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Alignment of fluorescent molecules vapour-deposited on to highly oriented PTFE substrates

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The alignment of six fluorescent materials (*p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, diphenylstilbene, 1,4-bis(2-methylstyryl)benzene, and 1,4-bis-2-(5-phenyloxazolyl)benzene) grown from the vapour phase on to friction-deposited, highly oriented poly(tetrafluoroethylene) (PTFE) films was studied. The dichroic ratio of the fluorescent films produced was determined by polarized spectroscopic fluorescence measurements, and the crystallographic orientation of these materials was determined by transmission electron microscopy. The measured dichroic ratios ranged from 1.7 for diphenylstilbene to 5.0 for the *p*-quaterphenyl film. Electron diffraction patterns revealed that five of the fluorescent materials grew epitaxially on the single crystal-like PTFE films, the fluorescent crystals adopting particular orientations with respect to the crystallographic planes of PTFE. On the other hand, crystals of 1,4-bis-2-(5-phenyloxazolyl) benzene aligned in a fibre pattern, apparently by a grapho-epitaxial mechanism.

1. Introduction

It has been shown [1] that highly oriented poly(tetrafluoroethylene) (PTFE) films are very effective at promoting oriented growth of a wide selection of materials, including polymers, liquid crystals, and organic and inorganic small molecules, deposited onto them from the melt, solution, or vapour phase. Such highly oriented PTFE films can be conveniently produced by friction-transfer of the polymer on to smooth substrates, as originally discussed by Tabor and co-workers [2, 3]. The polymer chains of such films are aligned parallel to the substrate surface and along the deposition direction. The remarkable orientation-inducing ability of these films is believed to be due to the presence of small-scale grooves at their surfaces and the presence of crystalline order perpendicular to the PTFE chain direction [1, 4]; at temperatures above 19 °C, where oriented growth is generally carried out, the PTFE crystal structure largely lacks order along the chain axis [5, 6].

The structure of these friction-deposited PTFE films has been investigated at room temperature [4, 7–9], where PTFE is in its hexagonal phase IV [10]. The polymer chains of the film are arranged in a single crystal-like pattern, with a close-packed plane parallel to the surface upon which the film is deposited [7]. Atomic force microscopy (AFM) measurements have shown that the surface of these films consists of small-scale grooves running parallel to the PTFE chain direction [4, 8, 9].

The original study [1] of oriented growth of materials on PTFE films was intended as a general discussion of an orientation technique, and thus the degree of alignment or crystallographic orientation of many of the materials deposited onto the PTFE films was not examined in detail. Recently, Yang and co-workers (11) used transmission electron microscopy (TEM) to study the structure and orientation of dimethyl-oligothiophene crystals grown on PTFE films. The oligothiophenes were found to orient on the PTFE substrates with the a-axis of the oligomers (length = 0.598 nm) generally parallel to the interchain (a or b) axis of PTFE (length = 0.566 nm), but the direction of the b and c-axes of the oligomers was not uniquely determined; for some crystals the c-axis was parallel to the PTFE chain direction, whereas for other crystals the c-axis was normal to the surface of the PTFE film.

In the present work, we investigated the alignment of a number of small, fluorescent molecules deposited onto highly oriented PTFE films from the vapour phase. Films of aligned, conjugated molecules produced by this method are of interest because of their potential use as components in optical devices such as light-emitting diodes (LEDs) that emit polarized light. The dichroic ratio of the fluorescent films produced was determined by polarized spectroscopic fluorescence measurements, and the crystallographic orientation of these materials was determined by TEM.

2. Experimental method

2.1. Oriented PTFE film production

Oriented PTFE films were produced by sliding a bar of commercial-grade PTFE on cleaned glass slides at a temperature of 300 °C, a contact pressure of 1 MPa, and a sliding rate of $1\,\mathrm{mm\,s^{-1}}$ using equipment now manufactured by DACA Instruments, Goleta, CA. The friction-deposition method used is described in previous publications [7, 12].

