Supporting Information for

"Synthesis and Self-Assembly of Fluorine-Containing Amphiphilic Graft Copolymer Bearing Perfluorocyclobutyl Aryl Ether-Based Backbone and Poly(acrylic acid) Side Chains"

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Experimental Section

Materials

tert-Butyl acrylate (*t*BA, Aldrich, 98%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$ and distilled twice from CaH_2 under reduced pressure prior to use. Copper (I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying at 40°C *in vacuo* for one day. Anisole (Aldrich, 99%) and diphenyl ether (Aldrich, 99%) were dried over CaH_2 and distilled under reduced pressure prior

to use. *N*-Bromosuccinimide (NBS, Aldrich, 99%) was recrystallized from water and dried *in vacuo* at 35°C for one day. Benzoyl peroxide (BPO, Alfa Aesar, 97%) was purified by dissolving in acetone and precipitating in water followed by drying *in vacuo* at room temperature for one day. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. Tetrahydrofuran (THF, Aldrich, 99%), dichloromethane (CH_2Cl_2, Aldrich, 99.5%), and toluene (Aldrich, 99%) were dried over CaH_2 and distilled from sodium and benzophenone under N_2 prior to use. 2-Methyl-1,4-bistrifluorovinyloxybenzene (MBTFVB) and 4-methoxytrifluoro-vinyloxybenzene were prepared according to previous report.[1] *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), acetonitrile (CH_3CN, Aldrich, 99.8%), trifluoroacetic acid (TFA, Aldrich, 99%), and carbon tetrachloride (CCl_4, Aldrich, 99.5%) were used as received.

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. All ^1H (500 MHz), ^{13}C (125 MHz), and ^{19}F (470 MHz) NMR analyses were performed on a Bruker Avance 500 spectrometer in $CDCl_3$, acetone-d_6, and DMSO-d_6, tetramethylsilicone (^1H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards and CF_3CO_2H was used as external standard for ^{19}F NMR. The bromine content was determined by the titration with $Hg(NO_3)_2$. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic

HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000) and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Thermogravimetry analysis (TGA) measurements were run on a TA Q500 system under N_2 purge with a heating rate of 10°C/min. Steady-state fluorescence spectra were measured at 20°C on a Hitachi F-2700 fluorescence spectrophotometer with the bandwidth of 5 nm for excitation and emission, the emission intensity at 418 nm was recorded to determine the critical micelle concentration (*cmc*), where the excitation wavelength (λ_{ex}) was 340 nm. TEM images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

Preparation of PMBTFVB Homopolymer

PMBTFVB **1** homopolymer was prepared via thermal step-growth cycloaddition polymerization of MBTFVB aryl TFVE monomer followed by end-capping with 4-methoxytrifluorovinyloxybenzene according to previous literatures.[2,3] GPC: M_n = 4,200 g/mol, M_w/M_n = 1.21. FT-IR: ν (cm^{-1}): 3053, 2933, 1599, 1498, 1315, 1267, 1203, 1120, 1009, 962, 925, 813, 743. ^{1}H NMR ($CDCl_3$): δ (ppm): 2.07, 2.26 (3H, CH_3), 3.75 (3H, OCH_3), 6.99, 7.09 (3H, phenyl). ^{13}C MNR ($CDCl_3$): δ (ppm): 16.1 (*C*H_3), 55.4 (O*C*H_3), 105.5, 109.4, 112.8 (4C, cyclobutyl), 116.5, 121.3, 131.2, 148.4 (3C, phenyl). ^{19}F NMR ($CDCl_3$): δ (ppm): -128.2 to -132.3 (6F, cyclobutyl-F_6).

