Beyond Polythiophenes:

Exploring the Impact of Precisely Controlled Microstructure of

Group 16 Conjugated Polymers on their Supramolecular

Organization and Properties

By

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Dedication

To my family whose optimism, love and support has given me the courage to pursue all of my dreams

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List of Abbreviations

AFM	Atomic Force Microscopy
GIWAXS	Grazing Incidence X-Ray Scattering
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
¹ H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
¹³ C NMR	Carbon Nuclear Magnetic Resonance Spectroscopy
GPC	Gel Permeation Chromatography
UV-Vis	UltraViolet-Visible Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
OLED	Organic Light Emitting Diode
PV	Photovoltaics
FET	Field Effect Transistor
OPV	Organic Photovoltaics
OFET	Organic Field Effect Transistor
rr	regio-regular
r	random copolymer
-a	alternating copolymer
D-A	Donor-Acceptor Copolymer
P3AT	
P3HF	Poly(3-hexyl furan)
РЗНТ	Poly(3-hexyl thiophene)
P3HSe	Poly(3-hexyl selenophene)
T-T-Se	periodic copolymer: 33% Selenophene Content
T-Se	periodic copolymer: 50% Selenophene Content
T-Se-Se	periodic copolymer: 66% Selenophene Content
<i>r</i> -T-Se ₃₂	random copolymer: 32% Selenophene Content
<i>r</i> -T-Se ₅₃	random copolymer: 53% Selenophene Content
<i>r</i> -T-Se ₆₅	random copolymer: 65% Selenophene Content
P3HEF	

P3HF- <i>a</i> -P3HT	Poly(3-hexyl furan- <i>alt</i> -3-hexyl thiophene)
P3HEF-a-P3HT	Poly(3-hexylester furan- <i>alt</i> -3-hexyl thiophene)
P3HET	Poly(3-hexylester thiophene)
P3HET-a-P3HT	Poly(3-hexylester thiophene- <i>alt</i> -3-hexyl thiophene)
CTP	Catalyst Transfer Polycondensation
НОМО	
LUMO	Lowest Unoccupied Molecular Orbital
$\Delta E_g \ldots \ldots$	Band Gap
VEdge	Optical Band Gap
μ , cm ² V ⁻¹ s ⁻¹	charge carrier mobility, SI units
Si	
S	Sulfur
Se	Selenium
O	Oxygen
S ₀	Electronic Ground State
S ₁	First Electronic Excited State
RB	
M.W	
DP _n	Degree of Polymerization
M _n	Number Average Molecular Weight
Ð	Dispersity
Tg	Glass Transition Temperature
T _c	Crystallization Temperature
T _m	
ΔH_m	
ΔH_c	Enthalpy of Crystallization

Abstract

Well-defined, regio-regular conjugated polymers such as P3HT have been extensively explored over the past few decades for applications in the field of organic electronics. Methods to explore the microstructure of this benchmark material (such as atomic force microscopy (AFM) and X-ray scattering techniques (i.e. grazing incidence X-ray scattering (GIWAXS)) have enabled the scientific community to discern how atomic-scale periodicity and nanoscale organization can influence the polymer's physical properties such as its thermal, photo and electronic response.

The development of novel conjugated polymers with various heteroatom sequence and side-chain architecture is of particular interest as a way to tune the physical properties and enhance photo-stability in light and air. Correlation between polymer microstructure and the resulting macroscopic properties is paramount to develop next generation materials. Therefore, the scope of this work entails an overview of conjugated polymers (Chapter 1) with insights to examining structure-property relationships of Group 16 family homopolymers (Chapter 2), including a 'model' fitting of solid-state UV-vis spectra inspired by Spano and co-workers.

Beyond polythiophenes, assessment of periodic and random copolymers with similar composition of thiophene and selenophene units (Chapter 3) revealed that regular placement of selenophene improved polymer organization with enhanced charge delocalization (characterized by 'model' fitting of UV-vis spectra). And finally, ester side-chain substitution in polyfurans not only showed improved photo-stability in the presence of light and air (Chapter 4), but also favored an all-cis conformation resulting in a helical packing arrangement. This favored conformational structure was also shown to extend to alternating copolymers containing ester substituted furan rings. In contrast, ester substituted polythiophene exhibited extended configurations with higher

degrees of disorder. In the alternating copolymer, the placement of ester groups along the polymer backbone, resulted in the low band-gap structures.

Chapter 1

Introduction

1.1 Preface

Pushing the boundaries of polymer science requires that we as chemists develop methods to generate and study materials with control of composition, topology and functionality.¹ Examining how polymer structure impacts its physical attributes is paramount for its use in a desired application. Our interests lie in the development of conjugated polymers for organic electronic applications (*Section 1.2*). Modulation of the polymer structure through framework design (*Section 1.3*) affords materials with an array of tunability and chemical composition to influence desired physical properties. The synthesis of these polymers (*Section 1.4*) with architectures ranging from homopolymers to periodic sequences, *Figure 1.1*, afford regio-regular materials with controlled molecular weight and low dispersity. These materials in turn easily facilitate systematic investigations of structure-property relationships with respect to polymer composition. These materials intrinsic properties, nanoscale organization and macroscopic properties (*Section 1.5*) can be studied more in-depth utilizing methods such as ultraviolet-visible spectroscopy (UV-vis), atomic force microscopy (AFM), grazing incidence X-ray scattering (GIWAXS) and differential scanning calorimetry (DSC) with additional consideration of



Figure 1.1. Depiction of homopolymer (100% one component, A), varying composition and arrangement of copolymers (A: B) and an example of complex sequences: periodic copolymers (A-B-C).

environmental stability (*Section 1.6*). Relevant examples from literature with respect to studying how polymer structure impacts its physical properties and organization (*Section 1.7*) will highlight some key aspects our group considers in the ascribed studies in Chapters 2 - 4.

1.2. Target Applications for Conjugated Copolymers

Until the late 1970's polymers were thought to be insulating materials. This perspective changed once A. J. Heeger, A. G. Macdiarmid and H. Shirakawa probed doped polyacetylene, and found it to have semi-conducting behavior, *Figure 1.2*, was recognized with the 2000 Nobel Prize in Chemistry.^{2,3} The capability of a carbon-based polymer to have semi-conducting character opened an entirely new field in science deemed as organic electronics.

Producing a cheap material that is environmentally stable and mechanically flexible (sufficiently high molecular weight), is the ideal avenue for organic electronic applications. This allows films to be



Figure 1.2. Range of conductivity for conductors (metals), insulators (glass) and semi-conducting materials (inorganic, organic).

easily processed by manufacturing methods such as roll-print processing.⁴ Carbon-based conjugated polymers offer these potential advantages over inorganics due to a wide substrate scope with lower temperature and solution processing conditions.

Extensive studies of carbon-based materials have been explored for applications suited for semi-conducting materials. Depending on the chemical structure of the carbon-based materials and the material's processing, a wide-range of semi-conducting behavior can be realized, making them versatile candidates. Commercialization of energy converting carbon-based semiconductors has been realized in the form of light-emitting diodes (OLEDs)⁵ commonly seen in television displays

and smart-phones. Extensive studies are currently being explored to further develop carbon-based materials for applications such as organic field effect transistors (OFETs)⁶⁻⁹ and organic photovoltaics (OPVs),⁹⁻¹³ but commercialization is further away due to other limiting factors such as environmental stability and lower charge-carrier mobility. Therefore, developing efficient, easy processing, stable materials is of high interest in the conjugated polymers community.

1.2.1. The Origin of Electrical Conductivity in Conjugated Polymers



Figure 1.3. Examples of delocalized conjugated frameworks ranging from *Top:* polyacetylene to *Middle*: more aromatic structures, including *Bottom:* heterocycles and fused-ring systems.

The semi-conducting character of conjugated polymers is rooted in the electronic band structure¹⁴ of the polymer that supports the generation and flow of charge carriers. The polymer structure that can provide this capability is a carbon framework with alternating single and double bonds (aka. conjugated), whose electron density is delocalized over porbitals with sufficient orbital overlap. The

simplest example of this would be trans- and cis-polyacetylene, *Figure 1.3*. Other delocalized systems include more aromatic structures such as poly(phenylene),¹⁵ poly(p-phenylene vinylene),¹⁶ poly(analine)¹⁷ and heterocycles such as poly(pyrrole)¹⁸ or poly(thiophene)^{19,20} and more complex structures such as fused ring systems like poly(fluorene).²¹

The framework of a conjugated polymer is built from monomeric units with a molecular orbital structure characterized by the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy. Addition of more monomer units extends the conjugated framework and effectively lowers the energy difference between the HOMO and LUMO. The addition of degenerate states creates a continuous band structures known as the valence band (occupied states) and conduction band (unoccupied states) separated by the respective band gap (ΔE_g) of the HOMO and LUMO, *Figure 1.4*.

The band gap, determined from the effective conjugation length, governs the amount of energy required to promote an electron from the valence band into the conduction band as a free charge-carrier. The resulting absence of an electron (aka. positive hole) in the valence band, is also a free charge-carrier. Additional charge-carriers are provided by doping a material with either an oxidizing (electron removal from the HOMO) or reducing agent (electron addition into the LUMO) aka. "dopant". An intrinsic semi-conductor has a balance between electrons and holes in the conduction/valence bands. Therefore, to induce conductivity in materials, an additional dopant, such as an impurity is needed. Group 13/ Group 15 elements have been used as oxidizing/ reducing doping agents for silicon semiconductors and halogens like iodine are commonly used for P3HT.²²



Figure 1.4. Developing band structure from monomer to conjugated polymer

Overall, conductivity of the material is determined by the density of charge carriers either electrons (–) or holes (+), and their inherent mobility (μ , cm²V⁻¹s⁻¹). Mobility characterizes the flow of charges through material via intra/inter–molecular charge transport pathways. The more

organized the structure, the less resistance a charge-carrier encounters and hence higher mobility. The most organized structures are crystalline structures such as crystalline Si that has high mobility in its doped state. However, Si is also mechanically rigid and difficult to process, similar to polyacetylene, who is highly insoluble and oxidatively unstable.²³

In OFET devices, the applied electric field acts as the effective dopant, either through introduction of electrons (n-type semiconductor) or removal of electrons (p-type semiconductor). OPVs are more complex in their design because both n-type and p-type semiconductors are needed to facilitate the separation of photo-generated excitons (electron-hole pairs). Band gaps less than 3 eV are ideal for OPVs since this requires visible light to generate excitons. Studies pursuing low band-gap materials with the ability to absorb more of the light spectrum, near IR, with lower lying LUMO levels are potential candidates for more efficient solar cells with ambient stability. With this in mind, a large portion of research in organic electronics has focused on alternating



Figure 1.5. General considerations of framework engineering i) conjugated backbone ii) heteroatom placement (Blue, Orange), iii) side-chain placement (Red) and iv) substitution (Green)

copolymers of donor-acceptor sequences.

1.3. Designing Conjugated Polymers

The design of a conjugated framework that is stable, easy to process and has an appropriate band structure, described in *Section 1.2*, can potentially be tuned through heteroatom placement and substitution along the material's backbone, *Figure 1.5*. Framework

engineering of the conjugated core/ backbone of the polymer, requires sufficient length, at least 6-10 units to reach the effective conjugation length with the appropriate band structure.²⁴⁻²⁶ The backbone determines not only the base electronic properties, but also the organization of the material through molecular packing and its intra/inter-molecular interactions. Heteroatom placement is a useful avenue to tune the electronic properties, introduce polarizable species that promote dipole-dipole interactions, where larger atoms can better accommodate charge carriers upon doping.^{5,27-30} Substitution and side-chain engineering along the backbone can fine-tune the HOMO and LUMO levels with either electron-donating or accepting groups to make the core more electron-rich or electron-poor. More electron deficient materials tend to be more insoluble, due to tighter molecular packing. Alkyl side-chains help with solubility of a material and also alter the organization of the material depending on the chain length. Side-chains can also effect the torsion along the chain, either promoting planarity of the core or hindering it (therefore enhancing solubility but potentially reducing the effective conjugation length).³¹ This illustrates that fine-tuning the types of substituents along the backbone and its side-chain architecture not only influences its electronic structure, but also its processability and its overall organization.

1.3.1. Regio-Regularity of Alkyl Side-Chains in PolyThiophenes

An example of side-chain placement impacting polymer properties is the development of regio-regular poly(alkylthiophene) (*rr*-P3AT). Unsubstituted polythiophene was insoluble in common organic solvents, therefore, the addition of alkyl side-chains allowed the material to be more processible. However, the irregular placement of side-chains through a mixture of head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT) couplings, *Figure 1.6*, causes steric strain and backbone twisting between neighboring rings. This in turn impacts the effective polymer conjugation length, reducing electrical conductivity. Polythiophenes with ~50 – 80 % regio-regularity resulted in electrical conductivity ~ 40 S cm⁻¹.³²⁻³⁴ Development of regioselective synthetic methods using Kumada cross-coupling methods was reported by McCullough and coworkers,³⁵⁻³⁷ and later by Rieke and coworkers^{38,39} to afford materials that were (> 98 %) HT

couplings. McCullough and coworkers furthered the development of *rr*-P3ATs, using Grignard Metathesis Polymerization (GRIM)^{40,41} to afford P3ATs with only one TT coupling. The development of regio-regular P3ATs produced materials with electrical conductivities as high as 1000 S cm⁻¹.³⁵ Therefore, not only did the addition of alkyl side-chains improve the processability of polythiophenes, but the regio-regular placement of side-chains improved material organization



Figure 1.6. (a) Solubilizing alkyl chain at 3-position of thiophene ring. Examples of coupling between neighbor thiophene units (b) 5,5' tail-to-tail (TT) (c) 2,2' head-to-head (HH) (d) 2,5' head-to-tail (HT).

manifesting improved conductivity in doped rr-P3AT films. Kumada cross-coupling methods will be discussed in more detail, *Section 1.4*.

1.4. Polymerization Techniques to Synthesize Conjugated Polymers

Most commonly, conjugated polymers are synthesized by step-growth polycondensation using cross-coupling metal catalysts such as palladium, whereby only high molecular weights are achieved at high conversion, using elevated temperatures and long reaction periods.^{42,43} Generally monomers are fitted with a transmetallating agents such as tin (–SnR₃), boronic esters (–BOR₂), magnesio (MgX) or zinc (ZnX) for Stille, Suzuki, Kumada or Negishi cross-coupling reactions.⁴⁴ The catalyst fully dissociates from the chain after one coupling event, therefore offering limited control over molecular weight and dispersity (D > 2) with significant batch to batch variation, *Figure 1.7.* Both electron-rich (donor) and electron-deficient (acceptor) monomers and fused ring systems are produced this way, including most donor-acceptor (D-A) alternating copolymers.



It wasn't until McCullough⁴⁵ and Yokozawa⁴⁶ independently reported the synthesis of

Figure 1.7. Step-Growth Polycondensation: a) Monomer conversion vs. molecular weight plots illustrating high molecular weight only at high conversion b) Graphic of monomer generating dimers, tetramers and polymers after high monomer conversion. $Pd(0)L_2$: Palladium catalyst (oxidation state zero) with 2 ligands (L) attached c) types of conjugated motifs commonly used for conjugated polymers synthesized via this route.

P3AT, using a nickel-bidentate complex with a Kumada transmetallating agent, were low dispersity and controlled molecular weights realized by catalyst transfer polycondensation (CTP). They demonstrated a linear increase of molecular weight with monomer consumption, unlike stepgrowth polymerizations. The polymerization is initiated by a double transmetallation event transforming Ni(II) to Ni(0) prior to the first oxidative addition. It has been proposed that the metal forms an associated π -complex with the polymer chain end and therefore acts as both the initiating agent and propagating agent in Kumada CTP.⁴⁷⁻⁴⁹ The catalyst associates with only a single chain, therefore the desired chain length can theoretically be governed by the catalyst loading with uniform results and low dispersity, *Figure 1.8*.

Controlled monomer addition provides an avenue to synthesize more complex architectures, such as block⁵⁰⁻⁵² and gradient copolymers.⁵³⁻⁵⁵ However the large majority of successful Kumada CTP polymers are electron-donating materials.⁵⁶⁻⁵⁸ This points to a limited monomer scope, due to the nature of the cross-coupling agents, with very few examples of acceptor

materials that maintain control^{59,60} including D-A copolymers.⁶¹⁻⁶⁶ Efforts to expand CTP beyond Kumada include the use of Stille CTP⁶⁷ and our current work utilizes Suzuki CTP⁶⁸⁻⁷¹ to afford conjugated polymer architectures and other side-chain derivatives such as ester functionalized polymers. The question of side-chain variation and its impact on structural organization and physical response will be addressed in *Chapter 4*.

1.5. Tools to Assess Structure–Property Relationships



Figure 1.8. *Left*: Linear increase of molecular weight with monomer conversion due to the *Right*: proposed main catalytic cycle for Kumada catalyst transfer polycondensation (CTP). Nickel-Polymer π -complex allows for Ni catalyst to stay associated with chain-end and provide controlled addition of monomer units.

How these materials behave can be deconstructed to three scales of interaction: i) molecular arrangement (Å), ii) assembly into nanoscale morphologies (nm – μ m) which govern iii) macroscopic properties (mm – cm).⁷² On a molecular scale, the connectivity, geometry, reactivity, inter/intra–molecular interactions governs its molecular properties, intrinsic to a single polymer chain. These interactions in turn influence how the polymer organizes. The relative order and disorder at a nanoscale level can be highly influenced by processing conditions (solvent, temperature) to promote aggregation in solution and film formation. Self-assembled structures can

be utilized as a means to promote other desired nanoscale morphologies, which in turn can have a tailored physical response.⁷³ The polymer's atomic structure, nanoscale organization and overall quality, including its composition, molecular weight and dispersity will influence material properties such as stability, crystallinity, mechanical and photo-physical properties. These considerations build a general framework for in-depth structure-property studies necessary to develop more complex architectures directed for desired applications.

1.5.1 X-Ray Scattering and Atomic Force Microscopy

For thin films, structural analysis of conjugated polymers by solid state organization is of critical importance. This can be accomplished with the use of atomic force microscopy to probe the surface topography which is complemented by the measurements of atomic-scale packing arrangements by X-Ray scattering experiments. Placement of an X-ray beam at a close angle with respect to the substrate provides the grazing-incidence geometry,⁷⁴ Figure 1.9 a. The incidence beam (wavevector k_i) at incidence angle (α_i) penetrates the polymer film and the resultant scattered beam (wavevector k_f) scatters at various angles with respect to the surface.⁷⁵ Periodic structures with constructive interference patterns produce Bragg peak features with scattering patterns both parallel (q_{xy}) and perpendicular (q_z) to the substrate surface with a sample azimuth range (ϕ) of 0° - 90°. Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS), Figure 1.9 b, probes angstrom length scales (atomic-level order),⁷⁵⁻⁷⁹ whereas Grazing Incidence Small-Angle X-Ray Scattering (GISAXS), Figure 1.9 b, probes nanometer length scales (long range order), useful for characterizing nanofibril widths or phase separations in block copolymers, or PCBM: P3HT solar cell layers.^{75,78,80-82} An example showing regio-regular P3HT illustrates structural organization probed by GIWAXS with lamellar spacing of layered polymer "sheets" governed by the length of side-chains (16 Å, (100)) and π -stacking interaction (3.8 Å, (020))⁸³⁻⁸⁶ between adjacent chains forming highly crystalline domains, *Figure 1.9 d*. Grazing incidence is also useful for characterizing the orientation of organized polymer chains, since it provides diffraction patterns both in the xy-plane and z-plane with respect to the substrate surface.

A good example of this, is the study of different regio-regularity, molecular weight and dispersity P3HT under various casting conditions for OFET devices.⁸⁷ Once polymers were spin-



Figure 1.9. a) Illustration grazing incidence X-Ray scattering (GIXS) wavevector (k_i) probing a surface by incidence angle (α_i) resulting in directional (α_f , 2 θ_f) scattering wavevector (k_f). (original artwork by Dr. A. Meyer - Institute of Physical Chemistry - University of Hamburg) b) *Top*: Grazing incidence wide-angle (GIWAXS) and *Bottom*: small-angle (GISAXS) X-ray scattering 2-D profiles of *rr*-P3HT c) AFM of nanofibril morphology of *rr*-P3HT d) a depiction of the polymer organization by atomic-scale (Å) and long-range order (nm).

coated, the polymer chains could either lay flat on the surface (face-on) or aggregate through π -stacking and lay perpendicular to the substrate (edge-on). The highest performing material had the highest regio-regularity (96%, μ : 0.05 – 0.1 cm² V⁻¹ s⁻¹).



Figure 1.10 Schematic of AFM setup (original artwork from the Institute for Surface Chemistry YKI, Stockholm, Sweden).

A complementary technique to GISAXS, which probes periodic structures with long-range order, is atomic force microscopy (AFM) to study surface morphology. This method is a proximal probe technique, with a probe comprised of a sharp tip mounted on a cantilever illustrated in *Figure 1.10*. The probe tip interacts with the surface of the sample through intermolecular forces, either through contact, non-

contact or intermittent contact (tapping mode) AFM. The tip deflection or amplitude is measured by a photodetector that catches the deflection of a laser pointed at the top of the cantilever. The tip is tuned by the resonance frequency and its drive amplitude. Monitoring the phase-shift between the drive and response results in sensitive detection of topographic changes in the surface (i.e. smooth, soft, hard surfaces). This is extremely valuable in block copolymers which have phase-separated domains and semi-crystalline materials. A great illustration of this is shown in *Figure 1.9 c* for P3HT, whose nanofibrils of a given length and width can be visualized.

P3HT being one of the most extensively studied conjugated polymers, has been shown to form nanowires.⁸⁸⁻⁹² Work in our group demonstrated that the nanofibril widths (~ 10 – 30 nm) correspond to the contour length of polymer chains and importantly that the mobility (μ) increases exponentially with increasing the fibril width. Saturation of fibril width due to chain-folding led to the saturation of mobility in P3HT ($\mu \sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), *Figure 1.11.*⁹³ These observations provided incentive for structure optimization and film quality of regio-regular, low dispersity materials to generate well-defined morphologies useful for organic electronics. Additionally, the 2D organization of P3HT and its analogs, assures charge transport through the nanofibril axis as well as an intra-chain transport, indicating that organization through fibril formation is just as significant as delocalization along the polymer backbone.

Characterization of fibril widths in conjugated polymers provides insight to chain packing in the solid-state. Lower molecular weight P3HT exhibits a linear correlation between increasing fibril width with respect to increasing molecular weight.⁹³ Whereas, higher molecular weights of P3HT (degrees of polymerization above 62 monomer units or ~10,000 molecular weight) begin



Figure 1.11. *Left:* AFM Phase Images: Molecular weights in a) through i), respectively: 2.4, 4.8, 5.1, 7.0, 7.5, 11.8, 15.7, 17.3 and 18.4 kDa. *Right*: Relationship of nanofibril width, molecular weight, weight average contour length and charge carrier mobility $(cm^2V^{-1}s^{-1})$. Reprinted with permission Reference 93, Copyright 2006, American Chemical Society.

chain-folding, generating a saturation limit for fibril width with respect to molecular weight.⁸⁰ The limitation of fibril widths influences crystallite size, as the nanofibril width of P3HT corresponds to the crystal thickness.⁹⁴ Therefore, AFM imaging can provide further

insight into the crystalline quality by other methods such as differential scanning calorimetry (DSC), described below.

1.5.2 Differential Scanning Calorimetry

The semi-crystalline nature of conjugated polymers can be further probed by studying the thermal transitions in polymer samples.⁹⁵ Thermal analysis by DSC can provide information about the glass transition temperature ((T_g °C), melting temperature (T_m °C) and crystallization temperature (T_c °C). T_g describes the amorphous region transitioning between a glassy state where

the polymer is brittle and stiff to a rubbery state. In semi-crystalline materials, the melting of a crystalline region is manifested as an endothermic peak transition with an integrated area corresponding to a change in enthalpy, the heat of fusion, ($\Delta H_m J g^{-1}$). The crystallization (exothermic peak) is observed upon cooling from the melt with its own respective enthalpy of crystallization ($\Delta H_c J g^{-1}$). Generally, tacticity, strong intermolecular interactions and increased

chain stiffness will increase Tm.96,97 Chain flexibility, disorder, crystal site imperfections and increased amorphous content will decrease T_m due to an increase in entropy within the system. This is well documented in classical polymer systems such as polyethylene, isotactic polypropylene and polyamides,^{96,97} and remains true for conjugated polymer samples. Examples of P3HT show regio-regularity and side-chain organization that formation.⁹⁸⁻¹⁰⁰ influence crystalline Regio-random P3HT is completely amorphous⁹⁸ exhibiting a $T_g = -3$ °C, whereas regio-regular P3HT has a melt transition from crystallites with organized side-chains above 225 °C, Figure 1.12.