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2.2. Fluorescent film production

The following fluorescent materials were used in this study: *p*-terphenyl ($C_{18}H_{14}$), *p*-quaterphenyl ($C_{24}H_{18}$), *p*-quinquephenyl ($C_{30}H_{22}$), 4,4′-diphenyl-trans-stilbene or "DPS" ($C_{26}H_{20}$), 1,4-bis(2-methylstyryl)benzene or "Bis-MSB" ($C_{24}H_{22}$), and 1,4-bis-2-(5-phenyloxazolyl)benzene or "POPOP" ($C_{24}H_{16}N_2O_2$). Vapour deposition of these molecules onto the PTFE-coated substrates was conducted within a bell-jar evacuation chamber at pressures of $2.7–6.7 \times 10^{-3}$ Pa. The molecules were allowed to sublime at temperatures $\sim 100\,^{\circ}C$ below their respective melting points (except for Bis-MSB, which sublimed at temperatures closer to the melting point) while the PTFE-coated glass slide was maintained at a temperature between 30 and 130 °C. Films with thicknesses $< \sim 1\ \mu m$ were produced over a period of 10–20 min; the average deposition rate was $< \sim 1\ nm\ s^{-1}$.

2.3. Characterization

The fluorescent films were analysed by polarized spectroscopic fluorescence measurements. For each sample, the luminescence spectrum (intensity versus wavelength) was measured for light polarized parallel and perpendicular to the PTFE chain axis. A schematic of the apparatus employed to execute these measurements is shown in Fig. 1. A sample was exposed to unpolarized u.v. light (wavelength = 254 or 365 nm) from an Ar lamp, and the light emitted from the sample passed through a polarizer and a monochromator (Spex model 340S) to a detector (Photometrics CCD array camera model CE 200A). The spectrum measured was not the true intensity versus wavelength; the monochromator produced greater intensities at intermediate wavelengths. However, the ratio of the intensities for both polarization directions at a given wavelength was accurate to within 5%.

The crystallographic orientation of the fluorescent materials was determined by transmission electron microscopy (TEM). For this purpose, samples were coated with carbon and subsequently detached from the glass substrate by a previously described method [7]. Images and diffraction patterns were recorded with a Jeol 100CX instrument operated at 100 kV. *p*-Terphenyl crystals, which were relatively large and more widely spaced than the crystals of other molecules, were also examined by optical microscopy.

The lattice structure of DPS was deduced from electron diffraction patterns of oriented films and X-ray diffractometer measurements of DPS powder, which were performed using the Scintag diffractometer model 2000.

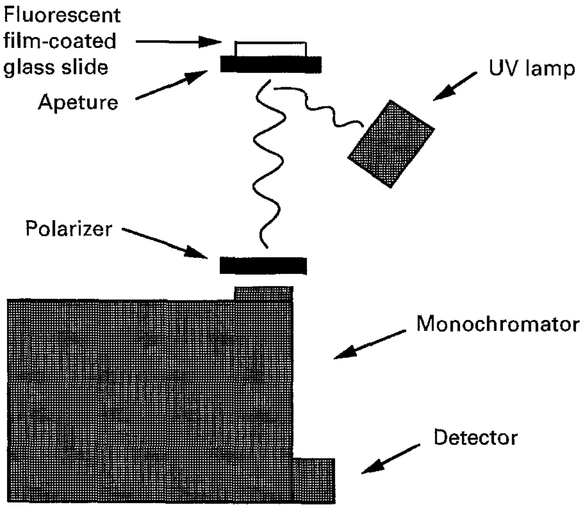

Figure 1 Schematic of the apparatus used for polarized spectroscopic fluorescence measurements.

