SURFACTANT FORMULATIONS FOR WATER-BASED PROCESSING OF
POLYTHIOPHENE DERIVATIVES

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Cameron Dean Danesh
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COMMITTEE MEMBERSHIP

Title:	Surfactant Formulations for Water-based Processing of a Polythiophene Derivative
Author:	Cameron D. Danesh
Date Submitted:	June 2013
Chair:	Dr. Shanju Zhang, Assistant Professor, Department of Chemistry & Biochemistry
Member:	Dr. Robert Echols, Associate Professor, Department of Physics
Member:	Dr. Derek Gragson, Professor, Department of Chemistry & Biochemistry

ABSTRACT

Surfactant Formulations for Water-based Processing of Polythiophene Derivatives

Cameron Dean Danesh

Conjugated polymers are semiconducting materials that are currently being researched for numerous applications from chemical and biological sensors to electronic devices, including photovoltaics and transistors. Much of the novel research on conjugated polymers is performed in academic settings, where scientists are working to prepare conjugated polymers for commercially viable applications. By offering numerous advantages, inherent in macromolecular materials, conjugated polymers may hold the key to cheap and environmentally friendly manufacturing of future electronic devices. Mechanical flexibility, and solvent-based coating processes are two commonly cited advantages. Transitions in the backbone conformation of polythiophenes (PT) in organic solvents have been widely observed to influence thin-film morphology. However, conformational transitions of water-soluble PT derivatives, with respect to their intramolecular versus intermolecular origin, remain largely obscure. Here, conformational transitions of a water-soluble polythiophene in aqueous ionic surfactants are investigated by means of Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), polarizing optical microscopy (POM), ultraviolet-visible (UV-Vis) absorption and fluorescence

spectroscopy, and various X-ray scattering techniques. As-prepared complexes exist as stable hydrogels. Upon dilution, a significant time-dependent chromism occurs spontaneously. A coil-to-rod conformational transition is identified in this mechanism and verified using small-angle x-ray scattering (SAXS). Study into the corresponding kinetics demonstrates an inverse first-order rate law. It is found that the conformational transition is thermally reversible and concentration-independent. The critical transition temperature is largely dependent on the surfactant formulation. A theoretical model is presented to explain this new phenomenon and the mechanisms behind its influence on the optoelectronic and solid-state morphological properties. A relationship between the dilute-solution processing with surfactants and the final properties of the system is substantiated.

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1. Introduction

1.1 History

In 2000, the Nobel Prize in Chemistry was awarded to three scientists “for the discovery and development of electrically conductive polymers”. Alan Heeger, Alan McDiarmid, and Hideki Shirakawa jointly received the prize for their work, which was focused on polyacetylene films (Shirakawa, 1977; Ito, 1974; Chiang, 1977) and resulted in significant progress towards understanding and altering conjugated polymers. However, as is the case with many discoveries in chemistry and materials science, there are other individuals with which the identification and preparation of conjugated polymers can be first attributed. In 1862, for example, at the College of London Hospital, aniline was oxidized in a sulfuric acid solution by Henry Letheby to obtain a partially conductive material, most likely what is known today as a conjugated polymer, polyaniline (Inzelt, 2012). In electrochemical experiments, Dr. Letheby observed a green-colored precipitate forming at the anode that turned colorless after reduction and this material piqued his curiosity. Little did he know he had electrochemically polymerized aniline onto the anode. Dr. Letheby had begun studying aniline because it was found in coal tar residues and was poisoning workers in the gas industry for years.

Throughout the 19th century, various forms of conjugated polymers were being prepared by chemical or electrochemical oxidation methods. However, the concept of macromolecular chains that contain many covalently bonded, repeating molecular units had not been entirely accepted by the scientific

community. Only in the early 1920's, when renowned experts like Hermann Staudinger, Wallace Carothers and Paul Flory began to substantiate the chemical structures of polymers, would conjugated polymers (CPs) be understood as a distinct category (Inzelt, 2012). The first presentations of CPs would have been as black, insoluble, powders with poor conductivity and little attention paid to them.

Since the early 20th century CPs had remained a minor research area by scientists who were merely curious about their properties and with little practical importance. In 1970, however, Shirakawa, Heeger, and McDiarmid began doping solid films of polyacetylene to produce the first highly conductive plastic films (Shirakawa, 1977). In 1990, at Cambridge University, Richard Friend's publication in *Nature* popularized the idea of conjugated polymer light-emitting diodes (Burroughes, 1990) and today CPs are widely studied materials, at the forefront of nanotechnology.

1.2 The Conductivity of Conjugated Polymers

Conjugated polymers (CPs) are long-chain macromolecules with overlapping *p*-orbitals that allow for electronic conductivity along their backbone. Many circumstances dictate a CP's conductivity: doping, chemical structure, microstructure and morphology, processing, etc. As such, the conductivity of a CP can range drastically from an insulator to a metallic conductor, as shown in Figure 1.

Figure 1. The conductivity of conjugated polymers ranges well into the insulator and metal categories (Inzelt, 2012).

The conductance of CPs is the result of conjugated π -bonds along the backbone that impart a high mobility of the corresponding valence electrons by reducing their band gap. This is in contrast with the overlapping d -orbitals in inorganic conductors, where valence electrons are farther from the atomic nuclei and have relatively low binding energies. In semiconductor terminology, the band gap refers to the energy required to excite electrons from the valence energy level to the unfilled conduction energy level. What separates insulators, semiconductors, and conductors is their band gap, as shown in Figure 2. In metals, the binding energy, which is what keeps electrons in their respective orbitals, is essentially zero and electrons exist as free particles. In the presence of a voltage, the electrons in a metallic conductor will freely travel down the potential to create current. In semiconductors they must be excited first and in insulators the electrons are bound to a specific atomic center. In inorganic

semiconductors, the energy levels are essentially continuous throughout inorganic crystals in three-dimensions because the molecular orbitals are evenly spaced throughout. CPs, however, have more localized orbitals with less continuity and the conduction pathway is one-dimensional (Roth, 1995).

Figure 2. Material conductivity depends upon the band gap. The band gap is the energy necessary to excite electrons from the conduction (black) to valence (gray) bands.

The one-dimensional electron pathway allows for the band gap energy of a CP to be ideally modeled in terms of a free-particle in a one-dimensional, infinite potential box. The wavefunctions of such a particle corresponds to discrete energy levels, according to the energy eigenvalues E_n of equation 1.1

$$E_n = n^2 h^2 / (8m_e(L)^2), \text{ with } n = 1, 2, 3, \dots, \quad (1.1)$$

Where, n is the energy level, h is Planck's constant, m_e is the mass of an electron, and L is the length of the one-dimensional box.

The difference between the energies of valence band, also known as the highest occupied molecular orbital (HOMO), and the conduction band, also known as the lowest unoccupied molecular orbital (LUMO), is the band gap. The idealized band gap's value can be calculated according to equation 1.2.

$$\Delta E = E(\text{LUMO}) - E(\text{HOMO}) = [n(\text{HOMO})^2 - n(\text{LUMO})^2] / [8 m_e (L)^2] \quad (1.2)$$

It can be seen that as the length of the box increases the energy spacing, or band gap, decreases. As the polymer length approaches macroscopic dimensions, the band gap approaches zero, allowing for metallic conductivity.

Figure 3 depicts a theoretical relationship for a polythiophene oligomer (Van Mullekom, 2001). Using the 1D particle-in-box model, assuming a carbon-carbon bond of 0.14 nm (the length of C-C bonds in a benzene ring), the maximum wavelength of absorption of 1,3-butadiene is expected to be approximately 207 nm and by experiment it is found to be 217 nm (Soderberg, 2012), showing that this method is somewhat reliable.

Figure 3. The theoretical band gap, E_g , of polythiophene decreases with increasing number of monomer units, in agreement with the particle-in-a-box model (van Mullekom, 2001).

Incident photons, of wavelength corresponding to the CP's band gap, will excite electrons from HOMO to LUMO to form a bound hole-electron pair, also known as an exciton, a neutral quasiparticle. Excitons only form in semiconductors because in true metal conductors the valence electrons are essentially free particles. The absorption spectrum of a CP is thus dependent on the distribution of transition energies from the HOMO to LUMO of the excited electrons. Depending on the circumstances, the fate of an exciton in the CP can be one of three outcomes: it can relax thermally (1), it can re-emit the photon resulting in fluorescence or phosphorescence (2), or it can dissociate into distinct

hole and electron charge-carriers (3) (Inzelt, 2012). Exciton dissociation is the working mechanism by which photovoltaics produce a potential, and the opposite of the mechanism by which light-emitting diodes produce light, this will be discussed in more detail later in the chapter.

Chemical doping of CPs with oxidative or reductive agents imparts a net positive or negative charge along the backbone, respectively, and doping drastically increases conductivity. The development of doping CP films to drastically improve their conductivity is what brought research on CPs to the forefront of materials science. The term 'doping' is used by analogy to inorganic semiconductors, although little commonality exists between them other than the dopant's ability to alter electrical properties. Alkali metals or halogens are typical dopants used with CPs. By doping polyacetylene, its conductivity can be increased by up to 13 orders of magnitude, to the same order as copper's conductivity (approximately 10^8 S/m). By comparison, typical polymers, such as Teflon, have conductivities below 10^{-10} S/m (Inzelt, 2012). The necessity for doping arises from the kinetics of electron transport in the backbone of the chain. The removal of an electron from the backbone via oxidative doping, for example, produces a radical cation, or polaron in this context. The polaron is relatively localized because of electrostatic interactions with the dopant counterion. The mobility of the counterion thus dictates the mobility of the polaron. Therefore, with increasing dopant concentration, the polaron mobility increases and so does conductivity. Figure 4 shows an example of a doped polyacetylene backbone with a stationary counterion.

