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Recent experiments on a combined small-angle/wide-angle X-ray scattering beam line at the ESRF

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Recent results using a new combined small-angle/wide-angle X-ray scattering (SAXS/WAXS) beam line at the European Synchrotron Radiation Source (ESRF) will be presented. This beam line is specifically designed to be able to handle complicated sample environments required to perform time-resolved experiments mimicking processing conditions used in material science. Besides the attention that has been given to the interfacing of these sample environments to the beam line data acquisition system also the developments in detector technology will be discussed. The influence that a high count rate and low noise WAXS detector can have on the accuracy of experimental results in polymer crystallisation will be shown. It is shown that it is feasible to detect crystalline volume fractions as low as 10^{-3} – 10^{-4} in polymeric systems.

Keywords: SAXS/WAXS; polymers; glass; crystallinity

1. Introduction

It has already been recognised for a long time that the combination of small-angle/wide-angle X-ray scattering (SAXS and WAXS) in time-resolved experiments can be very fruitful in a large number of cases. To this end it has recently become more or less routine to equip synchrotron SAXS beam lines with an additional WAXS detector. However, SAXS detector technology is still lingering behind the performance of most beam lines with respect to the combined parameters of achievable time-resolution, dynamic range and count rate. This being the case the situation for WAXS detectors is even more problematic since, in contrast with SAXS experiments where the scattering features are generally spread out over a large number of detector pixels, in WAXS the diffraction peaks map onto only a limited number of pixels. When one wants the statistical significance of both experiments to be compatible it will be clear that the requirements on dynamic range, instrumental noise, pixel resolution and local count rate will be much more severe for WAXS detectors than for SAXS detectors. The more so when the ultimate goal is to be able to perform millisecond time resolution experiments.

When beam line BM26B at the ESRF (part of the DUBBLE project [Borsboom *et al.*, 1998]) was designed this was recognized to be an important issue [Bras, 1998] and consequently a large development effort was made to design a detector that would be able to cope with the requirements outlined above [Zhukov *et al.*, 1997]. Using Micro Strip Gas Chamber technology (MSGC), so far mainly used in high energy physics experiments, we have succeeded in

constructing a very high count rate WAXS detector [Dolbnya *et al.*, 2002] system.

The particular importance of this instrumentation development is observed in time-resolved experiments where the sequence of structure development covering different length scales is of great interest. One of these fields is the crystallisation behaviour of semi-crystalline polymers. At present there broadly are two schools of thought. One favouring the classical ideas of nucleation and growth originated by [e.g. Keller 1995; Hoffman *et al.*, 1997] and the other, more recent one, in which the primary nucleation step is thought to be a mechanism with kinetics resembling those of spinodal decomposition [Terrill *et al.*, 1998; Olmsted *et al.*, 1998]. Although, a polymer melt in principle is a single phase system for which the theory of spinodal decomposition is not completely valid, there are indications that local polymer chain conformational changes effectively create a two phase system. [Tashiro *et al.*, 1998]. One aspect of the problems in this debate is that the theoretical developments [Olmsted *et al.*, 1998] should be supported by experimental evidence [Terrill *et al.*, 1998; Wang *et al.*, 2000]. Combined SAXS and WAXS experiments are invaluable tools for this area of investigation. However, in the past WAXS data quality has not been of a sufficient standard, thus, false assumptions could be made on the basis of the poor statistical quality of the data. Therefore, the task was to develop the experimental method so far that the underlying physics of the problem becomes the limiting factor.

Experimental evidence favouring a certain theoretical model therefore can be found in the sequence in which structure at different length scales develop. In the nucleation and growth model the occurrence of a signal in the SAXS region due to the scattering from the polymer lamellae should be simultaneous with the occurrence of diffraction peaks in the WAXS region due to the crystalline ordering of the polymer stems. In a spinodal type model the density fluctuations, at approximately the same length scale as the subsequently developing lamellar scattering, should precede the occurrence of the WAXS peaks. So far there is in a large number of systems the indication that the latter situation is the case. However, there is doubt about what level of crystallinity can be detected with the WAXS measurements. Experimentally it is shown that a level of 1 vol% can be detected by WAXS and 0.1 vol% by SAXS [Wang *et al.*, 2000]. These types of experiments are disregarding the crystallite size, which might be so small that due to thermal intensity reduction, Scherrer broadening and crystal imperfections, the intensity of the diffraction lines above the background might become too small that it is intrinsically undetectable. We have attempted to make a sensible estimate of what level of crystallinity can be detected in both weakly and strongly scattering systems.

