Scanning Probe Microscopy Studies of the Properties of Conducting Polymers

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Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy
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(Spine title: Scanning Probe Microscopy Studies of Conducting Polymers)

(Thesis format: Integrated-Article)

by

Kevin D. O’Neil

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The School of Graduate and Post-doctoral Studies
The University of Western Ontario
London, ON

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THE UNIVERSITY OF WESTERN ONTARIO
The thesis by

Kevin D. O’Neil

entitled:

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is accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Date__________________________

Chair of the Thesis Examination Board
ABSTRACT

Electronically conducting polymers (ECPs) have been growing in interest as important materials for a variety of different applications such as charge storage devices and photovoltaics. However, in all of these applications, the performance of conducting polymers are strongly dependent upon their local properties such as morphology, local conductivity and carrier mobility, local chemical composition, etc. All polymer materials feature a distribution of these parameters and therefore, they are considered heterogeneous. In this work, we use atomic force microscopy (AFM) and its related techniques such as current-sensing AFM (CS-AFM), Kelvin probe force microscopy (KFM) and phase imaging (PI-AFM) to directly investigate the heterogeneity of ECPs, specifically poly[2,2’-bithiophene] (PBT), in order to determine how their performance depends on their local properties and their distribution.

Chapter 4 will address the correlation between topography, local conductivity and local surface potential/work function of various conducting polymers such as PBT and poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV). To explain this correlation, a model has been proposed which relates these properties to the molecular weight distribution during electropolymerization of conducting polymers. Chapter 5 will investigate further into this model by studying the nucleation and growth of conducting polymers. It will utilize phase imaging to determine how the distribution of molecular weight, and therefore, crystallinity can directly affect the overall properties such as conductivity and surface potential in these materials. Chapter 6 will focus on the effect of common electrochemical techniques used to prepare these materials and their influence on the local properties of conducting polymers, specifically morphology and crystallinity, in both thin and thick conducting polymer films. Chapter 7 and chapter 8 will add to the previous chapters by investigating the charge/discharge (doping/undoping) efficiencies of these materials as charge storage devices in relation to the local properties of these conducting polymer films in order to effectively prepare these materials to increase efficiency for use in electronic devices.
**Keywords:** Electronically Conducting Polymers (ECPs); Polybithiophene; Mesoscopic Inhomogeneity; Nucleation; Doping-Level Distribution; Local Conductivity; Local Work Function; Crystallinity; Atomic Force Microscopy (AFM); Current-Sensing AFM (CS-AFM); Kelvin Probe Force Microscopy (KFM); Phase Imaging (PI-AFM); Electropolymerization.
CO-AUTHORSHIP

This doctoral thesis has been prepared according to the regulations for an integrated-article format thesis stipulated by the Faculty of Graduate and Postdoctoral Studies at the University of Western Ontario and has been co-authored as follows:

Chapter 3: On the Origin of Mesoscopic Inhomogeneity of Conducting Polymers

All experiments were conducted by K.D. O’Neil under the supervision of Dr. O.A. Semenikhin. Preliminary studies were started by B. Shaw. A draft of chapter 3 was prepared by K.D. O’Neil and reviewed by Dr. O.A. Semenkhin. Further edits and revisions were carried out by both K.D. O’Neil and Dr. O.A. Semenkhin. A copy of this chapter has been published at: O’Neil, K. D.; Shaw, B.; Semenikhin, O. A. Journal of Physical Chemistry B 2007, 111, 9253-9269.

Chapter 4: AFM Phase Imaging of Electropolymerized Polybithiophene Films at Different Stages of Their Growth

All experiments were conducted by K.D. O’Neil under the supervision of Dr. O.A. Semenikhin. A draft of chapter 4 was prepared by K.D. O’Neil and reviewed by Dr. O.A. Semenkhin. Further edits and revisions were carried out by both K.D. O’Neil and Dr. O.A. Semenkhin. A copy of this chapter has been published at: O’Neil, K. D.; Semenikhin, O. A. Journal of Physical Chemistry C 2007, 111, 14823-14832.

Chapter 5: AFM Phase Imaging of Thin Films of Electronically Conducting Polymer Polybithiophene Prepared By Electrochemical Potentiodynamic Deposition

All experiments were conducted by K.D. O’Neil under the supervision of Dr. O.A. Semenikhin. A draft of chapter 5 was prepared by K.D. O’Neil and reviewed by Dr. O.A. Semenkhin. Further edits and revisions were carried out by both K.D. O’Neil and Dr. O.A. Semenkhin. A copy of this chapter has been published at: O’Neil, K. D.; Semenikhin, O. A. Rus. J. Electrochem. 2010, 46, 1345-1352.
Chapter 6: The Effect of Electropolymerization Method on the Nanoscale Properties and Redox Behaviour of Poly[2-2’-bithiophene] Thin Film Electrodes

All AFM experiments and characterization were conducted by K.D. O’Neil under the supervision of Dr. O.A. Semenikhin. Electrochemical experiments on Pt were carried out by A. Forrestal under the supervision of both K.D. O’Neil and Dr. O.A. Semenikhin. A draft of chapter 6 was prepared by K.D. O’Neil and reviewed by Dr. O.A. Semenkhin. Further edits and revisions were carried out by K.D. O’Neil, A. Forrestal and Dr. O.A. Semenkhin. A copy of this chapter has been submitted for publication at: O’Neil, K. D., Forrestal, A., Semenikhin, O.A. Electrochim Acta 2012.

Chapter 7: The Effect of Cycling on the Nanoscale Morphology and Redox Properties of Poly[2-2’-bithiophene]

All experiments and characterization were conducted by K.D. O’Neil under the supervision of Dr. O.A. Semenikhin. Preliminary electrochemical measurements on HOPG were performed by A. Smith under the supervision of K.D. O’Neil and Dr. O.A. Semenikhin. A draft of chapter 7 was prepared by K.D. O’Neil and reviewed by Dr. O.A. Semenkhin. Further edits and revisions were carried out by K.D. O’Neil, and Dr. O.A. Semenkhin.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisor, Dr. Oleg Semenikhin. For the past 5 years, he has always motivated and inspired me to bring out the best in myself and to never give up and always keep moving forward.

I have also had the honor of having amazing laboratory partners throughout my time at UWO. Trissa Kantzas, Joshua Byers and Adam Forristal have always been around to give insight into new ideas, help teach unfamiliar concepts or just to have a great conversation to give our minds a break from research.

Finally, I would like to thank my friends and most importantly, my family. My father, mother and sister have always been there for me. When times were hard and stressful, they reminded me of my past and the previous struggles that I always overcame to continue moving forward. They always took the time to listen and always supported me in any possible way they could and for that, there are no words to express the magnitude of how truly grateful I am to have them.
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**Figure 7.1.** (a) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.3 V. Two quasi-isosbestic points are observed on the reverse scan located at B (ca. 0.8 V) and C (ca. 0.6 V). There is an indication of an isosbestic point on the direct scan around 1.25 V; however, it is not well pronounced. (b) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.4 V. One quasi-isosbestic point on the direct scan is located at A (ca. 1.1 V). Two quasi-isosbestic points are observed on the reverse scan located at B (ca. 0.75 V) and C (ca. 0.55 V). An inset in the upper left hand corner shows a zoomed-in section of B and C. (c) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.45 V. One quasi-isosbestic point on the direct scan is located at A (ca. 1.1 V). One special point is observed on the reverse scan located at B (ca. 0.75 V) and one quasi-isosbestic point is seen at C (ca. 0.55 V). (d) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to
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direct scan is located at A (ca. 1.0 V). One special point is observed
on the reverse scan located at B (ca. 0.75 V) and one quasi-isosbestic
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All CVs were recorded after every fifth scan cycle.

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**Figure 7.4.** Simultaneous 1 µm by 1 µm images of the topography (left) and phase (right) for polybithiophene films deposited on an HOPG substrate for (a) as-prepared, non-cycled, (b) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.4 V, (c) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.45 V, and (d) subjected to 100 doping and undoping cycles to the anodic potential limit of 1.45 V. All samples were prepared under galvanostatic conditions at a current density of 1 mA cm\(^{-2}\) for 50 s.

**Figure 7.5.** Simultaneous 500 nm by 500 nm images of the topography (left) and phase (right) for polybithiophene films deposited on an HOPG substrate for (a) as-prepared, non-cycled, (b) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.4 V, (c)
subjected to 50 doping and undoping cycles to the anodic potential limit of 1.45 V, and (d) subjected to 100 doping and undoping cycles to the anodic potential limit of 1.45 V. All samples were prepared under galvanostatic conditions at a current density of 1 mA cm$^{-2}$ for 50 s.
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### LIST OF ABBREVIATIONS

<table>
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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AcN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>BT</td>
<td>2-2’ bithiophene</td>
</tr>
<tr>
<td>CPD</td>
<td>Contact potential difference</td>
</tr>
<tr>
<td>CS-AFM</td>
<td>Current-sensing atomic force microscopy</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
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<tr>
<td>ECP</td>
<td>Electronically conducting polymer</td>
</tr>
<tr>
<td>EFM</td>
<td>Electrical force microscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast fourier transform</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<tr>
<td>HOPG</td>
<td>Highly oriented pyrolitic graphite</td>
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<tr>
<td>KFM</td>
<td>Kelvin probe force microscopy</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2’ethyl-hexyloxy)-1,4-phenylene vinylene]</td>
</tr>
<tr>
<td>Mw</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>OLED</td>
<td>Light emitting diode</td>
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<tr>
<td>P3HT</td>
<td>Poly3-hexylthiophene</td>
</tr>
<tr>
<td>Abbreviation</td>
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</tr>
<tr>
<td>PA</td>
<td>Polyacetylene</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybithiophene; poly[2,2’-bithiophene]</td>
</tr>
<tr>
<td>PI-AFM</td>
<td>Phase imaging atomic force microscopy</td>
</tr>
<tr>
<td>PT</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>RR</td>
<td>Regioregular</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>T</td>
<td>Thiophene</td>
</tr>
<tr>
<td>TBAPF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>Q</td>
<td>Quadrant</td>
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Chapter 1: Introduction

Virtually all materials naturally have some degree of inhomogeneity, or in other words, they are considered heterogeneous. When designing a material for applications, micro- and nanostructure and the corresponding nanoscale heterogeneity of the material play an enormous role. Without addressing this key issue, it is impossible to create a material that will be effective for a specific purpose or furthermore, be able to improve a material in order to increase its efficiency.

This apparent heterogeneity is extremely important in the field of electronically conducting polymers (ECPs) for use as organic semiconductor devices such as solar cells or charge storage devices\(^1\)-\(^3\). In these devices, the polymer layer can vary from ten to several hundreds of nanometers in thickness. At this scale, any disorder caused from heterogeneity has a direct impact on the properties and overall performance of these materials. Specifically, the effects of inhomogeneity are directly related to the charge transport efficiency in these materials, which is a crucial parameter for solar cells or batteries. Therefore, there is an interest in investigating the origin of the heterogeneity of these materials and the related effect of this heterogeneity on their properties.

Recent advances in the field of scanning probe microscopy, specifically atomic force microscopy (AFM) have provided researchers with a new powerful tool for visually characterizing the micro- and nanoscopic inhomogeneity, which will be referred to as the mesoscopic inhomogeneity, of ECPs. The mesoscopic scale can be understood as the length scale at which one can study the properties of a material without having to consider the properties of individual atoms. Importantly, this scale (5-500 nm) is also the size of the typical morphological features of most ECPs.

AFM is typically considered a powerful imaging technique for characterization of the morphology of materials on the nanoscale. However, one of the main advantages of this tool lies in the variety of different auxiliary scanning techniques to measure a host of additional parameters simultaneously with the topography. Some of these techniques
include: current-sensing AFM (CS-AFM), which can determine local electrical properties and, specifically, local conductivity; Kelvin probe force microscopy (KFM), which can be used to assess the local work function of materials and, through it, the chemical composition and the oxidation degree; and phase imaging AFM (PI-AFM), which can determine local mechanical properties and, in particular, local crystallinity. Again, it is important to note that all of these parameters are acquired simultaneously with the topography and therefore these techniques are especially useful in exploring correlations or the lack thereof between the sample morphology and local chemical or electrical properties. The presence or absence of such correlations is important for determining the origin of various nanoscale morphological features and the relation to local electrical and structural properties and whether or not such properties can be controlled through modification in the polymer morphology, for instance, through the use of different deposition techniques.

Most studies on ECPs using AFM have been focused on characterizing just the morphological features of these materials. However, the inhomogeneity of ECPs should not solely depend to their apparent morphological features but should also extend to their local internal properties such as conductivity, oxidation degree, crystallinity, etc. In this work, we utilize AFM and its extensions to study the origin and effect of the heterogeneity of ECPs and relate their local properties and their distribution to the performance of these materials in various devices. The majority of the studies were performed with polymers of the polythiophene series and specifically poly[2,2’-bithiophene] (PBT), which is a typical conducting polymer and an excellent model system; however, some other important polymers such as poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were investigated as well.

Chapter 4 describes our early study of the origin of mesoscopic inhomogeneity of conducting polymer films, such as polybithiophene (PBT) and poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), prepared by electropolymerization and spin coating using Kelvin probe force microscopy (KFM) and current-sensing atomic-force microscopy (CS-AFM)\(^4\). In this chapter, a well-pronounced
correlation between the polymer morphology, the local work function (which is related to the polymer oxidation degree) as well as polymer conductivity is found. In order to explain this correlation, a model is proposed that relates the observed inhomogeneity to preferential deposition of polymer molecules with higher molecular weight at the early stages of the polymer phase formation.

In Chapter 5, we further strengthen our proposed model of the polymer inhomogeneity by studying the nucleation and growth of conducting polymer films using AFM phase imaging. It was found that, at the early stages of the polymer nucleation and growth, the polymer films were predominantly crystalline. At the later stages, the polymer contained both crystalline and amorphous phases, with the crystalline polymer located in the grain cores and the amorphous phase found at the grain periphery. It was found that these results are in remarkable agreement with the results of the KFM and CS-AFM measurements from the previous chapter, which relates such inhomogeneity to the presence of both high and low molecular weight polymer fractions (polydispersity) in the electropolymerization solution during deposition.

Chapter 6 focuses on the effect of the electropolymerization method used when preparing conducting polymer films. In this chapter, the properties of polymer films made under potentiostatic and potentiodynamic conditions were compared using AFM and AFM phase imaging (PI AFM). It was found that while the morphologies of the films prepared using the two techniques were quite similar, the phase contrast measurements revealed a profound difference in the mechanisms of potentiostatic and potentiodynamic electropolymerization, as well as in the nanoscale crystallinity and grain structure of the resulting polymer films and that these differences were especially pronounced at the early deposition stages.

Chapter 7 builds upon the results found in the previous chapters by studying the cyclability and the charge storage capacity of conducting polymers prepared using different electropolymerization methods. It was shown that potentiodynamically prepared films featured a much higher stability and reversibility of the doping-undoping
processes approaching 100% over multiple cycles in comparison to potentiostatically prepared films. This was related to the difference in the nanoscale morphology, crystallinity and degree of disorder of polymer films, as evidenced by AFM and PI-AFM.

Finally, chapter 8 further develops the work performed in chapter 7 by characterizing the morphology and crystallinity of conducting polymer films using AFM and PI-AFM after they have been subjected to repeated charging-discharging cycles in order to explain the mechanism of the polymer film degradation and to how to effectively prepare these materials in order to increase the efficiency for use in charge storage devices.

1.1 References

(8) O'Neil, K. D.; Forristal, T. A.; Smith, A.; Semenikhin, O. A. 2012 Manuscript in Preparation
Chapter 2: Literature Review

2.0 Background

The field of conducting polymers is very diverse due to the wide range of uses for these materials. As a consequence, the attention of the scientific community is constantly shifting to whichever application will have the greatest impact in the present time. As a result, very often the focus of studies involving conducting polymer inhomogeneity has been based on the needs of specific applications with little attention being paid to developing an overall understanding of where the underlying inhomogeneity of all conducting polymers originates from.

In the 1980-s and 1990s, most studies were focused on the metallic state of conducting polymers. The common polymers studied at the time were mainly polyacetylene, polyaniline and polypyrrole. Electrochemical and related studies of the inhomogeneity of the doping level distribution were initiated at this time as well. Starting in the new millennium, the scientific community began to shift its focus towards semiconducting polymers and applications such as organic light-emitting diodes (OLEDs), organic electronics and plastic solar cells. As a result, studies of the polymer inhomogeneity from the previous generation of conducting polymers were replaced with newer polymers such as polythiophenes and its derivatives such as polybithiophene (PBT) and poly(3-hexylthiophene) (P3HT) (refer to figure 2.1). However, despite the very different functions that polymers such as polyaniline and polypyrrole have in comparison to polythiophenes, the fact remains that these polymers are closely related and therefore, the factors that govern their inhomogeneity should be similar.

The mesoscopic inhomogeneity of conducting polymers was first addressed in 1987 by Zuo, Angelopoulos, MacDiarmid, and Epstein who proposed the model of a granular polymer metal on the basis of their DC-conductivity measurements. In a follow up study, this model was strengthened by the results of X-ray measurements, microwave frequency-dependent conductivity and NMR relaxation measurements and was
summarized in a paper by Prigodin and Epstein\textsuperscript{6}. In this model, it was envisioned that these materials consisted of a network of small, conducting/crystalline domains or islands separated by an insulating/amorphous matrix. The conducting/crystalline domains would be assembled from regularly packed polymer chains with good interchain overlapping. It was thought that this highly packed configuration would occur randomly and only in certain regions of the polymer matrix while the rest of the polymer matrix would consist of amorphous or less conducting polymer fragments where the chain alignment is poor. As a result, the transport of charge within the polymer involves two mechanisms: metallic-like conductivity within the crystalline regions and hopping or resonance tunneling between these domains\textsuperscript{6}.

The most prevailing point of the Prigodin-Epstein model is that it could explain why conducting polymers cannot be 100\% doped and why even in the fully doped state the dominant charge transport mechanism in these materials is still hopping rather than band transport. On the other hand, this model does not provide any insight into the mechanisms and properties that control the formation of the crystalline regions embedded into the amorphous matrix.

The Prigodin-Epstein model has been developed to explain the properties of conducting polymers in their doped/metallic state as well as their semiconductor-metallic transition. However, the inhomogeneity also manifests itself during the reverse transition; when a doped conducting polymer is switched to its neutral semiconductor form. It is especially important for materials that are prepared by electrochemical polymerization, i.e., by electrochemical oxidation of the corresponding monomers, and thus are formed in the oxidized or doped state, as in this work. There is a considerable body of evidence\textsuperscript{7-11} suggesting that materials obtained in this way cannot be fully undoped; there is a certain amount of residual doping charge trapped within the polymer matrix. This residual or trapped charge is localized in a number of conducting nanometer-size domains surrounded by nonconducting polymer phase\textsuperscript{12}. 
Therefore, while the Prigodin-Epstein model of the polymer inhomogeneity was developed to explain the properties of the conducting state of conducting polymers and related materials, its concept of isolated highly ordered domains embedded into a disordered polymer matrix is applicable to reduced/semiconducting polymers as well. This conclusion is especially important from a practical viewpoint since the majority of prospective applications utilizing conducting polymers and related materials make use of their semiconducting rather than conducting properties (OLEDs, organic electronics, solar cells, etc.). In all these applications, the polymer inhomogeneity is likely to play a major role. For example, in organic solar cells, it can be detrimental to both the photogeneration of charges in the polymer phase (doped polymers are very poor semiconductors) and their collection (the inhomogeneity can significantly impede the transport of photogenerated carriers).

Currently, the only way to obtain very ordered and regular materials is to use certain monomers that can be arranged in a specific way during their polymerization. A well-known example is regioregular 3-alkyl substituted polythiophene\textsuperscript{13,14}. These materials were shown\textsuperscript{15} to spontaneously form microcrystalline domains or lamellae very similar to those described by the Prigodin-Epstein model. As a result, such materials indeed demonstrated superior performance in devices such as solar cells\textsuperscript{15-19}. However, these molecules have their drawbacks, such as reduced interchain interactions, limited potential of chemical and structural modifications, more pronounced charge trapping, etc. Therefore, it is desirable to find a more general solution that would be applicable to all polymer-based materials, not only regioregular polythiophenes. To be able to do this, we need to look beyond the Prigodin-Epstein model and further understand the origins of the polymer inhomogeneity and then ultimately find ways to control it.

In this work, the focus is in using AFM and its extensions in order to determine the origin of conducting polymer inhomogeneity. The main advantage of our approach is that AFM and its extensions allow for direct, visual measurements of the material topography while simultaneously providing additional information on the properties (local conductivity, work function, crystallinity, etc.) of these materials on the nanoscale.
All previous studies were based on indirect measurements which could not provide any local and especially nanoscale information. Furthermore, there was no way to relate the measured properties to any specific locations or morphological features of the materials under study.

For this work, we use poly[2-2’-bithiophene] (PBT) shown in figure 2.1. The reason for this is that PBT is a good model system that possesses all the typical properties of conducting polymers. At the same time, PBT is an extremely versatile polymer that can be prepared using a variety of chemical or electrochemical routes and can feature very diverse properties as dependent on the polymerization mechanism, treatment, etc. Its properties can also be tailored to the needs of specific applications.

Figure 2.1. Molecular structures of (a) poly(3-hexylthiophene) (P3HT) (b) poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and (c) poly[2-2’-bithiophene] (PBT).
2.1 Atomic Force Microscopy

2.1.1 Introduction

Atomic Force Microscopy is a versatile technique that allows the visual characterization of surface structure and the measurement of numerous crucial sample properties on the nanoscale. It was invented in 1986 by Binning, Gerber and Quate\textsuperscript{20} to broaden the usefulness of its precursor technique, scanning tunneling microscopy (STM), by allowing measurements on insulating materials. The first commercial AFM was introduced in 1989.

AFM is rather different from other microscopes in the way that it does not form an image by focusing light or electrons onto a surface like an optical or electron microscope. The AFM physically “feels” a sample’s surface by rastering over a specified area with a sharp probe building a map of the height of the sample. A laser is deflected off of an AFM cantilever (of which the sharp probe is attached to), and into a photodetector which records the deviations in height as the probe scans over the surface. A general schematic of AFM is shown in figure 2.2. This is then translated by the computer into physical data points to form a corresponding image.
AFM can be performed using two base methods of scanning: contact mode AFM and tapping mode AFM. The important advantage of AFM lies with the availability of related auxiliary techniques, or AFM extensions, which allow determination of a number of important additional parameters simultaneously with the topography scanning and at specific well defined points at the sample surface. The auxiliary techniques used in this work include Kelvin Probe Force Microscopy (KFM), Current-sensing AFM (CS-AFM) and phase imaging AFM (PI-AFM).

2.1.2 Contact Mode AFM

Contact AFM mode operates by scanning a tip attached to the end of a flexible cantilever while monitoring the change in cantilever deflection with a photodiode detector as the tip makes physical contact with the sample. To ensure the best results without damaging the sample, the tip should exert a low (typically attractive) force on the sample, which is lower than the effective force holding the atoms of the sample together. The tip-sample interaction causes the cantilever to bend, which in turn allows the variations in the sample topography to be measured with a very high (sub-nanometer) resolution.

A feedback loop within the system is used to maintain a constant deflection of the cantilever and hence, a constant force between the tip and the sample by vertically moving the scanner at each (x,y) data point. The specific force applied to the sample is maintained through setting a user controlled “set-point” deflection, which determines how strongly the tip interacts with the sample. The force is calculated using Hooke’s law:

\[ F = -kx \]  

(Eq. 2.1)

where  
\( F \) = force,  
\( k \) = spring constant of the tip  
\( x \) = cantilever deflection
The distance the scanner moves vertically at each (x,y) point is stored in the computer and forms a topographic image of the sample surface.

**2.1.3 Tapping Mode AFM**

Tapping mode AFM allows for high resolution topographic imaging of samples that are easily damaged or difficult to image by other AFM techniques such as contact mode AFM. It works by oscillating the cantilever at or near the cantilever’s resonant frequency using a piezoelectric crystal. The motion caused by the piezoelectric crystal forces the cantilever to oscillate with a high amplitude when the tip is not in contact with the surface of the sample. As the oscillating tip is moved towards the sample, an intermittent contact is established (the tip “taps” the surface). As a result, the oscillation amplitude is reduced due to an energy loss caused by the tip contacting the surface. This change in the oscillation amplitude is utilized to identify and measure surface features in much the same way as the cantilever deflection is used in contact-mode AFM. Specifically, a feedback loop maintains a constant root mean square (RMS) of the oscillation signal acquired by the photodiode detectors in order to achieve a constant tip to sample interaction during imaging.

**2.1.4 Kelvin Probe Force Microscopy (KFM)**

Kelvin probe force microscopy (KFM), also known as scanning surface potential microscopy, is a two-pass system where surface topography and surface potential can be measured simultaneously with nanometer resolution\(^2\). On the initial pass of the sample, regular tapping mode AFM is used to image the sample topography. In tapping mode, the cantilever is vibrated mechanically near its resonance frequency and brought toward the surface of the sample until it makes contact and an image is formed. The sample topography determined during this first pass is then used during the second pass to maintain a certain tip-sample separation with the help of an additional technique called LiftMode\(^\text{TM}\). Typical tip-sample distances vary from 10 to 50 nm. During the second pass, the drive piezo that vibrates the cantilever during the first pass is disabled. Instead,
an AC voltage is applied between the tip and the sample. In this case, there will be a
coulombic force between the tip and the sample at the AC voltage frequency, which will
be proportional to the amplitude of the AC voltage and the DC potential difference
between the sample and the tip. This will cause the cantilever to vibrate at the same
frequency, which will be detected in the usual way. In surface potential measurements,
there is an additional feedback loop that adjusts the dc voltage on the tip until the
vibration of the cantilever is cancelled out (figure 2.3).

This procedure can be illustrated as follows. The energy of a parallel plate
capacitor, $U$, is given by:

$$U = \frac{1}{2} C(\Delta V)^2$$

(Eq. 2.2)

where $C$ is the local capacitance between the AFM probe and the sample and $\Delta V$ is the
voltage difference. The force between the tip and sample is the rate of change of the
energy with the separation distance:

$$F = -\frac{1}{2} \frac{dU}{dZ} (\Delta V)^2$$

(Eq. 2.3)

In the operation of surface potential, the voltage difference, $\Delta V$, consists of both
DC and AC components. The AC component is applied from the oscillator, $\Delta V_{AC} \sin \omega t$, where $\omega$ is the resonance frequency of the cantilever:

$$\Delta V = \Delta V_{DC} + \Delta V_{AC} \sin \omega t$$

(Eq. 2.4)

Parameter $\Delta V_{DC}$ includes applied DC voltages (from the feedback loop or externally applied), work function differences, etc. Squaring $\Delta V$ and using the relation:

$2 \sin^2 x = 1 - \cos(2x)$, we get:

$$\Delta V^2 = \Delta V_{DC}^2 + 2 \Delta V_{DC} \Delta V_{AC} \sin \omega t + (\Delta V_{AC} \sin \omega t)^2$$

(Eq. 2.5)
The first term is the DC term, the second is the term at the frequency \( \omega \) and the third is the term at the frequency \( 2\omega \). Only the oscillating electric force at \( \omega \) acts as a sinusoidal driving force that can excite periodic motion of the cantilever (the cantilever responds only to forces at or near its resonance). The goal of the surface potential feedback loop is to adjust the voltage on the tip until it equals the voltage of the sample \( (\Delta V = 0) \), at which point, as follows from (Eq. 2.6), the cantilever amplitude should be zero \( (F_\omega = 0) \).

The DC voltage that is applied to cancel this effect is the same as the contact potential difference (CPD) between the tip and the sample. At this point, the voltage at the tip is the same as the surface potential of the sample so there is no dc electric field between the tip and the sample. This CPD can be used to determine the local work function of the sample and from this, an image of the surface potential and its correlation with the topography can then be obtained.

Figure 2.3. Explanation of the surface potential measurements. The feedback voltage cancels out the electric field between the tip and the sample when it is equal to the contact potential difference.

This is of great significance because the work function of a material provides information about its chemical composition and oxidation degree. Specifically for conducting polymers, the work function increases upon oxidation and decreases upon
reduction. This correlation is important for conducting polymers because oxidation-reduction, also called doping/undoping, is known to drastically change the polymer properties. Specifically, doped (oxidized) polymers are conducting, while undoped (neutral) polymers are insulating or semiconducting. Therefore, mapping the variations in the surface potentials allows us to determine the doping-level distribution in conducting polymers with nanometer resolution.

The KFM technique can be also used without engaging the feedback loop. In this mode, called Electrical Force Microscopy (EFM), there is no nullifying bias applied and the tip senses the vertical gradient of the local electric field. However, the data acquired in this mode are very much prone to artifacts due to a pronounced cross-talk between the morphology and the measured electric field (e.g., sharp morphological features will augment the local electric field), so it is less used. In this work, we used only the KFM feedback mode, which is considered to be free of such cross-talk.

