Morphological Evolution of Tetrachlorinated Perylene Bisimides with Lengthy Alkyl Substituent Polycrystalline Thin Films during Reversible Phase Transitions

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ABSTRACT: The phase behavior and related morphological evolution of thin films of lengthy alkyl substituted core-tetrachlorinated perylene bisimide (C18-4ClPBI), a large π-conjugated molecule, have been studied. It is found that the C18-4ClPBI can exist in two different crystalline phases depending on temperature, which transform reversibly in heating and cooling processes. The X-ray diffraction results demonstrate that the two crystalline forms of C18-4ClPBI exhibit a similar packing geometry but with different unit cell dimensions. It is confirmed that the low-temperature phase is packed more compactly than its high-temperature counterpart. During high-temperature to low-temperature crystalline phase transition, nonbirefringent protrusions were observed, which disassembled in the reverse crystalline phase transition process during heating. The exact formation mechanism of the protrusions is not clear at the moment. Nevertheless, their influence on the transfer characteristics of the polycrystalline C18-4ClPBI thin film has been clearly illustrated.

INTRODUCTION

Organic semiconductors are an essential part of electronic materials, which offer fascinating prospects for many benefits, such as high throughput, light weight, easy processing, and flexibility of the devices. Perylene dyes, which consist of two linked naphthalene units in peri position, have attracted a great attention as organic semiconductive materials because of some sophisticated advantages. Among them, perylene tetracarboxylic acid bisimide (PBI) derivatives represent an important role in n-type semiconductors. The comparatively great electron affinity among large-band gap materials, outstanding photochemical property, excellent thermal stability, high quantum yields of photoluminescence, and strong visible light absorption make them promising in applications including organic field effect transistors (OFETs), organic photovoltaics, organic light-emitting diodes (OLEDs), and so on. However, their use is still limited, even though the fundamental steps of charge transfer in combination with various donor polymers are excellent.

It is well established that the structure and morphology of materials in the condensed state can be different according to the processing condition and show significant influence on their performance. Organic electronic materials are no exception, especially for the polycrystalline thin film systems.

For example, the tetrachlorinated perylene bisimides are confirmed to exhibit excellent electron mobility in filed effect transistors even in air. A recent study on the core-tetrachlorinated perylene bisimides (4ClPBIs) with alkyl and fluoroalkyl substituents indicates that different alkyl substitutions result in different molecular arrangement and phase behavior, which in turn influence the optoelectronic properties greatly. Moreover, it was reported that the electron mobility of PBI with unsymmetrical oligoethylene glycol substituents in the ordered liquid crystalline state can increase by 2 orders of magnitude with respect to its amorphous state (7 × 10⁻³ vs 6 × 10⁻⁵ cm² V⁻¹ s⁻¹), while the alkyl substituted PBI in crystalline phase drops by a factor of 4 (8 × 10⁻⁶ vs 3 × 10⁻⁵ cm² V⁻¹ s⁻¹). Furthermore, pulse-radiolysis time-resolved microwave conductivity measurements show that the N,N'-dioctadecyl-3,4,9,10-perylenebiscarboximide has a charge carrier mobility of 0.2 cm² V⁻¹ s⁻¹ in the crystalline phase, while only of 0.1 cm² V⁻¹ s⁻¹ in the liquid crystalline phase. This leads to extensive studies on the properties of organic semiconductors in different states.

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pointed out that the diverse charge-transport properties are actually related to multiscale structures and morphologies of the thin films. However, the structural and morphological changes of organic semiconductors during phase transition are rarely studied.

Herein, tetrachlorinated perylene diimide with lengthy alkyl substituent (C18-4ClPBI), an air-stable and good-mobility n-type organic semiconductor, was chosen to reveal the structural and morphological evolution during heating and cooling processes. It was found that C18-4ClPBI exhibits two different crystalline phases, which transfer reversibly during the cooling and heating processes. The temperature-dependent morphological evolution was monitored by optical, scanning electron, and atomic force microscopies. The intriguing finding of this work is the formation of some protrusions during high-temperature to low-temperature crystalline phase transition, which show great influence on the transfer characteristics of the C18-4ClPBI thin film transistor. This may provide useful information for fabricating high performance devices.