Mono-Bromination of PMBTFVB

The pendant methyls of PMBTFVB **1** homopolymer were mono-brominated by NBS and BPO. In a typical procedure, PMBTFVB **1** ($M_{n,GPC}$ = 4,200 g/mol, M_w/M_n = 1.21, 1.00 g, 3.52 mmol -CH_3 group), NBS (0.187 g, 1.05 mmol), and BPO (0.171 g, 0.70 mmol) were first added to a 500 mL three-neck flask (flame-dried prior to use) fitted with a reflux condenser followed by deoxygenating under N_2. Next, 200 mL of CCl_4 was charged via a gastight syringe and the solution was refluxed at 80°C for 24 h. After filtration, CCl_4 was rotary evaporated from the filtrate. The obtained solid was dissolved in ethyl acetate (250 mL) and the resulting solution was washed with distilled water (200 mL×2) followed by drying over $MgSO_4$. The solution was concentrated and precipitated into methanol. After repeated purification by dissolving in THF and precipitating in methanol, 0.683 g of white powder, PMBTFVB-Br **2a** macroinitiator, was obtained after drying *in vacuo* overnight. GPC: M_n = 5,800 g/mol, M_w/M_n = 1.19. EA: Br%: 6.71%. ^{1}H NMR ($CDCl_3$): δ (ppm): 1.97, 2.19 (3H, CH_3), 3.67 (3H, OCH_3), 4.16, 4.34 (2H, CH_2Br), 6.88, 7.04, 7.15 (3H, phenyl). ^{13}C MNR ($CDCl_3$): δ (ppm): 15.3 (*C*H_3), 24.5 (*C*H_2Br), 54.5 (O*C*H_3), 105.0, 107.9, 111.9 (4C, cyclobutyl), 116.7, 118.6, 120.7, 129.4, 148.0 (3C, phenyl). ^{19}F NMR ($CDCl_3$): δ (ppm): -127.2 to -132.8 (6F, cyclobutyl-F_6).

ATRP Graft Copolymerization of *t*BA

ATRP graft copolymerization of *t*BA was initiated by PMBTFVB-Br **2** macroinitiator using CuBr/PMDETA as catalytic system. In a typical procedure,

PMBTFVB-Br **2a** ($M_{n,GPC}$ = 5,800 g/mol, M_w/M_n = 1.19, Br% = 6.71%, 195 mg, 0.1636 mmol -CH_2Br group) and CuBr (23.4 mg, 0.1636 mmol) were first added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, *t*BA (2.37 mL, 16.36 mmol), anisole (1.18 mL), and PMDETA (34.16 μL, 0.1636 mmol) were introduced via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing and the mixture was stirred at room temperature for 20 min so that the mixture became homogeneous. The flask was immersed into an oil bath preset at 80°C to start the polymerization. The polymerization was terminated by putting the flask into liquid N_2 after 30 min. The reaction mixture was diluted by THF and passed through an Al_2O_3 column to remove the residual copper catalyst. The solution was concentrated and precipitated into methanol/H_2O (v:v = 1:1). After repeated purification by dissolving in THF and precipitating in methanol/H_2O (v:v = 1:1), 165.0 mg of white powder, PMBTFVB-*g*-P*t*BA **3a** graft copolymer, was obtained after drying *in vacuo* overnight. GPC: M_n = 10,500 g/mol, M_w/M_n = 1.32. FT-IR: ν (cm^{-1}): 2977, 2938, 1729 ($\nu_{c=o}$), 1481, 1448, 1395, 1369, 1257, 1152, 965, 845, 809, 750. ^{1}H NMR (acetone-d_6): δ (ppm): 1.36 (9H, C(CH_3)$_3$), 1.71 (2H, CH_2CHCO$_2$), 2.18 (3H, $C_6H_5CH_3$ and 1H, CH_2CHCO$_2$), 3.66 (3H, OCH_3), 6.92-7.26 (3H, phenyl). ^{13}C MNR ($CDCl_3$): δ (ppm): 15.3 (CH_3), 27.5 (3C, $CO_2C(CH_3)_3$), 35.8, 37.3 (CH_2CHCO), 42.1 (CH_2CHCO), 80.5 ($CO_2C(CH_3)_3$), 105.0, 107.8, 111.7 (4C, cyclobutyl), 116.5, 118.7, 120.8, 129.3, 148.1 (3C, phenyl), 173.3 ($CO_2C(CH_3)_3$). ^{19}F NMR (acetone-d_6): δ (ppm): -126.6 to -133.0 (6F, cyclobutyl-F_6).

