

A Two-Dimensional X-ray Scattering System for *In-Situ* Time-Resolving Studies of Polymer Structures Subjected to Controlled Deformations

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A two-dimensional X-ray scattering system developed around a CCD-based area detector is presented, both in terms of hardware employed and software designed and developed. An essential feature is the integration of hardware and software, detection and sample environment control which enables time-resolving *in-situ* wide-angle X-ray scattering measurements of global structural and orientational parameters of polymeric systems subjected to a variety of controlled external fields. The development and operation of a number of rheometers purpose-built for the application of such fields are described. Examples of the use of this system in monitoring degrees of shear-induced orientation in liquid-crystalline systems and crystallization of linear polymers subsequent to shear flow are presented.

Keywords: WAXS; liquid-crystalline polymers; shear flow; relaxation; polymers.

1. Introduction

The study of the deformation of polymer systems attracts much attention as it allows the polymers to be investigated in the conditions in which they are commonly processed by industrial techniques. In this regard shear flow has been particularly exploited by a number of workers studying polymeric and liquid-crystalline systems (Larson, 1992; Odell, Ungar & Feijoo, 1993; Moldernaers *et al.*, 1993; Gervat, Mackley, Nicholson & Windle, 1995; Kume, Asakawa, Moses, Matsuzaka & Hashimoto, 1995; Keates, Mitchell, Peuvrel-Disdier & Navard, 1996). Wide-angle X-ray scattering (WAXS) is selected as the probe because this provides unambiguous values of orientation and crystallinity in addition to more general structural information. Additionally, X-ray scattering offers particular advantages in comparison with optical probes for studying samples which are optically opaque.

The information available from WAXS studies is much enhanced by the ability to monitor molecular level responses in real time during deformation processes, and this paper presents a diffractometer system called AXIS (area X-ray imaging system) which has been developed specifically for this purpose. For real-time studies AXIS is used in conjunction with a high-flux synchrotron source, such as the facility at CLRC Daresbury (Bliss *et al.*, 1995). Area detectors comprising a solid-state charge-coupled device (CCD) have been developed and tested by a number of workers in recent years (Lumb & Hopkinson, 1983; Fuchs, Wu & Chu, 1990; Keates, 1990; Clarke, Lowe, MacHarrie, Brizard & Rodricks, 1992; Mahendrasingam *et*

al., 1992; Eikenberry, Tate, Bilderback & Gruner, 1992), and one of the first commercially available CCD systems is employed in this work as the detection device to provide the appropriate speed of image acquisition.

Recently, novel X-ray scattering systems have been presented by Bras *et al.* (1995) and Hughes *et al.* (1996). Both comprise simultaneous SAXS and WAXS detection systems using two area detectors, and have been employed in the monitoring of shear-induced phase changes and orientation development of polyethylene in uniaxial extension over a wide range of scattering vectors. The system of Hughes *et al.* (1996) also incorporates a frame-by-frame synchronized video input which allows the sample strain to be calculated, and thus coupled with the structural and orientational information which can be derived from the contemporary X-ray diffraction patterns.

We present an X-ray scattering system (AXIS) whose integrated capabilities extend from these existing systems. It draws together into a single integrated unit the required time-resolving X-ray detection, environment control and automatic data analysis. Simultaneous control of any one of a variety of different sample environment mounts (\$4) with the data acquisition allows accurate association of the structural condition of the sample revealed by X-ray scattering with the physical environment parameters (temperature, shear rate *etc.*). A powerful interpretative high-level programming environment enables the user to set up a rich variety of experiments and sequences of experiments without further modification of hardware or control software. In addition, the integrated acquisition and analysis routines allow meaningful physical data to be

obtained *in situ* directly from the scattering profiles without recourse to additional processing algorithms. The synchronized integration of these functions is achieved using three IBM-compatible PCs linked with a local area network. A schematic representation of the components of the AXIS system is given in Fig. 1. The development of this system has proven a substantial project which was initiated in 1990 and has formed the core of two PhD programs (Keates, 1994; Pople, 1996a).

2. Extraction of physical parameters from diffraction patterns

The principal employment of AXIS is in the quantitative determination of molecular orientation of deformed polymeric and liquid-crystalline samples. The area of the sample exposed by the incident beam is large in relation to such molecular units ($\sim 0.1\text{--}1\text{ mm}^2$) and therefore the orientation data are in the form of global averages. The orientation is quantitatively expressed as coefficients $\langle P_{2n}(\cos \alpha) \rangle$ of a Legendre polynomial series which are obtained from the azimuthal intensity distribution, $I(\alpha)$, at a fixed scattering vector (Mitchell, 1989; Lovell & Mitchell, 1981).

To extract other structural information, such as a correlation length, a linear section of the scattering pattern is required. For this reason the AXIS system is able to extract these portions of the data from the image, as shown in Fig. 2. For other applications AXIS is also able to extract within a high-level programming environment semicircles, quadrants and chords, as well as the fractions shown, each

of which can be positioned or centred at any point in the two-dimensional image field.

2.1. Orientation parameters from azimuthal profiles

The azimuthal profiles, used to calculate the orientational parameters, are primarily corrected for background, polarization and statistical noise.

The partial plane polarization of the synchrotron introduces anisotropy into the azimuthal profiles. This is experimentally corrected by creating an array of normalizing variables, which are established from the intensity trends observed within the azimuthal profile of the scattering ring from a known isotropic amorphous sample, with which all azimuthal profiles are corrected. This also serves to correct for any spatial non-uniformity of response of the detector.

A background level of intensity, which is attributed to a combination of air scattering and thermal noise within the CCD, is subtracted from all points within the profile. No corrections for multiple scattering or absorption are made, as absolute intensity values are not required.

The axis of the orientation is calculated using the symmetry of the full set of scattering data $I(\alpha)$ at a fixed scattering vector, and the orientation parameters $\langle P_{2n} \rangle$ are then calculated according to the theory described above (Mitchell, 1989; Lovell & Mitchell, 1981). The complete series of orientation parameters are available from X-ray scattering data, in contrast to the limited information available from measurements of birefringence and dichroism which yield only $\langle P_2 \rangle$ (Mitchell, 1989). All variables are recorded with the contemporary time and temperature measurements.

