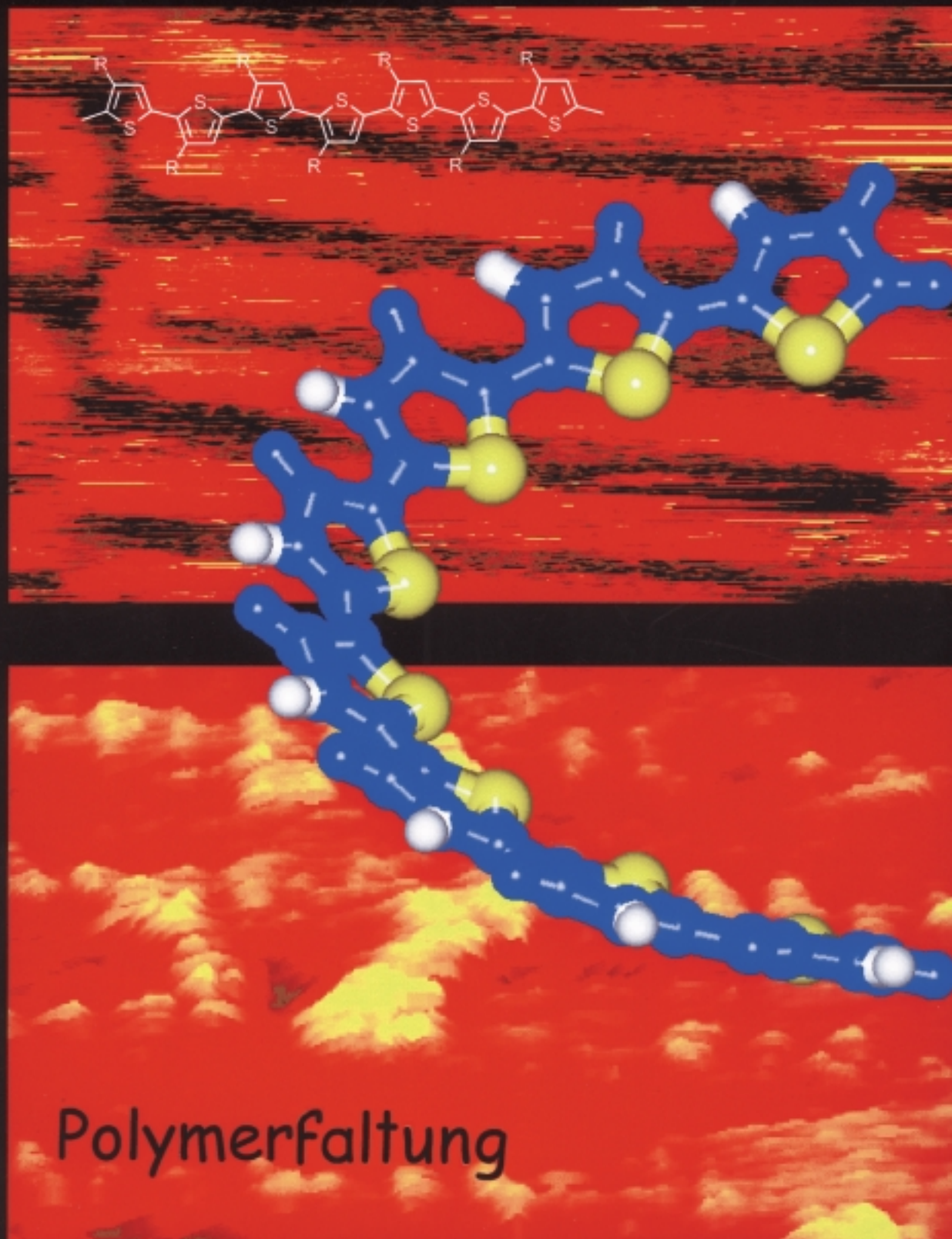


Faltungen und Konformationen von einzelnen konjugierten Polythiophenketten lassen sich mit der Rastertunnelmikroskopie-Technik abbilden und analysieren.



Mehr dazu auf den folgenden Seiten.