Figure 4. A radical cation (polaron) is shown propagating (top to bottom) along a negatively doped polyacetylene segment.

In reality, the macroscopic conductivity and bandgap of a CP is dependent upon more than the degree of polymerization and the oxidation state. Electrons must travel in more than one-dimension in a conductive film. Chemical doping improves charge-transport *within* a CP chain and the particle-in-a-box model only predicts the band-gap *within* a chain. CPs are often thought of as one-dimensional conductors, molecular wires with conductivity higher in the direction of their backbone than perpendicularly between backbones (Shacklette, 1980). In the bulk, however, electrons must be able to hop from chain-to-chain to produce an electrical current over any practical distance, otherwise each individual polymer chain must be long enough to span the entire material. For this reason, inter-chain ordering and alignment is critical to the overall mobility of charge-carriers. Defects in chain alignment inhibit the conductivity *between* polymer chains. Unfortunately, these defects are commonplace in bulk samples of polymer materials. In fact, no polymers exist with truly 100% crystallinity. The

covalent constraints between monomer units prevent an ideal orientation of them over long distances. Orientational freedom is required for crystallization and amorphous regions are therefore ubiquitous with polymers, even in highly linear and rigid CPs. Alignment of the backbone over large size scales is essential to encourage efficient charge-transport. For this reason, controlling the microstructure of CPs, to produce aligned, highly crystalline CP materials is of the utmost importance in improving their electrical properties. Crystalline morphologies of poly(3-hexylthiophene), for example, have been widely observed to impact photovoltaic device performance (Liu, 2012; Ren, 2011; Yang, 2005).

1.3 The Backbone Conformation of Conjugated Polymers

Beyond inter-chain ordering, even within an individual CP chain, the backbone conformation (the shape in three-dimensions) also drastically impacts the CP's band gap. As explained earlier, the length of conjugation dictates the HOMO-LUMO transition energy and theoretically this depends upon the degree of polymerization. In reality though, this also requires an idealized, perfectly rigid and linear chain over its entire length. Kinks and bends in the backbone of the polymer chain therefore increase the CP's band gap. The ensemble average length of the rigid portions of the backbone, with p-orbitals geometrically aligned, is termed the effective conjugation length (ECL). As shown in Figure 5, poly(3-hexylthiophene)'s ECL is directly related to its backbone conformation and therefore dependent upon the solvent the polymer is in. Solvent interactions with

the CP chain result in an equilibrium conformation. Coil-like CP chains have shorter ECLs, while rod-like chains have longer ECLs (Rodd, 2011).

Figure 5. The longer the effective conjugation length (ECL), the longer the wavelength of absorbed light. short ECLs (a) and long ECLs (b) result in an orange and purple color of P3HT in CHCl_3 and pyridine, respectively (Rodd, 2011).

In a poor solvent, P3HT chains exist as rod-like aggregates and in a good solvent, they exist as a coil-like solvated polymer (Xu, 2011; Rughooputh, 1987; Scharsich, 2012). Therefore the chain rigidity, which increases the ECL, occurs in concert with a poorer solubility. The rigid chains can have a higher surface area and aggregate or precipitate from solution. During film formation these aggregates produce an inhomogeneous and nonconformal film that results in a lower conductivity. Intermolecular forces, especially pi-pi dispersion interactions between backbones are the driving force for such aggregation and also mediate crystal formation in the solid-state, as shown in Figure 6. Thus, the choice of

solvent requires a balance of increasing the linearity and chain alignment of the polymers whilst maintaining polymer solubility.

Figure 6. Backbone crystallites of P3HT are shown here on a CdS nanowire surface. The crystallization is the result of pi-pi dispersion forces between conjugated backbones along the yellow line (Rodd, 2011).

In addition, the solvents used must be optimized for the coating process by considering the solvent vapor pressure at room temperature, solution rheology and desired film thickness. Spin-coating requires a good enough solubility for a homogeneous and conformal film but a poor enough solvent to favor crystallization. Many studies have focused on the optimization of the P3AT coating process and solvent choice to produce desired morphologies (Xu, 2011; Xie, 2009). As shown in Figure 7, various volume fractions of a poor solvent results in a gradual increase in the formation of crystalline nanostructures in films.

Figure 7. Increasing volume fractions of anisole in a CS₂:anisole solvent mixture: (a) 1:5, 12 h; (b) 1:7, 12 h; (c) 1:9, 12 h; (d) 1:11, 12 h; (e) 1:7, 24 h; (f) 1:7, after 2 months (Xu, 2011).

Conformational transitions and crystallization of P3AT can both be studied using spectroscopy because the absorbance spectrum of the polymer is highly dependent upon both the backbone conformation and pi-pi interactions. Pi-pi stacking of polythiophene chains provides additional orbital overlap between the backbone's molecular orbitals and thus alters the HOMO-LUMO transition energy in unison with changes in the ECL (Rughooputh, 1987; Xu, 2011). Experiments pertaining to the optoelectronic properties of polythiophenes in solution are therefore easily convoluted and require careful design to prevent confounded data. Using only absorbance spectrophotometry, Rughooputh, Heeger et. al.

suggested that a coil-to-rod transition *initiates* crystallization of P3HT during solvent-induced precipitation rather than vice versa (Rughooputh, 1987). The initial coil-rod transition and subsequent backbone crystallization of P3ATs, based upon solvent interactions, has been widely corroborated by other groups using optoelectronic analytical techniques, including UV-Vis spectrophotometry (Xu, 2011).

Alkyl side-chains along the polythiophene backbone greatly increase solubility and have been incorporated with the polythiophene backbone to improve processability and film properties (Causin, 2005; Lee, 2012; Biniek 2012). Polythiophene generally has a lower inherent conductivity than polyacetylene, but makes up for it by being far more stable under air. The lack of stability of polyacetylene in the presence of air is the result of its reaction with oxygen. The ionization potential of polyacetylene, approximately 4.7 eV, is low enough that oxygen can form a charge-transfer complex and oxidize the backbone. The oxidation of the backbone results in a further lowering of the ionization potential for subsequent oxidative attacks and overtime, polyacetylene can become cross-linked with significantly reduced ECLs. By comparison, polythiophene has an ionization potential above 5 eV in the undoped state (Inzelt, 2012). For applications, such as photovoltaic devices, the reliability of the material to ambient conditions is essential. For its stability and solubility, P3HT is one of the most widely used CPs in electrical devices (Tada, 2011; Minh Trung, 2011; Lobez, 2012; Treat, 2011).

1.4 Polythiophene Applications

Despite recent interest in using P3HT for electrical devices, inorganic compounds remain the most popular because they are more reliable long-term and they possess a regular crystalline structure over large distances. As shown in Figure 8, inorganic materials have allowed for the production of photovoltaic devices with power conversion efficiencies in excess of 40%. By comparison, polymer-based photovoltaics have yet to breach the 10% mark.

Figure 8. Efficiency break-throughs for various material systems used in photovoltaics (Wilson, 2013).

Still, inorganic solar cells are usually produced via expensive and highly sensitive vapor deposition processes. CPs offer a much cheaper route to

production via solvent-based coatings. Roll-to-roll coatings and printing are some of the commonly cited methods for highly scalable production of cheap polymer solar cells. In roll-to-roll coating production, substrates can be coated at more than one square meter per second by direct contact with wet polymer inks. Flexographic printing and rotary screen printing are two of the most common roll-to-roll methods for CPs (Sondergaard, 2012). The future of polymer photovoltaics will depend on the success of such high-throughput methods for producing efficient solar cells. Presently, most of the research on CPs for solar cells is performed in academic settings using spin-coating processes, often under controlled atmospheres. Recently large-scale coating processes have produced devices of over 3% efficiency, although this does not match up to research devices of over 8% efficiency (Sondergaard, 2012). In addition to the potential for reduced manufacturing costs, conjugated polymers may find niche applications requiring complex device shapes and novel mechanical properties (Liu, 2012; Brabec, 2010; Chen, 2010).

In a polymer photovoltaic cell, the semiconducting polymer is mixed with a more conductive charge acceptor in what is termed a 'bulk heterojunction'. A bulk heterojunction is a mixture of two species where at each interface between them an exciton may be dissociated into an electron and a hole. The hole propagates in the polymer phase while the electron is transferred to and transported by a lower-energy, more conductive species, such as carbon nanotubes or zinc oxide (Zhang, 2012). Photoactive layers in many polymer solar cells are thus composite materials containing inorganic and organic compounds.

The interface between the electron-acceptor and electron-donating polymer creates a chemical potential gradient for the electron to escape the exciton bound in the polymer phase. An energy level gradient in an example bulk heterojunction is shown in Figure 9.

Figure 9. Energy-level diagram of the components of a typical P3HT-based solar cell. At the PCBM-P3HT interface, an exciton dissociates into a hole, propagating towards the less negative potentials, and an excited electron, propagating down the more negative potential. The incoming photon thus results in a flow of direct current (Xie, 2009).

In the polymer phase, the exciton must propagate to the donor-accepter interface to dissociate and generate potential. For this reason, the exciton diffusion length, i.e. the distance over which an exciton may travel before relaxing to a ground-state electron, is a crucial dimension. Typical exciton diffusion lengths range from 7 to 15 nm (Salaneck, 1999). The polymer phase must have domain sizes equal to or below that of the maximum exciton diffusion length. The

morphology of the active layer of the device is therefore critical to overall efficiency. If domain sizes are too large, a newly generated exciton will recombine before reaching an interface and no power will be converted. If the domain sizes are too small, a continuous pathway for hole transport, after exciton dissociation, may be severed and less power converted. The optimal morphology is therefore an idealized pattern of interchanging domains just smaller than the maximum exciton diffusion length. Such an idealized morphology provides a direct pathway for non-tortuous charge-transport to the electrodes, as presented in Figure 10.

