

Supporting Information

Para-fluoro/thiol click chemistry-driven pentafluorostyrene-based block copolymers self-assembly: to mimic or not to mimic the solubility parameter?

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Experimental Section

Materials

Styrene (Aldrich) was purified by stirring through inhibitor remover and was kept in a refrigerator. The Bloc Builder® alkoxyamine and the nitroxide radical (SG1 solution) were obtained from ARKEMA. 2,3,4,5,6-Pentafluorostyrene, 1-hexanethiol (95%), 1-decanethiol (96%), 2-aminoethanethiol or cysteamine (95%), amylamine (99%) and 1,8-diazobicycloundec-7-ene (DBU) (98%) were purchased from Aldrich and were used as received. Anhydrous *N,N*-dimethylformamide (DMF) was purchased from Aldrich.

Characterization

The molar mass and molar mass distribution of the polymers were determined by size exclusion chromatography (SEC) using THF as eluent with a flow rate of 1.0 mL min⁻¹ at 30 °C. The SEC is equipped with a Viscotek VE 5200 automatic injector, a precolumn and two columns (Styragel HR 5E and 4E (7.8 ft, 300 mm)) and 4 detectors: UV-visible spectrophotometer (Viscotek VE 3210), a Multiangle Light Scattering detector (Wyatt Heleos II), a viscometer (Wyatt Viscostar II) and a refractive index detector (Viscotek VE 3580). The MW and dispersity of the polymers were

determined by using refractive index detector (Viscotek VE 3580) and polystyrene standards. SEC using DMF as solvent with a flow rate of 0.5 mL min⁻¹ was used to determine the molecular weight (MW) and molecular weight distribution (MWD) of the cysteamine modified BCP. Poly(methyl methacrylate) (PMMA) standards were used for the analysis.

¹H and ¹⁹F NMR spectra were recorded in a 400 MHz Bruker spectrometer at 25 °C. CDCl₃ and tetramethylsilane (TMS) were used as solvent and internal reference respectively.

Atomic force microscopy (AFM) was carried out using MultiMode® 8 Atomic Force Microscope from Bruker in a PeakForce Quantitative NanoMechanics QNM mode. The polymers were dissolved in toluene at ambient temperature to yield a 2.0 wt% solution. The thin films were prepared by spin coating the polymer solution onto the Si wafers at 2000 Tpm for 60 s.

The Small angle X-ray scattering (SAXS) measurements were conducted using a high-resolution X-ray spectrometer Xeuss 2.0 from Xenox. The spectrometer operates with a radiation wavelength of $\lambda = 1.54 \text{ \AA}$ (Copper K _{α} radiation). Scattering patterns were collected using a PILATUS 300K Dectris detector with a sample-to-detector distance of 1637 mm. The collected data were analyzed using Primus software. The film preparation for the SAXS experiment was done in a similar way than for the AFM analysis. The polymers were dissolved in toluene (2.0 wt%) and drop casted on a Kapton film. The SAXS intensity, I , is described as a function of the magnitude of the scattering vector, q ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle).

Differential scanning calorimetry (DSC) analysis was carried out using TA instrument (Model Q100, V9.9) with a heat-cool-heat programme following 40 °C to 150 °C and then cooled to -80 °C followed by heating to 150 °C at a heating rate of 10 °C/min for the homopolymers and 20 °C/min for the block copolymers respectively .

Synthetic procedures

Polymerization of styrene by NMP: In a typical procedure, styrene (15 g, 144 mmol), Bloc Builder (0.0785 g, 0.2 mmol) and the nitroxide radical (SG1 solution) (0.03 mmol, 15% wrt initiator) were taken in a 50 mL RB flask. The flask was sealed by a septum and kept in an ice bath. The solution was degassed by N₂ gas for 25 min and put into a preheated oil bath at 115 °C

for 4h. The mixture containing polymer and unreacted styrene was precipitated in methanol for two times. The polymer was dried in vacuum oven at 40 °C for 48h ^1H NMR (CDCl_3) (δ/ppm) = 7.2-6.9 (3H, *meta* & *para*), 6.8-6.3 (2H, *ortho*), 2.2-1.7 (1H, -CH-) and 1.6-1.3 (2H, -CH₂) (conversion was 45%, determined by ^1H NMR).

