Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One-pot polymer modification of carbon Nanotubes through mercaptoacetic acid locking imine reaction and π-π Stacking

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Experimental Section

1. Materials

Methoxypolyethylene glycol (mPEG, Mn ~ 5000, Aldrich), N, N'-dicyclohexylcarbodiimide (DCC, Aladdin, ≥ 99.0%), 4-dimethylamiopryidine (DMAP, Aladdin, 99%), 4-formylbenzoic acid (Aladdin, ≥ 99.0%), 1-aminopyrene (Aladdin, ≥ 99.0%) mercaptoacetic acid ((Aladdin, ≥ 99.0%), acetic acid (J&K Chemical, 99.8%) and methyl methacrylate (MMA, J&K Chemical, 99%) were used as purchased. 2, 2`-Azoisobutyronitrile (AIBN, J&K Chemical, 99%) was recrystalized twice from acetone before using. (4-Cyano-4-(((ethylthio)carbonothioyl)thio) pentanoic acid[1, 2] and 4-((6-hydroxyhexyl)oxy) benzaldehyde were synthesized as previous literatures[3-5].

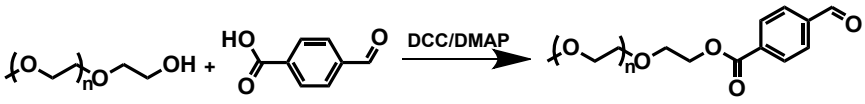
2. Instrumental Analysis

Gel permeation chromatography (GPC) analyses of polymers were performed using tetrahydrofuran (THF) as the eluent. The GPC system was a Shimadzu LC-20AD pump system consisting of an auto injector, a MZ-Gel SDplus 10.0 μm guard column (50 × 8.0 mm, 10^2 Å) followed by a MZ-Gel SDplus 5.0 μm bead-size column (50-10^6 Å, linear) and a Shimadzu RID-10A refractive index detector. The system was calibrated with narrow molecular weight distribution polystyrene standards ranging from 200 to 10^6 g mol-1. ^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400MHz) spectrometer for all samples. The FT-IR spectra were made in a transmission mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA). Thermal gravimetric analysis (TGA) was conducted on a TA instrument Q50 with a heating rate of 20 °C/min. Samples weighing between 2 and 5 mg were heated from 25 to 600 °C in air flow (60 mL/min), N_2 as the balance gas (40 mL/min).

Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 kV; the TEM specimens were made by placing a drop of the nanoparticle ethanol suspension on a carbon-coated copper grid.

3. Experiment

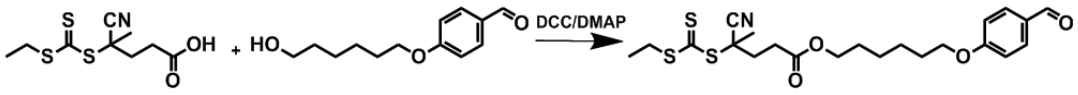
Synthesis of aldehyde terminated mPEG



Water in mPEG (M_n ~ 5000) was removed through azeotrope with toluene. 4-Formylbenzoic acid (0.18 g, 1.2 mmol) was dissolved into tetrahydrofuran (0.5 mL) priority while dehydrated mPEG (5.0 g, 1.0 mmol) was dissolved into dichloromethane (4.5 mL). The two solutions were mixed together, then DCC (0.41 g, 2.0 mmol) and DMAP (12 mg, 0.1 mmol) were added into the system under nitrogen atmosphere. The reaction was conducted for 4 h at 25 °C, and the aldehyde terminated mPEG can be obtained through precipitation in ethyl ether as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.07 (s, 1H, CHO), 8.18 (d, *J* = 7.4 *Hz*, 2H, CHOCC<u>H</u>CHCCOO), 7.92 (d, *J* = 7.4 *Hz*, 2H, CHOCCHC<u>H</u>CCOO), 4.47 (s, 2H, CH_2OCO), 3.80-3.30 (m, 464H, O<u>CH_2CH_2</u>O), 3.38 (s, 3H, CH_3O).

