

Supporting Information (SI)

RAFT synthesis of polyethylene glycol (PEG) and amino functionalized amphiphilic copolymers for dispersion of Carbon Nanofibers

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1. Preparation of Bis(dithiobenzoyl) Disulfide.

Bromobenzene (15.70 g, 0.10 mol) in 50 mL of dry THF was added over a period of 40 min, in the ice-water bath, to magnesium turnings (2.51 g, 0.102 mol), a catalytic amount of iodine and then reaction was started at 40 °C. CS₂ (7.6 g, 0.10 mol) was dropwised to the reaction mixture in the ice-water bath, when magnesium turnings was little. The Grignard product was hydrolyzed with 100 mL of cold, distilled water, and then formed salts and excess Mg turnings were filtered out. Diethyl ether (200 mL) was added to the solution and the mixture was acidified by the dropwise addition of fuming HCl until water layer was clear. Diethyl ether was removed under reduced pressure and red oil was gotten after the organic layer was washed by deionized water three times. Red oil was dissolved in 100mL of absolute ethanol and reacted with DMSO (7.80 g, 0.10 mol) and a catalytic amount of iodine at room temperature for 1 h. After keeping the reaction mixture at 0 °C for 12 h, the mixture was

filtered, redissolved in ethanol at 40 °C, and recrystallized for three times. After drying, a purple crystalline product was obtained, namely, bis(dithiobenzoyl) disulfide (yield 75%).

$^1\text{H NMR}$ (DMSO- D_6): $\delta = 7.50$ (m, 4H, Ph- C_3 and C_5), 7.65 (m, 2H, Ph- C_4), 8.15 (m, 4H, Ph- C_2) ppm

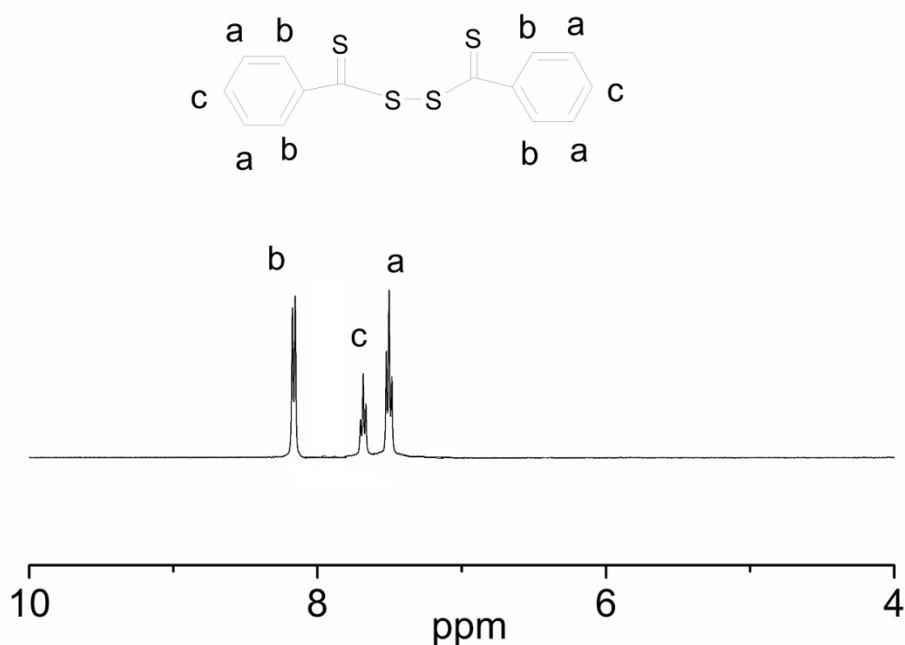


Figure S1. $^1\text{H-NMR}$ of bis(dithiobenzoyl) disulfide.

2. Synthesis of 2-Cyanoprop-2-yl Dithiobenzoate (CyDB)

Bis(thiobenzoyl)disulfide (2.01 g, 6.50 mmol) was mixed with 2,2-azobisisobutyronitrile (1.31 g, 7.80 mmol) in 40 mL ethyl-acetate and the mixture was refluxed for 18 hours. The red mixture was cooled to room temperature, solvent was removed by rotary evaporation, and the

red oily residue was purified by column chromatography with ethylacetate : petroleum ether 40:60 as eluent (yield 64 %).

