Experimental Report

Proposal: **9-11-1644** **Council:** 10/2012

Title: Oil-water reflectivity measurements for understanding polymer stabilization of multiple emulsions

This proposal is continuation of: 9-11-1511

Researh Area: Soft condensed matter

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Samples: water
toluene
polymer (Poly(styrene)-poly(2-(dimethylamino)ethyl methacrylate)
deuterated toluene
deuterated water

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	6	4	14/03/2013	18/03/2013

Abstract:

Copolymers of poly(styrene)-s-poly(daema) have been shown to be stimulable emulsion stabilizers by action of pH or temperature.
They are also promoters of multiple emulsions that are very stable over time. This promotion is intimately linked to a measured
minimum in the surface tension between water and oil as a function of pH. The position of this minimum and the whole behavior of
surface tension is very dependent of polymer architecture. There is then a strong need of quantitative information on the polymer
conformation at oil-water interface as a function of polymer nature. We propose to get such a knowledge thanks to reflectivity
measurement at the oil-water interface. A dedicated microfluidic cell was built, enclosing the fluid of thickness about 200 micrometers and anchoring a flat centimetric meniscus. The neutron beam will be collected after travelling through a sapphire window

Report about the experiment #9-11-1644 ‘‘Oil-water reflectivity measurements for understanding polymer stabilization of multiple emulsions’’

The goal of the experiment was to record the reflectivity signal of a copolymer layer at the interface between oil and water. Such a copolymer is a diblock copolymer made of a polystyrene (PS) miety linked to second block which is a statistically composed block of PS and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA). Some of these copolymers, depending on their architecture, were shown to stabilize multiple emulsions for a month and thanks to a one-step preparation. Moreover multiple emulsions were observed in a pH range located in between pH zones where direct (oil in water at low pHs) and inverse (water in oil at high pHs) simple emulsions are stable. This makes these multiple emulsions stimulable since an increase in pH (or in temperature since PDMAEMA is sensitive to both pH and temperature) turns the multiple emulsions to an inverse one, making a possible encapsulated molecule free.[1] It is then important to determine the polymer conformation at a flat interface whose curvature is, like for emulsions droplets, much larger than the polymer extension.

This was performed in March 2013 using an original cell validated in 2012 during a previous test (Figure 1).

Fig.1 : Image of the cell with the blue connectors for toluene inlet

The polymer PS48-*b*-(PS31-*st*-PDMAEMA60) is dissolved beforehand in the toluene phase which is added through the blue inlets (Fig. 1) above a macroscopic (mm thick) water phase. The water phase is then sucked out to reach about a hundred of microns thickness. The neutron beam enters from below through a sapphire window and is reflected at the toluene-water interface. The reflected signal (white beam) is collected at different thicknesses of water and is shown in Fig. 2.

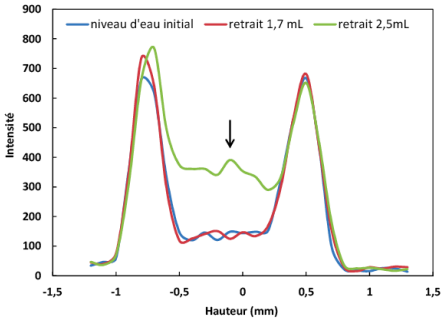

Fig. 2 : ‘‘Donkey’’ shape of the white beam reflected signal.

The ‘‘donkey hat’’ shape is due to side reflections of the beam but when the thichness is low enough (‘‘retrait 2.5 mL’’) a reflected beam at the correct 0 position appears. Data were

1 **Multiple Emulsions Controlled by Stimuli-Responsive Polymers**
Besnard, Lucie; Marchal, Frederic; Paredes, Jose F.; et al., ADVANCED MATERIALS Volume: **25** Issue: **20** Pages: **2844-2848** DOI: **10.1002/adma.201204496**, **MAY 28 2013**

accumulated at this position for two angles as well as for the direct beam at the same angles. The shape I(l) of the beam was also measured for different water thicknesses in order to correct for water scattering along the beam path. Reflectivity curves were then acquired for two different contrasts and the same polymer at an equilibrated pH value of 3. For the first contrast where the toluene is hydrogenated, the reflectivity and a fit are shown in Fig. 3.

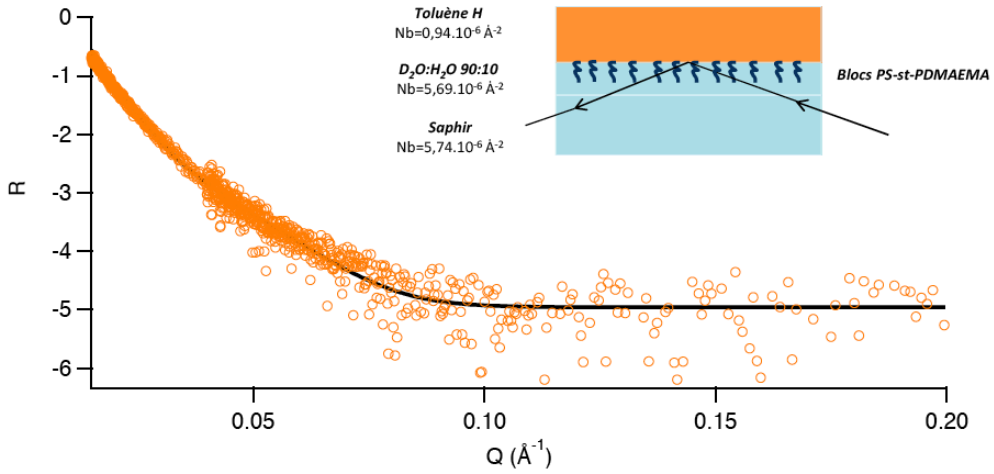

Fig. 3 : Reflectivity and fit to a 3 layers model for the contrast shown in the inset