Synthesis of poly(styrene-*b*-pentafluorostyrene) (PS-*b*-PPFS) block copolymer: In a RB flask, PS macroinitiator (0.335 g, 0.012 mmol) was dissolved in 0.82 mL DMF. The PFS (0.6 g, 3.1 mmol) and SG1 (0.0018 mmol) were added to the flask. The flask was closed by septum and purged by N₂ gas. The mixture was stirred at 115 °C for 2h. THF was added to dilute the viscous polymer followed by precipitation in methanol. The polymer was re-dissolved in THF and re-precipitated in methanol and then dried in vacuum at 40 °C for 48h. ^1H NMR (CDCl_3) δ/ppm = 7.2-6.9 (3H, *meta* & *para*), 6.8-6.3 (2H, *ortho*), 1.7-1.2 (2H, -CH₂-) for PS and 2.9-2.7 and 2.5-2.3 (1H, -CH-) for PPFS, whereas 2.1-1.7 are overlapped by -CH- and -CH₂- protons of PS and PPFS respectively. The molar composition of the block copolymers were determined using ^1H NMR spectroscopy by comparing the integral areas at δ/ppm = 6.8-6.3 (2H, *ortho*) of PS and 2.9-2.7 and 2.5-2.3 (1H, -CH-) of PPFS and were measured to be 80% and 20% for PS and PPFS blocks are respectively. The weight fractions of PS and PPFS were measured to be 68 and 32 respectively and were calculated by multiplying the individual molar mass of the repeating units (104.15 and 194.1 g/mol for St and PFS, respectively) with the molar composition (80/20 in St/PFS) determined from the ^1H NMR divided by the total weight. Using the same method the weight fractions of the modified polymers were calculated.

Para-fluoro/thiol click reaction: In a typical procedure, PS-*b*-PPFS (0.075g, 0.123 mmol wrt PFS unit) was dissolved in 1.5 ml of anhydrous DMF in a 10 ml RB flask. The flask was sealed by a septum and the solution was degassed by N₂ gas. To the solution, thiol (0.116 mmol, 0.94 eqv) and 1,8-diazobicycloundec-7-ene (DBU) (0.111 mmol, 0.90 eqv) were added and the solution was stirred for 6 h at room temperature. The polymer mixture was precipitated in methanol and dried in vacuum at 40 °C for 48h.

To completely substitute the *para*-fluorine by hexanethiol, \approx 1: 1.25: 1.20 equivalent of PPFS, hexanethiol and DBU were used keeping other reaction conditions fixed.

To achieve 90% *para*-fluoro substitution in cysteamine-modified PS-*b*-PPFS, ≈1: 1.50: 1.40 equivalent of PPFS, cysteamine and DBU were used using 3 mL of anhydrous DMF and 24h of stirring.

¹H NMR (1-hexanethiol) (400 MHz, CDCl₃), δ/ppm = 6.3-7.2 (5 aromatic protons of PS), 2.9 (2H, -SCH₂-), 1.2-2.5 (different aliphatic protons) and 0.9 (3H, -CH₃); ¹⁹F NMR (CDCl₃), δ/ppm = -134 (2 F, *meta*'), -143 (2 F, *ortho*), -154 (unreacted *para* F) and -161 (2 F, *meta*).

¹H NMR (1-decanethiol) (400 MHz, CDCl₃), δ/ppm = 6.3-7.2 (5 aromatic protons of PS), 2.9 (2H, -SCH₂-), 1.2-2.5 (different aliphatic protons) and 0.9 (3H, -CH₃); ¹⁹F NMR (CDCl₃), δ/ppm = -134 (2 F, *meta*'), -143 (2 F, *ortho*), -154 (unreacted *para* F) and -161 (2 F, *meta*).

In case of cysteamine substituted PS-*b*-PPFS, the polymer solutions were precipitated in a mixture of n-hexane and ether (1:1), and the polymers were used for different analysis.

¹H NMR (cysteamine) (400 MHz, CDCl₃), δ/ppm = 6.3-7.2 (5 aromatic protons of PS), 3.0 (2H, -CH₂-NH₂), 2.8 (2H, -SCH₂-) and 1.2-2.5 (different aliphatic protons); ¹⁹F NMR (CDCl₃), δ/ppm = -134 (2 F, *meta*'), -143 (2 F, *ortho*), -154 (unreacted *para* F) and -161 (2 F, *meta*).

