

**Controlling Polymer Molecular Structure and Morphology: From Illumination of
Conjugated Polymers to Polymer Chain Depolymerization**

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This dissertation is dedicated to my wife, Rachel Ramirez, and my daughter, Adelia.

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ABSTRACT

Polymers remain a prominent component of our lives, and finding methods to control their structure or morphology are needed to tune material properties. This dissertation reports methods to alter the conformation, morphology, or structure of polymeric materials. Chapter two describes the impact of exposure to white light during annealing of conjugated polymer blends on their morphology and optoelectronic performance. The observed changes in the morphology correlate strongly to the variation in photoluminescence (PL) with illumination, including that the PL varies less with illumination at higher Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] loadings, offering foundational understanding to guide the structure and optoelectronic performance of conjugated polymer blend films with illumination.

Chapter three describes the impact of exposure to synchrotron X-rays on the molecular structure of conjugated polymer solutions. These studies show that exposure of poly(3-hexylthiophene) in d-styrene to X-rays during synchrotron SAXS experiments results in the formation of radicals on the poly(3-hexylthiophene) (P3HT) that react to increase the polymer chain size, and continue to cascade long after the sample is removed from the X-ray beam. Supporting experiments reinforce the interpretation that deuterated polystyrene grafts to the P3HT, where the grafting reaction is dominated by X-ray exposure time. This reaction involves the rapid formation of graft points followed by the growth of deuterated polystyrene grafted chains. This study exemplifies the need to carefully plan synchrotron experiments, so as not to unexpectedly alter the structure of the targeted system.

Chapter four examines the evolution of chain structure during the glycolysis depolymerization of polyethylene terephthalate. We hypothesize that by intercepting intermediates in the depolymerization, telechelic oligomers can be captured that can also be used as reactants to produce value-added goods. These results show that a broad range of molecular weights (3,000 – 10,000 Daltons) are accessible at high yields with the heterogeneous reaction at lower temperatures, while increasing the temperature or using a homogeneous reaction limits accessible molecular weights and limits yield. This study shows that controlling the glycolysis depolymerization offers pathways to isolate targeted value-added oligomers. These materials can then serve as reactants to produce block copolymers, which are potential compatibilizers of PET blends.

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Chapter One-Introduction

Polymer Electronics

Polymers have gained a reputation as useful materials for the wide array of applications, mainly due to the extensive variety of properties that they exhibit, which leads to their use in multiple technologies. One application area that has seen a large amount of interest is in their use as organic semiconductors. Interest in this area of research was sparked in the mid-1970s, when Shirakawa, Heeger, and MacDiarmid discovered that doping of polyacetylene made the material electrically conductive.¹ This discovery led to a new class of polymers at the time, conjugated polymers. These materials possess alternating double bonds in the backbone of the polymer, which allow for the transport of electrons along the chain. The large array of chemical structures that enable polymers to exhibit conductivity has become the backbone of organic electronics. Conjugated polymers have been implemented as replacements or complements to traditional conductive and semiconductive materials, as these materials combine the electronic properties of traditional inorganic materials with the desired properties of organic plastics, such as lighter weight, increased flexibility, and potential lower production costs.^{2,3} These advances helped to propel conjugated polymers to their use in devices such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic thin film transistors (OTFTs).²⁻⁷

The conjugated polymers found in the active layer of such devices exhibit optoelectronic processes such as exciton formation, charge separation, recombination, trapping, and charge transport.⁸⁻¹² The final application of the devices dictates how these processes are utilized. For instance, in OPVs conjugated polymers absorb incident light to

produces excitons, that then produce an electrical current through the separation of the exciton at the phase interphase in the active layer and transport of charges to the electrodes. OLEDs luminesce when the charge carriers recombine, finding use as display components. There have been many studies that correlate the optoelectronic properties of conjugated polymers to the conformation of the polymer chains in the resulting devices.^{13–20} In this endeavor, there have been studies that examined methods such as thermal annealing, solvent vapor annealing, controlled crystallization, and induced dewetting to alter the polymer molecular and mesoscale structure, which have helped to further fundamentally understand the correlation of structure to performance in these materials as well as identify methods to increase performance of the resulting devices.^{14,17–23} Continued study into the correlation of polymer conformation and morphology to optoelectronic performance have kept these materials relevant today, and have resulted in the higher integration of these organic materials into devices.

Effects of White Light Illumination on Conjugated Polymer Films

A recent method used to alter the morphology of the active layer in an optoelectronic device containing a conjugated polymer is the use of light during the fabrication of the device. As light interacts with the conjugated polymers in the active layer, the conformation of the polymer chains is altered, which can manifest into changes in the morphology and performance of the active layer. For instance, Botiz et al. studied films of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and polystyrene (PS).¹⁹ This study examined the effect of illumination with white light below the glass transition temperature (T_g) of the polymers on the photoluminescence (PL) of the

films. The studies found an increase in the PL by as much as 42% when annealed with the presence of white light. Botiz et al. attributed this to the planarization of the MEH-PPV, increasing the conjugation length, which increases the PL of the films. Botiz et al. continued utilizing white light during processing to examine its effect on the dewetting of thin films containing a blend of MEH-PPV and polystyrene (PS).¹⁸ On surfaces that promote dewetting, the addition of the white light slowed the dewetting process, consistent with a conformational change in the polymer chains with exposure to light, suggesting the polymer adopts a more rigid and planar conformation. This work by Botiz et al. elucidates the effect of light on the photoluminescence and dewetting behavior of these conjugated polymer films, but does not provide direct evidence of any change in the morphology of the polymer blend films or of the conformation of the polymer chain. Previous work in the Dadmun group elucidated the changes to a conjugated polymer chain during illumination, including studying the conformation of poly(3-hexylthiophene) (P3HT) in dilute solutions via small angle neutron scattering (SANS).²⁴ These measurements directly observe the polymer chain conformation in the presence and absence of light, and found that the polymer Kuhn length, radius of gyration, and second virial coefficient decreased with exposure to white light. This study concludes that the most significant effect of white light exposure to conjugated polymers in solution was to alter the solubility of the polymer in solution, as formation of the exciton influences the polymer-solvent interaction. Another study by the Dadmun group, investigated how illumination alters the gelation of P3HT solutions at higher concentrations.²⁵ In this study, similar observations were made, as

exposure to white light slowed the gelation process, resulting in smaller aggregates and a lower volume fraction of gelled P3HT.

One last study by the Dadmun group investigated the impact of illumination during annealing on the depth profile of conjugated polymer blend thin films.²⁰ This study utilized neutron reflectivity (NR) to investigate the depth profile of MEH-PPV/deuterated polystyrene (dPS) thin films before and after annealing above the T_g in either illuminated or dark environments. The results show differences in the depth profile of the annealed samples dependent on illumination conditions during annealing. During illumination, the thermodynamic interactions between the conjugated polymer and polystyrene are altered, as are the surface energies of the components, which led to changes in the film density profile. These changes in the films depth profile may alter the optoelectronics of the system, but the correlation between structure and performance were not explicitly studied. These studies show promise for illumination with white light as a post processing method to alter the morphology and depth profiles of polymer films. There is, therefore, a need to correlate the illumination-controlled structure of conjugated polymer thin films more precisely to performance. Further studies are required to more fully understand the correlation of the variation in the film's depth profile to the change in the film's performance, and how these relationships can be harnessed as another tool to fabricate devices composed of conjugated thin films with targeted properties.

Effects of Ionizing Radiation on Conjugated Polymers

As previously discussed, much research has focused on studying the changes in the morphology and structure of conjugated polymers and their mixtures in devices. One group

of characterization techniques used on conjugated polymer systems has been different scattering and reflectivity techniques that use X-rays sources.²⁶⁻³⁷ These include grazing incidence small angle X-ray (GISAXS), grazing incidence wide angle X-ray scattering (GIWAXS), small angle X-ray scattering (SAXS) and X-ray reflectivity (XRR). These techniques have proven useful in studying conjugated materials, but the use of X-rays can also lead to damage to the samples. Synchrotron sources have become more potent than when they were initially put into use, which may lead to alterations to the polymer chain structure due the exposure to high energy ionizing radiation. As these techniques have become more widely available, evidence has emerged that document the damage and alteration of the polymer structure by exposure to x-rays.³⁸⁻⁴⁷ For instance, a study by Bras et al. focused on bringing awareness of the impact of brighter synchrotron sources on the molecular structure of soft materials analyzed with these sources.⁴⁶ The primary mechanisms of damage to polymeric materials when exposed to ionizing radiation are chain scission and cross linking events, where the authors correlate these events to the high amount of absorbed radiation. In regards to conjugated materials, Neuhold et al. studied the stability of several conjugated molecular thin films after exposure to synchrotron radiation.⁴² This work studied three different conjugated materials, P3HT, sexithiophene and pentacene and saw that P3HT showed a higher degree of damage when exposed to X-rays than sexithiophene or pentacene. The authors concluded that the alkyl side group on P3HT is susceptible to chain cleavage, which led to the formation of radical species that can react and cascade to produce changes in the film structure, via crosslinking. Vaselabadi et al. also studied the effects of synchrotron radiation on the structure of polymer thin films,

including P3HT and PS after exposure to synchrotron radiation in grazing incidence geometry.⁴⁰ The authors observed crosslinking of P3HT when exposed to X-rays in both air and vacuum, and also a decrease in the crystallinity of P3HT. The authors conclude that exposure to X-rays cause a change in polymeric structure via cross-linking or chain scission. These alterations are dependent on many factors such as molecular weight of the materials, film thickness, exposure geometry, photon energy and photon flux. The possibility and repercussions of this damage must be considered in experimental planning, where the minimum amount of radiation should be used to obtain the desired data so as to not induce any unintended alteration of the molecular structure of the sample.

Many of these studies have looked primarily at thin films composed of conjugated materials and how these materials are damaged by ionizing radiation, though few have looked at analysis of conjugated polymer solutions. Thus, there is a need to understand the kinetics of the structural changes in conjugated polymer solutions when exposed to synchrotron radiation, and what factors drive these changes (i.e., concentration of samples, exposure time to the beam, or the solvent used in the solutions). These studies can provide foundational insight into the limits of synchrotron x-ray experiments to analyze small changes induced by other stimuli (i.e., white light illumination) or if structural changes induced by the X-ray beam will dominate the conjugated polymer systems.

Polymer Recycling

Polymeric materials have integrated into multiple facets of society. Having uses in the industrial, agricultural, and residential sectors, polymer production has risen from this increased demand, which has caused an increase with the amount of waste produced from

these materials. The Environmental Protection Agency (EPA) reports that since the introduction of plastics in the 1960s, our plastic waste generated has increased significantly, with ~35,000,000 U.S tons of reported waste in 2017, as shown in Figure 1.1.⁴⁸ Though there have been attempts to lessen the impact of waste on our environment, mostly through recycling efforts, a large amount of the polymer waste enters landfills and the environment. Polyethylene terephthalate (PET) is one of the most highly recycled plastics used in society, as the material can be commercially recycled and either reused after washing and reprocessed into usable materials, or chemically recycled to form material that is a precursor to synthesize new PET material.⁴⁹ A general scheme to recycle polymeric materials is outlined in Figure 1.2.⁴⁹ Regarding chemical recycling of PET, there are a few chemical routes that can be used to produce monomers from the depolymerization of PET polymer chains, which can then be used to synthesize new polymer.⁵⁰⁻⁵³ These methods include hydrolysis, methanolysis, glycolysis, ammonolysis, and aminolysis, where each of these reactions are shown in Figure 1.3. The most used method to depolymerize PET commercially is glycolysis.⁵³ This is mainly due to the fact that there are a wide range of temperatures available for the process (180-240 °C), glycolysis is faster and more controllable than other methods, and there are a wide variety of catalysts that can be utilized.

Another widely used polymer in society is high density polyethylene (HDPE), but unlike PET, it cannot be readily chemically recycled. The most common method to recycle HDPE is via mechanical recycling of the plastic, which debuted in the 1970s. This method offers a process to manufacture new materials from recovered plastics. There have been

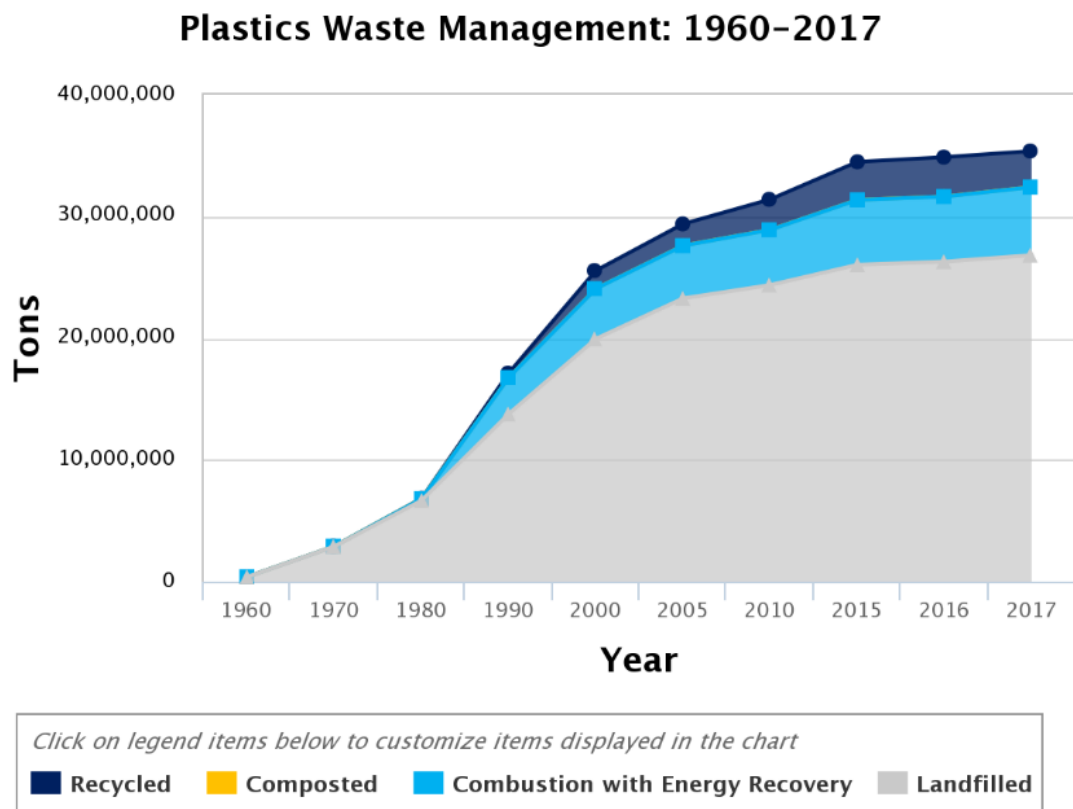


Figure 1.1- Outcome of plastic waste from 1960-2017 according to the EPA.⁴⁸

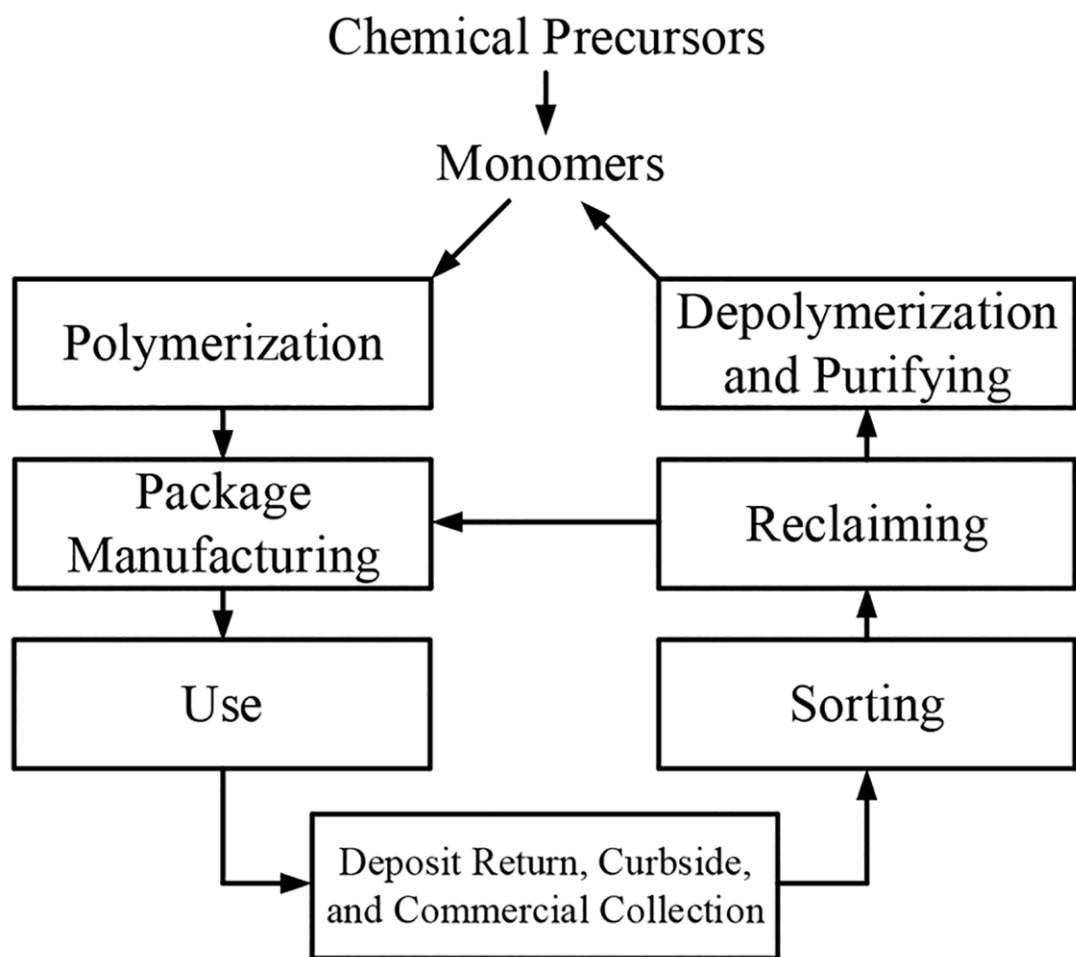


Figure 1.2-General scheme for production and recycling of polymeric materials, adapted from Smith et al.⁴⁹

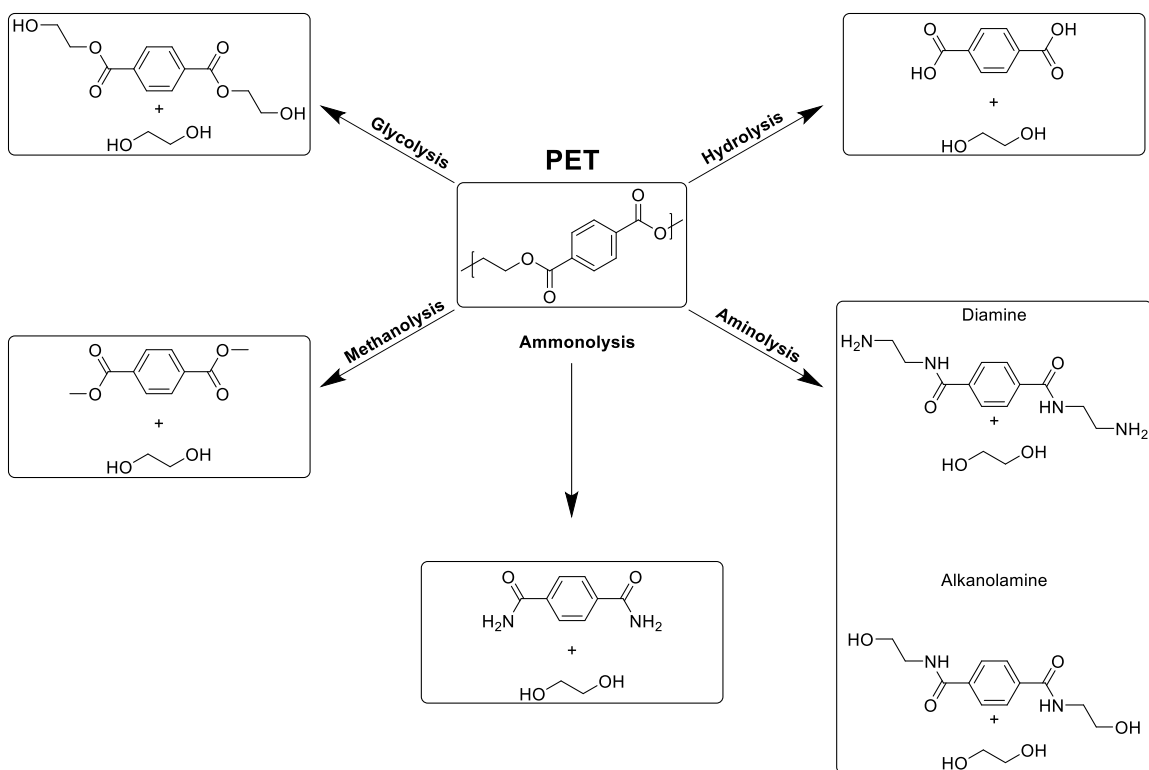


Figure 1.3-Possible routes that can be utilized in the chemical recycling of PET.

many hurdles in developing mechanical recycling as an economically viable process, but over the years, procedures have been developed to collect and clean PE products in a relatively economical fashion so that they can be reused. When it comes to waste streams, separation of the different polymers that co-exist to unique streams of pure polymer is needed, but adds to both the time and cost of the process. If these materials are not separated, the resulting blend will produce phase separated systems, as most polymers pairs are immiscible due to low entropy of mixing.⁵⁴⁻⁵⁶ At a macro scale, this phase separation creates less robust materials, with inferior mechanical properties to that of the pure blend components. The addition of interfacial modifiers, such as surfactants or compatibilizers which can be tailored for different polymer mixtures, can help stabilize the polymer blends, which increase the mechanical properties of the polymer blends compared to an uncompatibilized blend. Using these interfacial additives, the potential for less sorting of the polymer waste streams is possible, and has the potential to make the mechanical recycling process a more widely utilized process.

Compatibilization of Immiscible Polymer Blends

As mentioned above, most polymer pairs are immiscible with one another, where examination of the Gibbs free energy of mixing (ΔG_m) (Equation 1) provides insight into the immiscibility.⁵⁴⁻⁵⁶

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

A negative ΔG_m will result in a miscible blend. For most polymers, the enthalpy of mixing (ΔH_m) is endothermic, due to the repulsive van der Waals interactions of the polymer chains; and the entropy of mixing (ΔS_m) is generally low for polymer blends with high molecular weights, due to the limited number of conformations the chains can achieve, equating to a positive ΔG_m . This equation was further expanded by Flory and Huggins, where the Free energy of mixing of two polymers can be expressed by Equation 2,

$$\frac{\Delta G_m}{k_B T} = \left(\frac{\Phi_a}{r_a} \right) \ln \Phi_a + \left(\frac{\Phi_b}{r_b} \right) \ln \Phi_b + \Phi_a \Phi_b \chi_{ab} \quad (2)$$

where k_B is the Boltzmann constant, Φ is the volume fraction of each component a and b , r is the degree of polymerization, and χ is the Flory-Huggins polymer interaction parameter. The first two terms represent the entropic contribution, while the last term represents the enthalpic contribution to the free energy. The first two terms will generally be small (because r is large), so the value of χ dictates the sign of the Gibbs free energy of mixing. For most polymer blends, χ is sufficiently large and positive to result in an immiscible polymer blend. This drives the system to its most thermodynamically stable state, which results in phase separation of the blend. This phase separation can manifest into different morphologies, where the composition of the blend and processing history contributing largely to the final morphology. Examples of these morphologies can be seen in Figure 1.4. Regardless of the morphology of the immiscible polymer blends, an interface between the two components is formed. Stabilizing this interface is crucial in producing practical blends, as this will lead to stabilization of the blend and improved mechanical

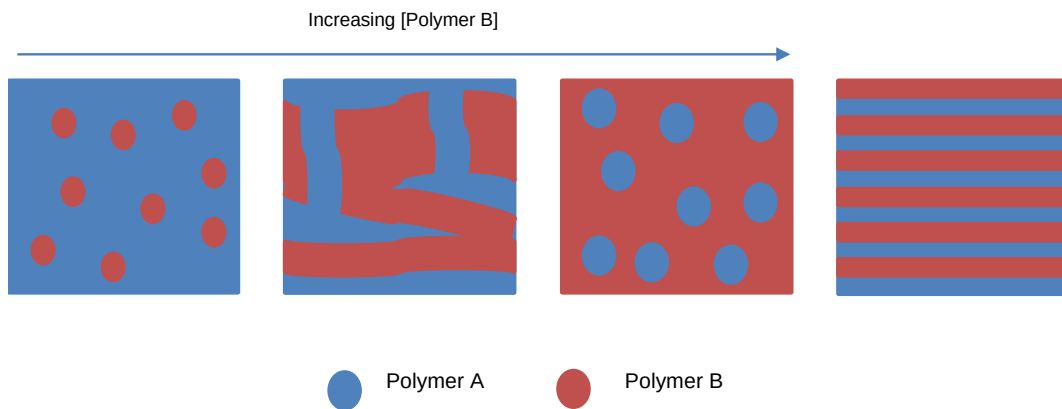


Figure 1.4- Possible morphologies that polymer blends can achieve. When the concentration of polymer $A > B$, then polymer B makes small domains. As the concentration of B increases in the system, a bi-continuous morphology may form and eventually transition the system where A forms droplets. The last morphology is a more lamella like morphology, which require mechanical stresses on the blends to form.

properties. Through the addition of compatibilizers, this can be achieved. The addition of a third species which has affinities for both blend components helps to stabilize the blend morphology by lowering surface tension, entangling with both polymers of the blend, and suppressing droplet coalescence.^{57–63}

Block copolymers are commonly studied compatibilizers in polymer blends, where the block copolymer may be either pre-synthesized or formed in-situ during processing of the blend, both of which have been studied extensively.^{61,63–85} The pre-synthesized block copolymers are macromolecules that can migrate to the interface of the blend during processing, interacting with both domains and stabilizing the dispersion. These block copolymers migrate to the blend interface and act as a “stitch” between the domains which is illustrated in Figure 1.5. The in-situ formed compatibilizers, referred to here as reactive compatibilizers, perform similarly to the pre-synthesized counterparts, but utilize reactive functional groups on homopolymers that can react to form block or graft copolymers in-situ at the biphasic interface. This can be achieved by introducing mutually reactive sites on both types of polymer chain that can react with each other during processing, such as amide formations from the reaction of carboxylic acids and amines, or ester formation from the reaction of epoxide and carboxylic acids.^{80,86} These in-situ reactions occur when homopolymers migrate toward the interface and react to form these block copolymers. Depending on the number and position of reactive sites on the homopolymers, the products can be simple diblock copolymers, multiblock copolymers, or graft copolymers as illustrated in Figure 1.5.

