

Small Angle Scattering of Biological and Polymer Samples under Pressure at the ESRF.

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Introduction

Small-angle scattering under pressure has been done up to now only with neutrons [1] because existing X-ray sources only deliver large cross sections of the X-ray beam with relatively low intensity. This would have led to high pressure cells with huge window apertures and, thus, thick windows and high absorption. These difficulties can be overcome with third generation synchrotron sources that deliver an X-ray beam of high brilliance. At the ESRF, we constructed a high pressure cell and used it for different types of samples. A short overview is given below.

The high pressure cell

The high pressure cell is a large volume cell of piston cylinder type (see figure 1) [2]. Pressure is applied and controlled by an oil hand pump from outside the experimental hutch. The pump drives a movable piston through a pressure amplifier that amplifies the pressure by a factor of 64. The pressure is transmitted to the sample through a liquid so that

hydrostatic pressure conditions are ensured. Depending on the type of sample being studied, different liquids have to be used. Silicon oil, for example, is chemically inert but solidifies at elevated pressure. Dioctylsebacate remains liquid throughout the whole pressure range but can react with the sample. Up to now we have used three different liquids [3]. Pressure can be increased from ambient pressure up to 1 GPa (10 kbar) and temperature from room temperature up to 300°C. The cell is heated from the outside with a heating rate of up to 3°C/min. Cooling is not yet available but is being planned.

The X-ray beam passes through the pressure cell perpendicular to the cell axis through two diamond windows of 1.5 mm thickness which have a transmission of 59% at 13 keV. The window aperture is 1 mm diameter and the maximum scattering angle is $2\theta = 3^\circ$ for a straight incoming beam. The samples can be either solid or liquid. Solid samples can be up to 6 mm thick. They can be introduced within 15 min. Liquid samples need to be separated from the pressure transmitting liquid and they are therefore filled into Teflon containers that are squeezed between the windows. This leads to 0.2 mm of Teflon in the beam path. Therefore, the containment for liquids will be re-designed.

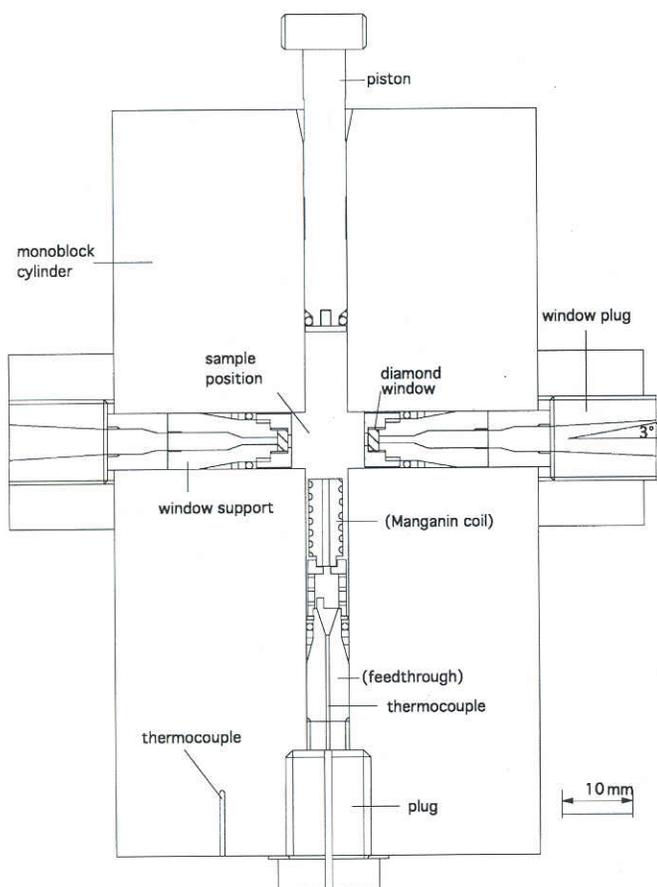


Figure 1: Schematic design of the SAXS-high pressure cell.

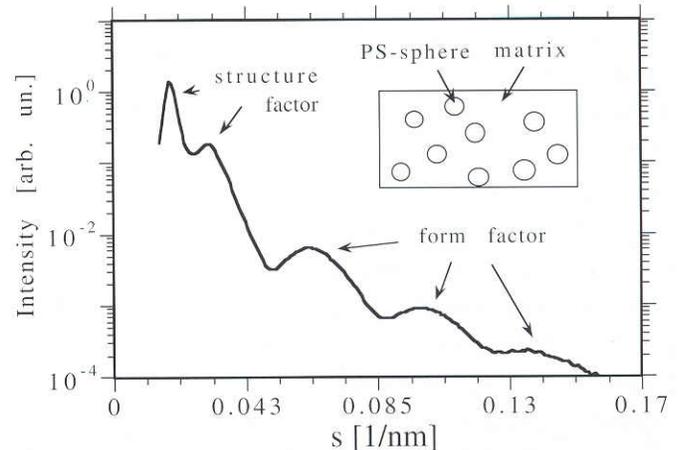


Figure 2: Small-angle scattering curve of a triblock-copolymer gel. Inset: Schematic morphology of the gel.

