Experimental report

18/01/2016

Proposal: 9-11-1756 **Council:** 4/2015

Title: Kinetic SANS study of mixed low molecular weight gelators

Research area: Materials

This proposal is a new proposal

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Samples: Amino acid derived gelators
glucono-delta-lactone

Instrument	Requested days	Allocated days	From	To
D11	3	2	26/11/2015	28/11/2015
D33	3	0		

Abstract:

Low molecular weight gels (LMWG) are new soft materials with the potential for a wide range of applications if their properties can be suitably tuned. The molecular structure of the gelator, the conditions and self-assembly mechanism by which the gels are formed are all important contributors to the final network characteristics and overall properties. The group has worked extensively on building a library of LMWG. We have found that the properties of gels can be enhanced or tuned by mixing two different gelators and controlling the order in which they assemble to form a gel. However the process by which the gelation of the two components occurs and how one gelator influences the structures formed by the other is unclear from other techniques. With this proposal we wish to understand how the structures, in particular worm-like micelles, evolve during gelation in order to understand the formation of the network over a range of length scales. Using the high flux available at the ILL the kinetic process will be tracked during gelation.

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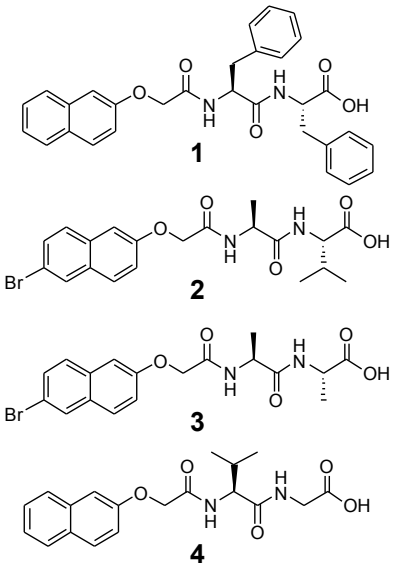
Abstract
The self-assembly of low molecular weight gelators (LMWG) into larger structures is complicated by the fact that gelation in water is a phase separation event, with insoluble fibrous structures being formed. Hence, the process of assembly is also extremely important. We are currently investigating mixtures of LMWG (both of which can form gels independently). A key question is how the presence of one network affects the other.

Introduction
We have been examining a range of dipeptide-based LMWG, focusing recently on gels prepared from two-component systems to identify whether the two LMWG self-sort, assemble separately, or co-assemble (specifically or randomly).[1-3] We have recently shown that mixtures of two gelators can form gels that are much stronger than might be expected from the individual components.[2] These materials have been characterized fully rheologically and using SEM. Also, using NMR it is possible to show that the assembly is sequential. However, it is unclear using most techniques how the two components are assembling. For example, we do not know if the formation of one network changes the self-assembly of the second component at the molecular level; it is also possible that the microstructure is affected by the presence of the first molecule.
We form gels by lowering the pH of the system from around pH 10 to around pH 4. Here, we use the hydrolysis of glucono-δ-lactone (GdL), which is highly reproducible, and occurs on the timescale of hours.[4] Hence, we can carry out experiments where we monitor the gelation over long periods of time and see how the scattering changes as gelation occurs. We can also relate the data to repeat experiments where the sample is measured using a rheometer.

Experimental
The LMWG were prepared as described elsewhere. 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 mixed solutions were added to pre-weighed aliquots of GdL, swirled gently and then the solutions were placed in 2mm quartz cuvettes.
SANS experiments were performed on the D11 diffractometer, a neutron wavelength of λ= 10 A˚ 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 A^{-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 of solutions of mixed LMWG was followed with time as the GdL hydrolyses, the pH drops and gels are formed. Specifically we followed the gelation of mixtures of LMWG where we had previously examined the structures formed at high pH (see experimental report 09-11-1757). Here, for example different structures were formed when **1** was mixed with either **2**, **3**, or **4** in different ratios.



The scattering on gelation was found to change very subtly with time in some cases, and hardly at all in others. It is clear from the data (Fig. 1) that the initial structures formed at high pH strongly determined the structures formed at low pH. This implies that the structures are essentially templated by the self-assembly at high pH before gelation. This opens up the intriguing possibility of being able to prepare very different materials by subtly varying the ratios of the two LMWG. We are in the process of fitting the data.

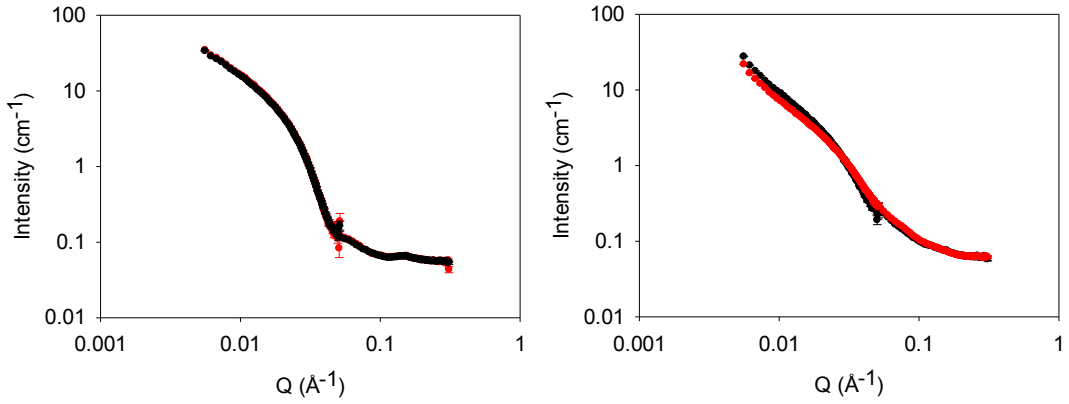


Fig. 1 Scattering from solutions of **1** diluted with either D_2O (left) or solutions of **3** (right). The black data is for time zero, and the red data for 6 hours after GdL addition.

References

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3. E.R. Draper, E.G.B. Eden, T.O. McDonald and D.J. Adams, *Nature Chem.*, **2015**, 7, 848-852.
4. D.J. Adams, W.F. Frith, M. Kirkland, L. Mullen and P. Sanderson, *Soft Matter*, **2009**, 5, 1856-1862.

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