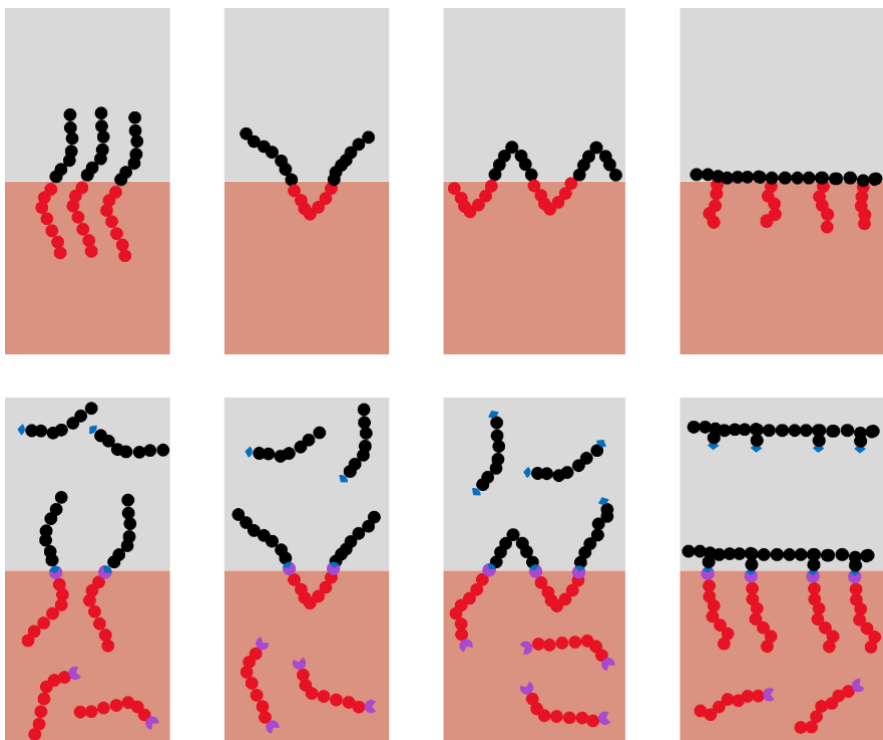


Figure 1.5- Examples of different types of block copolymers compatibilizers. The top row is nonreactive compatibilizers and the bottom row illustrates reactive compatibilizer architectures.

PET/PE compatibilization

As PET and PE are two of the most abundantly produced materials, blends based on these materials have been studied with the goal of producing useful materials for a relatively low cost.⁸⁷ Unfortunately, PET and PE are immiscible, driven by the polarity of PET and non-polarity of PE, resulting in phase separated blends. There have been studies to understand the compatibilization of PET/PE blends, with most efforts utilizing in-situ formation of compatibilizers during processing. The compatibilizers examined encompass copolymers that are formed from the reaction of the PET hydroxyl end groups with maleic anhydride, acrylic acid or acrylic ester groups grafted onto polypropylene (PP), PE, or styrene-ethylene-butene block copolymers (SEBS).^{62,88-92} Another form of compatibilizers for PE/PET blends involve the reaction of random copolymers composed of olefin and functionalized acrylates or anhydrides, such as poly(ethylene-co-acrylic acid), or poly(ethylene-co-glycidyl methacrylate), where the reactive functional group reacts with the PET end groups in the blends to form compatibilizers.^{91,93-100} Though these materials have been useful in the compatibilization of these blends, many of these studies required high loading of the copolymer additives (>5%) before the blend's properties show improvement.

In attempts to lower the loading of additives needed to effectively compatibilize PET/HDPE blends, further studies have examined the impact of varying the architectures of the copolymeric compatibilizer. For instance, work by Todd et al. used reactive compatibilization between PET and amino-terminated polyethylene (ATPE) to form block copolymers.¹⁰¹ The addition of ATPE into the blend lead to the in situ formation of multi

block copolymers that stabilize the interface between the two phases. The authors noted that the addition of as little as 0.5 wt% of ATPE increased the dispersion of HDPE in the PET phase, and improved the elongation at break by up to a factor of 12 relative to the behavior of the binary blend without the ATPE. Another study by Nomura et al. synthesized premade block copolymers composed of PET and PE.⁸⁷ The incorporation of 0.5 wt% of the pre-synthesized multiblock copolymer (MBCP) in PET/HDPE blends showed a reduction in size of the HDPE droplets in the PET phase, as well as a 30x increase in the strain at break compared to the blend without the MBCPs. These two studies show that the incorporation of MBCPs composed of PET and PE into blends show promise as compatibilizers for PET/HDPE blends, though they use newly synthesized materials as compatibilizers that could end up in the waste stream. Ideally, finding a way to utilize recycled materials as compatibilizers or their precursors would help in overcoming this hurdle. One such solution is to source PET as the precursor for these compatibilizers. Chemical recycling of PET is one option to access reactants to form compatibilizers, as there are a multitude of pathways available to produce value-added monomers. Unfortunately, most chemical recycling methods of PET focus on the complete depolymerization of the PET to monomer. It seems that the depolymerization can also access oligomers that can be useful in the production of value-added goods. Further investigation is therefore needed to understand the evolution of chain structures during the depolymerization process, to offer opportunities to intercept intermediates that can be used to synthesize value-added products, including compatibilizers.

Outline and Objectives

The remainder of this dissertation is outlined as follows. Chapter 2 will describe studies that continue the previous work in the Dadmun group. Morgan's previous work studied the effects of illumination on the depth profiles MEH-PPV/dPS thin films, where work reported in this thesis will examine the impact of illumination on MEH-PPV/dPS thin film structure and correlate these structural changes to the photoluminescence of the film. These observations will help in furthering the foundational understanding of how the combination of illumination environment during film fabrication and film composition alters their structure and optoelectronic performance. Chapter 3 will focus on the impact of ionizing radiation from small angle x-ray scattering experiments on the structure of P3HT in deuterated styrene solutions. Previous work in our group used neutron scattering and reflectivity techniques to study the impact of illumination on conjugated polymer structure, but could similar changes be noted in experiments using other radiation sources such as X-rays? As these X-ray sources get brighter, these techniques may lead to unintended changes during analysis. This chapter will investigate the impact of synchrotron radiation on the polymer structure, while providing insight into the kinetics of these structural changes. Finally, Chapter 4 focuses on understanding the depolymerization of PET during heterogenous and homogeneous glycolysis reactions, and how the products can be used as a feedstock for value-added goods. Many studies have examined the depolymerization of PET to monomer, but few focus on the intermediates that may be available. These studies offer insight into the opportunities and limitation of these depolymerization methods to produce oligomers that may be used to produce value-added materials. This work will

compare heterogenous and homogeneous glycolysis depolymerization reactions, with the aim of understanding the evolution of chain structures during the depolymerization process. This understanding provides an opportunity to intercept intermediates that can be used to synthesize value-added products, including compatibilizers. After these chapters, this dissertation will conclude with perspectives and prospects from the body of the work.

Chapter Two-The Correlation of Structure to Performance in MEH-PPV/DPS Thin Films Illuminated During Processing

Disclosure Statement: This chapter, “The Correlation of Structure to Performance in MEH-PPV/dPS Thin Films Illuminated During Processing” is a direct write up of “Correlation of the Structure with Performance in MEH-PPV/dPS Thin Films Illuminated during Processing” by the author, Dr. Tanguy Terlier, Dr. Ilia N. Ivanov, and Dr. Mark Dadmun, first published by ACS in the journal ACS Applied Polymer Materials on July 15th, 2021. This article can be found by the following hyperlink: pubs.acs.org/doi/abs/10.1021/acsapm.1c00410

Abstract

Thin films containing conjugated polymers have been used in a wide array of optoelectronic devices, and much research has focused on the conformation of the conjugated polymer as a key aspect to tuning the performance of the resulting devices. White light exposure has been studied as a post processing method to alter the film's morphology and photoluminescence (PL) in systems composed of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and polystyrene (PS). To date, there have been few studies that correlate the changes in depth profile to the PL performance of MEH-PPV/PS films. This study is designed to address this gap in knowledge. Thin films of MEH-PPV/dPS annealed above the glass transition temperatures (T_g) in an illuminated environment led to lower PL than found in annealed samples that are not illuminated. However, at higher MEH-PPV loading in the blend film, the extent of variation of PL with illumination diminished. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) and small angle neutron scattering (SANS) document the 3-dimensional morphology of the films with illumination conditions, which are correlated to the changes in PL. Illumination during annealing compressed MEH-PPV rich layers in the thin film blends at low loadings of MEH-PPV (below 10 wt%) but resulted in significant in-plane phase separation at higher loadings (above 15 wt%). Both changes increase interchain interactions and lower the PL of the illuminated samples. The changes in depth profile significantly alter the PL of the films, while the in-plane phase separation affected the optoelectronic properties to a lesser degree. This work, therefore, provides insight into how illumination and film composition

can be utilized to predictably alter the structure and optoelectronic performance of conjugated polymer blend films.

Introduction

Conjugated polymers have found many uses in devices such as thin film transistors, organic photovoltaics and organic light emitting diodes.⁴⁻⁷ Their use is driven, in part, by their lower cost and weight when compared to similar inorganic counterparts. The conjugated polymer found in the active layer of such devices exhibit optoelectronic processes such as exciton formation, charge separation, recombination, trapping, and charge transport.⁸⁻¹² There are many structural factors that can affect these properties, and there is significant evidence that a major contributor is the conformation of the conjugated polymers in the active layer.¹⁰²⁻¹¹² Moreover, there are several factors that affect the polymer conformation in the active layer, such as concentration of the polymer in pre-deposition solution, polymer-solvent interactions, and post processing methods such as annealing at elevated temperatures.^{21,23,113,114}

A recent method of post processing has been the application of light during fabrication to alter the performance of inorganic and organic semi-conductors.¹¹⁵⁻¹¹⁸ One method of interest utilizes illumination of conjugated polymer blend films with white light during annealing to alter the film's optoelectronic properties. For instance, Botiz et al. studied the impact of white light illumination on thin polymer blend films of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and polystyrene (PS) when illuminated at temperatures below the glass transition temperature (T_g) of the polymers. These studies found that the photoluminescence (PL) of the films increased by

much as 42% when annealed under white light.¹⁹ This change is attributed to planarization of the MEH-PPV polymer chains in the films, which in turn increases the chain's conjugation length and PL of the observed films. These studies also showed that this performance improvement is directly related to the annealing time when illuminated. This nondestructive method shows promise as a scalable method to tune the properties of conjugated polymer active layers. Botiz et al. continued to explore this phenomenon by investigating the dewetting of MEH-PPV/PS blend films when exposed to light.¹⁸ This work examined MEH-PPV/PS thin films on hydroxy terminated polydimethylsiloxane surfaces, which promoted dewetting of the blend film. This study concludes that exposure to white light slows the dewetting of the film, which is hypothesized to be driven by an alteration of the polymer chain conformation, with the conjugated polymer chains adopting a more planar/rigid conformation.

The work by Botiz et al. elucidates the effect of light on the PL and dewetting of conjugated polymer blend films, however, does not provide direct evaluation of the structure of the polymer blend films, including the polymer chain conformation or blend morphology. Work in our group has focused on directly measuring conformational and morphological changes of conjugated polymers due to light exposure. We studied dilute solutions of poly(3-hexylthiophene) (P3HT) via small angle neutron scattering (SANS) and found that the polymer Kuhn length, radius of gyration, and second virial coefficient decreased with exposure to white light.²⁴ This led to the conclusion that the most significant effect of white light exposure was to lower the solubility of the polymer in solution, as formation of the exciton changes the polymer-solvent interaction. Another study by our

group investigated how illumination alters the gelation of P3HT solutions at higher concentrations.²⁵ In this study, a similar response was observed, where exposure to white light slowed the gelation process, resulting in smaller aggregates and a lower volume fraction of gelled P3HT.

Of particular interest, is our previous studies that investigated the impact of illumination during annealing on the depth profile of conjugated polymer blend thin films.²⁰ This study utilized neutron reflectivity (NR) to investigate the depth profile of MEH-PPV/dPS thin films before and after annealing above the T_g in either illuminated or dark environments. The results of this study show variation in annealed depth profiles that is dependent on illumination conditions during annealing. As the films are illuminated, the thermodynamic interactions between the conjugated polymer and polystyrene are altered, as well as the surface energies of the components, which led to changes in the depth profiles of the fabricated films. The change in the depth profiles would in turn alter the optoelectronic performance of the films, but this was not explicitly examined.

The work presented here will expand on our previous work with conjugated thin film blends and investigate the correlation between the optoelectronic properties and depth profiles of conjugated polymer blend films fabricated with white light exposure. This work investigates thin films of MEH-PPV/dPS blends that are annealed above the T_g in different illumination environments, and correlates the observed PL to the film's depth profile and in-plane structure. This work will therefore provide new insights of how illumination can be used during film processing to tune the morphology and optoelectronic properties of conjugated polymer thin films.

Experimental Section

MEH-PPV was purchased from Solaris Chemical with a weight average molecular weight (M_w) of 100-250 kDa. Deuterated polystyrene (d_8) was purchased from Polymer Source with a number average molecular weight of 4000 Da and a molecular weight dispersity ($\mathcal{D}$) of 1.07. Tetrahydrofuran and toluene were purchased from Fisher Scientific. Poly(glycidyl methacrylate) (PGMA) with a manufacturer reported M_n =10-20 kDa, cyclohexanone, and 2-butanone were purchased from Sigma-Aldrich. All solvents were prefiltered with 1 μ m polytetrafluoroethylene (PTFE) filters before use.

Silicon wafers were cleaned using a piranha solution, composed of 1:4 hydrogen peroxide and sulfuric acid. The wafers were rinsed of the cleaning solution and then placed into a UV-ozone cleaner for 30 minutes. The silicon surfaces were coated with a thin layer of PGMA to limit the amount of dewetting of the MEH-PPV/dPS thin films. The bound PGMA film was formed by spin coating a 0.02 wt% solution of PGMA in 2-butanone at 1000 RPM for 20 seconds. The wafers were then annealed for 30 minutes at 100 °C to allow the reaction of the pendant epoxy groups to the SiO_x surface. After cooling, the wafers were sonicated in chloroform for 30 minutes to remove excess unbound PGMA. The wafers were washed once more with chloroform and put in a vacuum oven for 30 minutes at room temperature.

To fabricate the MEH-PPV/dPS blend thin films, 1 wt% solution of MEH-PPV and dPS in a solvent mixture of equal volume parts THF, Toluene, and cyclohexanone were made and allowed to stir overnight at 65 °C. The MEH-PPV/dPS blend compositions varied, with the ratios of MEH-PPV/dPS examined being 0/100, 5/95, 20/80, 35/65, 50/50

and 100/0. The solutions were first mixed for 2 hours at 65 °C before use to ensure homogeneity. The films were cast onto the PGMA treated wafers at 1000 RPM for 40 seconds, then moved to either a room temperature vacuum oven, or to a vacuum oven set to 125 °C for 15 minutes. This temperature was chosen since it is well above the T_g of both dPS (~83 °C) and MEH-PPV (65 °C) to focus on changes in the film structure but limit dewetting. Both samples were placed in the same oven, with the light annealed (LA) samples being exposed to a halogen light, and the dark annealed (DA) samples being shielded from the light with aluminum foil. After 15 minutes of annealing, the samples were moved to the room temperature vacuum oven and stored there shielded from light until further analysis of the films was performed.

PL of the thin blend films was performed on a Renishaw Invia© confocal Raman microscope (backscattering configuration) at the Center for Nanophase Materials and Science at Oak Ridge National Lab. The excitation wavelength was 532 nm, with a 10 second integration time, and the resultant PL was measured over a range of 550-800 nm. The PL data was collected using an average of a ten-point map scan, where a scan of blank silica was used in background subtraction. The 5% MEH-PPV films were analyzed at 100x magnification and 10% laser power, while the 20, 35, and 50% MEH-PPV samples were analyzed at 5x magnification and 0.05% laser power due to the increased PL at higher MEH-PPV loadings.

Positive high mass resolution depth profiles were determined using a TOF-SIMS NCS instrument, which combines a TOF-SIMS instrument (ION-TOF GmbH, Münster, Germany) and an in-situ Scanning Probe Microscope (NanoScan, Switzerland) at the

Shared Equipment Authority at Rice University. Bunched 30 keV Bi_3^+ ions (with a measured current of 0.2 pA) were used as the primary probe to analyze a field of view of $100 \times 100 \mu\text{m}^2$, with a raster of 128 x 128 pixels. The sputtering of the film was performed using Ar_{1500}^+ ions at 10 keV with a typical current around 1 nA, which was rastered over an area of $500 \times 500 \mu\text{m}^2$. The beams were operated in a non-interlaced mode, alternating 2 analysis cycles and 1 sputtering cycle (corresponding to 1.63s) followed by a pause of 3s for the charge compensation with an electron flood gun. An adjustment of the charge effects was realized using a surface potential of 0V. During the depth profiling, the cycle time was fixed to 200 μs (corresponding to $m/z = 0 - 3645$ a.m.u. mass range).

The total thickness of the films was measured using an Asylum Research MFP3D atomic force microscope. The thickness was measured using a scratch test, where a scratch was made in the film with a blade and the depth of the well created from this scratch was measured using an average of 5 measurements using ImageJ software.¹¹⁹

The films used in the SANS experiments were fabricated from polymer solutions that were mixed at ratios of 1/99, 2/98, 5/95, 15/85, and 20/80 MEH-PPV/dPS in the solvent mixture of THF/Toluene/cyclohexanone. Solutions were drop cast into quartz discs to create thin blend films, which were then hot pressed to produce films 1 mm thick. The SANS experiments were performed at the High Flux Isotope Reactor at Oak Ridge National Laboratory on the CG-2 GP SANS beamline, using three detector distances to give a Q range of 0.001-0.7 $\text{\AA}$. Q is the wave vector equal to $(4\pi/\lambda) (\sin(\theta/2))$, where λ is the neutron wavelength and θ is the scattering angle. Samples were placed in zero-gap copper cells with quartz windows. The samples were heated in the beam using a Peltier

sample holder to 90 °C. When samples were not in the beam line, they were kept in a laboratory oven at 70 °C. Samples annealed in the dark were shielded with aluminum foil. The same samples were then exposed to an optical illuminator that consisted of a 125-watt halogen bulb that exposed the samples to 50,000 lux at 5 cm. The samples equilibrated for 20 minutes under illumination before data collection. The raw data was reduced and corrected for empty cell scattering, with and without aluminum for dark and light samples respectively, dark current, and detector sensitivity.

Results & Discussion

A. Photoluminescence

The PL of the films was measured using Raman microscopy. Figure 2.1 shows the normalized PL of each set of MEH-PPV/dPS thin film blends for each blend concentration, with the unnormalized data plotted in Figure 2.7 in the appendix. The data are normalized for MEH-PPV concentration by dividing each set of curves by the maximum PL intensity of the as cast sample (AC), which occurs near 600 nm. In Figure 2.1, the PL spectra of the 5/95 sample shows a sharp peak near 560 nm, which is associated with the silica substrate and not a peak of interest for the film. The shape of the 5/95 PL curve differs from those of films with higher MEH-PPV concentrations. We believe that this variation is associated with the changes in the conditions of the Raman spectroscopy experiments, where a higher magnification and laser power was used to account for the lower MEH-PPV content. Previous studies have shown that higher excitation intensities result in a decrease in the peak at 570 nm, which is associated with intrachain interactions.^{120–123} As the samples are annealed at 125 °C, the PL decreases regardless of the illumination conditions. Closer

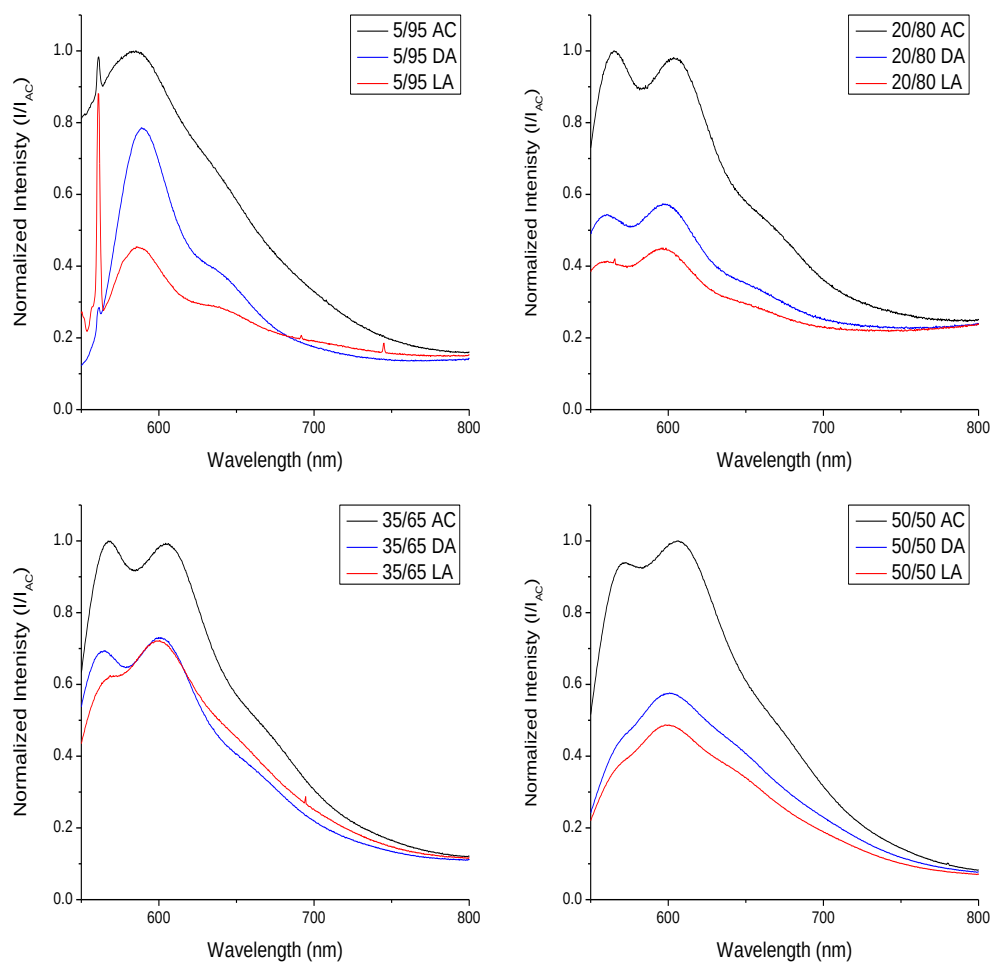


Figure 2.1- Normalized photoluminescence intensities for the 5/95, 20/80, 35/65, 50/50 MEH-PPV/dPS films. Black, blue, and red traces indicate the as-cast (AC), dark annealed (DA), and light annealed (LA) samples, respectively.

inspection shows that the PL of the sample annealed while illuminated (LA) is invariably lower than the PL of the samples annealed in the dark (DA). Moreover, the difference in PL curves between the DA and LA samples decreases as the concentration of MEH-PPV increases. These variations were quantified by tabulating the changes in PL at 600 nm with annealing for each sample and annealing condition in Table 2.1. The decrease in PL with the addition of illumination during the annealing process was 42.2% for the 5% MEH-PPV samples, while the decrease in PL was only 15.5% for the 50% MEH-PPV samples. The peaks in the PL curves for the 35/65 and 50/50 show interesting changes after they are annealed. The 35/65 shows a decrease in the peak near 570 nm when annealed in the presence of light, which indicates fewer intrachain interactions. For the 50/50 sample, when annealed, both the LA and DA samples show a decrease in this same peak, also indicating a decrease in the intrachain interactions.