2. Results

The experiments were done using beam line BM26B at the European Synchrotron Radiation Facility. This SAXS beam line is part of the DUBBLE CRG, collaboration between the Dutch and Flemish research councils (NWO/FWO).

The beam line receives 2 mrad of the radiation fan of an 0.8 Tesla bending magnet [Borsboom *et al.*, 1998]. The first optical element is a double crystal sagittal focussing monochromator, placed at 33 m from the source. This is a slightly adapted version of a monochromator that was developed at the ESRF [Freund *et al.*, 1998]. It was found that Compton scattering from the first crystal

heated up the second crystal to unacceptable high temperatures, necessitating the implementation of cooling on the second crystal. This is achieved by connecting flexible copper braids at one end to the sides of the bending mechanism and at the other end to a cryogenic finger that is inserted in the vacuum. This arrangement provides several Watts of cooling power.

The second optical element is a flat single crystal mirror placed at 37 m from the source. This mirror is 150 mm wide, thus allowing two strips of optical surface to be used. One of these strips is the bare Si surface, the other is coated with Pt. By keeping the angle of incidence fixed at 2.8 mrad higher harmonic rejection can still be achieved over the energy range 5 – 30 keV by applying a sideways translation and exposing the appropriate surface to the X-ray beam. The mirror surface is polished to 1.5 Å rms roughness and has a slope error of maximum 1.5 µrad. The mirror was manufactured by Reosc (Saint Pierre du Perray, France).

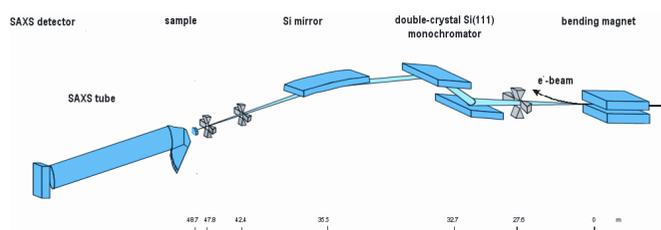


Figure 1

The schematic lay-out of the optical system of BM26B at the ESRF. The beam line accepts 2 mrad of the radiation fan of a 0.8 Tesla bending magnet. The sagittal focussing monochromator with Si 111 crystals is placed at 33 meter from the radiation source. A 1.4 m long single crystal Si mirror is placed under an angle of 2.8 mrad at 37 m and has the double function to suppress the higher harmonics from the primary energy and to focus in the vertical plane. The sample position is at 48 meter from the source. The optical bench allows a maximum sample-detector distance of 8 m. The scattering vector range of $1.57 \times 10^{-3} < q < 3.0 \text{ \AA}^{-1}$ can be covered ($q = 4\pi \sin\theta/\lambda$ with $\lambda =$ wavelength and $\theta =$ half the scattering angle).

Using this optical arrangement it is possible to obtain a flux of roughly 10^{12} photons/s (at 10 keV) in a 300 µm large spot on the sample. However, for isothermal crystallisation experiments on polymers this flux has to be reduced somewhat in order to avoid radiation damage to the sample.

The sample position is at 48 m from the source. After that there is the optical bench that allows a maximum sample-detector distance of 8 m. This has been described elsewhere [Bras, 1998].

The WAXS detector is of a novel design [Dolbnya *et al.*, 2002]. As mentioned in the introduction this detector was designed keeping in mind that it had to be able to handle very high local count rates and be able to achieve a high dynamical range as well as having good time framing capacities. An extensive description of the design and performance of this detector has been given by Dolbnya *et al.* (2002). Therefore a brief description will suffice here. The design is based upon micro-strip gas chamber (MSGC) technology. The major difference compared to conventional multiwire proportional counters is that here the anodes and cathodes do not consist of planes of wires but are deposited on glass substrates. This allows an accurate positioning of the detecting elements and even more important, they can be placed very close to each other. This reduces the problems of space charge build up inside the detecting gas and allows for a much higher counting rate.

