

Silsesquioxane-cored star amphiphilic polymer as an efficient dispersant for multi-walled carbon nanotubes

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Supporting Information

Experimental Materials

N, N-(Dimethylamine)ethyl methacrylate (DMAEMA) was purchased from Aladdin and purified by passing over a basic aluminum oxide column. Multi-walled Carbon Nanotubes (MWNTs) produced by the synthesized by a thermal chemical vapor deposition method (carbon content > 95%; OD×ID×L: 20-30 nm×5-10 nm×0.5-200 μm). Other reagents in analytical grade were all obtained from Aldrich. 2, 2-azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol before used.

Characterization

Size exclusion chromatography (SEC) was performed at 35°C using a Waters 1515 series system equipped with styragel HR4 and HR3 columns and a Waters 2414 refractive index (RI) detector. The system was calibrated with narrowly dispersed polystyrene standards and the mobile phase used was HPLC grade THF flowing at 0.60 ml/min.

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^1H NMR spectra were recorded in deuterated chloroform on a Bruker DMX-400 spectrometer equipped with a Varian probe.

Infrared spectra (IR) were obtained by Fourier transform infrared spectrometer (Bruker Tensor 27, Germany) using KBr method.

The UV/vis spectra (UV-2501, Shimadzu Co. Japan) of samples were measured in the range 200-800 nm.

Weight loss temperatures of the products were examined by a thermogravimetric analyzer (Netzsch TG209F3) at a heating rate of 10 °C/min under a nitrogen flow rate of 40 ml/min from 50-600 °C.

Transmission Electron Microscopy was performed on a Tecnai G2 F20 S-TWIN High Resolution Transmission Electron Microscopy (HR-TEM)

Polymer synthesis

Synthesis of CSQ-RAFT agent

Synthesis of Octa(aminophenyl)silsesquioxane(OASQ)¹:

Octa(nitrophenyl)silsesquioxane (ONSQ) was synthesized in our laboratory. ONSQ (1g, 0.716mmol, $-\text{NO}_2$ 5.74 mmol), FeCl_3 (20 mg), and 0.8 g active charcoal powder were charged into a three-necked 100 mL round-bottomed flask. THF (50 mL) was then added to the flask. The solution was stirred and heated to 60 °C under purified nitrogen. Hydrazine hydrate (4 mL) was added dropwise into the mixture. The reaction was continued for 6 h, and then the solution was cooled and filtered through Celite. The filtrate was combined with 40 mL of ethyl acetate and washed with H_2O four times. The organic layer was dried over MgSO_4 and poured into 200 mL hexane. The white precipitate was collected by filtration. The product was redissolved in the mixture of 15 mL THF and 20 mL ethyl acetate, and reprecipitated into 200 mL hexane. The obtained powder was dried in vacuum. FTIR (KBr): 3369, 3220 (w; N-H), 1119 cm^{-1} (s; Si-O-Si); ^{29}Si NMR (δ , ppm): -70.0, -77.5; ^1H NMR (DMSO- d_6 ,) (d, ppm): 7.8-6.2 (b, 2.0H), 5.2-3.7 (b, 1.0H).

Synthesis of BSPA:

3-Benzylsulfanylthiocarbonylsufanylpropionic acid (BSPA, RAFT agent) were synthesized according to the literature². ¹H NMR (DMSO, ppm): 7.35-7.25 (m, 5H, Ph), 4.60 (s, 2H, CH₂Ph), 3.65 (t, 2H, SCH₂CH₂COOH), 2.85 (t, 2H, SCH₂CH₂COOH). IR (KBr): 1710, 1490, 1450, 1240, 1070 cm⁻¹.