Figure 1.12. DSC thermograms of a) Glass transition temperature of regio-random P3HT and b) melting/crystallization transitions of *rr*-P3HT. Scanning rate: 10 °C min⁻¹. Reproduced with permission from Reference 98 Copyright 2004, Springer Nature.

1.5.3 Electronic and Vibrational Energy Transitions in Conjugated Polymers

Ultraviolet-visible (UV-vis) spectroscopy is commonly used to characterize the conjugated polymer's absorbance profile of irradiation ranging from (200 - 1000 nm) both in solution and in solid-state. The absorbance profile provides general information about the band gap measured by the absorption edge (v_{edge}, eV) as well as the regime of irradiation when the polymer absorbs



Figure1.13.Franck-Condonharmonicwells,Reproduced withPermissionReference137,Copyright 2016,John Wiley & Sons.

energy. A conjugated polymer chain contains multiple sites (chromophores) that can absorb energy to photogenerate an exciton. A large contribution to the optical absorption of a chromophore involves the electronic transition from the ground state (S₀) π orbitals to the excited state (S₁) π * orbitals. The electronic transition is coupled to vibrations of bonds occurring at the same site (i.e. electron-phonon coupling), described by the Franck-Condon principle.¹⁴ To better describe the how

excitons move through a material, we consider the coupling of Frenkel (localized) excitons and vibrations of carbon-carbon double bonds along the polymer chain. Classical one dimensional models can be used to describe the S_0 and S_1 states as harmonic potential wells with quantized vibronational levels ($\hbar\omega$), *Figure 1.13*.

This is extremely valuable when we begin to consider the shape of spectral profiles obtained by UVvis for conjugated polymers. The presence of vibrational fine-structure within solid-state absorption profiles indicates the weak to intermediate exciton coupling regime, where the transfer integral (coupling) between neighbor sites is relatively slower than the nuclear relaxation of the chromophore. The transport of excitons



Figure 1.14. Example of interchain coupling (J_{inter}) and intrachain coupling (J_{intra}) for adjacent polythiophene chains.

along the polymer chains (through-bond coupling) is governed by intra-molecular transfer (J_{intra}),



Figure 1.15. *Top*: Solid-state UV-vis of P3HT spun from different solvents. Theoretical fit of ordered aggregates (calculated from *Equations* 1 - 3), (Red). *Bottom*: Including evaluation of exciton bandwidth with respect to solvent boiling point. Reprinted with permission Reference 102, Copyright 2009 AIP Publishing.

while exciton hopping to adjacent chains (through-space coupling) is governed by inter-molecular transfer $(J_{inter}),^{101}$ Figure 1.14. When considering microstructures similar to P3HT, both inter-chain ($J_{inter} > 0$) and intra-chain coupling ($J_{intra} < 0$) is due to the π -stacking inter-molecular interactions and delocalization of varying conjugation lengths along the chain.

Spano and co-workers¹⁰²⁻¹⁰⁶ developed a modified Franck-Condon

fit to describe the aggregate character within P3HT films, *Figure 1.15*. Gaussian line shapes characterized by peak intensity (A_{*m*-*n*}), σ (width) and E_p (main intramolecular vibration) were used to describe the lower energy vibronic transitions from the ground state (*m* = 0) to excited state (*n* = 0, 1, 2, 3), including the exciton bandwidth *W*. These authors demonstrated that different processing conditions lead to different values of *W*, *Figure 1.15*. As illustrated in subsequent publications from this group,^{101,104} since P3HT exhibits both inter-chain (*J* > 0) and intra-chain (*J* < 0) exciton coupling, lower values of *W* correspond to higher delocalization with more order to promote intra-chain exciton transfer.



Figure 1.16. Experimental UV-vis of P3HT in solid-state (Black) and solution (Black, dashed). Theoretical fit of ordered aggregates (Blue), 'residual' from theoretical fit (Red). Illustrating that 'residual' represents disordered aggregates, similar to P3HT's behavior in solution. Reprinted with permission from Reference 105, Copyright 2009 AIP Publishing.

The resulting fits were in good agreement with the low energy transitions, and proved as a useful means to describe the shape and character of ordered aggregates in a polymer film. The 'residual' of this fit at higher energy was attributed to the disorganized amorphous phase of the material characterized conjugation short length, as disorganized chains. segments of polymer reminiscent of the solution absorbance spectra.¹⁰⁵ *Figure* 1.16.

1.6 Photo-stability of Conjugated Polymers

As mentioned above, the environmental stability of conjugated polymers is significantly limiting factor in their practical use. As with the potential advantages of light absorption to generate excitons (useful in OPVs), described *Section 1.5.3*, conjugated polymers can also act as classical photosensitizers and generate singlet oxygen, a highly reactive species.¹⁰⁷⁻¹¹⁰ Singlet oxygen can then react with the polymer through oxidation, leading to loss of conjugation, hence destroying the electronic properties. The main degradation mechanism of P3HT is still highly debated, ¹¹¹⁻¹¹⁵ with contention between a radical reaction through the alkyl side-chain and Diels Alder ring opening reactions. With this in mind, as we begin to develop more complex architectures using methods such as side-chain engineering or development of D-A copolymers,¹¹⁶ the materials oxidative stability^{117,118} is of paramount importance for their practical use.

1.7 Examples of Structure Variation in Conjugated Polymers Impacting Physical Properties and Organization

Beyond fundamental structure-property relationships, our understanding of how monomer order affects copolymer properties is relatively underdeveloped in comparison to biological systems such as proteins and DNA.¹¹⁹⁻¹²¹ While natural products and biology has inspired the development of sequence controlled polymers, the field is still in a nascent state. Polymer architectures such as random, alternating and block copolymers remain the most extensively studied, largely due to synthetic availability. Meanwhile, the impact of monomer arrangements on physical properties^{73,122,123} and relative order¹²⁴ has been far less explored.



Figure 1.17. a) Synthesis of random, gradient and block copolymers of 3-hexylthiophene and 3-hexylselenophene units. b) Resulting solidstate UV-vis and c) DSC endothermic melting transitions with respect to polymer compositions (50:50)varving monomer arrangements. Reproduced with permission from Reference 125 Copyright 2012 American Chemical Society.

An illustrative example of monomer order influencing physical properties was provided by McNeil and co-workers, who examined random, gradient and block copolymers of 3hexylthiophene and 3-hexylselenophene units.¹²⁵ UV-vis revealed prominent peaks in block copolymers indicative of phaseseparation, whereas gradient copolymers exhibited intermediate phase separation vs. random copolymers, with a more homogeneous composition (broad spectral absorption). This was reflected in DSC, as the

random copolymer had a reduced melting temperature, due to less favorable co-crystallization of the distinct monomer units, *Figure 1.17*.
Discussions of polymer composition is frequently highlighted when discussing block copolymers. Seferos and coworkers have performed studies on homopolymers, statistical and block copolymers composed of 3-hexylthiophene and 3-hexylselenophene units⁵¹ to characterize differences in phase separation and morphology. They employed side-chain engineering¹²⁶ as a means to improve morphology and enhance optical properties of statistical copolymers containing 3-hexylthiophene and 3-heptylselenophene. His group has additionally varied heteroatom substitution^{127,128} on alternating D-A copolymers to clarify the influence of single heavy atom substitution on optical response.



Figure 1.18. *Left*: D-A copolymers with varying thiophene-"spacer" content, P1 – P4. *Middle*: Respective solution UV-vis spectra and *Right*: 2D WAXS patterns. Reproduced with permission from Reference 131 Copyright 2009 American Chemical Society.

D-A copolymers commonly employ electron deficient units such as isoindigo, diketopyrrolopyrrole, napthalene diimide, benzothiadiazole as the strong acceptor unit component, paired with a strong donor unit.^{129,130} A good example of sequence modulation in D-A copolymers includes work by Reynolds and co-workers.¹³¹ They synthesized a series of D-A copolymers (P1 – P4) which varied electron-withdrawing character along the backbone with the inclusion of thiophene-unit 'spacers'. In doing so, they were able to tailor the absorbance of polymer P4 to span the entire visible spectrum range, *Figure 1.18*. Additionally, inclusion of the thiophene 'spacers' promoted backbone planarity, enhanced crystallinity with tight π -stacking (3.6 Å) (2D WAXS patterns), resulting in the highest OFET mobility (μ : 0.02 cm²V⁻¹s⁻¹) of the series.

Importantly, the above example highlighted a few key considerations for the development of novel materials for organic electronics. The design space altered the electron-withdrawing character, the materials planarity and overall organization (crystallinity). Typical conjugated polymers organize through aggregation from the π -stacking interaction of the conjugated backbone. These rigid-rod materials typically adopt an all-trans conformation, with consideration that the regio-regularity also promotes side-chain organization and enhances crystallinity, as discussed in *Section 1.5.2*. Conversely, recent efforts have begun exploring non-linear conformations for conjugated polymers,¹³² such as helical structures stemming from an all-cis



Figure 1.19. Side-chain substitution on polythiophene, inducing helical formation in poor solvents. Reproduced with permission from Reference 134, Copyright 2018 American Chemical Society.

conformation along the polymer backbone. This potentially affords materials that are optically active with applications extending to chiral sensing and generating molecular recognition sites and scaffolds.¹³³ Recently Koeckelberghs and coworkers¹³⁴ used Kumada CTP to synthesize polythiophene derivatives with bulky side-chains to induce

helicity in poor solvents. The use of a sterically hindered side-group¹³⁵ such as gallic acid helped to promote the desired self-assembly through π -stacking and van der Waals interactions, *Figure 1.19*.

Another interesting example is block copolymer poly(3-hexylthiophene)-*block*-poly(3-triethylene glycol thiophene), synthesized by Hayward and co-workers.¹³⁶ This block copolymer (with a uniform backbone but 'blocky' side-chain composition) showed that the addition of potassium iodide induced helical formation driven by self-assembly in solution. Visualization by

transmission electron microscopy (TEM) investigated varying block copolymer compositions and found that helicity did not occur in all samples. Thus, highlighting that a delicate balance was achieved between the crystallization of the P3HT block and the repulsive interactions of the P(3-triethylene glycol) thiophene block to favor helical formation, *Figure 1.20*.



Figure 1.20. a) Schematic of block copolymer P3HTb-P3(TEG)T forming a double stranded helix with the addition of KI. TEMs of block copolymer with composition (P3HT: P3(TEG)T) aka. (H:T) ratios of b) (2.2:1) c) (1:1) and d) (4:1). Note only (b) is helical with salt addition. Reproduced with Permission from Reference 136, Copyright 2011 American Chemical Society.

Both examples illustrate that helical formation with P3HT derivatives is possible with tailored solution conditions to drive selfassembly. Side-chain substitution was used as a means to introduce sterically bulky or functional groups that would favor intermolecular interactions to promote organization in the solid-state.

1.8. Summary

Studying conjugated polymers with controlled composition, molecular weight and low dispersities (ranging from homopolymers to complex sequences) enables chemists to examine the impact of polymer structure on its physical properties which are of importance in organic electronics applications. By considering the polymer's framework design, materials can be tuned to possess specific chemical compositions and monomer ordering to influence its structural organization, electrical and thermal response. Materials such as P3HT have been studied more indepth to examine its relative aggregate order and amorphous content by UV-vis, with AFM correlating fibril widths to OFET device performance and GIWAXS characterizing atomic scale

packing arrangements such as lamellar spacing and π -stacking that promote crystallinity in regioregular samples. P3HT's ability to act as a photosensitizer also leads to its eventual degradation as is true for materials absorbing in the visible light regime. As such, this parameter should be considered a main consideration in the development of new materials and their practical use.

Literature studies of structure-property relationships have shown that bulk morphology and optical properties seem to be more attuned to changes in composition. Extension of alternating copolymers to more complex systems such as D-A copolymers have been shown to be useful in organic electronics with low band gaps and good light harvesting capability. With these advantages, these types of materials are still prone to deviate from ideal behavior when more disorder is present. Therefore, favorable solid-state organization, packing and crystallinity are large factors for influencing materials' performance. A large majority of conjugated polymers, especially in the P3HT family, are linear, rigid rod self-assembled structures. However, more recent studies have shown that side-chain engineering combined with additional processing conditions, can be utilized to promote helical formation in polymers such as P3HT. This could be a potential pathway to exploring other avenues and applications for P3HT and its derivatives.

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Chapter 2

Influence of Heteroatom Substitution on the Behavior and Organization of Group 16 Conjugated Polymers

2.1 Introduction

Extensive studies of regio-regular poly(3-alkyl thiophenes) rr-P3ATs have demonstrated a wide range of their applications in organic electronics. The most widely studied analog, poly(3-hexyl thiophene), P3HT, has favorable packing in the solid-state, easy processing, with adequate charge-carrier mobility (0.1 – 0.01 cm² V⁻¹ s⁻¹) making an ideal candidate for both transistors and solar cell applications.¹⁻³ Utilizing aspects of framework design, heteroatom substitution may prove to be a fruitful strategy for tuning the behavior, response and organization of conjugated polymers similar to P3HT in both shape and size. Substituting group 16 heteroatoms such as oxygen and selenium varies the atomic size, influencing the aromaticity, ionization potential and intermolecular interactions within the polymer chain.⁴⁻⁸ These inherent characteristics and interactions may drastically impact the polymer's physical response and bulk organization. As such, it is important to probe these effects at different scales of interaction ranging from macroscopic to atomic-level arrangements.

Substitution of oxygen along the backbone is particularly attractive, since the furan monomer is both bio-renewable and biodegradable.⁹⁻¹³ Furan is less aromatic which enhances its quinoidal character,^{14,15} and with oxygen's smaller atomic size, smaller rings along the backbone enhance chain planarity,¹⁶ potentially improving charge transport. Selenium on the other hand is larger in atomic size, with strong intermolecular interactions. A systematic study is required to

assess how heteroatom substitution impacts its relative organization and its physical properties. This can be accomplished through characterization its i) macroscopic properties, such as its thermal response (TGA, DSC) ii) by assessing nanoscale morphologies (AFM) and atomic packing structures (GIWAXS) and iii) characterizing the electronic band structure by cyclic voltammetry (CV) and UV-vis.

Described here-in is i) the synthesis of homopolymers P3HF, P3HT and P3HSe and ii) thermal measurements will show melting enthalpy dependence on molecular weight that is independent of heteroatom identity. iii) Nanoscale morphologies and atomic packing arrangements will illustrate vastly different degrees of organization depending on the processing conditions and heteroatom identity. Scattering patterns will also reveal that despite the semi-crystalline nature of the described polymers, distinct patterns ascribed to a disorganized amorphous phase are noticeably absent. iv) Electronic band structure characterization will demonstrate that the electronic band gap can be modulated depending on heteroatom identity, in good agreement with theoretical and literature reports. v) Lastly, preliminary studies of ordered aggregates and amorphous character will be assessed from UV-vis deconvolution fits.

2.2 Synthesis of Homopolymers

The materials studied in this report include P3HF, P3HT and P3HSe that were synthesized via chain-growth mechanism Kumada catalyst transfer polycondensation (CTP).¹⁷⁻²¹ The use of CTP affords materials of controlled molecular weight and dispersity, with the ability to tune the materials organization and physical response. P3HT ²²⁻²⁴ and P3HSe²⁵⁻²⁹ have been far more extensively studied, and synthesized using CTP methods. P3HF^{8,30} has been reported by other synthetic methods, but it wasn't until recently that P3HF reported using Kumada CTP, synthesized

by Dr. Yunyan Qiu.³¹ The resultant P3HF material has relatively low molecular weight (M_n : 4,100) due to extensive aggregation during the polymerization, but maintained a low dispersity (D: 1.25). It was also found that P3HF degraded under the presence of air and light^{32,33} as visualized by atomic force microscopy (AFM). However, recent reports of oligofurans by Bendikov and co-workers^{4,5,33,34} produced relatively stable species, with high fluorescence, enhanced planarity and increased solubility.

The sulfur and selenium containing polymers, P3HT (*Scheme 2.1*) and P3HSe (*Scheme 2.2*) were also synthesized using Kumada CTP to afford regio-regular, low dispersity, controlled molecular weight materials, *Table 2.3*. Tetramethylpiperidine-magnesium chloride \cdot lithium chloride (TMP MgCl·LiCl) was used as a transmetallating agent via the deprotonation of the 5-position of the respective monomer to afford active species α and β for polymerization using catalyst (1,3-bis(diphenylphosphino)propane) dichloride nickel (II) (Ni(dppp)Cl₂). Synthesis of P3HSe at higher molecular weights (M/Cat. above ~ 50 rings) required a more dilute solution (0.01 M in THF) for polymerization due to the solubility issues.

Scheme 2.1. Polymerization of P3HT via Kumada CTP







P3HT (M.W. 11,300) and P3HSe (M.W. 10,000) were inspected by GPC and NMR, Appendix 1, to determine the resulting molecular weight, dispersity and polymer fidelity. Increasing molecular weight with reduced catalyst loading was confirmed by GPC, where number average molecular weight (M_n) determination also revealed low to moderate dispersity (Đ: 1.15 – 1.34). These materials were purified by re-precipitation into stirring methanol and was used without further modification.

2.3 Thermal Characterization of Homopolymers

Thermal characterization of homopolymers with varying heteroatom identities was carried out by thermogravimetric analysis (TGA) to measure the decomposition temperature range quantified by percent weight loss, *Figure 2.1*. The black dashed line references the 100 % weight.

Initial weight loss of ~ 2% was attributed to side-chain decomposition of alkyl chains.



Figure 2.1. Thermogravimetric analysis (TGA) of varying molecular weight (M.W.) for homopolymers P3HF (M.W. 4,100: Black), P3HT (M.W. 11,300: Red), P3HT (M.W. 19,000: Pink), P3HT (M.W. 37,500: Orange), and P3HSe (M.W. 10,000: Green), P3HSe (M.W. 19,700: Blue), P3HSe (M.W. 24,200: Purple)

Presented results show no significant impact of molecular weight on the decomposition of either P3HT or P3HSe. Instead, all homopolymers with the same heteroatom identity revealed similar initial carbonization profiles and relatively high 5% weight loss temperatures (T_{d5%}) of 373 °C and 431 °C for P3HSe and P3HT respectively. P3HF, revealed similar results, with a T_{d5%} of 373 °C. Interestingly, P3HF exhibited higher temperatures for carbonization of the polymer chain (~ 410 °C) in comparison to P3HSe (~ 390 °C) samples. The enhanced thermal stability of P3HF was attributed to its increased planarization due to smaller atomic size within the heterocycles along the polymer backbone. This is proposed to promote stronger inter-chain interactions such as π stacking (described in more detail, Section 2.4).



Figure 2.2. DSC thermogram of P3HF measured within a thermal range up to 320°C at a scanning rate 10 °C min⁻¹, with no visual melting or crystalline transitions.

Each homopolymer was then examined by differential scanning calorimetry (DSC) to characterize the crystalline quality of the materials. Initial studies probed P3HF from a temperature range of -20 °C up to 320 °C at a rate of 10 °C min⁻¹, with no apparent glass transition temperature $(T_g),$ melting (endothermic peak) or crystallization (exothermic peak) transitions, Figure 2.2. However, as P3HF exhibited no apparent glass transition temperature, and is shown to form nanofibrils from lamellar assemblies (Section 2.4), it is surmised that the material is in-fact crystalline. Given that the high temperature range exceeds the initial degradation of the polymer, extension to higher temperatures was not explored, and therefore limited the thermal analysis of this material. This study further suggests that P3HF is highly planar, promoting strong inter-chain interactions such as π -stacking, resulting in an increase in melting temperature beyond 320 °C.

DSC analysis of varying molecular weights (M.W.) of P3HT and P3HSe was carried out within a temperature range of 30 °C to 300 °C at a scanning rate of 10 °C min⁻¹. The crystallization and melting transitions of P3HT and P3HSe steadily increased with increasing molecular weight, *Figure 2.3*. The highest molecular weight P3HT (M.W. 37,500 \oplus : 1.18), *Appendix 1*, exhibited a T_m of 239 °C and T_c of 208 °C, in relatively good agreement with reported P3HT of similar molecular weight.³⁵⁻³⁹



Figure 2.3. DSC 2^{nd} cyclization (scanning rate of 10 °C min⁻¹) of different molecular weights (M.W.) of *Top*: P3HT a) M.W. 11,200, b) M.W. 19,000 c) M.W. 25,200 and of *Bottom*: P3HSe d) M.W. 10,000 e) M.W. 19,700 and f) M.W. 24,200. Integration limits (Black, dashed) used to calculate enthalpies. *Inset*: Crystallization (T_c) and melting (T_m) temperatures (°C), enthalpy of crystallization (Δ H_c, J g⁻¹) and heat of fusion (Δ H_m, J g⁻¹) for each sample.

The heat of fusion ($\Delta H_m J g^{-1}$) was calculated from the integrated melting peak area. The baselines were fitted by a 1st order approximation, and are shown as black dashed-lines. Extended melting transitions were evident in all samples. Comparison of the melting enthalpies in thiophene and selenophene-based polymer backbones required that enthalpy values were evaluated in terms of mole quantities, rather than mass. The enthalpy per ring within the polymer chain ($\Delta H_m ring^{-1}$) was calculated by multiplying the enthalpy (J g⁻¹) by the repeat unit molecular weight (g mol⁻¹). This was assessed against the inverse degree of polymerization (DP_n), (i.e. the number of rings

within a polymer chain) to determine the relationship of effective enthalpy per ring with respect to chain length, irrespective of heteroatom identity, *Figure 2.4*.

Data assessed in this manner included both the P3HT and P3HSe series of varying DP_n's conjunction with P3HT in polymers ((DP_n : 31 – 70), samples prepared as powders and films) measured by Dr. Emily Daniels Weiss (EDW). Low molecular weight P3HT samples provided higher sensitivity to processing conditions, whereas higher DP_n materials exhibited similar enthalpy values regardless of



Figure 2.4. Calculated enthalpy of fusion per ring within an average polymer chain, measured as (kJ per mol) (ΔH_m Ring⁻¹, kJ mol⁻¹) with respect to inverse degree of polymerization (DP_n)⁻¹. Homopolymer samples of i) P3HT (Black) and ii) P3HSe (Red) were compared to previous work conducted by Dr. Emily Daniels Weiss with analysis of iii) powder P3HT samples (Teal) and iv) film P3HT samples (Purple). Fits correspond to linear correlation of inverse DP_n vs. Enthalpy of fusion per ring including Dr. E. Weiss's powder samples (Teal, dashed) or Dr. E. Weiss's film samples (Purple, dashed).

processing conditions. Therefore, samples of sufficient molecular weight could be measured in powder form while maintaining useful comparisons to EDW measurements. A linear correlation with varying slope was calculated, depending on whether EDW powder samples vs. film samples were evaluated in the fit. These fits highlight the relative range of enthalpies that can be obtained depending on processing at low molecular weights. The one outlier of the series is the highest DP polymer P3HT (M.W. 37,500), showing a lower enthalpy per ring (3.6 kJ mol⁻¹). Very high molecular weight samples have shown similar reductions in enthalpy by other groups³⁷ which was

attributed to the effect of chain entanglements reducing the overall crystalline content by contributing more to the amorphous phase.

P3HT has been shown to organize as lamellar crystallite assemblies whose relative thickness (nanofibril width) is determined by the chain length⁴⁰, Section 2.4. Given that crystal thickness and size determines the melting enthalpy, it can be deduced that chain length will determine the enthalpy because it directly determines the lamellar crystallite width in these types of polymers. However, higher molecular weight P3HT has been shown to chain-fold,^{37,40} (commonly observed in other types of polymers such as polyethylene and isotactic polypropylene^{41,42}) resulting in limited fibril widths. Therefore, the enthalpy value should saturate at higher molecular weights because the chain-lengths (crystal width) will be limited by the occurrence of chain-folding. The linear correlation between enthalpy per ring and the polymer's chain-length reveals the range of DP_n in which chain-folding is likely limited and the chain is not entangled contributing to the amorphous phase. The studied samples have high regio-regularity and low dispersity, promoting highly organized, ordered structures. The use of these materials potentially extends the DP_n range in which this linear correlation holds true. And, most importantly, the enthalpy per ring for both P3HT and P3HSe are in excellent agreement with the expected enthalpy per ring of a given chain length. This indicates that the overall melting enthalpy of these polymers is largely dependent on the crystallite size and is independent of heteroatom identity.

