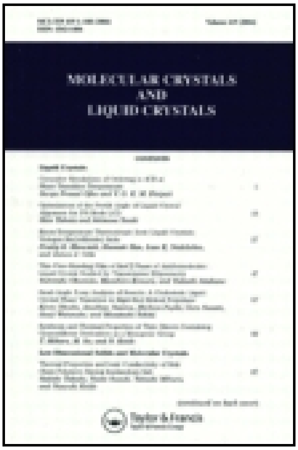

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Characterization of Defects in p-Quaterphenyl Single Crystals

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Characterization of Defects in p-Quaterphenyl Single Crystals

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Crystals of p-quaterphenyl were studied by synchrotron white beam x-ray topography. Leaves with (001) as the primary facet were grown from toluene solution by the solvent temperature gradient method. These leaves were shown to twin along the (201) plane. Two types of twinning were observed, a macroscopic twinning where two halves of the leaf were folded along the b-axis by 36.4° and a microscopic twinning, where narrow lamellae occur along the (201) plane, resulting in a flat crystal. These lamellae appear as lines in x-ray topographs. A low density of both growth dislocations were observed originating at the twinning planes.

Keywords: x-ray topography, polyphenyls, dislocations, twinning

INTRODUCTION

In previous papers in this series we described the defect structure of single crystals of p-terphenyl[1,2]. Here, we present a similar study of p-terphenyl's next highest homolog, p-quaterphenyl. The two organics have similar properties, both having the space group $P2_1/a$, a monoclinic unit cell. The chief difference in their structural parameters is that the c-dimension of p-quaterphenyl is longer (17.81 vs. 13.59Å)[3].

Synchrotron white beam x-ray topography is suited to the study of these substances for various reasons. Relative to many organics, linear polyphenyls are quite resistant to radiation damage by x-rays. Thin, wide plates can be crystallized in the nearly perfect quality that x-ray topography demands, using fairly simple and inexpensive apparatus. Fortunately they may be used in their as-grown condition, since sectioning and polishing of such soft materials would demand elaborate technique.

EXPERIMENTAL

While suitable leaves of p-terphenyl may be obtained simply by slow evaporation of toluene solutions from glass dishes[1], growing p-quaterphenyl crystals larger than 1mm by this method is impractical because of the chemical's low solubility at room temperature. Furthermore, the leaves of p-quaterphenyl grown in solution are more delicate than those of p-terphenyl, tending to deform under their own weight upon removal from the growth solution unless they have attained a fairly large size (1cm^2). While there are literature procedures to prepare large crystals of p-quaterphenyl from the melt, for example, by the Stockbarger technique[4], we desired to grow them from toluene solution, so they would be comparable to the p-terphenyl crystals we had previously studied. The solvent temperature gradient method was chosen, since it is more amenable toward materials of modest solubility. The arrangement used was a modification of a literature technique[5]. The leaves were spontaneously nucleated and grown over a period of several days on a flat surface at 45C in toluene solution, separated from the p-quaterphenyl feedstock by a 30C temperature gradient.

Like p-terphenyl[1,2], flat, parallelogram-shaped leaves of p-quaterphenyl with the {001} face are the predominant habit. Rhombus-shaped, twinned bicrystalline leaves frequently occur, where the crystal face is folded along the b-axis. The angle between the [001] face normals was measured by optical goniometry as 36.4°.

Synchrotron white beam topographs were taken by allowing the highly collimated beam of synchrotron white x-rays obtained from Beamline X19-C at the National Synchrotron Light Source, Brookhaven National Laboratory, to fall onto the crystal. The diffracted beams were recorded on 8x10" sheets of Kodak Industrex SR-1 film placed normal to the incident beam direction at a distance of 10cm from the crystal. An exposure took about 5sec. No radiation damage was evident in the topographs during a normal sequence of exposures.

RESULTS AND DISCUSSION

Examples of the three types of p-quaterphenyl leaves which obtain from temperature gradient toluene solution growth are shown in the optical photomicrographs in figure 1. While twinned specimens are prevalent, crystals I, II and III, single crystal specimens like IV may be observed

