[*Electronic Supplementary Information (ESI)*]

Synthesizing Amphiphilic Block Copolymers through Macromolecular Azo-Coupling Reaction

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Measurements and Materials. All the reagents and solvents were purchased commercially and used without further purification. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer (600 MHz for proton) by using DMSO-d$_6$ as the solvent. The GPC instrument was equipped with a Wyatt Optilab rEX detector and a PL gel 5 μm mixed-D column with THF used as solvent during measurements, which was calibrated by using polystyrene standards. UV-vis spectra were recorded by using an Agilent 8453 UV-vis spectrophotometer.

Synthesis of ATRP initiator 1. To a CH_2Cl_2 (10 mL) solution of a mixture of *N*-ethyl-*N*-hydroxyethyl-aniline (0.825g, 5 mmol) and triethylamine (2.5 mL) under ice bath was added 2-bromoisobutyryl bromide (1.69g, 7.5 mmol) in 10 mL CH_2Cl_2. The solution was stirred at room temperature over night. To the resulting solution was added CH_2Cl_2 and washed with water, dried over anhydrous $MgSO_4$. After solvent removal, column chromatography (SiO_2, CH_2Cl_2) was undertaken to afford the product. Yield: 85%. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ = 1.05 (t, 3H), 1.83 (s, 6H), 3.36 (m, 2H), 3.55 (t, 2H) 4.24 (t, 2H), 6.57 (t, 1H), 6.70 (d, 2H), 7.13 (d, 2H). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ = 170.4, 147.9, 129.7, 116.2, 112.4, 64.1, 57.6, 48.3, 44.9, 30.7, 12.5.

Synthesis of ATRP initiator 2. To a CH_2Cl_2 (20 mL) solution of a mixture of *N*,*N*-dihydroxyethyl-aniline (1.81g, 10 mmol) and triethylamine (7 mL) under ice bath was added 2-bromoisobutyryl bromide (6.9g, 30 mmol) in 20 mL CH_2Cl_2. The solution was stirred at room temperature over night. To the resulting solution was added CH_2Cl_2 and washed with water, dried over anhydrous $MgSO_4$. After solvent removal, column chromatography (SiO_2, ethyl acetate: petroleum ether=1:6) was undertaken to afford the product. Yield: 95%. ^{1}H NMR (600 MHz, DMSO-d_6) $\delta = 1.88$ (s, 12H), 3.70 (t, 2H), 4.29 (t, 2H), 6.64 (t, 1H), 6.80 (d, 2H), 7.17 (d, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) $\delta = 171.4$, 147.6, 129.7, 116.8, 112.5, 63.8, 57.6, 49.0, 30.7.

Synthesis of Azo monomer (AZO-M). ATRP initiator 1 (0.47 g, 1.5 mmol) was dissolved in DMF (30 ml) at 0 °C. A diazonium salt of ethyl-*p*-aminobenzoate was prepared by adding an aqueous solution of sodium nitrite (0.21g, 3.0 mmol in 0.6 ml of water) into a mixture of ethyl-*p*-aminobenzoate (0.42 g, 2.5 mmol), HCl (36%, 0.8 mL) and H_2O 1mL. The mixture was stirred at 0 °C for 15 min and then was added dropwise into above DMF solution. The solution was stirred at 0 °C for 12 h and then distilled under reduced pressure to remove DMF. To the residue was added ethyl acetate and washed with water, dried over anhydrous $MgSO_4$. After solvent removal, column chromatography was undertaken (ethyl acetate : petroleum ether (1:1)) to afford the product. Yield: 80%. ^{1}H NMR (600 MHz, DMSO-d_6) δ =1.17 (t, 3H), 1.35(t, 3H), 1.86 (s, 6H), 3.55(m, 2H), 3.77 (t, 2H), 4.35 (m, 4H), 6.93 (d, 2H), 7.83 (d, 2H), 7.86 (d, 2H), 8.09 (d, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) $\delta = 171.4$, 165.9, 155.8, 151.6, 143.3, 130.9, 130.5, 126.0, 122.4, 64.1, 61.4, 57.6, 48.3, 45.3, 30.8, 14.7, 12.5.

