Neutron Topography as a Tool for Studying Reactive Organic Crystals: a Feasibility Study

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Abstract

The feasibility of using neutron topography as a non-destructive imaging technique for the study of X-ray sensitive organic single crystals, with a view to applying it to the study of reactivity in such crystals, has been tested. Crystals studied range from relatively X-ray insensitive protonated and deuterated pyrene crystals to relatively highly X-ray sensitive 2,4-hexadiynylene bis(p-toluenesulfonate) (PTS) monomer crystals. The latter crystals are readily polymerized in an X-ray beam. Results indicate that neutron topographic imaging provides little advantage over X-ray topography for either the X-ray insensitive or X-ray sensitive crystals studied here. It was concluded that this is mainly due to limitations in spatial resolution attributed to geometric effects inherent to the technique. However, for X-ray sensitive crystals, neutron topography can provide useful information, in a non-destructive way, in the form of rocking-curve data, and as such can be regarded as a useful 'ally' technique to the analogous X-ray techniques. It is expected that in the case of extreme X-ray sensitivity, provided geometric losses can be minimized, neutron topography may be the only technique capable of non-destructively revealing bulk defect structures and strain distributions.

Introduction

In the past few years considerable effort has been directed towards the understanding of the role of crystalline defects in the reactivity of bulk single crystals. In order that one can carry out such studies usefully, it is necessary to find a non-destructive technique which combines high strain sensitivity with the capability of imaging defects and strain in bulk single crystals. Generally, electron microscopic techniques are not applicable in such studies owing to induced beam heating, the fact that the field of view of the technique is so small, and insufficient strain sensitivity. On the other hand, X-ray diffraction topography (Tanner, 1976; Tanner & Bowen, 1980) (for example the conventional monochromatic Lang technique) is a technique which allows both characterization of the bulk defect and general strain distribution in large (cm$^3$) single crystals prior to reaction and subsequent monitoring of this distribution during reaction, in a dynamic fashion. As such it has found application in this kind of study (Begg, Halfpenny, Hooper, Narang, Roberts & Sherwood, 1983). In many instances reaction-induced bending and strain make it necessary to utilize white-beam synchrotron-radiation topography which by nature has a greater inherent tolerance of lattice distortion than conventional monochromatic techniques. Unfortunately, many of the reactive systems of interest are also X-ray sensitive, which in some cases precludes extensive use of X-ray imaging techniques. In some systems, it has been shown that suitable filtering of a synchrotron beam to remove the generally more highly absorbed longer-wavelength X-rays can reduce X-ray induced reaction (or damage) to tolerable levels (Dudley, Sherwood & Bloor, 1986; Dudley, 1989). However, such methodology would not be applicable in cases of extreme X-ray sensitivity. In these latter systems, there is a need for a truly non-destructive imaging technique analogous to the X-ray topographic technique. Neutron topography is such a technique.

In the past, neutron topography has been applied to, for example, the characterization of crystals which have prohibitively high X-ray absorption (e.g. Baruchel, Schlenker, Zárka & Petroff, 1978). Without a doubt the major thrust in neutron topographic research has been in the area of imaging of magnetic...
structures in materials [for reviews see Schlenker & Baruchel (1986) and Baruchel (1989)] which exploits the magnetic scattering effect due to the interaction of the neutron magnetic moment with the magnetic configuration in the crystal. To date no application of neutron topography to the study of X-ray sensitive reactive organic crystals has been reported. Here we report the first systematic investigation of the feasibility of such applications of the technique.

Two systems were primarily studied: pyrene single crystals (both protonated and deuterated), which are relatively X-ray insensitive, and PTS monomer single crystals which can be polymerized readily in an X-ray beam. These latter crystals are consequently classed as relatively highly X-ray sensitive. The pyrene crystals were studied to enable detailed comparison of dislocation images formed in neutron topography to those already (readily) obtained from these crystals using both conventional and synchrotron X-ray topography. Both protonated and deuterated crystals were studied to assess the influence of the large differences in intensities of incoherent scattering expected from these crystals on topographic contrast formation. The PTS crystals were studied as part of an ongoing research effort investigating their reactivity. Again neutron topographic images could be directly compared with images obtained using synchrotron X-ray topographic techniques [conventional techniques are not feasible in these materials (Dudley, Sherwood, Ando & Bloor, 1982a,b)]. PTS monomer crystals were also studied during in situ UV induced polymerization. Again results from such experiments could be directly compared with those obtained from parallel experiments conducted in situ in a synchrotron X-ray beam.

Experimental techniques

For all systems studied here, neutron absorption is very low, so that neutron-induced reaction is not expected to occur. Consequently, restrictions on exposure times are not necessary.

Neutron topographic experiments, performed on both the S20 and D13 instruments at the Institut Laue–Langevin (ILL), were designed so as to make maximum use of the available neutron flux with minimum resolution loss. The neutron flux is so low compared with typical X-ray fluxes that a high-resolution collimated-beam experiment similar to the Lang technique is not feasible, owing to what could be prohibitively long exposure times. Thus, a ‘Barth–Hosemann’ (Barth & Hosemann, 1958) type geometry is utilized, monochromatization of the incident ‘white’ beam being provided, in this case, by a copper single crystal. However, this type of geometry inevitably implies some resolution loss compared with conventional Lang-type X-ray topographic geometries (or geometries used with synchrotron sources), since specimen–film distances must be made large enough to avoid impingement of the direct beam on the detector. As will now be shown, this increase in specimen–film distance can become significant.