B. Secondary Ion Mass Spectrometry

To correlate the PL to the structure of the polymer blend film, depth profiles of the blend thin films were acquired using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Pure films of PGMA, d-PS, and MEH-PPV were also characterized to verify the specific signals that can be uniquely ascribed to each compound, where the mass spectrums of each component are shown in Figure 2.2. The most prominent signals that could be used to distinguish between different polymers in the blend films were the $C_4H_9^+$ (57.07 amu), $C_7D_7^+$ (98.09 amu), and $C_2H_3O^+$ (43.02 amu) corresponding to MEH-PPV, d-PS, and PGMA, respectively. Figure 2.3 shows the depth profiles for the 5/95 MEH-PPV/dPS samples, with the depth of the films normalized by the thickness, (0 being the top of the

Table 2.1-Change in normalized photoluminescence of the light or dark annealed samples relative to the as-cast samples and between light and dark annealed samples.

Composition (MEH-PPV/dPS)	PL Percent Decrease at 600 nm of DA (AC→DA)	PL Percent Decrease at 600nm of LA (AC→LA)	PL Percent Decrease from DA to LA at 600 nm
5/95	21.4%	54.6%	42.2%
20/80	42.6%	54.9%	21.4%
35/65	27.0%	27.8%	1.10%
50/50	42.4%	51.3%	15.5%

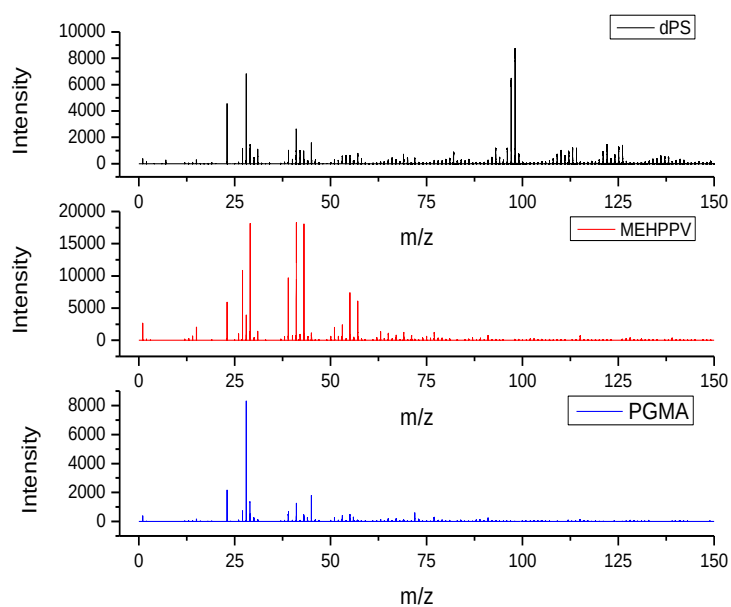


Figure 2.2- Positive mass spectra of the TOF-SIMS analysis of the pure polymer samples. The signals from top to bottom are deuterated polystyrene, MEH-PPV, and PGMA.

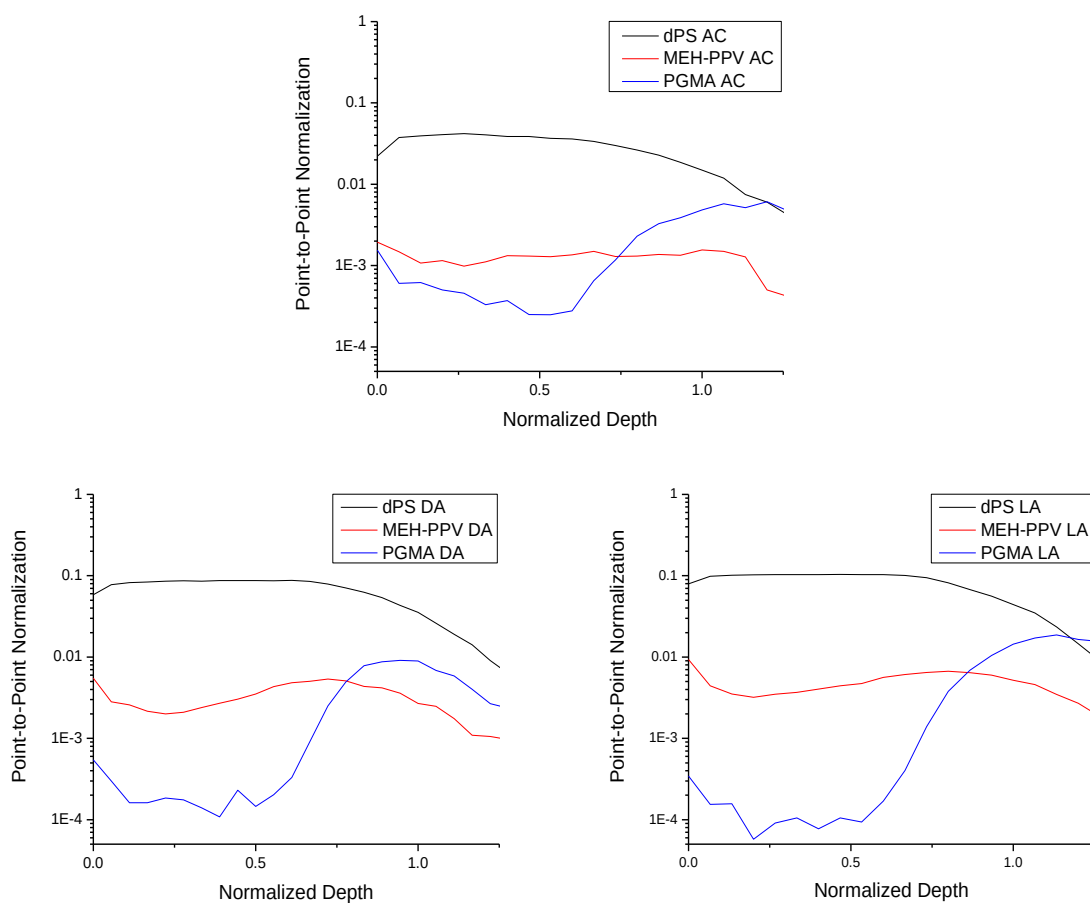


Figure 2.3- Depth profile data for the 5/95 MEH-PPV/dPS film on PGMA treated silicon wafers from TOF-SIMS. The black traces are for the deuterated polystyrene signals, red traces the MEH-PPV signals, and blue traces the PGMA signals.

film or the air/film interface) and the peak intensities normalized by total ion count, denoted as point-to-point normalization. These data show that the MEH-PPV in the blend moved toward the substrate with annealing, consistent with previous neutron reflectivity results that examined 10/90 MEH-PPV/dPS samples.²⁰ The depth profile of the 5/95 MEH-PPV/dPS samples shows that before the annealing process, both the signals for MEH-PPV and dPS varied little throughout the depth of the film. After annealing, the MEH-PPV migrated to the Si substrate, as evidenced by a peak in the MEH-PPV curve that starts to appear halfway through the film. The extent of segregation varies with illumination during annealing, with a narrower peak in the illuminated sample relative to the sample kept in the dark. This indicates that the MEH-PPV more strongly segregates and phase separates in the LA sample.

To understand how the stratification of the annealed sample changes with varying MEH-PPV composition, the signals from the depth profiles for the MEH-PPV were normalized by their maximum intensity and plotted in Figure 2.4 (unnormalized data is plotted in Figure 2.8 in the appendix). A peak in the MEH-PPV samples is clearly evident for all 5/95 blends, and the vertical distribution of MEH-PPV is narrower in the LA sample compared with the DA sample. This indicates that annealing of the samples leads to vertical stratification of the films, which results in local aggregation of the MEH-PPV. Aggregation can decrease PL, as more pathways are available for the exciton to be quenched before they can luminesce.^{120,124–126} Thus, the presence of the MEH-PPV rich layer is consistent with the lower PL of both LA and DA samples. Moreover, this interpretation predicts that the

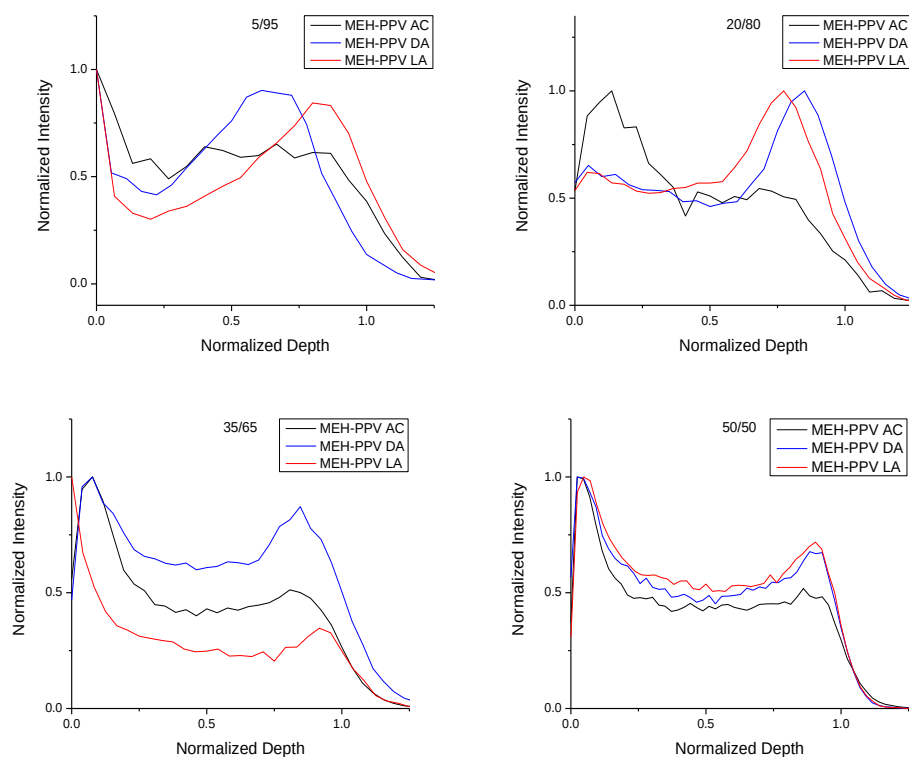


Figure 2.4- Normalized MEH-PPV signals from the depth profiles for the MEH-PPV/dPS films on PGMA coated silicon wafers. The black traces are for the signals from the as-cast samples, the red traces for the signals from the samples annealed at 125 °C in the presence of a light source, and the blue signals are from the samples annealed at 125 °C in the dark.

more compact MEH-PPV layer in the light annealed sample should exhibit lower the PL due to increased quenching, which is observed in Figure 2.1.

At higher MEH-PPV concentrations, however, more subtle changes were observed in the vertical distribution for the DA and LA samples. In the 35/65, the depth profiles do not change in shape with annealing, but there is a change in the breadth of the layers present in the film with annealing conditions. In the as-cast sample, there is an excess of MEH-PPV near the substrate, and after annealing there remains excess MEH-PPV near the substrate regardless of illumination. However, in the light annealed sample, the excess layer of MEH-PPV is more compact than in the dark annealed sample. The consistency in general stratification structure may also explain the lower extent of changes in the PL spectra for the 35/65 sample, where aggregated species present in all three 35/65 samples results in similar peaks at 590-500 nm. In the annealed samples, the intensity of the intrachain peak near 570 nm decreases. Moreover, this peak decreases substantially in the PL spectra with illumination during annealing where the more compact MEH-PPV excess layer at the substrate in the light annealed sample is consistent with more interchain and fewer intrachain interactions. The 50/50 sample exhibits even less variation in PL behavior and depth profile with annealing and illumination. There is an excess of MEH-PPV near the substrate for the AC sample, and after annealing, there is a further increase in MEH-PPV near the substrate but little variation in the depth profile with illumination. However, the PL of the DA and LA samples varies significantly (Figure 2.1). This suggests a factor other than stratification of the blend is contributing to changes in film PL.

C. Small Angle Neutron Scattering

The in-plane morphology of the thin films can also vary with illumination and influence film PL – changes that would not manifest in the depth profiles that are determined with SIMS. To examine this possibility, SANS was used to monitor the morphology of the conjugated polymer blend films as a function of composition and illumination conditions during annealing. These SANS experiments used 1 mm thick samples and consisted of 1, 2, 5, 15, or 20% MEH-PPV in deuterated polystyrene. The scattering of each blend was measured for dark annealed and light annealed samples.

The SANS curves of all the samples for both annealing conditions (light and dark) are shown in Figure 2.5. This figure clearly shows that there is very little difference in the scattering of each of the blends for the samples annealed under different illumination conditions. However, some features are evident in the plot of the difference in the absolute scattered intensity between these two samples. One would expect that this difference in scattering would be negligible and not q -dependent if the structure of the two samples with different illumination conditions were the same structure.

The differences in the absolute scattered intensities between the light and dark annealed samples are plotted in Figure 2.6. It is interesting that at low MEH-PPV loading, the scattering of the samples annealed in the dark scatter more than those annealed in the light. However, at higher concentrations of MEH-PPV, the scattering from the light annealed samples becomes greater than those of the dark annealed samples. This indicates that at higher MEH-PPV loadings (15-20%), the light annealed sample is more phase separated (and thus scattered more strongly) than the dark annealed sample. The opposite appears to

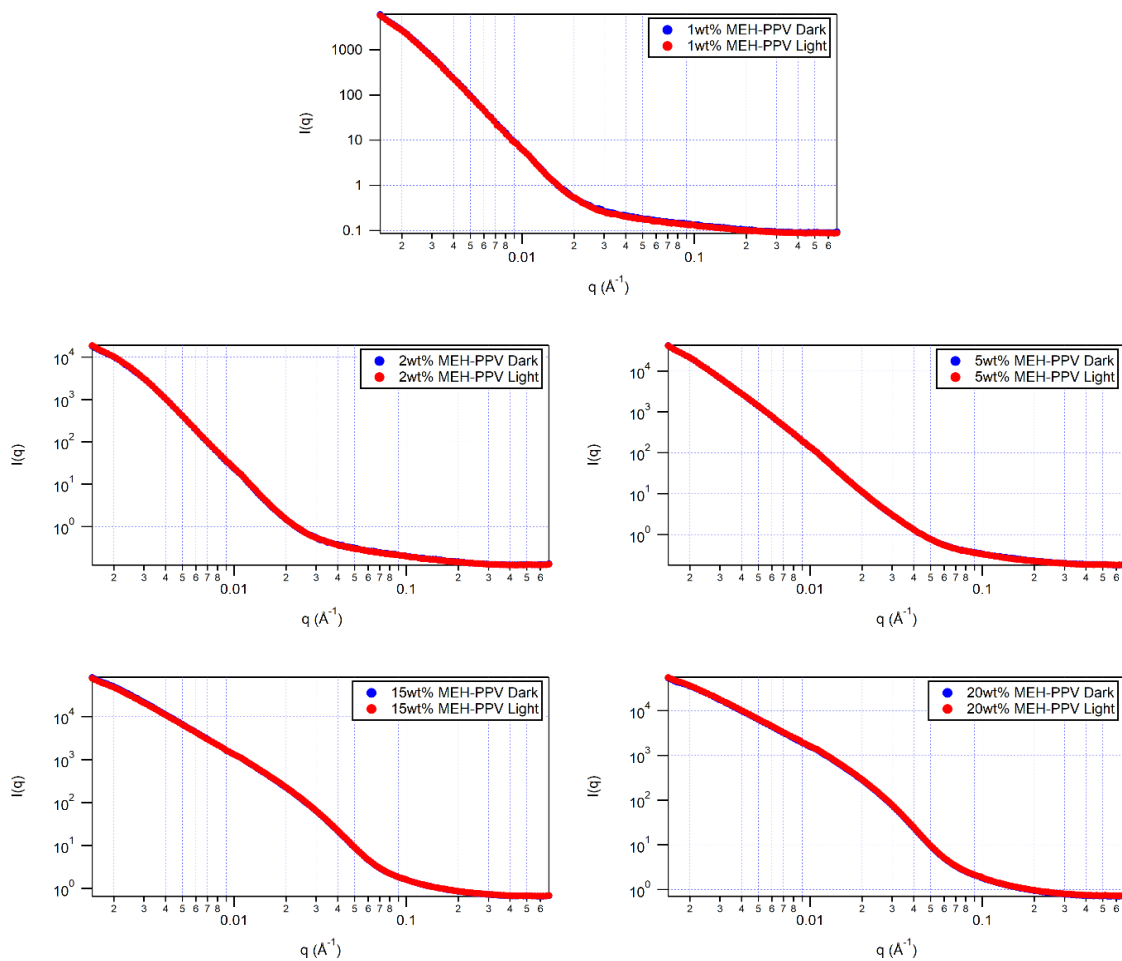


Figure 2.5- SANS curves for the 1mm MEH-PPV/dPS films. Red circles are for samples exposed to light during the analysis, while the blue circles are for samples that were shielded with aluminum foil, dubbed dark samples.

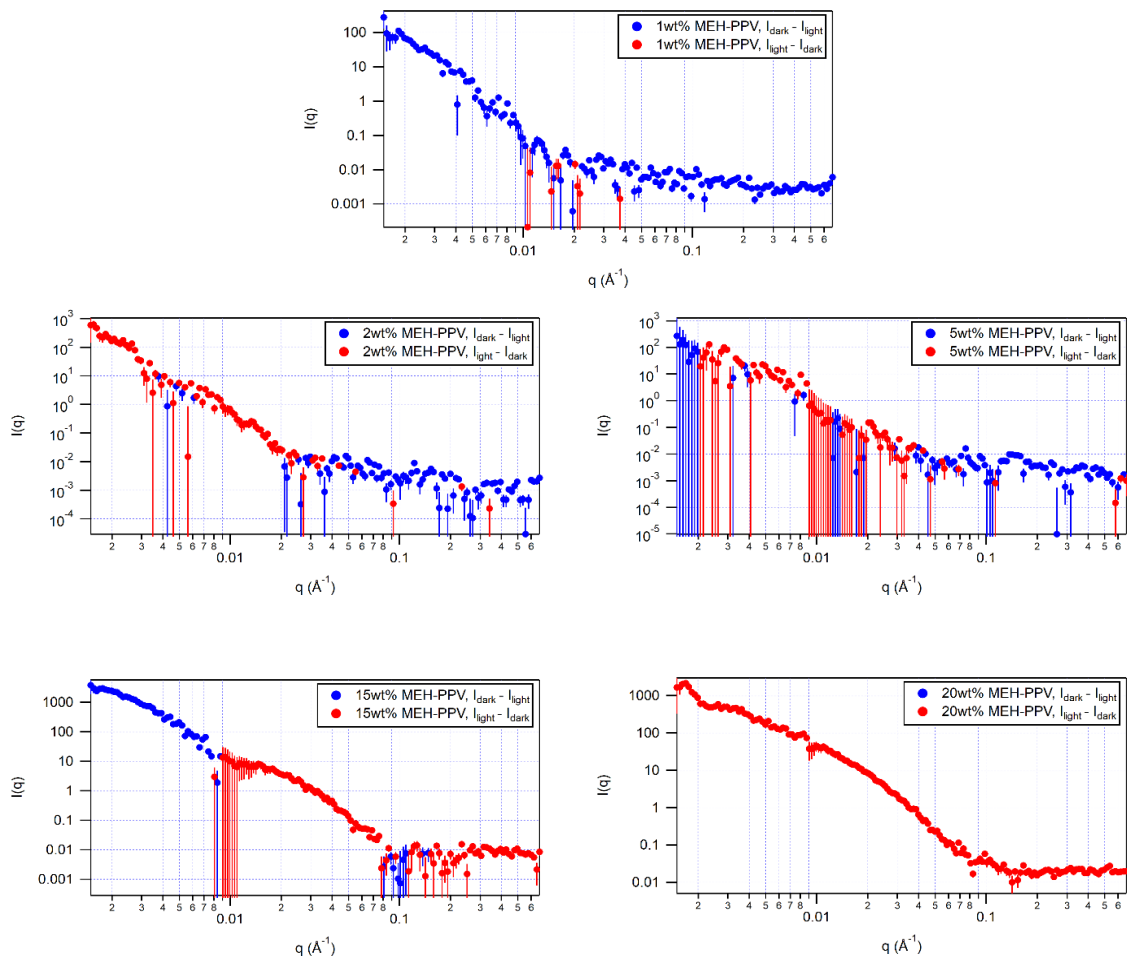


Figure 2.6- Subtraction of the scattering curves for the MEH-PPV/dPS films in different lighting environments. Blue circles are $I_{\text{dark}} - I_{\text{light}}$ and the red circles are from $I_{\text{light}} - I_{\text{dark}}$

be true for the 1% MEH-PPV in dPS sample, where the DA sample scatters more strongly than the LA sample.

These results demonstrate that the morphology of the phase separated polymer blends varies with illumination conditions during annealing, where illumination increases phase separation. Moreover, these changes in morphology are consistent with the observed variation in PL behavior of these films. At low MEH-PPV loadings, the variation in in-plane morphology with illumination during annealing are small, but the TOF-SIMS shows that there is significant variation in the vertical distribution of polymers in the film, where this stratification is consistent with changes in PL. However, as the concentration of MEH-PPV increases, the changes in in-plane structure of the blend with variation in illumination during annealing appear to dominate the PL. At higher MEH-PPV loadings ($> \sim 20\%$), annealing the blend thin film in the light results in increased aggregation of the conjugated polymer (i.e., a more phase separated blend) relative to the blends that are annealed in the dark. This increased phase separation creates more opportunities for quenching that lowers the observed PL of the blend films.

Considering these results holistically, the impact of illumination on the blend composition dependent 3-dimensional structure of MEH-PPV/dPS blend thin films emerges that is consistent with the observed PL. For all blends, it appears that annealing in the light results in a stronger drive for the MEH-PPV to phase separate from polystyrene than samples that are annealed in the dark. This is consistent with previous work in our group that has shown that the thermodynamic interaction between conjugated polymer and

solvent deteriorates when the sample is illuminated, presumably due to the formation of excitons on the conjugated polymer.^{24,25}

In these blends, this change in polymer-polymer interactions manifests as a variation in the vertical segregation of the MEH-PPV and polystyrene at low MEH-PPV loadings ($\sim < 5\text{-}10\%$), forming a more compact MEH-PPV rich layer in the light annealed sample. This increased partitioning of the conjugated polymer creates increased MEH-PPV intermolecular interactions that quench the PL. At higher MEH-PPV loadings, ($\sim >15\text{-}20\%$), the increased extent of phase separation with illumination manifests primarily in the in-plane morphology of the polymer blends thin films but little change in their depth profile. The resultant structure formed under illumination at all loadings, however, forms a construct that enables extensive MEH-PPV intermolecular interactions, which in turn promotes quenching and a measurable decrease in the measured PL. It also appears that the variation in depth profile has a more dramatic impact on the observed PL, while the changes in the in-plane morphology has a more attenuated impact on the blend optoelectronic performance.