A particularly important parameter in the surface potential imaging is a so-called drive phase, which specifies the sign of the applied nullifying bias and hence the sign of the contact potential difference as determined by this technique. The system determines the sign of the bias from the sign of an imaginary component of the tip deflection caused by the electric force between the tip and the sample, as measured by a lock-in amplifier built into the AFM controller. In the KFM feedback mode, there is always a phase shift between the applied ac voltage, which induces the cantilever vibrations, and the ac component of the tip deflection, which is used to detect the null conditions when the applied bias fully compensates the contact potential difference between the tip and the sample. This phase shift is determined by the mechanical properties of the tip-sample assembly, as well as by delays in the measurement circuitry (the system operates at rather high frequencies such as 300 MHz). The drive phase parameter is designed to compensate for the above phase shift by modifying the phase of the reference signal used by the lock-in amplifier. If this parameter is not set properly, then the sign of the imaginary component as measured by the lock-in amplifier may be incorrect, and hence the system will attempt to compensate the contact potential difference between the
sample and the tip by using a bias of the opposite sign. As a result, the surface potential values as measured by the system will lack any physical meaning, which, however, may not be apparent from the images.

The Veeco instrumentation manual recommends setting the drive phase parameter at certain negative values, varying from 0 to -70 degrees for high-frequency cantilevers. Our experience is that this setting does not necessarily work properly. Therefore, in this study, we have always performed additional checks by temporarily switching the output from the surface potential to the so-called surface potential input, which is essentially the raw DC potential difference sensed by the tip. If the feedback is working properly, the contact potential difference between the tip and the sample should be totally compensated, and the values of the potential input should be zero. If this was not the case, the driving phase parameter was adjusted until the proper feedback operation was restored.

As far as can been seen with literature, the first studies that involved KFM (as an extension to AFM) to study the inhomogeneity of polymers was by Semenikhin et al\textsuperscript{23,24}. In these studies, it was found that electrochemically prepared neutral and p-doped films of the conducting polymer, polybithiophene, showed a pronounced non-uniform doping-level distribution. In addition, it was found that the doping-level distribution showed a remarkable correlation with the surface morphology of the polymer. More doped regions of the polymer appeared on the top of polymer grains whereas the grain periphery was found to be less doped. Later, these results were corroborated by other studies\textsuperscript{24-27}.

The KFM measurements have demonstrated that there is a correlation between the doping level distribution (local work function), and the morphology of conducting polymer-based materials. However, despite the availability of the LiftMode\textsuperscript{TM}, the KFM technique is sometimes still subject to criticism (perhaps due to confusion with the electric field imaging) that a certain cross-talk could exist between the topography and the measured surface potential values. Therefore, it is usually not enough to draw significant conclusions on the polymer inhomogeneity using solely this technique. In this
case, it is more advantageous to corroborate the results found using KFM measurements with results obtained using other independent techniques, such as current-sensing AFM (CS-AFM) and phase imaging AFM (PI-AFM).

2.1.5 Current-sensing AFM (CS-AFM)

CS-AFM is a technique that allows one to measure, in addition to the surface morphology, the local current flowing between the conducting tip and the area of the sample it is in contact with. Since there should be a direct electrical contact between the tip and the sample, CS-AFM images are acquired in the AFM contact mode rather than in tapping mode as with KFM measurements. CS-AFM images are obtained by applying a bias, which is a changeable parameter, between the sample and a conducting cantilever tip, which is set to be on a virtual ground. As the tip runs along the surface of the sample, a linear amplifier with a range of 1 pA to 1 μA senses the current passing through the sample, which then allows an image of the local current and thus the sample conductance to be obtained. Since conducting polymers can vary their conductivity by several orders of magnitude as dependent on their doping level, measuring the local conductivity is yet another way to characterize the variations in the polymer doping level. Unlike other electrical characterization techniques such as scanning tunneling microscopy (STM), CS-AFM does not rely on conductivity as the source of the topographical information. Therefore, it can be used for poorly conducting samples such as semiconducting conjugated polymers.

There have been several studies involving CS-AFM of conducting polymers. Most notably were the studies performed by S.M. Park with various electropolymerized conducting polymers such as polypyrrole\textsuperscript{28-30}, polyaniline\textsuperscript{31,32} and derivatives of polythiophene\textsuperscript{33}. There has also been other CS-AFM studies involving chemically polymerized polyaniline\textsuperscript{34,35} and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV)\textsuperscript{36}. All these studies suggested that polymer materials, both doped and undoped, show considerable nanoscale inhomogeneity and possessed domains of either higher or lower conductivity. The domain sizes were estimated to be between 50-200
nm, however, the low quality of the images due to the probes used for CS-AFM at the time, introduced skepticism of the conclusions.

AFM probes are generally made of doped silicon. While this probe is conducting enough for studies involving EFM or KFM, they are not suitable for CS-AFM. Therefore, the probes must be coated with a thin metal layer to make them usable for CS-AFM. However, this coating introduces two main problems: the coating increases the size of the probe which reduces image resolution, and the coating can be easily damaged during contact mode scanning.

Originally in this work, a gold CS-AFM probe (see chapter 3, Section 3.2 for probe details) was used for conducting measurements. However, this probe produced poor images and the probe often would lose its coating in only a few scans. This made reproducibility of the images impossible to obtain. Not only that, with the coating lasting only a few scans, optimization of the applied contact forces to improve image quality could not be performed in time. This problem of probe coating was partially overcome with the introduction of a new type of conducting probe: boron-doped diamond film probes (see chapter 3, Section 3.2 for probe details). These probes possessed excellent electrical conductivity and superior anti-wear properties. Although the issue with the film coating increasing the probe size was still present, the conducting film now lasted several tens of scans. Therefore, the reproducibility of images could now be obtained. Furthermore, the longer lasting probe coating also allowed more time for force optimization in order to increase the image resolution. We first tested these probes on electrochemically deposited polythiophene in which the results were presented in studies by Trissa et al. These probes allowed remarkable resolution and provided great insight into the correlations between polymer conductivity and morphology; the results of which could now be compared with other techniques such as KFM and PI-AFM.
2.1.6 Phase Imaging AFM (PI-AFM)

Phase imaging is an extension of a regular tapping-mode AFM that allows simultaneous measurements of the topography and the local mechanical properties, such as adhesion, viscoelasticity, hardness, etc., of conducting or semiconducting samples with nanometer resolution. It is based on assessing the phase shift of an AFM cantilever as it is brought into contact with the surface of a material (through tapping mode) against the vibration of the cantilever when it retracted from the surface (a freely vibrating cantilever). When the AFM probe is brought close to a surface, at some point there will be a damping of the cantilever vibration amplitude. This is well known and is the bases of imaging in AFM tapping mode (see chapter 2, section 2.1.3). At the same time, the phase of the cantilever vibrations is also shifted depending on whether the probe-sample contact is elastic or inelastic.

![Figure 2.4](image)

Figure 2.4. A basic schematic of phase imaging AFM (PI-AFM) as the probe “taps” over a sample of varying hardness.

For an elastic response, the probe “bounces” back more readily upon contact with the sample and the phase shift of the cantilever vibrations stays near zero or becomes more positive in the case of a strong repulsive interaction with the sample (known as hard tapping). Likewise, for an inelastic response, the probe is delayed, or “sticks” to the surface, when it comes into contact and the phase shift of the cantilever is negative. This is illustrated in figure 2.4. Overall, the magnitude of the phase shift is dependent upon
the type of interaction (elastic/inelastic) or in short, it is based on assessing the dissipation of energy of the vibrating cantilever transmitted to the sample through the probe-sample contact. These processes are also influenced by the elastic modulus and other mechanical properties of the sample, which are related the crystallinity of the material. Since the crystallinity can be evaluated simultaneously with the regular topography information, phase imaging AFM is an excellent technique that can be used to study the distribution of crystalline and amorphous phases in a conducting polymer, or related materials.

An important parameter of this technique is the ratio of the set-point and free cantilever vibration amplitudes, denoted as $A_{sp}/A_0$. According to literature, it is ideal to maintain this ratio within the so-called moderate tapping region ($0.3 < A_{sp}/A_0 < 0.8$) in order to ensure proper interpretation of results. If the ratio is held higher than the range of the moderate tapping, then the phase image will not be in proper contact with the surface and simply, there will be no apparent phase contrast. On the other hand, if the ratio is held below this region, the sample will appear as if all regions have a positive phase shift since the strength of tapping will overcome the delayed response in amorphous regions of the material. Within this moderate tapping region, as was shown in the literature, a more positive phase corresponds to more crystalline regions of the polymer. Such regions would appear as bright spots in the phase images. Likewise, lower or a more negative phase corresponds to less crystalline or amorphous regions of the polymer and would appear as dark spots in the corresponding phase images.

### 2.2 Structures and Properties of Conducting/Semiconducting Polymers

Electronically conducting polymers are unique in the way that they are comprised of alternating single and double bonds along the polymer chain backbone. It is this configuration that makes these polymers also known conjugated polymers. The conjugation along the backbone of the polymer allows for a delocalized $\pi$-electron system to form. To help explain the unique bonding in conjugated polymers, polyacetylene (figure 2.5) will be used as it acts as a good base model due to its symmetry.
Polyacetylene is composed of numerous sp² hybridized carbon atoms. The sp² hybridization allows for the carbon atom to participate in σ-bonding and π-bonding with adjacent carbon atoms. Since carbon consists of four valence electrons, three of these electrons are placed into the sp² hybridized orbitals of carbon leaving one electron to be placed into the unhybridized pₓ-orbital of carbon. The electron in the pₓ-orbital of a carbon atom overlaps with the pₓ-orbital of an adjacent carbon atom to form the π-bonding system. This delocalized π-electron system allows for charge transport (conductivity) to occur in these materials. However, in the neutral state the conductivity is very low due to the lack of free sites on the backbone for the electron to move (the conduction band is not half-empty as in metals but filled). In order to make a polymer conducting, it needs to be doped by adding or removing electrons to create semi-filled bands. In other words, undoped polymers are semiconducting and doped polymers are conducting.

It must be noted that polyacetylene is different from the conducting polymers used in this work in the way that it has a degenerate ground state. “Degenerate” means that the energy does not change when the single and double bonds are interchanged. However, the other conducting polymers like polybithiophene are non-degenerate. In these polymers, the interchanging of single and double bonds from the aromatic state leads to a conjugational change to the quinoidal state (figure 2.6). In this case, the quinoid state has a higher energy than the aromatic state. Despite this difference, the charge transport mechanism still works in a similar way.
Figure 2.6. Molecular structure of polybithiophene in the aromatic state (top) and quinoidal state (bottom).

Figure 2.7 illustrates the process of doping/undoping of the conducting polymer polybithiophene (PBT). It shows a cyclic voltammogram (CV) of polybithiophene in a solution of supporting electrolyte without the monomer.

In these conditions, we are able to observe the redox behavior of the polymer. On the forward scan from 0 V to +1.5 V, the doping or oxidation of the polymer occurs which leads to the quinoidal structure that is shown in figure 2.8. In this form the polymer is conducting. Upon reverse scanning back to 0 V, the undoping/reduction of the polymer occurs resulting in the neutral aromatic form (which is in the undoped/semiconducting state) of the polymer, also shown in figure 2.8. The undoping/reduction curve is much wider and less pronounced than the doping/oxidation
curve due to the heterogeneity of the polymer resulting in the undoping process to occur more randomly and slower than the oxidation of the polymer film. Since the film is in a solution without the monomer, these curves are reproducible and very stable.

![Aromatic and Quinoid Structures]

Figure 2.8. The reaction mechanism for the doping/undoping of polybithiophene (PBT). In this reaction (and this work), PF$_6^-$ is used to maintain electroneutrality (see below).

### 2.2.1 Doping ability as Dependent on the Counter-ion Nature

Conducting polymers are able to be both anodically and cathodically doped. Anodic doping forms dications, as seen in figure 2.8, while cathodic doping produces dianions with both proceeding through similar processes. Regardless, in both states the polymer backbone is charged and requires counter-ions in order to maintain electroneutrality. The ability of a polymer to be doped (to form radical-anions/cations) is conditional on the ability of the counter-ion to stabilize the radical-cations/anions. This stabilization may be analyzed in terms of polarizability (hardness/softness) of the counter ions$^{38}$.

Polymer di-anions/cations are $\pi$-conjugated species and therefore, are readily polarizable. Furthermore, the charge is spread over considerable distances on the polymer backbone. Therefore, these materials can be considered as soft acids/bases. To stabilize these structures, relatively large and polarizable (soft) counter ions are required. If a counter ion is small and not polarizable (hard) it will not stabilize the charged polymer and doping would not occur. Specifically, it is well known$^{39,40}$ that a polymer can be readily doped anodically but cannot be doped cathodically under the same conditions, such as polythiophenes in acetonitrile solutions with an alkali metal salt as a
supporting electrolyte (hard acids). At the same time, with tetraalkylammonium cations (soft acids), cathodic doping readily occurs. The same is true with respect to anodic doping, which is readily observed with such anions as PF$_6^-$ and BF$_4^-$ but not in Cl$^-$, NO$_3^-$, SO$_4^{2-}$, etc$^{41,42}$. In this work, PF$_6^-$ is used to maintain the electroneutrality for polybithiophene.

2.2.2 Band Structure of Conducting Polymers

The delocalized $\pi$-electron system of the polymer backbone makes up the conduction band and the valence band, also known as the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) respectively. For the neutral/semiconducting polymers, the valence and conduction bands are completely full and empty respectively; therefore no conductivity can be observed. In order for the polymer to become a conducting, electrons must be removed from the valence band (oxidizing the polymer), or added to the conduction band (reducing the polymer). This process of oxidation or reduction creates elementary charge carriers in the polymer, which are called polarons. Upon further oxidation of the polymer, polarons pair up to form bipolarons and multiple bipolarons will combine to form bipolaron bands located in the band gap of the polymer (figure 2.9). It is within the bipolaron bands that conductivity takes place. Polarons and bipolarons are different from free electrons and holes in the conduction and valence bands because formation of these polarons and bipolarons requires a transformation of a portion of the polymer chain from the aromatic structure to the quinoidal structure.

![Diagram of band structure](image-url)

Figure 2.9. The evolution of the band structure in polybithiophene (PBT).
2.2.3 Trapped Charge Phenomenon

When polythiophenes are electrochemically polymerized, they are made in the doped/conducting form. To be used as solar cells or charge storage devices, they need to be converted into the undoped/semiconducting form. However, even after undoping the polymer film it will still feature some residual doping, also known as “trapped charge.” These trapped charge regions are fragments of the polymer chain that are still in the doped/conducting/oxidized form. These regions of residual doping charge appear as dark regions (oxidized) when performing surface potential (KFM) measurements. Additionally, this residual doping charge can also appear on a CV of the polymer as smaller “pre-peaks” at less positive potentials than the true oxidation peak of the polymer during the first cycle.\textsuperscript{40} For use in the field of solar cells, these regions of trapped charge are detrimental to the photocurrent generation ability of the polymer film as they serve as areas for recombination of the photogenerated charge carriers. In order to optimize the photocurrent efficiency, it is advantageous to locate these regions of trapped charge and find ways to reduce or eliminate it within these films.\textsuperscript{11,43}

2.3 Preparation Methods for Conducting Polymers

2.3.1 Introduction

Conducting polymers can be synthesized in a variety of different ways. Some of the more common methods include: radical chain growth, coordination polymerization, step-growth polymerization and electrochemical polymerization. For the purposes of this work, electrochemical polymerization, which is performed in solution, was chosen because it allowed for better control of the polymer film thicknesses and properties. In this method, a monomer is electrochemically oxidized to form an active radical cation which in turn will react with another oxidized monomer to form dimers. These dimers can then be oxidized and react with another oxidized group to form trimers, tetramers, etc. This process continues until the oligomers formed have grown to a point in which
they become insoluble in solution and then deposit onto an electrode surface as a polymer film. This polymerization is represented by the reaction scheme shown in figure 2.10.

This mechanism proceeds through a “non-living” radical polymerization. This implies that the radical needs to be regenerated after each radical coupling step. This mechanism is only a general representation of the electropolymerization process. In this work, the polymer films were electrochemically prepared using galvanostatic, potentiostatic, or potentiodynamic deposition methods. The benefits to using these specific methods of polymerization are that they allow for easy control of the deposition conditions of the polymer, ie. thicknesses, which is helpful in determining the possible origin of inhomogeneity of these materials.

![Figure 2.10](image)

*Figure 2.10. Polymerization of polybithiophene through a non-living radical mechanism. A new radical must be created electrochemically after each radical coupling step in order to continue polymerization.*

### 2.3.2 Galvanostatic Deposition

For the galvanostatic deposition method, a constant current is applied at the electrode in the monomer containing solution for a selected amount of time. The same radical-radical coupling mechanism occurs during synthesis but the films produced are in the charged/doped state. Therefore, if the goal is to study a semiconducting polymer, discharging/undoping of the film after deposition is required and often carried out under potentiostatic conditions (see below). The main disadvantage of this technique is that while the overall deposition rate is controlled through the electropolymerization current, the mechanism of electropolymerization is not.
2.3.3 Potentiostatic Deposition

The potentiostatic deposition method works by applying a constant potential during deposition. Again, the radical-radical coupling mechanism is observed and the film being produced in the charged/doped state, the same as in a galvanostatic deposition. Undoping/discharging of the film is performed to reduce the polymer to its semiconducting state. Unlike galvanostatic deposition, electropolymerization at a constant defined potential allows much better control of the electropolymerization mechanism and properties of the obtained films. However, this method has more difficulties in controlling the film thicknesses and deposition charges. Multiple depositions must be performed into order to find the proper deposition charge at which to terminate the polymer growth in order to have a specific thickness.

2.3.4 Potentiodynamic Deposition

In this method, the electrode potential is cycled over a potential range for a specified number of scans (also known as cycles) in the monomer-containing solution. The resulting scans/cycles are combined to form a cyclic voltammogram (CV) of the process (figure 2.11).

![Figure 2.11](image.png)

Figure 2.11. A typical cyclic voltammogram illustrating the potentiodynamic synthesis of polybithiophene. Every subsequent scan results in the deposition of more polymer onto the surface of the electrode (red arrows).

On the forward scan (0 V to +1.5 V) of the CV, two peaks can be observed. The first peak is attributed to the oxidation of the polymer already deposited on the electrode.
surface. It is important to note that on the very first scan of the CV, this peak is not present. This is because there is no polymer phase present during the initial scan. The second peak located at more positive potential is due to the oxidation of the monomer in the solution. On the reverse scan (+1.5 V to 0 V), the peak located at negative current values is due to the reduction of the polymer on the electrode surface. Every subsequent scan results in the deposition of more polymer onto the surface of the electrode (the red arrows in figure 2.11). As a result, the oxidation and reduction currents can be seen to increase with each cycle (thick arrows) as more and more polymer phase is present. In this particular method of polymerization, the film thickness can be directly controlled through the adjustment of the number of scans performed; the greater the number of scans, the greater the thickness of the polymer film.

2.4 References


Chapter 3: On the Origin of Mesoscopic Inhomogeneity of Conducting Polymers

3.1 Introduction

There is a growing understanding that the properties of organic functional materials and devices utilizing these materials are very much determined by their local structural/morphological features\(^1,2\) and, specifically, their inhomogeneity. However, despite an increasing number of studies that are aimed at studies of local properties of such materials, there is still a great uncertainty as to how exactly the local features affect the overall properties of materials and devices and especially why such materials are inhomogeneous in the first place and whether or not such inhomogeneity can be controlled. Furthermore, while the role of such a parameter as the local morphology is becoming more and more apparent, much less attention is paid to the local characterization of other properties of materials, such as electrical properties, chemical composition, etc., as well as their relation (or the lack thereof) to the local morphology.

In this work, we are particularly interested in the mesoscopic inhomogeneity of organic functional materials, such as electron-conducting polymers. The mesoscopic scale is usually understood as the length scale at which one can study the properties of a material without having to consider the properties of individual atoms. In practical terms, this scale corresponds to lengths of ca. 10 nm and up. Importantly, this is also the size of the smallest morphological features of most conducting polymers. Therefore, the mesoscopic inhomogeneity here will be considered in relation to the non-uniform local morphology of conducting polymers, which may or may not be accompanied by a variation in other material properties.

The mesoscopic inhomogeneity of conducting polymers and related materials was first addressed in 1987 by Zuo et al.,\(^3\) who proposed the model of a granular polymer metal on the basis of their DC-conductivity measurements. Later, this model was corroborated by the results of X-ray,\(^4\) microwave frequency-dependent conductivity\(^5,6\)

A version of this chapter has been published:
and NMR relaxation\textsuperscript{7} measurements, and was recently summarized in the paper by Prigodin and Epstein.\textsuperscript{8} In terms of this model, such materials are considered as consisting of a network of small (tens of nanometers) conducting/crystalline domains embedded into an insulating/disordered polymer matrix. Such conducting domains are assumed to consist of regularly packed polymer chains with good interchain overlapping of the electron wave functions. This highly ordered packing or folding occurs randomly and only in certain regions within the polymer phase; in the rest of the polymer the chain alignment is poor and therefore the polymer outside the conducting domains is amorphous and poorly conducting. As a result, the transport of charge within the polymer phase involves two mechanisms: metallic-like conductivity within crystalline domains and hopping or resonance tunneling between such conducting domains.\textsuperscript{8}

A strong point of the Prigodin-Epstein model is that it could explain why conducting polymers cannot be 100\% doped and why even in the fully doped state the charge transport in such materials shows a considerable contribution of hopping rather than the band transport mechanism. However, the model does not provide an insight into the mechanisms that control the formation and properties of such crystalline domains, as well as their distribution within the less ordered polymer phase.

The Prigodin-Epstein model has been developed to explain the properties of conducting polymers in their doped/metallic state as well as their semiconductor-metallic transition. However, the inhomogeneity also manifests itself during the reverse transition, when a doped conducting polymer is switched to its neutral semiconductor form. It is especially important for materials that are prepared by oxidative polymerization, i.e., by electrochemical or chemical oxidation of corresponding monomers, and thus are formed in the oxidized or doped state. There is a considerable body of evidence\textsuperscript{9-13} suggesting that materials obtained in this way cannot be fully undoped; there is a certain amount of residual doping charge trapped within the polymer matrix. This residual or trapped charge is localized in a number of conducting nanometer-size domains surrounded by non-conducting polymer phase.\textsuperscript{14}
Therefore, it is easy to see that, while the Prigodin-Epstein model of the polymer inhomogeneity was developed to explain the properties of the conducting state of conducting polymers and related materials, its central concept of isolated highly ordered domains embedded into a disordered polymer matrix is applicable to reduced/semiconducting polymers as well. This conclusion is especially important from the practical viewpoint since the majority of prospective applications utilizing conducting polymers and related materials make use of their semiconducting rather than conducting properties (OLEDs, organic transistors, solar cells, etc.). In all these applications, the polymer inhomogeneity is likely to play a major role. Specifically, in organic solar cells, it can be detrimental to both the photogeneration of charges in the polymer phase (doped polymers are very poor semiconductors) and their collection (the inhomogeneity can significantly impede the transport of photogenerated carriers).

Recently, we have shown that the removal of the trapped charge from a semiconducting polymer, polybithiophene (PBT), gave rise to a significant increase in the polymer photoefficiency. However, this was achieved by means of post-treatment of an already prepared polymer. It would be advantageous if we could find a way to reduce or eliminate the inhomogeneity of such materials not after but directly in the process of their preparation. Currently, the only way to obtain very ordered and regular materials is to use certain monomers that can be arranged in a specific way during their polymerization. A well-known example is regioregular 3-alkyl substituted polythiophenes. These materials were shown to spontaneously form microcrystalline domains or lamellae very similar to those described by the Prigodin-Epstein model. As a result, such materials indeed demonstrated superior performance in organic field-effect transistors and solar cells. However, these molecules have their drawbacks, such as reduced interchain interactions, limited potential of chemical and structural modifications, more pronounced charge trapping, etc. Furthermore, the regularity and the performance of such materials are not necessarily directly related to each other. Therefore, it is desirable to find a more general solution that would be applicable to all polymer-based materials, not only regioregular polythiophenes. To be able to do this, we need to look beyond the Prigodin-
Epstein model and further understand the origins of the polymer inhomogeneity to find ways to control it.

In this work, we present the results of our studies of mesoscopic inhomogeneity of conducting polymers using scanning probe techniques, namely, Kelvin probe force microscopy (KFM) and current-sensing atomic force microscopy (CS-AFM). These techniques have been selected because they allow one to characterize not only the morphology of a material, but also the distribution of its electrical properties such as surface potential (KFM) and local conductivity (CS-AFM) with nanometer resolution. Furthermore, these parameters can be determined simultaneously with the topography information. The latter feature is especially instrumental since it allows one to find out if there is a correlation between the electrical parameters and the surface morphology of the conducting polymer materials under study. This is of particular importance because, if there is no correlation with the morphology, this fact would strongly support the random character of the conducting domain formation as specified in the Prigodin-Epstein model. However, if such a correlation does exist, one can reasonably argue that the inhomogeneous distribution of the electrical parameters and non-uniform surface morphology are related to each other and are likely to be controlled by the same underlying mechanism.

The Kelvin probe force microscopy (KFM), also known under the more general name of the electric force microscopy (EFM), is an extension of a regular tapping–mode AFM technique which allows simultaneous measurements of the topography and local electrostatic properties of conducting or semiconducting samples with nanometer resolution. It has two measurement modes: the electric field gradient imaging, and the surface potential imaging. In the first mode, a conducting AFM tip is positioned over the sample and is used to sense the vertical gradient of the local electric field as the tip is moved over the sample surface. Usually, a two-pass system is used. On the first pass, the topography information is acquired as usual, in the tapping AFM mode. On the second pass, the topography information acquired on the first pass is used to maintain the tip at a constant height over the sample surface, and the local electric field is measured. Such a
two-pass system (also called LiftMode™) allows one to minimize the effect of the
crosstalk between the topography and the electric field measurements. However, despite
this improvement, the data acquired in this mode are still very much prone to topography-
induced artifacts and sometimes may be difficult to interpret.

In the surface potential imaging mode, an additional feedback loop is engaged,
which is used to apply an external bias to the tip until the Coulombic interaction between
the tip and the sample is nullified. As a result, the tip is maintained at the same electrical
potential as the sample region immediately beneath it. Generally speaking, this technique
is a microscopic analog of the well-known Kelvin probe technique; hence, the name
Kelvin probe force microscopy. As in the macroscopic Kelvin probe technique, the
voltage necessary to achieve this nullifying condition is equal to the contact potential
difference between the tip and the sample. Since the values of the contact potential
difference are directly related to the work functions of the materials in question, the
Kelvin probe force microscopy allows one to image the local variations in the work
function and hence in the chemical composition and/or oxidation degree of a material
under study with very high (<10 nm) resolution. Importantly, since no electric field exists
between the tip and the sample when the surface potential is acquired, its values are not
affected by the sample topography as is the case with the electric field imaging.

Since conducting polymers are switched from their neutral (semiconducting) state
to their conducting state by means of electrochemical or chemical oxidation or reduction
(also referred to as p- and n-type doping), the work function of a doped conducting
polymer material will be different from the work function of the same material but in its
undoped (neutral) form. Specifically, a p-doped (oxidized) polymer will feature a higher
work function as compared to its neutral form, while the work function of an n-doped
(reduced) polymer will be lower. The measured surface potential values will reflect this
change in the local work function. It should be noted that this change results from a shift
in the position of the polymer Fermi level upon doping-undoping and does not contain an
electrostatic component since the charge of the reduced or oxidized polymer chains is
compensated by counter-ions so that the polymer phase carries no net charge. Therefore,
the KFM technique can be used to image the local variations in the doping level of conducting polymer materials.

The first study of this kind was performed by the corresponding author of this work with co-workers in 1996. It was found that electrochemically prepared neutral and p-doped films of a conducting polymer, polybithiophene, showed a pronounced non-uniform doping-level distribution. Furthermore, it was established that the doping-level distribution showed a remarkable correlation with the polymer surface morphology. Specifically, the more doped regions were encountered on the top of the polymer grains, while the grain periphery was found to be less doped. Later, these results were corroborated by other studies with polythiophenes and other conducting polymers, including n-doped ones. Recently, there has been an increasing interest in using the KFM technique to characterize various conducting polymer blends. However, these studies were quick to conclude that the observed inhomogeneity was due to phase segregation and not inherent to the individual components of the blends, which at the very least needs further justification. In some cases when the images of pristine materials are presented as well, one can actually see some correlation between the topography and surface potential images, which, however, was completely disregarded by the authors.

