ESRF	**Experiment title:** pH responsive triblock colpolymer gels	**Experiment number**: SC1127
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Report:

We have determined the d-spacing within a pH responsive phase separated triblock copolymer gel when exposed to acid and basic environments by SAXS. The material studied is a ABA triblock of poly(methylmethacrylate)-co-poly(methacrylic acid)-co-poly(methylmethacrylate). The composition of the polymer is such that upon removal of the solvent system a body centred cubic microphase-separated morphology is generated with PMMA constituting the spheres surrounded by a matrix of PMAA. The application of a selective solvent for the PMAA (aqueous base) results in the swelling of the matrix of the BCC arrangement without affecting the PMMA spheres. The gel's structural integrity is maintained by the PMMA endgroups spanning the BCC unit cell and being locked in place due to the glassy nature of the PMMA.

Before attempting to study the behaviour of the gel in an aqueous environment the structure of the solvent-swollen system after shear and drying was determined. Having generated an ordered system pieces of the dried polymer were exposed to acid (pH 3) and base (pH 10) for a period of one hour. The results are shown below.

System	Q ($Å^{-1}$)	d-spacing (Å)
Acetone:Methanol (15:85 v/v) at 33 wt.% after shear	0.01739	361.3
Dried – following shear	0.02164	290.4
Dried piece placed in pH 3 for 1 hour*	No peak detectable	
Dried piece placed in pH 10 for 1 hour*	0.01343	467.8

* to measure the pieces exposed to acid and base the swollen gel was placed between kapton and placed in the beam.

The sample cell for dynamic liquid studies was designed such that the gel piece (1mm x 3mm) was held between two mica windows 3 mm appart placed on the ends of plastic tubes (internal diamter ~ 5mm) held within a liquid reservior (~100 mm). The beam is incident upon the sample by travelling through the tube, through the window, into the 3mm gap composing of the solution and the sample held between tweezers ,and then through the exit window and tube onto the detector. At the same time as collecting the SAXS data the pH was recorded every 5 seconds and images of the gel were recorded using a high magnification camera system at 3 frames per minute. This then allows for the macroscopic behaviour of the gel to be coupled with microscopic structure as revealed by SAXS.

The dynamics of the pH response of the gel were initial investigated by manually changing the pH of the solution surrounding the gel. A cycle of acid-base-acid-base-acid was condcuted over 2½ hours and for each step 30 frames of 1 min were collected.

Figure 1 (right) shows the 1D sector averaged response as a function of Q for the pH change from 9 to 3. This causes the gel to collapse and this is shown by the movement of the scattering peak to higher Q. The data has only been adjusted for intensity (.din) and detector response (.add). It clearly shows a peak at Q = 0.130 (t = 1 min) moving to Q = 0.170 (t = 30 min). This corresponds to a change in the unit cell of 483 Å to 369 Å. It can be also seen that this unit cell change approaches its final size within 7 minutes. (7 scan lines)

Figure 1. Gel collapsing in acid

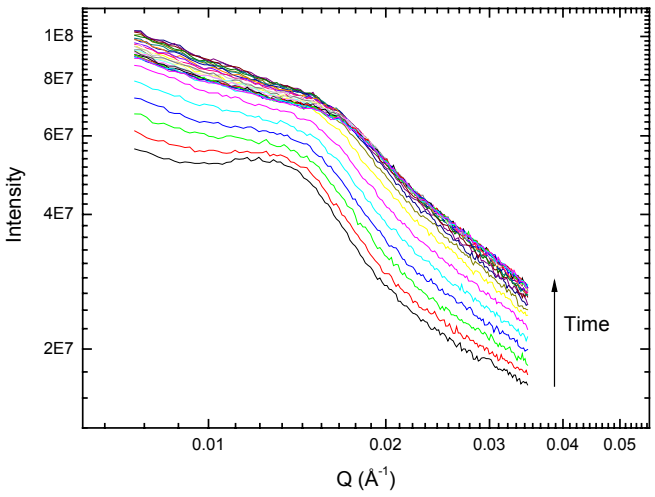
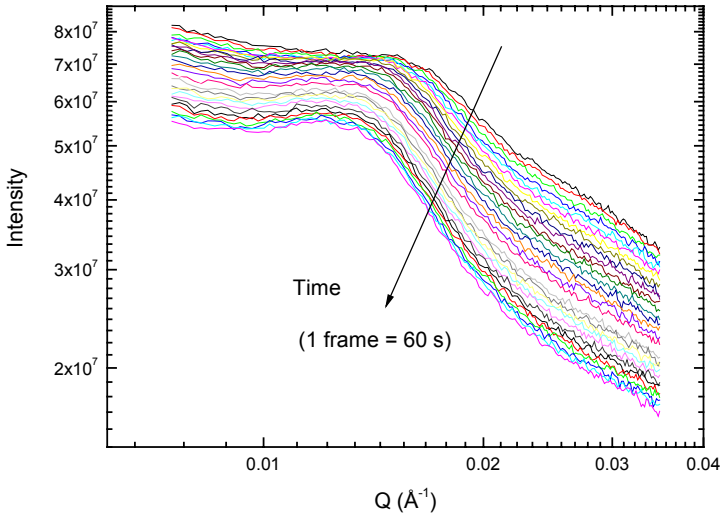


Figure 2. Gel expanding in base.



The increase in scattering intensity is attributed to the swollen gel collapsing and increasing the thickness of the liquid surrounding the sample through which the beam is transmitted through.

As can be seen from Figure 2. the expansion of the sample shows a similar behaviour in terms of unit cell size. The peak starts at 0.015 and end at 0.130. However, it is clear that the dynamics of the swelling process are not the same as those observed for the collapse.

The observed pH swelling behaviour as observed by SAXS is corresponds well to that seen with images recored on a macroscopic level.

The gel was then placed in a mixed landolt oscialltor which is capable of generating an oscillating pH over a 28 minute period with a range of pH 3 to pH 7. However, no noticible change in scattering was observed and we sumise that this is due to a combination of sample thickness and diffusion limited flow within the gel.