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 (tBA, Aldrich, 98%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over CaCl₂ and distilled twice from CaH₂ under reduced pressure prior to use. Copper (I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH₃CO₂H 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 CaH₂ 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$_2$Cl$_2$, 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-methoxytrifluorovinyloxybenzene were prepared according to previous report.$^1$ N,N,N’,N’,N”-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), acetonitrile (CH$_3$CN, 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 $^1$H (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 ($^1$H NMR) and CDCl$_3$ ($^{13}$C NMR) were used as internal standards and CF$_3$CO$_2$H 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 Styrage 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 N₂ 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 (λex) was 340 nm. TEM images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

**Preparation of PMBTFVVB Homopolymer**

PMBTFVVB 1 homopolymer was prepared via thermal step-growth cycloaddition polymerization of MBTFVB aryl TFVE monomer followed by end-capping with 4-methoxytrifluorovinylxybenzene according to previous literatures.² Three GPC: $M_n = 4,200$ g/mol, $M_w/M_n = 1.21$. FT-IR: $\nu$ (cm⁻¹): 3053, 2933, 1599, 1498, 1315, 1267, 1203, 1120, 1009, 962, 925, 813, 743. $^1$H NMR (CDCl₃): $\delta$ (ppm): 2.07, 2.26 (3H, CH₃), 3.75 (3H, OCH₃), 6.99, 7.09 (3H, phenyl). $^{13}$C MNR (CDCl₃): $\delta$ (ppm): 16.1 (CH₃), 55.4 (OCH₃), 105.5, 109.4, 112.8 (4C, cyclobutyl), 116.5, 121.3, 131.2, 148.4 (3C, phenyl). $^{19}$F NMR (CDCl₃): $\delta$ (ppm): -128.2 to -132.3 (6F, cyclobutyl-F₆).
Mono-Bromination of PMBTFVB

The pendant methyls of PMBTFVB 1 homopolymer were mono-brominated by NBS and BPO. In a typical procedure, PMBTFVB 1 \( (M_{n, GPC} = 4,200 \text{ g/mol}, M_w/M_n = 1.21, 1.00 \text{ g}, 3.52 \text{ mmol -CH}_3 \text{ group}), \) 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\(^{\circ}\)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, PMBTFVBr-Br \( 2a \) macroinitiator, was obtained after drying \textit{in vacuo} overnight. GPC: \( M_n = 5,800 \text{ g/mol}, M_w/M_n = 1.19 \). EA: Br\%: 6.71\%. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) (ppm): 1.97, 2.19 (3H, CH\(_3\)), 3.67 (3H, OCH\(_3\)), 4.16, 4.34 (2H, CH\(_2\)Br), 6.88, 7.04, 7.15 (3H, phenyl). \(^{13}\)C MNR (CDCl\(_3\)): \( \delta \) (ppm): 15.3 (CH\(_3\)), 24.5 (CH\(_2\)Br), 54.5 (OCH\(_3\)), 105.0, 107.9, 111.9 (4C, cyclobutyl), 116.7, 118.6, 120.7, 129.4, 148.0 (3C, phenyl). \(^{19}\)F NMR (CDCl\(_3\)): \( \delta \) (ppm): -127.2 to -132.8 (6F, cyclobutyl-F\(_6\)).

ATRP Graft Copolymerization of tBA

ATRP graft copolymerization of tBA was initiated by PMBTFVBr-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$_2$Br 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, tBA (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$_2$O$_3$ column to remove the residual copper catalyst. The solution was concentrated and precipitated into methanol/H$_2$O (v:v = 1:1). After repeated purification by dissolving in THF and precipitating in methanol/H$_2$O (v:v = 1:1), 165.0 mg of white powder, PMBTFVB-g-PtBA 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: $\nu$ (cm$^{-1}$): 2977, 2938, 1729 ($\nu_{C=O}$), 1481, 1448, 1395, 1369, 1257, 1152, 965, 845, 809, 750. $^1$H NMR (acetone-$d_6$): $\delta$ (ppm): 1.36 (9H, C(CH$_3$)$_3$), 1.71 (2H, CH$_2$CHCO$_2$), 2.18 (3H, C$_6$H$_5$CH$_3$ and 1H, CH$_2$CHCO$_2$), 3.66 (3H, OCH$_3$), 6.92-7.26 (3H, phenyl). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm): 15.3 (CH$_3$), 27.5 (3C, CO$_2$C(CH$_3$)$_3$), 35.8, 37.3 (CH$_2$CHCO), 42.1 (CH$_2$CHCO), 80.5 (CO$_2$C(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$_2$C(CH$_3$)$_3$). $^{19}$F NMR (acetone-$d_6$): $\delta$ (ppm): -126.6 to -133.0 (6F, cyclobutyl-F$_6$).
Acidolysis of PMBTFVB-g-PrBA

In a typical procedure, PMBTFVB-g-PrBA 3a ($M_{n, GPC} = 10,500$ g/mol, $M_w/M_n = 1.32$, 165 mg), CH$_2$Cl$_2$ (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-$d_6$): $\delta$ (ppm): 1.49, 1.75 (2H, C$_6$H$_2$CHCO$_2$), 2.19, 2.26 (3H, C$_6$H$_5$CH$_3$ and 1H, CH$_2$CHCO$_2$), 6.83-7.29 (3H, phenyl), 12.30 (1H, COOH). FT-IR: $\nu$ (cm$^{-1}$): 3386 ($\nu_{\text{OH}}$), 2977, 2938, 1724 ($\nu_{\text{c=O}}$), 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


Table S1. Preparation of PMBTFVB-Br 2 Macroinitiator

<table>
<thead>
<tr>
<th>Sample</th>
<th>NBS (eq.)</th>
<th>Br%b (%)</th>
<th>$M_n$GPCc (KDa)</th>
<th>$M_w/M_n$e</th>
<th>$N_{ATRP}^d$</th>
<th>$D_{ATRP}^e$ (%)</th>
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<td>2a</td>
<td>0.3</td>
<td>6.71</td>
<td>5.8</td>
<td>1.19</td>
<td>7.6</td>
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<tr>
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<td>1.18</td>
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<tr>
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<td>1.0</td>
<td>16.23</td>
<td>6.1</td>
<td>1.19</td>
<td>20.4</td>
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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-PrBA 3 in THF.
Figure S2. TGA (A) and DTG (B) curves (in N₂) of PMBTFVB-g-PrBA 3e and PMBTFVB-g-PAA 4e graft copolymer with a heating rate of 10°C/min.

Figure S3. Third heating DSC scan (in N₂) of PMBTFVB 1 with a heating rate of 10°C/min.