Two-Dimensional Crystals of Poly(3-Alkylthiophene)s: Direct Visualization of Polymer Folds in Submolecular Resolution**

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The control of structural order on the molecular level in semiconducting, self-organizing conjugated polymers has important consequences on their electronic properties.^[1] In particular, X-ray diffraction (XRD) on solution-processed, semicrystalline, head-to-tail coupled poly(3-alkylthiophene)s (HT-P3ATs)^[2] indicates a lamella structure with two-dimensional (2D) sheets formed by interchain stacking.^[1a] Like all other synthetic polymers, chain folding is very likely and XRD on semicrystalline whiskers of regiorandom poly(3-alkylthiophene)s indicates strands 15 nm in size, in which the thiophene rings adopt an all-*trans* conformation between the polymer folds.^[3] However, valuable information concerning the molecular parameters are very limited and only an educated guess of polymer conformations within folds is possible because of the lack of appropriate techniques to study these folded conformations at the atomic level.

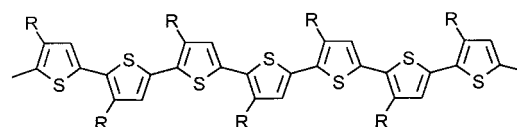
Herein, we report the direct observation of two-dimensional crystals of HT-P3ATs at the solution/HOPG (highly oriented pyrolytic graphite) interface, by means of scanning tunneling microscopy (STM). Lamellar structures formed by interchain stacking uniformly cover wide ranges of the surface. In the in situ measurements, we achieved submolecular resolution and, besides lattice constants, various molecular parameters of the conjugated polymers were determined directly. Supported by quantum chemical calculations, interchain distances, chain lengths, conformations in linear regimes, and folding of the polymeric conjugated chains were identified and analyzed. The formation of a second layer, in which diverse, oriented polymer chains are highly resolved, provides intriguing images: Higher electronic coupling from parallel π – π stacked “molecular wires” is directly visualized.

Conjugated polymers and oligomers show excellent electronic and transport properties in the solid state, which allows their application to organic electronic devices.^[4] In particular, poly-^[5] and oligothiophenes^[6] have been intensively studied in order to understand how structural parameters affect the physical properties^[7] and, consequently, the performance of

the devices.^[1a, 8] In this respect, we and others have developed a rational design and synthesis of model oligothiophenes that, strongly dependent upon their molecular structure, physisorb from solution either onto the basal plane of HOPG^[9] or onto MoS₂^[10] and form highly ordered, 2D crystalline monolayers which were imaged by STM. In particular, head-to-tail coupled oligo(3-alkylthiophene)s, that represent models for the above mentioned HT-P3ATs, show excellent self-assembly and film-forming properties.^[11] In some cases, the 2D ordering at the HOPG surface is, notably, fully coincident with the molecular packing in the 3D crystal, which provides an excellent way to receive information on the molecular packing in the solid state when it is otherwise impossible to perform single-crystal X-ray analyses.^[12]

Mono- and multilayers of macromolecular systems are, however, typically imaged with atomic force microscopy (AFM) on a longer length scale. Packing features have been shown for, among others, double- and single-stranded DNA,^[13] nylon 6,^[14] carbon nanotubes,^[15] and polymeric brushes; the latter are composed of graft- or dendritic block copolymers and form cylindrical^[16] or rodlike supramolecular assemblies.^[17] The resolution to image polymer chain conformations, other than in extended chains of well defined linear arrays, is limited primarily due to the lack of order in regimes of high electron mobilities. Therefore, π -conjugated polymers seem to be ideal candidates to observe the chain conformations in folds. However, STM investigations undertaken so far on conducting polymers, in particular on adsorbed films of regiorandom P3ATs on gold or HOPG surfaces,^[18] typically show only very small areas of ordered domains and allow only a crude determination of structural parameters. Individual strands have been recently found in STM images of the self-assembled rodlike poly(*p*-phenyleneethynylene)s, which form a nematiclike order on HOPG.^[19]

Motivated by the notable self-assembly properties of head-to-tail coupled oligo(3-alkylthiophene)s, the long- and short-range ordering of the corresponding polymers were investigated in self-assembled 2D crystals at the solution/HOPG interface by means of in situ STM. Importantly, HT-coupled poly(3-hexylthiophene) (**P1**) and HT-coupled poly(3-dodecylthiophene) (**P2**) comprised high regioregularities—the



P1: R = C₆H₁₃, **P2:** R = C₁₂H₂₅

percentage of alkyl side chains attached stereoregularly (head-to-tail) to the 3-position of the thiophene ring—of 95 % and 98 %, respectively.^[2] Samples of polymers with lower regioregularity could not be imaged because they do not self-assemble on the substrate surface.

