Experimental report

05/02/2017

Proposal: **9-11-1802** **Council:** 4/2016

Title: Mixing LMWG solutions and the effect of mixing on the final gel properties

Research area: Materials

This proposal is a continuation of 9-11-1757

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Samples: $C_{30}H_{28}N_2O_5$
$C_{30}H_{32}N_2O_5$

Instrument	Requested days	Allocated days	From	To
D22	3	0		
D11	3	2	13/09/2016	15/09/2016

Abstract:

Mixing different gelators together is a means of preparing gels with interesting and useful properties. However, understanding what happens when two different gelators (both of which gel alone) is difficult. Here, we aim to characterise what happens when two gelators are mixed before gelation and what effect this has on the properties of the final gels.

Experiment Number: 9-11-1802

Experiment Title: Mixing LMWG solutions and the effect of mixing on the final gel properties

Abstract The effect of mixing solutions of low molecular weight gelators (LMWG) at high pH was studied by SANS. A specific and important LMWG, 2-naphthalene-diphenylalanine (2NapFF), has been shown to form worm-like micelles at high pH that scatter well. Solutions of 2NapFF were diluted with either D_2O or solutions of another (2NapVG), chosen such that its scattering at high pH was low. On the basis of this, it was possible to determine whether the presence of the other LMWG affected the self-assembled worm-like micellar structures formed by 2NapFF. We also followed the gelation of the mixed system and were able to show that the assembly was a complicated mixture of self-sorting and co-assembly, depending on the ratio of the two LMWG.

Introduction We have been examining a range of dipeptide-based LMWG. These form solutions at high pH, and gels when the pH is lowered. We are specifically interested in mixed systems with two or more LMWG. These mixed systems are very complicated; it is possible for self-sorting, separate assembly, co-assembly (specifically or randomly), or most appealing, templated gel-on-gel assembly to occur.[1-3]

Up until now we (and others) have focused on one ratio of LMWG. However, we have recently found that a number of properties (e.g. the mechanical properties) vary non-linearly with composition. Whilst we can characterize the samples using microscopy, this does not inform us greatly since the gels have to be dried, which affects the data.

To form the gels, we mix solutions of the LMWG at high pH and then lower the pH. We do not know whether the two LMWG form two independent structures at high pH. We have assumed that this is the case, but have no proof. Additionally, we generally get sequential assembly on lowering the pH. Hence, one network forms in the presence of a non-assembled LMWG. This may lead to significant differences in structure. Hence, the aim of this proposal was to understand whether the structures at high pH were affected by the presence of other LMWG and also whether the final structures in the gel were different at different ratios of the two LMWG.

Experimental The LMWG were prepared as described elsewhere.[4] Solutions at 10 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. Solutions of the LMWG were either diluted with D_2O or a solution of another LMWG prior to measurement. The solutions were placed in 2mm quartz cuvettes.

SANS experiments were performed on the D11 diffractometer, a neutron wavelength of $\lambda = 10$ Å was employed at three different detector distances, D = 1.2, 8 and 40 m. This set-up corresponds to a Q range from 1.0 × 10-3 to 0.31 Å^{-1}. 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.

Results The scattering from solutions of 2NapFF (**1**) agreed with previous data.[5] We mixed this LMWG with 2NapVG, a LMWG that does not scatter significantly at high pH. Hence, we hypothesized that it would be simple to determine the effect of the added 2NapVG on the assembly of the 2NapFF. We examined a range of solutions, mixing 2NapFF and 2NapVG in varying ratios. The SANS data for solutions of 2NapFF at high pH can be fitted to a hollow cylinder model, combined with a power law component to fit the low Q region.[5] The scattering data from all of the solutions of 2NapFF and 2NapVG at high pH fitted well to this model, apart from the data for pure 2NapVG (Fig. 1a), which exhibited very low scattering at high pH that could be fitted well to a power law alone. The internal and external radii of the hollow cylinder do not vary much across the dilution series. For pure 2NapFF, the core radius determined from the fit is 1.50 ± 0.11 nm, and the external radius is 4.06 ± 0.10 nm. At 70 %, 50%, and 30% 2NapFF, the core radii are 1.66 ± 0.18, 1.58 ± 0.22, and 1.57 ± 0.3 nm respectively, and the external radii 3.79 ± 0.13, 3.86 ± 0.15, and 3.90 ± 0.22 nm respectively. Further, from the scattering intensities, it is clear that there is not a linear decrease in intensity across the dilution series (Fig. 1d).

