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ORIGINAL CONTRIBUTION

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Semicrystalline morphology in thin films of poly(3-hexylthiophene)

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Abstract The thermodynamic phase behavior and the morphology in thin films of poly(3-hexylthiophene) (P3HT) has been studied using calorimetry, X-ray scattering, and scanning force microscopy (AFM). Around 225 °C a phase transition from the crystalline state to a layered, liquid crystalline structure occurs in regioregular P3HT, while the regiorandom counterpart material is disordered at all temperatures and displays a glass transition temperature $T_g \approx -3$ °C. Regioregular P3HT is semicrystalline and forms needle or plate like crystallites which in solution cast thin films are oriented with respect to the substrate. Films produced by spin coating display a non-equilibrium structure with reduced order and orientation. Annealing of these films in the liquid crystalline state leads to the formation of a morphology similar to the one observed in solution cast films.

Keywords Semicrystalline morphology · Thin films · Poly(3-hexylthiophene) · Thermodynamics · Phase behavior · Morphology · Crystals

Introduction

Organic semiconductors have gained a lot of attention during the past few years, driven by their potential for applications as low cost electronic materials for devices not requiring the high specifications which can only be fulfilled by inorganic semiconductors [1, 2, 3, 4]. Of special interest are devices based on polymeric materials prepared by simple solution processing. Head-to-tail coupled poly(3-hexylthiophene) (P3HT) is one of the most promising materials for this purpose, since it combines the straightforward processability with a high charge carrier mobility [4]. The electronic transport mechanism in P3HT though, is not well understood, with one reason being that the material displays a complex heterogeneous structure on a mesoscopic length scale. The fact that structural order and orientation influences the electronic properties has been established (cf., e.g., [5]).

P3HT is a stiff polymer with flexible side chains, introduced for greater solubility. In the melt this kind of polymers generally exhibit a microphase separation between the stiff main chain and the alkyl side chains leading to a layered, liquid crystalline structure [6]. Upon crystallization the layered structure is preserved and the main chains as well as the side chains order onto a common crystalline lattice. In this respect, aspects of side chain crystallization as they are observed in comb-like polymers consisting of an amorphous main chain and crystallizable alkyl side chains like, e.g., poly(*n*-octadecyl methacrylate) [7, 8] are combined with aspects of the usual main chain crystallization as it occurs for polymers consisting of chemically regular, flexible chains [9]. In both cases a semicrystalline structure results, which for the case of crystallization of flexible chains has been studied in detail and is well characterized in bulk [9] as well as in thin films [10]. While it is well known that alkyl substituted polythiophenes develop oriented structures in thin films, neither the driving forces for orientation nor the exact relation with the semicrystalline morphology is well understood [5, 11].

Here we report a study of the morphology in thin films of regioregular P3HT on SiO_2 using a combination of X-ray scattering and scanning force microscopy (AFM) as imaging method. Films prepared by solvent casting and by spin coating are compared. The results indicate that the structure obtained from spin coating is a trapped non-equilibrium structure. In addition we present data concerning the phase behavior, since the transition temperatures observed depend on the regioregularity of the material used and values obtained from studies on different materials cannot be compared in a straightforward manner (cf., e.g., [12] and [13]).

The main structural feature of regioregular alkyl-substituted polythiophenes is a layered structure, in which laterally packed thiophene main chains are separated by the side chains as schematically shown in Fig. 1 [14, 15, 16]. At room temperature the material is semicrystalline; the crystal axes are defined in Fig. 1. Generally a side chain structure without interdigitation but with a finite tilt of the side chains with respect to the layers is reported [15]. At higher temperatures a phase transition to a liquid crystalline structure takes place with the transition temperature T_{clc} depending on the extent of regioregularity. Here it is important to realize that only recently, it has been become possible to synthesize almost completely regular head-to-tail coupled molecules [18, 19, 20]. While regiorandom P3HT is amorphous, the lower regioregularity of P3HT synthesized, e.g., with the $FeCl_3$ method (head-to-tail-regioregularity 80% and below, [21]) is also sufficient to allow crystallization.