In general, the major factors affecting resolution in neutron topography are as follows [for a review see Baruchel, Malgrange & Schlenker (1983)]: (1) dislocation image width; (2) film converter resolution and associated statistics; (3) geometric resolution; (4) effect of incoherent scattering, compared with coherent. Each of these will be dealt with separately.

(1) The ability to resolve between two adjacent dislocation images clearly depends on the individual widths of the images. The resolving power can never be greater than the sum of the half widths of the two images. It therefore becomes important to consider the influence of image width on optimum resolving power. In neutron topography one is nearly always in the direct, or kinematical contrast, regime as neutron absorption is so tiny for most elements. For many systems, for example silicon (Malgrange, Petroff, Sauvage, Zarka & Englander, 1976), the intrinsic rocking-curve widths in neutron topography tend to be, in general, narrower than those encountered in X-ray topography. Therefore, the distorted regions of crystal giving rise to direct dislocation images on neutron topographs usually tend to be situated farther from the dislocation core, which usually gives rise to wider direct dislocation images. However, as will be demonstrated later, inherent perfect-crystal neutron reflection curve widths are often greater than the corresponding X-ray widths for the systems studied here. Consequently, direct dislocation images might be expected to be narrower on neutron topographs than on X-ray topographs, constituting superior spatial resolution capability, based on strain sensitivity considerations alone.

(2) Statistical errors will always give rise to a resolution which is never better than $\sim 10 \mu m$. This is because with standard photographic detection methods (e.g. Malgrange et al., 1976), $2 \times 10^7$ neutrons need to fall on an area of $1 cm^2$ in order to record a good image. This means that on an area of $5 \mu m^2$ only one neutron may arrive, giving rise to the figure of $10 \mu m$. 

(3) Geometrical resolution can be determined by defining the angular divergence of diffracted rays emanating from a given point in the specimen crystal. This divergence is what gives rise to a ‘blurring’ effect on the detector. Two divergence angles can be distinguished, one in the vertical plane (perpendicular to the plane of diffraction, i.e. the plane defined by the incident and diffracted beam vectors, and the reflection vector) and one in the horizontal (parallel
to the plane of diffraction). Following Baruchel et al. (1983), the vertical divergence of rays issuing from a point in the specimen crystal, $\Phi_v$, depends on both the vertical divergence 'seen' by the first crystal, $\alpha_v^0$, along with the vertical mosaicity, $\eta_m^v$, of the first crystal, according to

$$\Phi_v = \left[ (\alpha_v^0)^2 + (\eta_m^v)^2 \right]^{1/2}.$$  \hspace{1cm} (1)

On the other hand, the horizontal divergence of rays issuing from a point in the specimen crystal, $\Phi_h$, depends on the diffraction geometry, and is given by

$$\Phi_h = a \alpha_h^0 \eta_{hm}^h / \tau,$$

where $a = \tan \theta / \tan \theta_m$, $\alpha_h^0$ is the horizontal divergence of the incident 'white' beam, $\eta_{hm}^h$ is the horizontal mosaicity of the monochromator, $\tau$ is the half width of the experimental rocking curve of the sample crystal, $\theta_s$ is the Bragg angle of the sample crystal, and $\theta_m$ is the Bragg angle of the monochromator.

(Note that in the case of a neutron guide, the divergence $\alpha_h^0 = \alpha_v^0$ results from the critical angle of total reflection on the nickel coating of the guide.)

It can be shown (Baruchel et al., 1983) that

$$\tau = \left[ (2 - a)^2 (\eta_{hm}^h)^2 + (1 - a)^2 (\alpha_h^0)^2 + (\eta_h^s)^2 \right]^{1/2},$$

where $\eta_h^s$ is the horizontal mosaicity of the sample.

Minimization of this function is achieved at a value of $a = 1.27$. The mosaic spread of the copper 111 reflection which was most commonly utilized was $-8^\circ$, and a typical value for $\alpha_h^0$ is $-13^\circ$. If $\eta_h^s$ is effectively zero for the crystals studied here (this is a valid assumption in all cases except that involving studies of a crystal undergoing in situ UV-induced polymerization), this yields a minimum attainable value of $-6.8^\circ$.

In general, the desire to minimize the influence of such geometrical factors on spatial resolution imposed serious geometric restrictions on the experimental design. Unfortunately, in some cases configurations leading to the desired value for $a$ could not be accessed owing to both crystallographic and spatial constraints, which would have caused unavoidable resolution loss. Because of the significance of these effects, criteria used in selection of diffraction geometries will be discussed in a separate section.

(4) Background noise resulting from a large intensity of incoherent neutron scattering is expected to contribute to resolution loss in neutron topography. A comparison of neutron topographs recorded from protonated and deuterated crystals is likely to demonstrate this effect, with the deuterated crystals expected to provide the cleaner image, with consequently higher effective resolution.