BSPA (2.52 g, 0.01 mol) and 7 mL of carbon tetrachloride were mixed in a dried 25 ml schlenk flask. Freshly distilled thionylchloride (2.5 ml) was added dropwise to the reaction mixture until the mixture was clear. After keeping the reaction mixture at reflux for 1 h, removed the solvent by Vacuum Freeze Drying, a yellow liquid was obtained. It was further dried under a high vacuum overnight at room temperature before used. The 3-benzylsulfanylthiocarbonylsufanylpropionic chloride (BSPA-Cl) was not characterized before use in the next step.

OASQ (0.54 g, 0.05 mmol) and 0.5 mL distilled pyridine were mixed with 6 ml distilled THF in a dried 25 ml schlenk flask. The freshly prepared BSPA-Cl was diluted in 6 ml of distilled THF. The solution was added dropwise into the flask at 0 °C for 30 min. After stirring for 24 h at room temperature, 10 ml chloroform was added into the mixture and then the mixture was washed repeatedly by saturated sodium bicarbonate, deionized water and diluted hydrochloric acid. Finally the organic layer was precipitated in n-hexane and the solid powder was CSQ-RAFT agent (1.27 g, yield 85%). (¹H NMR (DMSO ppm): 8.00-7.50 (m, 72H, Ph), 4.60 (s, 16H, CH₂Ph), 3.65 (t, 16H, SCH₂CH₂CONH), 2.85 (t, 16H, SCH₂CH₂CONH), IR (KBr): 1650, 1490, 1110, 1050 cm⁻¹)

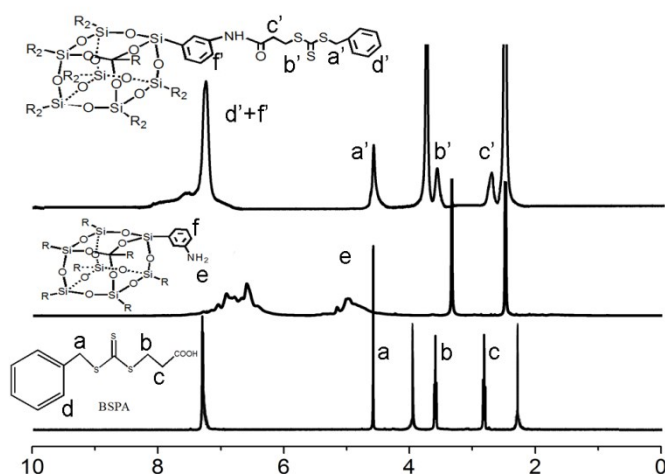


Fig. S1. ^1H NMR spectra of BSPA, OA-POSS and CSQ-RAFT agent.

Synthesis of CSQ-based star-shaped copolymer (CSQ-PDMAEMA)

DMAEMA (1.05 g, 0.0067 mol), SQ-RAFT agent (19.5 mg, 0.0065 mmol), AIBN (1.0 mg, 0.0061 mmol) were loaded into Schlenk tube with 3 ml of dioxane as a solvent. The tube was sealed and subjected to three freeze-pump-thaw cycles. The polymerization was allowed to proceed under continuous stirring at 70 °C for 2 h. The polymerization was quenched by liquid nitrogen. Then, the mixture was purified by precipitation into cold petroleum ether/diethyl ether (10:1). ($M_n=72920$ and $PDI=1.59$ by SEC, ^1H NMR (CDCl_3 ppm): 4.05 ($\text{CH}_2\text{-O}$), 2.54 ($-\text{CH}_2\text{-N}(\text{CH}_3)_2$), 2.24 ($-\text{CH}_2\text{N}(\text{CH}_3)_2$) 1.56-2.04 ($-(\text{C}-\text{CH}_2)-$), 0.92-1.04 ($\text{C}-\text{CH}_3$))