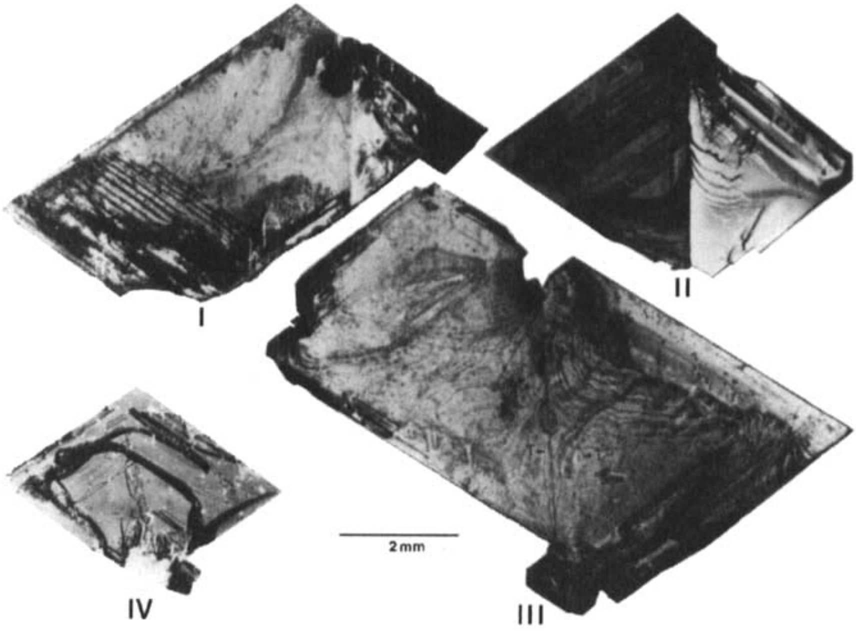

FIGURE 1. Optical micrographs of crystals of p-quaterphenyl. The right hand sides of crystals **I** and **II** are tilted by 36.4° toward the observer. The two lamellae in crystal **III** are marked **T**.

occasionally.

Macroscopically twinned bicrystalline leaves whose {001} primary faces were inclined to one another by 36.4° occur frequently. Such macroscopic twins are usually symmetrical, as in the case of II shown in figure 1, with their twin plane running through the center of the crystal, dividing it into two equal halves. However, topographs of few such symmetrically divided crystals don't show extensive asterism in the region of its twinning plane.

Figure 2 shows a white beam synchrotron Laue pattern of specimen I. This crystal has one small corner macroscopically twinned in this way, which is free of gross distortion. The (001) face of the larger parent matrix grain is oriented perpendicular to the incident beam. In figure 2, no misorientation

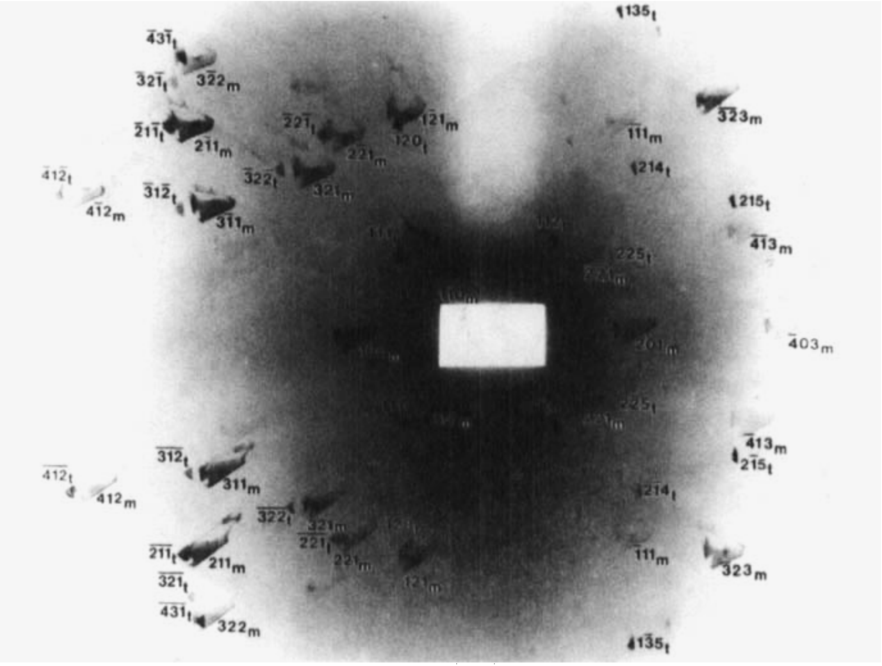

FIGURE 2. Indexed Laue pattern recorded from macroscopically twinned crystal **I**. Matrix reflection indices have the subscript **m**, while those of the twin have subscript **t**. The (001) face of the matrix was perpendicular to the incident beam. The specimen-to-film distance was 10cm.

