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Anisotropic Charge Transport in Spherulitic Poly(3-hexylthiophene) Films

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Poly(3-hexylthiophene) (P3HT) is one of the most important semiconducting polymers for organic photovoltaics and optoelectronics.^[1] Yet, because of the structural complexity of semicrystalline polymers, comparatively little is known conclusively about the relationship between charge transport and microstructure in P3HT-containing semiconductors.^[2-9] This lack of information arises mainly from an inability to manufacture samples with spontaneous long-range crystalline order approaching macroscopic dimensions, that allow characterisation in a similar fashion to inorganic single crystals. We have overcome this limitation and grown well-ordered P3HT spherulites, sufficiently large to measure charge transport within single oriented crystal domains, enabling measurements of the charge mobility both parallel and perpendicular to the characteristic π -stacked nanocrystalline lamellae and across spherulite boundaries.

The importance of local order and molecular orientation in determining the electronic properties of polymer semiconductor films is now well established.^[3] In the case of the poly(alkylthiophenes) (PAT)s an edge-on orientation of the molecules, such that the alkyl sidechains (*a*-axis) stand vertically and both the chain backbone (*c*-axis) and π -stacking direction (*b*-axis) lie in the plane of the film, is critical in achieving high in-plane



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charge mobility since this facilitates the assembly of adjacent chains into π -stacks with relatively close, regular intermolecular separation that promotes an effective interchain component of in-plane charge transport. Lan et al. predicted that even in this favourable relative orientation, charge mobility between adjacent chains (interchain) along the stacking direction would be some 2-3 orders of magnitude slower than along a single backbone (intrachain).^[10-12] However, real polymer chains are not infinite in length, and the full semicrystalline morphology comprises ordered, nanocrystalline π -stacked lamellae separated by amorphous regions containing chain folds and chain ends that interrupt this idealised single-chain transport (Figure 1a,b) over macroscopic distances. Charges are able to travel either along the lamellae by hopping between adjacent π -stacked chains, or perpendicular to the lamellae along individual chains before traversing the amorphous interlamellar boundaries. Transport through the amorphous region is most likely a combination of hopping between disordered segments on neighbouring chains, and intrachain transport where a single chain spans adjacent lamellae and is able to act as a high mobility bridge. Given the complex interplay of inter and intrachain pathways and their relative orientation within ordered and disordered regions it is not trivial to state, in spite of the predicted ultra-fast transport within a single chain, whether over macroscopic distances the mobility will be greater parallel or perpendicular to the nanocrystalline lamellae.

Under typical solvent casting crystallization conditions the nanocrystalline lamellae have random in-plane orientation at scales much longer than the polymer chain because of the very high and uncontrolled nucleation density. It is therefore extremely difficult to study the impact of structural anisotropy and grain boundaries on charge-transport mobility in simple spin-cast films using macroscopic probes such as field-effect transistor (FET) channels since the device measurement necessarily averages over a very large number of randomly oriented boundaries.^[9] One approach is to induce global orientation in the sample using mechanical rubbing,^[13–15] imprinting,^[16–18] alignment layers,^[19] or directional solidification.^[8,20] However, these methods introduce additional complications such as anisotropy in surface roughness (scratching) whose influence on the measured charge mobility (μ_{FET}) competes with and can obscure the effect of molecular orientation. Moreover, rubbing and directional solidification conditions thus far studied typically achieve an a-c in-plane orientation, that is, with the π -stacking axis directed out-of-plane and the alkyl side chains in-plane. Jimison et al. measured an anisotropy of at least one order of magnitude in predominantly a-c oriented P3HT films aligned by directional solidification in a crystallisable www.advmat.de