Acidolysis of PMBTFVB-*g*-P*t*BA

In a typical procedure, PMBTFVB-*g*-P*t*BA **3a** ($M_{n,GPC}$ = 10,500 g/mol, M_w/M_n = 1.32, 165 mg), CH_2Cl_2 (25 mL), and TFA (5.0 mL) were added to a 50 mL three-neck flask. The solution was stirred at 0°C for 1 h followed by stirring at room temperature for another 24 h. The solution was concentrated and precipitated into cold *n*-hexane. After filtration, 75.2 mg of white powder, PMBTFVB-*g*-PAA **4a**, was obtained after drying *in vacuo* overnight. ^{1}H NMR (DMSO-d_6): δ (ppm): 1.49, 1.75 (2H, CH_2CHCO_2), 2.19, 2.26 (3H, $C_6H_5CH_3$ and 1H, CH_2CHCO_2), 6.83-7.29 (3H, phenyl), 12.30 (1H, COO*H*). FT-IR: ν (cm^{-1}): 3386 (ν_{OH}), 2977, 2938, 1724 ($\nu_{c=o}$), 1452, 1390, 1369, 1257, 1152, 965, 845, 750.

Determination of Critical Micelle Concentration

PNA was used as fluorescence probe to measure the *cmc* of PMBTFVB-*g*-PAA **4** amphiphilic graft copolymer. Acetone solution of PNA (2 mM) was added to a large amount of water until the concentration of PNA reached 0.002 mM. Next, different amounts of THF solution of PMBTFVB-*g*-PAA **4** graft copolymer (1, 0.1, 0.01, or 0.001 mg/mL) were added to water containing PNA ([PNA] = 0.002 mM).

Micellar Morphology

PMBTFVB-*g*-PAA **4** graft copolymer was first dissolved in THF with different concentrations. Next, deionized water was added slowly (0.36 mL/h) to 1 g of THF stock solution until the desired water content was reached. The solution was sealed

with a PTFE plug for equilibration under stirring for another 12 h. The solution was then dialyzed against deionized water with slow stirring for 5 days to remove THF, and deionized water was changed twice one day. pH of micellar solution was about 4.9-5.1. For TEM studies, a drop of micellar solution was deposited on an electron microscopy copper grid coated with carbon film and the water evaporated at room temperature.

References and Notes

(1) Kennedy, A. P.; Babb, D. A.; Bermmer, J. N.; Pasztor, A. J. *J. Polym. Sci. Polym. Chem.* **1995**, *33*, 1859-1865.

(2) Liu, H.; Li, Y. J.; Zhang, S.; Yang, D.; Hu, J. H.; Huang, X. Y. *J. Polym. Sci. Polym. Chem.* **2011**, *49*, 11-22.

(3) Liu, H.; Zhang, S.; Li, Y. J.; Yang, D.; Hu, J. H.; Huang, X. Y. *Polymer* **2010**, *51*, 5198-5206.

Table S1. Preparation of PMBTFVB-Br **2** Macroinitiator[a]

Sample	NBS (eq.)	Br%[b] (%)	$M_{n,GPC}$[c] (KDa)	M_w/M_n[c]	N_{ATRP}[d]	D_{ATRP}[e] (%)
2a	0.3	6.71	5.8	1.19	7.6	26.5
2b	0.7	12.11	5.8	1.18	14.5	51.2
2c	1.0	16.23	6.1	1.19	20.4	72.1

[a] Reaction temperature: 80°C; reaction time: 24 h; feeding ratio: [methyl]:[BPO] = 1:0.2. [b] Determined by the titration with $Hg(NO_3)_2$. [c] Measured by GPC in THF at 35°C. [d] The number of benzyl bromide ATRP initiating group per chain obtained from ^{1}H NMR. [e] Density of benzyl bromide ATRP initiating group.

