Experimental report

Proposal:	**EASY-573**

Council: 10/2019

Title:	Contrast-variation SANS of dispersions of transparent diblock copolymer micelles in a nonpolar solvent
Research area:	Soft condensed matter

This proposal is a new proposal

Main proposer:	**Gregory SMITH**
Experimental team:	
Local contacts:	Sylvain PREVOST

Samples: Poly(stearyl methacrylate)–poly(2,2,2-trifluoroethyl methacrylate) in tetradecane (H and D)

Instrument	Requested days	Allocated days	From	To
D11	36	36	09/01/2020	11/01/2020

Abstract:

Several dispersions of transparent diblock copolymer micelles will be prepared at different solvent scattering length densities (SLDs) and particle concentrations. The two blocks of the copolymer have sufficiently different SLDs so that they can be differentiated by contrast-variation SANS. The data will enable the segregation of the two blocks to be studied (dilute dispersions) and the perturbation of the stabilizer to be studied (concentrated dispersions).

Contrast-variation SANS of dispersions of transparent diblock copolymer micelles in a nonpolar solvent

ILL Experiment EASY-573

Main proposer: Gregory Smith (Niels Bohr Institute and ISIS Neutron and Muon Source)

Local contact: Sylvain Prévost

Abstract Several dispersions of transparent diblock copolymer micelles will be prepared at different solvent scattering length densities (SLDs) and particle concentrations. The two blocks of the copolymer have sufficiently different SLDs so that they can be differentiated by contrast-variation SANS. The data will enable the segregation of the two blocks to be studied (dilute dispersions) and the perturbation of the stabilizer to be studied (concentrated dispersions).

Overview

Four series of samples were prepared. The solvent backgrounds and particle dispersions were most informative.

- *n*-Tetradecane mixtures as solvents.

- Dilute particles (1%) in six solvent mixtures.

    - H-tetradecane

    - Shell matched

    - Zero-average contrast (ZAC)

    - Core matched

    - ZAC above core matched

    - Shell matched above core matched

- Shell polymer (1%) in four solvent mixtures.

- Concentrated particles (20%, 30%, and 40%) in two solvent mixtures

    - Shell matched

    - Core matched

The particle samples were measured at four different instrument configurations (from low Q to high Q).

- Sample-to-detector distance of 1.4 m, Neutron wavelength of 4.6 Å

- Sample-to-detector distance of 8 m, Neutron wavelength of 4.6 Å

- Sample-to-detector distance of 8 m, Neutron wavelength of 4.6 Å (high resolution with long collimation)

- Sample-to-detector distance of 21 m, Neutron wavelength of 4.6 Å (high resolution with long collimation)

- Sample-to-detector distance of 39 m, Neutron wavelength of 4.6 Å

- Sample-to-detector distance of 39 m, Neutron wavelength of 10 Å (lowest Q)

The solvents mixtures were used as backgrounds for the remaining measurements. They were also informative in their own right, because the *n*-alkane molecules themselves are large enough to scattering in SANS *Q*-range. This is only observed for mixtures of H and D solvents because the mixtures have sufficient isotopic contrast.

The scattering was modelled using a Debye function assuming that the molecules were Gaussian chains. This is the same as would be done for polymer mixtures. The figure below shows five mixtures (volume percentage of D solvent shown in the legends) fit to Debye function plus a constant background. The table below shows the best fit parameters for the Debye function (I_0 - intensity at $Q=0$, R_g - tetradecane radius of gyration) and constant background (c_0).
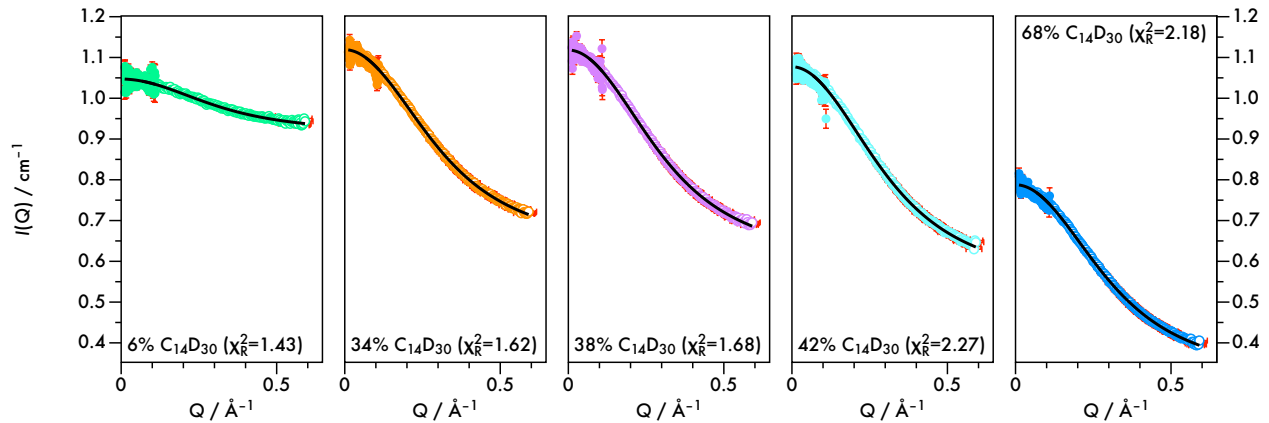

