



**Experiment title:**

SAXS studies of pH-responsive electrospun triblock copolymer fibre networks

**Experiment number:**

SC-2023

**Beamline:**

BM26

**Date of experiment:**

from: 12 July 2006 to: 17 July 2006

**Date of report:**

3/1/07

**Shifts:**

6

**Local contact(s):** Nicolas Vilayphiou

*Received at ESRF:*

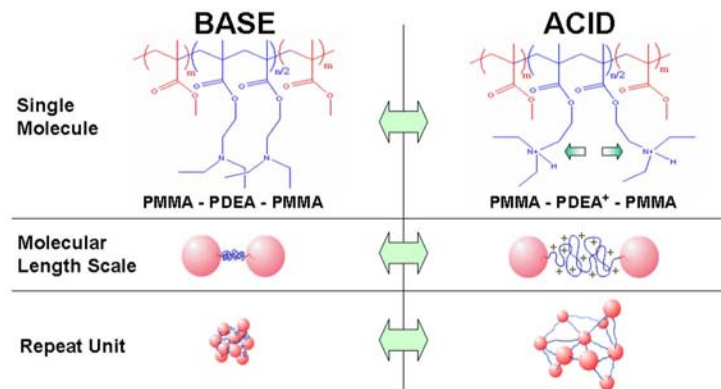
**Names and affiliations of applicants (\* indicates experimentalists):**

- \* Mr Joshua Swann, Dept of Chemistry, Sheffield University, Sheffield. S3 7RH
- \* Dr Jonathan Howse, Dept of Physics and Astronomy, Sheffield University, Sheffield. S3 7RH
- \* Dr Robert McKean, Dept of Chemistry, Sheffield University, Sheffield. S3 7RH
- Prof Tony Ryan, Dept of Chemistry, Sheffield University, Sheffield. S3 7RH

**Report:**

The phenomenology of shape-change polymer gels and brushes has been extensively studied theoretically and experimentally. Recently these stimuli responsive polymer gels have become of interest as novel intelligent materials with sensor, processor and actuator functions. The swelling-deswelling behaviour is a change toward a stable equilibrium state following an external stimulus and an on-off oscillating state can be induced by oscillating the external conditions. Such external stimuli may be temperature, pH, or ionic strength. We have previously demonstrated with a combination of SAXS and video microscopy that a self-assembled microphase separated triblock copolymer gel with a “sphere” structure comprising of Polymethylmethacrylate-Polymethacrylic acid-Polymethylmethacrylate (PMMA-PMAA-PMMA) undergoes affine changes in size when placed in a self-oscillating pH reaction<sup>1</sup>. Coupling the self-assembled gel to a load in this environment allows for mechanical work to be obtained from the chemical reactions taking place. The pH responsive nature of the material is attributed to the PMAA polyelectrolyte midblock. Below the  $pK_a$  of the PMAA chains the acid groups are protonated and hydrophobic so when in an aqueous environment the chain is collapsed. Above the  $pK_a$  of the midblock the individual polymer chains become deprotonated and the chain becomes hydrophilic with charge repulsion between individual chains causing expansion of the entire network.

Building on the success of the polyacid system efforts were driven towards synthesis of a polybase triblock. In contrast to the polyacid system, such a “polybase” should demonstrate an inverted pH response where the polymer is charge neutral above pH 5 (collapsed) and positively charged below (expanded). A suitable candidate was found in a triblock copolymer which contained a Polydiethylaminoethylmethacrylate (PDEA) midblock and end groups of PMMA<sup>2</sup>. The volume fraction of the PMMA endgroups is such that it self assembles into spheres of PMMA surrounded by a matrix of PDEA. A schematic diagram of the molecular and meso- structures of PMMA-*b*-PDEA-*b*-PMMA is shown in Figure 1.

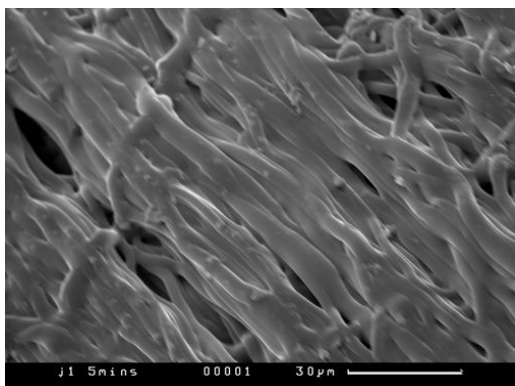


**Figure 1.** Schematic diagram of three different length scales of the chemical and meso-lengthscale changes of the polybase triblock copolymer under acidic & basic conditions.

