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Vapor Phase Epitaxy of Perylo[1,12-*b*,*c*,*d*]thiophene on Highly Oriented Polyethylene Thin Films

Shidong Jiang,[†,‡] Hualei Qian,[‡] Wei Liu,[‡] Chunru Wang,[‡] Zhaohui Wang,*[,‡] Shouke Yan,*[,†,§] and Daoben Zhu[‡]

[†]*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China,* [‡]*Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, China, and* [§]*Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Fudan University, Shanghai 200433, China*

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ABSTRACT: Epitaxial crystallization of PTH on highly oriented PE substrate from vapor phase has been achieved. The epitaxial growth of PTH on highly oriented PE substrate leads to the formation of lathlike PTH crystals. The lathlike PTH crystals exhibit well-ordered structure with their long axes preferentially parallel to the chain direction of the PE substrate crystals, while a small part of PTH lathlike crystals aligned with their long axes perpendicular to the chain direction of the PE. Electron diffraction further demonstrates that the epitaxial crystallization of PTH on oriented PE substrate results in an alignment of PTH with the *c*- and *b*-axes in the film plane. The *c*-axis of PTH is oriented either perpendicular, preferentially, or parallel, less frequently, to the PE chain direction. The former originates from a two-dimensional lattice matching, while the latter is based only on a one-dimensional intermolecular matching. The observed epitaxial growth provides an effective way for preparing large area well-arranged PTH films with unique crystalline structure.

Introduction

Over the past decades, organic field-effect transistors (OFETs) based on soluble conjugated oligomers or polymers have attracted considerable attention.[1−11] Enormous effort has been devoted to improve the key performance parameters of OFETs, such as carrier mobility, on/off ratio, and threshold voltage. It is well-known that the performance of the organic materials depends strongly on their molecular structure and spatial organization. For example, polycyclic aromatic hydrocarbons (PAHs) are known to be one of the most versatile and effective molecular scaffolds for organic functional materials. Integrating a S atom into the PAHs skeleton, as shown in left part of Figure 1, produces perylo[1,12-*b*,*c*,*d*]thiophene (PTH), which is a new class of semiconductive material. These molecules can be regularly stacked along the *b*-axis with intermolecular distances of 3.47 Å (right part of Figure 1), which is different from the sandwich herringbone packing of perylene crystal.[12,13] In this packing manner, marked S...S short contacts (3.51 Å) were found between the neighboring columns related by an inversion center. This makes the material of excellent performance with a high mobility up to 0.8 $cm^2 V^{-1} s^{-1}$, comparable to that of polycrystalline silicon.[14−16] It should be pointed out that the achieved high mobility has been measured by individual wire with single crystal structure. The mobility measured for spin-coating PTH thin films is only 0.05 $cm^2 V^{-1} s^{-1}$.[16] Therefore, increasing interest has been seen in fabricating large-area well-defined thin films with unique single crystal organization of semiconducting materials.[17−21]

It is well confirmed that epitaxy provides an effective way for preparing well-defined thin films. It can control not only the crystalline structure but also the crystal orientation of the epitaxial materials. As examples, in the early 1980s, Lovinger[22] has controlled the crystallization of PVDF from melt in its piezoelectric and pyroelectric β-form at atmospheric pressure through polymer epitaxy. Another example is the modification modulation of melt-crystallized isotactic poly(1-butene) through regulating the crystalline structure of the substrate polymers, performed by Lotz et al.[23,24] Therefore, a large number of conjugated oligomers and polymers have been grown epitaxially on the surface of inorganic single crystals for fabricating photovoltaic and electroluminescent devices.[25−29] Also some efforts have been made in the epitaxial growth of organic molecules on highly oriented polymeric substrates.[30−33] Actually, polymer dielectrics are ideal because of their diverse properties, easy film-forming, and tunable surface chemistry for controlling the device critical interfacial trap state densities. Very recently, Marks et al.[34,35] reported a substantial enhancement in performance of OFETs by fabricating the semiconductor/dielectric interfacial properties through use of thin polymer films. Taking all these into account, epitaxy on highly oriented polymeric substrates may provide a highly promising way for fabricating large area well-ordered thin films of semiconducting materials since large size highly oriented polymer thin films can be easily obtained. Herein, an example is presented to show the feasibility of preparing large area well-ordered layers of PTH, as model system, via vapor phase epitaxy on highly oriented polyethylene (PE) film.