Despite the hydrogenated polymer chains under study, it was shown that a 3 layer model was needed to fit the data, showing that the polymer layer is indeed detectable at this contrast. A thickness of 54 Å is found for the polymer layer thickness and 4.4 10^{-6} $Å^{-2}$ for scattering length density. The second contrast where solvents are matched is shown in Fig. 4 and the 4-layers fit result in both Fig.4 and Fig.5.

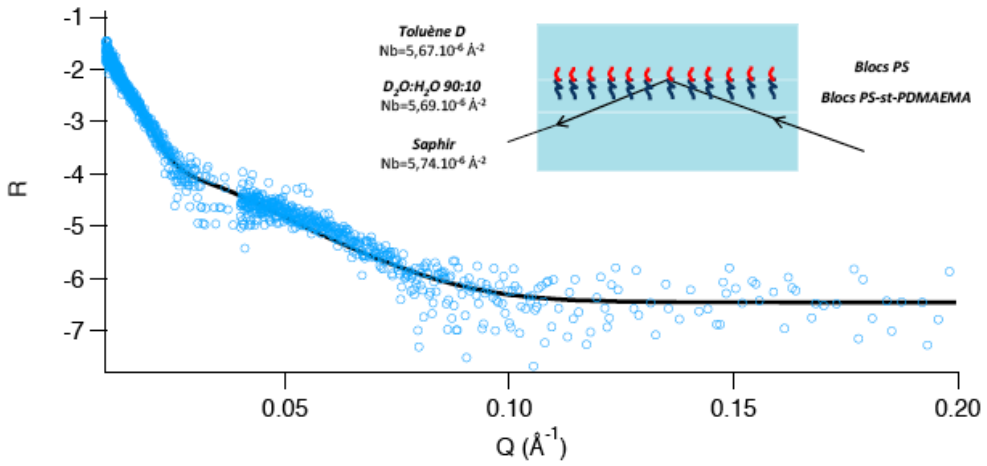

Fig. 4 : Reflectivity and fit to a 4 layers model for contrasts shown in the inset

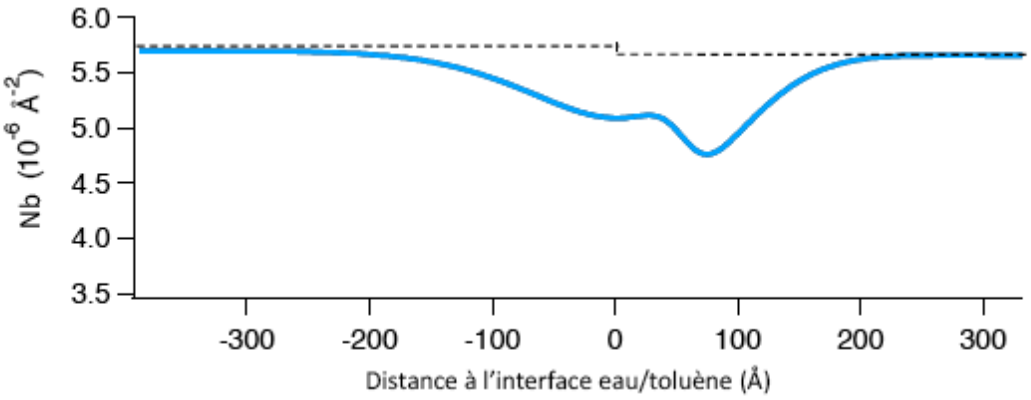

Fig.5 : Scattering length density contrast deduced from the fit in Fig. 4

For this configuration a thickness of 50 Å (roughness 20 Å) is found for the PS polymer layer thickness and 4.8 10^{-6} Å^{-2} for scattering length density. The PDMAEMA layer is of extension 59 Å (roughness 15 Å) and of scattering length density 4.8 10^{-6} Å^{-2}. By assuming an Alexander-de Gennes profile, areas per chain can be determined from the scattering length densities and the average thickness. The average area per chain is found to be 107 Å^2, a value in agreement with a brush conformation where the thicknesses are found larger than the Flory radii of both chains. The value of 59 Å (pH 3) is somewhat smaller than the PDMAEMA extension of 66 Å determined in spherical geometry at pH 1.2 where the PDMAEMA chains are fully charged and much larger than at pH 6 where chains are shown to be mostly adsorbed flat around a toluene core in spherical geometry (neutron scattering results).
To summarize, the major result obtained is that reflectivity profiles obtained in our original configuration can be made fully quantitative to determine the polymer layer conformations. Results are in full agreement with previous small-angle scattering results and bring important complementary piece of data.