Experimental Report

Proposal: **9-10-1304** **Council:** 10/2012

Title: On the structure of hydrogels - what length scale is important ?

This proposal is a new proposal

Researh Area: Materials

Main proposer: **GRIFFITHS Peter Charles**

Experimental Team: GRIFFITHS Peter Charles
ADAMS Dave
ZAMITH CARDOSO Andre
CATTOZ Beatrice

Local Contact: SCHWEINS Ralf
GRILLO Isabelle

Samples: Amino acid derived gels

Instrument	Req. Days	All. Days	From	To
D11	2	2	29/07/2013	31/07/2013

Abstract:

Understanding the gelation of liquids by low molecular weight solutes at low concentrations gives an insight into many molecular recognition phenomena, and also offers a simple route to modifying the physical properties of the liquid. More importantly, these gels are potential new soft materials, but their mechanical properties are critical to the final application. Depending on the application, different properties may be required. Recent work from our respective groups has focused on understanding the correlation between the molecular structure of the gelator, the kinetics of the gelation mechanism and the ultimate network characteristics. This opens up the potential to prepare gels with very different properties at the same final conditions, allowing the effect of microstructure to be probed. This proposal seeks to identify those factors that define the local and global structure of the gels, and to optimise the structures obtained from simple pH and counterion triggers.

Experiment Number: 9-10-1304

Experiment Title: On the structure of Low Molecular Weight Hydrogels

Abstract

The effect of assembling a key low molecular weight gelator (LMWG), 2-naphthalene-diphenylalanine (2FF) in a range of different ways was studied by SANS. 2FF was self-assembled in water by the addition of salts (Ca^{2+} and Na^{+}), the addition of an acid, or by the addition of water to a solution of 2FF in DMSO. All these methods lead to self-supporting gels in the bulk. The kinetic profile for the self-assembly was studied, as was the effect of concentration. The data show that the 2FF is initially self-assembled into long anisotropic structures in water. On addition of a salt, the network is formed by subtle changes in the self-assembled structure. However, the addition of acid results in a distinct structural change.

Introduction

The self-assembly of LMWG into larger structures is complicated by the fact that gelation in water is generally a phase separation event, with insoluble fibrous structures being formed. Hence, the *process* of assembly is also extremely important and, without care, gelation can be stochastic. The fibrous structures can be nanofibres, helical structure or nanotubes, with evidence in many cases of co-existence of different morphologies. However, it is extremely difficult to acquire data that can be said to be truly representative of the system by microscopy (for example TEM of these gels requires drying and a stain and can only possibly examine a fraction of the sample), and over a wide enough length-scale. We have been examining a range of dipeptide-based LMWG.[1-4] We know that the macroscopic properties are very different when different assembly techniques are used.[5] A key question is: what are the underlying differences in fibre network that lead to these differences?

Experimental

2FF was prepared as described elsewhere.[6] Solutions at a concentration of 2FF of 5 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 2FF had dissolved.

For the salt triggers,[7] an aliquot of a stock solution of $CaCl_2$ or NaCl in D_2O was added to 1 mL of the 2FF solution and the mixture immediately added to a 2mm quartz cell. Measurements were started as soon as possible after addition. For the acid trigger, 1 mL of the 2FF stock solution was added to a pre-weighed amount of glucono-δ-lactone (GdL),[8] the solution rapidly mixed and added to a 2mm quartz cell. Measurements were started as soon as possible after addition.

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. The scattering data were fitted using a Kholodenko-Dirac worm model with axial core –shell cylinder and surface fractal.

Results

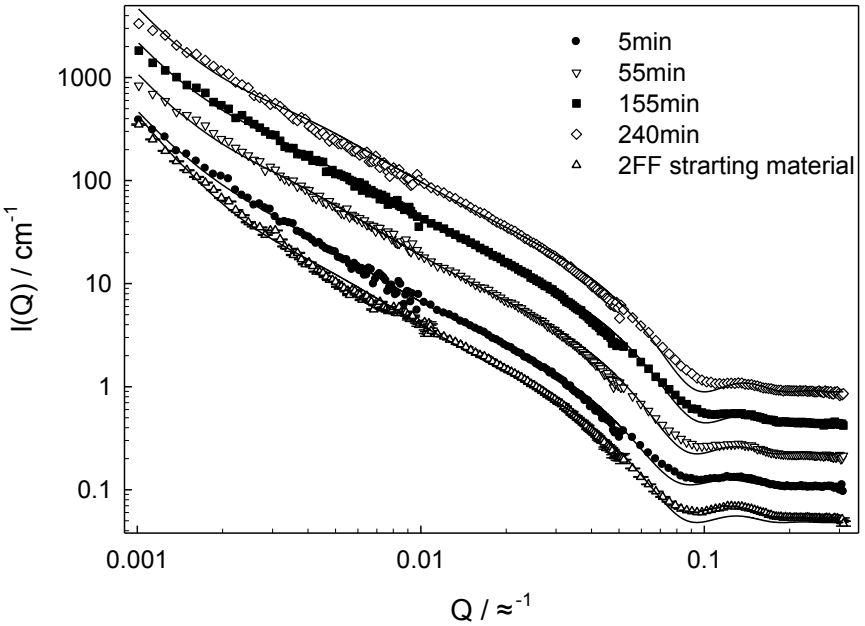

Figure 1 – SANS of the evolution of gelation for 5mg/mL 2FF with $CaCl_2$ added as trigger. Data have been shifted vertically for clarity. Solid lines are fits to the Kholodenko-Dirac worm model with axial core –shell cylinder and surface fractal.

Figure 1 shows the evolution of scattering of 2FF with gelation triggered by $CaCl_2$, the parameters extracted from fitting of the curves are summarized in Table 1. The scattering curves can be divided into 2 regions: one for $Q>0.006A^{-1}$ and another for $Q<0.006A^{-1}$. The 1st region corresponds to the core shell cylinder length scale, the plots show that the overall radius does not significantly changes upon gelation but that the core/shell feature (at $Q=0.12A^{-1}$) gets weaker during gelation indicative of a less ordered system. The Kuhn length varies but does not follow a particular trend indicative of rearrangements occurring during gelation. The other region represents the surface fractal dimension of the sample, a change is observed at the beginning of the gelation, i.e. a decrease in ds indicative of the formation of a smoother surface, but no significant evolution is observed afterwards.

	n / no of segments	l / Kuhn length	Core radius	Shell thickness	ds / surf fractal dimension
2FF starting material	9	320	18	19	2.58
5min	8.3	422	29	10	2.79
55min	9.4	374	24	13	2.78
155min	9.4	374	20	14	2.78
240min	8.3	354	20	15	2.77

Table 1 – Fitting results from analysis of 2FF gelation triggered with $CaCl_2$ with the Kholodenko-Dirac worm model with axial core –shell cylinder and surface fractal.

References

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