

Supplementary Material

Honeycomb films from perfluoropolyether-based star and micelle architectures

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Experimental

Materials.

tert-Butyl acrylate (*t*BA) (99 %), ethylene glycol diacrylate (EGDA) (90 %, technical grade) were purchased from Sigma-Aldrich and stirred with inhibitor remover (Sigma-Aldrich) for 18 h and filtered before use. 2-Bromo*isob*utyryl bromide (98 %), copper(I) bromide (CuBr) (98 %), *N,N,N',N'N''*-pentamethyldiethylenetriamine (PMDETA) (99 %), α,α,α -trifluorotoluene (≥ 99.0 %) and perfluorobenzoic acid (PFBA) were purchased from Sigma-Aldrich and used as received. Activated neutral aluminium oxide was purchased from Merck. 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) was purchased from Santa Cruz Biotechnology. Potassium trifluoroacetate (KTFA) (≥ 99.0 %) was purchased from

Fluka. Sodium chloride (NaCl), toluene (HPLC grade), *N,N*-dimethylformamide (DMF), chloroform (CHCl₃) (AR grade) and methanol (MeOH) (AR grade) were purchased from Chem-Supply and used as received. Triethylamine (TEA) (LR grade, Chem-Supply) was distilled from CaH₂ prior to use. Argon (UHP) was purchased from BOC, Australia. Copper TEM grids (300 mesh) were purchased from ProSciTech Pty Ltd.

Measurements.

Gel permeation chromatography (GPC) was performed on a Shimadzu liquid chromatography system fitted with a Wyatt DAWN HELEOS LS detector ($\lambda = 658$ nm), Shimadzu RID-10 refractometer ($\lambda = 633$ nm) and Shimadzu SPD-20A UV-Vis detector, using three identical Polymer Laboratories PLgel columns (5 μ m, MIXED-C) and DMF with 0.05 M LiBr (70 °C, 1 mL/min) as mobile phase. ASTRA software (Wyatt Technology Corp.) was used to process the data using either known dn/dc values or based upon 100 % mass recovery of the polymer where the dn/dc value was unknown. MALDI ToF MS was performed on a Bruker Autoflex III Mass Spectrometer operating in positive/linear mode. For analysis of polymers **1** and **2** the samples were deposited onto the target plate via a thin layer method. Firstly, 0.3 μ L of a saturated NaCl solution in methanol was spotted onto the plate and allowed to air dry. Secondly, 0.1 μ L of a solution containing the analyte (1 mg/mL) and matrix (PFBA; 10 mg/mL) dissolved in 1,1,1,3,3,3-hexafluoropropan-2-ol was spotted on top and allowed to air dry before analysis. For analysis of polymer **3** a dried droplet method was employed, whereby the analyte, matrix (DCTB) and cationisation agent (KTFA) were dissolved in THF at concentrations of 10 mg/mL, 10 mg/mL and 1 mg/mL, respectively, and then mixed in a ratio of 10:1:1. 0.3 μ L of this solution was

then spotted onto a ground steel target plate and the solvent allowed to evaporate prior to analysis. ^1H NMR spectroscopy was performed on either a Varian Unity400 (400 MHz) or Bruker AV-500 (500 MHz) spectrometer using the deuterated solvent or an external standard as reference. ^{13}C NMR spectroscopy was performed on either a Varian Unity400 (100 MHz) or Bruker AV-500 (126 MHz) spectrometer using the deuterated solvent or an external standard as reference. ^{19}F NMR spectroscopy was performed on a Bruker AV-200 (186 MHz) spectrometer using CFCl_3 as reference. Contact angle measurements were conducted with Data Physics OCA 20 Tensionmeter. Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano ZS with a maximum power of 4.0 mW He-Ne laser operated at 632.8 nm. HC films were imaged by SEM using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging.

Procedures.

