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Crystal Structure and Polymorphism of Dimethyl-Oligothiophenes Crystallized Epitaxially on Highly Oriented PTFE Thin Films

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Crystal Structure and Polymorphism of Dimethyl-Oligothiophenes Crystallized Epitaxially on Highly Oriented PTFE Thin Films

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The crystal structure of dimethyl-oligothiophenes grown by epitaxial crystallization on highly oriented PTFE thin films has been studied by transmission electron microscopy. The dimethyl-oligothiophenes crystallize principally in a monoclinic phase with common lattice parameters a, b, and β, but with different c for different numbers of thiophene rings: $a = 0.598$ nm, $b = 0.789$ nm, and $\beta = 98°$; and $c = 1.866$ nm for the tetramer, $c = 2.234$ nm for the pentamer and $c = 2.596$ nm for the hexamer. The space group is $C2/m$. The calculated crystallographic densities are 1.36 g/cm^3, 1.39 g/cm^3 and 1.40 g/cm^3 for the tetramer, pentamer and hexamer respectively. Polymorphism is found, with coexistence of monoclinic and orthorhombic crystal structures. The dominant phase, however, is monoclinic. The relationship between the different phases is discussed.

Keywords: Crystal structure, oligothiophenes.

INTRODUCTION

The epitaxial crystallization of a polymer from solution upon an alkali-halide substrate was originally observed by Willems[1] and Fischer[2] in the 1950s. Epitaxial crystallization of polymers on organic and polymeric substrates has been reviewed by Wittmann and Lotz.[3] The potential use of epitaxially crystallized layers has attracted attention since the discovery of the method of preparation of highly oriented thin films of

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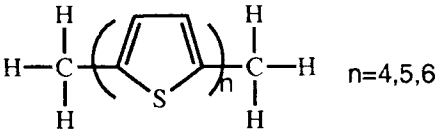
poly(tetrafluoroethylene) (PTFE) as a substrate which induces orientated growth of organic materials.[4]

Oligothiophene epitaxial layers are electronically interesting materials with potential for use in thin film transistors.[5,6] Recently, the synthesis and characterization of oligothiophenes with alkyl end-groups have been carried out. The crystal structure of dimethyl-quaterthiophene was determined using a four-circle X-ray diffractometer on single crystals and reported as orthorhombic;[7] the results are summarized in column 1 of Table 1. Two sets of monoclinic unit cell dimensions were found for the crystallites in sexithiophene films (also by X-ray diffraction); the results are summarized in column 2 of Table 1.[8]

In this paper we report the crystallographic data, obtained using transmission electron microscopy (TEM), for the dimethyl-oligothiophenes (tetramer, pentamer and hexamer) epitaxially crystallized on highly oriented PTFE thin films.



The unit cell dimensions of the major phases are listed in Table 2. In each case, the principal phase is monoclinic. Since a minor orthorhombic phase is also found, the dimethyl-oligothiophenes are polymorphic.

EXPERIMENTAL DETAILS

(1) The epitaxial crystallization procedure

The highly oriented PTFE substrate was prepared by the method described in Reference 4. Epitaxially crystallized oligothoiphenes with 4, 5 and 6 thiophene rings were obtained by vacuum deposition on PTFE while maintaining the substrate temperature at 80 °C. The desired slow evaporation was controlled by setting the temperature of evaporation boat slightly above the melting temperature for each oligothiophenes (192 °C, 243 °C and 298 °C for 4, 5 and 6 thiophene rings, respectively). This slow evaporation process typically lasted for about 30 minutes under 10^{-6} torr vacuum. The thicknesses of the epitaxial layers prepared for TEM examination were about 100 nm (controlled by the amount of material evaporated). The dimethyl-

TABLE I

The Crystallographic Data of Dimethyl-quaterthiophene (Reference 7) and of Sexithiophene (Reference 8)