Table 2. *Best fit parameters for SANS data of n-tetradecane and n-tetradecane-d$_{30}$ mixtures to Equation 2 (Figures 1 and 2).*

Volume fraction $C_{14}D_{30}$	I_0 / cm^{-1}	R_g / Å	c_0 / cm^{-1}	χ^2_R
0% (pure $C_{14}H_{30}$)	0.0197 ± 0.0004	5.4 ± 0.2	0.9820 ± 0.0005	1.17
6%	0.1370 ± 0.0004	5.04 ± 0.03	0.9132 ± 0.0005	1.43
34%	0.5037 ± 0.0004	5.121 ± 0.007	0.6187 ± 0.0004	1.62
38%	0.5373 ± 0.0003	5.135 ± 0.006	0.5841 ± 0.0004	1.68
42%	0.5510 ± 0.0003	5.113 ± 0.006	0.5294 ± 0.0004	2.27
68%	0.4896 ± 0.0003	5.142 ± 0.005	0.3005 ± 0.0003	2.18
100% (pure $C_{14}D_{30}$)	0.0031 ± 0.0007	31 ± 5	0.07907 ± 0.00003	1.25

The fit scattering from the solvents was then subtracted from all measurements of particles.

Dilute particles

The scattering from the dilute particles was fit simultaneously. The same model (core-shell sphere) was applied to all contrasts, with all parameters constrained to be the same, except for the solvent scattering length density, which was known from preparation. The experimental and fit scattering are shown in the figure below. Filled symbols are the experiment data, empty symbols are the subtracted experimental data, and the the lines are the fits to the data. Good agreement between this model and the experimental data are found. The best agreement is for samples where the scattering intensity are highest, but this is to be expected as the degree of certainty for these data are greater.
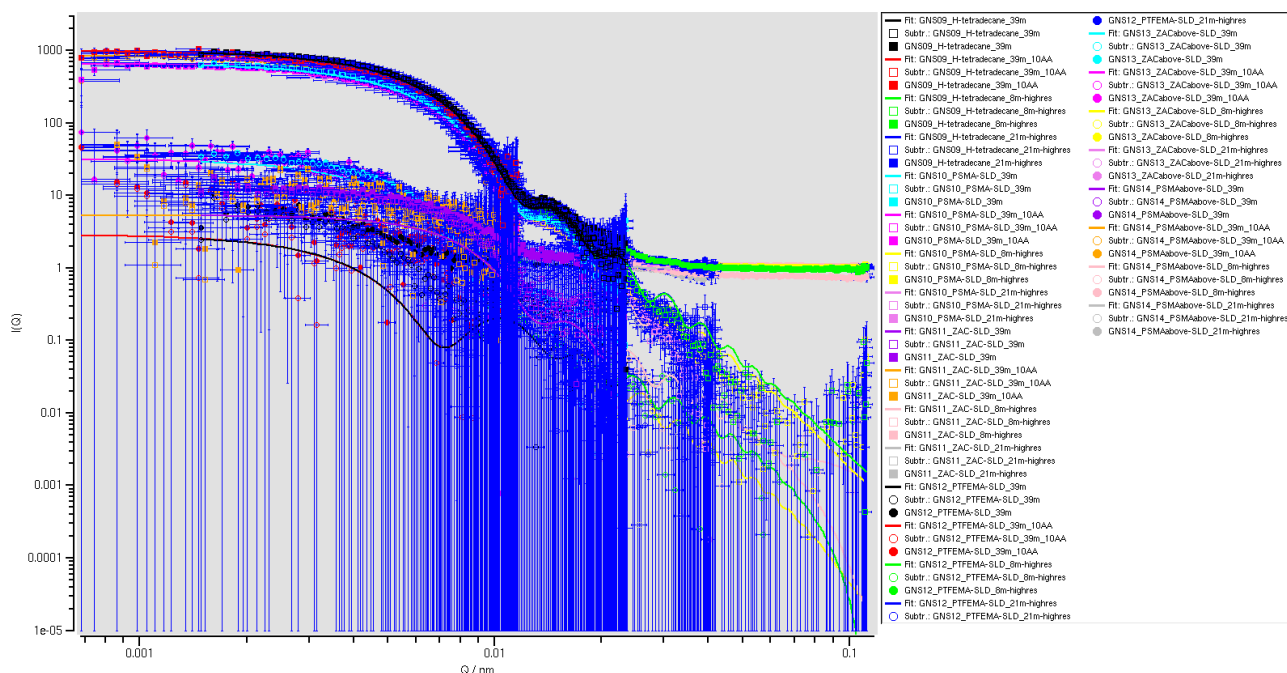
Concentrated particles

