Supporting information for

Construction of Semi-Fluorinated Amphiphilic Graft Copolymer Bearing Poly(2-methyl-1,4- bistrifluoro-vinyloxybenzene) Backbone and Poly(ethylene glycol) Side Chains via the Grafting-Onto Strategy

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Experimental

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.[25,26] GPC: M_n = 6,100 g/mol, M_w/M_n = 1.23. FT-IR: ν (cm^{-1}): 3054, 2931, 1598, 1498, 1312, 1269, 1201, 1122, 1009, 963, 926, 812, 742. ^{1}H NMR: δ (ppm): 2.07, 2.27 (3H, CH_3), 3.76 (3H, OCH_3), 6.98, 7.10 (3H, phenyl). ^{13}C MNR: δ (ppm): 16.0 (*C*H_3), 55.4 (O*C*H_3), 105.6, 109.3, 112.9 (4C, cyclobutyl), 116.5, 121.4, 131.0, 148.5 (3C, phenyl). ^{19}F

NMR ($CDCl_3$): δ (ppm): -127.2 to -132.6 (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** ($M_{n,GPC}$ = 6,100 g/mol, M_w/M_n = 1.23, 2.00 g, 7.04 mmol -CH_3 group), NBS (0.375 g, 2.11 mmol), and BPO (0.341 g, 1.41 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, CCl_4 (350 mL) was charged via a gastight syringe and the solution was refluxed at 80^{o}C for one day. After filtration, CCl_4 was rotary evaporated from the filtrate. The obtained solid was dissolved in ethyl acetate (400 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, 1.301 g of white powder, PMBTFVB-Br **2a** macroinitiator, was obtained after drying *in vacuo* overnight. GPC: M_n = 6,900 g/mol, M_w/M_n = 1.26. EA: Br%: 6.19%. ^{1}H NMR: δ (ppm): 1.99, 2.18 (3H, CH_3), 3.68 (3H, OCH_3), 4.17, 4.34 (2H, CH_2Br), 6.86, 7.04, 7.16 (3H, phenyl). ^{13}C MNR: δ (ppm): 16.2 (*C*H_3), 25.4 (*C*H_2Br), 55.4 (ArO*C*H_3), 105.8, 109.0, 112.8 (4C, cyclobutyl), 117.5, 119.7, 121.7, 130.0, 149.1 (3C, phenyl). ^{19}F NMR ($CDCl_3$): δ (ppm): -127.1 to -132.7 (6F, cyclobutyl-F_6).