2.4 Atomic Force Microscopy and X-Ray Scattering of Homopolymers

Atomic force microscopy (AFM) was used to visualize the nanoscale morphologies of homopolymers P3HF (M.W. 4,100), P3HT (M.W. 25,200) and P3HSe (M.W. 24,200). All materials in the bulk appeared to have very different features within the surface topography, shown *Figure 2.5*. Homopolymer P3HF developed patches with large holes over several scanning periods with featureless regions intermittently across a surface of thin nanofibrils, ~ 10 nm in width. Similar fibril widths have been noted in samples of P3HT with comparable molecular weight, indicating fully extended, π -stacked polymer chains parallel to the substrate surface.⁴³ We propose



Figure 2.5. Morphology of thin-film depositions of homopolymers visualized by AFM phaseshift images including a) Poly(3-hexyl furan) P3HF, b) Poly(3-hexyl thiophene) P3HT and c) Poly(3-hexyl selenophene) P3HSe where the *Inset*: of c) is an ultra-thin layer of P3HSe illustrating aggregate formation. Scale bar (white) measures length scales of 200 nm.

that the smooth features and holes in P3HF are a result of degradation from exposure to light and air, due to its high photosensitivity. This marked photosensitivity, highlights limitations to the materials use, since its surface structure was drastically altered just by the act of scanning. This observation helped to determine that the strictest protocols were necessary to handle P3HF for any subsequent tests and its photosensitivity will be discussed in more detail in *Chapter 4*.

In contrast, P3HT revealed a regular nanofibrillar structure with ~ 32 nm fibril width, indicating a highly favorable ordered arrangement. By comparison, once P3HSe was characterized in the bulk, it appeared to have a rough surface, potentially disordered aggregates. Further examination of mono-layered films revealed some fibrillar nanowires inter-mixed with polymer aggregate clusters. Therefore, it is gathered that higher concentration bulk films have a large majority of clustered polymer aggregates with mixed orientations with respect to the substrate. It is possible that the processing solvent (CHCl₃) is less favorable due to its low boiling point. Therefore, processing of P3HSe in other higher boiling solvents and/or casting conditions would be needed to find a more optimal bulk film structure.

Overall, comparison of nanoscale morphologies revealed very different surface topographies. This highlights that simple heteroatom substitution can lead to drastically different organization, each requiring a range of care, either with respect to light sensitivity or optimizing



Figure 2.6. Illustration of GIWAXS 2-D images: *Left*: P3HF (face–on), *Middle*: P3HT (edge–on) and *Right*: P3HSe (isotropic) orientations with respect to the substrate for lamellar structures and π -stacking (circled in red) with as-cast polymer thin-films.

processing conditions. Further analysis of atomic-scale packing organization would facilitate further clarity of polymer orientation and structure that promotes nanoscale assemblies.

As described in *Chapter 1*, *Section 1.5.1*, atomic-scale packing was studied by grazingincidence X-Ray scattering (GIWAXS) studied at Cornell High Energy Synchrotron Source (CHESS) facility. X-rays probed films cast atop silicon dioxide substrates, where periodic structures with Bragg peak features in the range of $(0.22 \text{ Å}^{-1} < q < 2 \text{ Å}^{-1})$. 2D scattering patterns covered the ranges of wave vectors parallel (q_{xy}) and perpendicular (q_z) to the substrate surface with an azimuthal range (ϕ) of 0° – 90°. The limits of the Ewald sphere are depicted as a "missing wedge" in the top left corner. All images were background subtracted and scaled by the scattering invariant to account for the scattering in the high–q regime. 2-D GIWAXS arrays for P3HF, P3HT and P3HSe as-cast films from chlorobenzene are shown in *Figure 2.6*.

The comparison of homopolymers with varying heteroatom substitution revealed distinctly different orientations with respect to the substrate surface. Two distinct Bragg features effect the structural organization and orientation of polymer films including i) the lamellar spacing dictated by the length and inter-digitation of alkyl side-chains between layered polymer chains and ii) π -stacking of the conjugated backbones of adjacent polymer chains. Polymers that organize with π -stacking perpendicular to the substrate surface (out-of-plane, $80^\circ < \phi < 90^\circ$), where polymer chains lay flat-on the substrate surface have a "face-on" orientation, as highlighted in polymer P3HF. Polymers that organize with π -stacking parallel to the substrate surface (in-plane, $0^\circ < \phi < 10^\circ$), where polymer chains are oriented perpendicular the substrate surface have an "edge-on" orientation, as highlighted in polymer P3HT. Polymers that have mixed organization with π -stacking orienting at all angles with respect to the substrate surface ($0^\circ < \phi < 90^\circ$) are "isotropic," as highlighted in polymer P3HSe. Anisotropy and higher order Bragg peaks are indicative of well-

organized structures, whose peak widths (FWHM) can be used to characterize the relative disorder within the polymer structures.

The organization and orientation of polymer chains is highly processing-dependent. Different processing conditions, such as temperature annealing and the use of different solvents can drastically alter polymer organization.⁴⁴ As shown in *Figure 2.7*, thermal treatment proves to be an effective method to drastically alter P3HSe (isotropic) orientation to reorganize to a more



Figure 2.7. Illustration of GIWAXS 2-D images of annealed films of homopolymers P3HF (left), P3HT (middle) and P3HSe (right) cast from chlorobenzene. Lamellar spacing and π -stacking peak assignments labeled in each profile. All images scattering intensities colored according to scale bar in logarithmic scale.

anisotropic, edge-on orientation. P3HF (face-on) orientation transitioned to a mixture of both edgeon and face-on orientations. This was indicative that additional optimization of P3HF's film may promote more edge-on orientation with additional thermal treatment.

Bragg features were characterized from radial profiles, evaluated over an average azimuthal range of in-plane: (ϕ : 0° – 10°) and out-of-plane: (ϕ : 80° – 90°). The d-spacing and full-width at half maxima (FWHM) analysis is tabulated in *Table 2.1*. After annealing, in-plane π -stacking (020) features of P3HF (3.84 Å) is similar to P3HT (3.82 Å). Substitution of the larger

heteroatom (Se vs. S) revealed that after annealing P3HSe exhibited a π -stacking of 3.9 Å, in good agreement with literature.²⁹

Polymer	M.W.ª	Casting Solvent ^b	π- Stacking (Å)	Lamellar Spacing (Å)	Radial FWHM (100)	Azimuthal FWHM (100)
P3HF	4,100	C.B.	3.84	17.5.	0.020 Å ⁻¹	38° ^{IP} 18° ^{OP}
РЗНТ	25,200	C.B.	3.82	16.1	0.038 Å ⁻¹	20.2°
P3HSe	24,200	C.B.	3.90	15.6	0.043 Å ⁻¹	19.2°

Table 2.1. GIWAXS Analysis of Homopolymers: d-spacing and FWHM of (100) Bragg Peak

a. Estimation of molecular weight from GPC in THF (40°C) eluent, calibrated with polystyrene standards

b. Films cast from chlorobenzene (C.B.) solvent, annealed at 150 °C for 30 minutes

c. IP: in-plane, OP: out-of-plane

Interestingly, out-of-plane lamellar spacing (100) of homopolymers decreased with increasing heteroatom size. Larger π -stacking of adjacent chains provides more volume available for side-chains to arrange more tightly. Further examination of lamellar features revealed higher order interlayer spacing features up to the 3rd order, after annealing, indicating a well-organized intermolecular structure. Additional FWHM analysis of (100) lamellar spacing in annealed films revealed similar azimuthal FWHM for P3HT and P3HSe whereas mixed orientations of P3HF revealed different levels of disorder, with broad azimuthal FWHM, *Table 2.1*.

Another feature commonly observed in X-Ray scattering experiments is the pronounced amorphous halo common to amorphous polymers.^{45,46} In conjugated polymers, the amorphous fraction stems from the chain ends, disorganized side-chains and low conjugation segments with chain torsion and defects within the polymer lattice. Therefore, to determine the contribution of amorphous content characterized in X-ray scattering experiments, a more in-depth study of different molecular weights P3HT and P3HSe, cast from CHCl₃, was pursued. In-plane and out-

of-plane radial profiles were superimposed to determine if there is any amorphous halo present at lower molecular weights before (as-cast) and after thermal annealing, *Figure 2.8*.



Figure 2.8. Radial profiles of in-plane and out-of-plane Bragg peaks from as-cast (top row) and thermally annealed (bottom row) films cast from CHCl₃ of *Left Panel*: P3HT: M.W. 11,300 (Pink); M.W. 19,000 (Red); M.W. 25,200 (Blue); M.W. 37,500 (Black) and profile overlays of *Right Panel*: P3HSe: M.W. 10,000 (Red); M.W. 19,700 (Blue); M.W. 24,200 (Black).

Absence of an amorphous halo is readily apparent both before and after thermal annealing in both P3HT and P3HSe. Diffuse scattering is more apparent in as-cast films, with baseline resolution not reaching zero for higher molecular weight materials. As cast-films of P3HSe, regardless of molecular weight, revealed a broad hump in the high q-regime above 1.5 Å⁻¹ both inplane and out-of-plane. Once P3HSe was thermally annealed the Bragg feature due to π -stacking (020) became apparent, with an increasing molecular weight resulting in increased intensities of (020) and (100) Bragg peaks. Remarkably, after annealing, the π -stacking feature of in-plane P3HT profiles almost matched perfectly regarding both shape and intensity, despite molecular weight. This π -stacking was accompanied by a wide pedestal ranging from q ~ 1.2 – 1.5 Å⁻¹. Current ongoing work entailing 2D GIWAXS pattern simulations of P3HT (not shown here) attributes this feature to a slight chain off-set between adjacent chains such that sulfur heteroatoms do not sit directly across from each-other. This feature is notably absent in P3HSe profiles, as larger chalcogens favor dipole-dipole interactions of neighboring heteroatoms. Therefore, the potential "amorphous" features in both P3HSe and P3HT, (regardless of molecular weight) showing broad shoulder and pedestal features, can be ascribed to broad π -stacking and adjacent chain off-sets inplane of the substrate, and not the amorphous content within the semi-crystalline structures.

2.5. Band Structure Characterization

Band structure characterization of homopolymers with varying heteroatom substitutions along the polymer main-chain can be probed by electrochemistry and absorbance spectroscopy. The relative onset of oxidation and reduction potentials obtained through cyclic voltammetry provides



Figure 2.9. Electrochemical analysis of the second cyclization of *Top*: P3HT and *Bottom*: P3HSe; Corrected vs. Ferrocene reference, using a glassy carbon working electrode combined with a Pt counter electrode and silverwire pseudo reference in a 0.1M TBAF/MeCN electrolyte solution. *Inset*: Measured oxidation (E_{ox}) and reduction (E_{red}) potentials (eV) for respective samples.

the oxidation and reduction potentials of HOMO-LUMO bands that can be compared with the optical band gap estimate from absorption edge of the solid-state UV-vis spectra. Reducing the band gap with heavier heteroatom substitutions such as transitioning from oxygen to sulfur to selenium, due to lowering of the LUMO is an effective means to tune the band structure⁴⁷⁻⁵⁰ for either wide band gap or low band gap materials.

Electrochemical properties of homopolymer P3HF were probed using cyclic voltammetry (CV). P3HF measurements were carried out by Dr. Yunyan Qiu and is described in Reference 31, using a platinum disk working electrode in dry acetonitrile. The polymer showed quasi-reversible oxidation peaks with onset potentials of -0.013 V (referenced vs. ferrocene internal standard). The reduction peak was not readily apparent, therefore the band gap was estimated from the absorption band edge (2.21 eV). Additionally, electrochemical properties of homopolymers P3HT and P3HSe were also probed using CV, *Figure 2.9*. Thin films were cast upon a glassy-carbon disk working electrode and measured in dry acetonitrile (referenced vs. ferrocene internal standard). P3HT and P3HSe showed onset oxidation peaks potentials of 0.143 V and -0.205 V respectively. The quasi-reversible onset of the reduction peaks were estimated at -2.11 V and -2.04 V. Electrochemical band gaps were estimated as 2.25 eV and 1.84 eV for P3HT and P3HSe.



Figure 2.10. *Left*: Theoretical HOMO-LUMO band energies, Reference 47, with experimental UV-vis spectra in *Middle*: solid-state and *Right*: solution of P3HF (Black), P3HT (Red) and P3HSe (Blue).

Optical properties of all three polymers were probed both in solution and in the solid state, *Figure 2.10.* Homopolymer P3HF had a solution absorption peak at 470 nm, which was slightly red-shifted from P3HT ($\lambda_{max} = 453$ nm). Closer examination of the P3HF's solution spectra revealed the presence of shoulders, indicating a highly aggregated solution, with vibronic finestructure beginning to appear at higher wavelengths. The aggregation in solution could explain the apparent red-shift in solution, as solution and solid-state spectra have similar absorption maxima. P3HSe produced the most red-shifted solution spectra with ($\lambda_{max} = 490$ nm). In comparison to the solid-state spectra, both P3HT and P3HSe have red-shifted spectra as polymers transition from solution to solid-state with an absorption edge (ν_{edge} , eV) estimated as (1.9 eV and 1.65 eV) respectively. The increase in heteroatom atomic size correlates well with decreasing band gaps, in good agreement with predicted theory calculations.⁴⁷ The absorption profile of P3HSe extends into the near-IR regime, indicating that selenium heteroatom substitution could be advantageous in expanding the absorbance range of conjugated polymers for applications such as solar cells.⁵¹

2.6. Model of Electronic-Vibronic Coupling Estimated by UV-Vis Spectroscopy

The absorbance profiles of P3HF, P3HT and P3HSe has vibronic fine-structure which can be ascribed to the weak coupling regime, described by Shoo and co-workers⁵² and Brown and coworkers⁵³. The electron-phonon coupled transitions from the electronic ground state (S₀) to the first excited state (S₁) can be deconvoluted using a modified Franck-Condon style fit, described by Spano and co-workers.⁵⁴⁻⁵⁸ Information gleaned from these profiles include i) the exciton bandwidth *W* (*Equation 1, Appendix 1*) calculated from the ratios of the first two peak intensities



Figure 2.11. Example of experimental data (Black) for P3HT with aggregate fit (Gaussians: Teal, Total: Red) with the resulting 'Residual' (Pink).

(A₀₋₀: A₀₋₁), ii) Gaussian distributions of respective width (σ) and vibronic spacing (E_p) and iii) the remaining 'residual', *Figure 2.11*. The total Gaussian fit describes the contribution from ordered aggregates, whereas the 'residual' from the fit was attributed to the disordered aggregates within the amorphous fraction of the semicrystalline material.⁵⁶ Our interests were to develop a fit of the entire absorbance profile with the inclusion of an appropriate function, such as a gamma function in place of the 'residual' to describe the disordered fraction. In our work thus far, the contribution of the amorphous component has been noticeably absent, with a non-discernable glass transition temperature (DSC) and lack of amorphous halo witnessed in X-ray scattering (GIWAXS). Therefore, any insight into the contribution of the amorphous fraction is readily welcomed and of interest to our group.

Initial examination of solid-state curves revealed up to 3 distinct peaks of varying intensity, appearing from low to high energy with *almost* regular spacing; accompanied by a smooth curve tailing off at higher energy, (*Figure 2.10, middle*). The irregular vibronic spacing has been reported in literature as an effect of inhomogeneous spectral broadening.^{53,57}

The shape of the 'residuals' from Spano's fits (*Figure 2.11*, see also: *Figure 1.15*, *Chapter 1*) has a sharp onset, with a skewed, unsymmetrical peak intensity that maintains some peak structure. Considering that the amorphous phase consists of i) site imperfections, ii) polymer-chain ends, and iii) chain entanglements, we hypothesize that the disordered contents should generate a high degree of spectral broadening resulting in a smooth curve. The use of a gamma distribution function, characterized by its location (μ), shape (α) and inverse scale (β) parameters, generates skewed curves with sharp onsets by using smaller values of (α). We also acknowledge that other distribution shapes may be a better descriptor of the amorphous fraction. However, as a first pass at attempting to fit the total spectra, the gamma distribution will suffice. We additionally acknowledge that Spano's assumptions in fitting P3HT (Huang Rhys parameter, S =1)⁵⁷ may not hold true for systems other than P3HT. However, its exact determination would require more indepth theoretical models which is beyond the scope of this work.



Figure 2.12. Spano's modified Franck-Condon fit, for *Left*: P3HF, *Middle*: P3HT and *Right*: P3HSe depicting *i*) Experimental data (Black) *ii*) Individual Gaussians (Blue, dashed) and *iii*) Total curve as the sum of Gaussians (Red, Dashed) Inset: Values of exciton bandwidth (*W*).

Spano's fitting of ordered aggregates was applied to homopolymers P3HF, P3HT and P3HSe. Tables of the resulting parameters are in *Table S2.1*, *Appendix 1*. Overlays of Gaussian peaks and their resulting sum are depicted in *Figure 2.12*. The resulting fit had Gaussian widths that were relatively narrow ($\sigma < 0.08$) with vibronic spacing in the range of 0.171 – 0.185 eV. Analysis of the exciton bandwidth, *W*, revealed slightly higher values for P3HF, and similar values for P3HT



Figure 2.13. P3HT Solid-state UV-vis deconvolution using Mean Squared Root Deviation (RMSD) with respect to the onset of the gamma distribution (y onset, eV). *Inset*: Examples of fits depicted as an overlay of i) Experimental data (Light Blue) *ii*) Individual Gaussians (Blue) iii) Gamma distribution (Black) and iv) Total curve fit from the integrated sum of (ii + iii) (Red). Best fit highlighted (\bigstar , Red Star).

and P3HSe, corresponding to a more delocalized structure.⁵⁴

The total absorbance spectra were fitted using both Gaussian and gamma functions (described in *Appendix 1*). The root-mean-square deviation (RMSD) was calculated for each fit vs. experimental data to determine the best fit (lowest RMSD). An example of the RMSD calculation for P3HT is shown with examples of various fits (insets), *Figure* 2.13. The remaining RMSD calculations are shown in *Appendix 1*. Comparisons of the best fit with the inclusion of the gamma function for P3HF, P3HT and P3HSe are depicted in *Figure 2.14*. Tabulation of the resulting fitted parameters are given in *Table S2.2* of *Appendix 1*. The inclusion of the gamma function generated a fit that was in relatively good agreement with the spectral shape of the experimental results (low RMSD). Gaussian distributions remained relatively narrow ($\sigma < 0.09$) with vibronic spacing in the range of 0.163 – 0.189 eV.



Figure 2.14. UV-vis spectra for *Left*: P3HF, *Middle*: P3HT and *Top*: P3HSe with optimized fits depicted as an overlay of *i*) Experimental data (Light Blue) *ii*) Individual Gaussians (Blue) *iii*) Gamma distribution (Black) and *iv*) Total curve fit from the integrated sum of (*ii* + *iii*) (Red).

The fitting of the gamma function's onset, peak shape and absorbance intensity closely matched the position and area of the 'residual'. The main difference between the two profiles resided in the smooth curvature of the gamma function. Comparison of the 'residual' shape and the gamma functions used to describe the amorphous fraction is shown in *Figure 2.15*.



Figure 2.15. Overlay of 'residual' from Spano's fit (Black) and fitted gamma function (Red, Dashed) for *Left*: P3HF, *Middle*: P3HT, and *Right*: P3HSe.

All spectra overall had relatively narrow linewidths for vibronic transitions within ordered aggregates, and approximately ~ 45 % - 49 % of the total spectra stemming from the amorphous fraction (either accounted for by the 'residual' or gamma function). P3HF revealed slightly broader linewidths and a larger exciton bandwidth, potentially indicating a less organized structure in comparison to P3HT and P3HSe. Variation in the vibronic spacing may potentially be due to the rigidity of the polymer chain, however, better accountability of Huang Rhys parameter is needed to better elucidate these differences. The agreement of the gamma function with the 'residual' profile is highly promising for its use to describe the amorphous contribution to the absorbance spectrum. The use of the gamma function enabled us to fit the entire absorbance spectrum, described by the sum of ordered and disordered components. This style of fitting could potentially be extended to more complex systems such as donor-acceptor copolymers, side-chain sequenced copolymers and other conjugated polymer families of various shape and size. This requires proper accountability for the Huang-Rhys parameter (S), the vibronic spacing and the effect of aggregation on higher energy transitions.

2.7. Summary of Findings

The synthesis of homopolymers P3HF, P3HT and P3HSe were carried out using Kumada CTP to afford regio-regular, low dispersity molecular weight materials. This enabled the characterization of thermal properties by TGA and DSC revealing a molecular weight dependence on melting enthalpy that is independent of heteroatom identity. P3HF showed no thermal transitions up to 320 °C, indicating a highly crystalline material with strong inter-chain interactions induced by small heteroatom size promoting high chain planarity. Further probing of nanoscale morphologies and atomic packing arrangements of as-cast polymer films displayed different

degrees of organization ranging from face-on, edge-on and isotropic orientations. Thermal annealing was also shown to promote more edge-on character in both P3HF and P3HSe, indicating a sensitivity to processing conditions and bulk organization. Radial profiles also revealed no distinct amorphous halo to indicate the presence of a disorganized amorphous phase in different molecular weights of P3HT or P3HSe. Intrinsic characterization of the materials electronic band-structure demonstrated that the electronic band gap can be modulated depending on heteroatom identity, in good agreement with theoretical and literature reports. Lastly, inspired by Spano and co-workers, deconvolution fitting of the vibronic fine-structure within UV-vis profiles were carried out describing ordered aggregates using Gaussian distributions with the amorphous component described by a gamma function. The combination of both Gaussian and gamma functions fitted the entire absorbance profile to describe the total contribution of ordered and disordered phases within respective homopolymers.

2.8 Experimental Procedures

Physical analysis followed standard experimental procedures described in Appendix 2.

All spectral analyses were performed using Mathematica Software. AFM images were processed using Gwyddion Software[®]. 2D GIWAXS images were recorded at Cornell High Energy Synchrotron Source (CHESS) at station D1 which is run by Dr. Detlef Smilgies. The work at CHESS is supported by the National Science Foundation under award DMR-1332208.

Scheme E1. Synthesis of monomer 2-bromo-3-hexylthiophene, Compound 1.



2-bromo-3-hexylthiophene. This compound was prepared according to a literature procedure.⁵⁹ ¹H and ¹³C NMR spectra were compared to a previous report.⁵⁹





2-bromo-3-hexylselenophene. This compound was prepared according to a literature procedure.⁵⁹ ¹H and ¹³C NMR spectra were compared to a previous report.⁵⁹

<u>Polymerization of *rr-P3HF*</u>. Regio-regular poly(3-hexyl furan) (rr-P3HF) was synthesized in collaboration with the Dr. Yunyan Qiu in Dr. Noonan's group. These materials were reported in Reference 33. The highest molecular weight (Mn 4,100 Đ 1.25) were used for the described studies. All materials were maintained in an inert, dark environment prior to any tests. Combined ambient light and air exposure led to excessive degradation both in solution and the solid-state. Therefore, all tests performed worked to minimize light exposure, at night, either covered with foil or within a black box environment.

Polymerization Considerations: Several considerations of the techniques involved in the polymerizations are as follows: i) The use of a Schleck line helped to maintain an inert environment for the magnesio active species, where upon ii) the powder catalyst was added under a nitrogen blanket with a moderate purging flow. iii) The solution maintained a steady stir rate, with little splashing on flask walls. These techniques combined, enabled the catalyst powder to add to the respective solution at one time, such that all chains were ideally initiated at once with assurance that all monomer was supplied and not wasted on the flask walls. Sloppy catalyst addition resulted in undesired molecular weights or greater chain dispersity, whereas excessive solution splashing reduced polymer yields. iv) All materials were stored in sealed glass vials, covered in foil and placed either in an inert environment or in-vacuo to reduce exposure to light, air and moisture. These precautions were taken to ensure that the materials quality was maintained over extended periods of time.
Polymer	M/Cat	Mn ^a	Đ	% Yield
	50	11,300	1.15	70
РЗНТ	75	19,000	1.28	60
	100	25,200	1.18	82
	200	37,500	1.18	61
P3HSe	50	10,000	1.32	73
	75	19,700	1.16	67
	100	24,200	1.18	49

Table 2.2. Homopolymers resulting weight and yields

^aGPC traces were recorded at 40 °C versus polystyrene standards using THF as the eluent.

In a N₂ filled glovebox, a larger batch of 0.1M solution of Polymerization of rr-P3HT. compound **1** in THF was prepared prior to all polymerizations. Then (4 - 6 mL) of the crop solution (0.10 - 0.15 g, 0.4 - 0.6 mmol) was added to an oven-dried 20 mL glass vial equipped with a magnetic stir bar. TMPMgCl·LiCl solution (0.8 M, 1.2 equiv.) was then added to the reaction solution, and the solution was stirred at room temperature for 2 hours. The reaction mixture was then transferred in the glovebox to a 250 mL Schleck flask equipped with a magnetic stir bar and diluted to a (0.04 M, 0.04 M, 0.01 M and 0.01 M) concentration respectively in THF for the (M/Cat. = 50, 75, 100, 200). The flask was then sealed and removed from the glovebox and then placed on a Schleck line atop a stir plate. Under a N2 purge, Ni(dppp)Cl2 (2, 1.33, 1 and 0.5 mol %) was quickly added to the solution in one portion. The polymerization was stirred at room temperature for 15 min, then quenched with 6 M methanolic HCl and stirred for an additional 10 minutes. The resulting precipitate was collected by gravity filtration, washed with methanol and dried overnight. The polymer was then re-dissolved in 1-2 mL THF, re-precipitated in methanol (200 mL), washed with methanol, acetone in several successions and dried overnight. Yield: M/Cat. = 50 (58.4 mg, 70 %), M/Cat. = 75 (42 mg, 60 %), M/Cat. = 100 (99 mg, 82 %), M/Cat. = 100 (52 mg, 61 %). ¹H NMR (500 MHz, CDCl₃) δ 6.99 (s, 1H), 2.82 (t, 2H), 1.72 (m, 2H), 1.54 – 1.37 (m, 6H), 0.93 (m, 3H). ¹³C NMR (126 MHz, THF-d8) δ 139.9, 133.6, 130.4, 128.6, 30.4, 29.2 (2 overlapping signals), 22.5 and 13.46 (2 overlapping signals).

