

Structure-Phase Behavior-Performance Relationships in Non-Fullerene Acceptor based Organic Solar Cells: Insight from Thermal and Spectroscopic Characterization

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To Sheikh Nazim, with love and gratitude.

I Declaration

The work presented in this thesis is the product of my own efforts, unless stated otherwise.

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أكبر و أحن شكري لأمي و لأبي من أجل حب و حنان و تشجيع و تضحية و صداقة كل منهما؛ اشكر ربي على
نعمة وجودهم في حياتي الذي مكنني من المضي في و إكمال هذا الطريق. أعز و أعمق شكري لشيخ
الشيخ ناظم القبرصي النقشبندى الحقاني و لخليفته الشيخ محمد عادل الرباني من أجل توجيهاتهم و اشكر
ربي على حظ معرفتهم وحبهم. ألد و أحلى شكري لإخوتي منتصر، عبد الحليم و شرف الدين من أجل حبهم
وقدوتهم وفكاهتهم ومكانة كل منهم في قلبي، و لأختي شريفة من أجل مكانتها الخاصة في قلبي وحنانها و
صداقتها. جزيل شكري لجدي الحاج طاهر سرور من أجل دعمه المادي و المعنوي، و لخالي الاستاذ خالدون
سرور من أجل رعايته لي منذ بداية دراستي الجامعية.

IV Abstract

In the context of increasing interest in faster material screening and blend component selection for organic solar cells, this thesis explores thermal analysis as a tool towards a more in-depth understanding of the relationship between material structure, phase behavior and performance in organic solar cells (OSCs). Firstly, the phase behavior of PffBT4T-2DT/O-IDTBR polymer donor/non-fullerene acceptor (NFA) system is investigated using differential scanning calorimetry. The observed monotectic temperature-composition ($T-\phi$) diagram is used to rationalize optimal donor/acceptor (D/A) ratio in devices based on morphological changes, and is supplemented by transient absorption spectroscopy and X-ray techniques to probe the morphology in thin films directly. It was found that a D/A ratio within the inferred miscibility gap induces excessively large polymer domains which are not well interconnected, thus limiting performance. Secondly, the relationship between phase behavior and device performance is further explored in P3HT blends with either O-IDTBR or EH-IDTBR, where it was found that the dependence of eutectic composition on M_w in blends with the former acceptor correlates with a dependence of performance, while both eutectic composition and performance are largely invariant in blends with the latter. This difference was attributed to the difference in degree of crystallinity of the two acceptors, which is further explored in the fourth chapter where acceptor crystallization kinetics and phase structure are investigated using differential scanning calorimetry and variable temperature X-ray diffraction. It was found that O-IDTBR crystallization persists at faster rates compared to EH-IDTBR. The latter acceptor was found to form a liquid crystalline phase that is more robust towards fast rates compared to the crystalline phase.

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V Abbreviations

a/a	Amorphous/amorphous
BHJ	Bulk Heterojunction
D/A	Donor/Acceptor
DSC	Differential scanning calorimetry
DMTA	Dynamic mechanical thermal analysis
FH	Flory-Huggins
GIXD	Grazing incidence X-ray diffraction
LAADF-STEM	Low-angle annular dark field scanning transmission electron microscopy
HOMO	Highest occupied molecular orbital
J_{sc}	Short-circuit current
LUMO	Lowest unoccupied molecular orbital
LBG	Low band-gap
L-L	Liquid-liquid
M_w	Molecular weight
NFA	Non-fullerene acceptor
OPV	Organic Photovoltaic
PCE	Power Conversion Efficiency
PCBM	Phenyl-C ₆₁ -butyric acid methyl ester
P3HT	Poly (3-Hexylthiophene)
PDI	Perylene diimide
PDI	Polydispersity index
ϕ_{mo}	Monotectic composition
ϕ_{eu}	Eutectic composition

R-SoXS	Resonant soft X-ray scattering
RHC	Rapid heat-cool calorimetry
SIMS	Secondary ion mass spectrometry
STXM	Scanning transmission X-ray microscopy
T_g	Glass transition temperature
T_{cc}	Cold-crystallization temperature
V_{OC}	Open-circuit voltage
VT-XRD	Variable temperature X-ray diffraction
χ_{FH}	Flory-Huggins interaction parameter

CHAPTER 1: Introduction

1.1. Organic Photovoltaics

With the growing demand on energy and the current climate change crisis, further development and large-scale implementation of renewable energy resources is crucial. Solar energy is particularly important given the large amount of energy supplied by solar radiation and which is available throughout the year.

While Silicon solar cells continue to dominate the solar energy market, organic photovoltaics (OPVs) have made significant progress commercially. However, further improvements in terms of power conversion efficiency (PCE) and stability are required for it to become a more prominent player in the market.^[1] Its advantages lie in material availability, ease and cost of manufacture via roll-to-roll printing,^[2-4] as well as flexibility and lightness, which are important for facile integration into existing structures. Single-junction OPVs offer the possibility of simpler and cheaper manufacture compared to tandem cells (a vertical stack of two or more organic solar cells); the former have made significant improvements in efficiency, with certified PCEs surpassing 13 %, ^[5-8] and approaching the 15 % benchmark for commercialization.^[9,10]

1.2. Operating Principles

Upon photo-excitation of an organic semi-conductor, an exciton (bound electron-hole pair) is generated. This contrasts with the direct generation of free charge carriers in solar cells based on inorganic materials and is due to the low dielectric constant of organic semi-conductors. As a result, state-of-the-art OPVs comprise at least two components: an electron donor and an electron acceptor. Upon photo-excitation of the donor, the energetic offset between donor and acceptor lowest unoccupied molecular orbital (LUMO) energy levels acts as a driving force for exciton dissociation into free charges as the electron is transferred onto the acceptor. Following exciton dissociation, holes and electrons are transported via donor and acceptor domains, respectively, to

the relevant electrodes. Two types of recombination losses are possible: geminate concerns loosely bound electron-hole pairs following photo-excitation, while non-geminate recombination refers to when free charges originating from different excitons recombine.

The light-absorbing (active) layer in organic solar cells is processed to form a bulk heterojunction (BHJ) structure, i.e. an interpenetrating network of donor and acceptor domains. This ensures a much higher donor/acceptor (D/A) interfacial area than in a bilayer structure, which greatly enhances the probability of exciton dissociation at a D/A interface before decay to the ground state. The active layer is sandwiched between the anode and cathode. Inverted devices display the reverse polarity of their conventional counterpart, which improves the oxidative stability of the device as the low work function electrode is at the bottom instead of being in contact with air.

1.3. Materials Development

The chemical structures of the materials discussed herein are shown in figure 1.1. The most widely investigated blend type comprises Poly (3-hexylthiophene) (P3HT) as a semi-crystalline polymer donor and Phenyl-C₆₁-butyric acid methyl ester (PCBM) as fullerene acceptor, leading to an average efficiency of $\approx 3\%$.^[3] Despite the advantages of P3HT in terms of scalability,^[2-4] its wide bandgap means the more abundant low-energy photons are lost. This led to the development of low bandgap (LBG) polymers which absorb in the abundant region of the solar spectrum. Similarly, while fullerenes are widely used given favourable properties such as isotropic charge transport, the need for alternative non-fullerene acceptors (NFA) was required to circumvent costly fullerene synthesis, poor optical absorption, limited energy level tuning and morphological instability.^[3,11-13]

Blends incorporating P3HT with NFAs led to improvements across several parameters compared to their fullerene predecessors. NFAs such as FBR and IDTBR display higher lying LUMOs

compared to PCBM,^[3,11] which helps reduce voltage losses induced by large LUMO/LUMO offsets. FBR and IDTBR fall into the category of acceptor-donor-acceptor (A-A-D-A-A) type molecules and are based on a fluorene and an indacenodithiophene electron-rich (donor) core, respectively, flanked by electron-deficient (acceptor) benzothiadiazole and rhodanine units. IDTBR was reported to achieve an efficiency of 6.4 % when blended with P3HT, which at the time was the best performance for a P3HT/NFA blend.^[3] Furthermore, both FBR and IDTBR displayed improved morphological stability compared to fullerene-based devices, with IDTBR additionally improving J_{SC} due to its complementary absorption to that of P3HT.^[3,11]

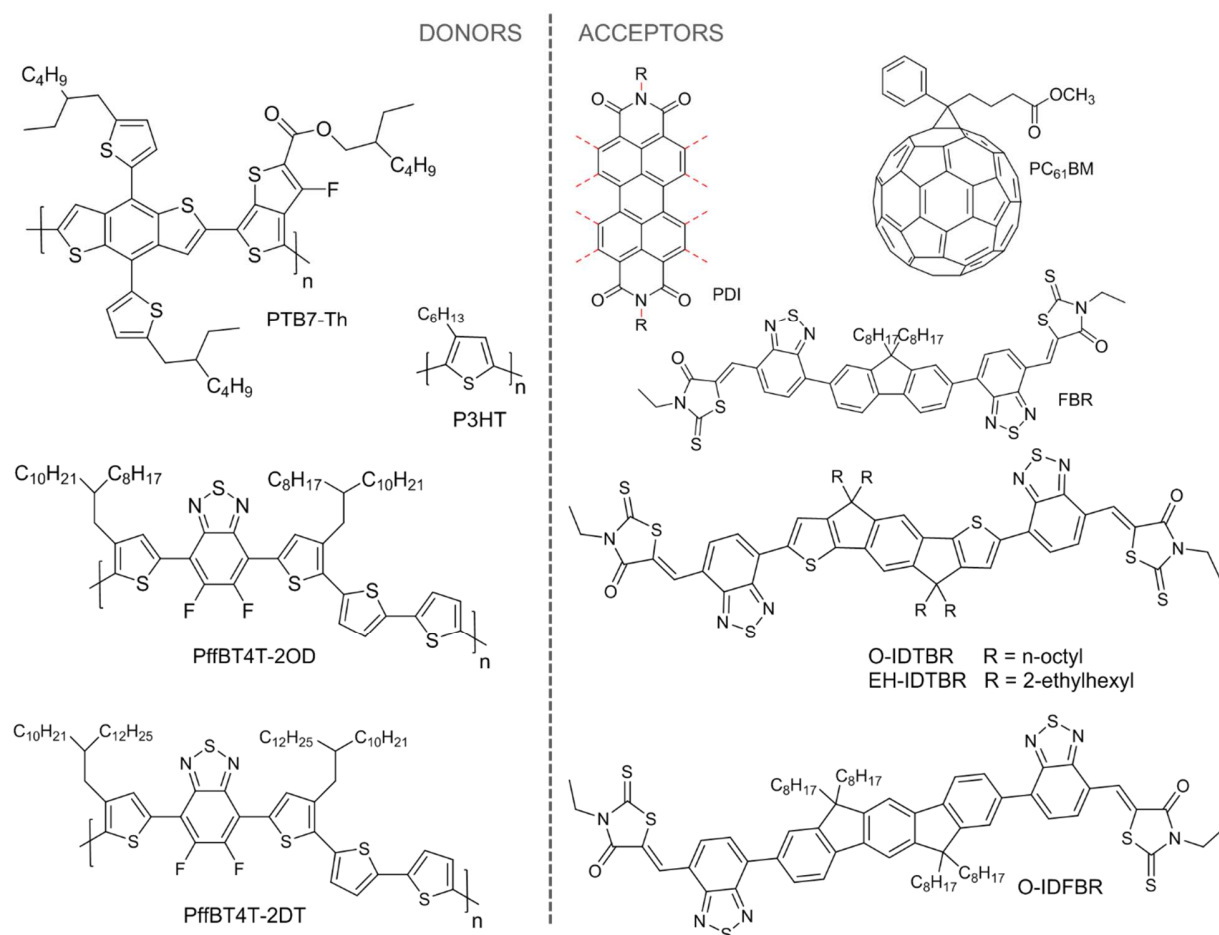


Figure 1.1. Chemical Structures (PDI functionalization positions are indicated in red).

Another important and widely used class of NFAs is that based on perylene diimide (PDI). PDI-based acceptors generally display similar electron affinity as fullerenes, with added advantages such as strong optical absorption.^[14] However, PDI acceptors generally tend to aggregate excessively, forming micrometer-size domains which reduce the probability of exciton dissociation and limit performance. As a solution to this, these acceptors are functionalized in order to reduce the extent of aggregation by inducing highly twisted structures.^[15] The best performances reported for P3HT:PDI blends remain below 2 %.^[16] Higher efficiencies are obtained when PDI acceptors are blended with low bandgap polymers like PTB7-Th; such blend types lead to an improvement in V_{OC} due to a smaller energy offset, as well as improved J_{SC} given the complementary absorption of donor and acceptor.^[17] The amorphous nature of such low bandgap polymers is also an important parameter for efficient devices incorporating PDIs as acceptor; blends of highly crystalline low bandgap polymers such as PffBT4T-2OD with PDIs may be limited by an unfavorable morphology.^[4,18]

Many high-performing devices at the moment rely on PTB7-Th or PffBT4T-based polymers as low bandgap donors.^[19,20] The former is an amorphous polymer while the latter displays strong temperature-dependent aggregation (TDA). The aggregation behavior of PffBT4T polymers is believed to be responsible for many unique properties which are not observed in other high-performing polymers; these properties include a highly favourable crystalline morphology which is robust towards several types of fullerenes and a wide range of processing parameters.^[21,22] This favourable morphology is maintained in blends with NFAs such as FBR and IDTBR, with the added advantage of additional improvements in V_{OC} ,^[23] stability (both thermal and burn-in degradation),^[24] as well as performance and shelf-life when processed from non-chlorinated solvents.^[19]

1.4. Active Layer Morphology

1.4.1. Morphology and Device Performance

The morphology of the active layer is one of the key parameters which need to be optimized to ensure high device performance and good stability. Several factors come into play with respect to optimizing the active layer structure. In order to ensure a high efficiency, the morphology must allow efficient exciton dissociation, i.e. a low probability of geminate recombination. This generally requires that the size of donor and acceptor domains are on the order of the exciton diffusion length ($< \approx 10$ nm),^[25] such that excitons generated within either domain are likely to reach a donor/acceptor (D/A) interface before the exciton decays to ground. Additionally, both domain types must be sufficiently pure to enable efficient charge transport to the electrodes by minimizing non-geminate recombination. In fact, the initial picture of the ideal BHJ morphology was based on a two-phase morphology comprising pure donor and acceptor domains. However, since the observation of partial miscibility in the benchmark P3HT:PCBM blend,^[26] it is accepted that the presence of a third amorphous mixed phase is in fact beneficial as the energetic cascade between pure and mixed regions enhances exciton dissociation.^[27]

However, the aforementioned requirements in terms of domain size and purity are general guidelines. The optimal morphology varies significantly depending on material and blend properties. While many optimized blend types have been shown to display a three-phase morphology (crystalline polymer domains, crystalline or amorphous acceptor aggregates and an amorphous polymer-rich matrix), blends relying on amorphous polymers can form a two-phase morphology at most. The degree of mixing in the amorphous mixed phase varies depending on the miscibility between blend components.

This diversity in morphology types highlights the need for a rational approach to materials design, synthesis and subsequent blend selection, instead of the costly and time-consuming trial-and-error-based approach which has thus far dominated progress in the field of OPVs.

Morphology formation during spin-coating is governed by both kinetic and thermodynamic factors. The former concerns variables such as drying rate and the kinetics of crystal nucleation and growth, while the latter includes solubility limits and the interactions between donor and acceptor molecules, which govern the liquid-liquid (L-L) two-phase region (i.e. the binodal or miscibility gap).^[28] In terms of material-relevant variables, understanding the crystallization behavior of a given crystallizable component in the neat state, as well as the miscibility between components, and its effect on crystallization kinetics, is crucial for achieving favourable microstructures. The advantage of ordered polymer domains in blends incorporating crystalline donor polymers has long been observed.^[21,29] Depending on the choice of acceptor, donor crystallization may remain relatively unperturbed in the blend,^[30] or may be severely disrupted due to excessive miscibility between blend components.^[31]

In contrast, a system where donor and acceptor display a low level of miscibility (i.e. large miscibility gap) is likely to induce domains which are excessively large and pure; additives are commonly used in such cases to control the extent of demixing. Apart from device performance, morphological stability also depends on the degree to which blend components are miscible. Stability of the active layer structure is governed by a combination of how far domain composition is from the binodal and by the glass transition,^[12,32] which determines the temperature above which quenched compositions may over-purify due to diffusion.

1.4.2. Miscibility Considerations and Flory Huggins Interaction Parameter

There has been increasing interest in quantifying miscibility between blend components in OPVs. Such reports have been typically based on the Flory-Huggins (FH) interaction parameter (χ_{FH}), which governs the energetic contribution to the free energy of mixing in a blend of A and B molecules (in contrast to the entropic contribution, which always favors mixing). χ_{FH} is a measure of the relative strength of AB interactions compared to interactions between like molecules (i.e. AA and BB). Larger χ_{FH} values indicate a lower energetic driving force for mixing. χ_{FH} is commonly estimated using the melting point depression method,^[33–39] although other methods and approximations are used.^[40,41] However, most of these analyses are narrow in scope and/or unclear in the true meaning of the extracted interaction parameter. In its original formulation, χ_{FH} is a measure of the amorphous/amorphous (a/a) miscibility in a polymer solution of a semi-crystalline polymer mixed with an amorphous solvent.^[42] It quantifies the degree to which the amorphous diluent is mixed in amorphous polymer domains; this is dictated by the molecular interactions between polymer and diluent, which in turn are governed by the chemical structures of both components. However, direct extraction of χ_{FH} (i.e. amorphous/amorphous miscibility) from melting point depression data is only valid for certain crystalline/amorphous blend types. In contrast, in other blend types, melting point depression data must first be corrected for the effect of crystalline/amorphous interactions in order to accurately estimate a/a miscibility.^[32,42–44] Additionally, the melting point depression method evaluates the interactions near the melting point,^[39] which is much higher than device processing temperatures. Recently, two methods have been reported as a more quantitative approach to the evaluation of the temperature dependence of χ_{FH} , i.e. $\chi_{FH}(T)$.^[43]

The first method uses secondary ion mass spectrometry (SIMS) to measure the degree of inter-diffusion between polymer and acceptor films stacked in a bilayer configuration as a function of annealing temperature. The temperature-composition (T - ϕ) data points thus obtained are then fitted with the FH equation for the binodal, allowing $\chi_{FH}(T)$ to be determined. The second method uses scanning transmission X-ray microscopy STXM to measure an effective (uncorrected) interaction parameter after aggressive thermal annealing to induce maximal demixing; this provides a measure of the maximum possible purity of the polymer-rich amorphous phase. To obtain $\chi_{FH}(T)$, they correct the value from STXM with the crystalline/amorphous interaction parameter ($\chi_{c/a}$) determined from Differential Scanning Calorimetry (DSC). These methods are easiest to apply to blends incorporating an amorphous polymer and acceptor. Crystalline polymers incur an added complexity in that the degree of crystallinity must be taken into account.^[32]

While a lot of work on quantifying miscibility and understanding its effects on performance and stability has focused on fullerene-based blends, investigation of the more promising blends incorporating NFAs lags behind.^[45]

The reported model according to which temperature-dependent miscibility is extracted from STXM or SIMS and correlated with device performance is evidently an important milestone in building a more rational approach to material design and blend selection in OPVs.^[43] However, these techniques are not widely accessible. Thermal analysis, a simpler and more accessible tool, can also provide valuable information in terms of morphological structure and stability. Some thermal analysis techniques are commonly used in the field of OPVs, such as DSC. However, the potential of several thermal analysis techniques to provide a more quantitative method for morphology characterization,^[46] or a more rational approach to the optimization of morphology structure and stability,^[47] has only recently gained interest, as will be discussed in the next section.

1.5. Role of Thermal Analysis in Morphology Characterization

1.5.1. General Insights from Thermal Analysis

The thermal analysis techniques most commonly used in OPVs are DSC and thermogravimetric analysis (TGA). The former can be subdivided into standard DSC and flash or hyper-DSC (also known as rapid heat-cool calorimetry (RHC) or fast scanning calorimetry), where much faster scanning rates can be achieved.^[48]

In terms of its basic purposes in the field of OPVs, DSC is used to characterize the melting/crystallization behavior and glass transitions of materials. It should however be noted that determination of the glass transition temperature (T_g) is not always possible using standard DSC, and other thermal analysis techniques are sometimes required for increased sensitivity, such as RHC or dynamic mechanical thermal analysis (DMTA).^[49–51] The temperature and magnitude of melting/crystallization transitions in OPV blends compared to neats provides an indication of the degree of mixing.^[2,4,34,35] Fusion enthalpies are also important for understanding the relative degree of crystallinity of a given material,^[39] and can also be used to validate temperature-composition ($T-\phi$) diagrams in blends.^[52]

Recently, it has been suggested that information from DSC can be used for a more predictive understanding of the relationship between component crystallinity, relative degree of phase separation, device performance and stability in a given blend.^[47] The suggested model is based on the commonly observed shift in non-fullerene acceptor cold-crystallization temperature (T_{cc}) upon blending with a polymer donor.^[2,45] The strength of the T_{cc} depression, dictated by the polymer's degree of crystallinity, was found to correlate with domain size and purity, as well as morphological stability.^[47]

Apart from crystallinity considerations, the glass transition is also a very important parameter for morphological characterization. T_g indicates the maximum temperature below which the morphology is stable in a given organic solar cell,^[53] as well as the minimum temperature for morphology optimization via thermal annealing.^[54] Furthermore, the glass transition provides information on the extent of phase separation in amorphous films, or in amorphous phases in films comprising both crystalline and amorphous domains. The presence of one or two glass transitions in a binary blend may be related to the degree of phase separation in the amorphous phase (i.e. one or two-phase system);^[55] the occurrence of two glass transitions has also been attributed to the presence of two mixed amorphous phases which differ in composition.^[56] In addition, monitoring the changes in T_g of one of the binary components as a function of composition can also provide a measure of the change in purity of the mixed amorphous phase; in P3HT:PCBM, the drop in T_g above 66 wt% PCBM has been attributed to the formation of a purer P3HT-rich amorphous phase.^[50] In fact, using T_g as a measure of domain composition is currently being explored as a promising new method to quantify absolute composition in the mixed amorphous phase.^[46] This method relies on fast scanning calorimetry; in contrast to DSC, very little material is required such that investigation can be performed directly on spin-cast thin films, prepared in the same way device active layers are processed.^[46] The larger sample size required for DSC means that spin-casting cannot be used as films are not thick enough, so samples are instead drop-cast.

With this in mind, apart from the promise of quantitative measurement of domain purity, we believe that fast scanning calorimetry will likely play a significant role as a fast screening tool for rational material selection based on blend miscibility. Nonetheless, standard DSC has led to important developments in morphology optimization, especially in terms of temperature-composition (T - ϕ) diagrams. These developments are discussed in the next section.

1.5.2. Temperature-composition diagrams

Early work on T - ϕ diagrams of binary blends in organic electronics involved applying blend phase behavior understanding to control organic semiconductor crystallization for optimizing both electrical properties, as measured in field-effect transistors, as well as thin-film mechanical properties.^[57,58] For simplicity, we will focus here on crystalline-crystalline or crystalline-amorphous polymer-small molecule binaries. Eutectic and monotectic behavior are two commonly observed types of (non-equilibrium) phase diagrams. They differ in miscibility between binary blend components. Eutectic behavior is characteristic of blends where the melting temperature of both components is comparable and/or where they are miscible in the liquid state,^[59] and display partially miscibility in the solid state.^[60] In the case where crystallization of either component may be super-cooled, liquid-liquid phase separation may be observed below the liquidus in eutectic blends. In fact, miscibility gaps ‘submerged’ below the liquidus curve affect its shape.^[61,62] When a given blend additionally displays partial miscibility in the liquid phase (above the liquidus), monotectic phase behavior develops (figure 1.2).^[60,63]

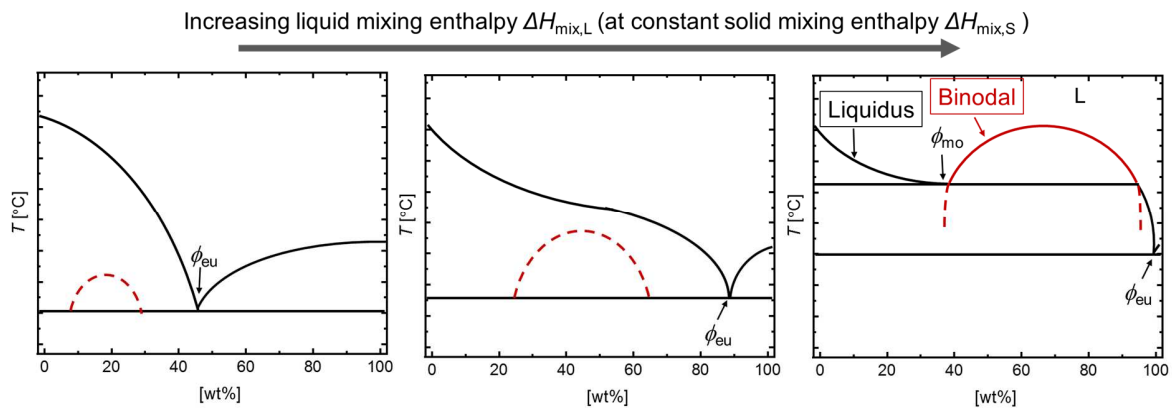


Figure 1.2. Effect of increasing liquid immiscibility on the shape of the phase diagram within the framework of regular solution theory; the simple eutectic on the left develops a monotectic, at compositions ϕ_{eu} and ϕ_{mo} , respectively. Modelled after Pelton and Thompson,^[64] and Matkar and Kyu.^[60]

According to the type of phase behavior, different microstructures are possible depending on the rate of solidification and the blend composition.^[59,65]

In the field of OPVs, over a decade ago, a model was suggested for rationalizing optimal D/A ratios in crystalline-crystalline polymer-small molecule binaries based on $T-\phi$ diagrams, whereby device performance of a eutectic blend is maximized at hyper-eutectic compositions (with respect to acceptor wt%).^[66] The improved performance was attributed to the formation of a favourable morphology which not only comprised a fine grained D/A matrix (from solidification at the eutectic composition), but also acceptor primary crystals which are formed at more acceptor-rich compositions relative to the eutectic (i.e. hyper-eutectic).^[66,67] Eutectic phase behavior has since been reported for many OPV blends comprising P3HT with either fullerene or non-fullerene acceptors,^[4,67] as well as in blends based on other donor polymers.^[52,68–70]

In the case of monotectic phase behavior, monotectic solidification precedes the eutectic reaction upon cooling from the melt (i.e. occurs at a higher temperature). As the size of the liquid miscibility gap increases (i.e. covers a larger composition range), the eutectic point is increasingly pushed towards the neat acceptor composition (figure 1.2).

Liquid-liquid phase separation is hard to detect from DSC due to limited sensitivity towards T_g detection. However, when precise determination of the miscibility gap is not required, its presence can be inferred from the shape of the liquidus curves determined from DSC.^[58,65]

As mentioned above, the benefit of hyper-eutectic compositions in optimizing active layer morphologies is now widely accepted and observed. However, we believe the analysis of $T-\phi$ diagrams have thus far been incomplete since additional (qualitative) information can be extracted on liquid miscibility. The type of phase behavior can in many cases be used to distinguish between

low- and high-miscibility blends.^[32] In view of this, in the next section we discuss the motivation behind the work presented herein and provide its outline.

1.6. Motivation

As highlighted above, crystallization dynamics of OPV blend components and their mutual miscibility are very important parameters for optimizing device performance as they dictate the active layer morphology. An increasing number of studies focus on developing a quantitative and predictive approach to active layer optimization based on miscibility and crystallinity considerations.^[43,47] Some of the suggested methods rely on techniques which are not easily accessible, namely STXM and SIMS.^[43] The use of DSC as a tool to evaluate relative miscibility within the framework of Flory Huggins Theory is interesting, and has become common given its appeal as a simple and easily accessible tool. However, similar to what occurred in the field of polymer blends after the middle of the 20th century,^[42] the values reported are likely inaccurate and their significance is clouded by the approximations made, such that the interaction parameters are only a measure of relative miscibility within the context of the work in question. Even then, other issues arise. For instance, χ_{FH} is a measure of the strength of molecular interaction between a polymer and a small molecule diluent *near the melting point of the polymer*. This invalidates comparing interaction parameters for two polymer:small molecule blends where the melting point of both polymers are significantly different, as in the case of P3HT and PPC4.^[37] Hence, we find that a more accurate qualitative method of comparing miscibility in such cases would be to simply compare the magnitude of the melting point depression.

