

*SOLID STATE PROCESSING OF ORGANIC
SEMICONDUCTING POLYMER BLENDS*

by

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degree of Doctor of Philosophy*

in the

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To my parents

DECLARATION

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ABSTRACT

Organic electronics is an exciting scientific frontier that holds great promise for the manufacture of low-cost, flexible electronic devices. The advancement of these technologies relies on gaining a deeper understanding of important structure/processing/property interrelationships in organic semiconductors. Addressing such fundamental questions enables the employment of well-defined schemes to efficiently improve device performances and optimise industrially relevant processing routes. Compression molding, a solid state process, is for example an excellent candidate for the manufacture of mechanically robust, freestanding organic semiconductor films with a high degree of molecular order and anisotropy. Regrettably, research into the use of such promising processing means are to date sorely lacking, limiting their applicability for future commercialisations. This thesis explores the solid state processing of the model semiconductor poly(3-hexylthiophene) (P3HT) and several blends with thermoplastic insulators. Studies herein address key areas in which solid state pressing has not yet been optimised and demonstrate versatile schemes that facilitate enhanced microstructure formation, molecular ordering and charge transport pathways in the freestanding films. Investigations further verify for the first time the highly anisotropic charge transport properties (as determined by time-of-flight photoconductivity measurements) that arise from solid state processing. Moreover, these flexible films, with well-defined semiconducting architectures, are envisaged as outstanding candidates for the regeneration of electroresponsive biological tissues and as regenerative platforms. The solid state processing protocols are therefore augmented with facile patterning techniques to replicate biologically relevant surface topographies, in the form of microgrooves, onto the film surfaces. Preliminary cell studies, using a cardiac-like cell line, indicate that the substrates support cell culture practices, and that the cells aligned on the groove surfaces. The results presented herein thereby demonstrate that solid state processing of neat organic semiconductors and their blends is a versatile and facile avenue to generate highly structured semiconducting architectures with potential bioelectronic applications.

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1 INTRODUCTION

1.1 Context

The field of organic electronics is one of the most promising and exciting scientific frontiers of today thanks to the high versatility of organic semiconductors.^{1,2} These novel materials offer great potential for low-cost and large area manufacture for a wide range of applications, owing to their tuneable nature for each specific usage. The advantages of organic electronics over the established inorganic semiconductors technologies include tuneable mechanical flexibility and optoelectronic responses (by chemical design or processing schemes). From a processing point of view, these materials are notably compatible with solution-processing (e.g. ink-jet, wire-bar coating, and perhaps even roll-to-roll processes) as well as other traditional polymer processing routes (e.g. compression molding and extrusion methods), making them highly promising for high-throughput manufacture of flexible electronics.

One of the most successful uses of organic semiconductors is as active materials, for instance, in organic light-emitting diodes (OLEDs) for flexible display applications and large area lighting.^{3,4} Decades of extensive efforts by both academia and industry have brought this arena forward and into the market. In fact, these technologies are becoming a part of our everyday life and can be found in many cellular phone and TV displays. Other widely explored applications of organic semiconductors include photovoltaic cells (OPVs), field effect transistors (OFETs), logic circuitry, radio frequency tags and sensors.^{5,6} Some of these applications are nearing commercialisation, while others have already reached market but require further optimisation in order to surpass the cost-effectiveness of already established technologies. More recently, there has also been a

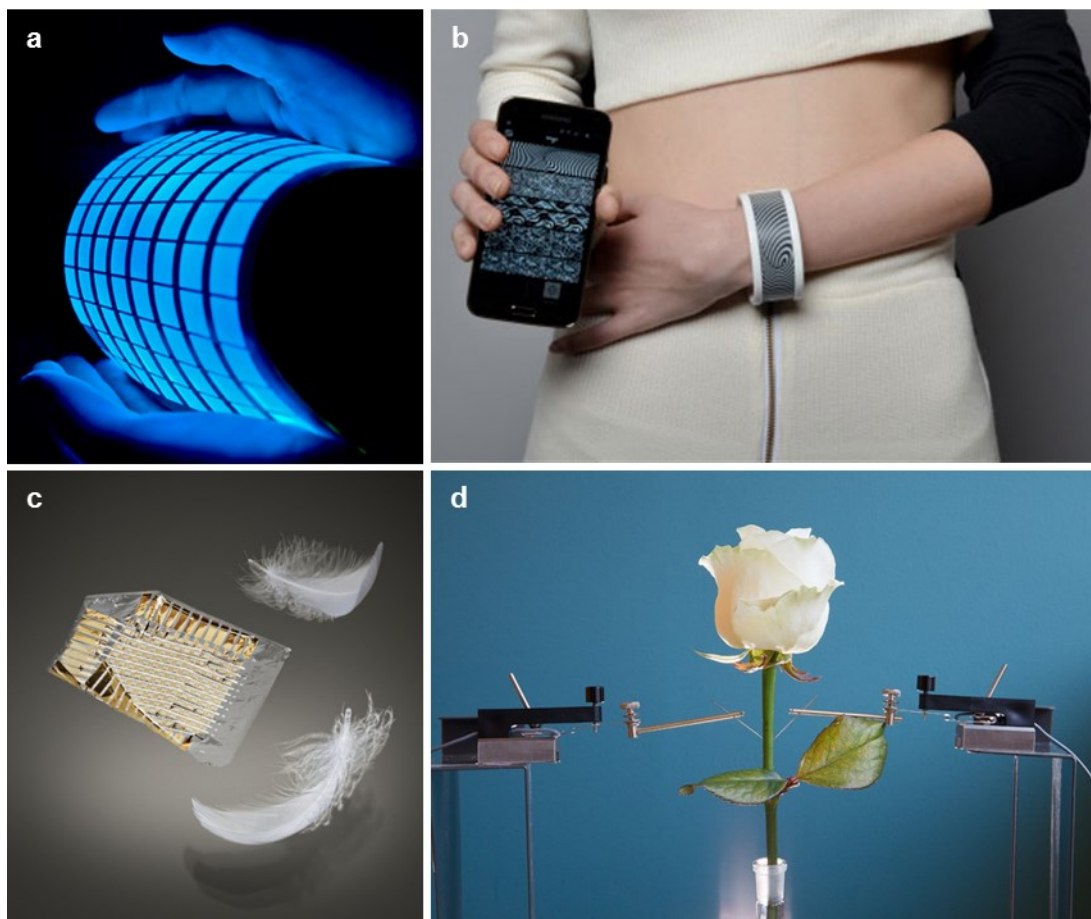


Figure 1.1 Applications of organic electronics. a) GE's roll-to-roll processed flexible OLED lighting (image from www.ge.com). b) Plastic Logic's conformable and wearable displays (image from www.plasticlogic.com). c) Feather light and imperceptible electronic skin (image from www.buinessinsider.com).⁷ d) Organic electronic plants (image from www.newscientist.com).⁸

growing interest in the use of organic semiconductors in bioelectronics as biosensors, switchable surfaces, implantable devices, electronic skin, tissue engineering platforms and plant-interfaces for alternative energy harvesting applications.^{2,9} Organic bioelectronics are especially promising because of the 'soft' and malleable nature of organic materials that, in contrast to 'hard' silicon based technologies, may improve the ability to interface electroactive materials with biology.¹⁰

There are however, many challenges associated with organic electronics that are highly specific to each application. For instance, the use of organic semiconductors in electronic technologies that demand high performances (e.g. transistors) is often constrained by low charge carrier mobility (μ). Unlike well-ordered inorganic semiconductors, organic electronic materials, such as conjugated polymers or small molecules, arrange in highly complex structures. These materials typically exhibit a

large degree of disorder and defects, resulting in charge carrier mobilities that are orders of magnitude lower than their inorganic competitors. However, ultrahigh mobilities of up to $43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have recently been reported in organic thin film transistors.¹¹ The ultrahigh mobility was attributed to band-like transport behaviour and is in the realm of state-of-the-art inorganic semiconductors (e.g. $\mu \approx 20\text{-}50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for metal oxides and $\mu > 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for polycrystalline silicon).¹² This value is also in agreement with ultrahigh mobilities ($40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) obtained for single crystal organic semiconductors.¹³ Unfortunately, the process used to obtain this milestone mobility (i.e. spin-casting) is not compatible with the high-throughput manufacturing of flexible devices. It is however possible that mobilities on the order of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ will be sufficient for commercialisation of other types of devices, where the requirements of alternative properties dominates at the expense of lowered mobility. For example, the compatibility and energetic structures of acceptor and donor OPV materials are more important than the mobility in photovoltaic cells.¹⁴ Additionally, in the relatively new field of bioelectronics there are no obvious constraints with regards to charge carrier mobility, as there are still many questions remaining regarding how best to interface these types of electroactive materials with biology. Limitations in this field instead concern the biocompatibility, biological activity, mechanical and topological properties, and potentially bioerosion of the organic semiconductor.¹⁵

There are many relatively unexplored avenues by which to further these technologies, making them more cost-effective and improving their charge mobility, mechanical properties and device stability. Examples of promising areas of investigation include: chemical design of novel conjugated polymers or small molecules to develop materials with specified energy levels or enhanced molecular packing;^{16,17} novel synthesis schemes to create more versatile and/or cost-effective conjugated structures;¹⁸ blending strategies to control optoelectronic responses or influence semiconductor crystallisation behaviour;¹⁹ processing techniques to orient π -conjugates systems and induce charge transport anisotropy;²⁰ and alternative industrially relevant processing methods to transition from the laboratory to large-scale fabrication settings.²¹

The microstructure and phase morphology of organic semiconductors can be manipulated by a multitude of processing means to influence their optoelectronic responses and charge carrier mobility. By studying the molecular order, arrangement and important functions arising from such processing schemes (e.g. optoelectronic responses, mechanical properties and device stability), researchers have been mapping

the relevant structure/processing/property interrelationships in these novel materials.^{19,22,23} This enables employment of such schemes for rational optimisation of device performances and to further deepen our understanding of these interrelationships.

1.2 Scope of this thesis

The focus in this thesis is on exploring means by which to improve upon the molecular order and arrangement of organic electronic materials, to optimise their charge transport properties. More specifically, the solid state processing of organic semiconductors and semiconductor:insulator polymer blends is investigated as an industrially relevant method to manufacture novel semiconducting architectures with both anisotropic order and charge transport and impressive charge carrier mobility. The thesis is thereby divided into chapters that consider particular questions regarding the processing schemes and their influence on structure and properties (such as bulk charge carrier mobility).

Chapter 2 outlines fundamental concepts regarding the structure and function of organic semiconductors, while Chapter 3 describes the experimental methods and protocols used to obtain the data pertinent to this thesis. The chapters to follow constitute the main chapters and body of work in this thesis. Chapters 4, 5 and 6, address several key areas in which solid state pressing has not yet been optimised and demonstrate versatile schemes that facilitates improved microstructure formation, molecular ordering and charge transport pathways in freestanding semiconducting films. More specifically, the focus is divided into the solid state pressing of the neat model semiconductor poly(3-hexylthiophene) (Chapter 4), semiconductor:insulator blends comprised of the previously mentioned semiconductor and the elastomer polystyrene-block-poly(butadiene)-block-polystyrene (Chapter 5) and blends with other polystyrene based thermoplastics (Chapter 6). In Chapter 7, the solid state processing protocols are augmented with facile micropatterning techniques to replicate biologically relevant micropatterns onto the films, extending the potential uses for such semiconducting constructs for bioelectronics to guide alignment and regeneration of electroresponsive tissues.

1.3 Publications

List updated as of April 2017.

Chow, L. W., Armgarth, A., St-Pierre, J-P., Bertazzo, S., Gentilini, C., Aurisicchio, C., McCullen, S. D., Steele, J. & Stevens, M. M. Peptide-directed spatial organisation of biomolecules in dynamic gradient scaffolds. *Adv. Healthc. Mater.* **3**, 1381-1386 (2014).

Gabrielsson, E. O., Armgarth, A., Hammarström, P., Nilsson, K. P. R. & Berggren, M. Spatiotemporal control of amyloid-like A β plaque formation using a multichannel organic electronic device. *Macromol. Mater. Eng.* **301**, 359-363 (2016).

Spicer, C. D., Booth, M. A., Mawad, D., Armgarth, A., Nielsen, C. B. & Stevens, M. M. Synthesis of hetero-bifunctional, end-capped oligo-EDOT derivatives. *Chem.* **2**, 125-138 (2017).

Armgarth, A., Pavlica, E., Dyson, M., Dattani, R., Bannock, J., Bratina, G., Stingelin, N. & Stevens, M. Solid state processing of poly(3-hexylthiophene) – elastomer blends. (To be submitted).

Guex, A. G., Puetzer, J. L., Armgarth, A., Littmann, E., Stavrinidou, E. Giannelis, E. P. Malliaras G. G. & Stevens, M. M. Highly porous scaffolds of PEDOT:PSS for bone tissue engineering. (Submitted).

Pacheco-Moreno, C. M., Amdursky, N., Dautel, O., Stavrinidou, E., Armgarth, A., Schreck, M., Stevens, M. M. & Stingelin, N. Derivative polythiophene:PVA blends towards versatile mixed transport materials. (Submitted).

2 FUNDAMENTALS

This chapter reviews fundamental principles of organic semiconductor materials. It begins with an explanation of the origin of their charge transport properties, and proceeds with descriptions of the highly complex structures that these exciting materials can adopt across different length scales and their influence on key electronic properties. Lastly, a brief description of organic bioelectronics applications is provided.

2.1 Charge transport in organic semiconductors

Organic semiconducting materials can be comprised of small molecules (weight-average molecular weight, $M_w \approx 100\text{-}1,000 \text{ g mol}^{-1}$), oligomers or long polymer chains ($M_w \approx 10,000\text{-}1,000,000 \text{ g mol}^{-1}$), with the common feature in all being their π -conjugated backbone. An illustrative example of π -conjugation in polyacetylene is shown in Figure 2.1.²⁴ The alternating single and double-bonds lead to contiguous sp^2 hybridised carbons along the backbone. Three of the four carbon valence electrons are in this configuration localised in σ -bonding orbitals between each neighbouring atom; in the case of polyacetylene, between two adjacent carbons and one hydrogen atom. The remaining valence electron, located in a p_z -orbital, overlap with adjacent electron clouds and form delocalised π -orbitals along the molecule backbone (Figure 2.1a).²⁵ These π -orbitals can be extended over the entirety of a small molecule or a number of units in a conjugated polymer, referred to as the conjugation length. How well the p-orbitals overlap dictates the effective conjugation length and is partially related to conformational fluctuations and chemical or physical disruptions of the planarity of the backbone. The charge mobility along the polymer backbones in these materials arise

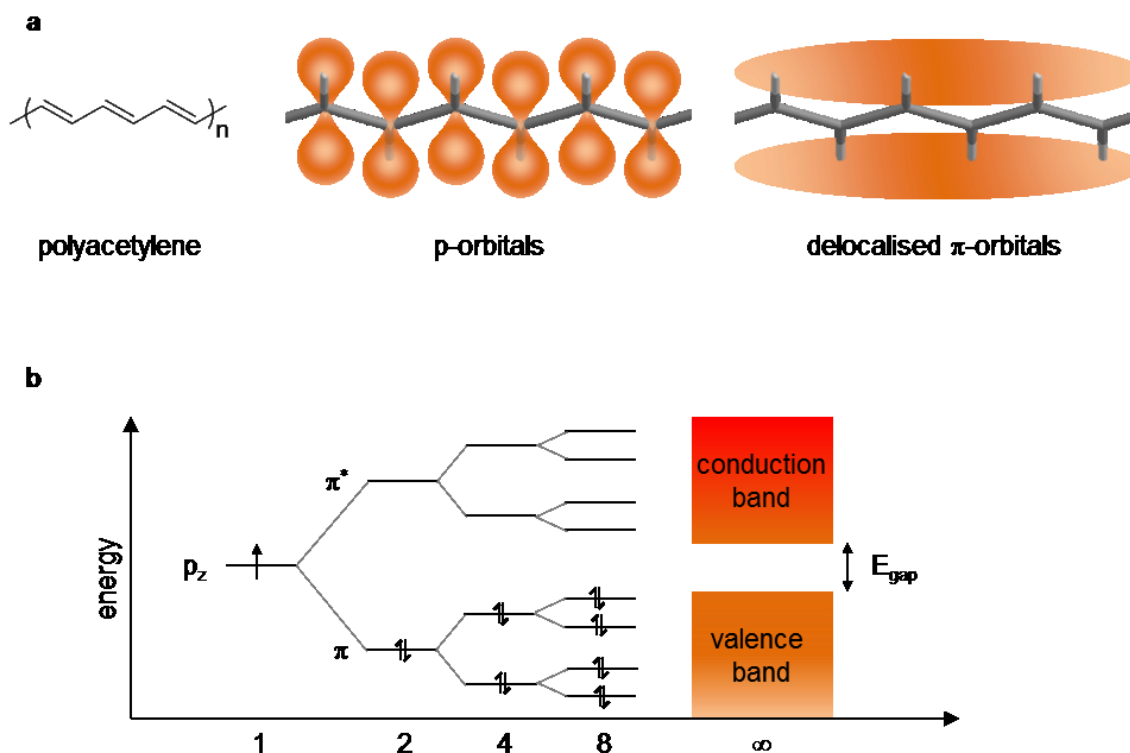


Figure 2.1 (a) Illustrative example of a π -conjugated system, polyacetylene, in which p_z -orbitals at each carbon centre overlap and delocalise along the conjugated backbone. **(b)** An idealised picture of the molecular orbitals that split into π -bonding (filled) and π^* -anti-bonding (empty) energy levels and are separated by an energy gap (E_{gap}). As number of contiguous sp^2 carbons increases (approaches infinity) the energy states can be viewed as the conduction and valence band of the organic semiconductor.

from such electronic delocalisation.^{26,27}

Semiconducting properties of organic materials are generally interpreted within the framework of molecular orbital (MO) theory. In this context, the π -molecular orbitals can be expressed as a linear combination of the atomic orbitals, which splits the molecules' π -energy levels into a stable π -bonding and a higher energy π^* -antibonding state (Figure 2.1b). Unless the molecule is excited, the lower energy state (π) will be occupied (by two anti-parallel spin electrons), and the higher energy state (π^*) will be empty. The energy difference between these orbitals, designated the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), is the π - π^* energy gap, which generally range from 1 to 5 eV for organic semiconductors. This means that the conjugated system act as semiconductors in which the continuous occupied π -states can be considered the valence band and π^* -states the conduction band into which electrons can be promoted.²⁶ However, the transport mechanism is quite

different compared to their inorganic and metallic counterparts, which will be addressed here next.

From a fundamental perspective, the electronic property in any material is classified by its conductivity (σ), which is described by the following expression:

$$\sigma = en\mu \quad (2.1)$$

where e is the fundamental charge, n the charge carrier density and μ the mobility of the charge carrier. The conductivity of intrinsic (undoped) conjugated polymers is highly limited, due to their low charge carrier density, with conductivity values similar to that of insulators. In ambient environments at room temperature these polymers are often weakly doped, by for example oxygen in the air, leading to increased conductivities ($< 10^{-4} \text{ S cm}^{-1}$). However, the conductivity of these semiconductors is typically orders of magnitude lower than the conductivity of metals (10^6 S cm^{-1}). Therefore, greater amount of charge carriers must be created in these materials to generate substantial currents. This can be achieved by chemical means, such as doping, or injection from external sources (electrodes). Alternatively, charges can be generated by optical excitation, which promotes electrons to transition across the HOMO-LUMO gap. When a charge transits through the energy gap to the lowest unoccupied state it is accompanied by a lattice distortion. The basic charge carrier unit created are for brevity commonly referred to as holes and electrons. However, the correct terminology for a singly or doubly charged unit is a polaron and bipolaron respectively.²⁸ Upon photo-excitation it is also possible to generate both hole- and electron-polarons. In this case, the localised charges can form a neutrally charged anion-cation pair bound by Coulombic interactions. In order to overcome these strong Coulombic attractions, separate and collect the charges, large electric fields are typically required, otherwise, the charges may recombine and decay radiatively or non-radiatively. Generated excitations can move or 'hop' to adjacent sites on either the same or different molecules, so called intra- or interchain hopping. Such processes are only permitted if it is energetically favourable for the excitation to hop. The charge transport in conjugated systems are therefore highly sensitive to the local environment's structural and energetic landscape.²⁹ Additionally, the macroenvironment becomes highly important from a device perspective, since the electronic and optoelectronic properties must function efficiently across suitably long distances.

The mobility of charges as well as the recombination effects in these conjugated systems can thereby be utilised for various optoelectronic devices through separate working principles. For example, conjugated systems can be used as active layers in photovoltaic cells (OPVs), in which sunlight generate charges that can separate at favourable interfaces and be driven towards the collecting electrodes owing to the energetics of the system.¹⁴ In contrast, in organic light emitting diodes (OLEDs) charges are injected from the electrode to the active material and the recombination and radiative decay of those charges are used to generate light.³ Understanding the complex charge transport nature in these materials and their interfaces across all length scales and in the context of their application is therefore of great importance.

2.2 Structure of conjugated systems

Conjugated systems can adopt highly complex structures via physical or chemical processing means. Such manipulations affect the order and arrangement of this class of materials from the molecular to the macroscopical level, resulting in tuneable electrical and optoelectrical responses. The performance of organic electronic devices is highly specific to the end-application. For example, desirable features in OPVs include high power conversion efficiency, long device life-times and environmental stability, while in contrast the brightness and colour purity becomes crucial to the performance of OLEDs. Meanwhile, in organic thin film transistors the performance is typically characterised by the charge carrier mobility, on/off ratios and operating voltages. For each desired application there are therefore different demands on the semiconducting architecture. Importantly, studies into the structure/processing/property interrelationships can help to reveal rational optimisation pathways to improve device performances. In addition, such studies allow researchers to quickly identify which application might be most suitable with regard to the structure and properties obtained via a specified processing route.

Organic electronic technologies seldom use single component systems in their final device architectures. This implies that additional effects have to be taken into consideration such as the interfaces in the bulk material (as in the case of bulk heterojunction OPVs) and/or at the electrode surface (e.g. field effect transistors, OFETs).^{14,19} In this context, it is crucial to characterise the structure and properties of a material across all relevant length scales to build up a comprehensive basis for their structure-property relationships (Figure 2.2). Investigations of the structure of organic

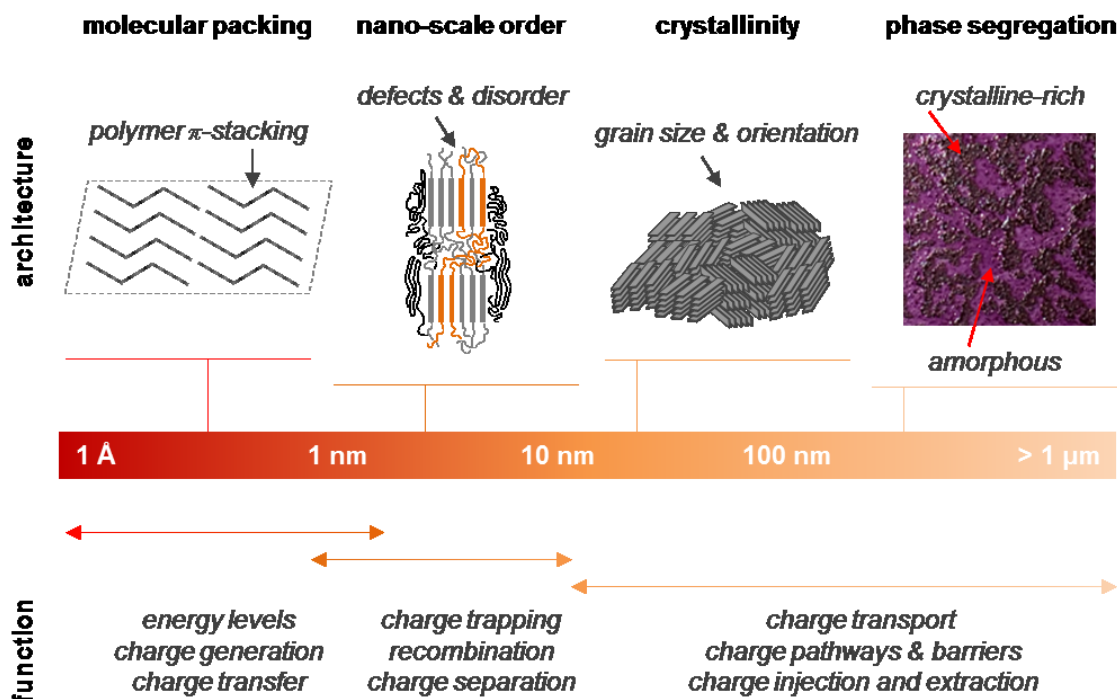


Figure 2.2 The arrangement and order of single component organic semiconductors and multicomponent systems (top) across relevant length scales, with each illustration assigned to a specific scale including: the molecular packing (i.e. polymer π -stacking), short- (nano-scale) and long-range (grain size) order and orientation of semiconductor, as well as potential phase segregations of crystalline-rich and amorphous regions that can range from nm to device scale range (> 1 μm). The resulting important optoelectronic responses are displayed (bottom) for each respective length scale.

semiconductors, from the nano- to macroscale, can be carried out using a wide range of technologies, each particularly suitable to a specific length scale.²³ Examples of characterisation methods include X-ray based technologies (e.g. small-angle and wide-angle X-ray scattering), atomic force microscopy (AFM), electron microscopy (transmission or scanning), optical microscopy and thermal analysis (differential scanning calorimetry). These methods will be discussed in detail in Chapter 3. This section addresses the structure of single and binary component systems used in organic electronics and the means by which to manipulate these materials at various length scales using the tools of material science. More specifically the focus in this thesis is on the model semiconductor poly(3-hexylthiophene) (P3HT). While advances in the field have brought forward novel materials with ultrahigh mobility and promising optoelectronic properties, P3HT is an excellent candidate to study structure/processing/property interrelationships. This material is arguable the most widely studied organic semiconductor and has well-documented structure-property

relations for a plethora of processing techniques.³⁰ Additionally, highly regioregular (RR) P3HT (RR > 98 %) can be obtained in large quantities and at low cost.¹⁸ Fortunately, many of the determined structure/processing/property interrelationships can be directly translated to other semiconducting systems, if specified in a proper framework including type (small molecule, conjugated polymer), nature (semicrystalline/ amorphous), molecular weight, regioregularity, molecular order etc..^{14,19,22,31} As such the fundamental structure and modulation of organic semiconductors described herein centres on this material.

2.2.1 Molecular packing

Starting at the molecular level (< 1 Å – 3 nm), the overlap of molecular wave-functions relates to the π -stacking of small molecules or polymer. The molecular packing thereby dictates important functions such as energy levels, charge generation and charge transfer properties in the materials. Crystal packing at the molecular level additionally serves as a template for the proceeding crystal growth and microstructure formation at large scales. Manipulation at the molecular scale is carried out by chemical design and encompasses various synthesis schemes that encourage planarity and π -stacking.⁵ For example, in polythiophenes the sulphur moieties in adjacent monomer units along the backbone leads to a favourable ‘anti’ configuration, which planarise the molecule (Figure 2.3a).³² The planarisation can further be extended by coupling multiple thiophene units and thus limiting the rotational freedom in the conjugated systems. Additionally, these materials are often decorated with solubilising side-chain units, typically linear or branched alkyl chains that extend away from the backbone and enable solution-processing, as for example in the case of P3HT (Figure 2.3b). If designed with appropriate lengths and regular spacings, these side-chains can encourage close packing by interdigitating with other aliphatic units in the formed crystal lamellae.³³ Typically, highly regioregular (RR > 96%) semiconducting polymers are required to achieve well-ordered packing and interdigitation (Figure 2.3c). The energy levels can further be modulated by designing copolymers with acceptor- and donor-like units along the conjugated backbone. When chemically designing high mobility organic semiconductors it is therefore important to simultaneously optimise both the energy levels and packing order.¹⁷

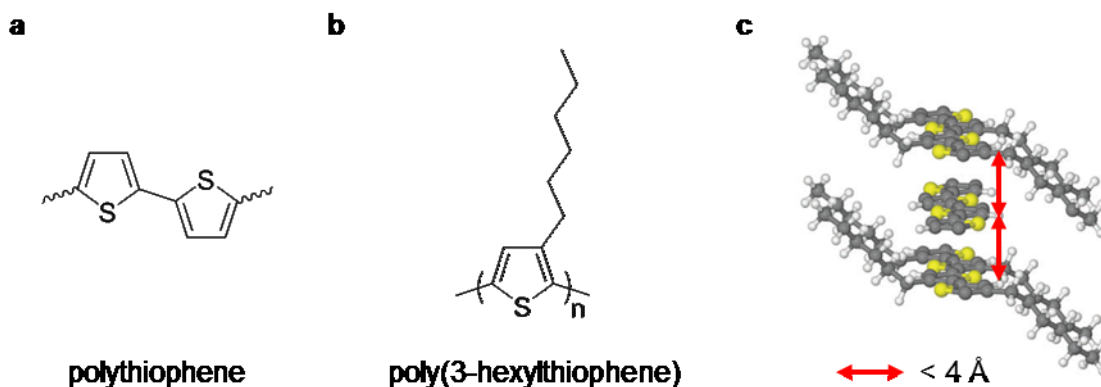


Figure 2.3 Chemical structure of (a) polythiophene in the favourable anti-configuration and (b) poly(3-hexylthiophene) (P3HT). (c) The packing of alternating P3HT chains with red arrows indicating π -stacking directions (figure adapted from ref.³⁴ with permission from Wiley-VCH). The thiophene backbones are separated by less than 4 Å. Note that the alkyl chains in the middle thiophene row were excluded for clarification.

2.2.2 Short-range order

Unlike conventional crystalline semiconductors, most organic semiconducting polymers are semicrystalline or amorphous with regions of varied degree of order, depending on their chemical structure and processing method. P3HT can for example be entirely amorphous or semicrystalline in the case of regiorandom and regioregular P3HT respectively. Crystallisation only occurs when it is energetically favourable for the polymer chains to stack together, and generally proceeds by chain-folding processes, where the polymer backbone folds 180° in on itself in a tightly packed fashion. Such packing eventually leads to the formation of nuclei from which crystal growth ensues. Due to preferential growth in one or more directions opposing the chain folding direction, the crystal lamellae thickness, l , is typically much smaller than the crystal widths and lengths. Moreover, depending on the molecular weight of the polymer and processing method the resulting crystalline lamellae can adopt different structures (Figure 2.4a). For instance, solution- or melt-processing of P3HT of low molecular weight grade ($M_w < 10 \text{ kg mol}^{-1}$) results in extended crystal lamellae. The size of the extended lamellae increases with the log scale of molecular weight until the polymers become entangled and chain extension is impeded. In contrast, high molecular weight grade ($M_w > 10 \text{ kg mol}^{-1}$) polymers instead tend to form ordered crystallites that are separated by interlamellar amorphous regions.^{31,35–37} This structure can be likened to the ‘switchboard’ model of irregularly folded crystallites proposed by Flory, or the ‘erstarrung’ model.^{31,38} In other words, their lamellar thicknesses are smaller than the

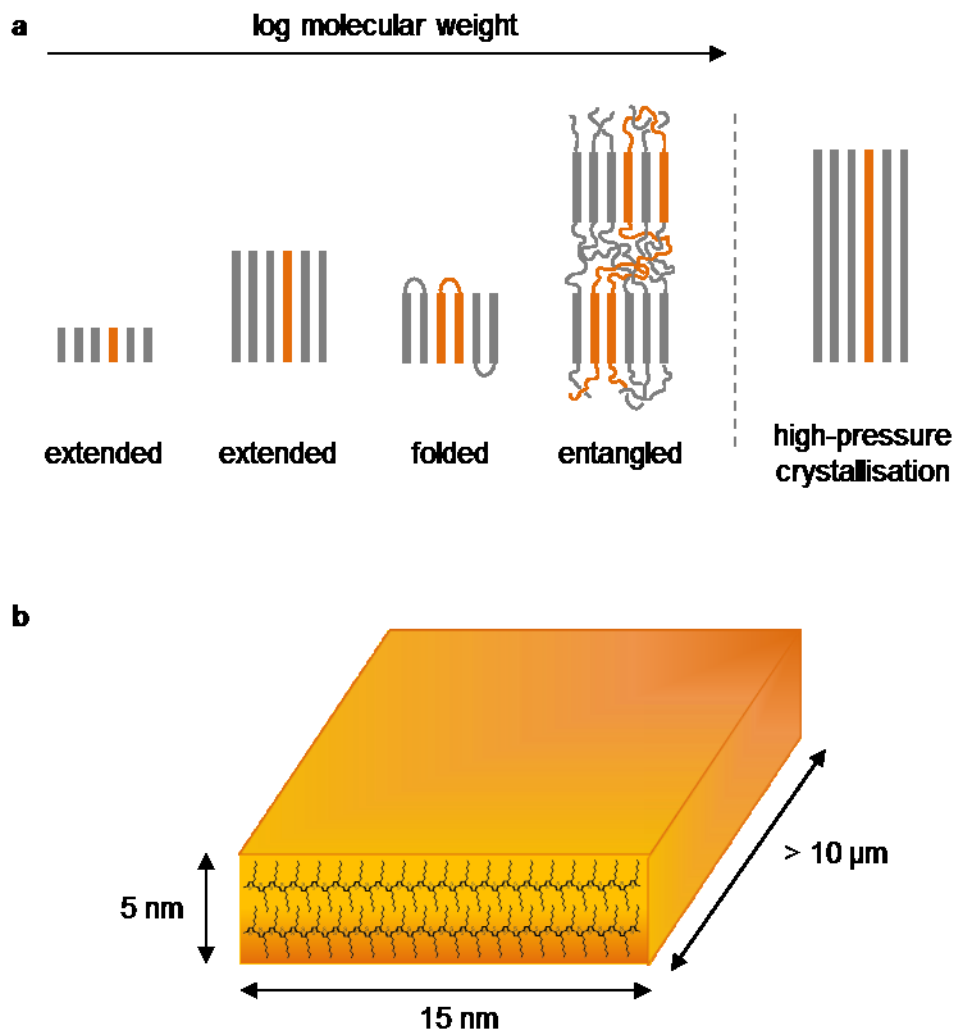


Figure 2.4 (a) Crystal lamellar structure development with increasing molecular weight (or macromolecule length) and processing history. Chain entanglements in high molecular weight macromolecules are impeded and intermixed crystalline and amorphous regions are formed, unless it is e.g. solidified from the melt and extended under high pressures. **(b)** Nanowhiskers formed in poor solvent environments with growth along the π -stacking direction (long-axis).

extended crystals and chains are intertwined between the separated crystalline regions. The lamellar crystals in high molecular weight grade P3HT can however, be extended when solidified from the melt under high pressures ($l_{\text{melt}} \approx 5 \text{ nm}$, $l_{\text{melt\&pressure}} \approx 8.9 \text{ nm}$; pressure of 50 kN cm^{-2}), similarly to chain extended commodity polymers.^{39,40}

On this structural scale (1-10 nm), processes involving charge generation, diffusion, recombination and collection are of great importance. When characterising the mobility in P3HT with varying molecular weights using time-of-flight photoconductivity measurements there are clear correlations to the structures described above. Ballantyne *et al.* demonstrated that P3HT of low molecular weight grade had consistently higher

mobility than high molecular weight grade ($M_W \approx 13 \text{ kg mol}^{-1}$, $\mu_{\text{TOF low } M_W} \approx 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $M_W \approx 121 \text{ kg mol}^{-1}$, $\mu_{\text{TOF high } M_W} \approx 2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$); i.e. they observed higher mobility in extended crystals compared to intermixed crystalline and amorphous domains.⁴¹ This was in accord with time-of-flight mobility reports by Müller *et al.*, in which P3HT solidified from the melt under pressures (i.e. extended crystals) had higher mobility than the same material solidified without the constraints of pressure ($\mu_{\text{TOF melt\&pressure}} \approx 1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $\mu_{\text{TOF melt}} \approx 5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). According to this old paradigm, high crystallinity and extended crystals are thereby considered desirable attributes in semiconducting architectures as it leads to structures which resemble defect-free single crystals.

However, in addition to lamellar solids, certain solution-processes may also result in the formation of nanowhiskers, or so called nanofibril aggregates. For instance, Ihn *et al.* showed that ribbon-like P3HT nanostructures precipitated in poor solvent environments, such as cyclohexanone, i.e. solvents in which P3HT has low or limited solubility.⁴² The whisker thickness, width and length were approximately 5 nm, 15 nm, > 10 μm long respectively (Figure 2.4b). Interestingly, whisker thickness was found to scale with the number of carbons in the side-chain units of poly(3-alkylthiophenes). These results implied that the alkyl chains were aligned parallel to the thickness, while growth of the nanowhisker (long axis) proceeded along the π -stacking direction, in agreement with observations from Xu *et al.*⁴³ The formation of such nanostructures occurs spontaneously under thermodynamically favourable conditions, i.e. when polymer-polymer interactions are less energetically costly than polymer-solvent interactions.⁴⁴ Nanofibril formation has since been reported for a wide range of poor solvents and ‘good’/‘bad’ solvent mixtures, but with different resulting nanofibril lengths depending on the solvent choice.^{45,46} Encouragingly, the length of the fibrils does not seem to be the limiting factor when it comes to charge transport conduction in such semiconducting architectures. In fact, P3HT aggregated in this fashion was shown to efficiently support long-range charge transport, due to the high degree of short-range order and aggregate interconnectivity, as elegantly demonstrated by Noriega and co-workers.⁴⁷ In this case, the small aggregated nanofibrils formed a larger network interconnected by tie-molecules (i.e. molecules that span the crystalline regions) that acted as efficient interchain-hopping sites. Here the local charge transport in conjugated polymers, of either low or high molecular weight, is limited only by the short-range ordered aggregates, as the barriers for interchain-hopping is low.^{48,49}

Moreover, local aggregation plays an integral part in determining the optoelectronic responses in conjugated systems. For instance, in conjugated systems that possess short-range order planarisation become apparent, as associated with a red shift in the absorption spectrum. As described in comprehensive studies by Spano *et al.* interchain and intrachain interactions in conjugated systems further give rise to H- and J-aggregate behaviour respectively that can be directly observed in their absorption and photoluminescence spectra.⁵⁰ For example, H-aggregates exhibit more structural and thermal disorder, whereas J-aggregates tend to be more rigid and planar. Conjugated polymers often behave as both and are then considered HJ-aggregates. The relative strength of the absorption of the 0-0 and 0-1 transitions can however, help to reveal which behaviour is dominant. In for example P3HT films with a large degree of disorder and short conjugation lengths (e.g. cast from low boiling point solvents), H-aggregate and interchain couplings dominate and the relative intensity of the oscillator strengths diminish.^{51,52} In contrast in short-range ordered materials, J-aggregate behaviour and intrachain coupling become more pronounced and the oscillator strength of the 0-0 transition increases.⁵³

2.2.3 Long-range order

The molecular order, local interfaces and electronic properties greatly contribute to the overall performance of the electronic devices. However, the disordered and crystalline domains must also be considered on the larger micro- and macroscopical scale, as this is in the realm of the functional devices. In this regard, the semiconducting polymer chain alignment and orientation of the crystalline domains in films become integral for their charge transport properties. For instance, semiconductors, such as P3HT, exhibit inherent charge transport anisotropy; the charge transport is fastest along the chain backbone and then across the π -stacking direction, whereas the alkyl chains are insulators.^{54–56} Typically, a distinction is made between edge-on and face-on orientations in semiconductors, i.e. if the π -stacking direction is parallel or perpendicular to the plane of the film respectively. Additionally, chain-on orientations are conceivable where the conjugated backbone and π -stacks are perpendicular and parallel to the substrate respectively. Depending on the device configuration and application different orientations are therefore desired. In the case of OLEDs/OPVs/vertical OFETs, efficient vertical (out-of-plane) charge carrier mobility is required, which necessitates a high degree of face-on or chain-on orientation.

Contrastingly, horizontal OFETs demand fast in-plane charge transport for which edge-on orientations are pertinent.

Edge-on orientation is most common and is typically obtained when solution-processing P3HT (e.g. from low boiling point solvents), due to interactions between the substrate and alkyl side-chains. To obtain vertical π -stacking there are several proposed routes including friction transfer, imprinting, epitaxy (via high boiling solvents), mechanical rubbing and substrate stretching.^{57–62} Furthermore it is possible to induce face-on orientations during the solid state pressing of organic semiconductors, which is the main focus of this thesis. The origin of such alignment effects and the influence on charge transport anisotropy is therefore discussed in greater detail in Chapters 4, 5 and 6.

2.2.4 Microstructure and phase segregations

The microstructure and potential phase segregations, of either disordered and crystalline domains or various blend components, are crucial for the function of various devices. For example, in bulk heterojunction photovoltaic cells, comprised of semiconductor and fullerene donor-acceptor blends, the presence of both locally and microscopically intermixed regions in the bulk material is beneficial to maximise the molecular interstitial area to drive charge separation and improve charge transport pathways.¹⁴ Meanwhile, in thin film transistors the microstructure at the electrode interfaces is instrumental for the device performance and bulk properties are a secondary concern.^{63,64} As such semiconductor:insulator polymer blends can be explored that have performances (i.e. charge carrier mobility, on/off ratios and operating voltages) similar to that of the neat semiconductor, while improving the mechanical properties and environmental stability of the devices.^{19,65,66} In this case, low threshold blends are allowed thanks to vertically stratified phase segregations in semiconductor:insulator blends.⁶⁷

There are many possible blend combinations that can be divided into the following scenarios: (i) fully miscible solids, (ii) eutectic and (iii) fully immiscible binary systems. In the first case, the mixing of two miscible components leads to the formation of one phase, in which the long-range order is not compromised. This phase is often referred to as solid solutions or cocrystals and examples include the previously mentioned intercalated regions in polymer:fullerene blends.^{14,68,69} More commonly, organic semiconducting binaries exhibit eutectic phase behaviour, which means that they are fully miscible in the liquid state but at least partially immiscible in the solid state. At the

eutectic composition the melting temperature is at its lowest. In this scenario, the composition and processing temperatures are therefore important factors to manipulate and optimise the amount of crystallisation and phase separation.^{67,70} In the last scenario, complete immiscibility in both the solid and liquid state (typically displayed in polymer:polymer blends) can cause large phase separations. From a device perspective large phase separations might limit the charge transport.

Blending strategies thereby offer great possibilities to manipulate the microstructure in the binary systems, in addition to incorporating new features and functionalities. More detailed discussions regarding blend microstructure and their effect on charge transport properties are addressed in Chapter 5 and 6.