Synthesis of PFPE-Br 2: A suspension of monohydroxy PFPE **1** ($M_n = 1.65$ kDa, 15.0 g, 9.09 mmol) in α, α, α -trifluorotoluene (5 mL) was cooled to 0 °C under argon and a solution of 2-bromoisobutryl bromide (1.55 mL, 13.63 mmol) in trifluorotoluene (5 mL) was added dropwise over 0.5 min. The reaction mixture was stirred at 0 °C for 3 h followed by 18 h at room temperature. The mixture was allowed to phase separate and the bottom layer was collected and washed with saturated NaHCO_3 solution (2×100 mL) and water (2×100 mL). The organic phase was concentrated *in vacuo* to afford **2** as a clear oil (12.8 g; 78 %), which was stored at < 5 °C until required. MALDI ToF MS: $M_n = 1.8$ kDa, PDI = 1.08; ^1H NMR (neat, 500 MHz, TMS external standard) δ_{H} 1.40 (*s*, 6H, $\text{C}(\text{CH}_3)_2$ end group), 4.13-4.34 (*m*, 2H, CH_2O end group)

ppm; ^{13}C NMR (neat, 126 MHz, TMS external standard) δ_{C} 28.6 (*s*, 2 CH_3 end group), 51.3 (*s*, $\text{C}(\text{CH}_3)_2$ end group), 59.7 (*d*, $\text{OCF}(\text{CF}_3)\text{CH}_2\text{O}$ end group), 97.5-127.0 (*m*, $(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ end group & $\text{OCF}(\text{CF}_3)\text{CH}_2\text{O}$ end group), 168.9 (*s*, $\text{C}=\text{O}$) ppm. ^{19}F NMR (neat, 186 MHz, CFCl_3 external standard) δ_{F} -147.5 to -146.6 (*m*, $(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n$), -136.2 to 135.7 (*m*, $\text{OCF}(\text{CF}_3)\text{CH}_2\text{O}$ end group), -132.4 (*m*, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ end group), -85.8 to -85.6 (*m*, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ end group), -84.5 (*m*, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ end group), -84.1 to -81.5 (*m*, $(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n$ & $\text{OCF}(\text{CF}_3)\text{CH}_2\text{O}$ end group) ppm.

*Synthesis of PFPE-*b*-PtBA copolymer 3:* PFPE-Br **2** ($M_n = 1.8$ kDa, 300 mg, 0.167 mmol, 1 equiv.), PMDETA (35 μL , 0.167 mmol, 1 equiv.) and *t*BA (1.96 mL, 13.36 mmol, 80 equiv.) were dissolved in a 1:1 toluene:trifluorotoluene solution to afford a total monomer concentration of 2.7 M. The solution was then added to a dried Schlenk tube complete with stirrer bar. The mixture was subjected to three freeze-pump-thaw cycles and backfilled with argon. The Schlenk tube was then immersed in liquid nitrogen and once the solution had frozen CuBr (24 mg, 0.167 mmol) was added under a flow of argon. Another three freeze-pump-thaw cycles the Schlenk tube was backfilled with argon and the mixture stirred at room temperature for 10 mins to ensure homogeneity. The reaction mixture was then heated at 80 °C for 8 h. The reaction mixture was diluted with CHCl_3 (1 mL) and passed through a column of basic Al_2O_3 to remove the copper catalyst. The filtrate was precipitated into methanol (50 mL), collected via centrifugation and dried *in vacuo* (0.1 mbar, 50 °C) to afford PFPE-*b*-PtBA copolymer **3**, 1.62g (80 %). GPC-MALLS: $M_n = 10.2$ kDa, PDI = 1.10; MALDI ToF MS: $M_n = 9.8$ kDa, PDI = 1.01; ^1H NMR (CDCl_3 , 400 MHz) δ_{H} 1.28 (*s*, $\text{C}(\text{CH}_3)_2$ end group). 1.29-1.61 (*m*, $\text{C}(\text{CH}_3)_3$ & CH_2), 1.81 (*br s*, CH_2), 2.22 (*br s*,

CH), 4.04-4.18 (*m*, **CHBr** end group), 4.55-4.76 (*m*, **CH₂O** end group) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ_C 27.7-28.1 (*m*, **CH₃**), 34.9-37.5 (*m*, **CH₂**), 41.4-42.3 (*m*, **CH**), 80.3-80.4 (*m*, **C(CH₃)₃**), 173.6-174.1 (*m*, **C=O**) ppm.