Conclusions

This work correlates the impact of morphological changes in phase separated conjugated polymer blends, as controlled by illumination conditions during annealing, on their optoelectronic performance. The illumination of annealed blend films composed of MEH-PPV/dPS create morphologies that exhibit lower overall PL than films that were not illuminated during annealing. Results from TOF-SIMS and SANS experiments elucidate the relationship between the 3-dimensional morphology of the blend thin films and the

observed changes to the PL. The depth profile of the films as determined by TOF-SIMS showed that, at low loadings of MEH-PPV, stratification of the polymers occurs with annealing, where the MEH-PPV migrates toward the substrate. This MEH-PPV rich layer encourages interchain interactions, thus increasing quenching and decreasing the observed PL. The illumination environment altered the compactness of this layer, as the illuminated sample exhibited a denser layer of MEH-PPV, which coincides with the lower PL of the illuminated samples. At higher loading of MEH-PPV, the depth profile varies only slightly with illumination. SANS results, however, showed that higher degrees of in-plane phase separation existed in samples that were illuminated during annealing. These in-plane morphology changes correlate well to the observed differences in the PL of the blend films with illumination during annealing at higher loadings of MEH-PPV, including the fact that the changes in PL are less dramatic at higher loadings than are observed at lower MEH-PPV blends. These observations provide further foundational understanding of how the combination of illumination environment and film composition alters the structure and optoelectronic performance of conjugated polymer blend films, and must be considered when fabricating their devices.

Acknowledgements

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University. The SANS experiments used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

Appendix

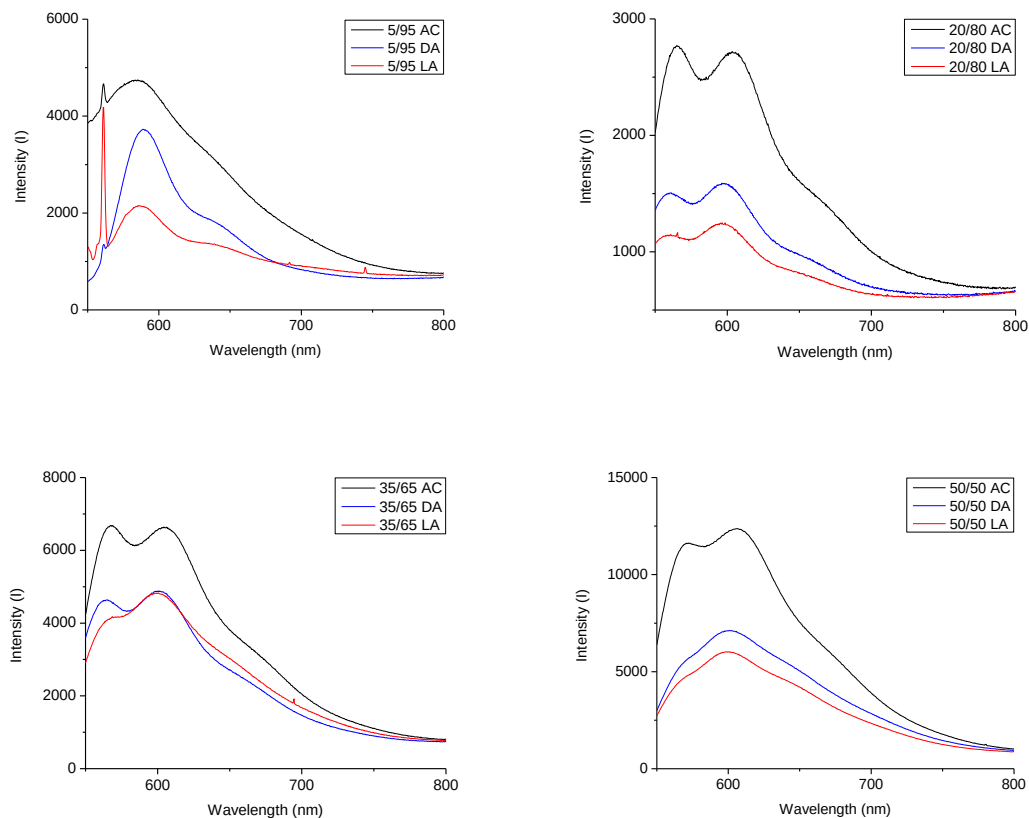


Figure 2.7- Photoluminescence for the 5/95, 20/80, 35/65, 50/50 MEH-PPV/dPS films. Black, blue, and red traces indicate the as-cast (AC), dark annealed (DA), and light annealed (LA) samples, respectively.

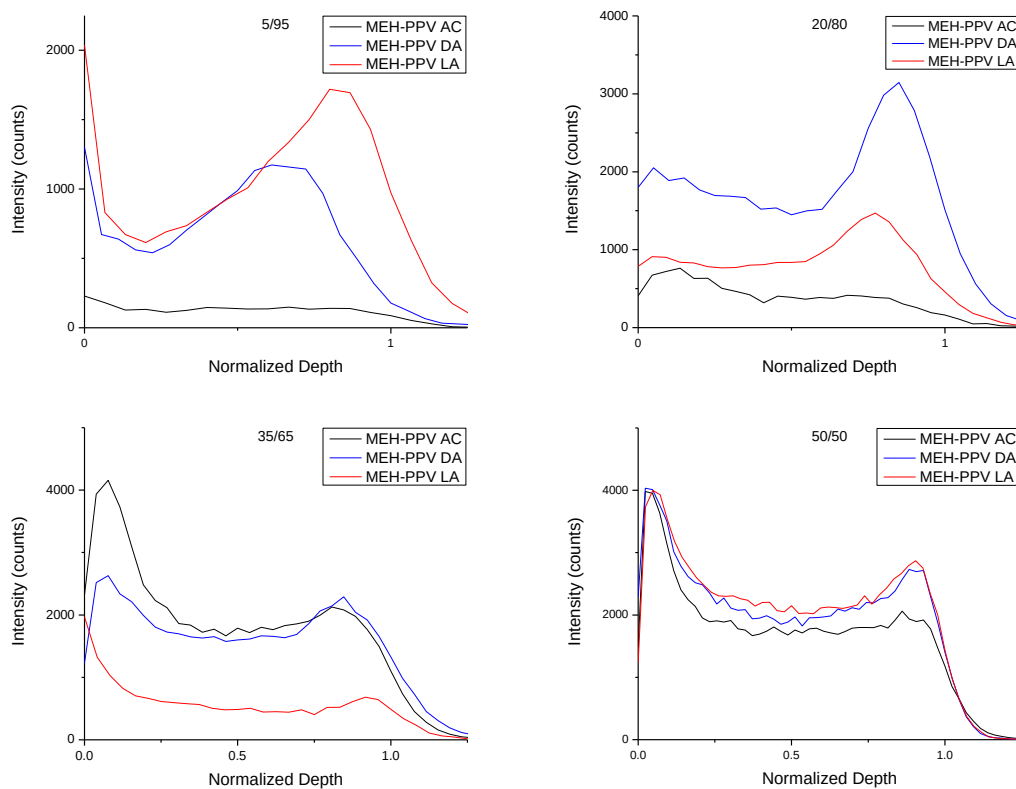


Figure 2.8- MEH-PPV signals from the depth profiles for the MEH-PPV/dPS films on PGMA coated silicon wafers. The black traces are for the signals from the as-cast samples, the red traces for the signals from the samples annealed at 125 °C in the presence of a light source, and the blue signals are from the samples annealed at 125 °C in the dark.

Chapter Three- Novel Ionizing Radiation Induced Reactions of Poly(3-Hexylthiophene)

Abstract

Conjugated polymers have been integrated into optoelectronic devices, and many studies have focused on the connection between polymer morphology and device performance. There are many methods used to probe this correlation, including the use of synchrotron sources for X-ray scattering and reflectivity experiments. Though these types of experiments are useful in studying these materials, as X-ray sources have gotten stronger, alterations to the polymer chains can occur from exposure to ionizing radiation. Most studies have examined thin films of conjugated polymers and the effects of ionizing radiation, with few examining solutions of conjugated polymers. This study monitors the time evolution of changes in poly(3-hexylthiophene) (P3HT) when dissolved in deuterated styrene with exposure to synchrotron X-rays. The scattering data, in conjunction with size exclusion chromatography and Fourier transform infrared spectroscopy, showed a change in the polymer structure that continues even after removal of the X-ray beam. Fitting the scattering data to the Gaussian Lorentz gel model and normalization to the sample concentration and exposure time offers insight into the relative dependence of the observed changes to the beam exposure time. These analyses lead to the conclusion that the structural changes are induced by the incorporation of styrene on the polymer chains, which can then further polymerize to produce grafts of deuterated polystyrene. The experiments show that such exposure to ionizing radiation can lead to irreversible changes in the polymer structures, and that reactions that drive these changes may continue to progress many hours after exposure. These experiments also show that using an easily polymerized monomer as

the solvent leads to grafted chains on the main polymer backbone, which demonstrates the need for careful consideration of all experimental parameters.

Introduction

Conjugated polymers are integrated into many devices, including organic light emitting diodes (OLEDs), thin-film transistors (OTFT) and solar cells, to name a few.^{4,5,7} Their light weight and flexibility make them cheaper to produce than their inorganic counterparts. These materials have been a topic of interest for many years, with a focus on correlating the structure of the polymer in an active layer of a device to its performance.^{102–107,110–112} Several techniques have been utilized to probe the influence of polymer morphology and structure on performance, including scattering and reflectivity that utilize ionizing radiation such as X-ray sources.^{26–37} These include grazing incidence small angle X-ray (GISAXS), grazing incidence wide angle X-ray scattering (GIWAXS), small angle X-ray scattering (SAXS) and X-ray reflectivity (XRR). These techniques have proven useful in studying these conjugated materials, but the use of X-rays can also lead to damage to the samples. As brighter synchrotron sources have become more prevalent in implementing these techniques, more evidence has emerged that document the damage and alteration of the polymer structure by exposure to X-rays.^{38–47}

For instance, the work by Neuhold et al. investigated the stability of several conjugated polymer films when exposed to synchrotron radiation.⁴² This work found that poly(3-hexylthiophene) (P3HT) showed a higher degree of damage when exposed to X-rays than sexithiophene or pentacene. The authors conclude that the hexyl side group on P3HT is susceptible to chain cleavage, which can form radical species that can react and

cascade to produce changes in the film structure, via mechanisms that include crosslinking. Further work by Vaselabadi et al. also studied the effects of synchrotron radiation on the structure of polymer thin films, including P3HT and PS.⁴⁰ This work looked at the impact of synchrotron exposure on the solubility of thin polymer films after exposure to synchrotron radiation in grazing incidence geometry. Regarding the P3HT, this study observed crosslinking of P3HT when exposed to X-rays in both air and vacuum, where a higher dose of radiation was needed to see crosslinking in vacuum environments. Exposure to radiation also decreased the crystallinity of P3HT. The authors conclude that exposure to X-rays in grazing incidence geometry alters the molecular structure of the P3HT via mechanisms that include cross-linking or chain scission. However, these changes are dependent on many factors such as molecular weight of the materials, film thickness, exposure geometry, photon energy and photon flux. Recently, a study by Bras et al. focused on bringing awareness of the impact of brighter synchrotron sources on the molecular structure of soft materials analyzed with these sources.⁴⁶ The primary mechanisms of damage to polymeric soft matter are chain scission events and cross linking, where the authors correlate these events to the high amount of absorbed radiation. They report that exposure to 10 keV of X-ray photons can cause up to 100 such events, depending on the material studied. The possibility and repercussions of this damage must be considered in experimental planning, where the minimum amount of radiation should be used to obtain the desired data.

This work aims to further elucidate the impact of synchrotron radiation exposure on the structure of P3HT in deuterated styrene solutions. In particular, the kinetics of structural

evolution after exposure to X-rays is of interest. This study seeks to understand the timescale of structural changes, i.e., are they instantaneous and short lived, or do the reactions cascade to continue over a longer period of time. Are these changes dependent on other factors, such as exposure time to the X-ray beam, or the concentration of the initial solutions? This study is also correlated to previous work by our group that has shown that exposure of conjugated polymers to white light alters the conformation and assembly of conjugated polymers in solution.^{20,24,25} These previous experiments used neutron scattering to monitor the change in the structure of conjugated polymers in the presence of a light source. These results open the question of whether such an effect can be observed by exposure to other radiation sources, such as X-rays. However, in order to tease out such an effect, the impact of exposure to synchrotron radiation on the conjugated polymer structure, and the kinetics of this structural evolution, is first needed.

Experimental

Poly(3-hexylthiophene) (P3HT) was purchased from Ossila, which had a regioregularity of 94.7%, a weight average molecular weight (M_w) of 34,100 Da and a molecular weight dispersity ($\mathcal{D}$) of 1.75 as reported by the manufacturer. Deuterated styrene (d_8) was purchased from Polymer Source. Deuterated styrene is chosen as a solvent to mimic previous studies in our group that elucidate the impact of light exposure on the conformation of P3HT in solution. Quartz capillary tubes (2.0 mm outer diameter, 0.01 mm wall thickness, overall length 80 mm) were purchased from Charles Supper company. The P3HT solutions were made at 0.25 and 0.5 wt% in styrene- d_8 to mimic samples examined in our previous studies. Solutions were wrapped in aluminum foil and heated to

60 °C to ensure complete dissolution of the polymer. The samples were transferred to a capillary tube and sealed with a rubber septum and Parafilm. The filled capillaries were kept in an oven set to 60 °C until the samples were analyzed.

Small-angle X-ray scattering (SAXS) measurements were conducted at Brookhaven National Laboratory National Synchrotron Light Source II on the Life Science X-ray scattering beamline, 16-ID. The scattering was completed in a custom-made sample holder composed of an insulated copper block that was heated using a water circulator that was set to 60 °C. The beamline's sample stage and detector were enclosed to limit the exposure of light to the samples. The raw data was reduced and corrected for empty cell and solvent scattering to provide the scattering in absolute intensity as a function of wavevector, q ($q = 4\pi/\lambda \sin(\theta/2)$; λ = the wavelength of radiation and θ is the scattering angle). For the 0.5 wt% solution, the sample was first exposed to the beam for 90 seconds, followed by measuring the scattering of the samples every 5 minutes for a 60-minute period with 1 second scans. Subsequently, one second scans were performed at 220-, and 240-minutes after the initial 90 second exposure. For the 0.25 wt% sample, the sample was first exposed to a shorter exposure time of 15 seconds. Following this exposure, the structural changes to the sample were followed by measuring the scattering pattern every 10 minutes over a 90-minute period with 1 second scans. The structural evolution of the samples was examined at 175-, 240-, 360-, and 710--minutes after the initial exposure with additional 1 second scans. Analysis of the SAXS data was performed using the SASview software.¹²⁷

Samples were extracted from the capillaries with tetrahydrofuran, and precipitated in acetone to remove residual d-styrene. Molecular weight and $\bar{M}_w$ of the P3HT before and

after exposure to the beam were measured using gel permeation chromatography (GPC) using a Tosoh EcoSEC gel permeation chromatography system equipped with two TSKgel SuperMultiporeHZ-M columns with THF as eluent at 40 °C and calibrated using polystyrene standards. Attenuated total reflectance Fourier transformed infrared (ATR FT-IR) spectroscopy was performed on a Thermoscientific FT-IR spectrometer with an ATR base.

Results

The SAXS curves that monitor the structural evolution of the 0.5 wt% sample after exposure to the X-ray source are shown in Figure 3.1A. This sample was initially exposed to the beam for 90 seconds, and the change in the structure of the sample for the subsequent four hours is monitored. After the initial 90 sec exposure, the first scattering pattern was obtained at 5 minutes, which showed an increase in the scattering of the sample over the entire q range. Moreover, an increase in scattering intensity is observed with time over the entire 4 hours, indicating the continual transformation in structure during this time. Figure 3.1B shows the scattering curves that monitor the change in structure of the 0.25 wt% sample after exposure to the X-ray beam. This sample was exposed for only 15 seconds to the X-ray beam (i.e., $1/6^{\text{th}}$ the time of the 0.5% sample). Inspection of this figure shows that the scattering curves increase at low q ($q < 0.1 \text{ \AA}^{-1}$; larger length scales) for the first 80 minutes, but does not vary at higher q (shorter length scales) over this time. Qualitatively, these variations in scattering indicate changes in the global structure, but very little change in the local structure of the polymer chains. At longer times, the

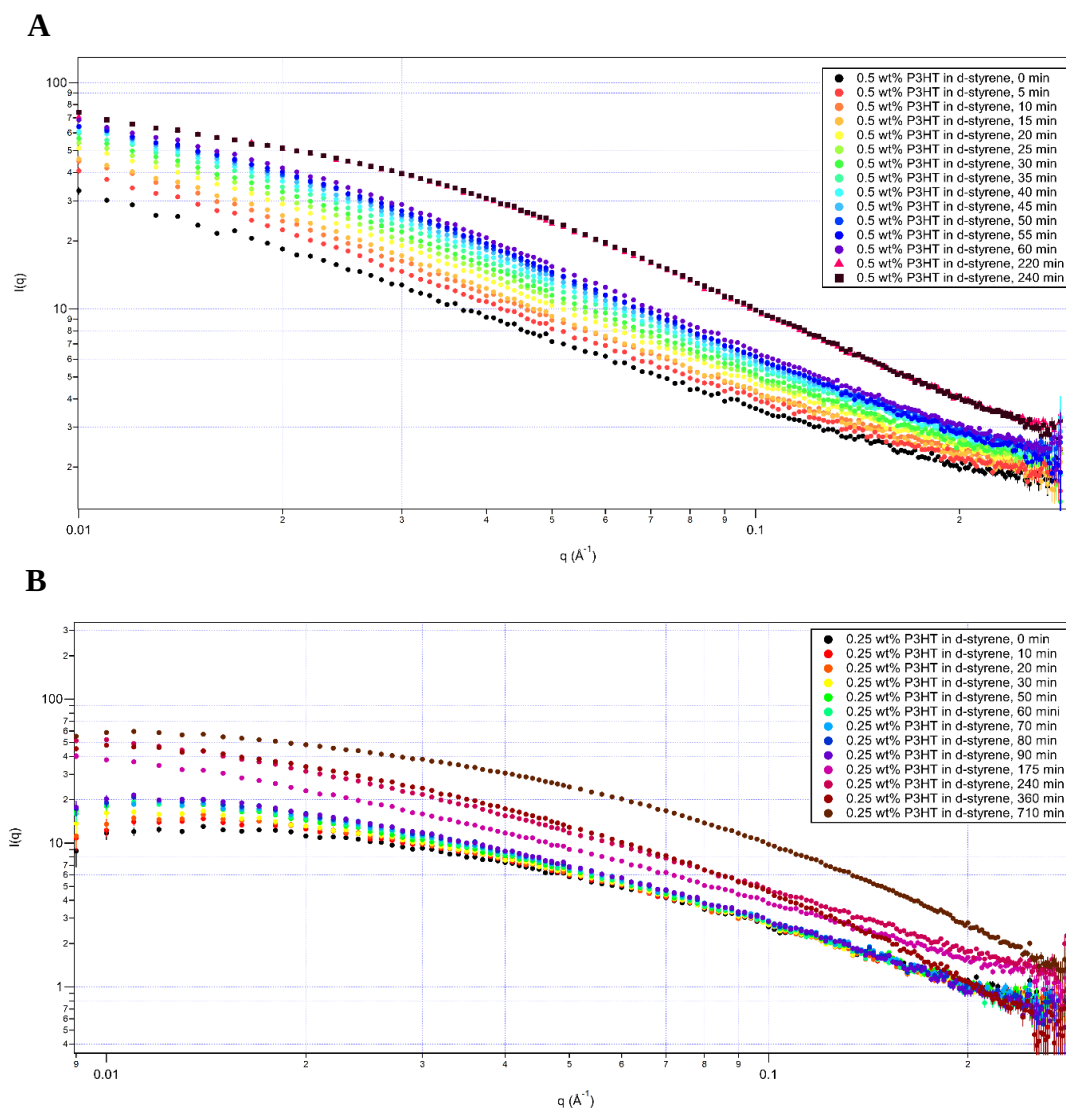


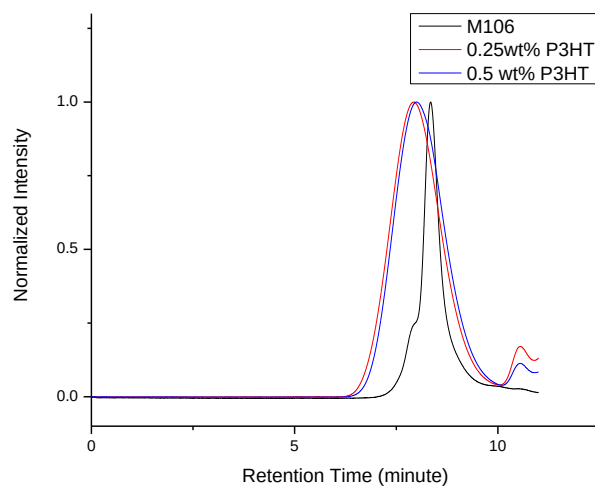
Figure 3.1- SAXS curves for P3HT in d-styrene. A) 0.5 wt % sample that was initially exposed for 90 seconds to X-ray before 1 second scans over 240 minutes. B) 0.25 wt % sample that was initially exposed for 15 seconds to X-ray before 1 second scans over 900 minutes.

scattering intensity over the entire q -range steadily increases, indicating changes in structure for all length scales at these later times after exposure.

These changes in scattering intensity monitor the variation in the polymer structure due to their initial exposure to the X-ray beam, and the analysis of these scattering curves provide quantitative insight into the evolution of structure that develops due to cascading radiation induced reactions. Previous studies indicate that either crosslinking or chain scission may result from radiation induced damage.^{40,42} However, the observed *increase* in scattering intensity is more consistent with crosslinking than degradation.

To provide corroborating evidence of the change in chain size and structure, the samples were removed from the capillaries after the X-ray experiment and analyzed via GPC and FTIR. The GPC chromatogram and peak analyses are shown in Figure 3.2. This data shows that the molecular weights of the two samples after exposure to the beam have a larger molecular weight and $\bar{M}_w$ than that of the initial P3HT. The starting P3HT sample had a molecular weight of 34,000 g/mol, while the molecular weight of both irradiated samples had almost doubled after exposure to the X-ray beam to 73,000 and 61,000 g/mol for the 0.25 and 0.5 wt% samples, respectively. The exposed samples also showed a broader $\bar{M}_w$, 1.8 for the 0.25 wt%, 1.9 for the 0.5 wt%, as compared to 1.3 for the starting material.

The FTIR spectra for the 0.25 wt% data and starting P3HT were also measured to provide insight into the changes in the functional groups present on the polymer as a result of exposure to the X-ray beam. These data are shown in Figure 3.3. Examination of the spectra shows that there are new peaks in the IR spectra of the P3HT sample after X-ray



Sample	M _w (kg/mol)	Đ
0.25 Wt%	72.7	1.8
0.50 Wt%	61.0	1.9
M106	34.4	1.3

Figure 3.2-GPC chromatograms of the samples compared to the starting P3HT. The table shows the calculated MW and Đ of the largest peak in the chromatograms.