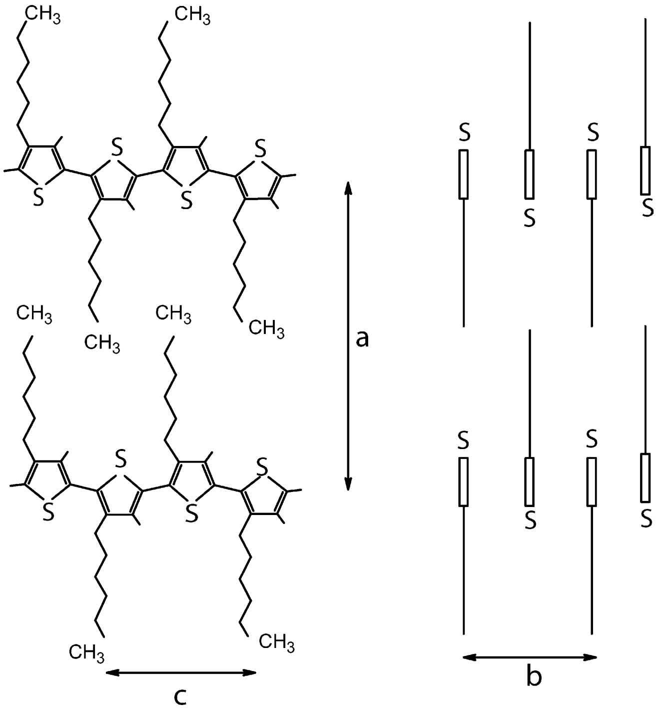

Fig. 1 Schematic illustration of the layered structure of regioregular P3HT with the definitions of the lattice parameters a, b, and c for the crystalline state (a = 16.8 Å, b = 7.66 Å, c = 7.7 Å [15]). The viewgraph is not intended to show a realistic model of side chain packing, which is, e.g., discussed in more detail in [15, 17]

In solvent cast thin films the crystalline part of the material is oriented with the a-axis perpendicular to the substrate [5, 11]. In spin coated films, the orientation was found to depend on the regioregularity as well as on the molecular weight [5]. High regioregularity (>91%) and low molecular weight was reported to lead to an orientation of the a-axis perpendicular to the substrate, while lower regioregularity (81%) and higher molecular weight produced films with an orientation of the a-axis parallel to the substrate. The morphology in these oriented films is not well known. Surface interactions have only been studied for the case of very thin films on graphite (HOPG) by STM [22, 23]. This substrate was found to have epitaxial effects on the polymer, resulting in an alignment with the a-axis parallel to the substrate. These studies though gave evidence for the existence of chain folds, whose existence in P3HT was postulated before based on indirect evidence from the morphology of solution grown whisker-like crystals [24].

Experimental section

Sample Regioregular and regiorandom P3HT, purchased from Aldrich Chemical Co., was used without further purification. The regioregularity of the regioregular material was specified as >98%, the nominal molecular weight M_w as 87000[1]. Our own NMR measurements, however, indicated a slightly lower regioregularity of only about 93% as determined from the signals of the α-methylene protons (cf. [20]).

Films were solvent cast from a 0.2% or 0.5% chloroform solution, or spin coated at 1500 rpm from a 0.5% chloroform solution onto silicon wafers covered with a natural oxide layer. While solvent cast films could easily be peeled off for X-ray measurements, this was not possible with spin coated films.

Experiments X-ray diffraction measurements were performed with a Siemens D500 powder diffractometer in reflection geometry (θ–2θ scans) equipped with a heat-

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[1] Values given by the supplier.

able sample holder (Anton Paar, Graz, Austria). X-ray diffraction measurements in transmission geometry were performed on a rotating anode equipped with an image plate detector (Schneider, Offenburg, Germany). Free standing solvent cast films were held by a sample holder which allows to adjust the incident angle. On both setups Cu-K$_\alpha$ radiation was used.

AFM experiments were performed with a Digital Instruments Multimode/Nanoscope III scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers (≈300 kHz). Typical scan speeds during recording were 0.3–1 lines/s using scan heads with a maximum range of 16×16 μm^2 . The phase images represent the variations of relative phase shifts (i.e., the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their elastic properties (e.g., amorphous and crystalline polymers).

Finally, a Perkin-Elmer-DSC7 has been used for the calorimetric measurements.