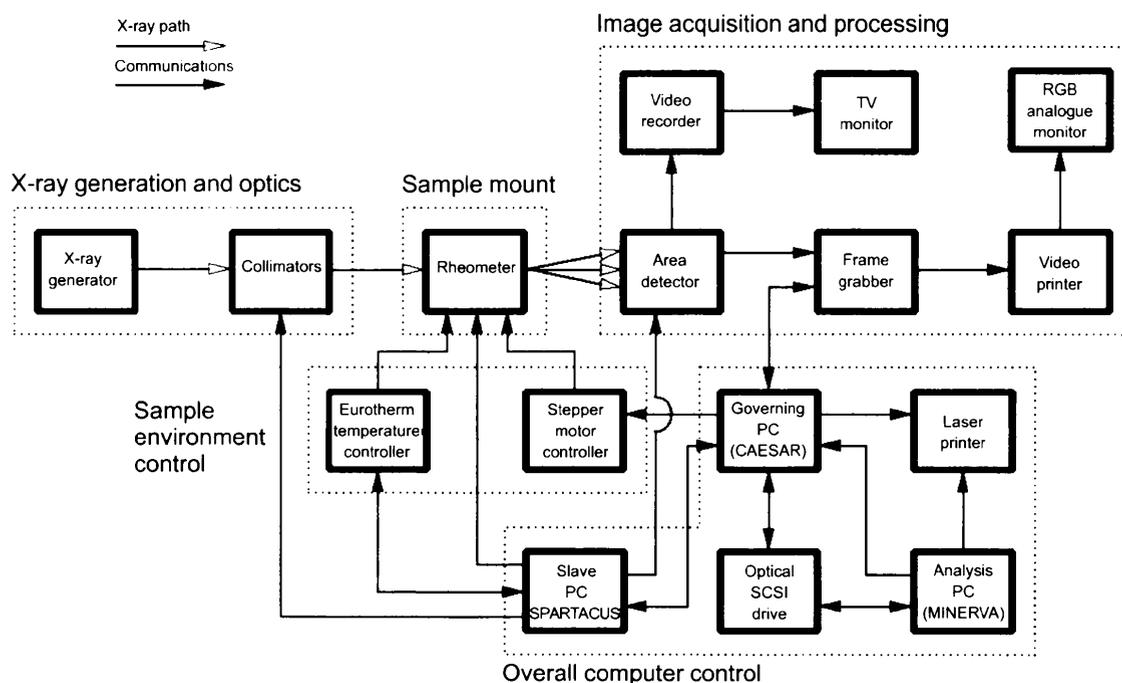


Figure 1
Schematic representation of the components of AXIS.

2.2. Structural parameters from scattering vector profiles

The linear intensity profiles, $I(s)$, shown in Fig. 2, are used to extract structural information. They are firstly corrected for polarization, and also for background and statistical noise in the manner described above. A Gaussian approximation is made to the scattering peak in order to isolate the peak from the other information. The Gaussian curve is then used to define the peak intensity and the scattering vector at which the peak intensity registered (referred to here as the principal scattering vector). The correlation length, l_c , is also established from this curve as

$$l_c = 2\pi/\Delta Q, \tag{1}$$

where ΔQ is the full width at half maximum of the simulated peak. As before, each of these parameters is logged with the contemporary time and temperature.

3. AXIS system hardware

3.1. X-ray area detector

The principal component of the detection system is a 50 mm diagonal area X-ray camera, based on an intensified CCD architecture, designed and manufactured by Photonic Science. Generically, CCD-based area detectors exhibit the fastest available readout times and evidence good

uniformity and linearity of response (Eikenberry *et al.*, 1992).

X-radiation scattered from the sample impinges on the area detector, where a gadolinium oxide scintillating screen acts as a wavelength converter in converting the incident X-rays to visible photons. A tapered fibre-optic bundle transmits the photons to a photocathode, through an image intensifier of microchannel plates, and onto a second scintillator placed before the CCD. Ambient light is excluded from entering the fibre optics by a 10 μm -thick Al foil on the front face of the camera.

The detector can be positioned along its linear rail at distances from the sample of between 25 and 450 mm, to an accuracy of 0.1 mm. For Cu $K\alpha$ radiation this permits the investigation of structural parameters in reciprocal space between vectors of $0.03 < |s|^\ddagger < 2.1 \text{ \AA}^{-1}$ with the detector in its regular position, *i.e.* centred around the non-diverged beam. This scattering vector range is ideal for studying such features as interlamellar spacings and segmental orientational correlations in polymer samples. The detector is also able to be moved radially between angles of $0 \leq 2\theta \leq 90^\circ$ to collect wider angle diffraction, although not all of the azimuthal extent of the scattering data can then be collected.

$^\ddagger |s| = (4\pi \sin \theta)/\lambda$ for radiation of wavelength λ scattered through an angle 2θ .

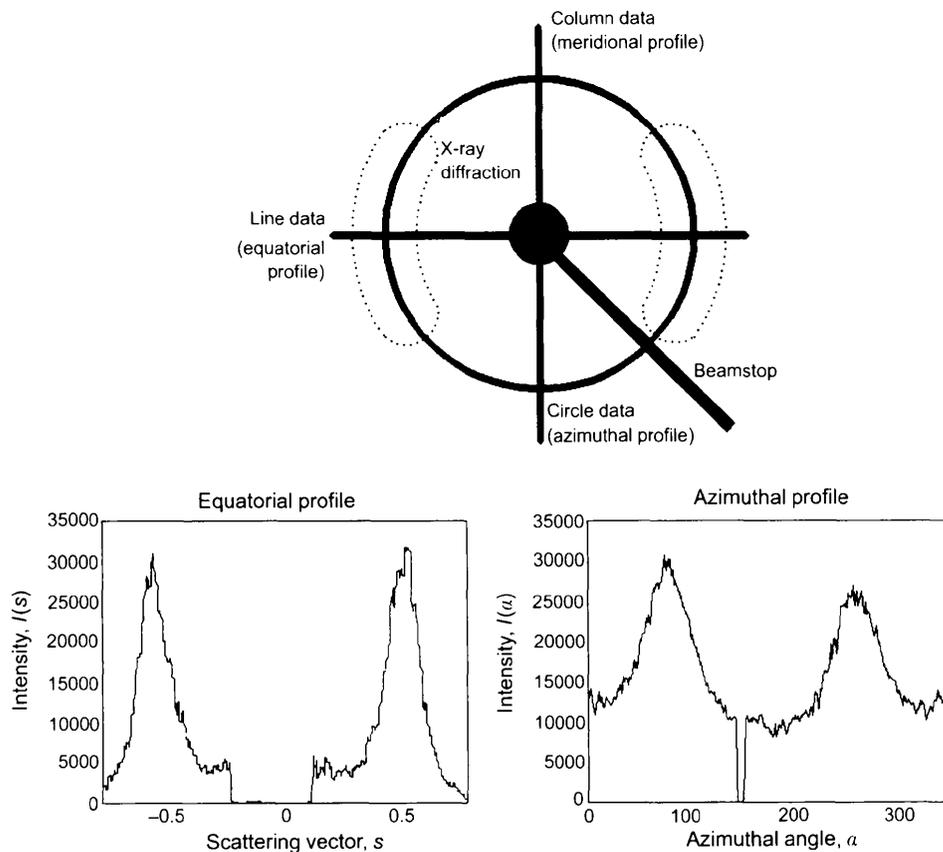


Figure 2

Some of the available profile geometries which can be extracted by AXIS from an area X-ray diffraction pattern. An example of a linear profile, $I(s)$, and an azimuthal profile, $I(\alpha)$, are shown.