Orthorhombic Dimethylquaterthiophene[7]	Monoclinic Sexithiophene[8]	
$a = 7.707$ Å	$a = 5.980$ Å	$a = 5.667$ Å
$b = 5.941$ Å	$b = 7.798$ Å	$b = 7.800$ Å
$c = 36.031$ Å	$c = 50.276$ Å	$c = 47.288$ Å
$\beta = 90°$	$\beta = 111.3°$	$\beta = 100.6°$
Space group Pbca	Space group $P2_1/c$	

TABLE II

The crystallographic Data of the Dimethyloligothiophenes

	Tetramer	Pentamer	Hexamer
a	0.598 nm	0.598 nm	0.598 nm
b	0.789 nm	0.789 nm	0.789 nm
c	1.866 nm	2.234 nm	2.596 nm
β	98°	98°	98°

oligothiophenes were supplied by Central Research Laboratories, Matsushita Electric Industrial Co., Ltd.

(2) Sample preparation for transmission electron microscopy, TEM

The epitaxially crystallized dimethyl-oligothiophenes on PTFE were carbon coated (thickness about 100 nm). In order to detach the epitaxial layer from its supporting glass slide, polyacrylic acid drops (~ 3 mm in diameter) were used (put on the carbon coated layer and dried). The dried drop-area with underlying sample layer was peeled from the glass by using a sharp knife edge. After dissolving off the polyacrylic acid in water, the sample layer was picked up on a Cu TEM grid. A JEOL EM 100cx instrument was used for this study at a beam accelerating voltage of 100 KV.

RESULTS AND DISCUSSION

a. Dimethyl-quaterthiophene (DQtT)

Figure 1a is an electron micrograph which shows the morphology of the epitaxial growth of DQtT on the oriented PTFE layer. Two types crystallites are clearly seen, plate-like and needle-like. The PTFE film substrate can be seen as well, with chain alignment direction indicated by the lines running from the upper-left to the lower-right corner of the micrograph. The grain size of the plate-like crystallites is about 0.5 μm in diameter, whereas the needle-like crystallites are about 1.5μm long and 0.15 μm wide.

The plate-like and needle-like crystallites are the crystallites with different orientation. The orientation of the crystallites can be determined from the electron diffraction patterns. Figure 1b is a [001] axis pattern of a plate-like crystallite (one of which is indicated by an arrow in Fig. 1a) with almost no tilt of the substrate with respect to the incident beam (sometimes a minor tilt adjustment, less than 10 degrees, is required to achieve the on-axis diffraction pattern). Therefore, the plate-like crystallites are aligned with **a** and **b** axes in the plane of the PTFE thin film, while the **c**-axis is perpendicular to that plane. The reflections in perpendicular directions, **a***, **b***, are indexed as (100) and (020), implying the following lattice parameters: $a = 0.598$ nm and $b = 0.789$ nm, and $\alpha = \gamma = 90°$.

Figure 1c is a [010] axis pattern obtained from a needle-like crystallite (one of which is indicated by two arrows in Fig. 1a). Note that **a*** indexed as (200), and **c*** are not orthogonal, implying that $\beta \neq 90°$. This means that the needle-like crystallites are aligned with **a** and **c** axes in the plane of the PTFE thin film, while the **b** axis is