Amine-*para*-fluorine click reaction: A similar reaction like thiol-*para*-fluorine click reaction of PS-*b*-PPFS with amylamine was carried out in presence of DBU, but no substitution reaction was observed from the ¹⁹F spectroscopy.

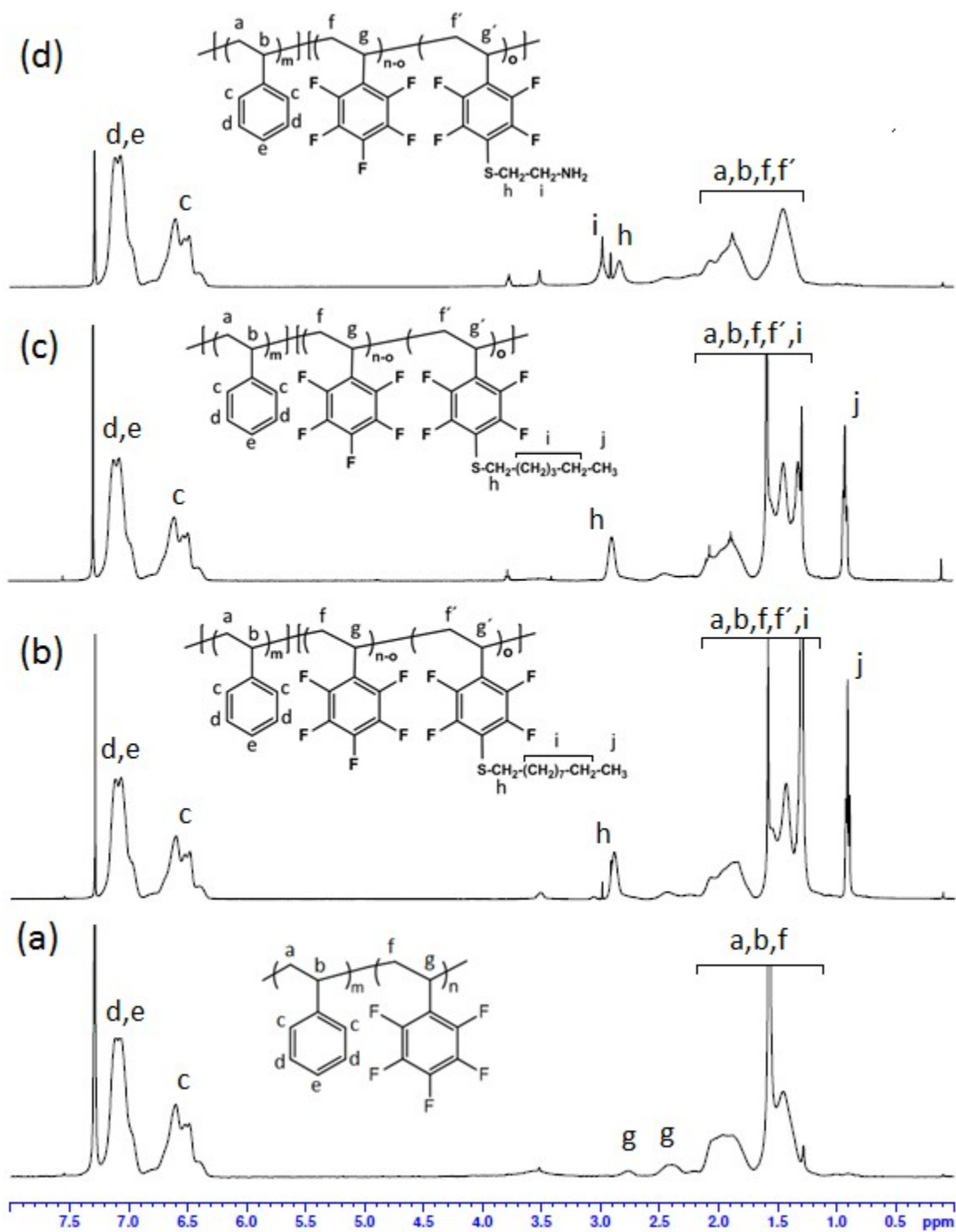


Figure S1. ^1H NMR spectra of (a) PS-*b*-PPFS, (b) decanethiol, (c) hexanethiol and (d) cysteamine substituted BCP.

