ESRF	**Experiment title:** A study of the phenomenon of crazing in glassy polymers through the use of μSAXS	**Experiment number**: SC-1099
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It has been well established over the last few years that the formation and breakdown of crazes in glassy polymers is of great importance in determining the overall fracture behaviour of the materials. In order to investigate this phenomenon we employed μSAXS and studied a series of well-defined polystyrenes (with a broad range of molecular weights (MW) and different polydispersities (PD)). The aim of the study was twofold. Firstly, we sought to understand the early phenomena associated with crazing, and secondly, we sought to investigate the effect of MW and PD on the phenomenon of crazing. In order to successfully conduct the experiment, a specially designed deformation rig, described in our previous reports, was mounted on the beamline, and a series of polystyrenes (PS) were tested in situ with SAXS. The geometry of deformation was that of a standard three point bending test, and the beam was set in the tension region, approximately 50 μm away from the sample edge (Fig.1a).

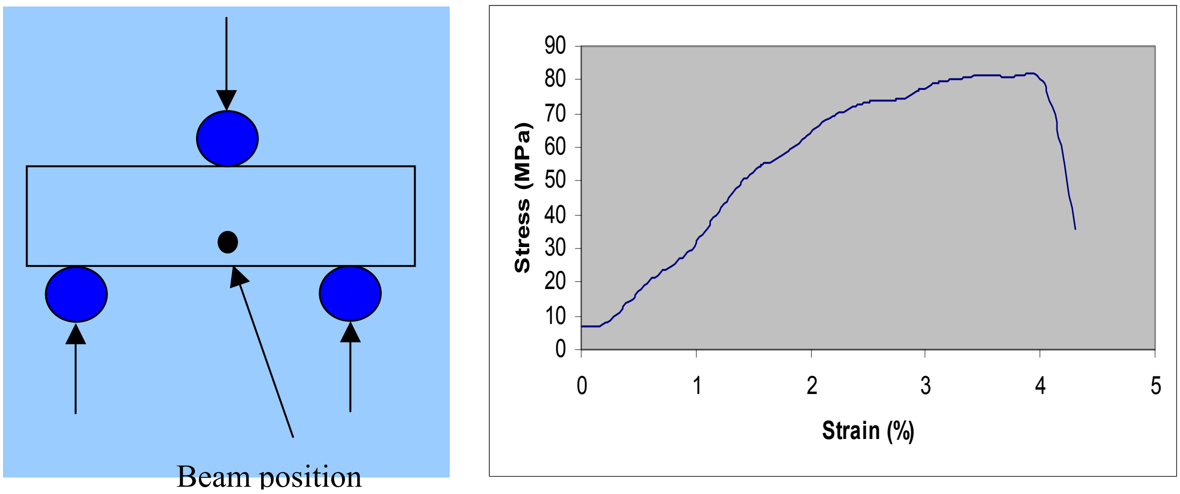
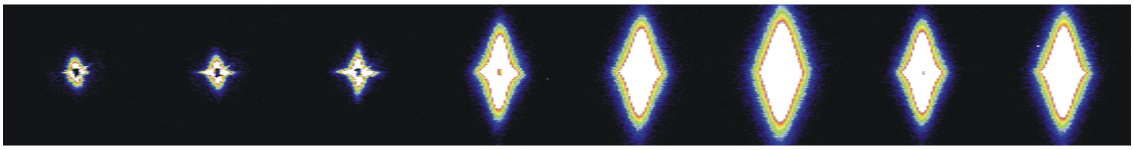


Figure 1. A schematic representation of the three point bending test for PS along with a typical stress-strain curve.

The choice of this geometry was necessary since (PS) is extremely difficult to handle in tension, and due to its high degree of brittleness premature failure occurs at the points of the higher concentration (that is in the clamps) much before it occurs in the sample, thus greatly skewing the results. Thin bars of PS were mounted on the deformation rig and the test proceeded with a strain speed of 0.0054 %/s. In addition, the deformation of the PS samples was monitored through the use of optical microscopy, as described in our previous reports. The data acquisition time was 12s for x-ray scattering patterns, 5s for images, and 5s for load-displacement. The results of the test, a small portion of which is given here, revealed many interesting phenomena taking place. Firstly, it was spotted that the formation of crazes proceeds with the generation of a very thin nanocrack which is then stretched to form an elliptical nanovoid, bridged with almost perfectly cylindrical shapes. The interesting aspect is that there was no interfibril bridging located, which has also been identified in the literature. Some of the results may be seen in fig. 2.