Synthesis of CSQ-PDMAEMA-CZ

CSQ-PDMAEMA (0.66 g, $M_n=72920$), AIBN (0.5 mg, 0.1 mmol) and vinyl carbazole (0.50 g, 2.6 mmol) with 3.5 ml dioxane were introduced into a dried 10 ml schlenk flask. The reaction flask was degassed by three freeze-pump-thaw cycles. The polymerization was allowed to proceed under continuous stirring at 70 °C for 2 h. The polymerization was quenched by liquid nitrogen. Then, the polymer solution was dropwised into diethyl ether and the unreacted vinyl carbazole was filtered out. After the filtrate was concentrated by rotary evaporator, the polymer was precipitated in n-hexane several times. The carbazole-contained star polymer (CSQ-PDMAEMA-CZ)

was gotten after drying under vacuum for several days. ($M_n=73614$ and $PDI=1.60$ by SEC, 1H NMR ($CDCl_3$ ppm): 7.0-8.0 (Ph), 4.05 (CH_2-O), 2.54 ($-CH_2-N(CH_3)_2$), 2.24 ($-CH_2N(CH_3)_2$) 1.56-2.04 ($-(C-CH_2)-$), 0.92-1.04 ($C-CH_3$))

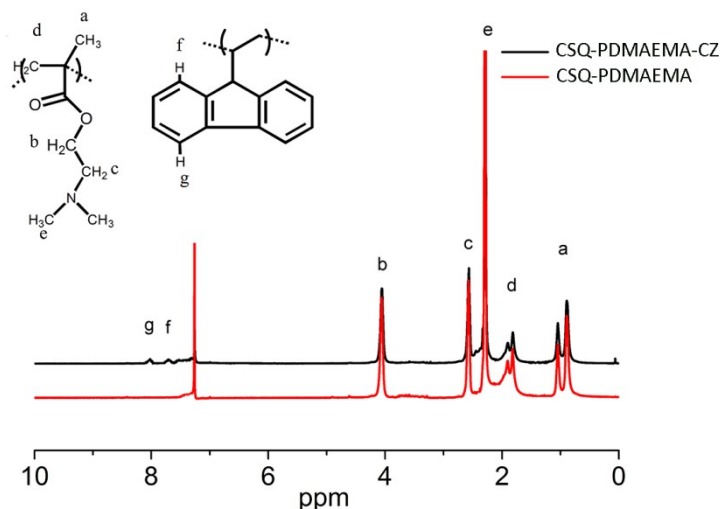


Fig.S2 1H NMR of CSQ-PDMAEMA-CZ and CSQ-PDMAEMA.

Synthesis of poly N, N-(Dimethylamino)ethyl methacrylate (PDMAEMA).

DMAEMA (1.57g, 0.01mol), BSPA (27.2mg, 0.1mmol), AIBN (3.28mg, 0.02mmol) were loaded into Schlenk tube with 3 mL of dioxane. The tube was sealed and /subjected to three freeze-pump-thaw cycles. The polymerization was allowed to proceed under continuous stirring at 70 °C for 2 h. The polymerization was quenched by liquid nitrogen. Then, the mixture was purified by precipitation into cold petroleum ether/diethyl ether (10:1). ($M_n=6236$ and $PDI=1.01$ by SEC, 1H NMR ($CDCl_3$ ppm): 4.01 (CH_2-O), 2.52 ($-CH_2-N(CH_3)_2$), 2.24 ($-CH_2N(CH_3)_2$) 1.72-1.98 ($-(C-CH_2)_n-$), 0.78-1.12 ($C-CH_3$))

Synthesis of PDMAEMA-CZ

The PDMAEMA-CZ was generated by the PDMAEMA-mediated free-radical solution polymerization of Vinylcarbazole in dioxane at 70°C for 2 h (Vinylcarbazole (0.579g, 0.003mol), PDMAEMA (0.6236g, 0.1mmol), AIBN (3.28mg, 0.02mmol), dioxane (3mL)). ($M_n=7350$ and $PDI=1.04$ by SEC, 1H NMR ($CDCl_3$ ppm): 7.0-8.0 (Ph),

4.11 (CH_2-O), 2.52 ($-CH_2-N(CH_3)_2$), 2.35 ($-CH_2N(CH_3)_2$), 1.65-2.04 ($-(C-CH_2)_n-$), 0.86-1.18 ($C-CH_3$)

Self-assembly of octopus-shaped amphiphilic polymer and contrast samples in Aqueous Solution

All modifiers were dissolved in deionized water and stirred for 24 h to ensure the system reached equilibrium.