2.3 Organic bioelectronics

An increasingly popular field of interest for applications of organic semiconductors is bioelectronics. The attractiveness of these materials comes from their malleability and inherently ‘soft’ nature of organic electronic materials, which can offer an improved interface with biology compared to inorganic electronic counterparts.¹⁰ Moreover, the rich and versatile chemistry of conjugated polymers makes them especially suitable for the development of novel biomaterials and healthcare solutions.

In a broad context, these electronic systems are unique in that they can interface with biology in either a sensing or a delivery capacity. In the first case, these polymers possess excellent capabilities as sensors to record various physiological signals, as well as selectively sense biological analytes. Such devices are, for instance, used to monitor brain activity or as sensitive diagnostic tools.^{63,71} These materials have also become increasingly popular in the development of sensors for electronic skin (e-skin) devices, owing to their processability and flexibility.^{7,72,73} The sensing attributes of organic electronics make them great candidates for many diagnostic applications, where a biological input results in a simple electronic readout. In their alternative capacity, these materials can instead be used to elicit a specific biological response and thereby acts as an actuator or therapeutic delivery system. In novel devices, such as the organic electronic ion pump and additional developed iontronic circuitry, an electrical input can be utilised for precise spatiotemporal delivery of ions or therapeutics.^{74–79} Alternatively the actuation triggered by the electrical signal can be a mechanical response, as demonstrated by conducting polymer actuators or so called ‘artificial muscles’.^{80–83} With these actuating or delivery devices it is thereby possible to translate electrical

signals to manipulate tissue or cell responses. However, as shown by studies into artificial retinas using conjugated polymers by Ghezzi *et al.*, it is further possible to stimulate cells and affect cell behaviour using light, rather than electrical signals. As demonstrated by the plethora of successes and applications of organic bioelectronics this novel class of materials thereby has immense potential as a bridge between electronics and biology.

The films generated herein are envisioned to mainly serve as tissue engineering platforms. Tissue engineering strategies are employed to overcome hurdles of limited self-repair in tissues that have been damaged or lost functionality, typically due to various detrimental pathologies. More specifically, the focus is on the regeneration of electroresponsive tissues, where brain, heart, muscle and bone are just a few examples of tissues that respond to electrical stimulation.⁸⁴ The use of conjugated polymers as either two- or three-dimensional (2D or 3D) tissue engineering constructs has been widely explored. There are many reported benefits for restoring functionality in tissues using electrical stimuli and electroactive architectures including improved electrical cell-couplings, cell self-alignment, as well as effects on cell migration and differentiation.^{85–89} The motivation and particular approaches pertinent to the organic bioelectronics applications pursued herein are described in greater detail in Chapter 8.

3 EXPERIMENTAL

This chapter outlines experimental techniques and procedures pertinent to the collection of data presented in this thesis. This includes characterisation techniques probing the (i) microstructure and (ii) bulk or surface material properties. Additionally protocols for the (iii) sample preparation, (iv) patterning techniques and (v) cell studies investigated herein are detailed. The sections concerning characterisation techniques will provide fundamental background and motivation for the utilisation of such methods and outline the experimental protocols. The motivation for the sample preparation, patterning techniques and cell studies will however be addressed in detail in the main chapters to follow. Here, the focus is instead on the experimental methods. Other methods utilised to a lesser extent will also be presented in this thesis, with additional information provided alongside the data.

3.1 Microstructure characterisation techniques

Determination of the microstructure in organic semiconductors is vital to study and understand important structure/processing/property interrelationships. The microstructure is a determining factor of the resulting properties of these tunable materials, such as their mechanical properties and optoelectronic responses. There are a plethora of techniques available to study the complex structures that may arise from the polymer processing schemes; each one being particularly suitable to a specific length scale or type of construct.

The following sections discuss various techniques used for investigating semiconducting semicrystalline freestanding films formed via solid state processing – a

process that will be discussed at great length in later chapters. The semiconducting crystallites are probed by thermoanalytical, X-ray scattering and optical spectroscopy techniques. These methods provide important information pertaining to the polymer processing history, phase transitions, semiconductor aggregate nature as well as the crystallite orientation. It should be mentioned that there are many other methods that can be used in conjunction with these techniques to gain further insight into the microstructure of such constructs. Such methods are proposed and explained in the main chapters.

3.1.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique that probes important phase transitions in polymers. It achieves this by measuring the difference in heat flow between a sample and a reference as a function of temperature. Typically a sample of known mass inside a crucible (e.g. aluminium) is placed next to a reference sample (empty pan) on a thermoelectric disk (sensor) in a furnace. As the furnace is heated and/or cooled at a specified rate (K min^{-1}), the heat flow can be measured since the sample has a different heat capacity compared to the reference. The sample can absorb (endothermic) or release (exothermic) heat due to various thermal effects such as chemical reactions or glass, crystallisation or melting transitions etc., thereby allowing detection and quantitative evaluation of such events.

Characteristic DSC thermograms of, for example, a semicrystalline polymer plot the heat flow versus temperature, which is proportional to time (Figure 3.1). The endotherm is in this schematic represented by an upward trend. The glass transition is noted by a step-change because the heat capacity of a polymer is increased as it changes from a brittle/glassy to a rubbery state. Melting or fusion is an endothermic process and heat is required to transition from the solid to the liquid state. This is shown by an endothermic peak. Crystallisation is, in contrast, an exothermic process and heat is released upon the formation of a more ordered structure when changing from a liquid to solid.

The enthalpy of fusion (ΔH_f) is directly related to crystallinity of the material. This can be determined by integrating the endothermic peak (Figure 3.1b, shaded area). Further insight can be gained from the shape of the endothermic peaks. For example, well-defined crystal lattices will give rise to sharp endotherms upon heating. Multiple endotherms can be related to either polymorphs or indicate the melting of primary

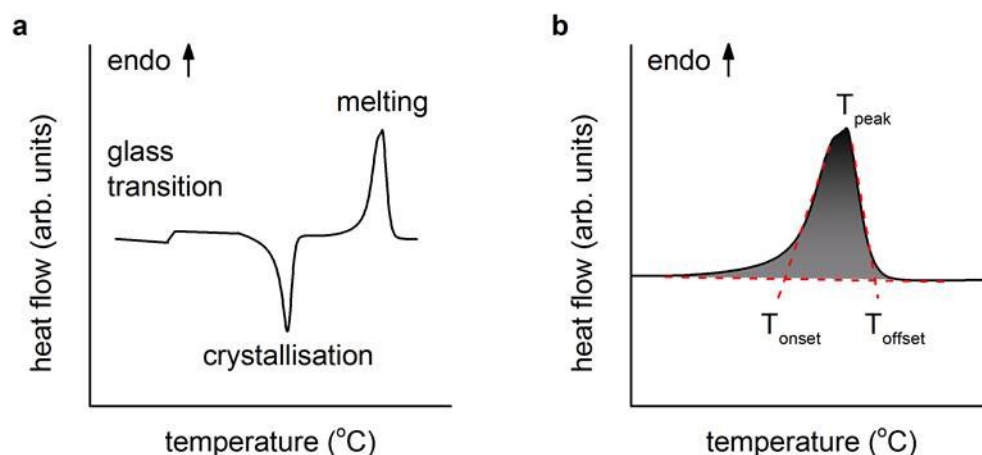


Figure 3.1 (a) Differential scanning calorimetry (DSC) thermogram displaying heat flow versus temperature with indicated glass, crystallisation and melting transitions, and endothermic direction. (b) Melting temperature (T_m) can be defined as T_{onset} , T_{peak} or T_{offset} . The enthalpy of fusion (ΔH_f) corresponds to the shaded area under the graph.

crystallites, followed by subsequent crystallisation and final fusion of the crystalline structures. The melting temperature, T_m , of a polymer can be denoted by the endotherm onset (T_{onset}), peak summit (T_{peak}) or offset (T_{offset}), as shown in Figure 3.1b. The on- and off-sets correspond to the initial and final melting temperatures and are extracted from the intersection of the baseline and the asymptotic lines. Defining T_m as T_{offset} is especially useful when a sample has multiple peaks or polymorphs, as one can assume that the total crystal population is melted at this point.

The same principles apply to the exothermic peaks and enable determination of the enthalpy of crystallisation (ΔH_c) and crystallisation temperature (T_c). Crystallisation exotherms are most commonly observed upon cooling crystalline or semicrystalline materials from the melt. However, it is also possible to crystallise materials upon heating, so called cold crystallisation. This can occur for instance when semicrystalline materials have been rapidly cooled. As the material is subsequently heated above its glass transition the quenched-in structure becomes sufficiently mobile to undergo further crystallisation.

Although DSC thermograms provide quantitative data, it is important to note that this information strongly depends on the heating and cooling rates, as well as number of heating and cooling cycles.⁹⁰ As mentioned above, rapid cooling rates may lead to quenching of the structure and significantly alter the exo- and endothermic behaviour in consecutive heating scans. Additionally, the first heating cycle reveals the processing

history of the semicrystalline polymer. Following cycles will provide information about the system as a whole for the conditions set during the experiment. Different cycles will therefore hold the answers to different questions such as: What is the melting temperature of the crystals formed via the chosen processing route? How well does the system crystallise at the given rate and what is the melting temperature of the crystals formed?

DSC measurements were here carried out using a Mettler Toledo DSC 1 Star^e system. Typically, 1.5-10 mg of sample to be examined was placed in an aluminium crucible and heated/cooled at a rate of 10 K min⁻¹. 2-3 heating/cooling cycles were performed and analysed, but with special focus on the first heating cycle pertaining to the influence of various processing conditions on polymer crystallites. Average melting temperatures, enthalpy of fusion and standard errors for each condition were determined from three different samples.

3.1.2 Wide-angle X-ray scattering

X-ray scattering techniques are useful to elucidate important morphological features or textures in crystalline or semicrystalline semiconductors. A plethora of available X-ray techniques and modes enable investigations of structural features, across a wide range of length scales and configurations, that are of great interest to the study of organic semiconductors, as neatly summarised by Rivnay *et. al.*²³ Arguably the most common X-ray technique is wide-angle X-ray scattering (WAXS). In this method, X-rays are formed by X-ray tubes, in which electrons are accelerated across a high voltage field, bombard a target (e.g. copper or molybdenum) and produce X-rays. The monochromatic radiation is then collimated to concentrate and focus onto the sample. As the incident rays interact with the sample they are diffracted by periodic planes (of atomic or molecular nature) and form constructive interference when conditions satisfy Bragg's law:

$$n\lambda = 2d \sin \theta \quad (3.1)$$

where n is the order of reflection, λ the incident wavelength, d inter-plane spacing and θ observed angle. The elastically scattered radiation is scanned over a range of angles (2θ), detected and analysed. The resulting diffractograms show scatter intensity versus scattering angle 2θ . Alternatively, results can be made independent of wavelength (recommended for comparisons where different sources are utilised) and represented by

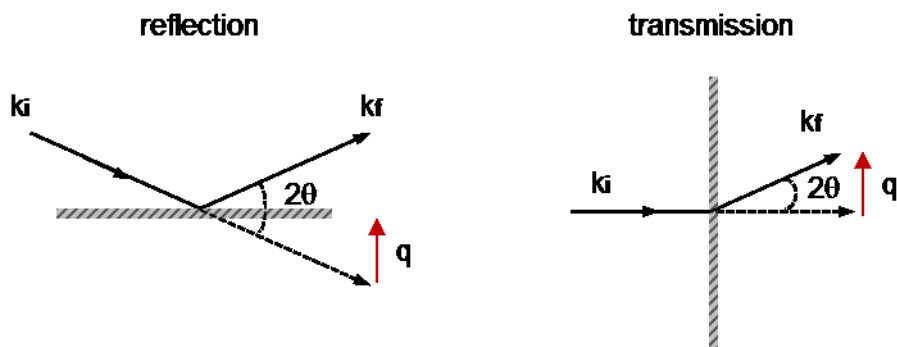


Figure 3.2 Reflection (*left*) and transmission (*right*) mode wide angle X-ray scattering schematics depicting incident (k_i) and scattered (k_r) rays at an angle of 2θ with respective out-of-plane and in-plane scattering vectors (q).

scattering intensity versus the scattering vector q :

$$q = \frac{4\pi}{\lambda} \sin \theta \quad (3.2)$$

The diffraction patterns give a quantitative measure of the order in the examined films or powders (detection of crystalline peaks and/or amorphous halos) and enables determination and comparison of unit cell parameters or lattice spacings of the observed peaks. Much research has been devoted to solving crystal structures of organic semiconductors, which allows simple comparisons of the obtained diffraction patterns to reference samples with known unit cell parameters.^{30,91,92}

A schematic of typical reflection mode WAXS is shown in Figure 3.2, also commonly referred to a θ - 2θ scans. In this configuration the scattering vector is normal to the plane of the film, or out-of-plane. In transmission mode the scattering vector can be considered in-plane of the film, assuming long detection distances or small 2θ angles. This combination gives complementary out-of and in-plane structural information.

In this thesis, reflection mode wide-angle X-ray scattering was carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu-K α 1 beam and X'CELERATOR detector (with $I = 40$ mA, $V = 40$ kV). Transmission mode small-angle and wide-angle X-ray diffraction measurements were carried out by Dr Rajeev Dattani on the beamline ID02 in Grenoble (ESRF, France).

3.1.3 Optical spectroscopy

Organic semiconductors absorb light in the ultraviolet, visible and near-infrared region of the electromagnetic spectrum. Their photophysical properties can be studied by a

wide range of techniques. In this thesis, a dual beam Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere was used to study the optical properties of both thin and thick organic semiconducting films. Measurements were carried out in collaboration with Matthew Dyson at Imperial College London. Due to the optical restrictions concerning film thickness different modes were investigated; the absorption spectra were characterised for thin wire-bar coated films (< 100 nm), whereas only the reflectance was measured for the thicker solid state pressed films (> 50 μm).

Absorption spectra were obtained from transmission measurements and corrected for the measured reflection and scattering losses (assuming: $1 = \text{absorption} + \text{transmission} + \text{specular reflection} + \text{diffuse reflection}$). The absorption was normalised to the maximum. During reflectance measurements the freestanding films were temporarily taped to glass slides. A fused silica substrate was used as a reflection standard. Measurements were carried out over wavelengths between 220-1400 nm.

Optical micrographs of wire-bar coated thin films were taken of various solution-processed samples, as noted in the following chapters. An Olympus microscope and Canon 5D Mark II was used to take the micrographs. Images of thicker cast films were taken using a phone camera.

3.2 Bulk and surface material properties

The material properties of the semiconducting polymer constructs are the last of the triage of important interrelationships (structure/processing/property). Often researchers start at this step, eager to assess the device performance of new materials or blend systems. However, one first needs to consider the effects that processing might have on the microstructure, to fully understand and appreciate the resulting material properties. When employing a materials science approach, as herein, this trinity of interrelationships is always central and functions as a feedback loop on how to improve the ultimate performance. Thereby the assessed bulk and surface material properties can be related to the applied processing methods and evaluated microstructure. This enables exploitation of the found interrelationships that may potentially be transferred to novel systems.

The bulk and surface material properties evaluated here include firstly the charge carrier mobility, for which time-of-flight photoconductivity measurements were utilised. Secondly, the mechanical properties of the films were measured by tensile testing.

Thirdly, atomic force microscopy was utilised to assess the surface interfaces of the films. Other techniques mentioned are also highly related to the bulk material properties of these novel architectures, but are discussed elsewhere.

3.2.1 Time-of-flight photoconductivity

Electronic properties are one of the key features of semiconducting materials. There are numerous methods by which to investigate the charge transport in organic semiconducting films, each with specific practical suitability, and advantages and disadvantages. Examples of common methods include current-voltage (I-V) measurements of organic thin film transistors, measurements of space-charge limited currents and time-of-flight photoconductivity measurements. The latter technique is considered a highly versatile and accurate tool to extract charge carrier mobility in organic semiconducting films. One of the constraints of this technique is however that the RC time constant of the system must be shorter than the transit times of the charge carriers examined. This technique is therefore limited to considerably thick films ($> 1\ \mu\text{m}$) and is unsuitable for most thin film applications. Herein, thick freestanding films (50-150 μm) are examined for which this method is ideal, as it forgoes any surface effects and probes the bulk electrical properties of the material in the low charge concentration regime.

In conventional time-of-flight photoconductivity measurements, the semiconducting film is sandwiched between two metallic electrodes, of which at least one is transparent or semi-transparent (Figure 3.3, left). A short laser pulse is applied to generate a thin ‘sheet’ of carriers near the illuminated electrode. The charge carriers are subsequently separated and drift towards the opposing electrode under an applied electric field, where they are collected. In such sandwich structures the investigated transport direction is perpendicular to the plane of the film. In-plane transport can likewise be examined using a coplanar electrode configuration (Figure 3.3, right).

The line shape of the resulting photocurrent transient will strongly depend on the energetic disorder and nature of transport in the semiconducting film. In an ideal crystal structure with non-dispersive transport, charges would travel with similar velocity. In this case, a knee corresponding to a change in dI/dt can easily be observed (Figure 3.4a,

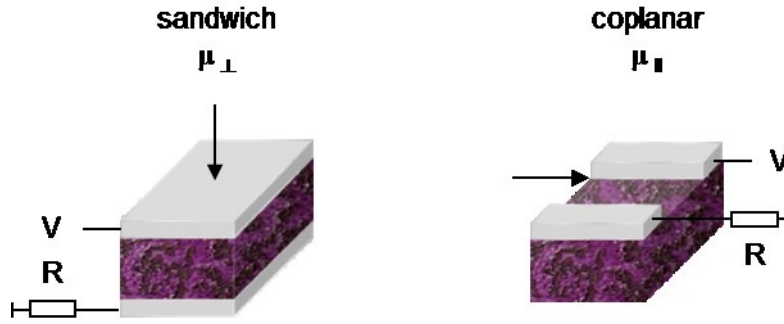


Figure 3.3 Illustration of time-of-flight photoconductivity set up using a sandwich (**left**) and coplanar (**right**) device configuration to measure the charge carrier mobility perpendicular to and in- plane of the organic semiconductor film.

top). The onset of this change notes the arrival, or transit time (t_{tr}), of the carriers at the collecting electrode. Organic semiconductors, especially polymers, have in contrast dispersive transport due to substantial structural and energetic disorder. The generated charge carriers do not travel at a uniform speed and it becomes difficult to distinguish a transit time on the linear-linear photocurrent plots (Figure 3.4a, bottom). The response of such systems can be plotted on a double logarithmic scale and transit times extracted from the intersection of asymptotic lines according to methods established by Scher and Montrell (Figure 3.4b).⁹³ This popular method to extract t_{tr} is justified by comprehensive theory employing appropriate transit time distribution simulations.⁹⁴

The effective velocity (v) is determined from the inferred transit time and the known electrode separation distance (d) as:

$$v = \frac{t_{tr}}{d} \quad (3.3)$$

The charge carrier mobility (μ) can thereby be calculated by a simple expression, assuming a known electric field ($E = V/d$):

$$\mu_{TOF} = \frac{d^2}{V t_{tr}} \quad (3.4)$$

While a constant electric field can be assumed for conventional sandwich devices, it is not entirely the case for coplanar devices. In a coplanar structure the field will be non-linear and slightly higher closer to the electrodes. This makes charges accelerate faster in the high field regions.⁹⁵ Pavlica *et al.* have developed models to describe this position dependent field behaviour, based on theory and Monte-Carlo simulations and verified

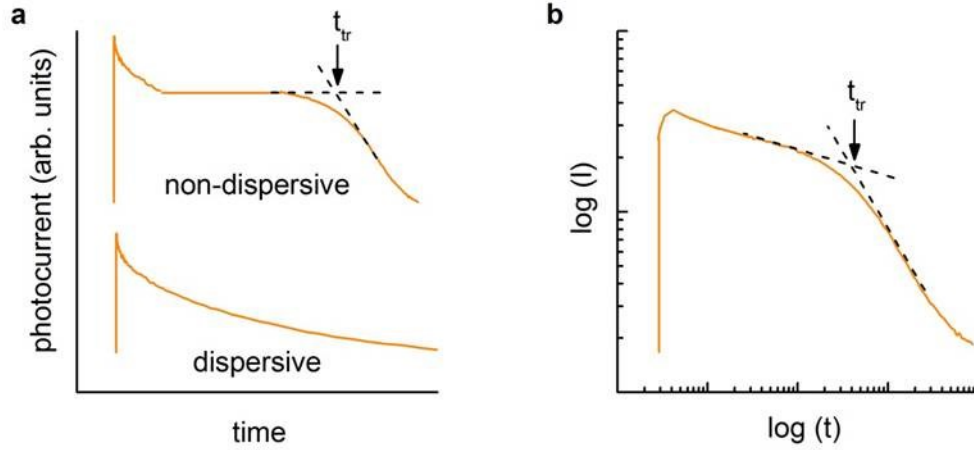


Figure 3.4 (a) Representative time-of-flight photoconductivity transients. In transients with non-dispersive transport the transit time (t_{tr}) can be easily determined in the linear-linear plot, but are less defined in transients with dispersive transport. (b) Transit times for dispersive transport become more distinguishable in a double logarithmic plot.

by experimental data.⁹⁵ The new expression for position dependent electric fields become⁹⁶:

$$\mu_{TOF} = \frac{\pi d^2}{8 V t_{tr}} \quad (3.5)$$

Interpretation of transit times with position dependent electric field assumptions therefore gives approximately 1.2 times higher mobility compared to conventional position independent electric field assumptions. As both sandwich and coplanar structures were investigated and compared herein, the mobility data was obtained assuming only position independent electric fields. It should therefore be noted that the mobility acquired for transport in-plane of the film may be slightly underestimated.

The photoconductivity measurements were carried out by Dr Egon Pavlica and Professor Gvido Bratina at University of Nova Gorica (Slovenia). Aluminium electrodes (Al, 30 nm thick) were vacuum-evaporated on the freestanding semiconducting films on both sides in sandwich devices (estimated electrode separations $d \approx 85\text{-}150 \mu\text{m}$) and on one side for coplanar configurations ($d \approx 50\text{-}200 \mu\text{m}$). A 3 ns laser pulse was applied to generate charge carriers near the illuminated electrode (with a photon energy of 2.34 eV that corresponded to the maximum absorption in P3HT). An optical density filter was selected to ensure linear dependence of photocurrent magnitude on illumination intensity. The sensing electrode was connected to a fast current amplifier (Femto DHPA-100), which was in turn connected

to a 2.5 GHz oscilloscope. This enabled measurement of the time dependence of the photocurrent. An external bias voltage was applied to the other electrode and ranged from 50-500 V. The photocurrent for each specified condition (e.g. composition and device configuration) was measured using multiple samples and sample spots; more specifically, two samples for each condition and up to 8 different spots. The mobility was calculated for a range of applied fields, to investigate potential electric field dependence.

3.2.2 Tensile testing

To gain fundamental knowledge into the mechanical properties of the manufactured freestanding films in this thesis, tensile testing was conducted. During this test a sample is typically exposed to a constant tension, or pull, until failure. A resulting stress-strain or stress-elongation (σ - ϵ) curve is represented in Figure 3.5. Important parameters such as the Young's Modulus (E), ultimate tensile strength (UTS) and elongations at break (ϵ at break) can be derived from such plots. The Young's Modulus, also referred to as the elastic modulus, is a measure of the material's stiffness. It is defined as the slope in the stress-strain curve for a given strain range.

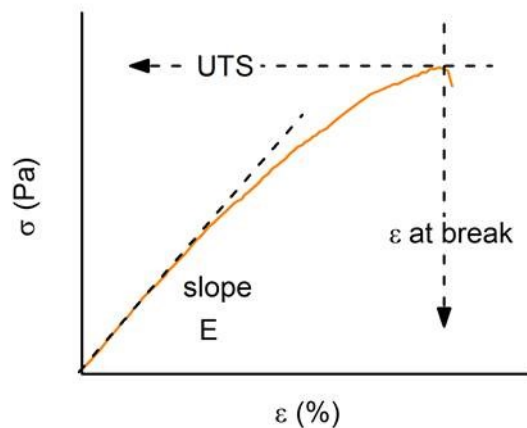


Figure 3.5 Stress-elongation (σ - ϵ) curve with indicated elastic region with slope for the Young's Modulus (E), ultimate tensile strength (UTS), and elongation at failure (ϵ at break).

Tensile test were conducted for 3-5 sample replicas using an ElectroForce 3200 System (Bose, Eden Prairie, MN, USA) equipped with a 22 N load cell. The samples were pre-loaded to 0.03 N before pulled at a constant strain rate of $0.1 \% s^{-1}$. The Young's moduli were calculated from slope of the linear regression of the stress-strain curve between 0-2 % strain. Analysis was accomplished with three to four sample replicates for each condition. Neat and blend films were strained until failure, with the exception of highly elastic films with elongations $> 500 \%$.

3.2.3 Atomic force microscopy

Atomic force microscopy (AFM) is a highly popular surface analytical method capable of high resolution topographical imaging and measuring of surface interactions and forces down to the sub-nm regime. Compared to other conventional electron microscopy imaging techniques AFM sample preparation is very straight forward and independent of the conducting properties of the examined surfaces. Unlike many vacuum based methods, AFM can further be carried out in a wide range of environments, such as air, fluid or gas media. One of the drawbacks of AFM is the limited imaging areas with a typical spatial range of 90-150 μm along the x- or y- axis and a height restriction along the z-axis of 10-20 μm .

To achieve high resolution imaging a sharp tip mounted on a cantilever is brought into contact with the sample (Figure 3.6). Forces (e.g. van der Waals, electrostatic, chemical bonding etc.) between the sample and the tip cause the cantilever to deflect. The tip is then scanned across the sample surface, while the cantilever deflection is monitored as a laser is reflected off the end of the cantilever and detected by a photodiode. The photodiode records the changes in effective cantilever deflection as a voltage. Feedback loop monitors and a z-piezoelectric scanner ensures that the z-position of the tip in relation to the surface is maintained constant. The collected x-, y- and z- data can then be viewed and processed using imaging software.

Available modalities of imaging include either contact (or static) or tapping (non-contact/alternating current, AC) modes. In the first case, the static tip is dragged across the surface, while in the latter the tip oscillates close to its resonances frequency as it scans the sample with minimal or no contact. This latter method typically leads to less damage to the surface and minimised drift effects.

Most commonly AFM is used to image 3D topographies. These topographical images also provide quantitative information about the sample surface roughness, which is

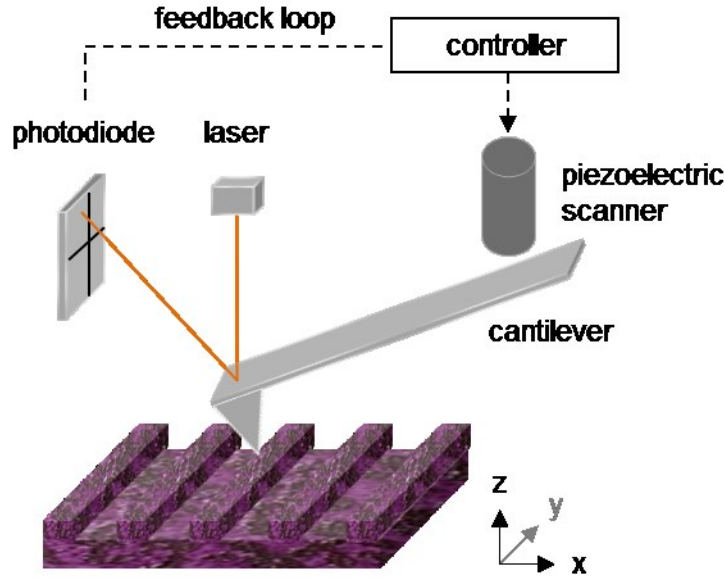


Figure 3.6 Schematic of atomic force microscopy main components (not drawn to scale).

generally calculated as the root-mean-square average (RMS) roughness:

$$\text{RMS} = \left[\frac{1}{N} \sum_{i=1}^N Z_i^2 \right]^{\frac{1}{2}} \quad (3.6)$$

where N is the number of data points and Z_i the distance from the mean surface plane. Additionally, phase images can simultaneously be acquired during AC mode topographical imaging. Changes in the phase of the tip oscillation are caused by tip-surface interactions. This reveals potential variances in the surface material properties that might go by unnoticed in topographical images. Such phase shifts can be related to differences in the material stiffness or adhesion. Generally, prior knowledge about the investigated material is required to draw conclusions from such phase shifts.

Alternatively, the stiffness (Young's modulus) and adhesion properties can be directly measured by AFM force spectroscopy. During force spectroscopy the cantilever begins to deflect due to the repulsive forces as it approaches the surface and is ultimately brought into contact. The cantilever is then further deflected as the z-piezo brings the tip to a set maximum deflection point. Finally, the tip is retracted from the surface until a zero-deflection point is reached. In order to plot the obtained data as force-distance curves multiple conversions are made. Firstly, the deflection voltages are converted into a known distance (e.g. meters), using the inverse optical cantilever sensitivity obtained from the inverse of the slope in the contact region. Secondly, according to Hooke's law the deflection is directly proportional to the forces acting on the cantilever. The

deflection distance can thus be converted into a force assuming a known spring constant of the cantilever. The Young's modulus can then be calculated from the slope of the force curves using established models and information regarding the indentation-force relationships.^{97,98}

Samples were imaged in AC mode using an Agilent 5500 AFM system. A SiNi tip with a nominal spring constant of 7.8 N/m was used (BudgetSensors). The images were processed and line profiles were extracted using Gwyddion software. Force spectroscopy was carried on several samples and multiple areas of interest within each sample, based on the obtained phase and topography maps. Analysis of the obtained data was carried out by Dr Amy Gelmi at Imperial College London. Young's moduli were calculated using the Hertz model and manufacturers spring constant values.

3.3 Sample preparation

This chapter details the protocols used for preparing samples via both solution-processing and solid state processing routes. The rationale for these approaches and the resulting structure/processing/property interrelationships from such schemes are discussed in-depth in the chapters to follow. Hence, only information pertaining to the actual procedures is addressed in this section.

Solvents and chemicals were purchased from Sigma-Aldrich, unless specifically noted, and used as received. Regioregular poly(3-hexylthiophene) (P3HT; $M_w = 150 \text{ kg mol}^{-1}$; PDI = 1.6; RR = 99 %) was supplied by Dr James Bannock in the group of Professor John de Mello at Imperial College London. The semiconductor was synthesised and purified as previously described.¹⁸ Insulators investigated herein included: polystyrene-block-poly(butadiene)-block-polystyrene (SBS; $M_w = 140 \text{ kg mol}^{-1}$; styrene 30 wt %), polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS; $M_w = 118 \text{ kg mol}^{-1}$; 29:71 mole ratio styrene: rubber), polystyrene (amorphous atactic polystyrene: a-PS, $M_w = 192 \text{ kg mol}^{-1}$; 90 % isotactic polystyrene: i-PS, $M_w = 400 \text{ kg mol}^{-1}$, Specific Polymers).

Polymer solutions were prepared with final concentrations of 10 mg ml^{-1} . Neat and blend material compositions were investigated with varied amounts of 100, 80, 60, 40, 20 and 0 wt % P3HT. Components were separately dissolved in chloroform (CHCl_3 ; boiling point, b.p. = 61°C) prior to addition of ethyl acetate (EtOAc; b.p. = 77°C) in a ratio of 2:1 by volume, stirred for 2 hours and cast at 30°C . As comparison, the neat semiconductor was also solubilised in pure CHCl_3 , stirred and cast at 50°C . Thin films

for optical micrographs and optical spectroscopy measurements were prepared using a temperature controlled wire-bar coater (K 101 Control Coater, Printcoat Instruments). Powders were obtained by scratching solution-processed films and placed between Kapton films (Cole-Parmer) in a custom-made, modular stainless-steel channel die, inserted in a hot press (Rondol Technologies). The channel die was heated at a rate of $\sim 10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $140\text{ }^{\circ}\text{C}$, compressed for 5 minutes, released of the pressure and thereafter cooled to room temperature at $\sim 10\text{ }^{\circ}\text{C min}^{-1}$. Pressure applied for neat P3HT film manufacture was $20\text{--}30\text{ kN cm}^{-2}$ and 3 kN cm^{-2} for blend materials. This resulted in $\sim 50\text{--}150\text{ }\mu\text{m}$ thick films with dimensions of $\sim 8 \times 10\text{--}15\text{ mm}$. Control experiments were carried out at additional operating temperatures of $80\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$.

3.4 Patterning techniques

The solid state processing manufacture was augmented by facile hot embossing techniques to generate biologically relevant microtopographies. As for the previous section, only protocols are outlined herein, as the background and motivation for such patterning techniques are described in a later chapter.

Parallel microgrooves with width, spacing and height dimensions of $10 \times 10 \times 10\text{ }\mu\text{m}$ were chosen as micropatterns based on previous successes regarding cell alignment and biological responses.^{99,100} A master silicon wafer with the patterned microgrooves was kindly supplied by Dr Ciro Chiappini at Imperial College. This was utilised to generate elastomeric stamp replicas of the pattern for hot embossing. Poly(dimethylsiloxane) (PDMS; Sylgard 184; Dow Corning) stamps was prepared using 5:1 weight ratios of pre-polymer and curing agent. PDMS was degassed by centrifugation for 30 seconds, cast onto the master wafer and cured at $110\text{ }^{\circ}\text{C}$ and thermally aged at $200\text{ }^{\circ}\text{C}$ for 2-4 hours in accordance with previously described protocols.¹⁰¹ The stamps were removed from the template, washed and sonicated in isopropanol 2-3 times and dried using pressurised air. The PDMS stamps with patterned gratings and unpatterned flat surfaces were placed on the pre-manufactured solid state pressed films, and embossed at $140\text{ }^{\circ}\text{C}$ for 4 minutes at a pressure of 2 N cm^{-2} , using a custom-made weight holder. The systems were heated and cooled at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$, for the embossing and de-embossing. Alternatively, hard stamps using an epoxy embedding medium were similarly generated from the elastomeric PDMS stamps. These were utilised in

conjunction with the solid state pressing protocols previously described to generate a facile single-step patterning technique.

The patterned and unpatterned solid state pressed films and original PDMS or epoxy stamps were imaged using an Olympus microscope and Canon 5D Mark II. Micropatterned films were further examined using scanning electron microscopy (JOEL JSM-5610 LV, and Zeiss Auriga cross beam) in collaboration with Shenyang Chen at Imperial College London. To prevent charging, a 10 nm Cr layer was sputter coated on the films prior to imaging. Additionally, atomic force microscopy was utilised to evaluate the relief structures, as discussed in the previous section.

3.5 Cell studies

The biocompatibility of solid state pressed P3HT films was investigated using a sub-clone cardiac-like cell line, HL-1-6, generously provided by Dr Manuel M. Mazo Vega at Imperial College London.¹⁰² Medium, solvents and chemicals were purchased from Sigma-Aldrich, unless specifically noted. Cells were grown in Claycomb medium supplemented with 10 % fetal bovine serum (v/v, FBS), penicillin/streptomycin (100 U ml⁻¹:100 µg ml⁻¹), norepinephrine (0.1 mM) and L-glutamine (2 mM), and passaged as needed upon full confluence. Medium was changed daily and only passages in which contractions in the confluent cell layers were observed, were utilised for the experiments.

Flat and microgroove P3HT substrates, manufactured as previously described, were sterilised in 70 % ethanol (v/v, 2 x 15 minutes) and washed with phosphate buffered saline (PBS). The films and tissue culture plastic (TCP) control samples were pre-coated with fibronectin (5 µg ml⁻¹) and incubated at 37 °C and 5 % CO₂ for 1 hour. 50,000 cells were seeded per sample and each experiment had 3 sample replicas with and without cells seeded on top for each respective condition. Metabolic activity and cell morphology studies were carried out with one and two experimental repeats respectively. The metabolic activity was assessed after 1 and 3 days in culture using a continual fluorescence assay (Alamar blue assay, Life Technologies – Invitrogen; SpectraMax 5M multimode microplate reader, Molecular Devices Ltd.). Duplicate measurements were carried out for each sample replica and the fluorescence background was subtracted from the samples without cells.

To study the cell morphology, samples were fixed with 4 % formalin (w/v, 20 minutes) after 1 and 3 days of culture. The cell membranes were permeabilised using 1% tween

(w/v, 15 minutes) and blocked with 5 % bovine serum albumin (w/v, BSA, 30 minutes). Cells were incubated with a cardiac troponin I antibody (2 hours; 1:100 volume ratio in 1 % w/v BSA; Abcam), donkey anti-mouse secondary antibody-Alexa Fluor[®] 488 conjugate (1 hour; 1:200 volume ratio in 1 % w/v BSA; Thermo Fisher Scientific) and cell nuclei stain, DAPI (5 minutes; 4',6'-diamidino-2-phenylindole; 1 in 1000 volume ratio). Multiple washes with PBS were carried out after each incubation step. Samples were imaged using a Leica SP5 upright confocal microscope. The Z-scan images were processed using ImageJ software and the obtained data from three separate channels (autofluorescence of the substrates, cardiac troponin and cell nuclei) were merged.

4 SOLID STATE PROCESSING OF SINGLE COMPONENT SYSTEMS

This chapter investigates solid state processing of a model semiconductor system, poly(3-hexylthiophene) (P3HT). During pressing in the solid state the semiconductor begins to flow radially outward due to the high pressure applied. This polymer flow has been shown to improve molecular order and enhance vertical π -stacking (face-on) orientation in P3HT films. As a result charge transport was greatly improved and a high charge carrier mobility, μ_{TOF} , of $\sim 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (as determined by time-of-flight photoconductivity measurements) has been reported, which was three orders of magnitude higher than for solution-processed material of the same molecular weight.¹⁰³ The semiconductors were processed as received and because they do not undergo melting during the hot pressing their previous processing history was intact. This leaves room for further manipulation of the semiconductor microstructure via pre-processing routes demonstrated herein. A facile solvent-assisted solidification pre-processing method, aimed at improving the semiconductor short-range order, was employed and demonstrations showed that the beneficial solid state processing outcomes (such as high degree of molecular order and enhanced vertical π -stacking) are maintained whilst modulating the overall microstructure. The microstructure formed via the solution-processing prior to the pressing, improved the charge carrier mobility in the resulting films ($\mu_{\text{TOF}} \sim 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for transport perpendicular to the plane of the film).

Further investigations into the charge carrier transport characteristics in the plane of the film revealed a high degree of charge transport anisotropy. Anisotropy was observed both when comparing through-plane and in-plane transport, as well as comparing different in-plane directions. Here, a channel die was utilised during the pressing, which induced polymer chain alignment along the long axis of the die, or rather the material flow direction. Studies suggest that this may be caused by shear stresses as polymer flow was constricted by the walls of the channel die.¹⁰⁴ The in-plane charge carrier mobility along the short axis of the die ($\mu_{\text{TOF}} \sim 3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was in fact an order of magnitude higher than the through-plane mobility. Along the long axis of the semiconducting films an even greater increase in charge carrier mobility was observed, reaching up to $\sim 8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The anisotropic transport in these films was attributed to the structural order in the films and the intrinsic anisotropic charge transport properties of the semiconductor.⁵⁴⁻⁵⁶ This chapter thus serves to demonstrate both the importance of utilising pre-processing methods in conjunction with solid state pressing, as well as using channel dies as a novel means to obtain highly anisotropic semiconducting constructs.

4.1 Introduction

Semiconducting polymers have attracted increasing attention over the last decades thanks to their great potential as large-area and low-cost flexible electronic devices for solar cells, light emitting diodes and more recently bioelectronics applications. While much industrial focus is on processing polymer semiconductors via solution based roll-to-roll technologies (e.g. ink-jet, gravure, screen and flexographic printing), excellent environmentally friendly and low cost solvent-free processing alternatives also exist. Examples of such methods that have a long-standing history when it comes to the processing of commodity polymers include melt and solid state processing (as a fluid or above the glass transition but well below the melt of the polymer respectively).²¹ Other solvent free methods include friction transfer and rubbing techniques.^{57,58,61,62,105} These methods are all attractive means by which to generate a high degree of alignment of the semiconductor resulting in improved charge transport properties.

Melt processing is commonly utilised in industry to process thermoplastics, such as polyethylene, polypropylene, polystyrene, polycarbonate and poly(methyl methacrylate). Some of the earliest reported synthesised poly(3-alkylthiophenes) were in fact melt processed, but the method was thereafter overlooked for many years, due to

the typically high melting temperatures of conjugated polymers.^{106–109} Melt processing was recently brought back into the spot light when Müller *et al.* demonstrated that the solidification of poly(3-hexylthiophene) under elevated pressures (50 kN cm⁻²) resulted in extended chain crystal structures with enhanced crystallinity and charge carrier mobility ($\mu_{\text{TOF}} \sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).³⁹ However, the authors pointed out that high-pressure melt processing remains an unlikely candidate for commercial fabrications (possibly due to the cumbersome and costly need for high operating pressures and temperatures, of several kN cm⁻² and $\sim 300 \text{ }^\circ\text{C}$ respectively), but continued by highlighting the importance of exploring novel methods to obtain advantageous semiconducting architectures. The mobility (as determined by single carrier space-charge limited current measurements) of P3HT crystallised from the melt without pressure has also been investigated.¹¹⁰ These studies showed that the charge carrier mobility strongly depended on the polymer molecular weight, and the maximum mobility was on the same order of magnitude as those found by Müller and co-workers. Fanous *et al.* further demonstrated that fibres of P3HT could be produced via melt spinning at temperatures $> 260 \text{ }^\circ\text{C}$.¹¹¹ The observed crystallinity in these P3HT fibres was poor, but could be significantly enhanced by drawing the fibres at a temperature of $150 \text{ }^\circ\text{C}$ (a temperature above the glass transition but below the melting temperature of P3HT). This post-processing method served to both increase crystallinity and re-orient the crystals in the drawing direction.

Overcoming the limitations of melt processing organic semiconductors, such as elevated pressures and temperatures and the requirement for post-processing methods, was later addressed by Baklar *et al.* They demonstrated that compression molding in the solid state, at $\sim 100\text{--}150 \text{ }^\circ\text{C}$ (a temperature above the glass transition but well below the melting temperature of the semiconductor) and at significantly lower pressures of 20 kN cm⁻², was sufficient to induce improved crystallinity and enhanced charge-carrier mobility in P3HT.¹⁰³ The charge carrier mobility (μ_{TOF}) in the freestanding, mechanically robust pressed films was $\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Similarly, μ_{TOF} of solution-processed P3HT are typically on the same order of magnitude.^{112–114} In this technique, the applied pressure induced radial flow of the polymer chains, with the P3HT side chains being forced perpendicular to the applied compression. Historically this behaviour is known as ‘plastic crystal’ flow, but can be viewed as accelerated creep behaviour under elevated pressures from a polymer science perspective.¹¹⁵ The ‘plastic crystal’ flow enabled restructuring of P3HT into highly ordered architectures with

significantly enhanced vertical π -stacking orientation of the semiconductor. The observed structural ordering effect induced by the pressure was also pronounced when solid state pressing various other organic semiconductors.

