# Experimental report

23/10/2018

**Proposal:** **9-11-1870** **Council:** 4/2018

**Title:** Interfacial behaviour of thermal and pH-responsive nanogels at Sapphire/water interface

**Research area:** Soft condensed matter

**This proposal is a new proposal**


**Main proposer:** **Ali ZARBAKHSH**

**Experimental team:** Ali ZARBAKHSH
Pengfei LIU

**Local contacts:** Armando MAESTRO


**Samples:** N-isopropylacrylamide (NIPAM)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| FIGARO | 3 | 3 | 14/09/2018 | 17/09/2018 |


## 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 charged thermo-responsive nanogels at the Sapphire/water interface as a function of the temperature, concentration and pH.

## 1 PRINCIPAL INVESTIGATOR

Name and institution of the Principal Investigator

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## 2 EXPERIMENT DETAILS

Experiment: 9-11-1870

Title: Interfacial behaviour of charged nanogels at the air/water and sapphire/water interfaces

Instrument: FIGARO

Dates scheduled: 14th September 2018 to 17th September 2018 | No. Days allocated: 3

Date of experimental report: 23 Oct. 2018

## 3 EXPERIMENT OBJECTIVES

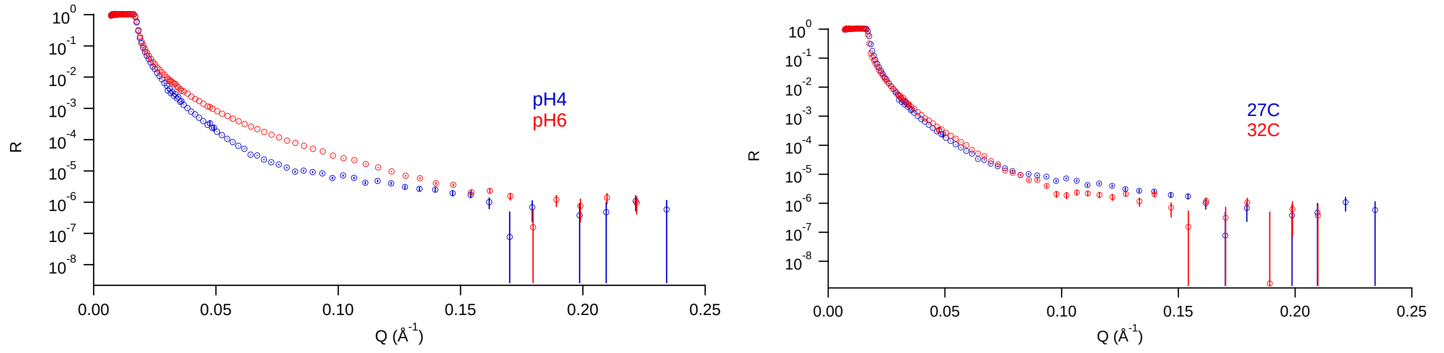
In the past we have successfully used neutron reflectivity (NR) to study the structural conformations of thermoresponsive N-isopropylacrylamide (NIPAM) based nanogels, cross-linked with methylene-bis-acrylamide (MBA), both at the air-water and hydrophobic solid (Si)-water interface. Results from neutron reflectivity and additional complementary experiments demonstrate that the adsorption process of NIPAM based nanogels onto the air-water interface can be described by lay-by-layer deposition with increasing layer thickness as the concentration of nanogels in the bulk and temperature increase in the absence of any bulk aggregation. For a well characterised hydrophobic (Si-C8) coated substrate, much thicker layers (order of magnitude thicker) than those at the air-water interface were observed.

We then have also investigated the interfacial behaviour of N-n-propylacrylamide (NPAM) based nanogels at air-water interface. NPAM, the linear isomer of NIPAM, was selected on the basis that it could increase the overall hydrophobicity of the nanogels, while keeping a similar monomer structure. The preliminary results suggest a better ordered and much more compact packing for the NPAM compared with those observed of NIPAM. This indicates that the hydrophobic interactions may play a major role governing the adsorption process of these thermal responsive nanogels onto the interfaces.