Apart from applications involving Flory Huggins theory, it is evident that the determination of T - ϕ diagrams using DSC has provided valuable insight into D/A ratio optimization of crystalline-crystalline polymer/small molecule binaries.^[66] However, the above discussion of phase behavior

fundamentals raises the question of the effect of liquid miscibility on the shape of the liquidus curves in the reported eutectic diagrams of poly(3-alkylthiophenes) with fullerene acceptors (figure 1.3).^[66] In fact, it may be suggested that P3DDT/PCBM evokes the case of a blend displaying monotectic phase behavior, whereby the miscibility gap intersects the liquidus curves at hyper-eutectic compositions, with respect to acceptor content.

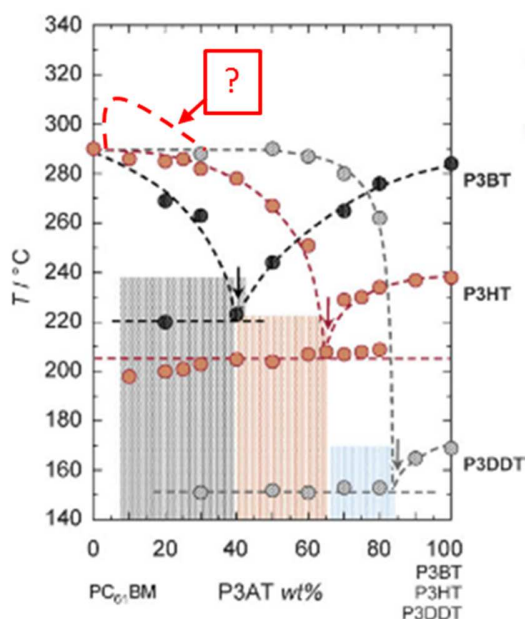


Figure 1.3. T - ϕ diagrams of P3AT/PCBM. Adapted with permission.^[66]

In light of this, here we focus on further exploring the potential of thermal analysis, specifically DSC, in helping understand the correlation between chemical structure, (non-equilibrium) phase behavior and performance (based on morphological considerations). Albeit far from quantitative, the richness of thermal analysis as a characterization tool is highlighted by the nature of ongoing efforts investigating its potential in developing a more predictive and quantitative method for morphology optimization,^[32,43,46,47,71] which brings the work presented herein in line with this promising approach. We do not attempt to calculate interaction parameters. Instead, the focus is on exploring the full potential of information provided from non-equilibrium phase diagrams to understand its effect on morphology.

We focus on two donor polymers with different degrees of crystallinity, P3HT and PffBT4T-2DT (the latter being more crystalline). Those are paired with O-IDTBR, EH-IDTBR and O-IDFBR as NFA. The change from octyl to ethylhexyl side chains in the O-IDTBR acceptors leads to a change in crystallization dynamics.^[3] Similarly, O-IDFBR has a more twisted core given the bulkier phenyl groups of the indenofluorene unit compared to thiophene aryl groups in indacenodithiophene of O-IDTBR. This leads to a predominantly amorphous acceptor.^[72]

1.7. Outline

In chapter 2, we investigate the phase behavior in blends incorporating PffBT4T-2DT with either O-IDTBR or O-IDFBR. In contrast to the commonly observed eutectic behavior, we find that these blends display monotectic $T-\phi$ diagrams, suggesting partial miscibility in the liquid phase. OPV devices were fabricated at several compositions to probe the effect of such phase behavior on D/A ratio optimization. It is observed that the best device performance (and short-circuit current) occurs near the monotectic composition, which we partly attribute to a finer morphology compared to more acceptor-rich compositions (hyper-monotectic), where a miscibility gap is expected in the liquid phase. A more in-depth understanding of the changes in morphology as a function of composition is obtained using a combination of microscopy, spectroscopy and X-ray techniques. We suggest that the size of acceptor domains is similar across all D/A ratios probed, while a significant increase in polymer domain size and purity occurs at hyper-monotectic compositions.

In chapter 3, we investigate the phase behavior of EH-IDTBR and O-IDTBR in binary blends with various molecular weights (M_w) of P3HT as polymer donor. Eutectic behavior is observed, with a variation in eutectic composition as a function of M_w in blends incorporating O-IDTBR, while the eutectic composition is observed to be M_w -independent when the branched side-chain acceptor is

used. We find that this correlates with the device performance dependence on M_w with O-IDTBR, and independence with EH-IDTBR.

Chapter 4 focuses on a more in-depth investigation of the thermal behavior of O-IDTBR and EH-IDTBR as a function of heating/cooling rates and annealing. We find that the O-IDTBR crystallization is robust towards a wide range of rates, while EH-IDTBR displays more complex, rate-dependent behavior, with a higher barrier to crystallization. The branched chiral side-chains induce a difference in isomeric purity between batches, which is observed to affect the rate of nucleation of the crystalline phase. Furthermore, combining DSC with variable temperature X-ray diffraction, we suggest the occurrence of a mesophase.

CHAPTER 2: Influence of Polymer Aggregation and Liquid Immiscibility on Morphology Tuning by Varying Composition in PffBT4T-2DT/Non-Fullerene Organic Solar Cells

In this chapter, we focus on understanding the effect of monotectic phase behaviour on D/A ratio optimization in blends of the low bandgap polymer PffBT4T-2DT with O-IDTBR as acceptor. Devices showed that the best performances were achieved at the estimated monotectic composition, observed at ≈ 50 wt% and 60 wt% O-IDTBR and O-IDFBR, respectively.

Using a combination of microscopy, spectroscopy and X-ray techniques, we investigate the changes in morphology and correlate them to the $T-\phi$ diagram and device performance. We also briefly explore the effect of acceptor crystallinity by using O-IDFBR as acceptor, which is largely amorphous given its twisted backbone due to the bulkier phenyl moieties of the indenofluorene unit compared to thiophene flanking aryl groups in indacenodithiophene. The observed phase behavior allowed a qualitative rationalisation of the optimal morphology in terms of the varying interplay between solid-liquid (S-L) and liquid-liquid (L-L) phase separation as a function of composition. We find that the best performance is dictated by control of the degree of phase separation by selecting a D/A ratio which doesn't lie within the liquid two-phase region inferred from DSC.

This work has been published in Advanced Energy Materials.^[73]

2.1. Background

Binary blends combining PffBT4T-2OD with fullerene acceptors display several advantages, such as the possibility of processing from hydrocarbon solvents, and a robust microstructure leading to high efficiencies even in thick films.^[21,74] However, studies on the phase behavior of such blends and its impact on optimal D/A ratios in devices are lacking. T - ϕ data have been reported for PffBT4T-2OD blended with PCBM as acceptor, but there was no comment on the resultant eutectic.^[40] It is thought that the temperature-dependent aggregation behavior of PffBT4T polymers is a key factor behind the favorable morphology in as-cast devices, leading to the formation of highly pure polymer crystallites around 40 nm in size for a variety of processing parameters (spin speed, temperature and concentration) and fullerenes.^[21,22] Blends of PffBT4T polymers (namely PffBT4T-2OD or its longer side-chain derivative, PffBT4T-2DT) with rhodanine-flanked non-fullerene acceptors show comparable crystalline polymer domains,^[23,75] but offer several advantages over their fullerene counterparts, namely higher voltages, reduced voltage losses,^[23] improved stability towards thermal and burn-in degradation,^[24] and also show enhancement in efficiency and shelf life when processed from hydrocarbon solvents.^[19] D/A ratio tuning and its impact on morphology in blends of the PffBT4T polymers with either fullerenes or NFAs is however not explored in detail.^[23,75]

To this purpose, here we focus on elucidating the effects of D/A ratio tuning on the morphology of devices incorporating PffBT4T-2DT with O-IDTBR. In contrast to the observation of eutectic T - ϕ phase behavior in crystalline/crystalline blends so far, DSC thermograms of neat materials and blends suggest monotectic phase behavior (indicating low liquid miscibility), with a monotectic point at intermediate composition. Such behavior has been referred to schematically before in the context of OPVs,^[32] as also illustrated in figure 2.1.

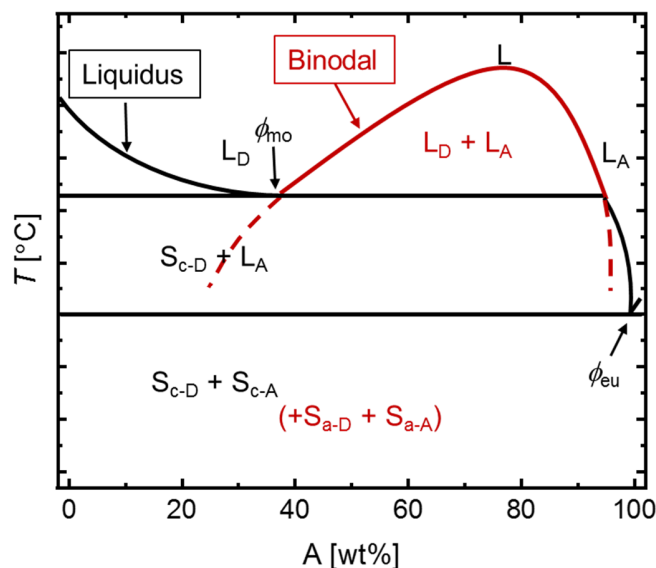


Figure 2.1. Schematic illustrating monotectic phase behavior with increasing small molecule acceptor (A) content in a polymer/small molecule binary; monotectic and eutectic points (ϕ_{mo} and ϕ_{eu} , respectively) are highlighted. L denotes the homogeneous liquid and L_D and L_A refer to donor-rich and acceptor-rich liquids, respectively. $S_{c-D(A)}$ denotes crystalline donor (acceptor), in contrast to the amorphous solid denoted as $S_{a-D(A)}$. The volume fraction of amorphous donor (acceptor) ($S_{a-D(A)}$) formed after cooling from the melt will depend on the starting composition of the liquid L as well as cooling kinetics. The eutectic is shown here for completeness; it lies practically at 100 wt % acceptor content given the large difference between polymer and acceptor melting temperatures.^[63] The difference in molecular size in such a blend leads to an asymmetric binodal (red curve). Modelled after Matkar et al. and Burghardt.^[60,63]

2.2. Bulk Phase Behavior in PffBT4T-2DT:NFA blends

DSC is used to examine the T - ϕ diagram of PffBT4T-2DT ($M_w = 41$ kDa) combined with either O-IDTBR or O-IDFBR as NFA. Thermograms of the neat materials and the blends, as well as the resultant T - ϕ diagrams, are shown in Figure 2.2. Pure PffBT4T-2DT shows one sharp melt with an endset temperature T_m at 260.5 °C and an enthalpy of fusion ΔH_f of 22 J g⁻¹. Pure O-IDTBR shows one sharp melt at 227.3 °C ($\Delta H_f = 46$ J g⁻¹) preceded by a cold crystallization ($\Delta H_{cc} = 21$ J g⁻¹) at $T_{cc} = 111.2$ °C. O-IDFBR shows two endotherms at 123 °C and 193 °C ($\Delta H_f = 28$ and 55 J g⁻¹).

g⁻¹). T - ϕ diagrams indicate monotectic phase behaviour, with a monotectic composition $\phi_{mo} \approx 50$ wt% and 60 wt% acceptor in the case of O-IDTBR and O-IDFBR, respectively. Using a higher molecular weight (M_w) in blends with O-IDTBR leads to a slight shift in monotectic composition (figure 2.3). Despite the two intense endotherms in the first heating of O-IDFBR, O-IDFBR is known to have a weaker tendency to aggregate compared to O-IDTBR,^[2,72] as illustrated in the DSC cooling and second DSC heating cycles, where no crystallization/ melting transitions occur (second heating is shown in figure 2.2). The lower crystallinity of O-IDFBR is also consistent with the difference in acceptor degree of crystallinity observed in thermograms of blends with PffBT4T-2DT. This is quantified by comparing measured vs. calculated fusion enthalpies for each component at a given D/A ratio, as illustrated in figure 2.2e & f as follows: in contrast to the complete crystallization of O-IDTBR at all compositions probed, O-IDFBR crystallization is inhibited from 60 wt% to 90 wt % O-IDFBR and is almost completely suppressed from 10 wt% to 60 wt %. The monotectic composition occurs at a more acceptor-rich loading compared to blends with O-IDTBR (around 60 wt % O-IDFBR). This is likely due to the lower melting temperature of O-IDFBR and weaker polymer/acceptor repulsive interactions with O-IDFBR compared to O-IDTBR,^[76] such that the polymer-rich melt tolerates a higher NFA content.

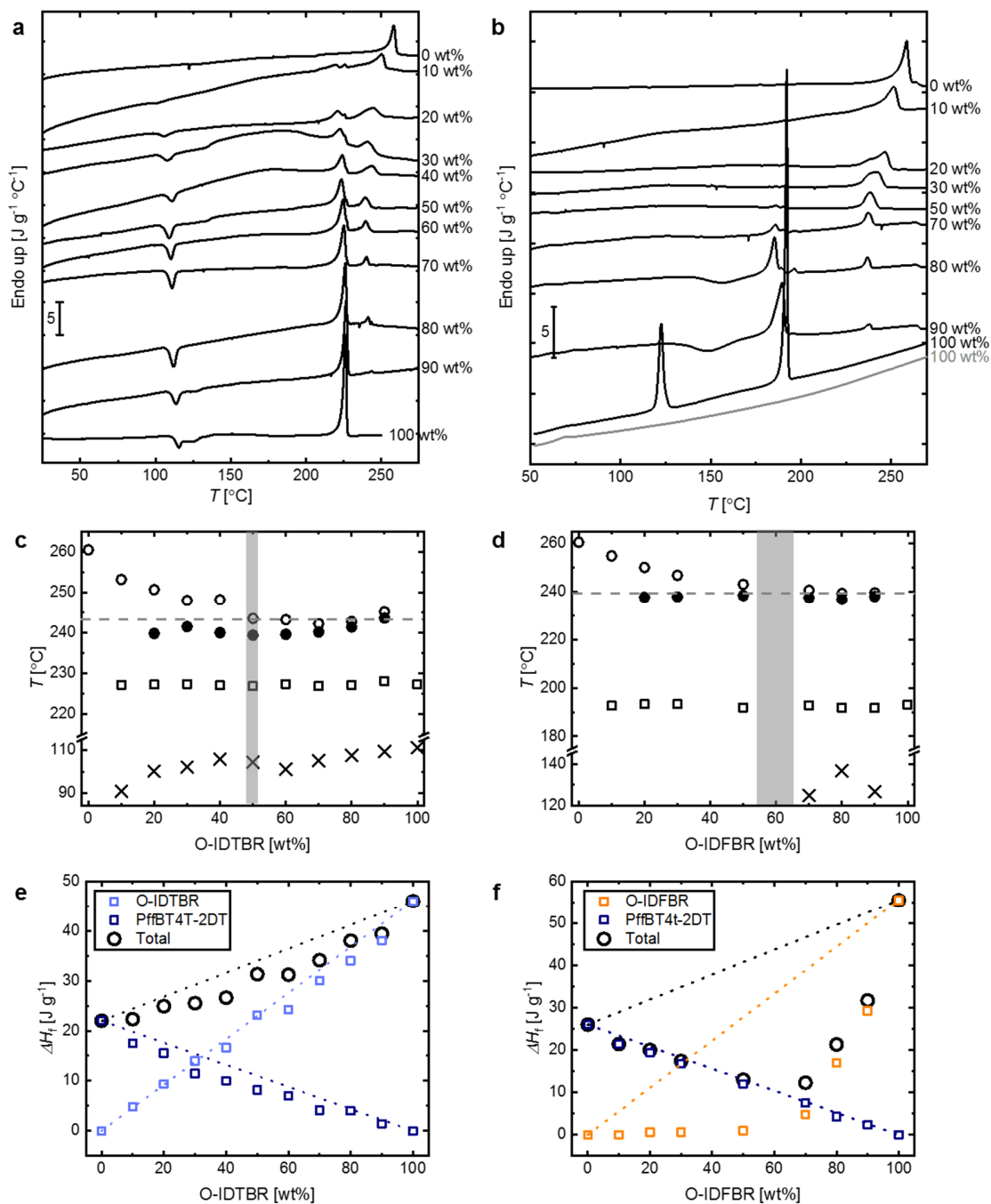


Figure 2.2. DSC first heating thermograms of 41 kDa PffBT4T-2DT with O-IDTBR (a) and O-IDFBR (b); the second heating cycle of neat O-IDFBR is shown in grey. Thermograms are offset for clarity and the scale bar indicates the Y-axis scale. The concentration of NFA is indicated on the right. (c,d) T - ϕ diagrams of PffBT4T-2DT with O-IDTBR and O-IDFBR, respectively; empty circles correspond to the polymer melt endset temperature; filled circles correspond to the peak of the low-temperature shoulder of the polymer endotherm from 10 to 40 wt % O-IDTBR (20 to 30

wt% O-IDFBR), and to the peak temperature of the polymer endotherm from 60 to 90 wt % O-IDTBR (50 to 90 wt% O-IDFBR); empty squares indicate the endset melting temperature of the NFA and crosses denote the onset temperature of acceptor cold-crystallization; vertical and horizontal lines are guides to the eye and roughly denote monotectic composition and temperature, respectively. (e,f) Fusion enthalpies ΔH_f of each component (and the combined total) for PffBT4T-2DT with O-IDTBR (e) and O-IDFBR (f), extracted from first heating DSC thermograms; symbols correspond to measured values while dashed lines are from calculated values obtained by weighting the enthalpy of fusion of the neat to its composition in the relevant blend. Very good agreement is observed in PffBT4T-2DT:O-IDTBR, suggesting that each component is able to crystallize almost completely at all compositions at the rates used during the DSC experiment. In contrast, while the trend in fusion enthalpy of the polymer is the same when combined with O-IDFBR, acceptor crystallization is inhibited between (60 to 90) wt % O-IDFBR and is almost completely suppressed between (10 to 60) wt %.

The processes governing solidification from the melt differ depending on the starting D/A ratio. At donor-rich compositions below ϕ_{mo} , polymer crystallization (S-L demixing) most likely initiates microstructure formation. A large activation energy for nucleation may delay the onset of crystallization (i.e. supercooled crystallization) such that L-L demixing would occur first,^[63] but this is unlikely for the system of interest here given the polymer's strong tendency to aggregate. Following S-L demixing, the composition of the remaining liquid phase is 'pushed' towards/into the L-L two-phase region. Hence, when the starting composition is within the range of the miscibility gap (above ϕ_{mo}) in the melt, L-L demixing likely dominates microstructure formation, which would lead to a highly phase separated microstructure. In contrast, for compositions $\phi \leq \phi_{mo}$, crystallization likely plays a more important role, which would freeze-in a smaller length scale.

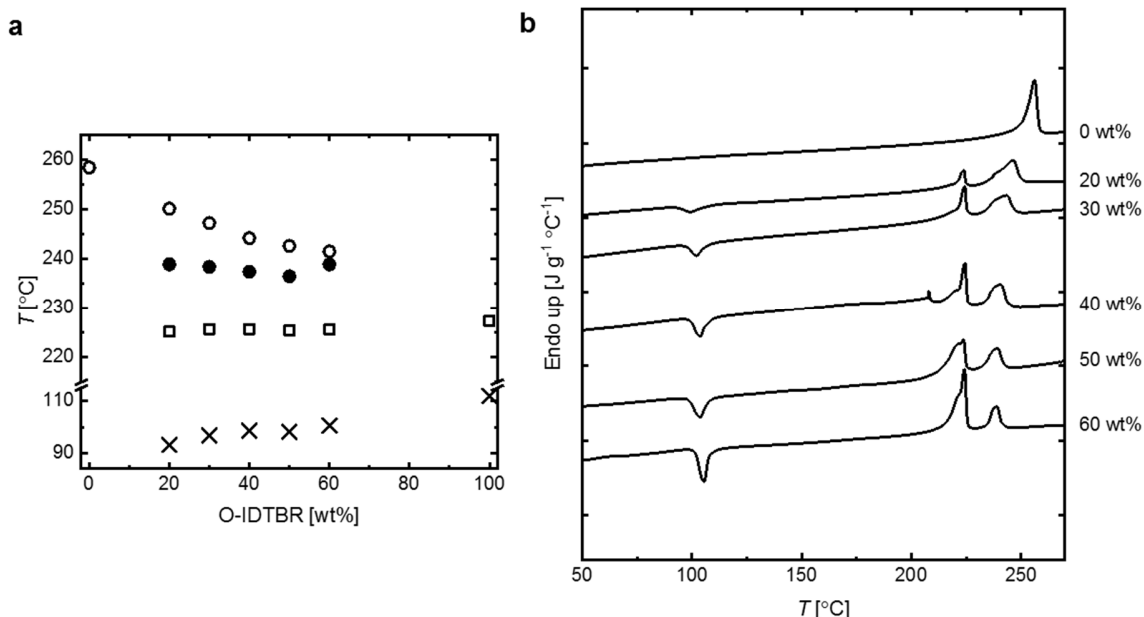


Figure 2.3. (a) T - ϕ diagram for 55 kDa PffBT4T-2DT:O-IDTBR constructed from (b) first heating thermograms DSC thermograms. The T - ϕ diagram suggests that the monotectic composition is slightly richer in acceptor compared to the 41 kDa batch; a slight shift in monotectic is indeed expected as M_w changes, similarly to eutectics.^[3] Symbols bear the same meaning as figure 2.2.

To evaluate the effect of monotectic phase behaviour on device composition dependence, in the next section we focus on device performance as a function of composition. The active layers in OPV devices are formed upon solidification from solution, which is evidently different from solidification from the melt. It should be noted, however, that the solvent does not dramatically affect the size and location of the L-L two-phase region, which is governed by donor/acceptor interactions.^[77] As such, in combination with the established understanding of the aggregation behavior of PffBT4T polymers, it is reasonable to use the phase behavior obtained from DSC to provide an idea of the interplay between L-L and S-L demixing during solution casting. As such, it is expected that spun cast active layers will display a coarser morphology when the composition is hyper-monotectic with respect to acceptor content.

2.3. Device Performance as a Function of D/A Ratio

We will first focus on devices fabricated using O-IDTBR as acceptor. Current-voltage (J - V) characteristics of devices as a function of D/A ratio for the two polymer molecular weights (41 kDa and 55 kDa) are summarized in **table 2.1**. The maximum efficiency obtained with a PffBT4T-2DT M_w of 41 kDa is lower than that previously reported for the same blend (6.9 vs. 10 %).^[23] The higher M_w batch was thus used to confirm the occurrence of efficiencies comparable to literature, although maximizing PCE is not central to this study. A maximum PCE of 8.4 % was obtained and we observe similar trends in the dependence of device parameters on composition for both batches (Figure 2.4).

Power conversion efficiency (PCE) is found to be largely dictated by J_{SC} . It can be seen that PCE and J_{SC} both peak around (50 to 55) wt % O-IDTBR (devices fabricated using the lower M_w batch show comparable performance at 50 wt % & 55 wt % acceptor). From the J - V characteristics, it can be seen that devices fabricated with the 41 kDa polymer batch with a 50 wt % acceptor loading display, on average, an efficiency of 6.1 ± 0.8 % with a J_{SC} of 11.2 mA m^{-2} and fill factor (FF) of 0.52. At higher and lower acceptor concentrations, average J_{SC} and PCE drop with a minimum observed at 74 wt % O-IDTBR (6.0 mA cm^{-2} and 3.3 %, respectively). FF varies very little, going from 0.49 ± 0.02 at 41 wt % to 0.54 ± 0.02 at 74 wt % O-IDTBR. The same can be said for V_{OC} , which remains around 1.00 - 1.04 V.

With the 55 kDa batch, similar behavior occurs in that average J_{SC} and PCE both peak at 50 wt % acceptor (13.4 mA cm^{-2} and 7.9 %). Average FF reaches its maximum of 0.62 at 41 wt % O-IDTBR, and remains around 0.59 ± 0.02 upon further acceptor addition.

Table 2.1. *J-V* characteristics and thicknesses of PffBT4T-2DT:NFA devices; active layer solution concentration is 15 mg mL⁻¹ unless stated otherwise. Measurements by Andrew Wadsworth and Sarah Holliday.

PffBT4T-2DT <i>M_w</i> [kDa] / NFA	NFA [wt %]	<i>J_{sc}</i> [mA cm ⁻²]	<i>V_{oc}</i> [V]	<i>FF</i>	average PCE ^{a)} [%]	Thickness ^{b)} [nm]
41 kDa / O-IDTBR	41	10.1	1.03	0.49	5.1 (±0.48)	104
	50	11.2	1.04	0.52	6.1 (±0.77)	85
	55	10.9	1.03	0.52	5.9 (±0.57)	88
	64	9.3	1.02	0.57	5.4 (±0.29)	77
	74	6.0	1.00	0.54	3.3 (±0.30)	72
55 kDa / O-IDTBR	41 ^{c)}	11.8	1.01	0.62	7.3 (±0.18)	60
	50	13.4	1.03	0.57	7.9 (±0.51)	69
	64	10.3	1.03	0.59	6.2 (±0.60)	66
	74	8.7	1.02	0.60	5.3 (±0.48)	68
41 kDa / O-IDFBR	50	7.1	1.04	0.38	2.8 (±0.65)	108
	64	8.5	1.02	0.42	3.6 (±0.49)	107
	74	6.7	1.04	0.46	3.2 (±0.48)	91

^{a)}The average PCE and standard deviation were calculated over 7-12 devices; ^{b)}Thickness values are averaged over at least three measurements for each device, taking into account the centre and edge of the active layer; ^{c)}13 mg mL⁻¹ active layer solution concentration was used to reduce the thickness from 77 to 60 nm

Comparing device performances of the two *M_w*, the lower *J_{sc}* and *FF* with the 41 kDa polymer compared to 55 kDa can be attributed to a sub-optimal morphology. This has been observed for PffBT4T-OD:PC₇₁BM, where lower *M_w* was found to induce larger, lower purity domains with poorer π - π stacking (as measured from the lower coherence length from GIWAXS), leading to reduced *FF* and *J_{sc}*.^[22]

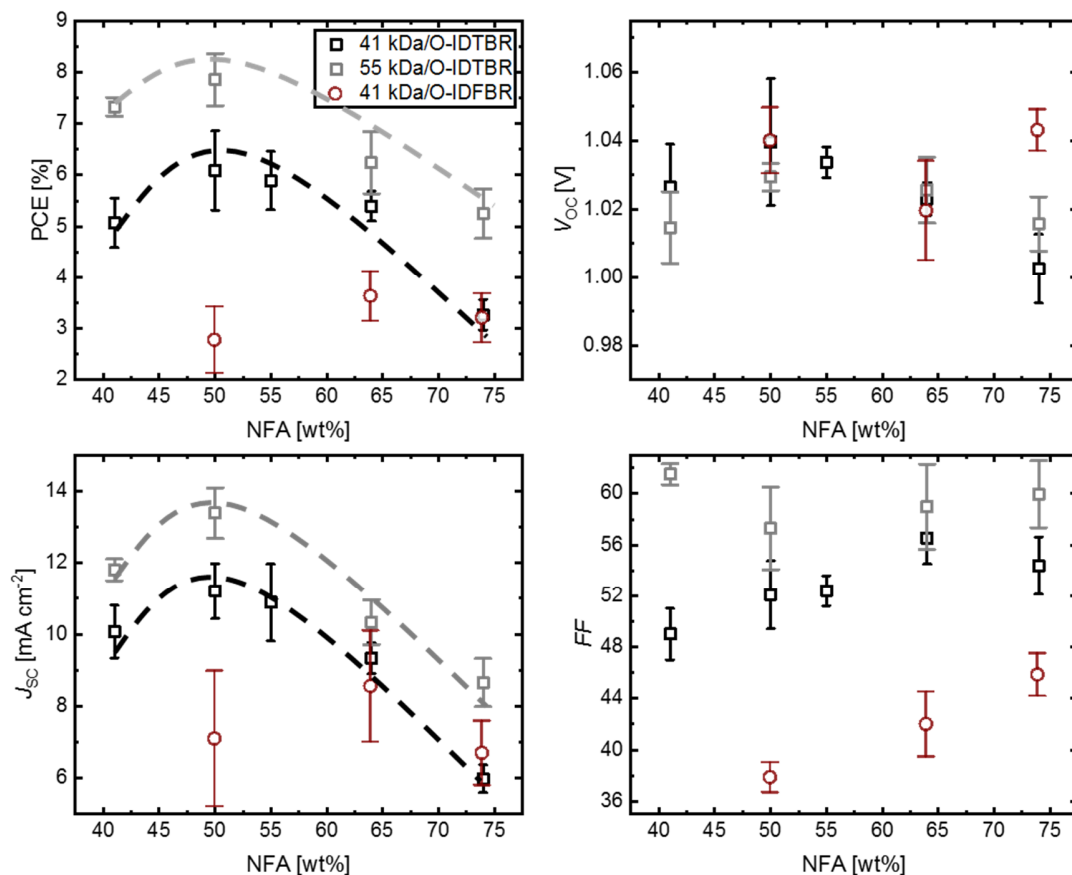


Figure 2.4. Device parameters of PffBT4T-2DT:NFA as a function of D/A ratio and polymer molecular weight (41 and 55 kDa); dashed lines were manually constructed as guides to the eye; average values and standard deviations were calculated over 6-14 devices. Measurements by Andrew Wadsworth and Sarah Holliday.