Evaluation of the performance of this detector has been undertaken to characterize temporal resolution, linearity and noise effects. The temporal resolution achievable with AXIS is highly dependent on the source flux and the scattering efficiency of the sample employed. Nevertheless, AXIS has the ability to collect and archive diffraction data with a cycle time of 0.6 s. The linearity of the detector is good to within 1.5%, calculated between 25 and 95% of the dynamic range of the device (Keates, 1994). Both linear and angular uniformity are good to within 4% across the spatial extent of the detector; the signal variation is caused by statistical fluctuations in the X-ray intensity rather than any progressive deterioration of response (Keates, 1994).

Noise in the detection system is anticipated from two sources: statistical fluctuations in the X-ray intensity and dark currents within the CCD, the latter of which afflicts all electronic-based detection devices. Measures employed to reduce statistical noise involve designing processing software which excludes the dark-current portion of the signal whilst preserving the full dynamic range of the device, discussed in §5.1. To combat dark currents in the CCD the area detector is cooled to 278 K by a recirculating cooler bath. In addition, the background subtraction mentioned above is incorporated into the analysis software to remove any remaining thermal noise.

3.2. Image-processing hardware

The signal is output from the camera as a standard analogue video signal of 25 lines and 460 columns at 50 Hz. These images are not normally analyzed directly, as the number of X-ray events contained in one 40 ms frame scattered from a polymer system is not usually sufficiently large to have any meaningful information derived from it. For this reason a frame grabber is employed to co-add incoming frames to provide a more intense image with reduced statistical fluctuations.

Image acquisition and processing is performed in the AXIS system using a Data Translation DT2867 integrated image processor. Real-time simultaneous pixel processing is performed at 25 MHz and the 16-bit dynamic range of the device has proven of invaluable use in monitoring deformations of polymer systems. The degrees of orientation developed in linear polyethylene melts in shear flow, for example, are very small: $\langle P_2 \rangle \simeq 0.01$ for shear rates up to $\gamma = 100 \text{ s}^{-1}$ (Pople, Mitchell & Chai, 1996, 1997). Such degrees of orientation, which were anticipated to be small (Bird, Armstrong & Hassager, 1987), were not detectable using an 8-bit imaging processing device which was originally employed in the AXIS system (Keates, Mitchell, Peuvrel-Disdier, Riti & Navard, 1994). The frame-grabber output is displayed on a separate monitor with a variety of display modes including false-colour enhancement.

3.3. Image storage and display hardware

The signal is taken from the camera to a video recorder, which provides an inexpensive method by which all of the

pixel data associated with the area images can be stored on standard video cassettes. This serves the useful function that the video recorder can be used as an input device to the frame grabber, replacing the area-detector camera, and thus pre-recorded experiments are able to be replayed and re-analyzed any number of times. This is a particularly valuable resource in cases where either sample quantity or beam time is limited. A Mitsubishi CP100B(H) colour video copy processor is employed to produce 8-bit colour hard copies of dimension $100 \times 75 \text{ mm}$, such as appear in this paper, in approximately 60 s.

It should be noted that AXIS operates by extracting only the required small fractions of the two-dimensional image from the frame grabber to the control PC (Fig. 2). This has two important consequences. Firstly, it means that the quantity of data transferred to the PC hard drive is very small, maximizing the efficiency of storage and allowing the experiment to run continuously for many hours or days. Secondly, the fact that only very small portions of data are transferred means that data transfer is fast, a key feature in the real-time operation of AXIS. Even though it is only small portions of the two-dimensional image which are transferred to the PC, all of the complete area images are archived to a video recorder in real time, so that any portion of the scattering patterns can be recovered for future analysis.

4. Sample mounts

A number of purpose-built sample environments have been constructed for use with the AXIS system. The simplest of these are a flat plate mount and goniometer, which simply position a sample in the beam path. For more exotic applications, where *in-situ* measurements are required whilst an external field is applied, a number of appropriate mounts have been developed.

4.1. XY translation stage

This stage consists of a mount which is able to be driven to a spatial accuracy of $\sim 0.05 \text{ mm}$ in both the X and Y orthogonal directions (where X and Y are also both orthogonal to the probe beam). This permits the *in-situ* characterization of orientational or peak parameters of a sample held in static ambient conditions over the whole area of the sample, *i.e.* up to maximum dimensions of $300 \times 300 \text{ mm}$. This enables the creation of two-dimensional maps of orientation parameters or axes of orientation over the entire spatial extent of a given sample.

4.2. Oven

A self-contained oven environment has been constructed in which samples can be held at controlled temperatures between 293 and 573 K, within an accuracy of $\pm 2 \text{ K}$. Apertures within the oven walls permit the transmission of the X-ray beam and are covered with 50 mm-thick mica windows to preserve thermal insulation.

4.3. Magnetic stage

This is a mount which has been constructed to hold samples within capillary tubes between permanent magnets which subject the sample to a field of 0.3 T. The sample environment is able to be maintained at temperatures between 293 and 573 K.

4.4. Tensiometer

The tensiometer is a tensile straining device which clamps a sample between two steel jaws and deforms it through symmetric uniaxial extension such that the centre of the sample remains stationary during extension. It is operable in the temperature range between 293 and 573 K, with a stability of ± 2 K over the entire sample, with minimum and maximum deformation rates of 1 and 110 mm min⁻¹. This device has been employed in the study of macroscopic deformation of liquid-crystalline elastomers and in determining the mechanisms by which a monodomain sample oriented in one direction can be caused to adopt an orthogonal alignment under uniaxial extension (Beattie, Lacey, Pople & Mitchell, 1997; Roberts, Mitchell, Davis & Pople, 1996; Mitchell, Davis & Guo, 1993).

4.5. Ambient shearing rheometer

For analysis of polymeric melts and fluids in shear flow a number of shearing cells have been constructed. A prototype was based on a parallel-plate design supported by a steel yolk to hold two circular 3.5 inch-diameter Al plates in the vertical plane. The rear plate is held fixed, with a small circular aperture for the X-ray beam to pass through. The front plate is rotated by stepping motor control to generate the shear field and is milled with radial apertures. All apertures are covered with rigid mica windows. The shear rate, γ , is determined by

$$\gamma = r\omega/t, \quad (2)$$

where r denotes the radius of the X-ray port from the centre of the rheometer plate and t denotes the sample thickness. The rheometer has permitted the study of the development of global orientation in lyotropic liquid-crystal systems subjected to shear flow and in relaxation upon cessation of flow (Keates *et al.*, 1994, 1996; Keates, Mitchell, Peuvrel-Disdier & Navard, 1993).