Typical figures for overall resolution [obtained by taking the square root of the sums of the squares of all these contributory factors, i.e. (1) to (3); the effect of (4) is rather more difficult to define quantitatively, and will only be considered qualitatively here] are of the order of 60 $\mu$m.

**Materials**

(a) Pyrene

Pyrene crystallizes in the monoclinic system with space group $P2_1/a$ (Wyckoff, 1963; Camerman & Trotter, 1965). The unit-cell parameters are $a = 13.6$, $b = 9.24$, $c = 8.47$ Å and $\beta = 100.28^\circ$. The molecular structure of pyrene is shown in Fig. 1(a). In the crystal structure, these molecules, which are planar, lie in parallel pairs at approximately $40^\circ$ to the $ab$ plane.

Large colorless ($10 \text{ cm}^3$) crystals of both protonated and deuterated pyrene (maximum impurity content 100 p.p.m.) were grown on previously prepared seeds by slow cooling of a saturated toluene solution (Hampton, Shah & Sherwood, 1974; Hooper & Sherwood, 1976). The tabular crystals exhibited well developed {110}, {001} and {101} faces. For the purpose of these experiments a tabular sample was cut parallel to the (001) plane using a solvent saw (see Fig. 1b). The section was cut so as to include the seed, so that the dislocations which propagated towards the {110} faces could be readily imaged.

(b) PTS

The diacetylenes are a unique class of compound which undergo a single-crystal-to-single-crystal

![Fig. 1. (a) Molecular structure of pyrene. (b) Schematic representation of the morphology of an as-grown protonated pyrene crystal. The slice studied here contains the seed crystal, indicated by S. Growth sector boundaries are denoted by G.](image-url)
polymerization. This can be achieved radiolytically, photolytically, thermally or mechanically. The polymerization is incurred via the rotation and subsequent adjoining of the monomer units (see Fig. 2a). A series of diacetylenes have been studied but results presented here concern 2,4-hexadiynylene bis(p-toluene sulfonate) (PTS). The molecular structure for the side group, R, for PTS is presented in Fig. 2(b).

PTS monomer was purified by successive recrystallizations from pure acetone. Single crystals (1 x 1 x 0.5 cm) were grown by slow controlled evaporation of saturated acetone solutions at 270 ± 0.5 K (Dudley, Sherwood, Ando & Bloor, 1983).

The resulting monomer crystals were pale pink in color and exhibited the morphology consisting of face forms {100}, {001} and {111} shown schematically in Fig. 2(c). They were transparent and free from visible imperfections.

Both PTS monomer and polymer crystallize in the monoclinic space group \( P2_1/c \) (Kobelt & Paulus, 1974; Bloor, Koski, Stevens, Preston & Ando, 1975) with the following lattice parameters: monomer: \( a = 14.60, b = 5.15, c = 15.02 \) Å and \( \beta = 118.4^\circ \); polymer: \( a = 14.49, b = 4.91, c = 14.94 \) Å and \( \beta = 118.14^\circ \).

**Selection of neutron diffraction geometries**

Generally, only transmission geometries were sought as the overall bulk defect structure of the crystals was of interest rather than near-surface structures. Criteria used in selecting diffraction geometries for the neutron topographs include:

(a) Accessibility; obviously not all reflections are accessible in the transmission Laue geometry. This can be assessed in a quantitative manner by computing the angle between the incident beam and the outward-drawn normal to the specimen entrance surface and that between the diffracted beam and the outward-drawn normal to the specimen exit surface. Obviously if either of these angles is greater than 90° then the reflection is not accessible in transmission. In addition, the condition \( \lambda < 2d \) must also, of course, be satisfied.

(b) Minimization of resolution losses; this is achieved through (i) minimization of \( \tau \) from (3), by choosing geometries with \( \alpha \) values close to 1.27, and (ii) choosing reflections with relatively large Bragg angles (small \( d \) spacing) so that specimen-film distances do not have to be excessively large to avoid impingement of the direct beam on the detector.

(c) Maximization of diffracted intensity; achieved through choice of high-structure-factor reflections (note also that, since inherent perfect-crystal reflection curve width is proportional to the structure factor, high-structure-factor reflections generally give narrower 'direct' dislocation images, improving the effective resolution of dislocation images).

(d) Correspondence with X-ray reflections; if possible, neutron reflections were chosen which also had both large X-ray structure factors and relatively broad inherent perfect-crystal X-ray reflection curve widths, so that neutron and X-ray images might be compared. The situations for pyrene and PTS will be discussed separately.

The neutron wavelengths mainly employed were 1.7 and 2.0 Å, to a certain extent determined by current flux availability (the neutron topography facilities were downstream from several other experiments which could tend to deplete the intensity, at a given wavelength, delivered to the topography station). Table 1 lists diffraction parameters considered in the selection of neutron diffraction geometry for the protonated pyrene crystal. The parameters listed are \( d \) spacing, neutron structure factor, product of X-ray structure factor and classical electron radius, the angle \( \varphi \) between the pole of the reflecting plane and the pole of the specimen surface, the \( a \) factor for the most commonly used
neutron wavelength (1.7 Å), and the Bragg angle and inherent perfect-crystal X-ray reflection curve widths at this wavelength, as well as the inherent perfect-crystal X-ray reflection curve widths at the two X-ray wavelengths employed in topographs presented here [A(Mo Kα1) and 0.5 Å]. The standard equation, from dynamical theory, used to calculate the inherent perfect-crystal X-ray reflection curve width is

$$\delta X(\lambda) = \frac{2|C|RA^2F_{hkl}^N}{\pi V\sin 2\theta_B} \left( \frac{\gamma_h}{\gamma_0} \right)^{1/2},$$

where C is the polarization factor, R is the classical electron radius, $F_{hkl}^N$ is the observed X-ray structure factor, obtained from Camerman & Trotter (1965), V is the unit-cell volume, and $\gamma_h$ and $\gamma_0$ are the direction cosines of the incident-beam vector and diffracted-beam vector respectively, with the inward-drawn entrance surface normal.

