

Preparation of Diblock Copolymer Films for the Localization of C₆₀ and Multiwalled Carbon Nanotubes on Aqueous Substrate

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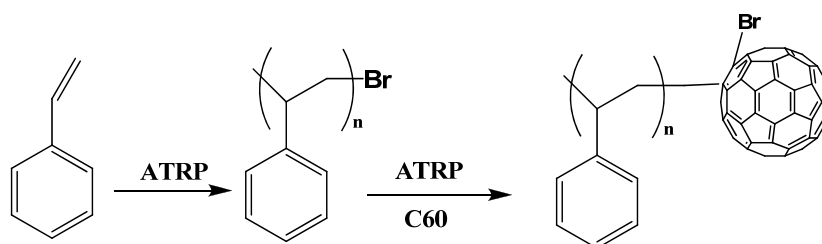
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Supporting Information

1. Preparation and characterization of C₆₀-PS

1.1 Preparation of PS-Br

ATRP was used to prepare bromine end-capped polystyrene (PS-Br) using benzyl bromide as an initiator. In a 50 ml round-bottom flask, 0.625g (4 mmol) 2,2-dipyridyl, 0.287g (2 mmol) CuBr, and 2 ml DMF were combined. After purging with dry argon for 10 min, 0.2379 ml (2 mmol) benzyl bromide was added to the flask. The reaction system was degassed by three freeze-pump-thaw cycles. Subsequently, 11.44 ml (0.1 mol) styrene was added. The system was then allowed to react at 110 °C for 4 h. The crude polymer was obtained by precipitation from methanol and then was dissolved in THF. The solution was passed through an alumina column to remove the catalysts. A white, fine powdery polymer was obtained after the polymer was precipitated from a large excess of methanol and dried under vacuum at 80 °C. The *M_n* and the polydispersity index (*M_w/M_n*) of PS-Br measured with GPC were 2812 g/mol and 1.114, respectively. The PS-Br was used for the functionalization of C₆₀. The synthesis scheme of PS-Br and C₆₀-PS is shown in Scheme S1.



Scheme S1. Synthesis scheme of PS-Br and PS- C₆₀

1.2 UV-vis spectra of C₆₀-PS

Figure S1 shows the comparison of the ultraviolet-visible (UV-vis) spectra of C₆₀-PS in toluene and C₆₀ in cyclohexane. C₆₀ has characteristic absorption peaks at 283 and 335 nm. C₆₀ absorbs at approximately 335 nm and is known to be sensitive to chemical reaction. Its absorption intensity weakens upon chemical modification to the molecular structure of the C₆₀ cage. The C₆₀-PS shows a weak but readily discernible absorption shoulder at 330 nm, confirming that the molecular structure of C₆₀ has been modified by the polymerization reaction. The color of the toluene solution of C₆₀ and C₆₀-PS differed markedly from purple black to brown, strongly supporting our conclusion.

