



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Exploring the relationship between changes in self-assembled structures and mechanical stimuli in dynamic hydrogel systems

Experiment number:
SC 5410

Beamline: BM26	Date of experiment: from: 04-07 to: 07-07	Date of report: 09/11/2023
Shifts: 9	Local contact(s): Martin Rosenthal	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Simona Bianco (UofG)* Chloe M. Wallace (UofG)* Emma L. Bowley (UofG)* Rebecca E. Ginesi (UofG)* Dave J. Adams (UofG, PI)		

Report:

Overview

Transient supramolecular gel systems can be designed such that pre-determined changes in state occur. Due to their dynamic nature and high degree of tunability, such systems are of great interest both for the potential analogy to out-of-equilibrium biological systems and the formation of novel stimuli-responsive materials.¹ For instance, regenerating materials for drug release or self-healing materials can be envisioned.² Two low molecular weight gelators were used prepare systems undergoing gel-to-sol-to-gel transitions by using a previously reported pH-cycle.³ In such systems, the final properties and morphologies of the material depend on both molecular structure and rate of pH change, allowing us to design a variety of materials starting from a single starting gel. A key question is to understand how the morphology of the self-assembled structures changes throughout the different phases and during re-assembly. Here, we have used *in-situ* SAXS to probe the systems as they evolve. This allowed us to observe how different gelators possessing different initial morphologies respond to the phase changes.

Experiment details

In the original beamtime proposal, a Rheo-SAXS set-up was proposed. However, due to unavailability of the rheometer, only SAXS data was collected. Small-angle data was collected of the samples prepared in borosilicate glass capillaries over a period of 16 hours with 10-seconds exposures every 5 minutes. The gels were prepared directly in the capillary right before starting the measurement. A script was provided by the local contact to measure SAXS data at different time intervals during the collection period.

Results

To enable us to study the changes in assembly during gel-to-sol-to-gel transitions, two different gelators with different initial morphologies were used, CarbFV and FmocFA. These materials form gels at a concentration of 5 mg/mL in DMSO/H₂O (20/8, v/v). To induce the pH cycle, two competing pH triggers were used by adding urea (4M), urease (0.4 mg/mL) and methyl formate (100 uL) as previously reported.³ At the start, a gel is formed

at low pH (~4.00), which transits to a solution phase as the pH increases above the apparent pK_a of the gelators due to the autocatalytic reaction between urea and urease. Re-gelation is then triggered once the hydrolysis reaction of methyl formate becomes dominant, leading to a reduction in pH below the apparent pK_a .

In both systems, a significant change in structure can be observed as the gel-to-sol transition takes place within the first 20 minutes (Figure 1). For the CarbFV system (Figure 1a), the SAXS patterns appear to shift from less persistent structures in the gel phase (Figure 1a, blue) to more cylinder-like structures in the solution phase (Figure 1a, orange and green), potentially related to the presence of worm-like micelles in solution. In the case of the FmocFA system (Figure 1b), the opposite behaviour can be observed. At the start, significant scattering can be observed due to the presence of persistent structures making up the gel network (Figure 1b, blue). As the sample transits to solution, the scattering pattern appears to change (Figure 1b, orange). This can be related to the presence of less self-assembled structures in solution or spherical micelles. In both cases, the new structure formed in solution appears to lock in during re-gelation (Figure 1, red data), suggesting that the gel-to-sol-to-gel process allows to form novel materials with different underlying structures by means of a pH change. The results from this beamtime allowed us to gain insights into how the molecular structure of the gelator affects initial gel properties and how it can be tuned to design novel materials using a pH cycle.

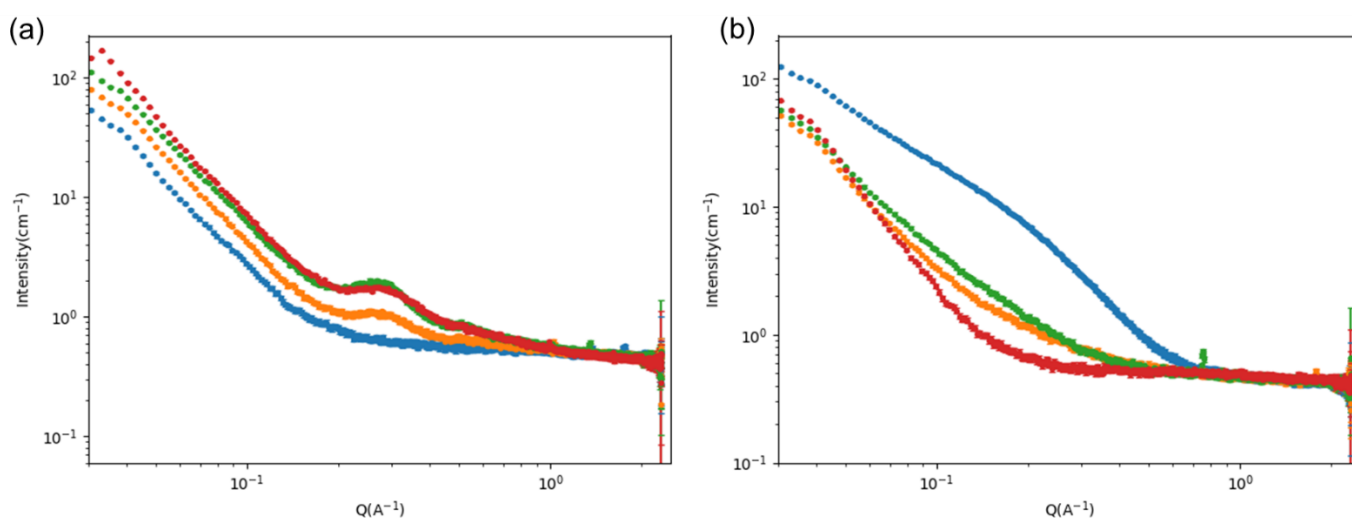


Figure 1. SAXS patterns of low-molecular weight gelators (a) CarbFV and (b) FmocFA as they undergo pH-triggered gel-to-sol-to-gel transitions. In all cases, the data for the initial gel (blue line), solution phase (orange and green lines) and final gel (red line) are shown.

Conclusions and Future work

The results from this beamtime gave us an insightful understanding in the way self-assembled structures can respond to pH-triggers and how this can be used to form novel materials with different morphologies. We are currently in the process of fitting the SAXS data to gain further information on how the different structures change over time (radius, length, etc.) at key points during the pH cycle. We plan to apply for further beamtime to carry out Rheo-SAXS to gather how these morphological changes affect the bulk properties of the final gel material.

References

1. Olivieri, E., Quintard, G., Naubron, J.-V. & Quintard, A. Chemically Fueled Three-State Chiroptical Switching Supramolecular Gel with Temporal Control. *J. Am. Chem. Soc.* **143**, 12650–12657 (2021).
2. Rieß, B. & Boekhoven, J. Applications of Dissipative Supramolecular Materials with a Tunable Lifetime. *ChemNanoMat* **4**, 710–719 (2018).
3. Panja, S., Fuentes-Caparrós, A. M., Cross, E. R., Cavalcanti, L. & Adams, D. J. Annealing Supramolecular Gels by a Reaction Relay. *Chem. Mater.* **32**, 5264–5271 (2020).