For the case of the X-ray topographs presented here, which are Lang topographs recorded using conventional X-ray sources, the polarization factor in (4) is the average value of (1 + cos2$\theta_B$)/2. For those which are synchrotron topographs with diffraction occurring in the vertical plane, $C = 1$, and for those with diffraction occurring in the horizontal plane, $C = \cos 2\theta_B$. The average polarization factor is used in calculating the values presented in Tables 1–3. All of the synchrotron topographs presented were recorded with diffraction occurring in the vertical plane. The correct value for inherent perfect-crystal reflection curve width in these cases is obtained by multiplying the value from the table by 2/(1 + cos2$\theta_B$).

The equation used to calculate the inherent perfect-crystal neutron reflection curve width is

$$\delta^N(\lambda) = \frac{2\lambda^2|F_{hkl}^N|}{\pi V\sin 2\theta_B} \left( \frac{\gamma_h}{\gamma_0} \right)^{1/2}. \quad (5)$$

Note the absence of the polarization factor (the neutron wave is a scalar wave) and the classical electron radius.

Among the reflections listed in Table 1 are those which have the highest neutron structure factor, while satisfying the accessibility criteria outlined above. Since the magnitude of the nuclear interaction of a neutron, the so-called scattering length, has the dimensions of length, structure factors calculated from these scattering lengths also have dimensions of length. Therefore, following standard practice the X-ray structure factors listed in Table 1 (and those in Tables 2 and 3) have been multiplied by the classical electron radius, $R$, so that they can be directly compared with the neutron structure factors. Also among those listed are reflections which have the highest X-ray structure factor.

Owing to the asymmetry of the reflections, two possible values of inherent perfect-crystal reflection curve width are listed corresponding to the two unique ways of accessing such reflections. In terms of (4) and (5) these values are calculated by inverting the term $(\gamma_h/\gamma_0)^{1/2}$.

Some 12 neutron topographs were taken from the protonated pyrene crystal chosen for study. Best results were obtained from the 441 reflection, which is one of the highest-neutron-structure-factor reflections. This image can be directly compared with the 441 X-ray reflection which has a large structure

Table 1. Comparison of neutron and X-ray diffraction parameters for protonated pyrene

| hkl | d (Å) | $|F_{hkl}^N|/|F_{hkl}^R|$ (× 10^-12 cm) | $\varphi$ (°) | $a^1$ | $\theta_B(\lambda_1)$ (°) | $\delta_X(\lambda_1)$ (μrad) | $\delta_X(\lambda_2)$ (μrad) | $\delta_X(\lambda_3)$ (μrad) |
|-----|-------|-------------------------------|------------|-----|----------------|----------------|----------------|----------------|
| 925 | 1.19  | 25.14*                        | 4.90       | 55.31| 2.31           | 45.84         | 10.73| 1.79           |
| 842 | 1.24  | 23.26*                        | 6.99       | 64.57| 2.11           | 43.27         | 6.59 | 2.52           |
| 563 | 1.17  | 22.65*                        | 5.02       | 60.20| 2.39           | 46.83         | 8.06 | 1.95           |
| 743 | 1.24  | 21.95*                        | 5.55       | 55.96| 2.13           | 43.47         | 8.20 | 1.79           |
| 744 | 1.29  | 21.35*                        | 4.99       | 60.02| 1.96           | 41.16         | 6.56 | 2.16           |
| 441 | 1.19  | 19.25*                        | 16.46**    | 82.71| 1.12           | 26.58         | 4.48 | 3.94           |
| 220 | 3.81  | 18.97*                        | 33.93**    | 84.19| 0.51           | 12.89         | 7.45 | 7.80           |
| 604 | 1.68  | 18.81*                        | 4.51       | 47.68| 1.31           | 30.35         | 6.83 | 2.08           |
| 10.02 | 1.18 | 18.44*                        | 5.55       | 63.98| 2.35           | 46.25         | 5.66 | 1.84           |
Table 2. Comparison of neutron and X-ray diffraction parameters for deuterated pyrene

Neutron structure-factor magnitudes calculated as for protonated pyrene, X-ray structure-factor magnitudes from observed data (Cameran & Trotter, 1965). $\lambda_1 = 1.7 \AA$, $\lambda_4 = 2.0$ and $\lambda_5 = 0.75 \AA$.

