

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:**

The specific power of pH-responsive microphase-separated triblock co-polymer electrospun fibres as studied by SAXS.

**Experiment
number:**
Sc1783

Beamline:	Date of experiment: from: 14 December 2005 to: 17 December 2005	Date of report: 1 march 2006
Shifts: 9	Local contact(s): Florian Meneau	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): (*)Dr Jonathan HOWSE Department of Chemistry, University of Sheffield, Sheffield Prof Anthony RYAN as above (*)Mr Paul TOPHAM as above (*)Mr Joshua Swann as above (*)Ms Carme Coll as above		

Report:

We have prepared responsive gels based on polyelectrolytes (polymethacrylic acid and polydiethylaminoethyl methacrylate) and a manganate-based reaction that oscillates pH. ^{1, 2} A weak polyacid will, at low pH, be essentially charge-neutral, because the degree of dissociation of the carboxylic acid groups is relatively low. In these circumstances water is a poor solvent for the polyacid and the gel collapses. However, as the pH is increased the acid groups dissociate and the polymer acquires a net charge; mutual repulsion between the charged chains causes them to stretch away from each other. The opposite pH response is observed for polybase. By oscillating the pH one can induce a macroscopic oscillation in the dimensions of a gel of a factor of 10 or more. Using triblock copolymers with hydrophobic end-blocks and polyelectrolyte mid-blocks we can make actuator systems that operate in one, two or three dimensions by use of lamellar, cylindrical and spherical gels, respectively. Previously, we have successfully studied the response of a polyacid and a

polybase triblock, which expand in 3 dimensions, in a pH oscillating chemical reaction both microscopically (SAXS) and macroscopically using an optical microscope. The change in volume was found to be affine over 5 orders of magnitude for both materials.³ The response of the polymer relies on the diffusion of $[H^+]$ ions throughout its structure; therefore a larger surface area increases the rate of diffusion and thus induces a more rapid response. A more rapid response will lead to more powerful systems.

Electrospinning polymer fibres enables one to fabricate extremely small (diameter ~ 5 microns), aligned strands of pH-responsive materials, which can be intertwined or woven together to create “rope” like structures. Such bundles of fibres resemble muscle structures found in the body. Nature’s approach to solving this problem is to use bundles of muscle fibres in a bath of chemical fuel (ATP) with the macroscopic contraction being the sum of small contractions by many microscopic fibres. Although the forces associated with synthetic pH-responsive polymer systems are many orders of magnitude lower than that of actin and myosin³, the fundamental principles are the same, fast diffusion by using small diameter fibres and macroscopic motion through the serial addition of many small contractions. The natural evolution of this research is therefore to move towards small gel pieces (fibres) that will give a faster response and therefore be more powerful. Electrospun fibres however, do not microphase separate into distinct microdomains (due to instantaneous removal of solvent during their production) and therefore their microscopic length scale changes cannot be followed by SAXS. To overcome this, the fibres can be annealed in a solvent atmosphere to allow the polymer chains to flow amongst one another to adopt a more ordered microphase separated conformation (Report SC-1783).

The PMMA-*b*-PDEA-*b*-PMMA fibre annealing process, using THF or DMF, follows the same fundamental steps; going from individual fibres with random polymer chain morphology to a dissolved material via a gel-like structure with a more ordered copolymer morphology. During annealing, the fibres coagulate as their external surface becomes dissolved, allowing the polymer chains to move around to adopt a lower energy conformation. The more the polymer is annealed, the more order is introduced (as confirmed by SAXS) until the material becomes close to a “holey” film-like structure, then the polymer starts to become dissolved. As the polymer dissolves the order is reduced until complete dissolution of the polymer chains is achieved. Using this information we can now optimise the morphology of the polymer fibres to give an internally ordered microdomain structure with a large external surface area to allow rapid response to pH. The internal morphology can then be monitored via SAXS.

Experiments were performed on the Dubble BM26 beamline for three different PMMA-*b*-PDEA-*b*-PMMA microphase separated samples. One of the samples was a cast film which was allowed several weeks of annealing in a saturated THF atmosphere to produce an equilibrium structure and the other two samples were electrospun fibre mats of different annealing times. Sample “Fibre 1” was annealed for 6 minutes in a 100% THF atmosphere, whereas “Fibre 2” was annealed for 6 minutes in a THF:DMF (50:50 v/v) atmosphere. The addition of DMF to the annealing atmosphere is to slow down the annealing process due to DMF having a much lower vapour pressure than THF. This results in samples with different porous properties. “Fibre 2” having the least annealing and hence most porosity. The experiments were designed to show how the different macroscopic fibre structures behave when immersed in the manganate-based pH-oscillating reaction compared to the solid gel material.