Figure 10. A typical bulk heterojunction morphology (top) compared to an idealized morphology (bottom) in the active layer of a polymer solar cell (Li 2012).

In an ideal bulk heterojunction, vertically aligned domains on the order of the typical exciton diffusion length of the polymer alternate with the charge-acceptor phase. This morphology provides the maximum interfacial area for charge-separation whilst maintaining pathways for charge-transport within each domain.

P3HT is by far the most widely employed in polymer photovoltaic devices due to its processability, low band-gap, and high charge-carrier mobility in the solid-state (Yang, 2005). The highest-efficiency polymer solar cells have been achieved with P3HT-based devices. P3HT has a larger proportion of its absorption in the visible region than conventional inorganic cells, where the sun's irradiance is of greater intensity. The bandgap of silicon is shown in Figure 11 for comparison with the sun's spectral irradiance.

Figure 11. The sun's incident spectrum at Earth's surface compared with Silicon's absorption (Myers, 2000).

In addition to solar cells, polythiophenes have been used for biomedical electrode coatings. CPs provide a better device-tissue interface and improve the biocompatibility of the device. By increasing the charge transfer from CPs to the surrounding neural tissue, polythiophene derivatives are observed to improve the

signal-to-noise ratio of implanted electrodes. In particular, a polythiophene based polymer, Poly(3,4-ethylenedioxythiophene) (PEDOT), is of great interest for its high conductivity, chemical inertness, and its long-term reliability (Patil, 1987; Zhang, 2005).

PEDOT coatings have been shown to make an electrode implant more reliable long-term by reducing neural tissue scarring, which can encapsulate the implant, as shown in Figure 12.

Figure 12. Glial scarring (a) can encapsulate the exposed metallic tips of implanted microelectrode arrays (b) (Bello 2007).

The impedance of an electrode-neural tissue interface is typically on the order of 1 kHz, the frequency of natural neural impulses. At this frequency PEDOT coated electrodes show a far lower impedance days after implantation (Bello, 2007). The lesser impedance provides a greater signal-to-noise ratio and indicates that the PEDOT-coating results in better contact with the surrounding

tissue. With a typical, insulating, biocompatible polymer the lack of conductivity would essentially nullify the purpose of the implant making PEDOT an ideal candidate for the improvement of electrode interfaces.

1.5 Water-soluble Conjugated Polyelectrolytes (CPEs)

Despite the utility of organic solvents in coating conformal polythiophene films, there is interest in water-based processing for industrial applications. One of the most important issues in reaching the ultimate goal of high-throughput CP-based solar cells, for example, is developing materials based on nontoxic and nonpolluting solvents. Aqueous solvents are cheaper and more environmentally friendly than organic solvents. However, CPs are typically insoluble in aqueous solution. By incorporating static ionic charges along the backbone, conjugated polyelectrolytes (CPEs) are water-soluble materials (Hoven, 2008; Wang, 2012; Lee, 2012; Franco, 2012; Duarte, 2011, Tennyson, 2009). In most cases, addition of ionic moieties has not been shown to alter the HOMO and LUMO energy levels of the backbone chromophores.

CPEs have been described by Attar et. al. as loosely aggregated together in aqueous solution, with their ionic moieties facing the solvent and their lipophilic backbones associated within the aggregates (Laurenti, 2008; Attar, 2007). CPEs based on polythiophene, have been studied for chemical and biological sensing applications due to their highly sensitive luminescent properties in the visible region. Luminescent quenching of CPs in water is thought to occur via inter-chain

charge transfer between adjacent backbones in aggregates. Various analytes impact the charge-quenching behavior of CPs to allow for fluorimetric detection (Attar, 2007). In addition, recent work has employed an anionic polythiophene, poly(3-potassiumhexanoate thiophene) (P3KHT), for electronic device applications. P3KHT has a similar band gap to that of P3HT and has therefore been incorporated into the composite active layer of a photovoltaic device, albeit with power conversion efficiencies of less than one percent (McClure, 2010).

1.6. Lyotropic Processing of Conjugated Polyelectrolytes

Lyotropic ordering of polymers plays an important role in the crystallization-process during water removal from the solution. Lyotropic liquid crystals were first studied in aqueous surfactants. Micelle formation becomes thermodynamically favorable at a certain concentration of an amphiphilic molecule in water, termed the critical micellar concentration (CMC). Above this concentration micelles exist in equilibrium with free surfactants in solution. By continuing to increase concentration, packing of micelles forms the first lyotropic phase. Here the micelles no longer have positional freedom and pack in a cubic arrangement. With increasing concentration, various lyotropic phases can form. Above roughly 70% amphiphile by weight in water, a lamellar morphology is typically favored, as shown in Figure 13.

Figure 13. Typical lyotropic liquid crystal phase diagram, where T_K is the Krafft temperature, below which solid-state crystals form (Fernsler, 2013).

The sliding of lamellae past one another in solution yields a significant drop in viscosity at the hexagonal to lamellar phase transition. It was the formation of a nematic lyotropic liquid crystals of an aqueous polyaramid that first drew the attention of scientists at DuPont when they discovered the polyaramid, Kevlar. Lyotropic ordering of Kevlar molecules can increase their attractive intermolecular interactions, such as hydrogen bonding, in the solid-state and result in a greater strength of Kevlar microfibers. As shown in Figure 14, shear-induced chain alignment of lyotropic crystalline Kevlar can produce high-strength films and fibers.

Figure 14. The chemical structure of Kevlar (a) and the liquid-crystal processing technique used by DuPont in the manufacture of Kevlar (b) (DuPont, 2013).

Lyotropic behavior of CPs has been shown to produce highly anisotropic film properties over long distances. The long-range order present in LC materials produces similar morphologies in the solid state. CP lyotropic self-assembly has recently been shown to produce thin films with three orders of magnitude faster charge mobility in the direction of the aligned polymer chains than in perpendicular direction (Kim, 2013). Typically, lyotropic CP polymers have bulky side groups that interact to assemble LC structures. In CPEs, however, static charges in the side chains are repulsive and limit the extent of chain interaction beyond aggregate formation. The aggregates are stabilized in the solution by Coulombic repulsion of the side-chains and lyotropic assembly has not been widely reported for CPEs. Addition of ionic surfactants to CPEs, however, has

been shown to result in lyotropic ordering based on the formation of supramolecular complexes (Zhang, 2010).

Surfactants are generally used as additives to CPEs for tailoring their optoelectronic and morphological properties. Studies on surfactant-CPE systems for electrical devices were performed by Thunemann, Antonietti and coworkers in the mid-to-late 1990s (Thunemann, 1999; Antonietti, 1994). By incorporating ionic surfactants with the otherwise brittle CPE, Thunemann produced the first highly flexible CPE films. It was found that CPE-surfactant systems assemble into highly ordered lamellar structures and are thermally stable.

Both ionic and neutral surfactants have been used with CPEs. In solution, individual CPE chains or aggregates may be incorporated into surfactant micelles. Micelle incorporation of CPEs can be detected using spectroscopy because it drastically alters their emission and absorption wavelengths.

Aggregated CPEs in solution often have weak fluorescence emission intensities because of inter-molecular quenching. By incorporating the chains into micelles and creating a greater distance between them, the quenching mechanism is inhibited and fluorescence emission is increased. Fluorescence detection by CPEs using surfactants has reported for fluorescence-based DNA detection (Attar 2007).

Unlike neutral surfactants, counterionic surfactants form supramolecular complexes with CPEs, mediated by Coulombic attraction. Using UV-vis spectrophotometry or fluorimetry, the formation of the supramolecular complex can be confirmed because incorporation of CTAB between CPE backbones interferes with interactions in aggregates and alters the optoelectronic properties

(Lavigne, 2003; Chen, 2000; Knaapila, 2010; Knaapila 2011) Many factors, such as the backbone structure of CPEs (Chu, 1991; Lanzi, 2008), the surfactant lipophile length (Laurenti, 2008), the molar ratio between surfactants and CPEs (Franco, 2012), and overall surfactant concentration (Treger, 2008), play a role in altering the optoelectronic properties in what is termed surfactochromism.

Because of complicated interplay among various intra- and interchain interactions, the physical origin of surfactochromism is still far from being understood and is yet to be described unambiguously. Supramolecular complexation between ionic surfactants and CPEs reduces the charge-repulsion of side-chains and can result lyotropic self-assembly. Lyotropic liquid crystal (LLC) formation has been observed for an anionic PT-CPE complexed with cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) (Zhang, 2010). Using shear-induced alignment, a high degree of hexagonal packing has been substantiated for PT CPE-CTAB complexes. Shear-alignment manufacturing processes to improve polymer properties have been well substantiated for non-conjugated polymers. As discussed earlier, the production of Kevlar uses shear-alignment of LLCs.

Figure 15. Hexagonal lyotropic packing of a polythiophene-based conjugated polyelectrolyte (in red) after complexation with the cationic surfactant (CTAB, in blue) (Zhang, 2010).

LLC phases of CPE-complexes allow for the formation of ordered morphologies of the polymer film after solvent removal. Hexagonal lyotropic ordering of PT-CTAB complexes have been verified using small-angle x-ray scattering (SAXS), as shown in Figure 15. In the hexagonal phases, supramolecular chains are aligned and extended. These self-assembled nanostructures provide an excellent platform for tailoring morphology for charge-transport

As described previously, P3HT crystallization is initiated by a coil-to-rod transition in the dilute regime. Similarly in aqueous PT-CTAB supramolecular complexes, hexagonal packing and LLC formation is driven by such a conformational transition in the dilute regime. The Onsager hard-rod model predicts, in some cases, an entropically-driven LLC formation in the case of rigid, anisotropic rod-like particles in a solvent, as shown in Figure 16.