In Figure 1, representative STM images of the conjugated polymers **P1** and **P2** are shown. The images are typically found on areas larger than the 1.0 μm scan range and display a long-range order with *molecularly resolved individual strands*.

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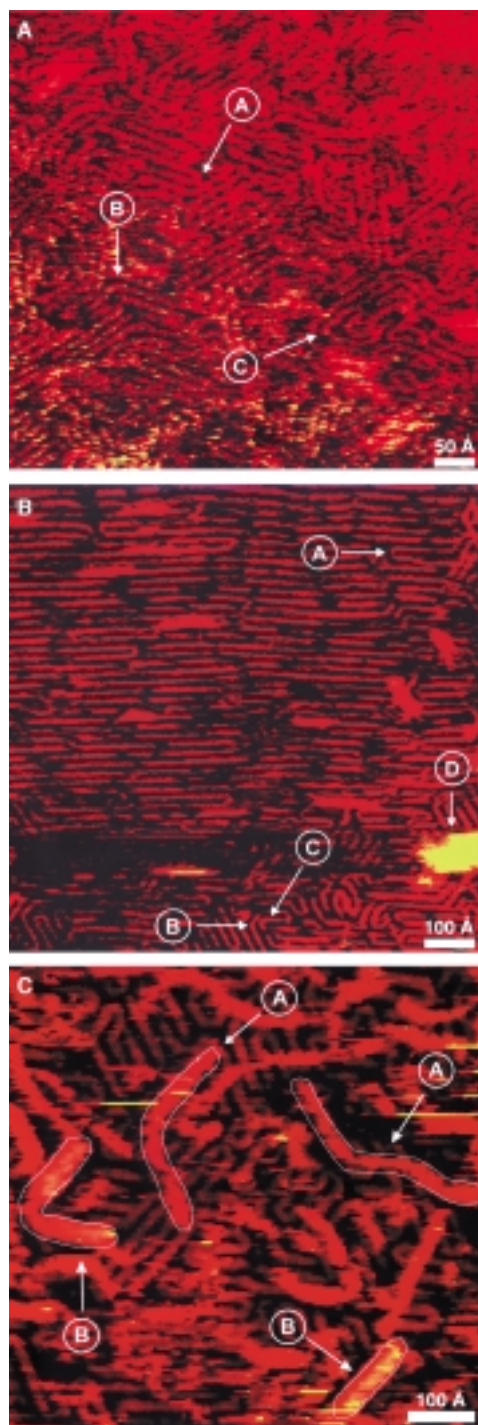


Figure 1. STM images of the long-range ordering of head-to-tail coupled poly(3-alkylthiophene)s on HOPG. A) **P1**, $600 \times 600 \text{ \AA}^2$; B) **P2**, $1000 \times 1000 \text{ \AA}^2$; C) multilayers of **P2**, $700 \times 700 \text{ \AA}^2$.

They are oriented according to the three crystallographic axes of the HOPG substrate, each 120° apart. Since the alkyl side chains prefer to organize in a planar, zigzag, interdigitated fashion along the three main graphite axes,^[11, 12] the conjugated backbones are oriented perpendicular to them in highly ordered lamellae. Over most of the surface, the conjugated chains are linearly arranged and therefore comprise an all-*trans* conformation of the thiophene repeating units. A closer look at the images reveals that the individual

strands are not only linear but chain folding is also clearly observed, in which *cis* conformations of the thiophene units are prerequisite for the fold. Regular, hair-pin folds angle can be seen (A) but also folds of 120° (B) and, rarely, of 60° (C) are evident.

STM images of the short-range ordering of the two conjugated polymers exhibit both formation of parallel lamellae and a regular folding of individual strands (Figure 2).