| hkl | $d$ (Å) | $|F_{dd}|$ ($\times 10^{-2}$ cm) | $|F_{dd}|/R$ | $a^1$ | $a^4$ | $\theta(\lambda_1)$ (°) | $\delta\sigma(\lambda_1)(\mu\text{rad})$ | $\delta\theta(\lambda_4)$ (°) | $\delta\sigma(\lambda_4)(\mu\text{rad})$ | $\delta\sigma(\lambda_5)(\mu\text{rad})$ |
|-----|---------|-----------------------------|--------------|------|------|----------------------|-----------------------------------|----------------------|-----------------------------------|-----------------------------------|
| 762 | 1.19    | 32.59* 7.05 79.91 2.29     | 2.83         | 45.53 | 6.84 4.74 57.09 11.46 | 6.52 0.46 0.39 |
| 321 | 3.14    | 21.11* 26.43* 75.45 0.63    | 0.62         | 15.71 | 11.22 9.69 18.57 13.60 | 11.42 4.64 4.31 |
| 102.2 | 1.18    | 27.30* 5.55 63.98 2.35    | 2.96         | 46.26 | 8.38 2.72 58.21 21.39 | 2.54 0.40 0.27 |
| 862 | 1.13    | 25.25* 4.99 81.33 2.56    | 3.47         | 48.72 | 5.31 3.73 62.14 9.96 | 5.49 0.30 0.24 |
| 10,3.2 | 1.13    | 25.02* 4.03 65.04 2.55    | 3.46         | 48.69 | 7.95 2.45 62.09 28.76 | 1.86 0.28 0.19 |
| 441 | 1.89    | 23.75* 16.46* 82.71 1.12   | 1.14         | 26.58 | 5.53 4.86 31.75 6.95 | 5.93 1.71 1.60 |
| 10,0,2 | 1.35    | 23.52* 5.33 81.68 1.82   | 2.02         | 39.00 | 4.73 3.73 47.77 6.72 | 4.86 0.39 0.35 |
| 754 | 1.19    | 23.05* 4.90 62.55 2.29    | 2.83         | 45.52 | 7.26 2.24 57.07 18.44 | 2.02 0.37 0.24 |
| 221 | 3.61    | 21.53* 29.62* 70.31 0.54  | 0.53        | 13.63 | 8.96 7.53 16.09 10.84 | 8.81 6.03 5.51 |
| 220 | 3.81    | 20.56 33.95* 84.19 0.51    | 0.49        | 12.89 | 8.07 8.46 15.21 9.55 | 10.09 6.90 7.07 |
| 311 | 3.88    | 12.64 20.57** 71.88 0.50   | 0.49        | 12.65 | 5.56 4.80 14.93 6.70 | 5.63 4.48 4.15 |

Table 3. Comparison of neutron and X-ray diffraction parameters for PTS

Neutron structure-factor magnitudes calculated as for deuterated and protonated pyrene, X-ray structure-factor magnitudes from observed data (Kobelt & Paulus, 1974). $\lambda_1 = 1.7$, $\lambda_4 = 2.0$ and $\lambda_5 = 1.0$ Å.

| hkl | $d$ (Å) | $|F_{dd}|$ ($\times 10^{-2}$ cm) | $|F_{dd}|/R$ | $a^1$ | $a^4$ | $\theta(\lambda_1)$ (°) | $\delta\sigma(\lambda_1)(\mu\text{rad})$ | $\delta\theta(\lambda_4)$ (°) | $\delta\sigma(\lambda_4)(\mu\text{rad})$ | $\delta\sigma(\lambda_5)(\mu\text{rad})$ |
|-----|---------|-----------------------------|--------------|------|------|----------------------|-----------------------------------|----------------------|-----------------------------------|-----------------------------------|
| 102 | 4.99    | 19.17* 43.62* 41.62 0.39  | 0.38        | 9.81  12.88 8.68 11.57 15.82 | 9.89 1.56 12.38 |
| 342 | 1.18    | 18.89* 4.31 68.06 2.34    | 2.95         | 46.23 | 2.24 5.48 58.16 2.49 | 11.69 0.24 0.36 |
| 9,3.10 | 1.06    | 16.13* 1.44 68.93 3.05    | 5.46         | 53.69 | 1.75 5.60 71.45 1.79 | 26.14 0.07 0.11 |
| 441 | 1.17    | 15.98* 6.09 65.98 2.37   | 3.00         | 46.51 | 4.93 1.78 58.59 11.66 | 1.82 0.51 0.33 |
| 223 | 1.96    | 10.84* 10.17 58.87 1.08   | 1.09         | 25.69 | 3.47 1.91 30.67 4.61 | 2.18 1.45 1.05 |
| 212 | 4.25    | 8.96 26.35* 88.57 0.46    | 0.44         | 11.55 | 4.21 4.25 13.62 4.99 | 5.05 7.09 7.14 |
| 214 | 3.03    | 2.73 15.75* 87.96 0.66    | 0.64         | 16.28 | 0.93 0.95 19.26 1.11 | 1.14 3.00 3.03 |
| 104 | 3.64    | 6.74 15.53** 76.06 0.54   | 0.52         | 13.49 | 2.92 2.59 15.93 3.52 | 3.79 3.72 3.47 |

factor, although a relatively narrow inherent perfect-crystal reflection curve width, leading to broader 'direct' dislocation images. Unfortunately such direct comparison is not possible for the 220-type reflections, since the Bragg angle (in the neutron case) for this type of reflection is so small that specimen–film distances have to be increased to avoid impingement of the transmitted beam on the detector, leading to unacceptable resolution loss. This is generally true for reflections with Bragg angles less than around 15°.