An example of what can be achieved is the development of crystallisation in cordierite glass. This $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ glass was given a double heat treatment in which the first stage ensured that heterogeneous nucleation would take place and the second (isothermal) stage was required for the development of crystallites with the spinel structure in the glassy matrix. This heat treatment results in a fixed number of monodisperse particles (see Fig. 2).

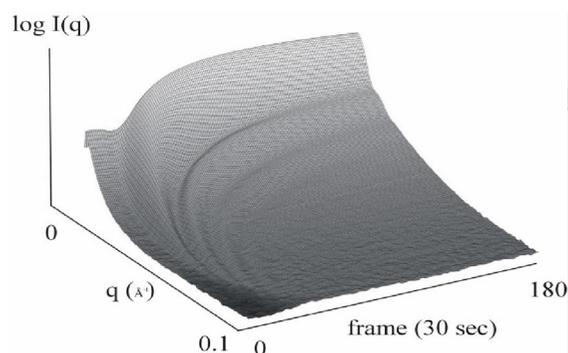


Figure 2

Time-resolved scattering curves of the formation of monodisperse crystalline spinel particles in an amorphous background composed of glass with the cordierite composition. The data was collected in 30 s time frames. The final volume fraction of the spinel particles is approximately 2%.

These SAXS/WAXS experiments have extensively been described elsewhere [Bras *et al.*, 2002]. In Fig. 3 the intensity of a representative WAXS peak of the spinel crystallites is co-plotted with the total integrated intensity on the SAXS detector.

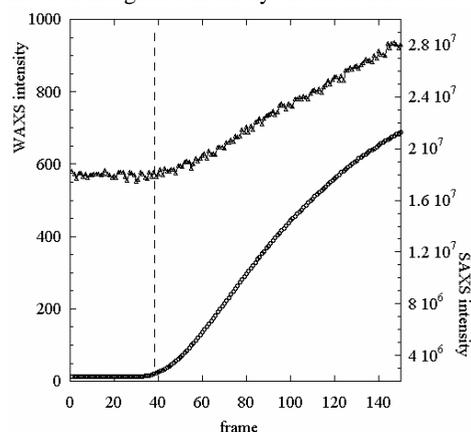


Figure 3

Total integrated SAXS intensity (circles) plotted on the same time-axis as the integrated intensity of a representative peak in the WAXS pattern (triangles) generated by the spinel particles. It can be seen that the increase in intensity in the SAXS range slightly precedes the increase in the WAXS peak. When the radius of the SAXS particles is approximately 40 Å the diffraction peak can be observed.

In Fig. 4 the radius of the spinel crystallites as function of frame number is shown. From our earlier experiments we know that the final crystalline volume fraction is about 2%. (This is corroborated by EXAFS, SANS and Molecular Dynamics experiments [Durville, 1983; Greaves *et al.*, 2002]). Using the fact that we are dealing with a fixed number of particles and taking the ratio of the final particle size to the earliest detectable particle size, we can deduce that a crystalline volume fraction of $V_c = 10^{-4} - 10^{-5}$ is detectable.

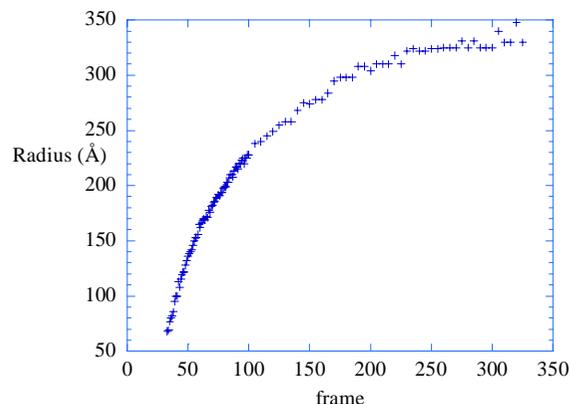


Figure 4

Time evolution of the radius of the spinel particles determined from the data shown in Fig. 2. The radius was determined by fitting a spherical form factor to the individual curves. The accuracy of the particle size is within 2%.

Obviously the situation is less favourable with more weakly scattering samples. In Fig. 5 the results of an isothermal crystallisation experiment on isotactic polypropylene (iPP) are shown. The sample was placed in a Linkam DSC cell [Bras *et al.*, 1995]. Isothermal crystallisation was initiated by rapidly quenching the samples from the molten state to the desired under cooling temperature. See Fig. 5.