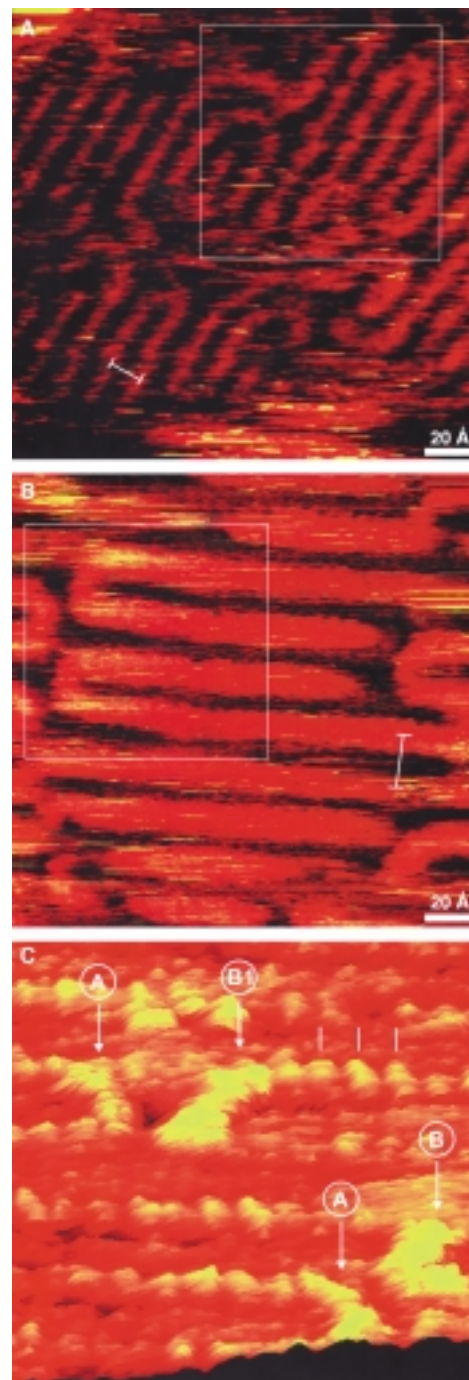


Figure 2. STM images of the short-range ordering of head-to-tail coupled poly(3-alkylthiophene)s on HOPG. A) **P1**, $200 \text{ \AA} \times 200 \text{ \AA}$, the chain-to-chain distance corresponds to $13\text{--}14 \text{ \AA}$; B) **P2**, $200 \times 200 \text{ \AA}^2$, the chain-to-chain distance corresponds to $19\text{--}20 \text{ \AA}$; C) individual chains and folds of **P2**, $93 \times 93 \text{ \AA}^2$, the periodicity of the repeating units at the submolecular resolution is $6.8 \text{ \AA}$. The white squares in (A) and (B) correspond to the areas which are shown in Figure 3 A and 3 B.

Supported by semiempirical calculations (Figure 3), the contour length of the conjugated chains can be measured due to the submolecular resolution, which allows the determination of the number of repeating units in individual strands. Mean values are 110–130 Å (33–40 thiophene units) for **P1** and 100–150 Å (30–44 thiophene units) for **P2**. In Figure 3C, a representative histogram of the chain length distribution, here for **P2**, determined from the whole area in Figure 1B, is shown. Although the average degree of polymerization estimated from STM is lower than those of GPC and MALDI-TOF, the deviations are acceptable and comparable to those published for poly(*p*-phenyleneethynylene)s.^[19]

Another important result obtained from the STM images is the chain-to-chain distance in the lamellae. Typically, distances of 13–14 and 19–20 Å for **P1** and **P2**, respectively, are found. This result is in excellent accordance with semiempirical calculations (**P1**: 13.3, **P2**: 20.8 Å; Figure 3A,B) and with highly ordered 2D crystalline monolayers of corresponding model oligomers, the head-to-tail coupled oligo(3-alkylthiophene)s on graphite (alkyl = hexyl: 12–13,^[20] alkyl = dodecyl: 20–21 Å^[11]) but is in contrast to XRD measurements on the same polycrystalline polymers. By XRD, a greater spacing between two individual conjugated backbones are found: 16.3 for **P1** and 27.1 Å for **P2**.^[21] Two models for the side chain organization in HT-P3ATs are often used: 1) a tilted structure in which the side chains tilt away from the plane of the conjugated backbone, to nearly eliminate alkyl chain interdigitation,^[21f] and 2) a structure with side-chain interdigitation.^[21g] The latter model agrees in full with the STM results of polymers and oligomers and with theoretical calculations. Evidently, due to epitaxial effects of the graphite surface, the intermolecular interactions and interpenetration of the alkyl side chains is maximized and “compressed” in the monolayer whereas, in the polycrystalline bulk material, the chains are less interdigitated by two (**P1**) or four (**P2**) methylene groups (Scheme 1) when the second model is adopted. In accordance, theoretical calculations show an energy minimum in the case of maximum interdigitation.

