Experimental report

12/04/2022

Proposal: **9-11-1966**

Council: 10/2019

Title: New electrochemical approach to monitor gelation self-assembly and kinetics

Research area: Chemistry

This proposal is a new proposal

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Samples: 2-bromo-naphthalene-valine-glycine

Instrument	Requested days	Allocated days	From	To
D11	2	2	16/05/2021	18/05/2021

Abstract:

The mechanism of the self-assembly of low molecular weight gelators (LMWGs) into gels is still poorly understood. Despite this their gels are used in diverse applications such as cell growth and differentiation, cosmetics, chromic displays and even catalytic hydrogen evolution. We have been looking at the gelation process in detail for a number of years. Using different techniques to monitor this process, such as, UV-vis absorption, rheology, NMR, SAXS, SANS and computational modelling. We are finding we need all these different techniques to look at different length scales during self-assembly, but there is so much more still to be learnt about these systems. Our work looks at self-assembly by using a slow pH switch such as glucono-∂-lactone (GdL) and more recently electrochemically by oxidising the hydroquinone to produce protons and reduce the pH locally on the surface of an electrode. We wish develop this electrochemical method of gel growth to examine more thoroughly how the kinetics of self-assembly effects the gel network, molecule aggregation and fibre formation and in turn how this effects their rheological properties.

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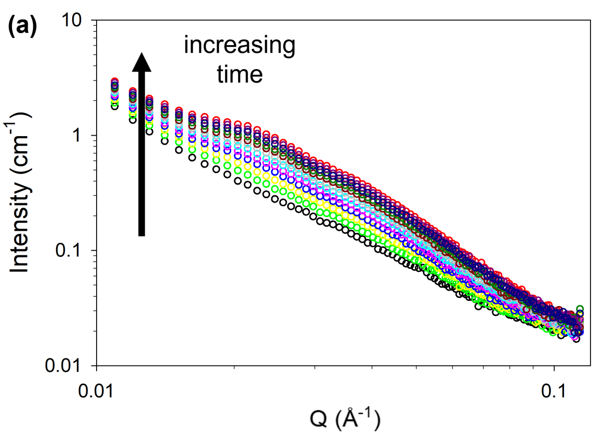
Abstract The mechanism of the self-assembly of low molecular weight gelators (LMWGs) into gels is still poorly understood. Despite this their gels are used in diverse applications such as cell growth and differentiation, cosmetics, chromic displays and even catalytic hydrogen evolution. Using different techniques to monitor this process, such as, UV-vis absorption, rheology, NMR, SAXS, SANS and computational modelling. We are finding more that these techniques need to be carried out *in situ* whilst the gel is forming to truly understand what is happening and be representative of the system. We therefore have developed an in situ electrochemical cell that can be used in the neutron beam.

Introduction Several self-assembling systems can be triggered electrochemically using the oxidation of hydroquinone (HQ) to allow for a lower pH on the electrode surface, causing gelation to occur. Performing electrochemistry on a sample in the beam itself has all the advantages of real time SANS measurements, allowing analysis of a larger variety of length scales than absorbance spectro-electrochemistry (which gives more information about molecular packing rather than overall structure in these types of systems and can be limited by factors such as concentration). The use of in situ electrochemistry combined with SANS (electrochem-SANS) and with other ex situ techniques has been reported mostly in the evaluation of batteries. The use of electrochem-SANS to the best of our knowledge has not been applied to organic materials. Here, we report a simple contained method of performing electrochem-SANS, able to be controlled from outside the beam. It requires small volumes (2 mL) of material and can be easily cleaned between measurements.

Experimental We focused on the gelator BrNapAV as we have collected the rheological data for this system. We measured the scattering of the pre-gelled solutions and then the end point of the gelation. We then collected scattering at 5 minutes intervals in the Q range where any change was happening for a total of 60 minutes whilst the gelation is occurring. We varied the speed of the gel growth by altering the amount of current and therefore the speed of the HQ oxidation. We looked 10 μA intervals from 10 to 50 μA. An end point scattering data was then be collected for all the different grown gels. We then left the gel once the current was stopped (and therefore gelation should also stop) for 30 minutes and then collected scattering again to see if the network was still evolving.

Results

We were able to monitor the growth of BrNapAV using the electrochemical method. The scattering was comparable to that of gels grown ex situ, despite the fine Pt mesh working electrode present. We then able to collect data every 5 minutes and watch the gel structures appear and then fit to an elliptical cylinder with a power law (Figure), which grew linearly. This agreed with data collected from other in situ techniques. We then we able to grow the gel at different speeds by varying the amount of current. The larger the current the faster the gel grew. We also found that when current was removed then the gel stopped growing. This means that gelation could be stopped and longer better resolved scattering could then be collected. This method not only is amazingly useful for gelation, but could be used in many systems were change in structure is happening on an electrode surface, the possibilities and range of uses is huge. We are currently writing this work up for a publication.



References

1. R. I. Randle et al., 2022, In submission