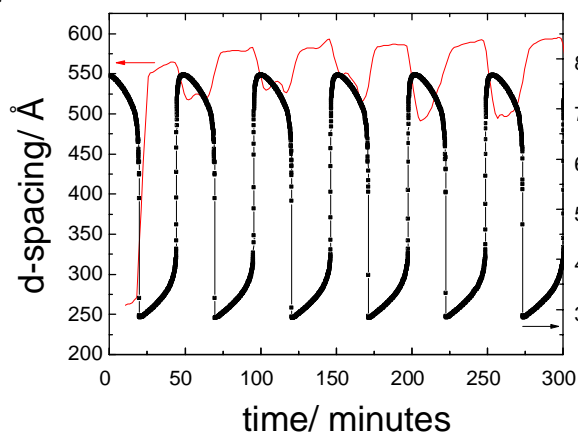


Figure 1. pH trace against time for the manganate-based oscillatory system (—●—) and the characteristic length scale (unit cell dimension) for a microphase separated bundle of PMMA-*b*-PDEA-*b*-PMMA electrospun fibres (---), “Fibre 1”) as revealed by SAXS.

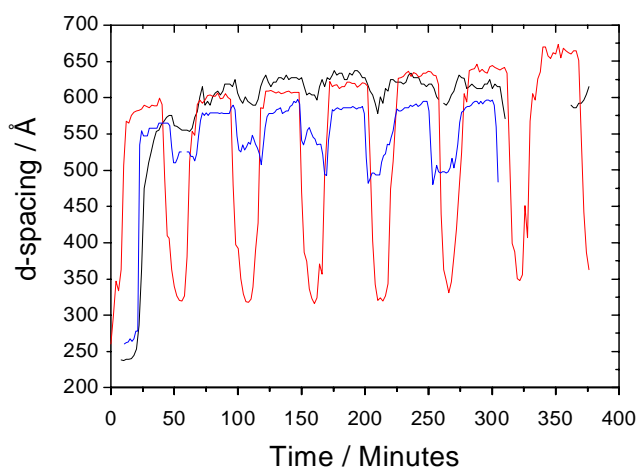


Figure 2. The characteristic lengthscale (unit cell) for three different PMMA-b-PDEA-b-PMMA samples in an oscillating chemical environment (— gel, — fibre 1, — fibre 2)

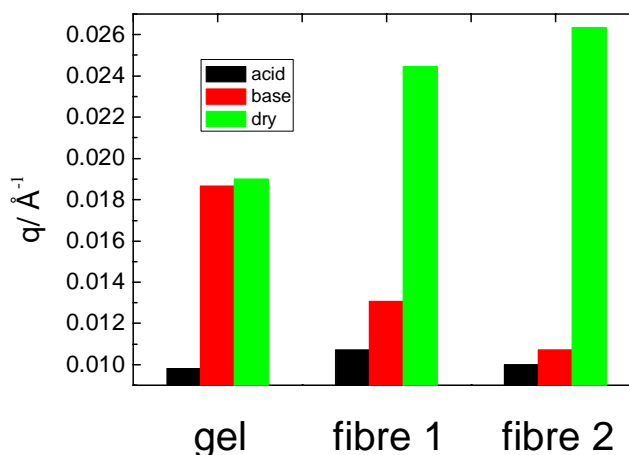


Figure 3. The characteristic lengthscale for three different PMMA-b-PDEA-b-PMMA samples in their dry state and the collapsed and expanded states in basic and acidic conditions, respectively.

The results show that we have been successful in generating microphase separated fibrous materials that are responsive to an oscillating pH environment. However, as can be seen from Figure 3, the peak position (q) for the electrospun fibres in their dry state is significantly different to that of the equilibrium position for the dry gel.

The process of annealing the samples has two effects. Firstly it allows the individual polymer chains to move and phase separate, moving towards an equilibrium structure. Secondly, the presence of the solvent allows for neighbouring fibres to “melt”. These two effects, are unfortunately conflicting. It is apparent that longer annealing times are necessary to achieve a phase separated structure. However, if the annealing process is conducted when the inter-fibre distance is small, the fibres melt together, ultimately resulting in a gel like structure.

We have also shown that to produce a significant collapse transition we must anneal the sample sufficiently. The magnitude of such a transition is given by the difference in unit cell size between the material in acidic and basic environments. The solid gel sample shows the greatest difference, with fibre 1 (greatest annealing time) showing a larger difference than fibre 2. (Figure 3) The annealing process promotes the microphase separation of the two polymers and as this happens the inter-digitation of unlike chains is reduced. As the unlike chains pull apart the domain spacing increases. As this occurs the length of the responsive chain segment spanning the separated domains increases. As this increases with increasing annealing time, the greater the difference between the expanded and collapsed states will be. To overcome this problem future samples will be made by annealing fibres separately and then combining them to produce macroscopic structures.

1. Crook, C. J.; Smith, A.; Jones, R. A. L.; Ryan, A. J. *Physical Chemistry Chemical Physics* **2002**, 4, (8), 1367-1369.
2. Okazaki, N.; Rabai, G.; Hanazaki, I. *Journal of Physical Chemistry A* **1999**, 103, (50), 10915-10920.
3. Howse, J. R.; Topham, P.; Crook, C. J.; Gleeson, A. J.; Bras, W.; Jones, R. A. L.; Ryan, A. J. *Nano Letters* **2006**, 6, (1), 73-77.