An intriguing result comes from a detailed, calculation-supported analysis of the folds in both polymers (Figures 2 and 3). The *cis* conformations must definitely be present in a folded chain. An intramolecular hair-pin fold is composed of seven thiophene units in an all-*cis* conformation for hexyl-substituted **P1** (Figure 3A) and eight units for dodecyl-substituted **P2** (Figure 3B). Larger curvatures include additional *cis-trans* conformations in the fold (see Figure 3A). An STM image of dodecyl-substituted **P2** at a submolecular resolution (Figure 2C) even permits conclusions about the composition of the conjugated chains to be made: chains periodicities of 6.8 Å can be observed, that corresponds to a “compressed” bithiophene repeating unit, which in the gas phase has a calculated extension of 7.4 Å. This evident compression can be rationalized by epitaxial effects of the underlying substrate surface on the alkyl side chains. Calculations show that only small variations (<5%) of the angles and the inter-ring bonds are sufficient to achieve this 0.6 Å difference. The periodicities conform to a model, in which MOs of each second thiophene ring match a similar electronic environment on the underlying graphite

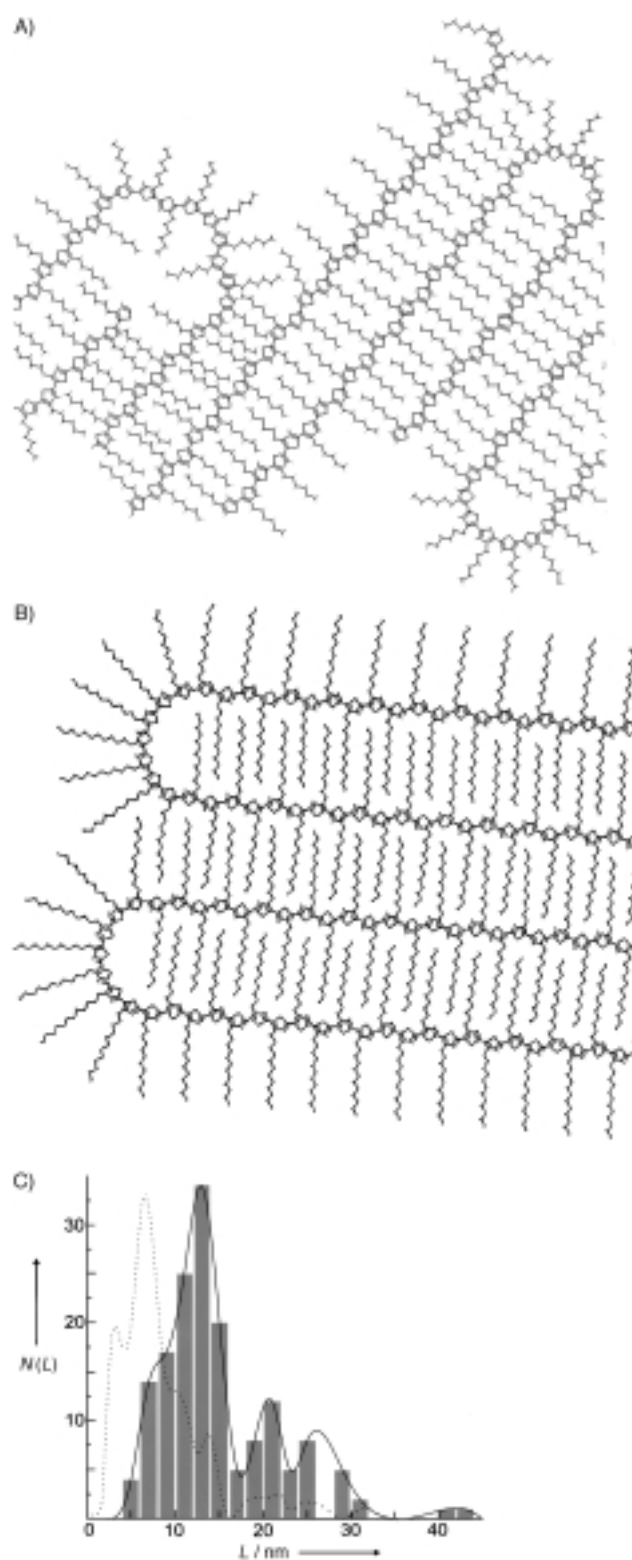
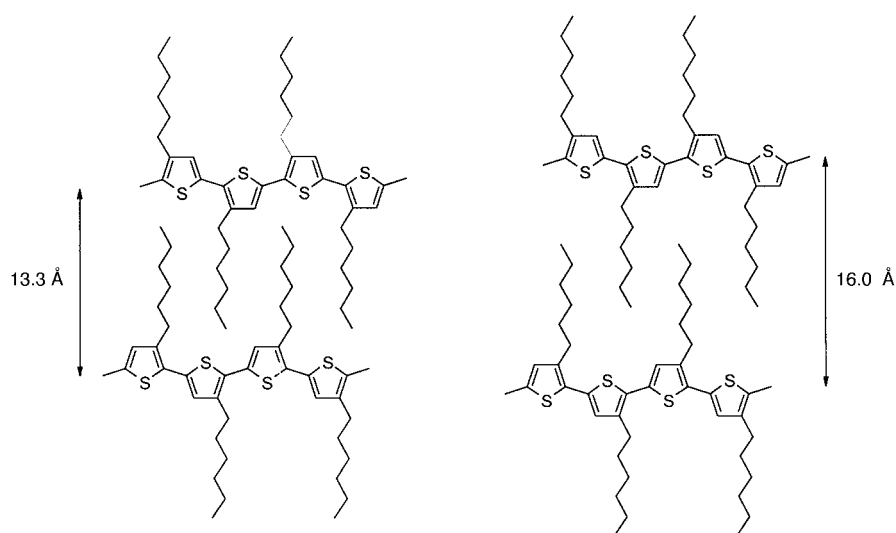