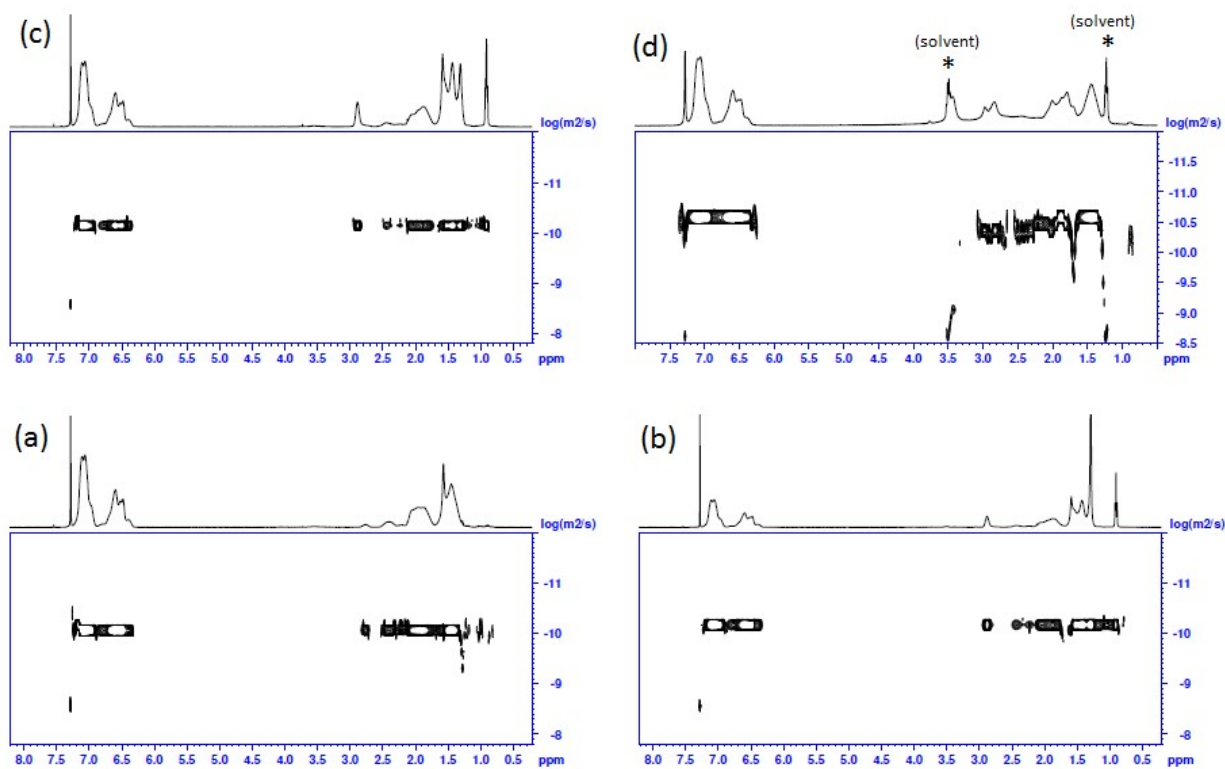


Figure S2. DOSY NMR spectra of (a) PS-*b*-PPFS, (b) decanethiol, (c) hexanethiol and (d) cysteamine substituted BCP.

