Structural studies on thin films of an unsubstituted oligo(para-phenylenevinylene)


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Abstract

Typically, thin films of the conjugated oligomer \( p \)-bis[(\( p \)-styryl)styryl]benzene (P5V4) prepared by vacuum deposition on substrates like silicon wafers and quartz plates are polycrystalline. Atomic force and electron microscopy reveal elongated clusters with characteristic dimensions of \( 20 \times 80 \) nm. X-ray and electron diffraction (ED) measurements indicate a close correspondence between the crystal structure of these micro-crystallites and the reported structure of single crystals grown from solution. However, we argue on the basis of ED measurements that P5V4 micro-crystallites found in thin films vapor-deposited on amorphous carbon substrates adopt a morphology that differs from the single-crystal structure. In the proposed polymorph, the molecular axis is nearly perpendicular to the substrate plane, though the molecular arrangement is otherwise very similar to that in the single crystal. We suggest that several polymorphs may coexist in the thin films.

Keywords: Electron diffraction; Evaporation; Organic semiconductors; Surface morphology

1. Introduction

Over the last decade, the ‘oligomer approach’ has proven to be of great value in resolving chain length versus property relationships in the field of conjugated polymers and oligomers [1]. Using oligomers instead of polymers enables one to work with chemically well-defined molecules which may be altered in a systematic way in order to study, for example, the optical absorption spectrum as a function of the oligomer chain length [2,3]. These studies on oligomers contribute to a better insight into the evolution of the electronic structure from the monomer to the polymer. Since the oligomers have a well-defined and defect-free molecular structure, extrapolations of measured properties to infinite chain length may be taken, with due caution, to represent the perfect, infinite polymer.

Another advantage of oligomers over polymers is their low molecular weight, which makes it possible to obtain the oligomer in a vapor phase. This is not only useful for measurements on isolated molecules; it also enables one to process the material by vacuum sublimation techniques in high-vacuum or ultra high-vacuum environment. It is possible to optimize the vacuum deposition technique in order to obtain high-quality molecular single crystals with low (active) impurity concentrations \( (10^{18} - 10^{12}) \) cm\(^{-3} \) for optical and transport measurements, revealing for example superconductivity at low temperatures [4–6]. Measurements on these well-defined samples show that intrinsic material properties are affected and often completely masked by defects, which demonstrates how sensitive these materials are towards chemical as well as structural imperfections [7,8]. Hence, knowledge of the thin film structure is important due to the direct link with the optical and electronic properties of these materials and thus with the characteristics of devices composed of these organic semiconductors.

In a consideration of structure–property relationships, it is important to distinguish between substituted oligomers and unsubstituted oligomers, since the substituents...
alter both, the tendency to crystallize, as well as the crystalline structure itself. Many substituted, ‘hairy-rod’ and dialkoxy-substituted oligomers tend to crystallize in a layered structure [9–13], while unsubstituted conjugated oligomers settle down in a herringbone structure in their crystalline state [14–19]. Effects from a higher level in the structural hierarchy are important as well. For example, disorder in the morphological structure causes inhomogeneous broadening effects in the electronic structure of the thin films.

As an illustration of morphological aspects, we show here how the oligomer chain length influences the thin film structure of \textit{para}-phenylenevinylene oligomers. Fig. 1 displays atomic force microscopy (AFM) images of P3V2 (\textit{para}-distyrylbenzene) (a), P4V3 (\textit{p}-distyryl stilbene) (b), and P5V4 (\textit{p}-bis[(\textit{p}-styryl)styryl]benzene) (deposition rate \(\sim 0.1\) nm/s, total layer thickness \(\sim 85\) nm deposited on quartz or sapphire substrates which were kept at room temperature). Thin films of P3V2 and P4V3 show clusters, though the average size of the P3V2 islands is much larger than that of the P4V3 islands. In the P5V4 film, individual islands are not identifiable on the scale of the AFM images shown in Fig. 1c.

Recently, the electronic structure at interfaces found in organic semiconductor devices attracts attention because of an unexpected misalignment of the vacuum levels at interfaces in (some) of these devices [20–26]. Furthermore, detailed studies on the interface formation reveal also other substrate effects on the electronic structure of the organic overlayer on metal substrates [26]. Since the electronic structure is related to the morphological structure one needs information on the morphological structure of very thin films to fully understand the modifications of the electronic structure induced by the substrate. Here we present experimental data (using transmission electron microscopy (TEM), electron diffraction (ED), scanning electron microscopy (SEM) and AFM techniques) collected on thin films of P5V4, an unsubstituted oligo(phenylenevinylene) containing five phenyl rings, vacuum-deposited on amorphous carbon films. The carbon substrates make it possible to use TEM and especially (high-energy) ED techniques to probe the (polycrystalline) structure of thin films.