Devices utilizing the low M_w polymer with O-IDFBR were also fabricated for 50 wt %, 64 wt % and 74 wt % acceptor (figure 2.4 and table 2.1), and the highest device performance occurred at 64 wt %, with an average PCE, J_{sc} and FF of 3.6 %, 8.5 mA cm^{-2} and 0.42, respectively. PCEs are lower compared to O-IDTBR, which is likely largely due to the negligible LUMO-LUMO offset limiting J_{sc} and FF,^[23] but ensuring a high V_{oc} between 1.02-1.04 V across compositions. A similar trend as that for O-IDTBR is observed, although weaker, whereby average PCE and J_{sc}

peak around the estimated monotectic composition, despite the low acceptor crystallinity observed from DSC around this composition window.

To understand the origin behind the dependence of J_{SC} on D/A ratio, it is important to first consider the effect of thickness variations, induced by different solution compositions. It is worth noting that it is difficult to efficiently control active layer thickness for such blend types incorporating polymers with strong temperature dependent aggregation (TDA) properties, where a variation in thickness, of up to 20 nm, was observed within a single film. Thickness values as a function of composition and M_w are reported in table 2.1. Blends with the low M_w batch vary in thickness by ≈ 30 nm, while the higher M_w batch displays smaller thickness fluctuations (only up to ≈ 10 nm, given the use of a lower solution concentration for the blend richest in polymer). Considering that the same J_{SC} -composition dependence is observed for both M_w , despite a difference in the magnitude of thickness variation, suggests that the trend in J_{SC} is dominated by the effect of composition, rather than thickness. In other words, this dependence is governed by the changes in morphology as the D/A ratio is varied.

To summarize, in line with the expectation of a coarser morphology at hyper-monotectic compositions, as inferred from the discussion of $T-\phi$ diagrams, we observe a drop in J_{SC} and PCE at these compositions. As the phase behavior from DSC describes the bulk-morphology in slow-dried thick films, we now turn towards an in-depth characterization of thin-films prepared under similar conditions as devices. The following sections will focus on devices based on 41 kDa PffBT4T-2DT with O-IDTBR.

2.4. Thin-Film Micro- and Nano-structure

To investigate thin-film morphological changes as a function of composition, we performed grazing incidence X-ray diffraction (GIXD), resonant soft X-ray scattering (R-SoXS) and low-

angle annular dark field STEM (LAADF-STEM) of thin films of 41 kDa PffBT4T-2DT:O-IDTBR. The packing characteristics of donor and acceptor were measured by GIXD. The 2D GIXD scattering patterns and sector averaged 1D profiles are shown in figure 2.5. The GIXD data indicate that for all the samples the polymer crystallites exhibit a strong preferential edge-on orientation with respect to the substrate with up to 4 orders of the (h00) diffraction peaks due to the lamella separation parallel to the surface normal. In contrast, a more face-on orientation is observed for O-IDTBR with a strong in-plane (100) peak around $0.4 \text{ \AA}^{-1}$.

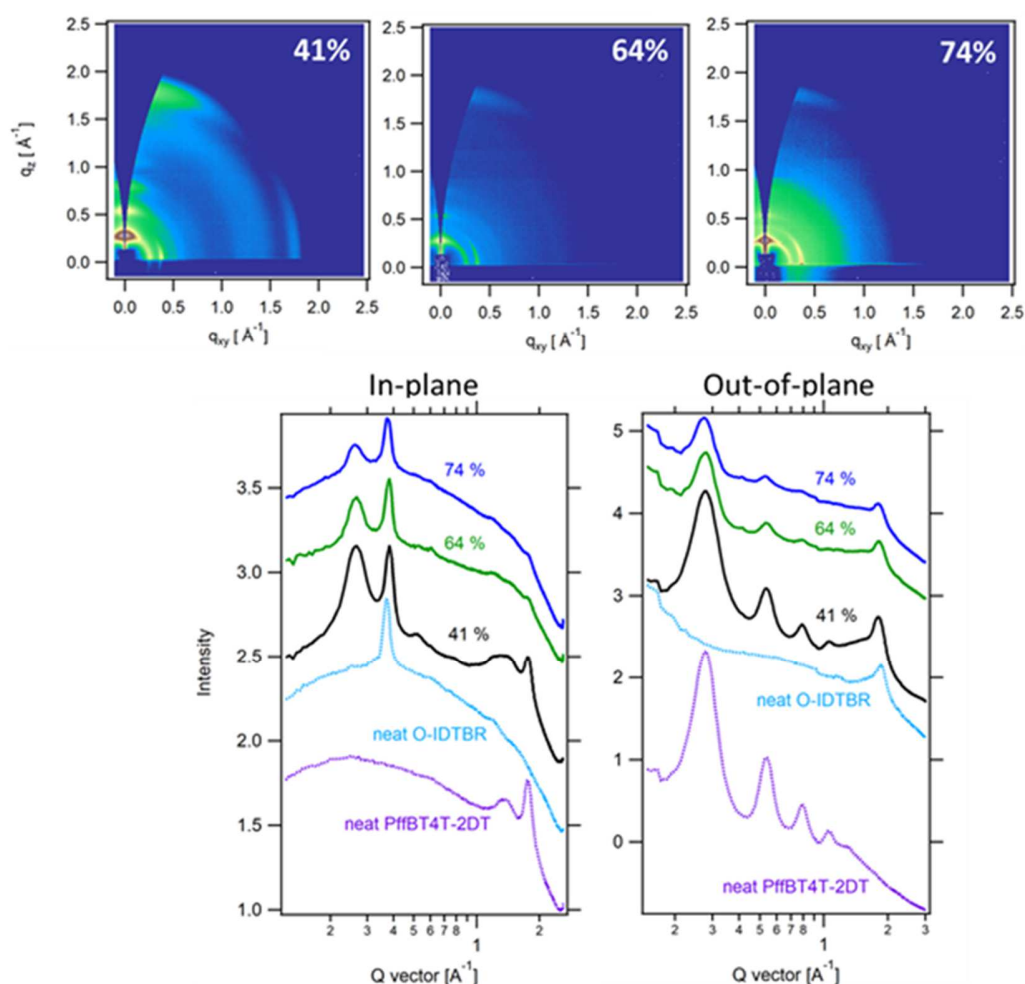


Figure 2.5. GIXD 2D images of PffBT4T-2DT:O-IDTBR blends with different O-IDTBR wt % and 1D in-plane and out-of-plane sector averaged scattering profiles from in-plane and out-of-plane 15° cake sectors. Data from Subhrangsu Mukherjee.

Volume-normalized pole figures from the (100) diffraction peaks of PffBT4T-2DT and O-IDTBR are shown in figure A1. The relative degree of crystallinity (rDoC) assessed from these pole figures is shown in figure 2.6a. Importantly, an increase of the rDoC of the polymer as well as the acceptor is observed for D/A ratios above ϕ_{mo} . This result suggests that polymer and acceptor aggregation plays a dominate role in governing the composition dependence of morphology and consequently the compositional dependence of J_{SC} as well.

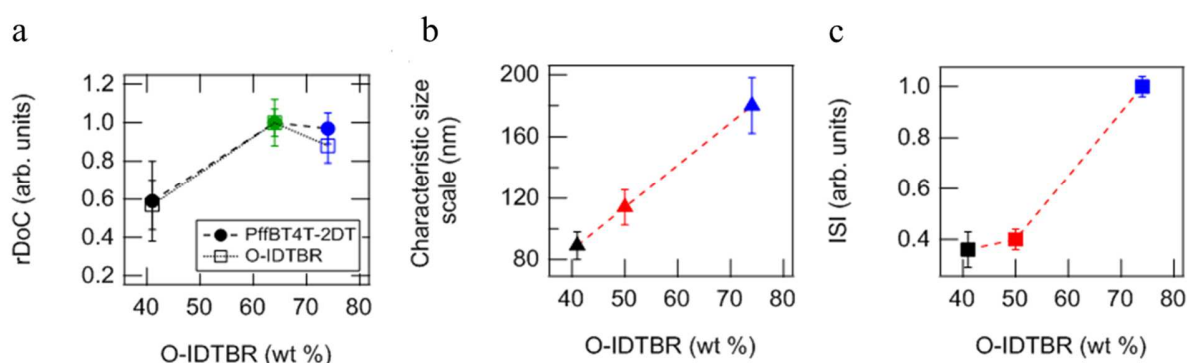


Figure 2.6. (a) Relative degree of crystallinity (rDoC) of PffBT4T-2DT and O-IDTBR from GIXD for 41 kDa PffBT4T-2DT:O-IDTBR at 41 wt %, 64 wt % and 74 wt %; (b) relative average purity and (c) size scales extracted from R-SoXS for 41 kDa PffBT4T-2DT:O-IDTBR at 41 wt %, 50 wt % and 74 wt %. Uncertainties in rDoC are from standard deviation in film thickness and sample length measurements. Uncertainties in size scales and scattering intensities are from standard deviation of the respective values from R-SoXS data acquired at high material contrast energies. Data from Subhrangsu Mukherjee.

R-SoXS was used to quantify the length scale of phase separation as well as relative scattering intensities. Scattering profiles obtained at 284 eV are shown in figure A2 and the extracted size scales are shown in figure 2.6b. A good fit was obtained using two log-normal peaks. The low- q peak, indicating micrometer size scales, likely originates from surface roughness and has a negligible contribution to the integrated scattering intensity (ISI). In agreement with the more uniform thickness at the highest acceptor loading, this peak disappears at 74 wt % O-IDTBR. The

high-q peak originates from D/A phase separation. As shown in figure 2.6b, extracted size scales for 41 wt %, 50 wt % and 74 wt % O-IDTBR are $\approx$ (90, 115 and 180) nm respectively, which is similar to previous reports of blends incorporating PffBT4T donors with fullerenes.^[21,22,78] Such size scales are quite large but the broad peaks imply a broad dispersion which likely arises from a hierarchical morphology. The normalised relative integrated scattering intensity (ISI) is shown in figure 2.6c. These ISI values are a measure of the contrast between two phases and the respective volume fractions.^[79] A step-like increase in ISI is observed for D/A ratios above ϕ_{mo} .

To summarise, the breadth of the R-SoXS peaks suggests the occurrence of a hierarchical morphology at all three compositions probed, with a gradual increase in median size scale. The fact that the largest median size scale at 74 wt % O-IDTBR also exhibits the highest ISI relative to the other compositions does indicate a more phase separated morphology.

LAADF-STEM was used to further consolidate the morphology picture (figure 2.7). In agreement with R-SoXS, results suggest the occurrence of a hierarchical morphology given the observation of features $\approx$ 100-200 nm in size. However, we do not observe a significant difference in the size of these features as a function of composition, as expected based on the varying degree of phase separation. In fact, obtaining a complete morphological picture from electron microscopy for such a blend system is complicated by the low level of contrast given the similarity in chemical composition of both components. Analysis is also complicated by the fact that the images are a 2D projection of a 3D morphology.

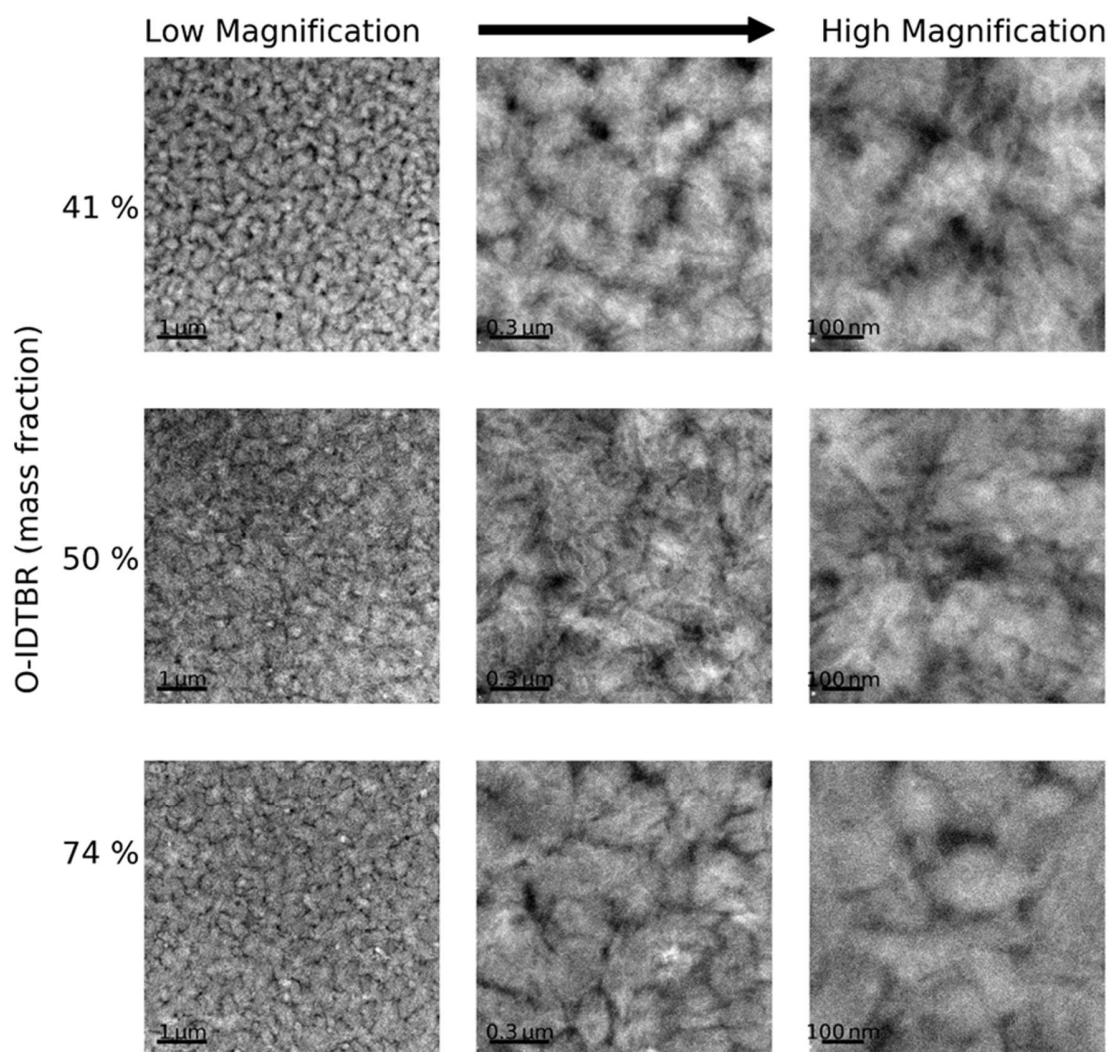


Figure 2.7. LAADF-STEM images of PffBT4T-2DT:O-IDTBR blends using the 41 kDa batch, where the image intensity scales with density. Data from Andrew Herzing.

The results from real-space microscopy and scattering studies thus agree reasonably well. Results from thin-film morphology characterisation reveal a complex hierarchical morphology and are consistent with the degree of phase separation expected from the bulk phase behaviour. For active layer solutions with compositions below the monotectic ϕ_{mo} , the suggested dominance of S-L demixing means there is less time for crystal/aggregate growth, which would freeze-in a smaller length scale, lower crystallinity and lower composition variation and/or pure phases with different

volume fractions. The occurrence of L-L demixing to a stronger extent in the 74 wt % blend ($\phi > \phi_{mo}$) (i.e. deeper quench depth) is consistent with the coarser morphology, higher degree of aggregation/crystallinity, and higher degree of phase separation. Hence, the large drop in J_{SC} upon increasing acceptor content from (50 to 74) wt % could suggest that device performance becomes limited by the exciton diffusion length as excitons need to travel further to reach a D/A interface, which would lead to a longer exciton lifetime at 74 wt %. However, this doesn't seem to be the case, as will be discussed in the next section. In order to elaborate further the morphology image and its impact on the trend in J_{SC} , we investigate the dynamics of charge generation and recombination.

2.5. Charge Generation and Recombination

Photoluminescence spectroscopy (PL) was employed to elucidate the impact of the observed changes in morphology on exciton dissociation, while femtosecond-transient absorption spectroscopy (fs-TAS) was used to elucidate their impact on charge generation and recombination in O-IDTBR blends with the 41 kDa batch.

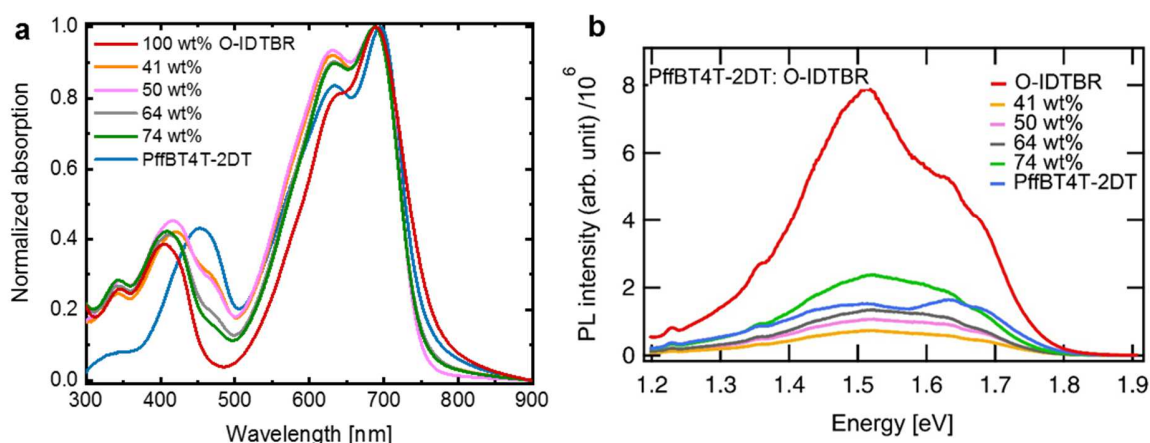


Figure 2.8. (a) Thin-film UV-vis absorption spectra of neats and blends; legend indicates wt% of O-IDTBR. (b) PL spectra of films excited at 630 nm. PL data in collaboration with Elham Rezasoltani.

Extracting values for PL quenching efficiency (PLQE) is complicated by overlapping absorption profiles (figure 2.8) which prevents selective excitation of either donor or acceptor. Thus an ‘overall’ PLQE is extracted by normalizing the PL spectra (figure 2.8b) with respect to the emission from neat O-IDTBR (PL spectra were initially normalized to the absorption at the excitation wavelength). It should be noted that neat O-IDTBR was cast from hot solution to match the conditions used for the neat polymer and polymer/acceptor blend films. An overall PLQE of $80 \pm 5 \%$ occurs between 41 and 64 wt % O-IDTBR (figure 2.9a). The relatively low quenching efficiency has been previously attributed to the formation of large, highly pure PffBT4T polymer domains.^[24] At 74 wt % acceptor, PLQE decreases to $\approx 65 \%$.

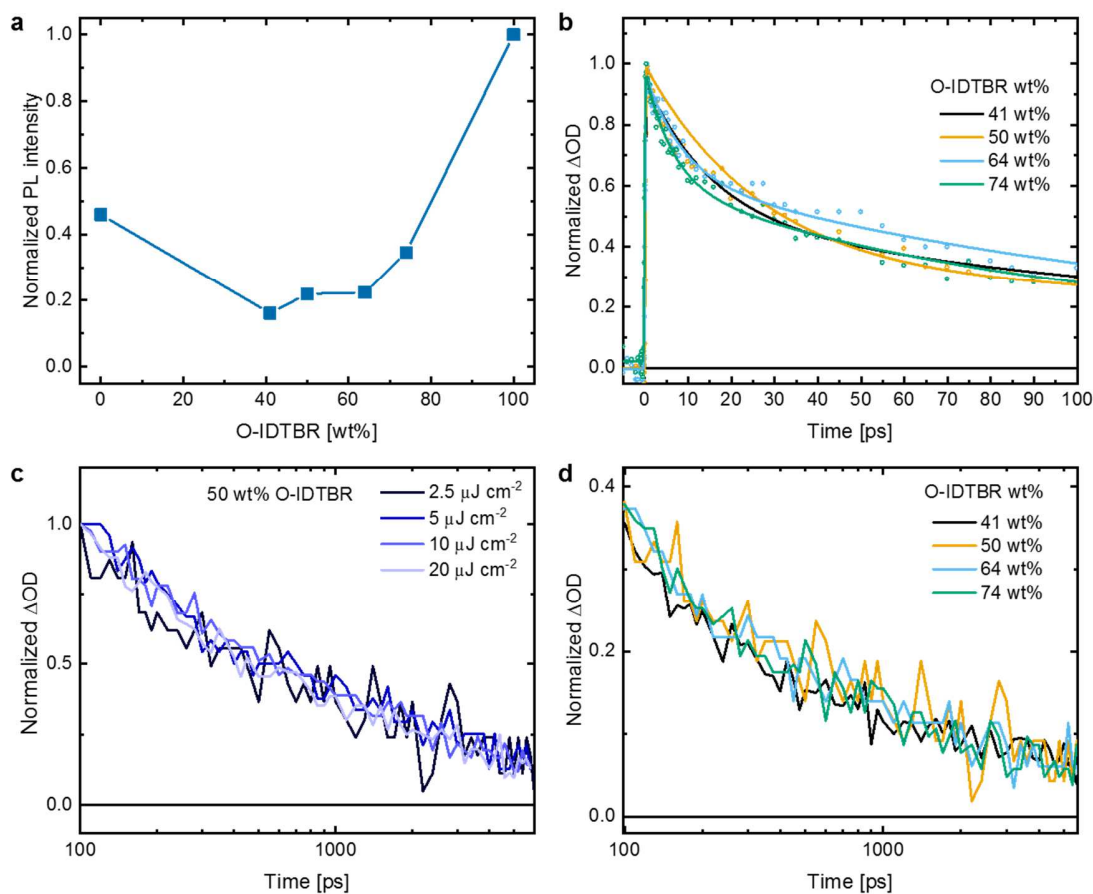


Figure 2.9. (a) PL intensity as a function of acceptor wt % in blends of PffBT4T-2DT:O-IDTBR excited at 630 nm; (b) Transient absorption kinetics probed at 1125 nm where the kinetics are normalized at 0 s. Similar decay rate is observed in all the blends; (c) Transient absorption kinetics probed at 1050 nm for the PffBT4T-2DT:O-IDTBR blend with an acceptor of 50 wt% at various pump fluences ranging from 2.5 to 20 $\mu\text{J cm}^{-2}$. The kinetics are normalized at 100 ps where most excitons have decayed to the ground state. (d) Transient absorption kinetics at 1050 nm for PffBT4T-2DT:O-IDTBR blends with different ratios with the kinetics normalized at 0 ps. All films were fabricated using the 41 kDa polymer batch and excited at 650 nm for TAS measurements. PL measurements in collaboration with Elham Rezasoltani; TAS data from Yifan Dong.

The occurrence of a coarser microstructure at higher acceptor loading is indeed expected to lead to a reduction in PLQE as excitons need to travel further before dissociating at a D/A interface, thus the probability of exciton dissociation is reduced. However, the 15 % drop in PLQE on going from (41 to 64) wt % O-IDTBR to 74 wt % is not sufficient to explain the 42 % decrease in J_{SC} and PCE. Hence, in order to further understand the trend in J_{SC} , TAS was used to investigate the dynamics of charge generation and recombination.

Transient absorption spectra as a function of time delay of the neat materials and the 41 wt %, 50 wt %, 64 wt % and 74 wt % O-IDTBR blends excited at 650 nm are shown in figure 2.10. Polymer and acceptor exciton absorption in the neat films peak at 1050 and 1125 nm, respectively. Due to the broad and featureless responses of donor and acceptor exciton/polaron excited states, we could not use global analysis procedures to accurately decompose the transient absorption spectra and unambiguously link the dynamics to specific excited states.^[80]

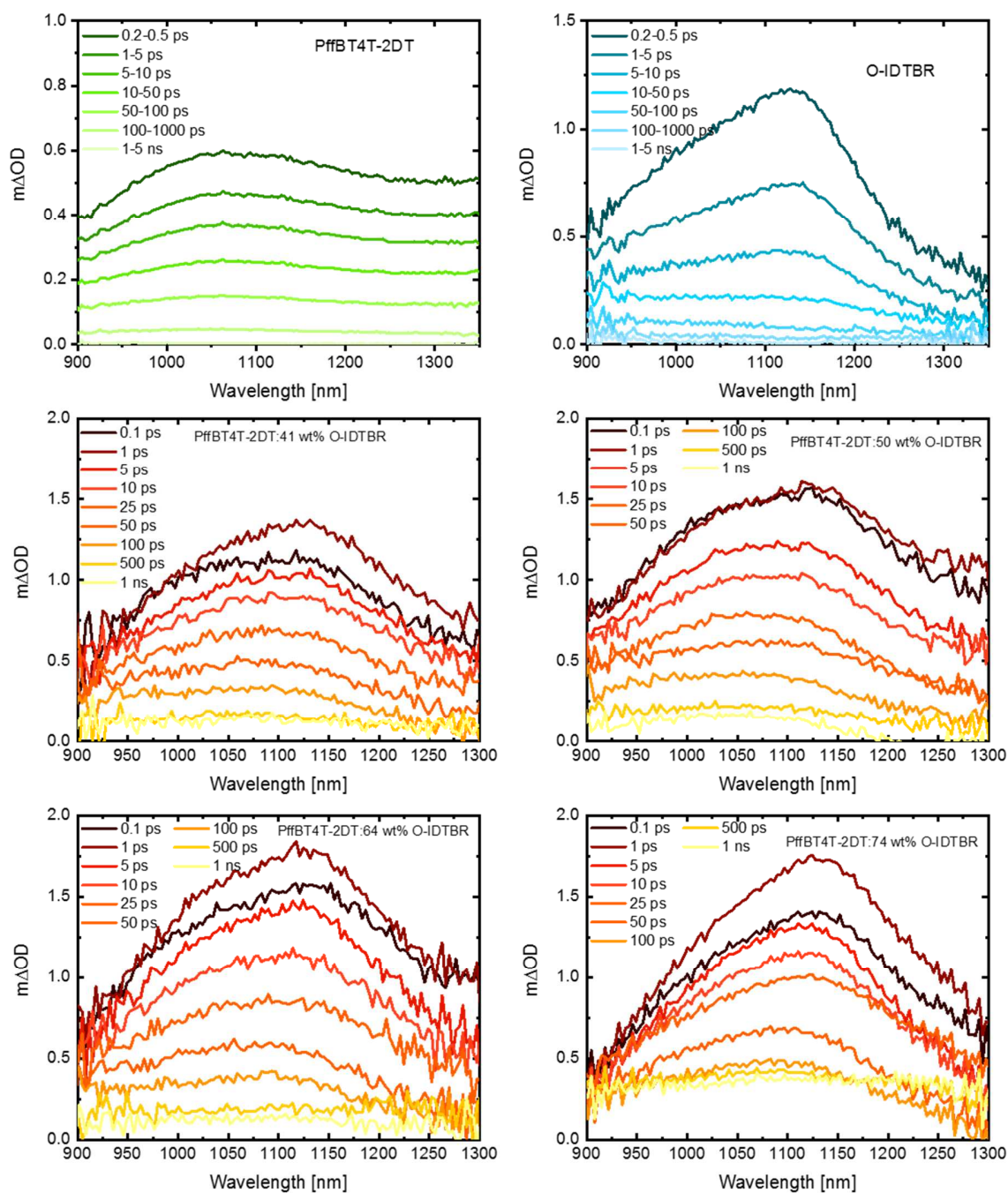


Figure 2.10. Femto-second transient absorption spectra of PffBT4T-2DT, O-IDTBR and blends thereof excited at 650 nm from 200 fs to 5 ns (neats) 100 fs to 1 ns (blends). Blend compositions are indicated on the graphs. The exciton lifetime in the neat polymer and neat acceptor is 127 and 145 ps, respectively. The absorption maximum for polymer and acceptor excitons occurs at 1050

and 1125 nm, respectively. No peak shift occurs in the spectra of the neats while a blue shift is observed in the blends, suggesting polaron formation. Data from Yifan Dong.