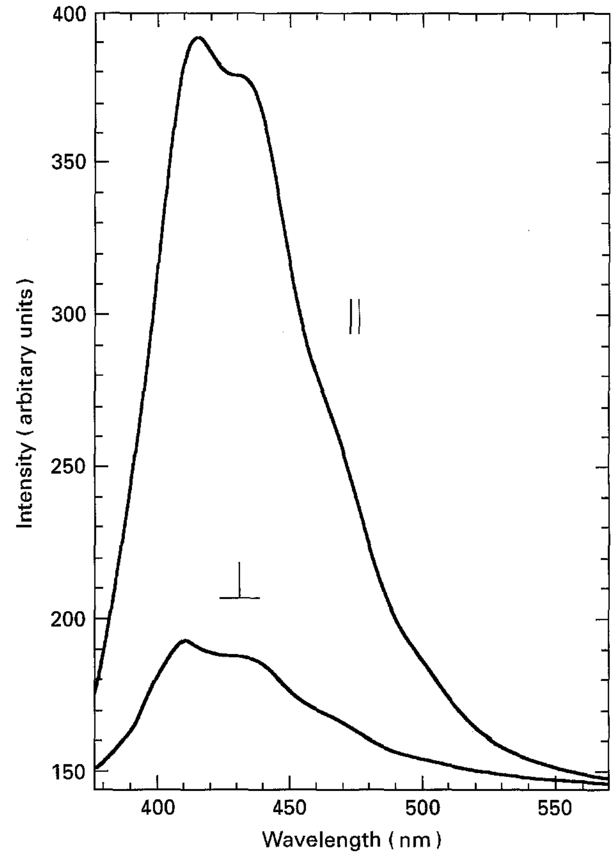

Figure 2 Fluorescence spectrum of an oriented *p*-quaterphenyl film for light polarized parallel (upper curve) and perpendicular (lower curve) to the PTFE chain direction.

3. Results and discussion

Each material deposited on the oriented PTFE films exhibited anisotropic or polarization-dependent fluorescence, indicating that the fluorescent molecules were aligned at least to some extent along the PTFE chain direction. The polarized fluorescence spectrum for *p*-quaterphenyl is shown in Fig. 2. For each fluorescent material the measured ratio, at a given wavelength, of the intensity of fluorescence polarized parallel to the PTFE chain direction relative to the intensity of light polarized perpendicular to this direction (the "dichroic ratio") is listed in Table I. Heating the PTFE substrate during vapour deposition did not have a dramatic effect on the alignment of any of the materials except for POPOP, which was optimally oriented at substrate temperatures of 110–130 °C. The dichroic ratio for POPOP listed in Table I is that of a film produced at a substrate temperature of 130 °C, whereas the other dichroic ratios listed in this table are those of films grown at temperatures below 70 °C.

p-Terphenyl, *p*-quaterphenyl, and *p*-quinquephenyl molecules crystallized on to the PTFE films in the form of needle-shaped and more irregularly-shaped crystals (see Fig. 3). The needle-shaped crystals were aligned with their long axis perpendicular to the PTFE chain axis. Electron diffraction patterns revealed that the *p*-phenylene crystals were in the equilibrium monoclinic phase (*p*-terphenyl: $a = 0.811$ nm, $b = 0.561$ nm, $c = 1.361$ nm, $\beta = 92°$; *p*-quaterphenyl: $a = 0.811$ nm, $b = 0.561$ nm, $c = 1.791$ nm, $\beta = 96°$; *p*-quinquephenyl: $a = 0.807$ nm, $b = 0.558$ nm, $c = 2.206$ nm, $\beta = 98°$) [13]. The crystal structure of these materials consisted of molecules that were perpendicular to the b-axis and inclined at a small angle with respect to the c-axis [13].

When the electron beam was approximately normal to the plane of the *p*-phenylene films, hk0 reflections from many of the irregularly-shaped crystals were detected (e.g. Fig. 4(a)), indicating that the a–b plane was parallel to the plane of the film, or a close-packed plane of PTFE. Thus, these crystals consisted of molecules that were nearly perpendicular to the surface of the PTFE film. The b-axis of many (but not all) of these crystals ($b = 0.56$ nm) was parallel to the PTFE interchain (a or b) axis (length = 0.57 nm).