*Synthesis of PFPE-*b*-PtBA CCS polymer 4*: PFPE-*b*-PtBA **3** (*M_n* = 10.2 kDa, 50 mg, 0.005 mmol, 1 equiv.), PMDETA (1 μL, 0.005 mmol, 1 equiv.) and EGDA (12 μL, 0.075 mmol, 15 equiv.) were dissolved in a mixture of toluene:trifluorotoluene with different ratios (a) 1:0; b) 1:1; c) 1:2; d) 1:10) to afford a total cross-linker concentration of 0.005 M. The solution was then added to the dried Schlenk tube complete with stirrer bar. The mixture was subjected to three freeze-pump-thaw cycles and backfilled with argon. The Schlenk tube was then immersed again in liquid nitrogen and once the solution had frozen CuBr (1.4 mg, 0.01 mmol) was added under a flow of argon. Another three freeze-pump-thaw cycles the Schlenk tube was backfilled with argon and the mixture stirred at room temperature for 10 mins to ensure homogeneity. The reaction mixture was then heated at 80 °C for 10 h. After 10 h, the reaction mixture was cooled in liquid nitrogen and precipitated into methanol after being washed with saturated EDTA solution for three times (50 mL). The precipitate isolated from the reaction conducted using 10:1 toluene:trifluorotoluene as the solvent was collected via centrifugation and dried *in vacuo* (0.1 mbar, 50 °C) to afford PFPE-*b*-PtBA CCS polymer **4**, 45 mg (yield 72 %). GPC-MALLS: *M_n* = 650 kDa, PDI = 1.23; ¹H NMR (CDCl₃, 400 MHz) δ_H 1.29-1.61 (*m*, **C(CH₃)₃** & **CH₂**), 1.81 (*br s*, **CH₂**), 2.22 (*br s*, **CH**) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ_C 27.7-28.1 (*m*, **CH₃**), 34.9-37.5 (*m*, **CH₂**), 41.4-42.3 (*m*, **CH**), 80.3-80.4 (*m*, **C(CH₃)₃**), 173.6-174.1 (*m*, **C=O**) ppm.

Characterisation of PFPE-OH 1.

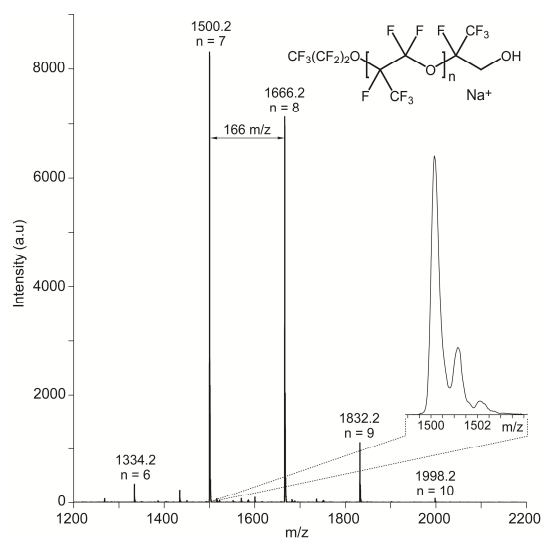


Figure S1. MALDI ToF mass spectra of monohydroxy PFPE **1** recorded in linear/positive mode using NaCl as the cationisation agent and PFBA as the matrix, which were deposited onto the target plate using a thin layer method.

Characterisation of micelle 5.

