Experimental Report

21/07/2014

Proposal:	**9-12-338**	**Council:**	10/2012

Title: Interactions between Block and Comb Copolymers and Single-Walled Carbon Nanotubes in Aqueous Media

This proposal is a new proposal

Research Area: Soft condensed matter

Main proposer: **KASTRISIANAKI-GUYTON Emma**

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Samples: Water/H2O/D2O
Methanol/CH3OH/CD3OD
Single walled carbon nanotubes/SWCNT
SDS/NaC12H25SO4
Pluronic P103 polymer
Comb copolymer

Instrument	Req. Days	All. Days	From	To
D33	0	2	07/08/2013	09/08/2013

Abstract:

Carbon nanotubes are of great interest due to their unique properties, such as their high aspect ratio and electrical conductivity. Many possible applications of CNTs require nanotubes to be well dispersed in suspension. One method commonly reported to disperse nanotubes is sonication with the addition of an adsorbing surfactant or polymer. We plan to investigate the adsorption of sodium dodecyl sulfate, Pluronic ABA block polymers and comb copolymers with grafted poly(ethylene oxide) side chains, which are all effective as dispersants for CNTs. By using contrast matching techniques, we hope to obtain detailed information about the adsorbed polymer layer and exactly how they act on CNTs to stabilise them in water.

Small-angle neutron scattering to investigate the adsorption of Pluronic block copolymer onto single-walled carbon nanotube surfaces

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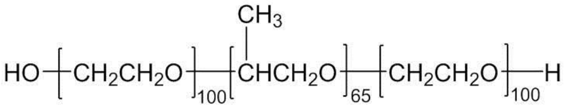
Introduction

Single-walled carbon nanotubes (SWCNTs) show potential for use in various applications, for example they could be used as semiconductors in next-generation electronic devices. Forming SWCNT dispersions in either aqueous or organic media is challenging due to their tendency to bundle. A number of methods have been investigated to overcome this problem, including covalent and non-covalent bonding to the SWCNT surface in order to minimise van der Waals attractions between the SWCNT walls. Non-covalent functionalisation is often preferred as it ensures the π-orbital interactions on the SWCNT surface, and thus the electronic properties of SWCNTs, remain unchanged.[1]

A small-angle neutron scattering (SANS) experiment was designed to investigate dispersions of SWCNTs in water using a Pluronic block copolymer (F127) as the stabilising surfactant. The Pluronic block copolymer was first contrast matched to a D_2O/H_2O mixture, allowing the contribution of the SWCNTs alone to be observed. This was then followed by experiments looking at the same system in D_2O with all components visible. Similar experiments were conducted by Granite *et al.*, who reported that the minimal scattering of F127 SWCNT dispersions occurred at 40% D_2O, much higher than the 15% D_2O which was predicted based on the scattering length density (SLD) of the Pluronic.[2] This was explained using a model where D_2O is preferentially adsorbed onto the F127 layer, and the scattering was unable to be modelled using a core-shell cylinder model. This contradicts the results we found in this experiment, as we have been able to contrast match the adsorbed F127 at the D_2O composition that would be expected based on its SLD.



$$\mathrm{HO}-\left[\mathrm{CH_2CH_2O}\right]_{100}-\left[\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HCH_2O}\right]_{65}-\left[\mathrm{CH_2CH_2O}\right]_{100}-\mathrm{H}$$

Pluronic F127

Fig. 1. The structure of Pluronic F127

Experimental

HiPCO single-walled carbon nanotubes (raw) were obtained from NanoIntegris and kindly provided by Merck chemicals. SWCNTs were added to dispersions of F127 (0.5 and 1% w/w) to a total volume of 2 ml and dispersed using a tip sonicator in pulsed mode at 57% max power for 1hr (QSonica Q125, max power 125 W), before being centrifuged using a Labnet Prism Microcentrifuge at 20100 g for 40 min (24 place rotor, 230 V) to remove larger impurities. The top ~1.5 ml of the resulting supernatant was removed for use in scattering experiments. It is important to note that the SWCNT concentrations are not the final concentrations, but those calculated before purification by centrifugation. The resulting dispersions were characterised using Transmission Electron Microscopy, which indicated that the SWCNTs were mainly present in bundles rather than as individual tubes. Final SWCNT concentrations were determined by taking UV-vis spectra of SANS samples (after dilution by a fixed amount) and comparing to a spectrum of a sample whose concentration was determined by dialysis and subsequent drying.