between the diffraction spots arising from the matrix and twin occurs for spots of the zone $\langle \bar{1}02 \rangle$ (i.e., $\{4\bar{1}2\}$, $\{2\bar{1}1\}$, $\{2\bar{2}1\}$, etc.), the direction of shear between the twin and matrix lattices. Additionally, the angle between [001]

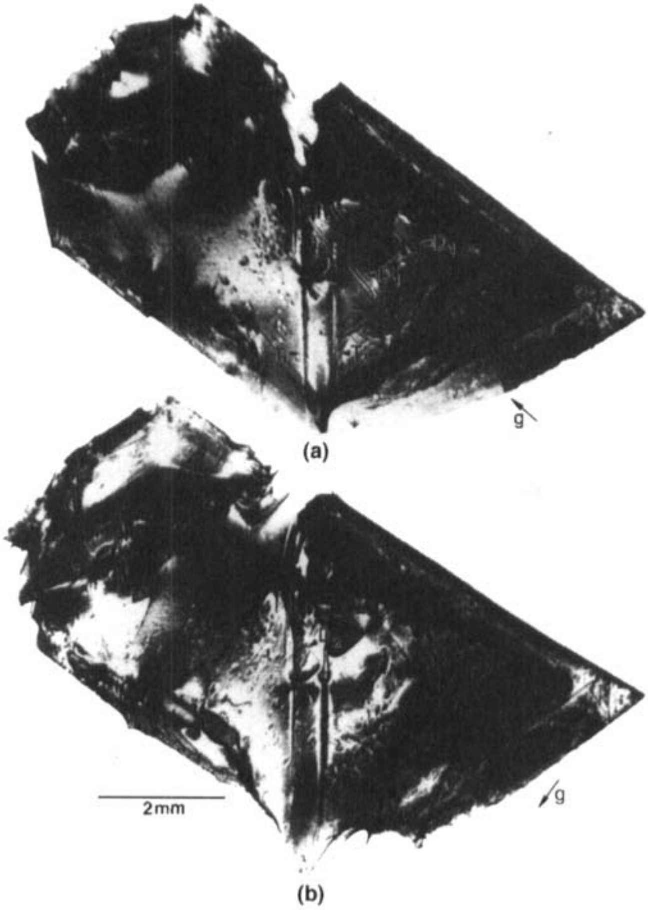

FIGURE 3. Synchrotron white beam transmission topographs of crystal III. Dislocations $\mathbf{D_1}$, which are associated with the twin lamellae, extinguish in (b) ($\mathbf{g}$ = (110), λ = 1.06Å), while $\mathbf{D_2}$ extinguish in (a) ($\mathbf{g}$ = $(1\bar{1}0)$, λ = 1.06Å).

and $[\bar{1}02]$ is 18.2°, half the observed twinning angle in the crystal. Therefore, the twin plane may be assigned as (201). This situation is also observed in twinned p-terphenyl crystals. The primary faces of the twins in such

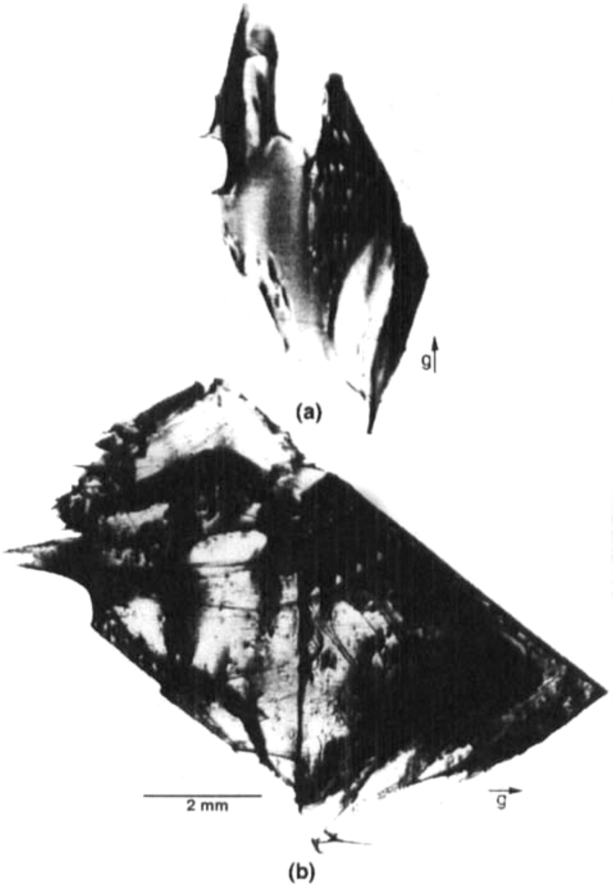

FIGURE 4. Synchrotron white beam transmission topographs of crystal III. In (a) (g = (001), λ = 1.03Å) the dislocations marked in figure 3 have extinguished. In (b) (g = (201), λ = 1.09Å) the contrast of one of the twin lamellae has disappeared.

macroscopic p-terphenyl twined leaves are similarly folded along the [010] axis by 37.5° [1,2].

