Supporting Information for

Synthesis and Self-Assembly of PMBTFVB-*g*-PNIPAM Fluorine-Containing Amphiphilic Graft Copolymer

Guolin Lu,[a,#] *Xiaojun Jiang*,[b,#] *Yongjun Li*,[a] *Xuliang Lv*,[b,*] *Xiaoyu Huang*[a,*]

[a] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[b] PLA University of Science & Technology , 88 Houbiaoying Road, Nanjing, Jiangsu 210007, People's Republic of China

Experimental

Materials

N-Isopropylacrylamide (NIPAM, Aldrich, 97%,) was recrystallized from a mixture of benzene and *n*-hexane (v:v = 1:3). Copper(I) chloride (CuCl, Aldrich, 99%) 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 *in vacuo* at 40°C for 1 day. *N*-Chlorosuccinimide (NCS, 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. *N,N*-dimethylformamide (DMF, Alfa Aesar, 99%) were dried over CaH_2 for several days and distilled under reduced pressure prior to use. Carbon tetrachloride (CCl_4, Aldrich, 99.5%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and *tert*-butanol (TBA, Aldrich, 99%) were used as received. 2-Methyl-1,4-bistrifluorovinyloxybenzene (MBTFVB) and 4-methoxytrifluorovinyloxybenzene were prepared according to previous report.[1]

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a 4 cm^{-1} resolution. All ^1H (400 MHz), ^{13}C (100 MHz), and ^{19}F (370 MHz) NMR analyses were performed on a Bruker Avance 400 spectrometer in $CDCl_3$, 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 chlorine 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 (sample concentration: 2 mg/mL) were carried out at 35°C using LiBr-added DMF ([LiBr] = 10 mM) as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Differential scanning

calorimetry (DSC) measurements were run on a TA Q200 system under N_2 purge with a heating rate of 10°C/min. The glass transition temperature (T_g) was recorded from the second heating process after a quick cooling from 200°C and the value was determined from the midpoint of C_p curve. Thermogravimetric analysis (TGA) measurements were run on a TA Q500 system under N_2 purge with a heating rate of 10°C/min. The decomposition temperature (T_d) is defined as the temperature with 10% weight loss. 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. Hydrodynamic diameter (D_h) was measured by dynamic light scattering (DLS) with a Malvern Nano-ZS90 Zetasizer, the samples were allowed to equilibrate for 2 min at changed temperature prior to the measurement. TEM images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

Preparation of PMBTFVB-Cl 2 Macroinitiator

Firstly, 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 literature.[1] GPC: M_n = 4,700 g/mol, M_w/M_n = 1.20. 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).

The pendant methyls of PMBTFVB **1** homopolymer were mono-chlorinated by NCS and BPO. PMBTFVB **1** ($M_{n,GPC}$ = 4,700 g/mol, M_w/M_n = 1.20, 2.00 g, 7.04 mmol -CH_3 group), NCS (2.00 g, 15.0 mmol), and BPO (2.00 g, 8.26 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 (400 mL) was charged via a gastight syringe and the solution was refluxed at 80^{o}C for 12 h. After filtration, CCl_4 was rotary evaporated from the filtrate. The obtained solid was dissolved in ethyl acetate (200 mL) and the resulting solution was washed with saturated brine (100 mL×3) 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, 1.3213 g of white powder, PMBTFVB-Cl **2** macroinitiator, was obtained after drying *in vacuo* overnight. GPC: M_n = 6,300 g/mol, M_w/M_n = 1.19. EA: Cl%: 4.83%. ^{1}H NMR: δ (ppm): 1.99, 2.18 (3H, C*H*$_3$), 3.68 (3H, OC*H*$_3$), 4.36, 4.59 (2H, C*H*$_2$Cl), 6.86, 7.04, 7.12 (3H, phenyl). ^{19}F NMR ($CDCl_3$): δ (ppm): -127.1 to -132.7 (6F, cyclobutyl-F_6).

ATRP Graft Copolymerization of NIPAM

In a typical procedure, to a 5 mL Schlenk flask sealed with a rubber septum, CuCl (13.5 mg, 0.137 mmol), PMBTFVB-Cl **2** macroinitiator (0.1 g, M_n = 6,300, M_w/M_n = 1.19, Cl% = 4.83%, 0.137 mmol -CH_2Cl initiating group), and NIPAM (1.5 g, 13.7

mmol) were first added for degassing and kept under N_2. Next, DMF (1.0 mL), TBA (1.0 mL), and PMDETA (28.4 μL, 0.137 mmol) were charged via a gastight syringe. The solution was degassed by three cycles of freezing-pumping-thawing followed by stirring for 20 min at room temperature. The flask was then immersed into an oil preset at 80°C to start the polymerization. The polymerization was quenched by immersed the flask into liquid N_2 after 48 h and the mixture was diluted with 10 mL of THF followed passing through a short Al_2O_3 column to remove the residual copper catalyst. The resulting solution was concentrated and precipitated into cold diethyl ether. After repeated purification by dissolving in THF and precipitating in cold diethyl ether, the crude product was drying *in vacuo* overnight to afford 0.1050 g of white powder, PMBTFVB-*g*-PNIPAM **3b** graft copolymer. GPC: M_n = 40,100 g/mol, M_w/M_n = 1.29. FT-IR: ν (cm^{-1}): 3519, 3294, 3074, 2970, 2927, 1644, 1538, 1458, 1386, 1204, 1170, 1130, 962. ^{1}H NMR: δ (ppm): 1.14 (6H, CH(CH_3)$_2$), 1.36, 1.64, 1.85 (2H, CH_2CHCONH), 2.10-2.36 (3H, PhCH_3, 2H, PhCH_2, and 1H, CH_2CHCONH), 3.74 (3H, OCH_3), 4.01 (1H, NHCH(CH)$_3$), 6.43 (1H, CONH), 6.96, 7.08 (3H, phenyl). ^{19}F NMR: δ (ppm): -128.1 to -132.2 (6F, cyclobutyl-F_6).