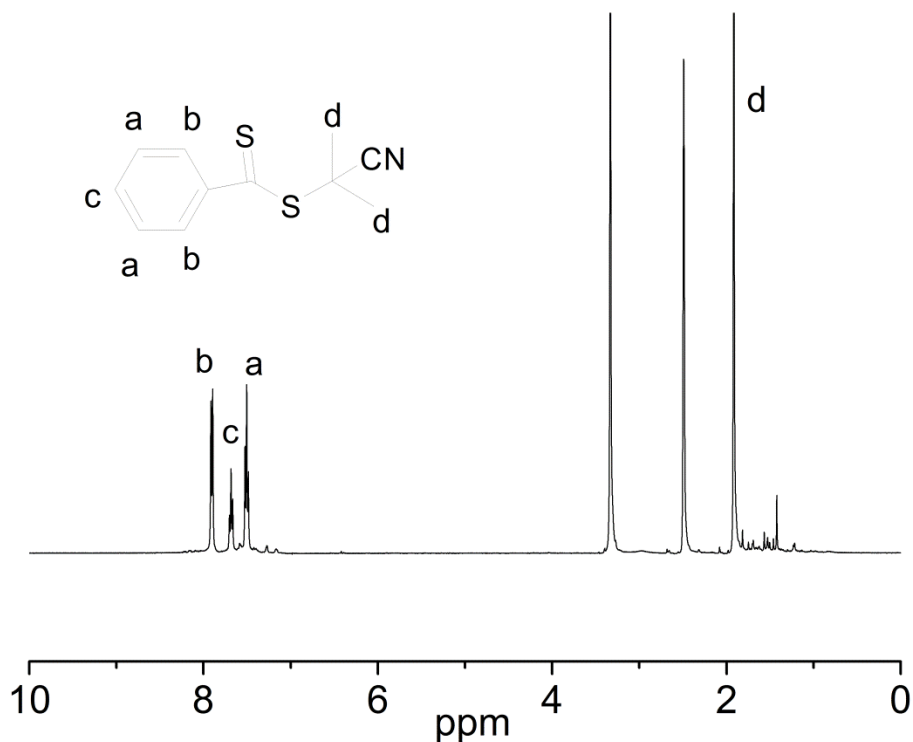


Figure S2. ¹H-NMR of CyDB. (DMSO-*D*)

3. Synthesis of the Macromolecular RAFT Agents (R_2) and the block copolymer (B_2)

Macromolecular RAFT Agents (R_2) The monomer PEGMA (3.96 g, 0.010 mol ~) and RAFT agent (CyDB, 44.2 mg, 0.20 mmol) were added to an 25 ml flask with 5.0ml 1,4-dioxane and AIBN (6.50 mg, 0.040 mmol). The reaction flask was degassed by three freeze-pump-thaw cycles. The polymerizations were then carried out in a constant temperature oil bath at 90°C for 2 hours. The polymerization was quenched by placing the flask into liquid nitrogen. The PPEGMA

polymerization mixture was purified by precipitation into petroleum ether/ diethyl ether (1:1).

Block Copolymer (B₂) The monomer BA (0.56 g, 0.010 mol) St(0.41 g, 0.0040 mol), DMAEMA (0.63 g, 0.010 mol) and R₂ (1.34 g, ~0.132 mmol) were added to an 25ml flask with 5.0 ml 1,4-dioxane and AIBN (3.00 mg, 0.018 mmol). The reaction flask was degassed by three freeze-pump-thaw cycles. The polymerization was then carried out in a constant temperature oil bath at 90 °C for 4 hours. The polymerization was quenched by placing the flask into liquid nitrogen. The (PPEGMA)-*b*-(PDMAEMA-*co*-PSt-*co*-PBA) (B₂) polymerization mixture was purified by precipitation into petroleum ether.

4. Synthesis of the Macromolecular RAFT Agents (R₃) and the block copolymer (B₃)

Macromolecular RAFT Agents (R₃) The monomer DMAEMA (3.14 g, 0.020 mol) and RAFT agent (CyDB, 126.80 mg, 0.20 mmol) were added to an 25ml flask with 7.0 ml 1,4-dioxane and AIBN (6.50 mg, 0.040 mmol). The reaction flask was degassed by three freeze-pump-thaw cycles. The polymerizations were then carried out in a constant temperature oil bath at 70 °C for 6 hours. The polymerization was quenched by placing the flask into liquid nitrogen. The PDMAEMA (R₃) polymerization mixture was purified by precipitation into petroleum ether.