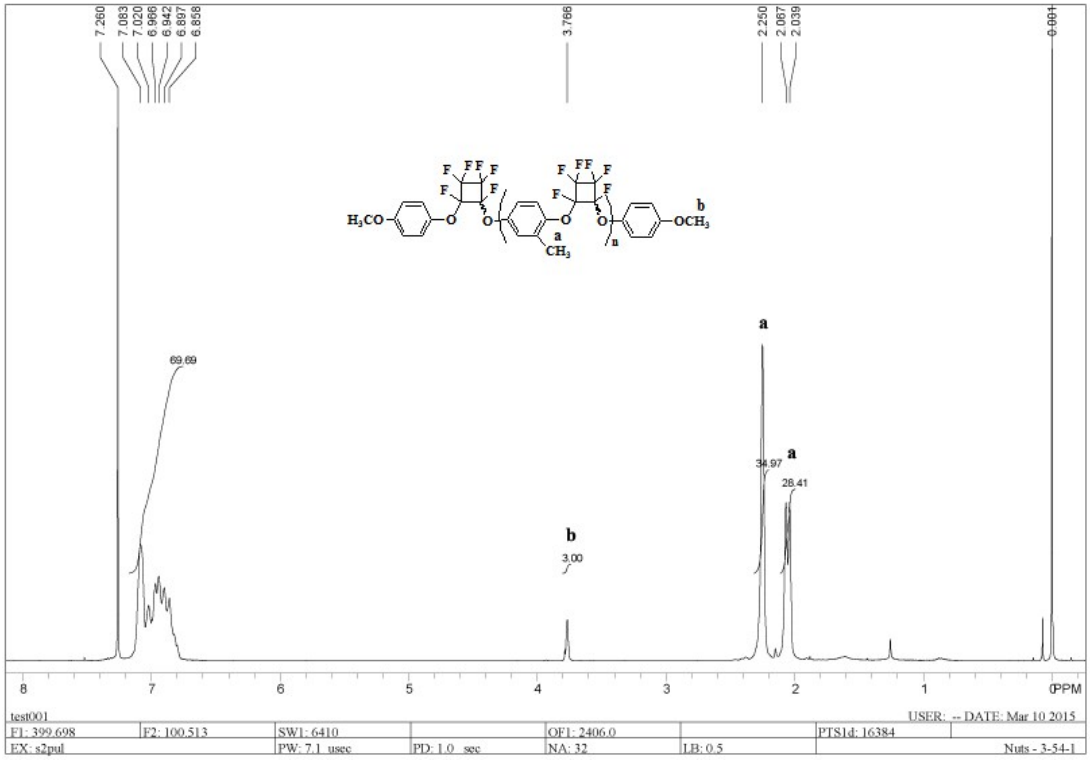

Figure S1. ^{1}H NMR spectrum of PMBTFVB **1** homopolymer in $CDCl_3$.

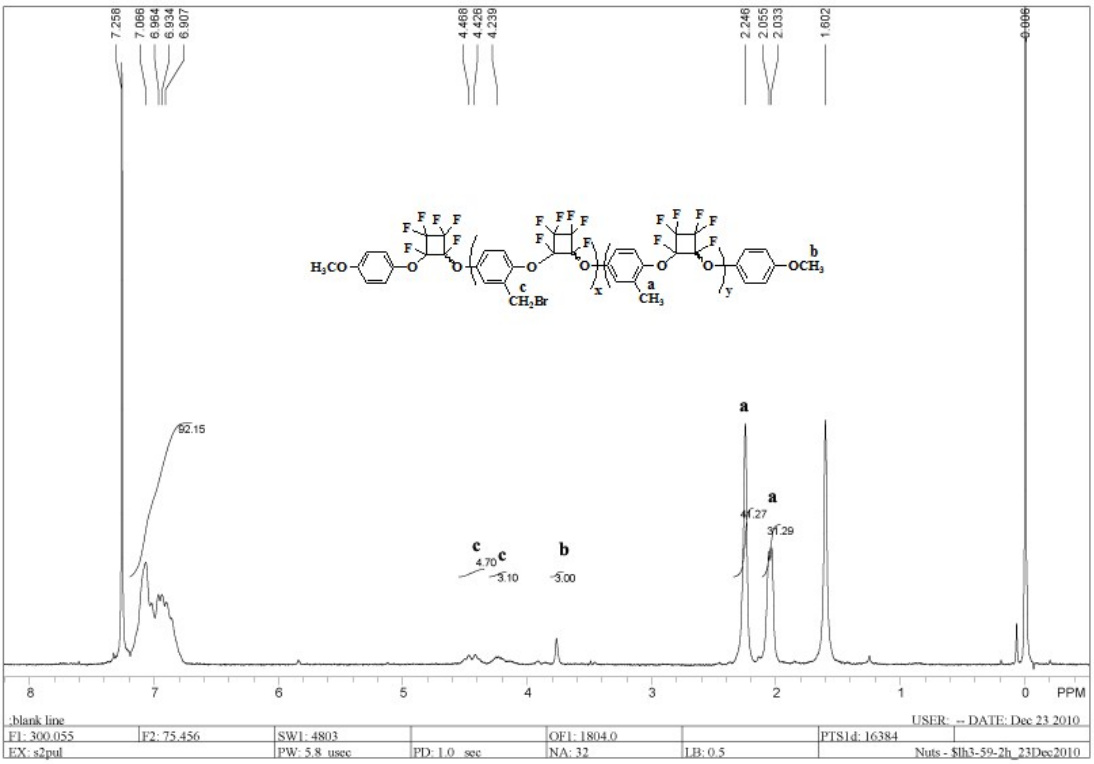

Figure S2. ^{1}H NMR spectrum of PMBTFVB-Br **2a** in $CDCl_3$.