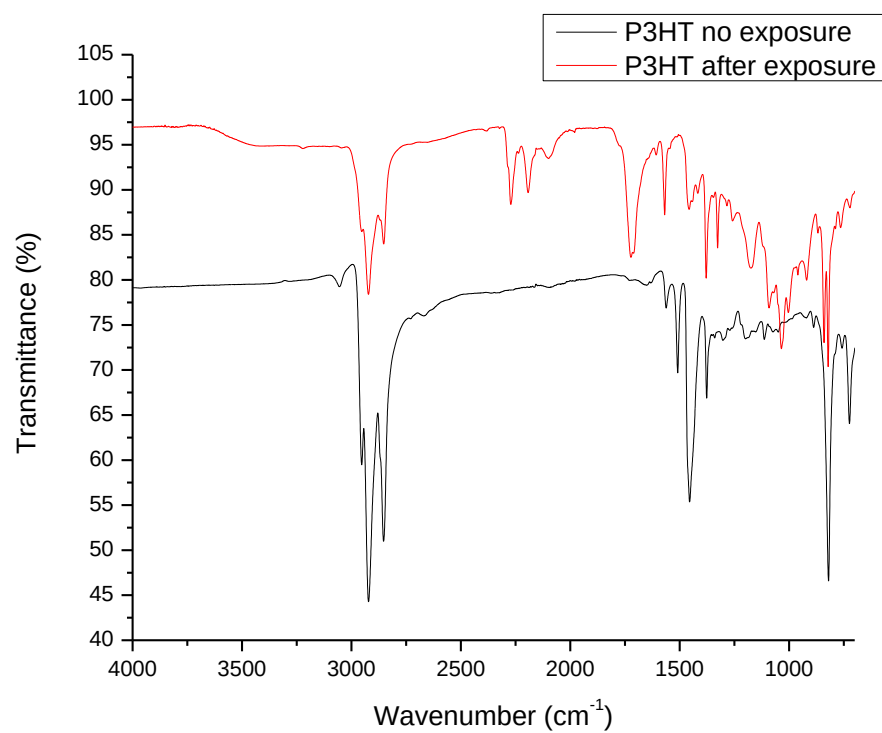


Figure 3.3- FTIR spectra of P3HT samples before and after irradiation from the synchrotron beam.

beam exposure at 2270-2090 cm^{-1} and 1700 cm^{-1} that are not in the initial sample. Work by Holdcroft and Ljungqvist found that there are different pathways available for the photo-oxidation of P3HT, and the main products of the potential pathways were distinguishable via IR.¹²⁸⁻¹³⁰ If the degradation occurred on the alkyl chain, a peak at 1700 cm^{-1} will be observed that relates to the formation of a ketone on the alkyl chain alpha carbon.¹²⁹ If this degradation leads to chain scission, this peak shifts to 1650 cm^{-1} which is indicative of the formation of a thionyl ketone.¹³⁰ As the IR spectra of the exposed P3HT shows a new peak at 1700 cm^{-1} , this hints that any reaction that transpires occurs mainly on the alkyl chain, but no chain scission occurs according to the IR. To assign a structure to the new peaks at 2270-2090 cm^{-1} , the FTIR spectra of d-styrene and d-polystyrene were measured and compared to the FTIR curves of the samples after exposure to the synchrotron. These data are presented in Figure 3.4. Examination of Figure 3.4 clearly shows that the new peaks near ~2250 cm^{-1} correspond to peaks associated with the deuterated styrene, while the two peaks at ~2200 and ~2100 cm^{-1} are present in d-polystyrene (dPS). This leads to the conclusion that the exposure of the sample to the X-ray beam results in the formation of deuterated polystyrene grafts or the separate polymerization of deuterated polystyrene. However, the steady progressive change in the scattering curve is more consistent with a grafting mechanism than the polymerization of deuterated styrene, where the formation of a second polymer would result in a phase separated structure and an abrupt increase in scattering at low q would be expected. The further observations that the GPC curve only presents one peak, and that the consistency of the sample does not change considerably are also more consistent with a grafting mechanism than the polymerization of d-styrene.

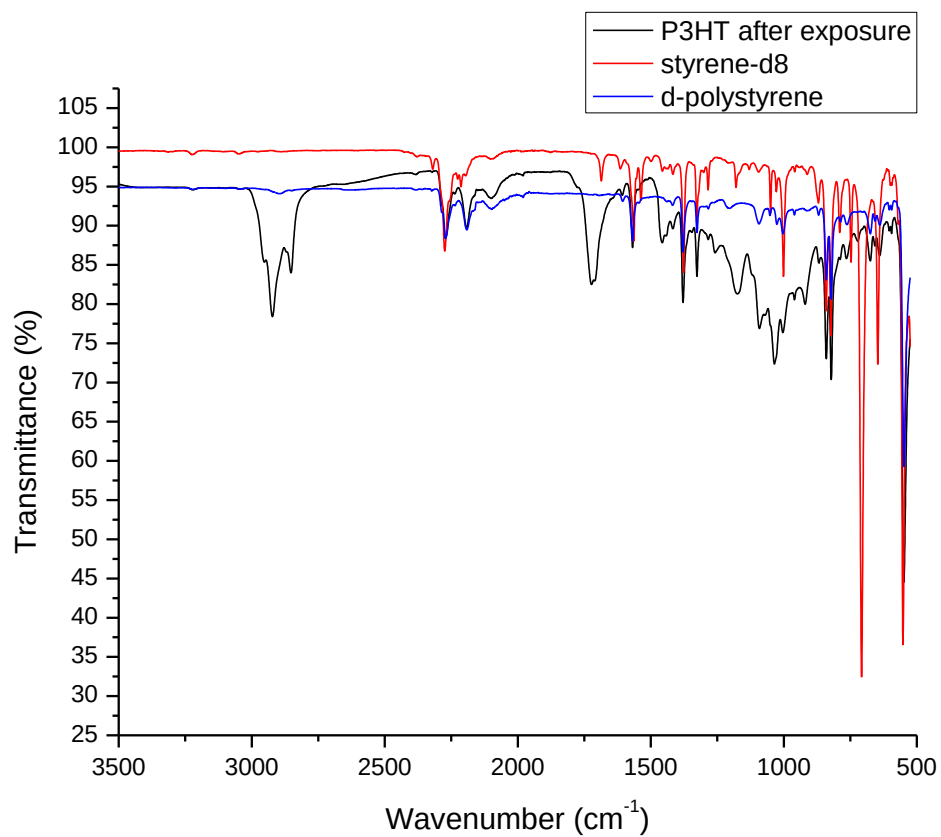


Figure 3.4-Comparison of FTIR spectrum of P3HT after exposure to the beam, deuterated styrene, and deuterated polystyrene.

Furthermore, there are previous studies that examined the radiation induced grafting of monomers, such as styrene, onto polymers chains.^{131–135}

The FTIR and GPC data thus leads to the initial interpretation that exposure of the sample to the synchrotron beam alters the chemical structure of the polymers in solution. The IR data shows that carbonyl carbons are formed, as well as the potential presence of dPS grafting to the P3HT. Both of these processes are consistent with the formation of a radical on the alpha carbon of the alkyl chain in the P3HT. The GPC data shows an increase in MW of the polymers after beam exposure, which could be the result of the formation of crosslinks between polymers or the grafting of dPS chains to the P3HT backbone. Therefore, with these potential pathways in mind, the Gaussian-Lorentz gel model (Equation 1) was used to model the scattering data, which provides a measure of the structures that emerge in the P3HT because of the exposure to X-rays. The Gaussian-Lorentz gel model fits the data well and describes a gel with graft points/crosslinks and fluctuating polymer chains attached to the graft points/crosslinks.

$$I(q) = I_g(0) \exp\left(-\frac{q^2 \Xi^2}{2}\right) + \frac{I_L(0)}{1 + q^2 \xi^2} \quad (1)$$

In Equation 1, Ξ is the static correlation length within the connected structure, and ξ is the dynamic correlation length, or the size of the density fluctuations attached to graft points/crosslinks. $I_g(0)$ and $I_L(0)$ are the intercepts ($q=0$) of the Gaussian (static) and Lorentzian (dynamic) terms, which are proportional to the amount of the graft

points/crosslinks and density fluctuations, respectively, that exist in the sample. If the sample is forming d-PS grafts on the P3HT backbone chains, the I_g term characterizes the number and size of the graft points, while the I_L term characterizes the length/size of the grafted chains.

This model fits all the scattering curves in Figure 3.1 very well, where an example of this fit is presented in Figure 3.5 for the 0.25% sample immediately after the 15 second exposure time. The parameters that emerge from these fits can then be plotted as a function of time after the initial exposure to the X-ray source, and their evolution reveals the progress of the radiation induced reactions and the growth of the structures that emanate from these reactions.

Figure 3.6 shows the plots that track the time evolution of the amount of graft points ($I_g(0)$) and dynamic fluctuations ($I_L(0)$) in the samples as well as the static and dynamic correlation lengths for the 0.5 wt% sample. The concentration of the graft points ($I_g(0)$) shows an initial increase after exposure to radiation, but then plateaus at around 20 minutes post exposure. The number of dynamic fluctuations shows a steady increase over the observed time frame. The sizes of both the grafts and fluctuating domains show minor change, with a small increase noted for both over the reaction time. Looking at both the concentration and size of the graft points, it appears that these form quickly to a maximum size, which occurs at about 20 minutes post exposure. After this time, the amount of graft points remains constant.

The 0.25 wt% sample was exposed to the beam for 15 seconds, 1/6th the time the 0.5 wt% sample was exposed. Figure 3.7 plots the number of graft points ($I_g(0)$) and

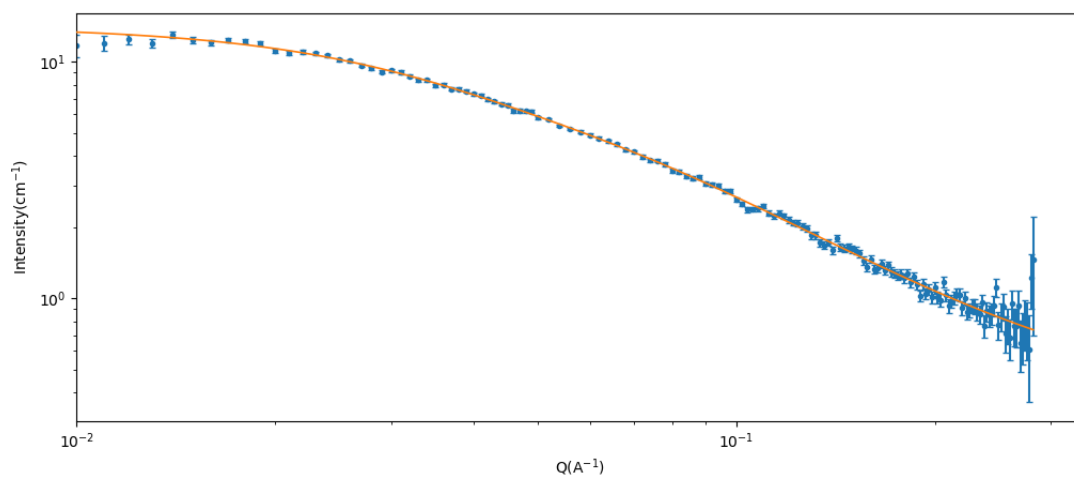


Figure 3.5-Example of fit using the Gaussian-Lorentz gel model on the sample that is 0.25 wt% zero minutes after exposure to the beam.

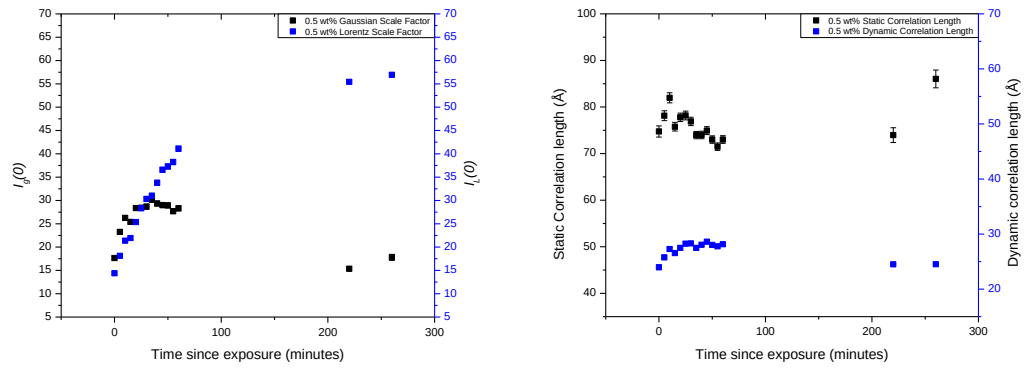


Figure 3.6-Time evolution of the concentration (left) and size (right) of the static and dynamic domains for the 0.5 wt% sample. $I_g(0)$ (black squares) and $I_L(0)$ (blue squares) of the left plot and the right plot shows the static (black squares) and dynamic (blue squares) correlation lengths.

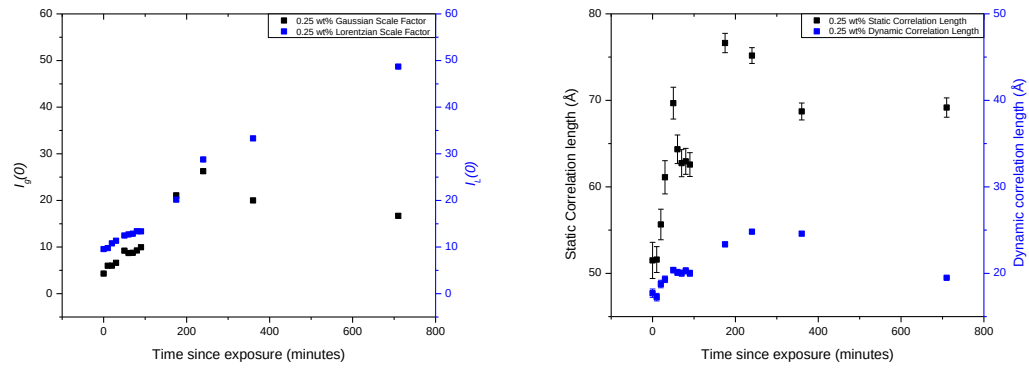


Figure 3.7- Time evolution of the concentration (left) and size (right) of the static and dynamic domains for the 0.25 wt% sample. $I_g(0)$ (black squares) and $I_L(0)$ (blue squares) of the left plot and the right plot shows the static (black squares) and dynamic (blue squares) correlation lengths.

dynamic fluctuations ($I_L(0)$) in the samples for the 0.25 wt% sample as a function of time after X-ray exposure. The concentration of graft points shows a similar trend to the 0.5 wt% data, where the number of graft points increases, plateaus after 50 minutes, then increases again after 90 minutes, before a small decrease and plateau after 240 minutes. Thus, the structural changes that occur in this sample after X-ray exposure appear to grow in a similar fashion, but at a slower rate than the 0.5% sample. At the same time, the concentration of fluctuating domains continuously increases, similar to the behavior of the 0.5 wt% data. The correlation lengths (Ξ and ξ) both show similar evolution with time, where the size of the graft points steadily increases until a maximum (~200 min) followed by a slight decrease in size with time after exposure. The size of the fluctuating domains shows a much smaller increase in overall size than that of the static graft points, and are similar in size to the fluctuating domains in the 0.5 wt% samples.

Discussion

The scattering data shows evidence that there are changes to the polymer structure after initial exposure to the beam, and the polymer structure continues to change well after the beam is turned off. The changes to the polymer structure with X-ray exposure in this work are not consistent with degradation of the polymer chain, as evidenced by the increase to the MW of the polymer from the GPC data and suggested grafting of dPS, as demonstrated by the FTIR data. To elucidate the processes by which these reactions occur, the radiation induced degradation pathways for P3HT will still be helpful in understanding the change in polymer structure after exposure to the beam. Most studies of P3HT that are exposed to synchrotron radiation have looked at thin films of the material. The work by

Neuhold looked at thin films composed of P3HT and other conjugated polymers exposed to synchrotron radiation from grazing incidence X-ray diffraction, and concluded that the alkyl chain in P3HT is susceptible to cleavage, which leads to the formation of radicals near the thiophene ring. These radicals can then form crosslinks between the polymer chains.⁴² Studies by Abdou et al. examined the photodegradation of poly(alkylthiophenes) in solution and Ljungqvist et al. monitored the photodegradation of poly(alkylthiophenes) thin films, with both using lower energy UV sources. These experiments showed that the polymers can undergo chain scission and cross-linking events depending on the radiation source and atmosphere.^{128,129} The authors state the start of all these reaction pathways require the formation of a radical at the α -carbon of the alkyl chain (Figure 3.8), which can undergo reaction with oxygen that can lead to chain scission or cross-links. The radical can resolve through different pathways, with some of these shown in Figure 3.9. Though these studies used much weaker energy sources, a stronger source should induce similar changes to the P3HT.

The samples in our study use d-styrene as the solvent, which can react with any radical formed to initiate the grafting of the styrene to the P3HT backbone. The grafted styrene can then further react with additional styrene monomer to form dPS chains grafted to the P3HT polymer. Fitting the scattering to the Gaussian-Lorentz gel model provides quantitative insight into this grafting process. The static domains represent the formation of graft points, while the dynamic domains represent changes in the grafted polystyrene chains. Furthermore, comparing the scattering data from both samples can provide additional insight into the reaction processes that underly the change in scattering

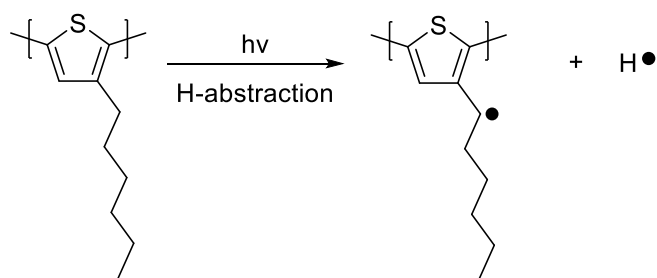


Figure 3.8- Formation of radical on the alkyl chain of P3HT.

Adapted with permission from Ljungqvist et al.¹²⁹ Copyright
1995 American Chemical Society.

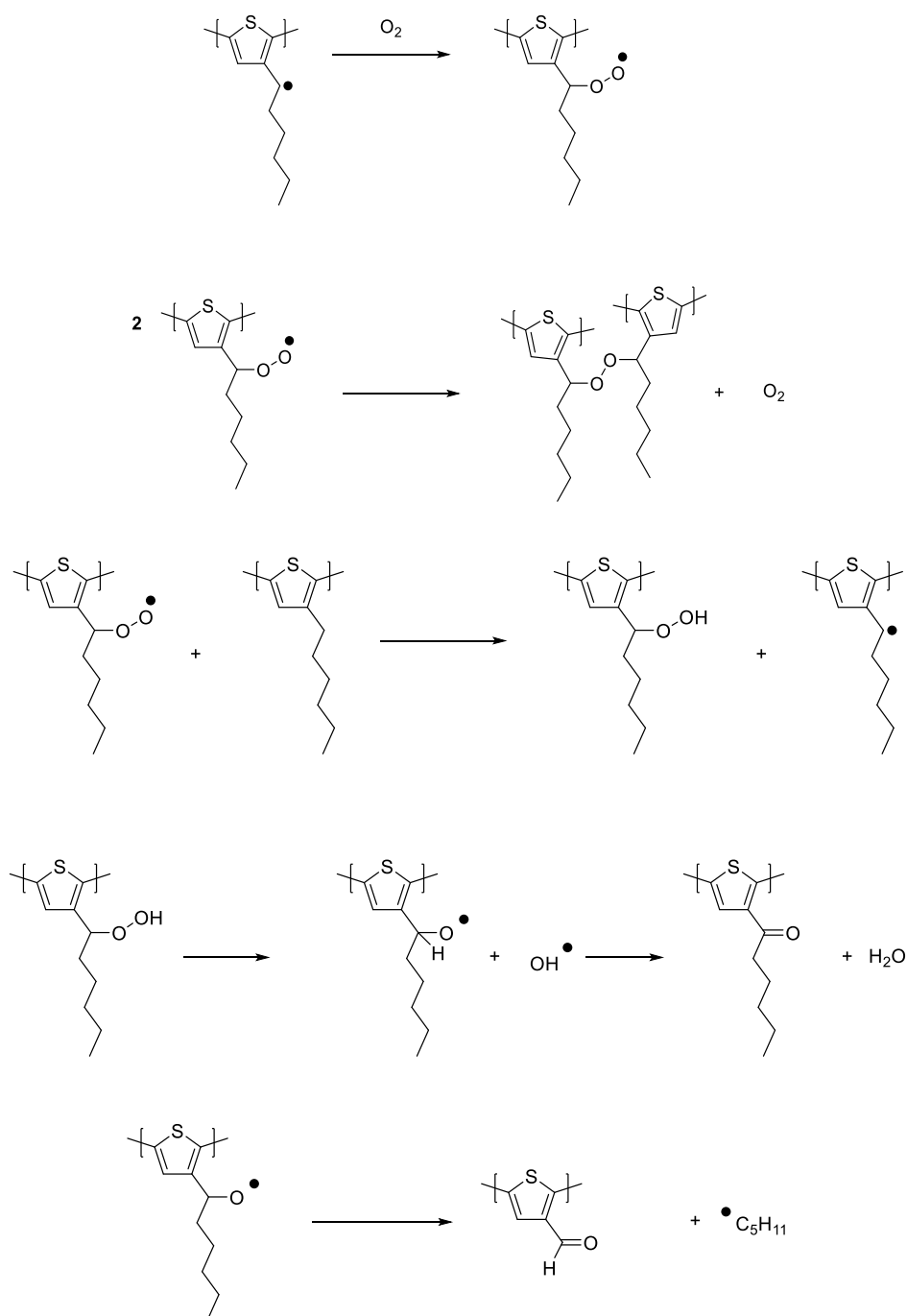


Figure 3.9-Oxidative pathways to molecular enlargement or formation of carbonyl group. Adapted with permission from Abdou et al.¹²⁸ Copyright 1993 American Chemical Society and Ljungqvist et al.¹²⁹ Copyright 1995 American Chemical Society.

pattern. Inspection of the time evolution of the structural changes in the two samples (Figures 3.6 and 3.7) shows similar trends but with different rates of change, where the structural changes in the 0.25% sample evolve more slowly than the changes in the 0.5% sample. The slower rate of change of the 0.25% sample may be governed by the lower P3HT concentration or the shorter exposure time to the X-ray beam. To determine the relative importance of the P3HT loading and the X-ray exposure time, we assume that the reaction rate of the post exposure changes is first order in P3HT loading and X-ray exposure time, T. This assumes that the X-ray exposure time correlates to the number of radicals formed.

$$\text{Reaction rate} = k [\text{P3HT}] [T]$$

Thus the rates of the reaction for each sample can be described as:

$$\text{Rate}(0.5\%) \sim k [0.5][90 \text{ s}]$$

$$\text{Rate}(0.25\%) \sim k [0.25][15 \text{ s}]$$

The reaction rates denote the number of reactions (G_r) that occur per unit time (t):

$$\text{Rate}(0.5\%) = G_{r1}/t_1$$

$$\text{Rate}(0.25\%) = G_{r2}/t_2$$

From this, the ratio of the Rate(0.5%) and Rate(0.25%) will result in some factor, X:

$$(G_{r1}/t_1)/(G_{r2}/t_2) = X$$

where $X = 2, 6$, or 12 . $X = 2$ if the reaction is dominated by the P3HT concentration and is independent of exposure time (or number of radicals formed), however $X = 6$ if the reaction is dominated by the exposure time/# radicals but is independent of P3HT

concentration, and $X = 12$ if the reaction is dependent on both P3HT concentration and exposure time/radicals formed.

The times when both reactions have progressed equivalent amounts, $G_{r1} = G_{r2}$, can be expressed by:

$$(1/t_1)/(1/t_2) = t_2/t_1 = X$$

This can be rearranged to give a relationship that defines the factor (X) that the timescale of the 0.5% reaction (t_1) must be multiplied by to observe equal extents of reaction for both samples.

$$t_2 = Xt_1$$

Thus, Figures 3.10, 3.11, and 3.12, show the size and number of graft points and graft chain length for both samples when $X = 2, 6$, and 12 , respectively.

Comparison of Figures 3.10-3.12, show that the data for the two data sets overlap the most when $X=12$, which indicates that both the exposure time and P3HT concentration impact the rate of the reaction. Comparison of Figures 3.10 and 3.11, however show that the data in Figure 3.11 overlap much better than those in Figure 3.10, which we interpret to indicate that the exposure time is more dominant than the P3HT concentration in driving these reactions. This limited dependence of the reaction rate on P3HT concentration is consistent with little intermolecular reaction in the structure development, i.e., there is little P3HT-P3HT crosslinking. This is not surprising as at these dilute solutions, one would expect any radicals to more readily find and react with the deuterated styrene solvent than other P3HT chains. Thus, the formation of the static domains are primarily intramolecular reactions, with few P3HT-P3HT intermolecular reactions. The graft points on the P3HT

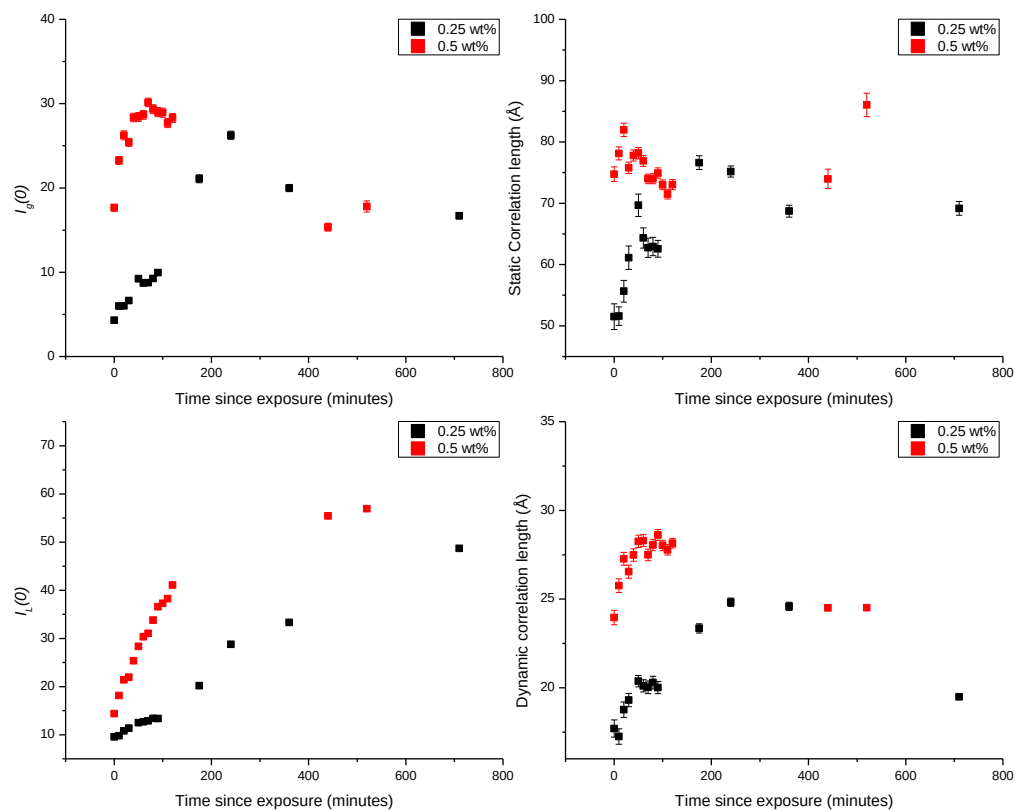


Figure 3.10- Comparison of the concentration and size of the static and dynamic domains of the 0.25 and 0.5 wt% samples, after normalization of the 0.5 wt% time axis by only the P3HT concentration (multiplying by a factor of 2).