Measurements were carried out at 15 and 35 °C (below and above the critical micellisation temperature (CMT) of the F127, respectively) on the D33 instrument at the Insitut Laue-Langevin in Grenoble, France. A neutron wavelength of 10.0 Å was used with detector distances of 2.0 and 12 m to gain an overall Q range of 0.0022 to 0.1376 $Å^{-1}$. The samples were transferred to Hellma rectangular quartz cells with either a 1.0 or 2.0 mm path length, depending on the relative amounts of H_2O and D_2O in the samples.

Results

The scattering of a dispersion of SWCNTs (0.3% w/w) and F127 (1% w/w) in water was first measured with the solvent contrast matched to the SLD of the F127 (calculated as 0.5×10^{-6} $Å^{-2}$) corresponding to a solvent composition of 15% D_2O and 85% H_2O. The resulting scattering is shown in fig. 2. The contribution of the SWCNTs to the scattering is given in fig. 3, where the scattering from 1% w/w F127 in H_2O/D_2O has been subtracted from the scattering of 1% w/w F127 + 0.3% w/w SWCNTs in H_2O/D_2O. The resulting scattering has been fit to a homogeneous cylinder model, and gave an average core radius of 17 Å, corresponding to a small SWCNT bundle (e.g. a bundle of 4 nanotubes with 10 Å radius).

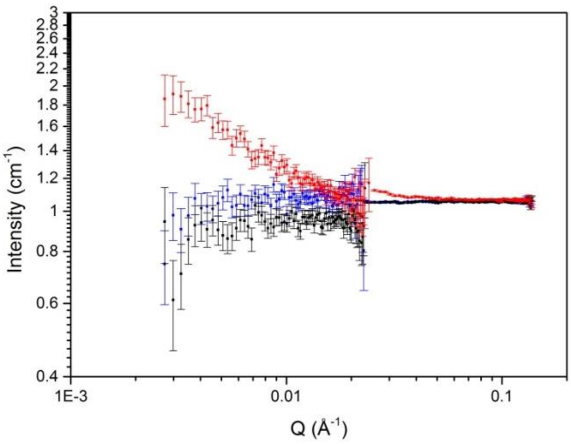


Fig. 2. Scattering from 1% w/w F127 in cm-H_2O/D_2O with and without SWCNTs present. Red: 1% w/w F127 + 0.3% w/w SWCNTs in H_2O/D_2O, black: 1 % F127 in H_2O/D_2O, blue: H_2O/D_2O background.

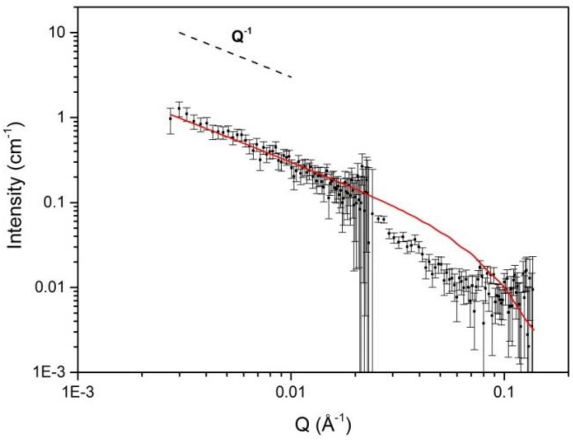


Fig. 3 Scattering from 1% w/w F127 in H_2O/D_2O subtracted from 1% w/w F127 + 0.3% w/w SWCNTs in H_2O/D_2O and fit to a homogeneous cylinder model.

We then investigated the scattering of 1% w/w F127 in D_2O with and without SWCNTs, using a core-shell cylinder model to fit the data. The scattering curves obtained are shown in fig. 4. 1% w/w F127 in D_2O was fit to a Debye-Guinier model for free polymers, and this was then subtracted from the data for 1% w/w F127 + SWCNTs in D_2O to give the contribution from the decorated SWCNTs, which were then fit to a core-shell cylinder model. This fit gave an average core radius of 5 Å (including a lognormal polydispersity (S.D./mean) of 0.7) and an adsorbed layer thickness of 57 Å (with a lognormal polydispersity of 0.4).