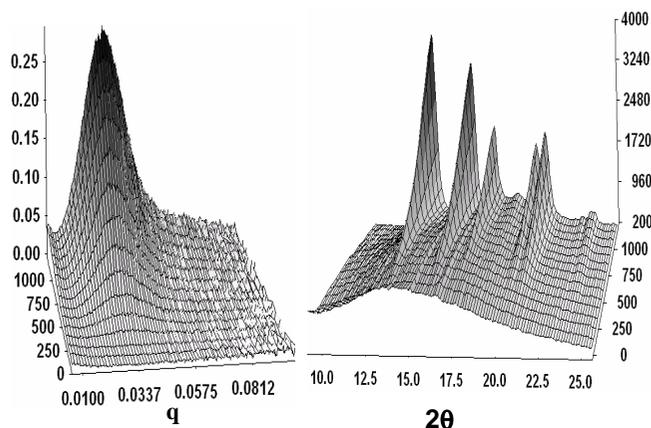


Figure 5

Time-resolved SAXS (left) and WAXS (right) data obtained during isothermal crystallisation of isotactic polypropylene (Daplen iPP, M_w 622 kg/mol). Time frame length 6 s/frame.

The crystalline peaks are superimposed on a high scattering background due to the molten polymer (see Fig. 6) and the electron density differences between the crystalline and amorphous phase are approximately a factor 10 lower than in the case of the cordierite glass. This would suggest that a crystalline volume fraction of approximately $10^{-3} - 10^{-4}$ could be detected. Here we ignore the effect that the temperature will have on the intensity of the diffraction peaks. The temperature difference of about 600 K

between the temperature where the glass was crystallising or where the polymer will crystallise will favour a lower detection limit in the polymeric system [Warren, 1969]. Depending on the degree of under cooling the number of nucleation sites can range from $10^{13} - 10^{16} / \text{m}^3$ [Eder, 2001]. Thus it can be calculated that, assuming an isometric shape of the crystallites, in favourable circumstances crystallites of approximately 10 lamellar stacks thick can be detected. Crystals of that size do not give any Scherrer broadening that would be detectable on the MSGC WAXS detector. The findings on the detectable level of crystallinity in weakly scattering systems have been corroborated by experiments on ethylene oxide-butylene oxide block copolymer solutions in hexane [Heeley, 2002].

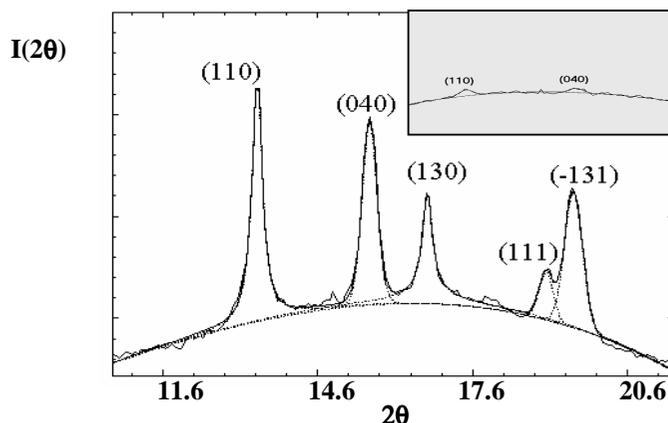


Figure 6

WAXS pattern of the final stage of the isothermal crystallisation experiment on iPP. The inset shows a pattern at the very early stages of crystallisation when only the strong 110 and 040 diffraction peaks are intense enough to be observable above the background.

3. Conclusions

The question what degree of crystallinity can be detected in combined SAXS/WAXS experiments using position sensitive detectors is an important issue in the study of crystallisation kinetics. Using a well characterised glass system that was devitrified by applying a thermal treatment we have been able to show that the detectable volume fraction for samples with a high electron density contrast between the scattering particles and the surrounding matrix is approximately $10^{-4} - 10^{-5}$ and for polymeric samples, with a low electron density contrast this is about $10^{-3} - 10^{-4}$. To be able to achieve this detection at these low levels clearly requires a low noise high count rate position sensitive detector in order to be able to obtain the required statistical accuracy in time scales relevant for the experiment. Obviously this makes the developed equipment suitable for fast time-resolved experiments as well.

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