Similar solid state processing approaches have since been used to manufacture P3HT rods and ribbons at room-temperature and moderately high pressures, with comparable effects on enhanced molecular ordering.^{116,117} In these methods extrusion dies with various circular or ribbon geometries were utilised to achieve the desired anisotropic molecular orientation of P3HT. It should be noted that during extrusion techniques the P3HT backbones became aligned with the long axis of the extruded species, i.e. parallel to rather than perpendicular to the applied pressure. This was found to be a result of the shear forces the extrudate experienced as it exited the circular and ribbon dies respectively. Pressure induced orientation of organic semiconductors is thereby sensitive to the set up that is utilised. Unfortunately, the charge transport properties in these constructs were not evaluated.

Together these studies into the important structure/processing/property interrelationships paint a rather incomplete picture. The microstructure and preferential molecular arrangement that arise from the various processing conditions have been demonstrated. The performance of solid state pressed films has to a small extent been evaluated in terms of charge carrier mobility determined from time-of-flight photoconductivity measurements. Additionally, post-processing, such as annealing, of these constructs has been shown to influence the lamellar crystal thickness.¹¹⁸ Yet, the impact of any potential pre-processing conditions has been overlooked, which is remarkable since the systems, by definition of the processing methodology, do not undergo melting. Hence, crystalline domains that become oriented during compression or extrusion in the solid state are expected to propagate from their original pre-processed state – leaving much room for the optimisation, further exploration and exploitation of important structure/processing/property interrelationships. This becomes especially important with regards to recent findings that suggest key design parameters for high charge carrier mobility constructs are short-range order in π -aggregates and high aggregate interconnectivity, rather than merely high crystallinity of the semiconductor.⁴⁷

This chapter therefore serves to demonstrate a material science approach towards obtaining semiconducting constructs with optimised performance centred on under-

standing and utilising such important interrelationships. Herein, solid state processing was investigated using a channel die set up, as shown in Figure 4.1. The organic semiconductor is depicted in its original powder form and as a compressed film in Figure 4.1a-b to signify the importance of its pre-processed powder and final freestanding film state. Different pre-processing protocols of polymer powders were investigated. Their effect on the resulting microstructure, crystallinity and molecular order in the solid state processed films was evaluated by optical microscopy, thermal analysis and X-ray based structural characterisation methods. Next, the performance of films with optimised microstructures was investigated by time-of-flight photoconductivity measurements to determine the bulk charge carrier mobility in the constructs. The modular channel die in the hot press in Figure 4.1c has a configuration similar to that reported by Baklar *et al.*¹⁰³ The material flow is therefore expected to flow radially outwards from the pressure applied perpendicular to the surface – leading

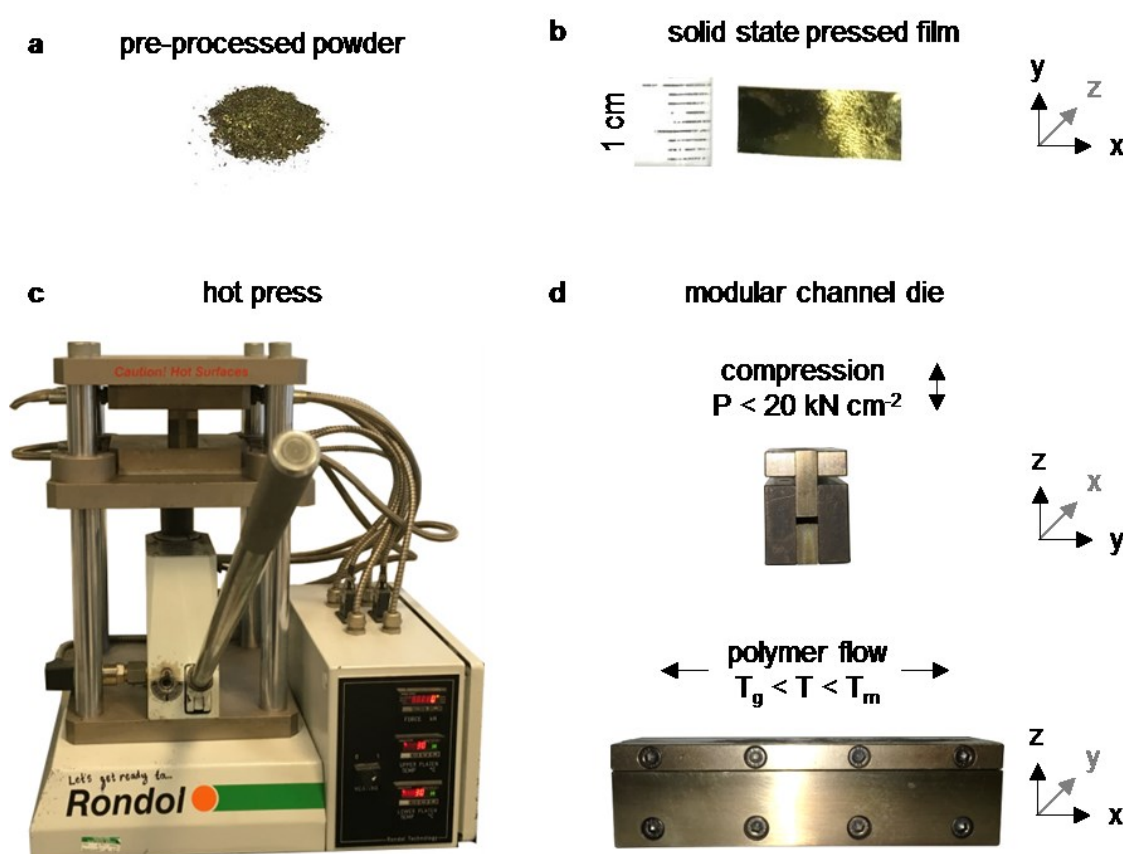


Figure 4.1 Solid state pressing of poly(3-hexylthiophene) (P3HT) in its (a) initial powder and (b) final freestanding film state (with scale bar) using a (c) hot press and (d) modular channel die (front and side view). Moderate operating pressures ($P < 20 \text{ kN cm}^{-2}$) and temperatures (T above the glass transition, T_g , and below the melting temperature, T_m) are sufficient to induce polymer flow. The material flow perpendicular to the applied pressure, as indicated in schematic, causes preferential molecular arrangement of the semiconductor and enhanced vertical π -stacking in the free-standing films.

to enhanced vertical π -stacking of the semiconductor. The additional constraint of restriction of polymer flow at the channel die walls can induce further alignment of the polymer chains along the channel die long axis (x), see Figure 4.1d, as previously demonstrated for insulating block copolymers.¹⁰⁴ Transport was therefore evaluated perpendicular to the plane of the film and in-plane both along the long and short axis of the film to assess the potential anisotropic behaviour arising from the solid state processing.

4.2 Results and discussion

4.2.1 Impact of pre-processing on microstructure

In the first set of experiments, poly(3-hexylthiophene) (P3HT) was used as a model material, because it has well-documented structure-performance relationships for a large set of processing techniques. In particular, the resulting microstructure, molecular ordering and performance of P3HT have been investigated after solid state processing of both semiconducting films, rods and ribbons.^{103,116,117} To the best of our knowledge, in these works neat P3HT was used as received without prior processing. In contrast, here well-established pre-processing techniques were used to obtain defined powders, via solution-processing, for pressing in the solid state.

The effects of pre-processing conditions on the neat semiconductor were studied by comparing the properties of P3HT films cast from a ‘good’ solvent versus a ‘good’/‘bad’ solvent mixture, such as chloroform (CHCl_3) versus chloroform/ethyl acetate ($\text{CHCl}_3/\text{EtOAc}$) mixtures. Crystallisation of the semiconductor was in the first case governed by the solvent evaporation rate, which is typically considered rather uncontrollable for low boiling point solvents. In the latter case, the semiconductor aggregated in solution (Figure 4.2a; colour shifted from bright orange to red), or rather formed highly defined nanowiskers or nanofibrils, as the solvent environment became less favourable. It should be noted that the assumption of nanofibril formation was extrapolated from extensive and comprehensive findings in previous studies and was not verified experimentally herein.^{42,43,46} Protocols developed by Scharsich *et al.* detail how the ratio of good to bad solvents leads to extremely fine control over the amount of fibrils formed.⁴⁵ Here ratios of 2:1 by volume of CHCl_3 and EtOAc were utilised for a final concentration of 10 mg ml^{-1} . This ratio was shown to be the saturation limit of aggregation of P3HT.⁴⁵ Moreover, Noriega *et al.* demonstrated that short-range intermolecular order that arises from such nanoaggregates was sufficient to support

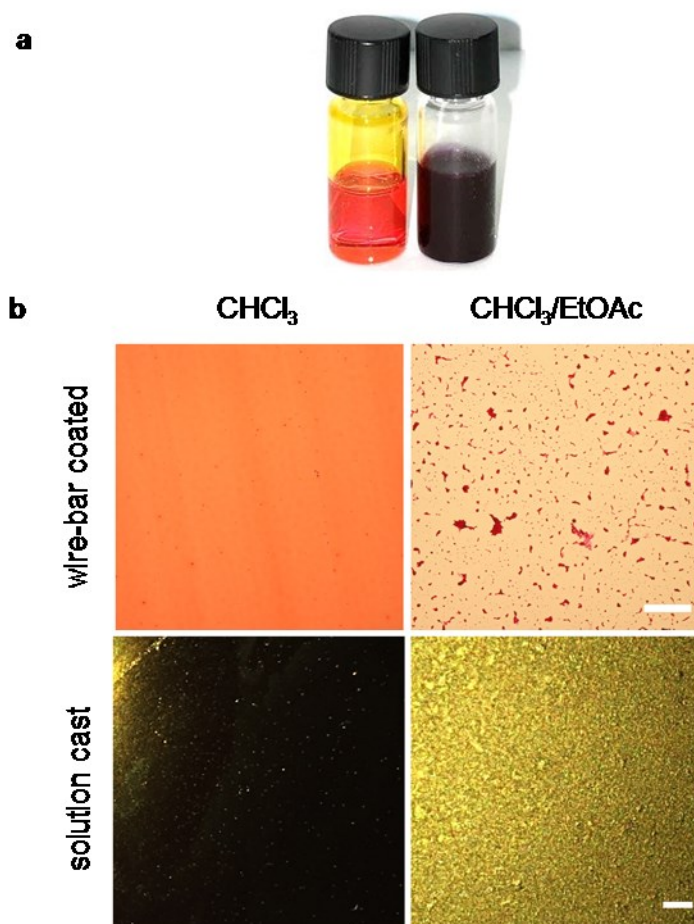


Figure 4.2 (a) Aggregates of P3HT were formed in 'good'/'bad' solvent mixtures, as evidenced by the shift from orange (in CHCl_3) to dark purple (in $\text{CHCl}_3/\text{EtOAc}$). (b) The resulting macroscale aggregates were observed in optical micrographs of wire-bar coated thin films cast from solvent mixtures, whereas films cast from CHCl_3 were largely homogenous. Contrast in microstructure remained as thicker films were cast. Scale bars are $100\ \mu\text{m}$.

efficient long-range charge transport in semiconducting constructs.⁴⁷ In their comprehensive study they revealed that the charge transport in high molecular weight semiconducting polymers (such as the one used herein) was predominantly impeded by their lattice disorder. In contrast to the previous demands of high crystallinity, the new key design parameters for high performing semiconductors dictate short-range order in π -aggregates and high aggregate interconnectivity. Solvent-induced aggregation, as this method is commonly referred to, is therefore a facile tool to control crystallisation of organic semiconductors.

The stark contrast between the two pre-processing conditions is evident in optical micrographs of thin wire-bar coated films cast from either chloroform or the solvent

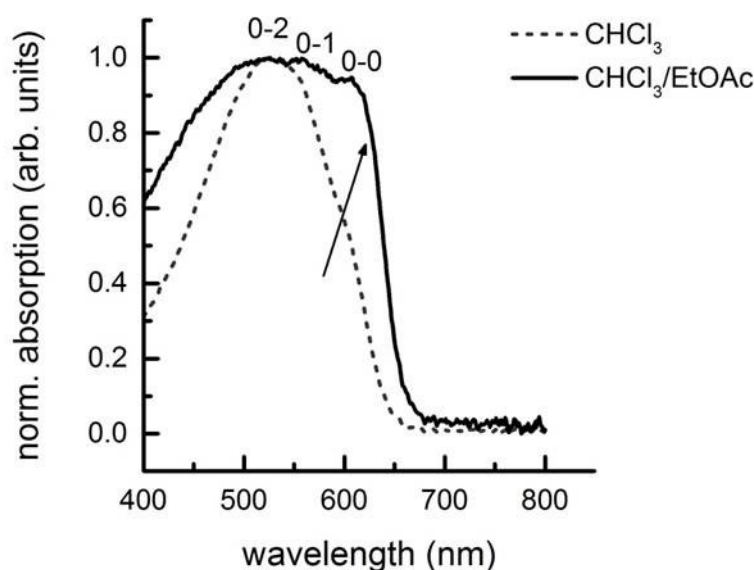


Figure 4.3 Normalised absorption spectra of neat P3HT thin films processed from CHCl_3 or solvent mixture, $\text{CHCl}_3/\text{EtOAc}$. The pronounced red-shift and appearance of the 0-0 transition in the solvent mixture system indicate aggregation of P3HT from the nano- to the microscale.

mixture (Figure 4.2b). Macroscopical clusters formed were visible in films cast from the mixed solvent system. Meanwhile, thin films of semiconductor cast from the CHCl_3 remained homogenous. Normalised absorption spectra of the thin films verified the aggregation of the semiconductor (Figure 4.3). The pronounced red-shift and strong appearance of 0-0 transition, upon addition of EtOAc, indicate aggregation of the semiconductor. It was noted that the detector was well below its saturation limit and that the high 0-0 transition was therefore not an artefact. The increased 0-0 compared to 0-1 transition can be related to increased intrachain excitonic coupling, or J-like aggregation behaviour as discussed extensively by Spano *et al.*⁵⁰ The aggregation and evident differences in film morphology was preserved when thicker films were obtained by solution casting (Figure 4.2b, bottom). From these pre-conditioned thick films, semiconducting polymer powders were obtained by scraping with a razor blade and utilised for the solid state pressing.

Calorimetric studies were conducted to further investigate the differences in the crystallites formed. Solution cast systems were compared to the solid state processed films to examine the effect these pre-processing steps imparted on the final systems. Figure 4.4a depicts the differential scanning calorimetry (DSC) thermograms of the solution-processed (from either CHCl_3 or $\text{CHCl}_3/\text{EtOAc}$ mixtures) and sequentially

solid state pressed films of neat semiconductor. The first heating cycle was examined, which detailed the polymer processing history. Samples originally cast from chloroform revealed multiple melting endotherms. Possible interpretations of this include either multiple lamellar crystal populations or partial melting of less well-defined crystals, followed by recrystallisation and final melting. The endotherm was considerably broader compared to the single sharp melting endotherm obtained for semiconductor cast from $\text{CHCl}_3/\text{EtOAc}$. The final melting temperature T_m (as defined by the offset described in Chapter 3) was significantly lower for samples solution-processed from the solvent mixtures (Figure 4.4a dashed lines and Figure 4.4b; $T_m^{\text{cast-CHCl}_3/\text{EtOAc}} \approx 250\text{ }^\circ\text{C}$, $T_m^{\text{pressed-CHCl}_3/\text{EtOAc}} \approx 251\text{ }^\circ\text{C}$, $T_m^{\text{cast-CHCl}_3} \approx 256\text{ }^\circ\text{C}$, $T_m^{\text{pressed-CHCl}_3} \approx 257\text{ }^\circ\text{C}$). The well-established correlation between T_m and lamellar crystal thickness l , is given by the Gibbs-Thomson equation:

$$T_m = T_m^0 \left[1 - \left[\frac{2\gamma}{\Delta H_f l} \right] \right] \quad (4.1)$$

where T_m^0 is the equilibrium melting temperature, ΔH_f the enthalpy of fusion per unit volume and γ the lamellar surface free energy.¹¹⁹ Combined these results suggest that the lamellar crystal thickness was smaller and more well defined when processed from solvent-mixtures compared to the crystallites formed from more uncontrollable crystallisation protocols, such as chloroform evaporation.

The melting temperature remained relatively constant (within experimental error) upon sequential pressing, indicating that the applied pressures and temperature were insufficient to induce chain extension in the lamellar crystals.^{39,40}

The enthalpy of fusion (ΔH_f) of the P3HT was slightly decreased for the samples solution-processed from solvent-mixtures (Figure 4.4c; $\Delta H_f^{\text{cast\&pressed-CHCl}_3/\text{EtOAc}} \approx 24\text{ J/g}$, $\Delta H_f^{\text{cast-CHCl}_3} \approx 27\text{ J/g}$, $\Delta H_f^{\text{pressed-CHCl}_3} \approx 20\text{-}33\text{ J/g}$). The enthalpy of fusion for the pressed samples initially cast from CHCl_3 had large variations due to poor baselines. Assuming an enthalpy of fusion for 100 % crystalline material (ΔH_f^0) of 99 J/g ,¹²⁰ this corresponds to a bulk crystallinity (X) of 24% for solvent-induced aggregated samples (both as cast and pressed), 20-33% for chloroform cast and pressed samples, as described by:

$$X = \frac{\Delta H_f}{\Delta H_f^0} \quad (4.2)$$

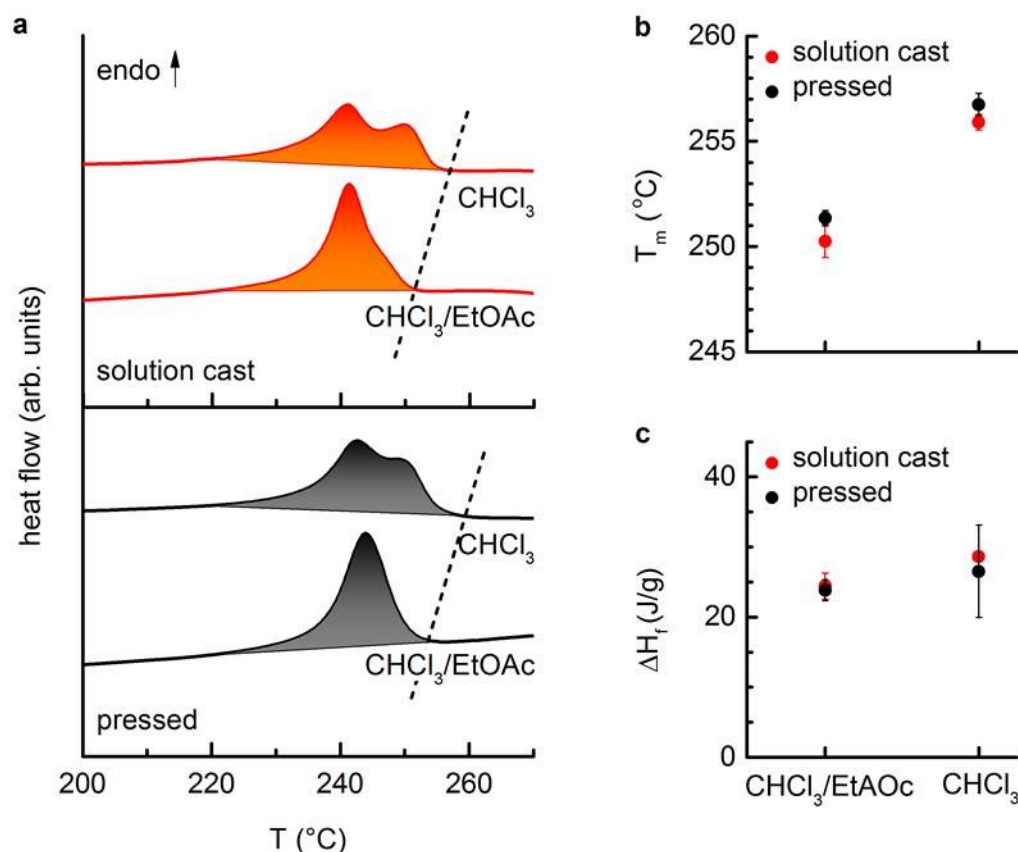


Figure 4.4 (a) Differential scanning calorimetry (DSC) heating thermograms of P3HT as initially cast (**red**) from CHCl_3 or solvent mixture, $\text{CHCl}_3/\text{EtOAc}$, and sequentially solid state pressed (**black**); dashed lines and shaded areas indicate melting temperature (T_m) and melting enthalpies respectively. (b) Derived melting temperatures (T_m) for the various processing conditions. Note the large decrease in T_m when processing from the solvent mixture, suggesting solvent-induced aggregation leads to formation of crystallites with smaller lamellar thickness. (c) Enthalpies of fusion of P3HT (ΔH_f) for the various processing conditions.

It should be noted that there are some controversies regarding the estimation of enthalpy of fusion provided for 100 % crystalline P3HT. The value of ΔH_f° of 99 J/g obtained by Malik and Nandi through crystallisation studies and DSC measurements has been widely used, resulting in crystallinities around 10-40%.¹²⁰ However, many consider this value a gross overestimation since it is not in agreement with crystallinities estimated from X-ray scattering observations. Balko *et al.* proposed an approximation of $\Delta H_f^\circ \approx 33$ J/g, based on DSC thermograms and temperature dependent small and wide-angle X-ray scattering measurements.¹²¹ This was in close agreement with a value of $\Delta H_f^\circ \approx 37$ J/g proposed by Pascui *et al.* based on ^{13}C solid state NMR studies and DSC analysis.¹²² However, these estimations of ΔH_f° would make the samples herein close to 100% crystalline, which is very unlikely. Regardless, the difference in crystallinity observed between the two pre-processing schemes remains. Therefore, it was concluded that the

developed pre-processing protocols represent a good system through which to compare between the traditional approach of aiming for high crystallinity and the more modern school of thought where short-range order is sought, even at the cost of lowered crystallinity.

4.2.2 Molecular order and anisotropic orientation

In the next set of experiments, the crystal structure and molecular orientation of P3HT was evaluated by reflection mode wide angle X-ray scattering (WAXS). Samples prepared via the two different pre-processing routes were compared in their solution cast, powder and solid state pressed film state. The crystallographic directions (hkl) of P3HT are schematically represented in Figure 4.5a by the alkyl chain (h00), π -stacking (0k0) and polymer backbone (00l) planes, with corresponding characteristic edge-on or face-on orientations. The diffractograms in Figure 4.5b reveal reflections at $q_{(100)} \approx 3.8 \text{ nm}^{-1}$ and $q_{(020)} \approx 16 \text{ nm}^{-1}$, with their corresponding $d_{(hkl)}$ -spacings summarised in Table 4.1. This corresponds well to the most common polymorph of P3HT, Form I, for which an orthorhombic unit cell was initially proposed by Prosa.⁹² Additionally, Brinkmann *et al.* suggested a monoclinic unit cell from studies of P3HT cast from high boiling point solvent.^{30,35}

The solution cast samples featured a strong (100) reflection and lacked a (020) reflection, indicative of characteristic edge-on orientation. This orientation was expected as enhanced face-on orientation is typically difficult to achieve from cast films without additional epitaxy processing techniques (such as the use of high-boiling solvents or rubbing).^{60,62} In powder XRD, isotropic orientation of crystals was evident by the strong (100) and (020) reflections. Finally, in solid state pressed films this isotropic nature was diminished by the more prominent (020) diffraction and slightly reduced (100) reflections. Compared to solution cast films these films had significantly enhanced vertical π -stacking (face-on orientation). This suggests that the enhanced vertical π -stacking in part came from the fact that isotropic powders were pressed and that further enhancement was attributed to reorganisation of the crystallites by ‘plastic crystal’ flow. The trends in orientation with respect to processing step (cast, powder to pressed) were the same for both pre-processing conditions.

The orientation in solid state pressed films was also verified by transmission mode WAXS measurements (Figure 4.6). These experiments were carried out by Dr Rajeev Dattani on the ID02 beamline in Grenoble (ESRF, France). These measurements probed

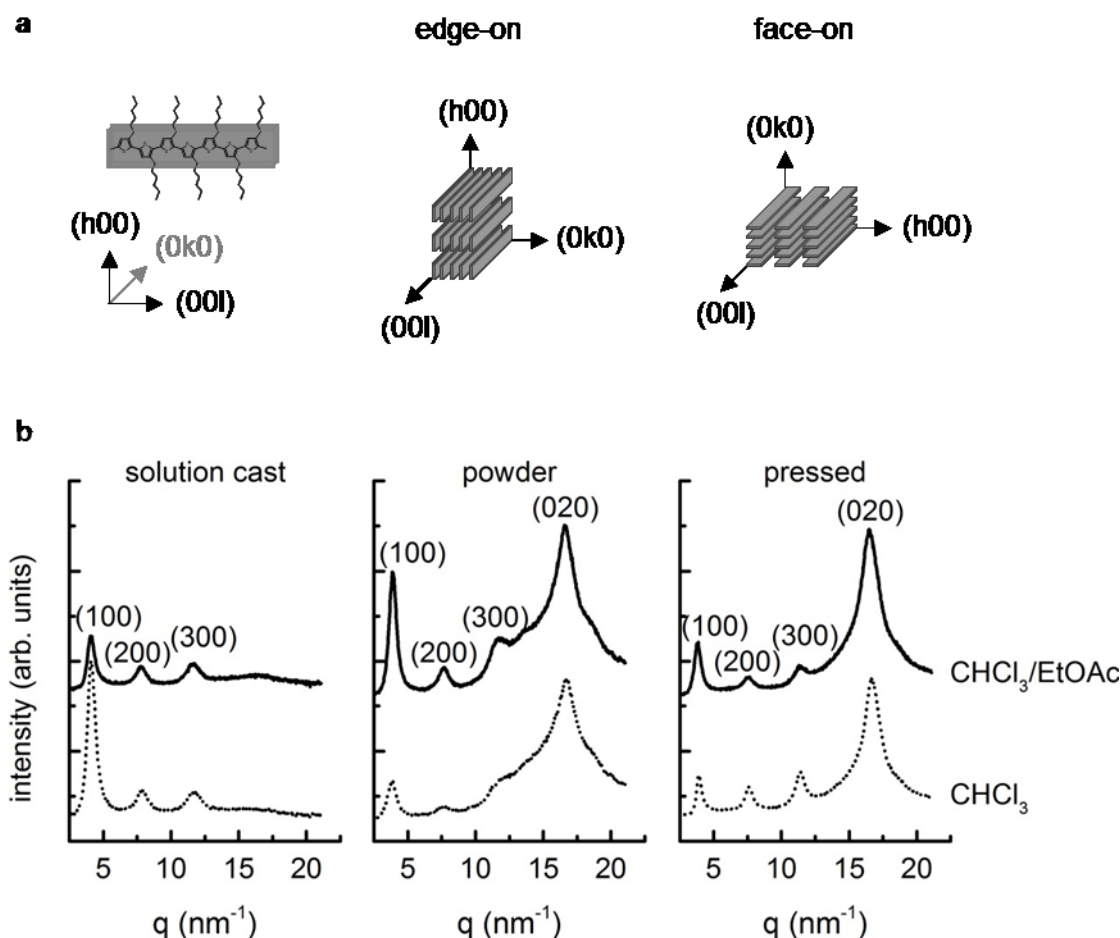


Figure 4.5 (a) Schematic of resulting molecular order with depicted crystallographic directions of P3HT: the (h00) alkyl stacking, (0k0) π -stacking and (00l) polymer backbone direction, and the typical edge-on and face-on orientations. (b) Reflection mode XRD of P3HT from solution cast films, with characteristic edge-on orientation, as isotropic powders, and pressed with reduced isotropic nature and enhanced vertical π -stacking (face-on) orientation. These observed molecular orientation trends remained similar regardless of the solvent system chosen.

Table 4.1 Wide-angle X-ray scattering $d_{(hkl)}$ -spacings for P3HT with different solution-processing protocol prior to solid state pressing.

solvent system	$d_{(100)}$ (Å)			$d_{(020)}$ (Å)		
	solution cast	powder	pressed	solution cast	powder	pressed
CHCl ₃ /EtOAc	16.1	16.1	16.2	3.7	3.7	3.8
CHCl ₃	15.7	16.6	16.2	3.8	3.7	3.8

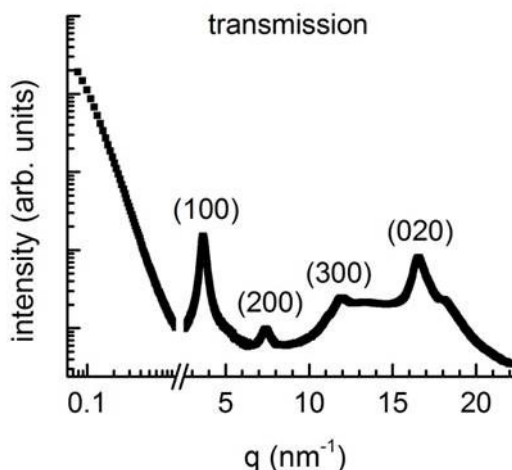


Figure 4.6 *The isotropic molecular order with enhanced vertical π -stacking in pressed P3HT films becomes more evident in transmission mode wide angle X-ray diffractograms (cast from solvent mixtures prior to pressing). Potential inhomogeneity in the long range ($q < 1 \text{ nm}^{-1}$) from the small angle XRD diffractograms could not be distinguished from the general background.*

the in-plane rather than the out-of plane orientations and showed opposite strengths of the (100) and (020) reflections. This confirmed the enhanced face-on orientation in the solid state pressed films. Long range order was investigated by complementary small angle X-ray-scattering measurements. However, no features could be distinguished from the general background.

From the structural and thermoanalytical findings it was concluded that the pre-processing steps were of importance for solid state processed films. During pressing in the solid state the operating temperatures were maintained well below the melting temperature of the semiconductor. Whatever microstructure that was formed prior to sequential pressing would thereby remain as bulk material properties in the free-standing films. Solid state pressing instead acted as a facile method to generate highly textured films with enhanced vertical π -stacking.

4.2.3 Charge carrier mobility and transport anisotropy

The next key evaluation concerned the electrical characteristics of the solid state processed films with a well-defined short-range order (defined by solvent-induced aggregation) and high degree of vertical π -stacking (induced by pressing). To assess the bulk transport properties of the solid state pressed films time-of-flight (TOF) photoconductivity measurements were carried out, as detailed in Chapter 3. The work presented in this section was carried out by Dr Egon Pavlica at University of Nova

Gorica (Slovenia). The charge carrier mobility perpendicular to the plane of the film ($\mu_{\text{TOF}\perp}$) was measured in device structures where freestanding films were sandwiched between two aluminium (Al) vacuum evaporated electrodes. The charge carrier mobility in-plane of the films ($\mu_{\text{TOF}\parallel}$) was measured using evaporated coplanar Al electrodes. The coplanar electrodes were aligned with the long axis ($\mu_{\text{TOF}\parallel x}$) or the short axis ($\mu_{\text{TOF}\parallel y}$) of the film as shown in Figure 4.7a. The long axis was the same direction as the material flow in the channel die. An image of the coplanar set up is shown in Figure 4.7b.

Dispersive hole transport photocurrents, characteristic to P3HT, were found for samples in all directions, as shown by the representative transients in Figure 4.7c. Interestingly the transit time increased by an order of magnitude for transport perpendicular to the plane of the film compared to the in-plane transit times. Transit times for in-plane

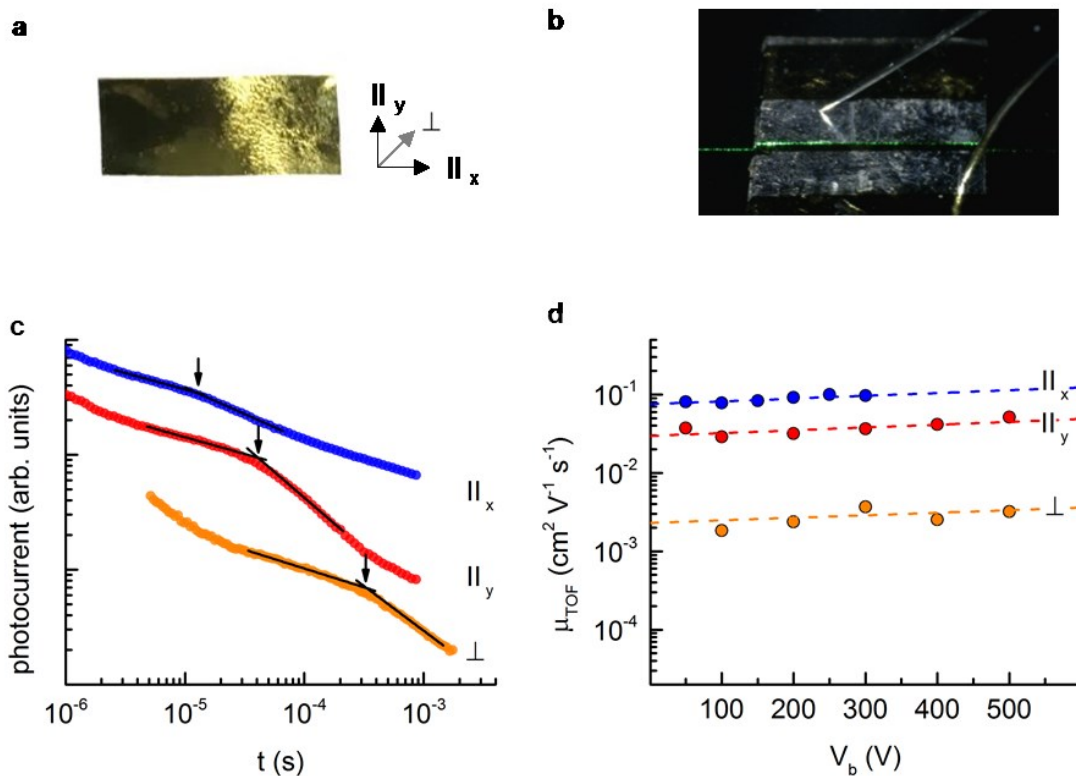


Figure 4.7 (a) Top-view image of freestanding P3HT film with investigated charge transport directions indicated as perpendicular to ($\perp$) and in-plane of the film along its long ($\parallel x$) and short axis ($\parallel y$). (b) Side-view image of the photoconductivity set up showing the laser beam photoexcitation close to one of the multiple coplanar evaporated Al electrodes on the P3HT film. (c) Representative time-of-flight (TOF) photoconductivity transients of solid state pressed P3HT films for the various configurations (at V_b of 200 V and $d_{\parallel}$ of 150-160 μm and $d_{\perp}$ approximately 125 μm) displaying the increase in transit time (arrows) with regard to directionality. (d) The field dependence of mobility in the pressed films.

transport were faster along the long axis compared to the short axis. The TOF mobility was calculated from the inferred transit times, assuming electric fields defined by the electrode separation distance and bias voltage. The dependence with respect to bias voltage for the respective directions of transport is represented in Figure 4.7d. These photocurrent transients and field dependence mobility plots correspond well to the median of the entire sample population for each specific device configuration.

The median charge carrier mobility of P3HT perpendicular to the plane of the film ($\mu_{\text{TOF} \perp}$) was found to be approximately $\sim 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is on the same order of magnitude as the previously reported mobility in solid state pressed films ($\mu_{\text{TOF}} \sim 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁰³ These films had similar molecular orientation in the through-plane (i.e. enhanced vertical π -stacking), but had not been processed to provide well-defined short-range order.⁴⁷ In comparison, previous time-of-flight hole mobility in solution cast, neat P3HT reported in the literature gave values on the same order of magnitude as the latter or lower.^{112–114} To the best of our knowledge, the highest mobility in P3HT films reported in literature is $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹²³ However, it needs to be noted that this was obtained through space-charge-limited-current measurements, which is not directly related to time-of-flight mobility. Additionally, the long-range mobility were measured in significantly thinner films ($< 1 \text{ } \mu\text{m}$) compared to the relatively thick solid state pressed films ($125 \text{ } \mu\text{m}$).

The median in-plane mobility along the short axis of the film ($\mu_{\text{TOF} \parallel y}$) was in comparison an order of magnitude higher at $\sim 3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Charge transport in P3HT is inherently highly anisotropic with transport most efficient along the polymer backbone axis, slightly less efficient along the π -stacking direction and slowest across the insulating alkyl chains, as shown in Figure 4.8.^{54–56} The increase in mobility can therefore be attributed to the preferential face-on molecular orientation. The highest median mobility of $\sim 8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained for in-plane transport along the long axis of the film ($\mu_{\text{TOF} \parallel x}$). This axis was also the main direction of material flow in the channel die. The charge transport anisotropy ratio of the in-plane mobility was ~ 3 ($\mu_{\text{TOF} \parallel x} / \mu_{\text{TOF} \parallel y}$). Enhancement of charge transport along the channel die suggests slight preferential alignment of the P3HT backbone, induced by the shear stress as polymer flow is constrained by the walls of the die.¹⁰⁴ The largest charge transport anisotropy ratio of ~ 26 ($\mu_{\text{TOF} \parallel x} / \mu_{\text{TOF} \perp}$) was found by comparing in-plane (long axis) and out-of-plane mobility.

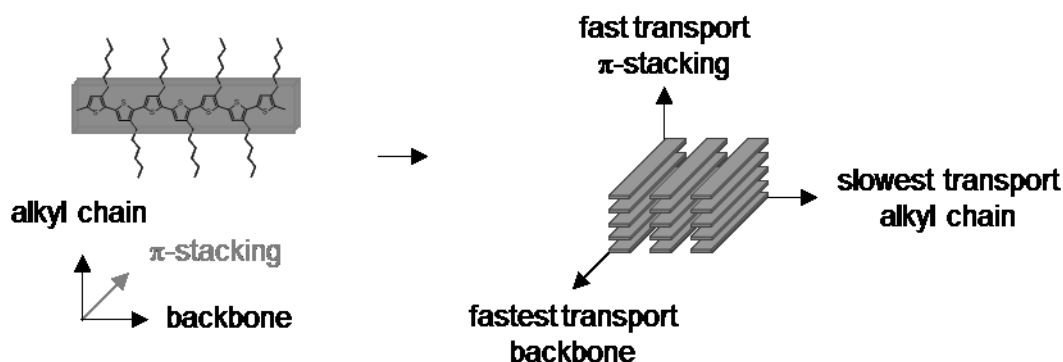


Figure 4.8 Schematic of the crystal structure of P3HT with intrinsic anisotropic charge transport as indicated by the fastest to slowest charge transport directions.

Variations in mobility between different samples and sample spots were observed. Boxplots showing the spread of the obtained mobility data are plotted in Figure 4.9a. The boxplots show the median (line), upper and lower quartile (box) and 1.5x interquartile range (whiskers). Data beyond the interquartile range are displayed as outliers. For example one set of data for transport along the short axis showed significantly higher mobility than the rest. The widths of the boxes were normalised to the square root of the sample size to limit skewing of their visual representation. A compilation of all data (comprised of multiple samples/sample spots and electrode separations for each direction) is shown in Figure 4.9b. This verified that discrepancies between different samples were significantly larger than any discernable field dependence.

It should be noted that there is a slight misrepresentation when directly comparing TOF mobility in sandwich and coplanar devices. Herein position independent electric fields were assumed for both types of devices, despite evidence suggesting that coplanar devices are better represented by position dependent electric fields.^{95,96,124} Assuming the latter for coplanar devices would increase the in-plane mobility by ~ 1.2 , as previously discussed in Chapter 3. The data presented herein may therefore be somewhat underestimated, but this becomes rather insignificant with respect to the large variances between samples. The conclusions of charge transport anisotropy, as made evident by the clear trends in Figure 3.9a, were thus justifiable and provided good approximations of the perpendicular and in-plane mobility in the solid state pressed films.

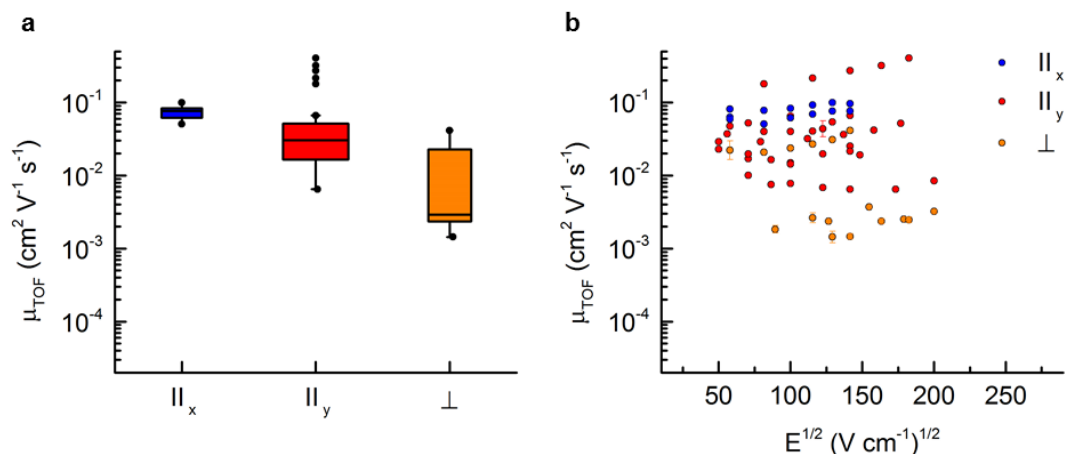


Figure 4.9 (a) Boxplots displaying the median (line), upper and lower quartile (box), 1.5x interquartile range (whiskers) and outliers (circles) to show the general variations in transport in the parallel and perpendicular directions. Box widths are normalised to square root of sample size. (b) Field dependence of charge carrier mobility for various samples, bias and configurations (bias of 50-500 V and electrode distances of 100-200 μm). Discrepancies between different samples were larger than any discernable dependence with regards to electrode distance or applied bias.

4.3 Conclusions

This chapter scrutinised the influence that pre-processing protocols have on the outcome of solid state processing, utilising a channel die hot press. Protocols were applied to obtain powders of P3HT as cast from chloroform or a ‘good’/‘bad’ solvent mixture (such as chloroform and ethyl acetate). The latter method of solvent-mixture induced aggregation lead to a high degree of short-range order and controlled crystallisation, compared to the neat chloroform that induced uncontrollable crystallisation. Investigations into solid state pressing of such distinct model systems revealed that the crystallites formed during different pre-processing conditions were maintained throughout the compression. Solid state pressing acted as a facile method to generate freestanding and mechanically robust films. As the semiconductor remained in its solid state during the process, the microstructure propagated from the initial pre-processing steps and P3HT crystals additionally became reoriented under the applied pressure to form films with a high degree of vertical π -stacking. Pre-processing of the semiconductor was therefore a crucial aspect for optimising the architecture in the solid state films.