Nonetheless, the shift in maximum transient absorption to shorter wavelengths over time in the blends can be clearly related to polaron formation. To compare the dynamics of excitons in different materials, we therefore focus on short-time (sub-100ps) transients in the 1125 nm region as transient absorption response at this time/wavelength has mostly excitonic character. To address the dynamics of charges we instead compare long time (>100 ps) transients in the 1050 nm region. Figure 2.9b shows the transient absorption dynamics probed at 1125 nm, where both PffBT4T-2DT and O-IDTBR singlet excitons absorb while the polaron absorption is less pronounced. Surprisingly, only negligible changes in exciton lifetime in blends are observed, with an average lifetime of 22 ± 4 ps. As such, the trend in exciton dynamics cannot be directly related to the significant morphological changes reflected in both size scale and ISI observed from R-SoXS. The invariance in lifetime with increased coarseness suggests that the signal is dominated by excitons which are travelling within domains of similar composition, and also size (if these domains are practically pure). Assuming a three-phase morphology, we must consider crystalline donor (D) domains, acceptor aggregates, and the amorphous D-rich matrix. Based on phase behavior fundamentals, polymer crystallization is more sensitive to processing conditions compared to small molecules given the difference in molecular size. The purity of small molecule acceptor aggregates is thus not expected to change much as a function of initial composition, in contrast to polymer domains. This is reflected in the asymmetry of the binodal in polymer/small molecule binaries, such that the small molecule-rich branch of the binodal is nearly vertical, meaning that the composition of the small molecule-rich liquid varies little as a function of temperature (schematically illustrated in figure 2.1). As a result, the purity of acceptor crystals/aggregates

formed from the acceptor-rich liquid L_A is similar irrespective of quench depth. These IDTBR crystals are also expected to be pure,^[3,81] which means that they must also display similar sizes within the (41 to 74) wt % D/A composition range in order to explain the invariance in exciton lifetime. As such, it seems the fast drying kinetics during spin-coating limit the growth of acceptor crystals at higher acceptor loading. While the lifetime of excitons generated in polymer/polymer-rich domains is expected to vary as polymer domain purity changes, the results from TAS suggest that the signal is dominated by excitons generated in acceptor domains. This is reasonable given the much higher absorption coefficient of IDTBR relative to PffBT4T polymers.^[3]

At long times (> 100 ps), the kinetics probed at 1050 nm provide insight on the decay of polarons as all excitons have decayed by that time and exciton absorption is red-shifted from this wavelength. By varying the pump fluence between 2.5 and 20 $\mu\text{J cm}^{-2}$, the kinetics at 1050 nm are found to be fluence-independent, indicating geminate recombination (example of 50 wt% O-IDTBR blend in figure 2.9c). This was also observed for PffBT4T-2OD:EH-IDTBR, where the dominance of geminate recombination was attributed to the modest LUMO/LUMO offset,^[24] such that following exciton dissociation, there is little energetic driving force to promote electron/hole transport away from the interface.^[82] These loosely bound charges were found to recombine geminately at the same rate irrespective of acceptor concentration (figure 2.9d), with a half-lifetime ≈ 300 ps. The invariance in the decay lifetime of charges across the composition series correlates with the largely invariant V_{OC} with respect to composition (table 2.1), such that there is little change in the driving force for charge separation at the interface.

To summarize, the trend in PL quenching supplements the morphology picture inferred from GIXD and according to which the polymer crystallinity/aggregation increases by 67 % on going from (41 to 50) wt % to 74 wt % O-IDTBR. This is further supplemented by an increase of R-

SoXS scattering intensity as well as size scales indicating an increase in domain purity. The negligible change in exciton lifetime, as observed in TAS measurements, is interpreted as being an effect of an invariance in the size of pure acceptor domains across this composition range. In consequence, the trend in relative domain purity when going from (41- to 50) wt % to 74 wt % O-IDTBR must be associated with the changes in polymer aggregation. The lower solution viscosity at 74 wt % O-IDTBR compared to (41 to 50) wt % facilitates molecular diffusion, allowing the formation of purer polymer domains. This translates into a larger difference in contrast between phases, which was observed in R-SoXS as higher scattering intensity. While higher purity is beneficial for charge extraction, the concomitant drop in J_{SC} is attributed to isolated crystalline polymer domains at low polymer loading, leading to a lower probability of efficient hole extraction. These changes in morphology as a function of composition are illustrated schematically in **figure 6**.

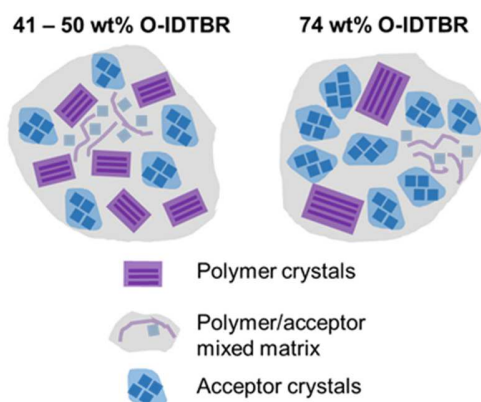


Figure 2.11. Schematic cartoon illustrating the change in morphology as acceptor concentration is increased above the monotectic composition around 50 wt%.

2.6. Phase behavior of low bandgap polymers with fullerenes vs. IDTBR/IDFBR

The observation of monotectic phase behavior in blends incorporating PffBT4T-2DT with either O-IDTBR or O-IDFBR raises the question of the impact of such behavior on the morphology as a function of D/A ratio in comparison to eutectic blends which have dominated the literature so far.

The suggested model for rationalizing optimal D/A ratios in eutectic blends is based on the need for pure acceptor percolation pathways.^[66] Based on our case study of PffBT4T-2DT/NFA blends, our results suggest that controlling the degree of phase separation dictates the optimal morphology in these monotectic blends. We propose that the key parameter to control in such blends is the degree of L-L phase separation which is governed by the strength of S-L demixing (i.e. polymer aggregation), thus dictating the phase separation length scale and preventing large scale phase separation. To elucidate the similarities/differences compared to fullerene-based blends, we note that PC71BM is known to display low levels of miscibility in blends with PffBT4T polymers.^[32] While the reported DSC thermograms for PffBT4T-2OD/PC71BM suggests eutectic behavior,^[40] visualizing the $T-\phi$ diagram evokes the case where the high melting temperature of the acceptor leads to a monotectic composition that is pushed towards the pure acceptor axis and a eutectic point which occurs at intermediate composition.^[63] This illustrates how in addition to the widely observed correlation between optimal D/A ratio and eutectic composition,^[4,52,66–69] additional insight into blend miscibility can be obtained from evaluating the shape of the liquidus curves constructed from DSC.

Another parallel can be drawn with blends incorporating IDTBR with another low bandgap polymer, namely PBDTTT-EFT. While we observe an invariance in charge decay kinetics on D/A ratio when semi-crystalline PffBT4T-2DT is used as donor, a strong dependence was observed when amorphous PBDTTT-EFT was used.^[81] This was attributed to the fact that increasing acceptor concentration above a threshold changed the morphology from an intimately mixed one-phase system to a two-phase system incorporating pure acceptor aggregates.^[81] In PffBT4T-2DT:O-IDTBR, the crystalline nature of the polymer leads to the formation of at least two phases across all the composition probed, making charge dynamics composition-independent.

2.7. Conclusion

This chapter explores the effect of the interplay between polymer aggregation from solution (S-L demixing) and L-L demixing on morphology optimization by varying solution composition in blends of PffBT4T-2DT with two NFAs, O-IDTBR and O-IDFBR. The blend displays a complex hierarchical morphology with a monotonic increase of the median size scale as acceptor loading is increased. Finer phase separation at or below the monotectic composition ≈ 50 wt % O-IDTBR was assigned to the dominance of polymer aggregation (S-L demixing) during microstructure formation compared to more acceptor-rich compositions, where L-L demixing likely dominates. The low polymer concentration at 74 wt %, combined with excessive phase separation, is considered as the factor limiting J_{SC} by reducing the probability of efficient hole extraction via crystalline polymer domains. Another limiting factors of these blends is the negligible LUMO-LUMO offset which leads to the dominance of geminate recombination. By varying the degree of crystallinity of the acceptor, we find that amorphous O-IDFBR displays a similar trend compared to crystalline O-IDTBR, although much weaker as device performance in the former system is limited by the even smaller LUMO-LUMO offset.^[23] The miscibility of the acceptor with the polymer influences the balance between S-L and L-L demixing, such that using a more miscible acceptor (O-IDFBR in this case) requires a higher acceptor loading to optimize performance. The experimental observation of monotectic phase behavior is interesting in that it contrasts with the dominance of eutectics in OPV literature so far and builds upon the rational understanding of D/A ratio optimization based on $T-\phi$ diagrams. Although limited in scope and far from quantitative, this study brings together the simplicity of bulk crystalline morphology evaluation from DSC with the importance of miscibility considerations, as highlighted by the growing number of quantitative investigation of component miscibility.

CHAPTER 3: Correlating temperature-composition diagrams to the effect of molecular weight on device performance in binaries of P3HT with two IDTBR acceptors

In the previous chapter we discussed the relationship between monotectic phase behavior and device performance as a function of D/A ratio. We now focus on another case study where we explore the relationship between phase behavior and device performance in terms of M_w dependence.

In this chapter, we investigate the relationship between P3HT molecular weight and device performance in 1:1 P3HT:NFA blends, with a particular focus on the role of morphology. The polymer is paired with either O-IDTBR or EH-IDTBR. Performance of devices incorporating the former acceptor were found to depend on the M_w of P3HT, with a maximum power conversion efficiency (PCE) of 7 % at an intermediate M_w of 34 kDa. In contrast, using EH-IDTBR lead to a maximal PCE of 6.3 %. However, the performance was found to be insensitive to M_w . We explore the dependence of microstructure on M_w using differential scanning calorimetry (DSC) by construct the non-equilibrium $T-\phi$ diagram. The trend in microstructure inferred from DSC is complemented by results from atomic force microscopy and scanning transmission electron microscopy.

We observe that device performance sensitivity and insensitivity to M_w in the case of O-IDTBR and EH-IDTBR, respectively, can be related to the phase behavior constructed from DSC. While both blends displayed eutectic behavior, the eutectic composition varies with M_w in blends with O-IDTBR but not with EH-IDTBR, following the trend in device performance. We propose that the optimal performance at 34 kDa is due to the fact that (i) device composition (1:1) is hyper-eutectic, leading to the formation of acceptor crystals which improve electron percolation and that (ii) the length scale of nanoscale phase separation allows good charge generation. For clarity, in this work compositions are consistently expressed in terms of acceptor concentration unless stated otherwise. In other words, reference to a hyper-eutectic composition refers to the concentration in terms of acceptor wt%.

This work was published in Advanced Energy Materials.^[4] Some new analysis of DSC data is added.

3.1. Background

Polymer molecular weight plays an important role in governing device performance. For simplicity, these effects will be discussed in terms of polymer:small molecule blends only. In contrast to NFA-based blends, M_w dependence has been extensively investigated in blends incorporating fullerenes as acceptors. The influence of M_w on microstructure can be discussed in terms of morphological effects, as well as concomitant optoelectronic effects. Higher M_w induces a higher solution viscosity which increases the degree of entanglements (i.e. reduces the degree of crystallinity) and thus hinders the mobility of acceptor molecules in solution. While chain entanglements have been suggested to reduce charge mobility,^[83] the reduced tendency of acceptor molecules to aggregate prevents large scale phase separation.^[84] At the other end of the spectrum, low M_w has been suggested to limit charge mobility as a result of grain boundaries.^[85] In terms of optoelectronic effects, the higher degree crystallinity for low M_w has been observed to improve light absorption but reduce V_{OC} due to a lower charge transfer state energy.^[86] It should be noted that the reverse effect in V_{OC} as a function of M_w has also been observed,^[39] highlighting the complexity of the dependence of these parameters as they rely on other polymer properties such as regioregularity (RR) and polydispersity index (PDI), as well as on processing conditions. This also underlines the importance of further investigating such relationships in non-fullerene acceptor solar cells which behave differently to fullerenes. Recently, several trends in M_w dependence of performance were reported for PDI-based blends as a function of both polymer and acceptor aggregation properties.^[87] It was concluded that the acceptor displaying the highest crystallinity governed morphology formation and inhibited M_w dependence of performance, while polymer M_w effects dominated morphology formation when a less crystalline acceptor was used. Herein, we focus on the relationship between P3HT M_w and device performance in blends with either O-IDTBR or EH-IDTBR as acceptor, where the former has a stronger tendency to crystallize.^[3]

3.2. Device Performance as a function of molecular weight

Four batches of P3HT with molecular weights of 17, 20, 34, 64 and 94 kDa were used (table 3.1). Regioregularity was relatively invariant across batches; while there was some variation in polydispersity index (PDI), it is reasonable to assume that its role on the trends observed is less important than the influence of the large differences in M_w .

Table 3.1. Summary of the properties of each neat batch of P3HT. Data from Andrew Wadsworth. Reproduced with permission.^[4]

P3HT Batch	M_w [kDa]	M_n [kDa]	PDI	RR [%] ^{a)}
A	17	13	1.31	96
B	20	15	1.34	96
C	34	26	1.35	95
D	64	35	1.83	96
E	94	59	1.59	97

^{a)} measured from ^1H NMR with CDCl_3 as the solvent.

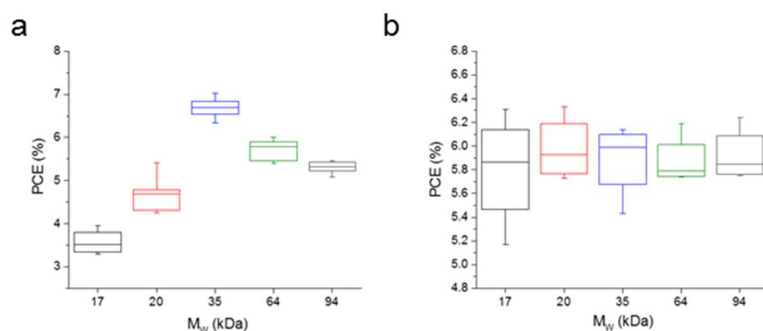


Figure 3.1. a) Box plots of the PCE achieved in P3HT:O-IDTBR devices, with varying polymer M_w , b) box plots of the PCE achieved in P3HT:EH-IDTBR devices, with varying polymer M_w . Data from Andrew Wadsworth. Reproduced with permission.^[4]

Table 3.2. Summary of the J-V characteristics of inverted architecture P3HT:IDTBR (1:1) OSCs. Data from Andrew Wadsworth. Reproduced with permission.^[4]

Active Layer	M_w [kDa]	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	Max PCE/Average PCE ^{a)} [%]	Standard Deviation ^{a)}
P3HT A:O-IDTBR	17	0.67	11.8	0.50	4.0/3.6	0.24
P3HT B:O-IDTBR	20	0.74	12.0	0.61	5.4/4.7	0.38
P3HT C:O-IDTBR	34	0.73	14.6	0.66	7.0/6.7	0.23
P3HT D:O-IDTBR	64	0.74	13.1	0.62	6.0/5.7	0.22
P3HT E:O-IDTBR	94	0.74	12.1	0.62	5.5/5.3	0.13
P3HT A:EH-IDTBR	17	0.79	12.0	0.65	6.3/5.9	0.34
P3HT B:EH-IDTBR	20	0.77	12.6	0.69	6.3/6.0	0.24
P3HT C:EH-IDTBR	34	0.77	12.0	0.68	6.1/5.9	0.28
P3HT D:EH-IDTBR	64	0.78	11.3	0.69	6.2/5.9	0.18
P3HT E:EH-IDTBR	94	0.78	11.7	0.68	6.2/5.9	0.20

^{a)} Average PCE and standard deviation were calculated over 8 devices.

J-V characteristics are summarized in figure 3.1 and table 3.2. Devices show that the highest performing device with O-IDTBR occurs with 34 kDa P3HT and achieves a maximum PCE of 7 %, which drops to 4 % and 5.5 % at the lowest and highest M_w , respectively. Maximum short-circuit current (J_{SC}) follows the same trend, peaking at 14.6 mA cm⁻² in the device based on 34 kDa, and dropping to 11.8 and 12.1 at 17 and 94 kDa, respectively.

The drop in J_{SC} at 17 kDa (lowest M_w) is unexpected based on the trend reported for P3HT:PCBM in a study of M_w between 11 and 91 kDa, where the improved current at lower M_w was attributed to improved light absorption.^[86] However, a similar drop in J_{SC} at the lowest M_w has been observed for P3HT M_w ranging from 6 kDa to 67 kDa, likely partly due to the observed lower crystallite perfection.^[39] The FF of P3HT:O-IDTBR devices followed the same trend as J_{SC} and PCE, increasing from 0.50 at 17 kDa to 0.66 at 34 kDa, before dropping to 0.62 at 64 kDa. In contrast, V_{OC} was found to remain ≈ 0.74 V for M_w between 20-94 kDa, but dropped slightly to 0.64 V at the lowest M_w . Devices incorporating EH-IDTBR display little change in PCE, J_{SC} and V_{OC} , with

efficiencies varying between 6.1 and 6.3 % across the five batches of P3HT. The drop in FF at the lowest M_w (0.65 vs. 0.68 to 0.69 between 20 and 94 kDa) is less significant than the variations observed in the blends based on O-IDTBR.

3.3. Non-equilibrium Phase Behavior

In an effort to understand the origin of M_w dependence of device performance in the case of O-IDTBR, and independence in the case of EH-IDTBR, the phase behavior is investigated using DSC to construct the non-equilibrium phase diagrams of O-IDTBR in blends with 20, 34, 64 and 94 kDa P3HT, and of EH-IDTBR in blends with 20, 34 and 94 kDa P3HT. It is worth noting that the samples for these measurements were drop-cast. The endset melting temperature is used to construct the liquidus curves. Eutectic phase behavior is observed for all blends (figure 3.2).

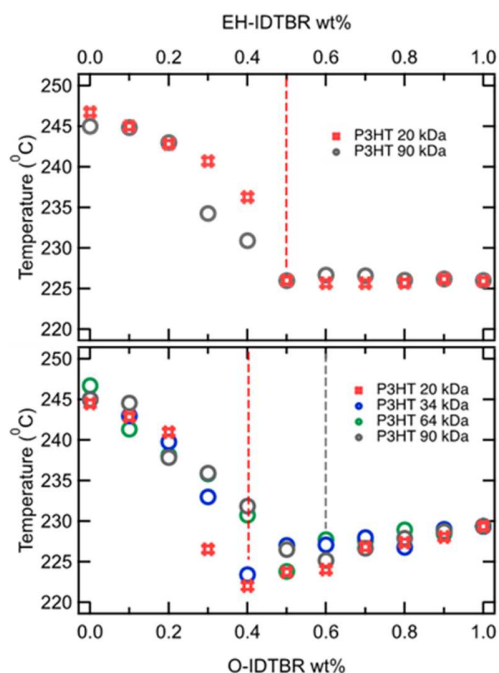


Figure 3.2. Phase diagrams of different molecular weight P3HTs and (EH-) and O-IDTBR binaries obtained on the basis of the DSC thermograms. The endset of the melting transition at each composition was used. a) P3HT: EH-IDTBR, 20 kDa (red) 34 kDa (blue) and 94 kDa (grey); b) P3HT: O-IDTBR 20 kDa (red), 35 kDa (blue), 64 kDa (green) and 94 kDa (grey). Measurements in collaboration with Elham Rezasoltani. Reproduced with permission.^[4]

In the case of O-IDTBR, the eutectic composition increases with increasing M_w , going from 40 wt% O-IDTBR at 20 and 34 kDa, to 50 and 60 wt% acceptor at 64 and 94 kDa, respectively. In contrast, for EH-IDTBR, the eutectic composition remains at 50 wt% acceptor irrespective of M_w . This means that the devices (fabricated using a 1:1 composition) incorporating the linear side-chain acceptor O-IDTBR go from being hyper-eutectic at the lowest two M_w (20 and 34 kDa), to hypo-eutectic at 94 kDa. In contrast, the composition of active layers employing EH-IDTBR coincides with the eutectic composition for all M_w . The shift in eutectic composition as a function of M_w is similar to what was previously observed for P3HT:PCBM.^[88] Active layers displaying hyper-eutectic compositions have been observed to optimize performance in many P3HT:fullerene blends, which is attributed to the formation of primary acceptor crystals which ensure the formation of percolation pathways for efficient electron extraction.^[66]

Upon further examination of the DSC thermograms (**figure 3.3a-d** and **figure 3.5**), it is observed that blends around the eutectic composition display lower intensity melting endotherms in the case of EH-IDTBR, indicating either a more amorphous blend or the formation of small nanometer size crystals which are not captured by DSC. The difference in crystallinity is further illustrated by the large depression in P3HT melting point which occurs between 20 and 50 wt% EH-IDTBR in blends with 20 kDa P3HT, and between 20 and 30 wt% EH-IDTBR in blends with 94 kDa P3HT (**figure 3.2**). Such a depression suggests the formation of a more amorphous microstructure within the relevant composition window. A similar effect occurs in the case of O-IDTBR, where the polymer melting point is strongly depressed from 20 wt% to 40 wt% in blends with 20 kDa P3HT. However, this does not occur for higher M_w batches, where the maximum depression of the P3HT melting temperature occurs at higher acceptor loading.

This difference in crystallinity is more quantitatively illustrated by comparing fusion enthalpies (ΔH_f), as shown in **figure 3.3e-f**. Given the overlap of P3HT and IDTBR acceptor endotherms at intermediate compositions, we extract the total (*measured*) fusion enthalpy ($\Delta H_f = \Delta H_{f, \text{P3HT}} + \Delta H_{f, \text{O-IDTBR}}$) across all blend compositions, and compare it to the theoretical (*calculated*) ΔH_f . The latter is obtained by combining the fusion enthalpy of neat P3HT and IDTBR acceptor, weighed against their respective compositions in a given blend.

Results from the 20 and 34 kDa blends show that *measured* values are much smaller than *calculated* values in EH-IDTBR relative to O-IDTBR, indicating the formation of a more amorphous microstructure in blends of the former acceptor.

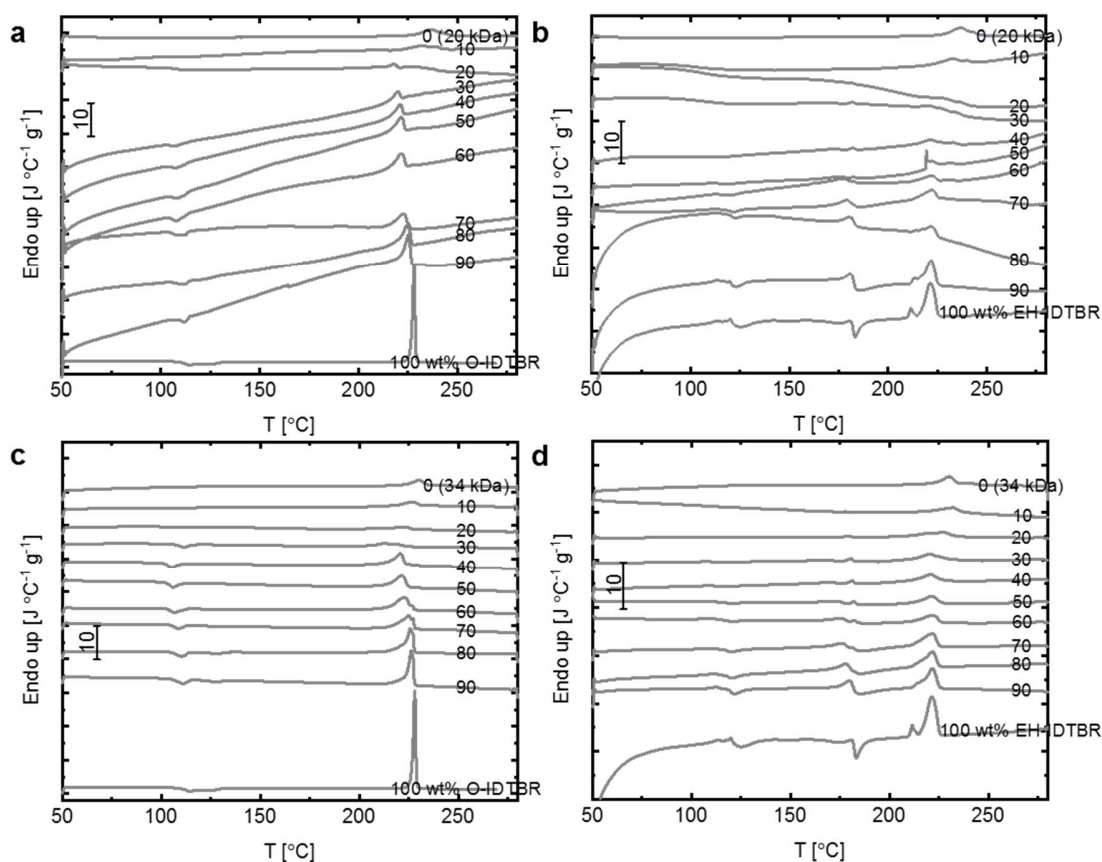


Figure 3.3. (Continued on next page)

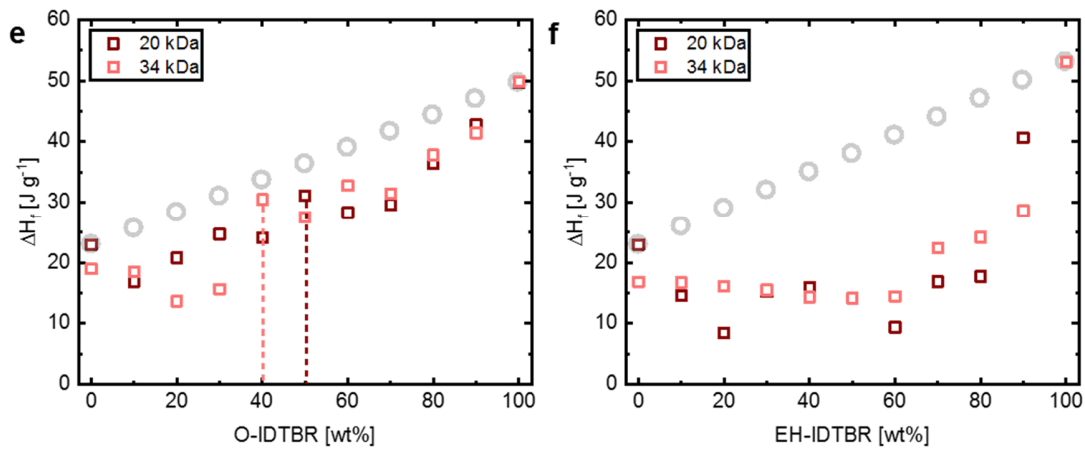


Figure 3.3. DSC first heating thermograms of 20 kDa and 34 kDa P3HT with O-IDTBR (a, c) and with EH-IDTBR (b, d); thermograms are offset for clarity; legends indicate acceptor concentration, polymer M_w and Y-axis scale (10 J g^{-1}); (e) comparison between total measured (empty squares) and total calculated (empty circles) fusion enthalpies ΔH_f for 20 and 34 kDa blends. Measured ΔH_f correspond to the area underneath the endotherms. Vertical dashed lines indicate the local maximum at which measured and calculated values are almost equal. (f) Total measured and calculated ΔH_f in P3HT:EH-IDTBR (20 and 34 kDa). The calculated values based on 20 and 34 kDa (e,f) differ slightly given the 5 J g^{-1} difference in P3HT fusion enthalpy; only values based on 20 kDa are shown for clarity. Measurements in collaboration with Elham Rezasoltani. Adapted with permission.^[4]

It is worth noting that a local maximum seems to occur in the measured ΔH_f for (O-IDTBR)-based blends, such that measured and calculate values are nearly equal at 40 wt% (34 kDa) and around 30 to 50 wt% (20 kDa). This agrees reasonably well with the estimated 40 wt% eutectic composition at these M_w , suggesting that eutectic solidification involves the formation of crystalline domains that are large enough to be captured by DSC, and with little mixing between components. In contrast, eutectic solidification in blends with EH-IDTBR seems to lead to a more fine-grained matrix that is largely amorphous and/or with small crystalline domains. To further

understand the difference in crystallization dynamics of the two acceptors, we investigate differences in crystallization upon cooling from the melt. Cooling thermograms of 20 and 34 kDa blends are shown in **figure 3.4a-d**. Acceptor crystallization is more strongly supercooled compared to P3HT crystallization, such that the high-temperature exotherm upon cooling is likely dominated by P3HT crystallization across most compositions. This is especially the case for blends of either acceptor with 20 kDa P3HT, and for 34 kDa P3HT with EH-IDTBR. In the case of 34 kDa polymer with O-IDTBR, the O-IDTBR crystallization exotherm can be distinguished in addition to the polymer's, from 40 to 90 wt% O-IDTBR. Measured crystallization enthalpies (**figure 3.4e-f**) are compared against the calculated crystallization enthalpy of P3HT only, weighed against its concentration across the compositions probed. The comparison confirms the fact that P3HT crystallization does indeed dominate during cooling given the good agreement between measured and calculated values across most compositions.

