

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 and mechanical work oscillations in triblock copolymers coupled to chemical oscillations as studied by small angle x-ray scattering

Experiment number:
SC-1782

Beamline: Bm 26b	Date of experiment: from: 27 april 2005 to: 29 th april 2005	Date of report: 01 sept 2005
Shifts: 6	Local contact(s): Florian Meneau	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Dr. Jonathan Howse*	Sheffield University, UK
Prof. Tony Ryan	Sheffield University, UK
Dr. Colin Crook *	Sheffield University, UK
Mr. Paul Topham*	Sheffield University, UK
Ms Claire Wilshaw*	Sheffield University, UK

Report:

SAXS studies were conducted on triblock copolymer gels with a mid-block consisting of a polyelectrolyte. The polymer gel was placed in a pH oscillating environment in a custom-built continuously stirred tank reactor which allowed for the simultaneous collection of SAXS and optical microscopy of the gel piece.

Figure 2a illustrates our experimental equipment. A nylon cell was fitted with 2 sets of orthogonal windows such that the macroscopic size of the gel could be captured by an inspection microscope and the synchrotron x-ray beam could be used to perform real-time SAXS. The pH was recorded using a combined microelectrode (Mettler Toledo) at a frequency of 0.33 Hz. SAXS images were typically collected at 60 seconds per frame for a maximum of 256 frames. Our Landolt pH-oscillator is based on a bromate/sulfite/ferrocyanide reaction and has a room temperature period of 25 minutes with a range of $3.1 < \text{pH} < 7.0$. The optimum flow rate for reliable oscillations was found to be $29 \mu\text{l s}^{-1}$ for each reactant with concentrations: $[\text{SO}_3^{2-}] = 0.3 \text{ M}$, $[\text{BrO}_3^-] = 0.26 \text{ M}$, $[\text{Fe}(\text{CN})_6^{4-}] = 0.08 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.04 \text{ M}$.

The time-course of the macro and molecular length-scales of a polymethacrylic acid based triblock gel are shown in Figure 1a (i) and (iii), respectively. As the pH oscillates the gel flips from expansion to contraction as it passes pH 5.5 (the pKa of polymethacrylic acid)(Figure 1c). The gel continues to expand, through mass transport of solvent, throughout the whole 10 minute period at high pH, contraction proceeds at the same rate and there is a period of constant length prior to expansion. The molecular size, as determined by the separation of the hydrophobic clusters, closely tracks the sample size. A plot of the time-course of the relative sizes, at the 10 nm and 1mm length scales, and when converted into relative expansion (Figure 1b) demonstrates that this self-assembling material affinely changes shape in responsive to its chemical environment over many cycles. That is, the serial addition of many molecular length changes is ultimately translated into the macroscopic length change.

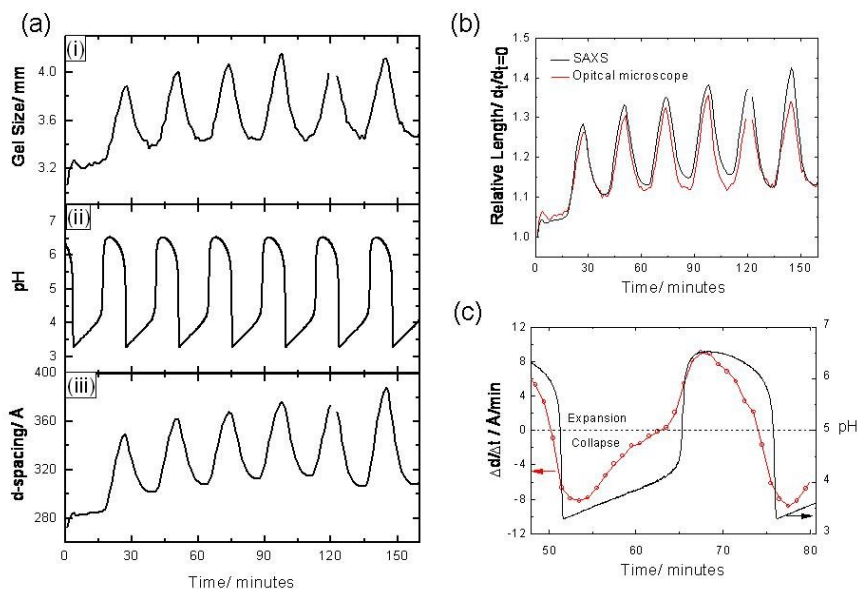


Figure 1 (a) The response of the macroscopic structure (gel-length)(i), and gel morphology (SAXS d-spacing)(iii) to the variation in pH (ii) induced by the bromate-sulfite-ferrocyanide oscillating reaction. (b) Time course of the relative size change for the morphology (—) and the macroscopic size (—) ($d_f/d_{f=0}$). (c) The rate of expansion ($\Delta d/\Delta t$, —) plotted with the pH (—) during the time-course of one oscillation.