The charge transport in the solid state films with optimised microstructures and good short-range order was investigated and compared to literature. The charge carrier

mobility was determined from time-of-flight photoconductivity measurements and evaluated for transport perpendicular and in-plane of the films (along the long and short axis). For the new systems with short-range order aggregates, presented herein, the charge transport perpendicular to the plane of the film was within the same order of magnitude as previous reports.¹⁰³ This was in line with studies by Noriega *et al.* who claimed short-range order was sufficient to induce efficient long-range transport.⁴⁷ The mobility obtained for transport in-plane of the film along the long axis of the channel die was increased by one order of magnitude. Comparing this to the in-plane transport along the channel die short axis, which was slightly lower, suggested preferential orientation of the polymer backbones along the material flow direction in the channel die. The charge transport anisotropy was attributed to the structural order, confirmed by X-ray scattering measurements, caused by the solid state pressing.

These studies imply that solid state processing is a versatile and facile tool to generate high mobility semiconductor films with a high degree of structural order, enhanced vertical π -stacking and anisotropic charge transport properties. Additionally, pre-processing measures can be taken to further optimise the performance of these constructs, due to the fact that the microstructure and crystalline domains will be carried on from their initial state.

5 SOLID STATE PROCESSING OF BINARY SYSTEMS

In this chapter the solid state processing of binary systems was explored. More specifically investigations concerned whether or not the reported beneficial enhancements during solid state pressing of neat semiconductors (such as enhanced molecular order, mobility and charge transport anisotropy) could also be achieved in semiconductor:insulator blends.^{103,116,117} Blending of semiconducting polymers with insulators are attractive and versatile means to improve processability and mechanical properties, reduce costs and introduce new features and functionalities into semiconducting architectures. In many reported blend systems device performances and charge carrier mobilities comparable to that of the neat semiconductor have been achieved. For the model semiconductor poly(3-hexylthiophene) (P3HT), blends with commodity insulators have in fact reached high bulk material hole mobilities (μ_{TOF}) on the order $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, measured by time-of-flight photocurrents.⁶⁵ This is on the same order of magnitude as the neat semiconductors. Demonstrations herein show that the blending of poly(3-hexylthiophene) (P3HT) with an elastomeric insulator, polystyrene-block-poly(butadiene)-block-polystyrene (SBS), not only greatly improved both the processability and mechanical properties of the pressed films, but also resulted in semiconducting architectures with a high degree of vertical π -stacking and highly anisotropic charge transport properties.

In these systems anisotropic transport was assessed by evaluating the charge carrier mobility from time-of-flight photoconductivity measurements, using device

configurations corresponding to each direction of interest. The in-plane mobility ranged from 3×10^{-2} to $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with decreased amounts of P3HT from 60 to 40 wt %. To the best of our knowledge, this is the highest reported μ_{TOF} for a P3HT:insulator blend. The through-plane mobility was overall decreased by an order of magnitude. These latter values are in agreement with other μ_{TOF} of both neat P3HT and P3HT:insulator blends previously reported in literature.^{103,112,113,125} The high mobility in the P3HT:SBS blends was attributed to two factors. Firstly, employment of well-defined pre-processing protocols, as discussed in Chapter 4, that ensured the maintenance of short-range order P3HT aggregates in the insulating matrix even upon sequential pressing. Secondly, the utilisation of a channel die during the pressing process which restricts the polymer flow at the die wall and lead to further reorganisation of the semiconductor and improved anisotropic molecular orientation and transport properties. These novel methods therefore have great potential for the manufacture of freestanding, flexible semiconducting substrates.

5.1 Introduction

The potential of low cost and large area manufacturing of flexible electronics makes organic electronics attractive in numerous applications, including organic optoelectronics (OLEDs), thin film transistors (OTFTs), photovoltaics (OPVs) and bioelectronics. One of the main current objectives is exploring novel methods to make the devices more cost-effective and improving their mechanical properties and stability. The use of multicomponent blended systems is one such avenue that has been pursued with great success. The benefit of blending lies in the ability to overcome the inherent limitations of organic semiconductors (e.g. small processing windows and poor mechanical and device performance stability), while extending their potential by introducing new features and functionalities in the semiconducting architectures. Additionally, by blending with commodity polymers the cost of manufacture can be greatly reduced. Binaries of low cost insulators and semiconducting polymers have been widely explored and shown to have numerous advantages.¹⁹ Electrically insulating polymers can for example be used to improve processability, modulate optoelectronic properties, enhance mechanical properties and device stability.^{52,66,126,127} The greatest opportunities in using binary systems come from investigating and exploiting crucial structure/processing/property interrelationships, in order to enable more versatile and finer control over tuning of desired features and functionalities.

There are countless variations and possibilities for creating binary systems and therefore many parts to take into consideration. One crucial aspect is for instance the crystallisation sequence in semiconductor:insulator blends to ensure percolating electrical networks. This was neatly demonstrated in a comprehensive study by Goffri *et al.*, which explored crystallisation sequences in P3HT blends with a range of insulators both of crystalline or amorphous nature.⁶⁷ In the case of a semicrystalline insulator, it is important to allow the semiconductor to crystallise prior to the insulator, since the insulator may hinder the crystallisation of the semiconductor.¹²⁸ Efficient electrical pathways are thereby deposited and the subsequent crystallisation of the insulator can further drive the solidified semiconductor to segregate at the film surface and interface. Such stratified (double-percolation) binaries have been shown to enhance the performances in field effect transistors (FETs), where interfaces are of utmost importance.^{67,129,130} For applications other than FETs, bulk transport properties may be more important. Even in bulk material characterisations impressive performances have been reported for semicrystalline:semicrystalline blends. For example, Kumar *et al.* demonstrated time-of-flight photoconductivity mobilities (μ_{TOF}) of $\sim 1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in P3HT:high density polyethylene (HDPE) blends with 80 wt % P3HT.⁶⁵ The reason for the high mobility in this specific blend composition could not be explained by simple percolation rationale and remains unknown. Nevertheless, blending of semicrystalline: semicrystalline polymers is often preferred as it allows much manipulation of structure/processing/property interrelationships.

Applying the same processing schemes to semicrystalline:amorphous polymer blends will on the other hand not necessarily have the same outcomes.⁶⁷ In such cases, the discussed double-percolation phenomena are not as readily observed and the performance of FETs of such binaries can consequently be degraded. This is often attributed to the increase in miscibility of the components in the liquid-liquid state, limiting phase separations and hindering crystallisation of the semiconductor. One way to overcome such limitations is by using solvent-assisted crystallisation methods, as described and demonstrated in Chapter 4. For instance, there are several reports on the stark improvement in the FETs performances of P3HT:amorphous polystyrene (a-PS) blends when switching from casting from ‘good’ to a ‘bad’ solvent systems (such as chloroform and dichloromethane respectively).^{131–133} Such improvements result from continuous nanofibrous networks, comprised of nanowhiskers/nanofibres formed in poor solvent environments, embedded in the insulating matrix. Similar processing

principles have also been applied to P3HT:elastomer blends with the additional benefit of improved elasticity of the binary system.¹³⁴

All of the blend processes mentioned above are solution-processing methods and alternative attractive and industrially relevant processing techniques are often overlooked. As discussed in Chapter 4, melt or solid state processing (compression molding) techniques are commonly used in industry to process commodity polymers. There is as such a pre-existing broad knowledge base when it comes to processing plastics that can potentially be applicable to the processing of semiconductor:insulator blends. Yet, there are very few studies on the use of these processes with semiconducting binary systems.^{135,136} To date, most studies utilising compression molding or melt extrusion methods involve blends of insulators and organic conductors, such as graphene or carbon nanotubes, or conducting polymers such as polyaniline.^{137–140} In these studies the potential benefits that solid state processing has to offer, such as enhanced molecular order and anisotropic orientations, were not addressed.

This chapter therefore investigates the important structure/processing/property interrelationships in hot-pressed binary systems comprised of the semiconducting polymer poly(3-hexylthiophene) (P3HT) and the insulating elastomer polystyrene-block-poly(butadiene)-block-polystyrene (SBS). First the benefits of hot pressing of a binary system are highlighted by demonstrations of improvements in both processability and mechanical properties of the semiconducting freestanding films. Second, the effects of solution-processing prior to solid state pressing on blend microstructure were probed by optical, thermoanalytical and structural characterisation methods. As demonstrated in Chapter 4, solution-processing protocols were crucial to establish a well-defined semiconductor microstructure in neat P3HT and it was observed to be equally important as well as practical to obtain homogenous blend powders. Third, the bulk charge carrier mobility in the solid state pressed blends was assessed using time-of-flight photoconductivity measurements. The charge transport properties were evaluated in all relevant directions to discern if anisotropic transport could be observed in blends as well, as in the previously noted neat semiconductor in Chapter 4. Lastly, other important processing conditions were addressed and how these can potentially be optimised to achieve optimal performances in solid state pressed blends is discussed.

5.2 Results and Discussion

5.2.1 Solid state processing of blends

The first set of experiments investigated the effects of solid state processing of blends comprised of poly(3-hexylthiophene) (P3HT) and the A-B-A type block copolymer polystyrene-block-poly(butadiene)-block-polystyrene (SBS) (chemical structures in Figure 4.1a). SBS is a widely-used commodity rubber, also known under the trade mark name of Kraton (D polymer series). In addition to being low cost, it is an easily processed thermoplastic elastomer that is typically molded as a melt fluid at temperatures of 140-200 °C. Meanwhile the semiconductor, P3HT, is arguably the most widely studied semiconductor and processing/structure/performance interrelationships have been well characterised. Specifically, pertaining to solid state processing there are both reports by other groups and new developments described in the previous chapter.^{103,116,117,135,136} It should be noted that the semiconductor remained in the solid state during the processing used in this chapter, whereas the elastomer was in its melt state. The term solid state pressing may therefore be misleading. However, it is considerably preferable over other terminologies such as melt processing, since the solid semiconductor is of interest herein.

Following the methods described and illustrated in Chapter 4, solid state pressing of blends was a facile and versatile multistep process. Uniform blend powders with well-defined microstructure (controlled by pre-processing conditions, as discussed later on) were obtained from solution cast films. The blend powders were placed in a stainless-steel channel die, inserted in a hot press and compressed at a temperature of 140 °C. This operating temperature was well below the melting temperature (T_m) of the semiconductor and above the glass transition (T_g) temperature of both blend polymer constituents (P3HT, $T_g \sim 12$ -14 °C; SBS, $T_{g, \text{poly(butadiene)}} \sim -95$ °C, $T_{g, \text{polystyrene}} \sim 90$ °C).^{141,142} Solid state processing of neat P3HT at 20-30 kN cm⁻² resulted in ~ 50 -150 μm thick films (dimensions of $\sim 8 \times 10$ -15 mm). P3HT:SBS blend films of similar thickness could be manufactured by applying a significantly lower pressure of 3 kN cm⁻². Processing of the blends at higher pressures, or contrastingly of neat P3HT at reduced pressures, resulted in mechanically unstable films that could not be further investigated; they were either too thin in the first case or not mechanically coherent in the latter. The introduction of the elastomer in fact considerably eased the process by which ‘plastic crystal’ flow of the semiconductor could be induced.

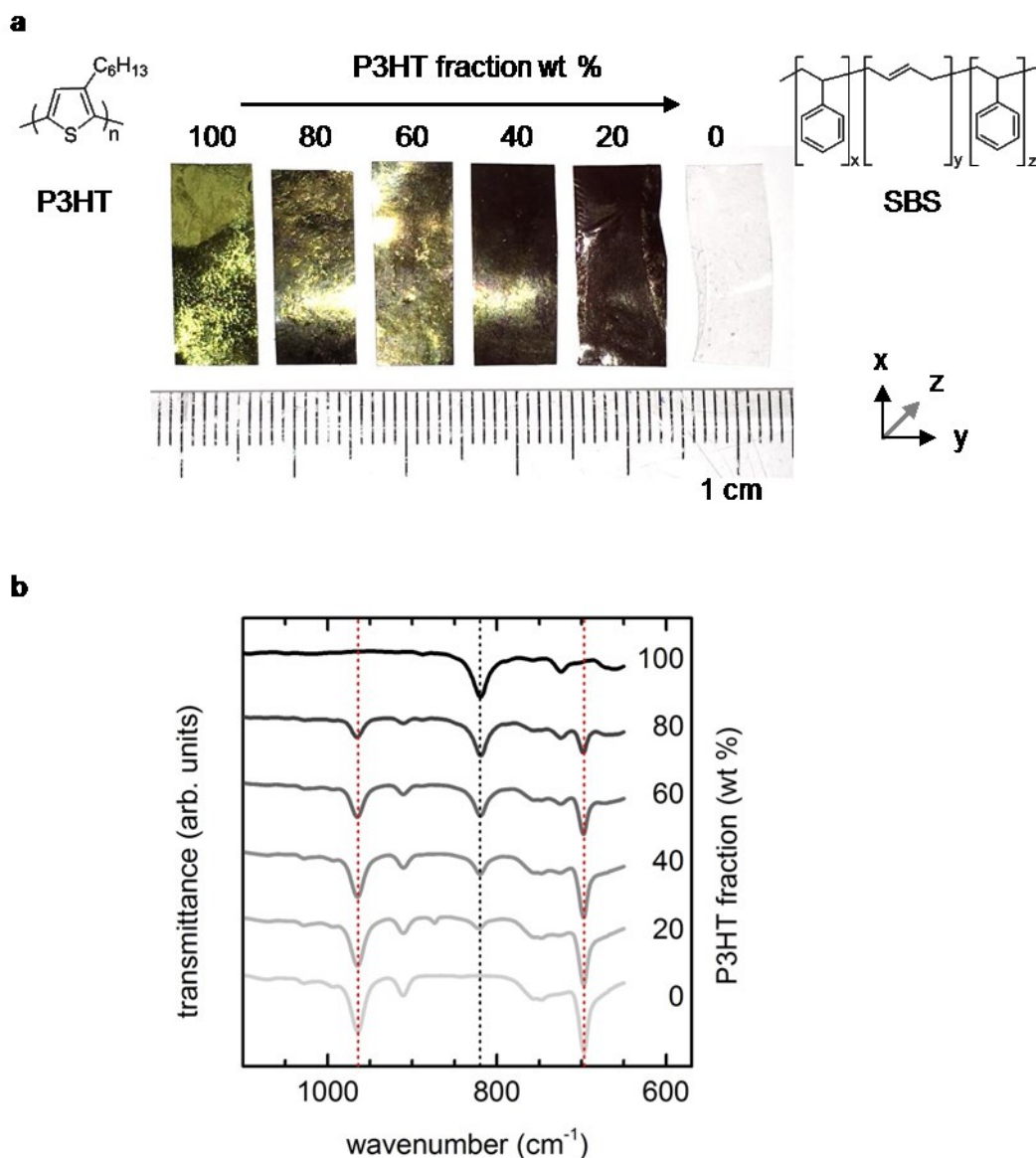


Figure 5.1 (a) Images of solid state processed blend films comprised of the semiconductor poly(3-hexylthiophene) (P3HT) and the elastomer polystyrene-block-poly(butadiene)-block-polystyrene (SBS) (chemical structures shown). As moderate pressures and temperatures are applied to the polymer powders placed in a channel die (width, y), material begins to flow (along the length of the die, x) resulting in freestanding mechanically robust films (thickness, z). **(b)** The incorporation of elastomer was confirmed by FTIR spectroscopy. Vibrational features corresponding to the styrene and butadiene blocks (**red dashed lines**) respectively became more pronounced with increased SBS content, while vibrational features related to the thiophene are diminished (**black dashed line**).

Solid state processing of P3HT:SBS blends enabled the manufacture of mechanically robust freestanding films with striking reflectivity (Figure 5.1a). Blend compositions investigated included 100, 80, 60, 40, 20 and 0 wt % P3HT. Successful incorporation of the insulator in to the films was clearly visible (as the rubber was completely transparent) and further verified by FTIR in Figure 5.1b. The vibrations at 699 and 966

cm^{-1} (Figure 4.1b, red dashed lines), ascribed to the out-of-plane $-\text{CH}$ bending in the styrene phenyl group and $-\text{CH}$ wagging near the butadiene unit's double bond respectively, became more pronounced with increasing SBS content, whereas the vibration at 825 cm^{-1} (Figure 5.1b, black dashed line) corresponding to the out-of-plane $-\text{CH}$ deformation of the thiophene diminished with decreasing P3HT content.^{143,144}

Introduction of an elastomer in the P3HT blends significantly enhanced the mechanical robustness and flexibility of the solid state pressed films as demonstrated by stress-elongation (σ - ϵ) curves (Figure 5.2a-b). Blends with predominately SBS content were highly stretchable and featured elongations at break, ϵ , of $> 260 \%$, whereas blends with P3HT as the major constituent exhibited elongations at break up to 10% . As shown in the zoomed in σ - ϵ curves in Figure 5.2b, the Young's modulus (E ; determined by the slope between ϵ of 0 - 2%) decreased, from ~ 120 to 33 MPa , with increased insulator amounts (Appendix Table A5.1).

The reflectivity observed in the freestanding films was assessed by optical spectroscopy, using a quartz substrate as reference. Figure 5.2c depicts the change in reflectance with increased insulator content, with a normal glass substrate being shown as a control. The films were found to be highly reflective and comparable to previous reports on solid state pressed films.¹⁰³ In contrast to these previous findings, the studies herein further revealed very distinct vibrational features in the 500 - 750 nm region. These spectral features were attributed to the well-defined microstructures in the films that were governed by the solution-processing steps. Under elongation of the films (ϵ of 0 - 200%) the shape of the reflectance spectra remained the same, suggesting that the applied elongation was insufficient to induce further planarisation of the semiconductor (Figure 5.2d). The decrease in reflectance was most likely due to the decrease in the exposed surface area of the films as they became narrower upon stretching. The high reflectivity of these semiconducting films is a result of the 'plastic crystal' flow under high pressure, which caused polymer chains to diffuse over grain boundaries.¹¹⁵

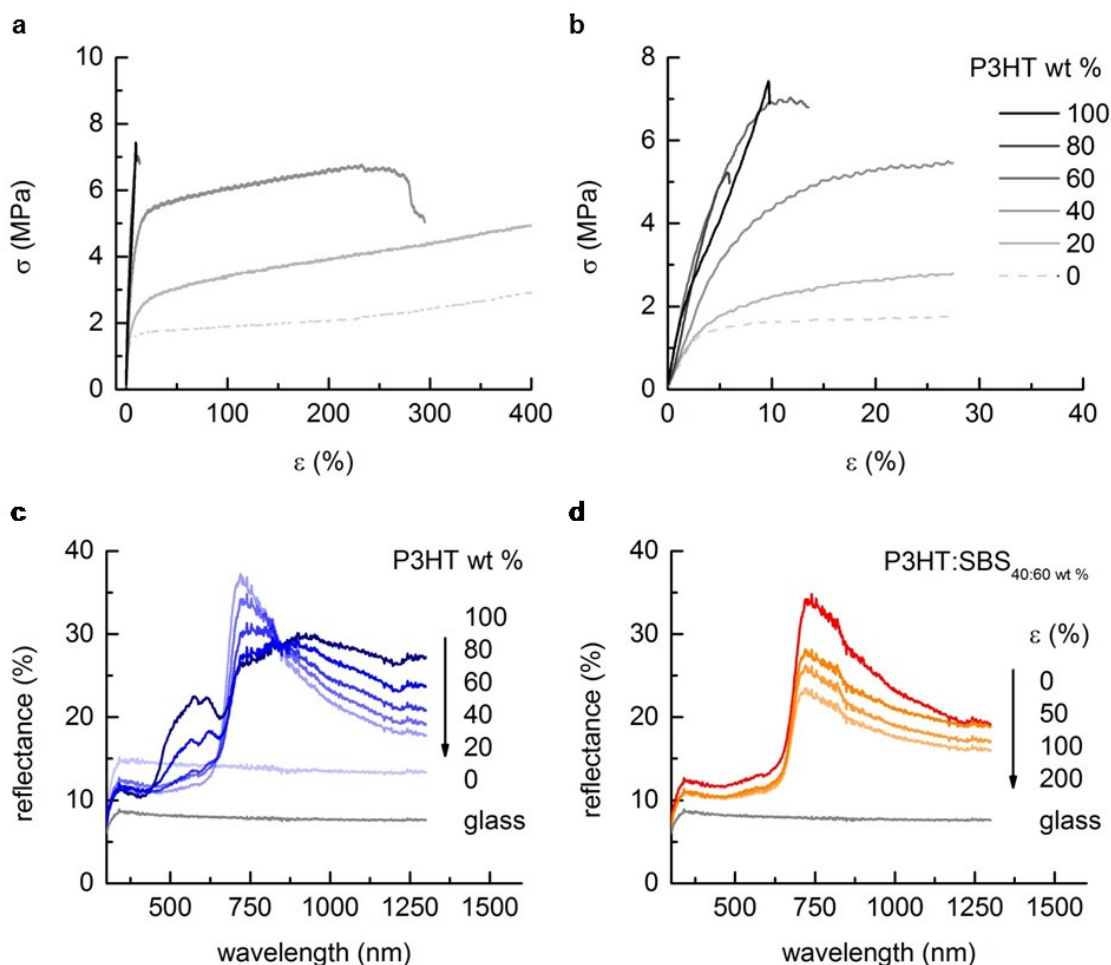


Figure 5.2 (a) Stress-elongation (σ - ϵ) curves of P3HT-SBS blends showing improved stretchability with increasing amounts of elastomer (P3HT fractions of 100, 80, 60, 40, 20 and 0 wt %). (b) Zoomed-in view of the stress-elongation curves revealing the blend compositions (80 and 60 wt% P3HT) previously overlapped by the neat P3HT. (c) Reflectance of blends with a glass substrate as comparison and (d) as a function of elongation of a blend film with 40 wt % P3HT.

5.2.2 Impact of pre-processing on blend microstructure

As demonstrated previously in Chapter 4, solution-processing steps are a crucial means by which to control the resulting microstructure of the solid state pressed films. From a practical perspective it is also highly useful to obtain homogenous blend powders to press for these studies. For industrial translations however, it will be imperative to seek out industrially applicable solutions by which to obtain well-defined microstructured blend powders. To generate short-range ordered aggregates in the blend films solvent-assisted aggregation methods were used, to enable efficient long-range charge transport in the solid state pressed semiconductor films, as described in Chapter 4. Semiconductor aggregates were prepared separately in solution mixtures of chloroform and ethyl

acetate ($\text{CHCl}_3/\text{EtOAc}$, 2:1 by volume), according to previously optimised protocols.⁴⁵ SBS solutions were similarly prepared in $\text{CHCl}_3/\text{EtOAc}$ solvent mixtures and added in different amounts to the semiconductor aggregate solutions.

Normalised absorption spectra of blends with varying compositions (100, 80, 60, 40 and 20 wt % of P3HT) cast from $\text{CHCl}_3/\text{EtOAc}$ solvent mixtures compared to the neat P3HT cast from CHCl_3 , showed a strong red-shift accompanied by a pronounced 0-0 transition aggregation of P3HT (Figure 5.3a). This strong 0-0 transition, indicative of increased intrachain excitonic coupling,⁵⁰ suggests that the solvent-induced aggregation of the semiconductor was not impeded by the addition of the SBS rubber. Optical micrographs of wire-bar coated thin films depict the aggregates and microscopical

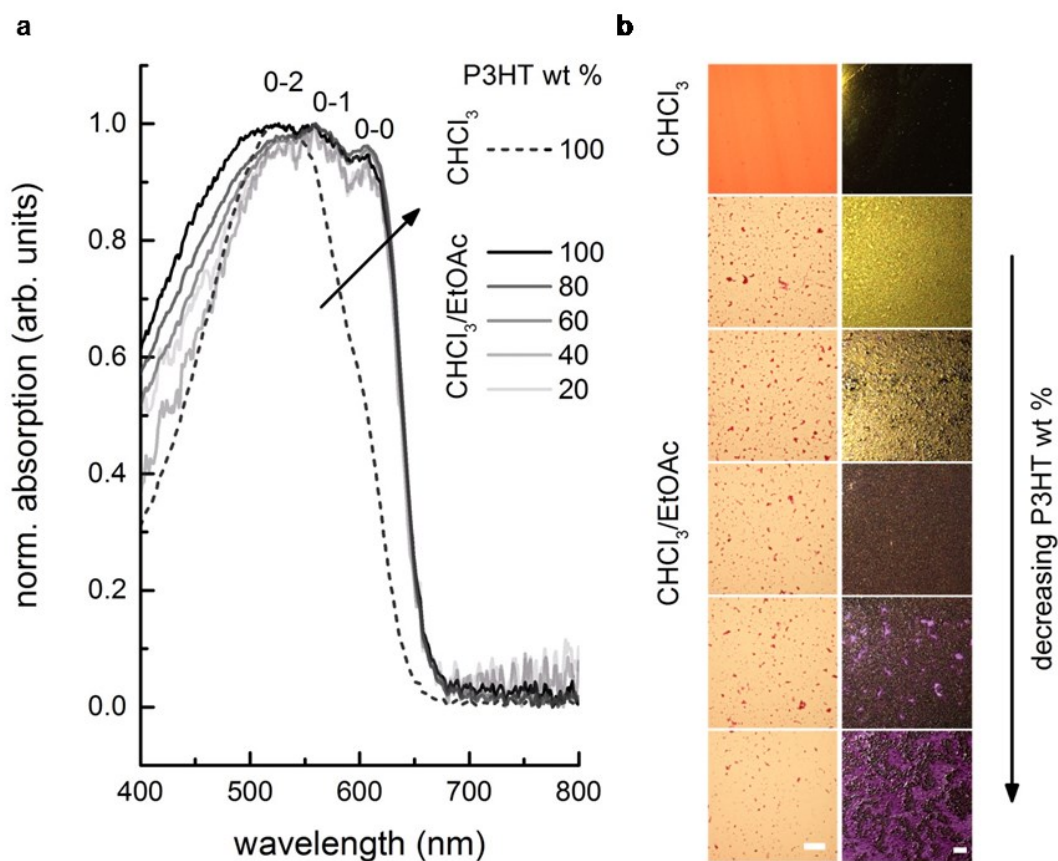


Figure 5.3 (a) Normalised absorption spectra of neat P3HT films processed from chloroform (CHCl_3) or solvent mixtures of chloroform and ethyl acetate ($\text{CHCl}_3/\text{EtOAc}$). The pronounced red-shift and appearance of the 0-0 transition indicates aggregation of P3HT from solvent mixtures, which was also pronounced in P3HT:SBS blends. **(b)** Optical micrographs of P3HT obtained from CHCl_3 and $\text{CHCl}_3/\text{EtOAc}$, as well as P3HT:SBS blends with decreasing fraction of P3HT of 80, 60, 40, 20 wt %, as thin wire-bar coated (**left panel**) and images of thick solution cast (**right panel**) films. Scale bar = 100 μm .

clusters of these aggregates that were formed when cast from solvent mixtures (Figure 5.3b, left panel). This morphology was in stark contrast to the homogenous films formed when cast from chloroform. The large clusters of semiconductor aggregates were relatively uniformly sized and homogeneously distributed across the films. It should be noted that the total mixing time was kept constant at 2 hour and that thermal equilibrium was not reached.⁴³ Longer stirring lead to a more fine distribution of the microscopic aggregate clusters (Appendix Figure A5.1). The semiconductor remained aggregated even when thicker films were cast, and the film morphology changed quite drastically with increasing insulator content. At low semiconductor content, P3HT-rich domains comprised of the clustered aggregates became increasingly interspersed in the surrounding matrix. The purple colour of the matrix however suggests that P3HT fibrils were still present in these regions as well. This was supported by the absorption spectra of the thin films (Figure 5.3a). From the thick films, blend powders were obtained and sequentially pressed.

Thermal analysis of the solution cast (from mixed solvent systems) and pressed blend films were conducted to assess the crystal structures formed. Particular attention was paid to the first heating cycle of differential scanning calorimetry (DSC) measurements, to gain information about the polymer processing history. Figure 5.4a shows the DSC thermograms of the various blends with compositions ranging from 0-100 wt % P3HT. Single peak melting endotherms were found for all samples, except for the completely amorphous insulator SBS. The final melting temperatures (T_m) of the blends, both cast and sequentially pressed, were determined from the offset, as described in Chapter 3, and generally remained relatively constant ($T_m^{\text{cast-pressed}} \approx 251 \text{ }^\circ\text{C}$, Figure 5.4b). However, it was observed that the P3HT:SBS_{40:60 wt %} blends had a higher melting temperature ($T_m^{\text{cast&pressed 40:60 wt \%}} \approx 255 \text{ }^\circ\text{C}$). These findings could be related to the lamellar crystal thickness, as given by the Gibbs-Thomson equation (Chapter 4 eqn. 4.1).¹¹⁹ This suggests that the crystals in the previously mentioned blend composition were larger than in the remaining systems. It should also be noted that the endotherms became less pronounced with increasing insulator content, and as a result it became increasingly more difficult to distinguish the final melting temperatures, as indicated by the large error bars. More importantly, there were no clear indications of differences from the initial and sequential pressing states, suggesting that similarly to demonstrations in Chapter 4 the crystallite structures were governed by the solution-processing step.

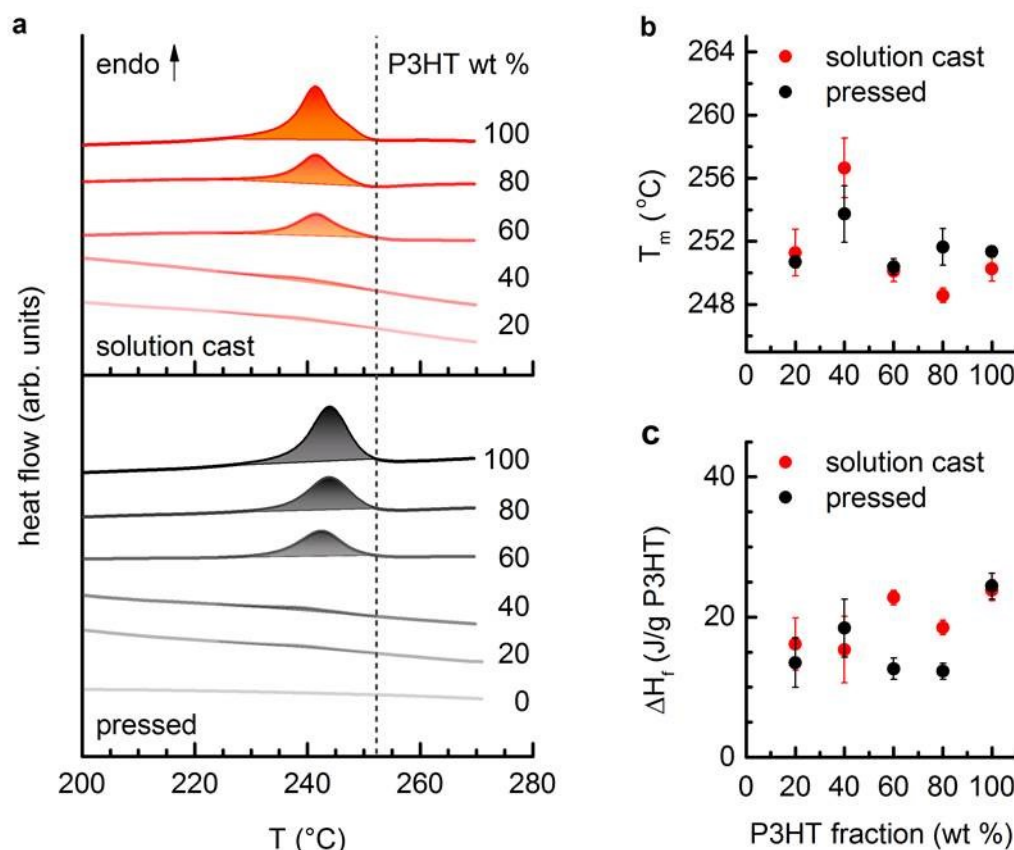


Figure 5.4 (a) Differential scanning calorimetry (DSC) heating thermograms obtained for P3HT:SBS blend films from the initial solution casting step (**top panel**) and the sequential solid-state pressing (**bottom panel**). (b) The final melting temperature (T_m) of the solution and solid state processed blend films. (c) Enthalpies of fusion (ΔH_f) of P3HT:SBS films normalised to P3HT content. The slight decrease in enthalpy upon introduction of insulator indicated partial miscibility of the two blend components.

The enthalpy of fusion (ΔH_f) of the semiconductor was in general greater for the neat material than for the blends, when normalised to P3HT content (Figure 5.4c; $\Delta H_f^{\text{cast\&pressed}} \approx 24$ J/g P3HT, $\Delta H_f^{\text{cast\&pressed blends}} \approx 12\text{--}18$ J/g P3HT). Assuming an enthalpy of fusion for 100 % crystalline material (ΔH_f^0) of 99 J/g, discussed in Chapter 4 (eqn. 4.2), this corresponds to a bulk crystallinity of 24 % for P3HT and 12–18 % for the blends.¹²⁰

The decrease in enthalpy observed upon blending is indicative of either partial miscibility of the amorphous insulator and semicrystalline semiconductor (in accordance with the Flory-Huggins solution theory).¹⁴⁵ Enthalpies in blends with low semiconductor content remain rather constant when assessed after solution-processing and upon sequential pressing. Enthalpies of blends with 60–80 wt% P3HT however, only drastically decreased after the sequential pressing. As a result, it is possible that

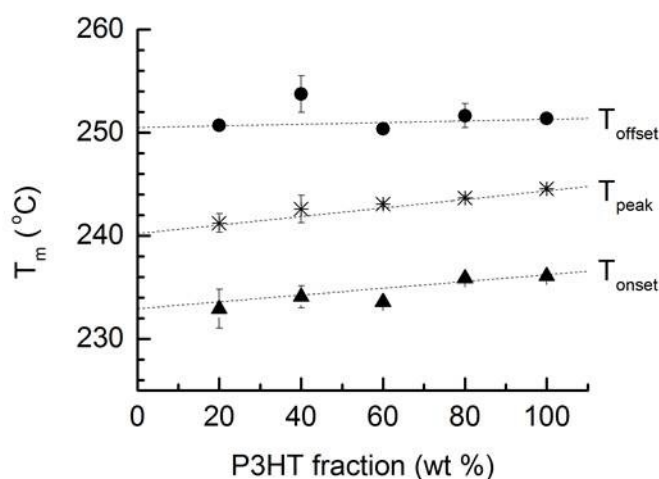


Figure 5.5 Melting point depression in solid state pressed blend films were observed, indicating that the binary components were either partially miscible or that crystallisation was hindered by the insulator.

partial miscibility occurred to a certain degree both in the initial casting step but also in the liquid-solid state during processing. In the latter case, the melt fluid, SBS, was considered the solute. Alternatively, these trends might also be explained by the insulator hindering the crystallisation of the semiconductor during the various processing steps.

Partial miscibility and hampering of crystallisation is typically also accompanied by a melting point depression.¹⁴⁶ From the previous observations it was difficult to discern any evidence of such melting point depression in these blend films. A closer look into the melting temperatures (defined by either onset, peak summit or offset as discussed in Chapter 3) revealed more pronounced contrasts with increasing insulator content. Figure 5.5 depicts the melting temperatures for solid state pressed blend films. T_{onset} corresponds to the initial melting of the crystallites – the smallest crystallites that are easiest to melt. In contrast, T_{offset} corresponds to the final melting, i.e. of the largest crystallites that require significantly more energy to melt. T_{peak} can be viewed as the mean population of crystallites in a uniform endotherm such as these. For both T_{onset} and T_{peak} a decrease in melting temperature with increased insulator content was observed, in support of either partial miscibility of the system or hindering of the semiconductor crystallisation.

Potential large vertical phase separations in the solid state pressed films could not be observed by conventional methods such as contact angle measurements (Figure A5.2).

Both blend components were found to be equally hydrophobic. As indicated by the optical micrographs (Figure 5.3b), in the films it was more likely that there were certain P3HT-rich regions, but that the aggregates overall remained interspersed in the insulating matrix. The partial miscibility or alternatively crystallisation-impeding insulator suggestions noted herein should additionally decrease the driving force for the segregation of the semiconductor and insulator.

5.2.3 Molecular order and anisotropic orientation

As discussed in Chapter 4 and in previous reports, the major beneficial outcome of solid state pressing is the ordering into highly anisotropic architectures.^{103,116,117} In order to investigate whether or not these ordered structures also could be formed in blend systems, wide-angle X-ray scattering techniques were employed. The diffractograms feature reflections of the semicrystalline P3HT at $q_{(100)} \approx 3.8 \text{ nm}^{-1}$ and $q_{(020)} \approx 16 \text{ nm}^{-1}$, and their corresponding $d_{(hkl)}$ -spacings are tabulated in Table 5.1. Figure 5.6 shows reflection mode diffractograms of the P3HT:SBS blends in their cast, powdered and solid state pressed forms. An amorphous halo of SBS appeared at $\sim 14 \text{ nm}^{-1}$ and became more prominent with increased amounts in the blends, somewhat over-lapping with the (020) reflection of the P3HT π -stacks.

Solution cast films displayed typical edge-on orientations with characteristic strong (100) reflections that diminished with increasing SBS content (Figure 5.6a), since the systems overall crystallinity was reduced. In the isotropic powders both (100) and (020) reflections, indicative of the alkyl chain and π -stacking directions respectively, were evident (Figure 5.6b). The isotropic nature was maintained after pressing of the powders and the films featured both strong (100) and (020) reflections (Figure 5.6c). Compared to solution cast samples these novel blend constructs had significantly enhanced π -stacking, or face-on orientation. In fact, the (020) reflection was prominent even at very high insulator loadings (20 wt % P3HT).

Table 5.1 Wide-angle X-ray scattering $d_{(hkl)}$ -spacings for P3HT:SBS blends.

P3HT fraction (wt %)	$d_{(100)}$ (Å)			$d_{(020)}$ (Å)		
	solution cast	powder	pressed	solution cast	powder	pressed
100	16.1	16.1	16.2	3.7	3.7	3.8
80	15.9	15.9	16.5	3.8	3.8	3.8
60	15.9	15.9	16.3	3.8	3.8	3.8
40	16.1	16.1	16.0	3.9	3.9	3.8
20	16.1	16.1	-	-	3.9	3.8

* Lack of distinguishable reflections noted by -

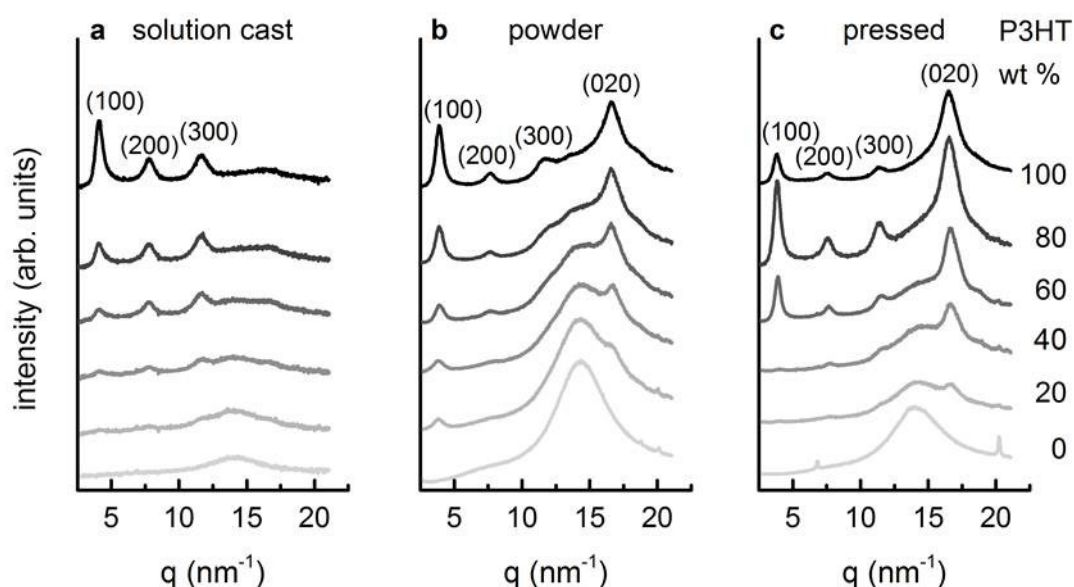


Figure 5.6 Reflection mode wide-angle X-ray scattering (WAXS) of P3HT:SBS blends as (a) solution cast films (with characteristic edge-on orientation), (b) isotropic powders, and (c) pressed with reduced isotropic nature and significantly enhanced vertical π -stacking (face-on orientation) even with increased SBS amounts.

The preferential orientation of the P3HT crystals in neat semiconductor films and P3HT:SBS_{20:80} wt% blends was confirmed by transmission mode X-ray diffraction (Figure 5.7), by probing the in-plane rather than out-of-plane reflections. The experiments were carried out by Dr Rajeev Dattani on the ID02 beamline in Grenoble (ESRF, France). Wide-angle X-ray diffraction of both pressed neat polymer and blends showed opposing intensity trends of the (100) and (020) reflections in contrast to the previous reflection mode findings. Additionally, small-angle X-ray scattering of the blend (P3HT:SBS_{20:80} wt%) showed that the long-range order of the insulator remained

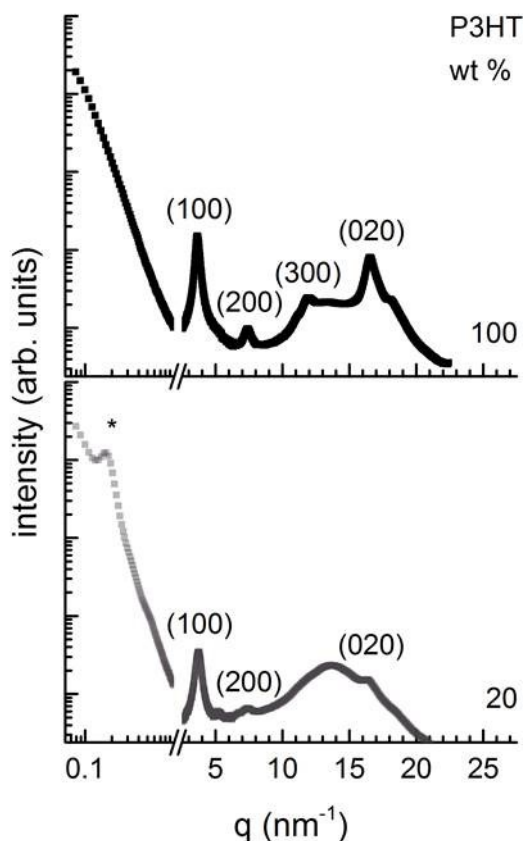


Figure 5.7 The isotropic molecular orientation in pressed P3HT and P3HT:SBS films (20 wt % P3HT) was further confirmed by transmission mode wide angle X-ray diffraction. The small angle X-ray diffractograms revealed long-range order typical of the A-B-A block polymer in the blends indicated by asterisk, but no features could be distinguished from the general background in neat P3HT films.

present in the blends. The SBS A-B-A type block copolymer is known to form ordered structures in the form of cylindrical microdomains.¹⁴⁷ The polybutadiene segments either ‘loop’ or bridge the polystyrene blocks that make up the outer core of the cylinder. These microdomains can further be preferentially oriented in the direction of the material flow during pressing, to give rise to anisotropic mechanical properties.^{104,148}

Whether or not this is also the case for these novel blend systems would require further investigations using both X-ray scattering techniques and mechanical testing. The small-angle X-ray scattering diffractograms for neat P3HT did not reveal any long-range order distinguishable from the general background.

