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Direct observation of the influence of chirality on the microstructure of regioregular poly-(3-alkylthiophene)s at the liquid/solid interface†

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The degree of order of poly(3-alkylthiophene)s on atomically flat surfaces is strongly influenced by interchain interactions. Regularly ordered, disordered and amorphous microstructures are observed for achiral, homochiral and meso poly(3-alkylthiophene)s, respectively, as revealed by scanning tunneling microscopy.

π -Conjugated conductive polymers are of interest because they are active materials in for instance organic field-effect transistors (OFET).^{1,2} Compared to inorganic semiconductors, polymers possess higher mechanical flexibility and better solution processability, but less crystallinity.³ The structural order of conjugated polymers, from chemical structure to micro- and mesoscopic scale organization, determines their carrier mobilities, which is an important parameter in plastic electronics.⁴ Numerous studies have been devoted to reveal the relation between the degree of order and electronic properties of these polymeric materials.^{5–8} Side chain engineering is widely utilized to improve solubility and achieve optimum charge transport by tuning the interchain interactions and π - π stacking distance.⁹ Different aspects such as the role of chain length,¹⁰ chain branching¹¹ and chain branching position¹² have been considered. Yet much less attention has been paid to the impact of chiral centers in the side chains.^{13,14} This is somehow surprising given the significant role of molecular chirality in molecular self-assembly,^{15–17} which motivated us to investigate the impact of chiral centers in the side chains on the microstructure of conductive polymers when adsorbed on atomically flat surfaces. On the one hand, the structural characteristics of these conjugated polymers at interfaces are relevant in relation

to organic electronics. On the other hand, scanning probe microscopies may give structural information at the nanoscale when the conjugated polymers are adsorbed on a solid substrate.¹⁸

Among the many possible polymeric systems, poly(3-alkylthiophene)s (P3ATs) are an important class that exhibit unique chemical, optical and electronic properties. In addition, its combination with C60 represents the workhorse in the field of polymer solar cells.¹⁹ To achieve optimum charge transport and therewith desirable performance of P3ATs systems, morphological control is the key. The adsorption behavior of various mainly achiral^{20–24,27,28} and few chiral poly(3-alkylthiophene)s (P3ATs)^{25,26} has been studied using scanning tunneling microscopy (STM) as visualization tool. Most often on the basal plane of graphite,^{20–26} but rarely on metallic substrates.^{27,28} The latter are relevant substrates though as noble metals are widely used as electrode materials for OFET. So far the only example showing regular structures of a long chain achiral P3AT on a metallic surface was demonstrated by Liu *et al.*, by taking advantage of an iodine adlayer to decrease the adsorbate–substrate interaction.²⁸

Herein we investigate the adsorption of three different P3ATs at the liquid/metal interface, aiming at bringing insight in the influence of the chirality of side chains on the degree of order of P3AT microstructures. In addition we also probe the adsorption of P3ATs/C60 mixtures. The three polythiophenes, termed as **P3OT**, **(S)-P3OT** and **(meso)-P3OT** according to the chirality of the lateral chains, have the same polythiophene backbone (Scheme 1).

P3OT, **(S)-P3OT** and **(meso)-P3OT** were dissolved in 1,2,4-trichlorobenzene (TCB) at low concentrations to avoid, or at least minimize, their self-aggregation in solution phase. The solutions were then deposited on Au(111) surface at ambient conditions *via* dropcasting and characterized by using STM with submolecular resolution.

In the STM topography images (Fig. 1), the conjugated polythiophene units can be recognized as the bright sometimes

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Scheme 1 Chemical structures of **P3OT** ($M_n = 9.3 \text{ kg mol}^{-1}$ and $D = 1.1$), **(S)-P3OT** ($M_n = 7.1 \text{ kg mol}^{-1}$ and $D = 1.1$) and **(meso)-P3OT** ($M_n = 7.8 \text{ kg mol}^{-1}$ and $D = 1.1$). M_n is the number average molecular weight; D = polydispersity. The regioregularity is 100% for all the three polymers.