Figure 16. Anisotropic particles forming nematic ordering upon solvent removal from the isotropic phase, as indicated by the Onsager hard-rod model of lyotropic liquid crystals.

According to the Onsager hard-rod model, while the packing of the rods in the solvent decreases orientational entropy, positional entropy is increased during alignment of individual rod-like particles in the solvent. If there is little orientational entropy, LLC formation may be favored. If rod-like particles approach each other in a non-parallel fashion, there is a larger excluded volume surrounding their center of mass and a reduction in positional entropy. The Onsager hard-rod theory was developed on the basis of a virial expansion of the Helmholtz free energy. With greater particle anisotropy, less virial coefficients are needed to calculate the free energy (Onsager, 1949). More spherical particles, more terms are necessary to accurately predict the particle densities required to cause an isotropic-nematic phase transition. As indicated by the Onsager model, coil-to-rod transitions of PT complexes can encourage LLC formation by increasing solute anisotropy and result in higher degrees of crystallinity after solvent removal. The relationship between the dilute solution behavior and solid-

state morphology is important to producing desired polythiophene-derivative materials. By adding aqueous surfactants it is possible to influence the dilute solution backbone conformation of water-soluble polythiophenes. Surfactant complexation may be used to produce 'green' solvent-based electrically conductive coatings without needing costly processing equipment, such as semiconductor deposition chambers.

In this work, a CPE is complexed with various cationic surfactants to form supramolecular complexes in water. The formation of the complex is verified and the dilute-solution behavior of the complex is investigated. A conformational coil-to-rod transition of individual supramolecular chains is confirmed in dilute solution. The parameters dictating the conformational transition, i.e., surfactant structure, temperature, concentration, relaxation time, and surfactant composition of the complex are studied. A model relationship between the dilute-solution backbone conformation and solid-state morphology is presented to explain the observations. The formation of lyotropic phases at intermediate concentrations is also observed in this mechanism. These findings have implications for optimizing the coating process of conductive polymer films using aqueous solvents to produce desirable optoelectronic properties.

2. Experimental Methods

2.1 Material Preparation

Regioregular (82-90% head-to-tail) poly[3-(potassium-6-hexanoate)thiophene-2,5-diyl] (P3KHT, average M_w = 60 kg/mol, Rieke Metals Inc.), cetyl trimethylammonium bromide (CTAB, Sigma Aldrich), and dihexadecyl dimethyl ammonium bromide (DHAB, Sigma Aldrich) were used as received, in preparation of the supramolecular complexes. CTAB and DHAB were received as fine white powders while P3KHT was received as a coarse, black powder. In a typical batch preparation, stock solutions of the surfactants (CTAB and DHAB) and P3KHT with nominal concentrations of 0.1 M monomer concentration were prepared in nanopure water (Milli-Q, 18M Ω). P3KHT and surfactant solutions were prepared separately and sonicated, vortexed, and heated to 60°C for approximately 20 minutes at each step at least twice to homogenize the stock solutions. Especially for stock surfactant solutions containing a large proportion of DHAB, sonication for longer times was needed due to the greater hydrophobicity of DHAB. Next complexes were prepared by drop-wise addition of homogeneous surfactant solutions, while still warm, to P3KHT solutions resulting in 0.05 M concentration of the complex. Complexes were heated, sonicated, and vortexed similarly to the reactant solutions (60°C for approximately 20 minutes at each step). Over time, more than 3h at room temperature, the viscosity of the complex solution rises and a hydrogel is formed, indicating the completion of the reaction. After complex formation, microcentrifugation (18-Centrifuge Biotechnical Services Inc.) at 18,000 RPM produced some phase separation.

The lesser solubility of the complex, relative to its isolated components further supports the formation of a supramolecular complex, where lipophilic tails of the surfactant point into solution, as depicted in Figure 17.

Figure 17. (a) Illustration of a complexation reaction between a side-chain conjugated polyelectrolyte and single-tail (CTAB) and double-tail (DHAB) surfactants. A 1:1 molar ratio complex is shown, referring to the equivalent number of carboxylic acid moieties to total (n+m) surfactant molecules. (b) Chemical structure of the reactants shown in Figure 2.1a.

At high concentrations of the double-tail surfactant, DHAB, complexes were especially insoluble, as shown in Figure 18. As such, for the purpose of this

study, DHAB surfactants were only added to complex with 30% of the carboxylic moieties, with the rest complexed by CTAB to maintain solubility of the complex at the concentrations studied.

Figure 18. Various as-prepared complexes with greater incorporation of DHAB into the supramolecules. Percentages shown are of the CTAB proportion, i.e., 90% refers to a 9:1 ratio of CTAB:DHAB grafted onto the backbone of the polyelectrolyte.

Spectroscopic measurements of solutions were performed by serial dilution of the reddish supernatant of the stock gels shown in Figure 17. Concentrations used for spectroscopy measurements are noted in this study in terms of the monomeric repeat unit (the carboxylate molarity).

2.2. Instrumental Methods of Analysis

2.2.1 UV-Vis spectrophotometry and Florimetry

UV-Vis absorbance and fluorescence spectra were obtained under stirring cuvettes on a Jasco *V-550* spectrophotometer and Jasco *FP-6500* spectrofluorometer, respectively. Both instruments employed temperature-control fixtures, and samples were sealed from the ambient atmosphere during measurement. UV-Vis measurements of all samples were performed to determine the concentration of the solutions. First, the stock 0.05 M complex hydrogels were oven evaporated at 60 °C to produce solids for confirmation the 0.05 M concentration using gravimetry. The volume of sample was measured using a syringe to prepare diluted complex solutions for UV-Vis spectrophotometry with known concentration. According to equation (3), Beer's law, the absorbance of an analyte is directly proportional to the concentration at a given wavelength.

$$\text{Absorbance} = \epsilon bc \quad (2.1)$$

Where, ϵ = molar absorptivity ($1/\text{M}\cdot\text{cm}$) b = path length (cm), c = concentration (M)

Using Beer's law, the absorbance was used to determine subsequent concentrations for dilute solution measurements. The relationship between absorbance and concentration appeared consistent regardless of the surfactant composition. For kinetic measurements, the sample hydrogel was diluted into the

cell containing water already placed in the instrument to begin obtaining the initial rate as quickly as possible. Absorbance versus time data was collected at 590 nm for approximately 5 minutes, however, the initial rate was calculated from the initial 30 seconds. The initial 30 seconds was used to find the rate law by a linear fit of each concentration ($R^2 > 90\%$ for all curves). The more dilute solutions had the fastest rate and therefore had the smallest R^2 in the range 90-100%. The slopes from each line were then plotted versus concentration to produce the rate law. All measurements were performed at 25 °C for kinetics measurements.

2.2.2 Small-angle X-ray Scattering

Small-angle (SAXS) X-ray scattering was performed on a pin-hole collimated Rigaku instrument (SMAX3000) with a 1.54 Å Cu K α radiation source. The Rigaku instrument, shown in Figure 19, was used in collaboration with Professor Osuji's lab in the chemical engineering department at Yale University. SAXS data can provide insight into both dilute solution three-dimensional structure of individual polymer molecules as well as large-scale anisotropic structural features in the solid state. SAXS is a powerful methodology and can provide direct physical evidence of structures in real space (Chabinyk, 2008). As with most X-ray scattering techniques, it provides spatially-averaged data throughout the sample, i.e., the average structural features.

The instrument was calibrated with a silver behenate standard. In this instrument, scattering data was collected in a transmission geometry, whereby X-rays passing through the sample are scattered at different angles onto a

photodiode detector surface at the end of the instrument. SAXS was performed with a transmission geometry and requires a large distance from sample to detector in order to amplify the otherwise small differences in the angle between the scattered photons and the incident beam. The working principle of the transmission geometry is illustrated in Figure 19. As with XRD, the functionality of SAXS depends on fully elastic photon-particle interactions.

Figure 19. Transmission geometry SAXS. The angle between the scattered beam and the collimated incident beams in blue is termed 2 theta (Andrej, 2013).

In the collection of SAXS data, a photodiode beamstop, far away from the sample, collects the transmitted and scattered photons. The photodiode records each photon's positioning in two-dimensions to produce a scattering pattern for the sample. The tube through which the X-rays pass to reach the sample is generally sealed from the ambient atmosphere because over the large distances required for transmission SAXS (approximately 10 feet) the X-ray scattering with the atmosphere is appreciable and causes a significant increase in background noise whilst lowering the incident intensity of the beam.

In the case of anisotropic materials, with regular structural features on the order of 10 nm – 1 nm (roughly the detectable range of the Rigaku instrument), a greater density of detected photons will appear at specific angles. When the scattering pattern is radially integrated, a scattering peak will appear at the specific angle that corresponds to the domain spacings in the material, according to Bragg's law, equation 2.2. An example of the SAXS operation to obtain the angle of scattering intensities is shown in Figure 20.

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta) \quad (2.2)$$

Where n is an integer, λ is the X-ray wavelength, d is the domain spacing, and θ is the angle between the scattered and incident beams.

Figure 20. Polar transformation and integration of raw SAXS data for a highly crystalline calibration material.

In the case of dilute solutions, however, no structural features are present in the solution (there would be no peaks in the graph shown in Figure 20).