4.6. High-temperature shearing rheometer

Many polymer samples require to be heated above room temperature in order to access their fluid phase. This fact has prompted the design of a high-temperature version of the original cell in which the two rheometer plates are constructed from steel and are enclosed in an oven environment. Available temperatures range between 293 and 613 K, with a stability of ± 2 K at the intersection with the probe beam. This has extended the range of the polymer samples open to investigation in our research programme enabling the elevated temperature study of shear-induced orientation

in polymer/liquid-crystalline-polymer blends (Tsakalos *et al.*, 1994) and deformations within the nematic phase of thermotropic co-polyesters (Pople, Mitchell & Chai, 1995).

4.7. Low-viscosity shearing rheometer

A third shearing rheometer has been constructed specifically for the purpose of retaining fluids of low viscosity, comparable with that of water, in the vertical plane. The elements of this rheometer are depicted in Fig. 3, with the driveshaft shown in half relative scale to that of the rheometer plates. Temperature control is available from Cu pipes containing circulating heated water, permitting temperatures between 293 and 338 K within an accuracy of ± 2 K to be obtained. This rheometer has been employed successfully in the study of low-molecular-weight liquid-crystal nematics, where it was demonstrated that the director field could be very highly oriented, $\langle P_2 \rangle_D = 0.96$, by shear fields of $\gamma = 1020$ s⁻¹ (Pople & Mitchell, 1997).

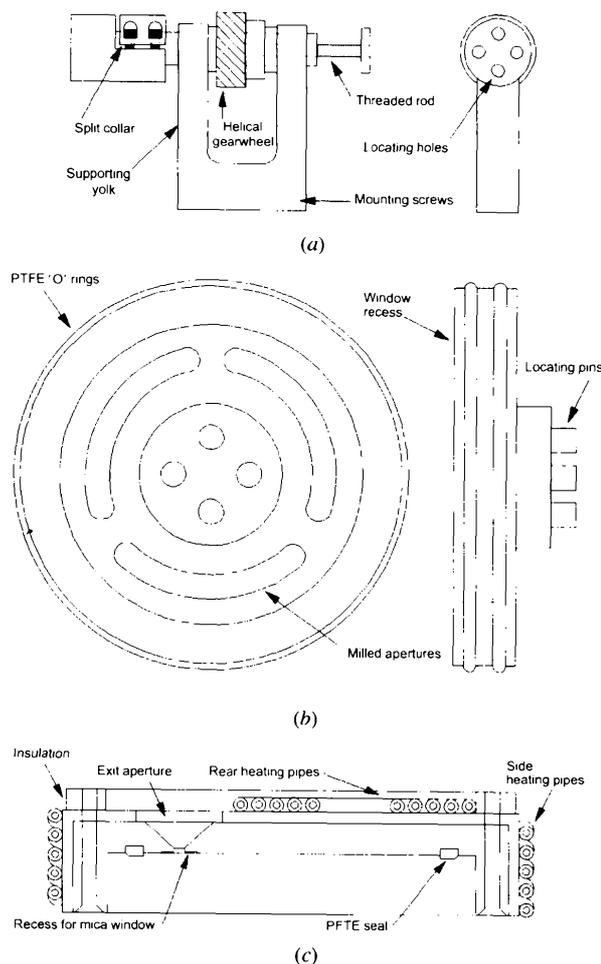


Figure 3 Scaled front and end elevations of (a) the driveshaft and (b) the rheometer plate components of the AXIS low-viscosity shearing rheometer. The driveshaft is shown in half relative scale to the plates. The fixed plate is shown as a cross-sectioned plan (c) with some hidden detail omitted for clarity.

All of the shear cells are driven by a common mechanism: a Unidex stepping motor connected by helical gears to the driveshaft of the given rheometer. The motor is governed by programs, written by the authors, contained within its own intelligent controller, and the capacities of these programs are outlined below (§5.2).

5. AXIS software control

The sum functions of the AXIS software are to regulate the sample environment and specify all parameters concerning simultaneous image collection, processing and analysis, including the archiving and time-stamping of all acquired diffraction data. The user is presented with a single high-level programming environment to control all aspects of operation

5.1. Software control of X-ray data collection

X-ray data collection and sample environment control are achieved with a program which responds to a library of mnemonics and associated syntax, and which can be run in a live mode where the user inputs mnemonics directly from the keyboard, or in remote mode where a previously compiled list of mnemonics is loaded. Using the

remote mode it is possible to run the system unsupervised for hours or days. Control of the sample environment is described in §5.2. The programming syntax is designed so that 'loops' can be used in the experimental execution: a series of commands is typed once in the program prefixed with a loop command which directs AXIS to perform the subsequent set of commands a certain number of times. This allows a lengthy experimental procedure to be conducted with a minimal number of pre-programmed mnemonics. An example of a complete experimental procedure programmed in these mnemonics is given in *Appendix A*.

The integrated image processor contains programmable input and output look-up tables (LUTs). An LUT is an electronically stored table containing an array of numbers which are used in the transfer of incoming intensity values. By appropriate programming of the input LUT the detection system can be configured to operate as either a proportional counting or pseudo photon-counting device, whichever proves more suitable to the given application. The pseudo photon-counting mode can be used to improve the smoothness of the collected data, at the expense of a longer data-acquisition period. A lower setting for the event unit than an average photon intensity allows the frame grabber to acquire an image over a long timescale (an