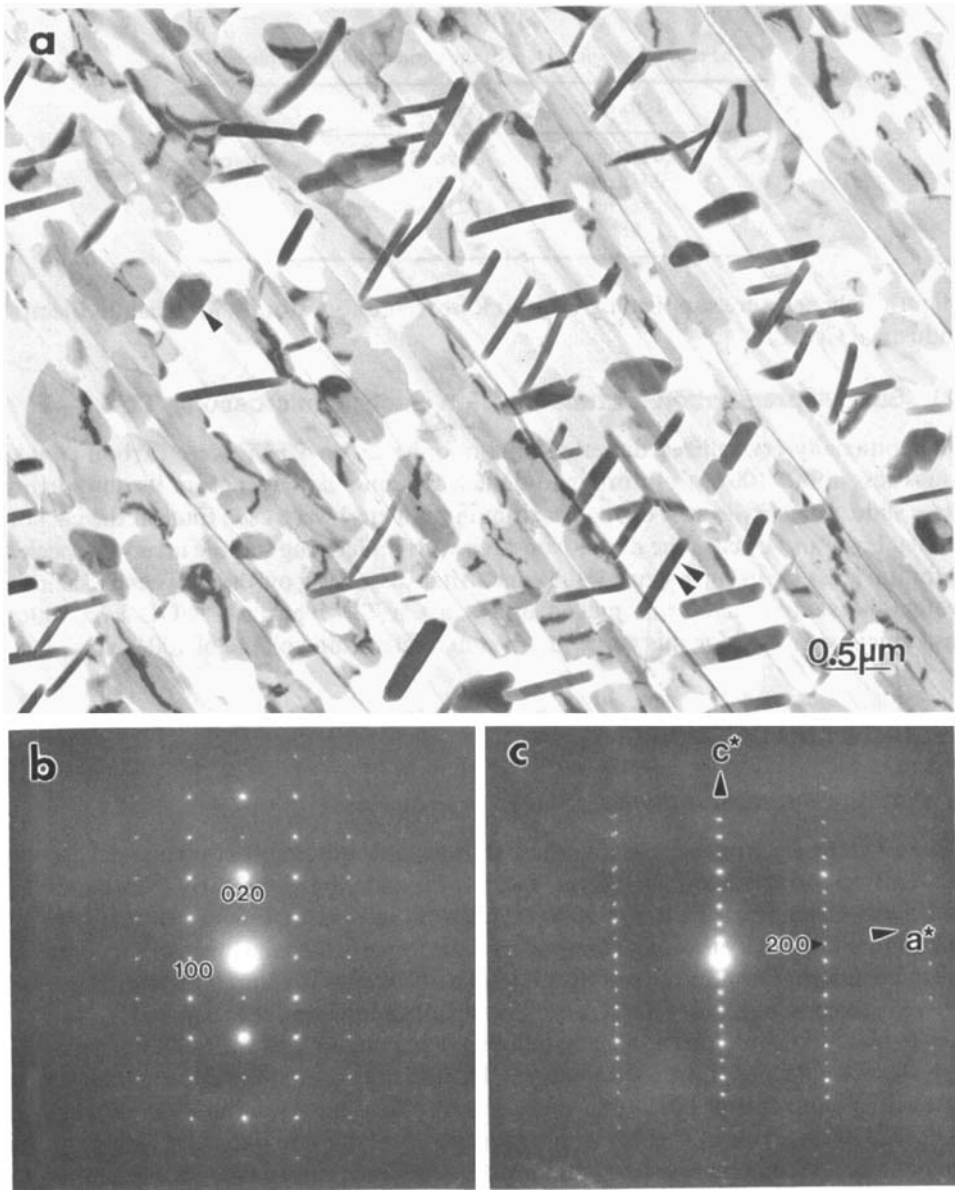
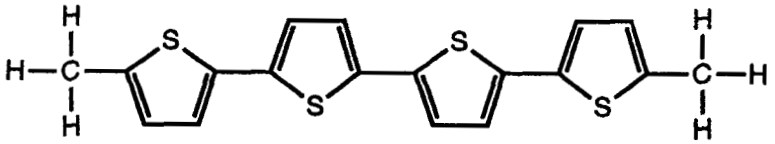


FIGURE 1 (a) Electron micrograph showing the two types of crystallite morphology: plate-like and needle-like; (b) [001] axis electron diffraction pattern from DQtT epitaxially crystallized on PTFE; (c) [010] axis electron diffraction pattern from DQtT epitaxially crystallized on PTFE; the angle between **a*** and **c*** is 98° indicating a monoclinic structure.

perpendicular to that plane. Therefore, the crystal structure of DQtT is monoclinic. The lattice parameters obtained from the pattern in Figure 1c are $a = 0.598$ nm, $c = 1.866$ nm and $\beta = 98°$. The unit cell dimensions are summarized in the first column of Table 2.