Determination of Critical Micelle Concentration

PNA was used as fluorescence probe to measure the *cmc* of PMBTFVB-*g*-PNIPAM **3** amphiphilic graft copolymer. Acetone solution of PNA (0.001 mol/L) was added to a large amount of water until the concentration of PNA reached 2×10^{-6} mol/L. Next, different amounts of THF solution of PMHDO-*g*-PNIPAM **3** graft

copolymer were added to water containing PNA ([PNA] = 2×10^{-6} mol/L). The concentration of PMBTFVB-*g*-PNIPAM **3** graft copolymer ranged from 1.0×10^{-6} g/L to 0.1 g/L. All fluorescence spectra were recorded at 25°C.

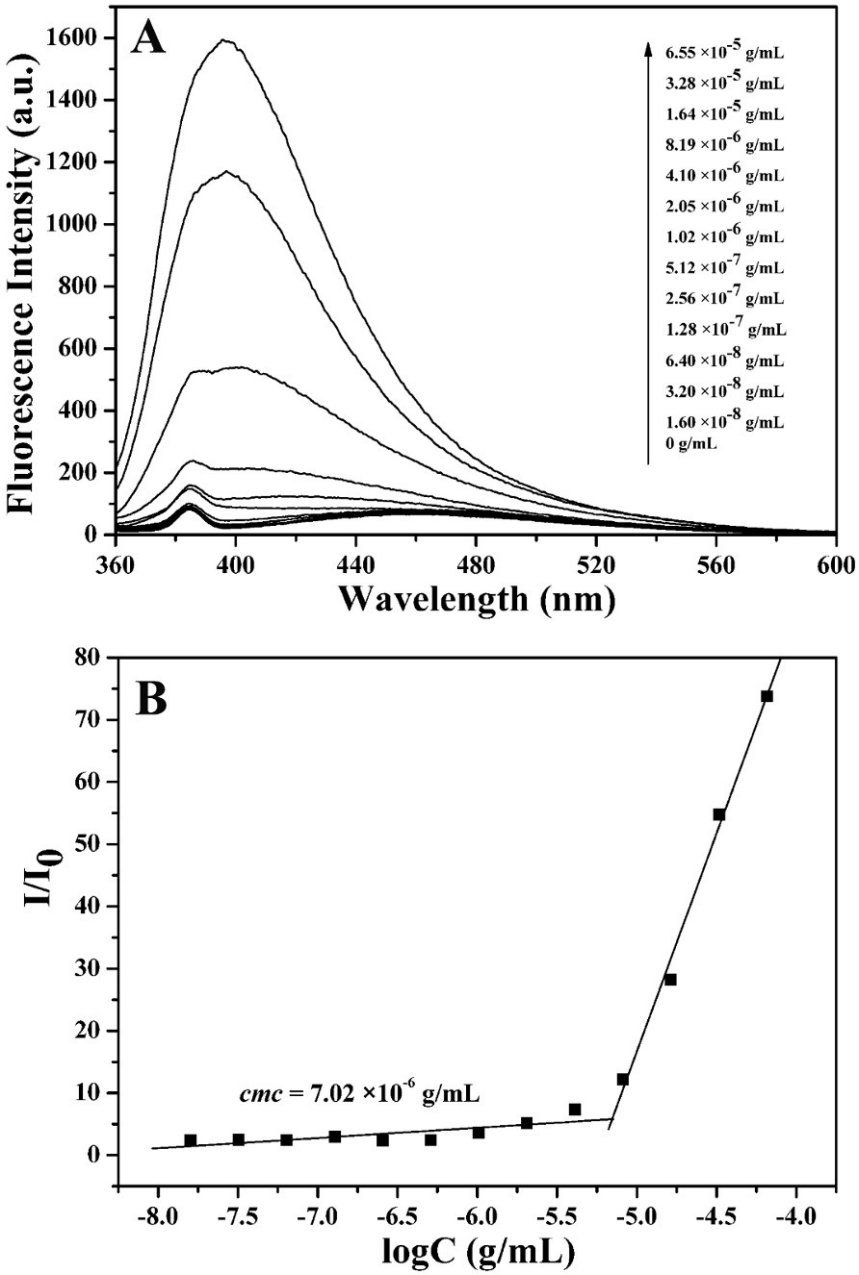

Figure S1. (A) Fluorescence spectra of PNA in aqueous solutions of PMBTFVB-*g*-PNIPAM **3b** graft copolymer and (B) Dependence of fluorescence intensity ratio of PNA emission band at 418 nm on the concentration of PMBTFVB-*g*-PNIPAM **3b** graft copolymer in pure water.

Micellar Morphology

THF solution of PMBTFVB-*g*-PNIPAM **3** graft copolymer (1 mg/mL) was quickly added to water under vigorous stirring until the desired concentration of graft copolymer was reached. THF was evaporated by stirring moderately at room temperature overnight to get the micellar solution. 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. Liu, H.; Zhang, S.; Li, Y. J.; Yang, D.; Hu, J. H.; Huang, X. Y. *Polymer* **2010**, *51*, 5198-5206.