Therefore, the KFM measurements have demonstrated that there is a correlation between the doping level distribution as inferred from the measurements of the local work function, and the morphology of conducting polymer-based materials. However, despite the availability of the lift mode, the KFM technique is sometimes still subject to criticism (perhaps due to confusion with the electric field imaging) that a certain cross-talk could exist between the topography and the measured surface potential values. Hence, it is desirable to corroborate the conclusions derived from the KFM measurements with results obtained using an independent technique. As such a technique, we selected the current-sensing AFM (CS-AFM).
The CS-AFM is a technique that allows one to measure, in addition to the surface morphology, also the local current flowing between a conducting tip and the area of the sample it is in contact with. Since there should be a direct electric contact between the sample and the tip, CS-AFM data are acquired in the AFM contact mode rather than the tapping mode, as is the case with KFM. Since conducting polymers can vary their conductivity by several orders of magnitude as dependent on their doping level, measuring the local conductivity is yet another way to characterize the variation in the polymer doping level and to find out if this variation is related to the polymer surface morphology.

There have been a few papers in the literature on CS-AFM studies of conducting polymers and related materials. A series of studies were performed by the group of S.M. Park with various electrochemically polymerized conducting polymers such as polypyrrole,\textsuperscript{37-39} polyaniline,\textsuperscript{40,41} polythiophene and derivatives,\textsuperscript{42} and poly(3,4-ethylenedioxy-thiophene).\textsuperscript{43} There have been also CS-AFM studies of electrochemically polymerized polypyrrole containing iron oxide nanoparticles,\textsuperscript{44} chemically polymerized polyaniline,\textsuperscript{45,46} and MEH-PPV.\textsuperscript{47} All these works have found that the investigated materials featured a considerable degree of inhomogeneity and possessed domains with higher and lower conductivity both in their doped and undoped forms. However, as far as the correlation between the morphology and the local conductivity was concerned, the results were more ambiguous. In many cases, a correlation has been observed generally similar to that predicted on the basis of KFM data. However, in other cases, no such correlation was found. Furthermore, in fact the quality and resolution of the CS-AFM data were often insufficient to make a confident conclusion whether or not such correlation existed.

As was the case with KFM, there have been a few CS-AFM studies of the polymer blends.\textsuperscript{48-50} However, while sometimes the topography data were not even shown, in other cases a correlation with the topography was observed but was again related to the phase segregation only. At least in one paper,\textsuperscript{50} one can easily see an
inhomogeneous current distribution within one of the segregated phases which, however, is not discussed by the authors.

Yet another concern is a great variety of the sample preparation conditions and imaging parameters employed in these works. Specifically, at least in some cases, the observed conductivity values could be attributed to insufficient dryness of the polymer films under study. The presence of the residual solvent can have a very considerable effect on the conductivity of conducting polymer materials due to combined contribution of ionic and electronic conductivity if the sample is not dry enough. Furthermore, in the majority of the studies, the main attention of the authors was concentrated on the studies of doped polymers. However, the doped state of the polymers is known to be unstable (as was also demonstrated\textsuperscript{39} by CS-AFM data). The oxidized polymer chains, which make the polymer conducting, can easily react with atmospheric oxygen and moisture and turn into neutral non-conducting polymer. Since the rate of these processes depends on the local availability of the depolarizer, the conductivity losses should occur non-uniformly across the polymer phase and may be expected to be related to the polymer morphology as well (obviously, the grain peripheral areas would be more accessible to oxygen or moisture than the inside of the grains). While this is an interesting scientific problem which has yet to be studied in any detail (characteristically, the authors of the work\textsuperscript{39} do not present any topography information when discussing the changes in local conductivity due to sample ageing), this factor could greatly complicate our task to prove or disapprove that there is a correlation between the polymer doping level and the polymer morphology that originates from the polymer formation mechanism and not from variations in the rate of the spontaneous undoping of the polymer.

Therefore, in this study we use the CS-AFM and KFM techniques to study the local electrical properties and the surface morphology of electron-conducting polymers. Undoped (semiconducting) polymers are used, which are more stable and also currently are more practically important than doped polymers. On the basis of our data, we propose a novel mechanism of the development of mesoscopic inhomogeneity of conducting polymers and related materials. We argue that the inhomogeneity is at least partially due
to preferential deposition of polymer molecules with higher molecular weight at the early steps of the polymer phase formation. These primary nuclei then form the highly ordered domains predicted by the Prigodin-Epstein model. However, in our model these nuclei also form the cores of the future polymer grains thus explaining the correlation between the topography and the electrical properties of conducting polymer materials. On the basis of our model, we conclude that, to ensure the formation of materials with low inhomogeneity and high quality, one should use the starting material with as narrow molecular weight distribution as possible.

3.2 Experimental

3.2.1 Preparation of the Polymer Samples

Three types of samples have been studied in this work: The first type was “regular” electrochemically deposited poly[2,2’-bithiophene] (PBT), with PBT film thickness of ca. 50 nm. The substrate in all cases was highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality). The second type was so-called “nucleated” PBT. The samples of this type were obtained by terminating the electrochemical deposition right after the primary nucleation step, as determined from the current-time transients. The average film thickness in this case was less than 1 nm, as estimated from the electropolymerization charge. The third type was poly[2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) samples kindly provided by the group of Prof. Fann Wunshain from the National Taiwan University. They were prepared by spin-coating from chlorobenzene onto the HOPG surface and dried in vacuum. The thickness of the polymer films in this case was ca. 100 nm. The images presented in this paper are typical ones selected from images taken for at least two different areas of at least three independently prepared samples in the case of PBT, and two samples in the case of spin-coated MEH-PPV.

The electropolymerization was carried out in a specially designed three-electrode Teflon cell mounted on top of the HOPG working electrode. The cell was equipped with
a silver pseudo-reference electrode (E= +0.05 vs. SCE) and a platinum counter electrode. A Princeton Applied Research (PAR) model 263A potentiostat/galvanostat controlled with a version 2.8 Corrware/Corrview electrochemistry software (Scribner) was employed. A 0.005 M solution of 2,2’-bithiophene in acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte was used for electropolymerization. The solution was deaerated with argon for 10 min before, but not during, the deposition. 2,2-Bithiophene (Aldrich) was purified through vacuum sublimation. Tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used as received. Acetonitrile (ultra-high purity) was purified using an in-house solvent purification system right before the experiments. The monomer and supporting electrolyte salt were stored at room temperature in a vacuum desiccator over silica gel to prevent from the moisture accumulation.

For the “regular” samples, the electropolymerization was performed in galvanostatic conditions at a current density of 1 mA cm$^{-2}$ for 40 s. The polymer film thickness was estimated from the deposition charge in view of our earlier data$^{51}$ to be ca. 50 nm. After the deposition, the polybithiophene films were reduced in the synthesis solution at a potential of -0.5 V (vs. the Ag pseudo-reference electrode) for 50 seconds in order to convert them into a neutral/undoped state. The samples were then rinsed three times with pure acetonitrile and dried in a vacuum desiccator at room temperature for at least 2 days to exclude the effect of the residual solvent content on the conductivity. The necessary drying time was determined in separate experiments (in order to avoid breaking the vacuum for the samples presented in this paper) by repeatedly imaging the samples over a period of several days and noting the time when the sample properties ceased to change. This time was then used for all samples.

The “nucleated” samples were obtained by terminating the electrochemical deposition at a stage when the primary polymer nuclei are already deposited on the surface but the nuclear growth step has yet to commence. Without going into a detailed discussion of various polymer deposition mechanisms, we adopt here the approach laid out by A.R. Hillman and co-workers.$^{52}$ Following their work, we assume that the polymer
deposition mechanism consists of instantaneous 3-D nucleation followed by the growth of the deposited nuclei to form polymer grains. It should be noted that the exact nature of the nucleation (instantaneous or progressive, 2 or 3-dimensional) was not studied in this work, nor it is expected that it would affect its main conclusions. Different steps of this process can be followed by recording the current-time transients during the deposition process. Such a transient is given in Fig. 3.1. One can see that after the initial peak the current decreases with time; then, after passing a characteristic saddle point, the current starts to grow eventually reaching a plateau. Such transients are very typical for polymer electrodeposition processes. According to Hillman et al., while it is impossible to totally separate the nucleation from the polymer growth, it is the rising portion of the i-t curve immediately following the saddle point when the nucleation has already occurred while the nuclear growth has not yet advanced enough so that the nuclei remain separated (hence, the 3-D growth rather than the 1-D one observed later when all the electrode surface is covered and the i-t transient levels off). Therefore, if we terminate the polymer electrodeposition process at a point immediately following the saddle point, we obtain a polymer sample consisting largely of primary nuclei that have yet to coalesce and form a totally continuous polymer phase. We call samples of this type “nucleated” samples. Specifically, for the sample shown in Figs. 3.6-3.7, the growth was terminated at a time of 6.4 s, as indicated in Fig. 1. The deposition potential for this sample was +1.35 V. The estimated deposition charge was as low as 0.43 mC cm^{-2}, as compared to the charge of 40 mC cm^{-2} for the “regular” samples. Such a charge would indicate the average film thickness of less then 1 nm. In fact, the height of the grains for this sample can be estimated from the AFM images (see below) as 5-10 nm, strongly indicating that the film was not continuous. As with the “regular” samples, after the deposition the samples were rinsed with pure acetonitrile and dried in a vacuum desiccator at room temperature.
Figure 3.1. A typical current transient of the potentiostatic electrodeposition of polybithiophene onto HOPG. The arrow indicates the point at which the deposition was terminated ($t = 6.4$ sec) in order to obtain a “nucleated” polymer sample.

### 3.2.2 KFM and CS-AFM Measurements

The atomic force microscopy (AFM) images were obtained in ambient conditions using a Multimode AFM (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco) and a CS-AFM extension module (Veeco). The Kelvin probe measurements were performed in the KFM feedback mode using RTESP n-doped Si probes (Veeco, force constant 20 N/m, resonant frequency 300 kHz). These tips were found by Veeco to be conducting enough to be successfully used for surface potential measurements. The advantage of using non-coated tips is that the absence of an additional coating allows one to maintain very fine tip curvature and obtain high-resolution images. The external bias in the feedback mode was applied to the tip (the sample was grounded). In this configuration, lower or more negative values of the surface potential corresponded to
regions with higher work functions (more oxidized polymer), which is also in agreement with the literature data.\textsuperscript{30,31} In the surface potential images, such regions of the sample would look darker than the ones with lower work functions. This conclusion has been confirmed by imaging the same samples with tips made of phosphorus-doped Si with and without Pt-Ir coating. The variations in the surface potentials measured with these two types of cantilevers followed the pattern expected from the work functions of n-type Si and Pt-Ir.

A particularly important parameter in the surface potential imaging is a so-called drive phase, which specifies the sign of the applied nullifying bias and hence the sign of the contact potential difference as determined by this technique. The system determines the sign of the bias from the sign of an imaginary component of the tip deflection caused by the electric force between the tip and the sample, as measured by a lock-in amplifier built into the AFM controller. In the KFM feedback mode, there is always a phase shift between the applied ac voltage, which induces the cantilever vibrations, and the ac component of the tip deflection, which is used to detect the null conditions when the applied bias fully compensates the contact potential difference between the tip and the sample. This phase shift is determined by the mechanical properties of the tip-sample assembly, as well as by delays in the measurement circuitry (the system operates at rather high frequencies such as 300 MHz). The drive phase parameter is designed to compensate for the above phase shift by modifying the phase of the reference signal used by the lock-in amplifier. If this parameter is not set properly, then the sign of the imaginary component as measured by the lock-in amplifier may be incorrect, and hence the system will attempt to compensate the contact potential difference between the sample and the tip by using a bias of the opposite sign. As a result, the surface potential values as measured by the system will lack any physical meaning, which, however, may not be apparent from the images.

The Veeco manual recommends setting the drive phase parameter at certain negative values, varying from 0 to -70 degrees for high-frequency cantilevers. Our experience is that this setting does not necessarily work properly. Therefore, in this study,
we have always performed additional checks by temporarily switching the output from the surface potential to the so-called surface potential input, which is essentially the raw dc potential difference sensed by the tip. If the feedback is working properly, the contact potential difference between the tip and the sample should be totally compensated, and the values of the potential input should be zero. If this was not the case, the driving phase parameter was adjusted until the proper feedback operation was restored.

The CS-AFM images were acquired in the contact mode using CDT-CONTR conducting diamond coated AFM probes (Nanosensors, force constant 0.2 N/m, resonant frequency 13 kHz). To ensure that no damage arose from the contact of the tip and the sample surface, the load forces were kept as close to zero as possible in order to still be able to obtain an image. This was controlled by repeatedly measuring the tip approach curves and adjusting the load if necessary. The absence of damage to the sample surface was evidenced by repeatedly scanning the same sample area. The current data were also highly reproducible. The choice of conducting diamond coating was very important. In earlier experiments, gold coated cantilevers were used; however, the conductive coating experienced severe wear after only a few scans and the data were inconclusive. No such problems were encountered with diamond coated cantilevers. However, as could be expected, the resolution that could be achieved with diamond-coated tips was lower due to an increase in the tip curvature as compared to non-coated tips. To ensure that the observed current images were due to variations in the sample conductivity, every area of the sample was scanned twice while applying biases of the same magnitude but with the opposite signs. In the CS-AFM measurements, the external bias was applied to the sample rather than to the tip; however, since the current was measured at the tip, in the subsequent discussion we will use the values of the tip bias equal to that of the sample bias but taken with an opposite sign.

In order to ensure that we had a good electrical contact between the tip and the sample and to estimate the contribution of the contact resistance to the polymer conductivity values measured by CS-AFM, frequency-dependent measurements were performed. To this end, the tip and the sample were brought into contact using a usual
engagement procedure as specified above, and then connected directly to a Solartron 1260 impedance/gain analyzer bypassing the CS-AFM module to avoid distortions due to its limited bandwidth. The value of the contact resistance was determined from the high-frequency limit of the frequency-dependent tip-sample impedance (frequency range 1 Hz – 1 MHz) and was found to be ca. 4 - 5 kΩ, which is several orders of magnitude lower than the values of the dc resistance measured in our CS-AFM experiments. Therefore, we conclude that the contribution of the tip-sample contact resistance was negligible and the measured values should be attributed to the resistance of the polymer films.

The topography images presented in the paper were manually plane-fitted. The surface potential images were offset. Since the measurements were performed in ambient conditions, no attempts were made to determine the actual values of the work functions. Therefore, the surface potential data presented in this paper (including cross-sections) are relative rather than absolute values. The CS-AFM current images were FFT-filtered to remove the 60-Hz noise and corrected for the amplifier offset. To ensure the accuracy of the current cross-section plots and to compensate for a certain drift of the zero of the current amplifier, the offset values were determined from corresponding I-V curves measured right before taking the CS-AFM images. Therefore, the current cross-sections always reflect the actual current values measured by the current sensor. However, to make the CS-AFM images more viewable, the zero current values in the images were not necessarily positioned in the middle of the color range.

3.3 Results

3.3.1 “Regular” Polybithiophene (PBT)

Figure 3.2a shows representative images of topography (left) and surface potential (right) typical for “regular” 50-nm thick polybithiophene samples. The images were acquired in the KFM feedback mode. Also presented in the figure are dual cross-sections taken along the same line in both the topography and surface potential images (Fig. 3.2b). The topography image shows the grainy structure typical for these materials. Each bright
spot in the topography image represents a polymer grain. The grains vary in size from ca. 20 to over 100 nm, although it can be easily seen that bigger grains are essentially conglomerates of smaller grains, and the size of these smaller grains is quite uniform and lies in the range from 20 to 50 nm. The average size of the grains was found to be 35.9 ± 5.0 nm. From the cross-section (Fig. 3.2b) one can estimate that the typical vertical grain size is of the same order of magnitude (20-30 nm). Since the average thickness of the film was estimated to be ca. 50 nm, it is clear that these grains represent only the uppermost layer of the polymer film. This may serve as indication of the occurrence of some progressive nucleation at longer polymerization times. The film is quite smooth: the rms roughness as found from the topography image is 8.1 nm, or less than 20% of the average film thickness.

The surface potential image (Fig. 3.2a, right) characterizes the lateral distribution of the local work function of the polymer material, which is related to the polymer structure and the oxidation state. One can see that the polymer is quite inhomogeneous. Furthermore, in line with the earlier data, there is a pronounced correlation between the topography and the surface potential data: the grain tops consistently feature more negative surface potential values as compared to grain periphery (and thus are seen as dark spots in the surface potential image). This is also evident from the dual cross-section of Fig. 3.2b. Since more negative surface potential values correspond to higher values of the polymer work function, this result positively confirms the results of earlier studies that the grain cores are more doped as compared to grain peripheral regions.
Figure 3.2. (a) Simultaneous 500nm by 500nm images of topography (left) and surface potential (right) acquired in the KFM feedback mode for a “regular” polybithiophene sample. The Z-scale was 200nm (topography) and 0.5V (surface potential). (b) Dual cross-section of the images of Fig. 4.2a indicating variations in the height (top) and surface potential (bottom) along the same line shown in the images.

The typical potential difference between the grain top and the grain periphery varies from -70 to -100 mV. Furthermore, the surface potential image clearly shows that indeed the large grains are in fact clusters of smaller grains that became agglomerated during the polymer growth: the core areas of these grains are clearly and separately visible in the surface potential image.
It is instructive to introduce the rms variation in the values of the surface potential (or, for this matter, the CS-AFM current) as a parameter characterizing the spread of these values over the sample surface and thus its inhomogeneity. This parameter is calculated in the same way as the rms roughness for topography images, except that the values of the surface potential or the CS-AFM current are used. For the image in Fig. 3.2, the rms variation of the surface potential was found to be 24.5 mV.

Figure 3.3. (a) Simultaneous 2 μm by 2 μm images of topography (left) and CS-AFM current (right) for the same “regular” polybithiophene sample as in Fig. 3.2. The Z-scale was 200 nm (topography) and 50 pA (current). An external bias of -250 mV was applied. To better indicate the correlation between the topography and CS-AFM current, the contours of a few grains from the topography image are repeated in the current image. (b) Dual cross-section of the images of Fig. 3.3a indicating variations in the height (top) and CS-AFM current (bottom) along the same line shown in the images.
Figure 3.3a shows representative CS-AFM images of topography (left) and current (right) for the same “regular” 50-nm thick polybithiophene sample shown in Fig. 3.2. The image was acquired using a tip bias of -250 mV. Therefore, the areas with higher conductivity should exhibit more negative current values and thus should appear as dark spots in the current image. Non-conducting or poorly conducting regions will feature low or zero current and will be seen as bright areas in the current image. Also presented in the figure are dual cross-sections taken along the same line in both the topography and CS-AFM current images (Fig. 3.3b). To enhance the readability of the images and to better indicate the correlation between the topography and CS-AFM current, the contours of a few larger grains from the topography image are repeated in the current image.

Comparing the topography and CS-AFM current images (Fig. 3.3a), one can immediately see that there is indeed a good correlation between the topography and the local conductivity of the polymer. Every time, the tops of the grains in Fig. 3.3a (left) correspond to dark spots in the current image of Fig. 3.3a (right). Since such a dark spot corresponds to a region of higher conductivity, we should conclude that indeed, the CS-AFM data unambiguously support the conclusion derived from the KFM measurements that the grain cores are more doped as compared to grain peripheral regions.

This conclusion is further supported by the cross-sections presented in Fig. 3.3b. We can see that the local CS-AFM current shows pronounced minima every time there is a grain in the topography cross-section (the current minima correspond to regions of higher negative current and thus higher conductivity), changing to almost zero over the regions between the grains (also called here grain peripheral regions). Sometimes, in the case of larger grains which can be seen to consist of two or more smaller ones, there are several conducting regions within the same polymer globule, like at the first grain in the left portion of the cross-section of Fig. 3.3b. Interestingly, when we follow the cross-section from left to right, we see that the CS-AFM current shows a pronounced minimum also over the “buried” grain of the 2nd layer, which is barely seen in the topography cross-section, but is readily observed in the CS-AFM current cross-section. This fact in particular indicates that there is no cross-talk between the measured CS-AFM current and
topography (e.g., because of variations of the load force over the elevated portions of the surface, as sometimes suggested in the literature), and the observed correlation between the topography and local conductivity is a real one. Also, while the grain tops are always more conductive, there is a pronounced variation between the current values observed on top of different grains and thus their conductivity.

The resolution in the topography images obtained in the CS-AFM mode is not as good as in the tapping-mode images of Fig. 3.2a. This can be expected given the fact that the CS-AFM imaging is performed in the contact mode, which is potentially more destructive to soft samples like thin polymer films. Therefore, to avoid damaging the polymer surface, we performed the scanning at very low load forces, which could not but affect the resolution. Furthermore, as has been already noted, CS-AFM requires the use of highly conducting tips, and conducting coating inevitably increases the tip curvature radius and reduces the resolution. Therefore, unlike the tapping-mode AFM images of Fig. 3.2a, the images of Fig. 3.3a cannot distinguish individual small grains that make up the polymer globules or grain conglomerates seen in Fig. 3.2a. The average grain size was found from the image of Fig. 3.3a to be 165.6 ± 12.0 nm, which is quite bigger than the average size of individual grains in Fig. 3.2a, but remarkably similar to the sizes of larger grain conglomerates seen in the image of Fig. 3.2a. Also, the values of the rms roughness as found from the topography images of Figs. 3.2 and 3.3 are almost identical: 8.1 and 8.9 nm. The typical vertical grain size as found from the CS-AFM images (ca. 25 nm) is also close to that found from the tapping-mode AFM data.

The rms variation of the CS-AFM current was 13.4 pA. The maximum current was 23 pA, the minimum 0.5 pA, the typical difference between the currents measured at grain tops and the grain periphery was ca. 18 pA. Therefore, the CS-AFM data showed that the polymer possessed a quite high degree of inhomogeneity and quite pronounced variations in its conductivity, the latter being related to the polymer surface morphology.

A more detail inspection of Fig. 3.3 reveals that the correlation between the local conductivity and surface morphology is in fact of a more complex nature. The most
conducting spots are not necessarily located on the very top of the grains. Some grains comprise more than one conducting area. To examine the correlation between the topography and local conductivity more closely, we obtained higher-resolution images of the topography and CS-AFM current showing fine details of the local current distribution. Furthermore, to prove that the variations in the CS-AFM current were related to the changes in the polymer conductivity, we obtained the images of the same portion of the surface at the opposite values of the applied bias. The images are presented in Fig. 3.4 together with corresponding cross-sections. It should be noted that to achieve the highest possible resolution, an area with a few larger than average grains was selected for these images.

Figure 3.4. (a) Simultaneous 1μm by 1μm images of topography (left) and CS-AFM current (right) for the same “regular” polybithiophene sample as in Fig. 3.2. The Z-scale was 100 nm (topography) and 30 pA (current). An external bias of -250 mV was applied. (b) The image of the same portion of the surface as in Fig. 4.4a taken in identical conditions except that an external bias of +250 mV was applied. (c) Dual cross-section of the images of Fig. 3.4a and Fig. 3.4b indicating variations in the height (top) and CS-AFM current (bottom) along the same line shown in the images. To better indicate the correlation between the topography and CS-AFM current, the contours of a few grains from the topography images are repeated in the current images.
The higher-resolution images do confirm the correlation between the topography and local conductivity. At the same time, it is now clearly seen that the grain structure is quite complex and often feature several conducting regions. This is especially evident in the cross-sections: each of the large grains clearly comprises two conducting regions. The grain periphery shows a pronounced drop in conductivity, especially in the case of large grains. Again, from the cross-sections it is clearly seen that some of the most elevated areas may be quite poorly conducting and, actually, the most conducting spots on the surface of the two large grains in Fig. 3.4c are not situated exactly at the top of the grains.

Different areas of the polymer also show quite distinct behavior with the change in the sign of the applied external bias (cf. Fig. 3.4a and Fig. 3.4b, as well as the corresponding cross sections in Fig. 3.4c). Some areas of the polymer show very little conductivity at either bias values. These are mostly associated with areas between the polymer grains or grain periphery. Some areas show high conductivity at both +250 and -250 mV, with the current absolute values being approximately equal. There are areas, however, which show a quite different conductivity at positive and negative biases. Specifically, this behavior is demonstrated by the smaller grain in the cross-section of Fig. 3.4c: the absolute values of the CS-AFM current taken at the same position over this grain is markedly higher at the negative bias.
The same behavior is evidenced by the $i$-$V$ curves taken at various points of the sample surface (Fig. 3.5). These curves were obtained by stopping the X-Y scanning over a point of interest with the tip engaged, and measuring the CS-AFM current at the tip while ramping the applied bias from -0.5V to +0.5V. Specifically, curves 1 and 4 of Fig. 3.5 represent typical dependences obtained on grain tops and grain peripheral regions, respectively. One can see that curve 1 shows a fairly good Ohmic behavior. From the slope of this curve we can estimate the polymer conductance, which was found to be $2.9 \times 10^{-11} \Omega^{-1}$. Taking into account the polymer film thickness of 50 nm, and assuming the tip-sample contact area of 50 nm$^2$, which is in line with the estimations given in the works of S.M. Park et. al.,\textsuperscript{37,39,41-43} we obtain the value of the polymer specific conductivity of $2.9 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$. While this value is a quite rough estimate due to uncertainties in both the tip-sample contact area and the actual local thickness of the polymer film, there is no doubt that this conductivity range is lower than the values typical for doped polymers. This was to be expected since all samples studied in this work were undoped upon synthesis. At the same time, as was demonstrated by studies
with semiconducting polymers and oligomers,\textsuperscript{53-55} fully neutral materials show conductivities as low as \(10^{-10} \ \Omega^{-1} \ \text{cm}^{-1}\). Therefore, the conductivity of \(2.9 \times 10^{-4} \ \Omega^{-1} \ \text{cm}^{-1}\) can be considered as quite high for an undoped polymer and should be attributed to the residual (trapped) doping charge.

The value of the specific conductivity as estimated for the grain peripheral regions from curve 4 is almost two orders of magnitude lower and is equal to \(6.7 \times 10^{-6} \ \Omega^{-1} \ \text{cm}^{-1}\). The curve is also quite symmetrical, which may indicate its Ohmic character, although it should be noted that the current values corresponding to curve 4 are near the resolution limit of our system and therefore the curve may possess some non-linearity that could not be recognized. In any case, this result further suggests that the material under study is highly inhomogeneous: the conductivity changes by as much as two orders of magnitude over a distance of less than 100 nm.

Of special interest is curve 2, which was taken over an area that showed different conductivity at positive and negative biases. One can see that the curve is indeed asymmetrical and exhibits certain rectification behavior indicating that the polymer here may possess good semiconductor properties. In our recent paper\textsuperscript{14} we have shown that indeed the areas with such asymmetrical \(i-V\) curves are able to produce higher photocurrents as compared to the rest of the polymer. When plotted vs. the square of the applied bias (not shown), the current demonstrated good linear dependencies both at positive and negative bias values, which is indicative of space-charge limiting currents (SCLC).\textsuperscript{56} This fact provides additional support for our suggestion that the polymer in this region features semiconductor properties. The slopes of the \(i-V^2\) plots at positive and negative bias differ by a factor of 3 indicating unequal mobilities of injected carriers. The corresponding specific conductivity as estimated from the linear portion of the \(i-V\) curve near zero bias is \(6.0 \times 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1}\).

Therefore, the KFM and CS-AFM studies for “regular” PBT samples have shown that indeed there is a general correlation between the polymer doping level, conductivity and surface morphology. The higher-resolution studies revealed that this correlation is of
more complex nature than co-existence of just “conducting” and “non-conducting” forms of the polymer on the grain tops and grain periphery, respectively, and also includes some transitional areas featuring semiconductor properties. Also, the images clearly show the heterogeneity of larger morphological features found on the polymer surface indicating that they are indeed built of several primary nuclei that became agglomerated during the polymer deposition process. Importantly, in these cases the above correlation was also observed, but now it was seen as correlation between the topography and doping level/conductivity of individual components of such agglomerates.

The latter fact provides further support to the hypothesis that the correlation and indeed the inhomogeneity of such materials originate from the early stages of the polymer nucleation and growth. In order to test this hypothesis, we performed the studies of so-called “nucleated” samples, the growth of which was terminated right after the nucleation stage in order to evaluate the roles of nucleation and the nuclear growth in the observed inhomogeneity of the polymer materials.