Synthesis of chain transfer agent (CTA) for Raft polymerization



4-Cyano-4-(((ethylthio)carbonothioyl)thio) pentanoic acid (3.0 g, 11.41 mmol) and 4-((6-hydroxyhexyl)oxy) benzaldehyde (3.8 g, 17.10 mmol) were dissolved into dichloromethane (5.0 mL), then DCC (4.7 g, 22.81 mmol) and DMAP (0.14 g, 1.14 mmol) were added into the system under nitrogen atmosphere. The system was maintained for 4 h at 25 °C. The CTA as a yellow oil (4.89 g, yield: 91.8%) could be obtained through chromatographic column using petroleum ether/ethyl acetate (3/1) as the eluant.

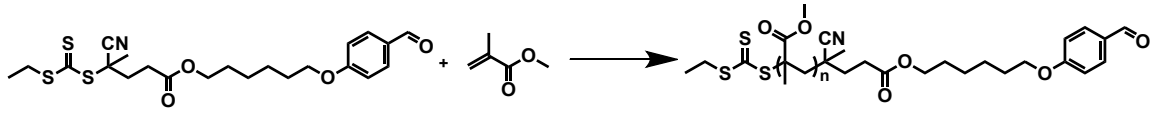
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 9.84 (s, 1H, CHO), 7.80 (d, *J* = 7.4 *Hz*, 2H, $CHOCC\underline{H}CHCOCH_2$), 6.96 (d, *J* = 7.4 *Hz*, 2H,$CHOCCHC\underline{H}COCH_2$), 4.21-3.93 (m, 4H, $C\underline{H_2}OCO$, $OC\underline{H_2}CH_2$), 3.32(m, 2H, $CH_3C\underline{H_2}$), 2.64-2.30 (m, 4H, $CC\underline{H_2}C\underline{H_2}CO$), 1.90-1.40 (m, 11H, $C(CN)C\underline{H_3}$,$OCH_2(C\underline{H_2})_{\underline{4}}CH_2O$), 1.31 (t, 3H, $CH_2C\underline{H_3}$).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 216.84, 190.91, 171.61, 164.22, 132.09, 129.87, 119.08, 114.81, 68.24, 65.09, 53.55, 46.44, 33.97, 31.45, 29.88, 29.02, 28.54, 25.75, 24.95, 12.84.

IR (v/cm^{-1}): 2932, 2858, 2738, 2117, 1732, 1688, 1599, 1576, 1509, 1451, 1426, 1394, 1311, 1254, 1215, 1182, 1175, 1110, 1075, 1031, 859, 831, 801, 734, 702

ESI-MS: observed (expected): 467.13 (468.13) [M+H^{+}]

Synthesis of terminated aldehyde group PMMA



MMA (3.00 g, 30.0 mmol), AIBN (10 mg, 0.06 mmol) and targeted synthetic CTA (140 mg, 0.3 mmol) were mixed into toluene (5.0 mL) in a dry Schlenk tube. The system were degassed through three freeze-pump-thaw cycles and then maintained for 10 h at 70 °C. The polymer could be purified through precipitation from THF to cold methanol three times. Then the obtained PMMA was kept under vacuum at 60 °C until constant weight.

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm):9.85 (s, 1H, CHO), 7.80 (d, *J = 8.1 Hz*, 2H, $CHOCC\underline{H}CHCOCH_2$), 6.96 (d, *J = 8.1 Hz*, 2H, $CHOCCHC\underline{H}COCH_2$), 4.12-3.95 (m, 4H, $C\underline{H_2}OCO$, $OC\underline{H_2}CH_2$), 3.72-3.45 (s, 305H, OCH_3), 3.20(m, 2H, $CH_3C\underline{H_2}$), 2.46 (t, 2H, $CC\underline{H_2}CH_2CO$), 2.10-1.58 (s, 202H, CCH_2C), 1.05-0.65 (s, 303H, CCH_3).

GPC data revealed the polydispersity index (PDI ~ 1.13) and the molecular weight (M_{nGPC} ~ 9500) of obtained PMMA. By comparison between peak (9.85 ppm) of chain-end aldehyde group and peak (3.75-3.45 ppm) of ester methyl group in the NMR spectra, the molecular weight of the obtained polymer was calculated as M_{nNMR} ~ 10500, consistent with the GPC analyzed result.

