Experimental Report

13/02/2015

Proposal:	**9-10-1349**	**Council:**	4/2014

Title: How to link multiple emulsions formation and the polymer conformationat the oil-water interface

This proposal is continuation of: 9-11-1644

Researh Area: Soft condensed matter

Main proposer: **GUENOUN Patrick**

Experimental Team:
MALLOGGI Florent
DAILLANT Jean
GUENOUN Patrick
PROTAT Marine
BLOT CHRISTIAN

Local Contact:
FRAGNETO Giovanna
CAMPBELL Richard

Samples: water/toluene

Instrument	Req. Days	All. Days	From	To
FIGARO	6	6	12/12/2014	18/12/2014

Abstract:

We have designed new polymer amphiphilic molecules which are able to stabilize such multiple emulsions depending on their architecture and on pH. We wish to determine whether the difference in conformation at the oil-water interface is correlated to this ability of forming multiple emulsions. To this aim, we propose to measure reflectivities of these different polymer layers at different pHs. We recently showed that such measurements are perfectly feasible with a new cell built in our group.

Experimental report on FIGARO test 9-10-1349: "How to link multiple emulsions formation and the polymer conformation at the oil-water interface" from 12/12/2014 to 18/12/2014

The goal of the experiment was to record the reflectivity signal of a copolymer layer at a liquid-liquid interface in order to determine the polymer conformation at a water-toluene interface and its influence on emulsions type and stability. In particular, very stable multiple emulsions are obtained in a precise range of pH and salt and it is not known how it is linked to a precise chain conformation. For this purpose, we made use of a home-made cell. In the previous experiment performed in 2013, the reflectivity curves obtained with the cell lead to a first determination of the polymer conformation on each side of the interface for one sample (1).

For this new experiment we have improved our cell's design in order to stabilize a larger and flatter interface. Such modifications have enabled us to get a better reflectivity signal which is stable over more than 8 hours without any dewetting.

Design of the cell

The new cell is composed of a pool of sapphire in which a sapphire bloc is inserted. The important depth of water near the border decreases the dewetting probability and facilitates the formation of a flat liquid-liquid interface on top of the inner sapphire bloc. Moreover, the surface covered by the water/toluene layers is approximately 2-times bigger than for our previous system. The cell is enclosed in a metallic structure and a PDMS spacer is used to seal the system (**FIGURE 1**).

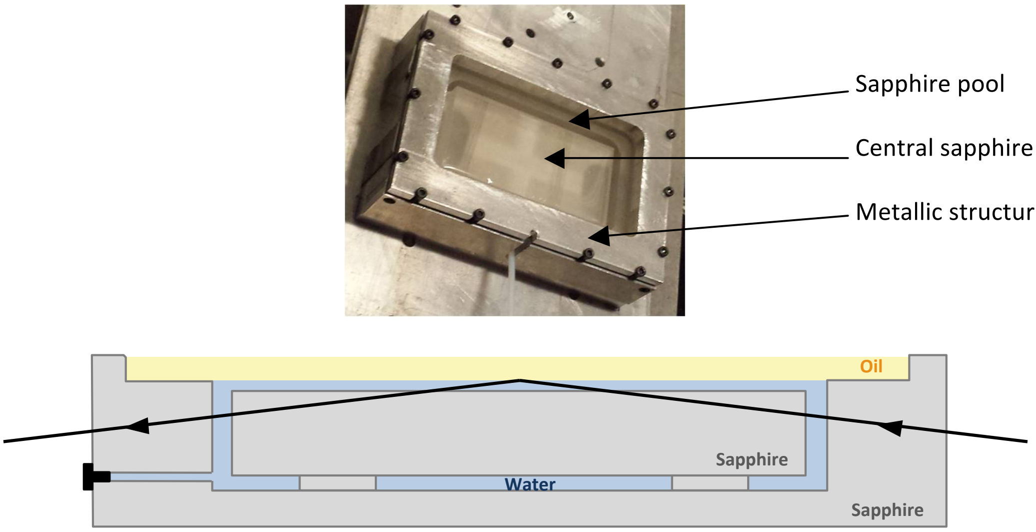

FIGURE 1: Picture of the cell in the metallic structure and sectional view of the filled cell.