The purpose of this paper is to present the detailed experimental procedure and structural features of PTH crystallized on highly oriented PE film from vapor phase. On the basis of the results of electron microscopy observation and electron diffraction, the origin of the epitaxial crystallization of PTH on PE was discussed. Also, the feasibility of epitaxy for preparing large area well-ordered layers of PTH was confirmed through optical microscopy observation.

Experimental Section

The perylo[1,12-*b*,*c*,*d*]thiophene (PTH) used in the present work was synthesized according to a known procedure[12] and

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*To whom all correspondence should be addressed: e-mail skyan@mail.buct.edu.cn; Tel 0086-10-64455928; Fax 0086-10-64455928.

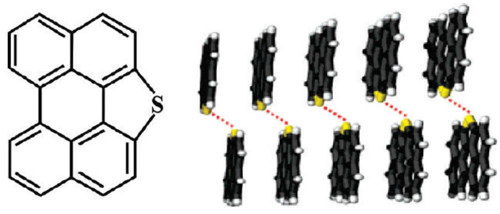

Figure 1. Chemical structure and crystal packing view of PTH.

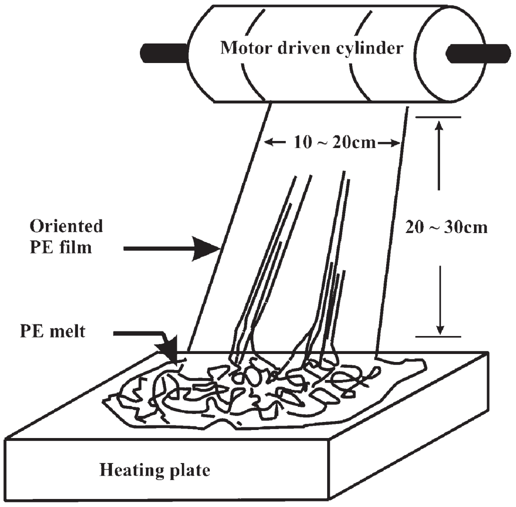

Figure 2. A sketch showing the melt-draw procedure of the PE substrate. The arrow in the bottom part indicates the thin PE melt on the glass surface. The straight arrow indicates the produced highly oriented PE thin film.

purified by recrystallization and sublimation. High-density polyethylene (PE), Lupolen 6021DX, was obtained from BASF AG Ludwigshafen, Germany.

Highly oriented thin films of PE were prepared according to a melt-draw technique introduced by Petermann and Gohil.[36] As shown in Figure 2, a small amount of 0.5 wt % PE xylene solution was poured and uniformly spread on a preheated glass plate at 130 °C, where the solvent was allowed to evaporate. After evaporation of the solvent, the remaining thin polymer melt on the glass surface was then drawn up with the help of a motor-driven cylinder at a drawing speed of ~20 cm/s. The resulting highly oriented films as indicated by a straight arrow, which are 30–50 nm in thickness and tens of centimeters in both lateral directions, can be collected by a glass slide. For structural analysis, the thin film was transferred onto copper grids and used directly for transmission electron microscopy (TEM) observation.

Vapor phase epitaxial crystallization of PTH on highly oriented PE thin films was realized through a homemade vacuum evaporation device. In this procedure, as shown in Figure 3, the powder of PTH was loaded in a ceramic boat, which was placed at the center of a quartz tube inserted in a horizontal tube furnace. Flat micaceous substrate covered by uniaxially oriented thin PE film was placed near the ceramic boat in the quartz tube. The ceramic boat was at the high-temperature zone, while the substrate was at the low-temperature zone. When the pressure in the quartz tube reached ca. 4 Pa, the furnace temperature was increased to 130 °C at a rate of 0.2 °C/s and then kept at that temperature for 5 min to prepare the TEM sample and 15 min to prepare the optical microscopy samples. Finally, the temperature was allowed to descend to room temperature. The prepared PTH/PE double-layered thin films were either used directly for optical microscopy observation or floated onto the surface of distilled water and mounted onto 400 mesh copper grids for TEM observation.

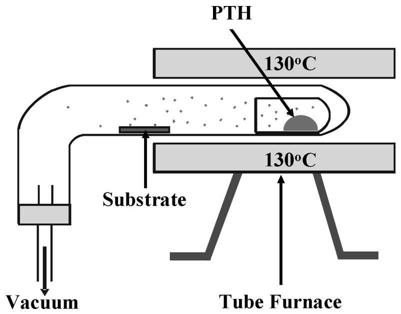

Figure 3. A sketch of a homemade vacuum evaporation device. The PTH powder is placed at the center of a quartz tube inserted in a horizontal tube furnace as indicated by a long arrow, while the substrate PE film is placed in the left side of the ceramic boat in the quartz tube.