Instead, an isotropic intensity distribution of scattering angles results from the

random shapes and orientations of free particles in a solvent. Once the contribution of the solvent scattering is removed, the net scattering of sample can provide information about the individual particles. Equation 2.3, where, X, P, PS, S, C, T, I, and BS refer to the mass fraction of polymer in solution, net polymer, total polymer solution, pristine solvent, empty sample cell, transmission factor, intensity at the beamstop, and beam stop intensity with no cell, is used to calculate the net scattering from the analyte (the P3KHT-surfactant complexes).

$$I^P = [I^{PS} / T^{PS} - I^S / T^S] + X [I^S / T^S - I^C / T^C], T = I / I^{BS} \quad (2.3)$$

Dilute solutions of the complex were prepared in sealed containers at various concentrations below 1% w/w total solids. This concentration was theoretically expected to be below the overlap concentration of the P3KHT solutions for nearly rigid chains, with repeat unit length of 0.446 nm. In the dilute regime the scattering patterns were obtained over a period of 5 hours of X-ray exposure. The data were plotted using Guinier and Porod, details of which are discussed in the results section. To obtain the dilute-solution data, boron-rich glass capillary tubes (Charles Supper Company) with outer-diameter of 2 mm were first used to collect data. The tubes soften at approximately 800 °C, and were flame heated to seal against the atmosphere to prevent solvent loss. The Boron-rich glass is expected to have a very low attenuation coefficient under the X-ray light. However, the diameter of the glass was close to the diameter of the

X-ray beam footprint yielding smeared data due to the edge surface of the capillary. The smeared pattern can be seen in Figure 21.

Figure 21. Scattering intensities appear at both edges of the capillary cell vertically (left). For confirmation, the cell was rotated 90 degrees to confirm that the pattern was the result of the cell (right).

For this reason, a Kapton capillary tube was used with an outer diameter much larger than the beam footprint. The empty Kapton cell produced a truly isotropic pattern, despite greater background scattering, as shown in Figure 22 and was used for the measurements. Kapton cells were sealed with an acrylic adhesive. Samples were heated in-situ by a custom-built temperature controller that heats the aluminum sample holder.

Figure 22. An empty Kapton cell showing a more isotropic scattering pattern and a more accurate background subtraction.

Wide-angle X-ray Scattering (WAXS) data was also collected on the Rigaku instrument by placing a data collecting plate behind the sample, essentially manually placing a 'beamstop' directly behind the sample and scanning the resultant pattern on the data collecting plate for digital analysis using SAXS GUI software.

2.2.3. Fourier-Transform Infrared Spectroscopy (FTIR)

Attenuated-total reflectance FTIR was used to confirm the carboxylate binding of P3KHT with the surfactants. Drop-cast films of 0.5 mM solutions were prepared on a glass slide, and evaporated at room-temperature to perform measurements on a Nicolet 380 infrared spectrometer.

2.2.4. Polarized Optical Microscopy (POM)

Visualization of solid-state and lyotropic samples was performed using a POM (Leica DM2500 P). POM is a widely employed tool for studying liquid crystal textures and provides information about the crystalline ordering of samples. Incident light from the bottom of the microscope is polarized before passing through the sample. After light has passed through the sample, the remaining polarization angles are filtered out again by a polarizer 90 degrees from the incident polarized light, as shown in Figure 23. The first and second polarizers are termed the polarizer and analyzer, respectively.

Figure 23. Working principle behind polarized microscopy. The incident beam is polarized by passing through a grating (Polarizer 1, vertical), a second grating positioned 90° to the first (the analyzer, horizontal) eliminates any incident light, unless a birefringent sample in between (not shown) repolarizes the light after Polarizer 1 to produce some throughput of light and creating an image (Fellers, 2012).

Thus, for an isotropic material, no light will be transmitted for observation because all polarization angles have been filtered out. In the case of samples that have long-range order, however, light will be repolarized before passing through the second filter by the oriented planes in the sample this will produce an image. Bright optical contrast under the crossed polarizers is defined as birefringence. Solid-state and high-concentration gels of the P3KHT complex showed strong birefringence and their crystalline texture were studied. Stock hydrogels (0.05 M carboxylate) were oven heated at 60 °C at drop casted onto glass cover slides for observation under POM.

Figure 24. Leica DM2500P microscope used for studying films in solid-state and in lyotropic liquid crystal state (Martinek, 2008).

2.2.5. Differential Scanning Calorimetry

Stock solutions (0.05 M hydrogels) were directly oven heated at 60°C for 48 hours to produce solids for differential scanning calorimetry measurements at 5 °C/min under Nitrogen flow, using TA Instruments DSC Q2000. Samples were studied from -20 °C to 200 °C to determine the thermal transitions. All measurements were performed after a heat-cool cycle to remove any thermal history. Without the heat-cool cycle, the extent of crystallization of some of the complexes was less, indicating that the heating may also anneal the samples. The T_g and T_m are determined by a second-order and first-order thermal transition in the sample, respectively. The enthalpy values for T_m were obtained by integrating the heat flow over the range of the transition.

2.2.6. X-ray Diffraction

A reflection geometry Siemens D5000 diffractometer, with a 1.54 Å Cu K α radiation source, was used to obtain X-ray diffraction patterns of oven-dried films of the complex at 60 °C. Data was collected from 2-60 degrees 2 theta for all complexes and the pristine reactants. Other than a drop in scattering intensity, no difference in the diffraction pattern appeared depending on the solution concentration used to make films. Six concentrations between 0.05 M to 0.001 M were used to confirm this, all producing films of varying thickness and color but without remarkable differences in the diffraction pattern. The stock concentration of 0.05 M gels were oven heated to produce films on glass slides which were then placed directly onto the sample holder for measurement. No background

subtraction was performed for the XRD data because it is assumed that the film covers the entirety of the substrate. Still, a background pattern of the glass slide showed no features in the angle regime of interest.

Figure 25. The Siemens XRD used in the experiment. The goniometer is visible through the window of the sample chamber surrounding the sample holder block in the middle of the window. The collimator is to the left of the sample holder block and the X-ray scintillator is to the right of the sample holder block.

3. Results & Discussion

3.1 Dilute Solution Spectroscopy

The preparation of the complexes yielded distinctly different hydrogel species from either the polyelectrolyte or surfactant solutions separately. The ratio of macroscopic phase separation of the hydrogel depended upon the proportion of mixed surfactant side-chains. Such phase separation behavior has been previously reported for polythiophene-surfactant complex hydrogels and other LC polymers (Yang, 2009). The proportion of the phases depended upon the ratio of surfactants used, which is expected when considering the greater hydrophobicity of DHAB relative to CTAB. The isolated supernatant is the focus of this study, however no differences in the spectroscopic and thermal properties were observed between the two phases.

The absorbance maximum of the diluted aqueous complex, shown in Figure 26, presents a gradual blue-shift with increasing surfactant incorporation and a disappearance of the vibronic fine structure seen in pristine P3KHT (Zhao, 2006; Lobez 2012). The fine structure of the pristine polymer appears with maxima at 560 nm and 590 nm ($\Delta E = 0.2$ eV). This fine structure has been widely observed in aggregated polythiophenes and corresponds to the Frank-Condon progression of the C=C stretching mode within the thiophene ring.

Figure 26. Normalized absorbance spectra of newly diluted P3KHT complexes with concentrations of 0.04 mM, with varying proportions of monomer complexation with CTAB.

The blue shift in absorbance with greater incorporation of the surfactant is attributed to the de-aggregating effects of complexation. The addition of the 16C alkyl side-chains of the surfactant onto the P3KHT side-chains results in a hindrance of aromatic stacking between thiophenes units (Yang, 2009). This consequently produces less inter-molecular interactions and increased Π - Π^* transition energies.

Aggregation is believed to cause photoquenching of the P3KHT due to inter-molecular charge-transfer, yielding non-radiative responses to excitation (Duarte, 2011; Yang, 2005). The fluorescence space, shown in Figure 27, shows no emission of the pristine P3KHT solution beyond instrumental noise.

Figure 27. Fluorescence space of aqueous P3KHT (0.04 mM).

The quenching was observed over a large range of concentrations (from millimolar to micromolar) suggesting that P3KHT aggregate formation is very favorable in water. As shown in Figure 28, the emission intensity increased proportionally with the addition of CTAB to P3KHT. The quenching mechanism is therefore eliminated during ionic complexation with the surfactant. These findings agree with the widely observed photoluminescent enhancement of CPs by surfactant addition and point to the deaggregation of P3KHT in solution (Franco, 2012; Tapia 2006). The increased emission, and the blue-shift in absorbance both support the formation of supramolecular complexes.

Figure 28. Fluorescence spectra ($\lambda_{\text{exc}} = 430 \text{ nm}$) of newly diluted P3KHT complexes with varying proportions of monomer complexation with CTAB.

The as-prepared complex was a stable hydrogel. Surprisingly, the system gradually altered color from orange to brown upon dilution, and eventually precipitates were observed after weeks, as shown in Figure 29b. Figure 29a shows the time-dependent spectroscopic properties of the diluted solution of the stoichiometric complex. The absorbance of the freshly diluted complex appears with a λ_{max} near 430 nm. However, a subsequent 120 nm red shift occurs spontaneously over an aging period at room temperature. A distinct isosbestic point is observed, indicating that two phases exist in the solution (Xu, 2011; Roux, 1992). They are identified as twisted coil-like and planarized rod-like conformations, with λ_{max} of 430 nm and 550 nm, respectively.

Figure 29. (a) Absorbance spectra of newly diluted 100% CTAB complex (1:1, P3KHT monomer:CTAB) taken at various time intervals at 25 °C (0.04mM). (b) Corresponding color changes and eventual precipitation of the complex shown one minute, three hours, and two weeks after dilution 100x from the 50 mM stock hydrogel.