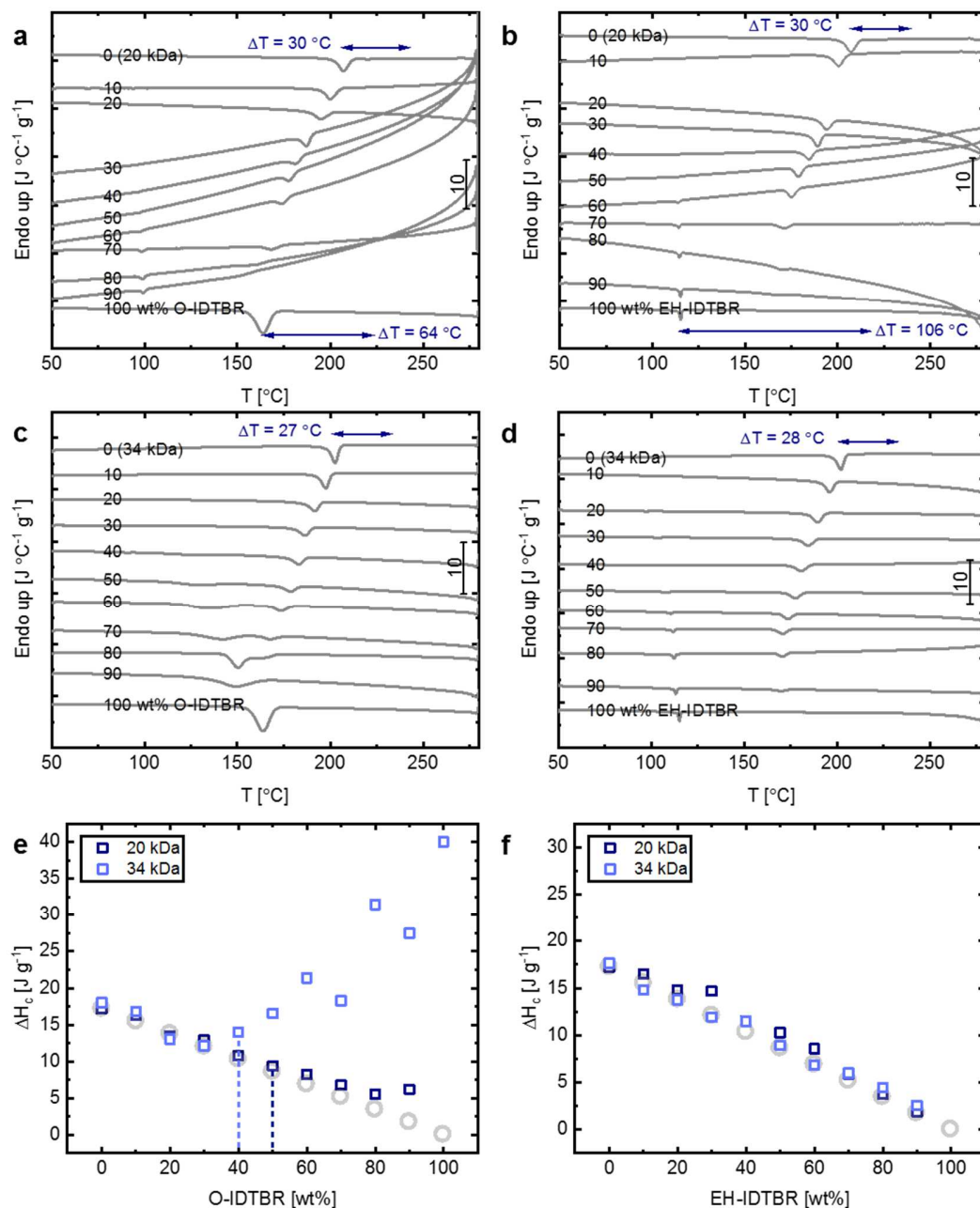


Figure 3.4. DSC 1st cool thermograms of 20 kDa and 34 kDa P3HT with O-IDTBR (a, c) and EH-IDTBR (b,d); thermograms are offset for clarity; legends indicate acceptor concentration, polymer M_w , and Y-axis scale (10 J °C⁻¹ g⁻¹). Difference between melting and crystallization temperature (i.e. degree of supercooling ΔT) for neat materials is annotated in blue. (e) Comparison between (total) measured (empty squares) and (P3HT) calculated (empty circles) crystallization enthalpies for 20 and 34 kDa blends. Measured ΔH_c correspond to the area underneath the exotherms.

Vertical dashed lines indicate the onset of O-IDTBR crystallization. (f) Total measured and (P3HT) calculated ΔH_c in P3HT:EH-IDTBR (20 and 34 kDa). In (e) & (f), the calculated values are based on P3HT crystallization only. Also, the calculated values based on 20 and 34 kDa differ slightly given the 1 J g^{-1} difference in P3HT crystallization enthalpy; only values based on 20 kDa are shown for clarity. Measurements in collaboration with Elham Rezasoltani.

However, O-IDTBR's stronger propensity for crystallization relative to EH-IDTBR is illustrated in the increasing difference between measured and calculated values from 50 to 90 wt% O-IDTBR with 20 kDa P3HT, and from 40 to 90 wt% with 34 kDa. This deviation occurs at more acceptor-rich concentration for 20 kDa suggesting that the higher P3HT crystallinity expected at lower M_w is more efficient at suppressing O-IDTBR crystallization. These concentrations also correspond relatively well with the eutectic window expected for these two M_w batches. No such deviation occurs in blends with EH-IDTBR with either M_w , where the measured values coincide with the theoretical values estimated based on P3HT crystallization only.

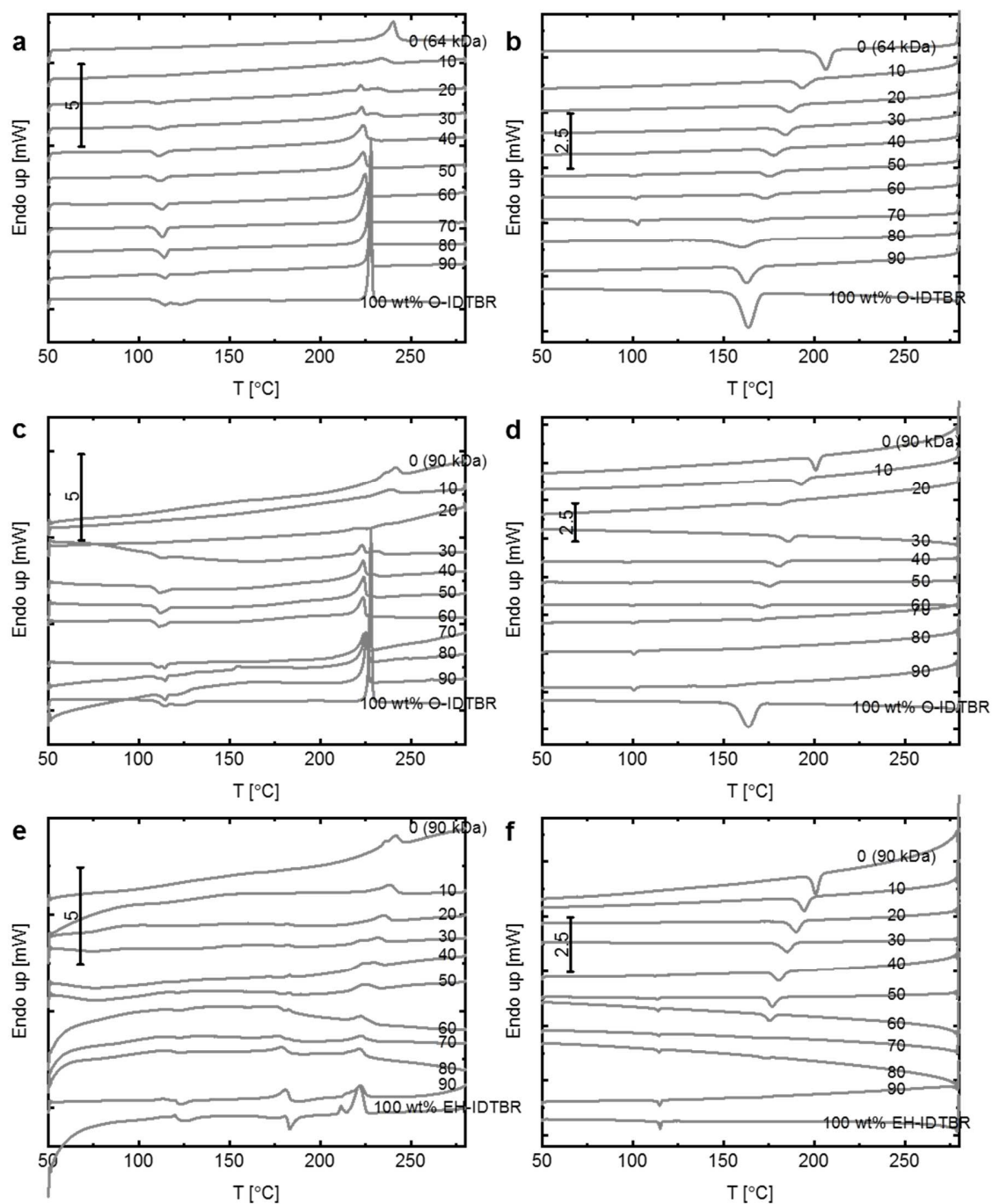


Figure 3.5. DSC first heating (a, c, e) and cooling (b, d, f) thermograms of blends incorporating 64 and 94 kDa P3HT; thermograms are offset for clarity; legends indicate acceptor concentration, polymer M_w and Y-axis scale (in mW). Measurements in collaboration with Elham Rezasoltani. Adapted with permission.^[4]

To further understand the relationship between phase behavior and device performance, we investigate thin-film morphology using various imaging techniques which provide insight into different length scales.

3.4. Thin-Film Micro- and Nano-Structure

Atomic force microscopy (AFM) of blends incorporating O-IDTBR with 17, 34, 64 and 94 kDa suggest the occurrence of a smaller feature size with increasing M_w on a micron length scale, as indicated by the small decrease in surface roughness from 21 nm at 17 kDa to 17 nm at 94 kDa (**figure 3.6a**). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to investigate the nanostructure of the same blends used in AFM (**figure 3.6b**). In-plane images at 34 and 64 kDa suggest the occurrence of a uniform distribution of domains around tens of nanometers in size. A more phase separated morphology is observed at higher M_w , with domains $\approx$ 80 nm in size, while a less clear and broader distribution of sizes is found at the lowest M_w (17 kDa).

Further information can be obtained by combining electron energy-loss spectroscopy (EELS) with STEM. EELS was used to construct sulfur (S) and nitrogen (N) elemental maps in the in-plane direction (**figure 3.6c**). These indicate the presence of impure polymer-rich and acceptor-rich domains across the four M_w . Upon going from 34 to 94 kDa, the stronger phase separation is accompanied by an increase in purity of acceptor-rich domains. This agrees with the stronger tendency for O-IDTBR to crystallize at higher M_w , inferred from the evaluation of crystallization enthalpy from DSC.

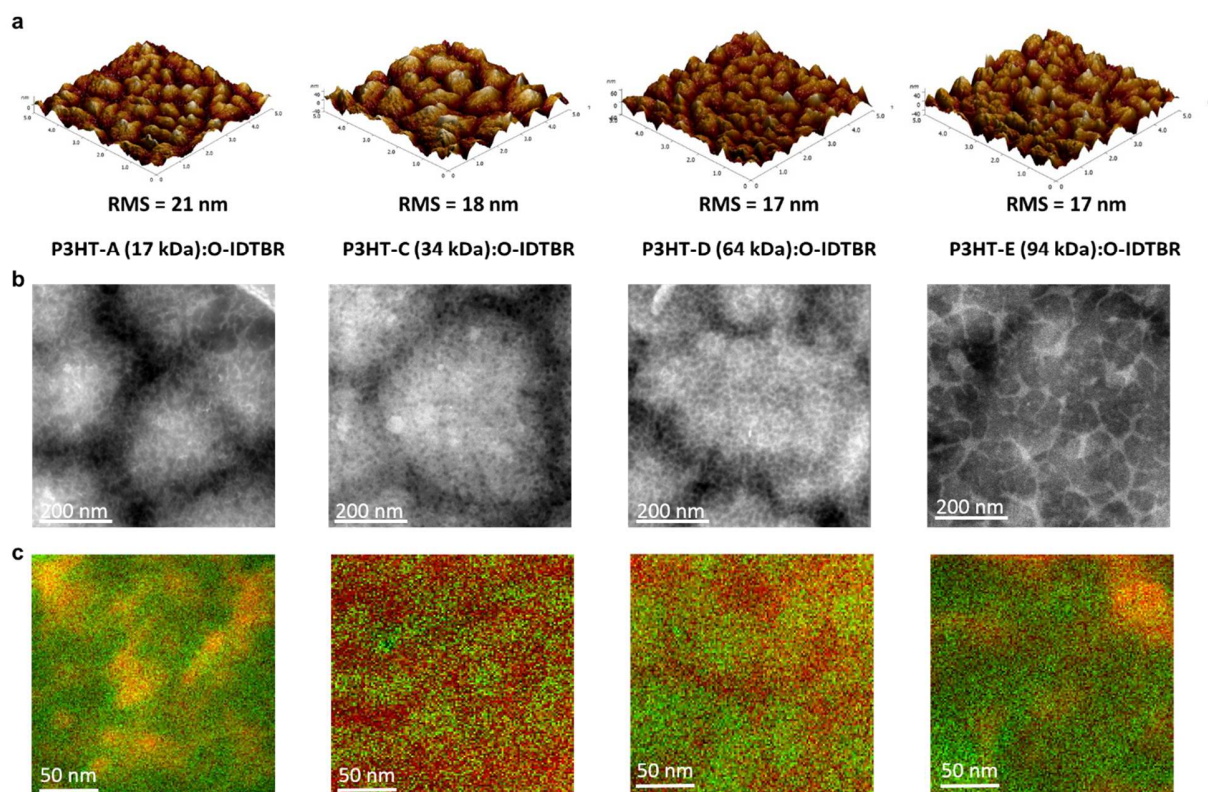


Figure 3.6. (a) AFM images of P3HT:O-IDTBR blends at different M_w (17 kDa, 34 kDa, 64 kDa, 94 kDa); (b) HAADF-STEM images of the same blends; (c) elemental mapping of STEM images where red denotes sulfur and green denotes nitrogen. AFM measurements by Marios Neophytou; STEM and EELS by Dalaver Anjum. Reproduced with permission.^[4]

The combined results from morphology characterization of devices based on O-IDTBR provide an explanation for the effect of P3HT M_w on device microstructure. The dependence of eutectic composition observed from the $T-\phi$ diagrams is concomitant with a dependence of amorphous miscibility on M_w . Amorphous miscibility is governed by the binodal, and although eutectic phase diagrams display complete miscibility in the melt,^[59] partial miscibility may occur if the melt is supercooled below the liquidus. This is analogous to device operating conditions, where the mixed blend solidifies from the liquid phase (i.e. from solution) at room temperature, far below the

eutectic temperature. The effect of miscibility on the nanostructure is observed from HAADF-STEM and EELS, where a greater degree of nanoscale phase separation occurs as M_w increases, with the formation of purer O-IDTBR domains. In contrast, on a micrometer length scale, AFM suggests the occurrence of micron size features which decrease slightly in size as M_w increases. This dependence of microstructure on M_w does not seem to occur in blends with the less crystalline acceptor, EH-IDTBR. The stronger tendency of O-IDTBR to crystallize leads to a stronger competition between polymer and acceptor crystallization, which affects the degree of miscibility between donor and acceptor.

3.5. Conclusion

In summary, we find that the dependence of device performance on P3HT M_w with O-IDTBR as acceptor, and performance independence with EH-IDTBR as acceptor, is correlated to the difference in phase behavior. This dependence is reflected in the changes in active layer morphology in devices fabricated at a 1:1 weight ratio with O-IDTBR. The degree of phase separation on the nanoscale in the amorphous P3HT matrix is governed by the miscibility between donor and acceptor and is observed to increase with M_w (i.e. coarser morphology at higher M_w). Active layers based on 34 kDa P3HT as donor combine the advantage of a hyper-eutectic composition, thus ensuring efficient electron percolation, with a favourable phase separation length scale which enhances charge generation. At higher M_w , device compositions are either at, or below the eutectic (hypo-eutectic), thus losing the advantage of acceptor percolation, while at lower M_w , the degree of phase separation is insufficient to ensure efficient charge generation. While devices employing EH-IDTBR are not as efficient as those incorporating the linear side-chain analogue, performance seems to be robust towards M_w changes, which is beneficial for large scale production. This study further highlights the importance of understanding phase behavior for

device optimization, but also the value of complementary techniques in capturing thin-film characteristics which are not observed from standard DSC.

CHAPTER 4: Influence of Side Chain on Phase Behavior in IDTBR Acceptors

In the previous chapter we observed how the difference in crystallinity between O-IDTBR and EH-IDTBR resulted in different dependencies of eutectic composition on P3HT M_w . In this chapter, we employ differential scanning calorimetry to further investigate the phase behavior of O-IDTBR and EH-IDTBR as a function of heating rate and seeding (or annealing) temperature. Importantly, we focus on the more complicated behavior displayed by EH-IDTBR given its branched, chiral, side-chains. We also employ variable temperature X-ray diffraction to assist in the identification of phases inferred from DSC.

The conclusions drawn from this chapter supplement the observations made in the previous chapter. The differences in crystallization kinetics highlight the role of side-chains in dictating the morphology in both neat and blend films.

4.1. Background

Apart from the importance of optoelectronic properties in matching a polymer donor with an electron acceptor in a bulk heterojunction blend, optimization of device performance and stability is also strongly dependent on active layer morphology. Thus, detailed understanding of small molecule acceptor phase behavior is crucial, especially since they lack the advantage of aggregate interconnectivity via tie chains in polymers, which is characteristic of macromolecules and which provides a pathway for charge transport even in amorphous polymers.^[48,66] Despite the well-documented advantages of fullerenes as acceptors in OPVs, alternative, non-fullerene acceptors, were required to enhance absorption and improve morphological stability, amongst other parameters.^[13] The structural differences between fullerenes and NFAs lead to different behavior, such that the established understanding of the behavior of fullerenes cannot be directly applied to NFAs. For example, while crystallization of traditional fullerene acceptors is known to be suppressed during solution casting of BHJ blends,^[12,32,89] high-performing IDTBR NFAs crystallize upon casting from solution.^[3,24] Apart from molecules which lie at the extreme ends of the crystallinity spectrum, there are small molecules which form metastable states upon rapid drying due to a large activation energy for nucleation. Such metastable states, which include liquid crystalline phases, have been investigated in the case of several small molecule donors.^[48,90] Herein we use thermal analysis to investigate the crystallization kinetics in O-IDTBR and compare it with the behavior of its branched side-chain analogue, EH-IDTBR. Results suggest that the latter forms a metastable liquid crystalline state upon casting from solution, which supplements previous reports where EH-IDTBR was suggested to form a different polymorph in blend thin films compared to neat films.^[3]

Throughout this chapter, T_m , T_c and T_{cc} denote melting, crystallization and cold-crystallization temperatures, respectively. Peak, onset or endset temperatures are further specified by the subscripts ‘P’, ‘O’ and ‘E’ (e.g. $T_{m/P}$ denotes the peak melting temperature).

4.2. O-IDTBR

We will first focus on the simpler of the two molecules in terms of phase behavior, namely O-IDTBR (figure 4.1). Upon first heating O-IDTBR at a low heating rate ($5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$), the acceptor undergoes a cold crystallization at $T_{cc/P} = 118\text{ }^{\circ}\text{C}$. This occurs above the glass transition T_g ; accurate determination of T_g is complicated by the weakness of the transition and overlap with the subsequent crystallization exotherm.^[45] As the temperature is further increased, the crystalline phase melts at $T_{m/P} = 227\text{ }^{\circ}\text{C}$ ($\Delta H_f = 53\text{ J}\cdot\text{g}^{-1}$).

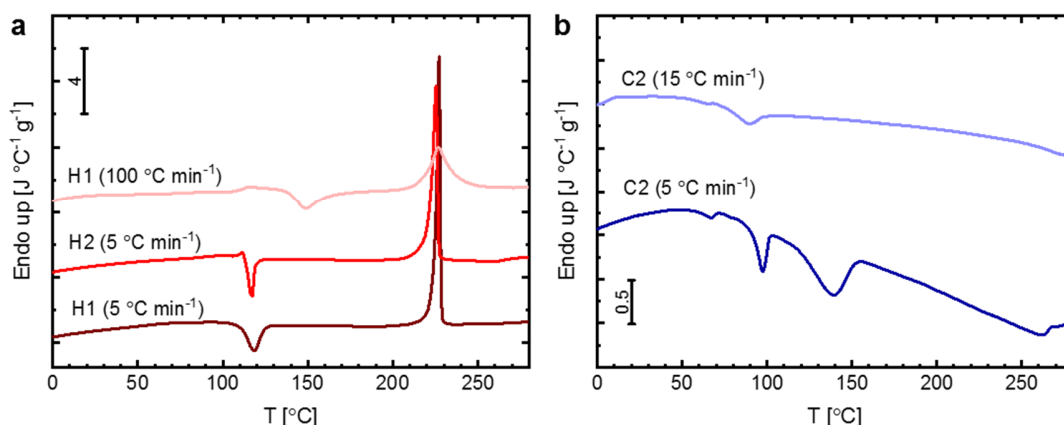


Figure 4.1. Differential scanning calorimetry heating (a) and cooling (b) thermograms of O-IDTBR. Thermograms are offset for clarity; annotations indicate the Y-axis scale, the scan rate and the cycle number (e.g. first heating as H1). The small exotherm at $\approx 70\text{ }^{\circ}\text{C}$ in (b) is due to an instrumental artifact.

Upon cooling, a broad exotherm is observed at $T_{c/O} = 155\text{ }^{\circ}\text{C}$ ($\Delta H_c = 10\text{ J g}^{-1}$), followed by a sharper and less intense exotherm at $T_{c/O} = 101\text{ }^{\circ}\text{C}$ ($\Delta H_c = 3\text{ J g}^{-1}$). The occurrence of multiple

exotherms upon cooling may suggest the occurrence of a liquid crystalline phase.^[90,91] To confirm whether or not this is the case here, the cooling rate is increased from 5 to 15 °C.min⁻¹ (figure 4.1.). It is found that both transitions display a cooling-rate dependence such that we only observe an exotherm at an onset of 145 °C with a transition enthalpy of 4 J g⁻¹. The rate dependence of the exotherm upon cooling generally suggests that the associated transition involves crystallization from the liquid phase or a solid-solid transition between polymorphs.^[91-93]

In the second heating cycle (figure 4.1), we observe the same series of transitions as in the first heating: a sharper cold crystallization occurs with a peak temperature of 117 °C, followed by melting at $T_{m/P} = 225$ °C ($\Delta H_f = 48$ J.g⁻¹). It is worth noting that exothermic peaks upon heating could be induced by other than a cold crystallization transition,^[92,94] but this is thus far the accepted interpretation in the case of IDTBR acceptors.^[3,45] Increasing the heating rate to 100 °C.min⁻¹ in the first heating does not change the sequence in transitions but shifts the cold crystallization to higher temperature ($T_{cc/P} = 149$ °C and $T_{m/P} = 227$ °C) as there is less time for nucleation just above the glass transition.

We now turn to variable temperature X-ray diffraction (VT-XRD) to investigate the phase structure of as-cast films as well as the effect of heating to, and cooling from, the melt. Figure 4.2 shows the diffractograms obtained upon heating, cooling and re-heating a drop-cast O-IDTBR film.

We will first focus on the 1st heating (figure 4.2a). The as-cast film displays a small sharp peak at a 2θ angle of 6.3 °, which corresponds to a lattice spacing of $d = 14$ Å. A broad peak is also observed at $2\theta = 7.2$ ° ($d = 12.3$ Å). The broad peak at $2\theta = 26.2$ ° ($d = 3.4$ Å) is consistent with π - π stacking distances.^[95] The diffractogram at 24 °C thus suggests that a predominantly glassy film is formed, with only a low degree of order. Upon heating the glassy phase, three transitions

can be discerned based on the trend in peak intensity and peak position as a function of temperature;

- (i) Upon increasing the temperature from 90 to 100 °C, the π -stacking diffraction peak undergoes an abrupt increase in sharpness and intensity, as well as a shift to higher angle (from $2\theta = 26.2^\circ$ to 26.6°), suggesting an increase in crystallinity. The transition from a glassy to a more ordered film at 100 °C coincides with the glass transition and onset of cold-crystallization from DSC. The peak at $2\theta = 26.6^\circ$ continues to increase in intensity and sharpness while shifting to lower angle up to 172 °C. At the same time, the peak at $2\theta = 6.3^\circ$ gradually increases in intensity. Additional (small) peaks can be discerned around $2\theta = 8$ and $20 - 22^\circ$.
- (ii) At 172 °C, the peak at $2\theta = 26.2^\circ$ drops in intensity, shows a shoulder at low angle and becomes a double peak between 192 – 222 °C. At 182 °C, additional diffraction peaks appear between $2\theta = 10 - 14^\circ$ and $15 - 18^\circ$. These changes in intensity and peak position do not seem to correlate to any observable change from DSC.
- (iii) Above 222 °C, the crystalline phase melts, as expected from the melting endotherm. The isotropic liquid is characterized by two amorphous halos, one centered at $2\theta = 6.9^\circ$ ($d = 12.8 \text{ \AA}$, shifted from $2\theta = 7.2^\circ$ in the as-cast film), and another more diffuse around $2\theta = 20^\circ$.

The above transitions can be visualized quantitatively by monitoring the change in integrated peak intensity as a function of temperature, as shown in figure 4.3a. This data suggests that the crystalline phase is gradually formed from the as-cast film once the glass transition is surpassed. The change in integrated intensity and peak position around 170 °C is unexpected upon examination of the DSC thermograms.

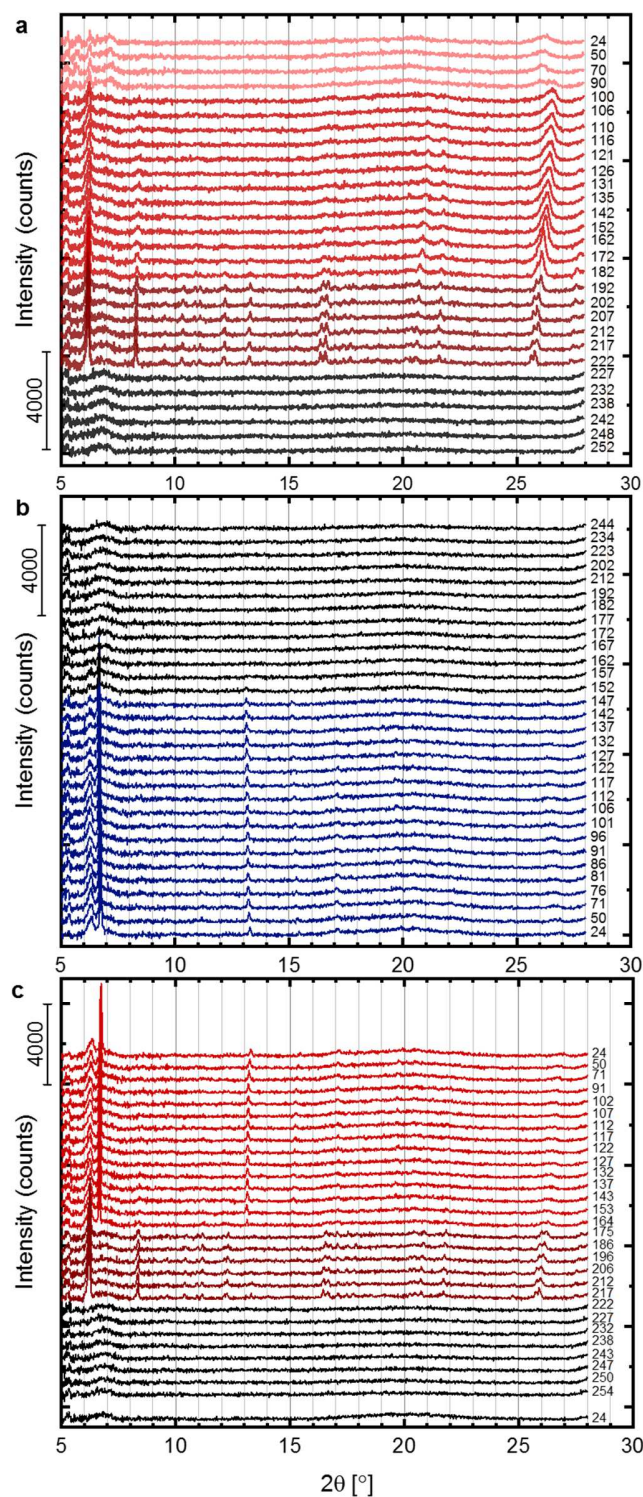


Figure 4.2. Variable temperature X-ray diffraction of O-IDTBR drop-cast on a silicon (Si) substrate. Diffractograms in (a), (b) and (c) correspond to the 1st heating, 1st cooling, and 2nd heating cycles, respectively. Diffractograms are offset for clarity and the Y-axis scale is indicated

by the scale bar, while temperatures are indicated on the right. Measurements by Marios Neophytou.