**RESULTS AND DISCUSSION**

The thermal stability of C18-4ClPBI was analyzed by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of 5% weight loss is 412.8 °C, indicating its good thermal stability. The phase behavior of C18-4ClPBI was investigated by differential scanning calorimetry (DSC). The DSC curves of C18-4ClPBI obtained during heating and cooling at a rate of 10 °C/min are shown in Figure 1. The second heating curve was used to exclude the influences of previous thermal history on the sample. From the DSC curves shown in Figure 1, it is clear that the C18-4ClPBI with lengthy alkyl chains (−C_{18}H_{37}) evidently shows two phase transitions in both the heating and cooling processes. In the cooling process from isotropic melt of C18-4ClPBI (Figure 1, bottom), a high-temperature transition was first appeared at 170 °C (peak temperature) and then a low-temperature transition takes place upon further cooling to 107 °C. In the subsequent reheating process (Figure 1, top), the low- and high-temperature phase transitions take place at 116 and 187 °C, respectively. This demonstrates that the C18-4ClPBI can exist in two different phases depending on temperature, which has also been confirmed by the X-ray diffraction shown later in Figures 3 and 10. The two phases can transform from one to another reversibly heating and cooling processes.

It should be pointed out that the chemical structure of C18-4ClPBI used here is essentially the same as the N,N′-dioctadecyl-3,4,9,10-perylenebiscarboximide (C18-PBI) reported in ref 40 except for the tetrachloro-substitutes at bay positions, see Figure 2. However, their phase behaviors are quite different. During heating process, at least three crystalline (transition temperatures: 111, 141, and 180 °C, respectively) and two highly ordered liquid crystalline (transition temperatures: 216 and 312 °C, respectively) phases were suggested for C18-PBI.43 By contrast, only two phases for the C18-4ClPBI were observed in both the heating and cooling processes. This illustrates the great influence of tetrachloro-substitutes on the phase behavior of the C18-4ClPBI. The high-temperature transition of C18-4ClPBI starts at ca. 171 and 182 °C (onset transition temperatures, i.e., T_{onset}) in the cooling and heating processes, respectively. On the other hand, the onsets of the low-temperature transition takes place essentially at the same temperature in both cooling and heating, which is typically observed during melt crystallization. By contrast, the occurrence of low-temperature transition at the same temperature reflects a transformation between equilibrium states. From this point of view, we assign the high-temperature transition of the C18-4ClPBI in the heating process to the melting of the C18-4ClPBI crystals (peak melting temperature T_m = 187 °C), which is very close to the crystalline to liquid crystalline phase transition temperature of C18-PBI, namely, the crystal melting temperature of C18-PBI. In the reverse cooling process, the high-temperature transition is then correlated to the crystallization of the C18-4ClPBI from isotropic melt at 170 °C (peak temperature). The low-temperature phase transitions started at 110.7 °C in both cooling and heating processes are then attributed to a reversible crystalline phase transition, which resembles the crystalline phase 1 to phase 2 transition of C18-PBI. It is reasonable because the molecular size of C18-4ClPBI obtained by energy optimization in Materials Studio, as schematically presented in Figure S1, is quite similar to that of the C18-PBI.

The X-ray diffractions of a C18-4ClPBI powder sample taken at different temperatures also support this conclusion. It was found that the sample did not show any Bragg diffraction after heating up to temperatures above 187 °C and before cooling from 200 °C down to 170 °C. Moreover, similar X-ray
Diffraction patterns were always obtained at temperatures below 100 °C and above 120 °C whether in heating or cooling process. Figure 3 shows two representative wide-angle X-ray diffraction patterns of the C18-4ClPBI powder sample taken at 100 and 120 °C, respectively. It can be seen that the two 2D X-ray diffraction patterns are essentially the same with a series of sharp diffraction rings, comparing Figure 3a,b. Their corresponding 1D wide-angle X-ray scattering (WAXD) profiles (bottom part of Figure 3a,b) are also quite similar with sharp reflection peaks, even though the d-spacing and reflection intensities varied slightly. The appearance of sharp and intense diffraction peaks confirms that the endothermic peaks in the DSC heating curves are not related to the customary crystallite melting. Otherwise, reduced reflection intensity and increased scattering of amorphous phase are expected. The X-ray diffraction results help to conclude that the C18-4ClPBI exhibits two crystalline forms with very similar crystal structure. Unfortunately, the exact crystal structures of the two crystalline forms cannot be precisely defined at moment. Therefore, we focus here mainly on the morphological changes during the phase transition because it is a crucial factor influencing the performance of the materials.