3.3.2 “Nucleated” Polybithiophene

Figure 3.6 shows representative images of the topography (left) and surface potential (right) typical for “nucleated” polybithiophene samples. Also presented in the figure are dual cross-sections taken along the same line in both the topography and surface potential images (Fig. 3.6b). One can see that the sample morphology is very different from that of “regular” PBT (Fig. 3.2): the grains are clearly smaller in size and there is virtually no aggregation (cf. Figs. 3.2a and 3.6a). Furthermore, the film seems to be not continuous, which agrees well with the expected structure of the “nucleated” sample as consisting of individual nuclei that had no time to grow and band together forming a continuous coverage. The average grain size as determined from the image is 27.0 ± 3.7 nm, which is markedly smaller than the value found for the “regular” sample (35.9 ± 5.0 nm) without aggregation (which increased the apparent grain size for the “regular” sample to 100 nm and more). This size difference was found by the t-test to be statistically significant (two samples, unpaired, unequal variances, two-tail, p=0.0245).
The typical vertical grain size as estimated from the cross-section of Fig. 3.6b is also markedly smaller than that for the “regular” sample (3-7 nm as compared to 20-30 nm). The average thickness of the film was estimated from the polymer synthesis charge to be less than 1 nm (see Experimental); therefore, the film is clearly non-continuous. The rms roughness as found from the topography image is also much smaller (1.3 nm vs. 8.1 nm for the “regular” sample).

Figure 3.6. (a) Simultaneous 500 nm by 500 nm images of topography (left) and surface potential (right) for a “nucleated” polybithiophene sample. The Z-scale was 50nm (topography) and 0.2 V (surface potential). The contours of a few grains from the topography image are repeated in the surface potential image. (b) Dual cross-section of the images of Fig. 3.6a indicating variations in the height (top) and surface potential (bottom) along the same line shown in the images.
Comparing the surface potential image (Fig. 3.6a, right) with the image of the polymer topography (Fig. 3.6a, left) and examining the cross-sections of Fig. 3.6b, we can see that again, as was the case with “regular” PBT, there is a correlation between the topography and surface potential data, with the grain tops featuring more negative surface potential than the grain periphery. However, the typical potential difference between the grain top and the grain periphery is now only 10-15 mV, as compared to 70-100 mV for “regular” PBT. The rms variation in the values of the surface potential for “nucleated” sample was found to be also much smaller (2.2 mV vs. 24.5 mV).

The same trend is observed in CS-AFM data (Fig. 3.7) despite the fact that, due to the reasons discussed above, the CS-AFM images cannot achieve the same high resolution as the tapping-mode KFM data of Fig. 3.6 and show certain averaged images of several adjacent grains rather than individual grains like in Fig. 3.6. Nevertheless, one can clearly see a correlation between the topography and conductivity as derived from the CS-AFM current. The typical current difference between the grain top and grain periphery (or the area between the grains) is now ca. 6 pA, as compared to 18 pA observed for “regular” PBT. The rms variation in the CS-AFM current is 5.5 pA rather than 13.4 pA.
Figure 3.7. (a) Simultaneous 1μm by 1μm images of topography (left) and CS-AFM current (right) for the same “nucleated” polybithiophene sample (figure 3.6). The Z-scale was 40 nm (topography) and 40 pA (current). An external bias of -500 mV was applied. (b) Dual cross-section of the images of Fig. 3.7a indicating variations in the height (top) and CS-AFM current (bottom) along the same line shown in the images.

Therefore, both KFM and CS-AFM data suggest that “nucleated” polymer is much less heterogeneous as compared to “regular” PBT. However, the most striking difference is that the grains in the CS-AFM images are now less conducting as compared to the area between the grains (since the applied bias was negative, bright spots in the current image correspond to regions of less negative current and thus lower conductivity).
The conductivity inside the grains is distributed more uniformly; there are no conducting domains inside polymer grains (or, at any rate, even if they exist but are not resolved due to a larger curvature radius of the conducting tips, such domains are much smaller than the domains clearly seen in the images of “regular” PBT). Furthermore, the currents measured at the polymer grains are markedly lower than the respective currents at “regular” PBT (and the film thickness is much smaller) thus indicating that the nucleated polymer grains are significantly less conducting as compared to “regular” PBT.

This conclusion is supported by $i$-$V$ dependencies. A typical $i$-$V$ curve taken at a nucleated polymer grain is presented in Fig. 3.5 as curve 3. One can see that the polymer conductance is clearly lower than that of the “regular” PBT grains (curves 1 and 2). Since the thickness of nucleated films were much lower than that of “regular” samples, the polymer specific conductivity should be even lower. Indeed, assuming the contact area to be equal to 50 nm$^2$ as in the previous case and taking the film thickness at the grains to be 5 nm from the cross-section of Fig. 3.7b, we estimate the polymer conductivity as $6.5 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$. This value is at least one order of magnitude lower than that found for the “semiconductor” portion of the “regular” polymer, and almost 2 orders of magnitude lower than the values for the grain tops of the “regular” PBT. These conclusions clearly indicate that, unlike “regular” PBT, the “nucleated” polymer shows much less inhomogeneity and virtually no charge trapping.

### 3.3.3 Spin-Coated MEH-PPV

So far, we have been discussing the properties of polymer samples obtained by electrochemical oxidation of corresponding monomers. However, despite many advantages of electrochemical polymerization, most researchers working with polymer-based semiconductor devices prefer to deposit polymer films by means of casting from solutions (spin-coating, dip-coating or drop-casting). Therefore, it was of interest to check if the same regularities as found for electropolymerized polymers will be observed with spin-coated samples of another polymer, MEH-PPV. Importantly, since MEH-PPV for spin-coating is made by chemical synthesis and is coated in its neutral/undoped form,
one could expect that this polymer will show no effects of charge trapping and thus there will be no local variations in its electrical properties. It turned out it was not the case.

Figure 3.8 presents representative images of topography (left) and surface potential (right) along with corresponding cross-sections (Fig. 3.8b) obtained for MEH-PPV spin-coated onto HOPG. The topography image clearly indicates that the sample is of high quality and features regular grains of rather small size. The average lateral grain size as determined from the image is 18.6 ± 3.3 nm, yet smaller than the values found for the “regular” and “nucleated” PBT. The typical vertical grain size as estimated from the cross-section of Fig. 3.8b is of the order of 1 nm only, with the rms roughness being as low as 0.2 nm. The surface potential image also shows remarkably little heterogeneity: the typical potential difference between the grain top and the grain periphery is only ~2 mV, and the rms variation in the experimental values of the surface potential is less than 0.1 mV. However, even then the images of Fig. 3.8 as well as the corresponding cross-section again show quite clearly the correlation between the surface potential and topography of the same type as was found for electopolymerized PBT samples.
Figure 3.8. (a) Simultaneous 500 nm by 500 nm images of topography (left) and surface potential (right) for an MEH-PPV sample spin-coated onto HOPG. The Z-scale was 5nm (topography) and 0.03V (surface potential). The contours of a few grains from the topography image are repeated in the surface potential image. (b) Dual cross-section of the images of Fig. 3.8a indicating variations in the height (top) and surface potential (bottom) along the same line shown in the images.

Unfortunately, the conductivity of these samples was found to be too low to allow us to obtain reliable CS-AFM data at reasonable bias values. Measurable currents started
to appear at tip bias values as high as -8 V, and only in the negative bias range. It is not clear if the currents measured at such a high bias can be compared to the rest of CS-AFM data obtained at much lower bias values. Work is in progress now to prepare more conducting MEH-PPV samples. In any case, we can say that the conductivity of these samples is much lower than that of any other sample measured in this work, which is in line with the trends observed for the topography and KFM data. Furthermore, our KFM measurements show that the correlation between the topography and inhomogeneity is not limited to PBT and electropolymerized films but is also found in spin-coated films of an entirely different polymer, MEH-PPV. This result indicates that there is a common underlying mechanism that controls the inhomogeneity of various conducting polymer materials and this mechanism should be common for both electropolymerized and solution-cast polymer films. The possible nature of such a mechanism is discussed in the next section.

3.4 Discussion

The experimental findings we need to explain can be summarized as follows:

1. There is a well-pronounced correlation between the polymer morphology, on the one hand, and the surface potential (which is related to the polymer composition and/or oxidation state), as well as the polymer conductivity (which is also related to the polymer composition, oxidation state and the degree of order) – on the other. Large polymer aggregates found in “regular” PBT samples may comprise several conducting regions, which correspond to primary grains coalesced during the deposition process. In this case, the most conducting regions are not necessarily found on the very tops of these large aggregates, but this fact does not affect the general nature of the morphology/surface potential/conductivity correlation. This correlation cannot be attributed to experimental artifacts such as morphology cross-talk effects since it was confirmed by two independent scanning probe techniques based on different physical principles.
2. For all samples, including “regular” and “nucleated” electrochemically deposited PBT, as well as spin-coated MEH-PPV, the grain tops or cores have consistently shown higher values of the local work function as compared to the grain periphery or the areas between the grains.

3. For “regular” PBT, the grain cores were consistently more conducting as compared to the grain periphery. The most conducting areas were encountered inside the grains and showed Ohmic behavior. They were surrounded first by a semiconductor-like phase showing rectifying behavior attributed to the space-charge limited mechanism, and then by an insulating polymer. The difference in specific conductivities between the grain cores and the grain periphery was two orders of magnitude.

4. “Nucleated” PBT showed a different pattern: the grains were found to be less conducting than the areas between the grains and ten times less conducting than the grain cores in “regular” PBT. The grain conductivity was distributed much more uniformly inside the polymer grains.

5. There is a pronounced trend showing that more uniform morphology corresponds to less variability in the other properties of the polymer. This is confirmed by topography, surface potential and local conductivity measurements. Specifically, “nucleated” PBT is much less inhomogeneous than “regular” PBT. The spin-coated MEH-PPV showed the finest morphology, very low conductivity and the least spatial variations in the surface potential.

Therefore, not only there is a pronounced correlation between the polymer morphology, on the one hand, and surface potential/conductivity, on the other, but this correlation is also both spatial (more doped grain tops) and qualitative (more uniform topography resulted in less variability of the other surface properties). These facts suggest that the observed inhomogeneity should have a common cause and probably originates from the early stages of the polymer phase formation. This conclusion is strongly supported by the pronounced difference in the conductivity distribution patterns for
“regular” and “nucleated” PBT. Furthermore, the same mechanism should apply not only to polymerization through in-situ electrochemical oxidation of corresponding monomers, but also to spin-casting from solutions of polymer prepared by separate chemical polymerization. This fact excludes all possible explanations related to variability in the kinetics of the electrochemical processes, non-uniform current distribution during the electrodeposition, etc.

A common feature of all polymer deposition methods, including electropolymerization, chemical in-situ oxidation, and various spin- and drop-casting techniques, is that in all these cases the polymer phase nucleates and grows from solutions that contain a mixture of polymer/oligomer molecules of very different molecular weights (Mw). In the case of chemical polymerization, there are synthetic approaches that allow one to keep the polymer polydispersity index quite close to unity, but even then, even with additional fractional separation, there is still a mixture of molecules of varying molecular weights in the casting solution. In the case of electrochemical polymerization, the situation is even worse because electropolymerization is a very complex process. It starts with a sequence of electrochemical-chemical-electrochemical (ECE) events involving electrochemical oxidation of the monomer, chemical coupling of the resulting radical-cations, re-oxidation of the formed dimers and their coupling with other monomer or oligomer molecules in solution, re-oxidation of the formed oligomers, and so on, again leading to formation of a mixture of oligomers of various molecular weights in the solution phase. The complexity of the mechanism and great variability of the kinetics of different stages of the electropolymerization process give rise to a quite wide distribution of the molecular weights of oligomer/polymer molecules obtained in this way.

The next step in either electrochemical deposition or solution casting is the nucleation of the polymer phase on the electrode/substrate surface, followed by the growth of the primary nuclei through further deposition of polymer molecules from the solution. In the case of electrochemical deposition, the driving force of the new phase formation is the supersaturation due to continuous formation of new and new portions of
the polymer, which eventually exceed their solubility limit. In the case of spin- or drop-casting, the supersaturation occurs due to evaporation of a portion of the solvent. Again, in the case of electropolymerization, the mechanism may be more complicated and involve further solid-state polymerization of the deposited oligomers,\textsuperscript{64,65} which may also involve oligomers from the solution.\textsuperscript{63} Furthermore, although the polymer molecules are deposited in their neutral (undoped) state, they become immediately re-oxidized at the electrode surface since the electrode is kept at a potential high enough to oxidize the monomer molecules, and the oxidation potential of oligomers is lower than that of the monomers and decreases with an increase in the conjugation length.\textsuperscript{64,66} Nevertheless, despite these complications, we can see that in either case the polymer phase is formed by deposition from solution containing a distribution of oligomer/polymer molecules of varying molecular weights.

Let us consider how the molecular weight of a polymer fraction in the casting or electropolymerization solution affects its nucleation and growth. As already mentioned, the driving force of the new phase formation is the supersaturation of the polymer molecules in the solution. The supersaturation, or supersaturation ratio $\zeta$, is defined as the ratio of the actual concentration $c$ of a species in solution to the saturated concentration of the species in given conditions, $c_s$:

$$\zeta = \frac{c}{c_s} \quad \text{(Eq. 3.1)}$$

The molecular weight is known to affect the solubility of the polymer molecules: the higher the Mw, the longer the molecule, the lower its solubility in the same solvent at a particular temperature. Therefore, at a given $c$, the supersaturation ratio and hence the driving force will be greater for molecules with higher Mw, and they should be deposited at earlier stages of the deposition process, as compared to molecules with lower Mw. This behavior should be observed for all methods of polymer deposition, provided that the deposition occurs from solution containing polymer fractions with variable molecular weight.
The mathematical description of the mechanism outlined above can be obtained from the nucleation theory. Nucleation is a spontaneous process of formation of clusters of a new phase on the substrate surface. These clusters can be of different sizes. If the size of a cluster is smaller than a certain critical radius \( r^* \), than this cluster is thermodynamically unstable and disappears. If a cluster is larger than the critical radius, it undergoes further growth and eventually forms the core of a polymer grain. The value of the critical radius \( r^* \) in the simplest case of the so-called capillarity approximation for clusters comprising sufficiently large number of molecules\(^\text{67}\) can be obtained using the famous Kelvin equation:\(^\text{68}\)

\[
 r^* = \frac{2 \cdot \sigma \cdot V_M}{R_{\text{gas}} T \cdot \ln\left(\frac{c}{c_s}\right)} 
\]

(Eq. 3.2)

where

- \( c \) is the concentration of a nucleating species;
- \( c_s \) is its saturated concentration;
- \( \sigma \) is the surface tension at the polymer/solution interface;
- \( V_M \) is the molar volume of the polymer;
- \( R_{\text{gas}} \) is the gas constant;
- \( T \) is the absolute temperature;
- \( r^* \) is the critical radius of a nucleus;
- \( \frac{c}{c_s} = \zeta \) is the supersaturation ratio.

Since the supersaturation ratio \( \zeta \) will be higher for molecules with higher Mw, Eq. 3.2 predicts that the critical size of the nucleus \( r^* \) will be smaller for polymer molecules with higher Mw. This means that the probability of survival is different for nuclei made...
of polymer with low and high molecular weights. Specifically, the nuclei made of polymer molecules with higher molecular weight will have more chances to survive and eventually form polymer grains. As the grains grow, their size becomes bigger, and deposition of molecules of lower molecular weight (higher $c_s$) becomes thermodynamically favorable. Therefore, this mechanism should result in segregation of polymer molecules according to their molecular weight between primary nuclei that become grain cores, and the grain peripheral regions. Specifically, higher Mw polymer will be located predominantly in the grain cores, while the grain periphery will consist of shorter, lower Mw oligomers.

The effects of the molecular weight on the properties of various conducting polymers have recently attracted a lot of attention in the literature. However, most papers examined the effect of the average molecular weight only. A few papers noted the positive effect of low polydispersity, without producing specific evidence or discussing this effect in any detail. To the best of our knowledge, only one paper specifically studied the effect of polydispersity on the performance of polymer-based devices. The authors showed that blending of low Mw pentamer of p-phenylenevinylene with higher Mw poly-(p-phenylenevinylene) (PPV) polymer, as well as blending of different fractions of di-alkoxy substituted oxadiazole-PPVs with high and low molecular weights, significantly degraded the performance of the resulting light emitting diodes. Furthermore, it was found that using a specially synthesized low Mw but narrow polydispersity PPV allowed the authors to prepare devices with the external quantum efficiency two orders of magnitude better than the efficiency of identical devices but made of high Mw but also high polydispersity PPV. However, the authors attributed the observed effects to the impediment of the carrier transport across polymer chains with varying lengths and energy levels. The effect of polydispersity on the nucleation and growth of polymer films was not considered, the authors assumed that the blending occurred uniformly and homogeneously.

Let us consider the effects of the molecular weight segregation in more detail. There is extensive experimental evidence suggesting that carrier mobilities in
conducting polymers and related materials drastically increase with an increase in the molecular weight. Typically, such an increase is accompanied by an increase in the polymer crystallinity. Unfortunately, the majority of the available data relates to regioregular poly[3-hexylthiophene] (P3HT), which can crystallize also in low Mw form,\textsuperscript{22,70,71} although the structure of the low Mw polymer is quite different from the structure typical to the high Mw one.\textsuperscript{22,70,75-78} For non-regioregular polymers, like those studied in this work, one can expect the formation of the crystalline phase only at high molecular weights, when the polymer chains are able to efficiently fold and stack together. The higher crystallinity of the grain cores for PBT was also inferred from molecular-resolution AFM data;\textsuperscript{27} furthermore, our preliminary phase imaging results show the presence of more crystalline phase within the polymer grains as compared to the grain periphery. In any case, even with regioregular-P3HT, the mobilities found for the low Mw polymer were several orders of magnitude lower than those for the high Mw polymer. This difference should be even greater in our case. Therefore, if the grain cores consist of polymer with higher molecular weight as compared to the grain peripheral regions, then the grain cores should feature higher mobilities and higher conductivity, which is indeed the case.

In the case of “regular” PBT samples, the more crystalline and more conducting grain cores are surrounded by lower-Mw polymer deposited at later stages of the polymer deposition process and featuring lower conductivity. This poorly conducting layer prevents the polymer inside the grain cores from being fully undoped after the deposition, thus giving rise to charge trapping. An intermediate, semiconducting polymer layer can be also formed. As a result, the “regular” PBT samples are very heterogeneous, with the conductivity values varying two orders of magnitude. However, in the case of “nucleated” samples, the poorly conducting outer layer made of lower Mw polymer is absent, since the deposition process was intentionally terminated right after the nucleation step. The polymer material is more homogeneous since it is formed only with high Mw polymer. A decrease in the polymer heterogeneity for very thin films was also noted by Park and co-workers.\textsuperscript{37,43} Furthermore, there is no charge trapping, and, as a result, the polymer can be fully undoped after the synthesis. As a result, the polymer grains feature
much more uniform conductivity distribution as compared to “standard” PBT. Furthermore, they should be less conducting as compared to “regular” samples, which is also observed. This very significant difference between the two samples indeed suggests that the observed inhomogeneous conductivity distribution has its origin in the nucleation and growth of polymer fractions of varying molecular weight.

The KFM data follow the same trend. The surface potential values as measured by KFM characterize the local work function of polymer regions immediately below the AFM tip. Generally speaking, the work function of a polymer is determined by two factors: its structure and its oxidation degree. More oxidized polymer should feature a higher work function and thus a more negative surface potential. The other factor is crystallinity. Since crystalline phases are more ordered and thus more energetically favorable, they feature higher work functions as compared to amorphous phases of the same composition. Since the crystallinity/degree of order should increase with Mw, the local work function should also increase. If, as postulated above, polymer of higher Mw is located in the grain cores, then the grain cores should feature a higher local work function and a more negative surface potential, which is indeed observed experimentally.

However, electropolymerization produces polymers in their oxidized (doped) state and, as has been discussed above, this doping charge cannot be always fully removed due to charge trapping. Therefore, there will be an additional contribution due to variations in the oxidation degree of the polymer. It is easy to see that, with “regular” PBT, the two factors work in the same direction: The higher Mw fraction is easier to oxidize due to its lower oxidation potential. It is more likely to retain at least some of the doping charge since it is surrounded by less conducting, lower Mw polymer. At the same time, the higher Mw polymer will also have a higher work function even in its neutral state due to increased crystallinity. As a result, the difference in the work functions between the areas of high and low Mw polymer (grain tops and grain periphery) for “regular” PBT samples, as determined from our KFM data, is as high as 100 meV.
The difference in the work function between the grain tops and grain periphery in the case of the “nucleated” sample is much smaller (10-20 meV). This fact correlates well with the absence of the poorly conducting low Mw polymer phase responsible for the charge trapping. As a result, the polymer is quite uniformly undoped, as is also evidenced by rather uniform conductivity distribution, and the variations in the local work function between the grain tops and grain periphery in this case are mostly due to a shift in the position of the Fermi level of the polymer with an increase in its crystallinity. Even smaller variability (2-3 meV) is observed for MEH-PPV, which is cast in its neutral form and therefore does not show any charge trapping. However, the type of the surface potential distribution as found by KFM measurements is the same for “regular”, “nucleated”, and MEH-PPV samples. Therefore, in all these cases the grain cores (or the whole grains as in the case of “nucleated” sample) are made of high Mw polymer, which is in its partially doped state in “regular” samples due to charge trapping, and in undoped non-conducting state in the case of “nucleated” and MEH-PPV samples.

Much lower heterogeneity of the MEH-PPV samples, including much smaller and more uniform grains, as well as much less pronounced variability of both conductivity and the local work functions, suggest that this polymer featured much less variation in the molecular weight as compared to electrochemically prepared polymers. Yet another possible reason may be that, in spin-coating, not all of the polymer is deposited, and a portion of it is blown away by the sample spinning and is not incorporated into the polymer film. In view of the above discussion, it could be expected that the polymer of lower molecular weight is more likely to be removed because it is more soluble then the higher Mw fraction and then will start deposit later than the high Mw fraction. This would result in a smaller grain size and less heterogeneous films. A counterargument here may be that the higher Mw polymer molecules should be moving faster due to the centrifugal effect and thus would be less likely to be deposited. While this issue certainly requires further consideration, it may be argued that any significant centrifugal fractionation of the polymer in the solution is unlikely at the normal rotation speeds employed in spin-coating (ca. 1000 rpm) and on the time scale of the polymer deposition.
In fact, it was noted in the literature that polymer films deposited from identical solutions but using different deposition techniques (dip-coating, spin-coating and drop-casting) featured very different morphology and other properties, such as mobility. Surin et.al.\textsuperscript{80} studied the effect of the deposition technique on the morphology and mobilities of poly[3-hexylthiophene] (P3HT) deposited from different solvents. The authors found that the highest mobilities were observed for dip-coated samples, although the mobilities measured for spin-coated films were generally not much lower. They also studied the effect of solvent and found that high quality and high mobility polymer films are obtained from low-boiling solvents in the case of dip-coating, and high-boiling solvents for spin-coating. They have attributed this behavior to the fact that high boiling point solvents evaporate slowly and allow for crystallization and self-organization of the deposited polymer. However, it is also possible that the effect discussed by Surin et.al. is at least partially due to the fact that, in a high-boiling solvent, there are more chances for the low Mw fraction to be removed and not become incorporated into the polymer film.

Verilhac et.al.\textsuperscript{75} studied the effect of both the molecular weight and the deposition technique on the properties of P3HT films. Unlike Surin et.al., they showed that the mobilities obtained for polymer prepared with either spin coating or dip- and drop-casting were roughly the same. At the same time, they observed a pronounced change in the morphology of the polymer films prepared using different deposition techniques from the fractions of the same molecular weight. Specifically, for all fractions the spin-coated films were the smoothest and featured the smallest morphological features, which is consistent with our hypothesis that this behavior may be due to preferential deposition of the polymer with higher Mw.

A similar effect was observed by Zhao et.al.,\textsuperscript{63} who studied the deposition of poly[3-methylthiophene] (P3MT) on the surface of a rotating disc electrode as a function of the electrode rotation speed. They found that rotation greatly affected the polymer morphology much in the same manner as in the work of Verilhac et.al.: an increase in the rotation speed produced more dense, high-quality films with much smaller grains. Furthermore, they observed that rotation affected the potentiostatic $i$-$t$ transients of the
polymer deposition predominantly after the saddle point, that is, during the nuclear growth step. Specifically, the current of the nuclear growth was very high at stationary electrodes, and was constant and close to zero at high rotation speeds. The nucleation itself was not considerably affected, just slowed down a little (apparently, due to a decrease in the concentration of the electrogenerated polymeric species). This behavior indicates that electrogenerated short-chain oligomers, which can be readily removed by rotation, are indeed involved mostly in the nuclear growth and not the nucleation step, which is in good agreement with our model.

Let us further test the model. One may argue that the effect of the decreased solubility of high Mw oligomers could be offset by lower abundance of molecules with higher Mw in the solution, so that the supersaturation ratio $\zeta$ will not increase with an increase in the Mw. However, in fact this is not the case. In electropolymerization, quite the opposite happens: gel-permeation chromatography of electropolymerized films$^{61}$ showed that the majority of electropolymerized molecules possessed a high molecular weight so that the distribution featured a sharp peak at the highest Mw values and a long tail into the area of smaller molecular weights indicating the presence of a certain concentration of shorter oligomers. Such type of distribution can be attributed to an increase in the polymerization rate with an increase in the molecular weight. The reason for this behavior is the already noted decrease in the oxidation potential of a polymer with an increase in Mw,$^{74}$ so that, at a given potential, the formed oligomers are immediately re-oxidized and undergo further coupling. This mechanism is somewhat similar to the well known autoacceleration effect in free radical polymerization.

Chemically synthesized polymers usually possess a certain molecular weight distribution featuring one or (rarely) two or more maxima (see, e.g., papers$^{21,57}$). The specific type and width of the distribution depend on the polymerization mechanism. However, in any case, since the solubility should monotonously decrease with Mw, we can see that the supersaturation ratio will peak at a higher Mw than the maximum of the original molecular weight distribution, thus resulting in enrichment of the primary nuclei with higher Mw molecules as compared to their content in the casting solution.
In any case, we would like to point out that the Kelvin model should be regarded as a useful approximation only. The use of the Kelvin equation to describe the nucleation phenomena has many limitations and it cannot be expected to describe with high accuracy all the aspects of the polymer deposition process. Further discussion of these issues can be found here.\textsuperscript{67} The Kelvin model also does not consider interaction of polymer molecules with ions\textsuperscript{81} (there are no electrostatic terms in the expression for the change in the free energy upon new phase formation), which is rather important since ions are known to enter the formed polymer phase to ensure its electroneutrality. Nevertheless, the use of the Kelvin model does provide a useful insight into the mechanism of the polymer deposition process. Specifically, it allows us to highlight the importance of the fact that the polymer deposition occurs from solutions containing a mixture of polymer fractions with different molecular weights and hence different solubilities, and thus the rates of deposition of these polymer fractions should be different as well and depend on the molecular weight. However, irrespective of the specific model used for the description of the polymer nucleation and growth, the fact is that polymer molecules with higher molecular weights feature lower solubility and should be deposited earlier than polymer fractions with lower molecular weights, thus giving rise to the mesoscopic inhomogeneity of these materials evidenced by AFM, KFM, CS-AFM, and other techniques.

### 3.5 Conclusions

In this work, we studied the mesoscopic inhomogeneity of conducting polymer films obtained by electropolymerization and spin-coating techniques. We have demonstrated, using the Kelvin probe force microscopy (KFM) and the current-sensing atomic-force microscopy (CS-AFM), that there is an unambiguous correlation between the surface morphology of the polymer films, on the one hand, and their conductivity and local work function, on the other. A model is proposed that relates the mesoscopic heterogeneity of conducting polymers and related materials to the polydispersity of polymer fractions inherent to both the electropolymerization and various solution-casting techniques. The difference in solubility between the polymer fractions of different
molecular weight (Mw) results in preferential deposition of higher Mw, better conducting and more crystalline polymer fractions at early stages of the polymer nucleation and growth. These primary nuclei are then coated with lower Mw, poorly conducting and substantially disordered polymer phase, which significantly worsen the overall polymer performance. Our results suggest that the best way to control the inhomogeneity is to use the polymer fractions with as low polydispersity index as possible. Yet another possibility is to use leveling solvents or systems (e.g., surfactants) which would bring down the differences in the solubilities of polymer fractions with different molecular weight. Further studies are required to fully evaluate the importance of the factors discussed in this work.

3.6 Acknowledgements

The support of this work by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Foundation for Innovation/Ontario Innovation Trust (CFI/OIT) is gratefully acknowledged. The authors are greatly indebted to the group of Prof. Fann Wunshain from the National Taiwan University for their kindly providing us with the samples of spin-coated poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV).