Table 2 shows a similar list corresponding to deuterated pyrene. In this case, neutron diffraction parameters calculated at two wavelengths (1.7 and 2.0 Å) are presented for comparison, as well as X-ray parameters at the X-ray wavelength employed (0.9 Å). The table shows that the only high-neutron-structure-factor reflections which have both high values of X-ray structure factor as well as relatively broad inherent perfect-crystal neutron reflection curve widths are the 321, 221, 220 and 311 reflections. Of these the 321 reflection has the largest Bragg angle, as well as the broadest inherent perfect-crystal neutron reflection curve width. Thus, even though the Bragg angle is not much greater than 15° the 321 reflection is chosen as optimum for neutron topography. This image could also be compared with the corresponding 321 X-ray image, which is among the best for this material.

Table 3 shows the list of diffraction data corresponding to PTS. Neutron diffraction parameters are listed at the two wavelengths employed in the neutron topographs presented here (1.7 and 2.0 Å), as well as the X-ray parameters at the relevant X-ray wavelength (1.0 Å). Again only those reflections which have the highest structure-factor values and which satisfy the accessibility criteria are listed. The five most intense neutron reflections are among those listed. It is notable that only one of the strong neutron reflections, the 102 reflection, is also a strong X-ray reflection. The large value for neutron structure factor led to the selection of this reflection for study despite its small Bragg angle (the 102 was the actual reflection used). The value for the factor $a$ from the 223 reflection was close to the optimum value so that this reflection was also chosen for study (the actual reflection used was 223). When recording X-ray topographs from PTS monomer crystals, filtered synchrotron white-beam topography must be used (Dudley et al., 1986; Dudley, 1989). Synchrotron white-beam topographic geometries are generally chosen on the basis of obtaining the maximum number of useful reflections simultaneously in a single exposure. Unfortunately, neither the 102 or...
223 reflections are among the images routinely utilized (those which include the \(104, 214\) and \(324\) reflections). Therefore, although a direct comparison of equivalent neutron and X-ray reflections from PTS is not possible in this paper, a general comparison of topographs obtained in the respective optimum neutron and X-ray configurations is presented.

Fig. 3. (a) Lang topograph \((g = 220, \text{Mo } K\alpha, \text{radiation})\) recorded from a protonated pyrene crystal, cut as shown in Fig. 1(b). (b) Lang topograph \((g = 220, \text{Mo } K\alpha, \text{radiation})\) recorded from the same crystal. Note the appearance of dislocation \(D\), which is not visible on (a). (c) Synchrotron white-beam topograph \((g = 220, \lambda = 0.75 \text{ Å})\) recorded at the SRS, Daresbury, from the same crystal.
Results

Results for pyrene and PTS will be presented separately. In each case examples of X-ray topographs recorded from the specimens will initially be presented, defect characterization outlined, and then neutron results presented for comparison.

(a) Pyrene

Fig. 3(a) shows a Lang topograph \((g=220, \text{Mo } K\alpha_1 \text{ radiation})\) taken from a protonated pyrene crystal which was cut parallel to the \((001)\) face (as described earlier). Note the growth dislocations propagating towards the \((110)\) growth faces. Fig. 3(b) shows a Lang topograph \((g=220, \text{Mo } K\alpha_1 \text{ radiation})\) recorded from the same crystal; note the appearance of dislocation \(D\) which was not visible on Fig. 3(a). Fig. 3(c) shows the same reflection as (b), recorded using synchrotron white radiation (recorded at the SRS, Daresbury, England; \(g=220, \lambda=0.75 \text{ Å}\)).

In general, clear dislocation image extinction was only observed for dislocation \(D\), with the remaining images persisting on all of the high-structure-factor reflections employed. This latter persistence can be attributed to the mixed character of the dislocations.

Fig. 4(a) shows a white-beam synchrotron X-ray topograph \((g=44l, \lambda=0.5 \text{ Å})\) recorded from the same crystal. The image is a composite made from several separate images, each recorded with the relatively small-area white beam available at the topography station X-19C at NSLS, Brookhaven, USA. The dislocation structure is seen to be the same as in Figs. 3(a)–(c), although the images are a little broader and more diffuse, owing to the narrower inherent perfect-crystal reflection curve width. For comparison, Fig. 4(b) shows the corresponding neutron topograph \((g=44l, \lambda=1.7 \text{ Å})\) recorded from part of the same crystal. The dislocation structure observed in (b) is recognizable as being the same as that in (a), although clearly the definition and resolution of the dislocation images on the neutron image are much inferior.

Fig. 5(a) shows a synchrotron X-ray topograph \((g=321, \lambda=0.9 \text{ Å})\) recorded at the NSLS, Brookhaven, from a deuterated pyrene crystal. Fig. 5(b) shows a neutron topograph recorded, with the same reflection vector, from the same crystal \((g=321, \lambda=1.7 \text{ Å})\). Again approximate correspondence between dislocation structures observed on both topographs is observable, although the dislocation images obtained on the neutron topograph are much broader and less well defined than those on the X-ray topograph. The reduced level of background noise on the deuterated pyrene neutron topograph, as compared with that on a typical protonated pyrene neutron topograph, contributes to the production of a much cleaner image. The dislocation images are also a little better defined (less diffuse) on the deuterated pyrene neutron topograph.