Encouragingly, the DSC studies and structural analysis showed that solid state processing of P3HT:SBS blends resulted in microstructures with a high degree of molecular order. Solid state processing thus enabled the structuring of both

semiconductors as well as semiconductor-insulator blends films with preferential orientation of the semicrystalline polymer.

5.2.4 Charge carrier mobility in blends and their transport anisotropy

In order to investigate if blending altered the electronic properties of the semiconducting pressed films, time-of-flight photoconductivity experiments were conducted. The work presented here was conducted by Dr Egon Pavlica at University of Nova Gorica (Slovenia). Different transport directions were investigated, since the transport in the neat semiconductor solid state pressed films was found to be highly anisotropic, as discussed in Chapter 4. The charge carrier mobility perpendicular ($\mu_{\text{TOF}\perp}$) to the plane of the film was measured using both neat and blended films that were sandwiched between evaporated Al electrodes. Conversely, in-plane transport was assessed using devices in which the Al electrodes were evaporated on top of the films in a coplanar configuration (detailed in Chapter 3). The in-plane charge carrier mobility was evaluated both along the film long axis ($\mu_{\text{TOF}\parallel x}$), which was also the direction of material flow, and along the short axis ($\mu_{\text{TOF}\parallel y}$).

Characteristic dispersive hole photocurrent transients were observed for both neat P3HT and P3HT:SBS blend films in the in-plane (Figure 5.8a; $\parallel x$ and $\parallel y$; left and mid) and through-plane ($\perp$; right) transport directions. These transients are representative of the median of the entire sample population. A shift towards longer transit times (t_{tr}), determined from the asymptotic lines in the double logarithmic plot, as described in Chapter 3, was observed both with respect to increased SBS content and when probing the transport perpendicular to the plane of the film. The charge carrier mobility was determined from the inferred transit time, and under the assumption of position independent known electric fields.⁹³ As discussed in Chapter 3 and 4, this may lead to slight underestimations of the in-plane mobility.^{95,96,124}

The field dependence of the time-of-flight mobility for the pressed films, with regards to their respective directionality, is depicted in Figure 5.8b. In most cases the electric field dependence was negligible. In some instances, it was observed that the slope of the field dependency of the mobility was negative. Negative field dependency has been ascribed to systems in which the spatial disorder dominates over the energetic disorder.¹¹⁴ Herein, negative field dependencies were predominantly, but not exclusively, found for the blends and in the perpendicular transport directions. Additionally, the line shape of the photocurrents provides information about how

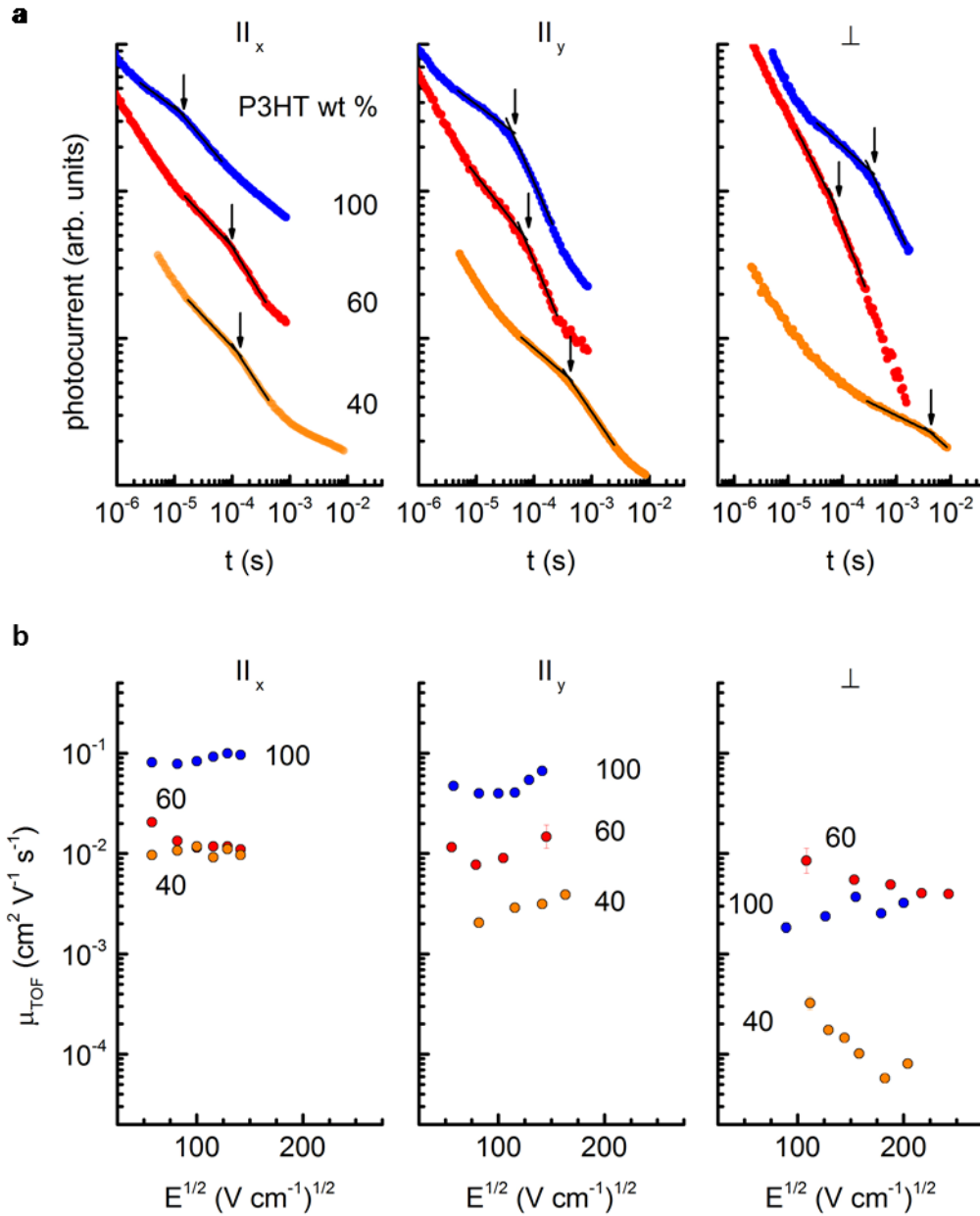


Figure 5.8 (a) Time-of-flight photocurrent transients representative of the median population for P3HT:SBS blend films with decreasing P3HT content (100, 60 and 40 wt %; **blue, red and orange** respectively; at a bias of 200 V and with electrode distances of 85-160 μm). Charge transport properties in solid state pressed films were assessed in-plane of the film long axis x (**left, I_{l_x}**) and short axis y (**middle, I_{l_y}**), and through-plane (**right, $\perp$**). **(b)** Field-dependence of charge carrier mobility for samples and respective directionality.

dispersive the transport is. For example, as P3HT content is decreased in sandwich devices the knee becomes less pronounced (Figure 5.8a, right), indicating that the charge carriers travel even less as a uniform packet. Overall, there were many discrepancies between different samples and sample spots with regards to photocurrent line shapes, mobility as well as their field dependence. To gain more information about

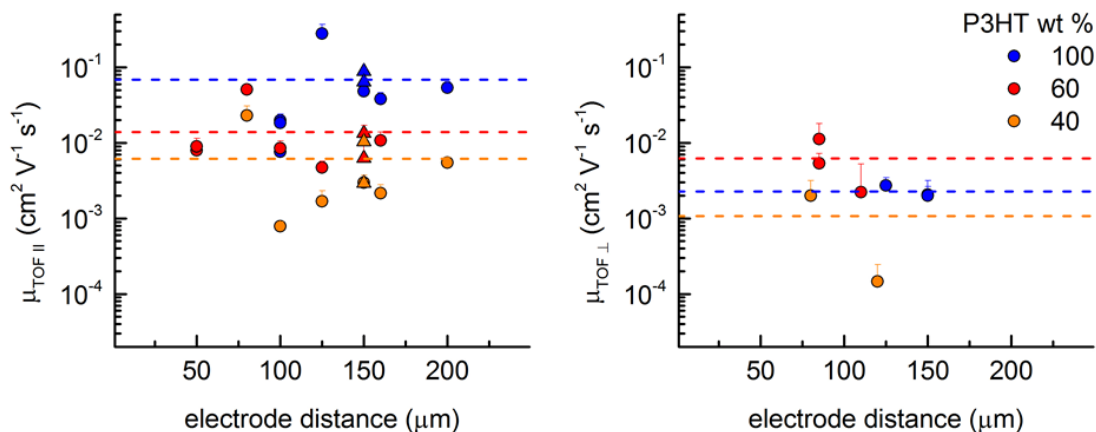


Figure 5.9 Time-of-flight mobility dependence on electrode separation distances for neat and blend polymers with 100 (blue), 60 (red) and 40 (orange) wt % P3HT. (a) In-plane charge transport along the short axis and long axis (circles and triangles respectively) and (b) through the plane of the film. The data sets shown here are averages of separate sample spots with varied voltage biases applied (50-500V). Dashed lines show average mobility for each respective blend composition. Discrepancies between different samples and sample spots were larger than any discernable dependence with respect to electrode distances.

different trap mechanisms would require further investigations into, for instance, the mobility temperature dependence in these systems. Alternatively, computational modelling of the experimental data and statistical analysis could give insight into the distribution of charge carrier velocity and their dispersiveness.

These findings however suggest that there were distinct regions in the solid state pressed films with more or less dispersive transport. This conclusion is further supported by the lack of mobility dependence on electrode separation distance for the different device configurations, as shown in Figure 5.9. Additional evaluation of the performance of these systems as a whole is therefore wise. Boxplots revealing the spread of the obtained mobility data are plotted in Figure 5.10. The boxplots show the median (line), upper and lower quartile (box) and 1.5x interquartile range (whiskers). Data beyond the interquartile range are displayed as outliers. The widths of the boxes are normalised to the square root of the sample size, so as to prevent skewing of their visual representation.

The boxplots illustrate that the mobility decreased overall with increased insulator content. The median charge carrier mobility obtained for neat pressed films and blend films in the in-plane transport direction $\mu_{\text{TOF} \parallel}$ ranged from $\sim 8 \times 10^{-2}$ to $6 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with decreasing P3HT content. In the through-plane transport direction $\mu_{\text{TOF} \perp}$ was

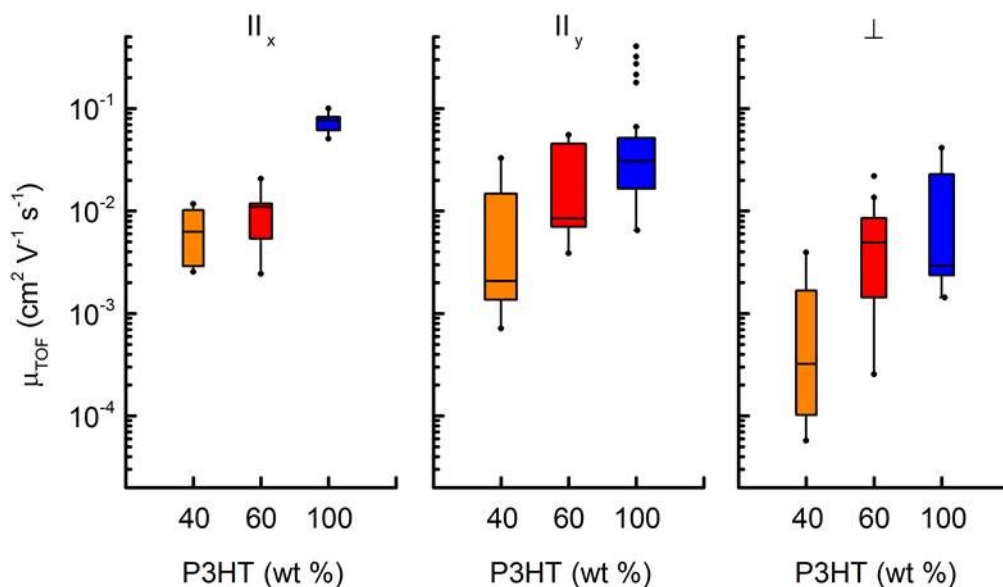


Figure 5.10 Boxplots displaying the median (line), upper and lower quartile (box), 1.5x interquartile range (whiskers) and outliers (circles) of the in-plane transport ($\parallel_x$ and $\parallel_y$) and through-plane ($\perp$) charge transport directions for films with 100 (**blue**), 60 (**red**) and 40 (**orange**) wt % P3HT. Box widths are normalised to the square root of sample size. Discrepancies between different samples were larger than any discernable field dependence.

between $\sim 3 \times 10^{-3}$ to $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These charge carrier mobilities are on the same order of magnitude as μ_{TOF} values previously reported in literature for neat P3HT.^{103,112,113,125} To the best of our knowledge there has only been one report on time-of-flight mobility in P3HT:insulator blend systems and the authors obtained μ_{TOF} of $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in high density polyethylene (HDPE) blends with 80 wt % P3HT.⁶⁵ Solid state processing of blends thus result in films with overall good hole mobility. This implies that novel alternative processes combined with blending strategies have great potential as highly efficient semiconductor architectures, with additional beneficial features such as flexibility.

The fastest transport direction was found to be in-plane along the long axis $>$ in-plane along the short axis $>$ through-plane of the films, with regards to the median of the population. The spread in the mobility was greatest in the slowest direction of transport, in line with the suggested increased dispersive transport. The median mobility and charge transport anisotropy in the blends observed in Figure 5.10 is summarised in Table 5.2. The high charge transport anisotropy is prominent in neat as well as blend films. For in-plane and through-plane mobilities anisotropy ratios ($\mu_{\text{TOF } \parallel_x} / \mu_{\text{TOF } \perp}$) of up to 26 and 19 were reached for neat and blended films respectively. As discussed in

Table 5.2 The median mobility and mobility anisotropy of blend films with 100, 60 and 40 wt % of P3HT, with respect to the corresponding charge transport directions in-plane along the long ($\parallel_x$) and short axis ($\parallel_y$), and through-plane ($\perp$) of the film.

P3HT (wt %)	median mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)			mobility anisotropy		
	$\parallel_x$	$\parallel_y$	$\perp$	$\parallel_x / \parallel_y$	$\parallel_x / \perp$	$\parallel_y / \perp$
100	8×10^{-2}	3×10^{-2}	3×10^{-3}	3	26	10
60	1×10^{-2}	8×10^{-3}	5×10^{-3}	1	2	2
40	6×10^{-3}	2×10^{-3}	3×10^{-4}	3	19	6

Chapter 4, charge transport anisotropy can be related to the structural orientation, because of the intrinsic anisotropic charge transport characteristics of P3HT.^{54–56} The solid state pressing employed thereby induced enhanced vertical π -stacking that resulted in significantly enhanced charge conduction in the plane of the film.

The anisotropy observed between the long and short axis of the sample suggest that the channel die further induced preferential orientation of the P3HT backbones in the direction of the material flow. This supports the use of solid state pressing as a promising method to generate highly oriented samples with charge anisotropy even upon blending. In fact this method performs very well compared to other methods used to orient semiconductors such as rubbing, epitaxy, nanoindentation lithography, friction transfer, strain orientation and flow coating.^{58–61,149,150} In comparison, in recent demonstrations by Hamidi-Sakr *et al.* charge transport anisotropy ratios of up to 20 were achieved by rubbing P3HT at various processing temperatures.⁶² The anisotropy was attributed to a switch from face-on to edge-on orientation of the oriented P3HT crystals. The same group had previously showed that the effects of rubbing were molecular weight dependent and mobility anisotropy ratios of up to 22 were obtained for low molecular weight polymers.⁶¹ Surprisingly, the anisotropy described in this thesis is significantly higher in the P3HT:SBS_{40:60} wt % blend films compared with P3HT:SBS_{60:40} wt %. The anisotropy in the latter blend is in fact only marginal (anisotropy ratios < 2). From the X-ray studies it was revealed that the blends with lower P3HT content show an increased amount of face-on versus edge-on orientation. This might give rise to the differences in charge transport anisotropy with regards to insulator content.

There are many factors at play that might influence the observed drop in mobility with increased insulator content. For example consider that the systems herein have well-defined short-range ordered semiconducting aggregates interconnected by crucial chain segments that act as tie-molecules, as described by Noriega *et al.*⁴⁷ Therefore, in these types of systems the aggregate interconnectivity, in addition to short-range order, is equally important to sustain efficient long-range charge transport. Introducing a high amount of insulator dilutes these aggregates, thereby decreasing the interconnectivity and reducing the potential pathways for the charge carriers to travel. This scenario is supported by the fact that even though the mobility is decreasing with insulator content by dilution, it still remains among the highest μ_{TOF} reported for P3HT:insulator blend systems. Additionally, the partial miscibility of the semiconductor and insulator or hindering of the crystallisation caused by the insulator (indicated by the overall decrease in enthalpy and melting point depression as discussed earlier) may lead to further phase separations that may contribute to a drop in mobility. As noted by Goffri *et al.* partial miscibility of a semicrystalline semiconductor and amorphous insulator can have dramatic detrimental effects on the charge transport properties in organic semiconductor blends.⁶⁷ This means that special care has to be taken with regards to, for example, the crystallisation sequence in blend systems. However, in solvent-induced aggregation systems the crystallisation of the semiconductor becomes decoupled and nanofibrous networks will be embedded in the insulator.^{131,132,134} As such the evident partial miscibility herein is most likely not the limiting factor with regards to reduced mobility in these films. This seems especially likely when considering that the lamellar crystal thicknesses and crystallinities in the two blend systems (containing 60 and 40 wt% P3HT) investigated remained comparable. Partial miscibility should in fact decrease potential phase separations in this case and maintain aggregate interconnectivity. The decrease in mobility with increased insulator content may therefore be rationalised by simple percolation considerations.

5.2.5 Further optimisation and potential of solid state processed blends

As noted in Chapter 4, the utilisation of pre-processing protocols in conjunction with solid state processing is a critical step in this process. This is because the solid state microstructure of the semiconductor is maintained throughout the processes, i.e. does not melt. This remains true for blend systems as well. Therefore, it is possible to optimise the pre-processing steps to further compatibilise the blends and achieve improved charge transport properties in the blends. For example, finer and more

homogenous distributions of the semiconducting aggregates in the insulating matrix could be obtained by increasing the stirring time prior to solution casting, as thermal equilibrium was not reached (Figure A5.1). This can in turn improve aggregate interconnectivity in the blends.

Another important factor to consider for optimised solid state processed binary systems concerns both the operating conditions (temperatures and pressures) as well as the choice of insulating component. Operating temperatures and other insulators are addressed in detail in the next chapter. The sensitivity to the pressure applied first becomes apparent in the wide range of resulting film thicknesses (50-150 μm), despite carefully controlling the amounts of materials pressed. This was attributed to the lack of fine control over the pressure applied (increased by increments of 1 kN). The polymer flow was only constricted by the channel die walls and not restricted along the long axis of the die. As a result blends with different propensity to flow could spread out more easily. This can in turn alter the shear forces exerted on the semiconductor and cause changes in structural and transport anisotropy as observed in the 60 wt % P3HT:SBS blends. Pressures and temperatures would therefore require optimisation for each specific blend condition for optimal performances.

Additionally, the environmental stability was not assessed herein. However, it should be noted that the neat P3HT and blend samples were all prepared under ambient conditions, unlike many other semiconducting films and devices that require preparation in clean rooms or under vacuum conditions. They were in fact kept in ambient environments for > 2 weeks prior to evaporating the Al electrodes under vacuum and conducting the electrical characterisations. Many P3HT:insulator blends show impressive stabilisation effects via self-encapsulation mechanisms dictated by the insulating polymer.^{65,66,129} This can potentially also be applied to rationalise the stability of the blends under investigation in this thesis, but would require further exploration. This stability makes solid state pressed binary systems of great interest for industrially relevant processing techniques and commercialisation purposes.

5.3 Conclusions

Hot pressing was demonstrated to be a highly versatile and facile means to achieve highly ordered architectures in neat polymer semiconductors as well as semiconductor:insulator polymer blends. With regards to the semiconductor poly(3-hexylthiophene) (P3HT), solid state processing acted as a tool to facilitate

rearrangement of the polymer into highly oriented structures independent of the inclusion of an insulator. Furthermore, incorporation of an elastomer polystyrene-block-poly(butadiene)-block-polystyrene (SBS) into binary systems with P3HT was found to improve both processability (by allowing processing at decreased pressures) as well as the mechanical properties of the semiconducting films.

Important structure/processing/property interrelationships were exploited to achieve well-defined blend microstructures that did not interfere with crystallisation of the semiconductor. More specifically, solvent-assisted crystallisation solution-processing protocols ensured that the short-range order of the semiconductor was maintained as the amount of insulator was increased.^{43,45} Similarly as reported in the previous chapter, the initial microstructure of the blends propagated through the sequential pressing step, but there were indications of partial miscibility of the blend components both in the pre-processing and pressing steps. The preferential arrangement of the semiconductor during pressing into highly ordered films with a high degree of vertical π -stacking was not affected by the presence of the elastomer.

The charge carrier mobility in the films was investigated by time-of-flight photoconductivity measurements for the respective directionalities of interest, i.e. through-plane and in-plane transport both in the long and short axis of the film. Compared to previous findings regarding charge transport in neat P3HT, the transport in blend films with low amounts of P3HT (40 wt %) were likewise found to be highly anisotropic. Blends with moderate amounts of P3HT (60 wt %) meanwhile resulted in insubstantial charge transport anisotropy. These anisotropy effects were attributed to the varying amounts of anisotropic orientation formed during the pressing and the intrinsic transport properties of P3HT.^{54–56} The mobility decreased by up to an order of magnitude with increasing amount of insulator. This could be explained by simple percolation considerations, whereby incorporation of an insulator diluted the semiconductor aggregate interconnectivity. The time-of-flight through-plane mobility in all blends remained on the same magnitude as the highest mobilities in semiconductor:insulator polymer blends reported in literature.⁶⁵ In contrast, the obtained in-plane mobility was an order of magnitude higher than these reports. To the best of our knowledge, this is therefore the highest reported μ_{TOF} for P3HT:insulator blends.

Overall the studies showed large variances in the line shapes of the photocurrent transients, mobilities and their field dependence between different samples and sample spots. This suggested there were distinct regions with more or less dispersive transport.

It is likely that further optimisation by increase solution-processing times would lead to more homogenous films with finely distributed semiconductor aggregates and higher aggregate interconnectivity in the blends being obtained.

These results suggest that solid state pressing of semiconductor:insulator binary systems is a highly promising industrially relevant processing route to obtain interesting semiconducting architectures in freestanding, flexible films. Crucial structure/processing/property interrelationships pertaining to solid state processing can be explored and exploited to further the developments of such novel constructs.

6 TRANSFERABILITY TO OTHER BLENDS

This chapter explores the transferability of the solid state processing schemes developed in Chapters 4 and 5 to other blend systems. One of the key features of the solid state pressing of organic semiconductors and their blends is the ability to form freestanding semiconducting films with enhanced vertical π -stacking (face-on orientation). This has been reported in the literature for a wide variety of organic semiconductors,¹⁰³ and further described in detail in previous chapters for both neat poly(3-hexylthiophene) (P3HT) and blends with the elastomer polystyrene-block-poly(butadiene)-block-polystyrene (SBS). Herein, the central consideration concerned if the observed orientation effects from pressing in the solid state could be maintained across a series of other binary systems comprised of P3HT and thermoplastics with different processability and amorphous or semicrystalline nature.

The studies show that vertical π -stacking was in fact obtained in all blends investigated as a result of the solid state pressing from isotropic powders. However, the investigations indicated that the degree to which this orientation occurs strongly depends on the blend constituents, compositions and operating conditions, such as temperature. For instance, while hot pressing of blends comprised of P3HT and SBS generate highly oriented and anisotropic films, minor changes to the chemical makeup of the copolymer insulator lead to drastic reductions in the molecular anisotropy. Likewise, changes in operating temperature generated films with less anisotropic nature. Hot pressing as a means to generate free-standing films with a high degree of molecular

anisotropy is therefore a delicate processes that requires optimisation for each specific system.

6.1 Introduction

The processing of bicomponent systems enables access to new desirable features and functionalities in semiconducting constructs, as described in Chapter 5. In semiconductor:insulator polymer blends the choice of insulator can for instance influence the system's optical response.^{52,126,151} Hellman and co-workers demonstrated that the absorption of semiconductors could be tuned by the presence of the insulator poly(ethylene oxide) (PEO).¹²⁶ The polar matrix utilised may, for example, be manipulated via post-processing methods to control inter- and intrachain exciton couplings of the semiconductor that dictated important light interactions. Moreover, the choice between a semicrystalline or amorphous insulator is likely a crucial factor in facilitating specific crystallisation pathways, as shown by Goffri *et al.*, leading to more favourable semiconducting microstructures. As long as the semiconductor is crystallised prior to the insulator any adverse effects on charge conduction can typically be avoided. Binary systems therefore open up a plethora of processing routes by which to further advance the control of crystallisation, molecular order and interactions of semiconducting polymers.

Solvent-assisted crystallisation strategies can be applied in pre-processing steps to generate blended powders that can be subsequently hot pressed, without negative impact on the well-defined microstructure, as previously noted. However, the choice of blend constituents might influence how well the pressing itself proceeds. Additionally, semiconducting systems might be sensitive to processing conditions, such as pressure and temperature. This chapter explored whether the processing schemes developed in Chapters 4 and 5 could be translated to other blend systems. More specifically, the focus herein was on the preferential structural organisation that arose from pressing in the solid state, since the influence of pre-processing protocols and resulting structural and charge transport anisotropy was already discussed in detail in the previous chapters. The results presented in this chapter demonstrated both the versatility as well as the complex nature of solid state processing.

6.2 Results and Discussion

6.2.1 Transferability of processing schemes to other blend systems

As concluded in the previous chapters, solid state processing of neat poly(3-hexylthiophene) (P3HT) and in blends with polystyrene-block-poly(butadiene)-block-polystyrene (SBS) resulted in freestanding films with preferential vertical π -stacking orientation and highly anisotropic charge transport properties. In order to investigate if these compression effects on orientation were transferable to other binary systems, a series of semiconductor:insulator blends were investigated. In all blends the model semiconductor poly(3-hexylthiophene) (P3HT) and composition (40 wt % P3HT) remained constant. The chosen commodity insulators were similar in structure to SBS, as polystyrene based thermoplastics, but differed in their processability and amorphous or semicrystalline nature. Firstly, the elastomer SBS was compared to its hydrogenated analogue polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS), which has a similar chemical composition, but differs in its melt fluid properties. SEBS has for instance improved thermal stability compared to SBS and is typically processed at higher temperatures ($T_{\text{SBS}} \approx 150\text{ }^{\circ}\text{C}$; $T_{\text{SEBS}} \approx 200\text{ }^{\circ}\text{C}$) for optimal performance. Secondly, the butadiene units were altogether eliminated and two types of polystyrene were investigated, atactic amorphous polystyrene (a-PS) and isotactic semicrystalline polystyrene (i-PS; chemical structures shown in Figure 6.1). The irregular structure of the former prohibits the polymer chains to form stacking in a regular manner, while the latter can readily crystallise. These comparisons thereby serve to demonstrate that small alterations in the chemical structure and polymer tacticity can lead to a wide range of interesting processing scenarios.

Previous studies demonstrated that the microstructure of the pressed semiconductor:insulator blends propagated from their pre-processed state. Identical pre-processing protocols were therefore exploited here in order to maintain short-range order in the semiconducting P3HT aggregates.^{45,47} In brief, P3HT was solvated in ‘good’/‘bad’ solvent mixtures ($\text{CHCl}_3/\text{EtOAc}$, 2:1 by volume) and formed nanowhiskers or nanofibres in solution.⁴² Insulators were then sequentially added to the solution, with the purple colour remaining, indicative of P3HT aggregates in the solutions. It should be noted that the various insulators may have additional effects on the resulting microstructure of the blends, for instance as noted in the discussions in Chapter 5 regarding the partial miscibility of P3HT:SBS blends. In this section

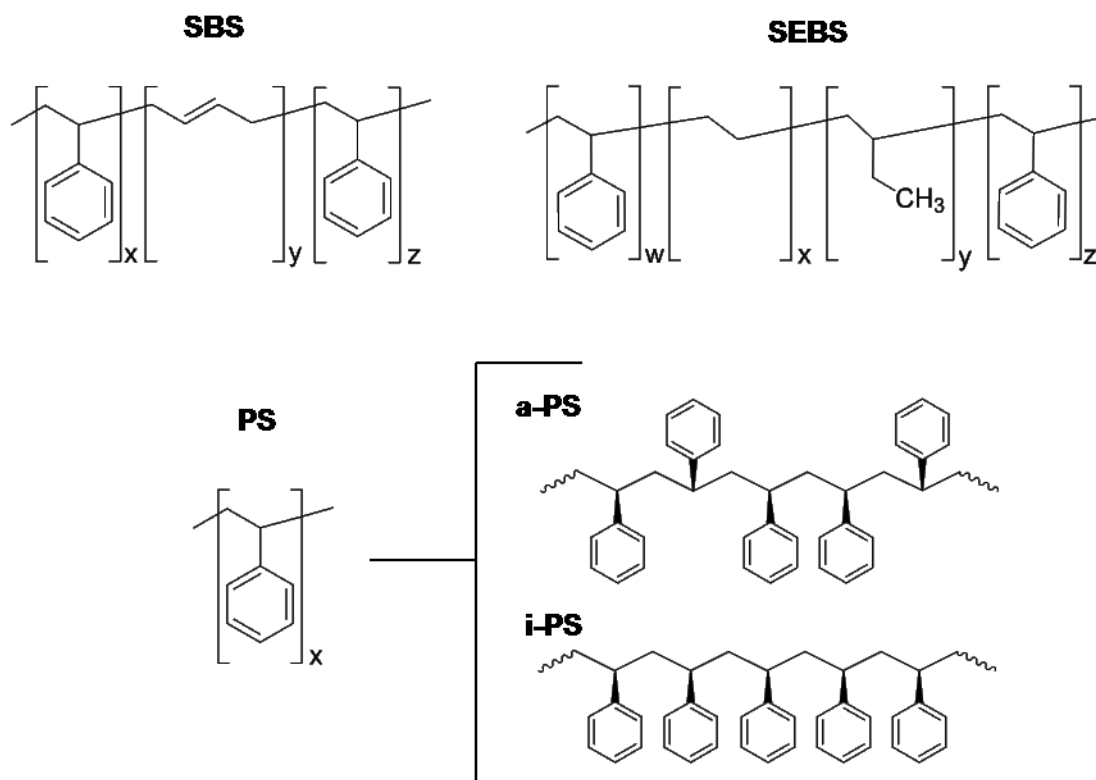


Figure 6.1 Chemical structures of the investigated insulators including: polystyrene-block-poly(butadiene)-block-polystyrene (**SBS**), polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (**SEBS**), and polystyrene (**PS**) – atactic amorphous (**a-PS**) and isotactic semicrystalline (**i-PS**).

however, the focus was on the orientation caused by the pressing. To this extent, the pre-processing protocols were deemed appropriate since the solvent-induced aggregation methods dictated the formation of P3HT crystals of similar sizes and distributions.

The powders were obtained by scratching solution-processed films using razor blades and subsequently pressed in a hot press using a channel die, as previously described. There were clear contrasts between the generated pressed blend films. The semicrystalline:semicrystalline polymer blends of P3HT:i-PS for instance were extremely brittle in contrast to the more pliable semicrystalline:amorphous P3HT:a-PS blends. Both P3HT:elastomer blends were highly flexible.

In the first set of experiments, the effects compression had on inducing preferential vertical π -stacking in the freestanding blend films were examined by wide-angle X-ray scattering, by reflection mode θ - 2θ scans. The diffractograms of blend powders and after pressing, depicted in Figure 6.2, revealed isotropic P3HT crystals. The

diffractograms featured (100) and (020) reflections at $q_{(100)} \approx 3.8 \text{ nm}^{-1}$ and $q_{(020)} \approx 16 \text{ nm}^{-1}$. These reflections correspond to the alkyl chain and vertical π -stacking planes of P3HT crystallites with $d_{(hk0)}$ -spacings summarised in Table 6.1. There were essentially no changes in the π -stacking $d_{(020)}$ -spacing, indicative of well-controlled solvent-induced P3HT crystallisation in all blends, and only small changes in the alkyl chain stacking with regards to different insulators. An amorphous halo appeared at $q \approx 14 \text{ nm}^{-1}$ in all blends. Even blends with semicrystalline i-PS had an amorphous halo, most likely due to the fact that it was not solidified sufficiently slowly. Additional reflections in blends with i-PS were observed (noted by asterisks) that correspond to the (110), (220), (211) and (410) reflections of the isotactic polystyrene crystals.¹⁵² Overall the (020) reflections remained pronounced for all blends, suggesting that pressing enhanced vertical π -stacking (face-on orientation) in the pressed films. This was especially evident when compared to solution-processed P3HT:insulator blends that resulted in predominant edge on orientation of the crystallites (see appendix Figure A6.1).

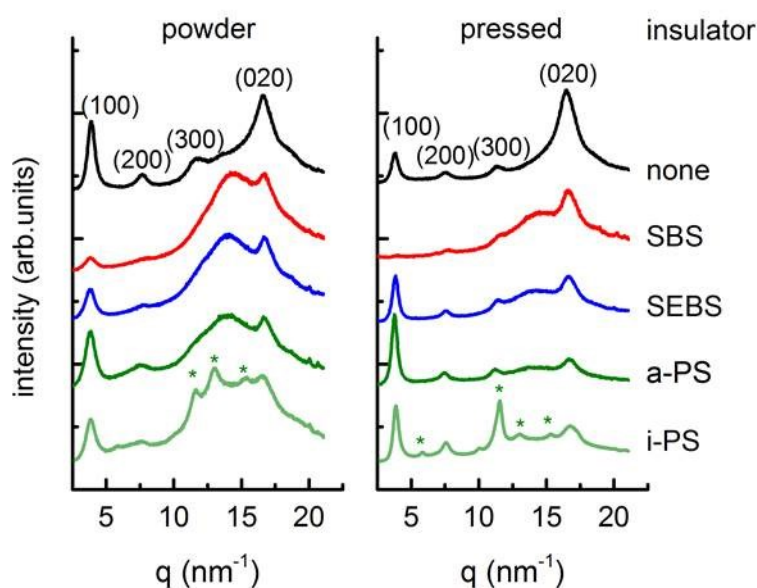


Figure 6.2 Reflection mode wide-angle X-ray diffractograms of neat P3HT and P3HT:insulator blends (40:60 semiconductor:insulator wt %) as isotropic powders or hot pressed films, showing prominent P3HT crystallites reflections corresponding to the alkyl chain (100) and π -stacks (020). Vertical π -stacking was enhanced in all blends. The largest anisotropy was found in P3HT:SBS blends, whereas P3HT:SEBS and P3HT:PS (atactic and isotactic) blends were largely isotropic, as shown by the addition of the strong (100) reflection. The main i-PS reflections are indicated by asterisks.

Table 6.1 Wide-angle X-ray scattering $d_{(hkl)}$ -spacings for neat P3HT and P3HT:insulator blends.

insulator	$d_{(100)}$ (Å)		$d_{(020)}$ (Å)	
	powder	pressed	powder	pressed
none	16.3	16.2	3.8	3.8
SBS	16.3	16.0	3.8	3.8
SEBS	16.5	16.5	3.8	3.8
a-PS	16.3	16.6	3.8	3.8
i-PS	16.2	16.2	3.8	3.7

* All semiconductor:insulator blends were 40:60 wt%

A simple means to probe the degree of orientation is by studying the intensity of the reflection peaks. Assuming the material and scattering geometry remains the same it is as such possible to get a sense of the preferential orientation when comparing different films by normalising to a specified (hkl) peak.¹⁵³ Figure 6.3 shows the resulting intensity of the (020) reflection normalised to the (100) reflection for the various blends investigated both in their powder and pressed forms. Additionally, a reference $I_{(020)}/I_{(100)}$ ratio from literature was included that has reported face-on orientation and anisotropic charge transport (Figure 6.3, dashed line).⁵⁶ It should be noted that this simplified comparison method only serves as a preliminary indicator for whether or not face-on orientations may be expected. Further characterisations are required to verify this, as discussed later on.

For the isotropic powder samples it was noted that the $I_{(020)}/I_{(100)}$ ratios were not proportional, i.e. not one to one. This is partly due to the fact that the intensities of different planes are not necessarily equal and because the scattering intensity is proportional to the scattering factors, which may differ. For example, edge-on orientations in P3HT systems are typically easily distinguished by a strong (100) reflection and lack of (020) reflection. Many reports claim strong face-on orientation in P3HT as soon as the (020) reflection becomes apparent. However, as exemplified by the intensity ratios in the blend powders it is perhaps more appropriate to describe the entire powder population as isotropic, with varying degrees of face-on orientation. It should also be noted that it was more cumbersome to produce fine powders in certain blends, which generate more representative isotropic powder reflections. The powders were

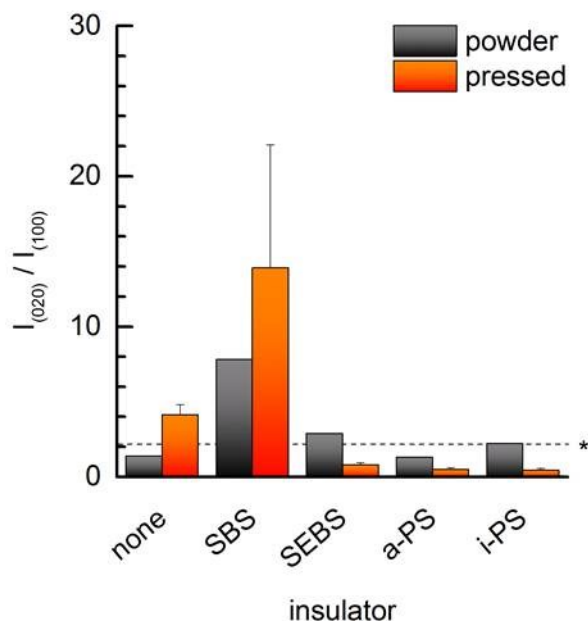


Figure 6.3 Normalised scattering intensities $I_{(020)}/I_{(100)}$ of neat P3HT and P3HT:insulator blends (40:60 semiconductor:insulator wt %) in their powder and sequentially hot pressed forms. Samples with previously demonstrated high degree of anisotropy, such as P3HT and P3HT:SBS blends had remarkably high intensity ratios. Reference included of a known neat P3HT sample with high degree of face-on orientation and anisotropic charge transport (dashed line, asterisk).⁵⁶

obtained by scratching cast films using razor blades, which worked excellently for brittle compounds or blends such P3HT or P3HT:i-PS blends. However, for sticky elastomer blends larger powder flakes were obtained. Therefore, even in isotropic samples the intensity ratios varied significantly.

For the pressed films, the $I_{(020)}/I_{(100)}$ ratio was high for both neat P3HT and particularly P3HT:SBS blend films. These ratios were significantly higher than those for their respective isotropic powders and in addition surpassed the reference sample $I_{(020)}/I_{(100)}$ ratio of a neat P3HT film, with known face-on orientation.⁵⁶ Both the pressed neat P3HT and P3HT:SBS blends had a high degree of enhanced face-on orientation induced via hot pressing. This was verified in the previous Chapters 4 and 5 by complementary transmission mode X-ray scattering measurements and anisotropic charge transport measurements. Interestingly, the $I_{(020)}/I_{(100)}$ ratio for the other blends were significantly decreased compared to their respective isotropic powders. This suggested that these films remained isotropic, and that the pressing did not induce further anisotropy in the films.

From these results it was clear that the enhancement of face-on orientation induced by solid state pressing was a delicate process. For instance, the hot pressing of P3HT:SBS generated highly oriented architectures, whereas small changes to the butadiene unit on the insulating block copolymer, in for instance P3HT:SEBS blends, seemed to reduce this anisotropy. The anisotropy was also reduced in P3HT:PS blends, where the butadiene unit was altogether eliminated. This was true irrespective of the amorphous or semicrystalline nature of the insulator. This suggest that although solid state pressing can be utilised to induce face-on orientations in semiconducting:insulator polymer blends, the degree to which this occurs is strongly dependent on the choice of blend constituents and likely their glass transition temperature.

One explanation that can explain the sensitive nature of vertical π -stacking enhancement during hot pressing is that small changes to the system can alter its propensity to flow, or melt fluid properties like the viscosity of the insulator or the blend. This will affect the transfer of stresses on to the solid P3HT during the pressing and thereby aid or hinder the preferential orientation of the crystals. The chosen insulators all have very different melt fluid properties (such as viscosity) dictated by their T_g and molecular weight.¹³⁹ Additionally, as discussed in the previous chapter it was evident that even alterations to the amounts of insulator in the blends caused significant differences in the amount of vertical π -stacking in the systems. Therefore, these effects induced by composition are not surprising.

6.2.2 Influence of processing temperature on molecular order

In addition to changes in the chemical nature of binary systems, the blend melt fluid properties during pressing strongly depend on the operating conditions such as pressure and temperature. To this end, two different P3HT:elastomer blends (SBS and SEBS) were processed at various operating temperatures and the resulting molecular order was studied by reflection mode X-ray scattering. These blends were expected to have relatively similar thermal behaviour.¹⁵⁴ The lowest operating temperature of 80 °C was above the glass transition (T_g) of the semiconductor (P3HT, $T_g \sim 12-14$ °C) as well as the poly(butadiene) and poly(ethylene-ran-butylene) units of the elastomers ($T_{g, \text{poly(butadiene)}} \sim -95$ °C, $T_{g, \text{poly(ethylene-ran-butylene)}} \sim -37$ °C), but below the glass transition of the polystyrene units ($T_{g, \text{polystyrene}} \sim 90$ °C).^{141,142,155} Additional operating temperatures of 140 and 200 °C were both well above all glass transition temperatures.