Figure 3. Semiempirical calculations of the head-to-tail coupled poly(3-alkylthiophene)s. The calculations were performed such that first chain fragments of at least ten thiophene units have been optimized in an all-*trans* or an all-*cis* conformation, the interaction of two strands was calculated subsequently, and finally the fragments were assembled in order to construct the polymer chains and to simulate the STM images. A) **P1**, the optimized chain-to-chain distance is 13.3 Å and is coincident with distances determined from STM images; B) **P2**, the optimized chain-to-chain distance is 20.8 Å and is coincident with distances determined from STM images; C) histogram of the chain length distribution (full line) and lamella thickness (dotted line) of **P2**.



Scheme 1. Schematic representations of the molecular arrangement of a monolayer of the regioregular head-to-tail coupled **P1** on graphite, derived from STM data (left) and in the bulk form derived from XRD data (right).^[2c]

surface and thereby give rise to intensive tunneling currents.

Details about the adsorption process can also be deduced from Figure 2C: If two complete hair-pin folds meet on the substrate surface, one fold will lie flat on the surface (A) whereas the second one is raised due to a dynamical processes (B), as indicated from the color which represents different height profiles. In excellent accordance with the calculations in one hair-pin fold (B1), four periodic features in the fold can be identified, which correspond to eight thiophene units in an all-*cis* conformation.

The data allows a detailed analysis of the chain conformations of the polymer fold and, evidentially, the polymer adopts the *cis*-conformation to fold without disorder. In case of a fold over longer distances, in which one chain lies within the folding chain (Figure 3A), the conformation adopts a low energy, well defined, and disorder-free conformation. Furthermore, the data quantification of 7.0 nm, the length of the all-*trans* strand of the polymer between the folding points. The corresponding histogram for the all-*trans* length is given in Figure 3C for **P2**, to show the regularity of the fold, yet the length of the all-*trans* strand is only half of the whisker width in the 3D crystal.^[3]

In an early stage of the adsorption process, the adsorption of individual chains and smaller aggregates onto the substrate surface may result in predominantly parallel lamellae. Because of the longer alkyl side chains, **P2** has a greater tendency to form aggregates and must therefore be used in lower concentrations. However, individual chains also seem to fold back quite regularly and bend completely by 360° without loss of interaction energy. After most parts of the surface are covered, macromolecules from the solution can only adsorb onto open areas and in the remaining gaps by randomly folding at angles of 360° or 120° (Figures 1 and 2). Interestingly for **P2**, a nearly perfect, parallel lamella-type ordering of the macromolecules is found over 70–80 % of the monolayer area (Figure 2B); for the remaining 20–30 % (on the bottom

of the image), folding processes are commencing. Despite the fact that hair-pin folds have been discussed for liquid crystalline polymers, the chains are probably not folded before adsorption onto the surface, as the experiment is at equilibrium conditions and the behavior of poly(3-alkylthiophene)s is not liquid crystalline.