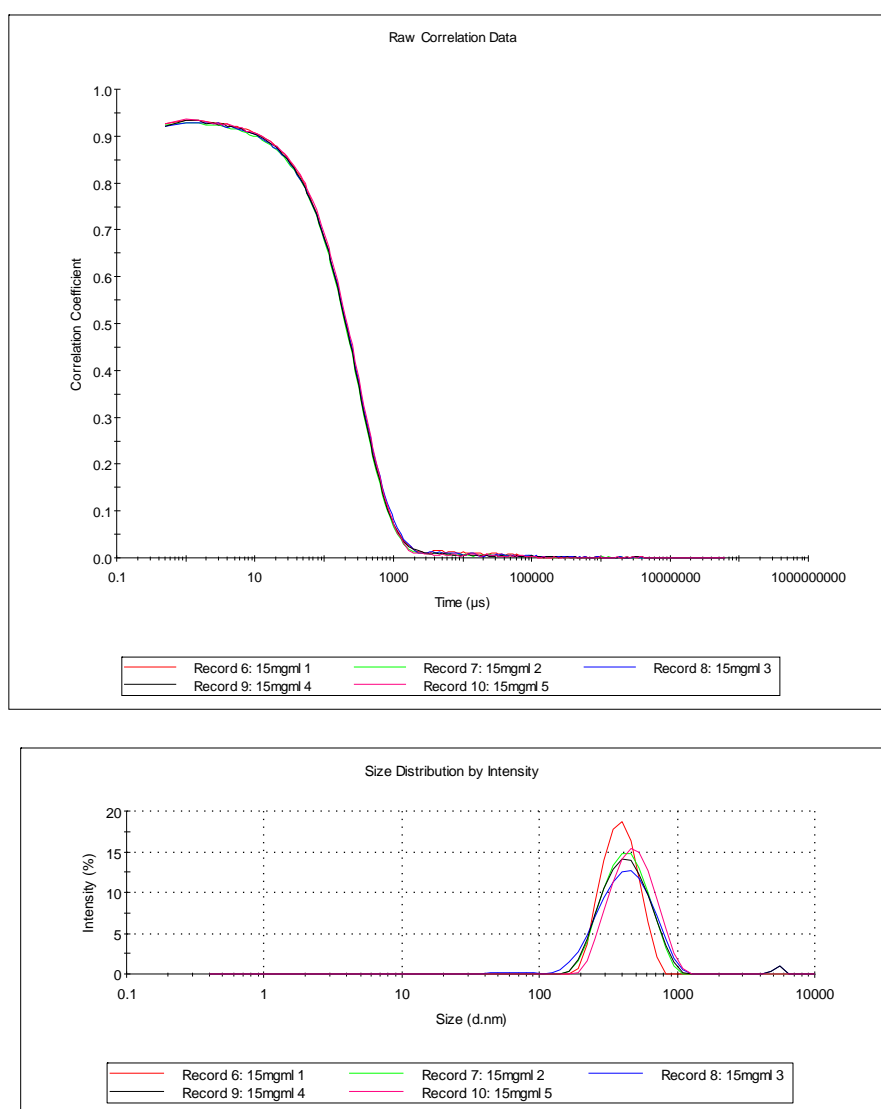


Figure S2. Dynamic light scattering analysis of poly(PFPE-*b*-*t*BA) micelle 5 in benzene (15mg/mL). (a) Raw correlation and (b) size distribution (*ca.* 400 nm) are provided.

Contact Angle Measurements.

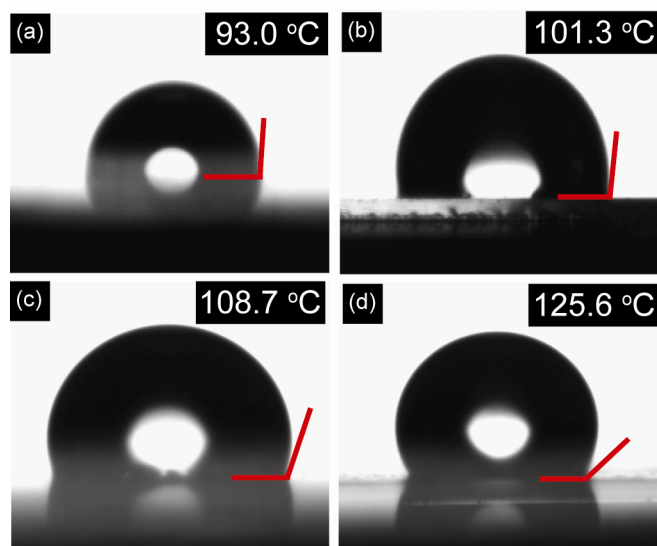


Figure S3. Images of contact angles on different films: Non-porous films of poly(PFPE-*b*-*t*BA) (a) micelle **5** and (b) star polymer **4**; Honeycomb structured films of poly(PFPE-*b*-*t*BA) (c) micelle **5** and (d) star polymer **4**.