3.7 Supporting Information

Discussion of the effect of the molar volume on the polymer nucleation according to the Kelvin model can be found in the Appendices.
3.8 References


Chapter 4: AFM Phase Imaging of Electropolymerized Polybithiophene Films at Different Stages of Their Growth

4.1 Introduction

The crystallinity of conducting polymer-based materials is an important parameter that considerably affects their properties, such as carrier mobilities, conductivity, etc. The crystalline polymer phases are more ordered and feature higher carrier mobilities, which is very important for a number of practical applications such as organic light-emitting diodes, transistors and solar cells. There is a large body of evidence ranging from X-ray diffraction\textsuperscript{1-3} and microwave conductivity\textsuperscript{4,5} to electrochemical\textsuperscript{6} and quartz microbalance\textsuperscript{7} data suggesting that conducting polymers represent a mixture of crystalline and amorphous phases. The question of the nature and origin of the distribution of the crystalline and amorphous phases in these materials has been the matter of discussion. The viewpoint most often advocated in the literature (the model of a granular polymer metal\textsuperscript{8}) is that the more crystalline phase forms certain mesoscopic crystalline domains (20-100 nm in size) that are randomly distributed within the polymer phase. In our previous paper,\textsuperscript{9} we have demonstrated using current-sensing atomic force microscopy (CS-AFM) and Kelvin probe microscopy (KFM) that such domains are indeed observed, but they are not randomly distributed but rather are embedded inside the polymer grains. The data suggested that each grain contains a more conductive/crystalline core surrounded by less conducting/disordered polymer phase. Such a distribution was related to the preferential deposition of a polymer of higher molecular weight (M\textsubscript{W}) at the early stages of the polymer deposition process. The high M\textsubscript{W} fractions are less soluble and therefore, the nucleation driving force for these fractions is higher as compared to more soluble, lower M\textsubscript{W} fractions. Therefore, the higher M\textsubscript{W} fractions will be deposited as polymer nuclei and eventually form the cores of the polymer grains. The fractions with lower molecular weights are deposited later and form less ordered/less conducting grain periphery. More details of this model can be found in our previous paper\textsuperscript{9} (see chapter 3).

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In order to further test this model, it is advantageous to directly measure the degree of crystallinity of conducting polymer films at different stages of their growth. This is done in the present work. The crystallinity is evaluated on nanoscale through the use of an AFM technique called phase imaging. Phase imaging is an extension of a regular tapping-mode AFM that allows simultaneous measurements of the topography and the local mechanical properties, such as adhesion, viscoelasticity, hardness, etc., of conducting or semiconducting samples with nanometer resolution.\textsuperscript{10-14} It is based on assessing the dissipation of energy of the vibrating cantilever transmitted to the sample through the tip-sample contact. These processes are influenced by the local Young’s modulus and other mechanical properties of the sample, which are related to crystallinity.\textsuperscript{11} The crystallinity can be evaluated simultaneously with the regular topography information by mapping the phase of the cantilever oscillations over various sections of the material with respect to the phase of a freely oscillating cantilever. The regions possessing a more positive frequency and phase shift are indicative of hard, or more crystalline, areas of the polymer.\textsuperscript{11} Likewise, regions of the polymer that are softer and less crystalline would show a negative phase shift. Therefore, if our model proposed in Ref.\textsuperscript{9} is correct, we expect that the polymer nuclei formed during the initial stages of nucleation should show a more positive phase indicating crystalline regions. These primary nuclei would be then coated with a lower $M_W$, substantially disordered polymer phase at later stages of the polymer growth, which could be indicated by the phase imaging as showing a more negative phase.

4.2 Experimental

4.2.1 Preparation of the Polymer Samples

A set of poly[2,2’-bithiophene] (PBT) samples (“nucleated” samples) were prepared by potentiostatic electropolymerization, which was terminated at different stages of the polymer nucleation and growth process. The samples varied in thicknesses from very thin non-continuous films to “thick” PBT films with thicknesses of ca. 80 nm. The substrate used for all samples was highly oriented pyrolytic graphite (HOPG)
(NTMDT, ZYB quality). This substrate features an extremely flat surface with very
typical morphology (flat terraces and atomic steps) and thus allowed us to unambiguously
separate the polymer properties from those of the substrate even at the very early stages
of the polymer deposition.

The electropolymerization was performed using a specially designed three-
electrode Teflon cell mounted on top of the HOPG working electrode (the electrode
surface area exposed to the solution was 0.28 cm$^2$). A silver pseudo-reference electrode
(E= +0.05 vs. SCE) and a platinum counter electrode were used. A Princeton Applied
Research (PAR) model 263A potentiostat/galvanostat controlled with version 2.8
Corrware/Corrview electrochemistry software (Scribner) was utilized. A 0.005 M
solution of 2,2'-bithiophene in acetonitrile containing 0.1 M of tetrabutylammonium
hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte was used for
electropolymerization. The solution was deaerated with argon for 10 min before, but not
during, the deposition. 2,2-Bithiophene (Aldrich) was purified through vacuum
sublimation. Tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used
as received. Acetonitrile (ultra-high purity) was purified using an in-house solvent
purification system. The monomer and supporting electrolyte salt were stored in vacuum
desiccators over silica gel to prevent from the moisture accumulation. Further details
concerning the preparation of the polymer samples used in this work can be found in our
previous paper.$^9$

The three “nucleated” samples presented in this paper were prepared by
terminating the electrochemical deposition at a charge of 0.07 mC cm$^{-2}$ (non-continuous
film), 1.2 mC cm$^{-2}$ (an average thickness of approximately 4 nm), and 5.7 mC cm$^{-2}$
(approximately 15 nm). Other samples (not shown) followed the same trends. The
deposition potential for each of these samples remained the same at +1.25 V (vs. the Ag
pseudo-reference electrode). A “thick” PBT sample was also prepared by
electropolymerization under galvanostatic conditions at a current density of 1 mA cm$^{-2}$
for 50s. The average thickness of the polymer film was ca. 85 nm. After the deposition,
the films were reduced in the synthesis solution at a potential of -0.5V (vs. the Ag
pseudo-reference electrode) for 50 s in order to convert them to a neutral/undoped state. The samples were then rinsed three times with pure acetonitrile and dried in a vacuum desiccator at room temperature for at least two days to prevent the effect of residual solvent on the measurements. Overall, the preparation procedure was as close as possible to that employed in our previous work.9

The thickness of the polymer films was determined using AFM by selectively removing a portion of the film by prolonged scanning in the contact mode at high load forces and subsequent measuring of the depth of the produced cavity in the AFM images. The typical cavity size was at least 2 μm by 2 μm to avoid the influence of the local morphological features on the values of the average film thickness as determined by this method.

4.2.2 AFM and Phase Imaging Measurements

The atomic force microscopy (AFM) images were obtained in ambient conditions using a Multimode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using RTESP n-doped Si probes (Veeco, force constant 20 N/m, resonant frequency 300 kHz). The ratio of the set-point and free cantilever vibration amplitudes $A_{sp}/A_0$ was maintained at 0.7 – 0.8, that is, within the so-called moderate tapping region ($0.3 \leq A_{sp}/A_0 \leq 0.8$).11 In this region, as was shown in the literature,11 more positive phase corresponds to more crystalline regions of the polymer. Such regions would appear as bright spots in the phase images. Likewise, lower or a more negative phase corresponds to less crystalline or amorphous regions of the polymer and would appear as dark spots in the corresponding phase images.

The Kelvin probe (surface potential) measurements were performed in the KFM feedback mode using the same RTESP n-doped Si probes, which are known to be conductive enough for this purpose.9 The external bias in the feedback mode was applied to the tip (the sample was grounded). In this configuration, lower or more negative values
of the surface potential corresponded to regions with higher work functions (e.g., more oxidized polymer domains). In the surface potential images, such regions of the sample would look darker than the ones with lower work functions. Further experimental details, including the procedure for the adjustment of the cantilever drive phase, can be found in our previous work. The topography images presented in the paper were manually plane-fitted. The phase and surface potential images were offset. The confidence intervals were determined using Student’s distribution for 10 measurements at 95% confidence level.

4.3 Results

Figure 4.1 shows representative 1 μm by 1 μm images of the topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 0.07 mC cm⁻². The images were acquired in the tapping mode, as were all images presented in this work. Bright areas in the topography image correspond to the polymer film. Also seen in the image are flat sections of the underlying substrate (HOPG) appearing as small “islands” throughout the sample. Importantly, these islands appear bright in the phase image, which confirms that more positive phase corresponds to harder, more crystalline areas of the sample. The film for this sample can be seen to be not continuous, showing very small grains with lateral dimensions of less than 15-20 nm and a height of less than 1 nm. However, these grains appear to be crystalline, since they correspond to bright spots in the phase image.
Figure 4.1. Simultaneous 1 μm by 1 μm images of topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 0.07 mC cm⁻². The Z-scale was 15 nm (topography) and 40° (phase).

This is confirmed by Figs. 4.2a and 4.2b, which show high-resolution images of the topography and phase typical of the sample shown in Fig. 4.1. Also presented in the figure are dual cross-sections taken along the same line in both the topography and phase images (Fig. 4.2c). Comparing the phase image (Fig. 4.2b) with the image of the polymer topography (Fig. 4.2a) and examining the cross-sections of Fig. 4.2c, we can see that there is a good correlation between the topography and phase imaging data. A similar correlation was observed between the topography and other polymer properties, such as the work function and conductivity, in our previous paper⁹ and was explained by a higher degree of crystallinity of the primary polymer nuclei. The phase images of Figs. 4.1 and 4.2 confirm this reasoning. The grains formed during the initial steps of nucleation, shown as bright spots in the topography image, feature more positive phase values which are indicative of a high degree of crystallinity. The darker areas in the phase images of Figs. 4.1 and 4.2 located around the polymer nuclei probably correspond to absorbed oligomers that have yet to crystallize.
Figure 4.2. Enlarged images of (a) topography and (b) phase for the “nucleated” polybithiophene sample shown in Fig. 4.1. The Z-scale was 10 nm and 20°, respectively. (c) Dual cross-section of the images of Fig. 4.2a and 4.2b indicating variations in the height (top) and phase (bottom) along the same line shown in the images.

Figure 4.3 shows representative 1 µm by 1 µm images of the topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 1.2 mC cm². The average film thickness of this sample was ca. 4 nm. The fact that the film is very thin is also confirmed by the visibility of an atomic HOPG step coated with polymer (Fig. 4.3). It can be seen that the sample consists of a layer of small, crystalline grains with the lateral dimensions of ca. 30-40 nm and the height of ca. 2 nm that cover the substrate almost completely and uniformly. This is especially evident from high-resolution images of Figs. 4.4a and 4.4b as well as dual cross-sections of Fig. 4.4c. Again we can see an excellent correlation between the topography (Fig. 4.4a) and the phase (Fig. 4.4b) data. The grains formed during this stage of nucleation and growth
feature more positive phase values and are entirely crystalline with no presence of an amorphous phase. This conclusion is confirmed by the dual cross-section of Fig. 4.4c.

Figure 4.3. Simultaneous 1 μm by 1 μm images of topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 1.2 mC cm$^{-2}$. The Z-scale was 15 nm (topography) and 40° (phase).
Figure 4.4. Enlarged images of (a) topography and (b) phase for the “nucleated” polybithiophene sample shown in Fig. 4.3. The Z-scale was 3 nm and 30°, respectively. (c) Dual cross-section of the images of Fig. 4.4a and 4.4b indicating variations in the height (top) and phase (bottom) along the same line shown in the images.

Figure 4.5 shows representative 1 μm by 1 μm images of the topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 5.7 mC cm⁻². The average film thickness of this sample was ca. 15 nm. It can be seen that the sample is now composed of two different layers: the first layer that consists of smaller grains with lateral dimensions of ca. 30-40 nm and height of 2-4 nm, which are entirely crystalline, and the non-continuous second layer composed of much larger grains (the lateral size of ca. 100 nm and the height up to 20 nm) containing both crystalline and amorphous phases. The film is very flat and uniform, especially the first layer.
Figure 4.5. Simultaneous 1 μm by 1 μm images of topography (left) and phase (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 5.7 mC cm⁻². The Z-scale was 30 nm (topography) and 60° (phase).

This difference between the layers is especially evident from Figs. 4.6 and 4.7, which show high-resolution images of the topography and phase typical for the first and second layer of Fig. 4.5. Also presented in the figures are dual cross-sections taken along the same line in both the topography and phase images (Figs. 4.6c and 4.7c). Once again, it can be clearly seen that there is a well-pronounced correlation between the topography and phase images; however, now the larger grains of the second layer (Fig. 4.6) are composed of both crystalline and amorphous phases. Specifically, the crystalline domains of the polymer are located in the centre of the large grains with the amorphous phase surrounding these crystalline regions. Conversely, the grains of the first layer (Fig. 4.7) can be seen to be entirely crystalline with no amorphous phase present. However, in both cases, we continue to see the correlation between the polymer morphology and crystallinity, which further support our model of the polymer nucleation and growth.
Figure 4.6. Enlarged images of (a) topography and (b) phase for the larger grains from the second layer of the “nucleated” polybithiophene sample shown in Fig. 4.5. The Z-scale was 50 nm and 60°, respectively. (c) Dual cross-section of the images of Fig. 4.6a and 4.6b indicating variations in the height (top) and phase (bottom) along the same line shown in the images.
Figure 4.7. Enlarged images of (a) topography and (b) phase for the grains from the first layer of the “nucleated” polybithiophene sample shown in Fig. 4.5. The Z-scale was 50 nm and 80°, respectively. (c) Dual cross-section of the images of Fig. 4.7a and 4.7b indicating variations in the height (top) and phase (bottom) along the same line shown in the images.

Figure 4.8 shows representative 1 µm by 1 µm images of topography (left) and phase (right) typical for “thick” polybithiophene samples. High resolution images of the same sample are given in Figs. 4.9a and 4.9b. Also presented in the figure are dual cross-sections taken along the same line in both the topography image and the phase image (Fig. 4.9c). The topography image shows a well-developed grainy structure typical for these materials. The grains are bigger both in lateral and vertical dimensions (50-70 nm and 20-30 nm, respectively). The average film thickness of this sample was determined by AFM to be ca. 85 nm; therefore, the sample clearly consists of several layers of polymer grains.
Figure 4.8. Simultaneous 1 μm by 1 μm images of topography (left) and phase (right) for a “thick” polybithiophene sample terminated at a deposition charge of 50 mC cm$^{-2}$. The Z-scale was 200 nm (topography) and 80° (phase).

The phase image of Figs. 4.8-4.9 characterizes the local crystallinity of the polymer material. One can see that now virtually all exposed grains have a complex structure with a more crystalline core and amorphous periphery, as predicted in our previous paper$^9$ (see chapter 3). As with the other samples, there is a pronounced correlation between the topography and the phase imaging data: the center of the grains consistently features a positive phase value (bright spots) as compared to the peripheral regions of grains which show a negative phase value (dark spots). This is especially evident from the high-resolution images of Figs. 4.9a and 4.9b and the dual cross-section of Fig. 4.9c.
Figure 4.9. Enlarged images of (a) topography and (b) phase for the “thick” polybithiophene sample shown in Fig. 4.8. The Z-scale was 100 nm and 80°, respectively. (c) Dual cross-section of the images of Fig. 4.9a and 4.9b indicating variations in the height (top) and phase (bottom) along the same line shown in the images.

In order to confirm that the correlation exists not only between the morphology and crystallinity but also between the morphology and local electrical properties of the polymer, as discussed in Ref., we used Kelvin probe force microscopy (KFM) to determine the distribution of the surface potential and hence the local work function for the samples described in this work. Of two electrical parameters used in Ref. (surface potential and local conductance), we selected surface potential because it is measured in the same tapping mode as the phase images. The local conductance is measured using current-sensing AFM (CS-AFM), which is performed in a contact mode and thus cannot provide the same high resolution with thin and soft polymer films.
Figure 4.10. (a) Simultaneous 1 μm by 1 μm images of topography (left) and surface potential (right) for a “nucleated” polybithiophene sample terminated at a deposition charge of 5.7 mC cm\(^{-2}\). The Z-scale was 40 nm (topography) and 0.1 V (surface potential). (b) Dual cross-section of the images of Fig. 4.10a indicating variations in the height (top) and surface potential (bottom) along the same line shown in the images.

Figure 4.10a shows representative 1 μm by 1 μm KFM images of the topography (left) and surface potential (right) obtained for the sample with a deposition charge of 5.7
mC cm$^{-2}$. Also presented in the figure is a dual cross-section taken along the same line in both the topography and surface potential images (Fig. 4.10b). As has been also demonstrated in our previous work$^9$ (see chapter 3), there is a pronounced correlation between the topography and surface potential (indicative of the local work function) of the polymer sample. The topography image is very similar to that in Fig. 4.5 and shows a continuous first layer containing small grains and a non-continuous second layer composed of much larger grains. The average height of the grains of the first layer is 2.5 ± 0.4 nm, while the average height of the grains of the second layer is 15.5 ± 2.3 nm. The surface potential image shows several dark areas that correspond to the large grains in the topography image. As has been already discussed, this means that the large grains are more doped as compared to the rest of the polymer. However, there is also a correlation (especially evident from the cross-section of Fig. 4.10b) between the topography and surface potential for the grains of the first layer as well, but the variations in the surface potential for the grains of this layer are much smaller than for the grains of the second layer (5.1 ± 0.8 mV between the grain top and the grain periphery, as compared to 21.6 ± 2.4 mV for the second layer). Similar values (5.3 ± 0.9 mV) were observed for the grains of the single-layer 1.2 mC cm$^{-2}$ sample, while for the “thick” sample such variations were as high as 100 mV (images not shown).

4.4 Discussion

Electropolymerization is a rather complex process. It starts with a sequence of electrochemical-chemical-electrochemical (ECE) events involving electrochemical oxidation of the monomer molecules, chemical coupling of the resulting radical-cations, re-oxidation of the formed oligomers in solution, their further coupling, and so on, leading to formation of a mixture of oligomers of various molecular weights in the solution phase. The next step is the nucleation of the polymer phase on the substrate surface, followed by the growth of the primary nuclei through further deposition of polymer molecules from the solution. This growth is typically accompanied by continued generation of new and new portions of oligomers, as well as solid-state polymerization of oligomers that are adsorbed/deposited on the electrode surface.
As a result, as has been discussed in more detail in our previous paper, the nucleation and growth of the polymer phase occur from the solution containing a mixture of oligomers of very different molecular weights (Mw). Since the solubility of a polymer fraction decreases with its molecular weight, the high molecular weight fractions will be deposited first and form the primary polymer nuclei, which later become the cores of the polymer grains. The lower molecular weight fractions will be deposited at later stages and form the grain periphery. Since higher molecular weight fractions are likely to form more crystalline polymer, it could be expected that the grain cores would be more crystalline as compared to the grain periphery. Further details of this model can be found in our previous paper (see chapter 3). In this work, this hypothesis was confirmed by direct measurement of the polymer crystallinity using AFM phase imaging. Indeed, it was shown that there is a well-pronounced correlation between the crystallinity and polymer morphology, with the more crystalline polymer found in the cores of the polymer grains and more amorphous polymer located at the grain periphery. Furthermore, as predicted by the model, thin “nucleated” films featured a total absence of the amorphous phase.

Indeed, when electropolymerization is performed in potentiostatic conditions after applying a potential step, as it is done in this work, at first the concentration of electrogenerated oligomers in the electrode vicinity is quite high. Some of them may also become adsorbed on the electrode surface. However, since it takes a certain time for the oligomers to react to form a high molecular weight polymer, at first there will be only a limited number of very small crystalline nuclei surrounded by amorphous low molecular weight oligomers. This situation corresponds to the thinnest “nucleated” PBT sample (Figs. 4.1-4.2). However, even at this stage, the nuclei feature a pronounced crystallinity.

As the polymerization time increases, the oligomers now have time to react and form a high molecular weight polymer. The concentration of the high molecular weight fractions is quite high, and so is the supersaturation ratio, which is the driving force of the polymer nucleation. This process is probably accompanied by solid-state polymerization of the adsorbed oligomers. The result is the formation of a large number of highly crystalline nuclei, which contain no low molecular weight fractions. This situation
corresponds to the second “nucleated” sample (Figs. 4.3-4.4) and the first layer of the third “nucleated” sample (Figs. 4.5-4.7).

However, as the electropolymerization time grows, the concentration of the electrogenerated oligomers decreases and it becomes more difficult for the oligomers to react to form high molecular weight polymer fractions. Furthermore, the deposition of oligomers on the already formed polymer layer is easier as compared to the polymer nucleation on HOPG. Therefore, at this step, low molecular weight fractions start to deposit forming amorphous grain periphery. This situation corresponds to the second layer of the third “nucleated” sample (Figs. 4.5-4.7) as well as the “thick” sample. Importantly, our data suggest that the mechanism of the polymer nucleation is not 3-dimensional instantaneous, as is often assumed in the literature, but rather 2-dimensional progressive.

The fundamental difference between the “thin” and “thick” polymer samples, as well as between the grains of the first and the second layer, is also evidenced by our KFM measurements (Fig. 4.10). The values of the surface potentials were found to be considerably more negative for large grains of the 2nd layer, as compared to small grains of the first layer. Furthermore, the difference in the surface potential at the grain core and grain periphery was markedly greater for the 2nd layer. However, phase imaging showed that the grains of the 1st layer are more crystalline. As has been discussed in our previous paper (see chapter 3), crystallinity may have a twofold effect on the polymer work function and thus on the values of the surface potential. First, crystalline materials should feature higher work function values as compared to amorphous materials of the same chemical composition because disorder increases the internal energy. In KFM images, this effect would result in the surface potential of more crystalline domains being more negative. However, there is another mechanism, which seems to play a dominant role in our case. It is called charge trapping.

When the polymer is undoped after the synthesis, a portion of the doping charge may become trapped in the polymer phase when the outmost layers of the polymer grains
become non-conducting. Since p-doped polymers have higher work functions as compared to neutral ones, these residually doped domains will show a more negative surface potential. This effect should be more pronounced for the large grains formed at the late stage of the polymer deposition process. As has been shown experimentally in this as well as in our previous work \(^9\) (see chapter 3), the periphery of large grains is more amorphous and less conducting as compared to the grain cores. Therefore, the doping charge will be trapped and the surface potential will be more negative, which is observed experimentally. The grains of the first layer are more crystalline but they are also more homogeneous, there is no non-conducting amorphous phase which would trap the doping charge inside the polymer grains.

Therefore, our KFM data indicate that the values of the surface potential and thus of the local work function are determined by the residual doping level and charge trapping rather than directly by the grain crystallinity. However, it is the variation in the polymer crystallinity between the grain cores and grain periphery as evidenced by the phase imaging that ultimately controls the charge trapping through the difference in conductivity of crystalline and amorphous polymer.

There have been several studies of the crystallinity of conducting polymers in the literature; \(^2,3,15-18\) however, the great majority of them are related to regio-regular poly(3-hexylthiophene), P3HT, which feature quite different properties as compared to electropolymerized polybithiophene studied here. Specifically, RR P3HT is known \(^18\) to crystallize also at lower Mw, although the structures formed at low Mw are very different and feature dissimilar properties (e.g., low carrier mobilities) as compared to high Mw P3HT. Nevertheless, the presence of the less crystalline, low Mw polymer has been shown to negatively affect the polymer properties, in particular, the carrier mobility in various polymer-based devices \(^3,15-22\) and the efficiency of polymer-based photovoltaic cells. \(^23,24\) However, in these papers the distribution of the more and less crystalline phases was considered to be purely stochastic due to random folding of the polymer chains. The results of this work provide further justification for an alternative viewpoint that the polymer inhomogeneity occurs not randomly but is related to the distribution of the
primary nuclei formed from solutions containing polymer fractions of different molecular weight. This conclusion not only explains the well-known correlation between the morphology of conducting polymer layers and their performance in various devices, but also shows the ways to control the inhomogeneity of such materials and further improve their properties.

4.5 Conclusions

Our studies of the evolution of the crystallinity of an electron-conducting polymer in the process of its electropolymerization provide the following main conclusion: the polymer materials are heterogeneous and feature a non-uniform distribution of crystalline and amorphous phases. This heterogeneity is not only longitudinal (different crystallinity of grain cores and grain periphery), but also latitudinal (change in crystallinity between the inner and outer layers of the polymer films). The inner polymer layer is almost 100% crystalline; however, the degree of crystallinity decreases notably with the film thickness. As a result, the outer polymer layers are the most heterogeneous and also feature pronounced charge trapping as indicated by Kelvin force microscopy (KFM). The results of this work confirm the model proposed in our previous paper9 (see chapter 3) that the heterogeneity is related to the presence of the polymer fractions of different molecular weights in the electropolymerization solution.

4.6 Acknowledgements

The support of this work by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Foundation for Innovation/Ontario Innovation Trust (CFI/OIT) is gratefully acknowledged.

4.7 References


Chapter 5: AFM Phase Imaging of Thin Films of Electronically Conducting Polymer Polybithiophene Prepared By Electrochemical Potentiodynamic Deposition

5.1 Introduction

Electrochemical deposition remains a versatile and popular method for preparation of conducting polymer modified electrodes. While there have been numerous studies of the mechanism of this process in the literature dating back almost 30 years, very little attention was paid to studies of the electrodeposition process on the nanoscale and especially of the nanostructure of electrogene rated polymer films. In 2007$^1$, we applied an extension of atomic force microscopy (AFM) known as phase imaging (PI) to studies of the early stages of electrodeposition of a conducting polymer, polybithiophene (PBT). Phase imaging is an extension of the regular tapping mode AFM which allows the imaging of the local nanoscale variations in the sample mechanical properties such as hardness, viscoelasticity and ultimately the local crystallinity$^{2,3}$ simultaneously with the sample topography. This is done by following the phase of a vibrating cantilever onto which the AFM tip is mounted.

In the AFM tapping mode, the cantilever is excited by an external voltage at a certain frequency and undergoes a periodic vertical motion. As a result, the AFM tip comes in contact with the surface only intermittently; however, each contact modifies the amplitude and phase of the vibrating cantilever with respect to the situation when the tip has no contact with the sample (a freely vibrating cantilever). The physical origin of such changes is the dissipation of energy of the vibrating cantilever within the sample material. If the tip is in contact with a soft portion of the material with pronounced viscoelastic behavior, the energy of the vibrations is readily dissipated, which results in the occurrence of a negative phase shift (the tip “sticks” to the surface and thus “bounces” back with a delay). If the tip is tapping a hard portion of the material, it will not “stick” and will readily “bounce” back, thus exhibiting less negative or zero phase shift. Therefore, following the variations of the phase of the vibrating cantilever during the

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AFM scanning, one can image the distribution of “hard” and “soft” portions of the material. Furthermore, since the regular topographic information is readily obtained simultaneously during the same scan, one can easily correlate the distribution of the hardness of the material with the sample morphology. Further details of the phase imaging technique can be found in literature\textsuperscript{1-3}.

As far as electrodeposition of electronically conducting polymers is concerned, the AFM phase imaging can provide valuable information concerning the electrodeposition mechanism. The hardness/softness of a material is related to the degree of disorder in the alignment of the polymer chains and ultimately to the material crystallinity. Furthermore, there is a direct link between the crystallinity/degree of order and molecular weight of the deposited polymer (see, e.g., [4] and references therein). Briefly, for non-regio-regular materials, the higher the molecular weight, the greater the degree of order and ultimately, the hardness/crystallinity\textsuperscript{5-7}. Therefore, AFM phase imaging can provide valuable information concerning the distribution of ordered and disordered domains as well as polymer chains with various lengths / molecular weights. Furthermore, when such studies are performed with films for which the electrochemical deposition was terminated at different stages of the polymer electrodeposition process, important information concerning the distribution of electrogenerated oligomers during the nucleation and growth processes can be obtained\textsuperscript{1}.

In our earlier paper\textsuperscript{1} (see chapter 4), we applied the AFM phase imaging to studies of the early stages of the deposition process for potentiostatically generated PBT films. It was shown that at the very early deposition stages almost 100\% crystalline films were obtained. As the film thickness increased, the film crystallinity decreased and thick (50-100 nm) films featured a very particular heterogeneous structure with the cores of the polymer grains being hard or crystalline, and the periphery of the grains being soft and amorphous. This behavior was related to different rates of deposition of electrogenerated oligomers at various stages of nucleation and growth. Specifically\textsuperscript{1,8}, it is argued that the nucleation of the polymer material onto the substrate surface and formation of the
primary nuclei involve predominantly high molecular weight (Mw) oligomers since for them the driving force of nucleation is the greatest. This is primarily due to two factors: their lower solubility in the electropolymerization solution, and a greater energy gain in the solid phase due to more efficient formation of favorable intermolecular interactions. Further details are available in references\textsuperscript{1,4,8}. As the grains grow, the deposition of the lower Mw oligomers becomes possible since the driving force required is now much lower. As a result, at the early stages of electrodeposition the grains were found to be almost fully crystalline, while at the later stages the crystalline cores become coated with amorphous disordered periphery that comprises lower Mw polymer.

However, the potentiostatic electrodeposition technique is only one of the techniques used for preparation of conducting polymer modified electrodes. An equally, or even more popular technique is CV or potentiodynamic deposition, which allows one to prepare high quality polymer films by repeatedly scanning the electrode potential into the region of the monomer oxidation and back. It was of interest to compare the nanoscale properties of films prepared by potentiodynamic deposition with those of films prepared by means of potentiostatic or galvanostatic deposition. This is the subject of the present work.

