Experimental report

09/02/2016

Proposal: **9-11-1746** **Council:** 4/2015

Title: Conformation changes of thermo-responsive nanogels at air/water interface

Research area: Soft condensed matter

This proposal is a continuation of 9-13-530

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Local contacts: Richard CAMPBELL

Samples: poly(N-isopropylacrylamide)
poly(N-n-propylacrylamide)
poly(N-isopropylmethacrylamide)

Instrument	Requested days	Allocated days	From	To
FIGARO	4	4	09/11/2015	13/11/2015

Abstract:

The mechanism and processes of controlling adsorption of thermo-responsive nanogels at interfaces are not well understood. There is a lack of in-depth knowledge regarding the adsorption dynamics of these particles. Resolving these outstanding issues is important in many applications of these systems. This proposal aims to address these by probing interfacial properties of thermo-responsive nanogels at air/water interface and examining them as a function of temperature.

# ILL Experimental Report 01/02/2016 **Ex. Number: 9-11-1746**		**Local Contact:**	Richard Campbell
Principal Proposer:	Ali Zarbakhsh, Marina Resmini, Katarzyna Zielinska	**Instrument:**	Figaro
Experimental Team:	Ali Zarbakhsh, Katarzyna Zielinska	**Date of Experiment:**	09-13/11/15

Introduction:

Countless everyday formulations such as drug delivery vehicles, foam stabilizers and emulsifiers as well as froth, flotation and food products use micro- and nanogels to optimize the interfacial properties. Surprisingly, however, the link between the bulk and interfacial structures in these systems with the surface tension has remained unresolved. Micro- and nanogels are colloidal particles that are cross-linked networks of polymer chains swollen in a good solvent. Nanogels can be easily designed to have desired size, rigidity and hydrophobicity for specific applications. They can also be made to respond to a variety of external stimuli (e.g. pH, temperature, ionic strength, magnetic field), which makes them "smart" materials. Thermo-responsive nanogels (among them *N*-isopropylacrylamide, NIPAM based ones) have a unique characteristic of being able to alter their size and hydrophobicity as a result of changes in the temperature. What more they can adsorb at the fluid/fluid interfaces reducing the surface tension.

The principal objective of this experiment was to use Neutron Reflectometery (NR) to probe the interfacial properties of NIPAM nanogels with 20% of cross-linker (*N*,*N'*-methylenebisacrylamide, MBA) and to examine how the related interfacial structure varies with the nanogels concentration (range $5x10^{-4}$ – $1.6x10^{-1}$ mg ml^{-1}) at the air-water interface at 25°C (below the transition temperature). Thermo-responsible nanogels (20 MBA-H) and their deuterated analogues (20 MBA-D) were used. NR technique was used to determine both the adsorbed amount and changes in conformations of the nanogels at the air/water interface as a function of bulk nanogel concentration. In the same time samples surface tension of all samples was measured.

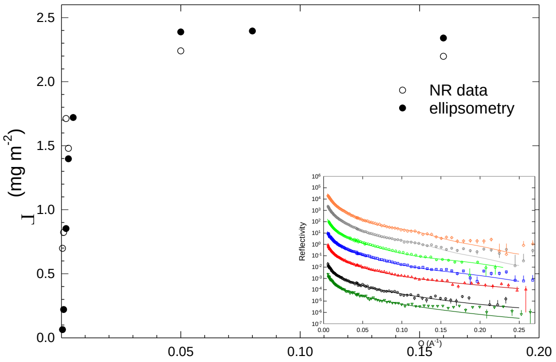

Fig. 1. Adsorbed amount determined by NR and ellipsometry. Insert shows the NR data for nanogels at different concentrations.