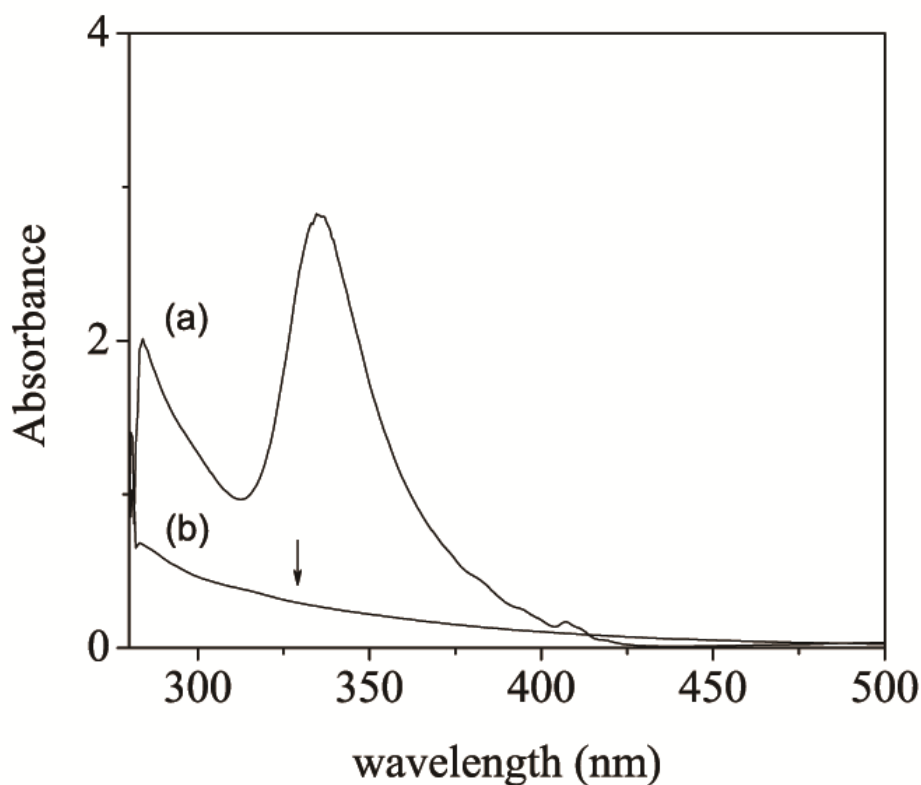
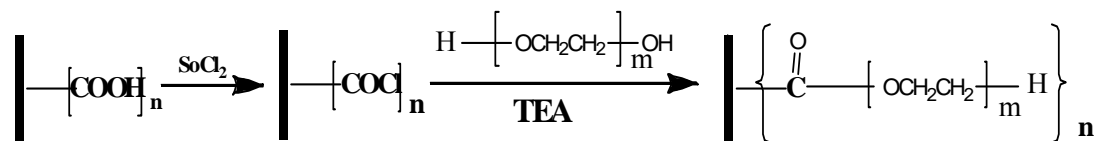


Figure S1. UV-vis spectra of (a) C₆₀ and (b) C₆₀-PS.

2. Preparation and characterization of MWNT-g-PEO

The synthesis scheme of MWNT-g-PEO is shown in Scheme S2.



Scheme S2. Synthesis scheme of MWNT-g-PEO.

We show the Raman spectroscopy of CNT before and after modification here. The Raman spectra in Figure S2 show the D- and G-bands of the MWNT at 1350 and 1584 cm^{-1} for both MWNT and MWNT-g-PEO, which were attributed to the defects and disorder-induced peaks and the tangential-mode peaks, respectively. These were the same as observed in the pristine nanotubes, which indicates that the electronic structure of the MWNTs remained essentially unperturbed after the incorporation of PEO molecules. However, a smooth shoulder band located at 1622 cm^{-1} was observed for the MWNT-g-PEO. This peak has been attributed to sp^2 hybridization of carbon and is evidence of the disruption of the aromatic system of p electrons by the attached molecules. The appearance of this obvious shoulder peak at 1622 cm^{-1} of the MWNT-g-PEO samples demonstrated that organic molecules had been covalently attached.