Figure 1. Molecular and crystalline morphology in P3HT films. a) Edge-on orientation of chains with side-chain (*a*-axis) standing parallel to the substrate normal form quasi-parallel nanocrystalline lamellae comprising π -stacked aggregates (solid rectangles) separated by amorphous zones (red lines) with occasional tie-molecules spanning adjacent lamellae. b) Ordered regions at inter-spherulite boundaries are far less likely to be bridged by tie-molecules. c) POM image of a spherulitic morphology at the micron scale in a 25 nm thick P3HT film crystallized at 83% P_{rap}^{cryst} . d) Tapping-mode AFM image (phase contrast) of a meeting point of two spherulites. Radial growth directions and the approximate location of a spherulite boundary are highlighted in (b) and (d). The orientation and position of spherulite boundaries corresponds precisely with the structure visible in POM (data not shown) and confirms the nanocrystalline lamellar structure of the spherulite at the free surface.

trichlorobenzene carrier solvent.^[8] The RMS roughness in the two transport directions was 16 nm in the low mobility (predominantly a-axis) direction compared to just 1.4 nm in the high mobility direction parallel to the chain axis. Ideally, we would like to measure the charge-transport anisotropy in the b-c orientation that is spontaneously adopted in typical high-performance PAT thin-film transistors. This measurement has, to the best of our knowledge, never been achieved.

We recently reported a method of controlled dissolution and recrystallization of preformed P3HT films swollen to a well-defined degree in vapours of a good solvent.^[21] The effective polymer concentration (ratio of initial thickness to swollen thickness) in the thin-film solution is controlled by the relative solvent vapour pressure while in-situ optical spectroscopy can identify the conditions (polymer concentration) at which the polymer crystals completely dissolve. Recrystallization proceeds by a nucleation and radial growth of spherulitic domains familiar from classical semicrystalline polymers comprising nanocrystalline lamellae emanating radially from the nucleation centre. Controlled nucleation and growth allows massive reduction in the nucleation density (i.e., increased spherulite diameter) to such an extent that a transistor channel can be placed entirely within a well-oriented domain, allowing direct measurement of transport anisotropy in a morphology truly representative of that found in high-performance PAT FETs without the need for external structure direction.

The boundaries formed where two crystal growth fronts meet (i.e., interspherulite boundaries) might be expected to represent a greater barrier to the passage of charge because of the significantly reduced likelihood of tie-chains bridging adjacent ordered regions compared to boundaries between quasi-parallel lamellae within the spherulite (Figure 1b).^[22] In order to study this conjecture we make use of a "self-seeding" methodology in which we dissolve all but a few remaining polymer aggregates in the solvent-swollen film that act as nucleation seeds for subsequent recrystallization.^[21,23] Crystal growth therefore occurs under identical conditions but with nucleation density varying over orders of magnitude, determining the relative abundance of crystalline-amorphous boundaries within spherulites to those between neighbouring spherulites and enabling the study of the effect on macroscopic charge transport.

P3HT purchased from Merck ($M_n = 30.9 \text{ kg mol}^{-1}$, PDI = 1.9, 96.2% regioregular) was used for all experiments described here. The molecular weight is above the plateau in lamellar width reported by Zhang et al. and we therefore assume that the P3HT contour length is long enough to allow both chain folding and the existence of tie molecules spanning adjacent lamellae.^[24,25]

25 nm thick P3HT films spin coated from toluene solution were used as the initial state for all experiments. The substrates were silicon wafers (cleaned by exposure to O_2 plasma for 300 s) with or without a 40 nm thick underlayer of sodium



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poly(styrene sulfonate) (NaPSS) spin coated from aqueous solution and used as a water-soluble underlayer for subsequent delamination of the P3HT film. Details of the controlled solvent vapour treatment are published elsewhere.^[21] In brief, a controlled solvent vapour pressure was achieved by mixing two streams of dry nitrogen carrier gas, one of which was saturated with solvent vapour by bubbling through a sintered glass frit in a CS₂ washbottle. The mixing ratio, and therefore relative solvent vapour pressure (denoted as $P_{\text{vap}} = P/P_{\text{sat}}$) was controlled using two mass flow controllers (MKS) with an accuracy of 0.01 sccm in a total flow of 20 sccm. The temperature of the solvent reservoir, sample-chamber walls and polymer sample were set independently using a water-circulating bath and Peltier stage, respectively.