Formation of the water/toluene interface

First, the sapphire bloc inside the pool was cleaned and treated under plasma to exhibit a perfect wetting behavior versus water. Then, a D_2O/H_2O 90:10 mixture (to match the contrast of the sapphire) is added in the sapphire pool. Finally, a polymer solution in deuterated toluene is gently spread on top of the water (**FIGURE 1**). The water level is eventually thinned down to a value of 150µm through a preformed hole in the pool.

With our new cell, oil-water interfaces can be stabilized for a long period of time (more than 8 hours) using the previous simple and reproducible filling procedure.

Setting of experiments

The neutron beam enters from below through the sapphire pool and is reflected at the water (contrast matched with sapphire)-toluene interface (**FIGURE 1**). To obtain a reflectivity curve with a wide range of q, three different angles: 0.6°, 1.4° and 2.7° were used.

To normalize the data, direct beams were measured at the three angles through sapphire and D2O/H2O 90:10. The normalization factor for each angle was determined and the shape I(λ) of the beam was also measured for different water thicknesses in order to correct for water scattering along the beam path.

Results

The polymer that we were studying is composed of a hydrophobic bloc of styrene and an hydrophilic bloc of 2-(dimethylamino)ethyl methacrylate (DMAEMA) statistically copolymerized with styrene and is soluble in deuterated toluene. With this stimuli-responsive polymer we can stabilize direct, inverse or multiple emulsions playing on the pH and the ionic strength of the water phase. The reflectivity curves were obtained for different samples corresponding to different types of emulsions (**FIGURE 3**). The data presented here are not yet corrected for transmission through the water layer.

Oil-in-Water 1	**Oil-in-Water 2**	**Multiple 1**	**Multiple 2**	**Multiple 3**	**Water-in-Oil**
Polymer A	Polymer A	Polymer A	Polymer A	Polymer B	Polymer A
pH=1	pH=2	pH=1	pH=1	pH=1	pH=7
[NaCl]=0M	[NaCl]=0.25M	[NaCl]=1M	[NaCl]=2M	[NaCl]=1M	[NaCl]=1M

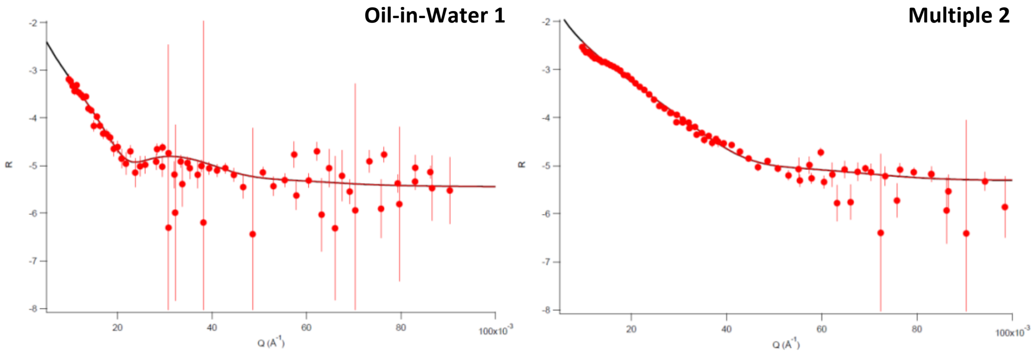

FIGURE 3:
Top: The six samples; PolymerA=PS_{40}-b-P(S_{21}-st-$DMAEMA_{68}$) ; PolymerB=PS_{48}-b-P(S_{32}-st-$DMAEMA_{60}$)
Bottom: Reflectivity data (symbols) and data fit (lines) to a 4-layer model obtained for two samples

All the data analysis has been done by fitting to a model where the interfacial region is represented by two discrete layers of different scattering length densityas represented in **FIGURE 4**.