<u>Polymerization of *rr-P3HSe*</u>. In a N₂ filled glovebox, a larger batch of 0.1 M solution of compound 2 in THF was prepared prior to all polymerizations. Then (3.5 - 6 mL) of the crop

solution (0.10 - 0.18 g, 0.35 - 0.6 mmol) was added to an oven-dried 20 mL glass vial equipped with a magnetic stir bar. TMPMgCl·LiCl solution (0.8 M, 1.2 equiv.) was then added to the reaction solution, and the solution was stirred at room temperature for 2 hours. The reaction mixture was then transferred in the glovebox to a 250 mL Schleck flask equipped with a magnetic stir bar and diluted to (0.04 M, 0.01 M and 0.01 M) concentration respectively in THF for the M/Cat. = (50, 75, 100) polymerizations. The flask was then sealed and removed from the glovebox and then placed on a Schleck line atop a stir plate. Under a N₂ purge, Ni(dppp)Cl₂ (2, 1.33 and 1 mol %) was quickly added to the solution in one portion. The polymerization was stirred at room temperature for 15 min, then quenched with 6 M methanolic HCl and stirred for an additional 10 minutes. The resulting precipitate was collected by gravity filtration, washed with methanol and dried overnight. The polymer was then re-dissolved in 1 - 2 mL THF, re-precipitated in methanol (200 mL), washed with methanol, acetone in several successions and dried overnight. Yield: M/Cat. = 50 (93 mg, 73 %), M/Cat. = 75 (50 mg, 67 %) and M/Cat. = 100 (36.2 mg, 49 %). ¹H NMR (500 MHz, CDCl₃) δ 7.14 (s, 1H), 2.75 (t, 2H), 1.7 (m, 2H), 1.55 – 1.37 (m, 6H), 0.93 (m, 3H). ¹³C NMR (126 MHz, THF-d8) δ 141.3, 139.5, 133.0, 132.0, 128.1, 31.5, 30.6, 30.4, 29.1, 22.4 and 13.5.

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Chapter 3

Impact of Sequence on Organization in

Thiophene-Selenophene Copolymers

3.1 Introduction

In recent years, there continues to be intense interest in controlling monomer sequence in polymer materials, as discussed in *Chapter 1*. Researchers strive towards the creation of more complex synthetic materials with a wide range of structural and functional properties.¹⁻³ Their efforts are reflected by recent numerous reports demonstrating increasing levels of control over monomer insertion in step-growth and chain-growth polymerization processes.⁴⁻¹⁰ For conjugated polymers, sequence has been used very effectively to tune the electronic and photo-physical properties of materials, because their electronic structure is highly delocalized.¹¹⁻¹⁴ This is manifested in the ability to generate low band gap polymers to form donor-acceptor copolymers,¹⁵⁻ ²¹ and developing other sequence architectures such as statistical copolymers,^{11,13,22,23} graft copolymers,²⁴⁻²⁹ block copolymers,³⁰⁻³⁵ stars³⁶, and side-chain varying copolymers.³⁷⁻³⁹ Keeping the π -conjugated framework intact while replacing heteroatoms within the backbone enables modulation of the electronic structure without large variations in the polymer chain's shape, therefore potentially limiting the impact on a material's morphology. However, reports of distinct nanoscale phase-separation in block copolymers of 3-alkylthiophene and 3-alkylselenophene⁴⁰⁻ ⁴³ indicate simple replacement of a heteroatom in the heterocycle may have a significant impact on solid-state packing. Furthermore, while studies of random copolymers of alkyl-thiophene and alkyl-selenophene have shown that electronic properties vary smoothly with composition,¹¹ the

differences in vibronic fine-structure have been noted,^{13,44} but not explored in extensive detail. This intrinsic character may be one of the more sensitive methods to characterize the impact of periodicity at a molecular level. Overall, this highlights a need to explore the impact of randomness and periodicity on its intrinsic properties, solid-state ordering and macroscopic physical response using a wide array of thiophene: selenophene compositions, *Figure 3.1*.

To further elucidate these aspects, in this report we developed a series of both random copolymers and well-defined periodic sequence copolymers of similar composition comprised of



Figure 3.1. Exploration of periodic vs. random copolymers and how monomer arrangements impact physical properties.

3-hexylthiophene and 3hexylselenophene units. To ensure that periodic sequence copolymers were well-defined, the copolymers were synthesized by linking short oligomers through catalyst-transfer polycondensation (CTP).⁴⁵ Polymer chains assembled through

polycondensation typically grow through a step-growth mechanism, which yields broad molecular weight distributions. CTP on the other hand, proceeds in a chain-growth process, yielding polymers with narrow molecular weight distributions and controlled molecular weights.⁴⁵

We will demonstrate both similarities and deviations from the expected physical behavior of periodic and random copolymers with respect to their relative composition. Impacts to the material's decomposition and crystallinity are explored by thermal analysis, with optimal structure arrangements predicted by theory. We also demonstrate that, similar to previous reports on random copolymers,¹¹ the optical bandgaps and redox potentials of well-defined periodic copolymers vary with composition in a predictable, linear manner. Both random and periodic sequences exhibit well-defined morphologies, and the packing patterns mimic those of *rr*-P3HT.⁴⁶

Further exploration of both periodic and random copolymers provides insights into the material's organization on a nanoscale and molecular level, including analysis of fibril widths, atomic spacing and vibronic character gleaned from X-ray scattering and absorption spectroscopy. Probing of atomic-scale organization by X-ray scattering reveal that packing patterns of random copolymers significantly differ from the periodic systems. Larger π -stacking distances and higher range of orientational disorder are present in the random copolymers in comparison to most periodic structures of similar composition. Periodic copolymers exhibit vibronic fine-structure in UV-vis absorbance with lower exciton bandwidths indicating a more delocalized structure in comparison to random copolymers.

Overall, periodicity is promoting improved chain-packing and charge-transporting potential, and as such, should be a crucial consideration in the design of conjugated architectures, particularly when attempting to promote structural ordering and charge-carrier mobility. This report also demonstrates that atomic-level analysis and examination of a material's intrinsic properties are the most sensitive to alterations in periodicity within a polymer chain.

3.2. Synthesis and Polymerization Fidelity of Periodic and Random Copolymers

The synthesis of periodic and statistical copolymers bearing 3-hexylthiophene and 3-hexylselenophene units was carried out using Kumada CTP. This controlled polymerization technique afforded high molecular weights polymers with relatively narrow weight distributions $(\Phi = 1.2-1.3)$. Since molecular weight and dispersity were eliminated as potential candidates for

deviations in behavior,⁴⁷ a more meaningful comparison of how monomer arrangement impacts a material's properties with respect to composition, could be conveyed.

3.2.1. Synthesis of Periodic Copolymers

The synthesis of periodic copolymers with exact placement of 3-hexyl selenophene rings within a thiophene copolymer backbone was conducted by Dr. Chia-Hua Tsai.⁴⁵ Her work entailed the synthesis of dimeric and trimeric units that were magnesio-functionalized for controlled placement of hexyl-thiophene (T) and hexyl-selenophene (Se) along the copolymer backbone. The polymerization of complex sequence copolymers varied selenophene content ranging from (33 % : T-T-Se, 50 %: T-Se and 66 % : T-Se-Se) was carried out following Kumada CTP methods. The resulting polymers have the following molecular weights and distributions: T-T-Se (M_n: 32,100 Đ 1.23), T-Se (M_n: 39,800 Đ 1.18), T-Se-Se (M_n: 39,000 Đ 1.17).

3.2.2. Synthesis of Random Copolymers

The synthesis of statistical copolymers (r-T-Se_n : r- denotes 'random' and 'n' denotes the X_i selenophene content), illustrated Scheme 3.1, was achieved similar to prior reports; though a slightly different method was used for monomer activation. 2-Bromo-3-hexylthiophene and 2-bromo-3-hexylselenophene were activated separately using 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex (TMPMgCl·LiCl).⁴⁸⁻⁵⁰ The active monomer solutions were then combined and polymerizations were initiated using Ni(dppp)Cl₂, *Scheme 3.1*. Typically, polymerizations were conducted in dilute solution (0.01 M)

to compensate for the limited solubility of the polymers bearing selenophene. After 15 min, reaction mixtures were quenched and precipitated with 6M HCl/MeOH and washed with methanol.

Gel permeation chromatography (GPC) of the crude polymer samples confirmed control over the molecular weights (*Table 3.1*). We have noted that incorporation of higher percentages of

Scheme 3.1. Synthesis of random P3HT-P3HSe (*r*-T-Se_n) copolymers using CTP.



the selenophene monomer while also targeting high molecular weights resulted in broader molecular weight distributions for the resultant samples. The reactivity ratios of the copolymerization for these two monomers was determined by McNeil and co-workers with an observation for a very slight preference for selenophene incorporation.

Name	X_i (Se) ^a	(M _T +M _{Se})/Cat.	$M_{ m n}{}^{ m b}$	Đ	Yield (%)
P3HT	0	100	25,200	1.18	81
<i>r</i> -T-Se ₃₂	32	150	32,300	1.31	38
r-T-Se ₅₃	53	150	30,300	1.26	31
r-T-Se ₆₅	65	150	28,700	1.23	55
P3HSe	100	100	24,200	1.18	49

 Table 3.1.
 Polymerization

^aPercent incorporation of 3-hexylselenophene was determined by integration of aromatic signals in the ¹H NMR spectrum (Appendix). ^bGPC traces were recorded at 40°C vs. polystyrene standards using THF as an eluent.

3.2.3. NMR Spectroscopy of Periodic and Random Copolymers

P3HT has been studied extensively using NMR spectroscopy.⁵¹ Model compound studies have been used to assign the four configurational triads from the regiochemical possibilities with hexyl chains of adjacent thiophenes in head-to-head (HH), head-to-tail (HT) or tail-to-tail (TT) arrangements. In our studies for random/statistical copolymers of 3-hexylthiophene and 3-hexylselenophene, the deprotonative method results in one active isomer for polymerization and



Figure 3.2. ¹H NMR spectra of the aromatic regions of the random copolymer *r*-T-Se₅₃ and periodic alternating sequence copolymer T-Se (CHCl₃ at 22°C, 500 MHz). The star symbols (*) indicate ¹³C satellite signals for the solvent.

consequently, only HT arrangements of the alkyl chains are accessible. However, the aromatic ring systems are sensitive to the adjacent heterocycle and result in multiple signals corresponding to backbone composition.

A periodic alternating copolymer of thiophene and selenophene (T-Se) was synthesized from a dimeric monomer, whose

triad arrangement along the backbone produces two signals: the thiophene-centered triad with two adjacent selenophenes (6.92 ppm, Se–*S*–Se, *Figure 3.2*) and a selenophene centered triad (7.18 ppm, S–*Se*–S, *Figure 3.2*) with two adjacent thiophenes. This spectrum was remarkably helpful for assigning the statistical copolymers and is consistent with the work from Seferos and co-workers.⁴⁴ Full triad resolution is not obtained and a total of four signals are observed. The signal at 7.19 ppm is essentially identical to the one observed in the alternating copolymer and

corresponds to the selenophene flanked by two thiophenes (S–*Se*–S). The signal at 7.12 ppm corresponds to the other two selenophene-centered triads, Se–*Se*–S and Se–*Se*–Se, which are overlapping. The selenophene triad assignment is consistent with the previous report by Heeney and co-workers who synthesized *rr*-P3HSe and noted the aromatic signal in the ¹H NMR spectrum was at 7.11 ppm.⁵² For the upfield thiophene-centered triads, the signal at 6.98 ppm matches *rr*-P3HT exactly and corresponds to the S–*S*–S triad while the signal at 6.92 ppm corresponds to the other two thiophene centered triads flanked by either the one or two selenophenes (S–*S*–Se and Se–*S*–Se). The signals at 7.12 and 6.92 are also larger in the ¹H NMR spectrum, as would be expected for signals of overlapping triads.

Two end-groups are also observable in the statistical copolymers, the signal at 7.52 ppm, which has been previously assigned in the alternating polymer.⁴⁵ This signal corresponds to the H-terminated selenophene end group. The signal at 6.82 ppm is tentatively assigned as a Br-terminated thiophene end group, consistent with prior reports on P3HT. We suspect the other two end groups (Br-terminated selenophene and H-terminated thiophene) are overlapping with the major aromatic signals of the polymer backbone. These signals were not used to conduct end-group analysis since all four signals could not be compared and a statistical mixture of all four end-groups should be observed.

3.3. Theoretical Predictions for Periodic Copolymers

Density Functional Theory (DFT) simulations were performed by Dr. David Yaron and Dr. Tomasz Kowalewski to examine the energy minimized geometric structure of dodecamers for periodic sequence copolymers containing 33 % selenophene content (T-T-Se) and 50 % selenophene content (T-Se), *Figure 3.3.* The energy minimum was found from an all-trans



Figure 3.3. *Top*: Calculated bond lengths and angles from dodecamer calculations for thiophene and selenophene in the oligomer chain (end groups were excluded) *Bottom*: Energy minimized T-T-Se and T-Se dodecamer structures.

conformation, with the perfect alternation of heteroatoms in an "up"-"down" direction for neighboring rings. This resulted in the perfectly alternating sequences of 3hexylthiophene and 3-hexylselenophene presenting backbone curvature once extended conjugation lengths were calculated. This curvature can be traced to the alternation of bond angles between the heteroatom bridge (88.3° for Se and 92.4°

for S). In homopolymers, the polymer chain remains linear because of the alternation of up/down direction of the monomer's heteroatom, whose neighboring rings are of the same identity. In the perfectly alternating periodic sequences all of the rings facing "down" are type of heterocycle (S or Se) and all of the neighbor rings facing "up" are the other identity heterocycle (Se or S), respectively. This means that the difference in bond angles becomes additive, with no bond angle corrections from a neighboring heterocycle (aka. …S–S… or …Se–Se…) to cancel out any curvature from bond alternation. This is also why the trimeric monomers used to synthesize the periodic copolymers are linear: the trimer units maintain that the central monomer is flanked by both types of rings (S and Se). The backbone curvature in the T-Se copolymer is potentially a large culprit for introducing disorder in the solid-state, which may also become apparent when probing its molecular, nanoscale and macroscopic properties. We additionally propose, that the random copolymers will not exhibit backbone curvature regardless of composition due to the statistical distribution of both thiophene and selenophene units.



Figure 3.4. Thermogravimetric analysis of *Top*: random and *Bottom*: periodic copolymers. Inset: 5% decomposition temperature ($T_{d5\%}$) for respective polymers.

Thermal characterization of periodic and random copolymers was carried out by decomposition measuring thermal by thermogravimetric analysis (TGA) and thermal transitions of melting and crystallization measured by differential scanning calorimetry (DSC). The thermal decomposition range measured by TGA points to good thermal stability of all copolymers with 5 % weight loss temperatures (T_{d5%}) above 370 °C, Figure 3.4. The homopolymer P3HT exhibits a $T_{d5\%}$

temperature measured at 412 °C, and P3HSe's 5% weight loss was measured at 372 °C. It is interesting to note that thermal decomposition temperatures for periodic copolymers decreased with increasing selenophene content, with T-T-Se exhibiting the highest decomposition temperature rivaling P3HT ($T_{d5\%}$ =412 °C), and the lowest decomposition temperature was exhibited from T-Se-Se ($T_{d5\%}$ =399 °C). Similarly, the random copolymer with the lowest selenophene content (*r*-T-Se₃₂) had the highest decomposition temperature ($T_{d5\%}$ =384 °C) in the random copolymers series. Random copolymers with higher selenophene content (*r*-T-Se₅₃ and r-T-Se₆₅) had decomposition temperatures 5 °C higher than P3HSe. Periodic sequences revealed higher thermal stability in comparison to the random copolymers of similar composition. The statistical nature of random copolymers produces longer segments (3 rings or more) of ...-

Se–Se–Se-···· neighboring heterocycles and result in skewing of decomposition temperatures towards the thermal response of homopolymer P3HSe at elevated temperatures.



Figure 3.5. Differential scanning calorimetry (DSC) 2^{nd} cyclization curves measured at a heating rate of 10°C min⁻¹. *Left*: random copolymers P3HT (Gray); *r*-T-Se₃₂ (Orange); *r*-T-Se₅₃ (Green); *r*-T-Se₆₅ (Purple) and P3HSe (Red). *Right*: DSC of periodic copolymers over same cycle range. P3HT (Gray); T-T-Se (Orange); T-Se (Green); T-Se-Se (Purple) and P3HSe (Red). Integration limits to determine heat of fusion ($\Delta H_m J g^{-1}$) drawn for each material (Black, dashed line).

DSC traces of periodic copolymers were compared to random copolymers, *Figure 3.5* Once traces were compiled next to homopolymers P3HT (M.W. 25,200, Đ 1.18) and P3HSe (M.W. 24,200, Đ 1.18), it became evident that regardless of monomer ordering, all copolymers exhibited lower crystalline and melting transition temperatures (°C). Similar trends were observed by McNeil and co-workers when comparing block, gradient and random copolymers¹³ where the reduced melting temperature range was attributed to less favorable co-crystallization of combined thiophene and selenophene heterocycles in the polymer backbone.

Polymer	X _i Se (%)ª	Mn ^b	T _m (°C)	T _c (°C)	ΔH _c (J g ⁻¹)	∆H _m (J g⁻¹)	∆H _m Ring ⁻¹ (J mol ⁻¹)
P3HT	0	25,200	235.5	204.7	23.0	28.5	4.73
<i>r</i> -T-Se ₃₂	32	32,300	232.3	201.0	17.9	21.9	4.00
T-T-Se	33	32,100	229.6	199.3	21.2	25.2	4.57
T-Se	50	39,800	219.3	160.8	5.6	9.3	1.76
<i>r</i> -T-Se ₅₃	53	30,300	230.8	202.9	16.0	14.8	3.40
<i>r</i> -T-Se ₆₅	65	28,700	233.3	206.2	19.3	21.2	4.17
T-Se-Se	66	39,000	235.3	204.4	15.6	19.7	3.89
P3HSe	100	24,200	248.2	221.0	19.0	22.8	4.86

Table 3.2. Table of Thermal Properties for Random and Sequence Copolymers with Respect toIncreasing Selenophene Content (Xi Se %)

^aPercent incorporation of 3-hexylselenophene was determined by integration of aromatic signals in the ¹H NMR spectrum (Appendix). ^bGPC traces were recorded at 40°C vs. polystyrene standards using THF as an eluent.

Tabulation of thermal transitions for both periodic and random copolymer sequences were reported with respect to mole fraction of selenophene rings (X_i Se Content), *Table 3.2*. The enthalpy of crystallization ($\Delta H_c J g^{-1}$) and heat of fusion ($\Delta H_m J g^{-1}$) was calculated from the integrated peak area. Integration limits using linear baselines spanned the interpretation range, illustrated by a black dashed-line to help visualize the early onset of melting, *Figure 3.5*.

Comparison of the melting enthalpies in thiophene and selenophene-based polymer backbones required that enthalpy values were evaluated in terms of mole quantities, rather than mass. The enthalpy per ring within the polymer chain ($\Delta H_m \operatorname{ring}^{-1}$) was calculated by multiplying the enthalpy (J g⁻¹) by the effective repeat unit molecular weight (g mol⁻¹), (*Experimental Procedures, Equation 7a*). This was assessed against the inverse degree of polymerization (DP_n), (i.e. the number of rings within a polymer chain) to determine the relationship of effective enthalpy per ring with respect to chain length, irrespective of heteroatom identity, *Figure 3.6*.



Figure 3.6. Calculated enthalpy of fusion per ring (Δ H_m Ring⁻¹) within an average polymer chain (kJ mol⁻¹) with respect to inverse degree of polymerization (DP_n)⁻¹. i) Random (Purple) and ii) periodic (Teal) copolymers compared against homopolymer samples iii) P3HT (Black) and iv) P3HSe (Red) of varying molecular weight. v) Linear fit of positive correlation between increasing chain length (crystal thickness) and enthalpy per ring (Black, dashed) for easy visualization of deviations from expected behavior.

Conjugated polymers similar to rr-P3HT form fibrillar crystallites, where the chain length corresponds to the crystal width.⁵⁵ As discussed in *Chapter 2*, increasing polymer molecular weight (M.W. ~ 25,000 and below) increases the enthalpy per ring (Figure 3.6 Black, dashed line). Higher molecular weight materials, such as P3HT (M.W. 37,500), presented a lowered enthalpy, due to chain entanglements contributing significantly to the amorphous phase, thereby crystallinity.53,56,57 reduce Therefore, materials of similar weights, are expected to present similar responses.

Comparison of copolymers comprised of thiophene and selenophene rings with high regioregularity and low dispersity revealed nanoscale organization similar to *rr*-P3HT (discussed in *Section 3.5* and *Section 3.6*). The majority of random and periodic copolymers exhibited lower enthalpies per ring with respect to chain length. Considering the molecular weight of the random and periodic copolymers (M.W. > ~28,000), the expected enthalpy per ring should be similar to high molecular weight P3HT (M.W. 37,500, ΔH_m Ring: 3.6 J mol⁻¹). Periodic copolymer T-Se showed the largest deviation from expected behavior with almost half the enthalpy per ring as high molecular weight P3HT. Drastic reduction in crystallization and melt temperatures points to smaller crystallites and higher structural disorder caused by chain imperfections.⁵⁶ For T-Se copolymer, chain curvature predicted by computational modeling produces more disorder and negatively impacts its thermal response. Interestingly, random copolymer r-T-Se₅₃ does not exhibit backbone curvature, increasing the enthalpy per ring to the range of polymers of similar molecular weight.

3.5. Atomic Force Microscopy of Periodic and Random Copolymers

Nanoscale morphologies of random and periodic copolymers were examined by atomic force microscopy (AFM). Phase-shift images were acquired for ultra-thin films prepared by drop-casting from dilute chloroform solutions directly onto silicon substrates with solvent vapor annealing, as shown in *Figure 3.7*. In all cases, nanofibril structures were observed with fibril widths ranging from 21 - 33 nm, reminiscent of those reported for *rr*-P3ATs.⁵⁸



Figure 3.7. AFM phase-shift images ultra-thin films visualizing nanofibril morphologies of random copolymers a) *r*-T-Se₃₂ b) *r*-T-Se₅₃ c) *r*-T-Se₃₂ and sequence copolymers d) T-T-Se e) T-Se and f) T-Se-Se (*Inset scale bar*: 400 nm).

The average distribution of fibril width with respect to copolymer composition was calculated from AFM phase-shift images. Ideal, extended polymer-chain lengths were estimated from the degree of polymerization calculated from GPC analysis in conjunction with theoretical predictions for heterocycle width and bond length (thiophene ring: 2.55 Å, selenophene ring: 2.64 Å, $C_{sp}^2-C_{sp}^2$ bond length: 1.47 Å), *Figure 3.3*. The tabulated DP_n, with respect to theoretical vs. calculated fibril widths are provided in *Experimental*, *Table 3.5*. Analysis of AFM phase-shift images are depicted in *Appendix 1*, "*Fibril Width Analysis*". Each AFM image (nm scale) had an average of 50 – 100 lines drawn across individual fibrils of varying width. The total number of counts per line width (nm) was tabulated to determine the average fibril width distribution. The theoretical extended chain-length (i.e. maximum fibril width, nm) was compared to average fibril width determined from AFM images, with respect to the degree of polymerization for copolymers, *Figure 3.8*.



