

W. Bras¹
Y.K. Levine²

¹ Netherlands Organisation for Scientific
Research (NWO)
DUBBLE@ESRF
BP220 Grenoble F38043 France

² Computational Materials Science, Debye
Institute, Ornstein Laboratory
P.O. Box 80.000, 3508 Utrecht, The Netherlands

Soft Condensed Matter Experiments Using Synchrotron Radiation

Abstract

The intense and well-collimated X-ray beams that can be generated by using synchrotron radiation have had a major impact on polymer science in the last decade. We give here a brief overview of the opportunities for polymer scientists when using such devices, and describe some experiments that have been performed. In addition, the advantage of having better access to this resource by operating a 'national' beam line at a larger institute will be discussed.

Key words: polymer science, synchrotron radiation, X-ray beams, SAXS, WAXS.

Introduction

The intense, energy-tuneable and highly collimated X-ray beams that can be generated at synchrotron radiation (SR) sources have been very beneficial to soft condensed matter research in recent years. The traditionally applied techniques of small- and wide-angle X-ray scattering can now be routinely performed in a time-resolved mode, whilst techniques like tomography [1] and coherent scattering [2, 3] have lately started to yield results as well.

Although generally overlooked, one of the most important aspects of the new generation of SR sources is that it has become feasible to construct beam lines with tuneability of the wavelength. At most older facilities, the X-ray scattering beam lines had a fixed wavelength due to the requirement of optimising the flux on the sample. With the new generation of equipment, the X-ray brightness is so high that one can afford to sacrifice photons in order to implement less efficient monochromators, which nevertheless can have variable X-ray energies. The tuneability allows the wavelength to be matched to the experiment. This means, for instance, that for very thin samples one can lower the wavelength in order to retain an acceptable scattering cross-section. For experiments where the sample environment itself is the cause of a large X-ray absorption (e.g. pressure cells), the energy can be increased in order to raise the penetration power.

Even in this situation, where the beam lines are not optimised for photon flux, it

is not uncommon that samples used in time-resolved experiment, where the sample is exposed to the X-ray beam for a considerable time (> 10 minutes), suffer from radiation damage.

Micro-focus beam lines can now generate beam sizes of around 2 microns and still have a flux that is higher than a rotating anode generator [4]. Also, the option of using optical elements in order to generate highly parallel monochromatic beams that extend over several centimetres in space make it possible to perform tomography on soft condensed matter samples, making it possible to follow the changes in microscopic structures as a function of externally applied forces, for instance, in the deformation of polyurethanes under mechanical pressure [1].

The use of scattering techniques has *inter alia* made a major contribution to the revival of the field of polymer crystallisation [5, 6, 7]. One question that can now be addressed is that of the events that take place during the early stages of the crystallisation process. The combination of time-resolved SAXS and WAXS can contribute to the answer to the question of what exactly the crystallisation mechanism is. However, it should be noted here that scattering experiments can elucidate the process, but are incapable of providing the ultimate answer.

An important aspect of synchrotron radiation sources is not only the experimental possibilities that they allow, but also that access to the facilities should be possible. Beam lines are often oversub-

scribed, and in some cases by many factors. Traditionally the Netherlands and Belgium have been relatively large users of SR facilities. When the decision was made to take part in the ESRF, it was also recognised that the public beam lines would not be able to satisfy the demands from these two communities. It was therefore decided to use the option that the ESRF offers to use a bending magnet port to construct a 'private' beam line [8, 9]. This has increased the productivity of the Dutch-Flemish research community, and increased the cost-effectiveness of the investments in the ESRF considerably.

Materials and Methods

The Dutch Belgian Collaborative Research Group (DUBBLE CRG) at the ESRF use the bending magnet radiation from a BM26 dipole magnet. Two beam lines have been constructed. One of these (BM26A) is dedicated to X-ray spectroscopy experiments. Recently the options to perform simultaneously time-resolved SAXS and WAXS experiments here have been undertaken as well. Here we use the quick scanning EXAFS mode, making it possible to work at time-resolutions of 5-10 seconds/data frame.