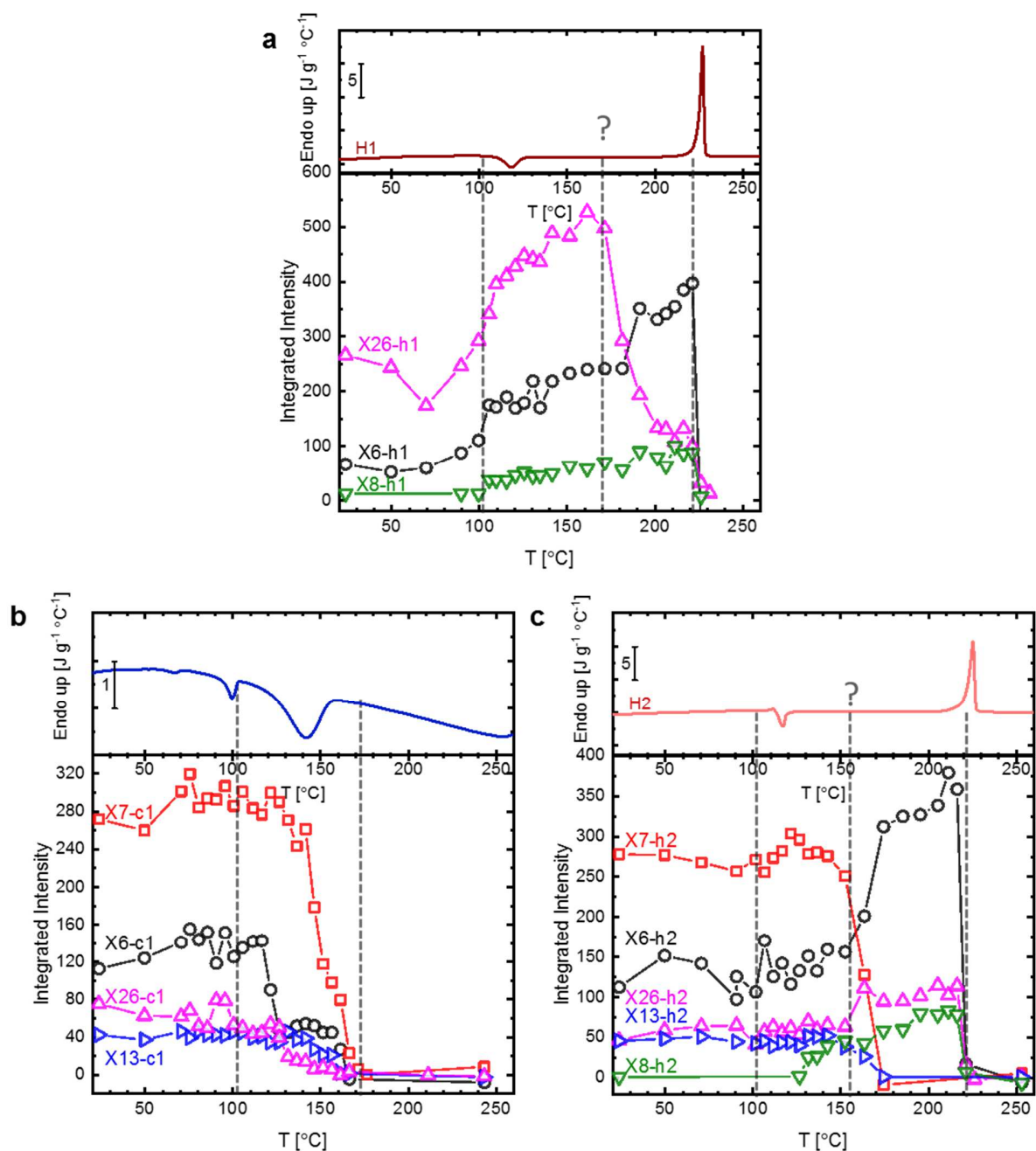


Figure 4.3. O-IDTBR thermograms (top panels) and integrated intensity (bottom panels) of select XRD peaks (e.g. X6 & X7 denote peaks at $2\theta = 6.3^\circ$ and 6.7° , respectively) as a function of temperature in first heating (a), first cooling (b) and second heating (c) cycles. Dashed lines are

guides to the eye to highlight the relationship between thermograms and diffractograms as explained in the text.

The diffraction pattern in most of the cooling and 2nd heating cycles (figure 4.2b and c) may be initially attributed to polymorphism when compared with the 1st heating. However, it is worth taking into account that the extensively studied O-IDTBR has not been observed to display polymorphism, in contrast to what has been suggested for EH-IDTBR.^[3] The transformation in diffraction pattern around 170 °C also puts into question the occurrence of polymorphism as no corresponding transition can be discerned from the DSC thermogram. We thus suggest that only one crystalline phase occurs, but that orientation effects play a significant role in the changes observed in diffraction pattern,^[96–98] as explained below. The diffraction pattern of the crystalline phase in the first heating is dominated by the sharp peak at 6.3 ° and broad peak at 26.3 °. The simulated powder diffraction pattern from single crystal data is shown in figure 4.4.^[99]

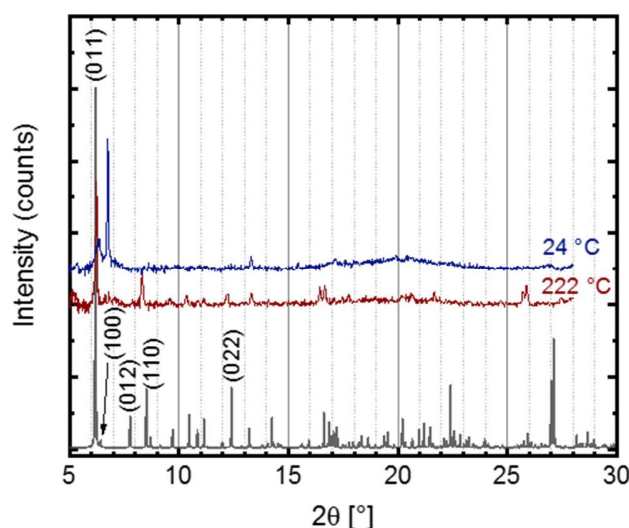


Figure 4.4. Simulated powder X-ray diffraction pattern from O-IDTBR single crystal data (grey) with main peaks assigned. Single crystal data from Andrew Wadsworth and Helen Bristow. Diffractograms at 222 °C and 24 °C from 1st heating and 1st cooling, respectively, are shown for comparison.

By comparing simulated and experimental patterns, the peak at 6.3° can be assigned to the (011) plane. This suggests the presence of a preferred orientation in the drop-cast film, which dictates the orientation of the crystals formed upon heating beyond the cold-crystallization temperature. As the film is further heated, additional diffraction peaks appear, such that the experimental diffractograms above 172°C are more similar to the simulated powder pattern, indicating the loss of preferential orientation.

Upon cooling from the melt and as shown in figure 4.3b, diffractograms show the onset of formation of an ordered phase from $\approx 155^\circ\text{C}$, as indicated by the appearance of three sharp diffraction peaks; the halo at $2\theta = 6.9^\circ$ in the isotropic phase develops two sharp peaks; one at $2\theta = 6.3^\circ$ (the same as that observed in the first heating), and a new one at $2\theta = 6.7^\circ$ which increases dramatically in intensity as crystallization progresses from the melt. An additional peak appears at $2\theta = 13.2^\circ$. These changes in diffraction pattern coincide with the high-temperature exotherm in the cooling thermogram. We suggest that the diffraction pattern obtained is due to a preferred orientation, different from that observed upon heating the drop-cast film given the difference in solidification conditions, i.e. drying from solution vs. solidification from the melt (see figure 4.2a & b).^[97,98] The diffraction peak at 6.7° can be assigned to the (100) plane by comparing to the simulated pattern (figure 4.4), suggesting that the peak at 13.2° arises from the higher order (200) diffraction. As the temperature is lowered, no change in diffraction pattern is observed but an increase in intensity occurs for the peak $\approx 6^\circ$ around 120°C . This may be related to either the breadth of the high temperature exotherm which seems to persist down to 110°C , or to the low temperature exotherm $\approx 100^\circ\text{C}$ (figure 4.3b). It is possible that the low-temperature exotherm corresponds to crystallization of the octyl side chains in O-IDTBR, which play an important role in dictating the NFAs crystal structure.^[99]

Similarly, in the second heating cycle, evidence of cold-crystallization can be discerned from the diffractograms at the expected temperature range based on DSC, although the difference between integrated intensity below and above the onset of cold-crystallization is smaller compared to the 1st heating (see figure 4.3a & c). We attribute this to the fact that the melt-solidified microstructure is more crystalline than the as-cast film. As observed in the 1st heating, the loss of preferential orientation is observed ≈ 160 °C. Finally, melting also occurs at the expected temperature range. However, a difference in fusion enthalpy and peak temperature between 1st and 2nd cycles can be clearly observed (figure 4.1a). We suggest this is due to the presence of impurities which induce batch to batch variations. This is further corroborated by comparison of DSC data of the O-IDTBR batch presented above (batch 2) with an older batch (batch 1). As shown in figure 4.5, batch 1 displays sharper melting and crystallization transitions. Furthermore, the crystallization exotherm is less supercooled compared to batch 2, where a lower purity is the likely reason behind the depressed and broader transitions.

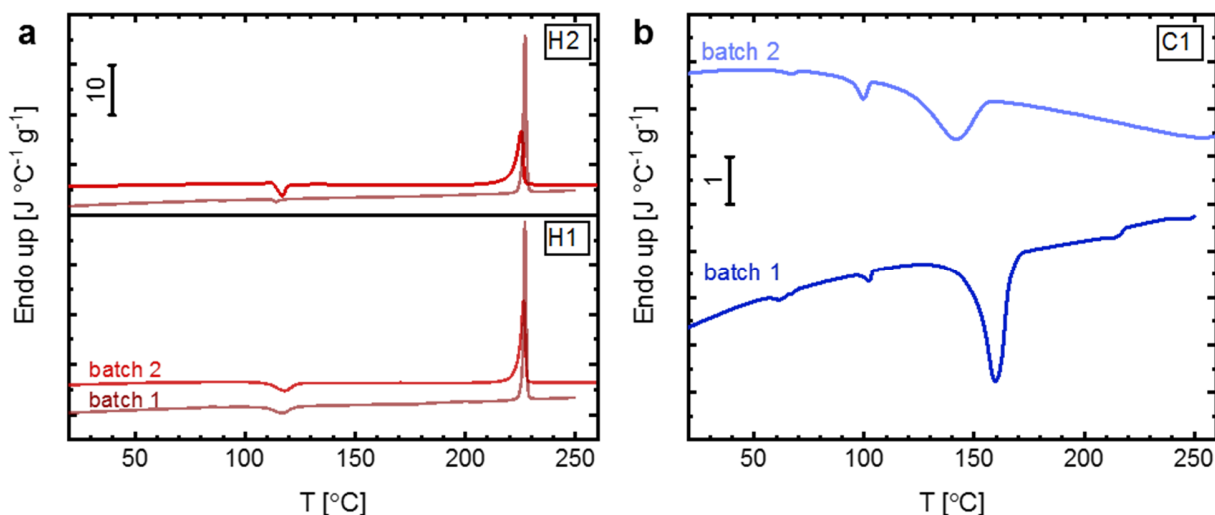


Figure 4.5. DSC heating (a) and cooling (b) thermograms of two O-IDTBR batches. H1, H2 and C1 denote first heating, second heating and first cooling cycles, respectively. C2 is identical to C1. The small exotherm at ≈ 70 °C in (b) is due to an instrumental artifact.

The above results show very good agreement between XRD & DSC results for O-IDTBR. We now turn towards the branched-side chain acceptor, EH-IDTBR.

4.3. EH-IDTBR

The phase behavior of EH-IDTBR was also found to display batch-to-batch variation, as shown in figure 4.6.

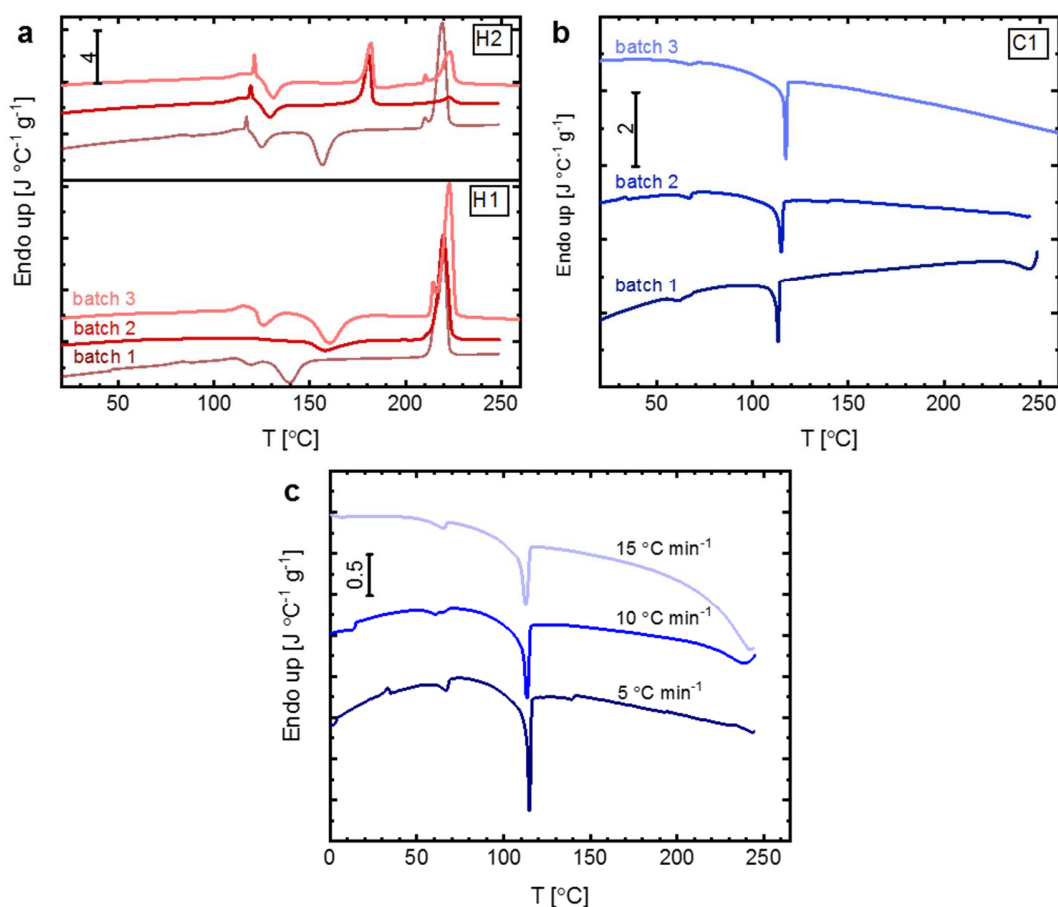


Figure 4.6. DSC heating (a) and cooling (b) thermograms of three EH-IDTBR batches. H1, H2 and C1 denote first heating, second heating and first cooling cycles, respectively. C2 (not shown) is identical to C1; (c) cooling cycle of batch 2 at various rates. All thermograms are offset for clarity and the scale bars indicate the Y-axis scale. The small exotherm at $\approx 70^\circ\text{C}$ in (b) and (c) is due to an instrumental artifact.

Apart from the effects of batch purity, we attribute the differences observed to the chiral side chains of the acceptor, leading to a mixture of stereoisomers.^[100,101] The discussion below will focus on batch 2 unless stated otherwise.

The first heating thermogram in figure 4.6a displays a single intense high-temperature melting endotherm ($T_{m/E} = 224\text{ }^{\circ}\text{C}$; $\Delta H_f = 48\text{ J.g}^{-1}$), preceded by a broad exothermic transition with $T_{cc/O} = 114\text{ }^{\circ}\text{C}$ and $T_{c/P} = 158\text{ }^{\circ}\text{C}$. Second heating thermograms also display the high temperature endotherm ($T_{m/E} = 227\text{ }^{\circ}\text{C}$; $\Delta H_f = 4.2\text{ J.g}^{-1}$), but this is broader and much smaller intensity compared to the 1st heating, and is preceded by two melt-recrystallization events, with peak temperatures at 119/129 $^{\circ}\text{C}$ and 181/191 $^{\circ}\text{C}$. For clarity, we will refer to the endotherms at 119 $^{\circ}\text{C}$, 181 $^{\circ}\text{C}$ and 227 $^{\circ}\text{C}$ as Endo-1, Endo-2 and Endo-3, respectively. Similarly, Exo-1 and Exo-2 will be used to denote the exotherms at 129 and 191 $^{\circ}\text{C}$, respectively. The second heating thus seems to suggest the presence of three phases, with each endotherm corresponding to the melting of each phase. We will use P1, P2 and P3 to refer to the suspected three phases which melt at Endo-1, Endo-2 and Endo-3, respectively. Upon cooling from the melt, a small, sharp, exotherm occurs at $T_{c/P} = 115\text{ }^{\circ}\text{C}$ ($\Delta H_f = 5\text{ J.g}^{-1}$). This matches the Endo-1 transition in transition enthalpy, peak shape and temperature, with only a small degree of supercooling ($\Delta T = 4\text{ }^{\circ}\text{C}$). This suggests that the exotherm upon cooling corresponds to the reverse of the transition at Endo-1 in the 2nd heating.

Interestingly, very similar heating and cooling phase behavior has been previously observed, and the equivalent of the Endo-1 transition was suggested to correlate with side-chain melting.^[92] To confirm this, we vary the cooling rate from 5 to 15 $^{\circ}\text{C min}^{-1}$ to study the effect on the exothermic transition since a cooling-rate dependence is expected if the transition corresponds to a crystallization.^[91,92] As shown in figure 4.6c, the transition does display cooling rate dependence as the crystallization enthalpy decreases slightly with increasing rate.

In an effort to understand the kinetics of the various transitions and the relationship between them, we investigate the effect of heating rate and seeding (i.e. annealing) on DSC thermograms.

Batch 3 was used for the heating rate experiments. Using a heating rate of $100\text{ }^{\circ}\text{C min}^{-1}$ on a fresh as-cast film shows the effect on the 1st heating cycle (figure 4.7). It is observed that the two exotherms which precede the melt of the crystalline phase at $5\text{ }^{\circ}\text{C min}^{-1}$ are replaced by a melt/re-crystallization transition. We suggest that at a slow rate, the phase present in the as-cast film has time to rearrange such that melting is suppressed. This is not the case at a fast heating rate, where the as-cast phase melts before rearranging into the crystalline phase.

The heating rate was also varied in the 2nd heating cycle and results are shown in figure 4.7. At $15\text{ }^{\circ}\text{C min}^{-1}$, Exo-1 is shifted to higher temperature, while Exo-2 and Endo-3 are significantly suppressed. Furthermore, while Endo-2 displays comparable intensity at both 5 and $15\text{ }^{\circ}\text{C min}^{-1}$, it is almost completely suppressed from $40\text{ }^{\circ}\text{C min}^{-1}$ onwards, as Endo-1 becomes broader.

To summarize the effect of heating rate on the phase behavior of EH-IDTBR, results from 2nd heating cycle show that there is a large barrier to the formation of the crystalline phase (P3), while the formation of P2 is more facile. The melt-processed morphology is dominated by a low-order phase (P1) which melts around $120\text{ }^{\circ}\text{C}$. By comparing the intensity of the Endo-3 transition in the 1st heating cycle at $5\text{ }^{\circ}\text{C min}^{-1}$ to that at $100\text{ }^{\circ}\text{C min}^{-1}$, it is clear that the as-cast morphology constitutes a lower barrier for the nucleation of the crystalline phase compared with the melt-processed morphology (in which case we observe near complete suppression of crystal phase formation at just $15\text{ }^{\circ}\text{C min}^{-1}$).

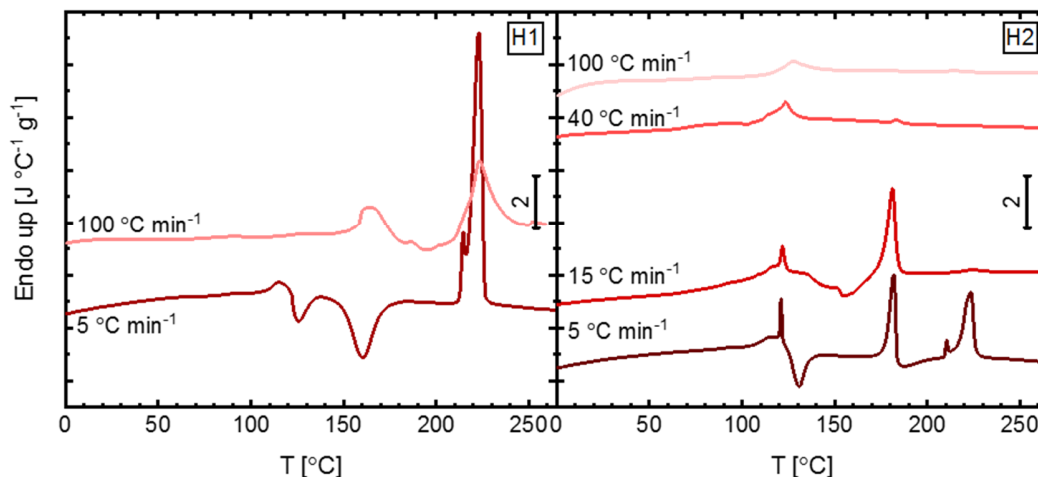


Figure 4.7. DSC first heating (H1, left panel) and second heating (H2, right panel) cycles of EH-IDTBR at various heating rates. Thermograms are offset for clarity and the scale bar indicates the Y-axis scale.

We now turn to the effect of seeding temperature to investigate the relationship between the various transitions in the 2nd heating cycle.

Two seeding (i.e. annealing) temperatures, 122 °C and 190 °C, were chosen based on the re-crystallization exotherms which occur during the second heating cycle (figure 4.8a).

After cooling from the melt at 5 °C min⁻¹, the sample was heated up to the seeding temperature at a rate of 5 °C.min⁻¹ and annealed for 20 min. After seeding at 122 °C, no additional transitions occur upon cooling. The trace of heat flow versus time during the isothermal segment (figure 4.8b) does in fact indicate that the exothermic transition is complete within ~ 7 min as the heat flow stabilizes from this point onwards. The extracted transition enthalpy is -5 J.g⁻¹. In the following heating, the Endo-1/ Exo-1 sequence is not observed, while the transitions at higher temperature are identical to those observed in the standard heating cycle (thermogram A3 in figure 4.8a).

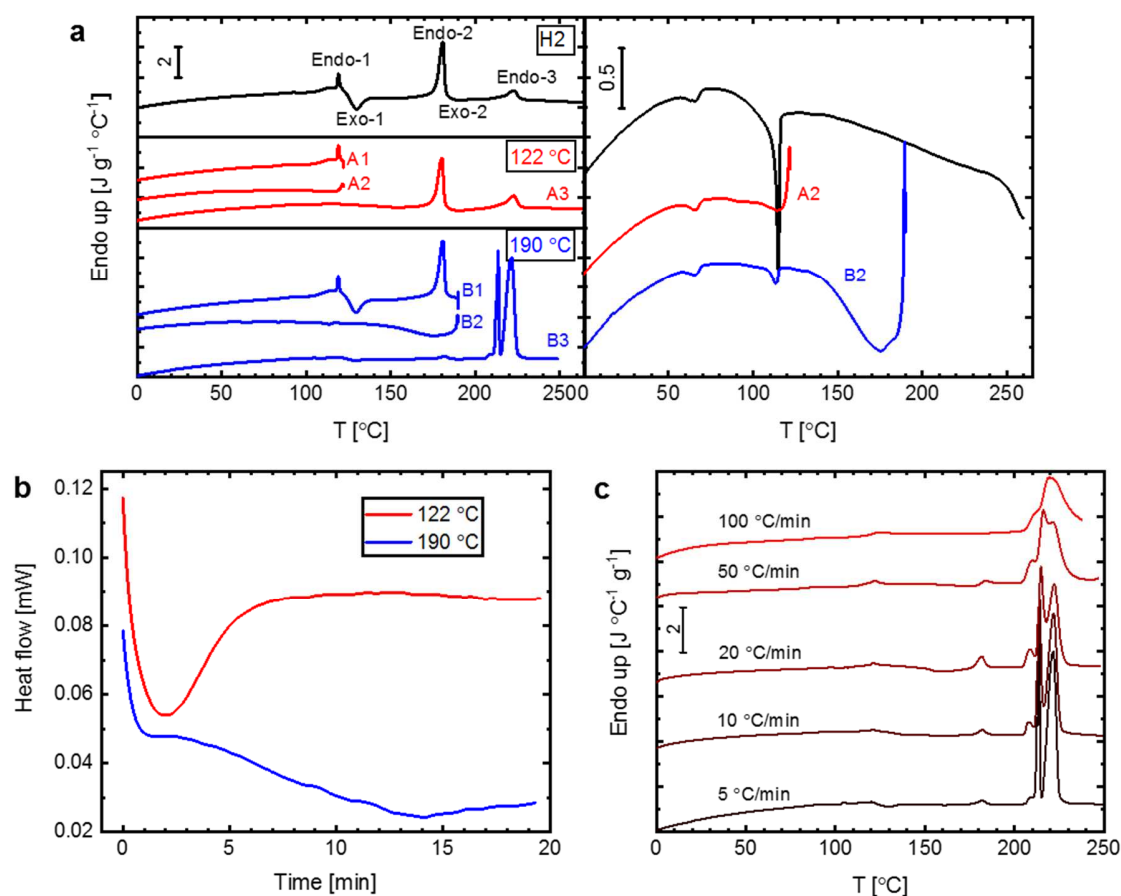


Figure 4.8. (a) Summary of DSC seeding experiments of EH-IDTBR at 190 °C (bottom, left panel) and 122 °C (middle, left panel). The standard second heating cycle (annotated) is shown for comparison (top, left panel). A1/B1 denote the heating cycles up to the seeding temperature, A2//B2 denote the cooling cycle after seeding for 20 min and A3/B3 indicate the subsequent heating cycle up to the melt. A2 and B2 are magnified in the right panel, with the standard cooling cycle (black curve) shown for comparison (the small exotherm at ≈ 70 °C is due to an instrumental artifact). Thermograms are offset for clarity and the scale bar indicates the Y-axis scale; (b) heat flow during isothermal seeding at 122 and 190 °C; (c) B3 cycles at various heating rates.

In contrast, during the isothermal segment at 190 °C, the heat flow does not stabilize within the annealing time, indicating that the exothermic transition is not complete within 20 min and continues during the subsequent cooling, as indicated by the broad exotherm from 190 °C to ≈ 130

°C in thermogram B2 in figure 4.8a. In the subsequent heating cycle, Endo-1 is not observed. Exo-1 and Endo-2 can be discerned around 130 °C and 180 °C but are significantly suppressed. Endo-3 occurs as multiple peaks and is much more intense compared to the standard heating cycle since the sample was crystallised isothermally for 20 min, in contrast to crystallization while heating over a period of only ≈ 6 min (i.e. an interval of 30 °C from ≈ 185 to 215 °C). The multiple peaks observed can be either due to close-melting polymorphs or are an effect of annealing as the crystals which melt first, recrystallize. The latter scenario would lead to a single melting peak at a sufficiently fast heating rate.^[102] As shown in figure 4.8c, these multiple peaks partly converge with increasing rate but at a low-temperature shoulder still remains at 100 °C.min⁻¹. Nonetheless, the highest-temperature endotherm is observed to decrease in intensity relative to the preceding endotherm with increasing heating rate, and also shifts to lower temperature, strongly suggesting an annealing effect. Faster rates are required to observe complete convergence, but are beyond the capability of our instrument.

