Simultaneous time resolved X-ray scattering experiments in the small and wide angle region

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Abstract

A SAXS synchrotron beam line is equipped with a second detector system so that simultaneous WAXS experiments can be performed. Modular sample environment cells give the possibility to obtain extra thermodynamical information. Experiments have been performed on a variety of samples.

Introduction

There is a wide variety of experiments in which it is essential to obtain structural information that spans the real space dimension range from 1 - 1000 Å. Polymers, liquid crystals and membranes are a few important examples. If one wants to study phase transformations in these systems it is crucial to collect the data in a time resolved mode.

A problem with performing independent time resolved Wide and Small Angle X-ray scattering experiments on a sample is to obtain a proper time correlation between the two experiments. When a third independent experiment, like Differential Scanning Calorimetry or Fourier Transform Infrared spectroscopy, has to be time correlated to the scattering experiments as well the situation is aggravated. Equipment in which these experiments can be combined would offer advantages for radiation sensitive biological samples as well.

Several attempts to build equipment that would allow simultaneous scattering experiments have been described in the literature [1,2,3]. Most of this equipment has some limitations in either the q-range that can be observed or in the obtainable time resolution.

A major problem in performing these experiments is that, in order to obtain a large q-range, one generally has to use position sensitive delay line detectors since solid state detectors in general are too short. For WAXS experiments this introduces a serious problem due to the parallax problem that these detectors exhibit when X-ray impinge on a large angle with respect to the surface normal of the detector.

Recently we have assembled equipment that could be utilised for the above described experiments with a larger obtainable q-range and a higher time resolution [4]. Here we describe the improvements to the initial equipment and show some results from the diverse set of recently performed experiments.

Description equipment

The optical system of station 8.2 at the Synchrotron Radiation source in Daresbury, which forms the basis of the equipment, has been described elsewhere in more detail [4]. A triangular bent Ge(111) crystal is used to focus the X-rays in the horizontal plane and monochromate at 1.51 Å. Subsequent vertical focusing is obtained by using an uncoated quartz mirror under grazing incidence. The total flux on the sample is 5×10^{10} photons/sec in a $3.5 \times 0.3 \text{ mm}^2$ spot. The horizontal and vertical divergence are, respectively, 5.0 and 0.25 mrad. The distance between the last two slit sets is increased by 1.0 meter with respect to the conventional set-up in order to reduce the parasitic scatter opening angle.

data quality is superior to a standard $\theta/2\theta$ diffractometer using filtered $\text{CuK}\alpha$ radiation. This can not be explained by a difference in bandpass for the radiation, since $\Delta\lambda/\lambda$ is roughly equal for both situations. The explanation can be found in the lower divergence of the synchrotron beam line.

The electronic system time resolution is 10 μs , but the practical time resolution that can be obtained with this equipment is approximately 100 ms. This limitation is imposed due to the limited count rate that the INEL can handle. Generally the scattering pattern has to be attenuated by a factor 30 - 300 times in order not to exceed the count rate limits of this detector. The quadrant detector only has to be attenuated by a factor 3 - 10.

Examples

Successful experiments have been performed on a variety of samples with an emphasis on material science research but also on some biological materials. Examples of the material science program are the study of the annealing behaviour of cordierite glasses, the freezing of undercooled water and a wide variety of temperature induced phase transitions in polymer systems. The growth process of starch granules, the temperature induced rearranging of lipid skin and artificial membranes and changes in structure of bovine cornea upon hydration are examples of the biological program. Below three example of experiments are shown.

Figure 4 Contour plots of time resolved experiment on a block copolyester sample.

The data in figure 4 is obtained during a heat $\rightarrow$ cool $\rightarrow$ heat cycle on a liquid crystal block copolyester. The SAXS and WAXS data are two intensity contour in Iq^2 and I respectively. The phase transitions from crystal 1 to crystal 2 are readily apparent. The sample was heated with $20^\circ\text{C}/\text{min}$. The data was collected in frames of 10 seconds.

The second example concerns the growth of starch granules (see figure 5). Here the gelatinization process under the influence from a temperature increase from 40° to 80°C was studied. The loss of crystallinity, as evidenced by the decrease in intensity of the WAXS peaks, is associated with the dissociation of the amylopectin double helices. The single peak in the SAXS region exhibits a similar loss in intensity due to the disruption of the lamellar structure as water penetrates the granule.

Figure 5
Gelatinization of 57% wheat starch under the influence of a temperature increase from 40° to 80°C

Figure 6 Fast temperature quench of HDPE

Data obtained from a fast temperature quench experiment on High Density Polyethylene. The sample was quenched from the molten state with $\approx 10^\circ\text{C/s}$. Time resolution 0.1 s. The SAXS invariant is shown (right scale) and the intensity of the 110 reflection (left scale), which can be used as a measure of the degree of crystallinity. This experiment indicates that it is feasible to work at a high time resolution, making this instrument very useful in the study of fast phase transitions.

Conclusion

The equipment described here is a very versatile instrument especially suited to the real time study of phase transitions. A time resolution of up to 0.1 s and a very wide scattering range can be studied. The combination of SAXS, WAXS and DSC will be tried out in the near future. Attempts to combine FTIR experiments with the scattering techniques will also be undertaken.

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