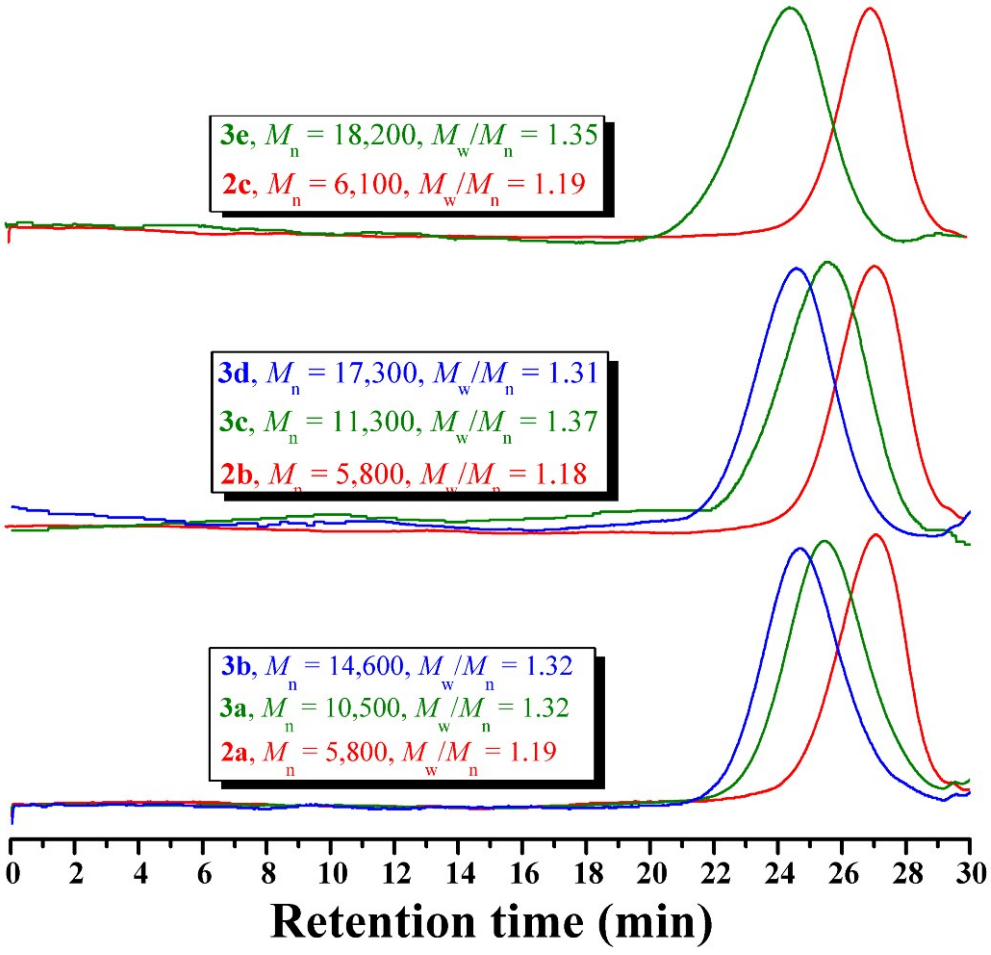

Figure S1. GPC traces of PMBTFVB-Br **2** and PMBTFVB-*g*-P*t*BA **3** in THF.

