	81.4	2.34	-2±4	N/A	DMF
2.00	72	100	2.76	-3±4	N/A	DMF
4.00	72	100	2.76	-3±2	N/A	DMF

Table S2. Reaction conditions and properties of sulfonated PFMA-*b*-PS-*b*-PFMA.

Acetyl sulfate/PS [mol/mol]	Reaction time [h]	Degree of sulfonation [%]	IEC ^{NMR}	T _g ¹ [°C]	T _g ² [°C]	Casting Solvent
0	0	0	0	33±2	106±1	TFT:Toluene=8:2
0.60	18	28.5	1.25	29±3	166±3	DMF:TFT=8.5:1.5
1.00	18	44.7	1.86	31±4	N/A	DMF:MeOH:TFT=7:2:1
1.00	67	61.2	2.41	N/A	N/A	DMF:MeOH:TFT=7:2:1
2.00	90	73.1	2.78	28±9	N/A	DMF:MeOH:TFT=5:4:1
3.50	90	100	3.51	36±6	N/A	DMF:MeOH=2:8