The second beam line (BM26B) is dedicated to fast time-resolved SAXS/WAXS experiments. It is a multifunctional beam line, but is mainly used for soft condensed matter experiments. For X-ray scattering experiments, the useable energy range ranges between 6 and 15 keV. The beam size in the focal spot is about 300 microns in diameter, and the maximum flux is 10^{12}

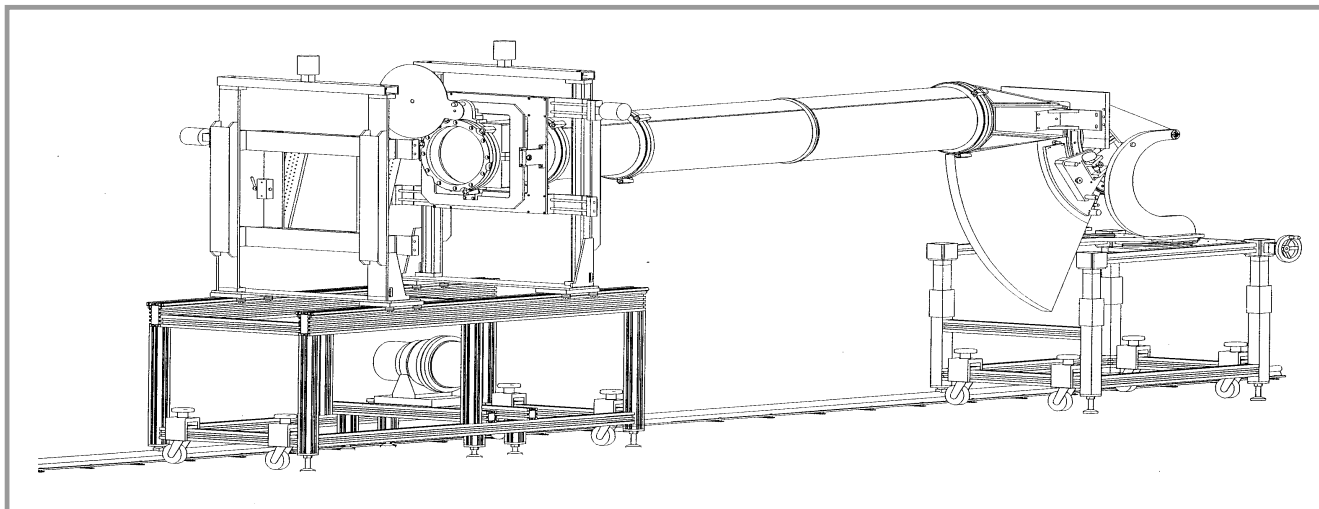


Figure 1. The optical bench of the SAXS beam line at BM26B of the ESRF. Picture courtesy of P. Lassing (NIKHEF-Amsterdam).

photons/sec (10keV) [9]. The low-angle resolution is such that Bragg spacings of 400 nm (real space) can routinely be resolved. In exceptional conditions, 1.4 microns has been resolved [10]. Experiments down to millisecond time resolution have been performed.

Nowadays a crucial property of this type of beam line is the option of installing complicated and often large sample environments. This calls for a flexible and spacious experimental hutch and appropriate services. So far, many different types of sample environments have been utilised on BM26B. This can range from a small on-line Differential Scanning Calorimeter [12] to large polymer extruders [11] and Reaction Injection Moulding machines [13]. More esoteric equipment such as flame chambers (required for the study of soot formation in open flames) or 30 Tesla pulsed magnets can be mentioned as well.

Another important issue is the question of which type of detector to use. For SAXS experiments, this is in general less of a problem than stated in the literature. The basic fact is that in an SAXS experiment, the scattering curves are in general mapped over a large number of pixels, and so it is not very difficult to achieve the required statistical accuracy by integrating. Only when experiments have to be performed at time-resolutions faster than 1 sec/frame, or when the dynamic range in the scattering curve exceeds the 16 bits (strongest/weakest = 64,000/1), or when one wants to detect a very weak signal on a high background, specialised detectors must be used [14]. However, the situation is different for

WAXS, or low-resolution powder diffraction, where the diffraction features are mapped upon only a small amount of pixels. Here one can integrate over only a few pixels, and it is thus hard to obtain an appropriate statistical data quality. The generation of a sufficiently intense X-ray beam is not the main problem here, but the ability to detect the scattered photons is. Therefore we have developed a detector which can handle a very high local count rate in order to detect the WAXS patterns.

When beam line BM26B at the ESRF part of the DUBBLE project [8] was designed, this was recognised as an important issue [9], and consequently a large development effort was made to design a detector that would be able to cope with the requirements outlined above [15]. Using Micro Strip Gas Chamber technology (MSGC), which so far has mainly been used in high energy physics experiments, we have succeeded in constructing a very high count-rate curved WAXS detector [16] system with a spatial, or angular, resolution sufficient for the study of the relatively broad WAXS peaks that semi-crystalline polymers generally exhibit.