Figure 3.8. *Left*: Example of line widths drawn across individual fibrils for random copolymer *r*-T-Se₆₅, with *Inset*: Scale Bar: 100 nm *Middle*: Histogram of number of counts per line width (nm) to represent fibril width distribution. *Left*: Comparison of theoretical chain length (maximum fibril width, nm) (Black) vs. calculated average nanofibril width examined by AFM phase-shift images (Red) with respect to the degree of polymerization (*r*-T-Se₃₂ DP_n: 107, *r*-T-Se₅₃ DP_n: 95, *r*-T-Se₆₅ DP_n: 87, T-T-Se DP_n: 105, T-Se DP_n: 126, T-Se-Se DP_n: 117)

Theoretical calculations of maximum fibril width were performed for both random and periodic copolymers. The positive, linear correlation between the theoretical fibril widths and the degree of polymerization set a baseline for comparison between samples of different molecular weight. Discrepancies between extended chain lengths and measured fibril widths indicate that in some cases, polymer chains are either contributing to the amorphous phase,^{56,59} acting as a 'tie molecule' ⁵⁹⁻⁶¹ between adjacent crystallites or that they undergo chain-folding.^{53,54,59} This is a common occurrence for high molecular weight conjugated polymers. With the exception of periodic copolymer T-Se and random copolymer *r*-T-Se₃₂, the majority of measured fibril widths also positively correlated with the increasing molecular weight, regardless of composition. Copolymers revealed a reduced fibril width, with greater than 65 % of a copolymer organized as a fully extended chain.

Random copolymer *r*-T-Se₃₂ showed a lower average fibril width indicating a higher degree of disorder, limiting chain organization. This is likely an effect of higher polymer dispersity (\oplus : 1.31) leading to a higher fraction of disorganized chain-ends. The most drastically hindered species was periodic copolymer T-Se, whose nanofibril width was less than half the fully extended polymer chain length. This is proposed to stem from backbone curvature of the perfectly alternating \dots -T-Se-T-Se- \dots sequences, predicted by modeling in *Section 3.3*.

Overall, in all instances, chain-folding is likely occurring at higher molecular weights resulting in limiting fibril width. Deviations from the expected nanofibril width with respect to molecular weight highlights that chain organization in nanofibrils is largely impacted by broad dispersity, non-linearity or changes in chain conformation.

3.6. X-ray Scattering of Periodic and Random Copolymers

Atomic-scale packing was studied using grazing incidence wide angle X-ray scattering (GIWAXS) recorded at the Synchrotron Radiation X-ray Source (CHESS). The gross appearance of 2D GIWAXS patterns, *Figure 3.9*, was again similar to the one widely reported for rr-P3HT⁴⁶ (*Chapter 1*, Figure 1.9) with a favored edge-on orientation with respect to the substrate. These studies revealed the presence of i) an in-plane reflection (020) originating from π -stacking of the polymer backbones parallel to the substrate surface ii) with out-of-plane reflections (100) resulting from the inter-layering of vertically stacked polymer chains, with spacing dictated by the organization and length of alkyl chains perpendicular to the substrate surface. Altogether, both random and periodic sequence copolymers showed a clear dependence on the overall content of selenophene rings.



Figure 3.9. a) GIWAXS 2-D patterns of random copolymers a) r-T-Se₃₂ b) r-T-Se₅₃ c) r-T-Se₃₂ and sequence copolymers d) T-T-Se e) T-Se and f) T-Se-Se. *Inset:* Assigned d-spacing *Scale Bar*: Log scale intensities

All copolymers exhibit an edge-on orientation with π -stacking distance linearly increasing from 3.7 – 4 Å as the proportion of selenophene rings increased, *Figure 3.10 top*. This points to

the incorporation of a larger heteroatom, (Se vs. S), increasing the inter-chain π -stacking distance, reported in *Chapter 2*. Interestingly, when examining the π -stacking distances of both periodic and random copolymers with regards to their respective selenophene content, the random copolymers exhibited a markedly higher π -stacking distance. This can be explained by the statistical distribution of selenophene rings along the random copolymer backbone. It is likely that longer



Figure 3.10. *Top*: π -stacking distance (Å) and *Bottom*: lamellar spacing (Å) for random and periodic copolymers with respect to selenophene content (%).

segments of the random copolymer sequence consist of only selenophene rings, therefore favoring the larger π - stacking observed in P3HSe (3.9 Å).

The lamellar spacing decreased from 15.8 to 15.2 Å as selenophene content was increased in both periodic and random copolymers, *Figure 3.10 bottom*. This decrease may be due to the increase in π -stacking distance, which makes more volume available for side-chains between the π -stacks. Seferos and coworkers have used the alkyl chain length as a tool to match the lamellar spacing between 3-alkylthiophenes and 3-alkylselenophenes in random copolymers previously.³⁰

Examination of relative disorder in periodic and random copolymers can be further investigated by calculating the full-width at half maximum (FWHM) of lamellar (100) Bragg peak,⁶³⁻⁶⁵ *Figure 3.11*. Periodic copolymer T-Se exhibited the highest orientational disorder with a broad FWHM, in agreement with predictions of computational modeling pointing to backbone curvature. Random copolymers revealed similar azimuthal FWHM, regardless of composition, but showed a broader FWHM in comparison to the periodic sequences of similar composition.

Periodic sequences T-T-Se and T-Se-Se revealed the highest degree of anisotropy with FWHM of demonstrating highly oriented packing with respect to the substrate surface.⁶⁴

Analysis of the atomic-scale packing arrangements of random and periodic sequence copolymers points to backbone curvature as a large culprit for introducing disorder in copolymer T-Se (*Figure 3.9 e*) with more isotropic character, broader Bragg peaks and more diffuse



Figure 3.11. *Top*: Azimuthal FWHM and Bottom: Radial FWHM of the lamellar (100) Bragg peak analysis comparing random and periodic copolymers with respect to selenophene content (%)

scattering. In stark contrast, periodic sequences T-T-Se and T-Se-Se show a high degree of anisotropy, linear correlation of π -stacking with respect to selenophene content, even with larger quantities of selenophene along the backbone. Looking at random copolymer *r*-T-Se₆₅ (*Figure 3.9 c*) highlights the latter, as it reveals mixed packing arrangements that require further processing optimization to promote better organization. These observations point to the possibility of using periodic sequence copolymers as a way to tune the π -stacking and promote inter-chain organization useful for charge transport in organic electronics. Incorporation of selenophene into a material, while maintaining organized

and ordered packing arrangements can be achieved with regular placement along a polymer chain as demonstrated with using periodic sequences. Therefore, all of the potential advantages of using the selenium atom, such as stronger dipole and larger atomic-size to promote favorable intermolecular interactions can be realized without the draw-backs of less favorable processing and mixed organization of conjugated polymer chains. 3.7. The Band Structure of Periodic and Random Copolymers Probed by Voltammetry and Absorption Spectroscopy

The band structure of random and periodic copolymers was probed using cyclic voltammetry (CV) to measure the oxidation (E_{ox} , V) and reduction (E_{red} , V) potentials of the respective HOMO and LUMO, coinciding with Ultra-Violet-Visible absorption spectroscopy (UV-vis) to estimate the optical band gap by measuring the solid-state absorption edge (v_{edge} , eV). These two techniques combined, provide a general overview of a conjugated polymer's band structure and the range of light absorption advantageous for photovoltaics.



Figure 3.12. Electrochemical analysis of the second cyclization measuring current (uA) vs. Potential corrected vs. Ferrocene (V) *Top*: Random copolymers and *Bottom*: Periodic sequence copolymers a) *r*-T-Se₃₂ b) *r*-T-Se₅₃ c) *r*-T-Se₆₅ d) T-T-Se e) T-Se f) T-Se-Se. *Inset*: Measured oxidation (E_{ox}) and reduction (E_{red}) potentials (eV) for the respective polymers.

Cyclic voltammetry measurements were performed using a glassy carbon working electrode, coupled with a platinum coil counter electrode, a silver wire pseudo reference immersed in 0.1 M TBAF/MeCN electrolyte solution. All series were corrected vs. ferrocene to determine the electrochemical potential onsets of the oxidation and reduction of the copolymers, CV curves were depicted in Figure *3.12*.

Polymer	X _i Se Content	Solution λ_{max} (nm)	Solid-State v _{Edge} (nm)	$(E_{ox} - E_{red})$ $E_{g} \; (eV)$	DFT: λ_{max} (CHCl ₃) (eV)
P3HT	0	453	1.90	2.25	2.43
<i>r</i> -T-Se ₃₂	0.32	465	1.79	2.12	-
T-T-Se	0.33	466	1.81	2.01	2.37
T-Se	0.50	473	1.77	2.17	2.34
<i>r</i> -T-Se ₅₃	0.53	473	1.73	2.05	-
<i>r</i> -T-Se ₆₅	0.65	476	1.71	1.86	-
T-Se-Se	0.66	480	1.72	1.88	2.32
P3HSe	1	493	1.65	1.84	2.27

Table 3.3. Electrochemical and Optical Properties of Random and Periodic Copolymers

With the exception of periodic copolymer T-Se, results obtained for random and periodic copolymers of similar selenophene content were in good agreement with each other with respect to measured quasi-reversible oxidation and quasi-reversible reduction potential onsets (\pm 0.1 eV), notated in *Figure 3.12*. Electrochemical analysis also revealed that the oxidation onset of both random and sequence copolymers decreased with increasing selenophene content. This indicated that the HOMO was raised with increasing selenophene content, regardless of composition. The difference between the oxidation and reduction potentials provided the electrochemical band gap

and showed that the inclusion of higher selenophene content reduces the band gap, *Table 3.3*.

Excitation energies (eV) of oligomers of different sequences and lengths of up to 12 heterocycles were calculated using DFT, *Table 3.3*. We considered planar structures since, in the solid state, packing forces from π stacking are expected to favor planar



Figure 3.13. *Left Panel*: UV-vis solution spectra and *Right Panel*: solid-state profiles of (top) periodic copolymers (T-T-Se (teal), T-Se (blue), T-Se-Se (pink)) and (bottom) random copolymers (r-T-Se₃₂ (teal), r-T-Se₅₃ (blue), r-TSe₆₅ (pink)).

configurations. Experimentally, the optical properties of periodic and random copolymers were also probed both in solution and by solid-state UV-vis spectroscopy, *Figure 3.13*. Solution spectra revealed a red-shift in absorbance maxima, *Table 3.3*, with the increase of selenophene content regardless of monomer ordering. Both the experimentally observed excitation energy (λ_{max} , nm) of periodic and random copolymers and those computed using TDDFT on oligomers of length 12 show linear dependence on the proportion of selenophene rings.

This correlation has also been observed for random copolymers reported in literature.¹¹ The maximum absorbance energy (eV) in solution was therefore compared for both periodic and random copolymers, including those reported in literature, illustrated in *Figure 3.14*. Overall, experimental results are in good agreement with literature



Figure 3.14. Comparison of the energy determined by the absorbance maxima in solution UV-vis profiles for both random (Teal) and periodic (purple) copolymers along with random copolymers reported in literature (Brown).

results are in good agreement with literature reports illustrating that the decrease in absorption maxima is dependent on the overall composition of the polymer, irrespective of monomer ordering.

Analysis of the solid-state UV-vis spectra, revealed that systematic reduction of band gap with increasing selenophene content is also observed for the bulk structures, *Table 3.3*. This trend is agreement with the calculated electrochemical band gap that is slightly higher in energy. The reduction in band gap can be rationalized as a result of incorporating a larger heteroatom selenium, which is more polarizable, into the delocalized polymer chain.⁶⁶⁻⁶⁸ Theoretical studies based on an exciton model of the excited state with the exciton coherently delocalized along the chain was carried out by Dr. David Yaron. The model ^{69,70} investigated the influence of oligomers ranging from 2 - 12 heterocycles with varying selenophene content. This demonstrated that the relative energy difference between heterocycles is small compared to the coupling energy, therefore the wavefunction describing the delocalized exciton averages over the heterocycles, and its respective energy depends on the overall composition, and not monomer ordering.

3.8. Characterizing Vibronic Structure of Periodic and Random Copolymer

As described in *Chapter 2, Section 2.6*, solid-state UV-vis spectra of random and periodic copolymers were deconvoluted into ordered and disordered components using a combination of Spano and co-workers ordered aggregate model⁷¹⁻⁷³ and a gamma function to describe the amorphous fraction of material. The outline and constraints of this fitting are described in *Appendix 1*. The exciton bandwidth (*W*), linewidths (σ) and vibronic spacing (E_p) were determined by using a series of Gaussians to describe the electron-phonon coupled transitions. A fitted gamma function with a given shape (α) and scale (β) characterized the amorphous contribution at higher energy.



Figure 3.15. Deconvolution of UV-vis profiles using Spano's modified Franck-Condon fit, depicting *i*) Experimental data (Black) *ii*) Individual Gaussians (Blue, dashed) and *iii*) Total curve as the sum of Gaussians (Red, Dashed) for *Panel a*) Random copolymers and *Panel b*) Periodic copolymers.

Tables of the fitted parameters are listed in *Appendix 1*. These parameters enabled us to evaluate how monomer ordering impacts the electron-phonon coupled transitions from the ground (S_0) to excited state (S_1) .

Initial examination of solid-state curves revealed up to 3 distinct peaks of varying intensity in the periodic copolymer series, whereas random copolymers showed a broad shoulder representing the A_{0-0} vibronic transition. Spano's fitting of ordered aggregates was applied to random and periodic copolymers, with fitting parameters



Figure 3.16. Exciton Bandwidth (W, meV) with respect to Selenophene Content for homopolymers P3HT and P3HSe (Purple), Random copolymers (Black) and Periodic copolymers (Red).

listed in *Table S3.1, Appendix 1*. Overlays of the Gaussian peaks and their resulting sum are depicted in *Figure 3.15*. In the resulting fit Gaussian components for periodic copolymers all showed relatively narrow linewidths ($\sigma < 0.07$) with vibronic spacing in the range of (0.167 – 0.170 eV). The random copolymer series revealed broader linewidths ($\sigma > 0.09$) with vibronic spacing in the range of (0.189 – 0.195 eV). An immediate trend became apparent when comparing the exciton bandwidth of random and periodic copolymers, *Figure 3.16*. Random copolymers exhibited larger values of *W*, calculated from *Equation 1, Appendix 1.*⁷³ Periodic copolymers revealed a lower value exciton bandwidth, pointing to a more delocalized structure.⁷¹⁻⁷³ This indicates that higher disorder, with more pronounced exciton localization occurring in random copolymers.



Figure 3.17. Deconvolution of UV-vis Profiles *i*) Experimental data (Light Blue) *ii*) Individual Gaussians (Blue) *iii*) Gamma distribution (Black) and *iv*) Total curve fit from the integrated sum of (ii + iii) (Red) for) for *Panel a*) Random copolymers and *Panel b*) Periodic copolymers.

The total absorbance spectra were fitted using both Gaussian and gamma functions (described in *Table S3.2, Appendix* 1). Comparisons of the best fit with the inclusion of the gamma function for random and periodic copolymers are depicted in *Figure 3.17*. Additional comparisons of the Spano fitting 'residual' shape and gamma functions used to describe the amorphous fraction are shown in *Appendix 1*. The amorphous fraction accounted for approximately 40 – 45 % of the total spectra. Random copolymers showed broader linewidths ($\sigma > 0.95$) with a gamma curve FWHM ($\gamma_{FWHM} > 0.75 \text{ eV}$) in comparison to periodic copolymers linewidths ($\sigma < 0.08$) and gamma curve FWHM ($\gamma_{FWHM} < 0.67 \text{ eV}$). This indicates less homogeneity and more spectral broadening for the random copolymers in comparison to periodic copolymers. Overall, these deconvolution methods point to the broader character of transitions in the random copolymer. This approach may prove to be one of the more sensitive methods to characterize the impact of monomer ordering at an atomic level.

3.9. Summary of Findings

In summary, we have designed and synthesized several copolymers both with random and periodic monomer arrangements, that systematically varied composition. Dimeric and trimeric monomer sequences were utilized in conjunction with applied CTP methods to afford periodic conjugated polymers with controlled molecular weights and relatively low dispersities. Random copolymers were also synthesized by CTP methods to afford high molecular weight materials with similar dispersities and composition as the periodic counterparts.

The random and periodic copolymer sequences have a predictable impact on the electronic properties of the materials as determined by UV-vis, CV and computation. Theory indicated that changes in bond lengths from the chalcogen to the diene may introduce curvature in the polymer backbone that can perturb organization, impacting macroscopic properties such as enthalpy of melting (DSC), reducing fibril widths (AFM), and generating higher disorder within atomic packing arrangements (GIWAXS). X-ray scattering revealed that inter-chain organization of random copolymers significantly differ from the periodic systems. Larger π -stacking distances and higher degrees of azimuthal disorder are present in the random copolymers in comparison to most periodic structures of similar composition. Deconvolution of solid-state UV-vis spectra revealed lower exciton bandwidths with more homogeneous electron-phonon coupled transitions for periodic sequences in comparison with random copolymers. This study demonstrated that systematic "sequencing" of thiophene-selenophene copolymers improved chain organization and order at a nanoscale level. As such, this design construct should be a crucial consideration for the development of more complex architectures, particularly when attempting to promote favorable inter-chain packing and structural organization in bulk films for organic electronics.

3.10. Experimental Procedures

Physical analysis followed standard experimental procedures described in Appendix 2.

All spectral analyses were performed using Mathematica Software. AFM images were processed using Gwyddion Software[®]. 2D GIWAXS images were recorded at Cornell High Energy Synchrotron Source (CHESS) at station D1, run by Dr. Detlef Smilgies. The work at CHESS is supported by the National Science Foundation under award DMR-1332208.

General Polymerization of Random Copolymers.

Table 3.4. Random copolymers polymerization conditions and resulting weight and yields

Polymer	AA	BB	CC	Target #	$X_{i} \operatorname{Se}$	Mn ^b	Ð	Yield
	(mmol)	(mmol)	Conc. [M]	Rings	Content ^a			(%)
<i>r</i> -T-Se ₃₂	0.4	0.2	0.01	150	32	32,300	1.31	38
<i>r</i> -T-Se ₅₃	0.3	0.3	0.01	150	53	30,300	1.26	31
<i>r</i> -T-Se ₆₅	0.2	0.4	0.01	150	65	28,700	1.23	55

^aPercent selenophene content determined by 500 MHz ¹H-NMR analysis in CDCl₃

^bGPC traces were recorded at 40 °C versus polystyrene standards using THF as the eluent.

Random Copolymer Polymerization. In a N₂ filled glovebox, separate 0.1 M stock solutions of both 2-bromo-3-hexylthiopene (Compound **AA**) and 2-bromo-3-hexylselenophene (Compound **BB**) in THF were prepared prior to all polymerizations. Appropriate volumes of compound **AA** (mmol) and compound **BB** (mmol) was added to separate oven-dried 20 mL glass vials each equipped with a magnetic stir bar. TMPMgCl·LiCl solution (0.8 M, 1.2 equiv.) was then added to each solution and was stirred at room temperature for 2 h. In the glovebox, the reaction mixtures were then transferred and combined to a 250 mL Schlenk flask equipped with a magnetic stir bar and diluted to (*CC* M) concentration respectively in THF for the (M/Cat.: 150) polymerizations. The flask was then sealed and removed from the glovebox and then placed on a Schlenk line atop a stir plate.

Under a N₂ purge, a calculated amount of Ni(dppp)Cl₂ (0.667 mol %) was then quickly added to the solution in one portion. The polymerization was stirred at room temperature for 15 min, and then quenched with 6 M methanolic HCl and stirred for an additional 10 minutes. The resulting precipitate was collected by gravity filtration, washed with methanol and dried overnight. The polymer was then re-dissolved in 1 - 2 mL THF, re-precipitated in methanol (200 mL), washed with methanol, acetone and hexanes in several successions and dried overnight.

Random Copolymers 33% Se content: Yield: M/Cat. = 150 (45 mg, 38 %). ¹H NMR (500 MHz, CDCl₃) δ 7.21 (s, 1H), 7.15 (s, 0.49H), δ 7.0 (s, 2.11H), 6.95 (s, 1.07H), 2.88 – 2.71 (m, 4H), 1.76 – 1.62 (m, 4H), 1.5 – 1.42 (m, 4H), 1.42 – 1.26 (m, 8H), 0.98 – 0.85 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 141.6, 139.9, 137.8, 135.8, 133.8, 131.7, 130.5, 128.7, 31.66 and 30.64, 30.57, 30.52, 30.47, 29.53, 29.44, 29.29, 29.23, 22.6, 14.08 (2 overlapping signals).

Random Copolymers 50% Se content: Yield: M/Cat. = 150 (35.4 mg, 31 %). ¹H NMR (500 MHz, CDCl₃ δ 7.21 (s, 1H), 7.15 (s, 1.14H), δ 7.0 (s, 0.86H), 6.95 (s, 1.06H), 2.88 – 2.71 (m, 4H), 1.77 – 1.67 (m, 4H), 1.51 – 1.42 (m, 4H), 1.42 – 1.22 (m, 8H), 0.98 – 0.80 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 141.3, 139.8, 137.7, 135.6, 132.2, 131.6, 129.1, 128.6 and 31.7 and 30.63, 30.56, 30.51, 30.46 and 29.53, 29.44, 29.29, 29.23, and 22.62 (2 overlapping signals) and 14.07. *Random Copolymers 66% Se content:* Yield: M/Cat. = 150 (59.6 mg, 55 %). ¹H NMR (500 MHz, CDCl₃) δ 7.21 (s, 1H), 7.15 (s, 1.87H), δ 7.0 (s, 0.53H), 6.95 (s, 1H), 2.88 – 2.71 (m, 4H), 1.76 – 1.62 (m, 4H), 1.5 – 1.42 (m, 4H), 1.42 – 1.26 (m, 8H), 0.98 – 0.85 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 141.4, 139.8, 137.7, 135.7, 132.2, 131.6, 129.1, 128.6, 31.94 and 31.67 and 30.63, 30.56,

30.50, 30.46 and 29.53, 29.29, 29.23 and 22.6 (2 overlapping signals) and 14.08.

Fibril Width Analysis

Experimentally Determined Fibril Width. AFM phase-shift images, were processed using Gwyddion Software©. (~ 50 - 100) lines were drawn across individual fibrils with a recorded length where the length of each line represented the nanofibril width (nm). The total number of lines was tabulated and depicted as a histogram to represent the fibril width distribution.

Calculated Fibril Width. The calculated fibril width was determined from the average total number of rings within the number average molecular weight (M.W.). (*Note:* GPC overestimates conjugated polymers molecular weight such as P3HT by a factor of 1.67) The total number of rings was calculated by dividing the M.W. by the average repeat unit weight. The average repeat unit weight was calculated by the mol fraction of (T: Se), *Equations 7a-b*. To calculate the chain width, the total number of thiophene and selenophene rings (ring width: 2.55 Å and 2.64 Å, respectively) and the total number of C_{sp}^2 - C_{sp}^2 bonds (length: 1.47 Å, (# rings – 1)) within the chain was added to determine the theoretical average chain length, *Equation 7c*.

$$(X_i \text{ Se}) * 213 \text{ g mol}^{-1} + (1 - X_i \text{ Se}) * 166 \text{ g mol}^{-1} = (repeat unit weight)$$
Equation 7a

$$r \cdot \text{T-Se}_{32} : X_i = 0.32 | \text{T-T-Se} : X_i = 0.33$$

$$r \cdot \text{T-Se}_{53} : X_i = 0.53 | \text{T-Se} : X_i = 0.50$$

$$r \cdot \text{T-Se}_{65} : X_i = 0.65 | \text{T-Se-Se} : X_i = 0.66$$

M.W. * (1.67⁻¹) ÷ (repeat unit weight) = Total # of rings Equation 7b

Theoretical Chain Width (Å) = $(x * width_T) + (x * width_{Se}) + ((1 - x) * bond_L)$ Equation 7c

x = Total # of rings

width_T = thiophene ring width (Å)

width_{Se} = selenophene ring width (Å)

$$bond_L = C_{sp}^2 - C_{sp}^2 bond length (Å)$$

Table 3.5. Calculated & experimental fibril width (nm) and # of rings within chain

Polymer	M.W.ª	Calculated Total # Rings ^b	Calculated Fibril Width (nm) ^c	Experimental Average Fibril Width (nm) ^d	Exp./Calc. % ^e
r-TSe ₃₂	32,300	107	43.2	27.7	64
r-TSe ₅₃	30,300	95	38.5	28.2	73
r-TSe ₆₅	28,700	87	35.4	26.8	76
T-T-Se	32,100	105	42.4	30.4	72
T-Se	39,800	126	51.1	21.4	42
T-Se-Se	39,000	117	47.6	33.0	69

^aMolecular weight determined from GPC traces (40 °C) vs. polystyrene standards using THF as the eluent ^bTotal number of rings calculated from Equation 7b.

^aCalculated fibril width determined from Equation 7c

^aAverage Fibril width calculated from average line widths drawn in AFM phase-shift images

^aThe experimental/calculated fibril width % represents the percent of total polymer chain length that contributing to average fibril width (nm).

