

## 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:** Shape change transitions in electrospun fibers of block copolymers coupled to chemical oscillations as studied by Small Angle X-ray Scattering

**Experiment number:**  
Sc1783

<b>Beamline:</b>	<b>Date of experiment:</b> from: 31 August 2005 to: 02 September 2005	<b>Date of report:</b> 1 march 2006
<b>Shifts:</b> 6	<b>Local contact(s):</b> 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

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(\*Dr James Wang as above

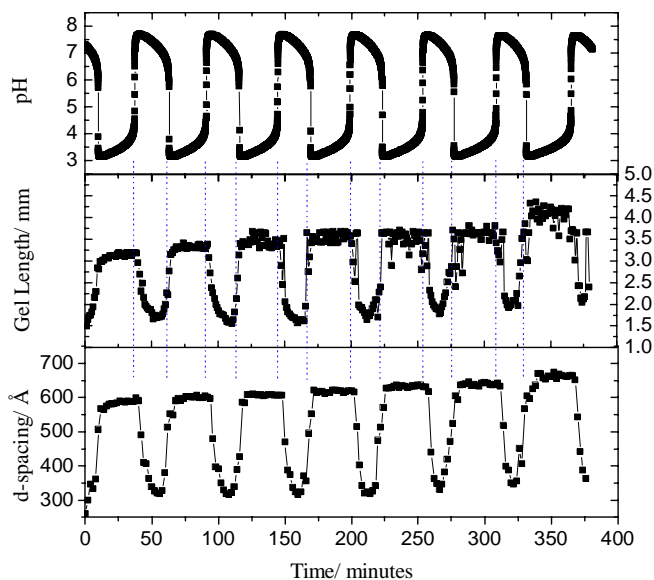
(\*Dr. Oleksandr Mykhaylyk as above

**Report:**

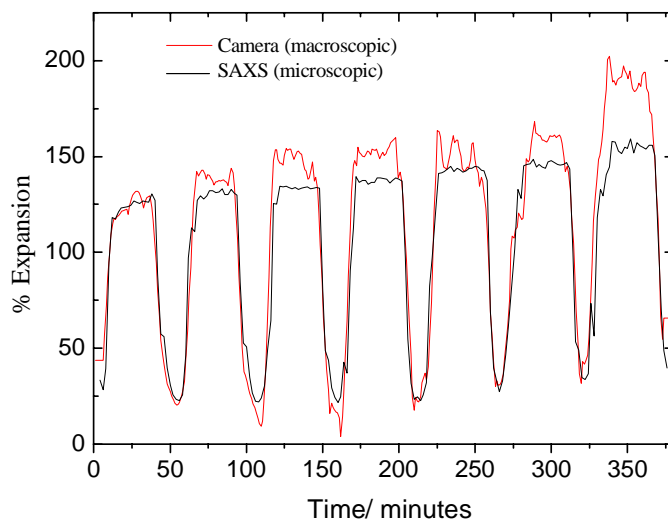
We have prepared responsive gels based on polyelectrolytes (polymethacrylic acid and polydiethylaminoethyl methacrylate) and a manganate-based reaction that oscillates pH. <sup>1, 2</sup> A weak polyacid will, at low pH, be essentially charge-neutral, because the degree of dissociation of the carboxylic 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 a 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 triblock,

which expands 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<sup>3</sup>.

Recently we have performed such experiments at Dubble using a polybase hydrogel, where we have monitored its pH-actuator behaviour. A sample of PMMA-*b*-PDEA-*b*-PMMA was held in the manganate-based pH-oscillatory system and was analysed via optical microscopy and SAXS. Autonomous volume transitions of the polymer gel were observed over 7 pH-oscillations, with a typical macroscopic collapsed gel length of 1.5 mm and an expanded length of 3.5 mm. The corresponding microscopic lengths varied between 325 Å (collapsed) and 650 Å (swollen). A plot of the micro- and macroscopic expansion showed that the polybase system affinely changes shape throughout the oscillations (see Figures 1 and 2).



**Figure 1.** pH trace (top), macroscopic data (middle) and microscopic, SAXS data (bottom) during the pH-oscillation reaction.