When the *p*-quinquephenyl film was tilted ~17° in the electron microscope about the PTFE interchain axis, 0kl reflections from many of the needle-shaped crystals were detected (see Fig. 4(b)). This observation revealed that these needle-shaped crystals consisted of molecules aligned parallel to the PTFE chain direction, since the *p*-quinquephenyl molecules were inclined at an angle of 17° relative to the *p*-quinquephenyl c*-axis (13). The b-axis of these needle-shaped crystals, like that of many of the irregularly-shaped crystals, was parallel to the PTFE interchain axis. No doubt, the needle-shaped crystals of *p*-terphenyl and *p*-quaterphenyl also consisted of molecules aligned parallel to the PTFE chain direction, with the b-axis parallel to the PTFE interchain axis, since the crystal structures of these materials were essentially identical to that of *p*-quinquephenyl. However, according to TEM and optical microscope

TABLE I Dichroic ratios of the fluorescent materials used in this study

Fluorescent Film	Dichroic Ratio[a]
p-terphenyl ($C_{18}H_{14}$)	2.9
p-quaterphenyl ($C_{24}H_{18}$)	5.0
p-quinquephenyl ($C_{30}H_{22}$)	3.9
diphenylstilbene ($C_{26}H_{20}$)	1.7
1,4-bis(2-methylstyryl)benzene ($C_{24}H_{22}$)	2.9
1,4-bis-2-(5-phenyloxazolyl)benzene ($C_{24}H_{16}N_2O_2$)	4.5

[a] Measured at wavelengths of (in descending order): 415, 415, 420, 460, 450, and 475 nm.

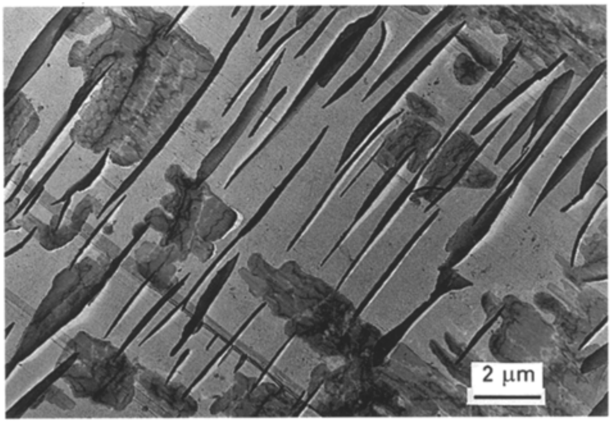

Figure 3 TEM image of *p*-quinquephenyl crystals grown on a highly oriented PTFE film. Scale bar 2 µm.