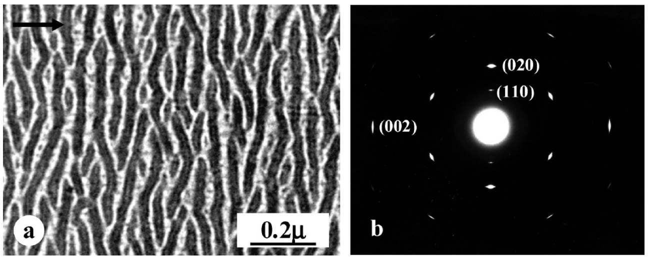

Figure 4. (a) BF electron micrograph of a melt-draw highly oriented PE film and (b) its corresponding ED pattern. The ED pattern is given in the same chain orientation as indicated by a black arrow.

To disclose the epitaxial relationship between PTH and PE, a JEOL J-2010 TEM operated at 200 kV was used in this study. Bright-field (BF) electron micrographs were obtained by defocus of the objective lens. To minimize radiation damage by the electron beam, focusing was carried out on an area, then the specimen film was translated to its adjacent undamaged area, and the image was recorded immediately. For optical microscopy observation, an Olympus BH-2 optical microscope was used in this study. The optical micrograph presented here was taken under crossed polarizers.

Results and Discussion

Figure 4 shows a phase-contrast bright field (BF) electron micrograph and its corresponding electron diffraction (ED) pattern of the highly oriented PE thin films. The arrow in the micrograph indicates the drawing direction during film preparation. In the phase-contrast BF image, the bright lines represent the amorphous regions, while the dark areas between the bright lines are the high-density crystalline lamellar regions; i.e., the PE crystals appear black. From the BF image of the PE film (Figure 4a), it can be clearly seen that the obtained PE substrate film consists indeed of highly oriented lamellar structure with the lamellae arranged perpendicular to the drawing direction. On the electron diffraction pattern (Figure 4b), which is given in the same orientation as the BF image, the appearance of sharp and well-defined reflection spots further confirms the high orientation of the PE films. The alignment of the (002) diffraction spots in the equatorial direction reflects an orientation with their chain axes oriented in the film plane and along the drawing direction. The appearance of strong (020) and weak (110) reflections but disappearance of the (200) reflections indicates a preferred orientation of the *b*-axis in the film plane.

Figure 5 shows the representative phase contrast BF images and corresponding electron diffraction patterns of PTH crystallized on the aforementioned highly oriented PE thin films. The diffraction patterns are given in the same orientation as the BF images, and the chain directions of the PE substrates are

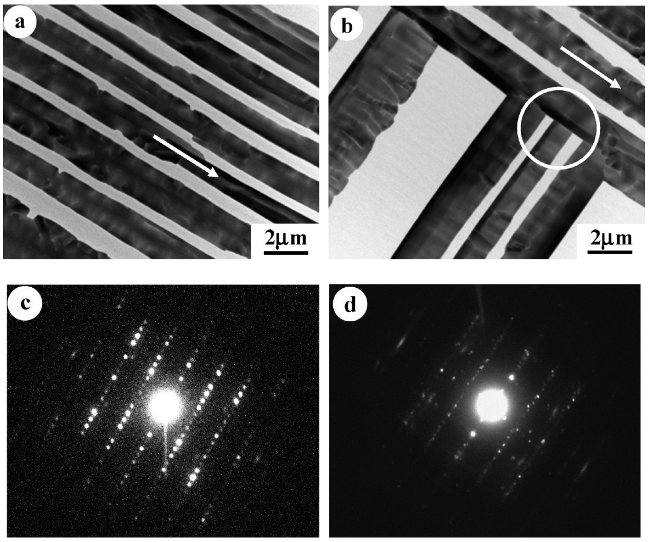

Figure 5. (a, b) BF electron micrographs of the PTH crystallized on highly oriented PE film; (c, d) corresponding electron diffraction patterns taken in different areas. The chain orientation of the PE substrate is indicated by two arrows, while the ED pattern is given in the same chain orientation as BF images.