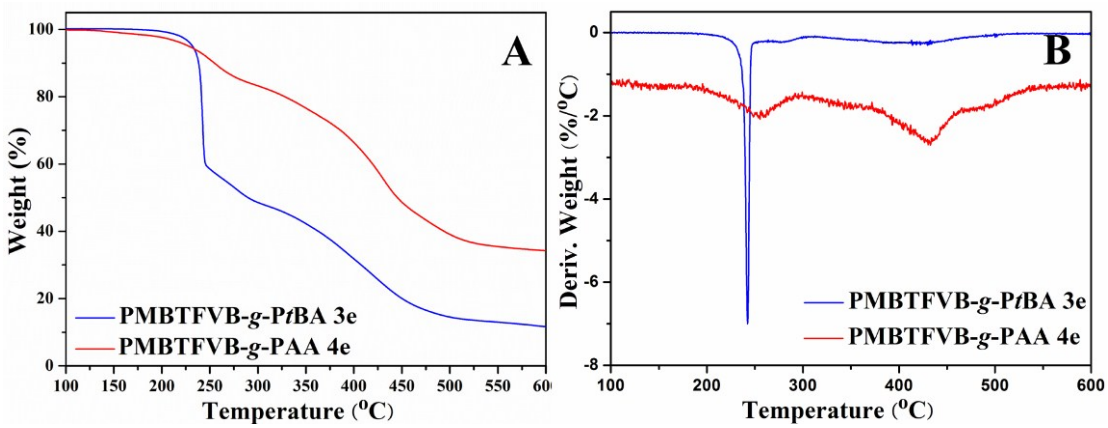

Figure S2. TGA (A) and DTG (B) curves (in N_2) of PMBTFVB-*g*-P*t*BA **3e** and PMBTFVB-*g*-PAA **4e** graft copolymer with a heating rate of 10°C/min.

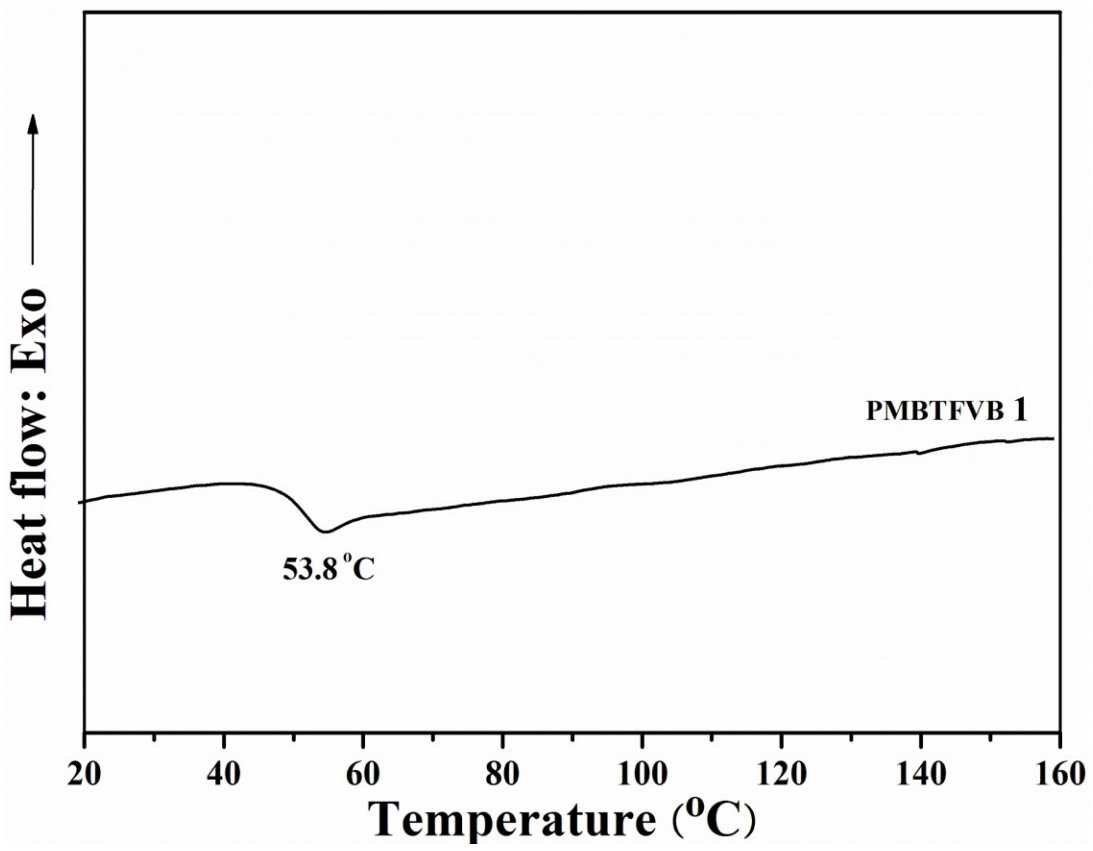

Figure S3. Third heating DSC scan (in N_2) of PMBTFVB **1** with a heating rate of 10°C/min.