Fig. 1 STM images of (a) **P3OT** ($2.7 \times 10^{-2} \text{ mg mL}^{-1}$), (b) **(S)-P3OT** ($3.0 \times 10^{-2} \text{ mg mL}^{-1}$) and (c) **(meso)-P3OT** ($3.1 \times 10^{-2} \text{ mg mL}^{-1}$) at the TCB/Au(111) interface. The bottom-left inset in the STM images is the two-dimensional fast Fourier transformation (2D-FFT). (d) A tentative model for a 'hairpin' arrangement of **P3OT** chain. (e) Structural illustrations for all-trans and all-cis conformations of a 8 units segment of **(S)-P3OT**. The red arrows mark the orientation of methyl groups on stereocenters, which are highlighted in black color.

curved lines. The brightest features in Fig. 1a are most likely individual polymer chains on top of the first layer. Individual alkyl chains are not visible but their presence typically leads to a less bright periphery. The occasional black features in Fig. 1b are probably the gold surface. When comparing the STM images that are typical for these compounds, a clear difference in morphology is revealed. **P3OT** furnishes an ordered linear structure, as shown in Fig. 1a and Fig. S1 (ESI[†]). Parallel aligned strands, corresponding to the aromatic backbones of

P3OT lie parallel to the surface, and are mostly oriented along the three main crystallographic axes of the Au(111) surface, as confirmed by the two-dimensional fast Fourier transformation (2D-FFT) images. Individual polymer chains are either straight or curved, and there is no visible grain boundary. The distance between adjacent parallel polythiophene chains is determined by the alkyl chains. An average value of about 1.6 nm (based on 8 observations in 5 images) is measured, which is smaller than the expected distance (1.78 nm) if the octyl chains are fully stretched and interdigitated (Fig. S1, ESI[†]). In addition, **P3OT** exhibits tendency to aggregate into a multiple-layered stacking. Similar structures of P3ATs were reported on HOPG.^{21–26} It has been suggested that the linear part of the conjugated backbone consists of all-trans conformations of repeated thiophene units while cis conformations of thiophene units are prerequisite for chain folding. A structural model for a hairpin arrangement of **P3OT** is shown in Fig. 1d.

In contrast, homochiral **(S)-P3OT** merely forms disordered structures (Fig. 1b and Fig. S2, ESI[†]). Though small well-aligned regions can occasionally be observed, the surface is dominated with spaghetti-like structures. The 2D-FFT pattern exhibits a hexagon-like shape but without scattering points, indicating that the conjugated backbones are not always aligned parallel to the axes of the underlying substrate. Chain bending and folding are of frequent occurrence. Interchain distance was found between 1.1 nm and 2.1 nm.

When it comes to **(meso)-P3OT**, barely any organized regions can be observed. The surface is fully covered with what appears as close-packed (Fig. 1c) or randomly adsorbed **(meso)-P3OT** chains (Fig. S3, ESI[†]) with no specific orientation. Bends and kinks are frequently observed in the curved polymer chains, especially in low density areas, probably because of the different bending directions of *S*- and *R*-segments. Curved chains are widely spread but hardly cross each other, in line with the nearly hexagonal or disk shape 2D-FFT patterns that are obtained. There is quite a spread in the distance between adjacent parallel polythiophene strands, ranging from 1.0 nm to 2.4 nm.

We hypothesize that the decrease in the degree of ordering in going from **P3OT** to **(S)-P3OT** and **(meso)-P3OT** is due to a less efficient interdigitation of the more bulky chiral side chains. The presence of two extra methyl groups hinders interdigitation interactions. Nevertheless, there are two ways to avoid the repulsion, one is by deforming the side chains (Fig. S5–S7, ESI[†]) and the other one is by *trans*-to-*cis* conformational isomerization of the oligothiophene backbone so that all the methyl groups are facing the same direction. Fig. 1e depicts tentative structural models for all-trans and all-cis conformations of a homochiral segment. If the all-trans conformation is adopted on surface, the methyl groups attached to the stereocenters are facing up on one side of the backbone, but pointing down on the other side, causing repulsion with the substrate. The former way to avoid repulsion results in loose and irregular interchain interdigitations, while the latter case favours the formation of curved chains.²¹ The disorder of polymers is therefore a

Fig. 2 (a) Statistics of the surface coverage of well-organized regions (blue shadowed area in the upright scheme, see ESI† for detailed information) for different polymers. (b) STM image of a mixture of **P3OT** and **(meso)-P3OT** at the TCB/Au(111) interface. Concentration: **P3OT**, 1.4×10^{-2} mg mL $^{-1}$; **(meso)-P3OT**, 1.5×10^{-2} mg mL $^{-1}$.

manifestation of *cis-trans* conformational isomerization of thiophene units.