To summarize, the second DSC heating cycle of EH-IDTBR suggests the occurrence of multiple phases which we assign as follows; the phase obtained upon cooling from the melt (P1) melts at 119 °C, which is followed by the crystallization of another phase (P2). P2 then melts at 181 °C, at which point the crystalline phase (P3) is formed. Only the melting of P3 is observed in the first heating cycle but the two exotherms which precede Endo-3 suggest that P3 crystallizes from a different phase which is present in the as-cast film. Furthermore, the seeding experiments provide insight into the kinetics of the formation of P2 and P3 at 122 and 190 °C, respectively, as well as the breadth of Endo-3. Melting of P3 occurs as a broad endotherm with a low-temperature shoulder due to melt/re-crystallization of P3 crystals during the heating cycle. It is also found that the crystallization of P3 is much slower than the formation of P2. Finally, Endo-1 only occurs when

the sample is cooled from the melt, and is the reverse of the exotherm at $T_{c/P} = 115\text{ }^{\circ}\text{C}$ in the cooling cycle of EH-IDTBR.

To further understand the difference between 1st and 2nd heating cycle and the nature of the phases which melt at Endo-1 and Endo-2, we employ VT-XRD of drop-cast films.

Diffraction patterns are shown in figure 4.9 and extracted integrated intensities as a function of temperature of select peaks are summarized in figure 4.10.

The as-cast film is characterized by a halo at $2\theta = 6.7^{\circ}$ ($d = 13.2\text{ }\text{\AA}$) and a weaker, diffuse, halo centered between 15 and 25° , suggesting a largely amorphous film (figure 4.9a & d). The first transition occurs as an increase in intensity and shift to higher angle (7°) of the low-angle halo between 110 and $120\text{ }^{\circ}\text{C}$ (figure 4.9a and 4.10a). At these temperatures, another halo can also be discerned at $2\theta = 25.8^{\circ}$ ($d = 3.4\text{ }\text{\AA}$), in agreement with π -stacking distances (figure 4.9d).^[3] This suggests an increase in the degree of order and coincides with the onset of the exotherm observed from DSC. These changes in diffraction pattern are then reversed above $140\text{ }^{\circ}\text{C}$, and other peaks appear (e.g. $2\theta = 5.9^{\circ}$, 9.6° , 10° , 23.2°), suggesting the formation of a crystalline phase. Above the melting temperature, the diffraction pattern of the isotropic liquid displays the same halo at 6.7° as in the as-cast film, only without the diffuse halo centered between 15 - 25° (figure 4.9d).

Upon cooling, diffraction patterns remain largely featureless. However, an increase in intensity of the halo around 7° at $\approx 120\text{ }^{\circ}\text{C}$ coincides with the exotherm observed from DSC (figure 4.10b). The difference between the isotropic melt phase and the melt-solidified microstructure is further illustrated in the difference in peak shape of the halo at 7° , which displays a ‘flatter’ peak at the end of the cooling cycle (figure 4.9d).

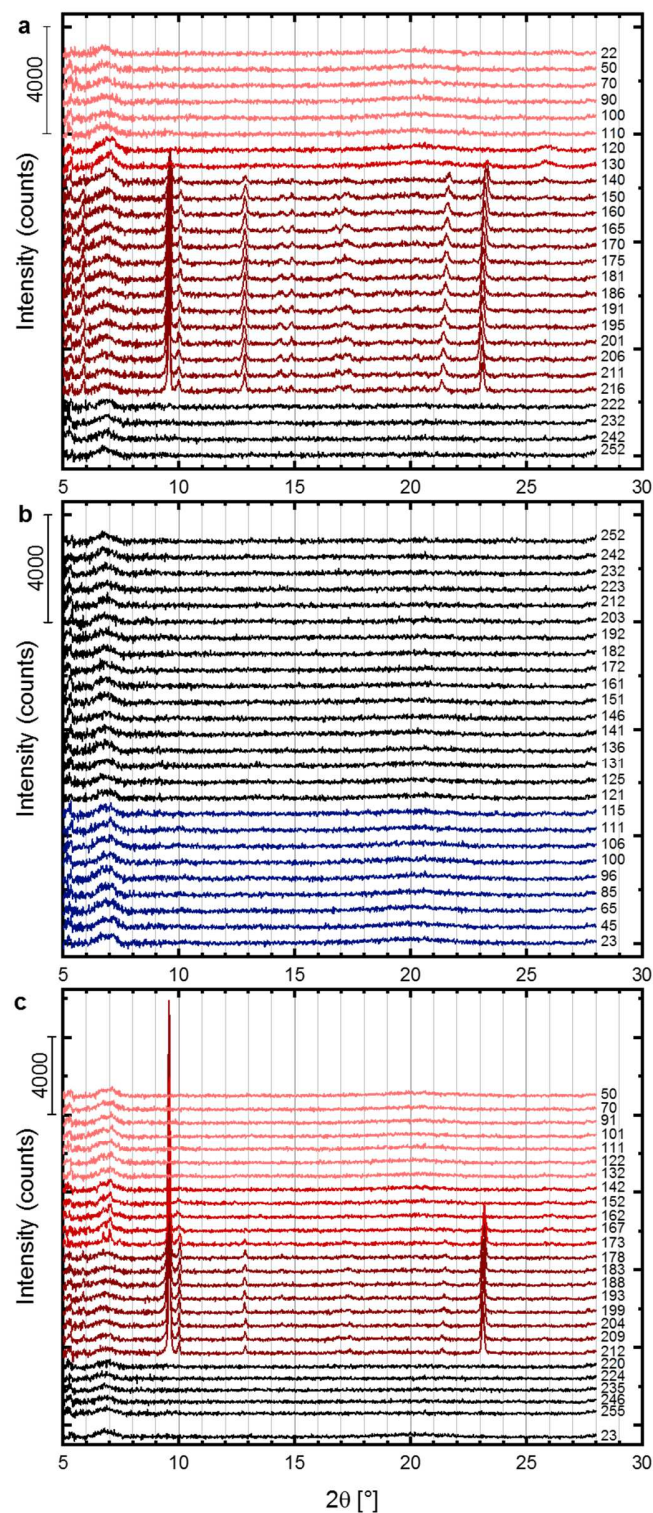


Figure 4.9. Variable temperature X-ray diffraction of EH-IDTBR drop-cast on a silicon (Si) substrate. Diffractograms in (a), (b) and (c) correspond to the 1st heating, 1st cooling, and 2nd heating cycles, respectively. (Continued on next page).

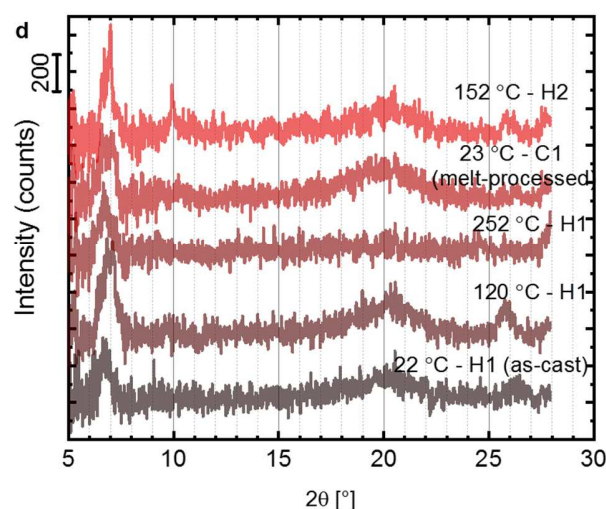


Figure 4.9. (d) Close-up of select diffractograms to highlight the intensity and shape of the halos around 7 ° and 20 °. H1, C1 and H2 denote first heating, first cooling and second heating cycles, respectively. In (a-d), diffractograms are offset for clarity and the Y-axis scale is indicated by the scale bar on the left, while temperatures are indicated on the right. Measurements by Marios Neophytou.

When the film is re-heated, the halo at 7 ° undergoes a drop in intensity above 100 °C, coinciding with the Endo-1/Exo-1 sequence (figure 4.10c). As the second heating cycle is continued, a clear difference can be observed between 1st and 2nd cycle diffractograms from ≈ 100 °C to 170 °C at low-angle; two sharp peaks emerge from the halo at 7 °, indicating the formation of another low-order phase, possibly liquid crystalline.^[92] This phase is completely melted by 178 °C, at which temperature the two peaks disappear (figure 4.9c). Simultaneously, the crystalline phase starts to form as indicated by the appearance of other peaks (e.g. $2\theta = 9.6$ °, 10 °, 23.2 °). This is similar to the 1st heating XRD cycle but occurs at a slightly higher temperature (140 vs. 170 °C), and coincides with the Endo2/Exo2 sequence from DSC (figure 4.10c).

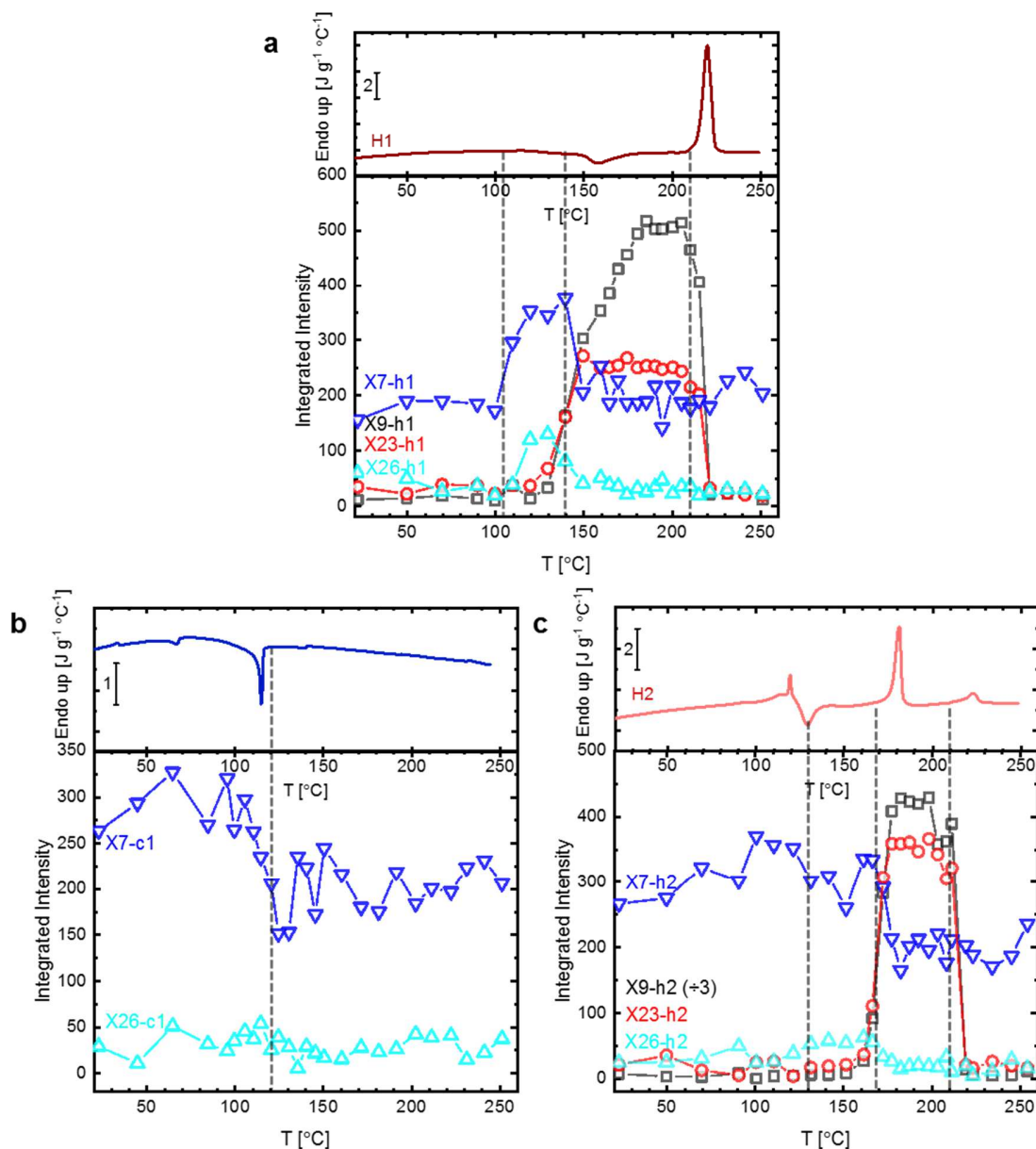


Figure 4.10. EH-IDTBR thermograms (top pannels) and integrated intensity (bottom pannels) of select XRD peaks (e.g. X7 & X9 denote peaks at $2\theta = 7^\circ$ and 9.6° , respectively) as a function of temperature in (a) first heating, (b) first cooling and (c) second heating cycles. Note that the integrated intensity of X9 in (c) is divided by 3 for clarity. Dashed lines are guides to the eye to highlight the relationship between thermograms and diffractograms as explained in the text.

Combining the results from DSC and VT-XRD, we suggest that the amorphous as-cast film undergoes a slight increase in order between 110 °C to 120 °C, with signs of π - π stacking (P0 phase). This phase then transforms into a crystalline phase (P3) from 140 °C. Upon cooling from the isotropic melt, another low order phase is formed (P1). P1 seems similar to P0, but the former is distinguished by a flatter baseline of the halo at $2\theta \approx 7^\circ$, shifting it to higher angle, and a more intense halo centered around 20° .

When the melt-cooled phase is reheated, P1 transforms into a higher-order phase (P2) from $\approx 100^\circ\text{C}$ as two sharp peaks emerge from the halo around 7° . This coincides with the Endo1/Exo1 event observed from DSC. P2 then melts from $\approx 170^\circ\text{C}$, concomitant with the crystallization of P3.

The effect of preferred orientation on diffraction pattern has already been discussed in terms of O-IDTBR. A similar effect occurs in the case of EH-IDTBR as the peaks originating from the crystalline phase (P3) are significantly more intense in the 2nd heating compared to the 1st cycle. This is especially the case for the peak at 9.6° , which is over twice the intensity. By comparing the experimental patterns with the simulated pattern from single crystal data (figure 4.11),^[99] the peak at 9.6° is assigned to the (100) plane.

Reasonable agreement is observed between the diffraction pattern of P3 and the simulated powder pattern from single crystal data, although the peaks seem to be shifted to lower angle in the experimental patterns. Since it is not certain that the batch used for growing single crystals is the same as that used in XRD, we tentatively attribute this difference to batch-variation induced by the chiral side chains, as mentioned at the beginning of this section on EH-IDTBR. The peaks originating from the suggested mesophase in the second heating do not correspond to any peaks in the simulated powder pattern, corroborating the idea that they correspond to a different phase, as opposed to being an effect of preferred orientation.

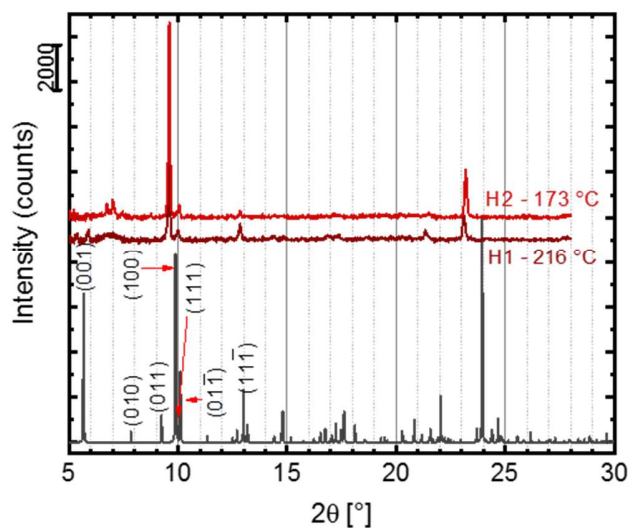


Figure 4.11. Simulated powder X-ray diffraction pattern from EH-IDTBR single crystal data (grey) with main peaks assigned. Single crystal data provided by Andrew Wadsworth and Helen Bristow. Diffractograms at 216 °C and 173 °C from 1st and 2nd heating cycles, respectively, are shown for comparison.

These results raise several questions, namely (i) the nature of the phase formed in OPV active layers when EH-IDTBR is blended with donor polymers and (ii) the effect of batch-variation on device performance under the same fabrication conditions. On the one hand, in terms of the former, it has been previously suggested that EH-IDTBR may form a different polymorph in a P3HT:EH-IDTBR thin film, compared to the neat film.^[3] Given the fast drying kinetics during spin-coating, it is likely that there is not enough time for nucleation of the crystalline phase. To support this idea, we refer to figures 3.3b & d, and figure 3.5e in chapter 3. The results shown in the previous chapter suggest that nucleation of the crystalline phase (P3) in the 1st DSC heating cycle of a (1:9) P3HT:EH-IDTBR blend is suppressed compared to the neat film, while the intensity of the endotherm assigned to melting of the suggested liquid-crystalline phase (P2) is enhanced in the

blend compared to the neat. We thus believe that the previously suggested polymorphism may be due to the dominance of P1 in the neat film, while P2 dominates the blend.

On the other hand, the effect of EH-IDTBR batch variation on OPV device morphology has not been previously explored. However, its effect may be insignificant if EH-IDTBR does not in fact form the high-melting crystalline phase upon casting blend solutions, and instead forms the lower-order liquid crystalline phase, which is more robust to batch-variations.

4.4. Conclusion

In this chapter, we investigate the effect of structural changes in the side chains of IDTBR acceptors on their phase behavior, which we relate to the performance in devices based on P3HT, as discussed in the previous chapter. Firstly, results highlight the effect of side-chain variation on phase behavior. The chiral branched side chains in EH-IDTBR lead to batch-to-batch variation in isomeric purity, which seem to induce significant changes in phase behavior. The impact is most significant in terms of the kinetics of nucleation of the crystalline phase. Meanwhile, two lower-order phases seem more robust towards isomeric purity, but to different extents. One of those is characterized by side chain crystallization, and is easily formed at rates as fast as $100\text{ }^{\circ}\text{C min}^{-1}$; the formation of the other, liquid crystalline, is almost completely suppressed at $40\text{ }^{\circ}\text{C min}^{-1}$. Secondly, results also highlight the effect of processing from solution vs. from the melt on film morphology. While this translates into differences in preferred orientation between solution- and melt-processing in the case of O-IDTBR, results suggest a difference in phase in the case of EH-IDTBR. We also find that nucleation of the crystalline phase is much more facile in the case of O-IDTBR, consistent with the observation of the same crystalline phase in both neat and P3HT-blend thin films.^[3]

CHAPTER 5: Conclusion and Future Work

In this thesis we explored the potential of thermal analysis as a tool for rational material design, blend selection and active layer optimization. The first chapter focused on a case study of monotectic low bandgap polymer/NFA binaries, which contrast with the dominating discussion of eutectics in the field of OPVs. The drop in device performance above the observed monotectic composition was attributed to the coarser morphology induced by melt immiscibility, as suggested by the phase behavior. Between the two (structurally similar) acceptors investigated, crystalline O-IDTBR displayed lower miscibility compared to amorphous O-IDFBR.

In the second chapter, we observe that the difference in degree of crystallinity between O-IDTBR and EH-IDTBR governs the M_w dependence and independence, respectively, of the eutectic $T-\phi$ diagrams. Once again, the higher crystallinity of O-IDTBR leads to a stronger competition between P3HT and acceptor crystallization, which induces a change in the level of miscibility as M_w varies, hence a change in eutectic composition. This change is not observed in the case of EH-IDTBR, a less crystalline acceptor. We explored this further in the fourth chapter, where the focus was on understanding the effect of branched vs. linear side chain on phase behavior. We observe a significantly lower barrier to crystallization in O-IDTBR. While crystallization of EH-IDTBR is suppressed under rapid solidification conditions, we suggest that a lower-order mesophase is formed more easily.

Understanding of the phase behavior of neat materials and blends has been used to characterize active layer morphology, but we suggest that the full potential of thermal analysis in the field of OPVs is yet to unravel, particularly in helping develop more quantitative active layer characterization and a more rational approach to materials design and blend selection. We discussed how certain aspects of blend phase behavior, as determined from standard DSC, have been usually overlooked but which are important. For example, the shape of the liquidus curve

provides insight into liquid miscibility, as exploited in chapters 2 and 3. Furthermore, there have been a few studies in the literature employing the potential of flash-DSC in mimicking the fast drying conditions during active layer processing.^[48,103] Although unable to replicate the rates accessible using flash-DSC, we further demonstrate the capability of such a method in chapter 4, where the study of crystallization kinetics and mesophase formation supplemented the discussion in chapter 3. Such information can be used as a rapid tool for understanding crystallization kinetics of given blend components, according to which casting conditions (e.g. blend composition, solution temperature, and whether or not an additive is required) can be determined more rapidly. Another exciting and novel application of flash-DSC remains in its application to quantitatively determine domain compositions in thin films processed under similar conditions as devices.^[46]

CHAPTER 6: Experimental Procedure

6.1. Materials

PffBT4T-2DT, O-IDTBR and O-IDFBR were synthesised according to literature procedures,^[2,3,104] and reactions were carried out under an inert argon atmosphere using conventional Schlenk techniques. P3HT batches were purchased from Ossila and BASF, or synthesized according to literature procedure.^[105] All other chemicals and solvents were purchased from Sigma Aldrich and Acros Organics and used as received.

6.2. Thermal characterization: differential scanning calorimetry

Samples for DSC were prepared by drop-casting neats and blends from chlorobenzene solutions. Two heating and two cooling cycles were recorded at a rate of 5 °C min⁻¹, unless stated otherwise, and under nitrogen. A concentration of 15 mg mL⁻¹ was used for blends incorporating PffBT4T-2DT, while 25 mg mL⁻¹ was used for neat P3HT, NFAs and blends thereof. A Mettler Toledo DSC 1 (instrument 1) was used for neats and blends of the 41 kDa PffBT4T-2DT batch (chapter 2) and for P3HT neats and blends (chapter 3). A TA Instruments DSC Q20 (instrument 2) was used for the neat and blends of the 55 kDa PffBT4T-2DT batch (chapter 2) and for the investigation of neat O-IDTBR and EH-IDTBR in chapter 4.

6.3. Device fabrication and characterization

Inverted architecture bulk heterojunction solar cells (glass/ITO/ZnO/polymer:NFA/MoO₃/Ag) were fabricated as follows. Glass substrates, prepatterned with ITO (15 Ω sheet resistance per square), were cleaned by sonication in acetone, detergent, deionized water, and isopropanol before oxygen plasma treatment for 10 min. A layer of ZnO, ≈ 30 nm (from Zn(OAc)₂ in monoethanolamine (60 μL) and 2-methoxyethanol (2 mL)), was deposited by spin-coating onto the ITO substrate at 4000 r.p.m. for 40 s, followed by annealing at 150 °C for 20 min. Active layer solutions (PffBT4T-2DT:NFA, of varying weight ratios) were prepared from CB with a total

concentration of 15 mg mL⁻¹, unless otherwise stated. The solutions were heated to 80 °C overnight, and the active layers were deposited by spin-coating from hot solution and substrates (100 °C) at 2500 r.p.m. for 1 min. The active layers were then annealed at 80 °C for 5 min, under an inert atmosphere. Active layer solutions (P3HT:IDTBR, weight ratio 1:1) were prepared from CB with a total concentration of 24 mg mL⁻¹. The solutions were heated to 70 °C overnight, and the active layer was deposited by spin-coating at 2500 r.p.m. for 1 min. The active layers were then annealed at 125 °C for 12 min, under an inert atmosphere.

A MoO₃ anode interlayer (10 nm) and Ag anode (100 nm) were then deposited by thermal evaporation through a shadow mask, giving an active area of 0.045 cm² per device. The *J-V* characteristics were measured under AM1.5G (100 mW cm⁻²) irradiation using an Oriel Instruments Xenon lamp calibrated to a Si reference cell to correct for spectral mismatch, and a Keithley 2400 source meter. Device active layer thicknesses were determined using a Veeco Dektak 150 profilometer.

6.4. Spectroscopic characterization

6.4.1. Transient absorption spectroscopy

A broadband pump-probe fs TA spectrometer Helios (Spectra Physics, Newport Corp.) was used to measure the TA spectra and kinetics for thin film samples. Ultrafast laser pulses (800 nm, 100 fs pulse duration) were generated by a 1 kHz Ti:sapphire regenerative amplifier (Solstice, Spectra Physics). One portion of the 800 nm pulses was directed to an optical parametric amplifier (TOPAS) to generate the visible pump pulses at 650 nm. The rest of the 800 nm pulses routes onto a mechanical delay stage (6 ns time window) and is directed through a sapphire crystal to generate white light probe ranging from (800 to 1600) nm in the near-infrared region. The pump and probe beams were focused onto the same spot on the samples. During the measurements, all the samples

were kept in a quartz cuvette under continuous N₂ flow. Samples were excited at a pump fluence of 5 $\mu\text{J cm}^{-2}$ unless otherwise stated.

6.4.2. Photoluminescence spectroscopy

PL spectra were acquired using a home-built set up with an Andor SR-163 spectrometer and a CCD array (Andor i-DUS). The excitation source provided the excitation wavelength of 630 nm (1.96 eV photon energy) and a low pass filter (650 nm) was in place to attenuate incident beam reflection. The emitted light was collected perpendicular to excitation focused into an optical fiber. The spectra were measured at 100 accumulated exposures of 0.1 s. Corrections were made by subtracting the constant background and accounting for the detector response, no change were made to the optical configuration between measurements. PL spectra were normalised with respect to the absorbance at the excitation wavelength.

6.5. X-ray characterization

6.5.1. Grazing incidence X-ray Diffraction

GIXD measurements were performed at the 11-BM Complex Materials Scattering (CMS) beamline of the National Synchrotron Light Source II (NSLS-II) with a beam energy of 10 keV. The 2D scattering patterns were collected at an X-ray incidence angle of 0.14° with a Pilatus 300K detector with a pixel size of 172 μm and placed about 150 mm from the sample. The data were analyzed using Nika analysis package based on Igor Pro.^[106] Sector averaged 1D scattering profiles were obtained from 15° cake sectors. Volume normalized pole figures were constructed from the 2D GIWAXS images corrected for the missing wedge by integrating the intensities at each detector azimuth within the q range of the lamellar diffraction peak. A linear background defined by the intensities at the two ends of the integrated q range was subtracted. The relative degree of crystallinity (rDoC) was calculated by integrating the intensities over the crystallographic

orientation sphere: $rDoC = \int_0^{\pi/2} I(\chi) \sin \chi d\chi$. Film thicknesses were measured using an ellipsometer (M-2000-XI, J. A. Woollam Co., Inc) and were found to be in the range 210 - 290 nm.

6.5.2. Powder X-ray diffraction

XRD was carried out on thin films of the acceptors drop-cast on silicon substrates from chlorobenzene solutions (25 mg ml⁻¹, 600 r.p.m.) using a PANalytical X'Pert PRO MRD diffractometer equipped with a nickel-filtered Cu-K α 1 beam and X'Celerator detector, with a current $I = 40$ mA and accelerating voltage $U = 40$ kV. Samples for variable temperature XRD were placed in a heating chamber and diffractograms were collected at a heating/cooling rate of 5 °C min⁻¹ from 20 to 250 °C (two heating and one cooling cycle were recorded). Heating and cooling were performed under nitrogen.

6.5.3. Resonant soft X-ray scattering

The scattering contrast is directly proportional to $\Delta n^2 = \Delta\delta^2 + \Delta\beta^2$, where $1 - \delta$ is the real part (related to dispersion) and β is the imaginary part (related to absorption) of the complex refractive index. R-SoXS measurements were performed in transmission geometry at the ALS beamline 11.0.1.2^[107] following procedures described earlier.^[108] BHJ films were cast directly onto UV-Ozone treated 100 nm Si₃N₄ windows (Norcada).^[107] The 2-D R-SoXS data were collected at beamline 11.0.1.2 at the Advanced Light Source using a Peltier cooled (-45 °C) in-vacuum (base pressure $\approx 10^{-9}$ kPa (10^{-8} mBar)) CCD detector (PI-MTE, Princeton Instruments, 2048×2048 pixels). 1-D scattering profiles were obtained from the reduction of the 2-D scattering patterns using a custom Nika^[106] analysis package and subsequently normalised for the instantaneous X-ray flux. The scattering intensity is affected by the distance travelled by the X-ray beam through the sample as well as the scattering volume. R-SoXS scattering intensities were therefore

normalised for absorption and film thickness.^[109] Film thicknesses were measured using an ellipsometer (M-2000-XI, J. A. Woollam Co., Inc). Films processed from 15 mg mL⁻¹ solutions had thicknesses ranging between 230 - 290 nm. R-SoXS contrast calculations were done using PEY NEXAFS measured on films cast on Si substrate at the Spectroscopy Soft and Tender (SST-1) beamline at NSLS-II. The QANT^[110] package based on Igor Pro was used to analyze the NEXAFS data.