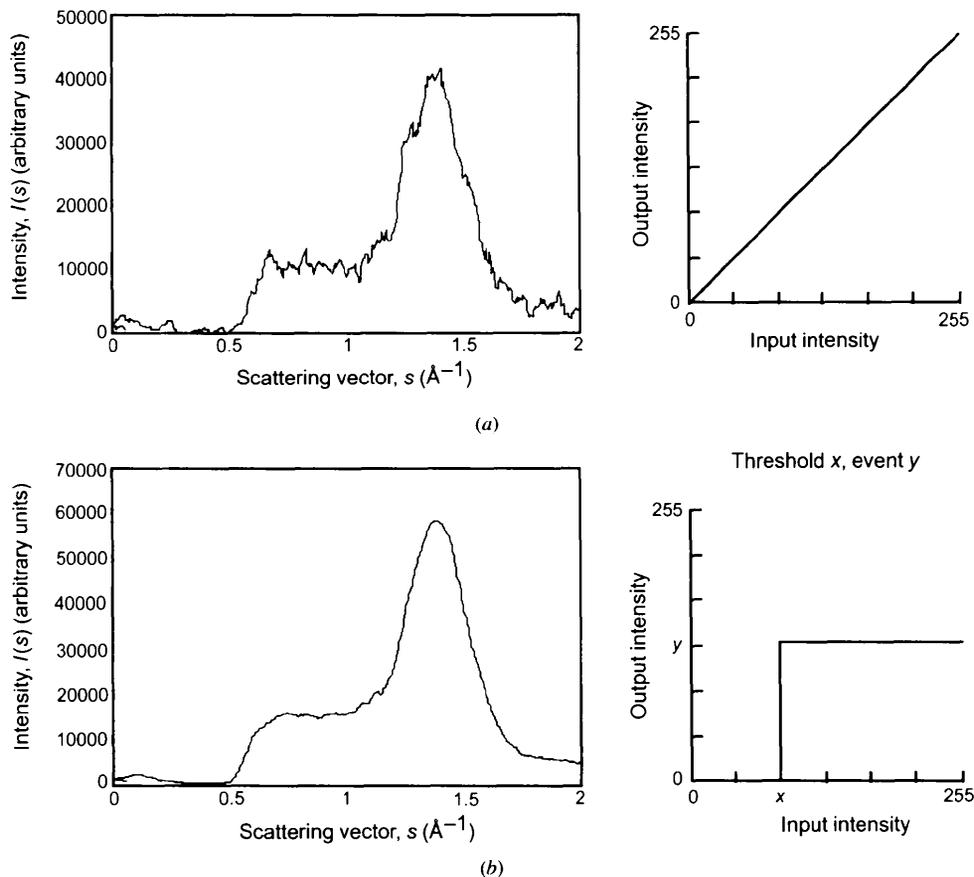


Figure 4

Commonly employed LUT configurations alongside profiles taken from a 1.5 mm polyethylene sample using a laboratory sealed-tube source. (a) True proportional counting mode, integration time $t = 60$ s. (b) Pseudo event counting mode, integration time $t = 900$ s.

hour or more) without saturation. Coupled with a suitable threshold this produces an image with optimized statistics in terms of the signal-to-noise ratio seen in the smoothness of the scattering peaks.

Fig. 4 graphically indicates this argument. The upper graph shows one half of an equatorial intensity profile extracted from a diffraction pattern obtained from a 1.5 mm-thick polyethylene sample obtained in 60 s, using a sealed-tube source in the laboratory. The configuration of the LUT used in obtaining this image is shown alongside. Below is a pattern obtained in 900 s using the event counting mode. The signal-to-noise ratio evidenced is clearly superior to the upper profile, and the smoothness of the scattering data indicates this device as a suitable facility for crystallographic analysis. At a synchrotron source the two images shown in Fig. 4 would be collected in 1 s (upper image) and 15 s (lower image).

LUT programming also provides a method by which dark-current noise can be subtracted. By prescribing a value of zero to all LUT entries below a certain threshold intensity the dark-current noise is eliminated. In addition, by appropriately rescaling the remaining LUT entries above the threshold limit the full dynamic range of the device is preserved, yielding a noise-free 16-bit X-ray detection capability.

5.2. Software control of sample environment

Remote computer control of the experimental arrangement is also achieved from the same single program running within the main AXIS console. This essentially offers the user synchronous control over all driving motors associated with positioning of the detector, collimators and rheometer; thermal control of the temperature of the high-temperature shearing rheometer; and the generation of shear fields from the rheometer motor. This latter task is achieved by serial link connection to a Unidex U100 motion controller. The programs within this device permit the motor to run continuously at shear rates between 0.05 and 4080 s^{-1} , and change direction with a single command. Alternatively, the unit is able to generate oscillatory shear rates of magnitudes $0.05 \leq \gamma \leq 204 \text{ s}^{-1}$ with any of the three shear rheometers detailed above.

A Eurotherm 815 temperature controller provides programmable ramp rates up to 10 K min^{-1} and a tuning sequence which permits the user to retune the instrument's control parameters to suit new process loop conditions. In this way the performance of the device is optimized to reach a given temperature most speedily and maintain that temperature with minimal fluctuation. Tuning to a desired temperature is achieved using a single command from the AXIS control PC.

6. Examples of the uses of AXIS

The principal advantages which the AXIS scattering system offers are the high degree of integration between sample

environment control and X-ray data collection, and the variety of sample fields which can be used in a fully coordinated procedure alongside the X-ray detection apparatus. The following examples are selected to illustrate the versatility of this system and the new scientific data which is made available.

6.1. In-situ measurements of orientation parameters

An injection-moulded ethylene/polypropylene copolymer sample was subjected to WAXS analysis using the AXIS system in order to characterize the degree and direction of molecular orientation throughout its spatial extent. The sample was mounted in the XY stage (§4.1) which allows precision translation of the stage to an accuracy of $\sim 0.05 \text{ mm}$ in both the X and Y orthogonal directions. The effective minimum step size is limited by the beam diameter, which in this case was set to be $\sim 1 \text{ mm}$. The experiment reported was performed in conjunction with the sealed-tube X-ray source in the laboratory and integration times for the diffraction patterns were 50 s (1250 frames). Of course, using a synchrotron beam source it would be possible to reduce the beam size, whilst maintaining sufficient intensity, and thereby increase the spatial resolution of the orientation measurements.

Fig. 5 shows the spatial variation of the global orientation parameter $\langle P_2 \rangle$ (top) and associated director aspect (bottom) from the WAXS diffraction at the user-specified scattering vector of 1.05 \AA^{-1} . The orientation parameter observed here is of relatively low order throughout the sample, *i.e.* $\langle P_2 \rangle < 0.3$ for all points, with its lowest points existing at the constricting walls of the mould due to the resulting turbulence. The director field of the most prominent scattering unit is parallel to the direction of injected flow along the line of injection (point A) and is continuously distorted at more distant locations. The highest levels of orientation in the sample are found to be in the same regions as those in which the director field is most distorted (point B). Theoretical observations in liquid-crystalline systems suggest that the highest degree of stability, and therefore molecular orientation, can be realized in the most heavily distorted regions of a shear flow (Marrucci, 1991; Marrucci & Greco, 1992; Larson, 1993). It is proposed that an analogous situation has been developed in this polymeric flow during the injection-moulding process, where the greater forces developed in the most distorted areas of the flow field yield the highest degrees of local molecular orientation (Fig. 5).

As has been mentioned, the inherent advantage of controlling the experiment in this way is that the AXIS control PC synchronously controls both sample position and X-ray data-collection parameters. This allows features observed within the X-ray data to be related to a user-specified portion of the sample material under software control with a confidence which would be unavailable by a less coordinated scattering system. Additionally, it should be noted that Fig. 5 represents calculated orientation

parameters and director aspects from over 2000 separate diffraction images. To store all of the raw diffraction data would require 2500 Mb using this detector system, yet all of the pertinent information, extracted by the integrated analysis routines, reduces the stored information to a single file of less than 1 Mb.