5.2 Experimental

The electropolymerization was performed using a specially designed three-electrode Teflon cell mounted on top of a working electrode made of highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality). The electrode surface area exposed to the solution was 0.28 cm\textsuperscript{2}. A silver pseudo-reference electrode (E = +0.05 V vs SCE) and a platinum counter electrode were used. All the potentials in the paper are given versus this pseudo-reference electrode. A Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat controlled with version 2.8 Corrware/ Corrview electrochemistry software (Scribner) was utilized. A 0.005 M solution of 2,2’-bithiophene in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate
(TBAPF6) as a supporting electrolyte was used for electropolymerization. 2,2’-Bithiophene (Aldrich) was purified through vacuum sublimation. Tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used as received. Acetonitrile was purified using a SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and a supported copper catalyst. The water content measured for this solvent was less than 10 ppm. The monomer and supporting electrolyte salt were stored in vacuum desiccators over silica gel to prevent moisture accumulation.

(a)

![Cyclic Voltammogram](image1)

(b)

![Chronoamperometric Curve](image2)

Figure 5.1. (a) A typical cyclic voltammogram of potentiodynamic PBT deposition onto the surface of a highly oriented pyrolitic graphite (HOPG) electrode. The potential scan rate was 100 mV s⁻¹. (b) A typical chronoamperometric curve of potentiostatic PBT deposition onto HOPG. The deposition potential was +1.45 V.
Two types of samples were prepared in this work. The first type was a set of poly[2,2’-bithiophene] (PBT) samples prepared by potentiodynamic deposition which was terminated after a varying number of potential scans. The electrode potential was scanned to a maximum potential of 1.45 V at a scan rate of 100 mV s\(^{-1}\). In this work, the results obtained for 1, 4 and 10 scan cycles will be shown. Typical cyclic voltammogram of potentiodynamic deposition of a 10-cycle film is presented in Fig. 5.1a. The figure shows the typical pattern of growing doping and undoping peaks that increase with every scan and indicate a progressive polymer growth. The thicknesses of the electrodeposited films were determined by AFM to be ca. 12, 40 and 60 nm (see below for the thickness determination procedure). A correction for the IR drop (R=320 Ohm) was introduced during the polymerization to ensure the accuracy of the electrodeposition potentials. The solution resistance was determined from an electrochemical impedance measurement performed right before the deposition experiment.

The second type was a set of PBT samples prepared by potentiostatic deposition at a potential of 1.45 V, again, with IR correction turned on. For these conditions, several “thin” and “thick” PBT samples were prepared by adjusting the deposition time. The results presented in this paper refer to samples with average thicknesses of 10, 25 and 72 nm (deposition charges of 0.35, 2.9 and 29 mC cm\(^{-2}\), respectively). A typical chronoamperometric curve for potentiostatic deposition is shown in Fig. 5.1b, with arrows indicating the times at which the film deposition was terminated. After the deposition, all the samples were reduced in the synthesis solution at a potential of -0.5 V for 100 s to convert them to a neutral/undoped state, rinsed with pure acetonitrile and dried in vacuum at room temperature for at least 3 days.

While it is possible in principle to perform phase imaging in situ directly during the electrodeposition process, the phase contrast in this situation is greatly distorted by the viscoelastic properties of the electrolyte solution which is present between the AFM tip and the polymer film as well as in the film itself. In fact, such distortions are observed even when the films are imaged ex-situ but are not sufficiently dry. Therefore, the films
were always thoroughly dried in vacuum before imaging to ensure that the obtained phase contrast distribution was due to variations in the properties of the polymer and did not arise from the distribution of residual solvent in wet polymer films.

The atomic force microscopy (AFM) images were obtained under ambient conditions using a Multimode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using Pointprobe n-doped Si probes (NCHR, Nanoworld, force constant 20 N/m, resonant frequency 300 kHz). The topography images presented in the paper were subjected to manual first-order plane fit to correct for the sample tilt; the phase images were offset. The thicknesses of potentiodynamically deposited films were determined directly using AFM following procedure developed in [9] by selectively removing in contact mode a portion of the film with a contact AFM probe (DDES, Nanoworld, force constant 40 N/m) using repeated scanning with high force reference over a certain area until the substrate surface is reached. The size of the areas is typically several μm squared and is selected to be much greater than the size of typical polymer morphological features. The film thickness is then determined from corresponding topography cross-sections measured over areas with and without the polymer. The procedure is repeated several times at different areas of the sample and an average value is found.

5.3 Results and Discussion

Figure 5.2 presents typical 1 μm by 1 μm topography (left) and phase (right) images of PBT films electrodeposited onto the HOPG surface using a varying number of potentiodynamic deposition cycles. For the sake of comparison, images of polymer films deposited in the same conditions but at a constant potential are also presented in the figure. The topography and phase images were obtained simultaneously in each experiment, as described above. Images a, b and c of fig. 5.2 correspond to films obtained using 1, 4 and 10 potentiodynamic scans, respectively, whereas images d and e of fig. 5.2
correspond to the “thin” and “thick” films obtained potentiostatically. The thicknesses of the films were ca. 12, 40 and 60 nm for potentiodynamically deposited films, and 10, 25 and 72 nm for potentiostatic films. The potentiostatic films with thicknesses of 25 and 72 nm showed essentially the same topography and phase distribution, so only the images of the former film are given in the figure. Brighter spots in the topography images correspond to elevated portions of the polymer (polymer grains). Brighter spots in the phase images correspond to hard, more crystalline, polymer, while darker areas represent soft, viscoelastic, amorphous polymer.

One can see that while both the topography and phase contrast images for the thick films look quite similar regardless of the deposition technique (cf. Figs. 5.2c and 5.2e), there is a remarkable difference in the nanoscale properties and especially the phase contrast at the early stages of the potentiostatic and potentiodynamic electrodeposition (Figs. 5.2a and 5.2d). Specifically, while thin films of polymer obtained using potentiostatic deposition (Fig. 5.2d) consist almost entirely of hard/crystalline grains, in accordance with our earlier data\(^1\), the polymer obtained at the first cycle of the potentiodynamic deposition shows quite complex grain structure that is very different from that observed for the potentiostatically prepared film. Specifically, while the topography of the films is not all that different from the films obtained in potentiostatic conditions (the potentiodynamically deposited films also show several well-known “cauliflower-like” structures originating from the potential scanning, which are absent in potentiostatically deposited films), the phase contrast indicates very little hard/crystalline phase. Only the very centers of the polymer grains show somewhat crystalline nuclei; however, these nuclei are surrounded by abundant disordered/amorphous polymer phase probably comprised of low Mw polymer fragments. Remarkably, this pattern becomes much less pronounced as the thickness of the polymer increases (with the number of potentiodynamic deposition cycles): the film grown for 4 cycles (Fig. 5.2b) shows an increase in the grain size and the relative abundance of the crystalline phase as compared to the film grown for 1 cycle. The film at 10 cycles shows a virtually identical structure to the “thick” film obtained at constant potential (Figs. 5.2c and 5.2e).
Figure 5.2. Simultaneous 1 μm by 1 μm images of topography (left) and phase (right) for: (a) Potentiodynamically deposited PBT sample after 1 scan cycle. (b) Potentiodynamically deposited PBT sample after 4 scan cycles. (c) Potentiodynamically deposited PBT sample after 10 scan cycles. (d) Potentiostatically deposited “thin” PBT sample (thickness ca. 10 nm). (e) Potentiostatically deposited “thick” PBT sample (thickness ca. 25 nm). For images A-C, the Z scales were 40 nm (topography) and 50° (phase). For images D and E, the Z scales were 20 nm and 100 nm (topography) and 50° and 80° (phase), respectively.

To further illustrate the differences in the nanoscale properties of the polymer deposited potentiostatically and using potential cycling, Fig. 5.3 presents higher resolution 500 nm by 500 nm topography and phase images for “thin” and “thick”
potentiodynamically and potentiostatically deposited films, as well as dual cross-sections of the topography and phase data for individual polymer grains. The term dual section means that both the topography and phase contrast values are determined across the same line in both the topography and the phase images, and the resulting profiles are analyzed. This is very convenient when establishing the correlation between the topography and phase contrast values, as well as determining the crystallinity and/or degree of disorder for various areas of the polymer grains. Figures 5.3 a-b correspond to potentiodynamic films obtained at 1 and 10 potential scans. Figure 5.3c shows the images as well as cross-sections for a “thin” potentiostatically deposited polymer film with approximate thickness of ca. 10 nm, while Fig. 5.3d corresponds to a “thick” (ca. 25 nm) potentiostatically deposited film. The locations of the grains for which the dual cross-sections were taken are marked in each image of Fig. 5.3 by white lines.
Figure 5.3. Simultaneous 500 nm by 500 nm images of topography (left) and phase (right) for: (a) Potentiodynamically deposited PBT sample after 1 scan cycle. The Z-scale was 40 nm (topography) and 50° (phase). (b) Potentiodynamically deposited PBT sample after 10 scan cycles. The Z-scale was 150 nm (topography) and 50° (phase). (c) Potentiostatically deposited “thin” PBT sample (thickness ca. 10 nm). The Z-scale was 20 nm (topography) and 50° (phase). (d) Potentiostatically deposited “thick” PBT sample (thickness ca. 25 nm). The Z-scale was 100 nm (topography) and 80° (phase). For all images, dual cross sections are also shown indicating variations in height (top) and phase (bottom) measured simultaneously along the white lines drawn across the same area for each sample, as indicated in the topography and phase images.

One can see again that thin films deposited potentiostatically feature grains that are predominantly crystalline (the phase contrast profile shows a sharp increase in the phase values as soon as the tip moves over a polymer grain and stays almost constant over the whole grain). The films deposited potentiodynamically are predominantly amorphous, as judged from considerably negative phase contrast values observed over the most part of the grains, with only the very centre of the grains showing an increase in the phase values. Interestingly, a number of grains also show an increase in the density/crystallinity at the grain boundaries possibly indicating the beginning of solid-state polymerization (see below).
The cross-sections for “thick” films of both kinds showed quite similar patterns in accordance to our observations made in other works: one can see an increase in the crystallinity/density at the grain cores (an increase in the phase contrast) together with significant presence of amorphous/disordered phase at the grain periphery (indicated by sharply lower phase contrast values). The amount of the crystalline phase for thick films is lower than in thin potentiostatic films, but considerably higher than in thin potentiodynamic films. Furthermore, the phase values for thick potentiostatic films are considerably higher, indicating possibly higher degree of crystallinity for these films.

The differences in the crystallinity/density and degree of disorder for potentiostatically and potentiodynamically deposited films, as revealed by the nanoscale phase contrast measurements, indicate very significant differences in the mechanisms of the potentiostatic and potentiodynamic electropolymerization processes, as well as the properties of the resulting films, especially, at the early deposition stages. Specifically, one can conclude that thin films of potentiodynamically deposited polymer are predominantly amorphous and quite disordered, while thin films of potentiostatically deposited PBT are almost fully crystalline. However, quite remarkably, such differences gradually disappear with an increase in the polymer film thickness. The potentiostatic films undergo grain enlargement due to subsequent deposition of some amorphous phase at the grain periphery, while the potentiodynamic films become considerably more crystalline.

As was discussed in our previous publications\textsuperscript{1,4,8} (see chapters 3 and 4), the variations in the phase contrast between different areas of the polymer sample can be ultimately related to the variations in the average molecular weight of the polymer chains found in this area. Higher molecular weight (Mw) polymer chains form more ordered/crystalline material, while the amorphous disordered regions are comprised of low Mw oligomers. Therefore, it can be concluded that at early stages of the potentiostatic deposition, the average molecular weight of the deposited polymer is significantly greater as compared to that deposited under potentiodynamic cycling.
Furthermore, in the process of potentiostatic deposition, the average molecular weight and the crystallinity decrease with the film thickness, while in potentiodynamic deposition the average molecular weight and crystallinity of the polymer films increase (but remain lower than in potentiostatically deposited films).

The reason for this behavior is probably related to the concentration and reactivity of oligomers generated in the electrode vicinity in either of the deposition techniques. In the potentiostatic deposition, the potential is shifted abruptly into the potential region of monomer oxidation, which gives rise to very high monomer oxidation currents observed right after the potential step. This results in generation of a high concentration of reactive oligomers in the electrode vicinity. These oligomers can thus undergo rapid coupling and elongation generating a considerably high content of high Mw polymer, which then form primary crystalline nuclei on the substrate surface. As the deposition continues, the monomer oxidation current drops and so do the concentration and reactivity of oligomers in the electrode vicinity. The average molecular weight of the electrodeposited polymer decreases, and the disordered, amorphous, low Mw grain periphery is formed.

Conversely, the potentiodynamic deposition produces only a limited amount of reactive oligomers at each of the deposition cycles. Furthermore, the formation of the oligomers is spread over a certain time, even at high potential scan rates. As a result, the rates of generation and coupling of oligomers will be lower than those observed during the early stages of the potentiostatic deposition, and the average molecular weight of the polymer produced in the electrode vicinity will be lower, too. Therefore, the amount of dense/crystalline polymer phase at the electrode surface will be quite lower, which is indeed evidenced by the phase contrast data. An additional factor may be that in the potentiostatic deposition the generated oligomers stay oxidized during the whole duration of electrodeposition, while in the potentiodynamic deposition the oligomers are repeatedly reduced to their neutral state and thus become non-reactive. Furthermore, neutral oligomers are less soluble and thus will be deposited earlier (before reaching high molecular weight) than oxidized oligomers generated in the potentiodynamic deposition.
These factors will further augment the difference in the average molecular weight of the polymer deposited at early stages of potentiostatic and potentiodynamic experiments.

However, as has been already mentioned, as the films grow thicker, the properties of the films prepared using the two techniques become quite similar. Therefore, there is a gradual conversion of low Mw disordered phase into higher Mw and more ordered polymer material in the course of potentiodynamic deposition. The mechanism of such conversion must be related to solid-state polymerization reactions that involve the deposited polymer at the surface. Such reactions are known to take place as the deposited polymer molecules become oxidized and therefore reactive. They may occur either between neighboring polymer chains in the solid state, or, more likely, involve the monomer molecules from the solution. It should be noted, however, that the overall crystallinity of potentiodynamically deposited films remains lower than that of potentiostatically deposited films.

5.4 Conclusions

AFM phase imaging of conducting polymer films obtained using various deposition techniques reveals a striking difference in the nanoscale properties of films deposited using potentiostatic and potentiodynamic electropolymerization. Specifically, the potentiodynamically deposited films showed relatively lower crystallinity and higher degree of disorder, while films grown potentiostatically were more ordered and more crystalline. This was especially pronounced for thin (ca. 10 nm) films. Such behavior was attributed to the differences in the average molecular weight of the polymer molecules formed using these two electropolymerization techniques. Moreover, the potentiodynamically deposited films are more heterogeneous on the microscopic scale and feature large irregular globules comprised almost entirely of amorphous disordered polymer, in addition to smaller regular grains typical to both types of polymer films. Such globules are absent in the images of potentiostatically deposited films. This may be due to two processes, formation of relatively disordered and irregularly shaped agglomerates
(“droplets”) of low-molecular weight polymer, evident in the images of thin potentiodynamically deposited films (Figs. 5.2a and 5.3a), and the well-known phenomenon of agglomeration of individual polymer grain due to repeated swelling-deswelling in the process of potential cycling (formation of “cauliflower”-like structures).

5.5 Acknowledgments

The authors gratefully acknowledge the financial support of this work by the National Science and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the University of Western Ontario Academic Development Fund (ADF).

5.6 References


Chapter 6: The Effect of Electropolymerization Method on the Nanoscale Properties and Redox Behaviour of Poly[2-2′-bithiophene] Thin Film Electrodes

6.1 Introduction

Organic electroactive and electron-conducting polymers are well known materials for electrical energy storage$^{1-4}$. The biggest advantages of electroactive polymers is that they are lightweight as compared to all metal based inorganic batteries, easier to recycle, and inexpensive to produce. Furthermore, they are not explosion-prone and do not contain toxic or hazardous metals and ions. At the same time, repeated attempts of building commercial polymer-based charge storage devices have been so far unsuccessful$^4$ due to a number of reasons, one of the most important being an insufficient ability of these materials to sustain repeated charging-discharging over the time required for a successful commercial device.

The problem of degradation and stability of organic conducting polymers has been addressed repeatedly in the literature since 1980-s, first with respect to overoxidation of such materials in solution$^{5-12}$, and lately, in solid-state electronic and photovoltaic devices$^{13-17}$. Various electrochemical and photochemical reaction pathways have been established that can be generally summarized as (i) oxidation and cleavage of the side chain; (ii) oxidation at the heterocyclic S atom to yield sulfone and sulfoxide moieties, (iii) oxidation at the β-position of the thiophene ring, if available, to yield C-OH and C=O moieties, and ultimately (iv) scissoring and cleavage of the polymer backbone. The degradation processes are greatly accelerated by the addition of nucleophiles, such as water. Over-oxidized materials rapidly lose the reversibility of their doping-undoping and in most cases their electronic conductivity; therefore preventing overoxidation and oxidative degradation of electroactive polymer materials is an important and yet to be fully solved problem of the science and technology of conducting polymers.

A version of this chapter has been submitted for publication:
In this work, we would like to concentrate on the role of microscopic structural factors involved in degradation and reversibility of electron-conducting polymer materials. The role of the deposition technique and its relation to the polymer morphology and nanostructure will be also considered. While the problem of chemical changes involved in oxidative degradation and deactivation has been to certain extent addressed in the literature, the role of the polymer morphology and the morphological changes in general in the course of repeated doping-undoping have attracted insufficient attention of researchers beyond the well-known swelling of the polymer films due to uptake of solvent\textsuperscript{18-22}. In some instances, the changes in the morphology upon cycling were noted in the literature\textsuperscript{22,23}, such as transformation of globular structures for freshly prepared polymers to chain-like or cauliflower structures, but no detailed analysis of these changes or the relationship between the morphology and nanoscale properties of the fresh and cycled films were performed. The atomic force microscopy (AFM) techniques employed were usual topography imaging, no advanced AFM characterization techniques such as phase imaging were applied to study these phenomena.

In this paper, we study the charge storage capacity and stability towards repeated charging discharging of a model conducting polymer, poly[2,2'-bithiophene] prepared using two electrochemical electropolymerization techniques. It was shown that otherwise identical polymer films prepared using potentiostatic and potentiodynamic electropolymerization demonstrated very different cyclability and charge storage capacity. The electrochemical data were related to mesoscopic structural factors such as crystallinity and degree of disorder determined using AFM and AFM phase imaging. Our results show that the low cyclability may be related to mechanical and structural factors rather than simple overoxidation of the polymer material. The main conclusion of the paper is that, unlike materials for solar cells and organic electronics, the best materials for charge storage applications are likely to be amorphous in order to accommodate repeated volume changes associated with doping-undoping without breaking.
6.2 Experimental

6.2.1 Preparation of Polymer Samples

Two types of samples have been studied in this work: The first type were electrochemically deposited poly[2,2’-bithiophene] (PBT) films on a 2 mm diameter platinum disk as a substrate for electrochemical measurements. The second type was electrochemically deposited PBT films on highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality) as a substrate for atomic force microscopy (AFM) measurements. The electrochemical measurements performed on Pt were of two kinds: usual CV characterization and galvanostatic cycling, both performed in monomer-free solutions. CV characterization in a monomer-free solution was also carried out for some PBT films deposited on HOPG in order to ensure that films grown on HOPG had similar properties to those grown on Pt; however, only freshly prepared films were used for AFM imaging.

All PBT films were produced from a 0.005 M solution of 2,2’-bithiophene (Aldrich) in acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (Aldrich) as a supporting electrolyte. The monomer was purified by sublimation at a reduced pressure; the salt was used as received. Acetonitrile was purified using an SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and copper catalysts. The water content was less than 10 ppm. A Princeton Applied Research (PAR) model 263A potentiostat/galvanostat controlled using version 2.8 CorrWare/Corrview software (Scribner) was used. The monomer and supporting electrolyte were stored at room temperature in a vacuum desiccator over silica gel to prevent from moisture accumulation.

Silver pseudo-reference electrode (E = +0.05 V vs. SCE) and platinum counter electrodes were used in all cells. The potential of the pseudo-reference electrode was periodically controlled vs. a ferrocene-ferricinium redox couple. To improve stability and consistency, between measurements the reference electrode was stored in a solution of
supporting electrolyte of the same concentration as during measurements. All potentials were measured and are presented with respect to this reference electrode.

6.2.2 Polymer Film Deposition on Pt

Electropolymerization of the first type of samples was performed in specially designed three-electrode Pyrex glass cells without separation of anodic and cathodic compartments. The working electrode was a 2 mm diameter platinum disc embedded in a teflon holder. Prior to deposition, the platinum working electrode was cleaned on a polishing cloth with 95% ethanol, rinsed with MilliQ water, and dried under a heat gun.

Two types of PBT films on Pt were prepared using either potentiostatic or potentiodynamic deposition techniques. For potentiostatic deposition, the Pt working electrode was held at a potential of 1.25, 1.3, or 1.35 V until the desired electropolymerization charge was reached. A post-deposition cyclic voltammogram (CV) was measured in identical conditions in monomer-free electrolyte solution in order to ensure that the thicknesses were consistent for all films created. The second type of PBT films were prepared by potentiodynamic deposition with the electrode potential scanned to a maximum potential of 1.3 or 1.4 V for a given number of cycles until a selected film thickness was reached. The potential scan rate was 100 mV s\(^{-1}\). Again, a post-deposition CV was measured to confirm consistent thickness across all films and specifically between the films prepared using potentiostatic and potentiodynamic deposition. After deposition, all films were discharged in the synthesis solution at a potential of 0 V for 100 s. All the solutions were deaerated with argon gas at all times before and after measurements, but not during deposition.

The samples made for CV characterization in a monomer-free solution had two thicknesses of 30 nm and 150 nm for both potentiostatically and potentiodynamically prepared films. The samples made for galvanostatic cycling had thicknesses of 150 nm only. The thicknesses were estimated from the comparison of their redox charges with those for PBT films deposited onto HOPG, for which the thicknesses were determined directly using AFM (see below).
6.2.3 Measurements of Films in Monomer-Free Solution

After polymer deposition, the electrode was rinsed with pure acetonitrile and transferred into a separate cell containing 0.1 M of TBAPF$_6$ without the monomer. In this cell, both potentiostatically and potentiodynamically deposited films were subjected to 25 galvanostatic charging-discharging cycles to the potentials limits of 1.3 V, 1.4 V and 1.45 V, with the exception of potentiodynamic films that were also cycled up to a maximum potential of 1.5 V. Potentiostatically synthesized films were not cycled to 1.5 V due to significant and fast degradation already apparent in films cycled to 1.45 V. The charging-discharging current density in these experiments was 0.634 mA•cm$^{-2}$. In addition, separate polymer films of the same types were also cycled 25 times at a current densities that varied from 0.634 mA•cm$^{-2}$ to 2.536 mA•cm$^{-2}$. The potential limit for these experiments was 1.3 V. It should be mentioned that the data for the first charging-discharging cycle after the film preparation were discarded for all experiments to avoid the contributions of the trapped charges and memory effects.

As with deposition, solutions were deaerated with argon gas before and after, but not during, all measurements.

6.2.4 Polymer Film Deposition on HOPG

Electropolymerization of the second type of samples was performed using a specially designed three-electrode teflon cell positioned on top of HOPG acting as the working electrode. The exposed surface area of the electrode to the solution was 0.28 cm$^2$. For this section, two types of PBT films were prepared for AFM analysis. The first type was a set of PBT films prepared by potentiodynamic deposition which was terminated after a selected number of potential scans. The electrode potential was scanned to maximum potential of 1.45 V at a scan rate of 100 mV s$^{-1}$. The results obtained for 1, 4 and 10 scan cycles will be shown in this work. The thicknesses of the electrodeposited films were determined by AFM to be ca. 12, 40 and 60 nm, respectively (for the thickness determination procedure, see below). A correction for the IR drop (R = 320 Ohm) was used during the polymerization to ensure accuracy of the electrodeposition
potentials. Electrochemical impedance measurements were performed prior to deposition in order to determine the solution resistance.

The second type was a set of PBT films prepared by potentiostatic deposition at 1.45 V, again, with IR compensation. Under these conditions, several “thin” and “thick” samples were prepared by adjusting the deposition time. The thicknesses of the films presented in this work were determined to be ca. 16, 25 and 72 nm (deposition charges of 0.71, 2.9 and 29 mC cm\(^{-2}\), respectively).

After the deposition, all samples were reduced in the synthesis solution at a potential of 0.0 V for 100 s to convert them to a neutral/undoped state. They were then rinsed with pure acetonitrile and dried in a vacuum at room temperature for at least 3 days.

6.2.5 AFM Measurements of Films on HOPG

The atomic force microscopy (AFM) images were obtained under ambient conditions using a Multi-mode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using Pointprobe n-doped Si probes (NCHR, Nanoworld, force constant 20 N/m, resonant frequency 300 kHz). The topography images presented in the paper were subjected to manual first-order plane fit to correct for the sample tilt; the phase images were offset. The thicknesses of potentiodynamically deposited films were determined directly using AFM by selectively removing a portion of the film with a contact AFM probe (DDESP, Nanoworld, force constant 40 N/m) by repeated scanning with high force reference over a certain area until the substrate surface is reached. The size of the areas is typically several \(\mu\text{m}^2\) and is selected to be much greater than the size of typical polymer morphological features. The film thickness is then determined from corresponding topography cross-sections measured over areas with and without the polymer. The procedure is repeated several times at different areas of the sample and an average value is calculated.
6.3 Results

6.3.1 Electrochemical CV Characterization

Figure 6.1 presents the results of electrochemical characterization of two sets of “thin” and “thick” polymer samples prepared by either potentiostatic or potentiodynamic deposition. The goal was to illustrate the evolution in the film properties during their growth and highlight the differences in the electrochemical behavior of thin and thick films as well as films prepared using potentiostatic and potentiodynamic deposition. Figure 6.1 (a) presents typical cyclic voltammograms obtained in identical conditions for thick polymer films (ca. 150 nm) prepared using the two techniques. To ensure the accurate comparison, the deposition charges and other polymerization parameters were carefully adjusted so that the doping-undoping charges of all films would be the same. Three films are presented in the figure: two potentiostatic films with the deposition potentials of 1.25 and 1.3 V, and a potentiodynamic film. Potentiostatic films with higher deposition potentials were also tested and showed behavior identical to the film prepared at 1.3 V. One can see that the voltammetric behavior of the films is quite different. Specifically, while the currents in the doping plateau region are quite similar for all films, the height of the doping peak is greater for the film prepared potentiostatically at 1.3 V, and the second undoping peak/shoulder at ca. 0.6 V is also better pronounced. The doping peak is also shifted towards less positive potentials. The height of the doping peak for the potentiodynamically prepared film is the lowest, and its position is shifted towards more positive potentials. The potentiostatic film prepared at low anodic potential shows intermediate behavior.

The same trend is observed for thin films (Fig. 6.1b): The height and the position of the doping peak change in the same manner for potentiostatic and potentiodynamic films and as dependent on the polymerization potential. Furthermore, the peak to plateau ratio is noticeably lower for thin films and the second undoping peak/shoulder at ca. 0.6 V is less pronounced.
Figure 6.1 (c) and (d) illustrate the voltammetric behavior of potentiodynamically deposited film with increasing the anodic scan limit. One can see a consistent pattern of broadening of the voltamograms and reducing of the doping peak height with an increase in the anodic scan limit. At the same time, we observe a remarkable feature that all voltammogram traces intersect at one potential producing a quasi-isosbestic point denoted as “B” in Fig. 6.1 (c). Generally, the occurrence of an isosbestic point suggests the co-existence of two redox-active forms with distinct redox potentials. Furthermore, one of the forms should be converted into the other but the total number of redox active sites should be preserved. This is further illustrated in Fig. 6.1 (d) which shows the dependence of doping charges derived from two portions of the cyclic voltamograms before and after the quasi-isosbestic point, as well as the sum of these charges. The same anodic and cathodic limits “A” and “C” were selected (see Fig. 6.1c). The results unambiguously show that while the charge in the region past the isosbestic point (between points “B” and “C”) indeed decreases with an increase in the anodic scan limit, this is exactly compensated by an increase in the charge before the isosbestic point so that the total doping charge remains the same. Therefore, the changes in the voltammetric behavior that are typically attributed to overoxidation and polymer degradation should rather be attributed to structural reorganization of the polymer films, without loss of the overall redox capacity. Yet another indication of the structural changes is the noticeable decrease in the intensity of the second undoping peak/shoulder at ca. 0.6 V.
Figure 6.1. (a) Typical cyclic voltammograms of “thick” polybithiophene films deposited (1) potentiostatically at a potential of 1.3 V, (2) potentiostatically at a potential of 1.25 V and (3) potentiodynamically by scanning to a maximum potential of 1.4 V for 7 cycles at a rate of 100 mV•s$^{-1}$. The deposition charge for film 1 was 85 mC•cm$^{-2}$ and was selected so that the doping-undoping charge of film 1 would match that of film 2 and 3. The thicknesses of these films are ca. 150 nm. (b) Typical cyclic voltammograms of “thin” polybithiophene films deposited potentiostatically at a potential of (1) 1.3 V and (2) 1.25 V as well as (3) a film deposited potentiodynamically by scanning to a maximum potential of 1.3 V for 1 cycle at a rate of 100 mV•s$^{-1}$. The deposition charges for films 1 and 2 were 5.8 mC•cm$^{-2}$ and was selected so that the doping-undoping charges of the films would match that of film 3. The thicknesses of these films are ca. 30 nm. (c) A cyclic voltammogram of the “thick” polybithiophene film of Fig. 6.1a taken while increasing the anodic scan limit from 1.15 V to 1.45 V in intervals of 50 mV. The arrows A, B, and C indicate the positions of special points in the voltammograms at the potentials of 0 V, 0.91 V and 1.15 V, respectively. (d) The dependencies of the doping charges calculated from Fig. 6.1c for the regions between points A-B (1) and B-C (2), as well as the sum of the charges for regions A-B and B-C (3).
6.3.2 Galvanostatic Cycling

Figures 6.2-6.3 compare the charging-discharging parameters of the films of identical thicknesses but prepared using either potentiostatic or potentiodynamic deposition. The parameters analyzed are the charges of charging and discharging processes achieved when the polymer electrode is subjected to galvanostatic cycles simulating the working regime of a polymer battery (charge and discharge at a constant current). This parameter characterizes the charge storage capacity of the polymer film. Yet another important parameter analyzed here is the charge recovery rate, which is the ratio of the charges of the discharging and charging processes in a given galvanostatic cycle. This parameter characterizes the fraction of the doping charge that can be recovered during the undoping cycle and thus illustrates the reversibility of the charging-discharging processes.