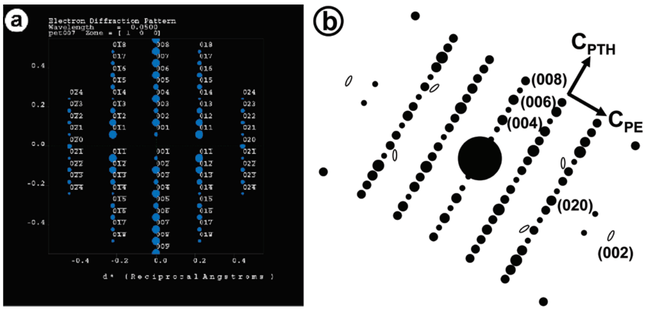

Figure 6. (a) Simulated diffraction pattern of the PTH single crystal along the [100] direction. (b) Sketch showing the electron diffraction pattern shown in Figure 4c.

indicated by the white arrows in both Figures 5a,b. As shown in Figure 5a, the PTH crystals grow as black long laths with width of a few hundreds of nanometers to micrometers. These PTH crystalline laths align mainly parallel to the chain direction of the PE substrate film and exhibit relatively smooth facets. Moreover, there are small domains, as indicated in Figure 5b, in which some PTH crystalline laths possess an orientation perpendicular to the chain direction of the PE substrate crystals. The preferred orientation of the PTH crystals grown on the oriented PE substrate suggests the occurrence of molecular epitaxy of PTH on the PE substrate. To disclose the epitaxial relationship between PTH and PE, electron diffractions for mutual orientation analysis were taken at different areas of the sample. Figure 5c shows the electron diffraction pattern taken at an area with parallel orientation. It shows well-defined sharp reflection spots. This unambiguously indicates the occurrence of epitaxial crystallization of PTH on PE oriented film, which results in the well-ordered electron diffraction pattern. The electron diffraction pattern taken in an intersection area with PTH crystals either perpendicular or parallel to the chain direction of PE film, as indicated by a circle, is shown in Figure 5d. With close inspection, one can find that the electron diffraction pattern of PTH crystals is actually composed of two identical diffraction sets with one of them rotated 90° about the incident beam compared to the other one. This makes the diffraction pattern very complicated and the intensities of each PTH reflection spot reduced remarkably. For simplification, a single diffraction set of the lathlike PTH crystals oriented along the PE chain direction has been analyzed. Actually, the diffraction pattern contributed by the PTH crystals has a close resemblance with the one simulated by using Cerius^2 program along the [100] direction according to a monoclinic unit cell with parameters a = 1.6921 nm, b = 0.452 52 nm, c = 1.7898 nm, and β = 112.655°,[12] as presented in Figure 6a. Therefore, all of the sharp reflection spots contributed by PTH crystals can be accounted for by a monoclinic unit cell proposed in ref 12. A sketch corresponding to the electron diffraction pattern shown in Figure 5c with some reflections being indexed is shown in Figure 6b, in which the reflections coming from the PTH crystals are presented in solid spots while those coming from PE substrate crystals presented as hollow ellipses. From Figure 6b, it can be clearly seen that in this orientation the *b*- and *c*-axes of PTH crystals are in the film plane with *b*-axis along the chain direction of PE. Hereby, in the other set of PTH diffraction, a 90° rotation leads to a parallel alignment of both *c*-axes for PTH and PE.

The above electron microscopy observation combined with electron diffraction indicate that the PTH can crystallize epitaxially from the vapor phase on the highly oriented PE substrate with its *c*-axes either perpendicular or parallel to the *c*-axis of PE crystals and the (100) lattice plane in contact with the PE substrate. This provides an effective pathway for fabricating well-ordered thin films of PTH with unique single crystal organization.

According to the above observed results, two aspects, i.e., (i) the origin of epitaxial growth of PTH on the PE substrate and (ii) the feasibility of epitaxy for preparing large area two-dimensional well-ordered films of PTH, should be clarified here. First of all, epitaxial crystallization is a widespread and much investigated phenomenon. Enormous studies on heterogeneous polymer epitaxies lead to an understanding of them at the molecular level.[37] It is generally accepted that the occurrence of epitaxy is based on some certain crystallographic matches, e.g., a coincidence of unit-cell dimensions. Therefore, the mismatching, sometimes refers also as disregistry or discrepancy, between atomic or molecular spacing is commonly considered, and a 15% disregistry is assumed to be the upper limit for the occurrence of the epitaxial growth. For the present case, by comparing the lattice parameters of PTH (a = 1.6921 nm, b = 0.452 52 nm, c = 1.7898 nm, and β = 112.655°) with the orthorhombic unit cell of PE (a = 0.74 nm, b = 0.494 nm, and c = 0.2534 nm), matches between the $(020)_{\mathrm{PTH}}$ and $(001)_{\mathrm{PE}}$ lattice planes can be found with a discrepancy of 10%. Also, the interplanar distance of $(004)_{\mathrm{PTH}}$ matches the interchain distance of PE in both [010] and [110] directions very well. The mismatchings along the $[010]_{\mathrm{PE}}$ and $[110]_{\mathrm{PE}}$ are 9% and 7%, respectively. Therefore, the observed most preferential orientation with the *b*- and *c*-axes of PTH crystals in film plane, and the *b*-axis along the chain direction of PE should rest on a two-dimensional lattice matching. As for the other orientation, one can find a one-dimensional matching between the intermolecular distances along *b*-axes of both PTH and PE crystals with discrepancy of 8%, well below the upper limit. Moreover, in this case, taking the almost planar molecular feature of PTH (see Figure 7a) into account, a common *b*-axes alignment results in a stagger parallel stacking of the molecular planes of both PTH and PE, as sketched in Figure 7b. This may decrease the interface free energy of the interacting pair. As a result, this one-dimensional matching also leads to the occurrence of the less pronounced epitaxial crystallization of PTH on the oriented PE crystals with *c*-axes of them parallel.