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Chapter 4

Evaluating the Impact of Ester Side-Chain Substitution in PolyFurans and PolyThiophenes

4.1. Introduction

One of the central considerations with conjugated polymers is their long term environmental stability.¹⁻⁶ While these materials have tremendous potential in electronic devices due to their interesting photo-physical properties and charge mobility, they often suffer from limited chemical stability, particularly in solution in the presence of oxygen. In general, a wide variety of aromatics are susceptible to oxidation upon reaction with singlet oxygen (${}^{1}O_{2}$, ${}^{1}\Delta_{g}$). The



Figure 4.1. Jablonski diagram of the formation of singlet oxygen from a photosensitizer. Reproduced with permission Reference 7.

formation of singlet oxygen is achieved by excitation of a discrete photo-sensitizer, which undergoes intersystem crossing to the triplet state, and then energy transfers with triplet oxygen forming singlet oxygen,⁷⁻¹⁰ *Figure 4.1*. Unlike small

molecule aromatics which may only absorb UV radiation and require an additional photosensitizer to generate singlet oxygen, conjugated polymers absorb within regions of the visible spectrum, and consequently can act as their own photosensitizer to generate singlet oxygen.⁹⁻¹² If a portion of the polymer is susceptible to oxidation by this reactive molecule, it can lead to loss of conjugation along the main chain and destruction of the desired electronic properties of the

macromolecule. The evaluation of this type of oxidation is complicated by the number of reactive sites within a single polymer chain, how reactive the aromatic repeat units are to singlet oxygen, and the efficiency of triplet formation for the polymeric material.¹³⁻¹⁷

Polyfuran presents an interesting test case for exploration of these photo-driven oxidation processes. The Diels-Alder reaction of furan with singlet oxygen is very efficient,¹⁸⁻²⁵ and consequently, information on decomposition can be achieved quickly. Moreover, homopolymers derived from Group 16 heterocycles such as polythiophenes, polyselenophenes and polytellurophenes are known to form triplets through intersystem crossing of singlet excitons.²⁶⁻²⁹ Herein, we evaluated how poly(3-hexylfuran) P3HF behaves in the presence of oxygen and light. Spectroscopic evidence points to the polymer acting as its own photosensitizer, generating singlet oxygen, forming endoperoxides along the chain, which subsequently result in polymer decomposition.^{11,18,19,24,30} Two paths were considered as a means to improve the photosensitivity of polyfuran i) Placing furan rings in-between other units with better photo-stability such as thiophene rings. ii) Attachment of electron withdrawing moieties, such as alkyl-ester side-chains. Homopolymer poly(3-hexylesterfuran) (P3HEF) alternating copolymer and poly(3hexylesterfuran-alt-3-hexylthiophene) (P3HEF-a-P3HT) were polymerized using Suzuki-Miyaura catalyst-transfer polycondensation³¹ affording materials with predictable molecular weights and relatively narrow molecular weight distributions.

Interestingly, these materials were found to be significantly more stable than their alkyl analogs in the presence of air and light. This stability is due to a number of factors, but the most interesting feature of P3HEF is its propensity for adjacent aromatic rings to adopt a cis configuration resulting in a helical structure. UV-Vis spectroscopy (solution and solid-state), Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) and computation (DFT) all provide corroborating evidence for this unusual helix formation. Additional structural studies of poly(3-hexylester thiophene) and alternating copolymer Poly(3-hexylesterthiophene-alt-3-hexylthiophene) (P3HET-*a*-P3HT) will show that the ester side-chain polythiophenes do not have a helical structure, but the side-chain does impact organization and physical properties such as thermal decomposition (TGA), crystallinity (DSC) and spectroscopic response (UV-vis). These studies will demonstrate the importance of framework design for conjugated materials, as simple adjustments by using oxygen and sulfur heteroatoms leads to dramatically different structures, physical properties and stimuli response.

4.2. Photo-stability Measurements of P3HF

We have explored catalyst-transfer polycondensation (CTP) as a method to construct P3HF previously.³² CTP enables the preparation of conjugated macromolecules via chain-growth polymerization rather than step growth, and it has been used extensively to synthesize P3HT³³⁻³⁷ as well as poly(3-alkylselenophene) P3ASe and poly(3-alkyltellurophene) P3ATe.³⁸⁻⁴³ While, the polymerization of 3-alkylfuran monomers does not proceed as smoothly as the other chalcogenbased rings, it can afford materials with lower dispersities, though it does not provide control over end groups and molecular weights.



Figure 4.2. UV-Vis normalized absorption spectra of *Left*: P3HF and *Right*: its relative change in peak intensity over time (sec).

The photo-stability of the synthesized P3HF was probed using UV-Vis spectroscopy. Its instability is apparent in a series of spectra collected upon exposure of the polymer solution (THF) to light and air, *Figure 4.2*. A blue shift in the absorption maximum (λ_{max}) is observed over a period of 5 h, along with broadening and a loss of signal intensity.

Scheme 4.1. Possible degradation products of furan via an endoperoxide intermediate.



These changes in the spectral features indicate a significant change in the polymeric material. We hypothesize that the polymer is behaving similarly to a photosensitizer, whereby upon photoexcitation it undergoes intersystem crossing to the triplet state which then activates singlet oxygen.⁹ Upon generation of singlet oxygen ($^{1}\Delta_{g}$), furan rings along the polymer main chain can react (*Scheme 4.1*) causing the observed loss of conjugation in UV-vis.



Figure 4.3. *Left*: P3HF, Normalized absorbance of IR vibrational frequencies (2000 – 700 cm⁻¹) before (Black) and after visible light irradiation in air (Red). *Right*: P3HF IR peak intensities of irradiation probed over time (sec), comparing the decay of furan ring peaks (1542 cm⁻¹, Black) and formation of carbonyl peaks (1667 cm⁻¹, red) due to exposure to visible light.

Another potential cause for the blue-shift in the λ_{max} is chain-scission of the polymer backbone. This was characterized using gel permeation chromatography (GPC) to examine any changes in molecular weight before and after exposure to light and air over time, *Appendix 1*. An initial rapid decrease in molecular weight over the first 15 min was followed by diminished rate of change after several hours with small molecular weight fragments forming. The change in the GPC profile is likely a consequence of two features: i) some chain scission which generating lower molecular weight fragments and ii) the loss of conjugation upon ring-opening limits aggregation of the polymer in solution with a hydrodynamic volume closer to the true polymer molecular weight.



Figure 4.4. *Left Panel*: Model Compound TFT *top*: UV-vis degradation studies and *bottom*: ¹H NMR *Right Panel*: Model Compound FFF *top*: UV-vis degradation studies and *bottom*: ¹H NMR

To better elucidate the photo-degradation products of P3HF, both FTIR and NMR were employed for structural analysis. P3HF produced two characteristic signals: a $v_{C=C}$ stretch corresponding to the furan ring (1542 cm⁻¹) and an aliphatic v_{C-H} stretch at 2856 cm⁻¹. Both signals are consistent with prior reports on oligofurans.^{44,45} Upon exposure of P3HF to visible light, the signal at 1542 cm⁻¹ disappeared and an isolated alkene stretch at 1574 cm⁻¹ appeared, along with three stretches tentatively assigned as $v_{C=O}$ bands at 1667, 1734 and 1781 cm⁻¹. The intensity of these signal's steadily increased over time (1667 > 1734 >> 1781 cm⁻¹), *Figure 4.3*. Additional IR assignments are summarized in *Table 4.1*.⁴⁴⁻⁴⁶

A model study was performed employing an alternating thiophene-furan-thiophene trimer (TFT) with one furan ring to assist in NMR analysis of the degraded P3HF. Initial tests of TFT by UV-vis revealed an onset absorbance in the UV range ($\lambda_{max} = 390$ nm). Visible light degradation studies required the use of a singlet oxygen generator, Rose Bengal (RB) over the course of 5 minutes. Photo-degraded TFT products could then be observed by UV-vis and ¹H NMR. UV-vis photo-stability tests in air revealed essentially complete loss of signal intensity with only 18.5% remaining, Figure 4.4. The main degradation products of the furan ring characterized by ¹H NMR, *Figure 4.4*, were readily assigned as either 1,4-dithiophene-2-butene-1,4-dione (δ 7.1 – 7.2 ppm, dd) and the enol ester (δ 6.2 ppm, d) or the epoxide analog (δ 4.7 ppm, s) as shown in *Scheme* 4.1. A second model study was performed utilizing an unsubstituted trimer of furan (FFF) to mimic the inclusion of furan ring end-groups that was exposed to visible light and air in the presence of RB of a period of 5 minutes. UV-vis studies of FFF showed an onset absorbance in the UV range with absorbance maxima at ($\lambda_{max} = 331$ nm), with a corresponding loss of signal intensity upon light exposure with only 24.5 % remaining, Figure 4.4. ¹H NMR photo-stability tests revealed similar degradation products as TFT, as well as proton shifts in the range of 9 - 11 ppm indicating the formation of aldehyde and carboxylic acid groups after exposure to visible light and air, Figure 4.4. These ¹H NMR signals corroborate with the observed formation of new carbonyl signals in IR for the polymer. As each furan ring is a potential reactive site, multiple product are possible,

where full assignment remained difficult, and therefore were mainly used to confirm formation of specific functional groups.

Degradation tests by ¹H NMR of P3HF also revealed complete loss of the ring peaks in the aromatic region, and the formation of new peaks in similar regions as the model compound degradation studies, *Appendix 1*. The disappearance of the signals for the furan ring along with the appearance of new alkene and carbonyl signals (*Figure 4.4, Right*) provides strong evidence for a change in the polymer microstructure. P3HF is acting as a photosensitizer, exciting oxygen which can then, in turn, react with the polymer backbone by a Diels Alder reaction and form an endoperoxide intermediate. Subsequent ring opening can result in multiple possible products particularly in the presence of H₂O. The formation of carbonyl stretches at higher frequencies (above 1750 cm⁻¹) point to the formation of carboxylic acid moieties, likely resulting from a chain scission process. A challenge in photo-degradation product assignment is the structure of the polymer chain itself.

4.3. Photo-stability Measurements of P3HF-a-P3HT

With the decomposition of P3HF well established and all evidence pointing to Diels-Alder reactivity with singlet oxygen, we then considered the possibility that a copolymer with hexyl-thiophene could be relatively more photo-stable than homopolymer P3HF. Previously reported P3HF-*a*-P3HT³² was utilized as a potential candidate, whereby it was exposed to visible light and air under similar conditions. Somewhat to our surprise, P3HF-*a*-P3HT seemingly degraded more rapidly than homopolymer P3HF, *Figure 4.5*. We believe this is potentially due to electron donation from hexyl thiophene into the furan acting as the 'diene' in the Diels Alder reaction.



Figure 4.5. UV-Vis normalized absorption spectra of *Left*: P3HF-*a*-P3HT and *Right*: its relative change in peak intensity over time (sec).

4.4. Synthesis and Characterization of P3HEF

Given that our pursuits entailed improving the photo-stability of P3HF and not increase the rate of degradation, further analysis of P3HF-*a*-P3HT was not pursued further for this study. However, it did point to a clear indication that tuning the electron density in the furan ring could greatly impact its photo-stability.⁴⁸⁻⁵⁰ This led us to take a second approach to improve the photo-stability using electron withdrawing side-chains. The Noonan group developed a synthetic method to access the ester functionalized polymer (P3HEF) using Suzuki–Miyaura CTP, *Scheme 4.2*.

Scheme 4.2. Suzuki-Miyaura CTP for Synthesizing Ester Side-Chain Polyfurans



Obtained polymers maintained good control over molecular weights with relatively narrow molecular weight distributions, (M_n : 3,100 \oplus : 1.04, M_n : 4,100 \oplus : 1.08, M_n : 5,800 \oplus : 1.06, M_n : 10,200 \oplus : 1.12). Interestingly, the polymerization was much more predictable as compared to the

polymerization of 3-hexylfuran using Grignard methathesis, which was partially attributed to the increased solubility with the ester side chain.



Figure 4.6. MALDI-TOF mass spectrum of P3HEF prepared using 4 mol % of Ni(PPh₃)IPrCl₂ (M_n : 4,100 \oplus 1.08).

The MALDI-TOF spectrum for the polymer, *Figure 4.6*, is indicative of the assigned structure and the MALDI provides further confirmation of the well behaved nature of the CTP reaction with a signal distribution corresponding to terminal H and Br end groups. Interestingly, the Mn values obtained from GPC for P3HEF are much closer to the values obtained by MALDI-TOF, so the overestimation of most conjugated polymers compared to polystyrene standards is less problematic for this type of polyfuran.



Figure 4.7. *Left*: ¹H NMR and *Right*: ¹³C NMR spectra for P3HET (top) and P3HEF (bottom). The NMR spectra for both polymers were collected in CDCl₃ at 22 °C. The star in the ¹³C NMR spectrum of P3HET is residual nonadecane (internal standard) from polymerization.

Subsequently, ¹H and ¹³C NMR spectra were collected for P3HEF, *Figure 4.7*. These NMR spectra were markedly different than spectra we had collected for polythiophenes previously, with broad signals appearing for essentially all nuclei of the repeat unit. Polyfurans have higher barriers to rotation and it is possible that slow molecular motion is producing the observed behavior. This was the first indicator of some unusual structural feature in the polymer. The chemical shifts are consistent with the assigned structure. The ¹³C NMR spectrum is particularly valuable for the assignment. Two signals for the C2 and C5 adjacent to the ring oxygen appear at 146.0 and 141.8 ppm respectively. The C3 and C4 signals are overlapping at 115.2 and 116.7 ppm.



Figure 4.8. *Left*: UV-vis absorption spectra of P3HET (solid line) and P3HT (dashed line) in THF. *Right*: UV-Vis absorption spectra of P3HEF (solid line) and P3HF (dashed line) in THF.

After confirmation of the assigned structure for P3HEF using NMR spectroscopy, we began probing its photo-physical response using absorbance spectroscopy. Replacement of alkyl groups with esters has been shown to impact the electronic transitions in polythiophenes previously. In solution, a relatively small blue shift (450 nm to 430 nm) is observed with P3HET as compared to P3HT, *Figure 4.8.*³² We suspect this is a consequence of increased steric strain imposed by the ester. We anticipated the impact of the side chain change would be minimal for polyfurans, which are much less susceptible to twisting due to steric penalties from specific side chain orientations. Surprisingly, the absorbance profile of P3HEF exhibits a strong absorption in the UV-region (333 nm) with the edge extended to 616 nm, resembling the absorption maxima of trimer FFF, *Figure 4.12*.

4.6. P3HEF Reactivity with Singlet Oxygen

Studies by Scarpati and co-workers⁴⁷⁻⁴⁹ have also found that ester substituted furan forms an endoperoxide and is stable at low temperatures (-15 °C),⁴⁷ indicating that the monomer 3hexylester furan does react with singlet oxygen. With this in mind, the interaction of polymeric form P3HEF with light and air was probed under ambient conditions over a period of 5 hours. Over this given time period, P3HEF's absorbance profile did not change as shown in *Figure 4.9*. This test alone illustrates an improved photo stability in visible light. The alkyl side-chain analog P3HF reveals approximately a 60% reduction in the λ_{max} over the same time period. The vast improvement of photo-stability of polyfurans to a range of hours in comparison to seconds is exciting, but begs questions as to the source of stability: i) What are the limits of P3HEF's stability under illumination, ii) does any degradation products assist in determining the degradation path (aka. Diel Alder ring opening or radical), iii) is P3HEF generating singlet oxygen by acting as a classical photosensitizer. iv) is P3HEF reacting with singlet oxygen. Once we establish P3HEF's behavior with respect to singlet oxygen, we can then re-visit other factors that may influence its photo-stability.



Figure 4.9. UV-Vis normalized absorption spectra of P3HEF illuminated by visible light and air over a period of 5 h.

To better elucidate any structural changes in P3HEF, both FTIR and ¹H NMR were employed to characterize any new functional groups appearing over extended light exposure periods. Special attention was paid to the vibrational frequencies associated with the furan ring $(v_{C=C}: 1542 \text{ cm}^{-1} \text{ and } \delta_{C=C}: 1588 \text{ cm}^{-1})$ whereby any reduction in peak intensities would potentially indicate ring–opening of the polymer backbone. Other characteristic frequencies similar to P3HF included the aliphatic v_{C-H} stretch at 2858 cm⁻¹, with additional IR assignments listed in *Table 4.1.*⁴⁴⁻⁴⁶ A sharp, strong carbonyl stretch around ($v_{C=O}: 1714 \text{ cm}^{-1}$) was apparent from the ester side chain functional group. New peaks did not appear once the sample was exposed to visible light and air over the period of 5 h with no reduction in peak intensities of either the furan ring (v_{Ring}) or formation of new carbonyl peaks ($v_{C=O}$), *Figure 4.10*.



Figure 4.10. *Left*: P3HEF, Normalized absorbance of IR vibrational frequencies (2000–700 cm⁻¹) before (Black) and after visible light irradiation in air (Blue). *Right*: P3HEF IR peak intensities of irradiation probed over time (sec), comparing the stability of furan ring peaks (1540 cm⁻¹, Black) and non-formation of carbonyl peaks (1667 cm⁻¹, red) due to exposure to visible light over 5 h.

Visible light exposure for extended periods of time, (24 hours and above) resulted in the reduction of absorbance intensities measured by UV-vis, and changes in IR peak intensities. From these studies, a few initial observations could be made: (i) Absorbance intensities measured by UV-vis at high energy ($\lambda < 400$ nm) depleted more quickly than absorbance above 400 nm (ii) the polymer solution remained colored over a period of days. (iii) IR peak intensities of the furan ring changed relatively little over a 24 h period, with slight formations of new carbonyl peaks observed around 1800 cm⁻¹, *Figure 4.11*.



Figure 4.11. *Left*: UV-vis of P3HEF exposed to light and air over a period of 7 days and *Right*: IR vibrational frequencies $(2000 - 700 \text{ cm}^{-1})$ before (Black) and after (24 h, Red) exposure to visible light and air.

Multiple changes in IR spectra occurred with longer exposure periods, including loss of furan ring peaks intensities coinciding with the formation of new carbonyl groups and the additional loss the main ester peak intensity. Therefore illustrating that multiple degradation products are being formed with longer light exposure periods. However, the caveat of longer exposure periods is that multiple degradation paths can come into play and as such the isolation of the dominant degradation mechanism remains a challenge.



Figure 4.12. Similar UV-vis degradation profiles developed over different time periods when trimer FFF is in the presence of singlet oxygen generators illuminated by a) Rose Bengal (t = 75 s) and b) P3HEF (t = 18000 s), respectively.

What can be more easily addressed is how oxygen interacts with P3HEF. The founded stability in visible light and air may possibly stem from P3HEF's inability to act as a classical photosensitizer. Therefore, the ability of P3HEF to act as a photosensitizer was compared against

known ${}^{1}O_{2}$ generator RB using model compound FFF. Trimer FFF was exposed to visible light and air with P3HEF acting as the photosensitizer over a 5 hour period, with absorbance measured by UV-vis. It was determined that FFF peak intensity reduced to 44 % after 5 h. A similar test utilizing RB as the photosensitizer showed a similar signal intensity loss after 75 s, *Figure 4.15*. This indicated that P3HEF was indeed generating ${}^{1}O_{2}$ through photosensitization, albeit a 250 times slower rate in comparison to RB.

P3HEF's slower generation of singlet oxygen may be a large contributor to its discovered stability in visible light and air. Therefore, comparative UV-vis model studies were performed with P3HEF as the analyte and RB as the photosensitizer to simulate P3HEF in an environment with a "large" influx of ${}^{1}O_{2}$. For reference, RB generates the same amount of ${}^{1}O_{2}$ that P3HEF is proposed to produce in 12.5 days. Over a period of 75 min, the P3HEF λ_{max} signal intensity degraded by ~0.08 %, with little change in the shoulder intensity above 400 nm, *Figure 4.13*. Notably, over the same time, the photosensitizer RB almost completely degraded.



Figure 4.13. UV-vis photo-degradation absorbance profiles of P3HEF in the presence of photosensitizer Rose Bengal (RB). Note that RB degraded with little impact on P3HEF when illuminated by visible light and exposed to air over the course of 75 min.

Polymer P3HEF revealed no degradation in the same time period that trimer FFF's peak intensity decreased by 44% in the presence of RB under similar conditions. This result strongly signifies that although P3HEF is a poor photosensitizer, the quantity of ¹O₂ produced by P3HEF

in-situ is not the attributor to its given photo-stabilization. The degradation of RB illustrates that ${}^{1}O_{2}$ is indeed being produced and reacting, but not with P3HEF over shorter periods of time. Given this result, we can now re-visit what structural or electronic features that may be influencing P3HEF's photo-stability.

4.5. Solid-State Characterization of P3HEF

To better elucidate the structure of P3HEF, solid-state characterization by UV-vis, thermogravimetic analysis (TGA) and differential scanning calorimetry (DSC), atomic-force microscopy (AFM) and grazing-incidence X-ray scattering (GIWAXS) were carried out to examine photo-physical and thermal response in the solid state, and examine the bulk morphology and packing structure.



Figure 4.14. *Left*: UV-vis absorption spectra of P3HF measured in solution (Black, solid line), and in solid-state (Red). *Right*: UV-Vis absorption spectra of P3EHF measured in solution (Black, solid line) and in solid-state (Red).

Solid-state absorbance profiles revealed no spectral red-shift or vibronic fine-structure (*Figure 4.14, right*), commonly observed in conjugated polymers such as P3HT. This is a highly unusual behavior, and when examining the alkyl-side chain analog, P3HF, we do see a red-shift when transitioning from solution to solid-state, with vibronic peaks (*Figure 4.14, left*) as expected.



Figure 4.15. *Left*: TGA of P3HEF and *Right*: DSC of P3HEF prior to decomposition with no apparent transitions (10 °C min⁻¹, Blue) and with fast scanning rates above T_d (50 °C min⁻¹, Red).

Further studies of the solid-state character of P3HEF involved thermal characterization. TGA explored the thermal decomposition range, revealing an initial decomposition temperature of 150 °C and a 5 % weight loss temperature of 238 °C, *Figure 4.15*. The dual peak decomposition is attributed to the initial loss of ester side-chains, followed by the carbonization of the polymer backbone above 400 °C. DSC scans up to 350 °C revealed no amorphous or crystalline transitions, suggesting that the material may be highly crystalline, but does not melt prior to decomposition. DSC scans above 350 °C were performed using faster scanning rates (50 °C min⁻¹) and revealed a melting transition peak at 368 °C, but sample degradation prohibited further analysis, *Figure 4.15*.

GIWAXS studies carried out at the Cornell's synchrotron facilities (CHESS) characterized thin-films cast atop native oxide (SiO₂) wafers that additionally exhibited additional Bragg features in an apparent hexagonal pattern, that are uncharacteristic of the P3HT family, *Figure 4.16 c*.

Before assignments to the structural features could be made, density functional theory (DFT) calculations of the geometry optimization of P3HEF with (6 - 13) -mers in length. The optimized structure showed a strong preference to an all-cis configuration, causing the chain to coil into a helix form, *Figure 4.16 a – b*. This was very exciting, as polythiophenes typically adopt an all-trans, linear configuration. Studies thus far for other helical conjugated polymers generally require bulky substituents to sterically confine the backbone into a cis-conformation.⁵⁰⁻⁵³

However, with P3HEF this appears to not be the case. Calculations show that a trans-conformation places the heteroatom of the furan ring in the least favorable energetic position with respect to the ester side-chain, due to steric repulsion. As such, the energy minima maximizes the distance between the furan heteroatom and the side-chain by adopting a cis conformation.



Figure 4.16. DFT calculations of all cis-conformation helical structures of P3HEF a) Top-view b) Side-view c) 2-D GIWAXS pattern of P3HEF with hexagonal pattern arising from d) stacked columnar helices and e) inter-coil π -stacking within individual of helices.

This structuring points all oxygen atoms in the ring towards the inner coil with all sidechains pointing away from the center of the helix taking on an overall cylindroid shape, *Figure* 4.16 a. A full helix turn is approximately 6.5 rings before a second coil layer of the helix begins to π -stack with favorable inter-coil interactions, *Figure* 4.16 b. As cylindroid helices begin to stack on top of each other, the overall structure appears as a well-organized hexagonally-packed array, comprised of multiple stacked helices, *Figure* 4.16 d–e. An inter-cylindroid, center-to-center helices spacing is approximately 24.36 Å, with a π -stacking of 3.4 Å between coil layers of individual helices. Full crystallographic assignments are currently underway, but unavailable at this time.

The hexagonal packing of multiple cylindroid helices gives rise to additional periodicity within the polymers structural organization. The combination of horizontal, vertical and diagonal spacing between helices measured center-to-center provides the hexagonal Bragg peak patterns highlighted in GIWAXS 2D patterns, shown in *Figure 4.16*. The ordered arrangement arises from adjacent cylindroid stacks lying with π -stacking parallel to the substrate surface.

Ultra-thin polymer films cast atop glass substrates were inspected under optical microscope to reveal aggregates that appear to grow radially from a center nucleation site, generating 'flower' aggregates depicted *Figure 4.17*, where the layering of the 'flowers', forms a non-continuous red film. AFM images examined individual polymer aggregates cast from dilute solutions of THF (nM), atop HOPG substrates. Structures revealed long filamentous co-facial aggregates of cylindroid particles with regularly spaced 'ridges' along individual aggregates, *Figure 4.17*. The hexagonal packing of these filaments in plane of the surface assists explaining GIWAXS patterns in *Figure 4.16 c*.