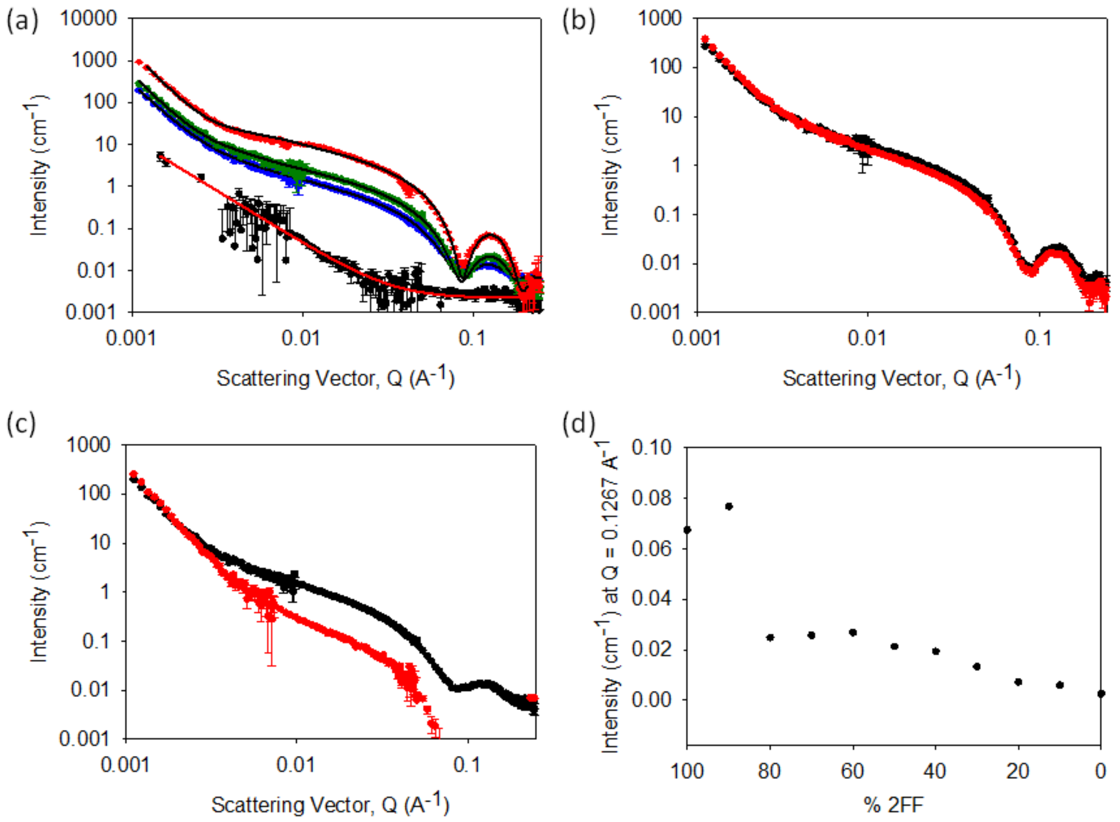

Fig. 1 (a) SANS profiles for solutions at 100% 2NapFF (red), 70 % 2NapFF (green), 50% 2NapFF (blue), and 0% 2NapFF (black). The fits to a hollow cylinder model combined with a power law are shown as black lines and, for the 0% 2NapFF only, the fit to a power law alone is shown as a red line. (b) Top: Overlay of the SANS profiles for a solution of 2NapFF diluted 1:1 with 2NapVG (black data) or 1:1 with D_2O (red data). Bottom: Overlay of the SANS profiles for a solution of 2NapFF diluted 3:7 with 2NapVG (black data) or 3:7 with D_2O (red data). For all of these data, the solutions were prepared in D_2O, with a pD of 11.4 ± 0.2. (d) Plot of scattering intensity at Q = 0.1267 $Å^{-1}$ for solutions containing different ratios of 2NapFF and 2NapVG.

We also investigated the gels at low pH and were able to show that the SANS data implies that all networks are very similar. Hence we conclude that that the non-linear differences in rheological data cannot be explained simply in terms of different types of fibres forming the networks.

This work is currently submitted for publication.

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