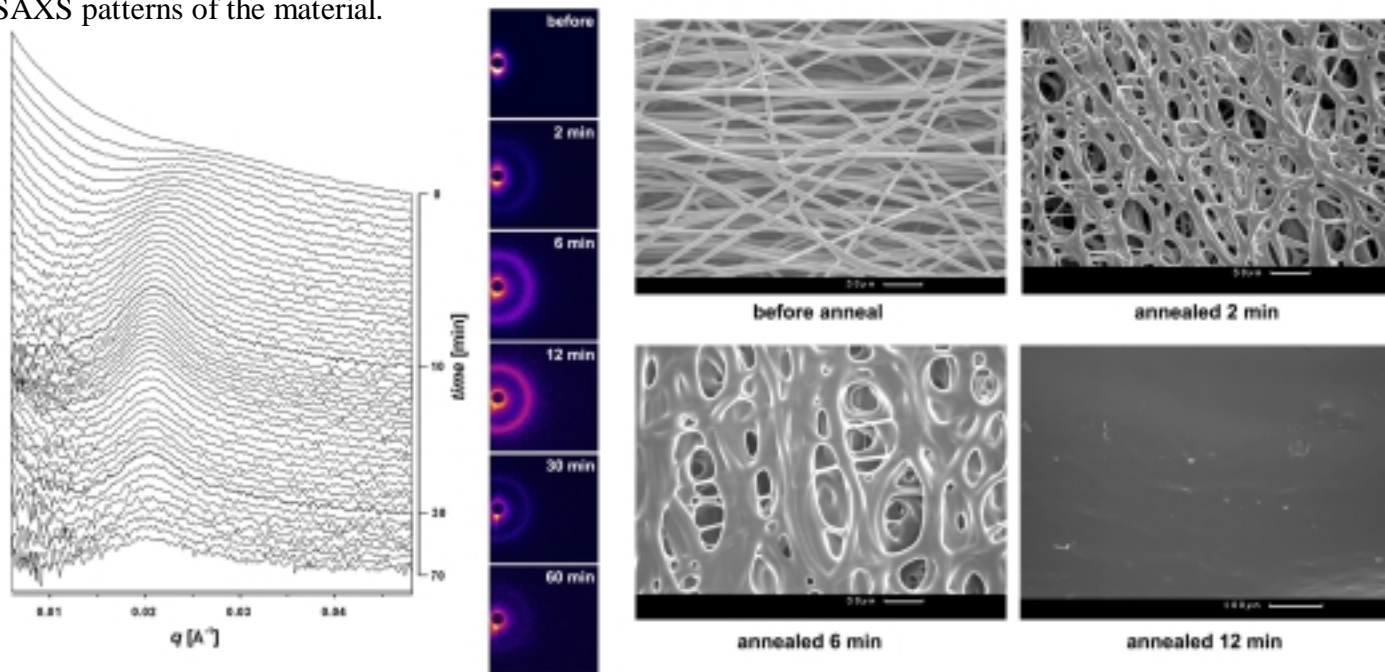
**Figure 2.** Micro- and Macroscopic Expansion for PMMA-*b*-PDEA-*b*-PMMA, shown as percentage expansion.

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  $\sim 5$  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 myosin<sup>3</sup>, 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.

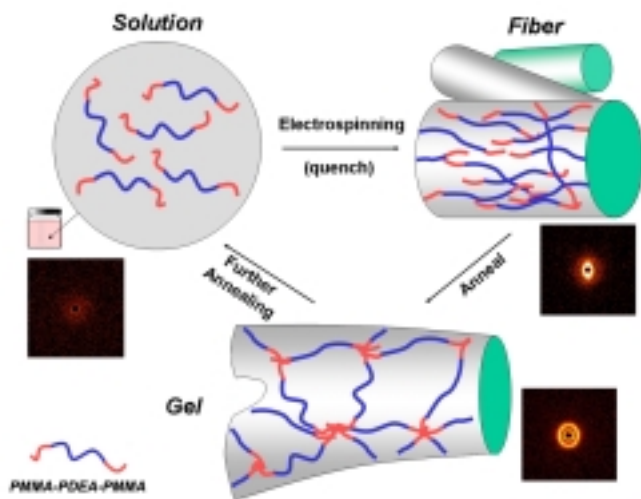
Electrospun fibres however, do not microphase separate into distinct microdomains (due to instantaneous removal of solvent during their production) and therefore their microscopic length scale changes cannot be followed by SAXS. To overcome this, the fibres can be annealed in a solvent atmosphere to allow the polymer chains to flow amongst one another to adopt a more ordered conformation whilst still maintaining its fibre

structure. The annealing process was monitored by SAXS (at Dubble) and Scanning Electron Microscopy (SEM) (Figure 3). Figure 4 shows how the annealing process alters the polymer conformation and consequent SAXS patterns of the material.



**Figure 3.** SAXS data and SEM micrograph images of the THF annealing process of electrospun fibres processed from a PMMA-PDEA-PMMA/THF solution (35 wt%).

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 fibre bundle to give an ordered microdomain structure with a large external surface area to allow the desired rapid pH-response.



**Figure 4.**

Schematic diagram of the block copolymer macromolecular arrangement after electrospinning and annealing (solution, electrospun fibre and gel) depicting the processes measured in Figure 3.

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.