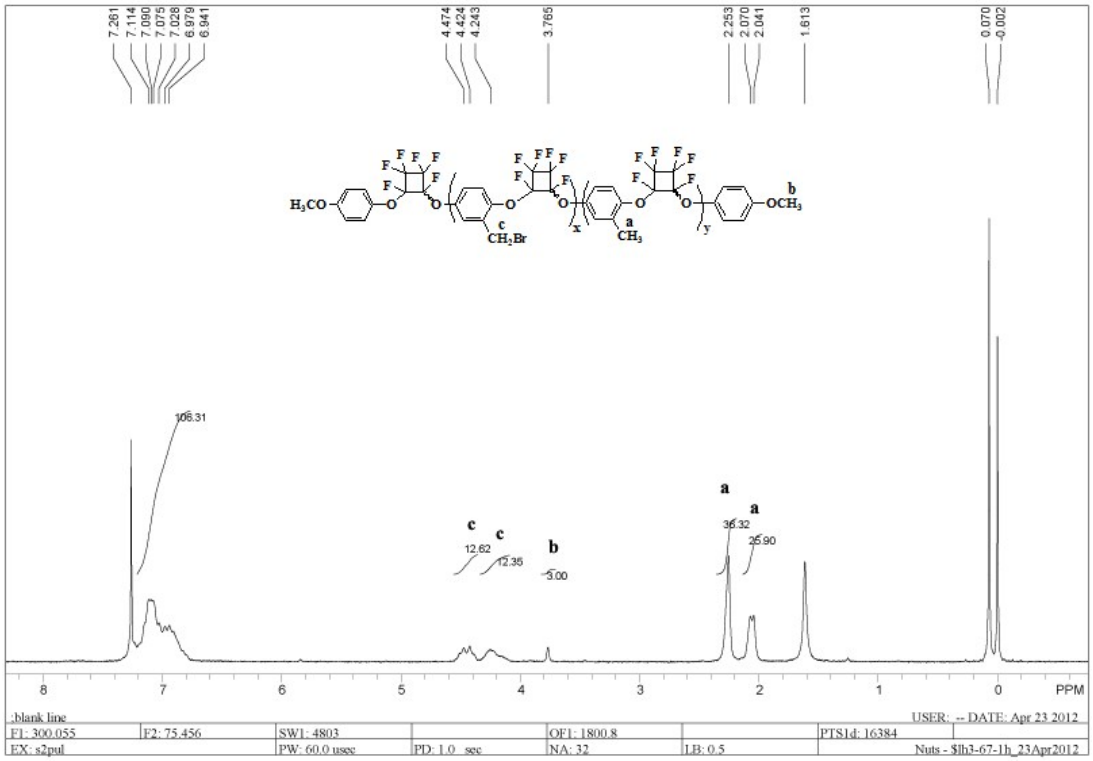

Figure S3. ^{1}H NMR spectrum of PMBTFVB-Br **2b** in $CDCl_3$.

