Experimental report

20/06/2016

Proposal: **9-10-1419**

Council: 10/2014

Title: Probing the Solution Structure of Monodisperse Cylindrical Micelles Prepared By Gradient Crystallisation-Driven Self-Assembly

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
(C12H14SiFe)n-block-(C3H5SiO)m with hydrogenous alkyl chains in deuterated hexane (C6D14)
(C12H14SiFe)n-block-(C3H5SiO)m with deuterated alkyl chains in mixed deuterated and hydrogenous hexane

Instrument	Requested days	Allocated days	From	To
D22	3	2	18/07/2015	20/07/2015

Abstract:

Micelles prepared by the crystallisation-driven self-assembly of a mixture of brush and linear PFS containing block copolymers (BCPs), display segmented coronas when analysed microscopically in the dried state. However, their structure in solution is as of yet undetermined. The principal aims of this experiment are: to determine the precise microstructure of cylindrical BCP micelles prepared by the co-assembly of linear and brush BCPs, to characterise the longitudinal structure of their coronas as a function of brush length and to elucidate the self-assembly mechanism that governs their formation. SANS represents the only technique available to conclusively achieve these aims. D22 is required for a wide Q range and high intensity.

Abstract

This experiment was conducted to determine corona structure of monodisperse, crystalline-coil block copolymer micelles. Previous work had shown that on addition of blends of linear and brush poly(ferrocenylsilane) (PFS)-based block-copolymers to a solution of preformed micelles, distinct linear and brush block domains would form in the corona.[1] Kinetic data and simple simulations strongly suggested that the microstructure of these micelles is a result of a segmented distribution of the two different BCPs that is a consequence the self-assembly process. However, due to the fact that the structure of these micelles had only been analysed using electron and force microscopy in the dried state, it could not be ruled out that the corona compartmentalisation was a result of sample preparation. This distinction is very important as segmented or 'patchy' structures could be used for the spatial isolation of functional nanoparticles and catalytically active small molecules. Analysis of the small-angle neutron scattering results taken in this experiment showed no evidence of a regular patchy structure in any of the samples but has shed light on the influence of the alkyl chains on the morphology of the corona.

Experimental Details

Two systems of cylindrical PFS-*b*-PMVS (poly(ferrocenylsilane)-*b*-poly(methylvinylsiloxane)) micelles were investigated in this experiment. One containing hydrogenous polysiloxane and alkyl chains, the other containing hydrogenous polysiloxane and deuterated alkyl chains. Both systems of PFS-b-PMVS micelles were prepared with three different alkyl chain lengths: 6, 12 and 18 units as well as a control with no alkyl chains, to determine the effects of brush length on corona structure (the chemical structure of a PFS-*b*-PMVS polymer with deuterated alkyl chains is shown in Figure 1a). All samples were prepared at 10 mg/mL and were measured in a deuterated hexane solvent to minimise the incoherent background. In order to discount the effects of possible interparticle interactions, measurements were also taken at 1 mg/mL and compared to the equivalent concentrated samples. To fully capture the cross-sectional geometry of the micelles, two sample-to-detector distances were used (5 m and 17 m) with a wavelength of 6 Å, giving a Q-range of 0.003-0.14 Å^{-1}. Finally, in an attempt to validate the model constructed to describe micelles with patchy coronae, an *in-situ* micelle growth experiment was conducted by sequentially adding block copolymer material with and without a brush block, effectively forming block comicelles.

Results

In order to facilitate further analysis and comparison, the 2-dimensional scattering data for all samples was first background subtracted and azimuthally regrouped to give 1-dimensional plots of scattered intensity vs. scattering vector. Figure 2a shows that scattering from the samples at concentrations of 10 mg/mL only differ from the dilute 1 mg/mL samples by a scaling factor. The cross-sectional dimensions, found by fitting the data to a model for long cylindrical micelles with uniform cores and coronae of decaying scattering length density,[2] were also found to be identical (within the uncertainties of the fit), confirming that at 10 mg/mL the micelles are sufficiently dilute to be in the non-interacting regime.

Figure 2b shows the azimuthally regrouped data for all of the samples self-assembled prior to the experiment and it can be seen that in all samples there are no identifiable peaks or fringes other than those from the core and corona dimensions (which are also visible in the sample with no alkyl chains in the corona). Even accounting for a decaying periodicity of the patches, one would expect to see a pronounced fringe at around 0.02-0.04 Å^{-1}, therefore the absence of any features at all appears to contradict the hypothesis of periodic patchy structures in solution. However, these fringes are also absent in Figure 3a, showing the regrouped scattering from the block comicelles produced *in-situ* via sequential addition of PFS-*b*-PMVS and PFS-*b*-PMVS with deuterated alkyl chains to short PFS-b-PMVS seed micelles. From Figure 3b, it can clearly be seen that these structures have a regular patchy structure when imaged in their dry state by transmission electron microscopy. By fitting the data to the core-corona cylindrical micelles model, it was possible to determine a volume fraction of the corona chains at the core corona boundary of ~0.16. This suggests that the corona is highly solvated which will reduce the scattering length density contrast between the blocks and supress any peaks in the data.

