Experimental report

13/02/2017

Proposal: **9-11-1786**

Council: 4/2016

Title: Structure and conformation of thermo-responsive nanogels at air/waterinterface

Research area: Chemistry

This proposal is a continuation of 9-11-1746

Main proposer: **Ali ZARBAKHSH**

Experimental team: Pengfei LIU
Ali ZARBAKHSH

Local contacts: Richard CAMPBELL

Samples: NIPAM

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	4	08/12/2016	12/12/2016

Abstract:

Stimuli-responsive nanogels have the unique characteristics of being able to alter their size, volume occupied and hydrophobic character as a result of changes in the temperature of the solution. Upon dissolution in water, polymer backbone forms favourable hydrogen bonds with hydrophilic amide groups resulting in negative entropy of mixing. In this proposal we would like to gain a better understanding of the interfacial properties of stimuli-responsive NIPAM-based gels by determining their conformation and structural changes at the air/water interface as a function of both concentrations at several temperatures below their (Volume Phase Transition Temperature) VPTT. The parallel characterisation of the bulk properties have been carried out in our Lab as well as the synthesis of both protonated and deuterated nanogels.

ILL Experimental Report 08/02/2017 **Ex. Number: 9-11-1786**		**Local Contact:**	Richard Campbell
Principal Proposer:	Ali Zarbakhsh, Marina Resmini, Katarzyna Zielinska	**Instrument:**	Figaro
Experimental Team:	Ali Zarbakhsh, LIU Pengfei	**Date of Experiment:**	09-13/11/15

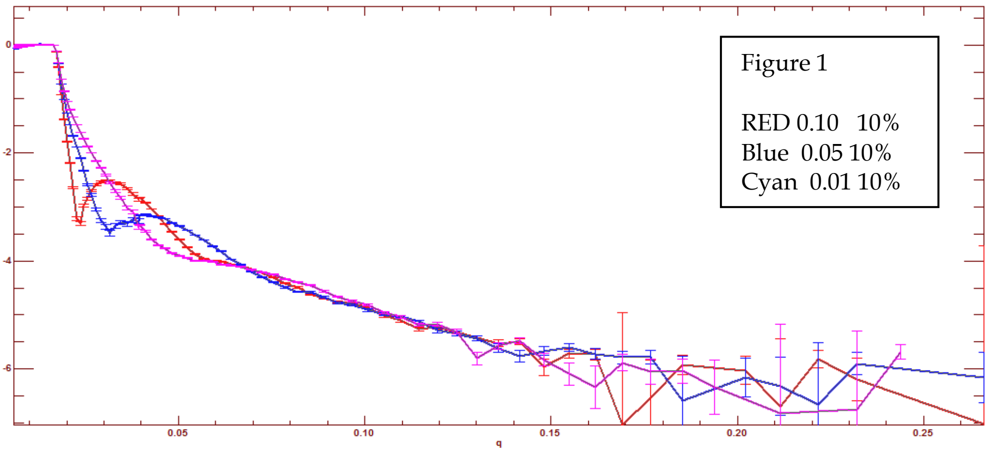
Structure and conformation of thermo-responsive nanogels at air/water interface

Introduction:

In surface tension studies of nanogels at the air/water interface as a function of concentration, the onset of the plateau region is normally taken in the literature to signify bulk aggregation. However, recently we have shown for the first time using a combination of DLS, surface tension, ellipsometry and NR measurements on FIGARO that the an inflection point in the surface tension data as a function of concentration is in fact be unrelated to bulk aggregation for these nanogels. 3 The behaviour of smart, thermo-responsive nanogels is therefore rather more complex than those of classical surfactants and their bulk and surface activity is driven by their intertwined structure, conformational rigidity and the structural changes that occur as temperature increases. We observed the lack of any bulk aggregation at high concentrations well above the inflection point in surface tension data for the NIPAM-based nanogels at 25°C. This behaviour is associated with the structural confinement of the hydrophobic moieties entrapped within the nanogel structures at this temperature.

However many questions related to these phenomena remained unanswered. For example what is the quantitative relationship between surface tension and adsorption? What are the factors influencing surface tension lowering and therefore the rate of adsorption? What is the structure of the adsorbed layer?

The aim of this proposal was to gain a better understanding of the interfacial properties of stimuli-responsive NIPAM-based gels by determining their conformation and structural changes at the air/water interface as a function of both concentrations at several temperatures below their (Volume Phase Transition Temperature) VPTT. The parallel characterisation of the bulk properties have also been carried out in our Lab .



In this study the adsorption of thermo-responsive pNIPAM – based nanogels with 5%, 10% and 20% of cross-linker (N,N'-methylenebisacrylamide, MBA) at the air/water interface were studied. A series of NR profiles at 25^{o}C to 46^{o}C as a function of concentrations 0.05, 0.01 and 0.1 mg ml^{-1} were obtained. The NR profiles are shown in Figure 1, for a 10% MBA cross-linker as a function of concentrations at 34 ^{o}C.

The data exhibit a clear set of fringes. These fringes indicate a well ordered multilayer adsorption at the air-water interface. The multilayer adsorption at the air-water interface occurs at the expense of bulk aggregation in order to minimise the free energy of the system. This supports the Derjaguin prediction, that a sphere's interaction with a plane (the thick adsorbed nanogel layer at interface) is much larger than the nanogel-nanogel (sphere-sphere) association in the bulk. These findings, in particular the changes in conformations and the thick layer adsorption at the interface as a function of concentration, can impact significantly on a number of applications for which nanogels are currently being investigated. These results contribute to the understanding of the behaviour of soft colloids at the interfaces.

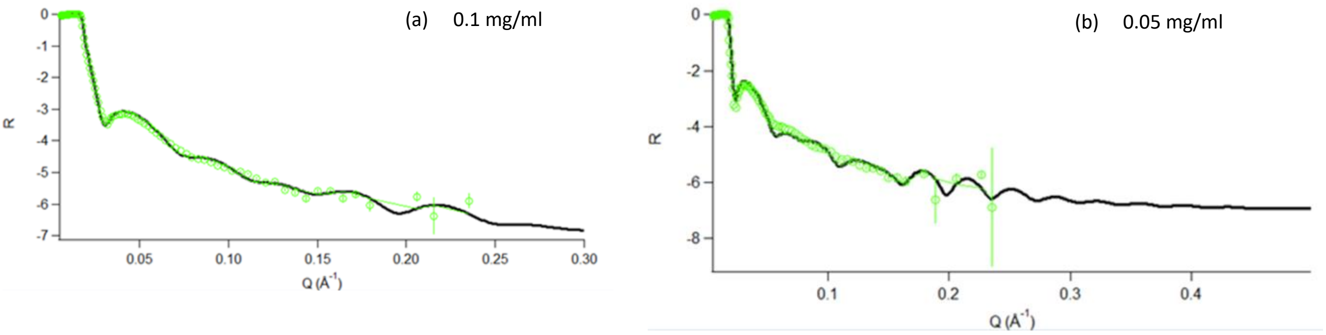


Figure 2. 10% MBA as a function of concentration at 34 ^{o}C (a) 0.1 and (b) 0.05 mg ml^{-1} at the air-D_2O

These preliminary fits shows a tri-layer model 28 (a collapsed nanogel layer), 31 (27% solvated) and 84 Å (extending into the bulk) for 0.05 mg/ml (The fit to the data is shown by the solid line, Figure 2 (b)) and as the concentration increases the data suggest an increase in layer 3 thickness to 145 Å (Figure 2 (a)). The analysis of the data is ongoing.