Block Copolymer (B₃) The monomer PEGMA (3.96 g, 0.010 mol ~) St

(1.04 g, 0.010 mol), BA (1.51 g, 0.012 mol) and R₃ (1.05 g, ~0.44 mmol) were added to a 25ml flask with 4.0 ml 1,4-dioxane and AIBN (3.00 mg, 0.018 mmol). The reaction was degassed by three freeze-pump-thaw cycles. The polymerization was then carried out in a constant temperature oil bath at 90 °C for 3 hours. The polymerization was quenched by placing the flask into liquid nitrogen. The (PDMAEMA)-*b*-(PPEGMA-*co*-PSt-*co*-PBA) (B₃) polymerization mixture was purified by precipitation into petroleum ether/ diethyl ether (1:1).

5. Part Characterization data of copolymers

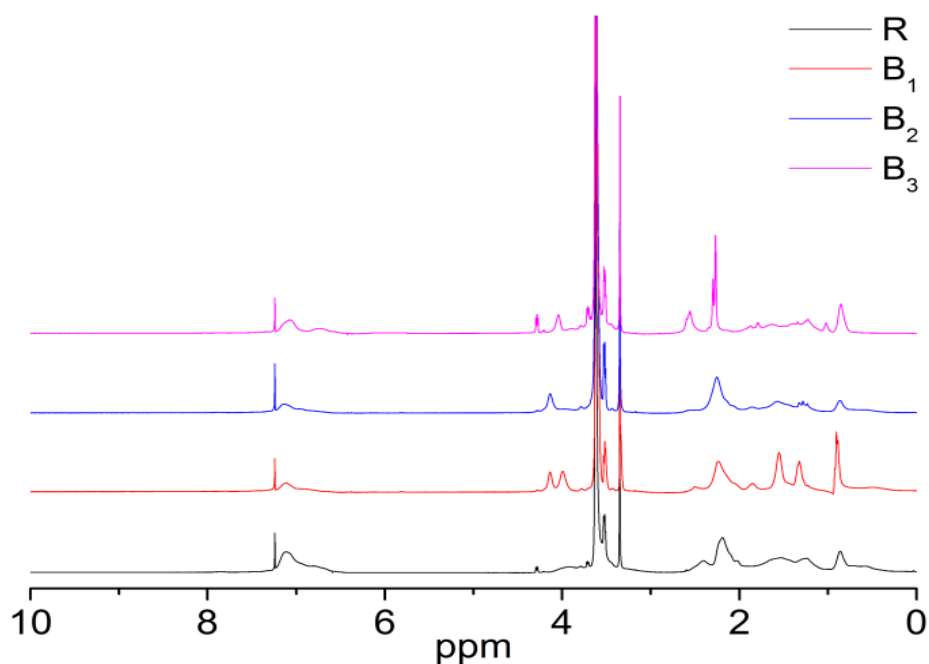


Figure S3. ¹H-NMR of R, B₁, B₂ and B₃ (CDCl₃).

Calculation of comonomer composition: The part chemical shifts at 2-3 ppm (d) can be assigned to (CH₂N(CH₃)₂) protons of the PDMAEMA block. Because typical chemical shifts of PDMAEMA block coincide with part chemical shifts of other blocks into one big peak, the mole

fraction of DMAEMA in copolymers are gotten subtraction formula (See Figure 2 about a b c d d₁ d₂ and d₃)

$$M = \frac{(D - D1 - D2 - D3)}{8}$$

Notes:

M is mole of DMAEMA in copolymer

D is total integration of chemical shifts at 2-3 ppm (d₁ d₂ and d₃)

D1 D2 and D3 are integration of chemical shifts of d₁ d₂ and d₃ in Fig. 2.

The mole fractions of each component in copolymer were calculated from ¹H NMR spectrum. We also tested and verified the mole fraction of PDMAEMA through the same method that was carried out to calculated chemical shifts at 1-2 ppm.