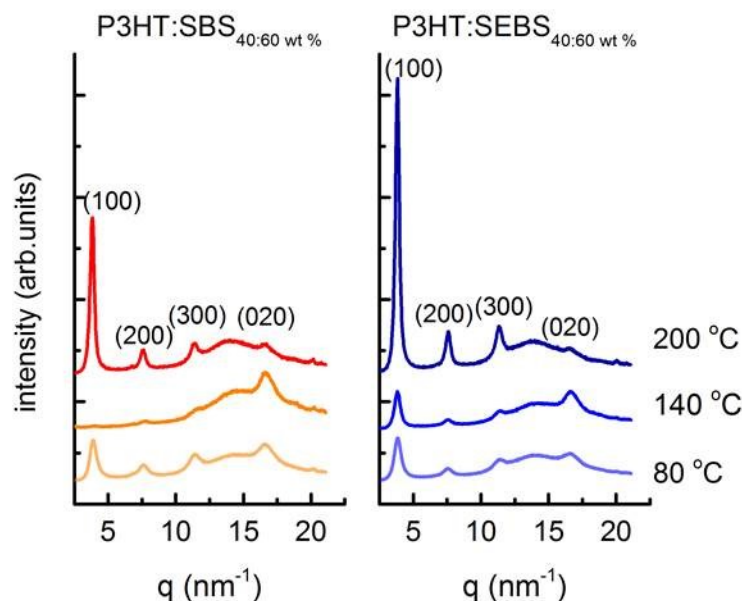


Figure 6.4 Reflection mode X-ray diffractograms of P3HT:SBS and P3HT:SEBS blend films (40:60 semiconductor:insulator wt %) hot pressed at various operating temperatures. The pressure-induced vertical π -stacking depicted by the strong (020) reflections seemed to strongly depend on temperature as well as elastomer component.

The diffractograms of both the P3HT:SBS and P3HT:SEBS blends in Figure 6.4, normalised to the sample volume, revealed large variations in the strength of the (100) and (020) reflections with respect to the various operating temperatures. The (020) reflection, which was apparent under all conditions, suggested an enhancement of vertical π -stacking was obtained regardless of operating temperatures after pressing. The isotropic nature of these films however, varied quite noticeably. In P3HT:SBS blends the (100) reflection was most prominent at both the 80 °C and 200 °C, while moderate operating temperatures of 140 °C resulted in the strongest (020) reflections. Perhaps, the re-orientation of the crystallites was inhibited at temperatures below the glass transition at 80 °C, leading to isotropic structures. Meanwhile 140 °C seemed to provide optimal flow of the semiconductor resulting in a highly anisotropic structure. A further increase in the processing temperature to 200 °C might have induced a significant amount of flow that reduced the shear forces experienced by the solid semiconductor. In P3HT:SEBS blends the alkyl chain reflections were generally stronger than the π -stacking reflections irrespective of operating temperature.

Hot pressing of neat P3HT at high temperatures (>190 °C) has been shown to anneal the samples and increase the crystal sizes, as seen by an increase in the $d_{(100)}$ -spacing.¹¹⁸ These annealing effects were not clearly observed in these samples (see summarised

Table 6.2 Wide-angle X-ray scattering $d_{(hk0)}$ -spacings for P3HT:SBS and P3HT:SEBS blends hot pressed at various operating temperatures (80-200 °C).

temperature (°C)	$d_{(100)}$ (Å)		$d_{(020)}$ (Å)	
	SBS	SEBS	SBS	SEBS
80	16.1	16.5	3.8	3.8
140	16.0	16.5	3.8	3.8
200	16.4	16.4	3.8	3.8

* All semiconductor:insulator blends were 40:60 wt%

$d_{(hk0)}$ -spacings in Table 6.2), where the $d_{(100)}$ -spacing in P3HT:SBS samples increased and decreased slightly in P3HT:SEBS blends. It is possible that longer annealing times are required to observe these changes. Here compression was only applied for five minutes, while the noticeable changes previously reported in the literature in d -spacings were observed only after seven hours.¹¹⁸ Temperature also did not affect the $d_{(020)}$ -spacing.

In order to investigate the influence of temperature on potential enhancement of face-on orientation, the (020) scattering intensity was normalised to the (100) reflection as described above. Figure 6.5 shows the drastic differences in $I_{(020)}/I_{(100)}$ ratio of the various blends and operating temperatures. The sample of P3HT:SBS pressed at 140 °C, with well-characterised predominant face-on orientation and anisotropic charge transport (as discussed in Chapter 5), had a remarkably high $I_{(020)}/I_{(100)}$ ratio. All other operating conditions and blends resulted in much lower scattering ratios. This indicated that in addition to blend composition, operating temperature strongly affected the resulting outcome of preferential orientation of P3HT crystals in the blends.

The differences in obtained anisotropy at various operating conditions indicated that there is a strong need to optimise the hot pressing protocols for each specific condition and blend composition. The strong (020) reflections evident in all binary systems and processing conditions arise from the isotropic nature of the powders that are being pressed. The additional enhancement in face-on orientation as a result of applied pressure however was more complex. The exact nature of these differences would have to be further investigated to build up a complete picture of important structure/processing/property interrelationships for such methods.

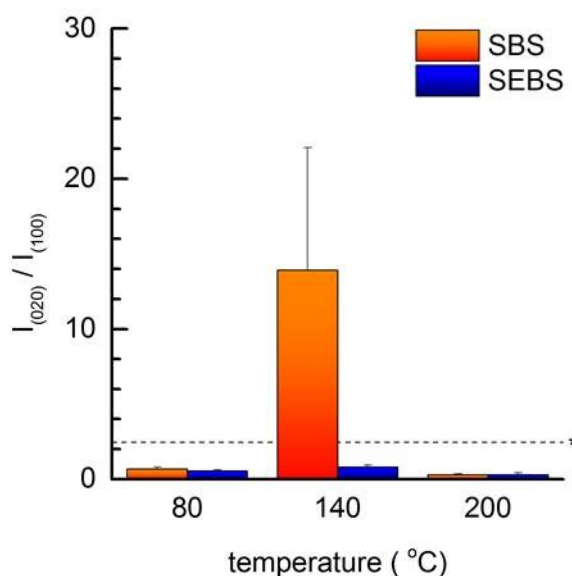


Figure 6.5 Normalised scattering intensities $I_{(020)}/I_{(100)}$ of P3HT:SBS and P3HT:SEBS blends (40:60 semiconductor:insulator wt %) hot pressed at various temperatures. P3HT:SBS blends manufactured at 140 °C, with previously demonstrated high degrees of anisotropy, had a remarkably high intensity ratio. Reference included of a known neat P3HT sample with high degree of face-on orientation and anisotropic charge transport (dashed line, asterisk).⁵⁶

6.2.3 Future characterisations

The above mentioned θ -2 θ scans allowed rapid structural investigation for a wide range of binary compositions and processing protocols. For further analysis of the diffraction patterns it should be mentioned that analysis of the peak intensity (as maximum) is not the conventional means by which to compare semicrystalline materials. More commonly the full-width at half maximum (FWHM) of the diffraction peaks is utilised, and the broadness of the peak is directly related to the crystallite size by the Scherrer formula. This has been readily applied to the well-defined (100) reflections obtained in neat semiconductors such as P3HT.^{133,149,156} However, FWHM peaks can become increasingly cumbersome to deduce for low intensity peaks and in areas where there might be significant overlap, as in the case of the amorphous halos overlapping the (020) reflections in the blend films. This leads to unreliable integration and interpretation of such peaks by conventional Scherrer techniques. Moreover, this method assumes that peak width is only affected by the finite crystal size, which is typically not the case for organic semiconductors that have a large degree of lattice disorder.²³ Herein, the study of crystallite size was not the preliminary aim of the investigations, and uniform crystallite distributions were assumed based on previous

findings for solvent-assisted aggregation of P3HT.^{45,47} Further investigations using rigorous Fourier-Transform peak shape analysis routines, as outlined by Rivnay and co-workers, would be required to support the validity of this assumption.¹⁵⁷ Unlike Scherrer techniques, these methods additionally investigate the cumulative disorder of the system that may arise from impurities, dislocations and chain backbone twisting.

The results herein only serve as preliminary indicators into the possible effects on the degree of vertical π -stacking in solid state pressed films. Additional X-ray based structural characterisations are therefore required for unambiguous proof. For example, grazing incidence X-ray scattering in various directionalities would allow direct comparison of structural information and the anisotropic charge transport measurements. Additionally, the texture and the degree of alignment of crystallites are conventionally investigated by performing azimuthal scans (φ -scans, or so called rocking curves). To this end, a (hkl)-plane reflection of interest is specified and the intensity is recorded as the film is rotated by an angle of φ around the substrate normal. Upon tilting of the substrates it would thereby be possible to detect the degree of π -stacks that are aligned in each respective direction, and whether the crystallites are misoriented.¹⁵⁸ These types of investigations would thus provide additional quantitative reassurance of the preferential alignment in the films. Preliminary studies have been carried out to investigate this, but such investigations are outside of the scope of this thesis. Additional future work is required before drawing conclusions.

6.3 Conclusions

The transferability of the developed solid state pressing protocols to other binary systems was explored using blends of P3HT and cheap commodity polymers that structurally resembled SBS. In previous chapters, it was demonstrated that hot pressing of P3HT:SBS blends generated highly ordered and anisotropic semiconducting architectures with significantly enhanced vertical π -stacking in the freestanding films. Similarly, vertical π -stacking was observed in all other blend systems investigated herein. However, the studies revealed great differences in the degree to which this enhancement occurred depending on both the chemical nature of the binary system as well as on the operating conditions. For instance, small changes in the chemical nature of the insulator in the blends imparted large changes in the degree of anisotropy in the films. Hot pressing of blends comprised of P3HT and the hydrogenated version of SBS, SEBS, for instance were largely isotropic, as were blends of P3HT and polystyrene

polymers, in which the butadiene unit was all together eliminated. Additionally, alterations in the temperature at which the blends were processed further led to changes in the structural anisotropy of the systems. This suggested that solid state pressing as a means to govern the face-on orientation of P3HT crystals is a delicate process that requires optimisation for each specific blend and composition. The studies herein did not elucidate the true mechanism behind these changes and further investigations were recommended and outlined.

7 PATTERNING TECHNIQUES AND BIOELECTRONIC APPLICATIONS

This chapter extends the potential uses of solid state processing methods by augmenting them with facile and versatile patterning techniques. Nano- or micropatterned semiconducting materials hold great promise for a wide range of scientific and industrial applications including optical devices, microfluidics, compact disk replication and bioelectronics to trigger highly specific biological responses.¹⁵⁹ The focus herein is on the latter application. To this end, biologically relevant microgroove surfaces were replicated to generate freestanding tissue engineering platforms.^{99,100} These semiconducting substrates are promising tools by which to study the regeneration of electroactive tissues.¹⁵

More specifically, experiments were conducted studying replication of relief structures on solid state pressed semiconductor (poly(3-hexylthiophene); P3HT), insulator (polystyrene-block-poly(butadiene)-block-polystyrene; SBS) and blend films, discussed in Chapter 5. Micropatterns were obtained via hot embossing at low pressures (2 N cm⁻²) and temperatures above the glass transition of the molding materials. The relief microstructures could be replicated onto surfaces of both SBS and P3HT:SBS blend films, but the investigated protocols proved insufficient in inducing structuring of neat P3HT. The ease of processability in the elastomer containing films was found to be

facilitated by decreased viscosity and reduced stiffness in presence of the insulator, as determined through atomic force microscopy (AFM) force curves.

Microstructured P3HT films, on the other hand, could be generated at moderately high pressures (20 kN cm^{-2}) in a single-step process by augmenting the solid state compression set up with a hard grating mold. The increase in pressure allowed for polymer flow into the cavities of the gratings and the resulting relief structures were uniform over large areas. These films were used for experiments with a cardiac-like cell line, HL-1-6.^{102,160} Preliminary cell studies suggest that the fibronectin coated semiconducting films supported cell adhesion. The cells were further found to be significantly more aligned on groove P3HT surfaces than their flat counter parts. While preliminary, the observations made during this study suggest that these novel solid state pressed substrates are promising for future applications as semiconducting tissue engineering platforms.

7.1 Introduction

7.1.1 Micropatterning techniques

In today's semiconductor industry nano- and micropatterning techniques are common practices. The optimisation of these technologies has spearheaded the downsizing of integrated circuits, making semiconducting technologies highly efficient, low cost and prolific across the globe, as predicted by Gordon Moore.¹⁶¹ The large driving force from the semiconducting industry has led to the development of innovative patterning techniques, which have found wide uses in alternative fields where micropatterning is favourable. Nano- or microstructured material are, for example, useful in optical devices to guide and manipulate light properties,^{162,163} as self-cleaning surfaces^{164,165} and in biology to elicit specific cellular responses.

Lithographic methods have long dominated the microfabrication field,^{166,167} but there are other methods by which to create nano- or microstructured materials including self-assembly processes, hot embossing and molding.^{159,168} These latter, high-throughput and cost-effective processes are for instance suitable for rapid prototyping and large volume manufacture. Scientific and industrial applications of these technologies include micro-optical devices (e.g. lenses, mirrors, waveguides and diffraction gratings),^{169–173} micro-fluidic devices (for lab-on-a-chip, life science analytical and 3D cell culture systems),^{174–176} compact disk replication (CDs and DVDs),¹⁷⁷ security features such as

holograms,¹⁷⁸ and in biology as a means to induce cell alignment and trigger biological responses.^{99,100}

Hot embossing processes are synonymous to nanoimprint lithography (NIL) of thermoplastics. Processes like UV nanoimprint lithography and microcontact printing (μ CP)¹⁷⁹ processes can also be found under the umbrella of NIL technologies, but have slightly different aims and methodologies. Regardless of methodology all of the NIL technologies have been very successful in replicating small features with high aspect ratios. NIL of thermoplastics have resulted in features with as little as 25 nm resolution,¹⁸⁰ and other NIL combinatorial methods have achieved impressive features in the sub-5 nm range.¹⁸¹

The principles of embossing are very simple and straightforward. Dating back centuries, embossing was used to replicate coins, and later on to print text using the Gutenberg press, where not only the ink was transferred to the paper but also relief structures. In industry today hot embossing typically begins with heating a semi-finished product to the processing temperature, i.e. above the glass transition temperature of the material. Isothermal embossing, using a patterned master, is then carried out at a specified pressure and/or velocity. The product is then de-embossed by lowering the temperature while keeping the force constant. The finished product with the new nano- or micropatterned surfaces can finally be removed from the set up.

The mold, or stamp, can be made from a range of materials including metals (nickel), inorganic (silicon) and polymers (either amorphous or semicrystalline in nature depending on the application). Molding materials also vary, but frequently amorphous polymers such as poly(methyl methacrylate) (PMMA), polystyrene and polycarbonates are used to replicate relief structures. Processing these polymers above their glass transitions allows the polymer to flow, conform to the mold and result in high aspect ratio relief structures.¹⁸² It is also possible to emboss relief structures in semicrystalline polymers. This can be achieved at high temperatures above the polymer melt, or in the solid state above the glass transition temperature if the molding polymer is ductile enough.¹⁸³

7.1.2 Uses in bioelectronic applications

As mentioned above there are many potential applications for microstructured materials. One especially attractive area for flexible organic semiconductor films is in the field of bioelectronics. This area encompasses a wide range of interests from sensing of analytes

using organic field effect transistors,⁶³ electrically triggered drug delivery,^{74–79} electrically switchable surfaces,^{184–186} actuators (as artificial muscles or for manipulation of cell behaviour),^{80–83} electronic skin or implantable devices^{7,72,73} to bio-inspired electronics using natural materials.^{187–189} Further, the rich chemistry and versatile processability of conjugated polymers makes these novel materials especially promising as tissue engineering constructs.¹⁹⁰ Brain, heart, muscle and bone are a few examples of electroactive tissues that respond to electrical stimulation.⁸⁴ Various strategies have been developed to investigate the potential benefits of electroactive 2D and 3D architectures for restoring functionality in these tissues.^{85–89} To govern the regeneration of such complex and hierarchical tissues well-designed constructs are required with appropriate biocompatibility or biological activity and mechanical and topological properties.¹⁵

Substantial efforts have been devoted towards exploring mechanically tuneable and patterned substrates, of insulating and semiconducting materials alike, to assess their influence on cellular behaviour.^{191–193} Such approaches are attractive because cells constantly sense or ‘pull’ on their environment, modulating their cellular responses and rebuilding the extracellular matrix (ECM) surrounding them accordingly. The ECM deposited by cells is fundamental for the form, function and health of both tissues as a whole and individual cell behaviour. Cells are connected to the ECM via integrins (receptors) on their membrane, which in turn are linked to the nuclear envelope via the cytoskeleton. The nucleus, which carries the cell’s genetic information, is therefore physically linked to the extracellular environment. Biophysical cues, such as topography and mechanical stresses, can thereby regulate the cell’s structural integrity, functionality and genetic landscape.¹⁹⁴ Likewise, other biological cues and material properties influence the cell behaviour and gene expressions through various complex pathways. Researchers have, for instance, utilised the fact that externally deposited or cell secreted ECM proteins adopt different conformations depending on the redox state of the electroactive material to develop electrically switchable surfaces that can steer stem cell differentiation (towards e.g. the neuronal lineage).^{184,195,196}

There is a great need for tissue engineering strategies, for example, to study the regeneration of cardiac tissues; a tissue that may be irreversibly damaged by cardiovascular diseases, in particular, pathological conditions such as acute myocardial infarction.¹⁹⁷ Due to the low regenerative capacity of the native myocardium alternative methods are currently being investigated to reprogramme other prevalent cell sources,

e.g. fibroblasts, towards the cardiac lineage.¹⁹⁸ Recent studies showed that the efficacy of such reprogramming schemes could greatly be improved by physical cues such as lithographically patterned microgrooves.^{99,100,199} As the cells elongate and align with the grooves, physical forces are exerted on the nuclear membrane that consequently alter the accessibility to the genetic code in the nucleus and thus enhance desired gene expression changes in conjunction with appropriate soluble biological cues.¹⁹⁸ Patterns with groove width, spacing and height dimensions of 10 x 10 x 3 μm have been shown to induce most prominent changes in gene expressions in progenitor cells derived from fibroblasts, but additional studies showed that this behaviour was also encouraged on aligned nanofibrous meshes.⁹⁹ Nanofibrous meshes of conjugated polymers have previously been demonstrated to support both cell adhesion and alignment.²⁰⁰ Alternative means to introduce micropatterns on electroactive substrates include surface wrinkling.²⁰¹ To the best of our knowledge cell alignment on semiconducting substrates with patterned microgrooves have, however, not been demonstrated.

This chapter therefore explores the augmentation of solid state processing protocols previously developed and discussed in Chapters 3 and 4, with hot embossing techniques. This was utilised to generate microgroove patterns, similar to those previously shown to result in advantageous alignment of reprogrammed fibroblast cells.^{99,100} The efficiency of the hot embossing procedures for pressed insulator, semiconductor and their blend films was investigated using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy techniques (AFM). Preliminary cell studies, using a cardiac-like cell line, were carried out to assess the biocompatibility of the novel constructs and their effect on cell alignment. These studies serve to show the potential extension of solid state processed semiconducting films and their blends, as mechanically robust and flexible micropatterned tissue engineering substrates for bioelectronic applications.

7.2 Results and Discussion

7.2.1 Micropatterning

In the first set of experiments, the block copolymer polystyrene-block-poly(butadiene)-block-polystyrene (SBS), poly(3-hexylthiophene) and their blends (with 40:60 semiconductor: insulator wt %) were utilised as model materials. The molding films were obtained by solid state pressing according to protocols previously described in Chapters 3. The sequential hot embossing of the films was carried out at a constant

pressure (2 N cm^{-2}) and at 140°C , a temperature well above the glass transition of all components but below the melting temperature of P3HT. A patterned grating and flat mold of poly(dimethylsiloxane) (PDMS) was utilised for the hot embossing. As detailed in Chapter 3, a PDMS formulation of 5:1 pre-polymer to curing agent by weight was chosen and thermally aged at higher temperatures for a few hours, because it is more resilient to pressures compared to the conventional 10:1 weight ratios. The former shows less than 10 % deformation under pressures of 15 N cm^{-2} , while the latter shows up to $> 60 \%$ deformation at the same pressure.¹⁰¹ Optical micrographs of the stamps (Figure 7.1a-b) are displayed together with hot embossed films with unpatterned flat and patterned microgrooves (Figure 7.1c-h). As seen in these images, the relief microstructures were accurately replicated in the neat insulator (Figure 7.1c-d). The patterns were uniform and defect free over large areas (up to $1.5 \times 1.5 \text{ cm}$). The relief structures were also replicated in the semiconductor:insulator blends (Figure 7.1e-f). In contrast, hot embossing of P3HT did not result in any discernable gratings (Figure 7.1g-h).

A closer look at the patterned films revealed slight differences in the uniformity of the patterns. As shown in the scanning electron microscopy images in Figure 7.2a-b, the SBS relief structures ($10 \mu\text{m}$ widths and spacings) remained well-defined over large areas. The data indicate that relief structures were more accurately reproduced in SBS compared to the blended materials (Figure 7.2c-d), which had an increased appearance of structure defects. Widths were often smaller in blends than in the original master, indicating that the material did not conform completely to the PDMS grating. P3HT did not conform at all during embossing at the specified pressures and temperatures (Figure 7.2e-f).

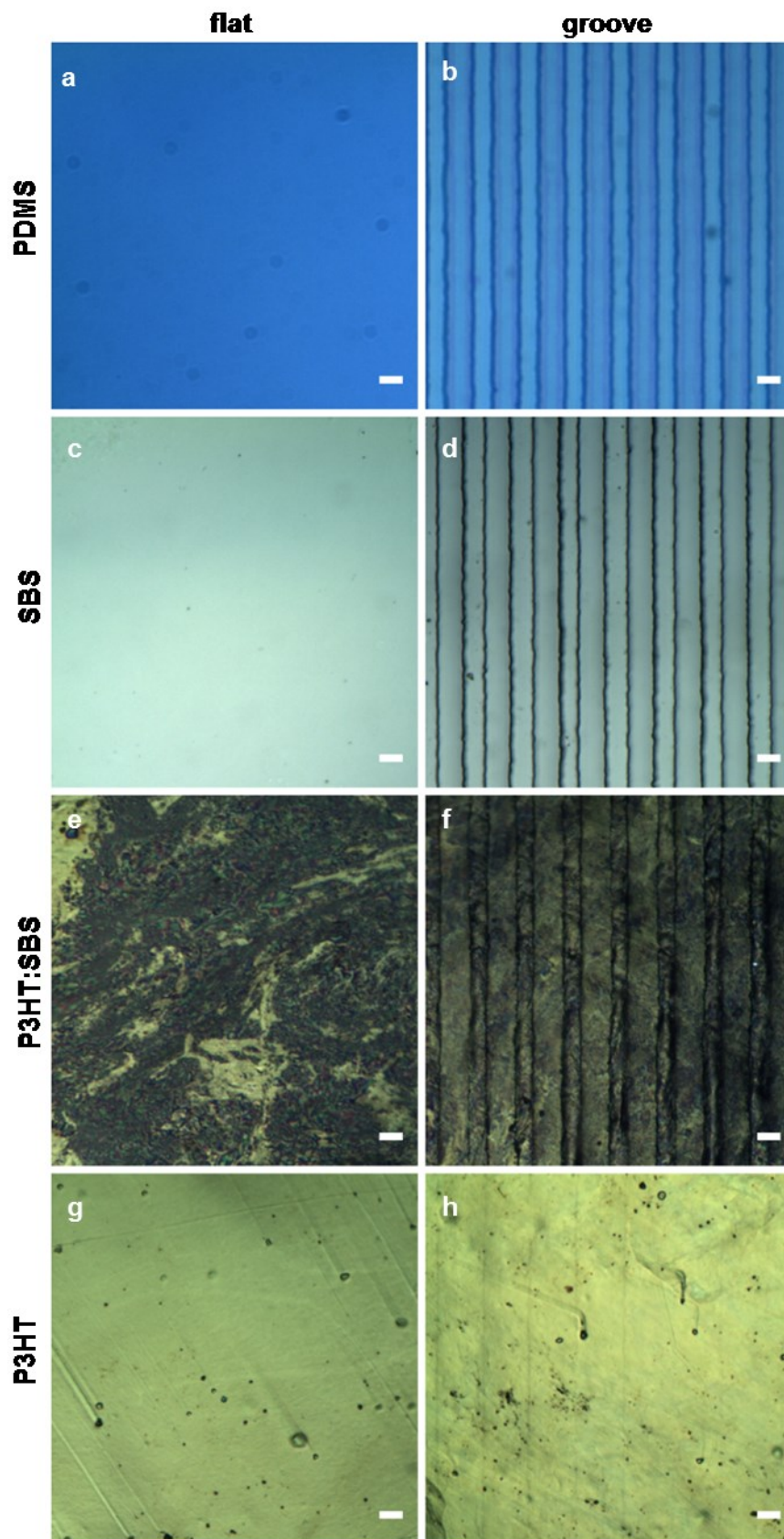


Figure 7.1 Optical micrographs of flat and microgroove (a-b) PDMS stamp utilised to hot emboss (c-d) SBS, (e-f) P3HT:SBS (40:60 wt %) and (g-h) P3HT films. Relief structures were accurately replicated onto: (d) SBS; and (f) P3HT:SBS films; but not onto (h) P3HT. Scale bars are 10 μm .

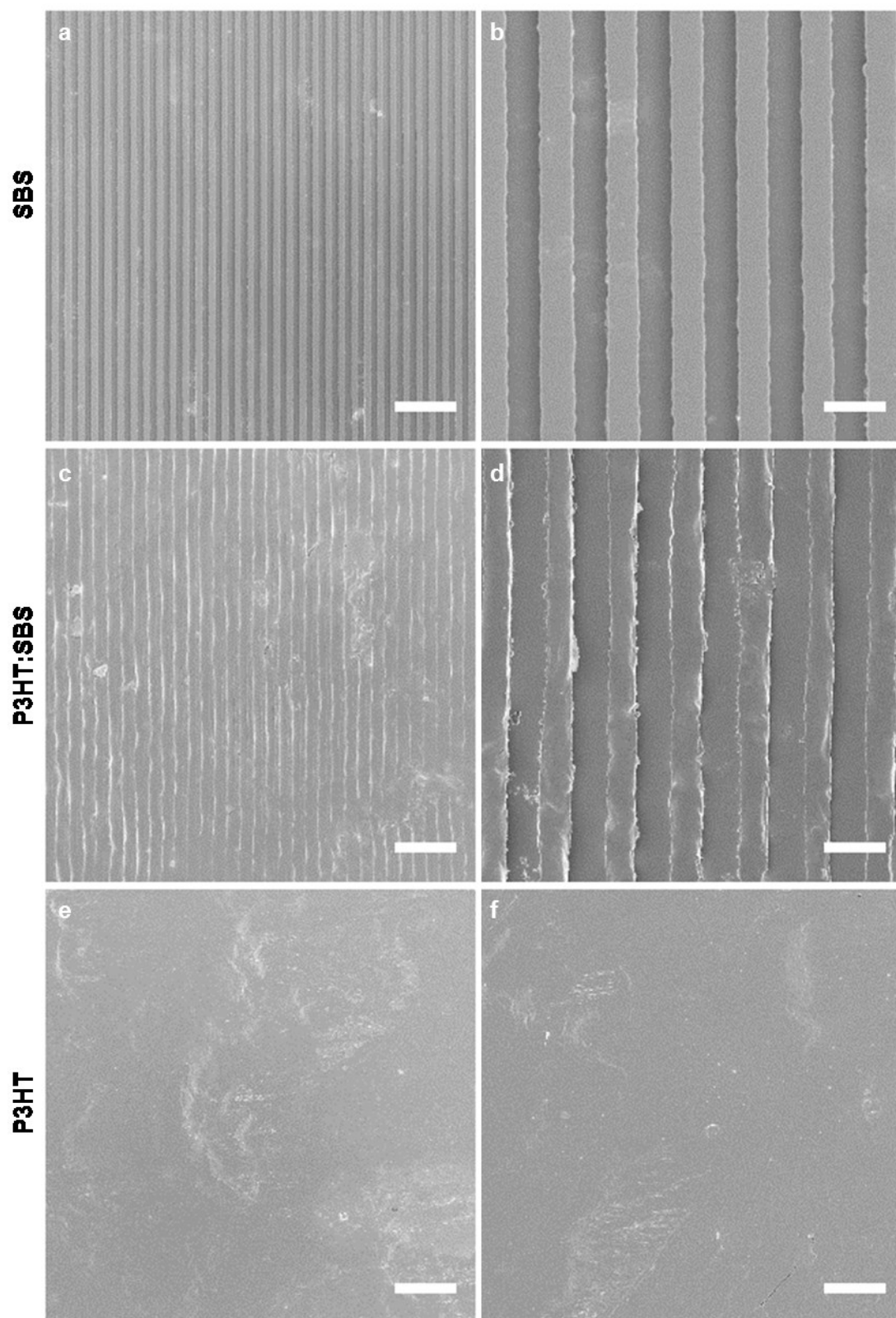


Figure 7.2 Scanning electron microscopy images of successful micropatterning of grooves on (a-b) SBS and (c-d) P3HT:SBS films. Micropatterning via hot embossing at low pressures was unsuccessful on P3HT surfaces (e-f). Scale bars are 100 and 20 μm for left and right panels respectively.

To further investigate the conformity during hot embossing, atomic force microscopy (AFM) measurements were carried out. Using tapping mode AFM the changes in topography and phase across the samples were studied. 3D representations of the topography of both flat and groove hot embossed samples are shown in Figure 7.3. The topography of the flat samples was quite heterogeneous in all samples. The surface root-mean-square (RMS) roughness for the flat samples was 30-40 nm for SBS, 80-120 nm for P3HT:SBS and 70-80 nm for P3HT samples. In the patterned films, the relief structures on SBS films (Figure 7.3b) were prominent in the 3D topography maps, but the grooves were less well-defined in the blend constructs (Figure 7.3d) and non-existent in neat P3HT samples (Figure 7.3f). The line profiles of the topographies in Figure 7.4 show the changes in gratings obtained for the various materials. The topographical data suggested that the PDMS cavities were not completely filled in any of the investigated polymer films. The groove heights in SBS films were only half of their intended dimensions, and even smaller in the blend films ($\text{height}_{\text{SBS}} \approx 4.5 \mu\text{m}$; $\text{height}_{\text{P3HT:SBS}} \approx 3 \mu\text{m}$). The topographies in patterned neat P3HT films were similar to the flat films (Figure 7.4, inset). Additional representative topography and phase images of the neat materials and their blends can be seen in the Appendix in Figure A7.1 and A7.2 respectively.

As evident by these results the microimprint procedures used require further optimisation. Replication of relief structures are facilitated by many factors including: (i) low adhesion between the stamp and sample, (ii) potential shrinkage of the polymer during the release, (iii) temperature and (iv) pressure or velocity of the imprinting. It is therefore important to choose compatible mold and molding materials. Shrinkage can be avoided by releasing first upon complete cooling of the materials, or alternatively by allowing long cavity filling times combined with slow cooling rates. Hot embossing at temperatures well above the glass transition of the thermoplastic is typically recommended to ensure that the molding material has sufficiently reduced viscosity.²⁰²

For polymers like SBS, processing at 140 °C has been reported to be sufficient to replicate relief microstructures with accurate groove widths, while for instance the hydrogenated analogue polystyrene-block-(poly(ethylene-ran-butylene)-block-polystyrene (SEBS) required higher processing temperatures of 200 °C.^{203,204} Similar to the results herein, the authors also noted a change in the height compared to the intended dimensions. This alteration did not seem to be related to any potential changes in the mold compared to the original master.²⁰³ It is likely that the optimal reduced

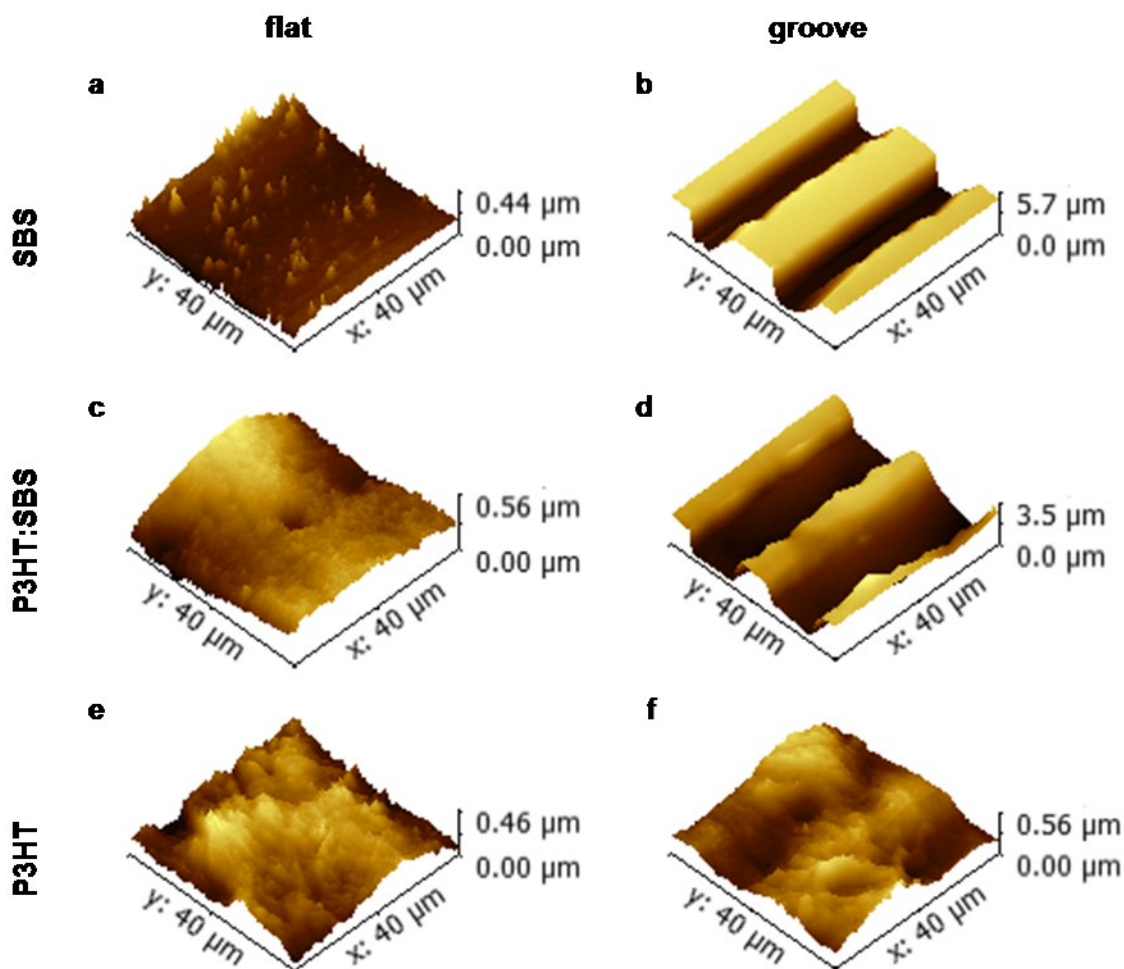


Figure 7.3 3D topography maps of flat (left) and groove (right) patterns from atomic force microscopy measurements of (a-b) SBS, (c-d) P3HT:SBS blends and (e-f) P3HT films.

viscosity was not reached and that the processing proceeded in the viscoelastic regime of the thermoplastic.

Encouragingly, the results herein, imply that the introduction of the insulator into semiconductor blends facilitate the replication of features. Blending is therefore a promising and versatile means to both improve the processability of semiconducting constructs, as pointed out in Chapter 5, as well as enhance microimprint patterning processes. This ease in processability most likely stems from the enhancement in viscoelastic properties of the blend and their reduced stiffness.

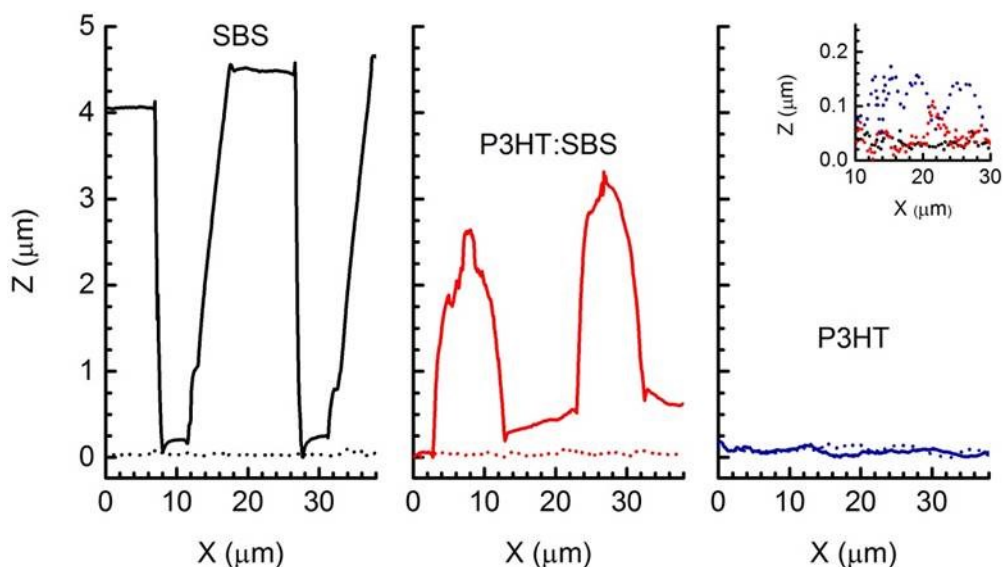


Figure 7.4 AFM topography line profiles of flat (*dashed lines*) and groove patterned (*solid lines*) films of SBS (*left*), P3HT:SBS (*middle*) and P3HT (*right*). Inset depicts a zoomed-in profile of the flat films that were quite inhomogeneous.

In order to investigate the potential reductions in stiffness, AFM force curve measurements were carried out and thereof the Young's moduli of the materials were derived by Dr Amy Gelmi as detailed in Chapter 3. Both flat and microgroove substrates were examined at areas of interest based on the obtained phase images (Figure 7.5). P3HT was found to be significantly stiffer than the neat insulator as well as the semiconductor:insulator blend. This was evidenced by the reduced Young's modulus in flat samples with increased insulator content (Figure 7.5a).

From the studies, it was further observed in the microgroove patterned SBS samples that specific regions, which displayed large phase shifts, were accompanied by clear differences in stiffness (Figure 7.5b). The top parts of the grooves showed uniform topographies and small phase shifts. The SBS material at the groove bottom meanwhile had large phase shifts and was less stiff and sticky, making the imaging of these regions difficult. In contrast, the Young's modulus in the micropatterned blend films

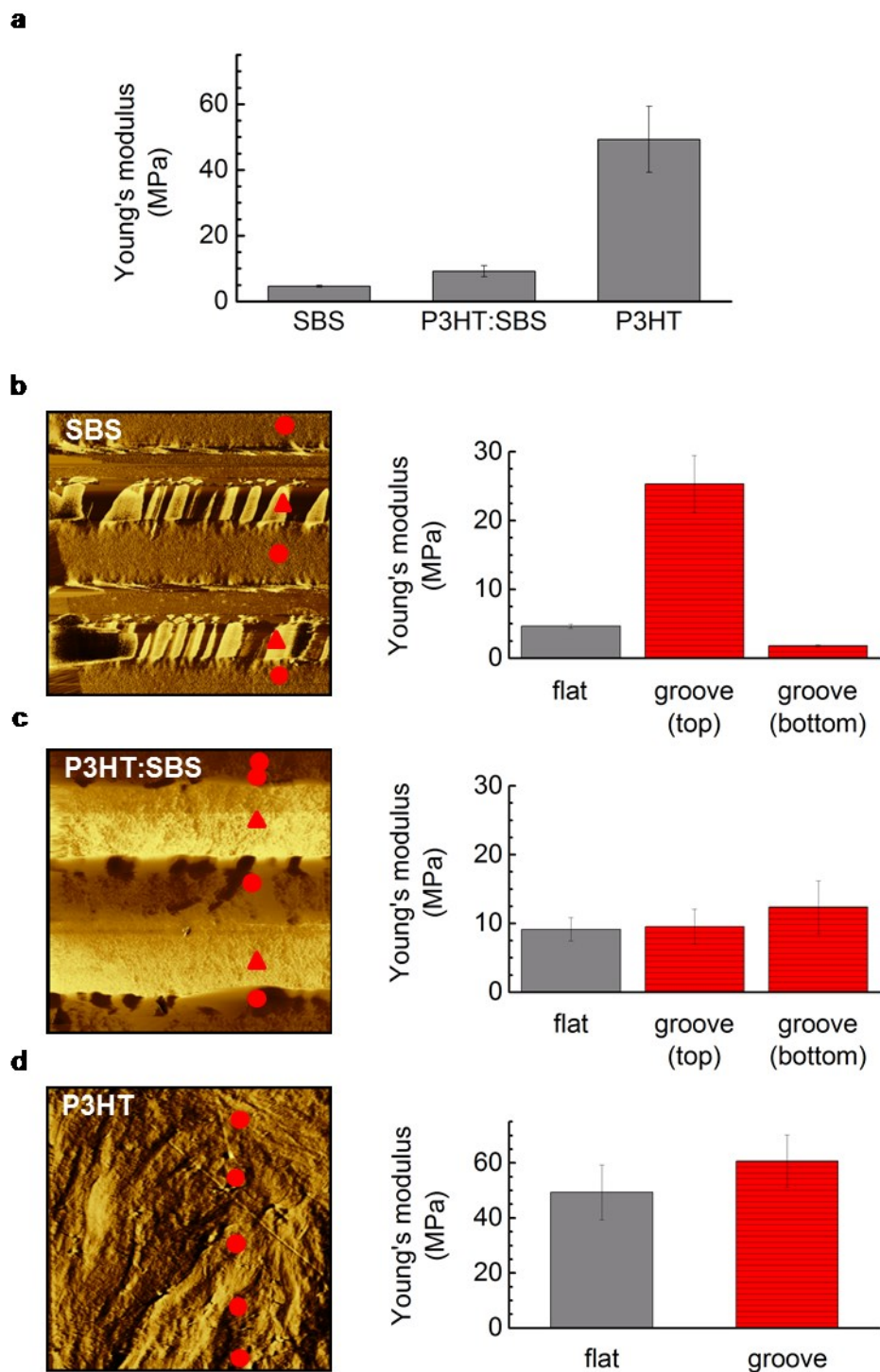


Figure 7.5 Young's moduli of (a) flat SBS, P3HT:SBS_{40:60 wt%} and P3HT films. Moduli were greatly reduced upon introduction of the insulator SBS. The moduli were derived from AFM force-curve measurements. Phase images (left) of (b) SBS, (c) P3HT:SBS_{40:60 wt%} and (d) P3HT mapping force-curve areas at the top (circles) and bottom (triangles) of the grooves that corresponded to different Young's moduli (right). As no discernable features were found in P3HT samples all areas were treated the same.