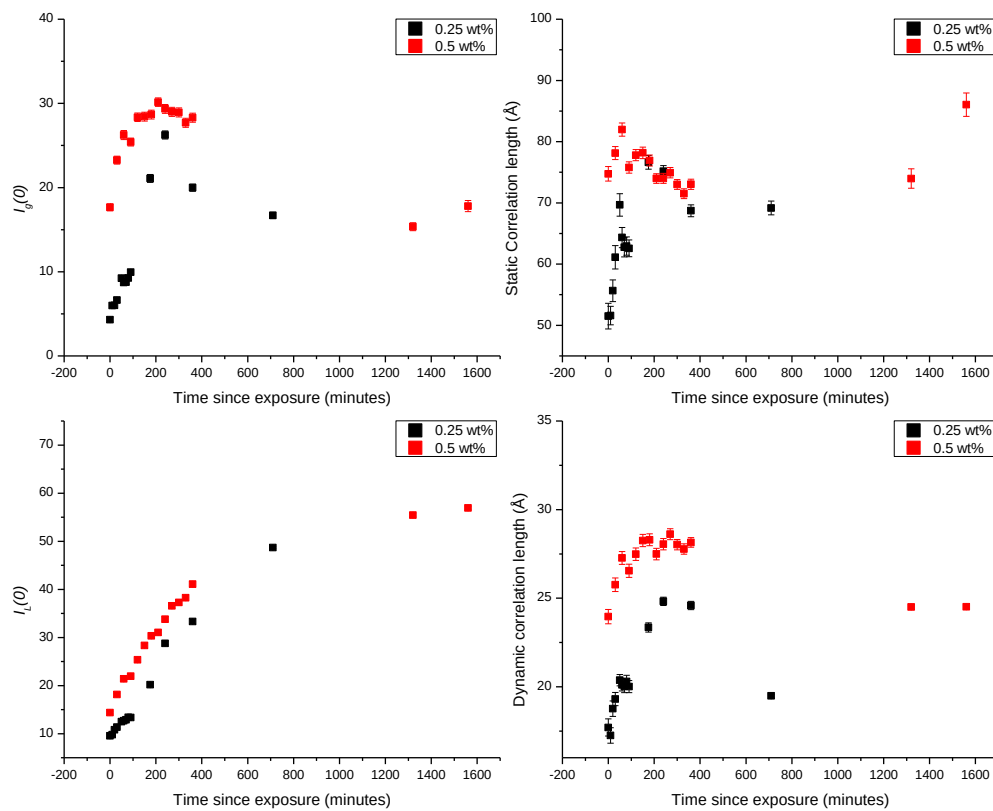


Figure 3.11- Comparison of the concentration and size of the static and dynamic domains of the 0.25 and 0.5 wt% samples, after normalization of the 0.5 wt% time axis by only the X-ray exposure time (multiplying by a factor of 6).

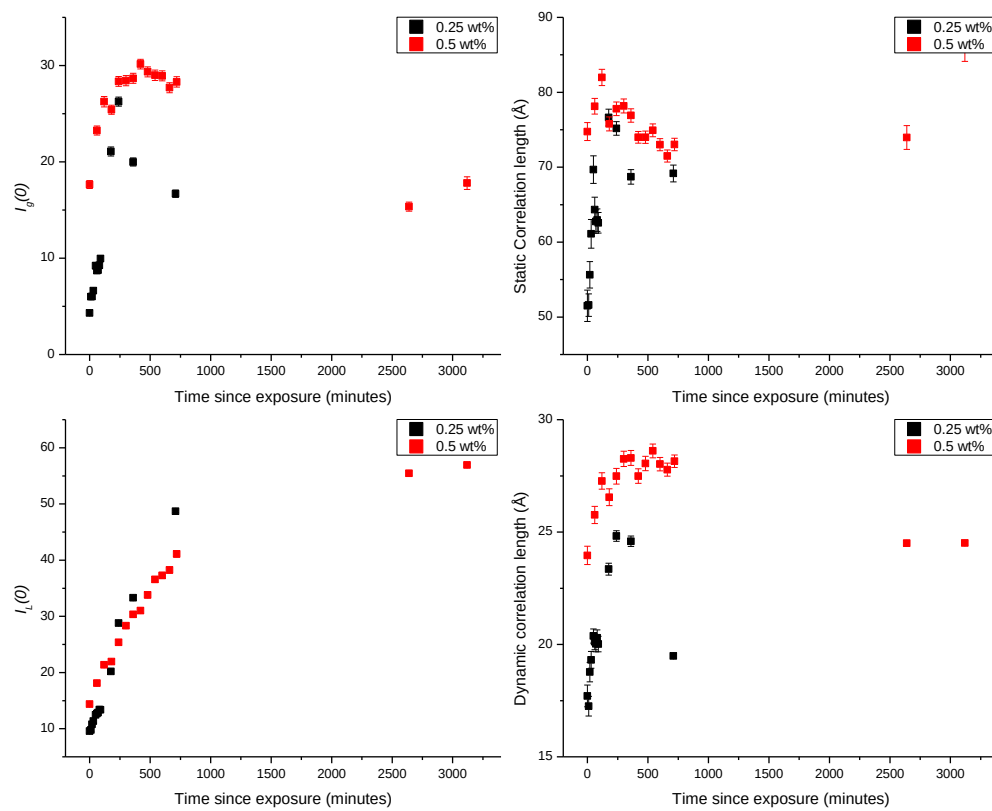


Figure 3.12- Comparison of the concentration and size of the static and dynamic domains of the 0.25 and 0.5 wt% samples, after normalization of the 0.5 wt% time axis for the P3HT concentration and the X-ray exposure time (multiplying by a factor of 12).

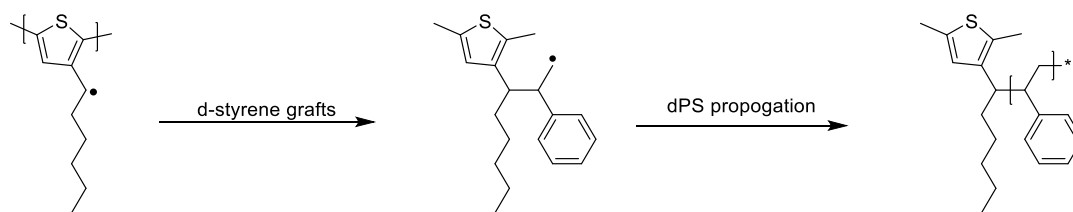


Figure 3.13- Proposed reactions for the irradiated P3HT with deuterated styrene.

chain then propagate to form dPS chains, which grow from the static (grafts points) to form the dynamic (dPS chains) structures in the fitting model, as shown in Figure 3.13. The concentration and size of graft sites reaches a maximum quickly, with little change noticeable after 200 minutes. The dynamic domains show slight change in the size after 200 minutes too, but the concentration continues to increase for these dPS chains through the observed time scale.

These and previous experiments argue that there are many pathways that the radiation induced formation of radicals can lead to alteration of the polymer chains. The SAXS data shows that there is an increase in structural size of the polymer chains, which is reinforced by the GPC data showing an increase in molecular weight and Đ. The FTIR data suggests that there is little chain degradation, and is consistent with the formation of radicals on the alpha-carbon of the alkyl chain. The FTIR also shows that there is dPS incorporated in the irradiated samples, which may also explain the increase in the MW of the samples. Normalization of the time scale for both samples offer a comparison of the rate of change of the structural changes, where this analysis indicates that the time of exposure to the X-ray beam is the major contributor to the rate of the radiation induced reactions in these samples. The limited dependence of P3HT concentration on the rate of reaction indicates that the increase in structure is primarily the result of grafting deuterated styrene to the P3HT chain, with little P3HT-P3HT coupling reactions.

Conclusions

This work presented in this manuscript shows that exposure of P3HT in d-styrene to synchrotron X-rays during small angle X-ray scattering experiments results in the

formation of radicals that further react to increase the polymer chain size. Further analysis shows that the rate of the reactions that drive these changes is most dependent on initial dosage of the X-rays. The SAXS data show an increase in the scattering intensity of the P3HT with time after exposure to the synchrotron beam, which correlates to the formation of radicals that serve as initiators of the grafting of dPS chains to the P3HT backbone. This interpretation is reinforced by analysis of the molecular weight of the polymer chains before and after X-ray exposure, which showed an increase in MW of the polymer samples after irradiation. FTIR data also supports this mechanism, as it shows no evidence of polymer chain degradation, but shows the presence of d-styrene and dPS in the irradiated samples. Analysis of the scattering data supports this interpretation as well and provides insight into the factors that govern the grafting process. All scattering data fit very well to the Gaussian-Lorentz gel model, which documents the change in the static (graft points) and dynamic (grafted dPS chains) correlation lengths with time after the X-ray exposure. Qualitatively, the scattering data show that higher doses of X-ray exposure result in faster grafting reactions. Quantitative analysis to account for exposure time and P3HT concentration showed that the grafting reaction is primarily dependent on the X-ray exposure time, which is interpreted to be responsible for forming radicals that act as graft sites. The concentration and size of the graft points increase quickly, but stop increasing after a short time post exposure. The formation of the dPS chains dominates the changes in these samples after these static domains quickly form, as the grafted chain length appears to increase for an extended period of time after exposure to X-rays. When exposed to the X-ray beam for short time, the rate of structural changes is slower, but continue for several

hours after the initial exposure. These experiments demonstrate that exposure to ionizing radiation can lead to irreversible changes in the polymer structures that can cascade after initial exposure to the ionizing radiation. These experiments also show that in the presence of an easily polymerized monomer, these alterations can result in the formation of new grafted chains on the main polymer backbone. This further exemplifies the need for careful consideration of all parameters in the experiment, so as not to induce unexpected changes in the system of interest.

Acknowledgements

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**Chapter Four- The Structural Evolution of Poly(ethylene
terephthalate) Oligomers Produced via Glycolysis
Depolymerization**

Abstract

Polymeric materials have become an integral material in our society, and their high demand has created a large quantity of polymers that end up in the waste stream. For instance, poly(ethylene terephthalate) (PET) is widely used in a broad range of applications, and can be recycled either mechanically or chemically. Chemical recycling of PET is of growing interest, as there are a multitude of pathways to deconstruct the polymer chain by reactions at the ester group with different functional groups. Most methods focus on the complete depolymerization of the PET to monomer, however pushing the equilibrium reaction to the monomer is time and energy intensive. We hypothesize that by intercepting intermediates in the depolymerization, telechelic oligomers can be captured that can also be used as reactants to produce value-added goods. To this end, this study monitors the products of the glycolysis depolymerization of PET and determines the effects of reaction type, catalyst loading, reaction time, and temperature on the evolution of product chain structure and yield. For the heterogeneous reaction at lower temperatures (165 °C), the rate of depolymerization is sufficiently slow to offer access to a broad range of molecular weight products (3,000 – 10,000 Daltons) at a high yield (nearly 100 %). At higher heterogeneous reaction temperatures (175 and 185 °C), the reaction rate increases, producing oligomers of a narrower molecular weight range (2,000-5,000 Daltons) with significant loss of the original PET, up to 40%, as water soluble products. In the heterogeneous reaction, little change was observed when altering the catalyst loading at higher temperatures, but lower temperatures and decreased catalyst loading produce higher molecular weight oligomers. Homogeneous catalysis of the glycolysis reactions rapidly

increases the rate of depolymerization, such that it is difficult to isolate oligomers with $M_n > 1000$ Daltons. The oligomers from heterogenous reactions were used as reactants to form block copolymers with ethylene glycol, exemplifying their use as precursors in the production of value-added materials. Through these experiments, the dependence of the structure of the depolymerization products as a function of reaction type, reaction temperature, catalyst loading, and reaction time is established, and gives crucial insight into how these parameters can be tuned to produce target telechelic oligomers of PET.

Introduction

Polymeric materials are used in many aspects of society, as they are integral to the industrial, agricultural, and residential sectors. With this demand, polymer production has risen, which in turn leads to problems in their end of life, as most plastics end up in landfills or the environment. For instance, the Environmental Protection Agency (EPA) estimates that the U.S produced ~35,000,000 U.S tons of plastics in 2018.⁴⁸ Of this large amount of polymers produced, poly(ethylene terephthalate) (PET) accounts for about 15% of the produced materials and polyethylene 42%. Moreover, these two polymers make up a large portion of the recycled polymer materials reported by the EPA.⁴⁸

There are a few methods that decrease the plastic waste burden, such as incineration or recycling.¹³⁶ Incineration is often the easiest and most cost effective but comes with the production of greenhouse gases and other undesirable byproducts, making this method suboptimal for several different types of polymers. Recycling falls into two main categories, mechanical and chemical recycling. Mechanical recycling is a method where the polymer is physically converted into usable precursors that can be reprocessed to

produce new products. Mechanical recycling is a common method used in recycling plastics, but there are many factors that decrease the quality and value of the recycled materials. A major issue is mechanical recycling results in degradation of the polymer every time it is recycled. This is due to the repeated melting and processing of the materials, that leads to degradation of the polymer chains, and in turn decreases the mechanical properties of the resulting materials.^{49,52,137–139} The inclusion of additives during original fabrication and contaminants from waste streams also make this recycling method more difficult. Mechanically recycling PET waste into usable bottles requires pristine, transparent, raw materials is feasible, however these materials can only be recycled about six times, after which the degradation renders the materials unusable.^{52,140}

Another recycling method that can overcome the shortcomings of mechanical recycling is chemical recycling. Chemical recycling depolymerizes the used polymer back to useable precursors (usually monomer) that can be repolymerized to synthesize new materials. There are quite a few reactions that can be used to chemically recycle PET due to the presence of the ester group on the backbone, which is susceptible to reactions with different functional groups. The most common method is glycolysis, which reacts a glycol with the ester linkage of PET to shorten the polymer chain and produce monomeric precursors that can be repolymerized to form PET.^{51,141–149} A common example of this reaction is the reaction of PET with ethylene glycol, which depolymerizes PET to bis(2-hydroxyethyl) terephthalate (BHET). BHET can be used as a monomer to repolymerize PET. Other reactants, and therefore reactions, can be employed, some of which include hydrolysis, methanolysis, or aminolysis, where each reaction will form a slightly different

precursor that can be utilized to form new materials.^{50–52} One drawback to the chemical recycling of PET is the solubility of the polymer itself. PET is a highly recalcitrant material, where it will not dissolve in most organic solvents. Thus, severe conditions are often required to realize these depolymerization reactions, such as harsh solvents and/or high temperatures.¹⁵⁰ These reactions also require a catalyst for high conversion to monomer, where organometallic catalysts are commonly employed, with the most prominent being zinc, lead, cobalt, or manganese acetates.^{141–143,151–153} Further studies have examined replacing these catalysts, as separation of the catalyst from the final product is often difficult. Alternative catalysts include nanoparticles, ionic liquids, and deep-eutectic solvents.^{144–146,154} Most recently, the use of protic ionic salts as catalysts in the depolymerization of PET have removed the metal component of the catalyst, resulting in products that are more benign.^{150,155}

Blending polymers together provides an additional pathway to use polymers at their end of life. Unfortunately, most polymers do not thermodynamically mix with each other. Due to the low entropy of mixing, these blends will usually phase separate, which will create materials that have inferior properties to the original materials.^{54–56} Compatibilization is a method to improve the properties of phase separated polymer blends where incorporation of an interfacial modifier may improve the interface between the two polymers in the blend, creating a more robust material.^{57–59} Copolymers that consist of monomers that are identical to either blend homopolymers are common compatibilizers, where block copolymers show significant improvement in the properties of the resulting blends. The formation of these block copolymers can occur before they are added to a

blend, or they may be formed by an in-situ reaction that occurs in the blend, known as reactive compatibilization.^{61,63–73} For the block copolymers that are synthesized before they are added to the blends, the copolymer will migrate to the interface between the polymers during processing and mediate the interactions between the two polymers, stabilizing the blend. Reactive compatibilizers perform similarly, but are formed in-situ in the blend, where each block contains mutually reactive groups such as carboxylic acids and epoxides, or carboxylic acid and amines. As these two functional homopolymers migrate to the blends interface, the groups react to form new bonds and create the copolymers only at the biphasic interface.

The simplest form of reactive compatibilizers are diblock copolymers, but through the addition of telechelic monomers, multiblock copolymers can be formed.^{74–85} These multiblock copolymers (MBCPs) have shown the ability to further improve the interfacial adhesion than diblock copolymers. This is mainly due to the compatibilizers crossing the interface multiple times, creating a “stitch” across the interface. Eastwood and Dadmun examined the incorporation of MBCPs as compatibilizers for blends of polystyrene and poly(methyl methacrylate).⁷⁸ These compatibilizers were different block copolymer architectures composed of styrene and methyl methacrylate. Their work found that the compatibilizers of pentablock architecture demonstrated the best reinforcement of the blend, followed by triblock, diblock, heptablock and then random copolymers. The study concludes that the ability to cross the interface multiple times increased the interfacial adhesion, but a critical molecular weight is required for the block lengths to adequately entangle with the homopolymers of the blend.

Blending of PET and HDPE is a potential method of recycling these materials. The production of useful materials from cheap sources can give new life to discarded materials. As these polymers are immiscible, there have been a number of studies that have examined the compatibilization of PET and HDPE blends using different block copolymer compatibilizers.^{87,89–91,91,93,95,97,99,101,101,156,157} A common compatibilizer is styrene-ethylene-*co*-butene-styrene (SEBS) triblock copolymer, where studies have shown improvements to the ductility of the compatibilized blend at higher loadings of the compatibilizer (>10%). Other compatibilizers that have been examined include linear low-density PE (LLDPE) or low-density PE (LDPE) with reactive groups, such as maleic anhydride, glycidyl, or amino functional groups, that can react with PET in-situ during the processing of the blends. Work by Todd et al. used a *tert*-butyloxycarbonyl protected amino-telechelic PE (Boc-ATPE) as a compatibilizer for blends of PET/HDPE (90/10 wt.%).¹⁰¹ The Boc-ATPE was added during melt mixing of PET and PE, where the Boc-ATPE was converted to ATPE and the unprotected amino groups react with the PET via ester aminolysis and form MBCPs of PET-*b*-PE. Even at low loadings, (0.5 wt.% ATPE), the authors saw a reduction in the size of the HDPE phase, as well as an increase in the elongation at break when compared to unmodified blends. Downsides to this reactive compatibilization scheme included that relatively long mixing times (~10 minutes) were needed to form the compatibilizer, and the by-products of the deprotection of the Boc-ATPE (carbon dioxide and isobutylene) form voids and defects during the melt mixing of the blends. Similarly, Nomura et al. synthesized multiblock copolymers composed of PET and PE via a coupling method using terephthaloyl chloride as a linker between hydroxyl

terminated PE and PET.⁸⁷ The incorporation of this pre-made compatibilizer to the PET/HDPE (80/20 wt.%) blends at low loadings (i.e., 0.5 wt.%) showed a reduction in size of the HDPE domains in the PET matrix, as well as a 30 times increase to the strain at break compared to neat blends. These two studies demonstrate the high potential of MBCPs to compatibilize PET/HDPE blends.

Though there have been strides to understand the compatibilization of PET and HDPE blends, all previous studies have used newly synthesized materials as compatibilizers. Though just a small amount of compatibilizer is needed, this still adds to the already high quantity of plastic materials produced. Chemically recycling polymers into usable compatibilizers or reactive precursor for compatibilization could overcome this hurdle as it would not increase the amount of produced polymers. This manuscript presents the results of a study that begins to address this concern, where the structural evolution of the products during the depolymerization of PET are monitored. Understanding this evolution of chain structure offers an opportunity to intercept the intermediates of the depolymerization process that can be used to synthesize value-added products, including compatibilizers.

This will be achieved by monitoring the products from the glycolysis of PET as a function of reaction time, where the product oligomers should have hydroxyl functional groups on both ends that can react to form potential compatibilizers. The impact of reaction type (homogeneous vs heterogeneous catalysis), temperature and catalyst loading on the progress of the depolymerization reaction of the PET will be examined to offer insight to obtain targeted molecular weight oligomers at a significant yield. The products of the

glycolysis depolymerization reaction will be used as reactants in reactive processing to determine their suitability in forming block copolymer compatibilizers. The results of this study will therefore offer researchers insight into the progression of the products in the glycolysis depolymerization of PET and how the products of this reaction may be used to form value-added materials.

Experimental

PET used in these experiments was obtained from commercial soft drink bottles that were washed with water, cut into flakes (4 cm x 4 cm) and dried in a vacuum oven at 85 °C overnight before use. Ethylene glycol, N-Methyl-2-pyrrolidone (NMP) and zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2$) were purchased from Fisher scientific and used without further purification. Poly(ethylene glycol) (4000 g/mol) was purchased from Sigma-Aldrich and used without further purification. 1,1,1,2,2,2-hexafluoroisopropanol (HFIP) was purchased from Oakwood chemical and deuterated chloroform (CDCl_3) from Cambridge Isotope Labs, both used without further purification.

The heterogeneous glycolysis reactions were adapted from procedures outlined in the literature.^{141,150} The general reaction includes the addition of dried PET (1 gram) to a vial with ethylene glycol (2.4 mL) and heated to 185, 175, or 165 °C. Once the temperature equilibrated, the catalyst (zinc acetate, 200:1 or 100:1 PET: $\text{Zn}(\text{Ac})_2$) was added to the vial and the reaction proceeded where vials were removed from the oil bath at 10-minute intervals over 80 minutes. Upon removal of the vial from the oil bath, the vials were quenched in room temperature water to stop the glycolysis depolymerization reaction. Subsequently, deionized water was added to the vials (15 mL) and heated to 90 °C for 20

minutes to remove all water-soluble reactants and products in the vial. The contents of the vial were filtered and the solid was washed with 10 mL of hot DI water to ensure complete removal of water-soluble materials. The recovered products of the reaction were then dried in a vacuum oven at 65 °C for 12 hours before weighing.

The homogeneous glycolysis reaction was adapted from procedures outlined in the literature.¹⁵⁸ Five grams of dry PET was added to round bottom flask with 48 mL of NMP, and 12 mL of EG. The flask was heated to 165 °C and 55 mg of Zn(Ac)₂ was added to the flask. A 3 mL aliquot was taken every 2 minutes until 10 minutes have elapsed. Each aliquot was analyzed in a similar manner to the products from the heterogenous reactions.

The mass and molecular weight of the products of the depolymerization reaction were determined, where NMR is used to determine the molecular weight of the PET. In this NMR experiment, the initial and depolymerized PET were dissolved in HFIP at a concentration of 20 mg/mL. The samples were agitated for 2 days to completely dissolve the PET. This PET solution (50 μ L) was added to 800 μ L of CDCl₃ in an NMR tube. Proton NMR analysis was performed on a Jeol JM-ECZS 400 MHz. NMR data was analyzed using MestReNova 14.2.3. The baseline was manually corrected. The number average molecular weight (M_n) was calculated using the method outlined by Falkenstein et al.¹⁵⁹ In this procedure, the NMR spectra for PET has two sharp singlets that correspond to the four protons from the terephthalate ring and the four proton oxyethylene units at ~8.1 and ~4.7 ppm, respectively. A weak signal near 4.0 ppm corresponds to the methylene protons of the α adjacent to the hydroxyl end group of the PET chains. Assuming each PET chain has one hydroxyl chain end on average, the degree of polymerization (DP) is calculated from

the ratio of the average integration from the peaks at 8.1 and 4.7 ppm and the hydroxyl end group at 4.0 ppm, then dividing by 4 (number of protons per repeat unit for the terephthalate or oxyethylene signals) to get the DP. Doing this for the starting materials gave a DP of 127 and 112, which corresponds to a M_n of 24,400 and 21,500 g/mol. This result was verified by a commercial size exclusion chromatography analysis by PolyAnalytik.