■ Experiments

Many of the experiments on polymer morphology and polymer crystallisation that have been performed on BM26B are well documented, and can be found on the web page of the DUBBLE project [17]. For instance, the importance in polymer crystallisation studies of the use of a very high count rate WAXS detector is

shown in [5, 9]. The minimum crystallite size that can be resolved is around 5-10 lamellar spacings. Below this size, the signal-to-noise ratio in the WAXS peaks falls below the level when it can generate reliable results. One of the main reasons for this is the Scherrer broadening of the peaks due to the finite crystallite size [9]. One can thus state that the experimental technology has brought the experiment as far as physically possible. What happens in the even earlier stages at the molecular level is not detectable by X-ray scattering methods.

Experiments on block co-polymer morphology, either in the quiescent state or in an external force field, such as shear, also make up a large part of the experiments that have been performed [18, 19]

High-resolution studies of photonic crystals made up of colloids are another field of research that has been pushing at the limits of what kind of experiment can feasibly be carried out. For this type of work, it is required that scattering patterns be detected at very low angles. This requires a high collimation and a high-resolution detector [10, 20]. It was shown in this work that by using a conventional transmission geometry it is possible to resolve Bragg spacings down to 1.4 micron. This is a range that using X-ray is normally only resolvable by using Bonse-Hart geometry. A great disadvantage of the latter technique is that time-resolved experiments are not feasible.

The real challenge of modern SAXS/WAXS beam lines, when used in the field

of polymer research, is to be able to accommodate the large range of sample environments required in the study of polymer processing and fundamental research, that requires for instance high pressure, high magnetic or electric fields, as well as the implementation of combined experiments, not necessarily based on X-rays. For the latter, we may consider the additional information that can be obtained via simultaneous light scattering [21], Raman scattering [22] or Fourier Transform Infrared spectroscopy [23].

An example is the behaviour of soft condensed matter in high magnetic fields [24, 25]. With the recent advances in superconducting magnet technology, it has become really feasible to utilise magnetic fields to influence the crystallisation and final morphology of even weakly diamagnetic samples.

The behaviour of nematic liquid crystals in rapidly changing magnetic (and electric) fields is a well-studied field, due to the industrial importance of liquid crystalline-based displays [26, 27]. However, certain classes of smectic liquid crystals have the optical characteristic that the director of the liquid crystal only has to be rotated over 45° instead of 90° to switch from a completely opaque to a transparent state, thus allowing a faster switching when used in an LCD display. In contrast to the case of nematics, very little is known about the behaviour of smectics in such circumstances. We have carried out a study of the model liquid crystal 4-octyl-4'-cyanobiphenyl (8CB), which was mechanically rotated inside a magnetic field of 7 Tesla, and performed time-resolved SAXS experiments [28]. The requirement to utilise a 250-kg split-coil superconducting magnet which has to be positioned on the beam line with an accuracy of 50 microns is an example of the complications that can arise when one wants to use such sample environments which occasionally must be used when studying soft condensed matter on a modern synchrotron radiation beam line.

The temperature was set so that the sample was in the smectic-A phase. Several interesting results were obtained. When rotated over an angle of $\leq 45^\circ$, it looks at first as if the sample rotates as a single domain, which is evidenced by the fact that the original diffraction peaks, although initially diminished in intensity, did not split up. In addition, the absolute

value of the scattering vector and the peak shape were not altered. A change in the value of the scattering vector would (for instance) indicate the presence of a smectic-C phase, whilst a broadening of the peak would indicate the presence of a more disordered nematic phase. The presence of such intermediate states could be ruled out. In Figure 2 we show the angular position of the peaks, which is equivalent to the angular deviation that the director has with respect to the original position.

Two important observations can be made. In the first place, the samples do not rotate back to the original position within the time scale of the experiment. This can take several hours. A second observation can be made, that at certain temperatures the sample actually rotates back, i.e. against the direction in which the mag-

netic field should force the material to move.

For rotations over angles $>45^\circ$, the situation is completely different. The rotations are faster by several orders of magnitude than in the experiments with rotations $\leq 45^\circ$, and the samples rotate back to their original position. Furthermore, the samples break up in several domains. The summation of the diffracted intensity of these domains is initially much lower than the original intensity, and only becomes comparable with the original intensity again when the sample has returned to the equilibrium position. This can partially be attributed to the fact that part of the material rotates out of the diffraction plane. However, it is unlikely that this effect is the main reason for this diminished intensity, since the rocking curve of the material is rather broad. Thus a large part