Figure 4 shows the optical micrographs of a C18-4ClPBI thin film in high-temperature phase, which was heated to 200 °C for 5 min and then cooled quickly down to and kept at 150 °C. The pictures were taken in situ at different times after reaching 150 °C. It can be seen that the crystallization of C18-4ClPBI takes place immediately after cooling down to 150 °C, which results in the appearance of strong birefringence of the sample, see Figure 4a. The crystallization propagates with time (Figure 4b,c) and completes within 4 min (Figure 4d). To display the morphological evolution of the C18-4ClPBI thin film during phase transition, the sample shown in Figure 4d was then cooled from 150 °C down to room temperature. Figure 5 shows the optical micrographs taken during the cooling process. One can see that the morphology remains essentially unchanged during cooling until 110 °C, comparing Figure 5a,b with Figure 4d. When the sample was cooled down to 100 °C, that is, after low-temperature phase transition, abundant light extinction bands appear in the optical micrograph as revealed in Figure 5c. The light extinction bands can be more clearly visualized in the enlarged micrograph shown in Figure 5d.

To show the formation process of the extinction band, in situ optical microscopy observation of the cooling and heating processes has been performed. Figure 6 shows the optical micrographs of a C18-4ClPBI thin film taken in situ during the cooling and heating processes at different temperatures under crossed polarizers. The related videos S1 and S2 can be seen in the Supporting Information. It was found that the crystallization of C18-4ClPBI starts when the sample was cooled from 200 °C down to 170 °C. The crystallization of C18-4ClPBI results in the appearance of strong birefringence of the sample, which remains unchanged until 110 °C (Figure 6a). With further cooling of the sample down to a temperature below the crystal-crystal phase transition temperature, for example, 105 °C (Figure 6b), some light extinction bands

![Figure 3. 2D WAXD patterns and the corresponding 1D WAXD profiles of C18-4ClPBI powder sample recorded at (a) 100 and (b) 120 °C.](image)

![Figure 4. Optical micrographs of a C18-4ClPBI thin film cooled from 200 to 150 °C taken at (a) 0, (b) 2, (c) 3, and (d) 4 min after reaching 150 °C.](image)

![Figure 5. Optical micrographs of a C18-4ClPBI thin film shown in Figure 4d taken during cooling at (a) 130, (b) 110, and (c) 100 °C. The rectangles highlight the identical positions. (d) Magnified picture illustrating the extinction bands.](image)
sparsely dispersed at certain places appear in the optical micrograph. These extinction bands stop at a strip as indicated by the white arrows in Figure 6b and develop further with temperature. As shown in Figure 6c, some of them grow further along their long axis as indicated by the circles, while abundant small ones are generated between the early formed ones. At temperatures below 100 °C, the morphology does not change anymore, indicating the completion of the crystalline phase transition. This is in good agreement with the DSC results shown in Figure 1. In the heating process, the extinction bands do not change until 110 °C (Figure 6d). With further heating, the extinction bands start to disassemble. It is noticed that the later formed smaller extinction bands disappear earlier at relative low temperature during heating (compare Figure 6d with 6e). All of the extinction bands disappear completely when the sample is heated to 120 °C (Figure 6f), indicating the completion of the reverse phase transition. This implies that the early formed extinction bands at somewhat higher temperature are more stable than those developed later at relative lower temperature. These in situ optical microscopy results combined with the DSC results indicate unambiguously that the extinction bands are caused by phase transition rather than an annealing process.