Fig. 4. (a) Synchrotron white-beam topograph \((g=44l, \lambda=0.5 \text{ Å})\) recorded at the NSLS, Brookhaven, from the same crystal. (b) Neutron topograph \((g=44l, \lambda=1.7 \text{ Å}, a=1.12)\) recorded from part of the same protonated pyrene crystal.
(b) PTS

Fig. 6(a) shows a filtered white-beam synchrotron X-ray topograph \((g = 104, \lambda = 1.0 \text{ Å})\) recorded on fast X-ray film [to minimize exposure; see Dudley et al. (1986)] from a PTS monomer crystal. Note the 'end-on' images of dislocations in the central growth sector. Fig. 6(b) shows a neutron topograph \((g = 102, \lambda = 1.7 \text{ Å})\) recorded from a similar crystal. It is obviously very difficult to discern any clear evidence for the end-on dislocations on the neutron topograph, and only by comparison with the X-ray image can the presence of very weak contrast in the dislocated volume of crystal be discerned.

Fig. 7(a) shows a filtered white-beam synchrotron X-ray topograph \((g = 104, \lambda = 1.0 \text{ Å})\) recorded from a PTS monomer crystal containing twin lamellae, composition plane \((122)\) [as observed previously by Young, Bloor, Batchelder & Hubble (1978)]. Figs. 7(b) and (c) show two neutron topographs \((g = 223, \lambda = 2.0 \text{ Å} \text{ and } g = 102, \lambda = 2.0 \text{ Å} \text{ respectively})\) recorded from the same crystal. While clearly being inferior in definition and resolution, images of the twins are nevertheless observable on the neutron topographs.

Neutron topographs recorded \textit{in situ} during UV-induced polymerization, from the PTS crystal imaged in Fig. 6(b), show little or no change in microstructural detail. An example is shown in Fig. 8 \((g = 102, \lambda = 1.7 \text{ Å})\). However, \textit{in situ} recording of experimental rocking curves revealed changes in both rocking-curve width and integrated intensity which accompany reaction. Figs. 9(a) and (b) show plots of measured experimental rocking-curve width and integrated intensity, respectively, as a function of time in the UV beam. The mosaic spread of the
crystal as a function of UV-irradiation time can then be obtained from the measured experimental rocking-curve widths, using (3). This is shown in Fig. 9(c). Clearly, although no microstructural changes are evident on topographs recorded \textit{in situ}, the mosaicity of the PTS crystal is increasing with increasing UV dose.

\section*{Discussion}

In general the width of a dislocation image on topographs recorded under low-absorption conditions is determined by the projection (in the diffracted-beam direction) of the limiting width of...
the zone surrounding the dislocation line for which the effective misorientation \( \delta(\Delta \theta) \) is greater than the inherent perfect-crystal reflection curve width (Miltat & Bowen, 1975). For a very narrow (wide) inherent perfect-crystal reflection-curve width the limiting distance from the dislocation line for which this is true will be quite large (small), and so wide (narrow) dislocation images would be predicted.

As mentioned earlier, contrary to the case for crystals such as silicon, inherent perfect-crystal neutron reflection-curve widths for the crystals studied here are often wider than their X-ray counterparts. This is mainly because the neutron scattering length for carbon can be greater than the product of X-ray scattering factor and classical electron radius [depending, of course, on the relevant value of \((\sin \theta_B)/\lambda\)], whereas in the case of materials such as silicon, the neutron scattering length can be up to an order of magnitude smaller (Bacon, 1975).

Unfortunately, as explained earlier, it is not always possible to perform a direct comparison between the same reflections recorded with both neutrons and X-rays, owing to serious experimental constraints. Indeed, only in the case of 441 reflection from protonated pyrene, and the 321 reflection from deuterated pyrene, could this be achieved. Consequently, only in these cases can information concerning the widths of dislocation images based on strain-sensitivity considerations be directly discussed. In all other cases only general comments, rather than direct comparisons, may be made. Results for protonated and deuterated pyrene and PTS, respectively, will be discussed separately.