Examples

1. Gels

Triblock-copolymer gels are studied that consist of some percent of triblock-copolymer (PS-PB/PE-PS) in an extender fluid. Their morphology has been elucidated by Mischenko et al [4]: The PS-endblocks separate from the rest (midblock + oil = matrix) and coagulate to form spheres (see inset of figure 2). This leads to small-angle scattering curves that show spherical oscillations at large s -values ('form factor')

and structural peaks at low s -values ('structure factor'). A typical curve is shown in figure 2 for a gel with 12 wt% of polymer in the sample. From the location of the oscillation maxima, the radius of the spheres can be derived; from the structural peaks, the distances between spheres can be obtained. In the example given, we will only show the pressure influence on the PS-spheres. In figure 3 the radius in relation to the pressure is given [5]. As can be seen, two regions of different slope occur: Up to 450 MPa the radius of the PS-domains decreases only slightly; above 450 MPa the decrease is pronounced. This behaviour is reversible. With the help of literature data for the compressibility, the radius of the glassy PS-spheres can be calculated (for details see [3]). As can be seen in figure 3, the experimental slope below 450 MPa is lower than the calculated one whereas, above this pressure, calculation and experiment do agree well. The difference below 450 MPa can be explained by a screening effect. This could be due to an interfacial layer with a compressibility smaller than the compressibility of the matrix. So far, no proof for this idea can be given. However, there is evidence for the existence of an interfacial layer [6].

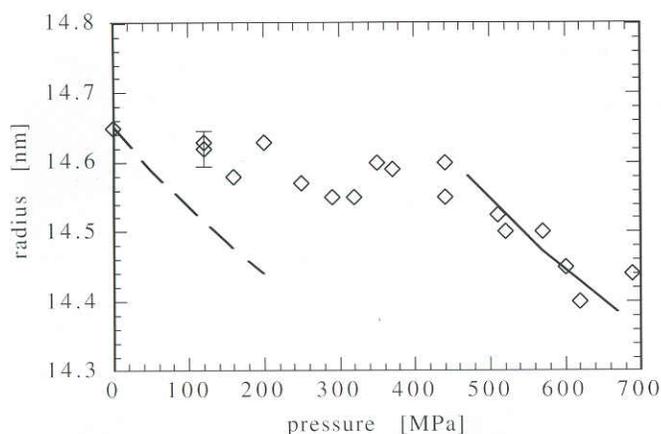


Figure 3: Radius of the PS-spheres as a function of pressure (diamonds: experimental data; solid and dashed line: calculations for different initial conditions).

2. Biological solutions

As an example for a biological solution, measurements on ATCase (Aspartic transcarbamoylase) are shown (see figure 4). As can be seen, the minimum smears out and the intensities decrease with increasing pressure. This can be interpreted as dissociation of the enzyme. According to our measurements, this behaviour is reversible.

Conclusions

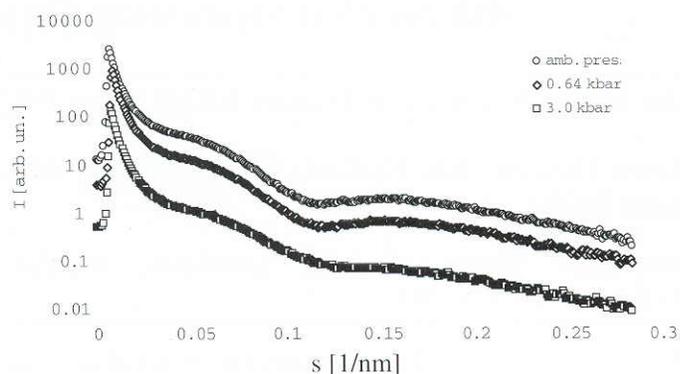


Figure 4: Scattering curve of ATCase as a function of pressure.

Although only a few examples are given, it can already be seen that small-angle X-ray scattering under pressure leads to interesting new results that need to be studied further. The application of pressure opens up a completely new branch of small-angle scattering studies. The high pressure cell is in use at the High Brilliance beamline (BL#4) [7] and the Microfocus Beamline (BL#1) [8] at the ESRF. Within the usual proposal procedure at the ESRF, anybody can apply for beamtime with the high pressure cell (the proposal form can be found in WWW: <http://fox.esrf.fr:3600>).

References

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