It should be pointed out that periodic light extinction under a polarized optical microscope is quite frequently observed in ring-banded spherulite caused by periodic twisting of the crystalline lamellae about the lamellar axis. In the present case, the lack of periodicity of the extinction bands rules out the possibility of lamellar twisting-induced extinction bands. The extinction bands can also be created by material depletion during solidification (as isotactic polystyrene) or formation of cracks due to anisotropic thermal contraction (as syndiotactic polypropylene). It is, however, also not the case for C18-4ClPBI as revealed by both atomic force microscopy (AFM) and scanning electron microscopy (SEM) observations. Figure 7a shows an AFM height image of a C18-4ClPBI thin film, which was cooled from 200 °C to room temperature. It can be found that the bands are neither the depletion zone nor cracks. They are actually a series of protrusions. As seen from the height analysis, the protrusions in C18-4ClPBI thin film are not uniform in size. They range from 200 to 1000 nm in height and around 2 µm in the transverse direction. SEM observation

Figure 6. Polarized optical micrographs of a C18-4ClPBI thin film obtained in situ during cooling from 200 °C down to 100 °C (a–c) and the subsequent reheating heating (d–f) processes at different temperatures as indicated. The cooling and heating rates are 10 °C/min.

Figure 7. (a) AFM height image with height profile and (b,c) SEM surface morphologies of a C18-4ClPBI thin film prepared by cooling from 200 °C down to room temperature. The images were taken at room temperature.
Figure 7b,c confirms the AFM results. Moreover, some cracks transverse to the protrusions are observed in the enlarged SEM picture (Figure 7b), which has not been observed in the AFM image and may be caused by gold sputter during SEM sample preparation.

The assembly and disassembly of the protrusions were further studied by in situ AFM equipped with a hot stage. Figure 8 shows the AFM height images of a C18-4ClPBI film taken in situ during the phase transition. It can be clearly seen that there are a series of protrusions at 100 °C (Figure 8a), which disassemble at 130 °C (Figure 8b). The surface of the sample is not quite flat even after the disappearance of the protrusions. Traces of the disassembled protrusions can be identified with close inspection. Moreover, some transverse ripples or undulations are created. After subsequent cooling of sample down to 100 °C, the protrusions reappear mostly at the same locations as those in the pristine sample (Figure 8c). With the help of height profiles of AFM, the temperature dependence of the film thickness as well as the heights of the protrusions were studied. Figure 9a shows the temperature-dependent AFM height profiles of a C18-4ClPBI film in the same region (89 × 2.5 μm) as that shown in Figure 9b. The sectional height profiles were got at the position marked by white lines in Figure 9b. The silicon substrate was set as baseline (0 μm). Five protrusions denoted by A, B, C, D, and E as well as five positions denoted by a, b, c, d, and e were chosen to follow the height variation of the sample during heating and cooling processes. From Figure 9b, it is clear that the thickness of the solution cast film is not uniform. Nevertheless, as presented in Figure 9d, the film is thicker in the high-temperature crystalline phase than in the low-temperature one. This means that the molecular packing in low-temperature crystalline phase is more compact than in high-temperature crystalline phase. As a result, shrinkage of the thin film happens during phase transition as illustrated by Figure 9d. This has further been confirmed by in situ X-ray diffraction experiment of the thin film.

Figure 10 shows the reflective X-ray diffraction profiles of a C18-4ClPBI thin film recorded at different temperatures during heating. It can be seen that sharp reflection peaks of the C18-4ClPBI film are observed at the measurement temperatures. For the diffraction profile taken at 105 °C, only reflection peaks with ratios of 1:1/2:1/3:1/4:1/5 for the d-spacings are observed, indicating the existence of only low-temperature crystalline phase and fixed crystal orientation in film normal direction. With further increase of the temperature

![Figure 8](image-url) AFM height images (90 μm × 90 μm) of a C18-4ClPBI film obtained in heating (a,b) and cooling (c) processes at different temperatures as indicated.