Spherulites with diameters as large as possible (lowest achievable nucleation density) are needed to probe in-plane charge-transport anisotropy in guasi-parallel lamellae within spherulites. It was found that the lowest nucleation densities were achieved with solvent bath and substrate temperatures of 25 °C and 23 °C, respectively, and a recrystallization solvent vapour pressure of 87% $P_{\rm vap}^{\rm cryst}$ following dissolution of the spin-cast starting film at 91% $P_{\rm vap}$ for 600 s. Figure 1c shows a typical spherulitic morphology in the film following recrystallization using polarised optical microscopy (POM). The molecular-scale P3HT crystalline surface morphology at the boundary between adjacent spherulites is visualised using tapping mode atomic force microscopy (AFM, phase contrast shown) in Figure 1d. The alternating bright and dark stripes are attributable to crystalline lamellae and amorphous interlamellar zones respectively. Wide-angle grazing incidence X-ray and transmission electron diffraction (not shown) are consistent with the edge-on orientation of the P3HT molecules ([100] alkyl chains standing parallel to the substrate normal). The b-c plane lies in the film with the *b*-axis [010] (π -stacking) parallel to the radial growth direction and c-axis [001] (chain direction) spanning the lamellar width.^[21] The position and orientation of the spherulite boundaries in AFM correspond precisely with those visible in POM, proving that the in-plane molecular orientation implied by optical microscopy is present at the free surface of the film.

The in-plane charge-transport mobility within spherulites was probed using a grid of short channel width $W = 40 \,\mu m$ and length $L = 30 \,\mu\text{m}$ source–drain contacts made by shadow-mask thermal evaporation of gold onto doped silicon substrates with a 300 nm thick thermally grown SiO_x insulating surface layer as gate dielectric. In thin-film FET devices the first few molecular layers in contact with the underlying gate dielectric dominate the measured charge transport.^[22] Since we are confident of the in-plane molecular orientation only at the free surface of the polymer film from AFM measurements, transistor devices were made by delaminating the recrystallized film from the NaPSS substrate and inverting it such that the free-surface is placed in contact with a new transistor substrate. In practice the NaPSS was dissolved in water after the controlled P3HT recrystallization, leaving a free-floating P3HT film on the water surface. The film was transferred to the transistor by placing the new substrate in gentle, tilted contact with the floating film from above (see the Supporting Information). The films were blown dry with nitrogen before drying at 20 mbar at 40 $^{\circ}\mathrm{C}$ for 12 h and transferal to a nitrogen atmosphere for electronic testing.





Figure 2. Charge-transport anisotropy within spherulites. a) Typical POM image of (40 μ m × 40 μ m) Au transistor contact pads for measurement of μ_{FET} within individual spherulites. Example source (*S*) and drain (*D*) electrodes for a single device are highlighted along with the radial growth direction at an angle (θ) to the transistor channel conduction direction. b) μ_{FET} within spherulites as a function of θ , the inset schematics show the spherulite growth direction in the transistor channels.

Figure 2a shows a typical POM image of the spherulitic P3HT crystal morphology (polarizer-analyzer angle 85° to highlight the radial growth direction) and the grid of Au contact transistor channels. The grid of source-drain contacts permits a large number of measurements to be made on a single P3HT film probing all angles between the source-drain transport direction and the radial spherulite growth direction (θ), shown in Figure 2b. The field-effect mobility was extracted from the saturated transfer characteristics as described in the Experimental Section (representative output and transfer curves are included in Supporting Information). Devices were measured in the same direction with respect to the transistor substrate in order to eliminate the possibility of stain-induced effects resulting from the floating transfer process.

We found average mobilities of $\mu_{\parallel} = 0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ parallel ($\theta = 0^\circ$) and $\mu_{\perp} = 0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ perpendicular ($\theta = 90^\circ$) to the