Results and discussion

Thermal behavior

Calorimetric measurements revealed an endothermic transition from a crystalline to a liquid crystalline state (cf. X-ray results) at 210–225 °C in regioregular P3HT and a glass transition in regiorandom P3HT ($T_g = -3 \pm 1$ °C), as shown in Figs. 2 and 3. The transition shows the typical features of a melting/crystallization transition. It is possible to supercool the sample. As commonly observed in polymers, the melting temperature depends on the crystallization conditions. A long isothermal crystallization at elevated temperature led to a higher nominal value for T_{clc}, e.g., isothermal crystallization for 12 h at 211 °C: $T_{clc} \approx 226$ °C (onset temperature). The range of the transition temperature T_{clc} of the regioregular material is consistent with the values given by Malik et al. [13]. The transition enthalpy as determined from the data shown in Fig. 2 was $\Delta H = 15.2$ J/g (integration range: 100–245 °C). X-ray diffraction measurements confirmed that around T_{clc} the crystalline structure melts while a layered liquid-crystalline structure is preserved. The scattering diagram of regioregular P3HT powder (Fig. 4) consists of a series of (h00)-reflections corresponding to the main chain/side chain layered structure and a strong reflection at a Bragg angle $2\theta = 23.4°$ reflecting the lateral packing in the crystals. At this angle, the (020) as well as the (002)-reflections are expected. However, it was shown previously that the first one is much stronger [14]. The lattice parameters calculated from the observed reflections are consistent with previously reported values. In the high temperature phase the (020)-reflection as well as the higher order layer reflections (200) and (300) disappear, while the (100)-reflection remains (cf. Fig. 4). This is in contrast to earlier observations [12] on P3HT of lower regioregularity, for which the (100)-reflection disappeared around 180 °C.

Note that regiorandom P3HT, on the other hand, showed no crystalline reflections, indicating that the regiorandom sample is amorphous. Instead, only a weak, broad peak around $2\theta \approx 7°$ is observed. Regiorandom P3HT is highly viscous at room temperature, consistent with the glass transition temperature observed in the DSC measurements ($T_g \approx -3°$, cf. Fig. 3).

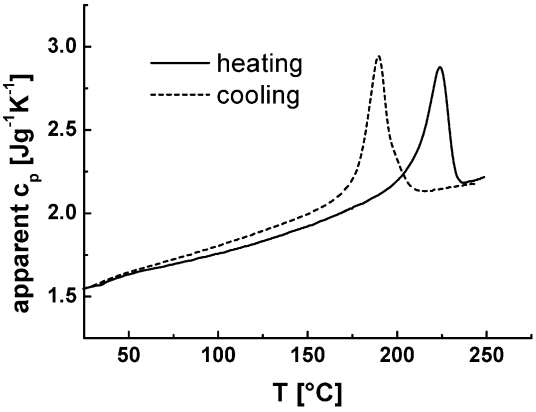

Fig. 2 Melting and crystallization of regioregular P3HT as measured by DSC (heating and cooling rates: 20 K/min). The signal obtained during heating is endothermic, while the one obtained during cooling is exothermic (heating scan: onset temperature: 209 °C, peak maximum 225 °C). Crystallization and cooling extend over a large temperature range as it is typical for semicrystalline polymers [9]

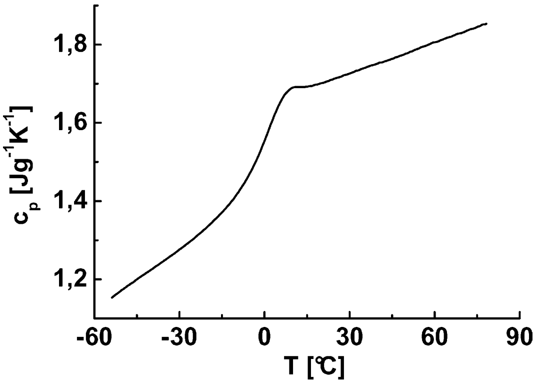

Fig. 3 DSC heating-scan of regiorandom P3HT (heating rate: 10 K/min). A glass transition occurs at about $T_g = -3$ °C

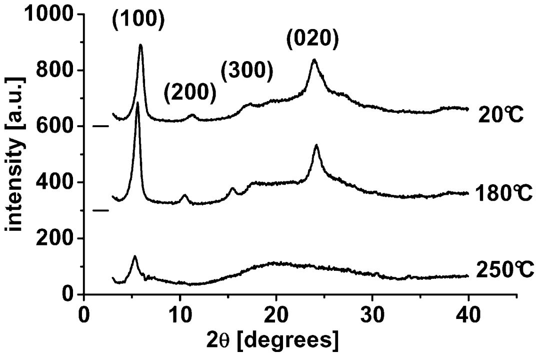

Fig. 4 Results of X-ray powder diffraction measurements on regioregular P3HT at different temperatures in the crystalline and in the liquid crystalline state (the data for 20 °C and for 180 °C have been offset vertically). Below $T_{c/c}$, the sample is semicrystalline, showing both crystalline reflections and an amorphous halo. The series of (h00)-reflections are due to the layered structure separating main and side chains, while the (020)-reflection reflects the lateral packing of the chains. A more detailed series of measurements (not included here) showed that the (020)-reflection disappears in the temperature range between 220 °C and 230 °C, corresponding to the transition observed in the DSC measurements (cf. Fig. 2)

