Experimental report

15/08/2019

Proposal: 9-11-1879 **Council:** 4/2018

Title: Electro and photochromic gels

Research area: Chemistry

This proposal is a new proposal

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Samples: C50H30N4O10

Instrument	Requested days	Allocated days	From	To
D11	2	2	20/09/2018	22/09/2018
D33	2	0		

Abstract:

Here we wish to use SANS to explore a gel made from a naphthalene diimide functionalised with a dipeptide on either end. These form worm-like micelles at high pH, and when the pH is dropped below that of the pKa the gel is formed. These gels are also able to change colour reversibly from a transparent material to dark brown/black colour. This is highly attractive for applications such chromic windows, where they can change colour automatically and with the push of a button. This can achieved by irradiation of the sample with UV light to go black, then left in the air to recover to transparent. This can also be achieved by the application of a small negative potential to get the sample to change to black, and then a small positive potential to return it to transparent. We know the gel structure changes upon irradiation as the rheological strain profile changes reversibly too. We want to investigate these structures further using SANS, does the bulk rheology match up to the microstructures, for example. We also want to add in deuterated glycerol as we want to see if we can make the chromic window more tolerant to different temperatures.

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Abstract We have a set of chromic materials that respond to different stimuli, giving the same change in colour. This is due to a reduction of the molecule causes a change in colour. This is of specific interest in chromic windows. From previous data collected we can that the materials self-assemble in solution to form aggregates. Upon reduction the rheology of the materials change, and upon oxidation return to the original state. We want to know what change happens to the aggregates upon this reduction, and whether the same happens suing the different methods of reduction. SANS is used to investigate this change.

Introduction We are currently developing materials where we utilise the self-assembly of small molecules to form fibrous structures. The entanglement of these fibres leads to the formation of gels. The formation of fibres is a result of the molecules stacking, and this can be used to form conductive materials due to stabilisation of charges and radical species. We have a range of molecules that can be successfully used to form such materials, and we have collected small angle neutron scattering data for a number of these at both ILL. One current set of materials of interest is chromic low molecular weight gels. We use different external stimuli to create this change in colour in the gels, such as light and electrical currents. Most examples show that the irradiation of the gel with light results in the gel be damaged and falling apart. However, we have a number of examples where the gels become stronger. This is highly unusual. We showed recently an example where this was the case and showed that the gel strength could be cycled repeatedly without any destruction of the gel.[5] This is hugely important when wanting to use the gels commercially. We have recently found another class that shows interesting optical properties on top of a really unusual change in the gel properties. The gel does not increase in absolute strength, but does become more resistant to strain. Our aims are to understand the changes in gel properties when the gels are irradiated vs. that of those when a current is used. We need to understand how the gel structure is affected by irradiation to be able to explain the extremely unusual rheological data. The materials are extremely unusual. They are currently being investigated for potential IP, and we aim to publish this work in a high-level journal, but this will only be possible if we can explain why these gels are so unusual.

Experimental The LMWG were prepared as described elsewhere.[1] Solutions at 5 mg/mL, were prepared in D_2O at high pD by the addition of one molar equivalent of NaOD (0.1 M), followed by stirring until the LMWG had dissolved. Gels were formed in situ by the addition of glucono-d-lactone (GdL). SANS experiments were performed on the D11 diffractometer, a neutron wavelength of λ= 10 Å was employed at a detector distance of, D = 1.1m, 8 m and 30 m. All spectra were normalised and corrected using the scattering of the empty cell. Scattering data were corrected for electronic noise and incoherent background subtraction and normalised by the intensity scattered for a 1 mm H_2O sample corrected by the intensity scattered from the empty quartz cell. The scattering of each of the samples were collected on irradiated (not in situ) and non-irradiated samples. We then used a larger cell which was a demountable quartz cuvette and could fit into the electrochemical cell with working, counter and reference included. We then collected data with no potential applied, reduced (-0.7 V) and oxidized (0.2 V) all for about an hour.

Results

Scattering collected for the irradiated and not irradiated samples fit to a power law. Upon irradiation there was a change in the gradient at high Q, showing there may be a change in the network. This gradient returned back to the original when allowed to oxidize in air. The electrochemical reduction has proved trickier. At first, we were using too small a pathlength and so we did not get sufficient scattering from the sample. We then moved to a different set up, with a larger pathlength, but this meant that the diffusion was too great for the sample. This meant that any change in the sample was too small in comparison to the rest of the bulk sample. We are in the process of getting custom cells prepared, to make a happy medium between diffusion of reduced state and enough smaple for good scattering and will try again.

References

1. E. R. Draper et al., *Chem. Commun.*, **2016**, *52*, 6934.