The scattering from the concentrated particles were also fit simultaneously. The geometrical parameters were fixed to those from the dilute particles. The volume fractions and effective particle radii were allowed to vary, but realistic values were obtained. It was not possible to find a fully accurate way to model the structure factor, due to polydispersity effects. Good fits are still obtained. The fits are worst for the the measurements with low scattering intensity, which is expected as these have the lowest certainty. These measurements provided valuable information about the concentration of particles in dispersion and perturbations in the amount of solvent in the shell as the particles were made more concentrated.
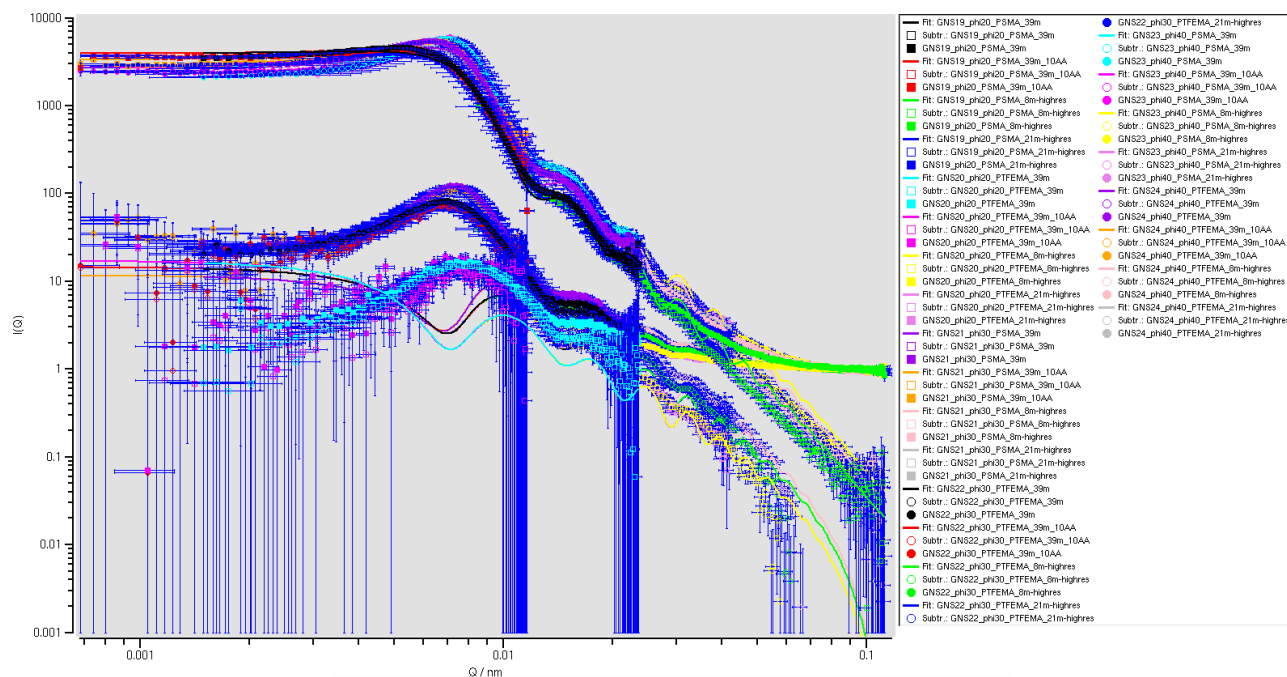
Summary

Contrast-variation SANS has proved to provide useful information about these novel polymer particles. This will hopefully support their uptake as model polymer spheres in the colloid science community.