Experimental report

15/06/2020

Proposal: 9-11-1906 **Council:** 10/2018

Title: Understanding Dynamic and Dissipative Gels

Research area: Materials

This proposal is a new proposal

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Samples: C30H32N2O5

Instrument	Requested days	Allocated days	From	To
D11	2	2	17/07/2019	19/07/2019

Abstract:

We are investigating low molecular weight gels for many applications. In some cases, stable gels are needed, but there is growing interest in the idea of gels that evolve over time. We have systems for example where gels form over around 10 minutes and then slowly return to a solution phase in a pre-determined manner by a triggered enzymatic reaction. It is also possible to prepare samples where a gel is only stable whilst a fuel is present. As the fuel runs out, the sample returns to a solution state, only to re-form a gel on the addition of more fuel. To understand these systems, we need to understand the way in which the fibre network leading to the gel phase is formed and degrades again. This will allow us to move from the current observations of gelation to the design of these systems for specific applications. We will understand the fibres, networks and changes in the systems using SANS.

Experiment Number: 9-11-1906

Experiment Title: Understanding Dynamic and Dissipative Gels

Abstract We are investigating gels formed by the self-assembly of small molecules. Gelation occurs when a trigger is applied to a solution of a pre-gelator. This trigger results in a decrease in solubility of the gelator, self-assembly and the formation of fibre-like structures that are generally around 10 nm in diameter and several microns long. These fibres entangle and immobilise the solvent. Typical triggers are a change in pH, a change in temperature, or a change in the solvent mixture. To understand these systems, we have been heavily using small angle scattering. This gets around drying issues which are prevalent in microscopy and allows bulk samples to be analysed.

Introduction In almost all cases, supramoelcular gels are triggered and used as is. There are however opportunities that are currently under-exploited. For example, we have now examples where we can form gels and then anneal them to form gels with different properties. This annealing can be by a heat/cool cycle. A second opportunity is to prepare gels which are dynamic. In these cases, the gelation occurs by a first trigger and then a second slower trigger results in either the gel falling apart again, or a further change in the gel properties. These are really exciting possibilities. A number of groups are looking at such gels, but there is limited understanding of the processes that lead to these changes in the properties. Almost all understanding that is in the literature comes from microscopy.

Here, we focussed on a specific issue. Since most characterisation comes from microscopy and we want to avoid drying, the most effective method is to use confocal microscopy. However, this generally requires the addition of a stain; a fluorescent additive that binds to the structures underpinning the gel phase. A key question is therefore whether the stain affects the structure formed and, in the case of dynamic gels, whether the structures that evolve are all equally (un)affected.
Hence, we examined a range of gels in their native state and compared the data with those from gels prepared in the presence of typical additives.

Experimental Solutions of LMWG were prepared as described previously.[1] Solutions were prepared in D_2O at high pD at 10 mg/mL by the addition of one molar equivalent of NaOD (0.1 M), followed by stirring until the LMWG had dispersed to give a free-flowing solution. Gels were prepared by the addition of GdL[2] to these solutions. The samples containing additives were prepared with the additives present in the high pH solutions. SANS experiments were performed on the D11 diffractometer, a neutron wavelength of λ= 10 Å was employed at three different detector distances, D = 1.2, 8 and 40 m, corresponding to a Q range from 1.0×10^{-3} to 0.31 $Å^{-1}$. All spectra were normalized and corrected using the scattering of the empty cell. Scattering data were corrected for electronic noise and incoherent background subtraction and normalized by the intensity scattered for a 1 mm H_2O sample corrected by the intensity scattered from the empty quartz cell.

Results We prepared a range of solutions and gels containing a range of typical additives used to monitor gels using microscopy such as Nile Blue and Thioflavin T. We probed whether the additives had an effect on the structures formed in solution at high pH and also in the gel phase. Typical dipeptide based gelators were used as we have described previously.[1]

Here, the data are complex and currently it seems difficult to pick out specific trends. However, importantly, the data do show that in some specific cases there are substantial changes in structure on addition of the additive. For example, in Figure 1, we compare the data for a specific dipeptide that forms hollow cylinders at high pH (green data). Addition of typical stains results in a change to a flexible cylinder (blue and red data).

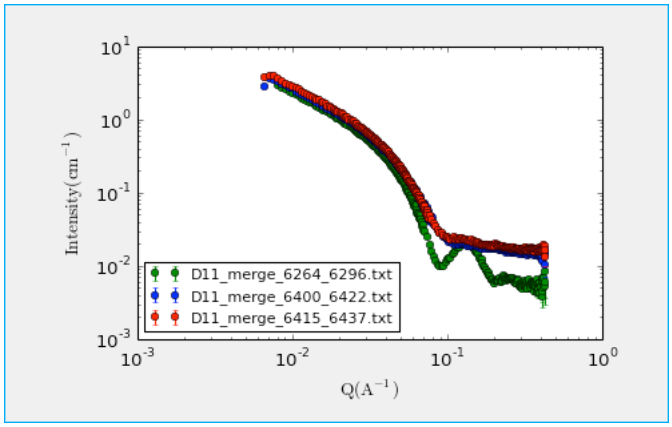

Figure 1. SANS data for a solution of a dipeptide at high pH (green data) and on adding eiher Nile Blue (red data) or Thioflavin T (blue data).

The data are currently being fitted and compared to viscosity rheology and confocal microscopy data to understand the systems. Some of the data fitted well into a different study we were examining where a specific additive can be used as a phototrigger. As such, these data were included in a recent paper.[3]

References

1. E.R. Draper, M. Wallace, R. Schweins, R.J. Poole and D.J. Adams, *Langmuir*, **2017**, 33, 2387–2395.
2. D.J. Adams, W.F. Frith, M. Kirkland, L. Mullen and P. Sanderson, *Soft Matter*, **2009**, *5*, 1856-1862.
3. L. Thomson, R. Schweins, E.R. Draper and D.J. Adams, *Macromol. Rapid Commun.*, **2020**, *41*, 2000093.