The molecular structure of DQtT is as follows:



with the thiophene rings arranged alternately up and down resulting in a linear (rather than a helical) conformation.[7,9] The length of DQtT is approximately 1.8 nm, consistent with the c-axis lattice parameter, implying that the DQtT oligomers are aligned in a stack with the molecular axis along **c**. In the **b** direction, neighboring oligomers are close-packed and tend to stack with backbones on top of one another in a nearly parallel manner. This close-packing gives two DQtT molecule in the unit cell.

Figure 2 is a schematic drawing of the crystal structure of the monoclinic phase of DQtT. The space group symmetry is inferred from the systematic absence of the reflections in the diffraction patterns ($k = 2n + 1$, for $0k0$; $h = 2n + 1$, for $h01$), and the lattice is C-centered if one equivalent DQtT molecular is considered as a lattice point. These data are consistent with the $C2/m$ space group. Actually, Figure 2 indicates a two fold axis along **b** and a mirror plane perpendicular to **b**, with a C-centered unit cell. The

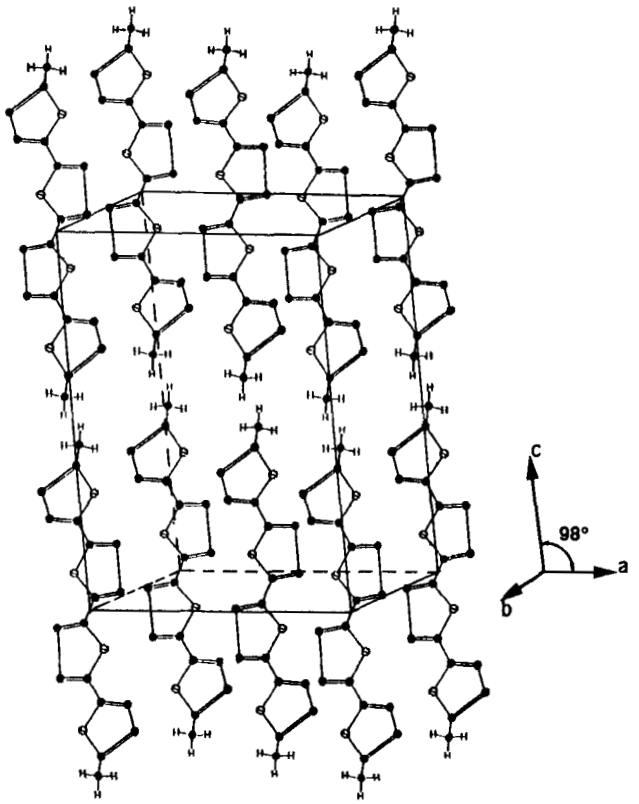


FIGURE 2 Schematic drawing of the crystal structure of DQtT, showing the monoclinic unit cell.

unique axis is **b**, and the angle between the **a** and **c** axes is 98°. To our knowledge this phase of DQtT has not been reported previously. The crystallographic density is $\rho = 1.36\,g/cm^3$.

b. Dimethyl-Quinquethiophene (DQqT)-the monoclinic phase

Figure 3a is an electron micrograph obtained from DQqT epitaxially crystallized on an oriented PTFE thin film. Again, two different morphologies can be seen, plate-like crystallites and needle-like crystallites. The crystallites are smaller than those of DQtT; the plate-like crystallites are about 0.3 μm in diameter, and the needle-like crystallites are about 0.4 μm long and 0.05 μm wide.