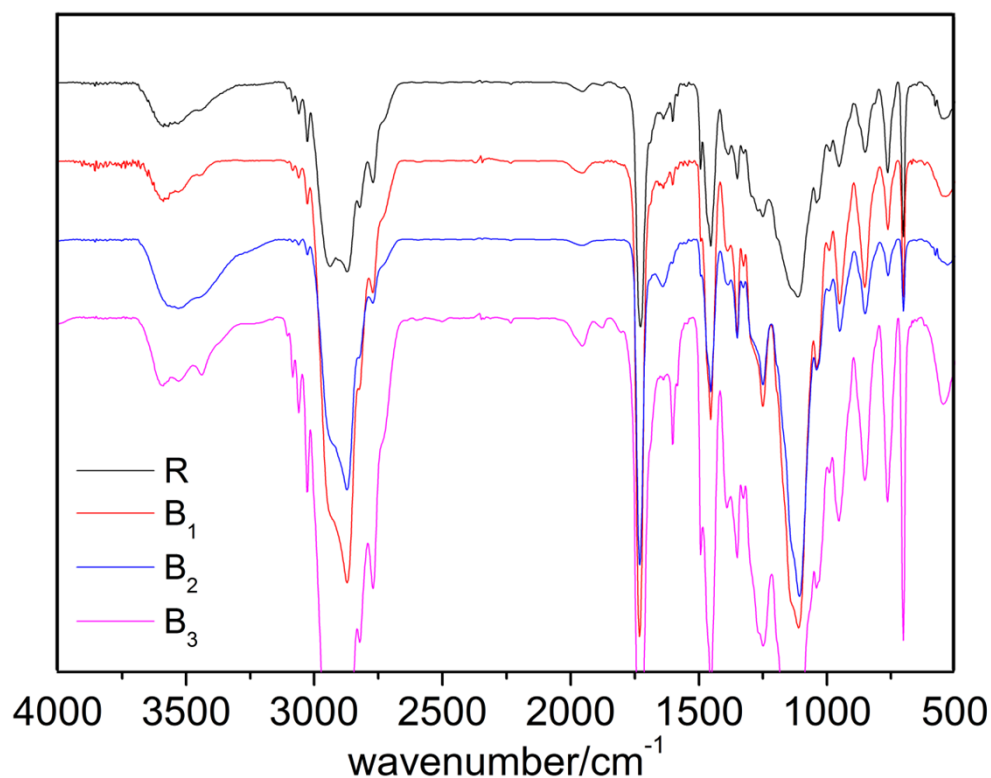


Figure S4. The FTIR spectrum of R, B₁, B₂ and B₃.