The emergence of a fine structure appears in the rod-like state of the complex, which is distinctly different from the fine structure of pristine P3KHT solutions; the relative absorptivity at 590 nm is much weaker and the spectrum presents a monotonic decrease in absorbance from λ_{max} . In most instances, the

vibronic structure of regioregular polythiophenes is reported in concert with an increase in the ECL, as a result of planarization among monomer units (Knaapila, 2010; Rughooputh, 1987), via single-molecule conformational extensions (Adachi, 2012) and/or ring stacking (Wu, 2009). The intensity of the lower energy absorption has been reported as indicative of the extent of lamellar-like stacking between chains. Such inter-chain stacking may be insulated by the 16 carbon supramolecular side-chains of the complex, however, the precise mechanisms contributing to the intensities of the fine structure are yet to be fully explored. We believe the time-dependent red-shift of λ_{max} to 550 nm is the result of conformational extensions of the individual complexes, while they remain less aggregated than P3KHT alone.

The intramolecular hypothesis is supported by the fluorescence data, as shown in Figure 30. The emission maximum shows a 50 nm red-shift with aging time. It is important to note that no significant photo-quenching is observed during the red shift, indicating that re-aggregation is not the cause of the red shift.

Figure 30. Normalized fluorescence spectra ($\lambda_{\text{exc}} = 560 \text{ nm}$) of newly diluted 100% CTAB complex at $25 \text{ }^{\circ}\text{C}$ ($4 \times 10^{-5} \text{ M}$).

The Stokes shift, defined as the difference between emission and absorbance band maxima ($\Delta\lambda = \lambda_{\text{em,max}} - \lambda_{\text{abs,max}}$), is found to progressively decrease from the initial coil-like ($\Delta\lambda = 130 \text{ nm}$) to final rod-like state ($\Delta\lambda = 60 \text{ nm}$). The reduction in the Stokes shift energy, by nearly 0.5 eV , supports the significant extension of the backbone, by providing improved overlap of fluorophores and a lesser extent of non-radiative electronic transitions (Chen 2000). The spectroscopic data collectively indicate a coil-to-rod transition. During this transition, polymer chains undergo a time-dependent change in conformation from a coil-like state, with twisting and bending between thiophene repeat units, to a rod-like state, with planarized thiophene rings. This transition would result in an increase in the ECL and a reduction in the band gap. In the rod-like conformation, surfactant side-chains interact closely and lipophilic interactions

may contribute to an energy barrier to free rotation of the thiophene units. With more rod-like regions in the backbone, less charge-trapping kinks are present along the chain (Tennyson, 2009). However, this rod-like conformation necessarily possesses a higher surface energy and is thermodynamically metastable (Xu, 2011). Therefore with much longer aging times, the polymer rods aggregate together to minimize interfacial area, as evidenced by flakey precipitates of the complex after weeks in Figure 29b.

In addition, it should be noted that a time-dependent chromism of the complex was not observed in the concentrated stock hydrogels, even after months of storage. This is attributed to entanglements of the coil-like complex chains. Upon dilution, these chains are freed from entanglements and over time, the coil-like conformation can transition into its favored conformation. Since the complex possesses long alkyl side-chains, π - π stacking between the polythiophene backbones is kinetically hindered, and may contribute to aggregation only with sufficiently long aging periods.

3.2. Kinetics of the Dilution-Induced Transition

To further understand the mechanism of the coil-to-rod transition of the aqueous polymer complex, UV-Vis absorption measurement is used to study the rate of time-dependent chromism for different concentrations (Figure 31). Interestingly, kinetics measurements display an inverse first-order rate law; the growth rate of the polymer rods is found to decline proportionally with

concentration. The method of initial rates was used to determine the rate law and to calculate the rate constant (Hall, 1976), as presented in Figure 31.

Figure 31. Change in absorbance ($\lambda = 590$ nm) with respect to concentration of the aqueous P3KHT-CTAB complex at 25 °C.

Figure 32. Initial rate plot fitted with a power function (dotted red line) taken from the initial rate data of the newly diluted P3KHT-CTAB complex. The uncertainty in the initial rates for each concentration results from the regression error of each

initial rate taken over the first 90 seconds. Images (inset) are taken 90 seconds after dilution corresponding to the indicated solution concentration, showing the difference in color.

Theoretically, the rate (R) is predicted to scale with concentration (C) as $R \propto C^n$, where the exponent determines the reaction order. As shown in Figure 32, the data points fall onto a line obeying the scaling relationship where $R \propto C^{(-0.98 \pm 0.01)}$. This inverse first-order relationship provides powerful evidence for the intrachain origin of the time-dependent chromism. Free of the high-viscosity environment in the gel, the more quickly the bulk of the chains can attain their thermodynamically favored extended conformation at room-temperature. As solution concentration approaches that of the stock hydrogel, the initial rate approaches zero. This phenomenon is in contrast with that of P3HT in a marginal organic solvent. The latter consistently shows a direct proportionality to concentration (Malik, 2001; Liu, 2009).

These results suggest that upon preparation of the hydrogel, the complex is topologically constrained from undergoing conformational transitions due to physically cross-linked networks. High concentrations may present a kinetic barrier to the thermodynamically favored rod-like conformation of the 100% CTAB complex, below a characteristic critical temperature. The transition manifests itself spontaneously at room-temperature in newly diluted solutions, when the polymer chains are freed of the entanglements.

3.3. Thermochromism of P3KHT Complexes

Figure 33 shows thermochromism of the aqueous complex in the dilute regime. At high temperature, the polymer chains adopt coil-like conformations to maximize the system's entropy and thus the absorption maximum shifts toward low wavelengths. With decreasing temperature, below a critical value, the polymer chains transform from coil-like to rod-like conformations to minimize the total free energy. As a result, the absorption maximum shifts toward higher wavelengths. Support along this line is provided by the temperature-dependent fluorescence of the complex (Figure 33b). High temperatures induce lower wavelength emission while lower temperatures result in a red-shift of the emission. The control P3KHT, however, shows no thermochromism from 5°C to 95°C.

Figure 33. Absorbance (a) and emission (b) spectra ($\lambda_{\text{exc}} = 430 \text{ nm}$) of the complex thermochromism. Measurements are performed during cooling for 30-minute equilibration times ($4 \times 10^{-5} \text{ M}$).

It should be noted that the thermochromism is reversible, with the presence of rate-dependent hysteresis, faster heating rates caused more hysteresis (Figure 34). In addition, due to the inverse-first order kinetics, more concentrated solutions showed greater hysteresis while at the dilute limit, no hysteresis is expected. For this reason, the critical transition temperature was calculated via quasistatic approximation, i.e., in dilute solutions at very slow scan rates.

Figure 34. Rate-dependent hysteresis of P3KHT-CTAB complex thermochromism (4×10^{-5} M). The heating rate is $2^{\circ}\text{C}/\text{min}$ at $\lambda = 590$ nm.

The critical temperature for the P3KHT-CTAB complex was calculated as $T_c = 37 \pm 3^{\circ}\text{C}$, corresponding to the magnitude of the thermochromism function's first-derivative ($|dA_{590}/dT|^{\text{max}}$). The sample standard deviation of repeated measurements is provided as the uncertainty because a slight variability between batches was observed. To understand the origin of transition mechanism,

thermochromism of the aqueous complex with different concentrations has been investigated. Figure 3.5 shows thermochromism of 0.06 mM and 0.74 mM solutions during slow heating rates. Within experimental errors, the thermochromism is concentration-independent, indicating an intrachain mechanism of the coil-rod transition (Rughooputh, 1987). Therefore, the transition is intrinsic to each polymer molecule.

Figure 35. Thermochromism of P3KHT-CTAB complex for different concentrations. The heating rate is 0.25 °C/min at $\lambda = 590$ nm.

To investigate the effect of surfactant structures on the critical transition temperature T_c , a certain amount of the double-tail surfactant, dihexadecyl dimethyl ammonium bromide (DHAB), was added to the P3KHT-CTAB complexes. The molar ratio of surfactants (CTAB and DHAB collectively) and P3KHT carboxylate units is stoichiometric (charge-balanced) in these complexes. With increasing the amount of the DHAB, the room-temperature absorption maximum shifts towards smaller wavelengths (Figure 36). This suggests that

more coil-like backbone structures are favored with higher loading of DHAB. The T_c of each complex was found to decrease proportionally with increasing the relative proportion of DHAB side-chains, as shown in Figure 37. These results indicate that the coil-like conformation is more favored in the complex with greater DHAB incorporation.

Figure 36. Absorbance spectra at 30 °C for 30-minute equilibration times during heating (0.04 mM)

Figure 37. Thermochromism functions of various side-chain compositions (2×10^{-5} M, $\lambda = 590$ nm, 0.25 °C/min). Ratios in the legend refer to the side-chain proportion (CTAB:DHAB) in the overall 1:1 (P3KHT:Surfactant) charge-balanced complex.

It is well recognized that the neutral P3HT chains adopt a coil-like conformation in good solvents. Upon addition of a poor solvent, P3HT chains undergo a structural transition from coil-like conformations to rod-like aggregates, accompanied by the formation of crystalline nanowires (Xu, 2011; Scharsich, 2012). Polymer solubility due to polymer-solvent interactions plays a crucial role in this structural transition (Park, 2011). Studies on the kinetics and thermodynamics of solvent-induced P3HT nanowire crystallization have revealed a possible intra- / inter-chain two-step mechanism (Xu, 2011; Malik, 2001; Liu, 2009) The first step is a coil-to-rod conformational transition of single polymer chains (Rughooputh, 1987) where backbones convert from a twisted coil-like

state to a planar rod-like state, which yields an elongation of effective conjugation lengths. However, this rod-like species has a larger surface energy and is therefore metastable (Xu, 2011). These rods will subsequently aggregate together via π - π stacking to minimize their surface energy. The first step, the conformational transition, is often too fast to be deconvoluted with respect to the optoelectronic properties of the system. The second step, aggregate formation, is the rate-determining step for polymer chromism (Mailk, 2001). As such, the kinetics and thermodynamics of aggregation/crystallization are used to describe polythiophene chromism (Rughooputh, 1987). For this reason, the dynamic behavior of crystalline nanowire growth rate against concentration obeys a first order rate law (Malik, 2001; Liu, 2009).