Synthesis of the tosylate ended poly(ethylene glycol) (PEG-Ts). Poly(ethylene glycol) monomethyl ether (PEG) (Mn =1 900, PDI =1.08) (6g, 3.16 mmol) and 3 mL triethylamine were dissolved in 30 ml CH_2Cl_2. This solution was cooled in an ice bath. Then 3 g of 4-toluenesulfonylchloride (15.7 mmol) was added. The reaction mixture was kept at 0 °C for 2 h and stirred at room temperature for 12 h. The product was then obtained by precipitated in cold diethyl ether and recrystallized from ethanol twice.

Yield: 60%. *Mn* (NMR) =2 100, *Mn* (GPC) =3 700, PDI =1.08. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 2.42 (s, 3H), 3.24 (s, 3H), 3.45~3.60 (m, 180H), 4.11 (t, 2H), 7.48 (d, 2H), 7.78 (d, 2H).

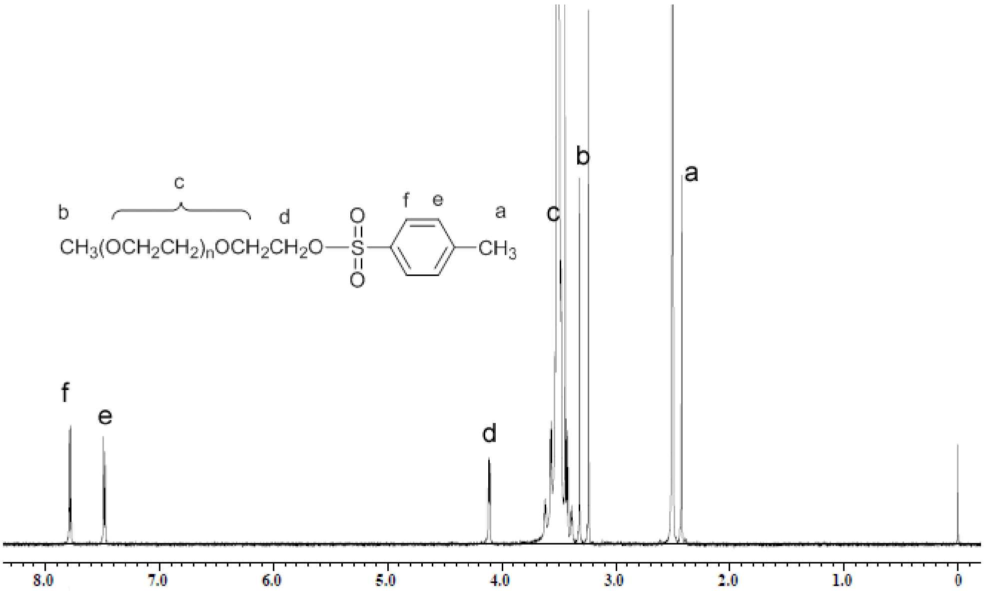

Figure S1 ^{1}H NMR spectrum of the PEG-Ts in DMSO-d_6 and structural identification.

Synthesis of aniline functionalized PEG (PEG-NH_2). PEG-NH_2 was prepared by the nucleophilic substitution reaction between PEG-Ts and p-aminobenzoic acid. PEG-Ts (6.3g, 3 mmol) and p-aminobenzoic acid (2.1 g, 15 mmol) were dissolved in DMF (50 mL) in a 250 mL round-bottom flask. Potassium carbonate (2.1 g) was added into the DMF solution. The reaction was carried out at 50 °C for 24h with stirring, and then the mixture was poured into an excessive amount of cold diethyl ether. The product was collected by filtration and recrystallization with ethanol. Yield 70%. *Mn* (NMR) =2 100, *Mn* (GPC) =3 700, and PDI= 1.08. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 3.24 (s, 3H), 3.45~3.60 (m, 180H), 4.26 (t, 2H), 5.96 (s, 2H), 6.56 (d, 2H), 7.63 (d, 2H).