Observations indicate that, in the case of protonated pyrene, dislocation images obtained on the 441 neutron topograph (Fig. 4b) are clearly broader, and thus inferior, in both resolution and definition, to those obtained on the 441 X-ray topograph presented (Fig. 4a). Table 1 shows that the inherent perfect-crystal neutron reflection-curve width for the 441 reflection (in Table 1, the value for the 441 reflection, which is equivalent to the 441 reflection, is listed) is broader than the corresponding X-ray width [the inherent perfect-crystal neutron reflection-curve width is 4.48 \( \mu \)rad, and the X-ray width, after multiplying the table value by \( 2/(1 + \cos 2 \theta_B) \), is 0.97 \( \mu \)rad], predicting narrower dislocation-image widths on the neutron topograph than on the X-ray topograph. Therefore, the poor resolution of dislocation images on the 441 neutron topograph of protonated pyrene, compared with that obtained on the corresponding X-ray topograph, cannot be attributed to differences in strain sensitivity deriving from differences in the respective inherent perfect-crystal reflection-curve widths. The explanation for the broad dislocation images on the neutron topographs lies in the geometric considerations described earlier. For the 441 neutron reflection it was, in fact, possible to approach the optimum conditions for geometric resolution \((a = 1.12\) for Fig. 4b), giving a measured experimental rocking-curve width of \(~7'\), in close agreement with the prediction of (3). However, even under these optimum conditions, this experimental rocking-curve width will contribute to a significant blurring effect at the sort of specimen–film distances required to ensure that the transmitted beam does not hit the film (this distance was typically between 1 and 1.5 cm; a blurring of around 20 \( \mu \)m is produced at a specimen–film distance of 1 cm). It is thus concluded that the ill-defined broad dislocation images are mainly due to the poor geometrical resolution attained in the neutron topographic set up even under optimum conditions. In addition the general noise due to the incoherent scattering from the hydrogen in the system is expected to contribute to the lack of resolution.

In the case of the deuterated pyrene crystal direct comparison could be made between neutron and X-ray topographs recorded with the 321 reflection vector (Figs. 5b and a, respectively). As in the previous case, the basic dislocation structure could be resolved on the neutron topograph, with the dislocation images appearing much broader, and more diffuse than on the X-ray image. Examination of Table 2 shows that the inherent perfect-crystal neutron reflection-curve width is again broader than the corresponding X-ray width [5.53 \( \mu \)rad for the neutron case and, after multiplication of the table value by \( 2/(1 + \cos 2 \theta_B) \), 1.81 \( \mu \)rad for the X-ray case], so that again strain-sensitivity considerations would predict narrower dislocation images for the neutron case. Unfortunately, possible diffraction geometries, for the deuterated crystal are quite restricted, and in fact make it impossible to approach optimum geometric resolution conditions \((a = 0.63\) for Fig. 5b). It is this latter consideration that is chiefly responsible for the relatively broad dislocation images on Fig. 5b. There is, however, a slightly improved clarity and definition to the deuterated pyrene neutron topographic image compared with the protonated case. This is considered to be the result of the absence of the contribution to resolution loss deriving from the presence of incoherent scattering from hydrogen.

In the case of PTS crystals it is not possible here to compare neutron and X-ray images recorded with the same reflection vector, as discussed earlier. It is, however, possible to compare neutron and X-ray images recorded under the respective optimum conditions. Examination of Figs. 6(a) and (b) shows that it is difficult to obtain a direct comparison between dislocations obtained on 104 synchrotron X-ray topographs and those obtained on 102 neutron topographs, since the latter are extremely difficult to
discern. It can be concluded that dislocation images obtained on neutron topographs recorded from PTS crystals are grossly inferior to their X-ray counterparts. On the other hand, neutron topographic images of twins obtained on 102 and 233 reflections, while being clearly inferior in resolution and definition to those obtained on the 104 X-ray topograph presented, are nevertheless resolved. Neutron topographs recorded during in situ UV-induced polymerization showed little evidence of image modification, not showing the kind of contrast changes routinely observed on synchrotron topographs. However, analysis of neutron experimental rocking curves, recorded during reaction, provides a unique insight into reaction-induced strains. The observed increase in experimental rocking-curve width is attributable to a calculable increase in the mosaicity of the specimen crystal. This increase in mosaicity is probably because the UV-induced reaction in PTS is restricted to the top few micrometres of crystal, so that the lattice-parameter changes accompanying reaction, in conjunction with the heterogeneous reaction profile, lead to the formation of inhomogeneous distortion fields. The decrease in extinction resulting from this increase in mosaicity would then account for the increase in integrated intensity with UV dose. This analysis of experimental rocking curves as a function of UV dose affords invaluable information on reaction-induced strains, under conditions where the investigative probe (the neutron beam) cannot itself induce reaction. This analysis provides an excellent complement to the extensive X-ray topographic imaging work already conducted on this system. As such it is a useful 'ally' technique to the analogous synchrotron topographic techniques, in which it is assumed that X-ray-induced reaction rates can be reduced to tolerable levels by filtering of the incident beam, while reaction induced by alternative means is studied, in situ, in the X-ray beam (Dudley et al., 1983). In fact, the neutron topographic studies provides further evidence in support of the previously calculated assumption of the limited non-destructive nature of filtered white-beam synchrotron-radiation topography. This evidence was gleaned from synchrotron X-ray topographic images recorded from the same crystal, following the neutron experiments. Contrast observed was identical to that observed in crystals which had undergone in situ UV-induced reaction using a filtered synchrotron X-ray beam to monitor the microstructure during reaction. Consequently, no spurious contrast effects were induced by the synchrotron beam itself. It should be noted that for PTS, similar in situ X-ray rocking-curve analysis is not possible since continued, rather than short intermittent, X-ray exposure induces polymerization, even in a filtered synchrotron beam.

For the case of extreme X-ray sensitivity it is envisaged that neutron topography may be the only non-destructive bulk imaging technique available for large single crystals which is capable of both detailed defect structure analysis and of monitoring distortions induced during solid-state reactions.

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