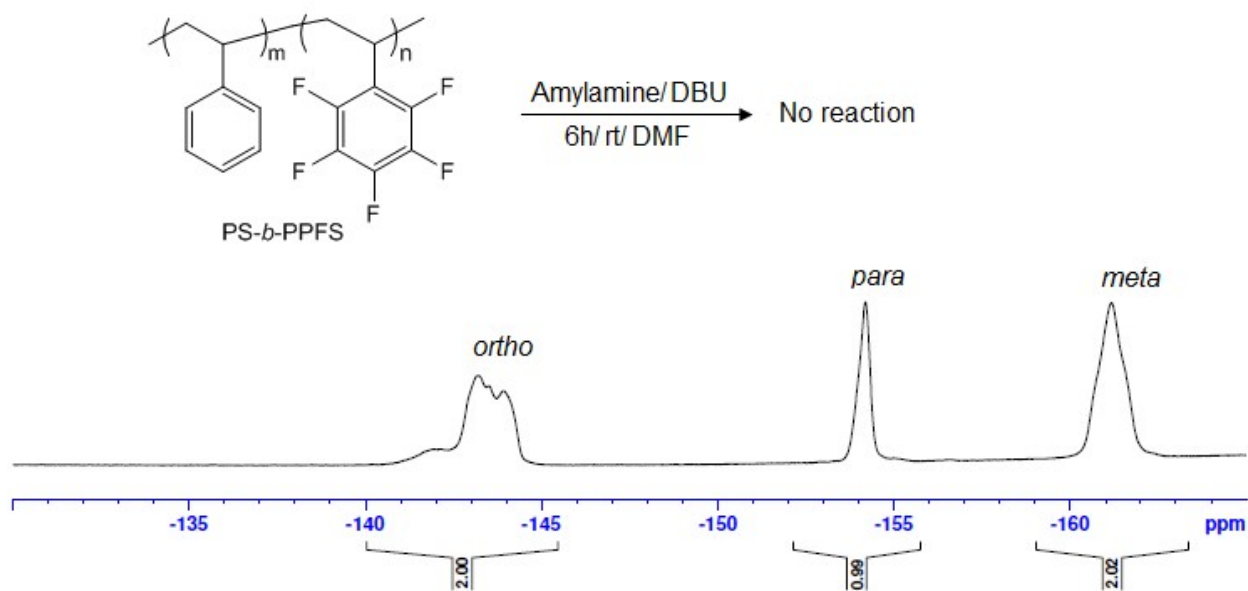


Figure S3. ^{19}F NMR spectrum of the unreacted PS-*b*-PPFS.

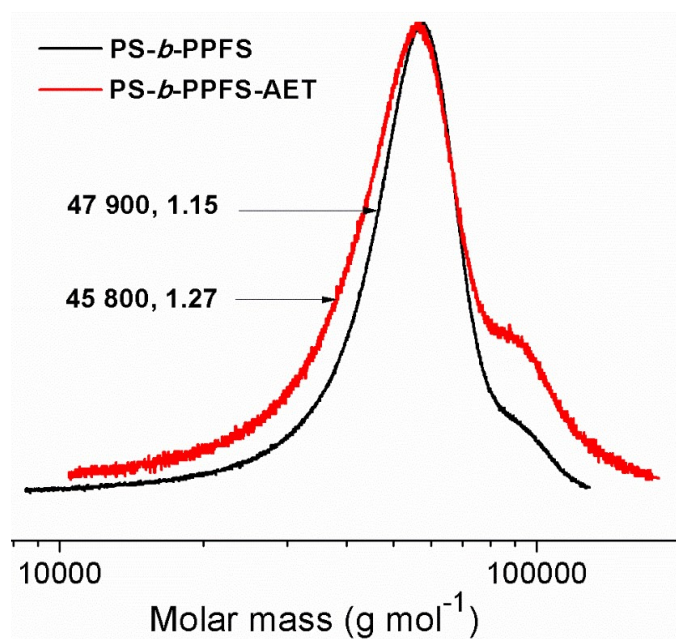


Figure S4. SEC traces of PS-*b*-PPFS and PS-*b*-PPFS-AET using DMF as eluent.