2. Experimental details

An all-\textit{trans} phenylenevinylene oligomer containing five phenyl rings, \textit{p}-bis[(\textit{p}-styryl)styryl]benzene, was used in this study. The structure of this oligomer is given in Fig. 1c. In the remainder of this paper we will refer to this compound as P5V4. After synthesis [19], the crude product was purified by several high-vacuum sublimation steps (\(p \sim 10^{-6}\) mbar, \(T \sim 300–340^\circ\text{C}\)) and recrystallized from \textit{trans}-stilbene. The product was subsequently filtered, washed with toluene and ether, and carefully dried under vacuum.

The purity of our P5V4 was proved by mass spectroscopy (only the charged and doubly charged ion detected) and IR spectroscopy. The carbon-coated electron microscopy (C-EM) grids (400 mesh) were mounted on a Cu substrate holder with a good thermal contact to the vacuum chamber (\(p_0<10^{-7}\) mbar). After outgassing the deposition cell overnight at \(\sim 150^\circ\text{C}\), P5V4 was vacuum-deposited on the C-EM grids. During the deposition, the temperature of the source was maintained at 300–330 °C, the pressure increased to \(\sim 4 \times 10^{-7}\) mbar, giving an deposition rate of 0.04–0.07 nm/s. During sample growth, the substrate holder was neither
deliberately heated nor cooled, yet the substrate temperature was probably somewhat above room temperature due to the thermal radiance of the source. Thin films grown on quartz and sapphire substrates were prepared in the same vacuum chamber under comparable conditions. Before mounting the substrates on the Cu substrate holder, the substrates were cleaned in an ultrasonic bath using acetone and toluene as solvents. Samples of P5V4 on Si-wafers for X-ray diffraction (XRD) measurements were prepared in a Balzers high vacuum deposition system. After degassing between 200 and 300 °C, two samples were prepared: one with the substrate at room temperature \( p = 1.2 \times 10^{-7} \text{ mbar} \), deposition rate 0.19 nm/s, thickness 3.5 \( \times \) 10^2 nm, according to the layer thickness monitor, LTM), and one with the substrate kept at approximately 250 °C \( p = 1.9 \times 10^{-7} \text{ mbar} \), deposition rate 0.29 nm/s, thickness 3.5 \( \times \) 10^2 nm).

The morphology of the films prepared on C-EM grids was studied with a JEOL 6320F Field Emission Scanning Electron Microscope, and with a JEOL 1200 EX Transmission Electron Microscope, operating at 100 kV, for bright field as well as selected-area diffraction patterns, using spot size 5. XRD patterns were recorded on a Philips X’pert MRD system equipped with a PW 3873/00 copper tube in line focus setting and operated at 40 kV, 40 mA, and a PW 3088/20 mirror monochromator to obtain Cu Kα radiation \( (\lambda = 1.542 \text{ Å}) \). A divergence slit of 1/8° was employed at the source. The Si-wafers with P5V4 film were measured in 0–20 reflection geometry.

The geometry of the two diffraction experiments differs in an essential way. In ED the electron beam is incident perpendicular to the sample surface, and hence the diffracting lattice planes are perpendicular to the sample surface. In the XRD experiments, the reflection geometry employed implies that the observed reflections originate from planes parallel to the sample surface.

The Cerius² program (Cerius² version 3.5, Molecular Simulations Inc., San Diego, CA) was employed for the calculation of powder diffraction data (module Diffraction-Crystal) and for the minimization of crystal structures (modules Crystal Builder, and OFF with Universal 1.02 force field).

The topography of the P5V4-covered C-EM grids and quartz plates was investigated with an Atomic Force Microscope, Nanoscope III, in Tapping Mode.

3. Results and discussion

Poly(para-phenylenevinylene) (PPV) as well as the related, unsubstituted oligomers consist of a large number of sp²-hybridized carbon atoms, forming flat, rodlike molecules with a π-system extending over the whole molecule. Both the shape of these molecules and their large π-system favor crystallization, which causes solubility problems, for example. It is expected that during thin-film growth from the vapor phase, the condensed oligomers have a strong tendency to form crystalline islands if certain experimental conditions are met (i.e., deposition rate, substrate temperature etc.).