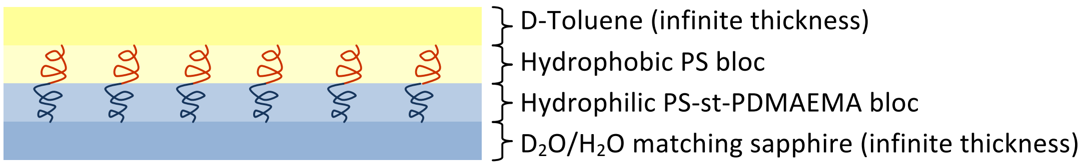

FIGURE 4: The 4-layer configuration used to fit the data

The thickness of the two polymer layers have been deduced from the fits (**FIGURE 5**). Although our data are not yet fully corrected for transmission effects, the first results demonstrate that the conformation is clearly related to the emulsion kind.

Emulsion	Thickness of PS-st-PDMAEMA layer	Thickness of PS layer
direct	190 Å	45 Å
multiple	70 Å	50 Å

FIGURE 5: Thickness of the polymer layers obtained with a 4-layer model

Comparing our two samples, the extension of the statistical moiety of the polymer is shown to be much smaller for the multiple case, in agreement with a modification in the curvature of the interface which would favor a change of the type of the emulsion. This seems also in agreement with qualitative SANS data which were previously obtained (1).

A start with biocompatible polymers

We have also designed a biocompatible system (oil and polymer) that can equally stabilize multiple emulsions. This system is very interesting for applications in cosmetics, foods and pharmaceuticals where multiple emulsions are able to encapsulate hydrophilic actives which need to be protected to the external medium before being delivered.The oil we are using for this system is isopropyl myristate, a biocompatible oil widely use in cosmetics and the polymer is a PDMS-*b*-PDMAEMA.

The reflectivity signal of [D_2O/H_2O 90:10]/H-isopropyl myristate has also been measured in presence of polymer (**FIGURE 6**) during the same run as a test. In spite of the poor contrast between the polymer and the hydrogenated oil, it seems that a polymer conformation can be extracted from this data curve since first fits to a pure water-myristate interface are not satisfactory. Moreover, this result demonstrated that a myristate-water interface can be equally stabilized for several hours of measurements.

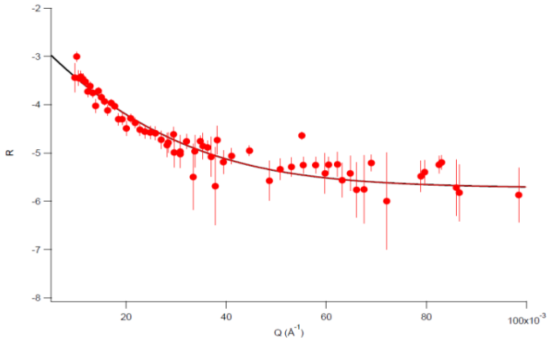

FIGURE 6: Reflectivity curve for a water/H-isopropyl myristate interface ($SLD_{isopropylmyristate}$= 0Å^{-2})

Conclusion

During this experiment, it has beenfirst demonstrated that our new cell has anexcellent designfor getting liquid-liquid reflectivity signal out of the noise in a wide q range: the stability and the quality (flatness) of the water-oil interface are the key points of this design. With this cell, we were able to record the reflectivity signal for six different samples.

Moreover, important results have been obtained and show for the first time that the polymer conformation varies with the types of emulsion that are obtained in the very same conditions. For example, the hydrophilic part of the polymer is shrinking when going to conditions where a direct emulsion is turned into a multiple one. This makes reflectivity a unique tool for this investigation since for instance, SANS was not able to detect polymer profile for the multiple case because the polymer corona over spherical analogues is too thin to be characterized (1). We are now treating all our results and we wish them to be published during the year.

In the future, we wish to pursue the study of our biocompatible system as shown above and also by improving the contrast by using deuterated polymers or oils.

(1) L. Besnard, M. Protat, F. Malloggi, J. Daillant, F. Cousin, N. Pantoustier, P. Guenoun, P. Perrin, *Soft Matter*, 2014, **10**, 7073-7087