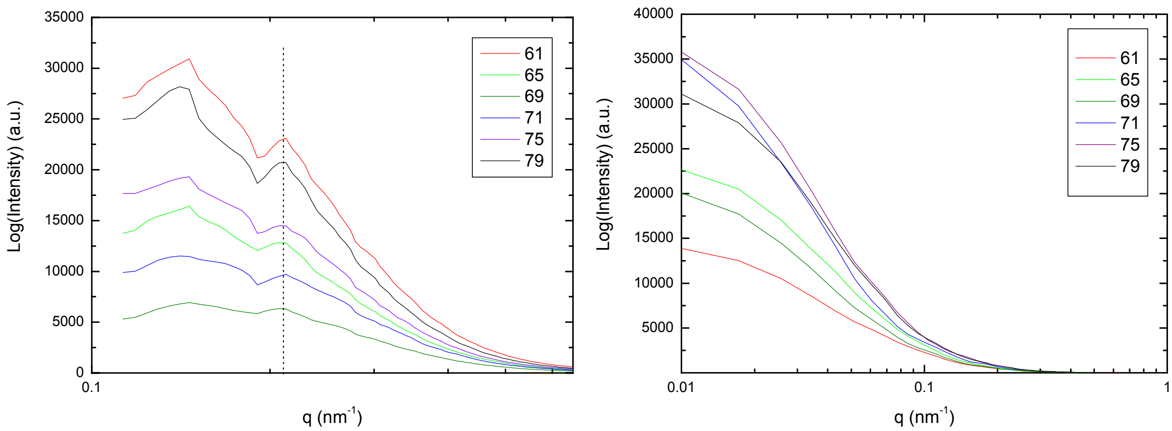


1.85	2.19	2.52	2.86	3.19	3.56	3.89	4.22	strain(%)
58.5	73.43	74.67	77.16	87.11	80.89	75.91	73.42	stress(MPa)
32	38	44	50	56	62	68	74	Frame

Applied stress

Figure 2. 2D SAXS patterns of PS (MW=900000, PD=1.09) under three point bending loading at the corresponding stress, strain and number of captured SAXS patterns frames.

As seen in fig. 2 in the very early stages of the test, there is only little scattering, but at about 2.2% strain (note the values correspond to the whole specimen and not for the beam illuminated point) a small streak appears, that is due to the formation of the nanocracks. As the test proceeds, the equatorial streak is joined by strong meridional scattering due to the formation of the bridging fibrils inside the nanovoids. From the 2D SAXS patterns one may obtain extra information by subsequent treatment. In fig. 3 the integrated intensities of the meridional and equatorial parts of the 2D patterns (±20° from the symmetry axis (0° for the equatorial part and 90° for the meridional part)) may be seen.



(a) (b)

Figure 3. Integrated intensities for the meridional (a) and equatorial (b) parts of the 2D SAXS patterns. The numbers in the legend represent the frame numbers of the SAXS 2D patterns.

From fig. 3 one may see that in the meridional parts there is a peak in the integrated intensities, corresponding to a long period of 29.8 nm. This is the repeat distance between two nanofibrils inside the craze, and it remains constant throughout the test. From the equatorial parts (b) one may see that there is a steady increase of scattered intensity due to the increase of the nanovoid density as the test proceeds. Furthermore, by fitting the form factor of a cylinder in the meridional part it was found that the average diameter of the fibrils corresponds to about 10 nm. This information may in turn be used for micromechanical modelling of the deformation behaviour of the material, with the ultimate goal to predict its macromechanical properties. However, what is of interest is the fact that the experiments did not reveal the formation of cross-tie fibrils in a large number of specimens, contrary to what has been reported in the literature. In addition, it was found that the mechanism of fibril formation was different for the different MW and for the different PD samples, and that the much celebrated meniscus model seems not to be well suited to describe the results. Further on going work is currently in progress and more experiments are needed in order to fully establish an understanding of the phenomenon of crazing.

References

1. N. E. Zafeiropoulos, R. J. Davies, K. Schneider, C. Riekel, M. Stamm, The effect of molecular weight and polydispersity on crazing of PS as revealed by synchrotron μSAXS, submitted in Macromolecules.