Figure 4.17. *Left*: Optical microscopy of P3HEF of films *Inset*: Scale bar 100 µm, *Right*: AFM phase-shift images of P3HEF, *Inset*: Scale bar 250 nm.

The structure of P3HEF may be a large contributor to its stability in air. It is possible that the outer 'layer' of the helices is acting as a 'barrier' helping to prevent access of singlet oxygen to the furan main-chain. The top and bottom 'faces' of the cylindroid remains exposed to air, but tight π -stacking (3.4 Å) may be preventing singlet oxygen access to the main chain furan rings. The relative access to oxygen may also explain the poor photosensitizing capability, as triplet oxygen needs to be in close proximity for singlet oxygen formation to occur. We propose that the structural organization of P3HEF forming a helical configuration from all cis-geometry conformations is likely helping to deter singlet oxygen from reacting with the polymer's main chain providing enhanced photo-stability.

A second source of stability most likely stems from the inclusion of an electronwithdrawing side-group on the 'diene' (i.e. furan ring). The side-chain could be electronically assisting photo-stability by pulling electron density away from the furan ring's active sites for Diels Alder activity. Therefore, ester-side chains placed along a polyfuran backbone has a twofold effect to helping improve photo-stability. Further studies include assessment of just the electronic contribution of the side-group with the study a linear, all-furan backbone, estersubstituted polymer. This would eliminate the effect of helicity, and directly compare two polymers with linear chain geometries. This work is currently underway.

4.7. Exploring Alternating Copolymers with 3-HexylEster Furan Units

Given the helical nature of P3HEF, studies employing GIWAXS was extended to alternating copolymer P3HEF-*a*-P3HT (M_n : 4,600 D: 1.39), *Figure 4.18*. The copolymer contained 3-hexylester furan and 3-hexyl thiophene units and synthesized by Suzuki CTP³¹ courtesy of Dr. Yunyan Qiu. The alternating copolymer also exhibited a similar hexagonal pattern as P3HEF.

This indicates that the alternating copolymer is also helical in structure, packing cylindroid stacks in hexagonal arrays, depicted in *Figure 4.16 d*. Therefore, the Bragg peaks features are tentatively assigned as the center-to-center inter-cylindroid spacing of 24.1 Å, with a π -stacking of 3.56 Å between coil layers of individual helices. Crystallographic assignments and further structural analysis including AFM and theoretical calculations are currently ongoing and unavailable at this time.



Figure 4.18. P3HEF-a-P3HT, *Left*: GIWAXS 2D scattering pattern, *Scale Bar*: Log-scale scattering intensities *Right*: Radial profiles of out-of-plane (*top*) and in-plane (*bottom*) Bragg features. *Inset*: Assigned d-spacing.

The UV-vis absorbance spectra of P3HEF-*a*-P3HT revealed a red-shifted, sharp, absorbance maxima ($\lambda_{max} = 372$ nm) with a broad absorbance edge extending to 656 nm, *Figure*



Figure 4.19. UV-Vis normalized absorption spectra of *Left*: P3HEF-a-P3HT and *Right*: its relative change in peak intensity over time (sec).

4.19 left. UV-vis degradation studies exposed P3HEF-*a*-P3HT to light and air over a 5 hour time period, and witnessed a peak intensity reduction to 55.4%, *Figure 4.19 right*. The degradation could also stem from the hexyl thiophene unit acting as an electron donor on the furan-ester 'diene'. Experiments with copolymer P3HF-*a*-P3HT also showed an increased rate of degradation in comparison to P3HF. Therefore, it can be proposed that the alternating copolymer P3HEF-*a*-P3HT is degrading by singlet oxygen stemming from electronic donation of the hexyl thiophene unit. The addition of the thiophene unit may also cause the helix to be not as thermodynamically stable with the helical structure partially unwound in solution. This example highlights, that the protection granted by the helical conformation is not the only factor influencing the photo-stability and that additional electronic effects are at play. Further analysis is needed to determine the degradation products and other potential mechanisms of degradation. Importantly, this illustrates that ester-side chain furan units are not impervious to reaction with ¹O₂, as seen by literature reports.

4.8. Exploring Ester-Side Chain Conjugated Polymers Beyond P3HEF

Variation of the side-chain identity has potential large implications on the material's overall behavior, influencing its chemical, electronic and physical properties. In light of the helical nature of P3HEF and alternating copolymer P3HEF-*a*-P3HT described above, heteroatom tuning with the use of sulfur vs. oxygen may have a drastic impact on the materials organization, ordering and overall physical response. Structural studies using GIWAXS and AFM were examined in conjunction with the materials thermal decomposition (TGA), crystallinity (DSC) and spectroscopic response (UV-vis) to better elucidate these properties. Poly(3-hexylester thiophene) (M_n:15,200 D: 1.23) and alternating copolymer Poly(3-hexylesterthiophene-*alt*-3-hexylthiophene)

(P3HET-*a*-P3HT) (M_n: 31,700 Đ: 1.24) was synthesized using Suzuki-Miyaura catalyst-transfer polycondensation³¹ by Dr. Yunyan Qiu and Dr. Joshua C. Worch.

The optical properties of P3HET and P3HET-*a*-P3HT were examined both in solution and in the solid state, *Figure 4.20*. P3HET ($\lambda_{max} = 429 \text{ nm}$) is significantly blue-shifted as compared to P3HT ($\lambda_{max} = 450 \text{ nm}$), whereas the absorption profile of P3HET-*a*-P3HT ($\lambda_{max} = 453 \text{ nm}$) is nearly identical to P3HT in solution. The solid-state spectra of the P3HET was red-shifted ($\lambda_{max} =$ 480 nm) from solution with an absorbance edge of ($\lambda_{max} = 582 \text{ nm}$, $E_g^{opt} = 2.13 \text{ eV}$). However, P3HET-*a*-P3HT ($\lambda_{max} = 627 \text{ nm}$, $E_g^{opt} = 1.85 \text{ eV}$) is red-shifted compared to both homopolymers in the solid-state as the first vibronic band (A₀₋₀) becomes the dominant absorption in this spectrum. The low band gap of P3HET-*a*-P3HT is a potential indicator of donor-acceptor character.



Figure 4.20. *Left*: UV-vis absorption spectra of P3HET measured in solution (Black, solid line), and in solid-state (Red). *Right*: UV-Vis absorption spectra of P3HET-*a*-P3HT measured in solution (Black, solid line) and in solid-state (Red).

Atomic-scale organization was characterized by GIWAXS for both ester-substituted polythiophenes, *Figure 4.21*. Neither P3HET nor P3HET-*a*-P3HT revealed a hexagonal Bragg peak pattern observed in both ester-substituted polyfurans, *Figure 4.16* and *Figure 4.18*. This is strongly suggesting that the polymers do not energetically favor an all cis-conformation nor form a helical structure. With this insight, Bragg features for P3HET are more likely reminiscent of a linear chain structure, with an edge-on orientation similar to the organization of P3HT. As such, Bragg peaks are assigned to π -stacking (3.69 Å) parallel to the substrate with a wide, isotropic

lamellar spacing (18.9 Å) corresponding to the inter-digitation of side-chains. The 2D profile reveals more diffuse scattering outside of the prescribed Bragg features indicating higher disorder, potentially caused by less favorable chain torsion.



Figure 4.21. 2-D GIWAXS profiles of a) P3HET (M.W. 15,200) with radial out-of-plane (top) and in-plane (bottom) profiles annotated with lamellar spacing (100) and π -stacking (020) b) P3HET-a-P3HT (M.W. 31,700) copolymer with radial profiles of out-of-plane (top) and in-plane (bottom) annotated with lamellar spacing (100) and π -stacking (020) *Scale Bar* represents Log-scale scattering intensities.

The alternating copolymer P3HET-*a*-P3HT also favored an edge-on orientation similar to P3HT, with a π -stacking (3.65 Å) parallel to the substrate surface, and a wider lamellar spacing (19.1 Å). However, the amount of diffuse scattering was significantly reduced in comparison to P3HET signifying that the alkyl side-chain 'spacers' are more beneficial for chain organization.



Figure 4.22. Surface morphology measured by AFM and visualized using phase-shift profiles of *Left:* P3HET (M.W. 15,200) *Right:* alternating P3HET-a-P3HT (M. W. 31,700) *Inset:* Scale bar: 200 nm)

Atomic force microscopy (AFM) revealed nanofibrillar morphologies for homopolymer P3HET (fibril width: ~ 17 nm) and alternating P3HET-*a*-P3HT (fibril width: ~ 27 nm), *Figure 4.22*, reminiscent of P3HT. The ideal fibril width of a fully extended chain for P3HET is approximately 20 nm, and P3HET-*a*-P3HT is approximately 40 nm. Therefore, initial observations point to either chain-folding or some disorganized fractions of polymer chains is present, reducing the fibril widths.

Thermal characterization of P3HET and P3HET-*a*-P3HT was carried out by TGA and DSC, *Figure 4.23*. The thermal decomposition range measured by TGA showed dual curves with weight loss features attributed to loss of side-chains and carbonization of the polymer backbone, *Figure 4.23 a*. The homopolymer P3HET exhibits a T_{d5%} temperature measured at 291 °C, and P3HET-*a*-P3HT produced a 5% weight loss at 372 °C, *Figure 4.23 a*. DSC traces revealing both crystallization and melt transitions were characterized by the enthalpy of crystallization (Δ H_c J g⁻¹) and heat of fusion (Δ H_m J g⁻¹). The peaks baseline was fitted by a 1st order approximation, shown as a black dashed-line to help visualize the early onset of melting, *Figure 4.23 b*. Comparison of the melting enthalpies in ester substituted polythiophenes was evaluated in mole quantities by converting the melt enthalpy (J g⁻¹) to the effective enthalpy per ring (Δ H_m ring⁻¹, J mol⁻¹). This was assessed against the inverse degree of polymerization (DP_n) to determine the relationship of effective enthalpy per ring in respect to chain width, irrespective of heteroatom identity or side-chain substitution, *Figure 4.23 c*.

Comparisons to the expected melt behavior for P3HT and P3HSe, as discussed in *Chapter* 2, revealed P3HET exhibited a drastic reduction in crystallization (151.2 °C) and melt (169.3 °C) temperatures with respect to the homopolymers. A corresponding lowered enthalpy of crystallization (ΔH_c : 11.3 J g⁻¹) and enthalpy of melting (ΔH_m : 11.6 J g⁻¹) points to smaller crystallites and higher structural disorder. However, copolymer P3HET-*a*-P3HT showed a melting (217.3 °C) and crystallization (192.6 °C) temperature with a corresponding enthalpy of crystallization (ΔH_c : 23.5 J g⁻¹) and enthalpy of melting (ΔH_m : 24 J g⁻¹), *Figure 4.23 b*.



Figure 4.23. Thermal characterization of P3HET (Red) and P3HET-*a*-P3HT (Teal) with a) thermal decomposition measured by TGA b) thermal transition curves measured by DSC ($10^{\circ}C$ min⁻¹) *Inset*: melt & crystallization temperatures with integrated areas (J g⁻¹) c) linear correlation of enthalpy per ring (J mol⁻¹) vs. inverse degree of polymerization (DP_n⁻¹) compared to P3HT (Black) and P3HSe (Purple) of varying molecular weights.

When the enthalpy per ring (J mol⁻¹) for both polymers was compared to P3HT and P3HSe, the melting enthalpies of P3HET-*a*-P3HT follows the trend expected for homopolymers (*Figure 4.23 c*, see also *Figure 2.4*, *Chapter 2*). Given the molecular weight of P3HET is well under the weight regime where we have shown that chain entanglements begins drastically effecting the crystallinity, it is more likely that the reduced crystallinity originates from disorder along the chain, such as chain twisting and site defects hence limiting crystal size.

The results obtained for P3HET caution that ester side-chain substitution on polythiophene leads to chain conformations with a higher disorder. It is proposed that significant chain torsion from steric repulsions between the side-chain and lone pairs of the sulfur heteroatom is the main culprit. Examination of P3HEF by DFT illustrates very well that steric repulsion between the lone pair on oxygen and the ester group favors an energy minima in a cis-conformation. Once the heteroatom is replaced with sulfur (a larger ring and heteroatom), steric repulsion is still present,

but due to slight differences in ring size and shape, does not adopt an all-cis configuration. Hence, the chain is twisting with a higher degree of conformational disorder that is contributing to the amorphous phase of material. As demonstrated by AFM, the chains are still organizing into fibrillar structures. However, GIWAXS additionally revealed diffuse scattering suggesting the presence of more scattering 'centers' or non-periodicity along the chain. This is corroborated by a lowered crystallization/melt temperatures and corresponding lowered enthalpy per ring from reduced crystallite size.

Once an alkyl side-chain 'spacer' is placed in-between ester groups, as accomplished by P3HET-*a*-P3HT, the steric effects are significantly reduced as we observe more organized structures (less diffuse scattering) by GIWAXS and corresponding expected melting enthalpy per ring with respect to P3HT of similar molecular weight and dispersity. Interestingly, the solid-state UV-vis of P3HET-*a*-P3HT shows some potential donor-acceptor character. This is very exciting as it is an example of a controlled molecular weight, low dispersity material; that is highly organized, with a low band gap, useful in organic electronics. As such, this material has the advantage granted from the electron-withdrawing nature of the ester side-chain without the additional drawback of inducing chain torsion as seen in homopolymer P3HET.

4.9. Summary of Findings

The photo-stability of P3HF, and P3HEF was examined in the presence of light and air by a variety of techniques including UV–vis, GPC, ¹H NMR and FTIR analysis. Polyfurans bearing an ester side-chain exhibited improved photo-stability in comparison to their alkyl side-chain analogs. It was demonstrated that Poly(3-hexylester furan) (P3HEF) is generating singlet oxygen, but seems insensitive to its presence over shorter periods of time. The discovered stability was partially attributed to P3HEF's helical structure with tight π -stacking, from an all-cis configuration of the polymer backbone. This structure was determined by the combination of experimental results in GIWAXS hexagonal Bragg feature patterning and DFT geometry optimizations of oligomers. Further investigation into the helical formation by the inclusion of ester side-chains involved studies of P3HEF-a-P3HT also revealed a hexagonal Bragg pattern in GIWAXS, indicating a helical structure. However, the alternating copolymer exhibited more photodegradation when exposed to light and air (UV-vis), to the electron donation of alkylthiophene rings. Once our attention turned to ester substituted polythiophenes, we observed higher disorder from chain-twisting in hompolymer P3HT resulting in a reduced crystallinity (DSC). Once an alkyl 'spacer' was incorporated, the steric effects stemming from inclusion of the ester group was not observed, therefore providing an alternating copolymer with donor-acceptor qualities useful for organic electronics. The presence of ester side-chains has been shown to improve photo-physical properties in polyfurans with an array of structural organization dependent on heteroatom identity. To our knowledge, this is the first report of the controlled synthesis of poly(alkylester furan) that exhibits a helical structure with improved photostability.

4.10. Experimental Procedures

Physical analysis followed standard experimental procedures described in Appendix 2.

All spectral analyses were performed using Mathematica (Wolfram Research).® AFM images were processed using Gwyddion Software©. 2D GIWAXS images were recorded at Cornell High Energy Synchrotron Source (CHESS) at station D1 which is run by Dr. Detlef Smilgies. The work at CHESS is supported by the National Science Foundation under award DMR-1332208.

Synthesis. Synthesis of ester side chain polymers was carried out by Noonan group members: Dr. Yunyan Qiu, Dr. Joshua Worch and later continued by Anthony Varni.

Fourier Transform Infrared Studies. FTIR analysis were performed using a Perkin Elmer Frontier FTIR Spectrometer. Degradation studies were also performed by analysis of powder samples. The initial (t = 0 s) spectra was collected using a pure powder sample (no solution) with no light exposure. Subsequent time points were collected by preparing films from ~ 2 mg/mL THF polymer solutions that were exposed to light and air under similar conditions as the previous stated UV-vis degradation tests. At each time interval a portion of the solution was used to cast a film of the light exposed sample atop a 22 cm × 22 cm glass slide placed inside a petri dish; dried under ambient conditions, in the dark. Power samples were collected by scrapping the dried polymer film off of the glass substrate using a razor blade. The powder was then placed directly atop the germanium plate of the FTIR for further analysis.

Quantitative analysis of FTIR Absorbance. All spectra were converted from transmittance (% T) to absorbance. Each spectra was baseline corrected with a first order approximation fit (fit₀) which was then applied as a baseline subtraction. The spectra were normalized by an "internal standard" peak area at ~1400 cm⁻¹. Therefore the area of the "internal standard" was the same across all spectra, and the respective peak intensities scaled accordingly. For photo–degradation studies: The normalized peak intensities of each time point were collected. The generation or loss of stretching (v), deformations (δ) or wagging (γ) vibrational frequencies (cm⁻¹) of different functional groups were be characterized in respect to the light exposure period.

P3HEF			P3HF		
No Light	Visible Light	Assignment	No Light	Visible Light	Assignment
859	859	δ(ring) & ν(C-O) furan ring, δ(CH)	920	920	δ (ring) & ν(C-O) furan ring, δ (CH)
1090	1090	δ(CH) & v(C-O) furan ring	1123	_	δ(CH) & ν(C-O) furan ring
1468	1468	δ(CH) alkyl side chain	1463	1463	δ(CH) alkyl side chain
1540	1540	δ(CH) & v(C=C) furan ring	1542	1542	δ(CH) & ν(C=C) furan ring
-	-	-	-	1574	δ(C=C) (endoperoxide ring opening)
		S(0-0)		1667,	v(C=O)
1714	1714	(ester group of side-chain)	1667*	1734, 1781	(endoperoxide ring opening & chain scission)
2800 - 3000	2800 – 3000	v(CH) aliphatic	2800 - 3000	2800 - 3000	v(CH) aliphatic

Table 4.1. IR Assignments for P3HEF and P3HF

Light Source Calibration. The visible and UV light sources were calibrated by distance and exposure time using a ThorLabs PM100D power meter with a photodiode sensor, UV-Si detector, 9.5 mm aperture; calibrated at 365 nm wavelength. Measurements were performed inside a black box at respective distances so that flux and calculated photon dose remain constant. The visible light source: Ecosmart Daylight LED (5000K, 1680 lumens, spectrum range: 400 – 700 nm) was calibrated at a distance of 10.6 cm, with an exposure period of 60 s.



Figure 4.24. *Left*: Normalized spectral power distribution for EcoSmart Daylight LED *Right*: Photon dose (mol m^{-3}) over time (s)

The corrected power (difference of when the light source was turned on vs. off) was converted into power per unit area, determined by the following Equation 8 - 9, using 9.5 mm as the diameter of the circular detector.

$$Power_{Corr} (\mu W) = Power Source (ON - OFF)$$
 Equation 8

Power per Unit Area
$$(J M^{-2} s^{-1}) = \frac{Power_{Corr}(\mu W)}{\pi (r (mm))^2}$$
 Equation 9

The photon flux was calculated as the flux per photon energy using Equation 10, where the photon energy was calculated at 365 nm.

Photon Flux
$$(M^{-2}s^{-1}) = \frac{Power per Unit Area(J M^{-2}s^{-1})}{Photon Energy (J)}$$
 Equation 10

Then the number of moles of photons provided per second per unit volume, was calculated over time (sec), by dividing the photon flux by Avogadro's Constant (NA) and 1 mm unit thickness using Equation 11.

Photons (mol
$$M^{-3}$$
) = $\frac{Photon Flux (M^{-2}s^{-1}) * 1 (s)}{NA (mol^{-1}) * 0.001 (M)}$ Equation 11

Table 4.2. Measurement, Calculations & Calibrations for Visible Light Source

Measurements,	Visible:		
Calculations &	Ecosmart Daylight		
Corrections	LED		
Power _{Corr}	(6300 – 1.88)		
(ON - OFF) (uW)			
Power Area ⁻¹	00.05		
(J M ⁻² s ⁻¹)	00.00		
Photon Flux	20 × 20		
$(M^{-2} s^{-1})$	1.633*10		
Photon Dose	0.074		
(mol M ^{⁻3})	0.271		
Exposure Time	60		
Correction (s)			
Sample Distance	10.6		
(cm)			

UV-vis Light Degradation Studies. Tests were performed in the dark, with samples placed in a calibrated distance from the respective light source. A black box with a black cover was used to shield any outside ambient light exposure during the test. Solutions were prepared in the glovebox from degassed solutions (Ar) of anhydrous THF at concentrations ranging from ~0.5 μ M – 120 μ M. Polymers were placed in a quartz cuvette exposed to air and a visible light source: 15W EcoSmart Daylight LED (5000K, 1680 lumens, spectrum range: 400 – 700 nm) set at a distance of 10.6 cm. Single solutions were repeatedly exposed to light for specific periods of time to generate successive time points.

¹**H NMR Degradation Studies:** Samples were prepared in THF- d_8 solutions (2 mg mL⁻¹) illuminated using the EcoSmart Daylight LED (5000 K, 1680 lumens; visible light) source set at a distance of 10.6 cm from the sample, set-up inside a covered black box, over a period of 3 h.

GPC Degradation Studies: Samples were prepared in THF solutions (2 mg mL⁻¹) illuminated using the EcoSmart Daylight LED (5000 K, 1680 lumens; visible light) source set at a distance of 10.6 cm from the sample, set-up inside a covered black box, over a period of X h. Samples were run according to *Gel Permeation Chromatography* Procedures (*Appendix 2*).

Sets of Control Experiments: Control experiments were set up for polymer UV-vis degradation studies with tests set-up under similar conditions (concentrations, solvent), but placed inside a sealed glass cuvette prepared in the glovebox (< 0.1 ppm oxygen present). Samples were *NOT* exposed to air, but illuminated over the course of 1 h. These tests ensured that the quick degradation visualized in P3HF was due to the presence of oxygen, spectra shown in (*Appendix 1*). Controls for UV-vis degradation tests of model compounds (absorption < 400 nm) placed the respective monomer (TFT or FFF) in a quartz cuvette (sealed to maintain concentration) and illuminated over the course of 30 min. This ensured that any degradation in the model studies was due to the singlet oxygen generated by respective photosensitizers.

Model Compound and Singlet Oxygen Degradation Studies. To assist in degradation product assignments in the polymers, model compound studies of were performed employing an unsubstituted alternating thiophene-furan-thiophene trimer (TFT) using both UV-vis and ¹H NMR. *In UV-vis*: Control experiments were performed on THF solutions of Rose Bengal (RB) (50 nmol) or the trimer (0.6 µmol), in conjunction with a mixed sample of trimer TFT with RB (12:1 mole ratio) illuminated using the EcoSmart Daylight LED (5000 K, 1680 lumens; visible light) source set at a distance of 10.6 cm from the sample, set-up inside a covered black box, over a period of 30 min. RB spectra were subtracted out of the resulting mixed samples spectra at each time interval generating an isolated spectra of only degraded products for the trimer.

*In*¹*H NMR*: Control experiments were performed on THF- d_8 solutions of RB (3.6 µmol) or trimer TFT (10 mg, 43 mM), in conjunction with mixed samples of trimer TFT with RB (12:1 mole ratio) illuminated using the EcoSmart Daylight LED (5000 K, 1680 lumens; visible light) source set at a distance of 10.6 cm from the sample, set-up inside a covered black box (3 h).

O₂ (${}^{1}\Delta_{g}$) Generation Studies using Model Compounds and P3HEF. To indirectly determine if P3HEF is generating ${}^{1}O_{2}$, UV-vis photo degradation studies employing P3HEF as the " ${}^{1}O_{2}$ generator" were conducted in the presence of unsubstituted trimer of furan, FFF. Samples were illuminated using the EcoSmart Daylight LED (5000 K, 1680 lumens; visible light) source set at a distance of 10.6 cm from the sample, set-up inside a black box, over a period of 5 hours. Control experiments for both trimer FFF (50 nmol) and P3HEF (0.6 µmol) in conjunction with mixed samples of P3HEF and FFF (1: 12 mole ratio) were measured by UV-vis. The control
spectra of P3HEF were subtracted from the mixed sample test spectra to produce the isolated spectra of degradation profile of trimer FFF.

Photosensitized generation of ${}^{1}O_{2}({}^{1}\Delta_{g})$ by Rose Bengal and the sensitivity of P3HEF under

illumination. To determine if P3HEF degrades in the presence of singlet oxygen, solutions of RB in THF (50 nmol) were mixed with P3HEF (0.6 μ mol, 1:12 mole ratio). Mixed samples were illuminated using the EcoSmart Daylight LED (visible light) source set at a distance of 10.6 cm from the sample, set-up inside a covered black box, over a period of 75 min. A separate test of only RB in THF was illuminated over a similar period with time points collected at the same intervals. The RB spectra was subtracted produce the isolated spectra of P3HEF.