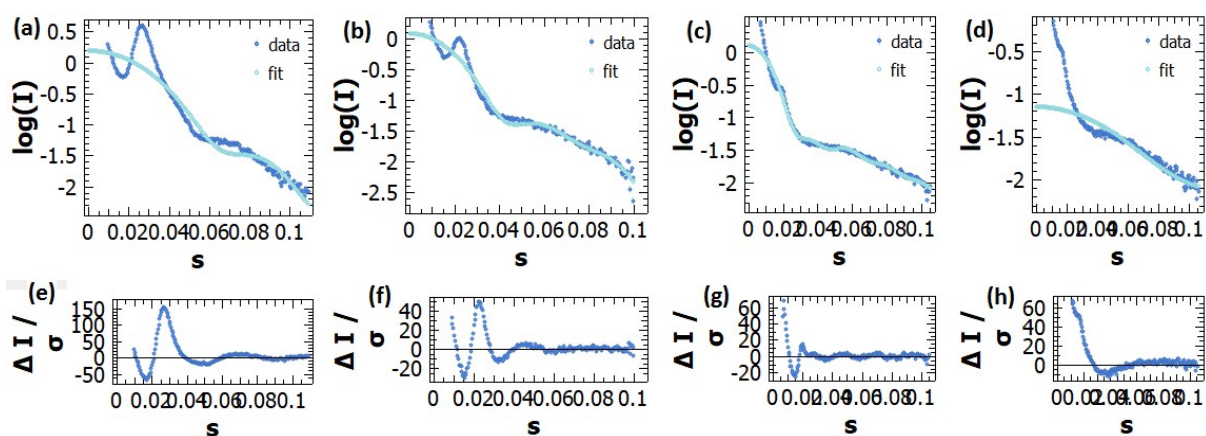


Figure S5. Primus distance distribution curves of (a,e) PS-*b*-PPFS, (b,f)PS-*b*-PPFS-AET, (c,g) PS-*b*-PPFS-HT and (d,h) PS-*b*-PPFS-DT.

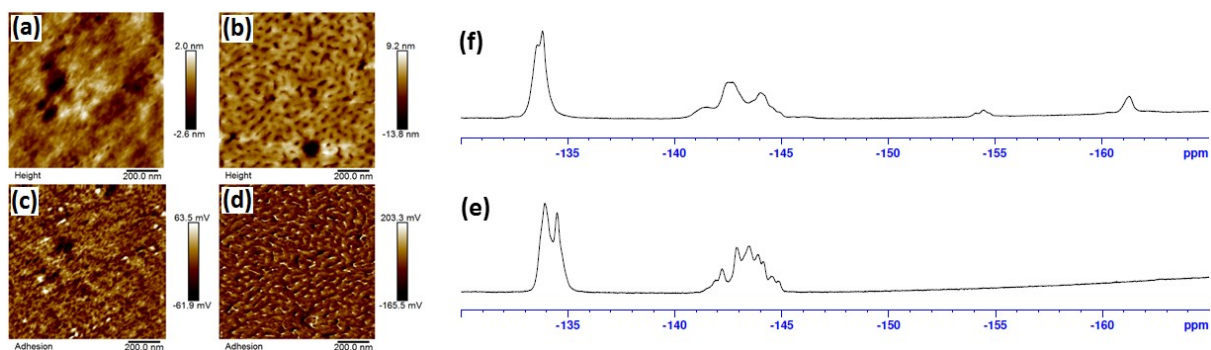


Figure S6. AFM height and adhesion images of (a,c) completely substituted PS-*b*-PPFS-HT and (b,d) PS-*b*-PPFS-AET at 90% *para*-fluoro substitution; (e) and (f) are their corresponding ^{19}F NMR spectrum respectively.

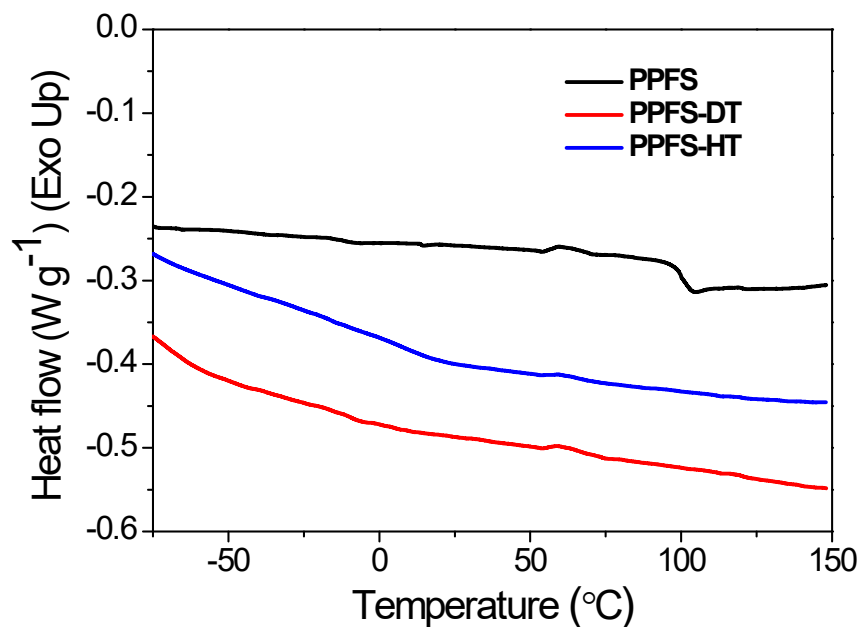


Figure S7. DSC thermograms of PPFS ($M_{nSEC} = 14\,500\text{ g mol}^{-1}$) and modified homologues (second heating scan).