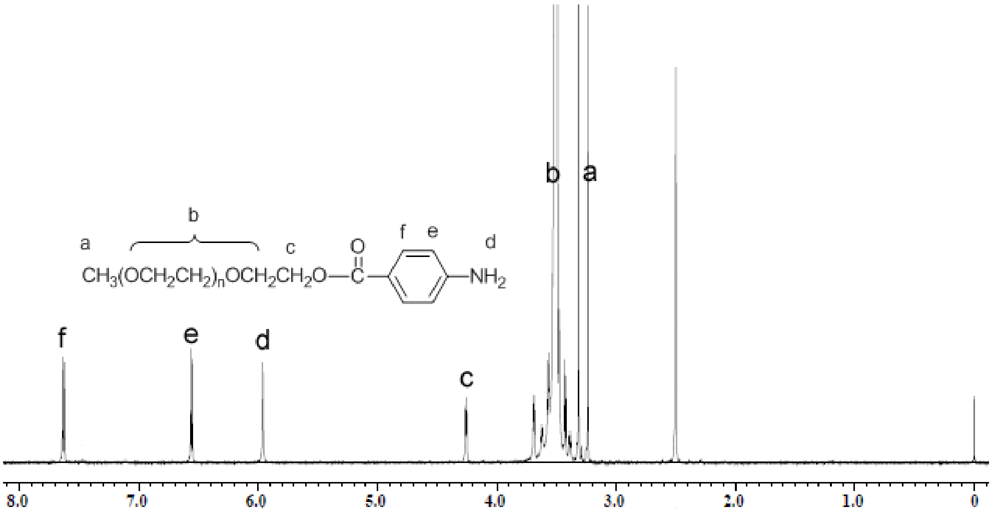

Figure S2 ^{1}H NMR spectrum of the PEG-NH_2 in DMSO-d_6 and structural identification.

Atom transfer radical polymerization for PMMA with terminal anilino functionality: CuBr (28.7 mg, 0.20 mmol) was added to a Schlenk flask. Then it was degassed and back-filled with argon three times. Following this step, deoxygenated ATRP initiator 1 (62.8mg, 0.2mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (54.4 µL, 0.2mmol), and MMA 6 mL were added via gas-tight syringes which had been previously purged with argon. After degassing by three freeze–pump–thaw cycles, the flask was immersed in an oil bath preheated to 100 °C. After the polymerization for 10 min, the reaction mixture was diluted with THF and passed through an alumina column to remove catalyst. The filtrate was concentrated and poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol and then dried in a vacuum oven for 24 h. *Mn* (GPC) =14000, and PDI= 1.24.

Atom transfer radical polymerization for PS with terminal anilino functionality: CuBr (71.8 mg, 0.5 mmol) and 2,2-dipyridyl (156.2 mg, 1 mmol) were added to a Schlenk flask. Then it was degassed and back-filled with argon three times. Following this step, deoxygenated ATRP initiator 1(157mg, 0.5mmol) and styrene 10 mL were added via gas-tight syringes which had been previously purged with argon. After degassing by three freeze–pump–thaw cycles, the flask was immersed in an oil bath preheated to 110 ^oC. After the polymerization for 2.5 hr or 1.5 hr, the reaction mixture was diluted with THF and passed through an alumina column to remove catalyst. The filtrate was concentrated and poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol and then dried in a vacuum oven for 24 h. *Mn* (GPC) =8800 and PDI= 1.29; *Mn* (GPC) =4200 and PDI= 1.31.

Atom transfer radical polymerization for PS with anilino functionality in the middle of polymer chain: CuBr (71.8 mg, 0.5 mmol) and 2,2-dipyridyl (156.2 mg, 1 mmol) were added to a Schlenk flask. Then it was degassed and back-filled with argon three times. Following this step, deoxygenated ATRP initiator 2(119.8mg, 0.25mmol) and styrene 10 mL were added via gas-tight syringes which had been previously purged with argon. After degassing by three freeze–pump–thaw cycles, the flask was immersed in an oil bath preheated to 110 ^oC. After the polymerization for 1.5 hr, the reaction mixture was diluted with THF and passed through an alumina column to remove catalyst. The filtrate was concentrated and poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol and then dried in a vacuum oven for 24 h. *Mn* (GPC) =6 300, and PDI= 1.29.