(Figure 7.5c) remained constant within experimental errors. The groove bottom regions were homogeneous, in terms of both phase and topography, and the small features observed in phase images on the top parts of the grooves could not be related to any major changes in stiffness. From this it was possible to conclude that the solid state pressing and hot embossing did not impart any major phase separation of the binary components. As micropatterning of neat P3HT films did not result in any discernable features the force-curves of all areas were treated equally. There was no significant difference in the Young's modulus between flat or 'grooved' P3HT samples.

Neat organic semiconductors are generally hard materials and it has been shown that moderately high pressures of $20\text{--}30\text{ kN cm}^{-2}$ are required to induce polymer flow in the solid state.¹⁰³ The applied pressure during hot embossing of 2 N cm^{-2} , (using a considerably soft stamp like PDMS) may not therefore be sufficient to induce polymer flow. The chosen pressure resilient PDMS formulation can however only withstand pressures up to 15 N cm^{-2} without significant deformation occurring.¹⁰¹ Increasing the pressure further will lead to deformation and breakage of the stamp rather than cause the semiconductor polymer to flow into the patterned cavities.

In order to investigate the effects of pressure during embossing of relief structures in hard semiconductors, a hard epoxy resin mold was generated with similar dimensions to the PDMS mold (see Figure A7.3). The epoxy stamp was utilised in conjunction with the solid state pressing of P3HT at room temperature and at pressures of 20 kN cm^{-2} . Gratifyingly, microgrooves could be replicated onto solid state pressed semiconductor films in a single-step process. Scanning electrode microscopy images in Figure 7.6 of the flat and groove patterned P3HT films showed that the relief structures were uniform over large areas. These micropatterning processes with hard stamps needs to be further investigated. The schemes require optimisation and verification of groove dimensions. Additionally, it is of great interest to study the molecular orientation of P3HT both in the bulk and on the surface of the novel grated substrates. Nanogroove imprint lithography has, for instance, been reported to confine semiconductors and consequently induce anisotropic orientation of the crystals.⁵⁹ These observations are thus indicative of new possibilities for generating constructs that combine anisotropic charge transport

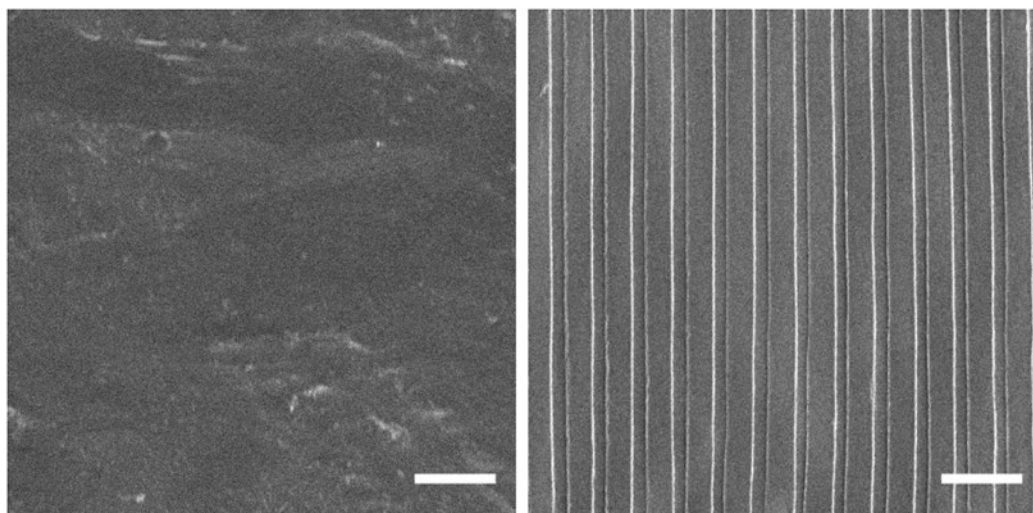


Figure 7.6 SEM images of unpatterned (left) and patterned (right) P3HT films using a hard epoxy mold during compression. Scale bars are 50 μm .

properties originating from the solid state processing, as demonstrated in Chapters 4 and 5, with micropatterned surfaces that carry other functionalities such as biologically relevant cues.^{99,100}

7.2.2 Bioelectronic applications

The biological moieties (microgrooves) investigated herein, are especially promising for the *de novo* generation and maturation of cardiomyocytes from adult heart-derived progenitor cells.¹⁰⁰ The use of microgroove electroactive substrates, such as P3HT, can potentially be beneficial in further improving the efficacy of such reprogramming schemes or the maturation of cardiomyocytes by enabling important excitation-contraction couplings.⁸⁶ The first crucial aspect in developing new materials for tissue engineering is to establish if such substrates are compatible with the intended cell types and cell culture practices. To this end, preliminary cell studies were conducted to assess the biocompatibility and cell morphology on flat and groove patterned semiconducting films. The immortalised cardiac-like cell line, HL-1-6, was utilised as a model system as it replicates certain electrophysiological aspects of cardiac-like tissues. HL-1-6 cells are for example able to contract in culture and carries many important cardiac-like markers.^{102,160}

It should be noted that the studies only had 3 sample replicas and one to two experimental replicates. These preliminary results should therefore be considered with

caution and are meant to establish a baseline for whether or not to proceed with further in-depth studies with cells cultured on these novel constructs.

Flat and microgroove patterned P3HT films were manufactured as previously described and coated with fibronectin prior to culture with HL-1-6 cells by 1 hour incubation. Coating substrates with adhesive proteins, such as fibronectin or laminin, is common practice when working with organic semiconductors, as cells typically do not adhere well to non-coated conjugated polymers.¹⁸⁴ Cells were simultaneously cultured on standard tissue culture plastic (TCP) as a positive control substrate. The metabolic activity of HL-1-6 cells on the P3HT films and TCP was assessed by an Alamar blue assay, as shown in Figure 7.7, after 1 and 3 days of culture. The metabolic activity of cells on the P3HT films (both flat and groove micropatterned) was similar to that on TCP at both time points. Overall there was an increase in metabolic activity after 3 days in culture. The reason for this increase in metabolic activity would need to be further investigated and possibly correlated to an increase in cell numbers.

In order to evaluate the cell morphology on the fibronectin coated flat and groove patterned P3HT films, cells were fixed with formalin after 1 and 3 days in culture. The cells were permeabilised, stained for cardiac troponin and cell nuclei (DAPI) and

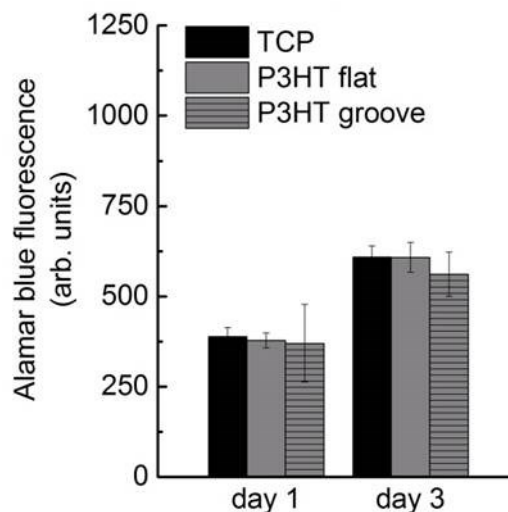


Figure 7.7 Metabolic activity of cardiac-like cells (HL-1-6) cultured on tissue culture plastic (TCP), and flat and groove patterned P3HT films, pre-coated with fibronectin over a 3 day period. There was no significant difference between P3HT substrates and TCP, as measured by Alamar blue assay.

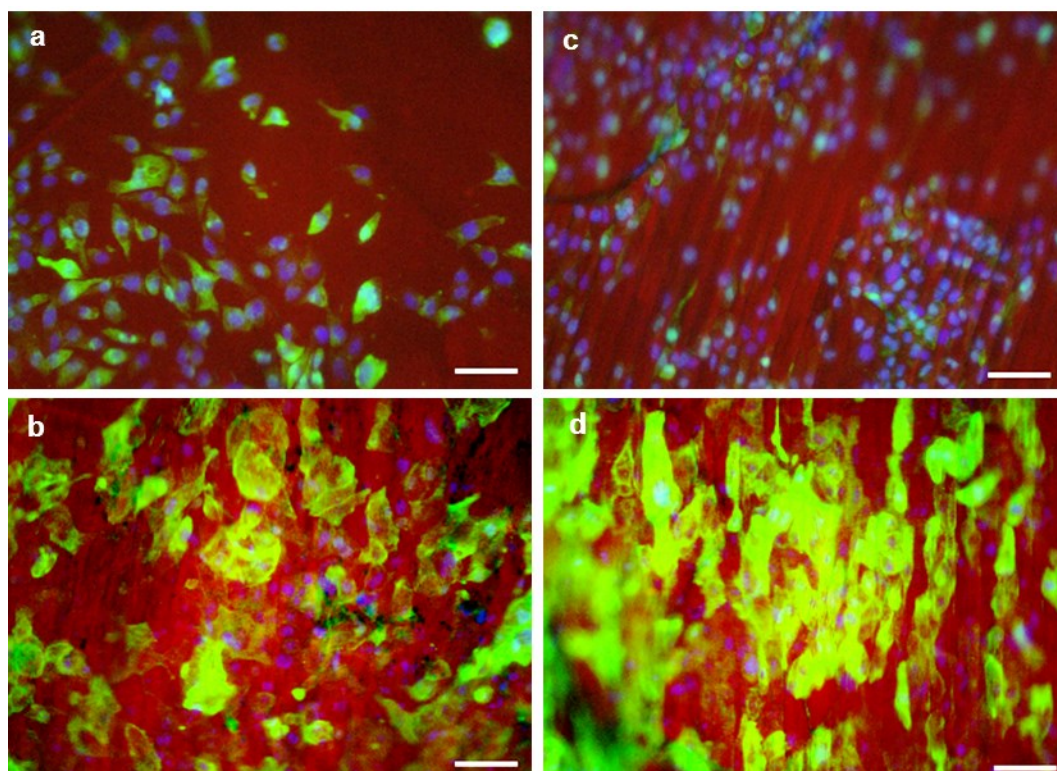


Figure 7.8 Confocal microscopy merged images show HL-1-6 cells on (a-b) flat versus (c-d) patterned P3HT films at day 1 and 3 respectively (top to bottom; scale bars = 50 μm). Cells were stained for cardiac troponin (green), and cell nuclei were stained with DAPI (blue). Autofluorescent sample background shown in red. Cell alignment was improved on micro-grooved P3HT films and cells were significantly elongated after only 3 days.

imaged using confocal microscopy as detailed in Chapter 3. Cardiac troponin is an integral protein for muscle contraction, whereas DAPI is a fluorescent stain that binds strongly to components in DNA. Combined these fluorophores constitute clear markers for the morphology of HL-1-6 cells, i.e. the cytoskeleton and the cell nuclei carrying the DNA. The P3HT substrates were autofluorescent and the grooves could be easily be visualised together with the cells. As seen in Figure 7.8a-b, the cells were attached to the flat films at day 1, and were more spread out and slightly hypertrophic (enlarged) at day 3. On the microgroove P3HT films cells became significantly elongated and hypertrophic after 3 days in culture. Cells on the groove substrates were remarkably aligned with the patterned features. The enlargement of cardiac-like cells can be indicative of cell growth in differentiated cells, but may also be an indicator of overload of stresses exerted on the cell.²⁰⁵ The results and cause of the hypertrophic behaviour therefore need to be further investigated and confirmed by more experimental replicates. However, the unaltered metabolic activity and the high degree of cell alignment on groove P3HT films make these constructs seem promising for future investigations.

Further cell studies on patterned blend constructs previously mentioned are currently under investigation, but are outside of the scope of this thesis.

These encouraging observations suggest that cell culture with cardiac-like cells is supported on semiconducting films of P3HT, and that hot embossed microgroove patterns can aid in their cell alignment. P3HT substrates have already been extensively reported to support neuronal cell cultures.^{206,207} In these reports P3HT functions as an optically active material that can absorb visible light pulses and thereby trigger action potentials in neuron networks. A promising application of such optoelectronic devices is to replace damaged light sensitive tissues in the eye as artificial retinas.²⁰⁸ In fact artificial retinas composed solely of P3HT has been reported to successfully restore light sensitivity in blind rats.²⁰⁹ Utilising similar principles of optoelectronic activation it may also be possible to induce responses in other electroactive tissues. These patterned semiconducting substrates can potentially be utilised to study changes in the epigenetic landscape as a result of biophysical cues in conjunction with further optoelectronic stimuli.

7.3 Conclusions

This chapter explored hot embossing techniques to generate biologically relevant microgroove patterned semiconducting substrates. Micropatterning was carried out by stamping solid state pressed films at temperatures above the glass transition of the molding materials using grated PDMS molds. Such processes were found to work well with insulating materials, such as the investigated block copolymer SBS, and resulted in uniform gratings across large areas. The introduction of the same insulator into blends with the semiconductor P3HT seemed to also facilitate imprinting of relief structures, but further optimisation of hot embossing protocols were encouraged to improve upon the accuracy of the replication. On the other hand, the benign hot embossing protocols were proven to be unable to reproduce microstructures onto the surfaces of solid state pressed P3HT films. The ease of hot embossing of SBS and P3HT:SBS blend films, in contrast to P3HT, was attributed to the reduced stiffness of the previous neat and blend materials, as shown by AFM force curves and derived Young's moduli measurements. These measurements further indicated that major phase separations of the binary components did not occur during the hot embossing. Blending was thereby shown to be useful means to facilitate improved processability both during solid state pressing, as discussed in Chapter 5, and during subsequent hot embossing procedures.

To replicate microgrooves in neat P3HT, the use of a hard epoxy mold was explored. The results showed that relief structures could indeed be generated in a novel single-step process during the solid state compression of the organic semiconductor. These films were utilised for cell studies using a cardiac-like cell line. The preliminary cell studies indicated that the novel constructs, coated with fibronectin, supported cell adhesion and further showed a high degree of cell alignment on the patterned films after 3 days in culture. The metabolic activity of the cells on P3HT films were found to be comparable to those grown on standard tissue culture plastic substrates. These studies indicate that microgroove P3HT films are promising tools for further investigations into the uses and effects of semiconducting substrates as tissue engineering platforms.

8 CONCLUSIONS AND FUTURE WORK

8.1 Motivation

To advance the field of organic electronics it is crucial to deepen our understanding of important structure/processing/property interrelationships in these novel and exciting materials. Addressing these fundamental questions enables employment of developed schemes to improve the device performances for a wide range of applications in a logical manner. This area of research is becoming increasingly important as many organic based electronic technologies progress towards commercialisation.¹ Unfortunately, many of the established structure-property relationships of organic semiconductors are only understood in the framework of processing methods that possess inherent flaws when transitioning from laboratory to large-scale fabrication (lab-to-fab) settings. For example, most of the well-characterised organic electronic devices are still manufactured by costly and time-consuming technologies, e.g. spin-coating. The promise of high-throughput, low-cost and large area manufacture of flexible organic electronics is thereby lost through the utilisation of such batch-to-batch processes. Meanwhile, roll-to-roll processes offer improved capabilities to reach these aims, but the intrinsic low viscosity of organic semiconductors greatly reduces the processing window of these materials.¹⁹ Alternative high-throughput and environmentally friendly processing methods are already commonplace in industry, including compression and extrusion molding (i.e. pressing of commodity polymers in the melt or solid state). To date, reports in the literature of using such methods to

process organic semiconductors at industrially relevant temperatures (i.e. in the solid state) are however surprisingly few, in-light of the demonstrated beneficial outcomes that such schemes have on the structure and performance of organic semiconductors.^{103,116,117,135} With limited research conducted in this area there is a strong necessity to further optimise compression techniques for organic electronics. These types of investigations will be useful to shine light on key structure-property relations in organic semiconductors within the framework of solid state processing. Moreover, compression molding of commodity polymers are often in industry augmented by facile patterning techniques, such as hot embossing, to generate micropatterned surfaces.¹⁵⁹ These processes therefore have great potential as means to both manufacture novel semiconducting architectures as well as replicate topographical features onto their surfaces. Demonstrating such novel applications of solid state pressing of this class of materials can broaden the potential uses of such processes and aid in the progression towards commercialisations.

8.2 Solid state processing

Solid state processing has previously been reported to result in mechanically robust freestanding films of a broad range of organic semiconductors with a high degree of molecular anisotropy. With regards to the model semiconductor poly(3-hexylthiophene) (P3HT), such enhancements of vertical π -stacking resulted in high charge carrier mobilities, μ_{TOF} , of $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (as determined by time-of-flight photoconductivity measurements), which was three orders of magnitude higher than for solution-processed material of the same molecular weight.¹⁰³ Molecular anisotropy has further been demonstrated when extruding P3HT in the solid state to form freestanding ribbons and rods, but the charge carrier mobility in these constructs was never investigated.^{116,117} Interestingly, the molecular order formed during the various solid state processes seemed to be highly dependent on the directionality of the material flow and shear stresses felt upon the extrudate. Remarkably, further optimisation of such industrially relevant schemes has not been carried out, despite their great potential as means to form anisotropic semiconducting architectures.

As the polymer remains in its solid state during the compression it is logical to assume that the processing history remains intact during the processes. The key hypothesis herein was therefore that the microstructure of a model semiconductor, such as P3HT, could be manipulated and optimised via solution-processing methods prior to the solid

state pressing. It was further conjectured that the anisotropic structuring that results from solid state pressing would give rise to anisotropic charge transport properties in these films, which had not yet been proven.

In order to investigate these hypotheses, solution-processing methods were employed to control the microstructure of the semiconductor in its initial powder state and investigate the effect this had on the subsequent solid state pressing (Chapter 4). The solution-processing protocols were carefully chosen to compare highly crystalline (with a large degree of disorder) and less crystalline (with a high degree of short-range order) neat semiconductor powders using chloroform and chloroform/ethyl acetate solvent mixtures respectively.^{45,47} The differences between the two chosen solution-processing methods were demonstrated by optical and thermoanalytical techniques. Further investigations into the solid state compression of the solution-processed powders demonstrated that the polymer processing history was in fact maintained throughout the pressing at temperatures below its melt. Wide-angle X-ray diffraction studies also revealed that the enhanced vertical π -stacking was obtained in the solid state pressed films, independently of prior solution-processing. Hence, microstructure modulation was enabled without any detrimental effects on the proceeding solid state pressing. Moreover, investigations into the charge carrier mobility by time-of-flight photoconductivity measurements revealed a median charge carrier mobility of $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the through-plane direction, which was slightly higher than previous reports in literature for neat semiconductors without well-defined short-range order in the same directionality.¹⁰³ More interestingly, using different device configurations it was possible to deduce that the median in-plane charge carrier mobility was further increased by an order of magnitude ($\mu_{\text{TOF}} 8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$); thus verifying for the first time the high degree of anisotropic charge transport in the solid state pressed films. The charge transport anisotropy was attributed to the molecular anisotropy arising from the solid state compression and the inherent anisotropic charge transport nature of P3HT.⁵⁴⁻⁵⁶ The use of a channel die herein, additionally, lead to in-plane charge transport anisotropy as the chain alignment was enhanced along the polymer flow direction due to constrictions at the channel walls.

The highest mobility in P3HT films reported in the literature is $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹²³ However, it needs to be noted that this was obtained through space-charge-limited current measurements, which is not directly related to time-of-flight mobilities. More importantly, this reported long-range mobility was measured in significantly thinner

films ($< 1 \mu\text{m}$) compared to the relatively thick solid state pressed films herein ($125 \mu\text{m}$). The results presented in this thesis thereby confirmed that that solid state processing is a highly useful and promising method to generate highly ordered and anisotropic semiconducting architectures with enhanced long-range charge transport. Additionally, these results further supports previous indicators of that the nature of the anisotropy is dictated by the set up utilised in the process.

In order to further demonstrate the versatility of compression schemes, studies were conducted investigating the solid state processing of semiconductor:insulator polymer blends comprised of P3HT and the elastomer SBS (Chapter 5). Blending of semiconductor:insulator polymers is a versatile strategy by which to introduce new features and functionalities into semiconducting architectures without necessarily hindering their electrical conduction pathways.¹⁹ In the literature there has only been one report of P3HT and insulator blends processed via compression routes, with a resulting mobility of $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (derived from field effect transistor measurements) for blends with 20 wt % P3HT.¹³⁶ However, the reported work did not assess the molecular ordering of the semiconductor, which is one of the major advantages of this processing route. Herein, demonstrations showed that introduction of an elastomer not only improved processability in the solid state, but also enhanced the mechanical properties and flexibility of the resulting films. Employment of the previously mentioned solution-processing methods prior to the pressing ensured that the semiconductor remained aggregated with a high degree of short-range order. The charge carrier mobility was thereby impressive in both neat and blend semiconductor pressed films. The mobility for blends with 60 to 40 wt% P3HT was 3×10^{-2} and $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. The decrease in mobility compared to the neat semiconductor could be explained by simple percolation rationale. Furthermore, the reported time-of-flight mobility for these novel constructs were, to the best of our knowledge, the highest reported for P3HT semiconductor:insulator blends, previously reported μ_{TOF} for a P3HT:insulator blend $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶⁵ It was noted that it might be possible to further enhance the charge transport pathways in blend systems by improving the semiconductor aggregate interconnectivity (via longer solution-processing times). The preferential orientation induced by the pressing was further maintained in blend systems and also resulted in highly anisotropic charge transport. As such, solid state processing of semiconductor blend systems has great potential to extend the functionalities of these novel constructs while retaining important key outcomes such as anisotropy.

Studies were carried out investigating the transferability of the solid state processing schemes to other blend systems (Chapter 6), including thermoplastic insulators such as the SBS hydrogenated analogue SEBS, and atactic/amorphous and isotactic/semicrystalline polystyrene (a-PS and i-PS). These studies revealed that vertical π -stacking of the semiconductor P3HT was observed in all blend films. However, the degree of anisotropy varied strongly depending on both the blend composition and chosen processing parameters such as operating temperature. These results suggest that the use of solid state pressing as a means to generate anisotropic constructs may need further optimisation when processing various blends. Additional structural characterisation techniques, such as grazing incidence X-ray scattering and rocking curves, were suggested that can further probe the texture in these films.

8.3 Outlook

These flexible, freestanding semiconducting films can be envisioned as excellent candidates for the regeneration of electroresponsive biological tissues and as regenerative platforms. There is a great need for such strategies, for example, to study the regeneration of cardiac tissues; a tissue that may be irreversibly damaged by cardiovascular diseases and pathologies, such as acute myocardial infarction.¹⁹⁷ Due to the low regenerative capacity of the native myocardium alternative methods are currently being investigated to reprogramme other prevalent cell sources, e.g. fibroblasts, towards the cardiac lineage.¹⁹⁸ Recent studies showed that the efficacy of such reprogramming schemes could be greatly improved by physical cues such as lithographically patterned microgrooves.^{99,100} Reprogramming and maturation strategies aimed at recapitulating healthy electroactive tissues can potentially be further improved by utilisation of electroactive substrates.

Therefore the schemes herein were extended to incorporate topographical cues (Chapter 7), onto solid state processed films, via single-step micropatterning techniques or subsequent hot embossing techniques in neat and blend materials.⁹⁹ Preliminary cell studies, using a cardiac-like cell line, revealed that fibronectin coated semiconducting substrates supported cell adhesion and that the metabolic activity of the cells on these substrates were comparable to those on control substrates. Furthermore, cells were significantly more aligned on the microgroove patterned films compared to flat ones. These novel optoelectronic constructs may therefore be further studied, firstly using appropriate progenitor cells and reprogramming cocktails, and secondly in conjunction

with optical activation methods, such as those described by Ghezzi and co-workers to potentially trigger electrical responses.^{100,208}

Furthermore, it would be of great interest to study the potential mechanical anisotropy in these novel constructs. The structural and charge carrier mobility investigations indicated a large degree of anisotropy in these films, both when comparing the through-plane as well as in-plane anisotropy of the semiconductor in various directions. The result of this anisotropy was attributed to the use of a channel die during solid state pressing, which constricts the polymer flow at the channel walls, aligns polymer chains along the long axis of the die and may result in mechanical anisotropy.^{104,148} Dual mechanical and charge transport anisotropy is advantageous for tissue engineering applications where mimicry of the highly hierarchical and anisotropic native tissue environment (e.g. the myocardium) is a key element to improve tissue regeneration.²¹⁰ One may envisage that future studies into these tunable anisotropic constructs might aid in the understanding of possible synergistic effects of mechanical, topographical and semiconducting properties on the reprogramming and maturation of electroresponsive cells into healthy tissues.

Solid state processing can also be utilised to manufacture flexible active layers for other device applications. Such uses were outside of the scope of this thesis, but applications including artificial skin and retinas, sensors and stretchable displays can also be envisioned.^{207–209,211–216}

In summary, this thesis demonstrate that solid state processing of neat organic semiconductors and their blends is a versatile and facile avenue to generate highly structured semiconducting architectures with potential application to bioelectronics.

9 REFERENCES

1. Das, R. & Harrop, P. Printed, organic & flexible electronics forecasts, players & opportunities 2016-2026. *IDTechEx* at <www.idtechex.com>
2. Malliaras, G. G. Organic bioelectronics: A new era for organic electronics. *Biochim. Biophys. Acta* **1830**, 4286–4287 (2013).
3. Burroughes, J. H. *et al.* Light-emitting diodes based on conjugated polymers. *Nature* **347**, 539–541 (1990).
4. Buckley, A. *Organic light-emitting diodes: Materials, devices and applications*. (Woodhead Publishing Ltd., 2013).
5. Arias, A. C., MacKenzie, J. D., McCulloch, I., Rivnay, J. & Salleo, A. Materials and applications for large area electronics: Solution-based approaches. *Chem. Rev.* **110**, 3–24 (2010).
6. Klauk, H. *Organic electronics: Materials, manufacturing and applications*. (Wiley-VCH, 2006).
7. Kaltenbrunner, M. *et al.* An ultra-lightweight design for imperceptible plastic electronics. *Nature* **499**, 458–63 (2013).
8. Stavrinidou, E. *et al.* Electronic plants. *Sci. Adv.* **1**, 1–8 (2015).
9. Berggren, M. & Richter Dahlfors, A. Organic bioelectronics. *Adv. Mater.* **19**, 3201–3213 (2007).
10. Owens, R. & Malliaras, G. Organic electronics at the interface with biology. *MRS Bull.* **35**, 449–456 (2010).

11. Yuan, Y. *et al.* Ultra-high mobility transparent organic thin film transistors grown by an off-centre spin-coating method. *Nat. Commun.* **5**, 3005 (2014).
12. Tsutsui, Y. *et al.* Unraveling unprecedented charge carrier mobility through structure property relationship of four isomers of didodecyl[1]benzothieno[3,2-b][1]benzothiophene. *Adv. Mater.* 7106–7114 (2016).
13. Hasegawa, T. & Takeya, J. Organic field-effect transistors using single crystals. *Sci. Technol. Adv. Mater.* **10**, 24314 (2009).
14. Treat, N. D. & Chabinyc, M. L. Phase separation in bulk heterojunctions of semiconducting polymers and fullerenes for photovoltaics. *Annu. Rev. Phys. Chem.* **65**, 59–81 (2014).
15. Hardy, J. G., Lee, J. Y. & Schmidt, C. E. Biomimetic conducting polymer-based tissue scaffolds. *Curr. Opin. Biotechnol.* **24**, 1–8 (2013).
16. Hamilton, R., Heeney, M., Anthopoulos, T. & McCulloch, I. in *Organic electronics: Materials, processing, devices and applications* (ed. So, F.) 393–425 (CRC Press, 2010).
17. Tsao, H. N. *et al.* Ultrahigh mobility in polymer field-effect transistors by design. *J. Am. Chem. Soc.* **133**, 2605–2612 (2011).
18. Bannock, J. H. *et al.* Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Adv. Funct. Mater.* **23**, 2123–2129 (2013).
19. Scaccabarozzi, A. D. & Stingelin, N. Semiconducting:insulating polymer blends for optoelectronic applications—a review of recent advances. *J. Mater. Chem. A* **2**, 10818 (2014).
20. Kline, R. J. Morphology and charge transport in conjugated polymers. *J. Macromol. Sci. Phys.* **46**, 27 (2006).
21. Brandão, L., Viana, J., Bucknall, D. G. & Bernardo, G. Solventless processing of conjugated polymers - A review. *Synth. Met.* **197**, 23–33 (2014).
22. Treat, N. D., Westacott, P. & Stingelin, N. The power of materials science tools for gaining insights into organic semiconductors. *Annu. Rev. Mater. Res.* **45**, 459–90 (2015).
23. Rivnay, J., Mannsfeld, S. C. B., Miller, C. E., Salleo, A. & Toney, M. F.

- Quantitative determination of organic semiconductor microstructure from the molecular to device scale. *Chem. Rev.* **112**, 5488–5519 (2012).
24. Su, W. P., Schrieffer, J. R. & Heeger, A. J. Solitons in polyacetylene. *Phys. Rev. Lett.* **42**, 1698–1701 (1979).
 25. Hadziioannou, G. & van Hutten, P. F. *Semiconducting polymers: Chemistry, physics and engineering*. (Wiley-VCH, 2005).
 26. Heeger, A. J. Semiconducting and metallic polymers: The fourth generation of polymeric materials (Nobel Lecture). *Angew. Chemie Int. Ed.* **40**, 2591–2611 (2001).
 27. Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J. & Shirakawa, H. Electrical-conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39**, 1098–1101 (1977).
 28. Ziemelis, K. E. *et al.* Optical spectroscopy of field-induced charge in poly(3-hexyl thienylene) metal-insulator-semiconductor structures: Evidence for polarons. *Phys. Rev. Lett.* **66**, 2231–2234 (1991).
 29. Rauscher, U., Bäessler, H., Bradley, D. D. C. & Hennecke, M. Exciton versus band description of the absorption and luminescence spectra in poly(p-phenylenevinylene). *Phys. Rev. B* **42**, 9830–9836 (1990).
 30. Brinkmann, M. Structure and morphology control in thin films of regioregular poly(3-hexylthiophene). *J. Polym. Sci. B. Polym. Phys.* **49**, 1218–1233 (2011).
 31. Virkar, A. a, Mannsfeld, S., Bao, Z. & Stingelin, N. Organic semiconductor growth and morphology considerations for organic thin-film transistors. *Adv. Mater.* **22**, 3857–75 (2010).
 32. Cui, C. X. & Kertesz, M. Two helical conformations of polythiophene, polypyrrole, and their derivatives. *Phys. Rev. B* **40**, 9661–9670 (1989).
 33. Kline, R. J. *et al.* Critical role of side-chain attachment density on the order and device performance of polythiophenes. *Macromolecules* **40**, 7960–7965 (2007).
 34. Dudenko, D. *et al.* A strategy for revealing the packing in semicrystalline π -conjugated polymers: Crystal structure of bulk poly-3-hexyl-thiophene (P3HT). *Angew. Chemie - Int. Ed.* **51**, 11068–11072 (2012).
 35. Brinkmann, M. & Rannou, P. Effect of molecular weight on the structure and

- morphology of oriented thin films of regioregular poly(3-hexylthiophene) grown by directional epitaxial solidification. *Adv. Funct. Mater.* **17**, 101–108 (2007).
36. Kline, R. J. *et al.* Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight. *Macromolecules* **38**, 3312–3319 (2005).
 37. Flory, P. J. & Yoon, D. Y. Molecular morphology in semicrystalline polymers. *Nature* **272**, 226–229 (1978).
 38. Flory, P. J. On the morphology of the crystalline state in polymers. *J. Am. Chem. Soc.* **84**, 2857–2867 (1962).
 39. Müller, C. *et al.* Enhanced charge-carrier mobility in high-pressure-crystallized poly(3-hexylthiophene). *Macromolecules* **44**, 1221–1225 (2011).
 40. Prime, R. B. & Wunderlich, B. Extended-chain crystals. III. Size distribution of polyethylene crystals grown under elevated pressure. *J. Polym. Sci. Part A-2 Polym. Phys.* **7**, 2061–2072 (1969).
 41. Ballantyne, A. M. *et al.* The effect of poly(3-hexylthiophene) molecular weight on charge transport and the performance of polymer: fullerene solar cells. *Adv. Funct. Mater.* **18**, 2373–2380 (2008).
 42. Ihn, K. J., Moulton, J. & Smith, P. Whiskers of poly(3-alkylthiophene)s. *J. Polym. Sci. Part B Polym. Phys.* **31**, 735–742 (1993).
 43. Xu, W. *et al.* Solvent-induced crystallization of poly(3-dodecylthiophene): Morphology and kinetics. *J. Phys. Chem. B* **115**, 6412–6420 (2011).
 44. Rughooputh, S. & Hotta, S. Chromism of soluble polythienylenes. *J. Polym. Sci. Part B Polym. Phys.* **25**, 1071–1078 (1987).
 45. Scharsich, C. *et al.* Control of aggregate formation in poly(3-hexylthiophene) by solvent, molecular weight, and synthetic method. *J. Polym. Sci. Part B Polym. Phys.* **50**, 442–453 (2012).
 46. Johnson, C. E. & Boucher, D. S. Poly(3-hexylthiophene) aggregate formation in binary solvent mixtures: An excitonic coupling analysis. *J. Polym. Sci. Part B Polym. Phys.* **52**, 526–538 (2014).
 47. Noriega, R. *et al.* A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* **12**, 1038–44 (2013).

48. Pingel, P. *et al.* Temperature-resolved local and macroscopic charge carrier transport in thin P3HT layers. *Adv. Funct. Mater.* **20**, 2286–2295 (2010).
49. Bolsée, J. C., Oosterbaan, W. D., Lutsen, L., Vanderzande, D. & Manca, J. The importance of bridging points for charge transport in webs of conjugated polymer nanofibers. *Adv. Funct. Mater.* **23**, 862–869 (2013).
50. Spano, F. C. & Silva, C. H- and J-aggregate behavior in polymeric semiconductors. *Annu. Rev. Phys. Chem.* **65**, 477–500 (2014).
51. Clark, J., Silva, C., Friend, R. H. & Spano, F. C. Role of intermolecular coupling in the photophysics of disordered organic semiconductors: Aggregate emission in regioregular polythiophene. *Phys. Rev. Lett.* **98**, 1–4 (2007).
52. Hellmann, C. *et al.* Controlling the interaction of light with polymer semiconductors. *Adv. Mater.* **25**, 4906–11 (2013).
53. Niles, E. T. *et al.* J-aggregate behavior in poly-3-hexylthiophene nanofibers. *J. Phys. Chem. Lett.* **3**, 259–263 (2012).
54. Jimison, L. H., Toney, M. F., McCulloch, I., Heeney, M. & Salleo, A. Charge-transport anisotropy due to grain boundaries in directionally crystallized thin films of regioregular poly(3-hexylthiophene). *Adv. Mater.* **21**, 1568–1572 (2009).
55. Crossland, E. J. W. *et al.* Anisotropic charge transport in spherulitic poly(3-hexylthiophene) films. *Adv. Mater.* **24**, 839–844 (2012).
56. Sirringhaus, H. *et al.* Two-dimensional charge transport in self-organized, high-mobility conjugated polymers. *Nature* **401**, 685–688 (1999).
57. Nagamatsu, S. *et al.* Backbone arrangement in ‘friction-transferred’ regioregular poly(3-alkylthiophene)s. *Macromolecules* **36**, 5252–5257 (2003).
58. Mizokuro, T., Heck, C. & Tanigaki, N. Orientation of α -sexithiophene on friction-transferred polythiophene film. *J. Phys. Chem. B* **116**, 189–193 (2012).
59. Aryal, M., Trivedi, K. & Hu, W. Nano-confinement induced chain alignment in ordered P3HT nanostructures defined by nanoimprint lithography. *ACS Nano* **3**, 3085–3090 (2009).
60. Müller, C. *et al.* One-step macroscopic alignment of conjugated polymer systems by epitaxial crystallization during spin-coating. *Adv. Funct. Mater.* **23**, 2368–2377 (2013).

61. Hartmann, L. *et al.* 2D versus 3D crystalline order in thin films of regioregular poly(3-hexylthiophene) oriented by mechanical rubbing and epitaxy. *Adv. Funct. Mater.* **21**, 4047–4057 (2011).
62. Hamidi-Sakr, A., Biniek, L., Fall, S. & Brinkmann, M. Precise control of lamellar thickness in highly oriented regioregular poly(3-hexylthiophene) thin films prepared by high-temperature rubbing: correlations with optical properties and charge transport. *Adv. Funct. Mater.* **26**, 408–420 (2016).
63. Torsi, L., Magliulo, M., Manoli, K. & Palazzo, G. Organic field-effect transistor sensors: a tutorial review. *Chem. Soc. Rev.* **42**, 8612–8628 (2013).
64. Torsi, L. & Dodabalapur, A. Organic Thin-Film Transistors. *Anal. Chem.* **1**, 2230–2236 (2005).
65. Kumar, A., Baklar, M. a., Scott, K., Kreouzis, T. & Stingelin-Stutzmann, N. Efficient, stable bulk charge transport in crystalline/crystalline semiconductor-insulator blends. *Adv. Mater.* **21**, 4447–4451 (2009).
66. Arias, A. C., Endicott, F. & Street, R. A. Surface-induced self-encapsulation of polymer thin-film transistors. *Adv. Mater.* **18**, 2900–2904 (2006).
67. Goffri, S. *et al.* Multicomponent semiconducting polymer systems with low crystallization-induced percolation threshold. *Nat. Mater.* **5**, 950–956 (2006).
68. Treat, N. D. *et al.* Interdiffusion of PCBM and P3HT reveals miscibility in a photovoltaically active blend. *Adv. Energy Mater.* **1**, 82–89 (2011).
69. Treat, N. D. *et al.* Polymer-fullerene miscibility: A metric for screening new materials for high-performance organic solar cells. *J. Am. Chem. Soc.* **134**, 15869–15879 (2012).
70. Müller, C. *et al.* Binary organic photovoltaic blends: A simple rationale for optimum compositions. *Adv. Mater.* **20**, 3510–3515 (2008).
71. Khodagholy, D. *et al.* In vivo recordings of brain activity using organic transistors. *Nat. Commun.* **4**, 1575 (2013).
72. Hammock, M. L., Chortos, A., Tee, B. C. K., Tok, J. B. H. & Bao, Z. 25th Anniversary article: The evolution of electronic skin (E-Skin): A brief history, design considerations, and recent progress. *Adv. Mater.* **25**, 5997–6038 (2013).
73. Reeder, J. *et al.* Mechanically adaptive organic transistors for implantable

- electronics. *Adv. Mater.* **26**, 4967–4973 (2014).
74. Isaksson, J. *et al.* Electronic control of Ca²⁺ signalling in neuronal cells using an organic electronic ion pump. *Nat. Mater.* **6**, 673–679 (2007).
 75. Simon, D. *et al.* Organic electronics for precise delivery of neurotransmitters to modulate mammalian sensory function. *Nat. Mater.* **8**, 742–746 (2009).
 76. Jonsson, A. *et al.* Therapy using implanted organic bioelectronics. *Sci. Adv.* **1**, e1500039 (2015).
 77. Jonsson, A. *et al.* Bioelectronic neural pixel: Chemical stimulation and electrical sensing at the same site. *Proc. Natl. Acad. Sci.* **113**, E6903–E6903 (2016).
 78. Gabrielsson, E. O., Tybrandt, K., Hammarström, P., Berggren, M. & Nilsson, K. P. R. Spatially controlled amyloid reactions using organic electronics. *Small* **6**, 2153–2161 (2010).
 79. Gabrielsson, E. O., Armgarth, A., Hammarström, P., Nilsson, K. P. R. & Berggren, M. Spatiotemporal control of amyloid-like A β plaque formation using a multichannel organic electronic device. *Macromol. Mater. Eng.* **301**, 359–363 (2016).
 80. Smela, E. Conjugated polymer actuators. *MRS Bull.* **33**, 197–204 (2008).
 81. Smela, E., Jager, E. W. H. & Inganäs, O. Microfabricating conjugated polymer actuators. *Science (80-.)*. **290**, 1540–1545 (2000).
 82. Gelmi, A. *et al.* Direct mechanical stimulation of stem cells: A beating electromechanically active scaffold for cardiac tissue engineering. *Adv. Healthc. Mater.* **5**, 1471–1480 (2016).
 83. Svennersten, K., Bolin, M., Jager, E. W. H., Berggren, M. & Richter Dahlfors, A. Electrochemical modulation of epithelia formation using conducting polymers. *Biomaterials* **30**, 6257–6264 (2009).
 84. Balint, R., Cassidy, N. J. & Cartmell, S. H. Electrical Stimulation: A Novel Tool for Tissue Engineering. *Tissue Eng. Part B* **19**, 48–57 (2012).
 85. Dvir, T. *et al.* Nanowired three-dimensional cardiac patches. *Nat. Nanotechnol.* **6**, 720–725 (2011).
 86. Radisic, M. *et al.* Functional assembly of engineered myocardium by electrical stimulation of cardiac myocytes cultured on scaffolds. *Proc. Natl. Acad. Sci. U.*

- S. A.* **101**, 18129–18134 (2004).
87. Schmidt, C. E., Shastri, V. R., Vacanti, J. P. & Langer, R. Stimulation of neurite outgrowth using an electrically conducting polymer. *Proc Natl Acad Sci U S A* **94**, 8948–8953 (1997).
 88. Iandolo, D. *et al.* Development and characterization of organic electronic scaffolds for bone tissue engineering. *Adv. Healthc. Mater.* **5**, 1505–1512 (2016).
 89. Wan, A. M.-D. *et al.* 3D conducting polymer platforms for electrical control of protein conformation and cellular functions. *J. Mater. Chem. B Mater. Biol. Med.* **3**, 5040–5048 (2015).
 90. Steinmann, W., Walter, S., Beckers, M., Seide, G. & Gries, T. in *Applications of calorimetry in a wide context - Differential scanning calorimetry, isothermal titration calorimetry and microcalorimetry* 277–306 (InTechOpen, 2013).
 91. Prosa, T. J., Winokur, M. J., Moulton, J., Smith, P. & Heeger, A. J. X-ray structural studies of poly(3-alkylthiophenes): An example of an inverse comb. *Macromolecules* **25**, 4364–4372 (1992).
 92. Prosa, T. J. & Winokur, M. J. Evidence of a novel side chain structure in regioregular poly(3-alkylthiophenes). *Macromolecules* **29**, 3654–3656 (1996).
 93. Scher, H. & Montroll, E. N. Anomalous transit-time dispersion in amorphous solids. *Phys. Rev. B. Condens. Matter* **12**, (1975).
 94. Scott, J. C., Pautmeier, L. T. & Schein, L. B. Mean mobilities of charge carriers in disordered media. *Phys. Rev. Lett.* **46**, 8603–8606 (1992).
 95. Pavlica, E. & Bratina, G. Time-of-flight mobility of charge carriers in position-dependent electric field between coplanar electrodes. *Appl. Phys. Lett.* **101**, (2012).
 96. Pathipati, S. R. *et al.* Graphene-induced enhancement of n-type mobility in perylenediimide thin films. *J. Phys. Chem. C* **118**, 24819–24826 (2014).
 97. Butt, H. J., Cappella, B. & Kappl, M. Force measurements with the atomic force microscope: Technique, interpretation and applications. *Surf. Sci. Rep.* **59**, 1–152 (2005).
 98. Clifford, C. a & Seah, M. P. Modelling of nanomechanical nanoindentation measurements using an AFM or nanoindenter for compliant layers on stiffer

- substrates. *Nanotechnology* **17**, 5283–5292 (2006).
99. Downing, T. L. *et al.* Biophysical regulation of epigenetic state and cell reprogramming. *Nat. Mater.* **12**, 1154–1162 (2013).
 100. Morez, C. *et al.* Enhanced efficiency of genetic programming toward cardiomyocyte creation through topographical cues. *Biomaterials* **70**, 94–104 (2015).
 101. Kim, M., Huang, Y., Choi, K. & Hidrovo, C. H. The improved resistance of PDMS to pressure-induced deformation and chemical solvent swelling for microfluidic devices. *Microelectron. Eng.* **124**, 66–75 (2014).
 102. Claycomb, W. C. *et al.* HL-1 cells: A cardiac muscle cell line that contracts and retains phenotypic characteristics of the adult cardiomyocyte. *Proc. Natl. Acad. Sci. U. S. A.* **95**, 2979–84 (1998).
 103. Baklar, M. A. *et al.* Solid-state processing of organic semiconductors. *Adv. Mater.* **22**, 3942–3947 (2010).
 104. Drzal, P. L., Barnes, J. D. & Kofinas, P. Path dependent microstructure orientation during strain compression of semicrystalline block copolymers. *Polymer (Guildf)*. **42**, 5633–5642 (2001).
 105. Nagamatsu, S. *et al.* Effects of molecular alignment on carrier transport in organic transistors. *Synth. Met.* **137**, 923–924 (2003).
 106. Österholm, J. E., Laakso, J. & P, N. Melt and solution processable poly(3-alkylthiophenes) and their blends. *Synth. Met.* **28**, 435–444 (1989).
 107. Laakso, J., Österholm, J. E. & P, N. Conducting polymers blends. *Synth. Met.* **28**, 467–471 (1989).
 108. Pomerantz, M. *et al.* Processable polymer and copolymers of 3-alkylthiophenes and their blends. *Synth. Met.* **41–43**, 825–830 (1991).
 109. Yoshino, K., Nakajima, S., Fujii, M. & Sugimoto, R. Conducting polymer fibre prepared by melt-spinning method from fusible polythiophene derivative. *Polym. Commun.* **28**, 309–310 (1987).
 110. Singh, C. R. *et al.* Correlation of charge transport with structural order in highly ordered melt-crystallized poly(3-hexylthiophene) thin films. *J. Polym. Sci. Part B Polym. Phys.* **51**, 943–951 (2013).