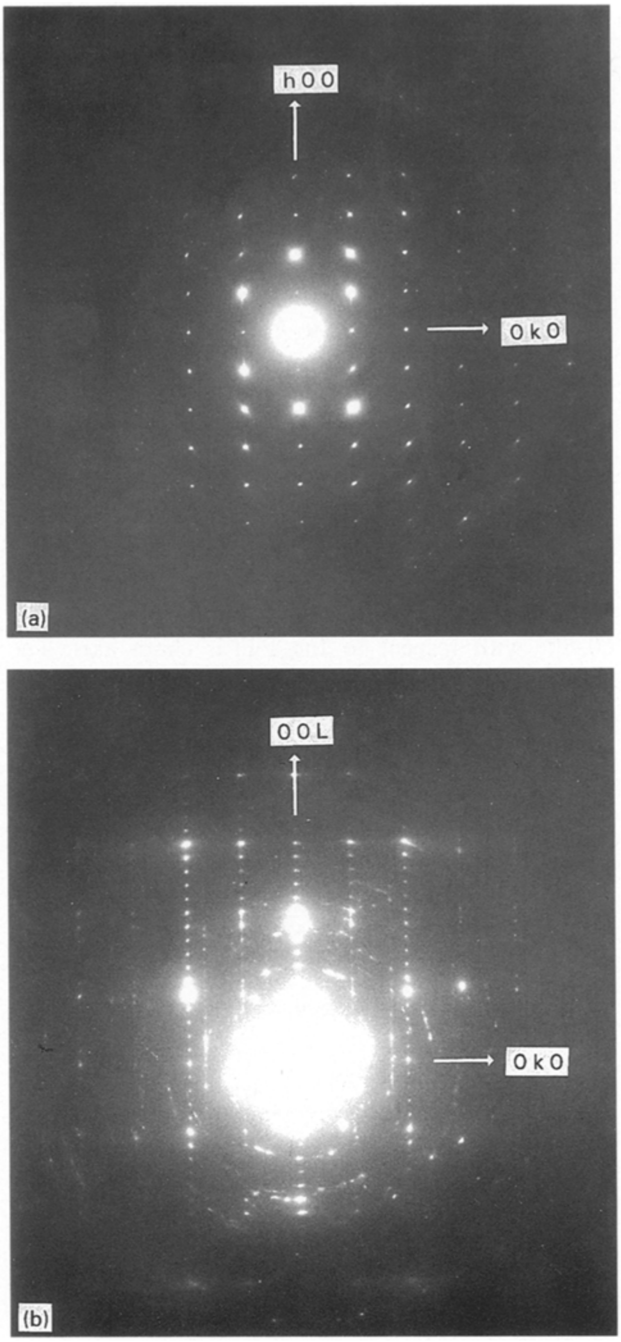

Figure 4 Electron diffraction patterns of (a) an irregularly-shaped crystal and (b) a needle-shaped crystal of *p*-quinquephenyl grown on a PTFE film. The hk0 reflections of the irregularly-shaped crystal (a) were recorded when the sample was tilted 8° about the PTFE interchain axis, whereas the 0kl reflections of the needle-shaped crystal (b) were recorded at a tilt angle of 17° about the same axis.

images, the needle-shaped crystals of *p*-terphenyl were not quite so well aligned as those of the other two materials. This was reflected in the lower dichroic ratio of the *p*-terphenyl film (2.9) compared to that of the *p*-quaterphenyl (5.0) and *p*-quinquephenyl (3.9) films. (The needle-shaped crystals of *p*-quaterphenyl and *p*-quinquephenyl were about equally well aligned. The dichroic ratio of the *p*-quaterphenyl film was slightly greater than that of the *p*-quinquephenyl film probably because of the greater volume of the needle-shaped crystals relative to that of the irregularly-shaped crystals for the former sample.)

The surface of the PTFE film consisted of close-packed planes at 60° intervals about the c-axis [4, 7], and thus the *p*-phenylene crystals grown on these films must have been oriented as shown in Fig. 5.

Like the *p*-phenylene molecules, DPS precipitated on PTFE films in the form of needle-shaped and irregularly-shaped crystals, as shown in Fig. 6. The needle-shaped crystals were inclined at an angle of 60–70° with respect to the PTFE chain axis. The crystal structure of this material is apparently unknown, but electron and X-ray diffraction patterns revealed that the lattice was either orthorhombic or monoclinic with $a = 0.76$ nm, $b = 0.60$ nm, $c = 1.90$ nm, and $\beta \sim 90°$. The lattice parameters were deduced from two different diffraction patterns originating from the irregularly-shaped crystals (see Fig. 7(a) and (b)) and from X-ray diffractometer measurements of DPS powder. The d-spacings corresponding to the electron diffraction spots were measured using the 0 0 15 reflection of PTFE as a standard.

hk0 reflections from many of the irregularly-shaped crystals of DPS were detected when the electron beam was normal to the plane of the sample (see Fig. 7(a)), and a different set of reflections (Fig. 7(b)) was recorded when the sample was tilted 18° about the PTFE c-axis. These diffraction patterns revealed that the a–b planes of the irregularly-shaped crystals were parallel to the close-packed planes of the PTFE film and that the b-axis of many of these crystals (length = 0.60 nm) was parallel to the PTFE inter-chain axis (length = 0.566 nm). Unfortunately, we did not observe a good diffraction pattern originating from the needle-shaped crystals of DPS, but it is

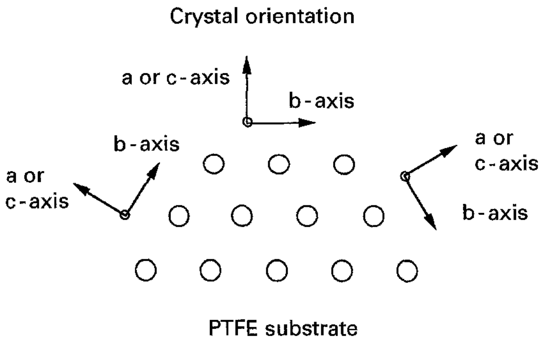

Figure 5 Orientation of a majority of the *p*-phenylene crystals grown onto PTFE films. The circles represent PTFE chains. The PTFE c- [chain] axis is normal to the plane of the figure.