Synthesis of MWCNT-polymer composite

MWCNT (50 mg), aldehyde terminated mPEG (472 mg, 0.09 mmol) and 1-aminopyrene(20 mg, 0.09 mmol) were dissolved into acetic acid (1.10 mL) at 25 °C for 1 h. Then, the mercaptoacetic acid (42 mg, 0.45 mmol) was added into the mixture and the system was kept at 25 °C for 5 h. The MWCNT-mPEG could be separated from mixture by centrifugation (8,000 rpm, 30 min), then washed with acetone (50 mL) for 3 times to removed unreacted polymer and other impurities.

MWCNT-mPEG was collected and kept in vacuum oven at 60 °C until constant weight.

The MWCNT-PMMA was prepared through same procedure.

Supporting Data

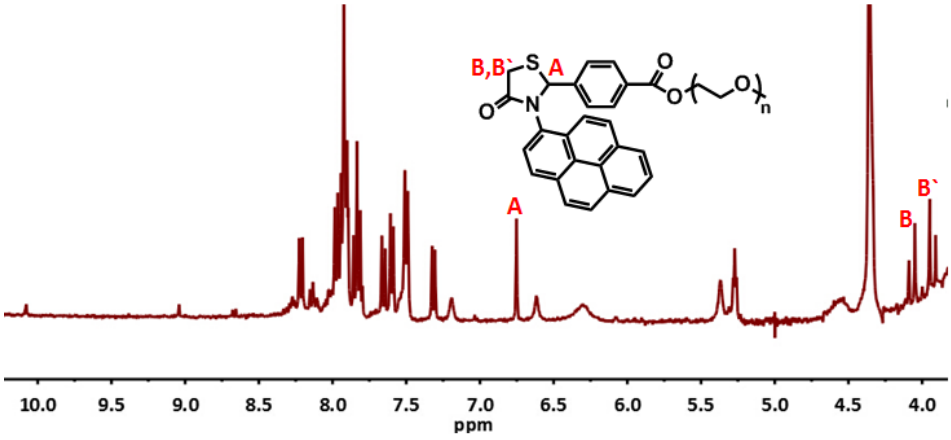


Figure 1S. [1]H NMR spectrum of model MALI reaction.

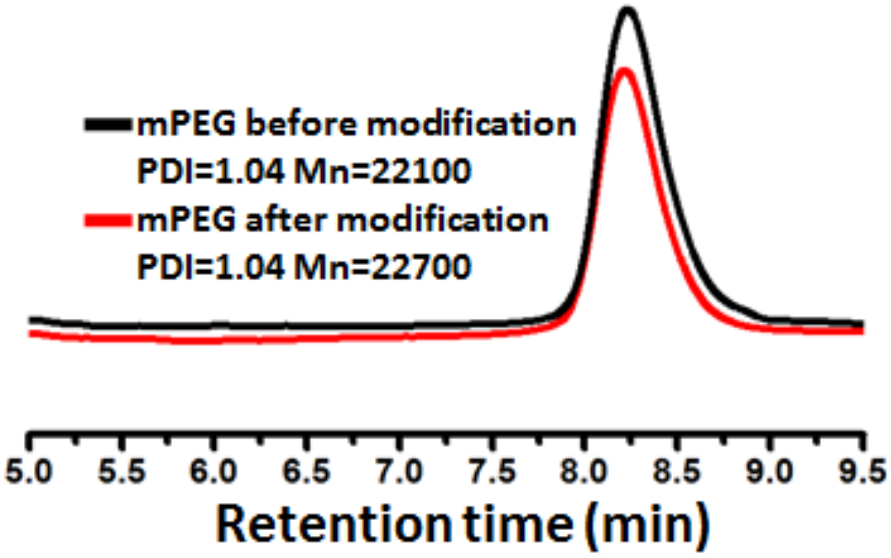


Figure 2S. GPC traces of mPEGs before and after modification.