6.2. Oscillatory shear-induced orientation in hydroxypropylcellulose

AXIS has been used in a number of time-resolving studies of the molecular effects of macroscopic deformation processes in polymer samples. An example is the study of the shear-induced global orientation parameter during

oscillatory shear flow in aqueous solutions of hydroxypropylcellulose (HPC) [a lyotropic liquid-crystal polymer (LCP) system]. These experiments were necessarily performed at a synchrotron source (beamline 7.2 of the SRS facility at Daresbury) with 2 mm-thick samples of 50% (*w/w*) aqueous solutions of HPC (Aqualan L) sheared *in situ* in the ambient shearing rheometer (§4.5).

A special rotating plate was employed which has a milled aperture of 180° azimuthal range to allow continuous transmission of the X-ray beam. The oscillatory nature of the motion was achieved by periodically reversing the direction of the shearing motor. It should be noted, therefore, that this does not result in the simple harmonic velocity profile normally associated with oscillatory shear, but rather a 'square wave' velocity profile in which there are periodic discontinuous changes of velocity from $+v$ to $-v$. These changes are assumed to occur instantaneously.

Previous work in HPC has revealed that the application of continuous simple shear flow causes global molecular orientation to be developed as directors are drawn into the shearing plane (Keates, 1994; Keates *et al.*, 1993). The first-order global orientation parameter, $\langle P_2 \rangle$, is shown to develop as a linear function of the shear rate for shear rates up to $\dot{\gamma} = 1 \text{ s}^{-1}$, and develops as a logarithmic function of the shear rate thereafter (Keates *et al.*, 1993). The transition between the different responses is hypothesized by Keates (1994) to be related to the rheological transition between the Newtonian plateau and the second shear-thinning region, observed by Ernst & Navard (1989) to occur at $\dot{\gamma} \simeq 1 \text{ s}^{-1}$.

Fig. 6 shows the time-resolved development of the first and second non-zero global orientation function coefficients and associated director aspect under this type of oscillatory shear flow at a shear rate of $\dot{\gamma} = 0.09 \text{ s}^{-1}$ over an amplitude of 60°. AXIS collects data using a cycle time of 10 s and therefore the figure reveals information collected from ~ 500 diffraction patterns.

It was anticipated that the degree of global molecular orientation would realize some fraction of the orientation parameter obtained in simple shear at the same shear rate. Fig. 6 shows that, contrary to expectation, the periodic reversals of the flow field produced orientation parameters whose magnitudes oscillated with respect to time. A form of steady-state behaviour has been adopted in that the orientation profile adopts a periodic response which is consistent through time and which exhibits the same period as the motion of the rheometer.

The close integration of AXIS allows the shear-rate profile to be accurately overlaid on the orientation data of Fig. 6. The shear motion is depicted by the broken line varying between magnitudes of $+v$ and $-v$ (Fig. 6). This is of particular importance for the axis of orientation values (displayed in the lower graph of Fig. 6) as it reveals that the change in direction of the rheometer plate coincides with the relatively sudden transition of the director aspect from its most positive to its most negative value, and that the maximum orientation parameters are coincident with the times at which the axis of orientation is close to zero.

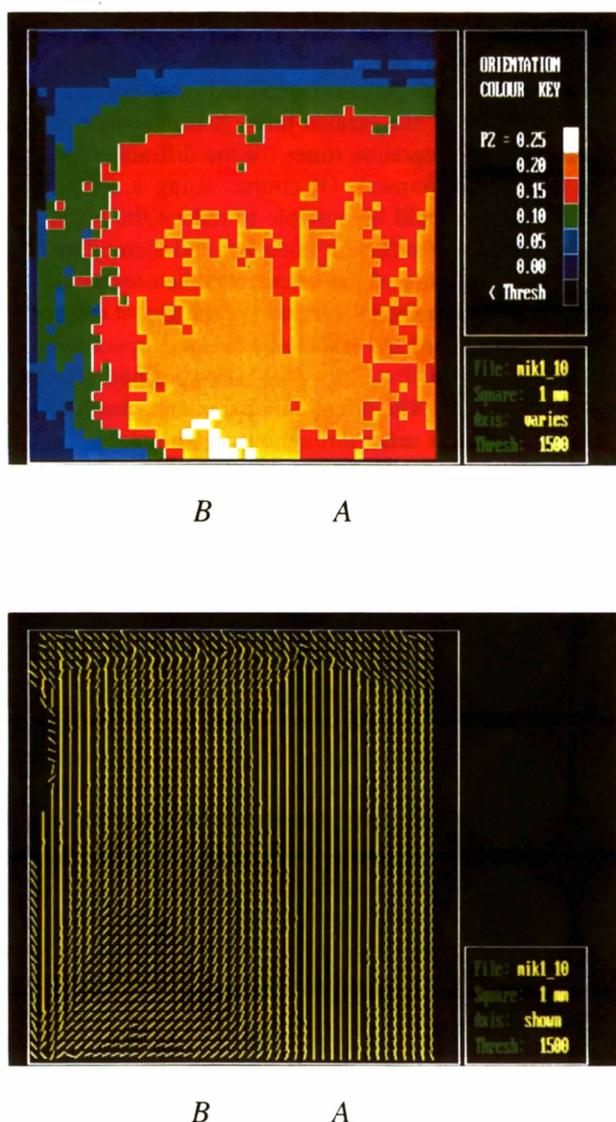


Figure 5

Global molecular orientation parameters $\langle P_2 \rangle$ (top) and associated director aspect (bottom), existent over the spatial extent of an injection-moulded polymer sample at a scattering vector of $|s| = 1.05 \text{ \AA}^{-1}$. Point A indicates the entrance of the injection moulding and B denotes the local region of highest orientation.

These two observations allow the response of the LCP system to the flow field to be understood. The oscillatory nature of the orientation parameter data yielded can be explained in terms of the out-of-plane aspects known to be adopted by the LCP directors in shear flow (Larson, 1993; Marrucci & Maffettone, 1989). It is proposed that the director is tilted in two planes during simple shear flow, and thus when the direction of shear is reversed the directors adopt the same angle to the shear plane but in the opposite sense, *i.e.* leaning in front of the shear plane where before flow reversal they tilted behind it, as illustrated in Fig. 7. (Note that the two directors are not in the same plane as each other, nor are either in the plane of the paper.)

Midway between this transition the directors are aligned in the shearing plane, and therefore the measurement of the orientation calculated from the X-ray scattering, which reveals interactions solely from this plane, increases to its maximum value midway between the transition, in accord with the observed data (Fig. 6).