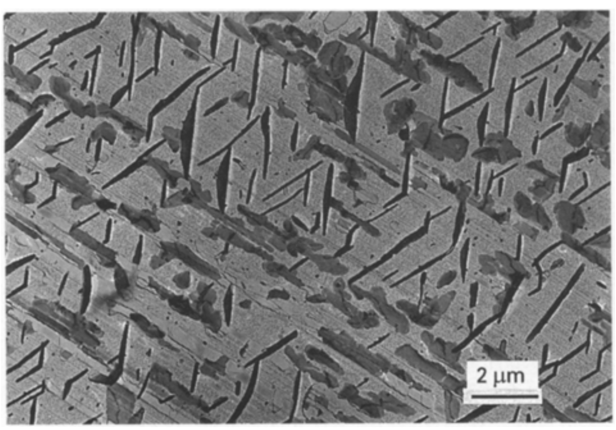

Figure 6 TEM image of DPS crystals grown on a PTFE film. Scale bar 2 μm.

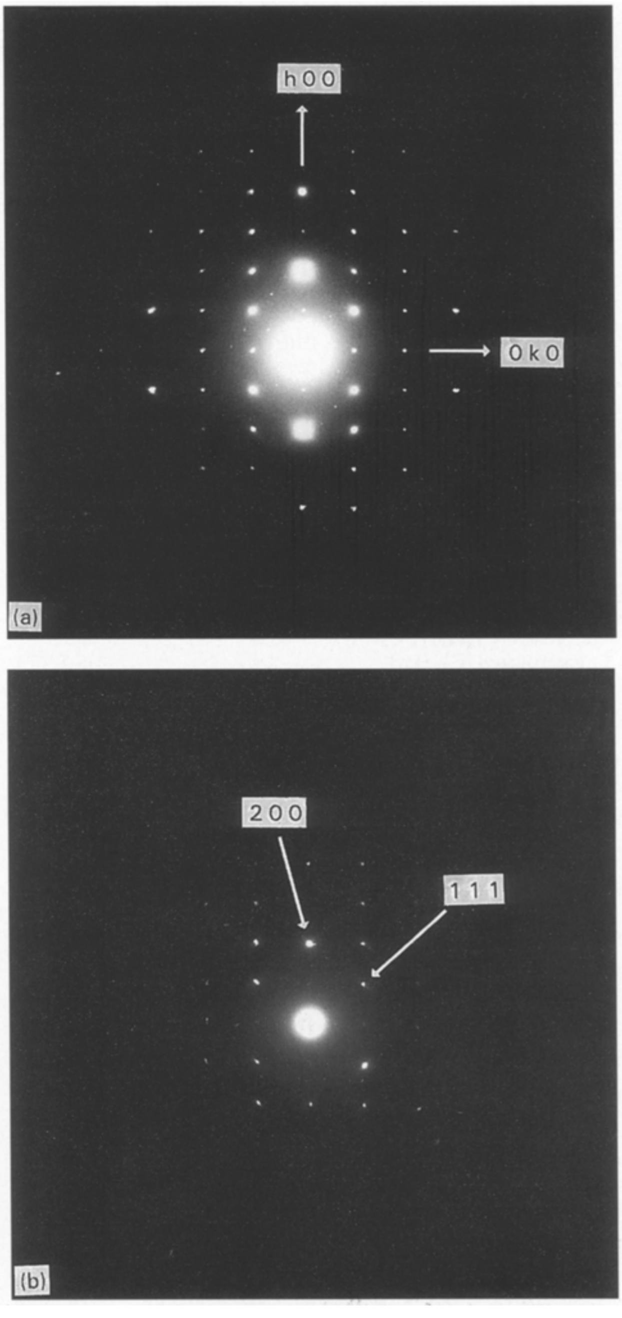

Figure 7 Electron diffraction patterns of an irregularly-shaped crystal of DPS grown on a PTFE film, recorded at tilt angles of (a) 0° and (b) 18° about the PTFE c-axis.