Due to the paucity of a tunneling current through nonconducting molecules, adsorbed monolayers can typically only be imaged by STM experiments. Surprisingly, in some cases at a later stage of the measurements, we observed a second layer of adsorbed macromolecules, as evident from height profiles (not shown) and the yellow areas (D) in Figure 1B. In contrast to STM experiments on oligothiophenes,^[11, 12]

in which a bias of about –600 mV is necessary in order allow a electron tunneling, a bias of only about –150 mV is sufficient to tunnel through two layers of these polymers. This clearly indicates superior semiconducting properties due to a more extended π -conjugation. The molecular arrangement of the second layer macromolecules can be seen in Figure 1C for **P2**. On top of the organized monolayer (red-brown region), a few individual, conjugated macromolecules are deposited in a second layer. Most chains cross the underlying molecules obliquely (A, red), however, parallel oriented molecules can be seen (B, yellow). Also in this case, chain folding of 60 and 120° turns are observed. Since the color in the image is dependent on the tunneling current, a greater tunneling current evidently passes through molecules aligned parallel rather than crossed. This is proof on a molecular scale that two conjugated molecules stacked parallel have more effective π - π interactions and, therefore, better electronic coupling than crossed ones. These results are fully consistent that macroscopic properties, such as conductivity, is better for conducting polymers which are stretched along the conjugated chains.^[22]

Since the self-organization process of highly stereoregular poly(3-alkylthiophene)s to form 2D crystals proved to be only weakly influenced by the substrate surface, the visualization of polymer chain or “molecular wire” conformations at the molecular level and the subsequent determination of molecular parameters, both in extended linear arrays as well as in chain folding, provides a powerful tool to further tailor properties of conjugated materials. The variations of polymer chain folding is visualized directly and shows different conformations, dependent upon the interchain packing. Additional elucidation of the growth of 2D crystal lattices into the third dimension is of interest in order to understand the crystallization mechanism of polymers and is particularly important for the future application of π -conjugated polymers as active elements in plastic^[23] and “molecular” electronic devices.^[24]

Experimental Section

HT-coupled poly(3-alkylthiophene)s were synthesized according the McCullough route.^[2b-d] The crude polymerization mixtures were purified by repeated Soxhlet extractions in methanol, hexane, and twice in chloroform. For the resulting fractions, a regioregularity of 95% (**P1**) and 98% (**P2**) was determined from the ¹H NMR signals at $\delta = 2.8$ and 2.6. Gel-permeation chromatography (GPC) measurements (polystyrene standards) gave polydispersities of 1.35 ($M_w = 28.1$, $M_n = 20.8$ kg mol⁻¹; **P1**) and 1.29 ($M_w = 45.2$, $M_n = 35.1$ kg mol⁻¹; **P2**). Comparison of GPC results of monodisperse model oligomers with MALDI-TOF mass spectra^[25] showed that the GPC results overestimated the number-averaged molecular weight M_n by a factor of 1.6–1.9. From this, we estimate that the number-averaged degree of polymerization amounts to 70 and 80 thiophene units for the hexyl- and dodecyl-substituted polymers, respectively.

The STM images were recorded at ambient temperature with the aid of a low-current STM (RHK Rochester Hills, Michigan, USA) equipped with a mechanically cut Pt/Ir tip and regulated by a STM 1000 control system (RHK). All of the images presented were obtained at quasi-constant height in the variable current mode without using either a voltage pulse to induce sample ordering or digital image processing. The bias voltages were typically about –150 mV and the setpoint currents around 1.0 nA. A freshly cleaved surface of HOPG was first characterized under ambient conditions, then solutions of the polymers in 1,2,4-trichlorobenzene were deposited onto the substrate. In situ STM imaging of the self-assembled 2D monolayers was performed at the interface between HOPG and concentrated solutions of the polymers. Distances determined from the images are of an accuracy of ± 0.1 Å.

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