However, STM is not very helpful to determine the exact conformation of thiophene units here. The *trans/cis* ratio, to a certain extent, determines the disorder. Contrariwise, the degree of organization can be used to reflect the changes in chain conformation. In order to reveal the influence of chiral side chains on chain conformation, we have performed a statistical analysis of the surface coverage of well-organized regions, in which the regular interchain interaction occurs (Fig. 2a). **P3OT** exhibits an excellent degree of order, and we find that 63% of the surface area is well-organized. It decreases sharply to 27% for **(S)-P3OT**, and 17% for **(meso)-P3OT**. As the disordered area is not necessary comprised of chains of all-*cis* conformations of thiophene units, we cannot tell the exact ratio of *trans* and *cis* conformations on the surface, but these values surely reflect the trend of *trans*-to-*cis* conformational isomerization from **P3OT** to **(S)-P3OT** to **(meso)-P3OT**.

Despite the huge difference in the morphology of **P3OT** and **(meso)-P3OT**, these two polymers mix well and form a disordered monolayer that shows a degree of order in between that of the pure polymers (Fig. 2b and Fig. S8, ESI†). As such, the degree of order of polymers can be modulated, which may provide an opportunity for future studies on revealing the relationship between the degree of order and performance of conductive polymers.

Polythiophene is well-known as a class of p-type polymer. Its combination with an n-type material, C60, has been widely used in organic photovoltaic devices. The nature of the polymer-fullerene complexation at the interface, which is largely dependent on molecular arrangement, is critical to its performance.¹⁹ Therefore, in a further attempt, we tried to study the polythiophene-fullerene interface on gold and explored the influence of polythiophene microstructure on polymer-fullerene interaction.

As a result of the totally different organization of **P3OT** and **(meso)-P3OT**, the mixing behavior of C60 with these two polymers exhibits distinct features, as shown in Fig. 3. Upon deposition a premixed solution of **P3OT** and C60 on gold surface, two layers can be clearly identified: a regular layer of **P3OT** with large C60 islands on top (Fig. 3a and Fig. S9, ESI†). The addition of C60 has no obvious impact on the

Fig. 3 STM images of (a–c) **P3OT**/C60 (**P3OT**, 1.4×10^{-2} mg mL $^{-1}$; C60, 5×10^{-5} M) and **(meso)-P3OT**/C60 (**(meso)-P3OT**, 1.5×10^{-2} mg mL $^{-1}$; C60, 5×10^{-5} M) at the TCB/Au(111) interface. Red dashed lines in (b) indicate C60 arrays. Inset in (d) is a close-up STM image of **(meso)-P3OT**/C60 mixture (20 nm × 20 nm).

self-assembled **P3OT** microstructures: well-organized monolayer can be easily identified under the C60 islands. The arrangement of C60 in the islands, however, shows no large scale periodicity (Fig. 3b). Nevertheless, the influence of the **P3OT** layer underneath can still be identified. From the high-resolution STM image of C60 island in Fig. 3b, we found that C60 arrays exist at some small regions (marked with red dash lines). A distance of about 1.5 nm is measured between these arrays, which happens to be the interchain distance of **P3OT**. In addition, small domains of a hexagonal network of C60 is also observed (Fig. 3c). Both C60 patterns are different from the spontaneously formed C60 arrays on bare gold, suggesting that the arrangement of C60 islands is being guided by the **P3OT** layer. The mixing of **(meso)-P3OT** with C60, on the other hand, results in randomly adsorbed C60 molecules on top of the **(meso)-P3OT** monolayer (Fig. 3c and Fig. S10, ESI†). Since **(meso)-P3OT**s barely assemble into well-organized structures, small aggregates instead of large regions of C60 are formed. The microstructure of the polymer layer is therefore manifested at the polymer/C60 interface.

To conclude, we have demonstrated the first example of the impact of the chiral nature of the alkyl side chains on P3ATs microstructures on gold. The chirality of alkyl side chains has a significant impact on the chain conformation of P3ATs and therewith influences the microstructures. Our results also show the possibility of using chiral side chains to tune the degree of order, which can be further applied to control the macroscopic properties of conductive polymers.

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