Experimental report

17/02/2022

Proposal: 9-10-1670 **Council:** 4/2020

Title: Using selective deuteration to understand gelation

Research area: Materials

This proposal is a new proposal

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Samples: 2NapFF
Deuterated 2NapFF

Instrument	Requested days	Allocated days	From	To
D11	3	2	14/03/2021	16/03/2021

Abstract:

Low molecular weight gelators self-assemble in solution to give nanofibres. These entangle to form the gel networks. Understanding how the molecules are packed in these fibres is difficult. Microscopy cannot provide this information and methods such as circular dichroism often have to be carried out at concentrations that are far lower than the concentration at which the materials are to be used. We have recently shown that contrast matching approaches can be used to work out how the molecules are packing (Matter, 2020, In press). Here, we wish to exploit this methodology for a wider range of gelation types. We know that the gel properties are very different between the pH-triggered, the solvent triggered and the calcium-triggered gels. What is not clear is whether this is driven by different underlying molecular assembly. Our method should allow us to answer this key, underlying and unanswered question

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Introduction We are investigating self-assembled structures formed from functionalised dipeptides such as L,D-2NapFF (Figure 1a) and FmocFF (Figure 1b). In water at high pH, such molecules assembles into long hollow cylinders.[1] Gels are formed when the pH is decreased or calcium salts are added. To investigate the packing, we have prepare a range of analogues of each gelator where either or both amino acids are deuterated. We have also prepared analogues where the N-protecting groups are deuterated. Using contrast matching approaches, we aim to understand the packing in the molecular aggregates.

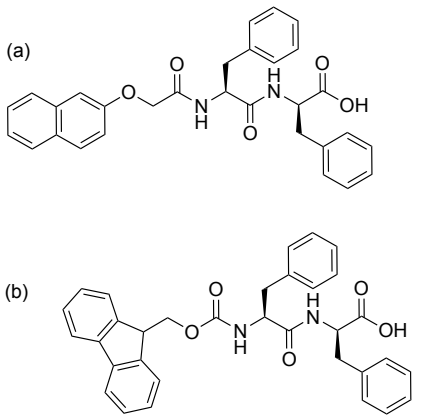

Figure 1. Structure of 2NapFF as (a) the sodium salt and (b) the TBA salt.

Experimental Solutions of 2NapFF 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. SANS experiments were performed on the D11 diffractometer, a neutron wavelength of λ= 6 Å was employed at three different detector distances, D = 2, 8 and 28 m. 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 Solutions were prepared from the various analogues of the different gelators. The solutions at high pH (before gelation) were examined as well as the samples after gelation. As expected, the more heavily deuterated the molecules, the lower the overall scattering, but good quality data could be collected in each case. Example data for one set of samples at high pH is shown in Figure 2. The data in this case can be fitted to elliptical cylinder models; for the analogue were the naphthalene ring is deuterated the model is essentially unchanged although the scattering is lower overall. When one of the amino acids is deuterated, there are changes to the apparent radius. Hence, we can understand the packing using the contrast matching approach. Our aim now is to pull out all of the packing for a range of systems. This has been slowed by the need to also collect SAXS data to show that the packing is not affected by the deuteration and hence changes in scattering and fitting are due to contrast matching only.

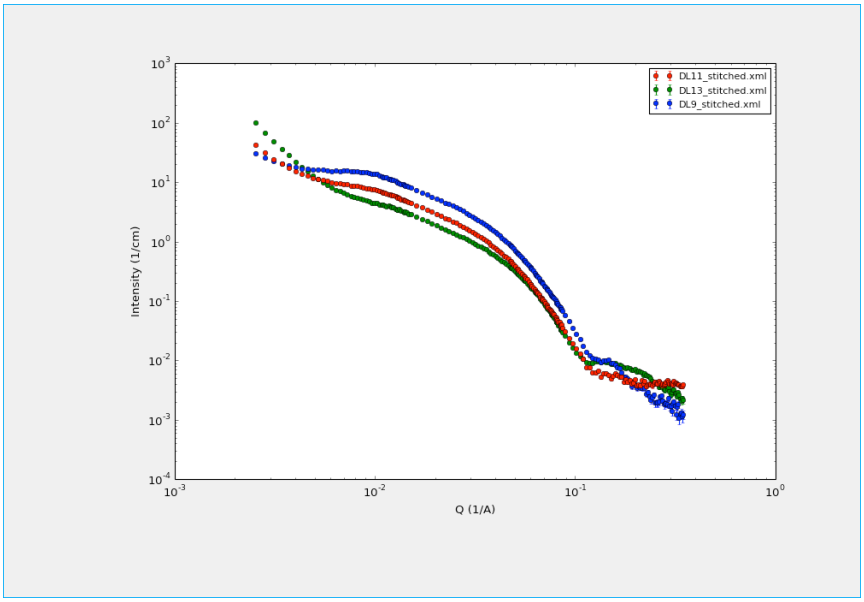

Figure 2. Example SANS data for a dipeptide at high pH for the parent (blue) with different analogues with either the naphthalene ring deuterated (red data) or one of the amino acids deuterated (green).

We are currently writing up the data for inclusion into a manuscript which we intend to submit this year.

References

1. E.R. Draper, K. McAulay, B. Dietrich, C. Brasnett, H. Abdizadeh, I. Patmanidis, S.J. Marrink, H. Su, H. Cui, R. Schweins, A. Seddon and D.J. Adams. *Matter*, **2020**, *2*, 764–778.