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radial spherulite growth direction, corresponding to a chargetransport anisotropy $(\mu_{\perp}/\mu_{\parallel})$ of 2.9 ± 0.8. In other words, the measured charge mobility is between 2 and 4 times faster in the direction perpendicular to the lamellar crystallites and not, as is sometimes assumed, in the π -stacking direction. This anisotropy should, strictly speaking, be considered a lower limit as we cannot be sure of the penetration depth of the lamellar orientation at the transistor substrate into the bulk of the layer. Buried layers might be isotropic or have a different in-plane orientation to that at the surface which would reduce the measured anisotropy. However, the charge accumulation layer under these operating conditions is known to be rather thin; Wei et al. estimated that in 26 nm thick P3HT transistors with insulator capacitance of 10 nF cm⁻² at $V_g = -60$ V, 90% of the charge density resides in the first two molecular layers (and 99% within the first 4).^[26,27] We believe, therefore, that this is a good approximation to the real room-temperature charge-transport anisotropy parallel and perpendicular to the lamellar axis in the b-c plane for this polymer. Importantly, we found no significant anisotropy in the film surface roughness (measured RMS roughness from AFM height images was 0.8 nm both parallel and perpendicular to the lamellae), in contrast to films exposed to external alignment processes such as alignment layers, mechanical rubbing or directional cystallisation.^[8,19]

To probe the effect of spherulite boundaries on in-plane FET charge mobility we prepared transistors from P3HT films recrystallized with a range of nucleation densities determined by self-seeding. The solvent reservoir and film temperatures were set to 21 and 19 °C respectively, in accordance with our previously published procedure.^[21] The spin coated films were first swollen to a fully dissolved state (determined by UV–vis absorption spectroscopy) at 91% $P_{\rm vap}$ CS₂ for 300 s and recrystallized at 30% in order that a comparable initial state is reached. Each film was then re-swollen to a chosen seeding concentration at $P_{\rm vap}^{\rm seed}$ for 600 s before de-swelling to a final recrystallization concentration at 83% $P_{\rm vap}^{\rm cryst}$ (see Figure 3b, inset).

Figure 3a shows the P3HT crystalline morphology observed in POM resulting from incrementally increasing the degree of self seeding (concentration of seed crystals). At low seed density (high $P_{\text{vap}}^{\text{seed}}$), individual spherulite nucleation events are visible optically, which grow radially at constant velocity before meeting at an inter-spherulite boundary. Increasing seed density results in incremental increase in the areal density of spherulites. The films were again delaminated after recrystallization and transferred in an inverted geometry onto prefabricated interdigitated bottom-gate, bottom-contact transistor substrates with channel length $L = 20 \ \mu m$ and a channel width $W = 10 \ mm$. Since the areal size of the transistor (500 μ m \times 500 μ m) is larger than the spherulites in all cases, the measurement effectively averages over all transport directions (Figure 3b, inset). Charge-transport mobilities extracted from the saturated transfer characteristics (μ_{FET}) are shown in Figure 3b as a function of the average number of spherulite boundaries intersected (*n*) by a line equal to the channel length *L*, where n = L/N with *N* the average areal nucleation density. Transfer and output curves are included in the Supporting Information.

There is a clear decrease in μ_{FET} visible when the average areal density of spherulite boundaries in the 20 µm channel exceeds n = 1. This is compared with a simple model for μ_{FET}

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Figure 3. Field-effect mobility of self-seeded P3HT films. a) Example POM images (100 μ m × 100 μ m) of a 25 nm thick P3HT film crystallized at 83% P_{vap}^{cryst} after first seeding at the stated P_{vap}^{seed} vapour pressure for 600 s. b) Measured field-effect charge-transport mobility in 20 μ m channel length interdigitated transistors (channel width 10 mm) as a function of the calculated number of spherulite boundaries along a 20 μ m channel (*n*). The dashed line is a fit of Equation 1 to the data.

which treats the film as a composite of higher mobility (within spherulites, μ_s) and lower mobility regions (located at the spherulite boundary μ_{sb}), by the dashed line in Figure 3b. The measured mobility is a composite value of mobilities weighted by respective characteristic lengths (L_s and L_{sb}) within the transistor channel:^[28]

$$\frac{L_{\rm s} + L_{\rm sb}}{\mu_{\rm FET}} = \frac{L_{\rm s}}{\mu_{\rm s}} + \frac{L_{\rm sb}}{\mu_{\rm sb}} \tag{1}$$