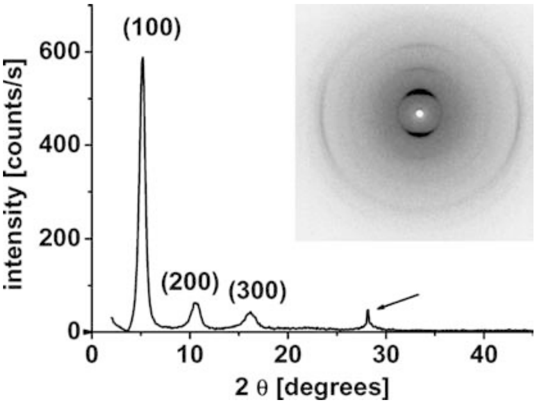

Fig. 5 X-ray diffraction data measured in reflection geometry from a solvent cast P3HT film (from 0.5% solution). The (h00)-reflections are visible, while the (020)-reflection at 23.4° is absent due to the orientated texture of the sample. (The peak indicated by the arrow at 28.1° is caused by the substrate.) *Inset*: X-ray measurement in transmission geometry of a solvent cast film under an angle of incidence of 25° (normal incidence 90°). The meridional position of the (h00)-reflections together with the equatorial position of the (020)-reflection confirm the above-mentioned preferred orientation of the crystallites. The pattern also indicates that the orientation is not perfect (modeling the orientation distribution of the angle between the a-axis and the substrate normal with a Gaussian leads to an estimate $\sigma \approx 20°$)

Thin film samples

In accordance with previous findings [5, 11, 20], films cast from solution with a thickness up to several micrometers were found to be oriented with their a-axis perpendicular to the substrate, as can be concluded from the corresponding X-ray measurements (cf. Fig. 5). Only the (h00)-reflections are visible in reflection geometry, while the lateral (020)-reflection is absent. Measurements in transmission on free standing films using an area detector support this result (cf. inset of Fig. 5).

The surface structure of the films was investigated with an AFM operating in tapping mode. Figure 6 shows the corresponding height and phase images. Since the phase image visualizes hard-soft contrast in the material it seems obvious to identify the structure observed with the crystalline-amorphous morphology in semicrystalline P3HT (lighter areas correspond to the harder, crystalline material). The crystallites have a highly anisotropic, needle or plate like shape. Given the X-ray results and assuming the structure at the surface to be identical to that one in the bulk of the film, we conclude that the crystals are visualized as seen along the crystal a-axis. The growth direction of the crystals is certainly perpendicular to the c-axis; we therefore identify the longer dimension of the elongated crystals with the b-axis, while the short dimension corresponds to the c-axis, as one would expect for a crystal for which chain folding occurs during growth (Fig. 7). This view is consistent with conclusions drawn from the morphology of whisker-like crystals grown from poor solvents [24]. The AFM images suggests some short range correlations between neighboring crystals with a period of ≈30–40 nm, but no well-ordered stacks of lamella are observed. Small angle X-ray measurements, on the other hand, showed no peaks that would allow the determination of a lamellar spacing neither in thin films nor in bulk samples, most likely due to limited resolution of the instruments available.

For investigations of the electronic properties spin coated films are often used. We also examined thin (≈50–100 nm) films produced in this way by a combination of scattering and imaging techniques. Generally the (020)-reflection could not be observed and even the (100)-reflection was very weak directly after spin coating, while after annealing at 250 °C in the liquid crystalline state the latter reflection became much stronger, as can be seen in Fig. 8. A similar increase can also be observed for the films obtained by solvent casting, but the effect is much smaller, indicating that the structure obtained by solution casting is closer to equilibrium (cf. also [25]). Corresponding AFM phase images obtained from samples as prepared and after annealing in the liquid crystalline phase are shown in Fig. 9. The images show a clear increase of the number of the needle or plate shaped structures after annealing, corresponding to a higher density of crystallites visible in the AFM.