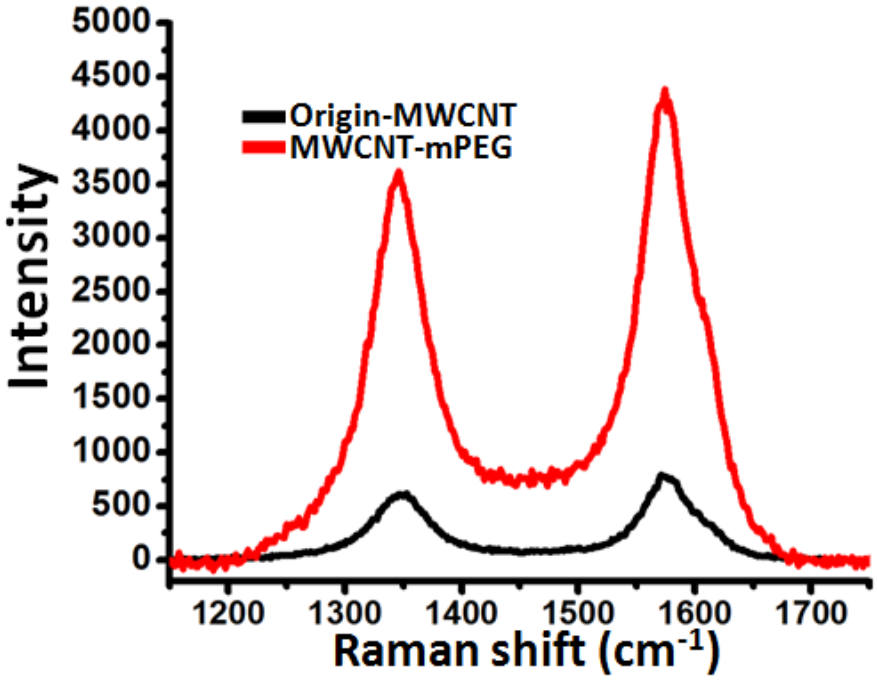


Figure 3S. Raman spectra for origin MWCNT and MWCNT-mPEG

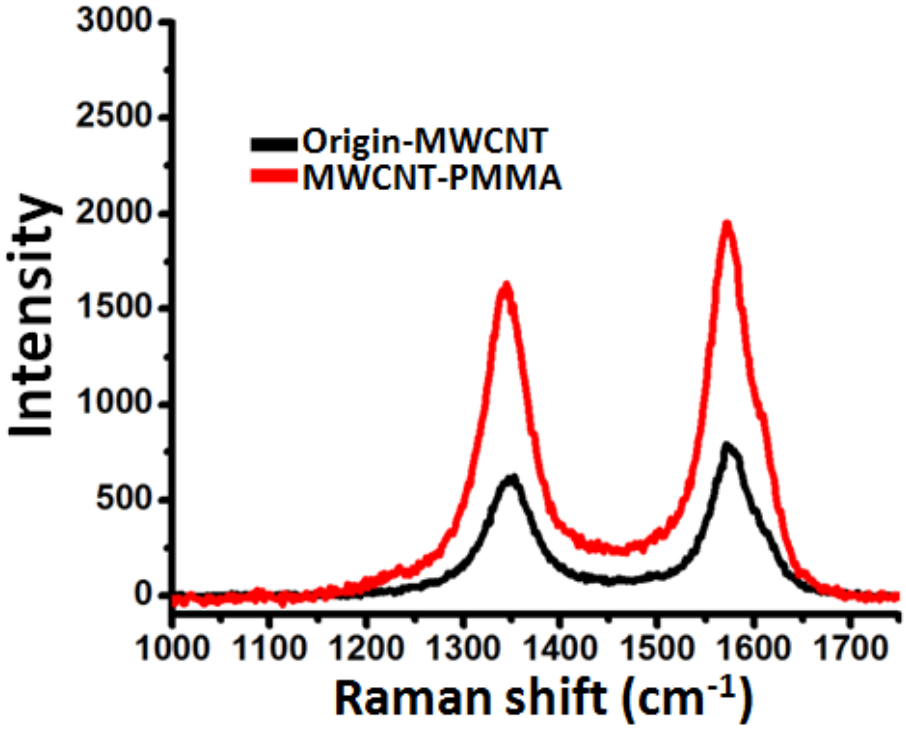


Figure 4S. Raman spectra for origin MWCNT and MWCNT-mPEG

NOTES AND REFERENCES

1. L. Tao, C. S. Kaddis, R. R. O. Loo, G. N. Grover, J. A. Loo and H. D. Maynard, *Macromolecules*, 2009, **42**, 8028-8033.
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