To see whether micro-crystallites are present in vapor-deposited P5V4, we used XRD on films (thickness \( \sim 350 \text{ nm} \)) grown on Si-wafers. Fig. 2 shows a semi-logarithmic plot of the intensity versus \( s \left( = 2 \sin \theta / \lambda = 1/d \right) \), collected on two different samples: one sample was grown with the substrate at room temperature at 0.19 nm/s (dashed line in Fig. 2), while the other sample was grown with a substrate temperature of approximately 250 °C at 0.29 nm/s (continuous line).

The sample prepared with high substrate temperature shows three distinct peaks in the XRD plot, which correspond to the (0 0 l) reflections of the known single-crystal structure (Table 1). However, the peaks are broad and the higher-order reflections (second and third peak) are strongly suppressed, which suggests crystalline order with a limited coherence length. Whereas the high-temperature sample shows clear diffraction peaks, the sample prepared with a substrate temperature of approximately 25 °C exhibits only shoulders. It is not possible to estimate the fraction of non-crystalline (amorphous) material from these measurements. The observation of only (0 0 l)-reflections indicates a preferred orientation of crystalline domains in the P5V4 film with the ab-plane aligned parallel to the Si-wafer substrate. This orientation corresponds to an almost upright position of the molecules on the substrate. Preferred growth at high substrate temperature of an oriented phase with the chain nearly perpendicular to the substrate was also found for sexiphenyl and pentacene films [27,28].

The much thinner films to be investigated by means of TEM in bright-field and selected-area ED mode were
also characterized for their morphology. Fig. 3 shows a
typical SEM picture of P5V4 deposited on a C-EM grid,
with a thickness of the oligomer layer of 75 nm. Small,
needle-like objects are present with typical dimensions
of \(20 \times 80\ \text{nm}^2\). The inset in Fig. 3 shows an AFM
image of the topography of the same sample (both
images have the same length scale). Clearly, the AFM
(height) image shows elongated structures, with typical
dimensions that are similar to those of the needle-like
structures shown in the SEM picture. However the
features are less sharp, presumably due to convolution
effects of the tip. This effect also prevents the imaging of
‘rods’ deeper in the film and results in an apparent
lower density of ‘rods’ per unit area as compared to
SEM measurements.

As we will discuss now, TEM shows that the ‘rods’
observed in SEM and AFM are micro-crystallites with
a random orientation towards the substrate. In Fig. 4
(left panel), we present a typical TEM image of the 75
nm thick P5V4 layer vacuum-deposited on a C-EM
grid. Elongated features are clearly visible in the film.
The ED pattern of the film is shown in Fig. 4 (center
and right-hand panel); at least four concentric rings are
identifiable. To see whether the known crystal structure
of P5V4 can be used for indexing the rings in Fig. 4 to
crystallographic planes in the micro-crystallites of the
film, we have calculated the powder diffraction pattern
from the single-crystal data for comparison. Table
1 summarizes the electron and XRD data on thin films
next to the 12 most intense reflections calculated using
the crystal data of the single crystal.

Three of the rings are attributed to reflections from
planes that are parallel to the \(c\)-axis, namely
\((3\ 1\ 0), (0\ 2\ 0)\) and \((3\ 2\ 0)\); the innermost ring originates from
the \((2\ 0\ 5)\) plane, which is parallel to the \(b\)-axis. Since
the electron beam is incident perpendicular to the sample
surface, reflections from planes that are perpendicular
to the substrate surface are observed.

Figs. 3 and 4 indicate that the micro-crystallites have
typical dimensions of 20 nm wide and 80 nm long.
While recording the ED pattern shown in Fig. 4, the
sample was moved around under the electron beam in
order to avoid beam damage and to probe a large
number of micro-crystallites. The diffraction pattern thus
obtained shows circles instead of distinct spots. This
indicates that the orientation distribution of the micro-
crystallites within the selected-area is isotropic with
regard to planes perpendicular to the substrate. So, for
the crystallites that contribute to the \((3\ 1\ 0), (0\ 2\ 0)\) and
\((3\ 2\ 0)\) reflections, the orientation around the \(c\)-axis is

\[
\text{Table 1}
\]
Calculated powder diffraction data using single-crystal structure of P5V4 [19], and observed \(d\)-spacings from ED and XRD measurements