![Figure 9](image-url) (a) AFM height profiles of a C18-4ClPBI thin film at different temperatures taken in the same region (89 × 2.5 μm) shown in part (b) at places marked with white lines. (b) Three-dimensional AFM height images of the C18-4ClPBI thin film taken at 100 and 120 °C. Temperature dependence of the protrusion height (c) and film thickness (d) at the positions marked in the part a.
to 110 °C, besides the already existing reflections of the low-temperature crystalline phase, diffraction peaks with weak intensity and slightly enlarged d-spacings but the same 1:1/2:1/3:1/4:1/5 ratios can be recognized, reflecting the beginning of crystalline phase transition. The later appeared reflection peaks get stronger while those observed already at 105 °C get weaker with temperature. When the temperature reaches 120 °C, only the reflections with enlarged d-spacings corresponding to the high-temperature crystalline form are observed. This demonstrates the completion of the phase transformation. Considering that only lattice planes parallel to the C18-4ClPBI exhibits two crystalline phases depending on temperature. The DSC results show that the high-temperature crystalline phase melts at 187 °C during heating and crystallizes again at 170 °C during cooling from the isotropic melt. Reversible crystalline to crystalline phase transition starts at 110.7 °C in both heating and cooling processes. The X-ray diffraction results demonstrate that the two C18-4ClPBI crystalline phases exhibit essentially the same packing geometry. However, the low temperature form packs more compactly than its high-temperature counterpart does. Morphological evolution during phase transition was followed via optical, scanning electron, and atomic force microscopies. The most intriguing finding of this study is the formation of protrusions during high-temperature to low-temperature crystalline phase transition, which are non-birefringent and can be disassembled in the reverse low-temperature to high-temperature crystalline phase transition.

It is further established that the protrusions exhibit great influence on the transfer characteristic of the C18-4ClPBI thin film. The electron mobility of the C18-4ClPBI thin film in high-temperature phase, $1.51 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, is about 1 order of magnitude higher than that in the low-temperature phase, $2.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This clearly demonstrates the great impact of morphology on the performance of the materials.

### EXPERIMENTAL SECTION

**Materials.** C18-4ClPBI was obtained on the basis of previous report. Solvents were purchased from commercial suppliers.

**Thin Film Preparation.** The C18-4ClPBI sample was dissolved in chloroform solvent with a concentration of 10 mg/mL. C18-4ClPBI thin films with thickness of ca. 1.25 μm (as measured by Dektak XT) were prepared by solution casting the solution onto silicon substrate after the evaporation of the solvent. The heat-treatment of the samples were conducted with a Linkam LTS 350 hot stage under nitrogen atmosphere.

**Characterization.** Heating and cooling DSC curves were recorded on a TA Q2000 differential scanning calorimeter at a cooling or heating rate of 10 °C/min in the nitrogen atmosphere. TGA was performed on a METTLER TOLEDO TGA/DSC 1/1100SF instrument. The thermal stability of this sample was confirmed by measuring the weight loss in the heating process with a rate of 10 °C/min from 30 to 800 °C.
under a nitrogen atmosphere. The optical micrographs were attained by an Axioskop 40A Pol optical microscope (Carl Zeiss) under crossed polarizers. SEM micrographs were recorded with a JEOI JSM 6300 F. The sample surface was sputtered by gold to enhance the contrast. The morphological evolution of C18-4CIPBI was observed in situ by an Agilent Technologies 5000 atomic force microscope (Agilent Technologies Co. Ltd., U.S.) equipped with a hot stage. The 2D wide-angle X-ray diffraction (WXRD) for powder sample was completed in a Xenocs-SAXS/WAXS system by X-ray wavelength of 1.5418 Å. The WXRD for the thin film sample was carried out using a Philips X’pert MRD diffractometer with Cu Kα radiation, and the sample was placed on a hot place to investigate the phase transition behavior of C18-4CIPBI film in the heating process. The θ/2θ scans were performed in the reflection mode with a 2θ increment of 0.05° and an integration time of 20 s.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03675.

* Videos showing the morphological evolution during cooling processes (AVI)*

* Videos showing the morphological evolution during heating processes (AVI)*

* Molecular size of C18-4ClPBI obtained by energy optimization in Materials Studio, transfer characteristics of a thin film transistor based on C18-4CIPBI at 100 and 120 °C, and schematic diagram of bottom-gate and bottom-contact OFET (PDF)*

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**Notes**

The authors declare no competing financial interest.

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