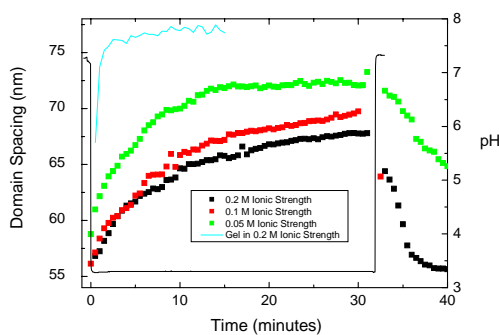
The response of such systems, both polyacid and

polybase, will ultimately be restricted by diffusion. Essentially the rate at which the chemical fuel is delivered to the active site determines the rate of response of the material. Having demonstrated the potential of these systems at converting chemical energy into mechanical energy, with an affine nature, then the proceeding work has focused on the understanding of the diffusion processes occurring in these systems.

To increase the rate of diffusion the sample must be made small, either thin sheets of gel material, or taking inspiration from mammalian muscle, fibres. Electrospinning is a process capable of producing aligned polymer fibres with diameters of 10s of microns from our chosen polymer. Following suitable solvent annealing and processing we are able to obtain microphase separated bundles of fibres that show an increased response to changes in pH over a simple, solvent annealed gel<sup>4</sup>. To further understand the effect that diffusion has on such a system we have used SAXS to follow the changes in domain spacing of electrospun fibre bundles and a gel piece. Initial tests to determine any effects of ionic strength on the swelling behaviour have also been conducted.



The dynamic behaviour of the polybase material was determined by placing microphase separated fibres into a manually oscillated pH environment using a pair of citrate and phosphate buffer solutions. Generating manual oscillations allowed greater control on the period of the pH oscillations, the pH and ionic strength. In addition manual oscillations ensure that various samples always encountered the same environment allowing any features to be explained in terms of the sample. Dynamic SAXS results obtained on responsive fibres is shown below in figure 2.



**Figure 4. (top)** SEM image taken of an annealed (6 minutes in THF) bundle of fibres showing the porous fibrous structure of triblock polymer fibres.

**(bottom)** Changes in fibre structure measured by SAXS (*d-spacing*) when placed in the oscillating citric acid-phosphate buffer at varying ionic strengths.

The dynamic behaviour of a polybase annealed gel was also measured to allow direct comparison with the fibres. Upon inspection of the results it appears that the gel sample is more responsive. This was an unexpected result as it was anticipated the fibres would be more responsive given their greater surface area. When electrospun, the PMMA-PDEA-PMMA triblock forms fibres which have no internal microphase separation due to the fast drying time, effectively quenching the structure and freezing in the disorder. In order to process fibres suitable for SAXS the fibres must be solvent annealed to generate microphase separated structures. The longer the fibres are annealed for the greater the degree of microphase separation. The higher the degree of separation between the adjacent polymer phases, the greater the expansion will be as the concentration of the charged domains will be higher, increasing the repulsing between neighbouring groups on the polymer chain. However the process of solvent annealing causes the

initially fibrous material to become more like a monolithic gel, due to solvent penetrating within the polymer and allowing the fibres to adhere to each other indicating that fibre annealing and response are inherently coupled.

[1] J. R. Howse, P. Topham, C. J. Crook, A. J. Gleeson, W. Bras, R. A. L. Jones, A. J. Ryan, Reciprocating Power Generation in a Chemically Driven Synthetic Muscle, *Nano Letters* **2006**, *6*, 73.

[2] P. D. Topham, J. R. Howse, O. O. Mykhaylyk, S. P. Armes, R. A. L. Jones, A. J. Ryan, Synthesis and Solid State Properties of a Poly(methyl methacrylate)-*block*-poly(2-(diethylamino)ethyl methacrylate)-*block*-poly(methyl methacrylate) Triblock Copolymer, *Macromolecules* **2006**, *39*, 5573.

[3] P. D. Topham, *Study of pH-Responsive Polymer Systems for use in Molecular Machines* **2005**, *PhD Thesis*, University of Sheffield.

[4] Linge Wang, Paul D. Topham, Oleksandr O. Mykhaylyk, Jonathan R. Howse, Wim Bras, Richard A. L. Jones, and Anthony J. Ryan, Electrospinning pH-Responsive Block Copolymer Nano-Fibres, *Advanced Material Communication*, IN PRESS.