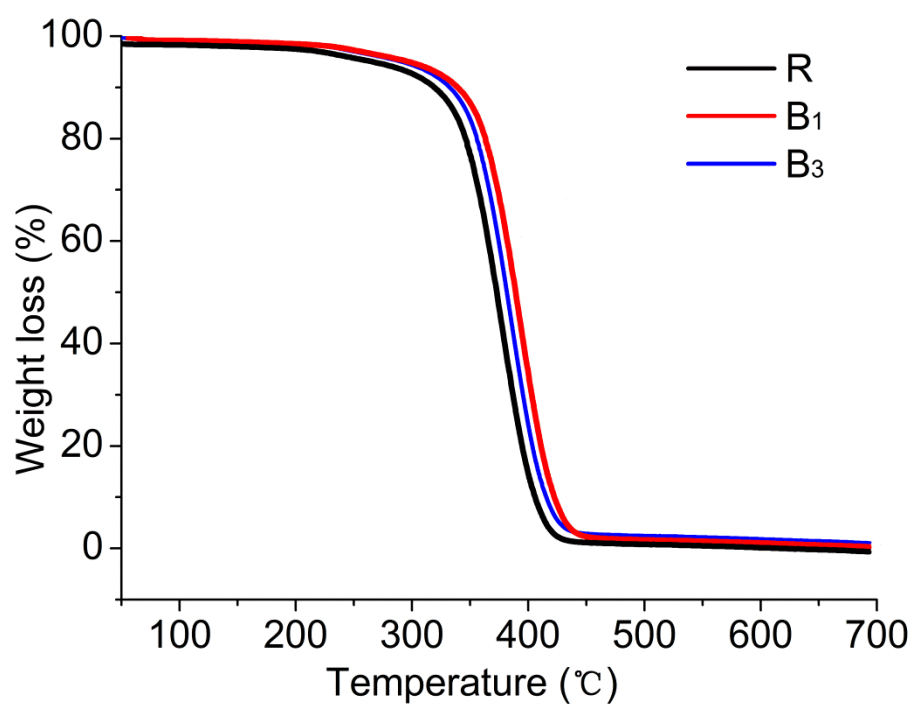


Figure S5. The TG curves of R, B₁ and B₃

6. Characterization datas

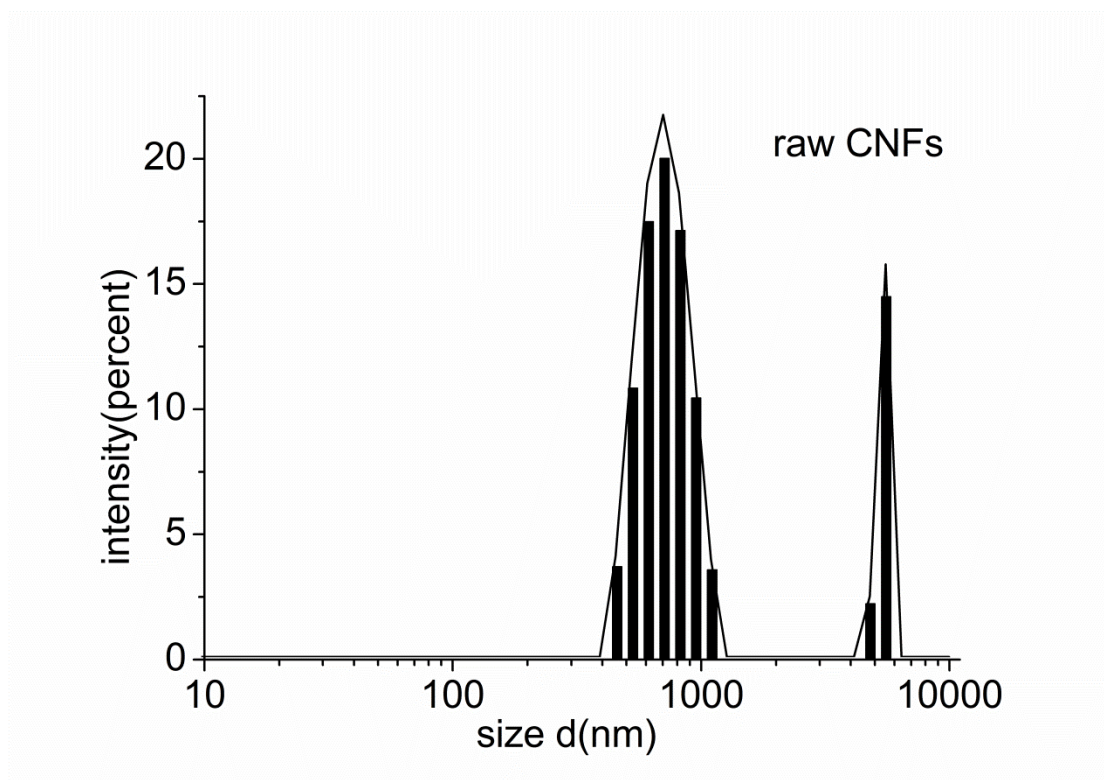


Figure S6. The size distribution of the raw CNFs dispersion by DLS.

The pure CNFs were difficult to disperse and there were little CNFs in its dispersion from the visual picture in Figure 3, so the size distribution of the raw CNFs dispersion was resulted from the little CNFs and the distribution the DLS results of the pure CNFs could almost not be compared.

7. Photograph of aqueous solutions of copolymers

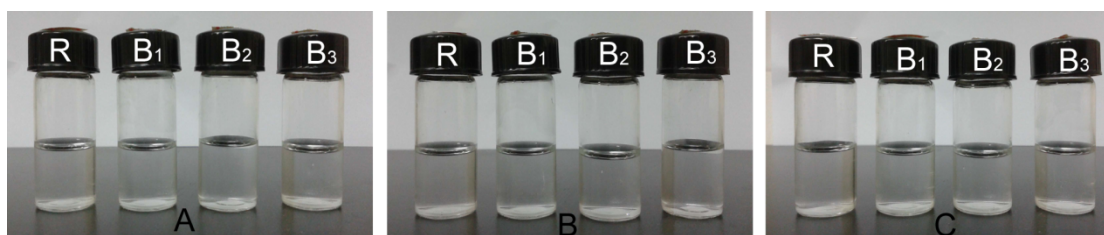


Figure S7. Copolymers were dispersed in water for 15 days (copolymers concentration: A 2 mg/ml, B 1mg/ ml, C 0.1g/ml).