reasonable to assume that the b-axis of these crystals was parallel to the PTFE interchain axis. Thus, the DPS and p-phenylene crystals, like those of dimethyl-oligothiophenes studied by Yang and colleagues [11], appeared to adopt a "dual orientation" on PTFE films, with lattice matching occurring along the PTFE interchain axis.

Although the DPS and p-phenylene crystals appeared to orient on PTFE films in a similar manner, the measured dichroic ratio of the DPS film (1.7) was significantly less than that of the p-phenylene samples (see Table I). Without knowledge of the crystal structure of DPS, the reason for this difference in the dichroic ratios is unclear.

POPOP crystallized on the PTFE films in the form of long needles aligned parallel to the PTFE chain (or groove) direction, as shown in another publication [4]. Electron diffraction patterns (e.g. Fig. 8) revealed that POPOP was in its equilibrium monoclinic phase ($a = 0.923$ nm, $b = 0.529$ nm, $c = 1.932$ nm, $\beta = 92.09°$) with the b-axis parallel to the long axis of the needles [14]. When the sample was rotated about the POPOP b-axis (or PTFE c-axis) no significant change in the intensity of the POPOP reflections was detected; evidently, the crystals were oriented in a fibre pattern. As discussed in another study [4], the fibre-like orientation of the POPOP crystals implies that oriented growth occurred because of the grating-shaped surface topography of the PTFE film; i.e. orientation occurred by a grapho-epitaxial mechanism rather than a lattice-matching or epitaxial mechanism. Although the POPOP crystals were well aligned along the PTFE chain direction, the measured dichroic ratio of these oriented crystals was only 4.5, no doubt a result of the criss-crossed arrangement of the POPOP molecules in the crystalline state [14].

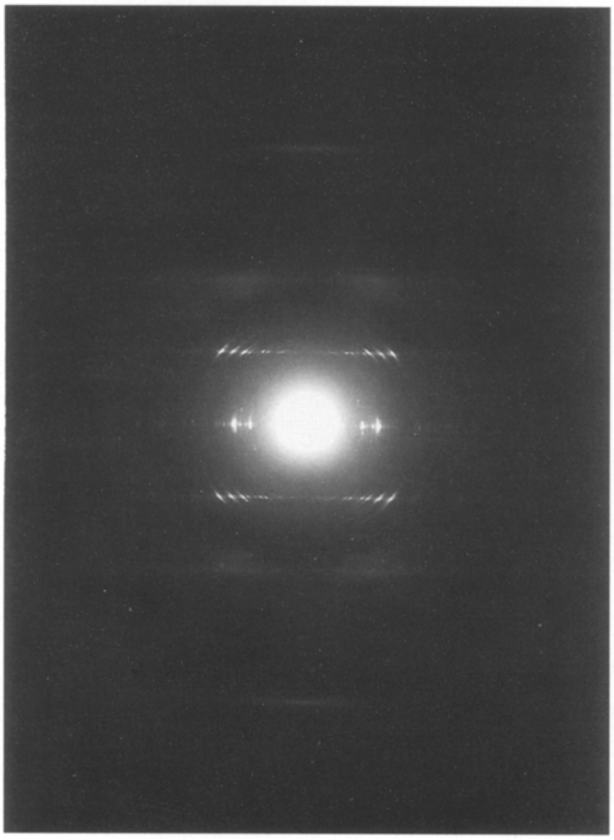

Figure 8 Electron diffraction pattern of POPOP crystals aligned on a PTFE substrate. The POPOP b-axis and PTFE c-axis are parallel to the meridional in the pattern.