Figure 3b is a corresponding diffraction pattern. Due to the small size of the crystallites, the diffraction spots are a superposition of the patterns from plate-like and needle-like crystallites. By analogy with DQtT, the needle-like crystallites have **c**-axis lying in the plane of the PTFE thin film (the longest dimension of unit cell, corresponding to the shortest reciprocal lattice translation period). Thus, the spots indicated with an arrow are diffracted from the needle-like crystallites with lattice parameter $c = 2.234$ nm. The diffraction spots with arc shape sitting on the Debye rings can be indexed as (100), (020), (210), (120) and so on, by using lattice parameters a and b identical to those of DQtT. Therefore, the unit cell of the needle-like crystallites of DQqT has the same construction as that of DQtT. The only difference is in the c parameter which is 0.368 nm longer, consistent with the additional thiophene ring in the DQqT molecular structure. The crystallographic density is $\rho = 1.39\,g/cm^3$.

c. Dimethyl-Sexithiophene (DSxT)-the monoclinic phase

Figure 4 shows the corresponding electron micrograph (Fig. 4a) and electron diffraction pattern (Fig. 4b) for DSxT. Again, the plate-like and needle-like crystallites can be

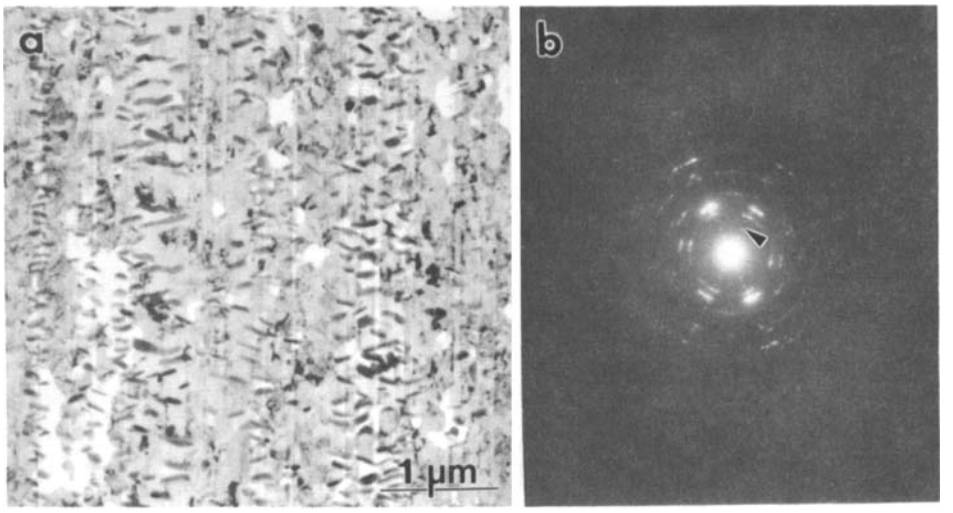


FIGURE 3 Electron micrograph (a), and correspoding electron diffraction pattern (b) of DQqT.

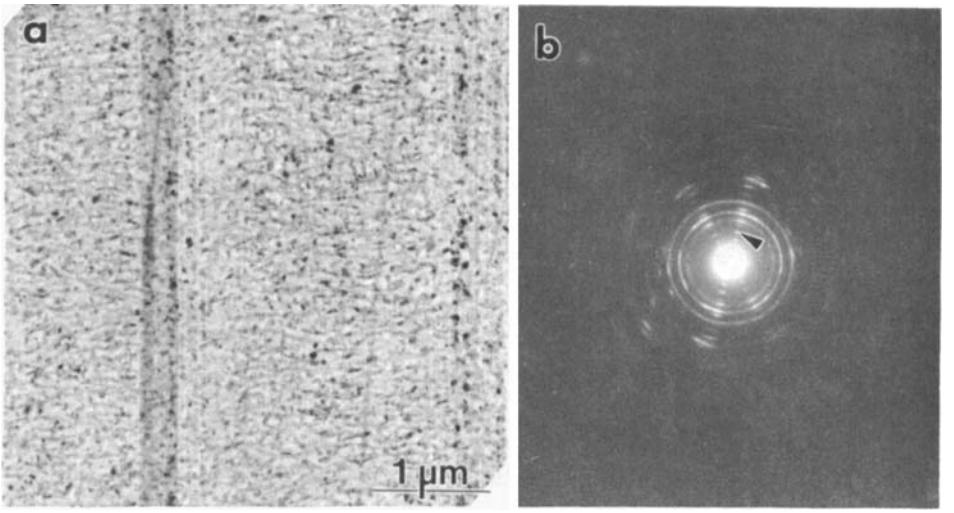


FIGURE 4 Electron micrograph (a), and corresponding electron diffraction pattern (b) of DSxT.