<table>
<thead>
<tr>
<th>Plane (h\ k\ l)</th>
<th>Calculated</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d)-Spacing (Å)</td>
<td>Relative ED intensity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 1 0</td>
<td>4.287</td>
<td>1</td>
</tr>
<tr>
<td>0 2 0</td>
<td>3.769</td>
<td>0.703</td>
</tr>
<tr>
<td>3 2 0</td>
<td>3.054</td>
<td>0.299</td>
</tr>
<tr>
<td>0 0 1</td>
<td>32.025</td>
<td>0.270</td>
</tr>
<tr>
<td>3 1 1</td>
<td>4.147</td>
<td>0.181</td>
</tr>
<tr>
<td>1 1 5</td>
<td>4.442</td>
<td>0.135</td>
</tr>
<tr>
<td>2 0 5</td>
<td>5.633</td>
<td>0.115</td>
</tr>
<tr>
<td>1 2 5</td>
<td>3.109</td>
<td>0.074</td>
</tr>
<tr>
<td>0 0 2</td>
<td>2.263</td>
<td>0.069</td>
</tr>
<tr>
<td>3 3 0</td>
<td>3.002</td>
<td>0.060</td>
</tr>
<tr>
<td>3 2 1</td>
<td>4.360</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Several reflections are expected close to the primary electron beam or zero order diffraction spot and are therefore absent or undetectable under these experimental conditions. In the table these reflections are indicated by the character ‘a’. Several reflections that were observed in the diffraction pattern of the ‘thick’ film were not observed in the pattern of the thin film. These reflections are indicated in the table by the acronym n.o.
isotropic, whereas for the crystallites that contribute to the \((205)\) reflections, the orientation around the \(b\)-axis is isotropic.

Fig. 5a shows the crystal structure of P5V4 according to van Hutten et al. [19]. In the monoclinic unit cell, six molecules are packed in a ‘herringbone’ type structure (space group \(P2_1/a\)). The long molecular axis is almost parallel to the \(c\)-axis. Fig. 5b shows the projection of the unit cell along the \(b\)-axis onto the \(ac\)-plane, whereas Fig. 5c represents the projection of the unit cell along the \(c\)-axis. Note that since the monoclinic angle \(\beta\) equals 103°, the \(c\)-axis is not perpendicular to the \(ab\)-plane and hence the \(ab\)-plane is at 13° relative to the drawing plane of Fig. 5c.

In order to visualize how the aforementioned crystallographic planes cause the diffraction patterns shown in Fig. 4, bold lines are drawn in Fig. 5. In the solution-grown cell, the \((310)\) plane is found to correspond to the most densely populated oblique planes through the lattice. The \((320)\) planes diffract even though they are interspersed with \((640)\) planes containing just as many molecules; the orientations of the molecules are different, however, which result in different density projections. The observed diffraction by \((205)\) planes represents the higher projected density of the phenylene rings relative to the vinylene linkages (Fig. 5b).

From the fact that we observe reflections from planes that are either parallel to the \(b\)- or the \(c\)-axis, we
conclude that the micro-crystallites form two ‘populations’. In one ‘population’, the molecules are oriented with their long axis nearly perpendicular to the substrate. This ‘population’ causes the (3 1 0), (0 2 0) and the (3 2 0) reflections observed in the ED measurements and the (0 0 1) and higher order reflections in the XRD measurements. The other ‘population’ of crystallites is oriented with the $ac$-plane along the substrate (i.e. the long molecular axis parallel to the substrate), causing the (2 0 5) reflections in Fig. 4. Only one reflection from this latter group of crystallites is observed, although one might expect to see also the (0 0 1), (0 0 2) and (0 0 3) reflections in the ED pattern. However, if present, the primary electron beam masks these reflections (indicated in Table 1 by ‘a’). Fig. 6 shows typical TEM results for a thinner film (≈ 10 nm) of P5V4 on a C-EM grid, obtained with a spot size that allowed us to probe individual crystallites. The bright-field image shows individual objects; in the diffraction picture, separate spots are observed. The spots observed in the ED of this very thin film all originate from the population with the molecular axis nearly perpendicular to the substrate; the (2 0 5) reflection is not observed. Although we must exert caution in drawing conclusions from the limited amount of data, this result suggests that the ensemble of crystallites in contact with the substrate is preferentially $c$-axis-oriented, the molecules being perpendicular to the interface. As the film grows in thickness, the correlation with the substrate-induced orientation is lost at some point. It depends on the deposition conditions, such as substrate temperature and deposition rate, when this occurs.

Since the $c$-axis of the crystal structure of P5V4 is at an angle of 103° with respect to the $ab$-plane, which is likely to be the contact plane of the crystallite to a substrate on which it grows, it is surprising that the (3 1 0), (0 2 0) and the (3 2 0) reflections are observed in the ED of the thin films. In principle, an orientation distribution of the substrate surface may cause these reflections to occur. Since an amorphous carbon film was used as substrate in ED samples, the substrate surface is certainly not perfectly flat and we may anticipate a distribution of crystallite orientations with respect to the sample surface, including orientations in which the $c$-axis is parallel to the (macroscopic) substrate normal. Such a distribution, however, would also lead to the appearance of several more spots relating to other sets of diffracting planes.

