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SYNTHESIS AND MORPHOLOGY OF MALEIMIDE VINYL ETHER ALTERNATING COPOLYMERS IN THE SOLUTION PHASE

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Major Professor's Signature

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Date

SYNTHESIS AND MORPHOLOGY OF MALEIMIDE VINYL ETHER ALTERNATING COPOLYMERS IN THE SOLUTION PHASE

By

Richard M. Bell III

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ABSTRACT

SYNTHESIS AND MORPHOLOGY OF MALEIMIDE VINYL ETHER ALTERNATING COPOLYMERS IN THE SOLUTION PHASE

By

Richard M. Bell III

Maleimide vinyl ether alternating copolymers were synthesized according to procedures established by the Blanchard group previously. The monomer reactivity of a 3 monomer system was studied by ^{1}H NMR to establish if one monomer was more reactive than the other. N-phenylmaleimide monomer was preferentially incorporated into the polymer chain relative to N-pyrenylmaleimide monomer. The resulting polymers were then studied using steady state fluorescence spectroscopy, and the results of this work were compared to a theoretical model to investigate the morphology of the polymers in various solvents. These studies suggest the polymer is coiled in solvents in which it is minimally soluble. As the solubility of the polymer in the solvent increased, it adapted a more linear conformation.

for Jimmy Wicks (October 9, 1955 - November 19, 2003)

ACKNOWLEDGMENTS

I would like to thank Gary Blanchard for his assistance in my research and the writing of this thesis. He has worked tirelessly in editing and advising on this document and I could not have done it without him. He has been a constant source of motivation in my research always encouraging me to pursue every detail and leave no stone unturned.

I also must thank group members past and present. Times can be hard when there are so many people in a lab but I always felt everyone was motivating me to succeed even when the motivation was a bit aggressive. I would especially like to thank Dr. Jaycoda Major whom started this project and provided a great deal of preliminary research on the topic.

My family and friends have been a constant source of support for me. They have always believed in me and knew I could do it when at times I felt I couldn't. I hope my example will motivate them to try things they never thought they could do and succeed where success may seem impossible.

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Images in this thesis are presented in color

LIST OF ABBREVIATIONS

AIBN	2-2'azobisisobutyronitrile
DMSO	Dimethylsulfoxide
GPC	Gel Permeation Chromatography
HPLC	High Performance Liquid Chromatography
MVE	Maleimide vinyl ether
QCM	Quartz Crystalline Microbalance
ZP	Zirconium Phosphonate

INTRODUCTION

Chemical separations are an essential part of academic and industrial chemistry. Academically they provide fascinating and challenging intellectual problems.[1] In industry chemical separations are essential for the purification of products ranging from petroleum fractions to pharmaceuticals and for the removal of toxins from waste water systems or other environmental processes. In the semiconductor device industry, purification of elemental silicon is a prerequisite for all subsequent fabrication steps.

Species in separations are partitioned between two distinct phases. For example, in High Performance Liquid Chromatography (HPLC) a separation occurs when the fraction of time spent in the stationary phase is different for two species. The chemical potential differences between these two phases are distinct and discontinuous. The Blanchard group seeks to separate analytes by creating a chemical potential gradient of molecular dimension normal to the stationary phase surface. Using this chemical potential gradient, separation would occur with small changes in chemical potential as compared to other analytical separations. In essence, we seek to create layered interfacial structures where separation occurs by a chemical potential gradient rather than a simple step function.

This thesis investigates the synthesis of a family of polymers which can be used to form chemical potential gradients on a variety of substrates. Chemical potentials are different for each analyte and the identity of each polymer layer. The methods by which these interfaces are synthesized afford layer-by-layer

means by which one can control the chemical potential profile at the resulting interface(s). Chemical potential can be controlled by substitutions made during polymer synthesis and deposition of these polymers on a surface by established methods.[2-3] This work focuses on the synthesis and morphology of MVE (maleimide vinyl ether) polymers in the solution phase. The research can be applied to a more detailed understanding of the morphological properties of these polymers and lead to an understanding of how these polymers may be adsorbed onto a substrate surface.

It is important to understand what a chemical potential gradient is and how is it possible to synthesize one. In practice we are trying to create a multilayer system on a surface. These multilayers consist of polymers where the concentration of side groups is adjusted to affect the chemical potential as an analyte encounters each layer. Factors such as dipole moment or dielectric constant of the polymers can influence the interactions of the analytes within the layer. Steric issues can be examined as well through the appropriate choice of polymer side groups and the use of cross-linking chemistry within and between polymer layers.

