Experimental report

09/01/2018

Proposal: 9-11-1823 **Council:** 10/2016

Title: Determination of the networks in two component self-sorted gels

Research area: Materials

This proposal is a new proposal

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Samples: C30H28N2O5
C20H23BrN2O5

Instrument	Requested days	Allocated days	From	To
D11	4	3	03/02/2017	06/02/2017
D22	0	0		

Abstract:

Low molecular weight gels have a number of exciting uses, for example in optoelectronics. We are investigating the use of two component systems, as potentially these could be used to form bulk heterojunctions. To do this, we need to understand how the networks formed from the two component systems are arranged in space; is the network from one component affecting the network of the second for example? To do this, we will use conditions where one of the networks has been contrast mapped to allow us to only scatter from the second network; the data will be compared to a network formed in isolation. These data will allow us to understand the networks; we envisage that by using different gelation conditions we will be able to control the network types and these data will be a key part of that understanding, allowing to us to prepare new optoelectronically efficient gels.

Experiment Number: 9-11-1823

Experiment Title: Determination of the networks in a two component system

Abstract Small molecules known as low molecular weight gelators (LMWG) can self-assemble to form a network of fibres, which trap and hold a vast amount of water forming a gel. When two different LMWG are mixed, multiple network types are possible. Understanding this is important if we are to be able to use these systems for applications in optoelectronics. Here, we use contrast matching experiments to allow us to understand how much one network is affected by the presence of the other.

Introduction In general, the anisotropic structures are fibres, which entangle. The properties of the gel arise from the network of the fibres that is formed. The properties of the gels are very dependent on sample history, and so a single gelator can form gels with a wide range of properties depending on how the gels were formed. It is often difficult to predict in advance what the properties will be. As such, there is a significant knowledge gap here. To design and control such gels, we need to understand the fibrous network to control the properties. This is especially true in multicomponent systems. Here, if both components can form a gel independently (i.e. in an orthogonal manner), then mixing gives the possibility of self-sorting, separate assembly, or co-assembly. Multicomponent systems can provide really interesting and unusual gels, but the characterization of these materials is even more complex. Here, we use contrast matching to allow us to investigate how much the networks differ in the presence of each other.

Experimental The LMWG were prepared as described elsewhere.[1] 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. Identical solutions were prepared in H_2O using NaOH. These were mixed to provide solutions at specific concentrations in mixtures of H_2O and D_2O to probe a range of contrasts, and as either pure LMWG or in mixtures of the two LMWG. Gels were prepared by the addition of GdL[2] to these 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. 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 We were able to prepare solutions at different ratios of H_2O and D_2O such that one of the two components in a mixture of two LMWG were contrast matched (Fig. 1)

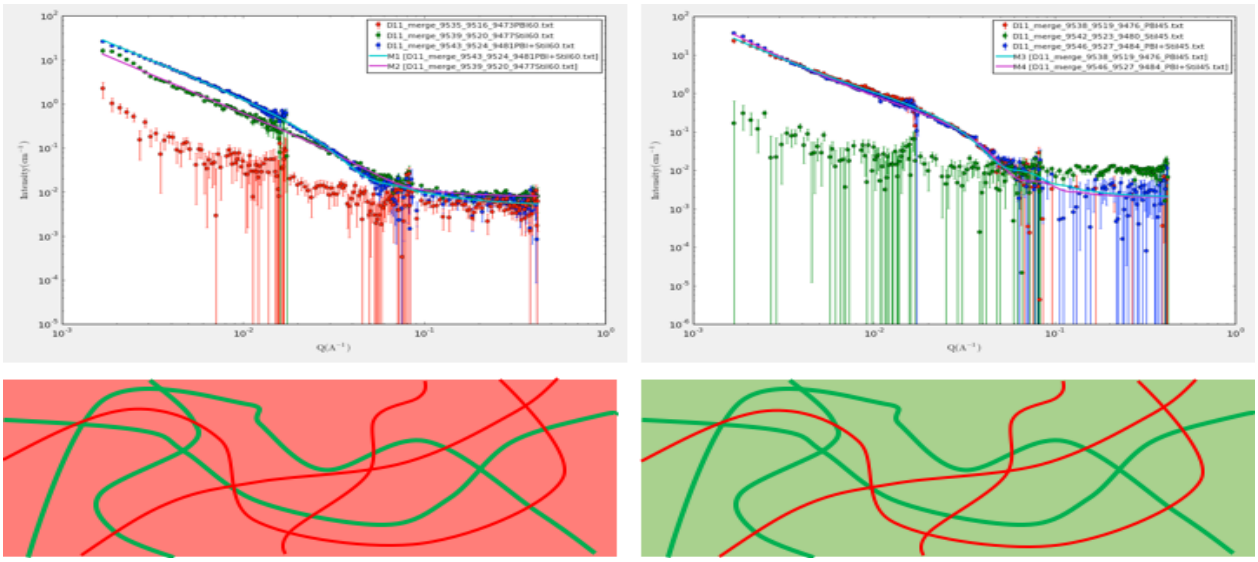

Fig. 1. Top: Preliminary contrast matching data. (a) Gelator **1** (red), gelator **2** (green) and mixture (blue) at 40% D_2O. (b) (a) Gelator **1** (red), gelator **2** (green) and mixure (blue) at 55% D_2O. Fits to the data are overlaid (no fits for weakly scattering components. Bottom: cartoon of assembly for contrast matched mixtures; in both cases, one of the components is matched, leaving the overall scattering (blue in the above) closely matching that of the relevant single component.

Fits to the data using a flexible cylinder combined with a power law imply that the scattering of the single component is subtly different in the mixture as opposed to alone. The radii are most strongly affected; the power law is very close (Table 1).

	Power Law	Kuhn Length / Å	Length / Å	Radius / Å	χ^2
Gelator **2** in 40% D_2O	1.62 ± 0.06	30.6 ± 0.1	> 1000	68.8 ± 0.1	1.8883
Mixture in 40% D_2O	1.74 ± 0.06	22.1 ± 0.1	> 1000	36.9 ± 0.08	1.7174
Gelator **1** in 55% D_2O	2.24 ± 0.03	>1000	>1000	70.9 ± 0.03	2.5978
Mixture in 55% D_2O	2.48 ± 0.01	> 1000	> 1000	59.2 ± 0.01	1.7859

Table 1. Unoptimised fits to the data shown in Fig. 3 to a flexible cylinder and power law model.

This has provided key data, as it is possible to separate out the scattering from the network and that of the primary structures. These data are currently being analysed and will be published in the future.

References

1. E. R. Draper, J.R. Lee, M. Wallace, F. Jäckel, A.J. Cowan, and Dave J. Adams, *Chem. Sci.*, **2016**, 7, 6499-6505.
2. D.J. Adams, W.F. Frith, M. Kirkland, L. Mullen and P. Sanderson, *Soft Matter*, **2009**, *5*, 1856-1862.