seen in Figure 4a, though they are even smaller than in DQqT. The plate-like crystallites are about 0.05 μm in diameter, the needle-like crystallites are about 0.3 μm long and 0.02 μm wide.

The diffraction pattern (Fig. 4b) is similar to that of DQqT. From the similar array of diffraction spots (**c*** direction) with those obtained from DQqT, we identify the *c*-axis lattice parameter as $c = 2.596$ nm, larger by 0.362 nm than in DQqT. Again, the pattern can be indexed with a, b and β the same as for the DQtT and DQqT oligomers (Third column of Table 2). The crystallographic density is $\rho = 1.40\,g/cm^3$).

d. Polymorphism of dimethyl-oligothiophenes

As shown above, the principal phase of the dimethyl-oligothiophenes crystallizes on the PTFE substrate in a monoclinic structure. These oligothiophenes are, however, polymorphic with a minority of crystallites in the same epitaxial layer in an orthorhombic phase. A series of diffraction patterns obtained from orthorhombic crystallites of DQtT are shown in Figure 5; Figure 5a is the diffraction pattern with the beam incident along [001], 5b with the beam incident along [010], and 5c with the beam incident along [100]. The morphology of the orthorhombic crystallites is similar to that of monoclinic crystallites. Figure 5a is obtained from plate-like crystallite, and both Figure 5b and Figure 5c are from needle-like crystallites. Figure 5d is a schematic drawing of the various patterns (in Figs. 5 a, b, and c.) obtained from the orthorhombic crystal structure of DQtT.

Note that the [001] pattern in Figure 5a is different from that of monoclinic DQtT (Fig. 1b) in the systematic absence of reflections. In Figure 5a there is systematic absence along **a***; when $h = 2n + 1$, the $h00$ reflections are absent in addition to the $0k0$ reflections which are absent when $k = 2n + 1$, as in Figure 1. These ($h00$) reflections are not missing in Figure 1b. Thus, the symmetry of the pattern in Figure 5a is orthorhombic.