6.6. Transmission electron microscopy

Blend solutions of 41 kDa PffBT4T-2DT with either NFA of varying weight ratios were prepared from CB with a total concentration of 15 mg mL⁻¹ unless stated otherwise. The solutions were heated to 80 °C overnight, and the active layers were deposited on Si (University Wafer) substrates coated with a water soluble sacrificial layer (PEDOT:PSS) (Sigma Aldrich) by spin-coating from hot solution and substrates (100 °C) at 2500 r.p.m. for 1 min. The samples were then annealed at 80 °C for 5 min, under nitrogen atmosphere. The films were then scored with a scalpel, and immersed in de-ionized water to dissolve the sacrificial layer. The delaminated BHJ films floating on the water surface were collected with a copper mesh TEM grid with a lacey carbon coating and allowed to dry in air prior to analysis. LAADF-STEM images were acquired with a FEI Titan 80-300 at operating voltage of 300kV. A 10 micron probe-forming aperture was employed to maximize the depth of focus resulting in a probe convergence angle of 3 mrad and a probe current of 60 pA. An annular dark field detector was employed to collect the scattered dark-field image signal over an angular range of 17 mrad to 96 mrad.

Bibliography

- [1] S. Chou, The Benchmark for Commercial Organic Solar Cells has Been Set, <http://lifeinism.com/2018/05/06/the-benchmark-for-commercial-organic-solar-cells-has-been-set/>, accessed: December, 2019.
- [2] D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant and I. McCulloch, *Nat. Mater.*, **2017**, *16*, 363.
- [3] S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant and I. McCulloch, *Nat. Commun.*, **2016**, *7*, 11585.
- [4] A. Wadsworth, Z. Hamid, M. Bidwell, R. S. Ashraf, J. I. Khan, D. H. Anjum, C. Cendra, J. Yan, E. Rezasoltani, A. A. Y. Guilbert, M. Azzouzi, N. Gasparini, J. H. Bannock, D. Baran, H. Wu, J. C. de Mello, C. J. Brabec, A. Salleo, J. Nelson, F. Laquai and I. McCulloch, *Adv. Energy Mater.*, **2018**, *8*, 1801001.
- [5] W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang and J. Hou, *J. Am. Chem. Soc.*, **2017**, *139*, 7148.
- [6] J.-D. Chen, Y.-Q. Li, J. Zhu, Q. Zhang, R.-P. Xu, C. Li, Y.-X. Zhang, J.-S. Huang, X. Zhan, W. You and J.-X. Tang, *Adv. Mater.*, **2018**, *30*, 1706083.
- [7] X. Xu, T. Yu, Z. Bi, W. Ma, Y. Li and Q. Peng, *Adv. Mater.*, **2018**, *30*, 1703973.
- [8] Raynergy Tek, Raynergy new world record on certified PCE 13.28% single junction OPV, <https://www.printedelectronicsworld.com/articles/15405/raynergy-new-world-record-on-certified-pce-13-28-single-junction-opv>, accessed: December, 2019
- [9] S. Li, L. Ye, W. Zhao, H. Yan, B. Yang, D. Liu, W. Li, H. Ade and J. Hou, *J. Am. Chem. Soc.*, **2018**, *140*, 7159.
- [10] University of Michigan, Organic solar cells reach record efficiency, benchmark for commercialization, www.sciencedaily.com/releases/2018/04/180423110813.htm, accessed: December, 2019.

- [11] S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson and I. McCulloch, *J. Am. Chem. Soc.*, **2015**, *137*, 898.
- [12] L. Yu, D. Qian, S. Marina, F. A. A Nugroho, A. Sharma, S. Hultmark, A. I. Hofmann, R. Kroon, J. Benduhn, D.-M. Smilgies, K. Vandewal, M. R. Andersson, C. Langhammer, J. Martín, F. Gao and C. Muller, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 21766.
- [13] C. B. Nielsen, S. Holliday, H.-Y. Chen, S. J. Cryer and I. Mcculloch, *Acc. Chem. Res.*, **2015**, *48*, 2803.
- [14] C. Li and H. Wonneberger, *Adv. Mater.*, **2012**, *24*, 613.
- [15] Y. Lin, Y. Wang, J. Wang, J. Hou, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, **2014**, *26*, 5137.
- [16] B. Jiang, X. Zhang, C. Zhan, Z. Lu, J. Huang, X. Ding, S. He and J. Yao, *Polym. Chem.*, **2013**, *4*, 4631.
- [17] Q. Wu, D. Zhao, A. M. Schneider, W. Chen and L. Yu, *J. Am. Chem. Soc.*, **2016**, *138*, 7248.
- [18] R. Singh, S. R. Suranagi, J. Lee, H. Lee, M. Kim and K. Cho, *Sci. Rep.*, **2018**, *8*, 2849.
- [19] A. Wadsworth, R. S. Ashraf, M. Abdelsamie, S. Pont, M. Little, M. Moser, Z. Hamid, M. Neophytou, W. Zhang, A. Amassian, J. R. Durrant, D. Baran and I. Mcculloch, *ACS Energy Lett.*, **2017**, *2*, 1494.
- [20] Y. Li, J.-D. Lin, X. Che, Y. Qu, F. Liu, L.-S. Liao and S. R. Forrest, *J. Am. Chem. Soc.*, **2017**, *139*, 17114.
- [21] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Commun.*, **2014**, *5*, 5293.
- [22] W. Ma, G. Yang, K. Jiang, J. H. Carpenter, Y. Wu, X. Meng, T. McAfee, J. Zhao, C. Zhu, C. Wang, H. Ade and H. Yan, *Adv. Energy Mater.*, **2015**, *5*, 1501400.
- [23] D. Baran, T. Kirchartz, B. S. Wheeler, S. Dimitrov, M. Abdelsamie, J. Gorman, R. S. Ashraf, S. Holliday, A. Wadsworth, N. Gasparini, P. Kaienburg, H. Yan, A. Amassian, C.

- J. Brabec, J. R. Durrant and I. McCulloch, *Energy Environ. Sci.*, **2016**, 9, 3783.
- [24] H. Cha, J. Wu, A. Wadsworth, J. Nagitta, S. Limbu, S. Pont, Z. Li, J. Searle, M. F. Wyatt, D. Baran, J.-S. Kim, I. McCulloch and J. R. Durrant, *Adv. Mater.*, **2017**, 29, 1701156.
- [25] J. Nelson, *Mater. Today*, **2011**, 14, 462.
- [26] B. A. Collins, E. Gann, L. Guignard, X. He, C. R. McNeill and H. Ade, *J. Phys. Chem. Lett.*, **2010**, 1, 3160.
- [27] T. M. Burke and M. D. McGehee, *Adv. Mater.*, **2014**, 26, 1923.
- [28] C. McDowell, M. Abdelsamie, M. F. Toney and G. C. Bazan, *Adv. Mater.*, **2018**, 30, 1707114.
- [29] Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha and M. Ree, *Nat. Mater.*, **2006**, 5, 197.
- [30] Q. Liang, X. Jiao, Y. Yan, Z. Xie, G. Lu, J. Liu and Y. Han, *Adv. Funct. Mater.*, **2019**, 29, 1807591.
- [31] Y. Qin, M. A. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T. J. Shin, H. Y. Woo and J. Hou, *Adv. Mater.*, **2016**, 28, 9416.
- [32] L. Ye, B. A. Collins, X. Jiao, J. Zhao, H. Yan and H. Ade, *Adv. Energy Mater.*, **2018**, 8, 1703058.
- [33] J. Perea, S. Langner, M. Salvador, B. Sanchez-Lengeling, N. Li, C. Zhang, G. Jarvas, J. Kontos, A. Dallos, A. Aspuru-Guzik and C. J. Brabec, *J. Phys. Chem. C*, **2017**, 121, 18153.
- [34] H. Bin, Y. Yang, Z.-G. Zhang, L. Ye, M. Ghasemi, S. Chen, Y. Zhang, C. Zhang, C. Sun, L. Xue, C. Yang, H. Ade and Y. Li, *J. Am. Chem. Soc.*, **2017**, 139, 5085.
- [35] H. Hu, Y. Li, J. Zhang, Z. Peng, L. Ma, J. Xin, J. Huang, T. Ma, K. Jiang, G. Zhang, W. Ma, H. Ade and H. Yan, *Adv. Energy Mater.*, **2018**, 8, 1800234.
- [36] H. Li, Y. Zhao, J. Fang, X. Zhu, B. Xia, K. Lu, Z. Wang, J. Zhang, X. Guo and Z. Wei, *Adv. Energy Mater.*, **2018**, 8, 1702377.

- [37] S. A. Dowland, M. Salvador, J. Perea, N. Gasparini, S. Langner, S. Rajoelson, H. H. Ramanitra, B. D. Lindner, A. Osvet, C. J. Brabec, R. C. Hiorns and H.-J. Egelhaaf, *ACS Appl. Mater. Interfaces*, **2017**, 9, 10971.
- [38] D. R. Kozub, K. Vakhshouri, L. M. Orme, C. Wang, A. Hexemer and E. D. Gomez, *Macromolecules*, **2011**, 44, 5722.
- [39] F. Liu, D. Chen, C. Wang, K. Luo, W. Gu, A. L. Briseno, J. W. P. Hsu and T. P. Russell, *ACS Appl. Mater. Interfaces*, **2014**, 6, 19876.
- [40] N. Li, J. D. Perea, T. Kassar, M. Richter, T. Heumueller, G. J. Matt, Y. Hou, N. S. Güldal, H. Chen, S. Chen, S. Langner, M. Berlinghof, T. Unruh and C. J. Brabec, *Nat. Commun.*, **2017**, 8, 14541.
- [41] D. Leman, M. A. Kelly, S. Ness, S. Engmann, A. Herzing, C. Snyder, H. W. Ro, R. J. Kline, D. M. DeLongchamp and L. J. Richter, *Macromolecules*, **2015**, 48, 383.
- [42] R. A. Matkar and T. Kyu, *J. Phys. Chem. B*, **2006**, 110, 12728.
- [43] L. Ye, H. Hu, M. Ghasemi, T. Wang, B. A. Collins, J.-H. Kim, K. Jiang, J. H. Carpenter, H. Li, Z. Li, T. McAfee, J. Zhao, X. Chen, J. Lin Yuk Lai, T. Ma, J.-L. Bredas, H. Yan and H. Ade, *Nat. Mater.*, **2018**, 17, 253.
- [44] P. Rathi, T.-M. Huang, P. Dayal and T. Kyu, *J. Phys. Chem. B*, **2008**, 112, 6460.
- [45] M. Ghasemi, H. Hu, Z. Peng, J. J. Rech, I. Angunawela, J. H. Carpenter, S. J. Stuard, A. Wadsworth, I. McCulloch, W. You and H. Ade, *Joule*, **2019**, 3, 1328.
- [46] J. Martín, presented at Interfaces in Organic and Hybrid Thin-Film Optoelectronics, València, Spain, March, **2019**.
- [47] J. Xin, X. Meng, X. Xu, Q. Zhu, H. B. Naveed and W. Ma, *Matter*, **2019**, 1, 1.
- [48] M. Abdelsamie, N. D. Treat, K. Zhao, C. McDowell, M. A. Burgers, R. Li, D. M. Smilgies, N. Stingelin, G. C. Bazan and A. Amassian, *Adv. Mater.*, **2015**, 27, 7285.
- [49] J. Kesters, P. Verstappen, J. Raymakers, W. Vanormelingen, J. Drijkoningen, J. D. ' Haen, J. Manca, L. Lutsen, D. Vanderzande and W. Maes, *Chem. Mater.*, **2015**, 27, 1332.

- [50] P. E. Hopkinson, P. A. Staniec, A. J. Pearson, A. D. F. Dunbar, T. Wang, A. J. Ryan, R. A. L. Jones, D. G. Lidzey and A. M. Donald, *Macromolecules*, **2011**, *44*, 2908.
- [51] M. Defour, N. Van Den Brande, L. Van Lokeren, G. Van Assche, W. Maes, D. Vanderzande and B. Van Mele, *RSC Adv*, **2016**, *6*, 92981.
- [52] N. C. Miller, R. Gysel, C. E. Miller, E. Verploegen, Z. Beiley, M. Heeney, I. McCulloch, Z. Bao, M. F. Toney and M. D. McGehee, *J. Polym. Sci. Part B Polym. Phys.*, **2011**, *49*, 499.
- [53] C. Müller, *Chem. Mater.*, **2015**, *27*, 2740.
- [54] J. Zhao, A. Swinnen, | Guy, V. Assche, J. Manca, D. Vanderzande and B. Van Mele, *J. Phys. Chem. B*, **2009**, *113*, 1587.
- [55] G. Bernardo, N. Deb, S. M. King, D. G. Bucknall and D. G. Bucknall, *J. Polym. Sci., Part B Polym. Phys*, **2016**, *54*, 994.
- [56] A. J. Pearson, T. Wang, R. A. L. Jones, D. G. Lidzey, P. A. Staniec, P. E. Hopkinson and A. M. Donald, *Macromolecules*, **2012**, *45*, 1499.
- [57] N. Stingelin-Stutzmann, E. Smits, H. Wondergem, C. Tanase, P. Blom, P. Smith and D. de Leeuw, *Nat. Mater.*, **2005**, *4*, 601.
- [58] S. Goffri, C. Müller, N. Stingelin-Stutzmann, D. W. Breiby, C. P. Radano, J. W. Andreasen, R. Thompson, R. A. J. Janssen, M. M. Nielsen, P. Smith and H. Sirringhaus, *Nat. Mater.*, **2006**, *5*, 950.
- [59] N. Stingelin, *Polym. Int.*, **2012**, *61*, 866.
- [60] R. A. Matkar and T. Kyu, *J. Phys. Chem. B*, **2006**, *110*, 16059.
- [61] T. Htira, C. Cogne, E. Gagnière and D. Mangin, *J. Chem. Eng. Data*, **2016**, *61*, 806.
- [62] D. Gebauer, M. Kellermeier, J. D. Gale, L. Bergströ and H. Cö Lfen, *Chem. Soc. Rev.*, **2014**, *43*, 2348.
- [63] W. R. Burghardt, *Macromolecules*, **1989**, *22*, 2482.
- [64] A. D. Pelton and W. T. Thompson, *Prog. Solid State Chem.*, **1975**, *10*, 119.

- [65] P. Wolfer, C. Müller, P. Smith, M. A. Baklar and N. Stingelin-Stutzmann, *Synth. Met.*, **2007**, *157*, 827.
- [66] C. Müller, T. A. M. Ferenczi, M. Campoy-Quiles, J. M. Frost, D. D. C. Bradley, P. Smith, N. Stingelin-Stutzmann and J. Nelson, *Adv. Mater.*, **2008**, *20*, 3510.
- [67] P. Wolfer, P. E. Schwenn, A. K. Pandey, Y. Fang, N. Stingelin, P. L. Burn and P. Meredith, *J. Mater. Chem. A*, **2013**, *1*, 5989.
- [68] C. Muller, J. Bergqvist, K. Vandewal, K. Tvingstedt, A. S. Anselmo, R. Magnusson, M. I. Alonso, E. Moons, H. Arwin, M. Campoy-Quiles and O. Inganäs, *J. Mater. Chem.*, **2011**, *21*, 10676.
- [69] F. C. Jamieson, E. B. Domingo, T. McCarthy-Ward, M. Heeney, N. Stingelin and J. R. Durrant, *Chem. Sci.*, **2012**, *3*, 485.
- [70] A. M. Ballantyne, T. A. M. Ferenczi, M. Campoy-Quiles, T. M. Clarke, A. Maurano, K. H. Wong, W. Zhang, N. Stingelin-Stutzmann, J.-S. Kim, D. D. C. Bradley, J. R. Durrant, I. McCulloch, M. Heeney, J. Nelson, S. Tierney, W. Duffy, C. Mueller and P. Smith, *Macromolecules*, **2010**, *43*, 1169.
- [71] I. Cardinaletti, J. Kesters, S. Bertho, B. Conings, F. Piersimoni, J. D'Haen, L. Lutsen, M. Nesladek, B. Van Mele, G. Van Assche, K. Vandewal, A. Salleo, D. Vanderzande, W. Maes and J. V. Manca, *J. Photonics Energy*, **2014**, *4*, 040997.
- [72] J. Luke, E. M. Speller, A. Wadsworth, M. F. Wyatt, S. Dimitrov, H. K. H. Lee, Z. Li, W. C. Tsoi, I. McCulloch, D. Bagnis, J. R. Durrant and J. S. Kim, *Adv. Energy Mater.*, **2019**, *9*, 1803755.
- [73] Z. Hamid, A. Wadsworth, E. Rezasoltani, S. Holliday, M. Azzouzi, M. Neophytou, A. A. Y. Guilbert, Y. Dong, M. S. Little, S. Mukherjee, A. A. Herzing, H. Bristow, R. J. Kline, D. M. DeLongchamp, A. A. Bakulin, J. Durrant, J. Nelson and I. McCulloch, *Adv. Energy Mater.* **2020**, 1903248.
- [74] J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, *Nat. Energy*, **2016**, *1*, 15027.

- [75] H. Cha, S. Wheeler, S. Holliday, S. D. Dimitrov, A. Wadsworth, H. H. Lee, D. Baran, I. McCulloch and J. R. Durrant, *Adv. Funct. Mater.*, **2018**, 28, 1704389.
- [76] A. A. Y. Guilbert, L. X. Reynolds, A. Bruno, A. Maclachlan, S. P. King, M. A. Faist, E. Pires, J. E. Macdonald, N. Stingelin, S. A. Haque and J. Nelson, *ACS Nano*, **2012**, 6, 3868.
- [77] S. Nilsson, A. Bernasik, A. Budkowski and E. Moons, *Macromolecules*, **2007**, 40, 8291.
- [78] H. W. Ro, J. M. Downing, S. Engmann, A. A. Herzing, D. M. Delongchamp, L. J. Richter, S. Mukherjee, H. Ade, M. Abdelsamie, L. K. Jagadamma, A. Amassian, Y. Liu and H. Yan, *Energy Environ. Sci.*, **2016**, 9, 2835.
- [79] B. A. Collins, Z. Li, J. R. Tumbleston, E. Gann, C. R. McNeill and H. Ade, *Adv. Energy Mater.*, **2013**, 3, 65.
- [80] W. Zhang, R. Hu, X. Zeng, X. Su, Z. Chen, X. Zou, J. Peng, C. Zhang and A. Yartsev, *Polymers (Basel)*, **2019**, 11, 408.
- [81] H. Cha, G. Fish, J. Luke, A. Alraddadi, H. H. Lee, W. Zhang, Y. Dong, S. Limbu, A. Wadsworth, I. P. Maria, L. Francàs, H. L. Sou, T. Du, J. Kim, M. A. McLachlan, I. McCulloch and J. R. Durrant, *Adv. Energy Mater.*, **2019**, 9, 1901254.
- [82] Y. Dong, H. Cha, J. Zhang, S. Tuladhar, I. McCulloch, J. R. Durrant and A. A. Bakulin, *J. Chem. Phys*, **2019**, 150, 104704.
- [83] A. M. Ballantyne, L. Chen, J. Dane, T. Hammant, F. M. Braun, M. Heeney, W. Duffy, I. McCulloch, D. D. C. Bradley and J. Nelson, *Adv. Funct. Mater.*, **2008**, 18, 2373.
- [84] J. J. van Franeker, M. Turbiez, W. Li, M. M. Wienk and R. A. J. Janssen, *Nat. Commun.*, **2015**, 6, 6229.
- [85] R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu and J. M. J. Fréchet, *Adv. Mater.*, **2003**, 15, 1519.
- [86] D. Spoltore, T. Vangerven, P. Verstappen, F. Piersimoni, S. Bertho, K. Vandewal, N. Van den Brande, M. Defour, B. Van Mele, A. De Sio, J. Parisi, L. Lutsen, D. Vanderzande, W. Maes and J. V. Manca, *Org. Electron.*, **2015**, 21, 160.
- [87] N. D. Eastham, A. S. Dudnik, T. J. Aldrich, E. F. Manley, T. J. Fauvell, P. E. Hartnett, M.

- R. Wasielewski, L. X. Chen, F. S. Melkonyan, A. Facchetti, R. P. H. Chang and T. J. Marks, *Chem. Mater.*, **2017**, 29, 4432.
- [88] C. Nicolet, D. Deribew, C. Renaud, G. Fleury, C. Brochon, E. Cloutet, L. Vignau, G. Wantz, H. Cramail, M. Geoghegan and G. Hadziioannou, *J. Phys. Chem. B*, **2011**, 115, 12717.
- [89] N. D. Treat and M. L. Chabinyc, *Annu. Rev. Phys. Chem.*, **2014**, 65, 59.
- [90] K. Sun, Z. Xiao, S. Lu, W. Zajackowski, W. Pisula, E. Hanssen, J. M. White, R. M. Williamson, J. Subbiah, J. Ouyang, A. B. Holmes, W. W. H. Wong and D. J. Jones, *Nat. Commun.*, **2015**, 6, 1.
- [91] A. J. Bourque, S. Engmann, A. Fuster, C. R. Snyder, L. J. Richter, P. B. Geraghty and D. J. Jones, *J. Mater. Chem. A*, **2019**, 7, 16458.
- [92] M. Park, Y.-J. Choi, D.-Y. Kim, S.-H. Hwang and K.-U. Jeong, *Cryst. Growth Des.*, **2015**, 15, 900.
- [93] C. McGregor and E. Bines, *Int. J. Pharm.*, **2008**, 350, 48.
- [94] T. L. Threlfall, *Org. Process Res. Dev.*, **2009**, 13, 1224.
- [95] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, **2006**, 5, 328.
- [96] T. Kellner, H. M. A. Ehmman, S. Schrank, B. Kunert, A. Zimmer, E. Roblegg and O. Werzer, *Mol. Pharm.*, **2014**, 11, 4084.
- [97] C. F. Holder and R. E. Schaak, *ACS Nano*, **2019**, 13, 7359.
- [98] C.-M. Tsai, G.-W. Wu, S. Narra, H.-M. Chang, N. Mohanta, H.-P. Wu, C.-L. Wang and E. Wei-Guang Diau, *J. Mater. Chem. A*, **2017**, 5, 739.
- [99] H. Bristow, K. J. Thorley, A. J. P. White, A. Wadsworth, M. Babics, Z. Hamid, W. Zhang, A. F. Paterson, J. Kosco, J. Panidi, T. D. Anthopoulos and I. McCulloch, *Adv. Electron. Mater.*, **2019**, 5, 1900344.

- [100] J. Liu, Y. Zhang, H. Phan, A. Sharenko, P. Moonsin, B. Walker, V. Promarak and T.-Q. Nguyen, *Adv. Mater.*, **2013**, 25, 3645.
- [101] M. Stolte, S.-L. Suraru, P. Diemer, T. He, C. Burschka, U. Zschieschang, H. Klauk and F. Würthner, *Adv. Funct. Mater.*, **2016**, 26, 7415.
- [102] C. Schick, *Anal. Bioanal. Chem.*, **2009**, 395, 1589.
- [103] J. Zhao, S. Bertho, J. Vandenberg, G. Van Assche, J. Manca, D. Vanderzande, X. Yin, J. Shi, T. Cleij, L. Lutsen and B. Van Mele, *Phys. Chem. Chem. Phys.*, **2011**, 13, 12285.
- [104] Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, J. Peng, Y. Ma and Y. Cao, *Adv. Mater.*, **2014**, 26, 2586.
- [105] J. H. Bannock, S. H. Krishnadasan, A. M. Nightingale, C. P. Yau, K. Khaw, D. Burkitt, J. J. M. Halls, M. Heeney and J. C. de Mello, *Adv. Funct. Mater.*, **2013**, 23, 2123.
- [106] J. Ilavsky, *J. Appl. Crystallogr.*, **2012**, 45, 324.
- [107] E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer and C. Wang, *Rev. Sci. Instrum.*, **2012**, 83, 045110.
- [108] B. A. Collins, J. E. Cochran, H. Yan, E. Gann, C. Hub, R. Fink, C. Wang, T. Schuettfort, C. R. McNeill, M. L. Chabinyc and H. Ade, *Nat. Mater.*, **2012**, 11, 536.
- [109] J. R. Tumbleston, A. C. Stuart, E. Gann, W. You and H. Ade, *Adv. Funct. Mater.*, **2013**, 23, 3463.
- [110] E. Gann, C. R. McNeill, A. Tadich, B. C. C. Cowie and L. Thomsen, *J. Synchrotron Radiat.*, **2016**, 23, 374.

Appendix

A. X-ray characterization

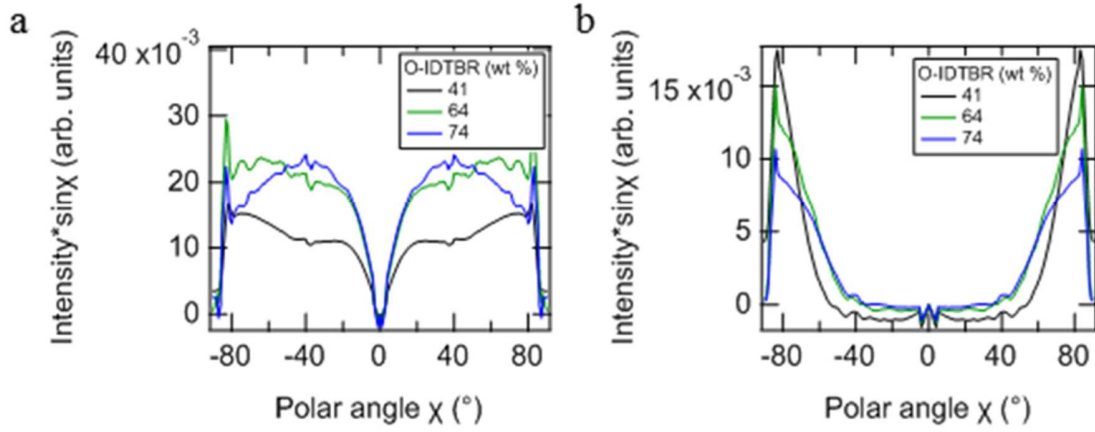


Figure A1. Volume normalized pole figures from (a) PffBT4T-2DT (100), and (b) O-IDTBR (100) peaks in GIXD data. Data from Subhrangsu Mukherjee.

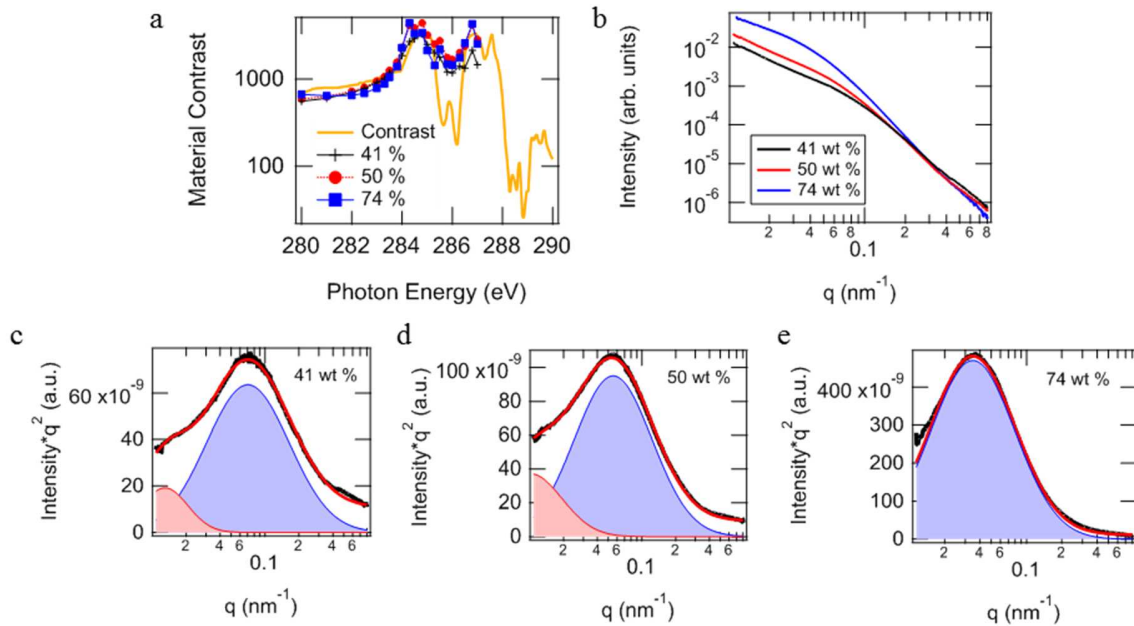


Figure A2. (a) PffBT4T-2DT:O-IDTBR material contrast calculated using PEY NEXAFS spectra superimposed on measured ISI at different photon energies; (b) Circular averaged R-SoXS scattering profiles measured at photon energy of 284 eV; (c)-(e) log-normal fits to q^2 corrected circular averaged scattering profiles acquired at photon energy 284 eV. Data from Subhrangsu Mukherjee.

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