The adsorption kinetic of the nanogels was measured at the air/CMAir water. As expected samples with lower particle concentration required more time to reach equilibrium (data not shown). The adsorbed amounts determined from both NR (one layer Box fitting) and ellipsometry measurements are shown in Figure 1. The adsorbed amount gradually increases with nanogel concentration and then levels off. There is good overall agreement for profiles obtained from NR and ellipsometry. What more data agree with the trend obtained by surface tension measurements (decrease at low concentrations fallowed by levelling off at concentrations higher than 2x10^{-3} mg ml^{-1}). The bulk behavior of nanogels as a function of concentration was measured by means of DLS. Data shows that there is no increase in nanogel sizes as a function of concentration at 25^{o}C hence bulk aggregation does not occur (up to 1.0 mg ml^{-1}).

While analysing the data we found reasonable to cluster them into three groups: (1) with concentration c < 2x10^{-3} mg ml^{-1} were data were fitted to two layers model, Fig. 2a, (2) fitted to three layers model (Fig. 2b, 2x10^{-3} mg ml^{-1} > c < 5x10^{-2} mg ml^{-1}) and (3) where two layers model was applied but the layer thicknesses were much higher than in the first group (Fig. 2c, c > 5x10^{-2} mg ml^{-1}).

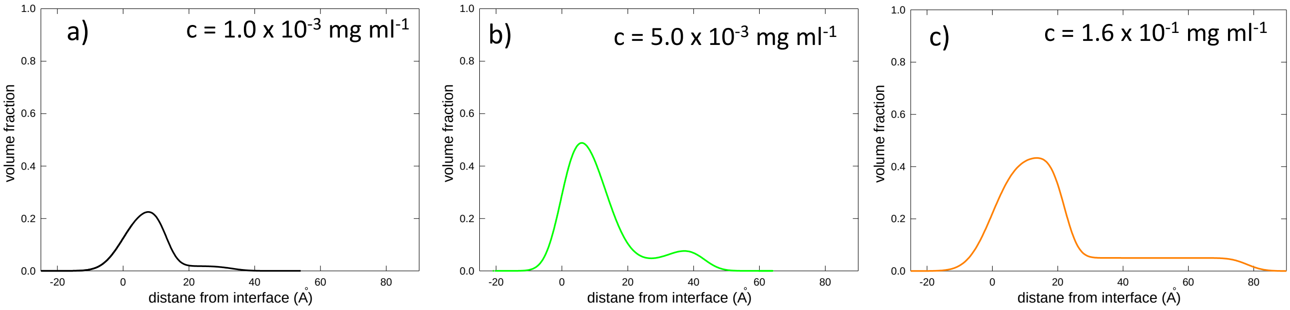

Fig. 2. Polymer volume fractions calculated from NR data for nanogel adsorption layers at air/water interface at different nanogel concentrations.

The first layer in all three groups was related with the fraction of nanogels exposed to the air. It is suggested that hydrophilic groups of the polymer at the hydrogel-air interface are preferentially drawn into the bulk of the hydrogel. It is possible because of the free rotation of polymer chain segments around C-C bonds and the long-range mobility of polymeric chains. When the polymer segments of a hydrogel are subjected to the asymmetric molecular force field at the gel/air phase boundary, it is energetically more favorable for the segments to orient in such a way as to expose the hydrophobic side groups of the polymer backbone toward the air (hydrophobic phase) and to bury the polar sites in the aqueous phase within the gel. This results in region with collapsed, relatively densely packed polymer chains (high Nb_{fited} values) and low water content. As the bulk concentration of the nanogels was increasing the increase of layer thickness and roughness was observed. This air exposed layer is then followed by the region where the polymer network is fully swollen by water. At very low bulk concentrations the amount of material in this subsequent layer is not enough to gain detailed structure (thus second layer with very low polymer volume fraction). Whit increase of concentration the measured signal is high enough to distinguish between the nanogel highly cross-linked core and loosely crosslinked shell (layer 2 and 3, respectively in the second concentration regime). However, with increase of bulk concentration, under the initial surface monolayer of nanogels more particles start to adsorb, the second layer gets thicker (56 Å) and it is not possible to distinguish between particle core and shell anymore (2 layers for c > 5x10^{-2} mg ml^{-1}).