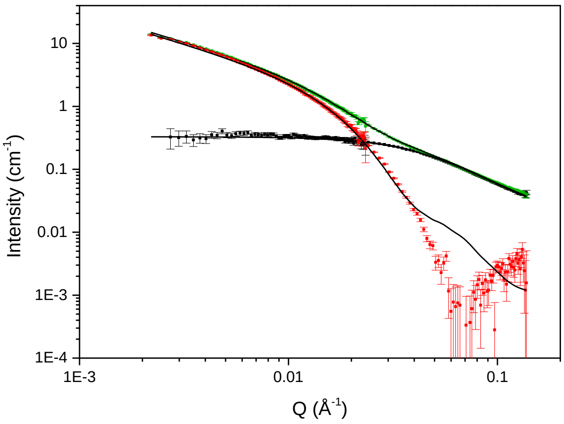


Fig. 4. 1% w/w F127 (black squares) below the CMT, fit to a Debye-Guinier model for free polymers. This fit was then subtracted from 1% w/w F127 + SWCNT data (green squares) to give the scattering from the decorated cylinders (red squares), which was fit to a core-shell cylinder model. The two fits were added together to give the fit for the 1% w/w F127 + SWCNT data

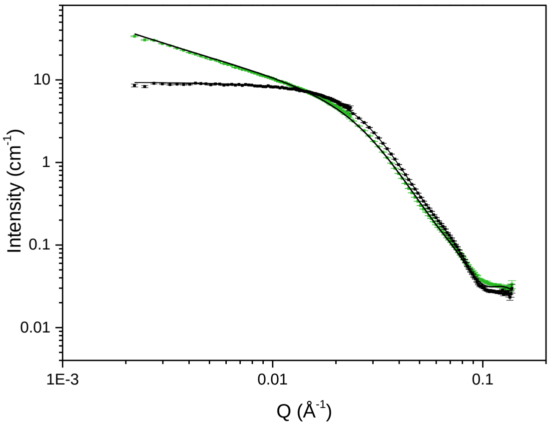


Fig. 5. 0.5% w/w F127 above the CMT with (green squares) and without (black squares) 0.3 % w/w SWCNTs present. 0.5% w/w F127 data was fit to a Pedersen model for Pluronic block copolymers, while the 0.5% w/w F127 + 0.3% w/w SWCNT fit is this Pedersen fit added to a core-shell cylinder fit for the contribution of the decorated SWCNTs. This gave a core radius of 20 Å and a thickness of 89 Å, with lognormal polydispersities of 0.3 and 0.2, respectively.

The same samples were also run at 35 °C, above the CMT of the polymer, and the resulting scattering is shown in fig. 5. The Pluronic data was fit to a Pedersen model, and this was subtracted from the 0.5% w/w F127 + 0.3% w/w SWCNT data to give the decorated SWCNT contribution, which was fit to a core-shell cylinder model. A summary of the parameters for the systems looked at in this experiment can be found in table 1.

System	**Core radius (Å)**	**Adsorbed layer thickness (Å)**
1% w/w F127 + 0.3% w/w SWCNTs in CM-H_2O/D_2O **below CMT of F127**	17	n/a
1% w/w F127 + 0.3% w/w SWCNTs in D_2O **below CMT of F127**	5	57
0.5% w/w F127 + 0.3% w/w SWCNTs in D_2O **above CMT of F127**	20	89

Table 1 A summary of the core radii and adsorbed layer thicknesses for the different systems studied

Conclusions

The small-angle neutron scattering of F127 has been studied with and without SWCNTs. Contrast matching experiments showed that it was possible to contrast match the F127 at the solvent composition expected by its SLD, in contrast to results published by Granite *et al.*[2] The data were fit to cylinder and core-shell cylinder models to give the radii of the inner SWCNT bundle and the thickness of the adsorbed polymer layer.

References

(1) Hersam, M. C. *Nat. Nanotechnol.* **2008**, *3*, 387.
(2) Granite, M.; Radulescu, A.; Pyckhout-Hintzen, W.; Cohen, Y. *Langmuir* **2011**, *27*, 751.