Macromolecular azo-coupling reaction (typical procedure):

PS with terminal anilino functionality (0.44 g, 0.05 mmol) was dissolved in DMF (50 ml) at 0 ^oC. A diazonium salt of PEG-NH_2 was prepared by adding an aqueous solution of sodium nitrite (14 mg, 0.2 mmol in 0.6 ml of water) into a mixture of PEG-NH_2 (0.21 g, 0.1 mmol), HCl (36%, 0.07 mL) and H_2O 1mL. The mixture was stirred at 0 ^oC for 15 min and then was added dropwise into above DMF solution. The solution was stirred at 0 ^oC for 72 h and then distilled under reduced pressure to remove most of the DMF. Then the result solution was precipitated with water. The precipitate was collected by filtration, washed with methanol and then dried in a vacuum oven for 24 h. Yield: 95%. *Mn* (GPC) =10000, and PDI= 1.27.

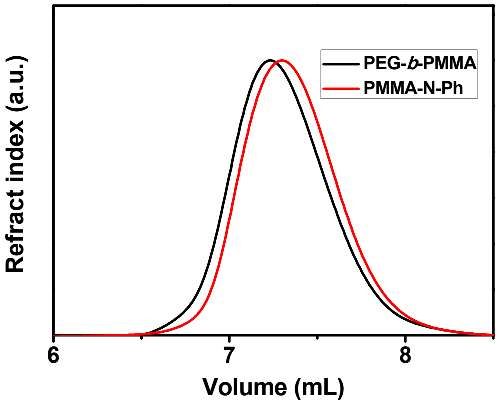

Figure S3 The GPC curves of PMMA-N-Ph (PDI=1.24, Mn=14000) and PEG-*b*-PMMA (PDI=1.24, Mn=15400).

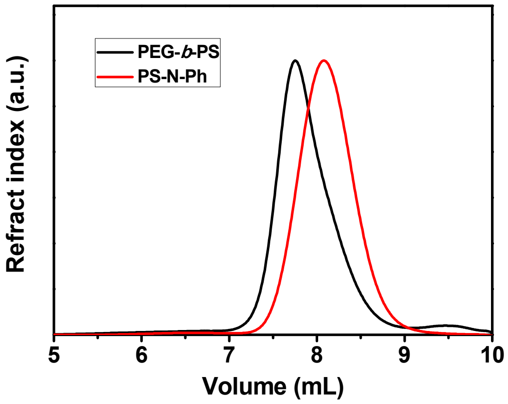

Figure S4 The GPC curves of PS-N-Ph (PDI=1.31, Mn=4200) and PEG-*b*-PS (PDI=1.32, Mn=5700).

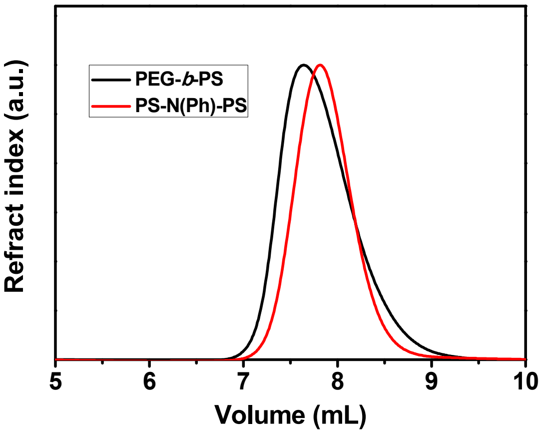

Figure S5 The GPC curves of PS-N(Ph)-PS (PDI=1.29, Mn=6300) and PEG-*b*-$(PS)_2$ (PDI=1.38).

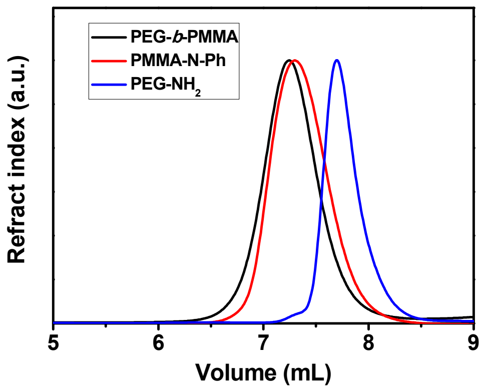

Figure S6 The GPC curves of PEG-NH$_2$ (PDI=1.12 Mn=6700, Mn (^{1}HNMR)=5000), PMMA-N-Ph (PDI=1.24, Mn=14000) and PEG-*b*-PMMA (PDI=1.24, Mn=19000).