The chromism of the water-soluble P3HT derivative presented in this work is different from that of neutral P3HT in organic solvents: First, the time-dependent coil-to-rod transition only occurs in a newly diluted solution. Second, the dynamic process of time-dependent chromism follows an inverse first order rate law. Figure 38 is a proposed chromism mechanism based on these observations. The pure P3KHT chains are present as loose aggregates analogous to other CPEs (Laurenti, 2008). During complexation, the surfactants breakup the P3KHT aggregates. The resultant coil-like complex chains entangle each other to form penetrated networks (Litmanovich, 2007). The chain entanglements serve as physical cross-linkers to stabilize as-prepared hydrogels. Therefore, the hydrogel is very stable at room temperature for months. Upon dilution the coil-like chains are freed from entanglements. Single polymer chains

spontaneously transform from a coil-like to rod-like conformation. This process is an intrachain phenomenon (Rughooputh, 1987) and can only occur below a critical transition temperature, T_c . This intrachain mechanism is strongly supported by the observed inverse first-order rate law and concentration-independent thermochromism. Thus, the coil-to-rod transition of single chains in the polymer complex is a rate-determining step.

From a thermodynamic viewpoint, the rod-like state possesses less entropy and must be enthalpically driven below T_c , where the system undergoes an exothermic process to minimize free energy (ΔG). The coil-to-rod transition only ensues in the newly diluted solution below the critical temperature, T_c , to attain a metastable equilibrium state, where $T_c = \Delta H/\Delta S$. However, upon increasing temperature ($>T_c$) the entropy of the coil-like state thermodynamically 'outweighs' the exothermic interactions present in the extended conformation. The entropic component of the system is believed to be driven by the reduction of the interfacial area of the complex (i.e., due the hydrophobic effect) while the enthalpic component is driven by the resonance of coplanar thiophene units (Tapia, 2006). The surfactant side-chain structure is crucial in determining T_c . The greater lipophilic character of the complex, with more double-tail side-chains, clearly contributes more to the entropy of the coil state because it results in a reduction of the critical transition temperature. The greater hydrophobicity was noted macroscopically, the complex was not entirely soluble with high proportions of DHAB loading. The favorable increase in surface area of the lesser hydrophobic complex (i.e., the favored rod-like state) with greater

proportion of CTAB, provides support for the initiation of aggregation via an intramolecular mechanism. Aggregation driven by hydrophobicity would be expected to be favorable at higher temperatures, if the molecules are more hydrophobic *and remained globular*.

While the intrachain mechanism explains the optoelectronic phenomena successfully, an interchain mechanism is clearly indicated in the much later precipitation of the rod-like complex, where the large surface area of the extended conformation makes it metastable. However, we believe that the surface energy of the aqueous P3KHT complex in the rod-like state is not as rapid of a driving force for aggregation, when compared to that of neutral P3HT in an organic solvent, because backbone interactions are kinetically hindered by the long supramolecular side-chains. Thus, the aggregation of polymer rods via π - π stacking is slower, once the coil-to-rod transition of single chains has occurred.

Figure 38. Illustration of the de-aggregating and gelating effects of surfactant complexation upon P3KHT, shown with the corresponding purple-to-red color changes. When the complexed hydrogel is diluted below a critical temperature, T_c , it spontaneously relaxes to its thermodynamically favored extended conformation and over time aggregates together. The conformational transition is thermoreversible.

3.4. Solution Small-angle X-ray Scattering

To support the coil-to-rod conformational transition with more direct measurements, SAXS was used to study the complexes in solution. In the low q regime, information about individual polymer particles can be obtained. Using a Guinier approximation, equation 3, a plot of $\ln[I(q)]$ versus q^2 has a slope which is proportional to the radius of gyration of the polymer particle. The Guinier equation assumes that the polymer chains are entirely isolated in solution, and is

most accurate for globular-shaped particles. If particles are aggregated, the Guinier plot approaches infinity as the angle approaches zero because the false R_g estimate of aggregate sizes approaches infinity (i.e., R_g value is dependent upon the angle and is no longer accurate). Example Guinier plots, depicting various states of aggregation is shown in Figure 39.

$$\ln[I(q)] = \ln[I_0] - [q^2 R_g^2] / 3 \quad (3.1)$$

Figure 39. Typical Guinier plots showing varying degrees of particle dispersion in solution (Wang, 2009).

As shown in Figure 40, the Guinier plot of various complexes reveals an upturn in $I(q)$ for low q -values indicating that polymer chains are not isolated particles in solution. This result is not unexpected, however, because of the sensitivity of the SAXS instrument, the minimum detectable concentration measured was 0.24% w/w (9.8 mM) and 0.01% w/w (0.5 mM). At these

concentration, the viscosity of the complex solutions was still above that of water. This suggests that entanglements exist in the complex solutions at this concentration and the polymer chains are not expected to be isolated in solution. Fitting of the Guinier plots to determine the radius of gyration provided a value of nearly 60 nm, although due to the aggregation this value is not expected to be accurate.

Figure 40. Guinier plot of complexes with different concentrations in water.

In the mid- q regime, X-ray scattering probes local structures smaller than the entire scattering object. The mid- q regime can be analyzed via the Porod plot. Using a Porod plot, the fractal dimension of local structures in the scattering object can be determined (Hammouda, 2013; Zhang, 2010). The Porod plot is obtained by plotting $\log(I(q))$ vs $\log(q)$. An example of the type of structural information obtained from the slope of the Porod plot is illustrated in Figure 41.

Figure 41. Structural information obtained from the fractal dimension of the scattering object (Hammouda, 2013).

The resultant data, shown in Figure 42, is found to fit $I(q) = q^{-1}$ (rodlike) and $I(q) = q^{-2}$ (sheet or coil-like) at low and high $\log(q)$, respectively, with $R^2 > 80\%$. The complexes are thus rod-like on smaller size scales while they present a more sheet or coil-like structure at larger size scales, essentially a coil-like overall shape with rod-like segments. It has been shown that the q^* transition from -1 and -2 slope values corresponds to the persistence length as $q^*(L_p) = 3.5$ (where q^* is the critical q value and L_p is the persistence length) (Lecommandoux, 2002 ; Knaapila, 2010). Longer rod-like segments in the chain will move q^* to larger values and more coil-like chains move q^* to smaller values. From the SAXS data (Figure 3.17) the changes in persistence length agree with the previous spectroscopic data because longer persistence lengths correlate to longer

effective conjugation lengths. With higher temperatures, for a given complex, the persistence length is reduced, and with greater proportions of DHAB complexation, the persistence length is also reduced for a given temperature. From Figure 42, it can be seen that these solutions do not show the large micellar hump as with pristine CTAB, and less obviously in the pristine P3KHT solution of Figure 42, despite the complex solutions being above the CMC of CTAB (approximately 1 mM). The broad halo in the CTAB solution of Figure 43 corresponds to loose correlation lengths between individual CTAB micelles and does not appear in the pattern for the complexes. In pristine P3KHT (Figure 3.17), however, a slight maximum is observed and no critical q -value is observed. This suggests that P3KHT aggregates have irregular fractal surfaces and associate to produce a broader interference pattern. These findings also suggest that in the complex solutions, free surfactant micelles do not form, supporting the formation of the supramolecular complex.

Figure 42. Solution SAXS of 0.6% w/w P3KHT-CTAB complexes and 0.2% w/w pristine P3KHT solutions.

Figure 43. Pristine CTAB solution, showing of broad interference pattern indicating the presence of micelles.

The persistence lengths, tabulated in Table 1, provide information about the rigid segments of the scattering objects, whether they be highly extended individual polymer chains or more likely aggregates which are rod-like. The uncertainty in the persistence length was taken from the largest of the regression errors in the linear fit of each scattering pattern, the high q regime generally had a larger regression error (the fit with a slope of -1 was used for uncertainty). For a thiophene monomer length of 4.46 angstroms, P3KHT contour length is 103 nm (calculated for $M_0 = 246$ g/mol and $M_w = 60$ kg/mol), calculated using equation 3.2.

$$\text{Contour length} = (M_w/M_0) * \text{Monomer length} \quad (3.2)$$

Table 1. Persistence length calculated for the complexes based on the solutions SAXS data.

Composition	Temperature (C)	q^*	Persistence Length (nm)	Uncertainty
100% CTAB	20	0.0243	14.4	0.4
85% CTAB 15% DHAB	20	0.0251	13.9	0.4
70% CTAB 30% DHAB	20	0.035	10.0	0.5
100% CTAB	70	0.0312	11.2	0.6
85% CTAB 15% DHAB	70	0.0325	10.8	0.5
70% CTAB 30% DHAB	70	0.035	10.0	0.6

The persistence length is expected to be well below the contour length of the chain, otherwise the polymer would be a 100% rigid object. According to the persistence lengths in Table 1, the P3KHT complex supramolecules have rigid units extending the length of approximately 30 monomer units. This value is

much larger than P3HT persistence lengths reported in literature that are typically below 5 nm (Rodd, 2011). These findings indicate that the scattering objects may not be individual chains, but instead aggregated objects in solution, as expected from the Guinier plots. Rod-like aggregates of other polythiophene-surfactant complexes in water have been previously observed using neutron scattering (Knaapila, 2010). The large persistence length for the P3KHT-CTAB complex likely corresponds to such rod-like rigid aggregates of the supramolecules.