This leads to the overall conclusion that the sign of the shear rate, as well as its magnitude, is instrumental in determining the oriented texture that develops in shear flow. The profundity of this unusual result is seen in the fact that no theory to date incorporates this parameter in the consideration of the generation of a globally oriented state by shear deformation. These results also indicate

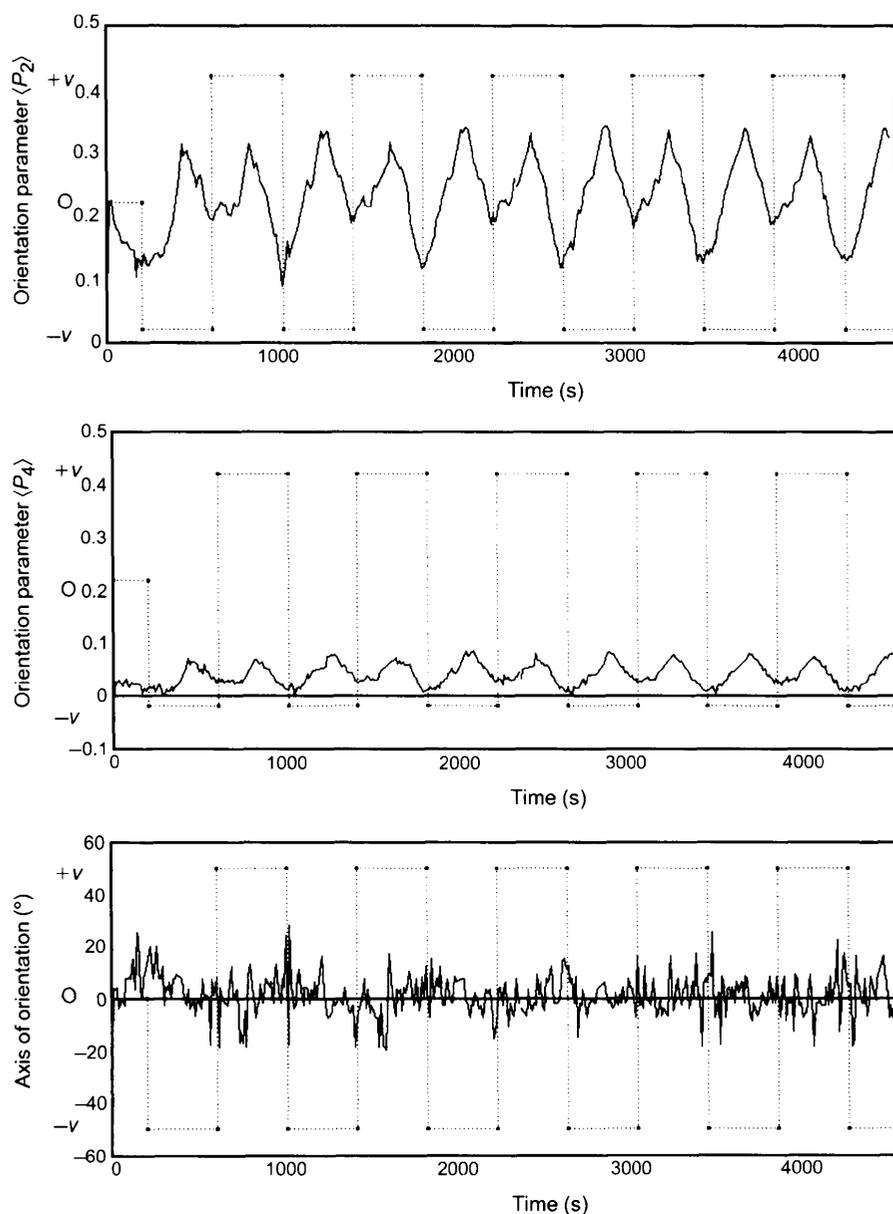


Figure 6 Orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ (top and centre, respectively) and director axes (bottom) developed in a lyotropic LCP 50% HPC water sample subjected to oscillatory shear of 0.09 s^{-1} over an amplitude of 60° . The shear profile of the rheometer is indicated by the broken line. The uncertainty associated with the orientation measurements is ± 0.02 .

the importance of the out-of-shearing-plane interactions in transient flows of LCP systems, which are not available from the X-ray scattering data.

6.3. Crystallization of sheared polyethylene melts

The use of the *in-situ* X-ray scattering probe AXIS has also enabled the continuous monitoring of the development of macroscopic orientation with the imposition of shear flow and the subsequent crystallization processes in polyethylene melts. These experiments were performed on beamline 16.1 of the SRS facility at Daresbury, UK.

Polyethylene discs of 100 μm thickness were sheared in the melt at 443 K for 60 s, and then the temperature of the sample stage was changed rapidly ($dT/dt \approx 20 \text{ K min}^{-1}$) to 393 K at the same time as the shearing was stopped. From the X-ray scattering patterns, AXIS provides, in real time, measures of the global orientation, the level of crystallinity, and the size of the crystals formed, in each case using the (110) reflection.

Previous work has shown that the degrees of orientation developed within the sheared melt were very small, $\langle P_2 \rangle \approx 0.01$, but higher degrees of orientational order, $\langle P_2 \rangle \approx 0.3$, were observed to develop during subsequent crystallization (Pople, Mitchell & Chai, 1997). These patterns, which are characterized by four maxima in the azimuthal intensity profile of the (110) diffraction ring, have been shown to be related to shish kebab morphologies, where the distribution of molecular relaxation times leads to an elongated nucleus chain of high molecular weight surrounded by epitaxial overgrowth of smaller crystalline units (Pople, Mitchell, Sutton, Vaughan & Chai, 1997).

Fig. 8 illustrates the percentage of crystalline scattering measured against the degree of orientation during the

crystallization process (the measurement of the orientation parameters relate to both the crystalline and non-crystalline components of the scattering). It is seen from the fact that the curve is convex in nature that the orientation is the faster developing feature of the crystallization process. This is in contrast to the expectation of the formation of the row nucleated structures which are known to develop under these conditions (Pople, Mitchell, Sutton *et al.*, 1997) in that the later stages of crystallization would be anticipated to involve higher levels of orientation and thus yield a concave curve for the data of Fig. 8. Nevertheless, the *in-situ* nature of the experimental procedure is advantageous in confidently establishing the thermal and deformation history of the sample prior to the crystallization process, and the availability of the time-resolving data is essential in establishing the relative developments of global molecular orientation and degree of crystallinity in the polyethylene samples.

7. Conclusions

AXIS was designed from the outset to provide a single operational environment in order to overcome the limitations of many experimental systems which consider X-ray detection, sample control and data analysis as rather separate items. As a consequence AXIS is a highly integrated system and thereby permits the development of physical parameters extracted from X-ray scattering patterns to be recorded either as a function of time or as a function of the imposed sample environment conditions. Control of both sample environment and X-ray data-collection parameters from a single console allows a given diffraction pattern to be accurately assigned to a given set of sample environment variables. The high degree of data analysis integrated into the data-collection process provides immediate knowledge

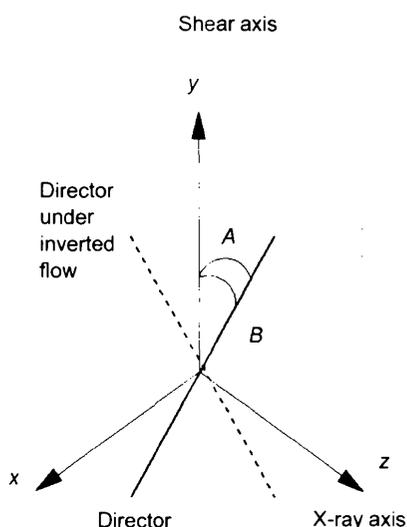


Figure 7

Schematic depiction of the aspect of a global director (solid line) in an LCP system subjected to shear deformation, tilted in two planes at angles A and B. The broken line marks the aspect of the director following inversion of the shear direction.