General Procedure for Dispersing MWNTs

The MWNTs were treated by ultrasonication in acetone for 10 min at 180 W and rinsing with water for several times to remove organic residues and part of inorganic impurity. The dispersion liquid was prepared by mixing treated-MWNTs and deionized water or acetone solution with aqueous polymer solution (concentration of polymer is 1% w/v) in a flask and then sonicated the resulting mixture for 20 min. All sonication processes were carried out with a horn sonicator. The output power was fixed at 180 W and the flask is placed in a bath of ice water during sonication to prevent the temperature rising. Then, the dispersions were centrifuged at a speed of 12500 rpm for 10min. The modified CNTs were obtained by washing and vacuum drying the residues. The centrifugal supernatant liquid and the washing liquid (the total volume of washing liquid was four times as much as the volume of dispersion) were merged for further testing.

IR characterization

The pristine MWNT and all the modified MWNT were dried under vacuum at room temperature for three days and characterized by FTIR spectroscopy (KBr).

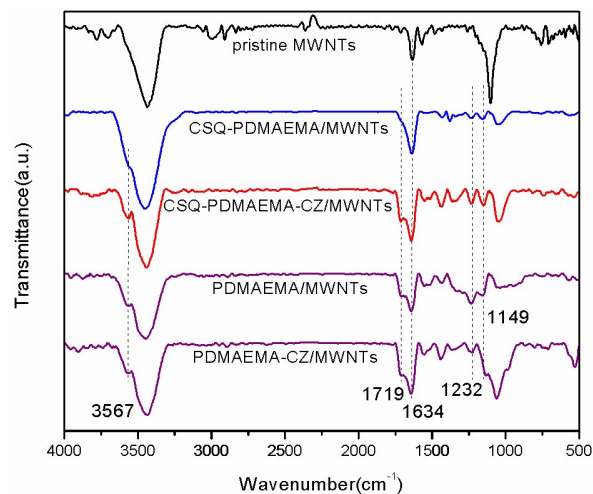


Fig.S3 The infrared spectrogram of pristine MWNTs and modified CNTs.

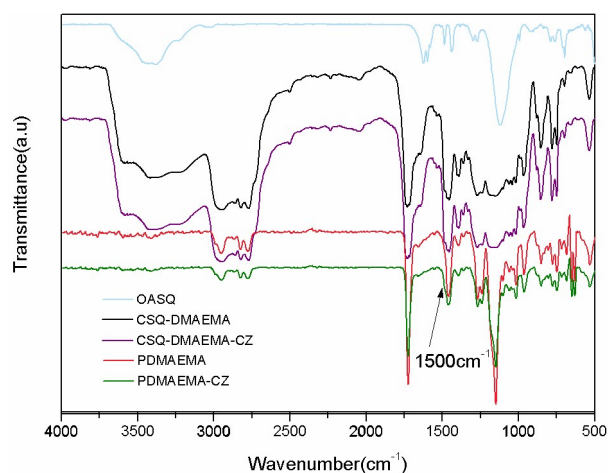


Fig.S4 The infrared spectrogram of modifiers.

The IR spectrum results are almost similar due to the overwhelming contributions of carbazole and CSQ in PDMAEMA structure. Only the curve of PDMAEMA-CZ has a little different with the curve of PDMAEMA at 1500cm^{-1} , which corresponds essentially to the cyclobenzene stretching vibration of carbazole.