We would like to gain more comprehensive information on the main factors influencing the surface behaviour of nanogels, and hence we wish to extend these studies and examine the interfacial behaviour of NPAM-MBA nanogels, when charges are introduced by adding N-acryloyl-L-Proline (A-Pro-OH) during the polymerisation. We believe that the combination of a pH-responsive system with a thermo-responsive polymer can further alter the dynamic of the adsorption process also providing a better control over the layer deposition architecture. Herein we would like to explore the behaviour of these NPAM and A-Pro-OH) based charged nanogels (short as NPAMP) at both the air-water and sapphire/water interfaces.

## 4 EXPERIMENT REPORT

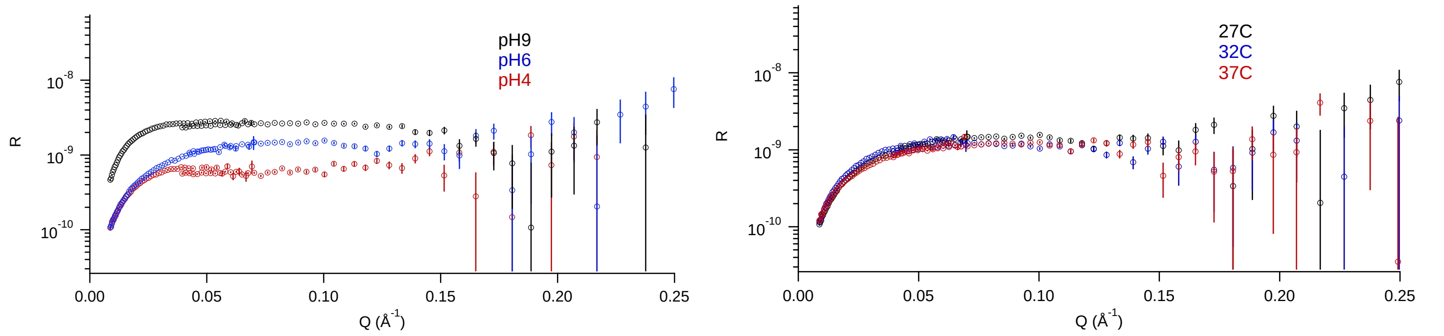
We have investigated adsorption behaviour of NPAMP based nanogels crosslinked with 5% and 10%MBA at the air/water interface at different pH (4 and 6) and temperatures (27 and 32ºC) for two aqueous sub-phase contrasts (D2O and NRW). Detailed data analysis is still ongoing. Exemplary NR profiles of NPAMP nanogels with 5% crosslinker are presented as a function of pH (Fig 1a) and temperature (Fig 1b). The data suggest the amount of nanogels at the air/water interface is much less at pH=6 compared with the value at pH=4.This can be attributed to the repulsion among the $COO^{-}$group of nanogel network at lower pH value. Another interesting observation is the weakened thermal responsiveness of these nanogels when charges has been introduced into nanogels matrix, indicating the electrostatic interaction dominates over the hydrophobic interaction.




(a) (b)

Fig. 1. NR profiles for 92.5%NPAM, 2.5%A-Pro-OH and 5%MBA nanogels at the air-water interface as a function of pH at 27C (a) and temperature under pH=4 (b)

We have also explored the same batch nanogels at the sapphire/water interface. Exemplary NR profiles shows that the pH effect seems to be enlarged while the temperature maintains the same negligible effect.




(a) (b)

Fig. 2. NR profiles for 92.5%NPAM, 2.5%A-Pro-OH and 5%MBA nanogels at the sapphire-water interface as a function of pH at 27C (a) and temperature under pH=6 (b)

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|---|---|
| **5 LIKELY OUTCOMEs FROM EXPERIMENT** *Please indicate what the experiment is likely to lead to by putting an 'x' next to one or more of the possible outcomes below.* | |
| *Likely outcome* | |
| Journal publication | *x* |
| Data for thesis | *x* |
| Follow-up experiment at ILL | **-** |
| Follow-up experiment at another facility | *x* |
| Other | *x* |
| No outcome anticipated | **-** |

## 6 SUGGESTIONS FOR IMPROVEMENTS TO YOUR EXPERIMENT, EQUIPMENT OR THE FACILITY

NA