Bis-MSB molecules crystallized on PTFE films in the form of irregularly-shaped crystals, as shown in Fig. 9. The crystal structure of this material is unknown, and its lattice structure was not solved in the current work. Electron diffraction patterns did suggest, however, that the orientation of this material occurred by conventional epitaxy, since the crystals did not appear to be oriented in a fibre pattern; the intensity of the diffraction spots strongly depended on the angle of tilt of the sample about the PTFE c-axis. A good diffraction pattern from many of the Bis-MSB crystals was detected when the film was tilted ~25° about the PTFE interchain axis (see Fig. 10).

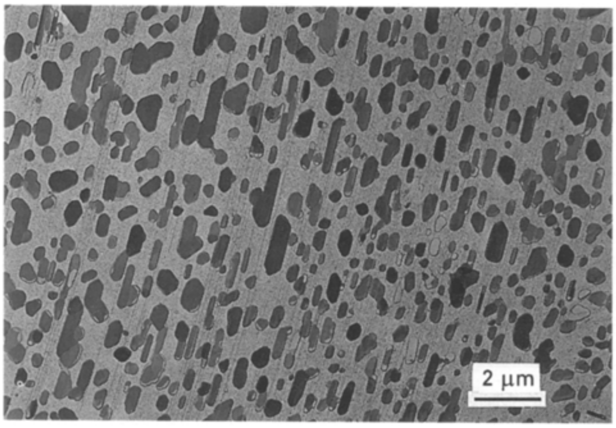

Figure 9 TEM image of Bis-MSB crystals grown on a PTFE film. Scale bar 2 μm.

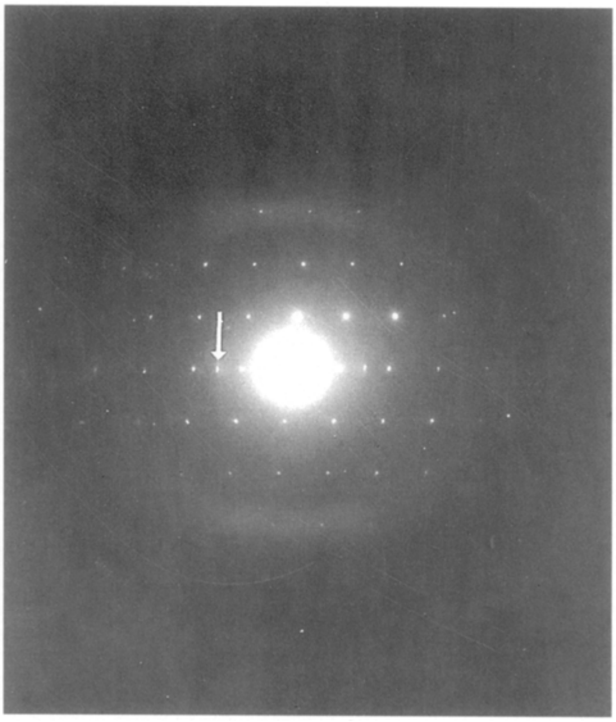

Figure 10 Electron diffraction pattern of a Bis-MSB crystal recorded at a tilt angle of 25° about the PTFE interchain axis. The reflection indicated by the arrow is the 1 0 0 reflection of PTFE.

4. Conclusions

Each of the fluorescent materials used in this study exhibited oriented growth on aligned PTFE substrates. *p*-Phenylene and DPS crystals generally adopted two different orientations with respect to the close-packed planes of the PTFE films, with lattice matching occurring along the PTFE interchain (a or b) axis. Although details regarding the lattice structure and orientation of Bis-MSB crystals were not determined, this material also appeared to orient epitaxially on the PTFE films. POPOP crystals, on the other hand, aligned in a fibre pattern, evidently by a grapho-epitaxial mechanism. The relatively modest values of the dichroic ratios of the fluorescent films, which ranged from 1.7 to 5.0, was apparently due to the multiple orientations of the crystals on the PTFE films and the fact that the molecules of at least one material were arranged in a criss-crossed pattern within the crystal lattice.

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