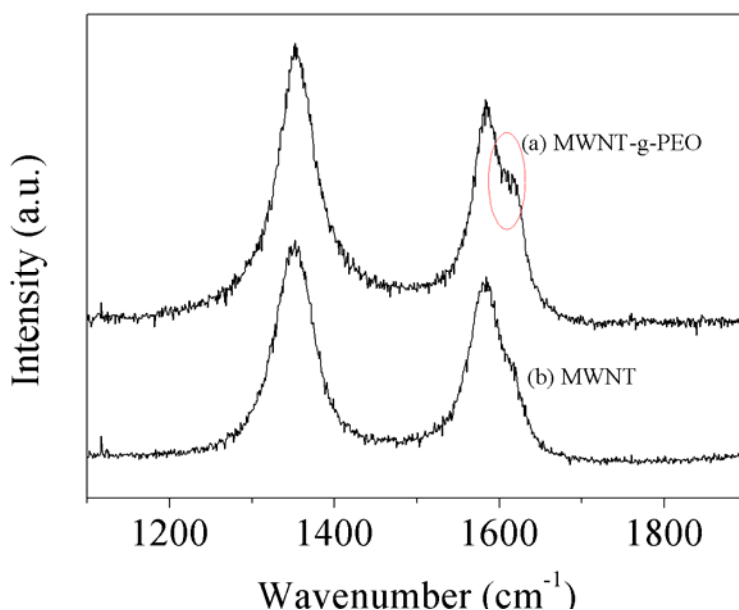


Figure S2. Raman spectra of (a) MWNT-g-PEO and (b) MWNT.

The morphology of the MWNT-g-PEO after the complete washing with chloroform was observed by using TEM as exhibited in Figure S3. As shown in Figure S3, a core-shell structure with MWNTs at the center can be clearly seen in the MWNT-g-PEO, indicating that the MWNTs were coated by the PEO layer. Comparing the mass gain after the grafting reaction with the thickness of the PEO layer observed in the TEM images of the MWNT-g-PEO samples, it can be clearly seen that the larger the amount of the grafted PEO.

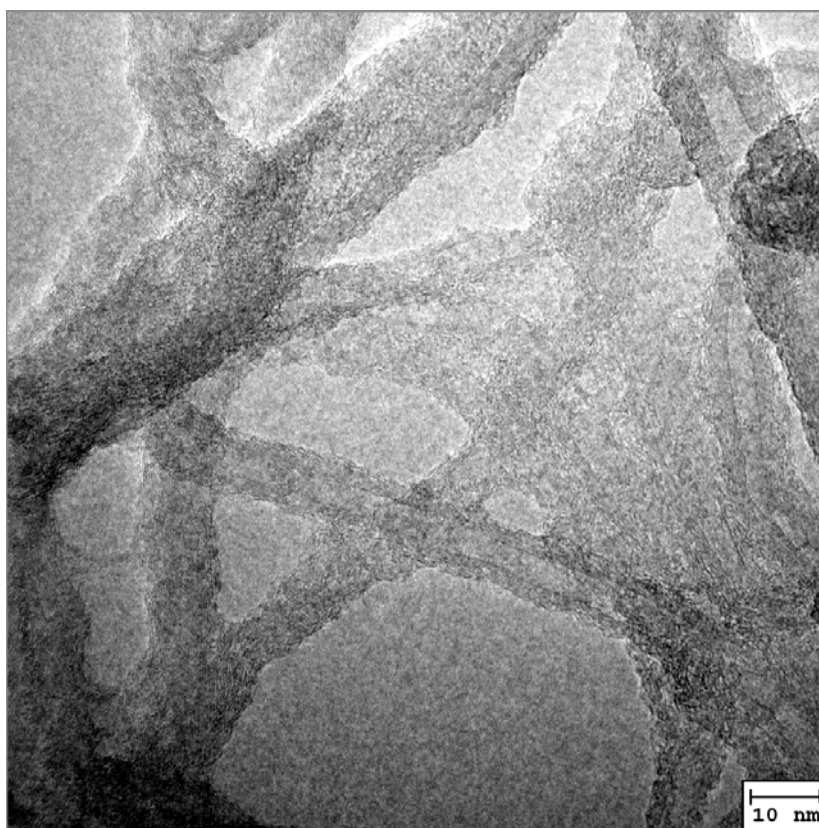


Figure S3. TEM images of MWNT-g-PEO

The amount of the PEO grafted to the MWNT, defined as the ratio of the mass of the immobilized PEO to that of the MWNT-g-PEO, was estimated from the thermogravimetric analysis (TGA) as shown in Figure S4. MWNT-g-PEO exhibited major weight loss in the temperature range of 300~400°C due to the degradation of the PEO grafted on the MWNT, as shown in Figure S4. The residual fraction at the temperatures above 600°C corresponds mainly to the MWNT. The amount of the PEO bound to the MWNT is about 29 wt %.