UV-vis characterization

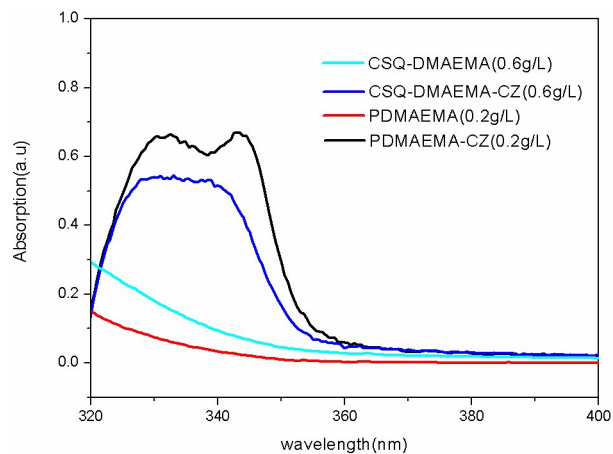


Fig.S5 UV-vis spectrogram of modifiers.

The solution concentrations of CSQ-DMAEMA, CSQ-DMAEMA-CZ, PDMAEMA, PDMAEMA-CZ were 0.6g/L, 0.6g/L, 0.2g/L, 0.2g/L respectively.

TGA characterization

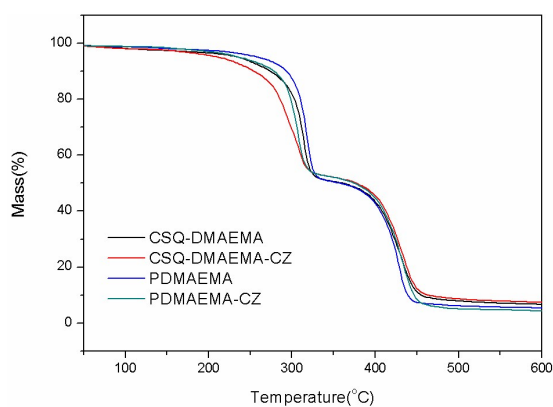


Fig.S6 TGA curves of CSQ-DMAEMA, CSQ-DMAEMA-CZ, PDMAEMA and PDMAEMA-CZ.

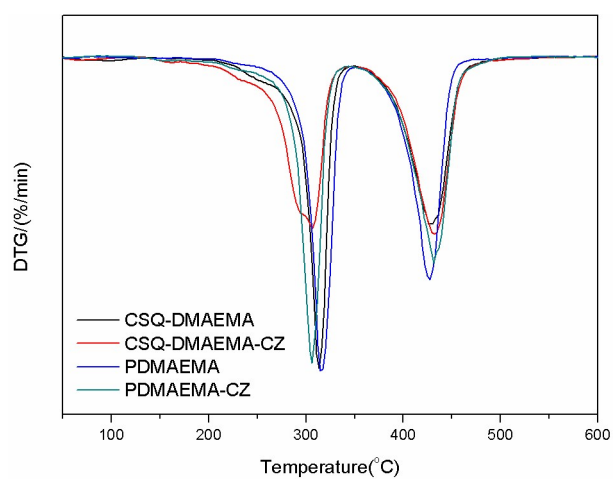


Fig.S7 DTG curves of CSQ-DMAEMA, CSQ-DMAEMA-CZ, PDMAEMA and PDMAEMA-CZ.