111. Fanous, J., Schweizer, M., Schawaller, D. & Buchmeiser, M. R. Crystalline and conductive poly(3-hexylthiophene) fibers. *Macromol. Mater. Eng.* **297**, 123–127 (2012).
112. Choulis, S. a. *et al.* High ambipolar and balanced carrier mobility in regioregular poly(3-hexylthiophene). *Appl. Phys. Lett.* **85**, 3890–3892 (2004).
113. Juška, G., Genevičius, K., Arlauskas, K., Österbacka, R. & Stubb, H. Charge transport at low electric fields in π -conjugated polymers. *Phys. Rev. B* **65**, 233208 (2002).
114. Mozer, A. J. & Sariciftci, N. S. Negative electric field dependence of charge carrier drift mobility in conjugated, semiconducting polymers. *Chem. Phys. Lett.* **389**, 438–442 (2004).
115. Timmermans, J. Plastic crystals: A historical review. *J. Phys. Chem. Solids* **18**, 1–8 (1961).
116. Rodrigues, A. *et al.* Low temperature solid state processing of pure P3HT fibers. *AIP Adv.* **3**, 52116 (2013).
117. Bernardo, G. *et al.* Solid-state low-temperature extrusion of P3HT ribbons. *Appl. Phys. A Mater. Sci. Process.* **117**, 2079–2086 (2014).
118. Canetti, M., Bertini, F., Scavia, G. & Porzio, W. Structural investigation on bulk poly(3-hexylthiophene): Combined SAXS, WAXD, and AFM studies. *Eur. Polym. J.* **45**, 2572–2579 (2009).
119. Wunderlich, B. A study of equilibrium melting of polyethylene. *Macromolecules* **10**, 906 (1977).
120. Malik, S. & Nandi, A. K. Crystallization mechanism of regioregular poly(3-alkyl thiophene)s. *J. Polym. Sci. Part B Polym. Phys.* **40**, 2073–2085 (2002).
121. Balko, J., Lohwasser, R. H., Sommer, M., Thelakkat, M. & Thurn-Albrecht, T. Determination of the crystallinity of semicrystalline poly(3-hexylthiophene) by means of wide-angle X-ray scattering. *Macromolecules* **46**, 9642–9651 (2013).
122. Pascui, O. F. *et al.* High crystallinity and nature of crystal-crystal phase transformations in regioregular poly(3-hexylthiophene). *Macromolecules* **43**, 9401–9410 (2010).
123. Skrypnychuk, V. *et al.* Ultrahigh mobility in an organic semiconductor by

- vertical chain alignment. *Adv. Mater.* **23**, 2359–2366 (2016).
124. Nawrocki, R. a, Pavlica, E., Celi, N. & Orlov, D. Fabrication of poly (3-hexylthiophene) nanowires for high-mobility transistors. *Org. Electron.* **30**, 92–98 (2016).
 125. Mozer, A. J. *et al.* Time-dependent mobility and recombination of the photoinduced charge carriers in conjugated polymer/fullerene bulk heterojunction solar cells. *Phys. Rev. B - Condens. Matter Mater. Phys.* **72**, 1–10 (2005).
 126. Hellmann, C. *et al.* Solution processing of polymer semiconductor: Insulator blends-tailored optical properties through liquid-liquid phase separation control. *J. Polym. Sci. Part B Polym. Phys.* **53**, 304–310 (2015).
 127. Müller, C. *et al.* Tough, semiconducting polyethylene-poly(3-hexylthiophene) diblock copolymers. *Adv. Funct. Mater.* **17**, 2674–2679 (2007).
 128. Müller, C., Radano, C. P., Smith, P. & Stingelin-Stutzmann, N. Crystalline-crystalline poly(3-hexylthiophene)-polyethylene diblock copolymers: Solidification from the melt. *Polymer (Guildf)*. **49**, 3973–3978 (2008).
 129. Salleo, A. & Arias, A. C. Solution based self-assembly of an array of polymeric thin-film transistors. *Adv. Mater.* **19**, 3540–3543 (2007).
 130. Qiu, L. *et al.* Versatile use of vertical-phase-separation-induced bilayer structures in organic thin-film transistors. *Adv. Mater.* **20**, 1141–1145 (2008).
 131. Qiu, L. *et al.* Organic thin-film transistors based on polythiophene nanowires embedded in insulating polymer. *Adv. Mater.* **21**, 1349–1353 (2009).
 132. Lim, J. A. *et al.* Inkjet-printed single-droplet organic transistors based on semiconductor nanowires embedded in insulating polymers. *Adv. Funct. Mater.* **20**, 3292–3297 (2010).
 133. Xu, Y., Liu, J., Wang, H. & Han, Y. Hierarchical network-like structure of poly(3-hexylthiophene) (P3HT) by accelerating the disentanglement of P3HT in a P3HT/PS (polystyrene) blend. *RSC Adv.* **3**, 17195 (2013).
 134. Shin, M. *et al.* Polythiophene nanofibril bundles surface-embedded in elastomer: A route to a highly stretchable active channel layer. *Adv. Mater.* **27**, 1255–1261 (2015).
 135. Ferenczi, T. a M. *et al.* Organic semiconductor: insulator polymer ternary blends

- for photovoltaics. *Adv. Mater.* **23**, 4093–4097 (2011).
136. Qiu, L. *et al.* Low-temperature melt processed polymer blend for organic thin-film transistors. *J. Mater. Chem.* **22**, 18887 (2012).
 137. Kuilla, T. *et al.* Recent advances in graphene based polymer composites. *Prog. Polym. Sci. Vol.* **35**, 1350–1375 (2010).
 138. Coleman, J. N., Khan, U. & Gun'ko, Y. K. Mechanical reinforcement of polymers using carbon nanotubes. *Adv. Mater.* **18**, 689–706 (2006).
 139. R. H. Cruz-Estrada, M. J. F. In-situ production of electrically conductive fibres in polyaniline-SBS blends.pdf. *J. Mater. Sci.* **35**, 5065–5069 (2000).
 140. Leyva, M. E., Barra, G. M. O. & Soares, B. G. Conductive polyaniline-SBS blends prepared in solution. *Synth. Met.* **123**, 443–449 (2001).
 141. Müller, C. On the glass transition of polymer semiconductors and its impact on polymer solar cell stability. *Chem. Mater.* **27**, 2740–2754 (2015).
 142. Cohen Addad, J. P. & Golebiewski, B. Polybutadiene network in a styrene–butadiene–styrene triblock copolymer. NMR observation. *Macromolecules* **31**, 8558–8565 (1998).
 143. Munteanu, S. B., Vasile, C., Poni, P., Ro, A. & Romania, I. I. Spectral and thermal characterization of styrene- butadiene copolymers with different architectures. *J. Optoelectron. Adv. Mater.* **7**, 3135–3148 (2005).
 144. Winokur, M. J., Spiegel, D., Kim, Y., Hotta, S. & Heeger, a. J. Structural and absorption studies of the thermochromic transition in poly(3-hexylthiophene). *Synth. Met.* **28**, 419–426 (1989).
 145. Flory, P. J. *Principles of polymer chemistry*. (Cornell Univ. Press, 1953).
 146. Nishi, T. & Wang, T. T. Melting point depression and kinetic effects of cooling on crystallization in poly(vinylidene fluoride)-poly(methyl methacrylate) mixtures. *Macromolecules* **8**, 909–915 (1975).
 147. Kämpf, G., Krömer, H. & Hoffmann, M. Long-range order of supramolecular structures in amorphous butadiene-styrene block copolymers. *J. Macromol. Sci. Part B Phys.* **6**, 167–190 (1972).
 148. Pakula, T., Saijo, K., Kawai, H. & Hashimoto, T. Deformation behavior of styrene-butadiene-styrene triblock copolymer with cylindrical morphology.

- Macromolecules* **18**, 1294–1302 (1985).
149. O'Connor, B. *et al.* Anisotropic structure and charge transport in highly strain-aligned regioregular poly(3-hexylthiophene). *Adv. Funct. Mater.* **21**, 3697–3705 (2011).
 150. Delongchamp, D. M. *et al.* Controlling the orientation of terraced semiconductor. *Nano* **3**, (2009).
 151. Kim, T. *et al.* Preparation and photoluminescence (PL) performance of a nanoweb of P3HT nanofibers with diameters below 100 nm. *J. Mater. Chem.* **21**, 14231–14239 (2011).
 152. Natta, G., Corradini, P. & Bassi, I. W. Crystal structure of isotactic polystyrene. *Nuovo Cim.* **15**, 68–82 (1960).
 153. Steinhart, M. *et al.* Coherent kinetic control over crystal orientation in macroscopic ensembles of polymer nanorods and nanotubes. *Phys. Rev. Lett.* **97**, 1–4 (2006).
 154. Abreu, F. O. M. S., Forte, M. M. C. & Liberman, S. A. SBS and SEBS block copolymers as impact modifiers for polypropylene compounds. *J. Appl. Polym. Sci.* **95**, 254–263 (2005).
 155. Ghosh, S., Bhowmick, A. K., Roychowdhury, N. & Holden, G. Influence of block molecular weight on the properties of styrene-ethylenebutylene-styrene block copolymers. *J. Appl. Polym. Sci.* **77**, 1621–1628 (2000).
 156. Cheng, Y. J. Morphological stabilization by in situ polymerization of fullerene derivatives leading to efficient, thermally stable organic photovoltaics. *Adv. Funct. Mater.* **21**, 1723 (2011).
 157. Rivnay, J. Quantitative analysis of lattice disorder and crystallite size in organic semiconductor thin films. *Phys. Rev. B. Condens. Matter* **84**, 45203 (2011).
 158. Kline, J. R., McGehee, M. D. & Toney, M. F. Highly oriented crystals at the buried interface in polythiophene thin-film transistors. *Nat. Mater.* **5**, 222–228 (2006).
 159. Worgull, M. *Hot embossing: Theory and technology of microreplication.* (William Andrew, 2009).
 160. White, S. M., Constantin, P. E. & Claycomb, W. C. Cardiac physiology at the

cellular level: use of cultured HL-1 cardiomyocytes for studies of cardiac muscle cell structure and function. *Am. J. Physiol. Heart Circ. Physiol.* **286**, H823-9 (2004).

161. Lee, J. B. Nanotechnology and smart materials for ‘ More than Moore ’ – It ’ s a small world after all ! *J. Nanotechnol. Smart Mater.* **1**, 1–3 (2014).
162. Clapham, P. B. & Hutley, M. C. Reduction of lens reflexion by the ‘Moth Eye’ principle. *Nature* **242**, 117–118 (1973).
163. Gale, M. Diffraction, beauty and commerce. *Phys. Worlds* **2**, 24–28 (1989).
164. Onda, T., Shibuichi, S., Satoh, N. & Tsujii, K. Super-water-repellent fractal surfaces. *Langmuir* **12**, 2125–2127 (1996).
165. Neinhuis, C. & Barthlott, W. Characterization and distribution of water-repellent, self-cleaning plant surfaces. *Ann. Bot.* **79**, 667–677 (1997).
166. Moreau, W. M. *Semiconductor lithography*. (Plenum Press, 1988).
167. Madou, M. *Fundamentals of microfabrication*. (CRC Press, 1997).
168. Becker, H. & Heim, U. Hot embossing as a method for the fabrication of polymer high aspect ratio structures. *Sensors Actuators, A Phys.* **83**, 130–135 (2000).
169. Chang, C.-Y. & Yu, C.-H. A basic experimental study of ultrasonic assisted hot embossing process for rapid fabrication of microlens arrays. *J. Micromechanics Microengineering* **25**, 25010 (2015).
170. Ting, C.-J., Huang, M.-C., Tsai, H.-Y., Chou, C.-P. & Fu, C.-C. Low cost fabrication of the large-area anti-reflection films from polymer by nanoimprint/hot-embossing technology. *Nanotechnology* **19**, 205301 (2008).
171. Choi, C.-G. Fabrication of optical waveguides in thermosetting polymers using hot embossing. *J. Micromechanics Microengineering* **14**, 945–949 (2004).
172. Loewen, E. G. & Popov, E. *Diffraction gratings and applications*. (Marcel Dekker, Inc., 1997).
173. Ulrich, R., Weber, H. P., Chandross, E. A., Tomlinson, W. J. & Franke, E. A. Embossed optical waveguides. *Appl. Phys. Lett.* **20**, 213–215 (1972).
174. Lee, G. Bin, Chen, S. H., Huang, G. R., Sung, W. C. & Lin, Y. H. Microfabricated plastic chips by hot embossing methods and their applications

- for DNA separation and detection. *Sensors Actuators, B Chem.* **75**, 142–148 (2001).
175. Gerlach, A. *et al.* Microfabrication of single-use plastic microfluidic devices for high-throughput screening and DNA analysis. *Microsyst. Technol.* **7**, 265–268 (2002).
 176. Jeon, J. S., Chung, S., Kamm, R. D. & Charest, J. L. Hot embossing for fabrication of a microfluidic 3D cell culture platform. *Biomed. Microdevices* **13**, 325–333 (2011).
 177. Schiff, H. *et al.* Nanoreplication in polymers using hot embossing and injection molding. *Microelectron. Eng.* **53**, 171–174 (2000).
 178. van Renesse, R. L. *Optical document security*. (Artech House, 1998).
 179. Kumar, A. & Whitesides, G. M. Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric stamp and an alkanethiol ‘ink’ followed by chemical etching. *Appl. Phys. Lett.* **4**, 2002–2004 (1993).
 180. Chou, S. Y., Krauss, P. R. & Renstrom, P. Imprint lithography with 25-nanometer resolution. *Science (80-.).* **272**, 85–87 (1996).
 181. Li, W.-D., Wu, W. & Stanley Williams, R. Combined helium ion beam and nanoimprint lithography attains 4 nm half-pitch dense patterns. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **30**, 06F304 (2012).
 182. Chou, S. Y., Krauss, P. R. & Renstrom, P. J. Imprint lithography with 25-nanometer resolution. *Science (80-.).* **272**, 85–87 (1996).
 183. Stutzmann, N., Tervoort, T. A., Bastiaansen, C. W. M., Feldman, K. & Smith, P. Solid-state replication of relief structures in semicrystalline polymers. *Adv. Mater.* **12**, 557–562 (2000).
 184. Herland, A. *et al.* Electrochemical control of growth factor presentation to steer neural stem cell differentiation. *Angew. Chemie (International ed.)* **50**, 12529–12533 (2011).
 185. Persson, K. M. *et al.* Electronic control of cell detachment using a self-doped conducting polymer. *Adv. Mater.* **23**, 4403–4408 (2011).
 186. Persson, K. M. *et al.* Matrix addressing of an electronic surface switch based on a

- conjugated polyelectrolyte for cell sorting. *Adv. Funct. Mater.* 7056–7063 (2015). doi:10.1002/adfm.201503542
187. Irimia-Vladu, M. *et al.* Indigo - A natural pigment for high performance ambipolar organic field effect transistors and circuits. *Adv. Mater.* **24**, 375–380 (2012).
 188. Amdursky, N., Wang, X., Meredith, P., Bradley, D. D. C. & Stevens, M. M. Long-range proton conduction across free-standing serum albumin mats. *Adv. Mater.* **28**, 2692–2698 (2016).
 189. Humphrey, E. *et al.* Serum albumin hydrogels prevent de-differentiation of neonatal cardiomyocytes. in *Cardiovascular Research* S80–S81 (OXFORD UNIV PRESS, 2016).
 190. Balint, R., Cassidy, N. J. & Cartmell, S. H. Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomater.* **10**, 2341–2353 (2014).
 191. Murphy, W. L., McDevitt, T. C. & Engler, A. J. Materials as stem cell regulators. *Nat. Mater.* **13**, 547–557 (2014).
 192. Kumar, S. Cellular mechanotransduction: Stiffness does matter. *Nat. Mater.* **13**, 918–920 (2014).
 193. Crowder, S. W., Leonardo, V., Whittaker, T., Papathanasiou, P. & Stevens, M. M. Material cues as potent regulators of epigenetics and stem cell function. *Cell Stem Cell* **18**, 39–52 (2016).
 194. Humphrey, J. D., Dufresne, E. R. & Schwartz, M. a. Mechanotransduction and extracellular matrix homeostasis. *Nat. Rev. Mol. Cell Biol.* **15**, 802–812 (2014).
 195. Svennersten, K., Larsson, K., Berggren, M. & Richter Dahlfors, A. Organic bioelectronics in nanomedicine. *Biochim. Biophys. Acta* **1810**, 276–285 (2011).
 196. Lundin, V., Herland, A., Berggren, M., Jager, E. W. H. & Teixeira, A. Control of neural stem cell survival by electroactive polymer substrates. *PLoS One* **6**, 1–8 (2011).
 197. Poole-Wilson, P. The prevention of cardiovascular disease worldwide: whose task and WHO's task? *Clin. Med. (Northfield. Il).* **5**, 379–84 (2005).
 198. Takahashi, K. & Yamanaka, S. Induction of pluripotent stem cells from mouse embryonic and adult fibroblast cultures by defined factors. *Cell* **126**, 663–676

- (2006).
199. Li, Y. *et al.* Biophysical regulation of histone acetylation in mesenchymal stem cells. *Biophys. J.* **100**, 1902–1909 (2011).
 200. Ku, S., Lee, S. & Park, C. Synergic effects of nanofiber alignment and electroactivity on myoblast differentiation. *Biomaterials* **33**, 6098–6104 (2012).
 201. Greco, F. *et al.* Microwrinkled conducting polymer interface for anisotropic multicellular alignment. *ACS Appl. Mater. Interfaces* **5**, 573–584 (2013).
 202. Schiff, H. *et al.* Fast heating and cooling in nanoimprint using a spring-loaded adapter in a preheated press. *Microelectron. Eng.* **84**, 932–936 (2007).
 203. Trimbach, D., Feldman, K., Spencer, N. D., Broer, D. J. & Bastiaansen, C. W. M. Block copolymer thermoplastic elastomers for microcontact printing. *Langmuir* **19**, 10957–10961 (2003).
 204. Luna, J. *et al.* Multiscale biomimetic topography for the alignment of neonatal and embryonic stem cell-derived heart cells. *Tissue Eng. Part C Methods* **17**, 579–588 (2011).
 205. Glennon, P. E., Sugden, P. H. & Poole-Wilson, P. A. Cellular mechanisms of cardiac hypertrophy. *J.Mol.Med.* **73**, 496–499 (1995).
 206. Martino, N., Ghezzi, D., Benfenati, F., Lanzani, G. & Antognazza, M. R. Organic semiconductors for artificial vision. *J. Mater. Chem. B* **1**, 3768–3780 (2013).
 207. Antognazza, M. R. *et al.* Shedding Light on Living Cells. *Adv. Mater.* **27**, 7662–7669 (2015).
 208. Ghezzi, D. *et al.* A hybrid bioorganic interface for neuronal photoactivation. *Nat. Commun.* **2**, 166 (2011).
 209. Ghezzi, D. *et al.* A polymer optoelectronic interface restores light sensitivity in blind rat retinas. *Nat. Photonics* **7**, 400–406 (2013).
 210. Engelmayer, G. *et al.* Accordion-like honeycombs for tissue engineering of cardiac anisotropy. *Nat. Mater.* **7**, 1003–1010 (2008).
 211. Rodgers, J. A., Ghaffari, R. & Kim, D.-H. *Stretchable bioelectronics for medical devices and systems*. (Springer Nature, 2016).
 212. Someya, T. *et al.* A large-area, flexible pressure sensor matrix with organic field-

- effect transistors for artificial skin applications. *Proc. Natl. Acad. Sci. U. S. A.* **101**, 9966–9970 (2004).
213. Webb, R. C. *et al.* Ultrathin conformal devices for precise and continuous thermal characterisation of human skin. *Nat. Mater.* **12**, 938–944 (2013).
214. Yamada, T. *et al.* A stretchable carbon nanotube strain sensor for human-motion detection. *Nat. Nanotechnol.* **6**, 296–301 (2011).
215. Larson, C. *et al.* Highly stretchable electroluminescent skin for optical signaling and tactile sensing. *Science (80-.).* **351**, 1071–1074 (2016).
216. Liang, J., Li, L., Niu, X., Yu, Z. & Pei, Q. Elastomeric polymer light-emitting devices and displays. *Nat. Photonics* **7**, 817–824 (2013).

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APPENDIX LIST OF ABBREVIATIONS AND ACRONYMS

AC	-	alternating current
AFM	-	atomic force microscopy
Al	-	aluminium
a-PS	-	atactic/amorphous polystyrene
arb. units	-	arbitrary units
b.p.	-	boiling point
CHCl ₃	-	chloroform
cm ² V ⁻¹ s ⁻¹	-	centimetre ² per volt second
dI/dt	-	rate of change of current
d	-	distance (electrode separation)
d _(hkl)	-	d-spacing
DAPI	-	4',6'-diamidino-2-phenylindole
DSC	-	differential scanning calorimetry
E	-	electric field
E	-	Young's modulus
ECM	-	extra cellular matrix
E _{gap}	-	energy gap (π - π^* gap)
endo	-	endotherm
EtOAc	-	ethyl acetate
FET	-	field effect transistor
FWHM	-	full-width half maximum
GHz	-	gigahertz
g mol ⁻¹	-	gram per moles
HDPE	-	high density polyethylene

HL-1-6	-	sub-clone of the cardiac like cell line HL-1
i-PS	-	isotactic/semicrystalline polystyrene
I-V	-	current voltage
kg	-	kilogram
kg mol ⁻¹	-	kilogram per moles
K min ⁻¹	-	Kelvin per minute
kN	-	kilo Newton
kV	-	kilovolts
l	-	lamellar thickness
mA	-	milliampere
mg	-	milligram
mm	-	millimetre
mM	-	millimolar
MO	-	molecular orbital
MPa	-	megapascal
M _w	-	mass-average molecular weight
NIL	-	nanoimprint lithography
nm	-	nanometre
N m ⁻¹	-	Newton per metre
N cm ⁻²	-	Newton per centrimetre ²
OFET	-	organic field effect transistor
OLED	-	organic light emitting diode
OPV	-	organic photovoltaics (solar cells)
OTFT	-	organic thin film transistors
PDI	-	polydispersity index
P3HT	-	poly(3-hexylthiophene)
PDMS	-	poly(dimethylsiloxane)

PMMA	-	poly(methyl methacrylate)
PS	-	polystyrene
q	-	scattering vector
RMS	-	root mean square
RR	-	regioregular
SAXS	-	small-angle X-ray scattering
S/cm	-	Siemens per centimetre
SBS	-	polystyrene-block-poly(butadiene)-block-polystyrene
SEBS	-	polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene
T	-	temperature
TCP	-	tissue culture plastic
T _g	-	glass transition temperature
T _m	-	melting temperature
T _{offset}	-	melting temperature offset
T _{onset}	-	melting temperature onset
T _{peak}	-	melting temperature peak
TOF	-	time-of-flight
t _{tr}	-	transit time
UTS	-	ultimate tensile strength
V	-	voltage (volts)
v/v	-	volume per volume
WAXS	-	wide-angle X-ray scattering
wt %	-	weight percentage (weight/weight)
w/v	-	weight per volume
X	-	crystallinity
XRD	-	X-ray diffraction
° C	-	degree Celsius

ϵ	-	elongation
ΔH_c	-	enthalpy of crystallisation
ΔH_f	-	enthalpy of fusion
ΔH_f^0	-	enthalpy of fusion of a 100% crystalline material
σ	-	conductivity
σ - ϵ	-	stress-strain
μ	-	mobility
μ_{FET}	-	mobility obtained from field effect transistor measurements
μm	-	micrometre
μ_{TOF}	-	mobility obtained from time-of-flight photocurrent measurements
$\parallel_x$	-	parallel to the x direction (in-plane)
$\parallel_y$	-	parallel to the y direction (in-plane)
$\perp$	-	through-plane direction

APPENDIX CHAPTER 5

Table A5.1 *Mechanical properties of P3HT:SBS blend films including Young's modulus (E), ultimate tensile strength (UTS) and elongation at break (ϵ at break).*

P3HT (wt %)	E (MPa)	UTS (MPa)	ϵ at break (%)
100	116 ± 12	6.1 ± 1.8	9 ± 0.4
80	161 ± 64	5.4 ± 1.4	4 ± 2
60	136 ± 51	6.1 ± 1.2	10 ± 2
40	68 ± 14	5.7 ± 0.9	215 ± 91
20	51 ± 24	6.3 ± 2.0	-
0	33 ± 29	3.7 ± 1.7	-

* Young's Modulus determined from the slope in σ - ϵ curves between 0 and 2%.

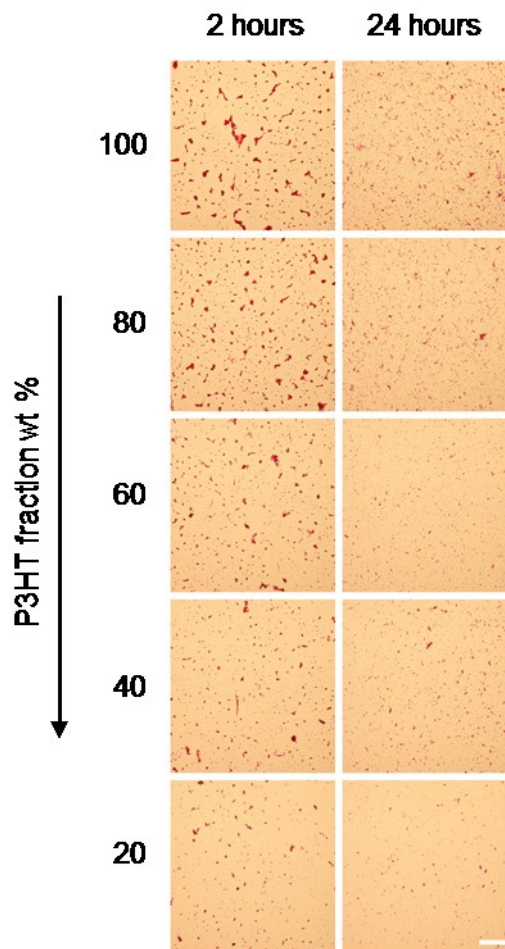


Figure A5.1 Optical micrographs of wire-bar coated thin films of P3HT:SBS blends cast from $\text{CHCl}_3/\text{EtOAc}$ stirred for 2 (*left*) or 24 (*right*) hours respectively (20-100 wt % P3HT). Thermal equilibrium was not reached at short stirring times and larger aggregate clusters were observed. Scale bar is 100 μm .

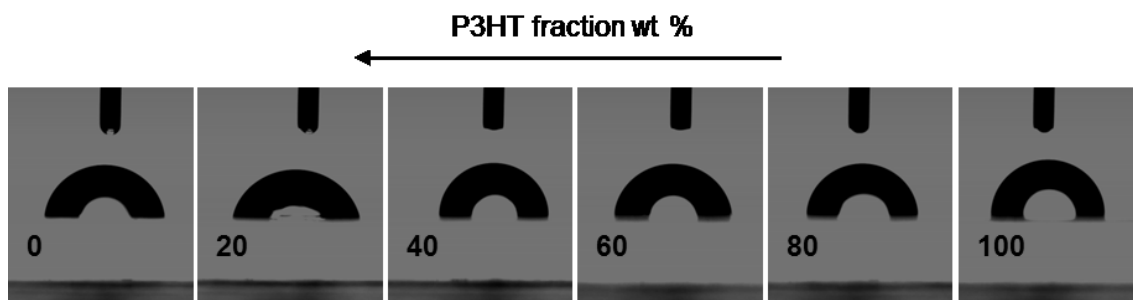


Figure A5.2 Water contact angles of P3HT:SBS blends with indicated varied amounts of P3HT (0, 20, 40, 60, 80 and 100 wt %). Contact angles varied between 76-92°, without obvious trends with regards to P3HT content, due to the equal hydrophobicity of the neat semiconductor and insulator.

APPENDIX CHAPTER 6

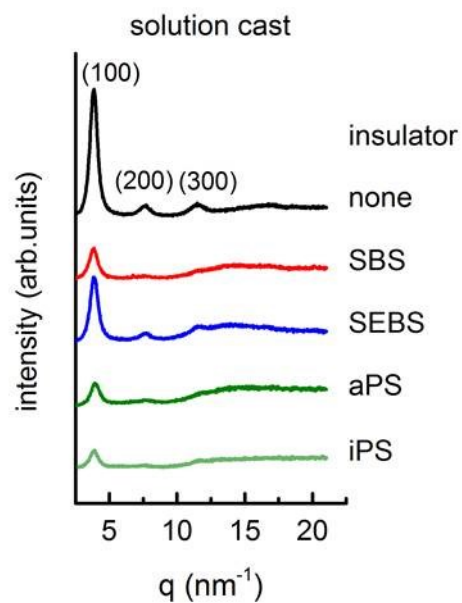


Figure A6.1 Reflection mode wide angle X-ray diffractograms of P3HT:insulator blend films (40:60 semiconductor:insulator wt %) cast from solution.

APPENDIX CHAPTER 7

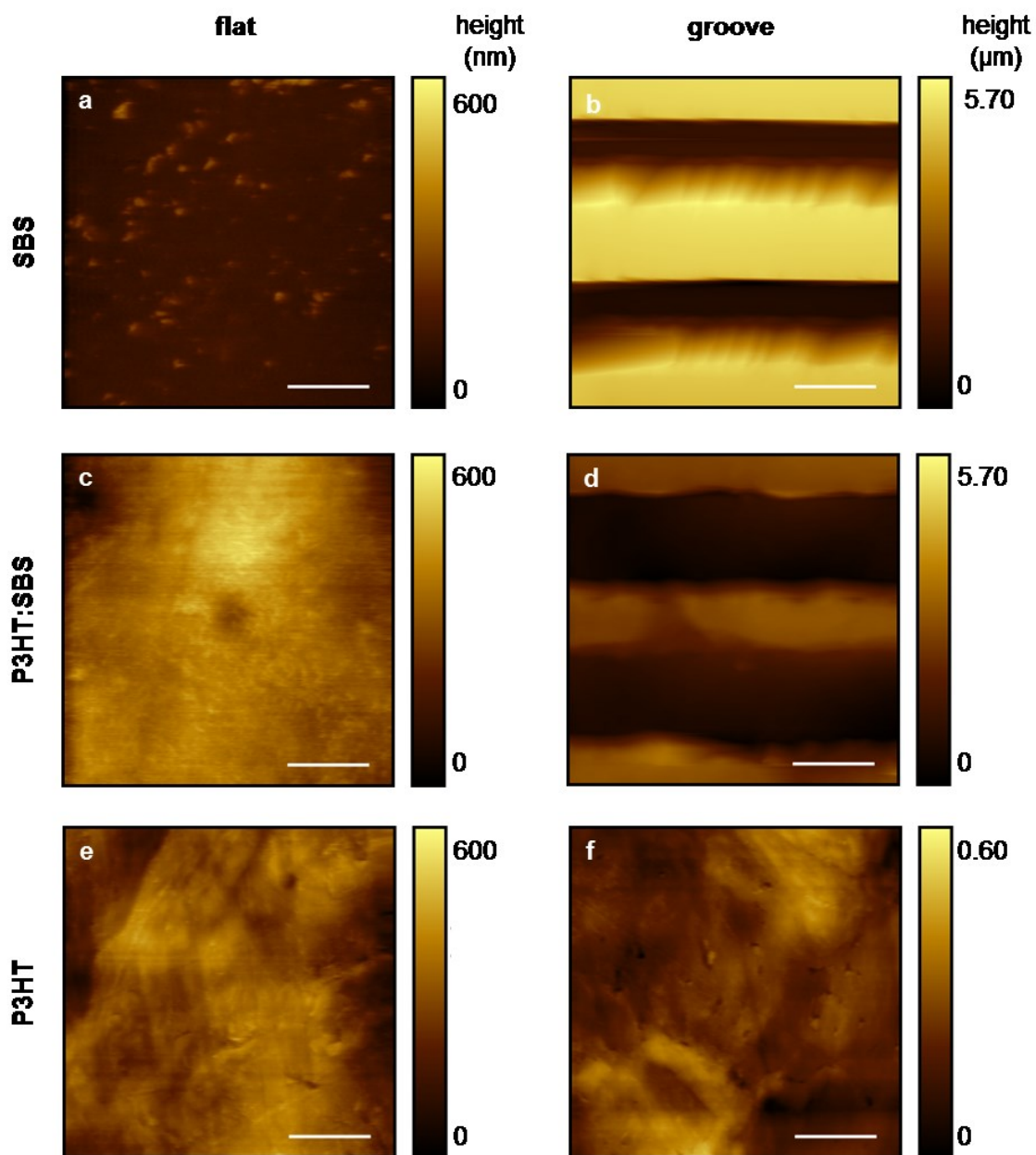


Figure A7.1 Atomic force microscopy topography images of unpatterned flat (left) and microgroove patterned (right) films of (a-b) SBS, (c-d) P3HT:SBS and (e-f) P3HT. Scale bars are 10 μm.

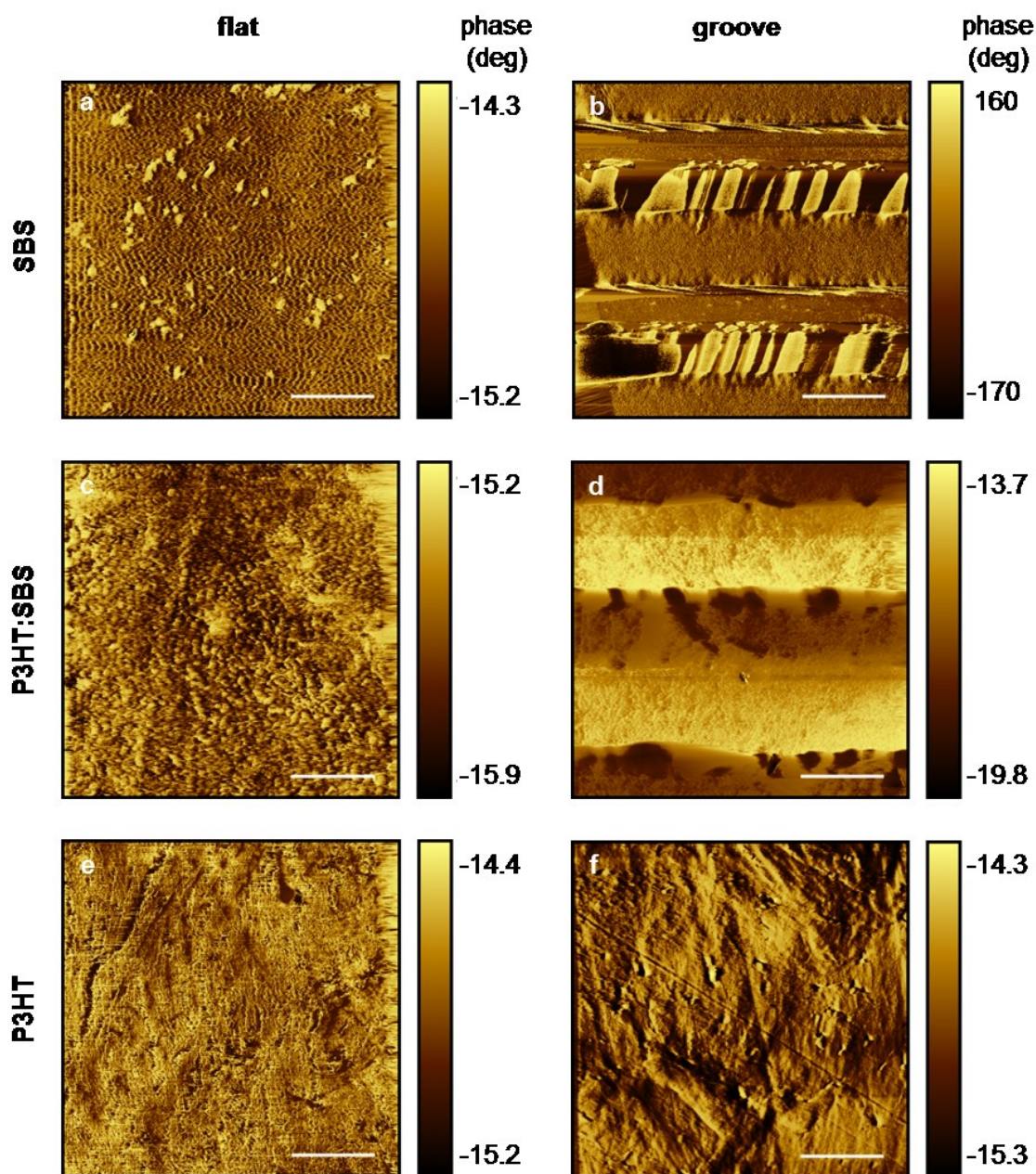


Figure A7.2 Atomic force microscopy phase images of unpatterned flat (left) and microgroove patterned (right) films of (a-b) SBS, (c-d) P3HT:SBS and (e-f) P3HT. Scale bars are 10 μm .

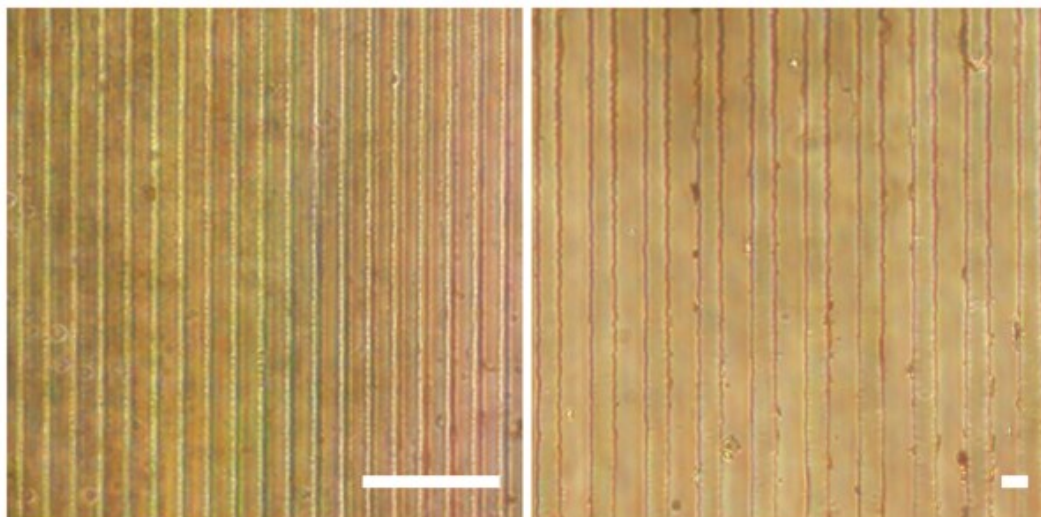


Figure A7.3 *Hard epoxy resin mold utilised for single-step patterning during solid state compression. Scale bars are 100 and 10 μm (left and right respectively).*

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