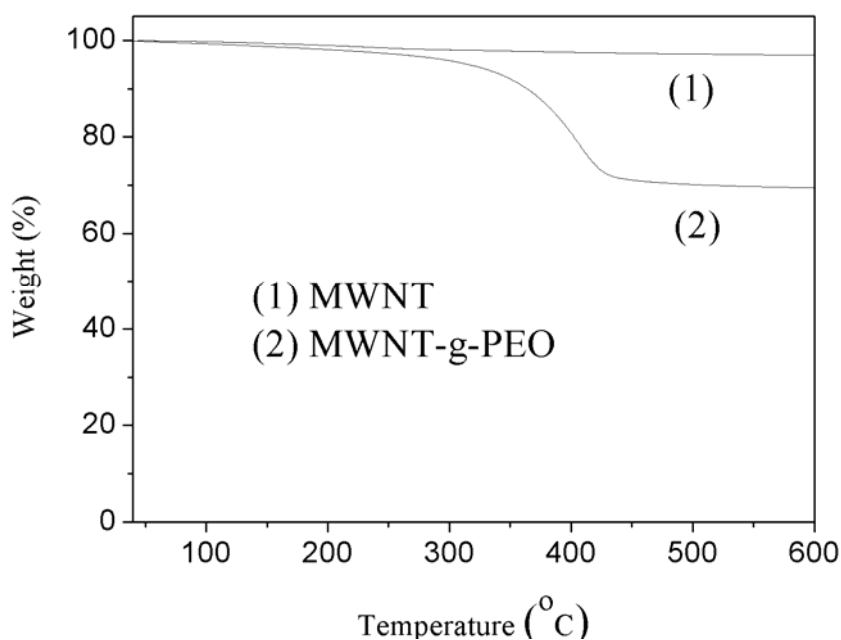


Figure S4. TGA traces of MWNT and MWNT-g-PEO.

3. The measurement of film thickness

Scheme S3 shows the structure of the film on aqueous substrate. The pink section is the film of PS-*b*-PEO or its nanocomposite, and blue section is deionized water or its solution.

The thickness of the PS-*b*-PEO thin film is calculated as the following equations:

$$d = \frac{V_p}{\pi R^2} \quad (1)$$

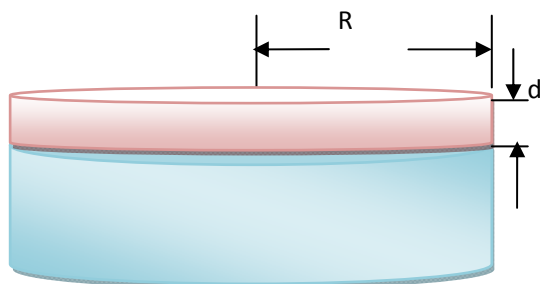
$$V_p = \frac{M}{\rho} \quad (2)$$

In our experiment, $V_s = 15 \mu\text{L}$, so $M = 0.15 \text{ mg} = 1.5 \times 10^{-4} \text{ g}$

$$d = \frac{V_p}{\pi R^2} = \frac{M}{\pi R^2 \rho} = \frac{1.5 \times 10^{-4}}{3.14 \times 3.75^2 \times 1 \times 10^{-2}} \text{ m} \approx 34 \text{ nm}$$

Here d is the thickness of block copolymer PS-*b*-PEO film that is formed after solvent evaporates on the air/water interface. V_p is the volume of PS-*b*-PEO film. R is the

radius of pertri dish, that is radius of film, here $R=3.75\text{cm}$. M and ρ are the mass and density of PS-*b*-PEO film, respectively, here $\rho=1\text{g/cm}^3$. V_s is the volume of PS-*b*-PEO solution injected. The concentration of PS-*b*-PEO solution is 10 mg/mL, 15 μL PS-*b*-PEO solution is injected every time, so $V_s=15\mu\text{L}$.



Scheme S3 The structure of the film on aqueous substrate