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GPC Analysis



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Figure **S25**. Gel Permeation Chromatography of random copolymer *r*-T-Se₆₅ (Target M/Cat = 150). *Top:* Refractive Index Detector Signal (RI Signal) vs. Elution Time (Time, min). Integration limits for characterization with baseline illustrated within profile (black lines with red arrowhead markers) *Bottom:* Mass Distribution from integrated limits. *Inset:* Number Average (M_n) and Weight Average (M_w) molecular weight with Dispersity (\oplus) values.

DSC Analysis









Figure **S27**. Fibril-width analysis of periodic copolymer T-T-Se illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.



Figure **S28**. Fibril-width analysis of periodic copolymer T-Se illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.



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Figure **S30**. Fibril-width analysis of random copolymer *r*-T-Se₃₂, illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.



Figure **S31**. Fibril-width analysis of random copolymer *r*-T-Se₅₃, illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.



Figure **S32**. Fibril-width analysis of random copolymer P3HET (M.W. 15,200 \oplus 1.23), illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.



Figure **S33**. Fibril-width analysis of random copolymer P3HT-*a*-P3HET, (M.W. 31,700 \oplus 1.24), illustrating *Left*: Example of lines drawn within AFM image (*scale bar*: μ m) and Right: Histogram of # of counts per fibril width (nm) determined by line widths in AFM image.

GIWAXS 2D Scattering Patterns



Figure **S34**. P3HT (M.W. 11,200) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S35**. P3HT (M.W. 19,000) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S36**. P3HT (M.W. 25,200) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S37**. P3HT (M.W. 37,500) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S38**. P3HSe (M.W. 10,000) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S39**. P3HSe (M.W. 19,700) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃



Figure **S40**. P3HSe (M.W. 24,200) 2D GIWAXS profiles of *Left*: as-cast and *Right*: annealed samples from CHCl₃

UV-Vis Deconvolution Fitting

Equations from Literature

Calculation of the Exciton Bandwidth *W* (*Equzation 1*)[Ref.S3], with Franck-Condon style fitting inspired by Spano's work. (*Equations 2 -3*) [Ref. S2, S5]

$$\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24 \, W/E_p}{1 + 0.073 \, W/E_p}\right)^2 \qquad Equation \ l$$

$$G_m = \sum_{n(\neq m)} \frac{s^n}{n!} (n-m)$$
 Equation 2

$$Abs \propto \sum_{m=0} \left(\frac{e^{-S} s^m}{m!}\right) \left(1 - \frac{W e^{-S}}{2E_p} G_m\right)^2 A e^{-\frac{(x-x_0 - m E_p)^2}{2\sigma^2}} \qquad Equation 3$$



Figure **S41**. Illustration of Spano's fit of experimental data (Black) for P3HT, and his total Gaussian fit (Red dots) extracted from literature, Reference S2. Overlays of our calculated fits using his aggregate model are depicted as the total sum of Gaussians (Blue, dashed) and its individual Gaussian line shapes (Orange) to describe the vibronic transitions (A_{m-n}) from electronic ground state (S₀, m = 0) to the first electronic excited state (S₁) with vibronic excitations (n = 0, 1, 2, 3).

As a self-check to validate that our use of Spano's model fitting, the experimental absorbance profile and total curve fit was extracted from Spano's work using Mathematica (Wolfram Research)® software, Figure 2.11. We then used (Equations 1 - 3, Huang Rhys factor S = 1 [Ref. S4] to apply a fit to his experimental data and then compared to the reported fit, Figure 2.11. We found that the extracted fit and our calculations were in excellent agreement, and therefore provided confidence in our use of Spano's fit to describe the ordered aggregate contribution to the total spectrum.

Fitting Total UV-vis Spectrum

Using a gamma distribution to describe amorphous content and Gaussian distributions to describe ordered aggregates, we outlined a series of constraints to properly fit the total absorption spectra.

To determine the contribution of the ordered component, we provided Gaussian peak parameters (x_0 , σ , δx), where (δx = vibronic spacing between Gaussian peaks, representing the main intra-molecular vibration (E_p)) and constant scaling factors A[0] and A[1], where (Huang-Rhys parameter S = 1)[Ref. S4], we can use *Equation 3* and calculate the (A₀₋₀, A₀₋₃) electronphonon coupled peaks:

The disordered component, describing the amorphous contribution was calculated using a gamma

Equation 4

$$Abs \propto A[0] \ e^{-\frac{(x-x_o)^2}{2\sigma^2}} + \sum_{m=1}^{\infty} \left(\frac{e^{-1} \ 1^m}{m!}\right) \left(1 - \frac{We^{-1}}{2 \ \delta x} G_m\right)^2 \ A[1] \ e^{-\frac{(x-x_o-m \ \delta x)^2}{2\sigma^2}}$$

Distribution function with parameters (μ , α , β) with constant scaling factor A[4]:

Equation 5

$$A[4] * \begin{cases} \frac{e^{-\frac{x-\mu}{\beta}} (x-\mu)^{\alpha-1} \beta^{-\alpha}}{\Gamma(\alpha)} & (x-\mu) > 0\\ 0 & True \end{cases}$$

The Fitting Constraints

- 1) The modified Gaussian Distribution fit, described by Spano et al, *Equation 3*, can be used to describe the S₀ to S₁ electronic excitations coupled with v₀ to v_n (n = 0, 1, 2, 3) transitions
 - i. The vibration energy levels are quantized by $\hbar\omega$ and equally spaced
 - a. The intramolecular vibration is characterized by the main-chain C=C vibration frequency generally in a range of (0.15 0.20 eV) [Ref. S1]
- 2) Electron-phonon coupling is prescribed to the weak (electronic) coupling regime
 - i. In the molecular limit, (J = 0) no coupling occurs

a. The exciton bandwidth ($W \ge 0$)

1.
$$(A_{0-0}/A_{0-1} \le 1)$$

- 3) The sum of Gaussian peak and gamma peak areas does not result in a discontinuity
- 4) Overall shape and curvature produced from the sum of Gaussian peak and gamma peak areas resembles the experimental curve in close approximation
 - i. Root-Mean-Square Deviations (RMSD) of spectrum peaks vs. fit peaks is in good agreement using formula: RMSD = $\sqrt{\langle (Exp.(x) fit(x))^2 \rangle}$
- 5) The sum of Gaussian peak (Gauss_m (x)) and gamma peak ($\gamma(x)$) areas is in relatively good agreement with experimental spectra's total area

$$\int Exp.(x) \, dx = \left(\int \sum_{m=0}^{3} Gauss_m(x) \, dx + \int \gamma(x) \, dx \right) \pm 2.5$$

References:

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Using Mathematica software, experimental data was baseline corrected with normalized in respect to maximum absorbance intensity (AU). The normalized absorbance (y) was tabulated vs. the respective Energy (eV, x) generating a list of $((x_1 \ y_1), \dots, (x_n \ y_n))$ points within the energy range of (1.55 - 3.5 eV). A non-linear model fit (NLMF (x)) was applied using the total sum of *Equations 5 & 6* with a total parameter set of (A[0], A[1], x₀, σ , δx , A[4], μ , α , β) including additional constraints: ($\delta x < 0.20 \text{ eV}$, $\mu > x_0$). The parameter constraints ensured i) that the intramolecular vibrational frequency ($\hbar \omega$) was characteristic of carbon double bonds within the polymer chain ii) the onset of the gamma distribution (μ) had very little mixing with the A₀₋₀ transition. Inspection of the 'residual' curve's onset reveals contribution mainly to the higher vibrational transitions supporting the use of this constraint to properly fit the gamma function.

A series of NLMF(x) for each sample was varied by gamma distribution onset (γ_{onset} (eV)) in a range of $\mu = (x_0 \text{ eV} \dots \sim (x_0 + 2 \delta x) \text{ eV})$. Each NLMF(x)'s parameters was tabulated in respect to the γ_{onset} (eV) to generate a list describing all individual Gaussian peaks and the shape and scale of the gamma distribution. The RMSD of each NLMF(x) fit was calculated in respect to each γ_{onset} (eV). Each overlay was compared against the RMSD to determine which NLMF(x) generated valid approximations of the experimental absorption curve following fitting constraints (# 1 – # 5). The optimized NLMF(x) corresponded to the lowest RMSD value.

In general, the following observations of the model fits were made: i) As the γ_{onset} approached the minimum position of ($x_0 \text{ eV}$), the overall fitted curve possibly agreed with the spectral curve, but the peak intensity the A₀₋₁ line shape decreased dramatically such that fitting constraint (# 2) was invalidated. ii) As the γ_{onset} approached the upper limiting position of (~ ($x_0 + 2 \delta x$) eV), the shape parameter α produced an extremely sharp peak onset generating discontinuities within the fitted curve, such that the fitting constraint (# 3) was invalidated. iii) Gamma fits with ($\alpha \ge 2.5$ and 0.17 > $\beta > 0.3$) generated fitted curves without discontinuities. iv) Lower RMSD values had a γ_{onset} (eV) within a similar energy range of the A₀₋₂ curve's onset.

Polymer	x ₀ (eV)			A ₀₋₀	A ₀₋₁
P3HF	2.335	0.0745	0.185	0.70	0.93
РЗНТ	2.045	0.077	0.181	0.72	0.93
P3HSe	1.787	0.0715	0.171	0.70	0.92

 Table S2.1. Spano's Aggregate Fit Parameters for Homopolymers

Table **S2.2**. NLMF(x) Fit Parameters for Homopolymers

Polymer	x ₀ (eV)	σ	δx (eV)	A ₀₋₀	A ₀₋₁	α	β	μ (eV)	γ_{Max}	γ _{FWHM} (eV)
P3HF	2.336	0.0879	0.189	0.64	0.72	3.31	0.22	2.355	0.48	0.75
РЗНТ	2.045	0.0810	0.172	0.68	0.79	2.84	0.24	2.140	0.53	0.76
P3HSe	1.786	0.0732	0.163	0.67	0.84	2.86	0.18	1.910	0.54	0.57



Figure **S42**. P3HF, Solid-state UV-vis fitting: Root Mean Squared Deviation (RMSD) in respect to the onset of the gamma distribution (γ onset, eV). *Inset*: Examples of fits depicted as an overlay of *i*) Experimental data (Light Blue) *ii*) Individual Gaussians (Blue) *iii*) Gamma distribution (Black) and *iv*) Total curve fit from the integrated sum of (*ii* + *iii*) (Red). Best fit highlighted (\bigstar , Red Star).



Figure **S43**. P3HSe, Solid-state UV-vis fitting: Root Mean Squared Deviation (RMSD) in respect to the onset of the gamma distribution (γ onset, eV). *Inset*: Examples of fits depicted as an overlay of *i*) Experimental data (Light Blue) *ii*) Individual Gaussians (Blue) *iii*) Gamma distribution (Black) and *iv*) Total curve fit from the integrated sum of (*ii* + *iii*) (Red). Best fit highlighted (\bigstar , Red Star).
Polymer	X _i Se Content	W (meV)	σ	δx (eV)	X ₀ (eV)	A ₀₋₀	A ₀₋₁
<i>r</i> -T-Se ₃₂	0.32	86.6	0.094	0.195	1.97	0.58	0.87
T-T-Se	0.33	78.4	0.068	0.167	1.95	0.69	0.93
T-Se	0.50	89.5	0.07	0.169	1.91	0.65	0.92
<i>r</i> -T-Se ₅₃	0.53	89.8	0.093	0.189	1.90	0.55	0.86
<i>r</i> -T-Se ₆₅	0.65	86.1	0.093	0.189	1.88	0.59	0.86
T-Se-Se	0.66	64.4	0.069	0.170	1.86	0.80	0.92

 Table S3.1. Spano Model Fit Parameters and Peak Intensities of Gaussian Components for Random and Periodic Copolymers

 Table S3.2. Fit Parameters and Peak Intensities of both Gaussian and Gamma Components for Random and Periodic Copolymers

Polymer	x ₀ (eV)	σ	δx (eV)	A ₀₋₀	A ₀₋₁	α	β	μ (eV)	γ_{Max}	γ _{εννης} (eV)
T-T-Se	1.94	0.076	0.167	0.64	0.78	2.99	0.19	2.02	0.42	0.66
T-Se	1.91	0.080	0.170	0.60	0.72	3.12	0.19	1.96	0.46	0.67
T-Se-Se	1.86	0.080	0.173	0.73	0.75	2.53	0.23	1.96	0.39	0.67
<i>r</i> -T-Se ₃₂	1.97	0.11	0.184	0.53	0.70	3.29	0.21	2.04	0.39	0.76
<i>r</i> -T-Se ₅₃	1.91	0.096	0.186	0.56	0.81	2.75	0.25	2.06	0.41	0.81
<i>r</i> -T-Se ₆₅	1.88	0.095	0.181	0.58	0.81	2.96	0.23	1.99	0.40	0.79



Figure **S44**. RMSD calculations for a) random and b) periodic copolymers. Best value highlighted with arrow.



Figure **S45**. Overlay of 'residual' from Spano's fit and gamma fitting for a) random and b) periodic copolymers

Photo Degradation Studies



Figure S46. GPC chromatogram overlay of P3HF evolution of molecular weight (top) when illuminated by visible light over the course of 5 h. Initial sample (black, t = 0 h) and final time point (red, t = 5 h).



Figure S47. GPC chromatogram overlay of P3HEF evolution of molecular weight (top) when illuminated by visible light over the course of 5 h. Initial sample (black, t = 0 h) and final time point (red, t = 5 h).



Figure S48. ¹H NMR Spectrum – 500 MHz, THF-*d*₈; P3HF before irradiation with visible light.



Figure S49. ¹H NMR Spectrum – 500 MHz, THF- d_8 ; P3HF after 5 h of irradiation with visible light, highlighting regime ~4 – 10 ppm (inset).



Figure **S50**. UV-Vis Normalized Absorption (AU) of P3HF (top) and P3HEF (bottom) illuminated by visible light (white LED) and no air (t = 0 - 60 min)



Figure **S51**. UV-Vis Absorption (AU) of model compound FFF illuminated by visible light (white LED) and air (t = 0 - 30 min)



Figure **S52**. UV-Vis Absorption (AU) of model compound TFT illuminated by visible light (white LED) and air (t = 0 - 30 min)



Figure **S53**. UV-Vis Absorption (AU) of Rose Bengal illuminated by visible light (white LED) and air (t = 0 - 5 min)

Appendix 2

General Experimental Procedures

Unless otherwise noted in the discussion, all materials and methods followed these general procedures.

Materials and Methods

All synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere or in an mBraun glovebox under an atmosphere of purified nitrogen. Column chromatography was completed using silica gel from Silicycle Inc. and analytical thin-layer chromatography (TLCs) using 0.2 mm silica gel plates (EMD). All solvents (dichloromethane, diethyl ether, tetrahydrofuran, toluene) were purchased from commercial sources, degassed with argon, and dried using a jcmeyer solvent system prior to use. Solvents used in work-up procedures and column chromatography were purchased from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources and used as received. All other chemicals were used as received from commercial sources except N-bromosuccinimide (NBS), which was recrystallized from hot water prior to use. 3-hexylselenophene¹ 3-hexylthiophene² were prepared according to literature procedures.

NMR Analysis. All NMR experiments were collected at 300 K on a two-channel Bruker AvanceTM III NMR instrument equipped with a Broad Band Inverse (BBI) probe, operating at 500 MHz for ¹H (126 MHz for ¹³C). The ¹H NMR spectra are referenced to residual protio solvents (7.26 for CHCl₃) and the ¹³C NMR spectra are referenced to CDCl₃ (77.23).

Gel-Permeation Chromatography. GPC traces were obtained using a Waters Instrument equipped with a 717 plus auto-sampler, a Waters 2414 refractive index (RI) detector and two SDV columns (Porosity 1000 and 100000 Å; Polymer Standard Services) with THF as the eluent (flow rate 1 mL/min, 40 °C). Molecular weights were determined by applying a 10-point calibration based on polystyrene standards (Polystyrene, ReadyCal Kit, Polymer Standard Services). Polymer samples for analysis were prepared by dissolving ~ 1 mg of dried polymer in ~1 mL THF, filtered through a 0.22 µm PTFE syringe filter and analyzed.

GC-MS Analysis. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Helium was used as the carrier gas. The following conditions were used for all GC-MS analyses: injector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 280 °C.

UV-Vis Spectroscopy. UV-Vis spectra of all polymers were recorded on a Varian Cary 5000 spectrophotometer. Prior to recording the spectra for all polymers, a 100% transmittance sample was taken of a "blank", either CHCl₃ (solution) in a quartz cuvette or cleaned glass substrate (solid-state). This "blank" was then ran a second time as a sample baseline.

Solution measurements were conducted in CHCl₃ at 0.0075 mg/mL concentration. Thin film samples were prepared from a spin-coating process, in the dark, under a dry nitrogen environment in a VAC glovebox. 22×22 mm glass cover slips were cleaned by spraying with acetone, isopropanol and dried under a jet of filtered, dry nitrogen. 5 mg/mL solutions of the desired polymer were prepared in dry toluene were heated to 80°C in glass vials for 10 min, filtered through a 0.22 μ m PTFE syringe filter using a glass syringe, and re-heated for 5 min prior to spin-casting from hot solutions. The spin-coating conditions consisted of three cycles, a 400 RPM spreading cycle for 5 seconds, a 1000 RPM main cycle for 30 seconds and a 2000 RPM wicking cycle for 15 seconds. The films were annealed at 150°C for 1 hour under a nitrogen environment.

UV-Vis Normalization and Spectra Correction Procedures. The UV-Vis sample tests were baseline shifted (δb) and baseline (*b*) subtracted and corrected using the following equation:

Sample –
$$(b - \delta b) = \text{Sample}_{Corr}$$

The Sample_{Corr} spectra were normalized by the absorbance maxima (λ_{max}). Therefore, in photo-degradation studies: All successive time points were scaled appropriately to the time zero spectra, and any reduction in area is still readily apparent with longer exposure periods. Therefore the normalization spectra were calculated as follows: $Sample_{Corr}/(\lambda_{max}) = Sample_N$

Electrochemical Analysis. For cyclic voltammetry, a three electrode system comprised of a silver wire pseudo-reference, a coiled platinum counter electrode, and a glass carbon working electrode was employed and was controlled with an EE&G Potentiostat Model 237A Series Electrochemical Analyzer with PowerSuite Software. The working electrode was balanced vertically using a punctured, upside-down septa-cap placed in the center of a petri-dish lined with CHCl₃ solution to provide a vapor-annealing environment. A solution of the polymer (0.5 mg/mL in CHCl₃) was drop cast onto the working electrode. The electrode was then encased by a domed glass lid that was covered in foil. The film was allowed to dry over a period of 5 minutes, prior to the measurement. The electrode was immersed in anhydrous acetonitrile with 0.1 M tetra-butylammonium hexafluorophosphate (Fluka, electrochemical grade). Potentials were scanned at 0.10 V/sec under a constant argon purge and were referenced to SCE via a ferrocene internal standard (Fc/Fc⁺). Considering the oxidation potential of ferrocene is +0.40 V versus SCE in acetonitrile and the SCE electrode is -4.7 eV from vacuum,⁴ the HOMO and LUMO energy levels were estimated according to:

 $E_{HOMO} = - (E_{[onset, ox vs. Fc/Fc^+]} + 5.1) (eV) \qquad E_{LUMO} = - (E_{[onset, red vs. Fc/Fc^+]} + 5.1) (eV).$

Differential Scanning Calorimetry. DSC experiments were performed on a TA instruments Q20 Series coupled with an RSC90 chiller. 3 - 5 mg of sample was placed inside an aluminum pan with an aluminum lid. A reference empty pan/lid of similar molecular weight to the sample pan was prepared to correctly calibrate the thermal transitions of the sample. Experiments were carried out under a nitrogen environment with a heating rate of 10 °C min⁻¹ and cooled at a rate of -10 °C/min within a range of 30 °C up to 280 °C -300 °C for a duration of two cycles. Temperatures above 300 °C were cycled at a rate of 50 °C min⁻¹ with a lower temperature range of 120 °C.

Thermogravimetric Analysis. TGA experiments were performed using a Perkin Elmer TGA 4000. Experiments were carried out under a nitrogen environment with a ceramic crucible. A heating rate of 10 °C /min within a range of 30 °C to 500 °C and a successive heating rate of 20 °C /min within a range of 500 °C to 800 °C was performed for each sample. Atomic Force Microscopy. These samples were prepared from (2 mg/mL and 0.02 mg/mL) solutions in anhydrous $CHCl_3$ (Sigma Aldrich) on 2 × 2 cm silicon wafers with native oxide for both "bulk" film and "monolayer" films, respectively. The wafers were cleaned by spraying acetone and isopropanol and dried under a jet of filtered, dry nitrogen, followed by UV/Ozone treatment at 120 °C for 45 min with an incubation period of 45 min until cooled to 42 °C (Novascan PSD-UVT). The wafers were then placed under vacuum, 10 mTorr, for 90 min.

In the glovebox, under a N_2 environment, the polymer solutions were initially heated to 50 °C in glass vials for 30 min, filtered through a 0.22 µm PTFE syringe filter using a glass syringe. Then, the solutions were pulled out of the glovebox, placed under ambient conditions and re-heated for 5 min prior to drop-casting hot solutions onto the wafers. The as-treated wafers were placed in a petri dish, lined with 1 mL of CHCl₃; completely covered with a minimum amount of solution, and allowed to dry slowly by solvent-vapor annealing. The as-obtained films were imaged with a Bruker Dimension V hybrid AFM in tapping mode.

"Bulk" film AFM images (2 μ m × 2 μ m) were traced with a (1024 pixel × 1024 lines) resolution. A Bruker Multi-190A cantilever (*model*: MPP 23100-10) with the following specifications: (0.01 – 0.025 Ω cm) Antimony (n) doped silicon tip with a cantilever (225 μ m × 40 μ m) length × width, with a spring constant of 35 N/m and resonance frequency of 190 kHz; was tuned 15% off resonance with a target amplitude of 250 mV, drive amplitude of 42 – 68 mV, and an amplitude set–point ranging from 160 – 200 mV. Height and phase–shift profiles were recorded at an integral gain of 0.35, a scan rate of 1 Hz, with a Z–limit of 2 μ m and a Z–range of 1.1 μ m. "Monolayer" films were recorded with a similar cantilever–tip tuning as the "bulk" film samples, with height and phase–shift profiles were recorded with an integral gain of 0.35, a scan rate of 0.5 – 0.75 Hz with a Z–limit of 1 um and a Z–range of 1.1 μ m.

All AFM images were data processed using Gwyddion 2.45 Software[©] with an initial image leveling by mean plane subtraction followed by a third degree polynomial horizontal–row alignment, with a final horizontal scar correction. A second iteration of data leveling was carried out using a three point plane fit.

The image scale range maintained a fixed zero point with maxima scale limits inclusive of the entire height (nm) or phase (degree) distribution for the appropriate image contrast.

Grazing-Incidence Wide Angle X-Ray Scattering.

The SiO₂ wafers (2 \times 2 cm) were cleaned with hexanes, acetone and isopropanol and dried under a jet of filtered, dry nitrogen, followed by UV/Ozone treatment at 120 °C for 45 min, followed by an incubation period of 45 min until cooled to 42 °C (Novascan PSD-UVT). The wafers were then placed under vacuum, 10 mTorr, for 90 min.

2 mg/mL solutions in anhydrous CHCl₃ (Sigma Aldrich) were prepared under a nitrogen environment prior to casting. The solutions were heated to 50 °C in glass vials for 30 min, filtered through a 0.22 mm PTFE syringe filter using a glass syringe, and re-heated under ambient conditions for 5 min prior to drop-casting hot solutions onto the wafers. The as-treated wafers were placed in a petri dish, lined with 1 mL of CHCl₃; completely covered with a minimum amount of solution, and allowed to dry slowly by solvent-vapor annealing. The films were then annealed at 150°C for 1 hour prior to measurement.

GIWAXS measurements were taken at the Cornell High Energy Synchrotron Source (CHESS) D1 (λ = 1.162 nm) station. A wide bandpass (1.47%) doublebounce multilayer monochromator supplied an intense beam of 10.1 keV photons. GIWAXS intensities were recorded with an area detector (Medoptics) with a resolution of 47.19 µm per pixel and a total area of about 50 mm by 50 mm at a distance of 10.62 cm from the thin film sample. The sample was mounted on a sample goniometer, in order to control the incident angle and the sample azimuth. An accurate calibration of the incident angle was performed in situ by measuring the X-ray reflectivity from the sample using an ion chamber. The measurements were calibrated using a ceria standard. The intense scattering close to the direct beam was blocked with a 1.5-mm-wide tantalum rod. Exposures times under these conditions ranged from 1 sec to 5 sec depending on the contrast and sample quality.