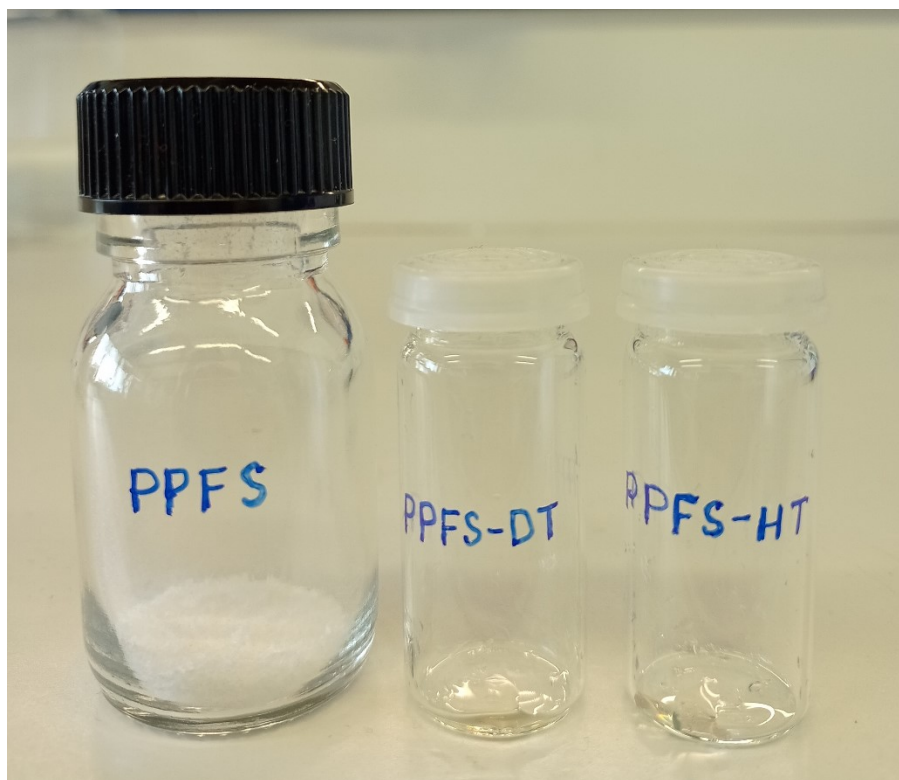


Figure S8. Visual appearances of poly(pentafluorostyrene) (PPFS) and after modification by decanethiol (PPFS-DT) and hexanethiol (PPFS-HT).

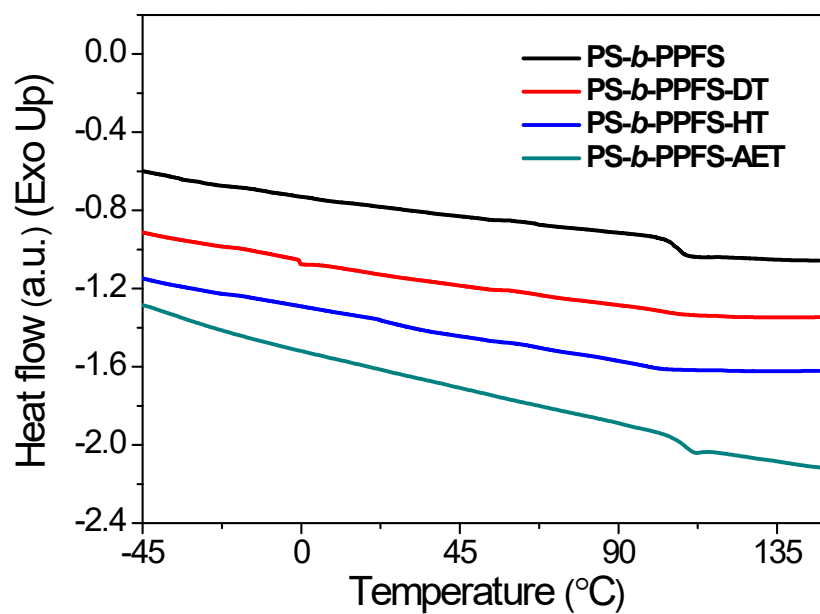


Figure S9. DSC thermograms of pristine and modified PS-*b*-PPFS block copolymer homologues (second heating scan).