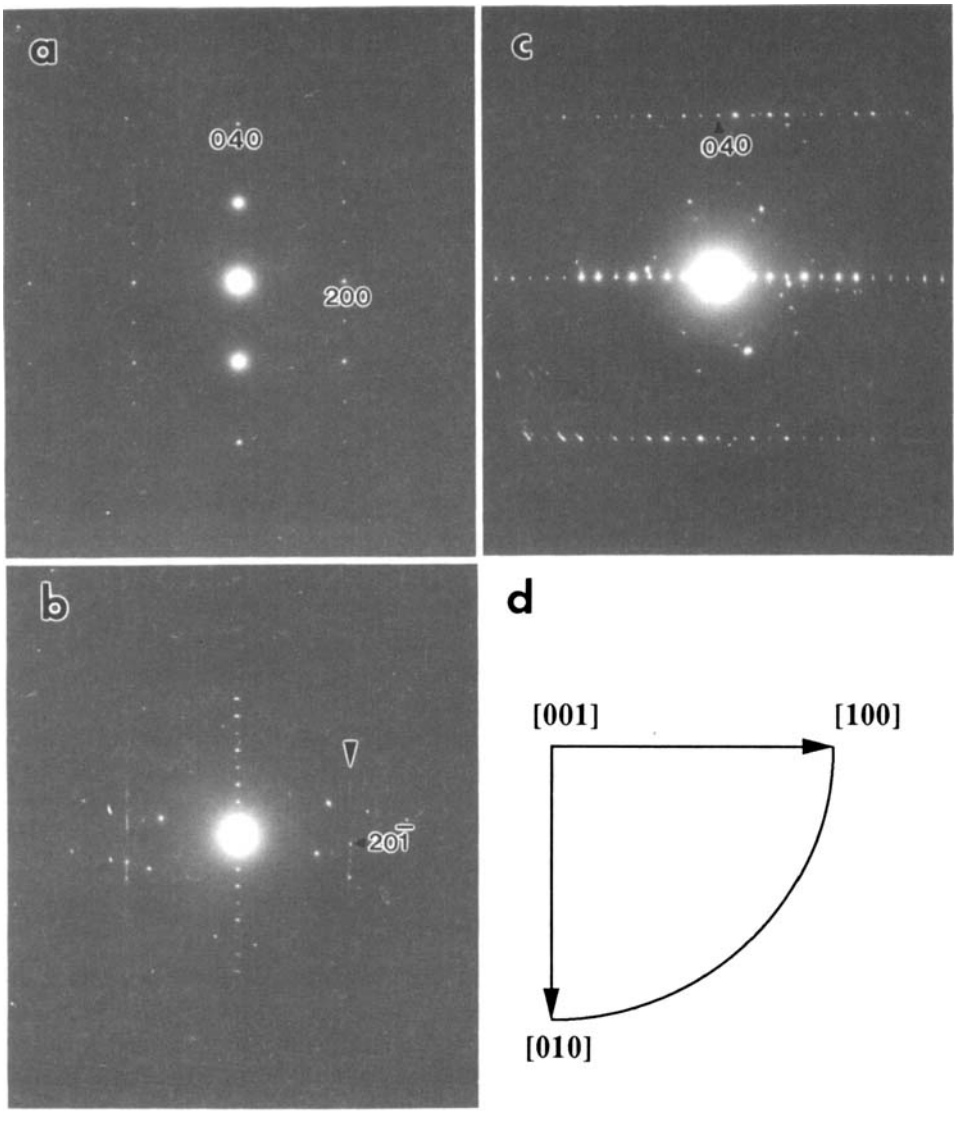


FIGURE 5 A series of diffraction patterns: (a) electron beam incident along [001]; (b) electron beam incident along [010]; (c) electron beam incident along [100]; (d) Schematic drawing of the map showing the orthorhombic crystal structure of DQtT.

The existence of orthorhombic crystallites can by seen also by carefully examining the [010] pattern shown in Figure 5b; the angle between **a*** and **c*** is 90°. Furthermore, the (001) reflections are absent when $l = 2n + 1$. This means that the c-axis lattice parameter is twice as long as that of the monoclinic DQtT phase, $c = 3.732$ nm, consistent with that reported in Reference 7. Note that the (201) reflections (indicated by an arrow in Fig. 5b) are mainly in the shape of streaks. There are a few diffraction

spots (*e.g.*, the (20l) spot) along with the streak; these spots were used to confirm both the 90° angle between **a*** and **c*** and the systematic absences. The streaks imply that the crystallites have a lamellar structure and/or planar defects. Figure 5c is a [100] axis electron diffraction pattern, which shows that the (0*k*0) reflections occur only with $k = 4n$.