Figure 6.2 shows the dependencies of the charges of charging (a) and discharging (b) and the charge recovery rate (c) on the number of charging-discharging cycles for potentiodynamically deposited polymer films. In this set of experiments, each of the films was charged/doped and discharged/undoped for 25 cycles to the various maximum potentials using the same current density of 0.634 mA cm$^{-2}$. The general trend shows that while all films tend to lose the charge storage capacity over the course of the cycling, films run to higher maximum potentials appear to lose their capacity more rapidly. In addition, the charge recovery rate determined over 25 cycles appears to show that films run to lower maximum potentials allow more than 90% of the stored charge recovered during the discharging process, while this value drops to less than 80% in PBT samples run to higher potentials. There was a consistent drop in the charge recovery rate with an increase in the charging potential limit indicating that less charge of the charging scan is associated with the polymer doping and more with polymer degradation.
Figure 6.2. Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiodynamically deposited PBT films on the number of doping-undoping cycles. The doping-undoping cycling was performed galvanostatically in solution without the monomer at a current density of 0.634 mA cm$^{-2}$ to the maximum potentials of (1) 1.3 V, (2) 1.4 V, (3) 1.45 V and (4) 1.5 V. The films were deposited potentiodynamically over 7 scans between 1.4 V and 0V at a rate of 100 mV s$^{-1}$. The thicknesses of these films are ca. 150 nm.

Figure 6.3 represents the charging (a), discharging (b) and recovery rate (c) dependencies for polymer films deposited potentiostatically at a deposition potential of 1.3V. As with the potentiodynamically deposited films, each of the films was charged/doped and discharged/undoped over 25 cycles to the various maximum potentials using the same current density of 0.634 mA cm$^{-2}$. Once again, a similar trend as above can be seen in these films. The charge storage capacity of films cycled to higher anodic potentials degrade more rapidly in comparison to those cycled at lower potentials. It is important to note that the drop in the charging and discharging charges occurred
more rapidly for potentiostatically deposited films and the recovery ratio observed for potentiostatically deposited films (Fig. 6.3c) was significantly lower than the recovery ratio obtained for potentiodynamically deposited films (Fig. 6.2c) for all charging-discharging conditions. This indicated a higher rate of degradation of potentiostatically deposited films. These results indicate that the charge storage capacity of potentiostatic films as determined from the recovered charge was considerably lower than that for potentiodynamically deposited films.

Figure 6.3. Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiostatically deposited PBT films on the number of doping-undoping cycles. The doping-undoping cycling was performed galvanostatically in solution without the monomer at a current density of 0.634 mA cm$^{-2}$ to the maximum potentials of (1) 1.3 V, (2) 1.4 V and (3) 1.45 V. The films were prepared at a deposition potential of 1.3 V. The thicknesses of these films are ca. 150 nm.

The effect of the charging/discharging current on the charge storage capacity was also studied. Figures 6.4 and 6.5 present the charging (a) and discharging (b) charges
obtained over 25 cycles for films prepared using potentiodynamic (Fig. 6.4) and potentiostatic (Fig. 6.5) deposition at varying current densities. The same charging potential limit of 1.3 V was used for all films. Overall, the polymers deposited potentiodynamically once again maintain higher charge stability over 25 cycles for all currents applied. This can be easily seen in the high values of the recovery rates (Fig. 6.4c) for these films approaching 100%. This indicates that very minimal degradation over 25 cycles is observed. The charge values themselves were quite stable and changed little during cycling and at different charging currents. This indicates excellent reversibility of the doping-undoping processes of potentiodynamically deposited films at various loads.

Figure 6.4. Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiodynamically deposited PBT films on the number of doping-undoping cycles. The films were prepared as those in Figure 6.2 and cycled galvanostatically in solution without the monomer at a current density of (1) 0.634 mA•cm$^{-2}$, (2) 1.268 mA•cm$^{-2}$, and (3) 2.536 mA•cm$^{-2}$ to the maximum potential of 1.3 V. The thicknesses of these films are ca. 150 nm.
The data for potentiostatically deposited films (Fig. 6.5) immediately shows a quite different trend. It is clear that all films now lose their charge capacity with cycling. Furthermore, films charged and discharged at higher currents lose their capacity much faster than films cycled at lower currents. The recovery rate values (Fig. 6.5c) between charging and discharging of potentiostatically deposited films are much lower and do not exceed 80%. These facts confirm the poor reversibility of the charging-discharging processes for potentiostatic films, which becomes even more pronounced at high load currents.

Figure 6.5. Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiostatically deposited PBT films on the number of doping-undoping cycles. The films were prepared at a deposition potential of 1.3 V and cycled galvanostatically in solution without the monomer at a current density of (1) 0.634 mA•cm\(^{-2}\), (2) 1.268 mA•cm\(^{-2}\), and (3) 2.536 mA•cm\(^{-2}\) to the maximum potential of 1.3 V. The thicknesses of these films are ca. 150 nm.
6.3.3 AFM Characterization

In order to understand the origins of such a profound difference in the performance of polymer films prepared using different polymerization techniques, we performed AFM studies of the morphology and heterogeneity of such films on the nanoscale. In order to obtain reliable high quality AFM data, HOPG was used as substrate rather than Pt; however, as was confirmed elsewhere\textsuperscript{24}, degradation patterns are similar for polymers deposited on HOPG and Pt. Figure 6.6 presents typical 1 μm by 1 μm topography (left) and phase (right) images of PBT films electrodeposited onto the HOPG surface using a varying number of potentiodynamic deposition cycles. For comparison, images of polymer films deposited potentiostatically are also presented in the figure. The topography and phase images were obtained simultaneously in each experiment. Since the topography and other properties of the films should depend on their thicknesses, we adjusted the deposition conditions to obtain films of comparable thicknesses. The thicknesses of the films investigated in this work were ca. 12, 40 and 60 nm for potentiodynamically deposited films (Figs. 6.6a, b and c, respectively) and 16 (Fig. 6.6d), 25 (Fig. 6.6e) and 72 nm for potentiostatic films. Potentiostatic films with thicknesses of 25 and 72 nm showed identical topography and phase distribution, so only the images of the former film are shown in this work. Brighter spots in the topography images correspond to elevated portions of the polymer (polymer grains). Brighter spots in the phase images correspond to harder, more crystalline polymer, while darker areas represent softer, viscoelastic, amorphous polymer. More details concerning phase imaging of the polymer films can be found in the literature\textsuperscript{25-27}.
Figure 6.6. (a,b,c) Simultaneous 1 µm by 1 µm AFM images of topography (left) and phase (right) for PBT films deposited potentiodynamically on an HOPG substrate by scanning to a maximum potential of 1.45 V for (a) 1 cycle, (b) 4 cycles, and (c) 10 cycles at a rate of 100 mV•s⁻¹. (d,e) The same images for PBT films deposited potentiostatically on an HOPG substrate at a potential of 1.45 V at a charge of (d) 0.71 mC•cm⁻² and (e) 2.9 mC•cm⁻². For images a-c, the Z scales were 40 nm (topography) and 50⁰ (phase). For images d and e, the Z scales were 20 nm and 100 nm (topography) and 50⁰ and 80⁰ (phase), respectively. The thicknesses of the films were (a) 12 nm, (b) 40 nm, (c) 60 nm, (d) 16 nm, and (e) 25 nm.

Comparing the images of potentiostatic and potentiodynamic films, one can see that while both the topography and phase contrast images for the thick films look quite similar regardless of the deposition technique, there is a significant difference in the nanoscale properties and especially in the phase contrast images of the early stages between the films prepared using potentiostatic and potentiodynamic depositions. Thin films prepared by potentiostatic deposition consist almost entirely of hard/crystalline
grains; whereas, films obtained through potentiodynamic deposition show a much different, complex grain structure. The phase contrast of polymer grains show very little hard/crystalline regions in comparison to potentiostatic films which are predominately hard/crystalline. Only the centers of the polymer grains show somewhat crystalline nuclei; however, these nuclei are surrounded by disordered/amorphous polymer fragments. Remarkably, this pattern becomes much less pronounced as the thickness of the polymer increases (with an increasing number of potentiodynamic cycles): films grown to 4 cycles show an increase in grain size and crystalline phase in comparison to films grown for 1 cycle. However, it can be inferred that even thick potentiodynamically deposited films still have higher amorphous polymer content as compared to potentiostatically grown films.

In order to better illustrate the above trends, higher resolution 500 nm by 500 nm images are presented in Fig. 6.7 together with simultaneous cross sections of both the topography and phase images across the same area of the polymer sample. For the sake of comparison, juxtapositions of the height and phase cross-sections are also presented. One can see that indeed there is a pronounced difference in the amorphous and crystalline content inside the polymer grains for materials deposited potentiostatically and potentiodynamically. Furthermore, there is a pronounced evolution in the crystalline content for potentiodynamically polymerized films with increasing thickness. This result indicates the continuing occurrence of solid-state polymerization in potentiodynamically deposited films. However, the crystalline content still remains lower in potentiodynamically deposited films than in potentiostatically deposited films in all cases.
Figure 6.7. (a,c) Simultaneous 500 nm by 500 nm AFM images of topography (left) and phase (right) for PBT films deposited potentiodynamically on an HOPG substrate by scanning to a maximum potential of 1.45 V for (a) 1 cycle and (c) 10 cycles at a rate of 100 mV•s\(^{-1}\). (b,d) The same images for PBT films deposited potentiostatically on an HOPG substrate at a potential of 1.45 V at a charge of (b) 0.71 mC•cm\(^{-2}\) and (d) 2.9 mC•cm\(^{-2}\). For images a and c, the Z scales were 40 nm (topography) and 50° (phase), and 150 nm (topography) and 50° (phase), respectively. For images b and d, the Z scales were 20 nm (topography) and 50° (phase) and 100 nm (topography) and 80° (phase), respectively. Also shown in all images are dual cross-sections indicating variations in height (top) and phase (bottom) along the same white line shown in the images. For the sake of comparison, juxtapositions of the height and phase cross-sections are also shown.
6.4 Discussion

For both potentiostatic and potentiodynamic deposition methods, it can be seen that films cycled to higher anodic potentials exhibit a rapid degradation of the charge storage capabilities over subsequent charge/discharge cycles. Likewise, when cycled to lower anodic potentials, the overall charge is decreased; however, the stability of films is much greater for both types of films. At the same time, there is a pronounced difference in both cyclability and the charge storage capacity as well as the charge recovery rate between potentiostatically and potentiodynamically prepared films. Overall, potentiodynamically prepared films possess a much higher stability and charge/discharge recovery over multiple cycles (Fig. 6.2) in comparison to potentiodynamically prepared films (Fig. 6.3). We propose that the origin of such a difference in the behavior of the polymer films synthesized using potentiodynamic and potentiostatic deposition methods lies in their nanoscale structural properties. As follows from our AFM data, although the morphology of the polymer films prepared using the two techniques look similar, one can see a pronounced difference in the crystallinity and heterogeneity for potentiostatically and potentiodynamically deposited films, as revealed by nanoscale phase contrast data. Specifically, it can be concluded that at the early stages of film deposition, potentiodynamic films are predominantly amorphous and disordered whereas PBT films deposited potentiostatically are dominantly hard/crystalline. As the films increase in thickness, these initial differences gradually become less pronounced but the potentiodynamically synthesized films still remain less crystalline than the films of similar thickness prepared using potentiostatic method.

This reasoning is supported by the results of CV electrochemical characterization (Fig. 6.1). These results can be summarized as following:

1. Potentiostatically deposited films have more pronounced doping peak and 2\textsuperscript{nd} undoping peak/shoulder as compared to potentiodynamically deposited films;

2. Thin films prepared using both potentiostatic and potentiodynamic polymerization techniques show lower peak to plateau ratio and less pronounced 2\textsuperscript{nd} undoping peak/shoulder as compared to thick film;
3. The same is true for potentiostatic films prepared at lower polymerization potentials as compared to films prepared at more anodic potentials.

4. Scanning with an increasing anodic limit results in a decrease in heights of both the doping peak and the 2$^{\text{nd}}$ undoping peak/shoulder, with the overall doping charge staying the same.

The explanation of these facts can be found in the models proposed by M. Skompska, M. Vorotyntsev and J. Heinze$^{28-30}$ that relate the doping peak and the 2$^{\text{nd}}$ undoping peak/shoulder to redox processes occurring in more crystalline portions of the polymer films that contain stronger interacting chains. Upon charging, these chains form various aggregates, such as $\pi$- and $\sigma$-dimers, that support extended electronic states delocalized across several interacting polymer chains. This charging process occurs in the vicinity of the doping peak, whereas the oxidation of more disordered polymer fragments (typically featuring shorter chain length) occurs later in the area of the doping plateau. On the reverse scan, such aggregates dissolve. This process requires extra energy and therefore occurs at less anodic potential and manifests itself as the 2$^{\text{nd}}$ undoping peak/shoulder. The difference in the kinetics of the doping processes occurring in crystalline and amorphous portions of polymer films was also observed in reference$^{22}$.

Therefore, the observed differences in the electrochemical behavior of potentiostatic and potentiodynamic films clearly support our hypothesis that potentiodynamically prepared films feature lower crystallinity. They show lower doping peak as compared to the doping plateau and less pronounced 2$^{\text{nd}}$ undoping peak/shoulder. Furthermore, the electrochemical results for thin and thick films clearly confirm our AFM data that thin films, especially thin potentiodynamic films, show much lower crystallinity.

Taking together, our electrochemical and AFM results suggest that the differences in the polymer cyclability and charge storage capacity can be related to the differences in the observed nanoscale properties of these films. When a polymer undergoes charging, solvent enters the polymer matrix causing the polymer to swell$^{18-22}$. When the polymer film discharges, the opposite occurs; solvent is pushed out of the film causing the film to
de-swell back to its original state. Unfortunately, the swelling and de-swelling is not a perfectly reversible effect. The best known manifestation of this fact is the occurrence of so-called “cauliflower” structures upon repeated doping-undoping of the polymer; individual polymer grains swell and come into contact with each other. Upon deswelling, it is energetically favourable to maintain the contact between the grains to reduce the surface energy. As a result, swelling-deswelling gives rise to redistribution of the polymer matter, which in particular exhibits itself as coalescence of the polymer grains and the emergence of the “cauliflower” structure. Inevitably, such redistribution creates mechanical stresses in the film that eventually lead to fracturing and loss of some polymer mass from the electrode. More crystalline and thus more rigid films are more brittle in comparison to films with less crystalline structure. Therefore, the repeated swelling and de-swelling process and the associated build-up of mechanical stresses are more likely to cause more damage to films prepared using potentiostatic electropolymerization. Likewise, potentiodynamically prepared films that exhibit a greater amorphous phase content should allow for a much greater flexibility in the polymer structure during the swelling and deswelling processes and thus would feature a greater reversibility of the repeated doping-undoping processes, greater cyclability and thus better charge storage performance, which is in fact observed experimentally.

The fact that one of the dominant degradation mechanisms in harder/more crystalline polymer films is the breaking-up and removal of polymer fragments from the electrode surface was also confirmed using direct AFM observations of the morphology changes in the polymer films upon doping-undoping\textsuperscript{24}. Taken together, our results suggest that the degradation of the conducting polymer electrodes upon repeated charging and discharging and the associated decline in the charge storage capabilities are not necessarily related to the process of over-oxidation, as is usually believed, but may to a great extent be related to significant irreversible morphology changes that take place in the polymer films upon redox cycling. The loss of capacity may be related to either direct loss of the active polymer mass from the electrode or inactivation of portions of the polymer, for instance, through the lost of accessibility of some polymer domain to solvent and dopant ions. Similar effects were inferred recently\textsuperscript{4} from EQCM
measurements of repeated cycling of a related conducting polymer, poly-3-octylthiophene.

Therefore, we must conclude that, in order to achieve high cyclability and charge storage capacity in conjugated organic polymer films, one must decrease the crystalline content in these films and prepare films that are largely amorphous. Interestingly, this is opposite of the requirements to polymer materials for such important applications as organic solar cells and organic electronics, which require highly ordered and predominantly crystalline films to ensure high carrier mobility. Our results suggest that to ensure better performance in polymer-based charge storage applications, the active polymer material must be largely amorphous.

It is important to understand the reasons for the experimentally observed difference in the crystallinity of conducting polymer films prepared using different electropolymerization techniques. As was discussed in our previous publications\textsuperscript{27,31}, the variations in the structural heterogeneity and crystallinity are likely attributed to the variations in the average molecular weight of the polymer chains formed at different stages of the polymer deposition process. In brief, higher molecular weight (Mw) polymer produces more ordered/crystalline material, while the amorphous disordered regions are comprised of low Mw oligomers. Therefore, it can be concluded that at early stages of the potentiostatic deposition, the average molecular weight of the deposited polymer is significantly greater as compared to films deposited potentiodynamically. Furthermore, in potentiostatic deposition, the average molecular weight and the crystallinity decrease or stay the same, while in potentiodynamic deposition the average molecular weight and crystallinity of the polymer films increases in subsequent cycles.

The reason for this behavior is related to the concentration and reactivity of oligomers generated in the electrode vicinity in either of the electropolymerization techniques. For potentiostatic deposition, the potential is switched abruptly and thus a high concentration of reactive oligomers is generated in the electrode vicinity immediately after the potential step. These oligomers are quite reactive and can undergo rapid coupling and elongation generating a considerably high content of high Mw polymer, which then continue on to form primary crystalline nuclei on the surface of the
substrate. As the deposition continues, the monomer oxidation current drops and so do the concentration and reactivity of oligomers at the electrode. The average molecular weight of the electrodeposited polymer decreases, and the disordered amorphous, low Mw grain periphery is formed (Figs. 6.6 (d-e)).

This mechanism is also supported by the results of our electrochemical studies, in particular, for potentiostatic films prepared at lower electropolymerization potentials (Fig. 6.1). The electrochemical data clearly demonstrate that such films feature a lower crystalline content as compared to potentiostatic films prepared at higher anodic potentials. Again, the concentration and reactivity of electrogenerated oligomers is decreased at lower electropolymerization potentials, which results in a decrease in the average molecular weight of electrodeposited polymer and in its crystallinity.

As the thickness of the films increase, the properties and crystallinity of the films prepared using the two techniques become more similar. This can be attributed to a gradual conversion of low Mw disordered phase into higher Mw polymer material through reaction of the electrodeposited polymer with oligomers from the solution. However, even in this case, the degree of disorder in films prepared potentiodynamically remains higher, which explains the results of the charging-discharging experiments with polymer electrodes prepared using potentiostatic and potentiodynamic deposition.

6.5 Conclusions

In this work, we compare the cyclability and the charge storage capacity of polymer electrodes prepared using potentiodynamic and potentiostatic electropolymerization techniques. It was shown that potentiodynamically prepared films featured a much higher stability and charge/discharge recovery rate approaching 100% over multiple cycles. Potentiostatically prepared films showed much lower performance and rapid deterioration in the charge storage capacity with cycling. Potentiodynamically prepared films showed little or no changes in their charge storage capacity over multiple cycles if the anodic potential limit was kept below +1.4 V. In contrast, potentiostatically prepared films displayed steady deterioration in the charge storage capacity even at the
lowest anodic potential limit tested, +1.3 V. This behavior was related to the difference in
the nanoscale morphology, crystallinity and degree of disorder of polymer films, as
evidenced by AFM and AFM phase imaging. Specifically, it was shown that
potentiodynamically deposited films were more amorphous, which enabled the films to
better withstand the mechanical stresses built up in the polymer phase due to repeated
swelling-deswelling. This was also evidenced by electrochemical data. The difference in
the degree of disorder and crystallinity in polymer films prepared using potentiodynamic
and potentiostatic methods was related to different concentrations and reactivities of
oligomers generated in the electrode vicinity. Our results point that structural factors
rather than (electro)chemical over-oxidation being one of the dominant reasons limiting
the cycle life of polymer-based charge storage devices. Specifically, for charge storage
applications, as opposed to solar cells and organic electronics, it is desirable to use
materials with an increased amorphous content. Moreover, the results suggest that for
polymer batteries, the issues of the purity of the electrolyte solution and the absence of
oxygen and water may play a less crucial role, again, as opposed to polymer-based
semiconductor devices and Li-based charge storage systems.

6.6 Acknowledgements

The financial support of this work by the Natural Sciences and Engineering
Research Council of Canada (NSERC), Canada Foundation for Innovation/Ontario
Innovation Trust (CFI/OIT), Ontario Centres of Excellence (OCE) and the Academic
Development Fund of the University of Western Ontario is gratefully acknowledged.

6.7 References

    (2010) 16823


Chapter 7: The Effect of Cycling on the Nanoscale Morphology and Redox Properties of Poly[2-2’-bithiophene]

7.1 Introduction

The problem of degradation of and stability of organic electron conducting polymers due to their overoxidation in solution has been addressed repeatedly in the literature\textsuperscript{1-7}. At the same time, much less attention has been paid to the morphological changes that occur in polymer films during repeated doping-undoping cycles, beyond the well documented swelling-deswelling of the polymer films due to uptake and release of the solvent\textsuperscript{8-12}. Furthermore, no detailed analysis of the changes in the redox responses of the polymer films in the course of repeated doping undoping has been performed, especially related to the changes in the polymer morphology and nanostructure. In most cases, the analysis concerned either the changes due to overoxidation, or the so-called memory effect (the difference in the position and height of the principal doping peak in the first and subsequent doping cycles, see, e.g., a recent review\textsuperscript{13}. In this work, we analyze in detail the evolution in the redox responses of the polymer films upon repeated doping-undoing beyond just the shift in the doping peak position. Furthermore, we demonstrate that these changes correlate well with the evolution in the nanoscale morphology of the polymer films observed by atomic force microscopy (AFM) and its extension, AFM phase imaging (PI-AFM). Taken together, our data support our earlier findings\textsuperscript{14} that degradation of the polymer films and a decrease in their redox activity and charge storage capacity may be related to mechanical and structural factors rather than simple overoxidation of the polymer material.

7.2 Experimental

7.2.1 Preparation of Polymer Samples

A set of poly [2,2’-bithiophene] (PBT) samples were prepared by galvanostatic electropolymerization. The substrate in all cases was highly oriented pyrolytic graphite
(HOPG) (NTMDT, ZYB quality). The cyclic voltammogram (CV) characterization was performed directly on the samples deposited on HOPG in a monomer-free solution.

All PBT films were produced from a 0.005 M solution of 2,2’-bithiophene in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte. 2,2-Bithiophene (Aldrich) was purified through vacuum sublimation and tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used as received. Acetonitrile was purified using an SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and copper catalysts. The water content was less than 10 ppm. A Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat controlled with version 2.8 Corrware/Corrview electrochemistry software (Scribner) was utilized. The monomer and supporting electrolyte salt were stored in vacuum desiccators over silica gel to prevent moisture accumulation.

Silver pseudo-reference electrodes (E = +0.05 V vs. SCE) and platinum counter electrodes were used in all cells. To improve stability and consistency, between measurements the reference electrode was stored in a solution of supporting electrolyte of the same concentration as during measurements. All potentials were measured and are presented with respect to this reference electrode.

The cyclic voltammograms and AFM images presented in this paper are typical ones selected from at least three independently prepared samples and in the case of the AFM images, also from at least three different areas of the sample.

### 7.2.2 Polymer Film Deposition and Characterization on HOPG

The electropolymerization was performed using a specially designed three-electrode Teflon cell mounted on top of the HOPG working electrode (the electrode surface area exposed to the solution was 0.28 cm$^2$).
All samples were prepared under galvanostatic conditions at a current density of 1 mA cm\(^2\) for 50 s. After the deposition, the PBT films were reduced in the synthesis solution at a potential of 0 V (vs. the Ag pseudo-reference electrode) for 100 s in order to convert them into a neutral/undoped state. The samples were then rinsed three times with pure acetonitrile in the apparatus. After rinsing, the synthesis solution was replaced with a solution of TBAPF\(_6\) in acetonitrile without the monomer. The samples were then subjected to 50 or 100 doping and undoping cycles at a scan rate of 100 mV s\(^{-1}\) from 0.0 V to specific anodic potential limits chosen for each sample; however, the CV was only recorded after every 5 cycles. These potential limits were: 1.3 V, 1.4 V, 1.45 V and 1.5 V. After cycling, the samples were rinsed again three times with pure acetonitrile and dried in a vacuum desiccator at room temperature for at least 3 days to prevent the effect of residual solvent on the measurements. In addition to the cycled samples, a non-cycled, as-prepared PBT sample was also made under the same conditions. The thicknesses of all films presented in this work were determined to be ca. 90 nm by the procedure described below.

### 7.2.3 AFM Measurements of Films on HOPG

The atomic force microscopy (AFM) images were obtained under ambient conditions using a Multimode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using Pointprobe n-doped Si probes (Nanoworld, force constant 20 N/m, resonant frequency 300 kHz). In this configuration, a more positive phase corresponds to more dense/crystalline regions of the polymer. Such regions would appear as bright spots in the phase images. Likewise, lower or a more negative phase corresponds to less dense/crystalline or amorphous regions of the polymer and would appear as dark spots in the corresponding phase images. The topography images presented in the paper were subjected to manual first-order plane fit and the phase images were offset. The thicknesses of all deposited films were determined directly using AFM by selectively removing a portion of the film with a contact AFM probe (DDESP, Nanoworld, force constant 40 N/m) by repeated scanning with high force reference over a
certain area until the substrate surface is reached. The size of the areas is typically several \( \mu m^2 \) and is selected to be much greater than the size of typical polymer morphological features. The film thickness is then determined from corresponding topography cross-sections measured over areas with and without the polymer. The procedure is repeated several times at different areas of the sample and an average value is calculated.

7.3 Results

7.3.1 Changes in the Redox Behavior of PBT Films in the course of Potential Cycling

Figure 7.1a-d shows representative cyclic voltammograms of PBT films of the same thickness deposited onto the surface of a HOPG electrode. The films were subjected to 50 doping and undoping cycles to anodic potentials limits of a) 1.3 V, b) 1.4 V, c) 1.45 V, and d) 1.5 V. The CVs were recorded after every fifth cycle during the scanning process.

One can see that all CVs show a remarkable feature that all voltammogram traces intersect around several specific points, which we will call quasi-isosbestic points, by analogy with isosbestic points defined in molecular spectroscopy\textsuperscript{15}. Specifically, we can define the following quasi-isosbestic points in Figs. 7.1a – 7.1d:

- Figure 7.1a: Two quasi-isosbestic points are observed on the reverse scan denoted as “B” at ca. 0.8 V and “C” at ca. 0.6 V. There is an indication of an isosbestic point on the direct scan around 1.25 V; however, it is not well pronounced due to its closeness to the anodic scan limit.
- Figure 7.1b: Three well pronounced quasi-isosbestic points are observed at potentials of ca. 1.1 V (“A”, direct scan), ca. 0.75 V (“B”, reverse scan) and ca. 0.55 V (“C”, reverse scan). However, the quasi-isosbestic point “B” occurs only for the first 20 cycles (see Fig. 7.1b inset).
- Figure 7.1c: The isosbestic point at ca. 0.8 V on the reverse scan is no longer observed; however, the isosbestic points “A” on the direct scan at a potential of
ca. 1.1 V and “C” on the reverse scan at ca. 0.55 V are still well pronounced. We still denote the potential of +0.75 V as a special point “B” for the sake of discussion; however, this point is no longer a quasi-isosbestic point.