3.5. Properties of Solid-state Complexes

Confirmation of the quaternary ammonium-carboxylate ionic bonding was obtained using FTIR spectroscopy of dried 1:1 films. As shown in Figure 44, the energy of carboxyl and carboxylate vibrations are different from one another, with the emergence of a triple-peak appearing in the case of carboxyl bonding. In the complex FTIR, shown in Figure 45, alterations in the vibrational energies of methylene bands ($2800\text{ cm}^{-1} - 3000\text{ cm}^{-1}$) as well as the carboxylate stretching bands ($1200\text{ cm}^{-1} - 1700\text{ cm}^{-1}$) were observed. Three peaks appear in the carboxyl region after complexation indicating a carboxy-like bonding, rather than a free carboxylate (Princeton, 2013). The slight red-shifts in methylene vibrations, and the substantial reduction in peak half-width, are attributed to the improved packing of the aliphatic side-chains in the complex films (Weiwei, 2012).

Figure 44. Carboxyl (blue) and carboxylate (red) vibrational energies of fulvic acid (Princeton, 2013).

Figure 45. Reflectance FTIR spectra of room-temperature drop-cast films showing the methylene and carboxyl regions of the 100% P3KHT-CTAB complex compared with the polymer, P3KHT, alone.

Complex films had crystalline textures that are in stark contrast with the non-birefringent P3KHT. The characteristic Maltese cross, shown at the inset of

Figure 46, identifies large spherulites in the 100% CTAB complex. These crystalline structures have not been previously visualized for water-soluble polythiophenes but are similar to films of P3ATs processed with organic solvents (Conio, 1984; Wu, 2009).

Crystallinity of the solid charge-balanced 1:1 (P3KHT:Surfactant) complexes was observed with DSC as well, in contrast with amorphous pristine P3KHT (Figure 46). No phase transitions for isolated CTAB nor DHAB were observed in the thermograms, supporting the completion of the complexation reaction. As shown in Figure 47, the complex presented a gradual reduction in crystallinity, and a lowered T_m , with increased proportion of DHAB side-chains. The lesser degree of crystallinity of the two-tail complex was found to agree with WAXS data shown in Figure 48, due to the appearance of a broad amorphous scattering halo. Enthalpy values for the sum of the first-order transitions, shown in Table 2, show a consistent reduction in percent methylene crystallites with more DHAB side-chains. In parallel with these observations, the gradual broadening of a double melting peak, from the shoulder peak of the 100% CTAB complex, indicates a greater proportion of imperfect crystallites with greater incorporation of DHAB (Worfolk, 2011). Previous studies on the thermal properties of CPE-alkyl surfactant complex films, by Thunemann and coworkers, have attributed similar transitions to side-chain crystallinity (Thunemann, 1999). These crystallites are analogous to paraffin-like ordering of covalent side-chain polymers, e.g. those based on acrylic acid, which show first-order transitions

above a critical alkyl side-chain length. These findings are in agreement with the increased methylene ordering in the complex shown by the FTIR data.

Figure 46. DSC of the 100% P3KHT-CTAB complex melt versus pristine P3KHT melt. The inset image shows spherulite crystalline textures of the complex under POM.

Figure 47. DSC of various 100% P3KHT complexes with varying ratios surfactant side-chains (CTAB:DHAB) heated at 5 C°/min.

Table 2. Normalized enthalpy values obtained for the sum of the melting peaks for each complex composition.

complex composition ^a	ΔH (J/gK)	w/w CTAB (%)	w/w relative CTAB (%)	ΔH_{norml} (J/gK) ^b
100% CTAB	51.39	58.44	100.00	51.39
90% CTAB 10% DHAB	24.42	54.62	93.46	26.13
80% CTAB 20% DHAB	17.61	46.46	79.50	22.15
70% CTAB 30% DHAB	13.02	38.98	66.70	19.52
60% CTAB 40% DHAB	10.5	32.09	54.91	19.12

^a Composition refers to the percent of carboxylate monomer units saturated by the indicated surfactant in the charge-balanced complex.

^b Normalization refers to the enthalpy per gram of the complex containing CTAB side-chains. Further examples of this calculation are available from reference 74.

Figure 48. WAXS of complexes with varying ratios surfactant side-chains (CTAB:DHAB).

Figure 49. XRD of pristine P3KHT compared with the complexes with varying ratios of surfactant side-chains (e.g., 8:2 = 80% CTAB:20% DHAB for overall 1:1 Monomer:Surfactant).

The crystallized complex is thus expected to have inter-digitated side-chains, observed before for P3ATs with side-chains of 12C and longer, where the inter-backbone distances are representative of a single-side chain length. Alternating alkane and ionic layers have been widely reported as the predominant molecular arrangement in films for CPE-surfactant complexes which are mediated by interdigitating side-chains (Thunemann, 1999). As shown in Figure 49, XRD of the solid samples presents a peak corresponding to a d-spacing of approximately 22 Å with a secondary peak near 11 Å. The 1:2 ratio of the peaks suggests a lamellar ordering in the film, which has been previously observed for CPE-surfactant complexes (Yang, 2009). The domain spacing is on the order of the length of a 16C side-chain of 39 Å, assuming a perfectly

extended sp^3 -bonded 16C side-chain (with bond angles of 109.5 degrees). This indicates that in the film, the side-chains are not entirely extended. It can be seen that with increasing incorporation of DHAB, the lamellar spacing increases and crystallinity rapidly decreases. This is in agreement with the calorimetry measurements. In addition, the lamellar ordering indicates that only one crystal form exists in the films, suggesting that the DSC melting peaks are not of different crystal forms but rather of imperfect crystallites. It can be seen that increased DHAB addition increases the proportion of the imperfect crystallites while reducing the overall enthalpy of the thermal transition. Collectively, these findings indicate the disruption of side-chain ordering by DHAB addition, which is in agreement with a less extended backbone during crystallization.

3.6. Research Outlook

In order to truly understand the mechanism by which dilute-solution polymer ordering mediates crystallization, higher concentration liquid crystal studies are of great importance. Shown in Figure 50 are images of lyotropic liquid crystal phases of P3KHT complexes at high concentration.

Figure 50. (a) Shear-aligned ~70% w/w P3KHT complex containing 8:2 (CTAB:DHAB) surfactants. (b) ~60% w/w P3KHT-CTAB complex containing only CTAB surfactants, 1:0 (CTAB:DHAB). Images are taken at room temperature under cross-polarizers.

As solvent is removed from the solution, birefringence appears above a certain critical concentration of LC formation. By studying the onset concentration of LC formation, the relative tendency for the complex to produce LC phases can be compared depending on the surfactant composition. Figure 50 shows preliminary data of lyotropic LC phases of the complexes with different surfactant side-chain compositions. The LC ordering is believed to be driven by anisotropic properties of the complex (Zhang, 2010). With a more rod-like shape, a nematic liquid crystal may form, in accordance with the Onsager hard-rod model (Onsager, 1949). With increasing concentration, cylindrical objects approach each other and exclude volume from their center of mass. This volume is larger if there is a significant angle between two approaching cylinders. For this reason, the net positional entropy of cylindrical objects in a concentration solution is increased by coaxial alignment of the cylinders. It has been clearly shown that

P3KHT-surfactant complexes undergo a coil-to-rod conformational transition in water, depending upon the surfactants used. It is important to understand how such a conformational transition effects the onset of nematic ordering of the complex. The processing of P3KHT solutions can be optimized by developing a phase diagram that shows the onset of LC formation (birefringence under POM) as a function of surfactant composition.

In addition to the development of such a phase diagram, solid-state memory of solution chromism is another interesting area of study. As shown in Figure 51, the solid-state absorbance is highly dependent upon the film casting temperature, which has been shown to effect the solution backbone conformation and of the complex.

Figure 51. (left) UV-Vis of various films at room-temperature depending on the casting temperature. (right) The pictures on the left column are of room-temperature casted films, observed at room temperature (above) and high temperature. (below). Right column images are of high-temperature casted films

being observed at room temperature (above) at high temperature (below). The high temperature used was a hot plate at 70 °C.

Films drop-casted show some mimicry of the chromism observed in solution. At high temperatures the color changes from purple to orange. However, a degree of film memory is apparent because the films casted at low and high temperatures do not behave the same with respect to their absorbance (Figure 51). The memory effect may be a result of the dilute-solution conformational transition. During film formation, inter-chain distances are reduced as the solvent is removed whilst the polymer chains retain their shape during drying. The red-shifted film, casted under vacuum at room temperature, is expected to have a greater crystallinity, as indicated by previous studies in polythiophene film absorbance and morphology.

The memory effect has important implications for the aqueous processing of polythiophene. By optimizing the processing parameters in water (e.g., temperature, concentration, surfactants), a higher degree of crystallinity can be obtained in the solid-state. Using this method, semiconducting films can be cheaply produced on a large scale with desirable optoelectronic and morphological properties.

4. Conclusions

In summary, the kinetics and thermodynamics of surfactochromism of aqueous P3KHT-CTAB complexes has been investigated. The diluted solution exhibits spontaneous time-dependent chromism at room temperature. Detailed analysis of this process reveals an inverse first-order rate law of the phase transition. Temperature-dependent chromism is completely reversible and is concentration- independent. An intrachain mechanism is proposed on the basis of the observed phenomena. Single polymer chains, once diluted from the entangled hydrogel conditions, spontaneously transform from a twisted coil-like conformation into a planar rod-like conformation. Surfactant architecture is crucial for determining the critical transition temperatures. In addition, solid-state crystallinity has been shown to be largely dependent upon the surfactant structure and in-turn the dilute-solution behavior. This work addresses an important fundamental issue concerning surfactant-induced ordering of nanostructures for water-soluble conjugated polymers. Because of an emerging demand for ordered nanostructures of water- soluble conjugated polymers in high-efficiency polymer electronic devices, this work represents a scientific foundation for the green manufacturing of these materials.

5. Works Cited

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