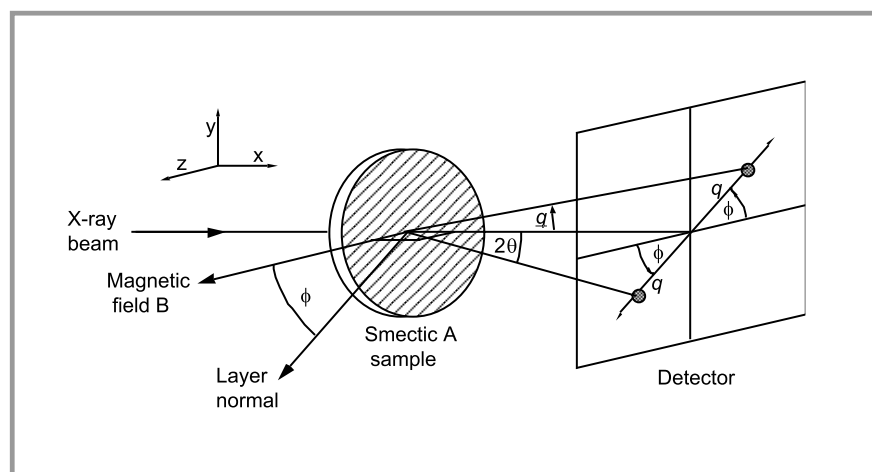


Figure 2. The experimental configuration and scattering geometry used in the experiments on rotating smectic-A liquid crystals. Figure courtesy of J. Seddon.

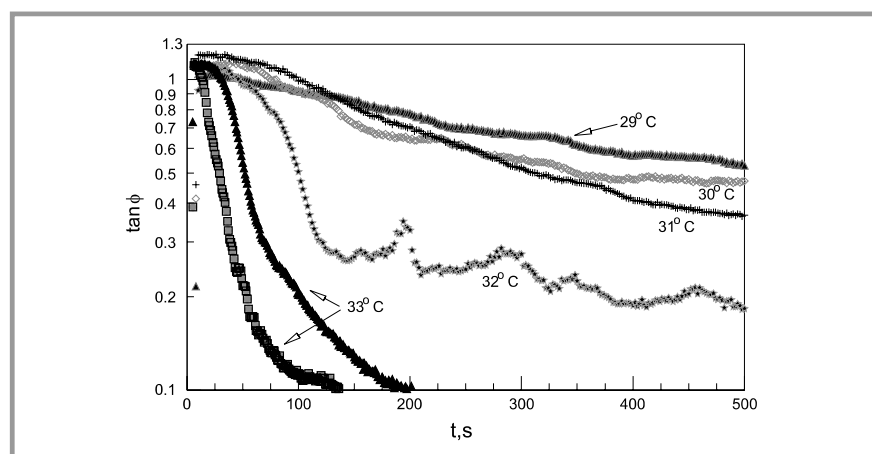


Figure 3. Angular position of the main smectic-A liquid crystal domain after a rotation over 45° as a function of time. The vertical axis is given as tangent, so that comparisons can be made to the case of nematic liquid crystals where this is conventionally used. The curve for the experiments performed at 32° shows the counter rotation that is often observed in these experiments.



Figure 4. The position and intensity of the liquid crystal domains after a rotation over 90°. The vertical axis is the time axis, and the horizontal one the angular position from 0 - 360°. The way the data was derived is described in the text above.

of the material would have to rotate out of the plane by more than 10° without a driving force in this direction, which is an unlikely event. However, there is even more convincing evidence that the reduction in intensity is caused by a partial disordering of the material, as will be made clear below.

The result of a representative experiment is shown in Figure 3. Here we plot the angular position of the different spots as a function of time. This graph was obtained by performing the integration

$$I(\phi, t) = \int_{q_{\min}}^{q_{\max}} I(q, \phi, t) dq.$$

It is clear that the sample does not rotate as a single domain, since in that case only two spots following the same trajectory would be observed. Evidence that the changes in intensity cannot be due to out-of-plane rotation is provided by the fact that in nearly all experiments transient domains arise at 45°. The material at that orientation is clearly not at equilibrium. Nevertheless, these domains can persist for many minutes before finally rotating back to their original position. It is very unlikely that the domains which rotate out of the plane will subsequently rotate back in the diffraction condition, remain in this position for a long time, and only then start to rotate back to the equilibrium position.

The results above suggest that after rotation the sample partly disorders, upon which the remaining fragmented domains

experience less hydrodynamic drag, and then ultimately become free to rotate in a rather turbulent fashion. This is supported by the observation that as soon as the main domain starts to move, diffraction intensity can be seen building up at the equilibrium position. This phenomenon is independent of the initial rotation angle.

Conclusions

Regarding the experiments with liquid crystals, it is clear that the rotational behaviour of these materials is a multi-step process. After the rotation, the original monodomain starts to partially disorder. Subsequently, the monodomain splits up into several smaller domains and a partially disordered phase.

These complicated experiments can only be performed with sufficient access to synchrotron radiation beam lines. The large publication output of these 'private' beam lines justifies the extra investment required to be able to operate these instruments. Even for countries with a smaller research budget, it is feasible to form consortia which enable this option.

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