Conclusions and Further Work

Despite a comprehensive investigation, it has not been possible to conclusively prove or refute the existence of a 'patchy' structure in the micelle coronae. The absence of a clear peak in the azimuthally regrouped data, even for the block comicelle structures suggests that the coronae are sufficiently well solvated such that the scattering length density contrast between the blocks is not large enough to produce well-defined peaks. In order to conclusively establish the presence or absence of the segmented corona in solution, it will be necessary to increase the scattering length density contrast of the different blocks. This could be achieved by using a fully hydrogenous polysiloxane block in conjunction with a fully deuterated polysiloxane block with deuterated alkyl chains, however this would synthetically very challenging. It may also be possible to image the micelles directly using synchrotron X-ray imaging techniques.

References

1. *J. Am. Chem. Soc.*, **2014**, *136* (39), 13835–13844

2. *Macromolecules*, **2015**, *48* (5), 1579–1591

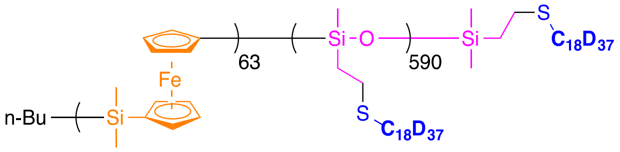

Figure 1 Representative chemical structure of PFS-based block copolymers studied in this experiment. Specifically, this is the polymer with deuterated octodecyl chains.

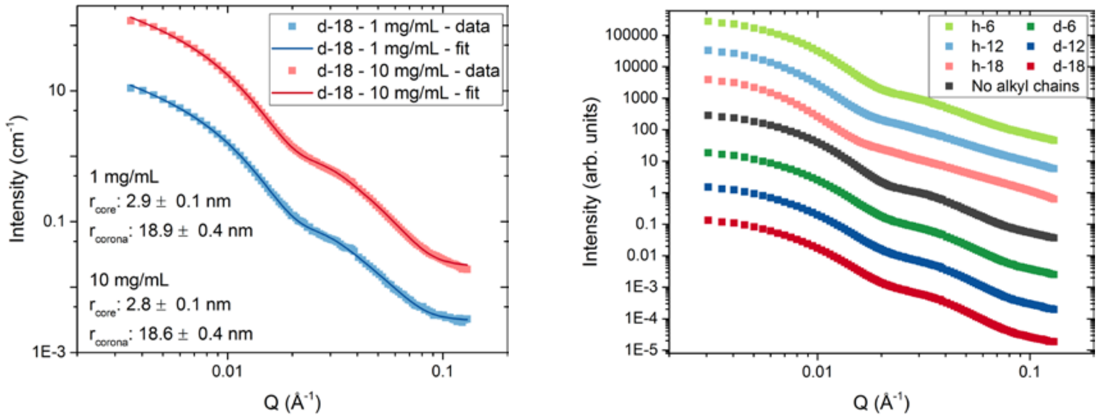

Figure 2 Plots of azimuthally integrated intensity vs scattering vector, Q for: (a) the micelles self-assembled using the polymer with deuterated octodecyl chains (Figure 1) at concentrations of 1 and 10 mg/mL and (b) all previously prepared micelles at a concentration of 10 mg/mL. The data in (b) are arbitrarily shifted in intensity for clarity.

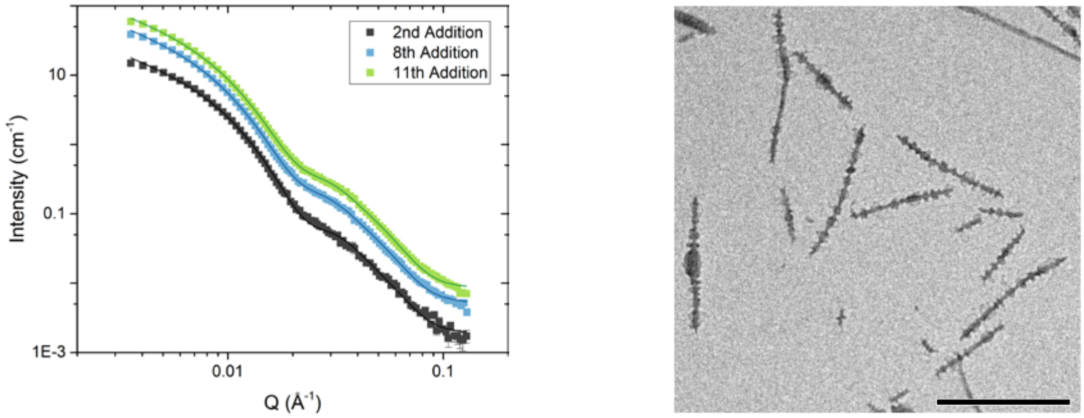

Figure 3 (a) Plot of intensity vs scattering vector for the micelles with segmented coronae prepared in-situ via sequential addition of block copolymer with and with deuterated alkyl chains. (b) Shows a transmission electron micrograph of the micelles after the 11th addition (6x polymer with deuterated octodecyl chains, 5x polymer with no alkyl chains).