The specific power of the polymethacrylic acid gel was measured by making the gel do work against a soft cantilever (0.47 N/m) whilst being driven by the oscillating reaction. Contemporaneous with these experiments the molecular orientation and relaxation of the structure was measured by SAXS, see Figure 2a. The deflection of the cantilever is measured by using the deviation of a laser beam reflected from a mirror attached to the cantilever. Thus the molecular structure, macroscopic deformation and force could all be measured simultaneously. Figure 2b is an AFM tapping mode phase-image of the collapsed block copolymer film and the insets are the (i) FFT of the morphology as measured separately by AFM and (ii) the SAXS patterns of the film under tension in the liquid cell. That the cantilever spring deforms the molecules is apparent from the SAXS patterns and the deformation changes systematically with the pH. Figure 2c is a plot of the time-course of the pH, length of the gel, l , the force, f , on the cantilever spring and the derived quantity the specific power, P_s . Work $w = f \times l$ and power $P = w/t$ so $P = f \times v = f \times (dl/dt)$ where t is time and v is velocity. The specific power is the power per unit mass obtained by normalising to the mass of the swollen gel and provides a lower boundary estimate of $P_s = 20 \text{ mW kg}^{-1}$.

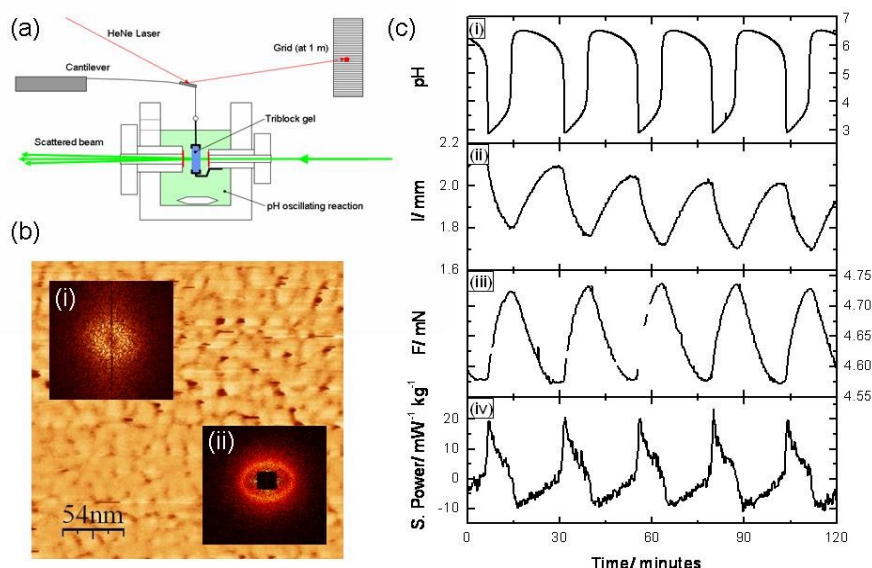


Figure 2 (a) A schematic diagram of the experimental apparatus for simultaneously measuring pH morphology and force generation. (b) An AFM micrograph of the dry polymer structure with inserts showing the FFT of the structure (i) and the SAXS patterns of the stretched (ii) gel. (c) The response to the variation in pH (i) of the gel-length (ii) and the force acting on the cantilever (iii) to the specific power generated (iv) by the gel.

In order to place the mechanical performance of our system in context, the specific power generated by our device can be compared to the performance of various cellular engines and an automobile engine $\sim 300 \text{ W kg}^{-1}$. The calculations of specific power are based on the molecular weight of the smallest unit, this favours the molecular motors and polymerisation based engines which are more powerful than the cellular structures in which they are found, and can be seen in the comparison between myosin at 20 kW kg^{-1} and striated muscle at 200 W kg^{-1} .