Flat leaves of p-quaterphenyl are also common. Most of these are also twinned, albeit microscopically. Like the macroscopic twins, their (001) faces are dominant. Their twins occur as narrow lamellae, visible by optical microscopy as pairs of parallel lines about 12µm wide, run along [010]. Two of these lamellae are marked **T** in the micrograph of III in figure 1.

They are also marked **T** in the x-ray topograph of III shown in figure 3a. Topographic images of the lamellae may be observed as narrow lines displaced from the images of their matrix, or in some reflections, coincident. Note that, for one of the lamellae, $\mathbf{T_2}$, in the $\mathbf{g}$ = (201) reflection shown in figure 4a, all contrast has vanished. The absence of lattice strain associated with this lamella implies that its twin plane is (201). The other lamella, $\mathbf{T_1}$, is still visible in this topograph. It apparently has another, unidentified twin plane.

The lamellae do not extend continuously along the [010] direction throughout the crystal. Where they terminate, dislocations are observed extending into the matrix. Dislocations also originate at the twinning plane, and either curve back to terminate there, or extend to the surface of the crystal. Some of them, $\mathbf{D_1}$, are in maximum contrast in the $\mathbf{g}$ = $(1\bar{1}0)$ reflection shown in figure 3a, and extinguish in figure 3b, the $\mathbf{g}$ = (110) reflection. Those labeled $\mathbf{D_2}$, behave oppositely, extinguishing when $\mathbf{g}$ = $(1\bar{1}0)$. Both $\mathbf{D_1}$ and $\mathbf{D_2}$ have minimal contrast in figure 4a, where $\mathbf{g}$ = (001), a reflection almost orthogonal to (110) and $(1\bar{1}0)$. Therefore, by the $\mathbf{g} \cdot \mathbf{b} = 0$ criterion it may be concluded the Burgers vectors of $\mathbf{D_1}$ are $\mathbf{b}$ = $[1\bar{1}0]$ and those of $\mathbf{D_2}$ are $\mathbf{b}$ = [110]. As their lines roughly follow the same directions, they are mainly screw in character.

Similar microscopic twin lamellae were observed in the case of p-terphenyl[1], with (201) as the twinning plane. The lamellae seen in p-terphenyl, were wider. These also had dislocations associated with them, determined to have different Burgers vectors, **b** = [100], with primarily edge character.

Crystal IV is an example of a single p-quaterphenyl crystal grown by this method. They are found in a minority, invariable smaller than the twinned leaves. The topographs in figure 4 show dislocations, **D**, some of which have the same extinctions as those occurring in III. The large gap in the topograph, C, is a distortion where a smaller crystal nucleated and grew on IV's surface.

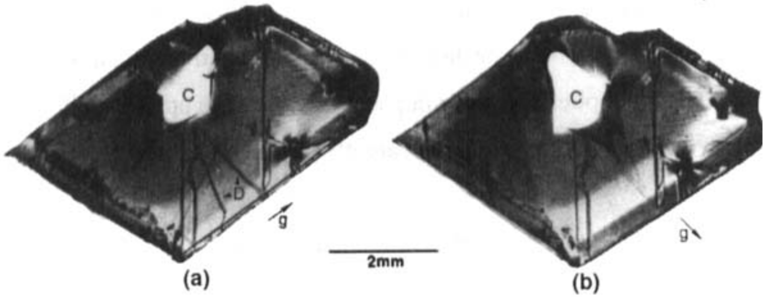

FIGURE 5. Synchrotron white beam topograph of crystal **IV**. The images are distorted at **C**, where a smaller crystal has grown on **IV**'s surface. Dislocations, **D**, visible in (a) (**g** = (110), λ = 1.06Å), extinguish in (b) (**g** = $(1\bar{1}0)$, λ = 1.06Å).

CONCLUSIONS

p-Quaterphenyl solution-grown crystals show similar twinning behavior to p-terphenyl, which is a homologous polyphenyl with a similar unit cell. The dislocations seen in the two crystals; however, have different Burgers vectors.

Acknowledgements

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