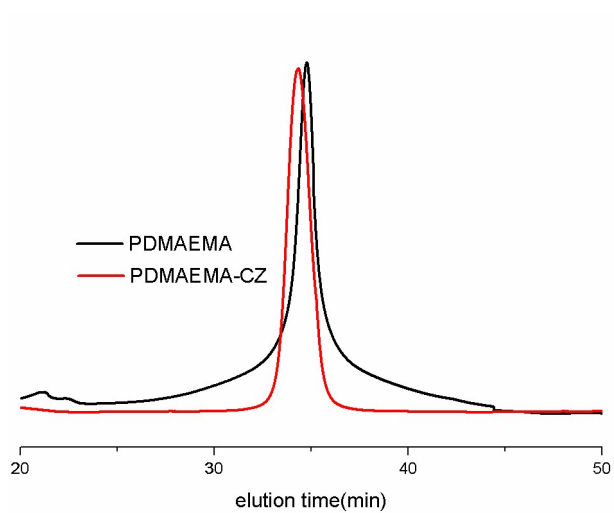
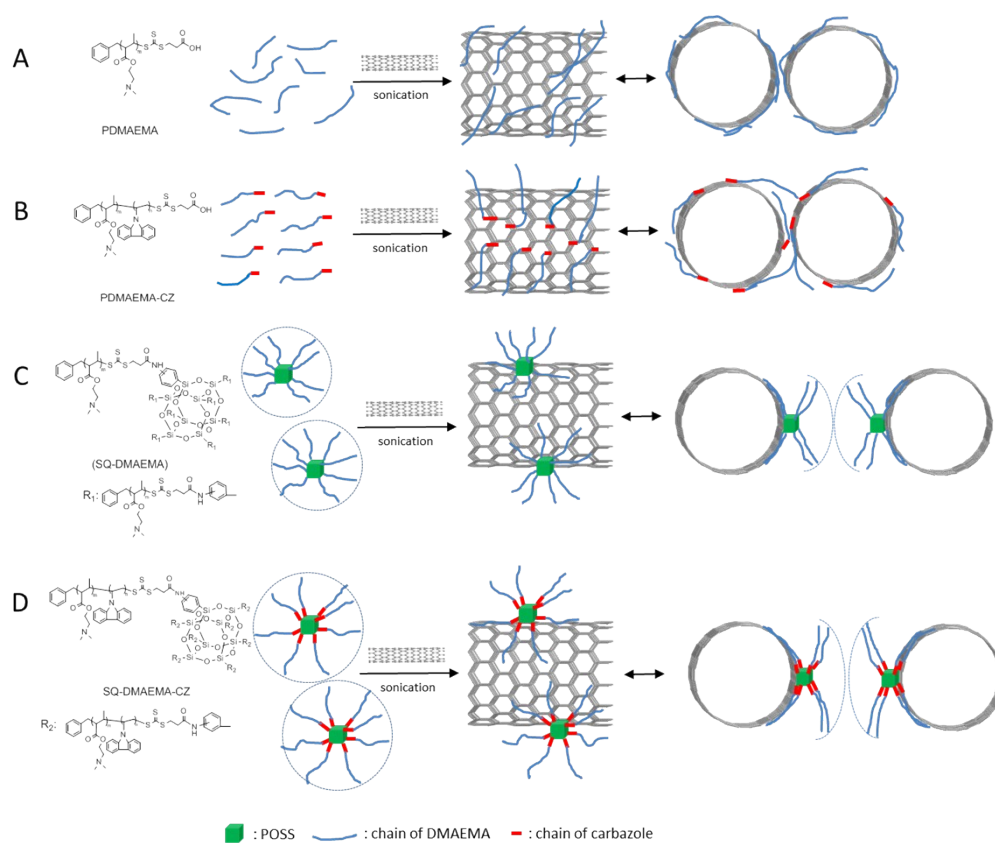


Fig.S8 SEC traces of the PDMAEMA and PDMAEMA-CZ



Scheme S1. Mechanism for the interaction between MWCNT and PDMAEMA (A), PDMAEMA-CZ (B), CSQ-DMAEMA (C), CSQ-DMAEMA-CZ (D).

1. R. Tamaki, Y. Tanaka, M. Z. Asuncion, J. Choi and R. M. Laine, *Journal of the American Chemical Society*, 2001, **123**, 12416-12417.
2. M. H. Stenzel and T. P. Davis, *Journal of Polymer Science Part A: Polymer Chemistry*, 2002, **40**, 4498-4512.