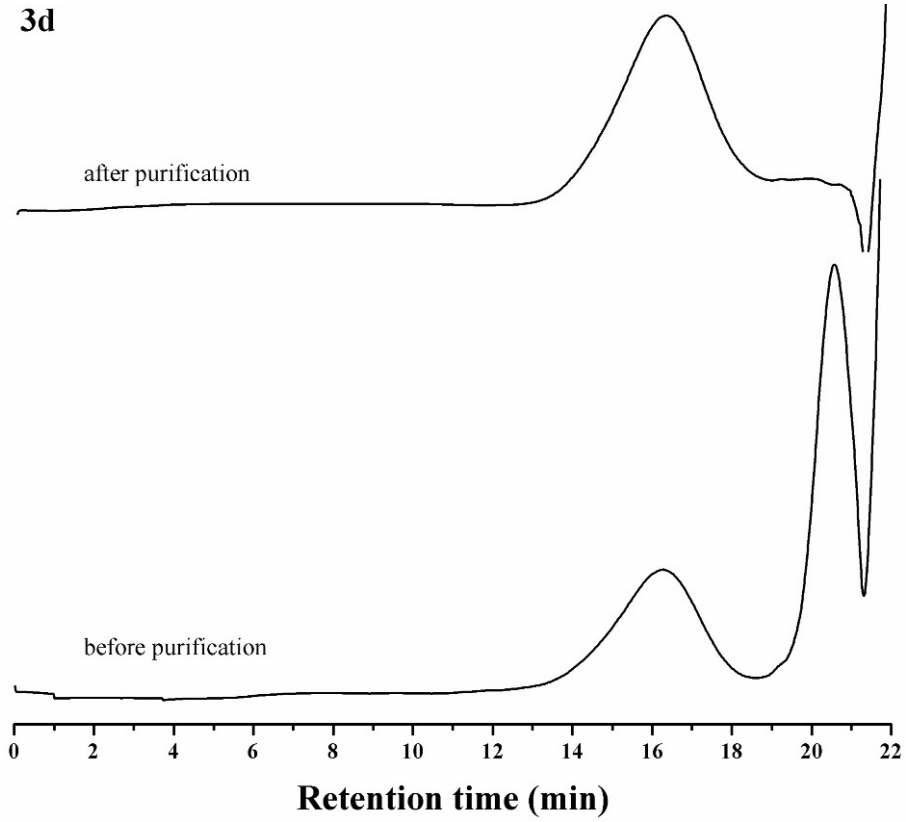

Figure S4. GPC curves of copolymer **3d** before and after the purification using preparative gel permeation chromatography.

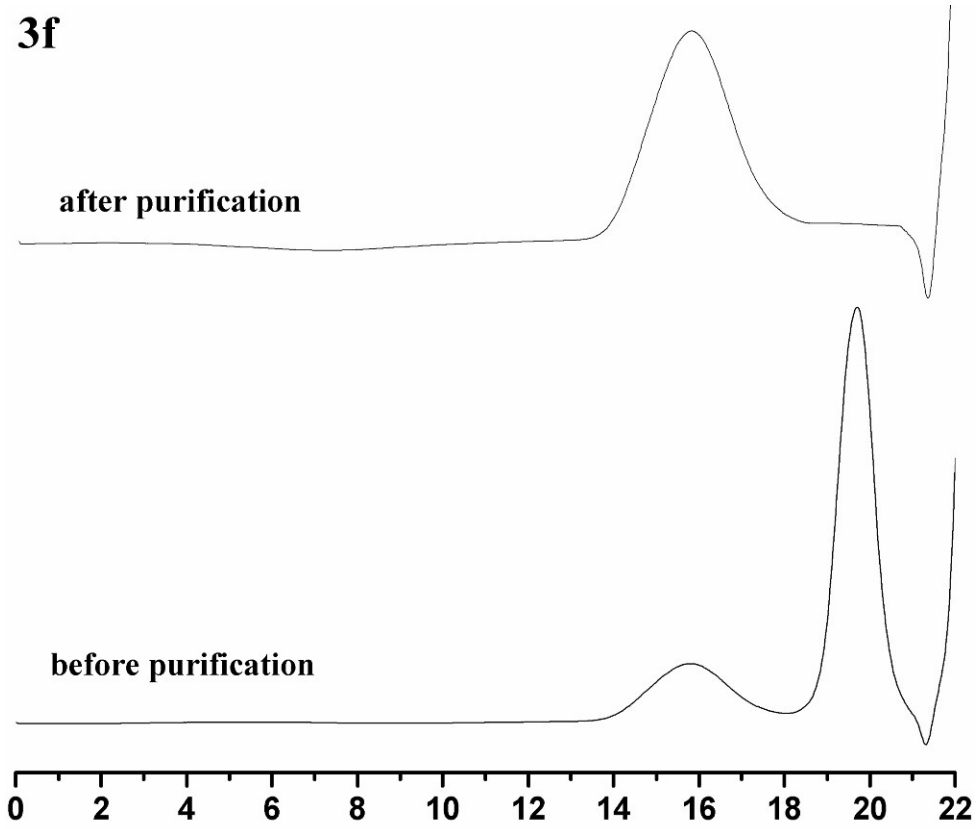

Figure S5. GPC curves of copolymer **3f** before and after the purification using preparative gel permeation chromatography.