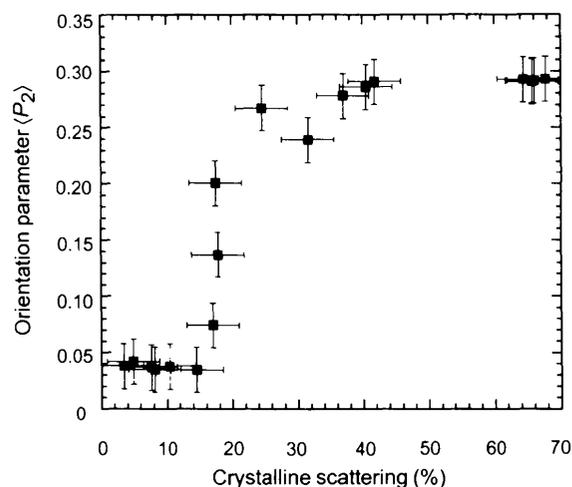


Figure 8

Global orientation developed as a function of the percentage of crystalline scattering during the crystallization at 393 K of a linear polyethylene melt which has been sheared at $\gamma = 8 \text{ s}^{-1}$ for 60 s at 443 K.

of pertinent physical parameters without recourse to additional processing algorithms and greatly reduces the storage requirements of raw data.

The AXIS system therefore proves both a powerful and versatile tool for the *in-situ* analysis of structural and orientational parameters in polymeric systems in non-equilibrium conditions using X-ray diffraction methods, providing data which permit new insights into the shear-induced phenomena of polymer and liquid-crystalline systems. It is found that the availability of time-resolving data during and subsequent to flow is essential in developing an understanding of the complex molecular reorganizations which occur in real processing conditions.

APPENDIX A

Example of operating procedure

In order to illustrate the high-level programming environment available to the AXIS user an example, taken

from a real experimental situation, is given in Fig. 9. The figure shows a typical instruction file used to govern an experiment concerning the *in-situ* X-ray scattering study of a polymer system at high temperature subjected to shear flow using the high-temperature shearing rheometer (§4.6).

The experiment is programmed to monitor the degree of orientation in the sample whilst it is melted by observing the azimuthal scattering intensities of the characteristic diffraction rings of both the crystalline and molten states. Once the sample has been melted it is sheared at a user-specified shear rate whilst information concerning the molecular orientation of the molten sample is continuously collected. The shear field is then stopped and time-resolving data concerning the relaxation behaviour of the shear-induced orientation are monitored. The annotation indicates how the experiment proceeds as each mnemonic is performed.

The example given in Fig. 9 employs only a few of the many mnemonics which are recognized by the AXIS

USER GARFIELD	This block sets all preliminary parameters appropriately. The user is logged on by the USER command, and INIT clears the frame-grabber buffers:
INIT	no accompanying syntax selects default values for references and gain.
LUTS 3 10 50	LUTS selects the photon-counting mode, as shown in Fig. 7, and LUTO determines display settings. SETL with no syntax selects the equatorial profile for analysis when LINE is called, SETC and SE2C select azimuthal profiles at 1.51 and 1.32 Å ⁻¹ , respectively, when CIRC and CIRC 2 are called.
LUTO 9	The Eurotherm is optimized for performance at 170°C (443 K), and directory EXPT1 on the control PC hard drive is selected for data storage.
SETL	Finally PAWS causes the program to wait until any key is pressed.
SETC 1.51	
SE2C 1.32	
TUNE 170	
PATH C:\EXPT1	
PAWS	
STPT 170	The rheometer is set to heat to 170°C (443 K) at a (default) rate of 10 K min ⁻¹ .
LOOP 100	All commands between this point and LEND are performed 100 times.
AVEG 250	A 16-bit image of 250 video frames is accumulated in the frame grabber.
LINE	A linear profile (set to be equatorial by SETL) is taken into the control PC, and stored by SAVL (in directory EXPT1) on the drive as a .LIN file.
SAVL	An azimuthal profile (set at 1.51 Å ⁻¹ by SETC) is taken into the PC, and stored by SAVC as a .CIR file in the EXPT1 directory.
CIRC	An azimuthal profile (set at 1.32 Å ⁻¹ by SE2C) is taken into the PC, and stored by SAVC 2 in the same directory as a .C2R file.
SAVC	The current temperature is stored in a .DAT file which bears the same filename as the .LIN, .CIR and .C2R files.
CIRC 2	
SAVC 2	
TEMP	
LEND	
SHER 1 50	The rheometer begins to shear at a rate determined by equation (2), which for a 1 mm-thick sample is 2.5 s ⁻¹ .
LOOP 20	[Note that should the rheometer have not yet reached 170°C (443 K) as it was set to do earlier, the program will automatically pause before commencing shear until the desired temperature has been attained.]
AVEG 250	Once again a 16-bit integrated image from 250 frames is built up in the processing buffer of the DT2867, and data are extracted and saved by the same following mnemonics. Note that no profile is taken from the 1.51 Å ⁻¹ azimuth, the sample by now having completely melted.
LINE	
SAVL	
CIRC 2	
SAVC 2	
TEMP	
LEND	
SSTP	Shearing is stopped by the SSTP mnemonic.
LOOP 200	Similar linear and azimuthal profiles are once more extracted from the integrated images, which will reveal the relaxation behaviour evidenced by the sample in the rheometer. Note that the temporal resolution of the data collected is 250 frames (10 s), and the AXIS system experiences a 'dead time' of about 2 s whilst all commands in the loop other than AVEG are being performed. The relaxation is monitored for 200 loops; for these loop commands this translates to a time of approximately 40 min.
AVEG 250	This command indicates to the control PC that the experiment is concluded.
LINE	
SAVL	
CIRC 2	
SAVC 2	
LEND	
END	

Figure 9
Typical instruction file.

system in the control of the various rheometric equipment (§§4.1–4.7) and the acquisition of various two-dimensional data profiles (Fig. 2), an exhaustive list of which is given elsewhere (Pople, 1996b). Nevertheless, the example program highlights the high degree of coordination which exists between the control of the sample environment and the data-acquisition processes.

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