The products of the heterogeneous depolymerization reaction were examined as reactants in the synthesis of block copolymers. In this reaction, the product of the depolymerization was added to a reaction flask with polyethylene glycol as described in the literature.¹⁶⁰ Following literature procedure, the flask was sealed and the atmosphere was replaced with nitrogen. The flask was then heated to 280 °C with stirring for 30 minutes. After the reaction was complete, the flask was cooled to room temperature where a brown solid was present. The solid was dissolved in HFIP and the product of this reaction was crashed out in water to remove any unreacted PEG. The material was filtered and dried in a vacuum oven at 60 °C overnight. Analysis of the product was performed using NMR and DSC. The NMR analysis mimics those described above for the pure PET materials. DSC analysis was performed on a TA Instruments Q-2000, with a heat ramp of 10 °C/min with a range from -85-285 °C. The samples were heat cycled once to remove thermal history and the second scan was used for analysis.

Results and Discussion

Evolution of Chain Structure during Heterogeneous Glycolysis of PET

A primary goal of this experiment is to elucidate the evolution of chain structure during the glycolysis of PET. Figure 4.1 plots the mass fraction of depolymerized PET from the heterogeneous catalysis reaction that is recovered after washing with water as a function of reaction time. Inspection of this figure shows that the amount of depolymerized PET that is recovered at any given reaction time decreases with an increase in reaction temperature, which is consistent with a faster depolymerization reaction at higher temperature. It is interesting that at 165 °C, nearly all of the mass of the original PET is recovered even after 80 minutes. This implies that the depolymerization reaction is sufficiently slow to create oligomeric products that are suitably large that they are insoluble in water. On the other hand, when the reaction is run at 185 °C, as much as 35-40% of the original PET is not recovered at later reaction times (70-80 minutes). This indicates that a significant portion of the PET has been depolymerized to create water soluble products under these conditions.

The number average molecular weights (M_n) of the products of the heterogeneous depolymerization reaction using a catalyst loading of 100:1 PET: $\text{Zn}(\text{Ac})_2$ are determined with NMR. The M_n of the products of the depolymerization reaction are plotted in Figure 4.2 as a function of reaction time for the three reaction temperatures. Figure 4.2 shows that the average chain length of the depolymerization products decreases rapidly in the first 10 minutes, but then gradually decreases further as the reaction proceeds. To account for a modest difference in the original molecular weight of the starting PET material, the relative

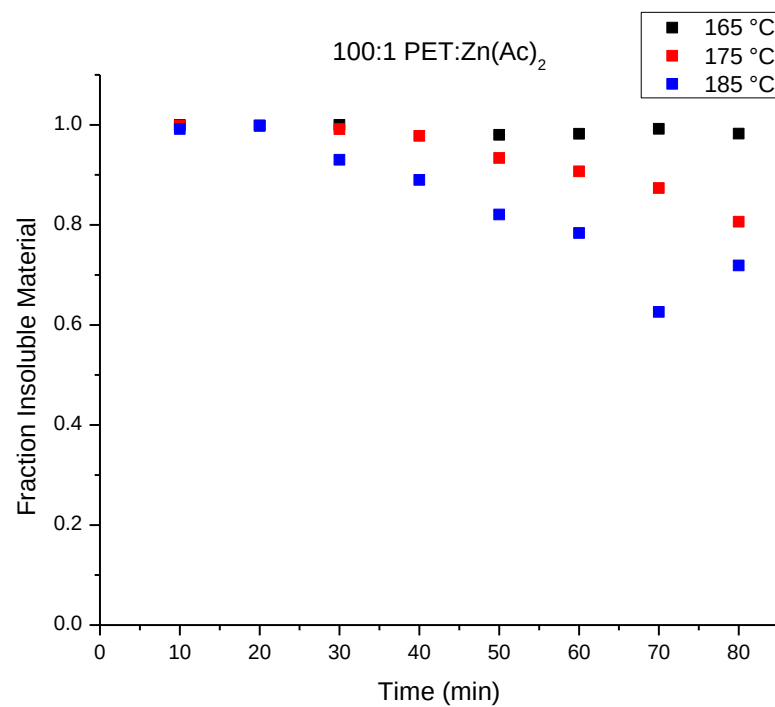


Figure 4.1- Fraction of water insoluble materials over the observed time for the heterogenous reaction at 165 °C (black), 175 °C (red) and 185 °C (blue).

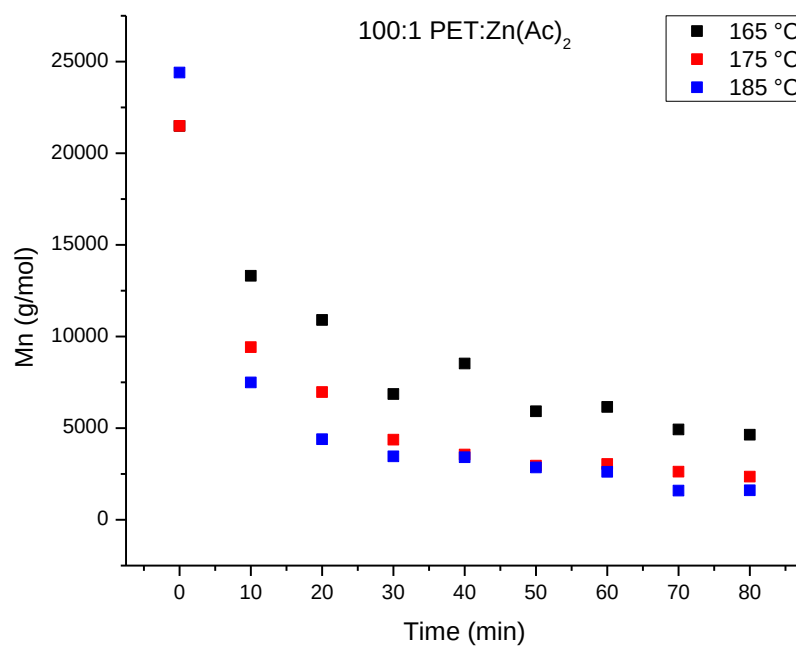


Figure 4.2- Decrease in M_n of the PET as a function of glycolysis reaction time at different temperatures for the heterogeneous reactions. The reaction conditions are PET: $Zn(Ac)_2$ of 100:1 at 165 °C (black), 175 °C (red) and 185 °C (blue).

change in molecular weight of the depolymerization products as a function of reaction time is determined by dividing the M_n of the depolymerization product at different reaction times by the starting M_n . This normalized progress of the decrease in chain length during the depolymerization is plotted in Figure 4.3 as a function of reaction time for the three reaction temperatures. Inspection of this figure further documents the acceleration of the depolymerization reaction with an increase in temperature, where the reactions at 185 and 175 °C reach a minimum chain that is *ca.* 10% of the original chain length after ~ 40 minutes of reaction time, while the chain length of the products of the heterogeneous reaction at 165 °C does not level off at longer reaction times. It is interesting that the limiting molecular weight that is accessible from the water washing at long reaction times is independent of reaction temperature. We interpret this to indicate that there is a maximum molecular weight of the depolymerization products that is water soluble, where these results suggest that this molecular weight is about 2,000-3,000 Daltons.

The loading of catalyst impacts the rate of reaction, where it has been shown that higher loadings of catalyst results in faster depolymerization of PET.¹⁴¹ The impact of catalyst loading on the evolution of depolymerization products from the heterogeneous reaction was examined, where the catalyst loading was halved to 200:1 PET:Zn(Ac)₂. The results were analyzed in similar fashion as the 100:1 PET: Zn(Ac)₂ samples. Figure 4.4 plots the mass fraction of depolymerized PET that is recovered after washing with water as a function of reaction time for the three different temperatures. Halving the amount of catalyst appears to slow the heterogeneous reaction at 165 and 175 °C, as the amount of recovered PET remain relatively unchanged over the observed reaction time. At 185 °C,

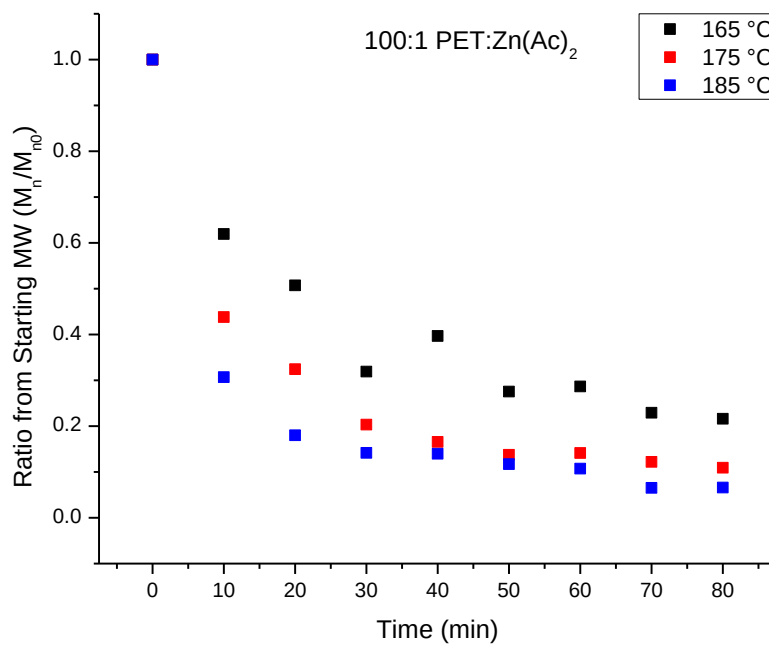


Figure 4.3- The normalized decrease in M_n as a function of glycolysis reaction time at different temperatures for the heterogenous glycolysis. The reaction conditions are PET: Zn(Ac)₂ of 100:1 at 165 °C (black), 175 °C (red) and 185 °C (blue).

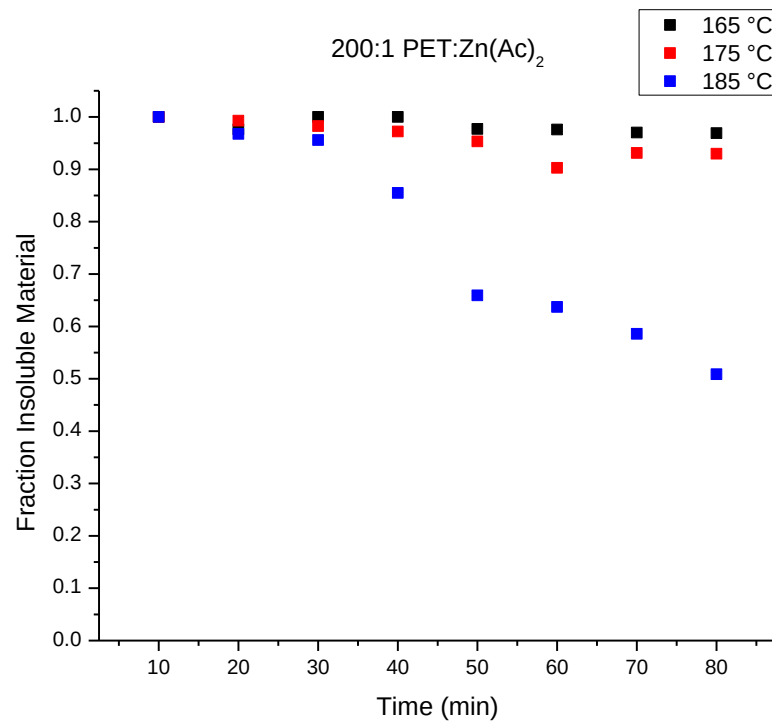


Figure 4.4- Mass fraction of water insoluble products from the heterogenous reaction as a function of the observed reaction time using 200:1 PET:Zn(Ac)₂ loading at 165 °C (black), 175 °C (red) and 185 °C (blue).

the rate of the reaction appears faster than the reaction using 100:1 PET: $\text{Zn}(\text{Ac})_2$ catalyst loading. For instance, the amount of PET recovered after 60 minutes is about 60% of the original PET in the 200:1 reaction, while *ca.* about 75-80% of the original PET is recovered after 60 minutes in the 100:1 reaction. Figure 4.5 plots the M_n of the depolymerized PET as a function of reaction time for the three temperatures for the 200:1 catalyst loading. The variation in amount of recovered PET as a function of reaction time can be correlated to this decrease in chain length with reaction. For the 165 °C and 175 °C reactions, the M_n of the recovered PET never decreases below 3000 g/mol. Thus, all of the products are insoluble in water, and all of the depolymerized PET is recoverable over the observed reaction time. For the 185 °C, the M_n of the recovered is ~ 2900 g/mol after 40 minutes of reaction. Thus, further depolymerization creates shorter PET chains that become soluble in water and product is lost during the water wash.

This initial analysis suggests that lowering the catalyst counterintuitively increases the reaction rate of the heterogenous reaction. To critically evaluate this interpretation, Figure 4.6 plots the normalized decrease in chain length as a function of reaction time for the two different catalyst loadings for all three temperatures to account for variation in original PET chain length. At 165 °C, there is a significant difference in the change in the chain length, where the higher catalyst loading reduces the chain length at a much faster rate than the lowest catalyst loading. As the temperature increases, this variation with catalyst loading is dampened, indicating that there is little impact on the rate of the depolymerization reaction by changing the catalyst loading at higher temperatures. Thus, it appears that monitoring the decrease in the normalized chain length with reaction time

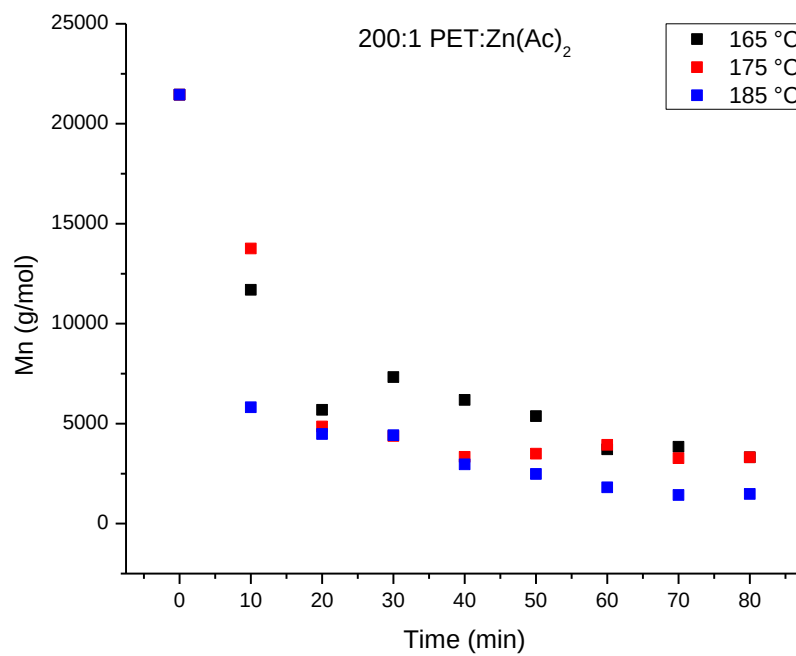


Figure 4.5- Decrease in M_n of the depolymerized PET as a function of reaction time at different temperatures for the heterogenous glycolysis reaction. Reaction conditions are 200:1 PET:Zn(Ac)₂ catalyst loading at 165 °C (black), 175 °C (red) and 185 °C (blue).

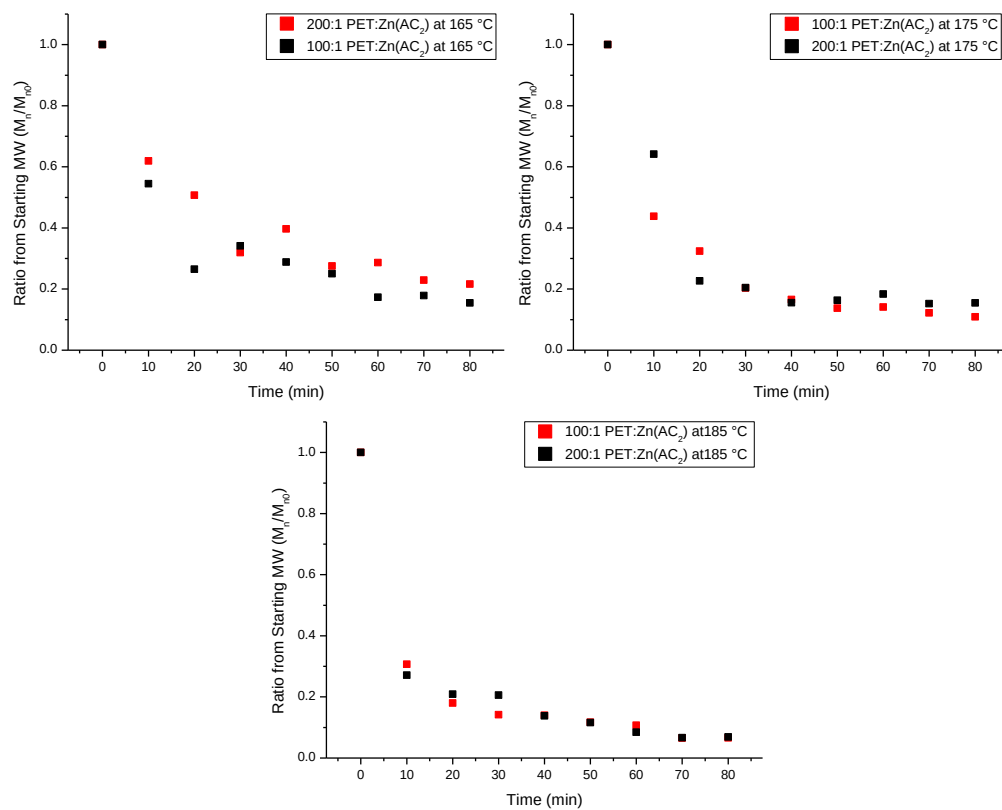


Figure 4.6- Normalized decrease in M_n as a function of reaction time for both catalyst loadings at 165 °C (top-left), 175 °C (top-right), and 185 °C (bottom).

is the most sensitive parameter to elucidate the impact of catalyst loading on the heterogenous reaction progress.

Evolution of Chain Structure during Homogeneous Glycolysis of PET

The homogeneous catalysis of the glycolysis of PET has also been studied, where previous work showed that dissolving the PET speeds up the reaction significantly. In a study by Liu et al., 82% of the PET was converted to BHET at a reaction time of one minute using solvents such as dimethyl sulfoxide or NMP at 180 °C.¹⁵⁸ By lowering the temperature, the reaction slows and the chain evolution may be observed in a similar fashion to the heterogenous reactions. Thus, the homogeneous depolymerization of PET was monitored at 165 °C, which is the lowest temperature that produced a homogenous solution. Figure 4.7 plots the mass fraction of depolymerized PET that is recovered from the aliquots after washing with water as a function of reaction time. Comparison of these results to those of the heterogenous reactions shows that the PET depolymerizes much more quickly, with approximately 50% yield in 4 minutes. This decrease is accompanied by rapid chain depolymerization of the PET, as shown in Figure 4.8. Figure 4.8 plots the M_n of the depolymerized PET from the homogeneous reaction as a function of reaction time. The homogeneous reaction leads to the rapid depolymerization of the PET chain in a matter of minutes. For instance, after two minutes of reaction, the molecular weight of the recovered PET is under 1000 g/mol. This molecular weight does not change significantly with further reaction time to 4- and 6-minutes. After 8- and 10-minute reactions, the products exhibited no distinguishable end group peaks in the NMR. The use of homogenous reaction conditions, therefore, leads to the quick depolymerization of PET,

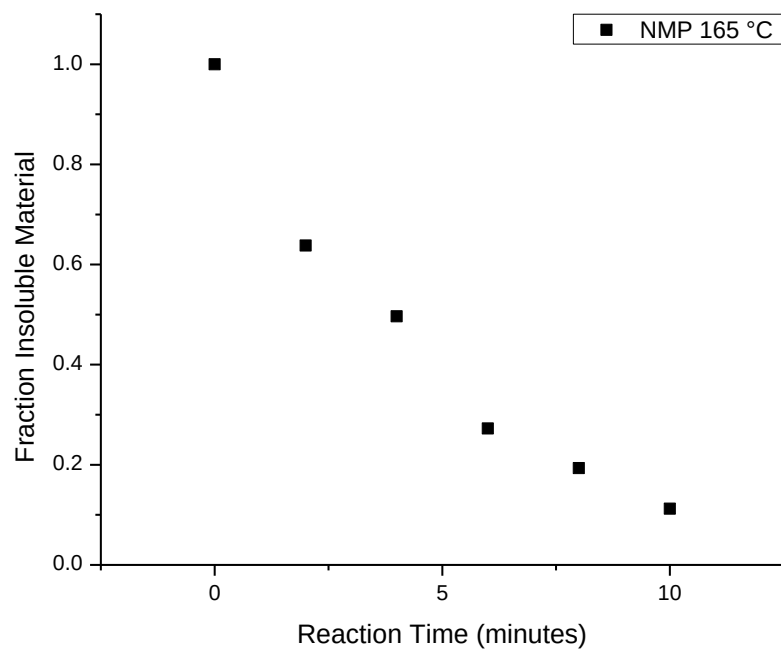


Figure 4.7- Mass fraction of water insoluble products as a function of the observed reaction for the homogeneous glycolysis in NMP at 165 °C.

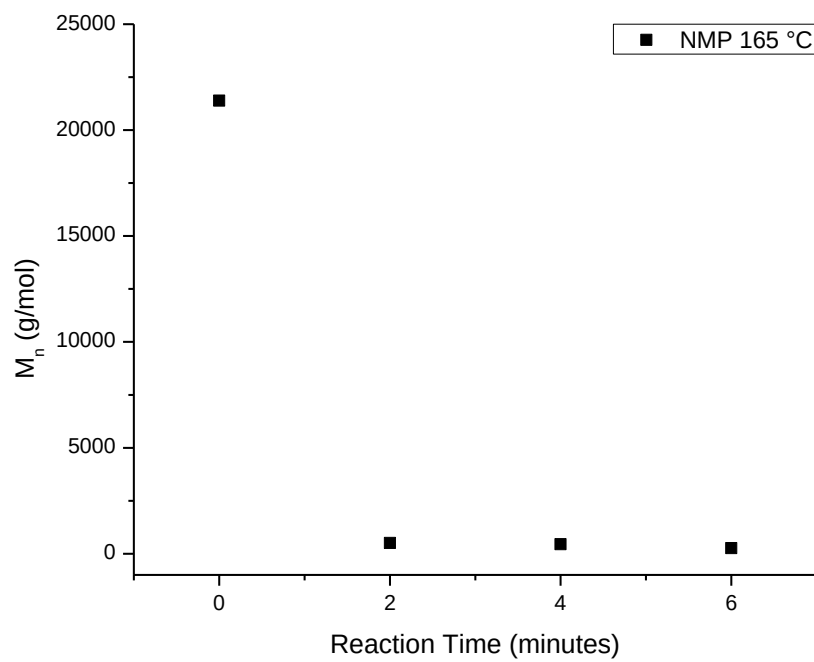


Figure 4.8--Decrease in M_n of the depolymerized PET as a function of reaction time for the homogeneous glycolysis in at 165 °C.

even at lower temperatures, and these rapid changes do not allow for the interception of telechelic intermediates that can be used to produce value-added products.

Block Copolymer Synthesis

We are interested in developing an understanding of how the intermediate products of the depolymerization reaction may be used as precursors to value-added products. One target is to use the telechelic oligomers that emerge from the depolymerization as reactants in the production of block copolymers. There are many reactions that can produce PET copolymers, but a method that can be readily scaled up is preferable. One approach that fits this criterion is the melt-mixing of PET telechelics with other polymers to form blocky copolymers. In our studies, we will examine the ability of the telechelic products of the depolymerization reaction to react with polyethylene glycol (PEG) to form block copolymers. The proposed melt-mixed reaction between PET and PEG is outlined in Figure 4.9. This reaction has some similarity to the glycolysis depolymerization reaction, where the -OH of the PEG will react with the carbonyl, replacing ethylene glycol in the PET backbone and inserting a PEG block.

