Amphiphilic Block Copolymer Micelles: New Dispersant for Single Wall Carbon Nanotubes

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TEM
The presence of the block copolymer micelles of PS-\textit{b}-P4VP20 in toluene was confirmed by spin coating the 0.1wt% solution on a Mica substrate before adding SWNTs. Figure S-1 shows a bright field TEM image of monolayer of nearly monodispersed P4VP/PS core/corona micelles (d \sim 30 nm) closely packed into a pseudo hexagonal structure.

UV-Vis Absorbance
We confirmed the observation by measuring concentration of the SWNTs in toluene by UV-vis spectrometer (UV2401PC, SHIMADZU). We monitored the absorbance of the solution with or without the block copolymer. Absorption spectrum of the SWNT with the block copolymer is shown in Figure S-2a. The spectrum is similar to one found in other well dispersed SWNT solutions (Chem. Commun. 2001, 193). The concentration was obtained based on the absorbance for the suspensions at the wavelength of 500 nm by Beer’s Law [1]. The linear calibration curve shown in the inset of Figure S-2b was obtained for the known SWNTs concentration and then used to determine the unknown amount of SWNTs in the suspensions. The same concentration of the block copolymer toluene solution was used as reference to eliminate the absorbance of block copolymer in the suspensions. Figure S-2b and c show the concentration of SWNTs on the top quartz tube versus time with and without block copolymer, respectively. The concentration of SWNTs in the solution with PS-\textit{b}-P4VP does not significantly change, which indicates that the well dispersed SWNTs with the block copolymer are considerably stable for more than 800 h.

Small Angle X-ray Scattering
In our block copolymer, PS-\textit{b}-P4VP20, that forms a lamellar structure in bulk, the absorbed layer structure formed by block copolymer wrapping around SWNT looks similar to the schematic in Figure S-3a. The structure seems to be a long cylindrical tube in which P4PV blocks contact with the surface of SWNT. The final thickness of the absorbed layer approximately corresponds to the center-to-center
distance in a hexagonally packed cylindrical P4VP microstructure which can be determined by \( \frac{2}{\sqrt{3}} d_{10} \) as shown in the schematic of Figure S-3b. In order to gain the information of the thickness of the absorbed layer, we employed another PS-b-P4VP block copolymer with cylindrical P4VP microdomains. PS-b-P4VP has 17,000 g/mol of PS block and 5,500 g/mol of PVP block. The (10) plane distance \( d_{10} \) was obtained by Small angle X-ray scattering conducted at the 4C2 beam line at Pohang Light Source. Figure S-3c shows the 1D intensity scan of the scattering data. The (10) reflection appears at \( q (= 4 \pi \sin \theta / \lambda) = 0.39 \) (nm\(^{-1}\)) and the (10) plane distance is 17 nm. The calculated center-to-center distance is approximately 20 nm. In our TEM samples, the absorbed layer with approximately 20 nm in thickness was not observed.

**Raman Spectroscopy**

To investigate the origin of interaction between micelles and SWNTs, Raman spectroscopy was used. Raman spectra were obtained at 532 nm laser excitation in LabRamHR and spectral resolution of 3 cm\(^{-1}\). Spectra were collected at various locations on each sample. Figure S-4 shows the Raman spectra of SWNTs, PS-b-P4VP20 and mixture of SWNTs and PS-b-P4VP20. The Raman resonance of PS-b-P4VP20 (Figure S-4a) is more than an order of magnitude lower in intensity than the one of SWNTs. The Raman spectrum of the SWNTs (Figure S-4b) features with the G band at ~ 1595 cm\(^{-1}\), D band at ~ 1310 cm\(^{-1}\). The G line band corresponds to the \( E_{2g} \) mode assigned to the movement of the two neighboring carbon atoms in opposite directions in graphite. The D line originates from carbon defects in the nanotube walls. There were reports that some Raman peaks of SWNTs may shift to higher frequencies upon their being incorporated into a polymeric matrix due to hydrostatic compression. However, such resonance shifts or no new peaks from chemical modification of SWNT surface are detected in the Raman spectrum of the mixture of SWNT and PS-b-P4VP20 (Figure S-4c). It implies that the micelles were physically absorbed on surface of the SWNTs.

Figure S-1
Figure S-3

(a) Schematic representation of PVP SWNT complexes with PS. The arrow indicates $\frac{2}{\sqrt{3}}d_{10}$.

(b) Diagram showing the arrangement of SWNTs with PS, where $d_{10}$ is the distance between the SWNTs.

(c) Graph showing the log intensity (AU) against $q$ (nm$^{-1}$) with two distinct peaks and a peak labeled $q_1$. The $q$-values range from 0.0 to 1.0.