Experimental report

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Proposal: 9-11-1732 **Council:** 10/2014

Title: Time resolved investigation of themicrostructure of dipeptide hydrogels

Research area: Materials

This proposal is a new proposal

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Samples: C32H32N2O5

Instrument	Requested days	Allocated days	From	To
D11	4			
D22	4	2	14/10/2015	16/10/2015

Abstract:

Low molecular weight gelators (LMWG) are molecules that self-assemble into one dimensional fibres that entangle and for a network. Under the right conditions, a self-supporting gel is formed. We have found that the process by which the self-assembly is conducted has a dramatic effect on the fins gel properties. To understand this, it is critical to understand the early time assembly processes that lead to the final network type. For dipeptide LMWG, a common method is to dissolve in a solvent and then add water. This leads to a nucleation and growth process (see for example Soft Matter, 2011, 7 9721). It is clear that the nucleation process determines the final properties, but the structures formed at early times are highly transient and difficult to characterise. Here, we propose to use the stop flow cell to probe the structures formed at early times.

Experiment Title: Time resolved investigation of the microstructure of dipeptide hydrogels

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Abstract

We have been examining the gelation of a range of dipeptide-based low molecular weight gelators using a range of different techniques. The rate and method of gelation can have a significant impact on the strength of the structures and network formed. A previous experiment identified that significant changes in scattering occur over the first few minutes of gelation. Therefore, the following experiment used the stopped flow cell to measure SANS during the initial stages of gelation. During gel formation there was an initial increase in the scattering intensity at low *Q* followed by a decrease. The intensity then increases in the regions at higher *Q* associated with fibre formation. This suggests the gel is formed in a two stage process when this method is used.

Introduction

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 extremely important to understand these materials. The fibrous structures can be nanofibres, helical structures or nanotubes, with evidence in many cases of co-existence of different morphologies. Gel properties are not only controlled by these primary structures, but by how they are arranged in space.

We have been examining a range of dipeptide-based LMWG,[1-3] focusing most recently on gels prepared from systems with two or more LMWG to identify what structural features determine self-sorting, separate assembly, co-assembly (specifically or randomly), or most appealing, templated gel-on-gel assembly. As part of these studies, kinetic measurements in which the gelation is simply followed after mixing the various materials have suggested that during the first 2 or so minutes, there is a considerable level of re-equilibration of structure. It is hypothesized that these nucleation events define the ultimate morphology of the gel, and control over these events would be instrumental in the ultimate design of programmed self-assembly. Therefore it is important to understand the mechanism by which this happens in single component systems.

Experimental

A widely studied low molecular weight gelator, FmocFF, was dissolved in deuterated DMSO to achieve a final gel concentration of 5 mg/mL FmocFF when mixed with D_2O, which forms 90 or 95% of the final gel. The stopped flow cell was cleaned and primed with the FmocFF in d-DMSO solution, the D_2O and a cleaning syringe of methanol. The instrument and stopped flow control software were set up to measure the scattering for the first five minutes in

logarithmic time steps, followed by the next ~30 minutes in 60 second time steps. Kinetic data were collected at two detector distances, 3 and 17.6 m, with a fixed neutron wavelength of 12 Å. Where necessary the first portion of the data was repeated to obtain the statistics required to produce sufficient quality data for model fitting. The 10% DMSO sample was also repeated using hydrogenous DMSO to better understand the role of the DMSO in the structures formed.

Results

Initially the data from the first 5 minutes of the 10% d-DMSO, 5 mg/mL FmocFF sample has been processed. The scattering intensity shows an initial increase in the low *Q* region, this corresponds to the time during which the solution becomes turbid and indicates large structures are formed first. As the intensity at low *Q* decreases the intensity increases at higher *Q* where features associated with fibre formation are evident. This is in good agreement with previous results[3] that the mechanism of gel formation is a multistage process when this method is used. Model fitting and analysis of the concentration and alternative contrast data will help to infer more information about the competing structures.

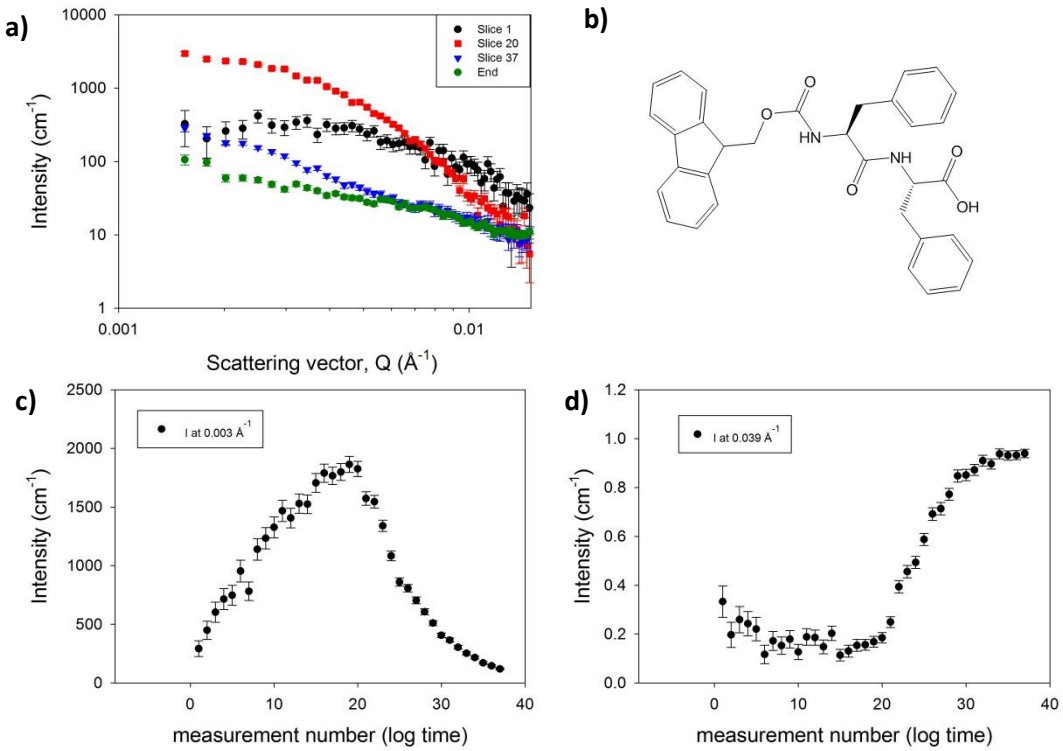

Figure 1. Data for the gelation of a 10% d-DMSO 5mg/mL solution of (b) FmocFF a) SANS curves at low Q during the 5 minutes and the end point after 30 minutes, c) the intensity at Q=0.003 Å^{-1} and d) the intensity at Q=0.039 Å^{-1} for the first 5 minutes.

References

1. K.L. Morris et al. *Nature Commun.,* **2013**, 1:1480. **2.** A.Z. Cardoso et al., *Faraday Discussions*, **2013**, 166, 101. **3.** L. Chen et al., *Soft Matter*, **2011**, *7*, 9721---9727.