The fit of Equation 1 to the measured data is rather sensitive to the choice of fitting parameters ($\mu_{\rm s}$, $\mu_{\rm sb}$ and $L_{\rm sb}$). Assuming a value of 50 nm for $L_{\rm sb}$ (i.e., on the order of one domain spacing) $\mu_{\rm s} = 0.11$ and $\mu_{\rm sb} = 0.005$ cm² V⁻¹ s⁻¹ gave the best fit (dashed



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line in Figure 3b). This fit is consistent with the spherulite boundaries presenting a greater resistance to the passage of charge than the boundaries between quasi-parallel lamellae within spherulites. In the model this difference could result from either the width or the mobility within the spherulite boundaries (or both). In fact, while μ_s is insensitive to choice of $L_{\rm sb}$, $\mu_{\rm sb}$ varies considerably. A range for $L_{\rm sb}$ between 10 and 100 nm resulted in best fit values for $\mu_{\rm sb}$ which were between 10 and 100 times smaller than μ_s . The ratio μ_s/μ_{sb} is considerably lower than values reported for typical small molecule devices (10³ to 10⁵).^[29] This is not surprising given that in small molecule films the difference between highly crystalline order within a grain to disordered zones confined to the grain boundary is considerable, while in the polymer morphology there is also disorder at the interlamellar boundaries distributed throughout the spherulite.

We observe a clear drop in measured field-effect charge mobility corresponding to a controlled increase in the number of non-parallel interspherulite boundaries within a transistor channel. These results support the model proposed by Salleo et al. that grain boundaries are not isotropic;^[22] crystallineamorphous boundaries separating adjacent quasi-parallel lamellae present less of a barrier to charge transport than the boundaries between distinct spherulites.

This observation could be explained by a difference in the relative abundance of intrachain links via tie-molecules connecting adjacent ordered regions. Spanning chains are far less likely to bridge between spherulites than between quasi-parallel lamellae within spherulites. Another (potentially coexisting) explanation would be a greater width of amorphous regions between spherulites compared to the interlamellar boundaries within, and differences in the ease of interchain hopping in these two environments. The well-controlled, ordered spherulitic crystalline morphology presented here will make possible future studies of the electronic properties of single, isolated grain boundaries using high-resolution techniques such as Kelvin probe force microscopy.^[30,31]

In conclusion, we have measured anisotropic charge-transport mobility in the *b*-*c* plane of moderately high-molecularweight P3HT films arising from a nanocrystalline morphology in which charge may travel either parallel to ordered π -stacked lamellar aggregates or perpendicular to them by moving along individual chains before traversing amorphous interlamellar zones. Using field-effect transistor channels placed within wellaligned domains of quasi-parallel lamellae, we found macroscopic charge mobility over distances much longer than a single chain three times faster in the direction perpendicular to the ordered π -stacks, despite the periodic amorphous inter-lamellar interruptions at the scale of the single chain. We attribute this observation to the presence of tie-molecules spanning adjacent quasi-parallel lamellae that provide fast intrachain transport bridges through the amorphous zone.^[11] The frequency of non-aligned grain boundaries occurring at the meeting point of neighbouring growth fronts was controlled using a self-seeding crystallization method. We observed a sharp reduction in μ_{FFT} as the number of non-aligned boundaries increased, suggesting that boundaries in which the frequency of tie-chains is expected to be much lower do indeed present a significantly greater barrier to charge transport than the low-angle boundaries between

adjacent quasi-parallel lamellae. While there are clearly many factors that must be considered simultaneously in order to optimise charge transport in semicrystalline polymer films, our results show that future synthetic and processing strategies for further increasing macroscopic charge mobility will rely on maximising the intrachain transport component of orderdisorder boundaries, and in controlling their placement and orientation with respect to the transport direction.

Experimental Section

Polymer Preparation: P3HT was purchased from Merck (M_n = 30.9 kg mol⁻¹, PDI = 1.9, 96.2% regioregular) and purified in a twostep procedure to eliminate bromine endgroups and to remove catalyst residues. Firstly, an excess of nBuLi n-butyllithium was added to an anhydrous toluene solution at room temperature and the mixture stirred and heated to 60 °C for 30 min. The polymer was precipitated in methanol. Catalyst residues were removed by vigorously stirring a P3HT solution in toluene with a 1 M solution of ethylenediaminetetraacetic acid (EDTA) sodium salt in water for 1 h. The organic phase was extracted and dried over magnesiumsulfate and passed through a short silica column before final precipitation in methanol to obtain the purified polymer.