To find out the feasibility of epitaxy for preparing large area two-dimensional well-ordered films of PTH, overview of the whole sample via optical microscope, which offers relatively larger area ordered structure, has been performed. Similar

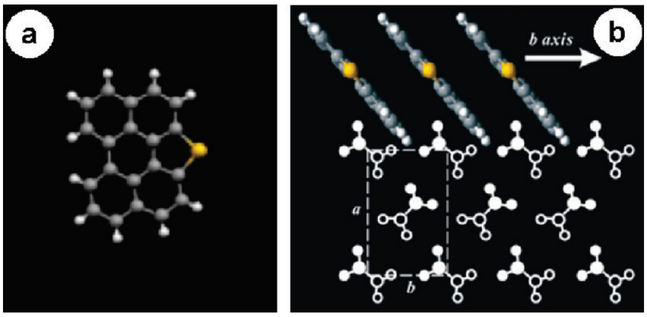

Figure 7. (a) Chemical structure of PTH and (b) its arrangement on PE substrate with common *b*-axis orientation.

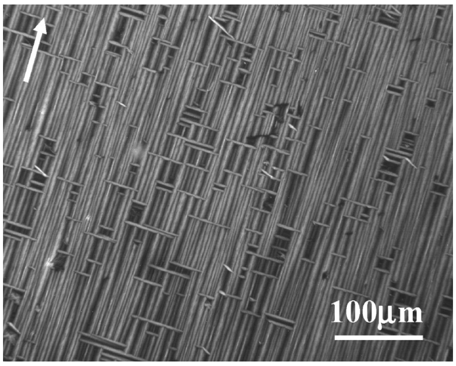

Figure 8. Optical micrograph taken from a PTH/PE double-layered thin film under crossed polarizers. The arrow indicates the molecular chain direction of PE.

oriented structure was found over the whole sample in the centimeter scale. Figure 8 shows a representative optical micrograph of the PTH crystallized on the PE oriented film. It can be seen that most of the rodlike PTH crystals align with their long axis preferentially along the PE chain direction, while some of them orient incidentally in the direction perpendicular to the PE chains. The lengths of the close packed rodlike PTH crystals are of hundreds of micrometers. It should be pointed out that there are very few crystals exhibit another orientation. These may be caused by an overgrowth on the first layer of crystals considering the long time vapor deposition. The optical microscopic observation clearly confirms the feasibility of epitaxy for preparing large area two-dimensional well-ordered films of PTH.

Conclusion

In summary, crystallization of PTH on highly oriented PE substrate from vapor phase has been studied by optical microscopy and TEM combined with electron diffraction. It is found that the PTH can grow epitaxially on the highly oriented PE substrate and form lathlike crystals. The lathlike PTH crystals exhibit well-ordered structure with their long axes preferentially parallel to the chain direction of the PE substrate crystals. There are some PTH laths aligned with their long axes perpendicular to the chain direction of PE. Electron diffraction confirms the occurrence of epitaxy of PTH on the PE substrate. The epitaxial crystallization results in an alignment of PTH with the *c*- and *b*-axes in the film plane. The *c*-axis of PTH is oriented either perpendicular, preferentially, or parallel, less frequently, to the PE chain direction. The former is explained in terms of a two-dimensional lattice matching, while the latter is based only on a one-dimensional intermolecular matching with likely an energetically favorable packing. The observed epitaxial alignment of PTH is found to cover the whole PE film uniformly, indicating the feasibility for preparing large area well-arranged films of semiconducting materials.

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