- Figure 7.1d: The quasi-isosbestic points “A” and “C” are still seen but their position now change slightly from 1.1 V to ca. 1.0 V and from 0.55 V to ca. 0.5 V, respectively. Again, as in Fig. 7.1c, we retain a special point “B” at 0.75 V for the sake of discussion.
Generally, by analogy with molecular spectroscopy, the occurrence of an isosbestic point on a cyclic voltammogram should suggest a co-existence of two redox-active forms with distinct redox potentials. Furthermore, one of the forms should be converted into the other but the total number of redox active sites should be preserved. The occurrence of any side reaction generally results first in a gradual shift in the position of the isosbestic point, and finally in its total disappearance.

Let us consider the CVs in Fig. 7.1b as showing the most typical behavior (features found in Fig. 7.1b can be to a certain extent found in all the other CVs of Fig. 7.1). The first quasi-isosbestic point “A” on the direct scan divides the overall doping process into two sections, before and after the quasi-isosbestic point. Specifically, in the course of scanning, the current before the point “A” gradually grows, whereas the current in the peak region including the peak height gradually decreases. On the reverse scan, the current before point “B” (on the right, at more anodic potentials) gradually increases, whereas the second undoping peak at ca. 0.6 V gradually diminishes and broadens transforming into a shoulder. This process also involves another quasi-isosbestic point denoted as “C”, the current past point “C” increases gradually in line with the already noted broadening and transformation of the second undoping peak.

While not all features as above are found in all CVs, the pattern still holds for all films scanned for various anodic potentials. Prolonged cycling gives rise to an increase in the currents in the region before the point “A” and a decrease in the current past this point, coupled with broadening and gradual disappearance of the second undoping peak. Moreover, scanning to higher anodic potentials results in a pronounced decrease in the current not only in the area of the second undoping peak but also before point “B”, in the area of the first undoping peak.

In order to quantify these observations, it is convenient to break down the anodic and cathodic processes into portions, or “quadrants”, and calculate the doping-undoping charges separately for each quadrant. The first quadrant (QI) will then extend from the beginning of the doping process to quasi-isosbestic point “A”, the second quadrant (QII)
will extend from point “A” to a fixed potential past the doping peak in the anodic potential scan to allow for comparison between data sets, quadrant III (QIII) will correspond to the undoping scan from again a certain fixed potential to point “B”, quadrant IV (QIV) will extend from point “B” to point “C”, and quadrant V (QV) will extend from point “C” to the end of the undoping cycle. To allow for comparison across the data sets, the potential of 0.0 V was selected as the start potential for QI and the end potential for QV. For QII, since different potential scan limits would obviously produce different charges, we ensured consistency by calculating the charges only up to 1.4 V, with the exception of PBT of Fig. 7.1a, the limit for which had to be taken at 1.3 V. However, the total doping and undoping charges charge were always calculated between 0.0 V and the maximum anodic potential scan limit for each CV. Also, since the quasi-isosbestic point A does not occur for films cycled to 1.3 V (Fig. 7.1a), no quadrant II was defined in this case. It should be also noted that while the positive current at the beginning of the reverse scan should be a part of quadrant III, we did not include this charge into the quadrant III values because in this region it is difficult to separate the anodic and cathodic processes. In any case, these charges were always quite small as compared to the total doping/undoping charges. However, the total undoping values include these charges.

Figure 7.2 presents the evolution of the charges calculated for each quadrant as defined above in the course of doping-undoping cycling to an anodic potential limit of a) 1.3 V, b) 1.4 V, c) 1.45 V, and d) 1.5 V. It can be seen that for all films cycled to various potentials, the charges for the quadrants QI and QV steadily increase with potential cycling, whereas the charges for QII (except films cycled to 1.3 V for which QII was not defined) and QIV steadily decrease. Importantly, the sum of charges for QI+QII and QIV+QV remained roughly the same, except QI+QII for the films scanned to the highest anodic potential of 1.5 V. This fact confirms the validity of our analysis that involves introduction of quasi-isosbestic points A and C (which separate QI / QII and QIV / QV, respectively): the redox activity of two individual components may change, but the sum of the redox activities of the two components remains the same. As for the charge of QIII, its behavior depends on the anodic scan limit. For films scanned to +1.3 V, it increases
continuously with cycling; for films scanned to higher anodic potentials, it first increases
then starts to decrease. This decrease starts earlier for films scanned to higher anodic
potentials: at cycle #25 for films scanned to 1.4 V, cycle #15 for 1.45 V, and cycle #10
for 1.5 V, for which the decrease becomes especially pronounced after ca. cycle # 40.

Figure 7.2. The evolution of charges for the samples in fig. 7.1 (a-d) calculated for quadrants 1
(■), 2 (●), 3(▲), 4(▼) and 5 (▲) as well as the total anodic (▲) and cathodic (●) charges to
the anodic scan limits of (a) 1.3 V, (b) 1.4 V, (c) 1.45 V and (d) 1.5 V. An exception to this is (a)
in which there is no defined quadrant 2 and the total anodic charge is represented by quadrant 1.

Also presented in fig. 7.2 are the total anodic and cathodic charges calculated for
CVs of fig. 7.1 without separation into quadrants. For films cycled until 1.3 V, both the
anodic and cathodic charges grow in the course of cycling, indicating that the redox
activity and the charge storage capacity of the polymer film actually increases. No overall
degradation was observed for films scanned to this potential. For films scanned to 1.4 V,
the overall doping and undoping charges change very little with scanning, and
furthermore the values of the anodic and cathodic charges closely match each other for all
cycles. This indicates that the doping-undoping process in these conditions is highly
reversible and no degradation of the redox activity is observed. The situation changes,
however, for films scanned to higher anodic potentials (Fig. 7.2 c-d): there is now a
marked decrease in both the doping and undoping charges, especially for 1.5 V. There is
also a pronounced difference between the anodic and cathodic charges indicating that the
reversibility of the doping-undoping process is lower for films scanned to higher anodic
limits.

Figure 7.3. A plot of the reversible undoping charge ($Q_r$) as well as the irreversible charge loss
(IrrQ) versus the number of cycles for the anodic scan limits of 1.3 V ($\square$, 1.4 V ($\bullet$, $\circ$), 1.45
V ($\Delta$, $\triangle$), and 1.5 V ($\diamond$, $\lozenge$). The fully colored shape represents the $Q_r$ and the half colored
shape represents the IrrQ for their corresponding anodic scan limits.

The difference between the total anodic and cathodic charges for a given cycle
represents the irreversible charge loss due to degradation. Figure 7.3 a plot of the
irreversible charge loss (IrrQ) as well as reversible undoping charge ($Q_r$) versus the
number of cycles. It can be clearly seen that samples of PBT cycled to anodic potentials
of 1.45 V and higher show pronounced degradation through an overall decrease in the
total undoping charge and a large increase in irreversible charge loss. However, PBT
cycled to 1.4 V and lower show virtually no degradation and very low irreversible charge
losses. The best overall charge storage capacity was shown by PBT cycled to 1.4 V since
at lower anodic limits the film does not charge in full, and at higher anodic limits the film
undergo rapid degradation.
7.3.2 AFM Imaging of PBT Films Cycled to Various Potential Limits

Figures 7.4 and 7.5 present AFM images of the typical structures found for PBT deposited onto HOPG before and after their repeated doping and undoping to the specific anodic potential limits listed above. Figure 7.4a-d compares 1 μm by 1 μm images, while Figure 7.5a-d represents higher resolution 500 nm by 500 nm images of some of the typical structures found for these samples. It is important to note that the topography and phase images were obtained simultaneously in each of the images presented. In the topography images, bright areas are indicative of elevated areas of the polymer surface (polymer grains). Brighter areas in the phase images represent regions of higher crystallinity or density, whereas darker areas correspond to less crystalline or amorphous, disordered polymer regions. More details concerning phase imaging of the polymer films can be found in the literature\textsuperscript{16-18}.

Figure 7.4. Simultaneous 1 μm by 1 μm images of the topography (left) and phase (right) for polybithiophene films deposited on an HOPG substrate for (a) as-prepared, non-cycled, (b) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.4 V, (c) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.45 V, and (d) subjected to 100 doping and undoping cycles to the anodic potential limit of 1.45 V. All samples were prepared under galvanostatic conditions at a current density of 1 mA cm\textsuperscript{2} for 50 s.
Figure 7.5. Simultaneous 500 nm by 500 nm images of the topography (left) and phase (right) for polybithiophene films deposited on an HOPG substrate for (a) as-prepared, non-cycled, (b) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.4 V, (c) subjected to 50 doping and undoping cycles to the anodic potential limit of 1.45 V, and (d) subjected to 100 doping and undoping cycles to the anodic potential limit of 1.45 V. All samples were prepared under galvanostatic conditions at a current density of 1 mA cm\(^{-2}\) for 50 s.

Figure 7.4a shows representative 1 \(\mu\)m by 1 \(\mu\)m images of the topography (left) and phase (right) for a non-cycled, ‘regular’ polybithiophene sample. Higher-resolution images of topography (left) and phase (right) of the same sample can be seen in figure 7.5a. The topography image shows a well-developed grainy structure typical for these materials with lateral grain dimensions of ca. 45-50 nm\(^{18,19}\).

The phase images for figures 7.4a and 7.5a characterize the distribution of the local crystallinity or density of the polymer material. Specifically, it can be seen that all polymer grains show a complex internal structure consisting of a more dense/crystalline core at the center of the grains surrounded by amorphous portions in the peripheral regions of the grain. The lateral dimensions of these crystalline cores are ca. 30-35 nm. This pattern is typical for these materials as was demonstrated in our previous paper\(^{18,19}\).

Figure 7.4b shows representative 1 \(\mu\)m by 1 \(\mu\)m images of the topography (left) and phase (right) for a polybithiophene sample subjected to 50 doping/undoping cycles to
an anodic potential limit of 1.4 V. High-resolution images of topography (left) and phase (right) of the same sample can be seen in figure 7.5b. The topography image shows a similar grainy structure as compared with the ‘regular’ polybithiophene sample with slightly smaller lateral grain dimensions of ca. 40-45 nm. In addition, one can now see numerous, well-pronounced, large conglomerations of polymer grains which are now present throughout the polymer surface. The appearance of this feature is a common in samples cycled to anodic potentials of 1.4 V and higher. These conglomerates are known as “cauliflower” structures and are likely to originate from repeated swelling-deswelling of the polymer film in the course of potential cycling. In the course of doping, individual polymer grains swell and come into contact with each other. Upon deswelling, it is energetically favourable to maintain the contact between the grains to reduce the surface energy.

At the first glance, the phase image of fig. 7.4b presents a similar local crystallinity distribution as the ‘regular’ polybithiophene samples showing a more crystalline core within the grain surrounded by amorphous grain periphery. However, the higher resolution phase images for these samples (Fig. 7.5b) show that the crystallinity is much more complex in comparison to what is typically found in the ‘regular’ polybithiophene samples. It can be clearly seen that the internal structure of the grain cores now consist of multiple crystalline components surrounded by amorphous grain periphery forming a “pea-pod” like appearance as opposed to the single crystalline core as observed in figure 7.4a and 7.5a. Cross-sections through these crystalline regions show that they have lateral dimensions of ca. 16-20 nm, nearly half the size of the crystalline regions found in ‘regular’ PBT samples.

Figure 7.4c shows representative 1 μm by 1 μm images of the topography (left) and phase (right) for a polybithiophene sample subjected to 50 doping/undoping cycles to a maximum anodic potential of 1.45 V. High-resolution images of topography (left) and phase (right) of the same sample can be seen in Fig. 7.5c. The topography images did not change much from the samples scanned to lower anodic limits and show mostly clusters of polymer grains with lateral dimensions of ca. 40-45 nm. However, the phase images of
figs. 7.4c and 7.5c clearly show further degradation of the crystalline cores and an increase in the amount of relatively amorphous, disordered phase. The lateral dimensions of these crystalline cores are much smaller (ca. 8-12 nm) in comparison to those in Fig. 8.5b (ca. 16-20nm). The “pea-pod” effect, which was beginning to show in fig. 7.5b, is now fully pronounced in fig. 7.5c.

Figure 7.4d shows representative 1 μm by 1 μm images of the topography (left) and phase (right) for a polybithiophene sample subjected to 100 doping/undoping cycles to an anodic potential limit of 1.45 V. High-resolution images of topography (left) and phase (right) of the same sample can be seen in fig. 7.5d. The images show a complete degradation of the polymer sample as a result of prolonged cycling to high anodic potentials. One can see that most of the regular grain structure of the polymer has been severely destroyed. The dominant structures now are much larger conglomerations of polymer grains that look like polymer grains melted together. A few surviving individual polymer grains possess the lateral dimensions of ca. 60-80 nm. The phase images show that the amorphous component has largely disappeared. The structure looks very rigid and rough.

7.4 Discussion

Both electrochemical and AFM data suggest that cycling results in profound changes in the redox behavior and nanoscale structure of polymer films, which are also dependent on the anodic scan limit and the number of cycles. In particular, the electrochemical data suggest that polymer films contain a number of distinct structural forms with different redox properties. Furthermore, the relative abundances of these forms gradually change in the course of repeated doping-undoping, indicating conversion of one of the forms into the other, as was evidenced by the measurements of partial doping charges associated with specific portions, or quadrants, of the charging-discharging curves. Specifically, it was found that cycling increases the charges for quadrants QI and QV and decreases the charges for quadrants QII and QIV. Furthermore, the changes occur in such a way so that a decrease in the charges for one quadrant is
compensated by an increase in the charges for the other, so that the overall redox activity of the two forms combined does not change. This was in particular corroborated by the occurrence of the quasi-isosbestic points in the cyclic voltamograms. Furthermore, since one of the quasi-isosbestic points was found on the anodic scan and the other on the cathodic scan, and the charges for quadrants QI and QV and quadrants QII and QIV show similar evolution with the number of cycles, it is natural to assign charges QI and QV to the one structural form, and charges QII and QIV to the other structural form. In this case, we can make the following observations:

1. The first structural form I that correspond to QI/QV possesses a lower redox potential than the second structural form II that correspond to QII/QIV;
2. During the scanning, the form II is gradually converted into form I.
3. Importantly, even when the polymer films were cycled to high anodic potentials, the overall content of forms I and II stay roughly the same, which indicate that degradation affects these forms less than the other portions of the polymer materials.

The identification of these structural forms inferred from the electrochemical data can be facilitated using our AFM data. AFM, especially phase imaging AFM, suggest that cycling results in a decrease in the amount of crystalline polymer phase and its conversion into more disordered, more amorphous polymer. However, except for the formation of aggregates, the overall morphology of the polymer films does not change much upon scanning, with the exception of really high anodic scan limits and numbers of cycles. Taking together the AFM and electrochemical data, we can make the following assignments:

Structural form II is likely to represent dense crystalline polymer cores evident in the phase images of non-cycled polymer films (Figs. 7.4a and 7.5a). They are made of long polymer chains with high molecular weight (Mw)\textsuperscript{18,19} and therefore they are oxidized in the vicinity of the polymer doping peak and reduced in the vicinity of the
second undoping peak\textsuperscript{20-22}. In the course of doping-undoping, the solvent and counter-ions repeatedly enter and leave the polymer matrix, which apparently results in gradual loosening of some of these dense crystalline polymer cores. This is confirmed by the evolution of the AFM phase images that show replacement of the more crystalline form II with a more disordered, less crystalline form forming the “pea-pod” structures (form I), as well as by the continuing reduction in the size of crystalline cores with cycling and with an increase in the anodic potential limit. As for the redox behavior, the doping of form I should occur at lower anodic potentials since it is easier now for the solvent and counter-ions to penetrate the polymer matrix. A similar observation was made earlier in reference\textsuperscript{12}. At the same time, while the more loose form I is now more disordered, it is still composed primarily by the long high Mw polymer chain and therefore will be oxidized at low anodic potentials.

The same conclusions can be reached from consideration of the cathodic portions of the cyclic voltammograms. Potential cycling clearly results in deterioration and broadening of the second undoping peak, which is related to redox transformation of interacting polymer chains and involve the formation and dissolution of extended electronic states encompassing several neighboring chains\textsuperscript{20-22}. The introduction of disorder through repeated cycling will reduce the probability of formation of such extended states and therefore will gradually abrogate the second undoping peak, which is actually observed. However, the overall redox activity in quadrants QI+QII and QIV+QV remains practically the same except the cases of scanning to the highest anodic potential limits. This fact suggests another interesting conclusion that repeated cycling, at least, while the potential limits are not very high, results in no or very little degradation of long polymer chains that feature the redox activity in these regions. It is likely that, at least at the first steps of degradation, the primary targets for degradation are the shorter polymer fragments, which is corroborated by the pronounced decrease in the redox activity corresponding to QIII.

The situation seems to change, however, when prolonged cycling to high anodic potentials. AFM imaging demonstrates that such cycling resulted in well pronounced
redistribution of the polymer material that gives rise to profound changes in the polymer morphology and crystallinity. One of possible mechanism for such restructuring could be partial dissolution and re-crystallization of the polymer fragments.

7.5 Conclusions

The evolution of the structural and redox properties of conducting polymer films in the course of repeated scanning to varying anodic scan limits was studied by AFM, AFM phase imaging, and cyclic voltammetry. It was shown that the cycling gave rise to irreversible structural changes in the polymer phase. Specifically, a portion of the dense crystalline fraction found in as-grown polymer films was converted into more loose and a more open structural form that featured a greater degree of disorder and less pronounced interchain interactions. However, while this process was irreversible, both more and less disordered phases continued to be redox active. The irreversible changes in the redox activity and charge storage capacity at the first steps of degradation were associated primarily with shorter polymer chains with redox response located at higher anodic potentials. However, scanning to higher anodic limits resulted in profound changes in the polymer morphology, which were likely caused by chain breaking due to overoxidation and removal of the resulting short fragments, as well as possible dissolution and re-crystallization of the polymer.

7.6 Acknowledgements

The financial support of this work by the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation/Ontario Innovation Trust (CFI/OIT), Ontario Centres of Excellence (OCE) and the Academic Development Fund of the University of Western Ontario is gratefully acknowledged.

7.7 References


Chapter 8: Conclusions

The overall conclusions are as follows:

1) We have demonstrated, using the KFM and CS-AFM, that there is an unambiguous correlation between the surface morphology, conductivity and local work function of conducting polymer films. A model was proposed that relates the mesoscopic heterogeneity of conducting polymers and related materials to the polydispersity of polymer fractions inherent to both the electropolymerization and various solution-casting techniques. The difference in solubility between the polymer fractions of different Mw results in preferential deposition of higher Mw, better conducting and more crystalline polymer fractions at early stages of the polymer nucleation and growth. These primary nuclei are then coated with lower Mw, poorly conducting and substantially disordered polymer phase, which significantly worsen the overall polymer performance. Our results suggest that the best way to control the inhomogeneity is to use the polymer fractions with as low polydispersity index as possible.

2) Our studies of the evolution of the crystallinity of a conducting polymer in the process of its electropolymerization shows that polymer materials are indeed heterogeneous and feature a non-uniform distribution of crystalline and amorphous phases. This heterogeneity is not only longitudinal (different crystallinity of grain cores and grain periphery), but also latitudinal (change in crystallinity between the inner and outer layers of the polymer films). The inner polymer layer is almost 100% crystalline; however, the degree of crystallinity decreases notably with the film thickness. As a result, the outer polymer layers are the most heterogeneous and also feature pronounced charge trapping as indicated by KFM. The results of this work confirm the model proposed in chapter 4 that the heterogeneity is related to the presence of the polymer fractions of different molecular weights in the electropolymerization solution.

3) AFM phase imaging of conducting polymer films obtained using various deposition techniques revealed a striking difference in the nanoscale properties of films
deposited using potentiostatic and potentiodynamic electropolymerization. Specifically, the potentiodynamically deposited films showed relatively lower crystallinity and a higher degree of disorder, while films grown potentiostatically were more ordered and more crystalline. This was especially pronounced for thin (ca. 10 nm) films. Such behavior was attributed to the differences in the average molecular weight of the polymer molecules formed using these two electropolymerization techniques. Moreover, the potentiodynamically deposited films are more heterogeneous on the microscopic scale and feature large irregular globules comprised almost entirely of amorphous disordered polymer, in addition to smaller regular grains typical to both types of polymer films. Such globules are absent in the images of potentiostatically deposited films.

4) It was shown that potentiodynamically prepared films featured a much higher stability and charge/discharge recovery rate approaching 100% over multiple cycles. Potentiostatically prepared films showed much lower performance and rapid deterioration in the charge storage capacity with cycling. Potentiodynamically prepared films showed little or no changes in their charge storage capacity over multiple cycles if the anodic potential limit was kept below +1.4 V. In contrast, potentiostatically prepared films displayed steady deterioration in the charge storage capacity even at the lowest anodic potential limit tested, +1.3 V. This behavior was related to the difference in the nanoscale morphology, crystallinity and degree of disorder of polymer films, as evidenced by AFM and AFM phase imaging. Specifically, it was shown that potentiodynamically deposited films were more amorphous, which enabled the films to better withstand the mechanical stresses built up in the polymer phase due to repeated swelling-deswelling. This was also evidenced by electrochemical data. The difference in the degree of disorder and crystallinity in polymer films prepared using potentiodynamic and potentiostatic methods was related to different concentrations and reactivities of oligomers generated in the electrode vicinity. Our results point that structural factors rather than over-oxidation being one of the dominant reasons limiting the cycle life of polymer-based charge storage devices. Specifically, for charge storage applications, as opposed to solar cells and organic electronics, it is desirable to use materials with an increased amorphous content.
5) It was shown that cycling gave rise to irreversible structural changes in the polymer phase. Specifically, a portion of the dense crystalline fraction found in as-prepared polymer films was converted into more loose and a more open structural form that featured a greater degree of disorder and less pronounced interchain interactions. However, while this process was irreversible, both more and less disordered phases continued to be redox active. The irreversible changes in the redox activity and charge storage capacity at the first steps of degradation were associated primarily with shorter polymer chains with redox response located at higher anodic potentials. However, scanning to higher anodic limits resulted in profound changes in the polymer morphology, which were likely caused by chain breaking due to overoxidation and removal of the resulting short fragments, as well as possible dissolution and recrystallization of the polymer.
Supporting Information for Chapter 3: The effect of the molar volume on the polymer nucleation according to the Kelvin model

The Kelvin equation gives the value of the critical radius $r^*$ in the simplest case of the so-called capillarity approximation for clusters comprising sufficiently large number of molecules (see references [67-68] in chapter 4):

$$ r^* = \frac{2 \cdot \sigma \cdot V_M}{R \cdot T \cdot \ln\left(\frac{c}{c_s}\right)} $$

(Eq. 1)

where $r^*$ is the critical radius of a cluster;

$c$ is the concentration of a nucleating species;

$c_s$ is its saturated concentration;

$\sigma$ is the surface tension at the polymer/solution interface;

$V_M$ is the molar volume of the polymer;

$R$ is the gas constant;

$T$ is the absolute temperature;

$r^*$ is the critical radius of a nucleus;

$$ \frac{c}{c_s} = \zeta $$ is the supersaturation ratio.

In addition to solubility, the molecular weight of a polymer fraction may affect also other parameters found in Eq. 1, specifically, the polymer molar volume. At a first glance, the molar volume should increase with the molecular weight thus increasing the resulting critical radius and favoring a larger critical grain size. However, this apparent contradiction is easily resolved if we remember that, in the case of nucleation of molecules with different Mw, the nuclei of the same size are comprised by a different number of molecules, and the survival of a nucleus will be determined not by its radius
per se, but rather by the number of molecules required to form a nucleus of this size. Evidently, a critical nucleus that comprises a smaller number of molecules is more likely to be formed than a nucleus containing a larger number of molecules.

In order to better demonstrate this reasoning, the Kelvin equation (Eq. 1) can be re-written as (see below for details):

\[
n^* = \frac{\pi}{6} \cdot \frac{(4\sigma)^3 \cdot V_M^2}{R_g T \cdot \ln(\zeta)}
\]

(Eq. 2)

where \( n^* \) is the number of molecules of given Mw in a critical nucleus;
\( V_M \) is the molar volume of the polymer;
\( V_M = N_A \cdot V_0, V_0 = \frac{V_{nucl}}{n} \)

(Eq. 3)

where \( V_{nucl} \) is the volume of a single nucleus made of \( n \) polymer molecules;
\( N_A \) is Avogadro’s number.

Equation 2 allows one to see more clearly the predominant effect of supersaturation on the polymer nucleation from solutions containing a mixture of polymer molecules with different molecular weights. It is worth noting that it is assumed here that the volume of a polymer nucleus consisting of \( n \) polymer molecules is obtained by simple addition of the volumes occupied by individual molecules (a so-called liquid droplet model). However, longer chains can be expected to fold more efficiently upon forming a solid phase, thus resulting in a more densely packed and more crystalline structure (see references [73] and [77] in chapter 3). Therefore, one could expect that in fact the volume of the polymer nuclei formed by polymer molecules with higher Mw will be less than the value calculated using Eq. 3. This should make the effect of supersaturation even more pronounced than predicted by Eq. 2.
Derivation of Equation 2

Following the paper of F.Q. Yu (see reference [81] in chapter 3), section let us use the liquid droplet model to find the Gibbs free energy for the addition of one polymer molecule to a cluster of \( n-1 \) polymer molecules of the same molecular weight:

\[
\Delta G_{n-1,n} = -kT \cdot \ln(\zeta) + \sigma \cdot (A_n - A_{n-1})
\]  
(Eq. 4)

Here \( \zeta = \frac{c}{c_s} \) is the supersaturation ratio;

\( \sigma \) is the surface tension at the polymer/solution interface;

\( A_n \) is the surface area of the polymer cluster containing \( n \) polymer molecules;

\( A_{n-1} \) is the surface area of the polymer cluster containing \( n-1 \) polymer molecules;

\( k \) is the Boltzmann constant;

\( T \) is the absolute temperature.

Since the volume \( V_n \) of the cluster containing \( n \) polymer molecules in terms of the liquid droplet model is equal to

\[
V_n = n \cdot V_0
\]  
(Eq. 5)

where \( V_\theta \) is the volume taken by one polymer molecule in the cluster,

we find the cluster radius \( r_n \),

\[
r_n = \left( \frac{3nV_0}{4\pi} \right)^{\frac{1}{3}}
\]  
(Eq. 6)
Therefore,

\[ A_n - A_{n-1} = 4\pi \cdot (r_n^2 - r_{n-1}^2) = \]

\[ = 4\pi \cdot \left( \frac{3V_0}{4\pi} \right)^\frac{2}{3} \cdot \left[ n^{\frac{2}{3}} - (n-1)^{\frac{2}{3}} \right] = \]

\[ = (4\pi)^{\frac{2}{3}} \cdot (3V_0)^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot \left[ 1 - (1 - \frac{1}{n})^{\frac{2}{3}} \right] \quad \text{(Eq. 7)} \]

from where we find when \( n \gg 1, \)

\[ A_n - A_{n-1} = (4\pi)^{\frac{2}{3}} (3V_0)^{\frac{2}{3}} \cdot \frac{2}{3} n^{\frac{2}{3}} \quad \text{(Eq. 8)} \]

For a critical nucleus,

\[ \Delta G_{n-1,n} = 0 \]

and

\[ kT \cdot \ln(\zeta) = \sigma \cdot (A_n - A_{n-1}) = \]

\[ = \sigma \cdot (4\pi)^{\frac{2}{3}} (3V_0)^{\frac{2}{3}} \cdot \frac{2}{3} n^{\frac{2}{3}} = \]

\[ = 4 \cdot \sigma \cdot V_0^{\frac{2}{3}} \cdot \left( \frac{\pi}{6} \right)^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \quad \text{(Eq. 9)} \]

From equation 9, it is easy to find the number of polymer molecules in a critical nucleus \( n^* , \)

\[ n^{\ast \frac{2}{3}} = \frac{4 \cdot \sigma \cdot V_0^{\frac{2}{3}} \cdot \left( \frac{\pi}{6} \right)^{\frac{2}{3}}}{kT \cdot \ln(\zeta)} \quad \text{(Eq. 10)} \]

Equation 10 can be readily transformed to the form of equation 2 by cubing and replacing the volume \( V_0 \) with the molar volume \( V_M \) and the Boltzmann constant \( k \) with the gas constant \( R \).
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Title: On the Origin of Mesoscopic Inhomogeneity of Conducting Polymers
Author: Kevin D. O’Neill et al.
Publication: The Journal of Physical Chemistry B
Publisher: American Chemical Society
Date: Aug 1, 2007
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