Film Formation and Controlled Crystallization: Silicon (p-doped, Si Materials) substrates were cleaned in a CO₂ snow jet followed by exposure to oxygen plasma (Diener Femto 100W) for 300 s. The clean silicon was coated with a 40 nm thick, water soluble poly(styrene sulfonate) (NaPSS, Aldrich) film by spin-coating a 30 mg mL⁻¹ solution in deionised water at 6000 rpm and dried for 1 h at 125 °C in air. P3HT solutions in toluene (6 mg mL^{-1}) were prepared by dissolution at 80 $^{\circ}C$ for 4 h under continuous stirring followed by filtering immediately at 25 °C through 200 nm PTFE filters (Acrodisc). Spin-coating at 4000 rpm produced uniform, optically smooth 25 nm thick P3HT films as determined by AFM profilometry. All polymer solutions and films were prepared in a dry nitrogen atmosphere. P3HT films with low and well-defined nucleation density were prepared by exposing the preformed films to a controlled vapour pressure of a good solvent (carbon disulphide, CS₂) as previously reported).^[21] The recrystallized films were removed from the substrate by floatation in deionized water. Transfer onto pre-fabricated transistor substrates was achieved by placing the (cleaned and surface-treated) transistor substrate in contact with the floating film at roughly 45° and gently pushing such that the free-surface of the film was in contact with the transistor surface (i.e., the film is flipped from its original orientation).

Prefabricated field-effect Field-Effect Transistors: transistors (FETs) were purchased from The Fraunhofer Institute for Photonic Microsystems (Dresden) in a bottom-gate, bottom-contact configuration on highly n-doped Si wafers with a thermally grown 300 nm SiO, layer serving as gate electrode and gate insulator, respectively. Gold source and drain electrodes defined interdigitated transistor channels with a length $L = 20 \ \mu$ m, and width $W = 10 \ m$ m. The transistors were cleaned by sonication in acetone and isopropanol followed by exposure to oxygen plasma (Diener Femto 100W) for 300 seconds. Before use, the substrates were exposed either to vapours of HMDS in a sealed glass jar on a hotplate at 100 °C for 12 h (interdigitated devices) or vapours of ODTS at 40 °C for 0.5 h (Au-grid devices). Electronic characterisation of the FETs was made in a nitrogen atmosphere using a Keithley 2636 Dual channel sourcemeter. Field-effect mobilities (μ_{FFT}) were extracted from the saturated transfer characteristics employing the relation:

$$\frac{\delta I_{sd} (V_g)}{\delta V_g} = \frac{C_i W}{L} \mu_{\text{FET}} (V_g, V_{sd}) \cdot (V_g - V_0)$$
(2)

where I_{sd} is the source-drain current in the saturation regime, V_g and V_{sd} are the source-gate and source-drain voltages, C_i is the insulator capacitance, W and L are the channel width and length, and V_0 is the turn-on voltage. Transistors for probing local transport anisotropy were



fabricated from grids of gold squares as contact pads 40 μ m × 40 μ m with spacing of 30 μ m fabricated by thermal evaporation (0.2 nm s⁻¹) of Au through a polyimide shadowmask (CADiLAC Laser, Germany) onto silicon substrates with a 300 nm thermally grown oxide layer as gate dielectric (Si Materials, Germany). The squares were contacted directly using Au-coated tungsten probes with 7 μ m diameter tips mounted in a micromanipulator probestation (SUSS MicroTec Test Systems, Germany). The channel width was predefined by making two parallel scratches at the ends of the desired channel using a third probe tip.

Structural Characterisation: AFM was performed on a Bruker MultiMode AFM with NanoScope IIIa Controller operating in tapping mode. Optical microscopy was performed with a Zeiss Axiovision polarizing microscope.

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