An alternative explanation for the observations may be based on the assumption that the crystals of the film have a unit cell that is different from that of single crystals grown from solution. Polymorphism is rather common for conjugated oligomers; it has been observed in sexiphenylene [27], pentacene [28, 29] and dialkoxy-substituted P5V4 oligomers [30]. Since there is a fair agreement between observed and calculated lattice periods (Table 1), we may anticipate a polymorph for P5V4 crystals in vacuum-deposited films in which the molecular arrangement is only slightly different from the molecular packing in P5V4 single crystals grown from solution.

An example of a hypothetical unit cell is shown in Fig. 7. It contains only four instead of six P5V4 oligomers but is very similar to the solution-grown cell (Fig. 5) as far as molecular packing is concerned. The main difference is that the monoclinic angle of the proposed cell (B) is close to 90°, which puts the molecules almost perpendicular to the substrate plane. The hypothetical cell was derived from the single-crystal cell by translations of molecules over a distance of one phenylene–vinylene unit, with a different alignment of the molecules’ ends as a result. Thereby, a different
pattern of the end rings is obtained. It seems quite probable that a more compact \( ab \) cell face should form on a foreign substrate rather than the less dense face of the cell formed in solution. The solution crystals were grown in liquid stilbene; because of the similarity between stilbene and P5V4, the interface free energy is likely to be low so that the molecules at the crystal facets may well remain more exposed to the medium. In both the original and the proposed cell there are two layers of molecules, displaced relative to each other along the \( b \)-axis by \( b/2 \) and along \( c \) by approximately 2 Å.

In the smaller cell (Fig. 7) proposed here for the film crystals, the relative orientation of the vinylene linkages in neighboring chains also differs from that in the original cell (i.e. some molecules have been deposited inverted with respect to their plane of \( \pi \)-symmetry). The smaller cell was optimized by energy minimization in the Cerius\(^2\) program, in which the \( b \)-axis length was kept fixed at 7.538 Å to remain close to the original cell. In the original cell (Fig. 5), the six molecules in the cell are generated from an asymmetric unit of only one and a half molecule by the \( P2_1/a \) symmetry; the reduced cell proposed here has the space group \( P2_1 \) and contains two molecules in the asymmetric unit. Minimizations without constraints indicate that there are only minor differences in energy and density between the various possible configurations. This outcome supports the idea of polymorphism and suggests that considerable disorder may be present in crystallites grown at a substrate.

In Fig. 7, the hypothesized cell is depicted along with diffraction planes that are equivalent to the ones identified before and shown in Fig. 5b and c. Note that the indices have changed because of the change in cell contents. The corresponding lattice \( d \)-spacings are listed in the caption to Fig. 7; they are close to the values for the solution-grown crystal (Table 1). Also note that in Fig. 7a, the cell base plane \( ab \) is in the plane of the paper and one easily observes the remaining tilt of the \( c \)-axis, the diffracting planes, and the molecules themselves with respect to the normal. This is due to \( \beta \) being 92° rather than 90°. A small orientation distribution together with the finite width of the diffraction spots would make the latter observable.

To test whether the structure of the hypothetical cell could give rise to the observed diffraction pattern of the 10 nm film (Fig. 6), we calculated the ED pattern of the proposed cell with the electron beam parallel to the \( c \)-axis. This pattern is shown as an overlay in Fig. 6 (right panel), with the diffraction spots indicated as open circles. Clearly, the most intense diffraction spots of Fig. 5 match well with the \((0 2 0)\) and \((2 1 0)\) reflections of the ED pattern calculated for an individual crystal with the structure of the proposed cell.

4. Conclusions

Thin films of P5V4, a phenylene–vinylene oligomer, were prepared by vacuum deposition and studied with several surface-sensitive techniques. We observed elongated micro-crystals with atomic force and electron microscopy. Diffraction studies suggested the presence of two populations of crystallites, one with the long molecular axis perpendicular to the substrate and another with the long axis parallel to the substrate. To make the perpendicular mode of crystallization plausible, a unit cell different from the one known for P5V4 crystals grown from solution is proposed for the vapor-deposited micro-crystals, though with very similar molecular packing. Both crystal structures closely resemble the structure of the parent conjugated polymer PPV.

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