Obviously in the initial state as obtained directly from spin coating either the crystallinity is much lower or the preferred orientation of the crystallites is different. With the techniques used here these two cases

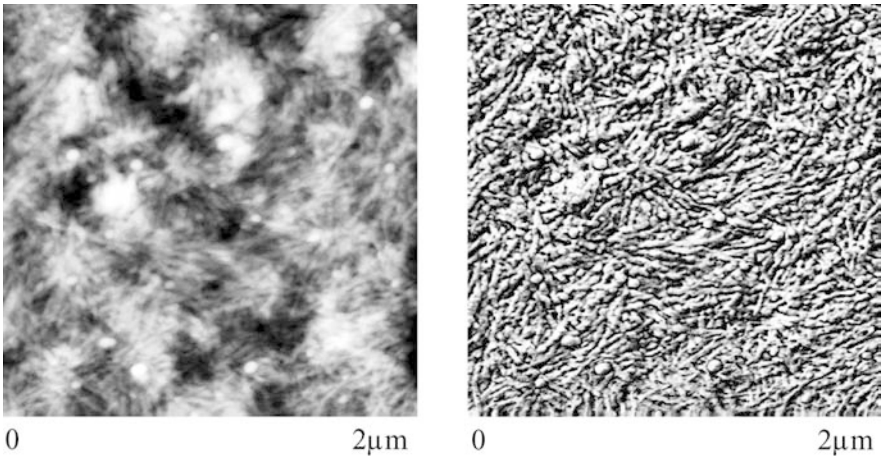

Fig. 6 AFM tapping mode height (*left*) and phase (*right*) images of a solvent cast P3HT film showing a two phase structure. We interpret the brighter anisotropic, needle or plate like structures as the crystalline parts of the semicrystalline material. The z-scale of the height image is 100 nm, the amplitude of the phase image is 40°

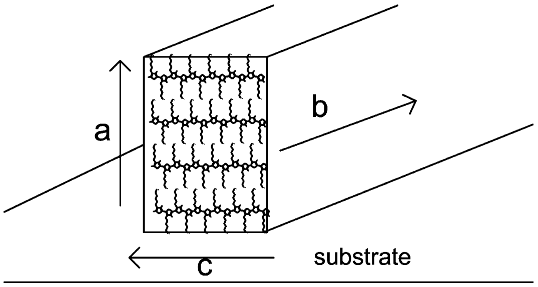

Fig. 7 Suggested schematic model for shape and orientation of the crystalline parts in solvent cast P3HT films, based on X-ray diffraction and AFM measurements (relative dimensions are not to scale)

cannot be clearly distinguished. Annealing above T_{clc} leads to an oriented liquid crystalline structure with the layers parallel to the substrate and as a consequence during subsequent cooling a crystallization within the existing layered structure takes place. We conclude that the state obtained directly after spin coating is a non-equilibrium state trapped by the fast drying process. It should be kept in mind also that a dry, amorphous film at room temperature is most likely in a state of reduced mobility, since it can be assumed that the glass transition temperatures of the regiorandom material and the supercooled regioregular material are similar. The alignment happening at high temperatures is most likely induced by a preferential wetting on one or both interfaces of the thin film, as it is common in thin films of microphase separated materials [26, 27]. Solvent casting obviously leads to films much closer to this final state. This could either mean that during slow drying the system goes through a swollen liquid crystalline phase which orients before crystallization takes place, or due to the presence of the interfaces crystals are nucleated in an orientated way leading to the same final structure as crystallization from an oriented liquid crystalline phase.

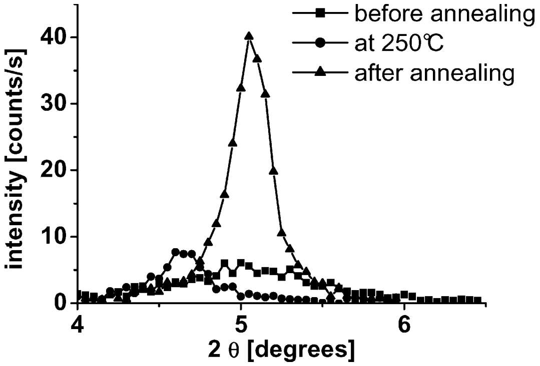

Fig. 8 X-ray diffraction data as measured from a P3HT film obtained from spin coating. Annealing (250 °C under vacuum for 20 min) of the sample in the liquid crystalline phase led to a strong increase of the intensity of the originally very weak (100)-reflection