The products of the material were analyzed using both NMR and DSC to evaluate the success of the proposed reaction. The NMR spectra of the PET and PEG starting materials and the product of the melt-mixed reaction are presented in Figure 4.10. The spectrum for the product of the melt-mixed reaction exhibit peaks for PET at 8 and 4.7 ppm, but also the peaks for PEG at 3.6 and 3.8 ppm, which indicate incorporation of PEG blocks in the product.¹⁶⁰ The recovery procedure of this product includes dissolution in HFIP, precipitation in water, and further heating and washing with hot water to remove

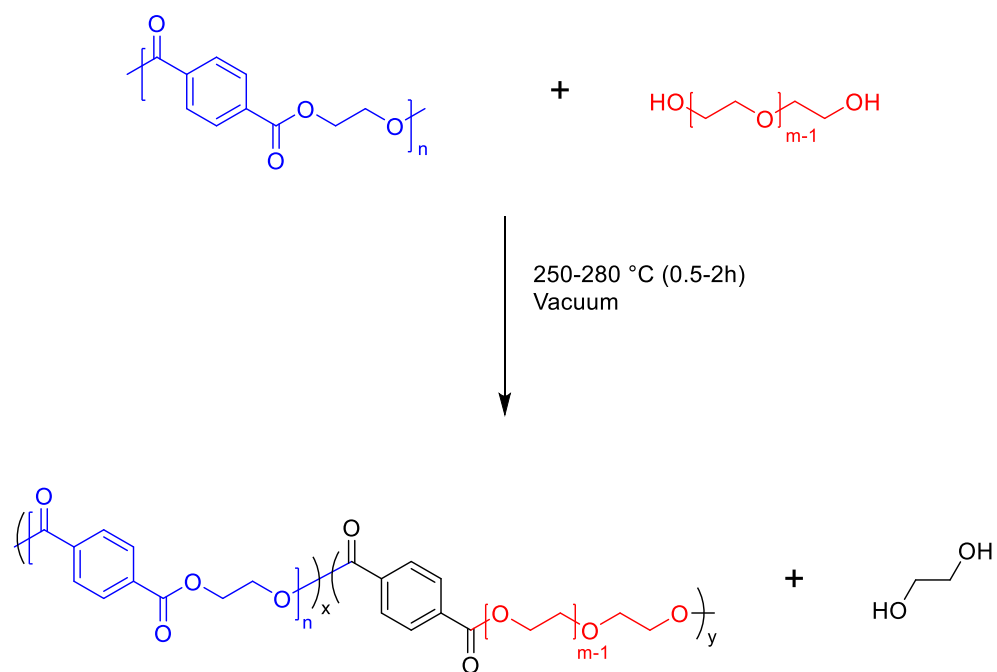


Figure 4.9- Reaction scheme for the synthesis of PET-b-PEG.

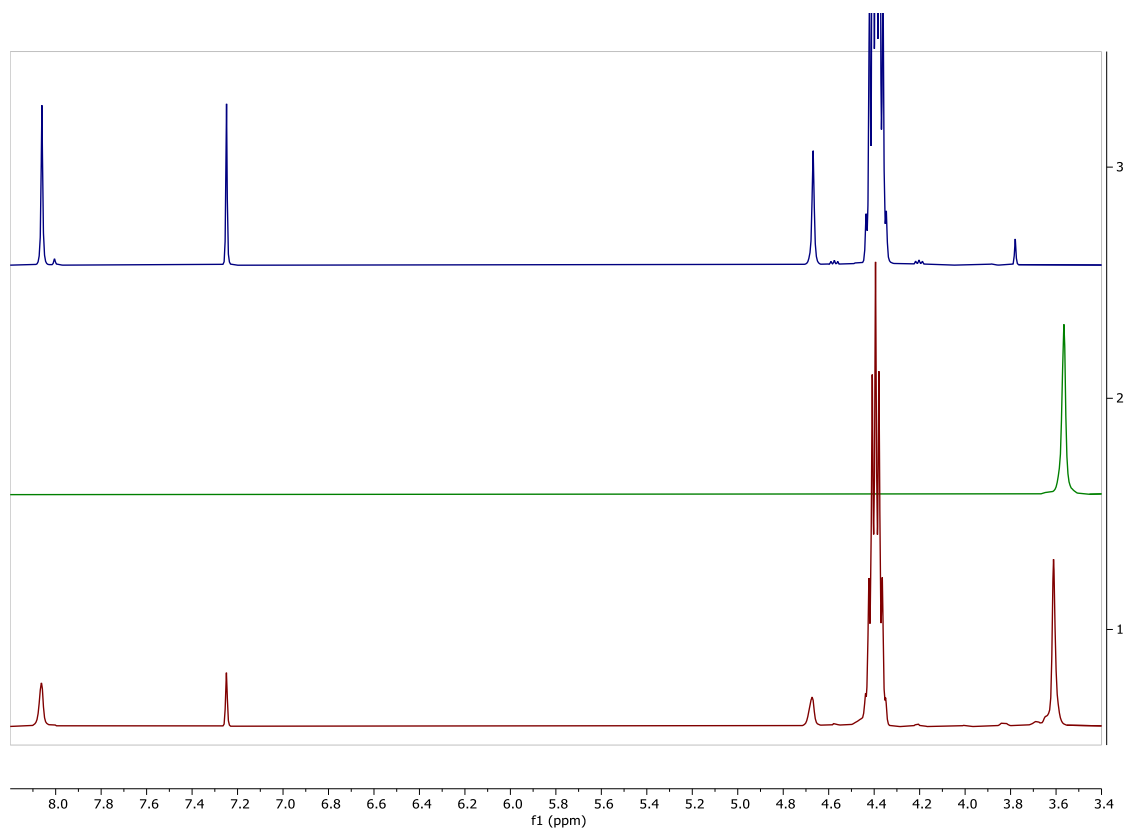


Figure 4.10- NMR spectra for PET, PEG, and melt mix product.

residual, unreacted PEG. Thus, we expect that the peak at 3.6 ppm indicates the incorporation of PEG into a copolymer. To further verify the successful formation of block copolymer during the melt-mixing, the DSC of the starting materials and product are shown in Figure 4.11. The DSC of the PET starting materials shows a melting peak near 246 °C, while the PEG shows a melting peak at ~60 °C. The DSC curve of the product of the melt-mixing shows two glass transitions, one at -48 °C and another at 7 °C, and two melt peaks, at 37 °C and 193 °C. These results are consistent with previous work that synthesized PEG/PET copolymers.¹⁶¹ Thermal analysis of the PET/PEG copolymers synthesized in these previous studies found two melting temperatures, one at ~37 °C that is ascribed to the melting of the PEG block and one at ~245 °C that is assigned to the melting of the PET block. The melting transition of the PEG block in our products is similar to this previous work, however, our melting peak for the PET block is lower than reported by Hu et al. We ascribe this to incorporation of more PEG in our block copolymers than those produced by Hu et al., where the copolymers synthesized by Hu et al. incorporate *ca.* 25% PEG. As our melt-mixed reaction involved ~1:1 molar ratio of PET:PEG in the melt-mixed reaction, we expect that the resulting block copolymers will incorporate more PEG. The decrease in the melting temperature of our PET block at ~193 °C is consistent with the disruption of the PET domains due to the presence of more PEG blocks.¹⁶⁰

To rule out the presence of a PET/PEG blend in the melt-mixed product, the DSC curve of a dry blend of pure PET and PEG was also obtained. This DSC curve is shown in

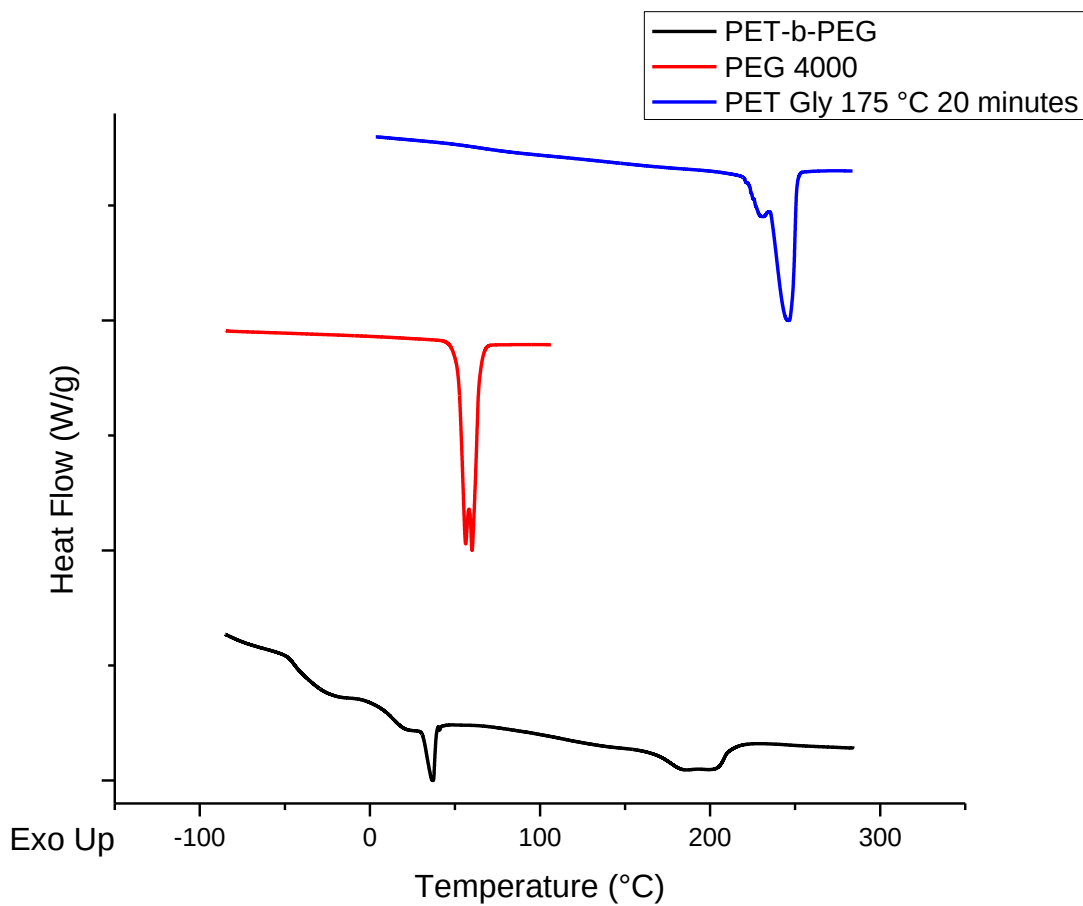


Figure 4.11- DSC thermograms for PET (blue trace), PEG 4000 (red trace) and the PET-b-PEG product from melt mixing the two materials.

Figure 4.12, showing the melt peaks of the two pure components. The melt peak of PEG is at 55 °C and that of PET presents at ~250 °C. These curves are very similar to the sum of the DSC curves of the individual components, verifying there is no reaction between these materials during the DSC experiment. Comparing the black trace for the melt mix product in Figure 4.11 and the curve in Figure 4.12 shows drastic differences, further supporting that the product of the melt mixed reaction are block copolymers and not an unreacted blend of the two reactants.

The results presented above elucidate the evolution of chain structure during the heterogeneous depolymerization of PET by glycolysis catalyzed by zinc acetate. The chain structure is monitored by following the decrease in the M_n of the products as a function of time. From these experiments, the effects of catalyst loading, reaction time, and temperature on the chain structure and percent of recovered PET are revealed. Altering the temperature appears to have the largest impact on the evolution of chain length of the products and yield. At higher loading of $\text{Zn}(\text{Ac})_2$, reactions at 165 °C show the largest range of accessible chain lengths from the reaction, with nearly complete yield of the products from the original PET. As the temperature increases, the reaction is faster making it harder to intercept intermediates with higher molecular weight. Moreover, the faster reaction converts more of the product to water soluble oligomers, lowering the yield. Decreasing the catalyst loading shows insignificant changes to the change in the chain length with reaction time for higher temperatures, but at 165 °C, the change in catalyst loading provides avenues to extract oligomers of higher M_n than using the higher catalyst loading. Tuning these parameters in conjunction to the time of reaction offers pathways to

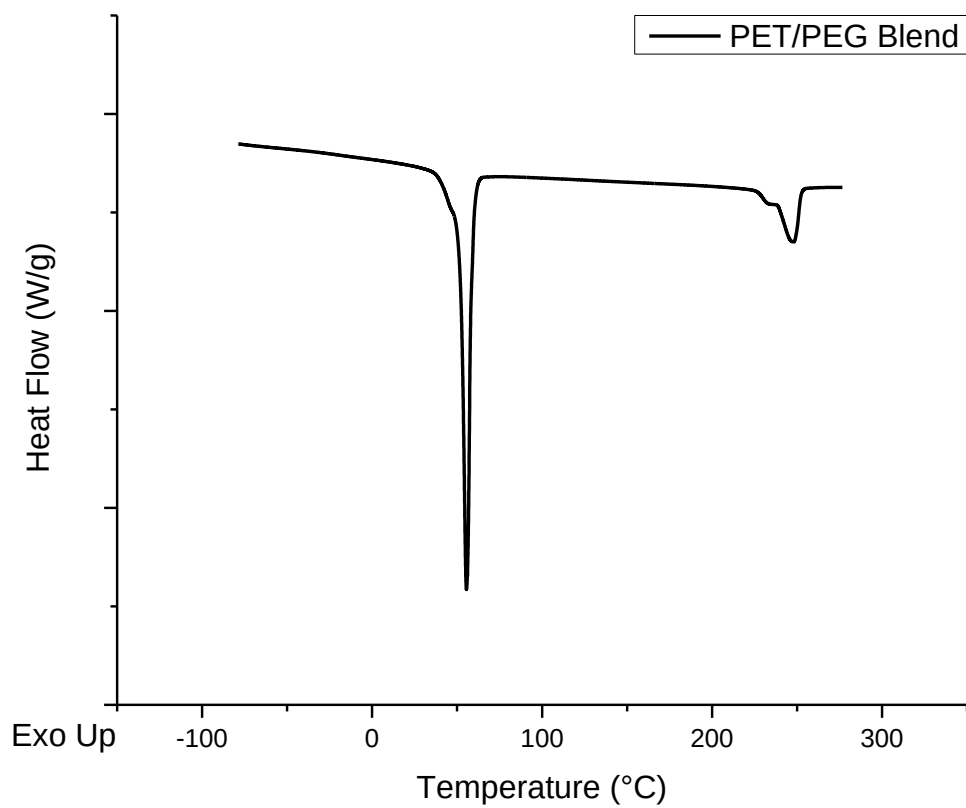


Figure 4.12-DSC thermogram of a blend of glycolyzed PET material and PEG 4000.

produce telechelic oligomers with target molecular weights using heterogenous conditions. The homogeneous glycolysis reaction in a solvent, such as NMP, leads to rapid depolymerization of the PET. Though advantageous in speeding up this reaction, this makes isolating useful intermediates very difficult when compared to the heterogenous reactions. The oligomers produced from the heterogenous reaction can then be used in the production of block copolymers, as demonstrated for the melt-mix reaction described above. These oligomers can be mixed with a broad range of diols, where transesterification reactions produce block copolymers that may be useful in the compatibilization of PET blends.

Conclusions

This work monitors the evolution of chain structure in the depolymerization of PET by glycolysis. The impact of catalyst loading, reaction type, reaction time, and temperature on the evolution of product chain length and yield was established. These results show that for the heterogeneous reaction, at lower temperatures (165 °C), the rate is sufficiently slow to access a broad range of molecular weight products (3,000 – 10,000 Daltons) at high yield (nearly 100 %). At higher temperatures (175 and 185 °C) the reaction is significantly faster, such that the resulting oligomers produced are of a narrower molecular weight range (2,000-5,000 Daltons) with significant loss of original PET, up to 40%, as water soluble products. Lowering the catalyst loading results in little change to the reaction products at higher temperatures, but produces higher molecular weight oligomers at lower temperatures. The use of NMP as a solvent speeds up the homogeneous reaction significantly, where the depolymerization occurred so quickly that it is difficult to intercept

oligomers of usable molecular weight. The products from the heterogeneous reactions can be further utilized in reactions to produce block copolymers. Through melt mixing the depolymerized PET with PEG, block copolymers were successfully synthesized. These experiments reveal the impact of temperature, catalyst loading, and reaction time on the properties of the oligomeric products of glycolysis, and how these parameters can be tuned to produce target oligomeric products of PET. These materials can then be used to produce block copolymers, which may prove useful as compatibilizers of PET blends.

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Chapter Five- Conclusions and Future Work

Conclusions

As polymer materials continue to be a prominent component of our everyday lives, finding methods to alter the structure or morphology can be a useful tool to tune the properties of the materials. The work presented in this dissertation utilized three methods to alter the conformation, morphology, or structure of polymeric materials. The first method was the continued study of using white light during annealing of blends containing conjugated polymers and the impact of this stimulus on the optoelectronic performance of a conjugated polymer thin film. Previous work examined the impact of white light on the optoelectronic properties of conjugated polymer thin films, which include the interpretation that the illumination alters molecular conformation of the conjugated polymer. Our work directly correlates morphological and conformational changes of the conjugated polymer film to their resulting optoelectronic properties. Our results show that morphologies that exhibit lower overall PL emerge from MEH-PPV/dPS blend films that are illuminated during annealing that differ from identical blend films that were not illuminated during annealing. Using TOF-SIMS and SANS, the relationship between the 3-dimensional morphology of the blend thin films and the observed changes to the PL was determined. The TOF-SIMS showed variation in the depth profiles of the films with illumination. At low loadings of MEH-PPV, stratification of the polymers occurs with annealing, where the MEH-PPV migrates toward the substrate. This MEH-PPV rich layer encourages interchain interactions, increasing the quenching of the exciton, resulting in a decrease in the observed PL. With illumination, the sample exhibited a denser layer of MEH-PPV, which coincided with the lower observed PL. As the loadings of MEH-PPV

increased, the depth profile varied slightly with illumination. However, small angle neutron scattering results show that the illuminated samples phase separate more than the samples annealed in the dark. These changes in the in-plane morphology correlate well to the observed differences in the PL of the blend films with illumination, including the observation that the changes in PL are less dramatic at higher loadings than are observed at lower loading of MEH-PPV. These observations provided further foundational understanding of the impact of illumination environment and film composition lead to alterations in the structure and optoelectronic performance of conjugated polymer blend films.

The second study investigated the impact of exposure to synchrotron X-rays to the molecular structure of conjugated polymer solutions. It has been well documented that soft matter is adversely affected by ionizing radiation, such as X-rays. Many studies have investigated the effects of ionizing radiation on conjugated materials, with many of these studies primarily studying thin films composed of conjugated materials, though few have examined conjugated polymer solutions. Our studies show that exposure of P3HT in d-styrene to synchrotron X-rays during small angle X-ray scattering experiments resulted in the formation of radicals that further react to increase the polymer chain size. Interestingly, these reactions continue to cascade long after the sample is removed from the x-ray beam. The rate of the reactions that drive these changes is most dependent on initial dosage of the X-rays. In the samples studied, the SAXS data showed an increase in the scattering intensity of the P3HT with time after exposure to the synchrotron beam, which correlated to the formation of radicals that serve as initiators of the grafting of dPS chains to the P3HT

backbone. This interpretation is reinforced by GPC analysis of the samples before and after X-ray exposure, which showed an increase in MW of the polymer samples after irradiation. FTIR analysis also supports this mechanism, as it showed no evidence of polymer chain degradation, but showed the presence of d-styrene and dPS in the irradiated samples. Further analysis of the scattering data provides insight into the factors that govern the grafting process. Qualitatively, the scattering data show that higher doses of X-ray exposure result in faster grafting reactions. Quantitative analysis to account for exposure time and P3HT concentration showed that the grafting reaction is primarily dependent on the X-ray exposure time, where the concentration and size of the graft points increase quickly, but stop increasing after a short time post exposure. The formation of the dPS chains dominates the changes in these samples after these grafts quickly form, as the grafted chain length appears to increase for an extended period after exposure to X-rays. Lower exposure times to the X-ray beam slowed the subsequent reaction, but continues for several hours after the initial exposure. These experiments demonstrate that exposure to ionizing radiation led to irreversible changes in the polymer structures that can cascade after initial exposure to the ionizing radiation. This study further exemplifies the need for careful consideration of all parameters, such as exposure time and solvents utilized, in the experiment, so as not to induce unexpected changes in the system of study.

Lastly, examination of the structural changes to the polymer chain by glycolysis of PET offers insight into the evolution of chain structure as the polymer depolymerizes, and offers a useful method to isolate value-added oligomers. There has been much interest in the chemical recycling of PET, with most work focusing on the complete depolymerization

of the PET into monomeric units. Our work monitors the evolution of chain structure in the depolymerization of PET via glycolysis. The study investigates the impact of catalyst loading, reaction type, reaction time, and temperature on the evolution of product chain length and yield of products. For the heterogeneous reactions at lower temperatures, the reaction rate was slow, but allowed access to a broad range of molecular weight products (3,000 – 10,000 Daltons) at high yields. Increasing the temperature to 175 and 185 °C significantly increased the reaction rate which resulted in access to oligomers in a narrower molecular weight range (2,000-5,000 Daltons), but this significantly decreased the yield of the original PET, up to 40%, as water soluble products. Varying the catalyst loading resulted in little change to the reaction products at higher temperatures, but produced higher molecular weight oligomers at lower temperatures. Using NMP as a solvent to create a homogeneously catalyzed reaction significantly speeds up the reaction, where intercepting oligomers of usable molecular weight was difficult. The oligomeric products from the heterogeneous reactions were further utilized in reactions to produce block copolymers, which were produced through melt mixing the depolymerized PET with PEG. These experiments reveal the impact of temperature, catalyst loading, and reaction time on the properties of the oligomeric products of glycolysis, and how these parameters can be tuned to produce target oligomeric products of PET. These materials can then be used to produce block copolymers, which may prove useful as compatibilizers of PET blends.

Future Work

These experiments showed that there are many parameters that can be controlled to rationally vary the morphological, structural, and conformational changes in polymer

chains. This in turn opens new avenues to further examine additional factors that may influence these changes, and are discussed below:

- I. Regarding the study of conjugated polymer thin films of MEH-PPV, factors such as fabrication and substrate materials could be useful in expanding our knowledge of how the annealing and illumination alter the films morphology. One aspect that was not investigated in our study was the impact of film thickness. As the concentration of MEH-PPV increased, the resulting film that was produced was thicker. In conjunction to the illumination and thermal environments, film thickness could play a role in the resulting morphology and properties of the film. The substrates used in this study were treated with PGMA to promote adhesion of the MEH-PPV/dPS layer, but other surface modifications could be used to treat the silicon surface, such as hydrofluoric acid treatment. Previous work showed this treatment changed the depth profiles of the films, so alternatives to substrate treatment could give further insight to how this influences the films depth profile, morphology and performance.
- II. The effects of ionizing radiation on conjugated polymer solutions can be expanded. The completed studies only examined only two P3HT concentrations in solution, and expanding the range of concentration to fully understand the effect of concentration on the observed grafting reactions would be beneficial to this study. To mimic previous work that used neutron scattering, our samples also used a poor solvent, styrene, for the sample preparation. This solvent was also susceptible to

radical reactions. If a poor solvent that was not as susceptible to radicals was used, such as toluene or chloroform, how would the structure and conformation of the P3HT be affected by the ionizing radiation and what pathways would be the reaction pathway of any resulting radicals?

- III. There are many avenues that the study of PET chain degradation can continue. The study showed that variations in the temperature, catalyst loading, and the type of reaction (homogenous vs heterogeneous) during the glycolysis of PET lead to changes in the oligomers produced during the reaction. One expansion of this study is to change the catalyst in the depolymerization. PET glycolysis has seen many studies that utilize different catalysts. The move from a heavy metal catalyst has seen the use of protic ionic salts, ionic liquids, or deep-eutectic solvents as the catalyst. Many studies have focused on the production of BHET or other monomers as a benchmark for success, but the structural chain evolution has not been explicitly studied and these catalyst may be useful to produce value added oligomers. Another parameter that could be of interest is the type of depolymerization reaction that is utilized. The chain evolution for the aminolysis or hydrolysis could be investigated in a similar fashion as outlined in this dissertation for glycolysis. These two methods also have the added caveat of the functional groups they produce, as both amine and carboxylic acid functionality provide many avenues to produce copolymers. Lastly, the synthesis of block copolymer compatibilizers needs to be further investigated. The work in this dissertation looked only at melt-mixing as the process to form these block copolymers, but other

methods can be used. Coupling reactions have been performed previously and offer more control over the resulting block copolymer. Though these methods are more complicated, there may be other avenues that can effectively synthesize the targeted block copolymers.

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Vita

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