From the electron diffraction patterns of the three main axis directions, as schematically shown in Figure 5d, the unit cell dimension of orthorhombic phase can be determined as $a = 0.598$ nm, $b = 0.789$ nm and $c = 3.732$ nm. However the space group of the phase is not obvious because the reflections which are systematically absent are not consistent with each other in the three diffraction patterns. For instance, according to possible reflection condition $k = 4n$ for (0*k*0), as shown in Figure 5c, there might be a *d*-glide plane in crystal, suggesting the Fdd2 space group.[10] This symmetry does not exist, however, in Figure 5a, *i.e.* (0*k*0) reflections also occur when $k = 2n$. This symmetry is also inconsistent with the space group proposed in Reference 7. Actually, these figures were taken from different crystallites, which may have different symmetry due to imperfections in the crystallites. There are only a few of the orthorhombic crystallites in the epitaxial layer, implying that the orthorhombic phase is not easy to form on the epitaxial layer. Evidently, the orthorhombic phase has a higher energy than that of monoclinic phase. However, there is no doubt that the orthorhombic phase coexists with the monoclinic phase in the epitaxially crystallized layers as confirmed by Figure 5, in which the orthorhombic lattice features are clearly seen and match each other very well in the three main axis patterns. This coexistence of monoclinic and orthorhombic phases is supported by Bernstein *et al.*,[11]

The relationship between monoclinic and orthorhombic structures is illustrated by the schematic drawing of Figure 6 (based on Ref. 11, which considered the polymorphism for organic molecules based on packing energy calculations). Figure 6a shows one unit cell of monoclinic phase of DQtT (the molecules are indicated schematically as ellipsoids). Figure 6b shows the same unit cell doubled along the **c** direction. If one monolayer is shifted in one direction (say in **b** direction) by **b**/2, then the face centered

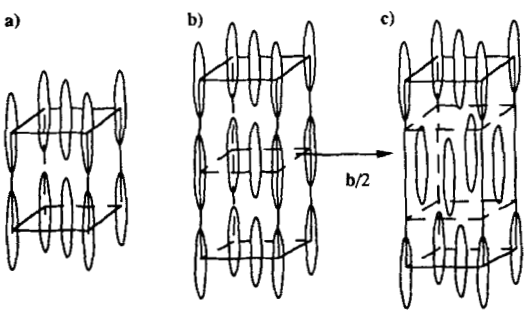


FIGURE 6 Schematic drawing illustrating the relationship between the monoclinic and orthorhombic unit cells of the polymorphic oligothiophenes; the tetramer chains are represented as ellipsoids. a) The monoclinic unit cell as shown in Figure 2; b) Two monoclinic cells; c) One of the molecular backbone layers is shifted by **b**/2; the orthorhombic symmetry and corresponding unit cell can be obtained with small molecular adjustment. The face centered orthorhombic unit cell with *c* axis lattice parameter twice that of the monoclinic cell forms.

orthorhombic unit cell with **c** twice that of monoclinic cell will be formed (see Fig. 6c). Thus, one concludes that the two structures are sufficiently close in energy and that the dimethyl-oligothiophenes are polymorphic. This polymorphism explains the differences and the similarities in both the crystal symmetry and the *c*-axis lattice parameter reported by Hotta and Waragai.[7]

The monoclinic crystallites are dominant when the epitaxially crystallized layers are grown with the PTFE substrate at room temperature, at 80 °C, and in samples subsequently annealed at 125 °C. Thus, the monoclinic structure is probably the lowest energy form. The monoclinic symmetry for dimethyl-sexithiophene is also found for sexithiophene[8] (see the second column of Table 1 and the third column of Table 2). Since, however, we do not find the systematic absences in the **c*** direction for monoclinic phase, the *c*-axis lattice parameter is half of that found in Reference 8 (and our results do not agree with the $P2_1/c$ space group.)[8]

CONCLUSION

The crystal structure of dimethyl-oligothiophenes epitaxially crystallized on PTFE has been studied by using TEM. The epitaxially induced orientation aids the determination of the 3-dimensional crystal structure. The crystal structure of the principal phase of the oligothiophenes is monoclinic with unit cell dimensions as summarized in Table 2. This crystallographic phase of the dimethyl-oligothiophenes has not been previously reported. Crystallites with orthorhombic symmetry are also found; the dimethyl-oligothiophenes epitaxially crystallized on PTFE are polymorphic. The *a* and *b* lattice parameters are identical in the two phases: however, the orthorhombic cell has *c*-axis lattice constant twice as large as that of the monoclinic crystallites.

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