Conclusions

By combining X-ray diffraction measurements with AFM data a morphological model for oriented, semicrystalline films of regioregular P3HT could be developed. P3HT films cast from chloroform on SiO_2 consist of oriented, needle or plate like crystalline structures embedded in an amorphous matrix. Highly regioregular P3HT undergoes a transition into a layered, smectic liquid crystalline phase at about 225 °C. The crystallinity and the orientation relative to the substrate of spin coated films increases by annealing the samples in this liquid crystalline phase. We understand the preferred orientation of the crystallites parallel to the substrate as a result of interfacial interactions, which leads to an alignment of the liquid crystalline phase parallel to the substrate. Initially, the spin coated films are far from equilibrium due to the rapid formation of the film. At higher temperatures, the mobility of the polymer chains increases, allowing the crystals to grow and to orient.

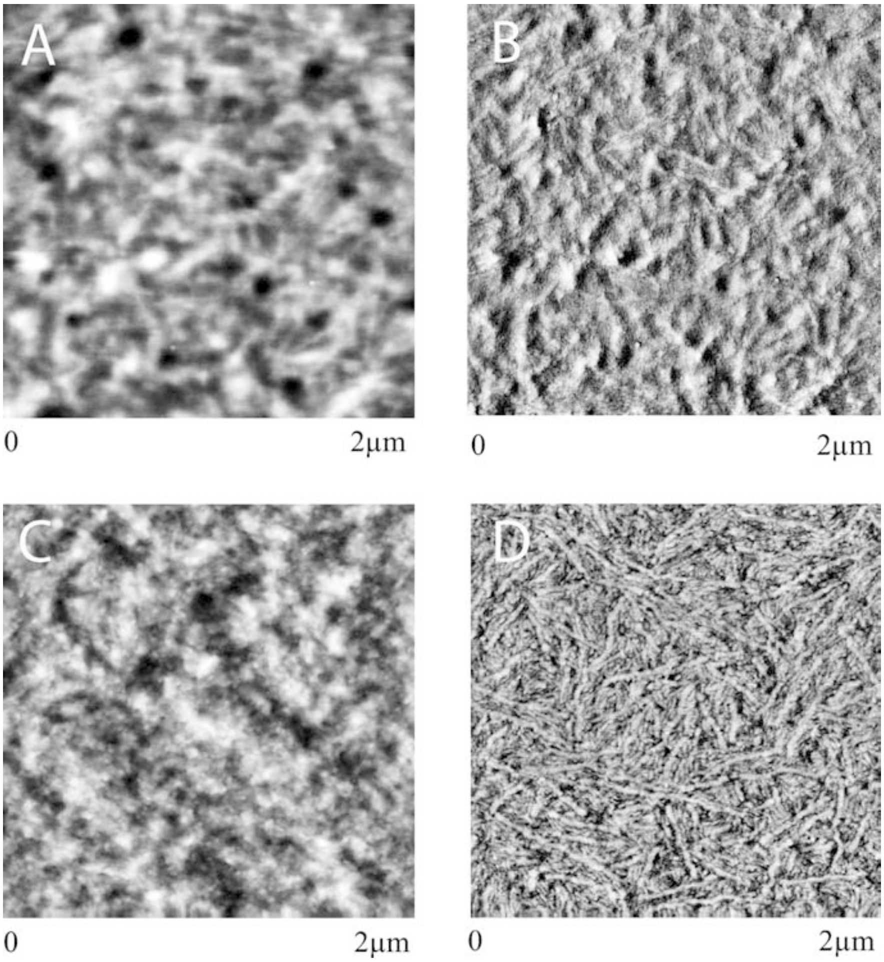

Fig. 9A–D AFM phase images of P3HT films produced by spin coating as prepared and after annealing in the liquid crystalline phase: **A** as prepared, height image—z-scale 40 nm; **B** as prepared, phase image—amplitude 40°; **C** annealed for 20 min at 250 °C, height image—z-scale 30 nm; **D** annealed for 20 min at 250 °C, phase image—amplitude 30°). The density of the needle-like crystalline structures has increased after annealing, indicating that the heat treatment induced a (re)organization of the liquid crystalline structure whose orientation is preserved during subsequent crystallization

Our study shows that in thin films of P3HT, self assembly is controlled by a complex interplay of microphase separation, surface induced orientation, crystallization and molecular mobility, as it is well known from other microphase separated polymeric systems. Assuming, as some experiments indicate, that the molecular order has a direct effect on the electronic properties in these materials, further understanding and control of these processes should be important.

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