A multilayer system can be constructed on a variety of substrates (Au and SiO_x) and polymer properties could be used to make a gradient normal to the surface. Synthesis of MVE polymers and bonding to a substrate surface has been documented in our group previously[2,4-6] and work has also been done to control the adsorption and desorption of methanol and cyclohexane on a layered polymer film.[7] We build on this work by seeking a deeper understanding of the

synthesis of MVE polymers and their morphology in the solution phase. With this knowledge, the bonding of the polymers to a substrate surface will be better understood and this understanding will be used to construct chemical potential gradients. To reach this goal we seek to create a chemical potential gradient on a polymer surface and control this gradient based on the choice and order of the polymer layers. An understanding of chemical potential is the first step.

The change in standard state chemical potential associated with the partioning of an analyte between two phases can be given by:

$$\mu^\circ_{A(1)} - \mu^\circ_{A(2)} = -RT \ln c_{A(1)}/c_{A(2)} = -RT \ln K \qquad (1)$$

where $\mu^\circ_{A(1)}$ and $\mu^\circ_{A(2)}$ are the chemical potentials of the analyte A in phases 1 and 2. The terms $c_{A(1)}$ and $c_{A(2)}$ are the concentrations of analyte A in phases 1 and 2. K is the equilibrium constant which can also be described by the rate of adsorption, k_a, and desorption, k_d, of the analyte between phases 1 and 2.

In a chemical separation the equilibrium constant K' for partitioning between two phases is determined by the ratio of the adsorption and desorption rate constants, k_{12}' and k_{21}'. Traditional systems such as gas and liquid chromatography do not allow substantial control of these rate constants unless the composition of one of the phases is changed. Changing the identity of one phase can be less molecule specific than changing the interface between two phases in a chemical potential gradient. A chemical potential gradient has the potential to give more degrees of freedom in chemical separations.

Using a structural gradient at the phase interface can afford greater control over the separation process. If we think of a multilayered system the

adsorption and desorption rate constants can be called k_{ij} and k_{ji} for each adjacent layer pair, i and j. Thus the equilibrium constant would be:

$$K = k_{ij}/k_{ji}$$

for partitioning between the i and j layers of an interface. If we were to use a two phase system the equilibrium constant would be:

$$K = k_{12}/k_{21}$$

or for a surface comprised of four layers:

$$K = k_{12}k_{23}k_{34}k_{45}k_{46}/k_{21}k_{32}k_{43}k_{54}k_{65} = K_1K_2K_3K_4K_5$$

We intend to control the polymer layers independently and thereby control the adsorption and desorption rate constants of each layer independently. Using this system, we can influence the kinetics of separation. This method is advantageous in that we can control the identity of each layer and thereby affect the separation substantially. Therefore, we seek to construct a chemical potential gradient on a surface where we can control the identity of the layers and the separation.

Our group uses MVE alternating copolymers for this research. We have garnered expertise with these polymers and the ability to bond them to a surface either ionically[4,6,15-16] or covalently.[2-3,17] Polymerization has been accomplished through photo, thermal and radical initiation. Photoinitiation has been accomplished through UV irradiation of a polymer matrix containing di(4-vionxloxybutyl) succinate and 1,5 bis(maleimide)-2-methyl pentane.[5] The same polymerization has been accomplished through thermal initiation when the temperature was raised to 60°C in $CHCl_3$ (b.p. 60.5°C) for 24 hours. During

these polymerizations addition across the maleimide occurs both *cis* and *trans*, which is advantageous for the multilayer bonding scheme we wish to use in our research. The vinyl ether can also have a terminal phosphonate that allows ionic bonding to a substrate.[6]

This research has focused on covalent bonding because of the avoidance of polarizability of the Zirconium-Phosphonate(ZP) layer which can occur with an ionic bonding scheme. This polarizability can interfere with multilayer measurements which makes covalent chemistry an interesting alternative. It is also possible to use mixed layering of ionic and covalent chemistry[4] but the dominant technique in our research has been covalent chemistry.

By reacting an amine with maleic anhydride, the amic acid can be formed and then closed forming a substituted maleimide. The resulting substituted maleimides can be polymerized and covalently bound to a surface.[2-3] Using a substituent such as pyrene we can study the spectroscopy of the polymers in solution and on a surface. We have also investigated the adsorption of gases such as hexane and methanol using a Quartz Crystal Microbalance (QCM).[7] Data from these measurements show that our multilayer assemblies can in fact alter the adsorption behavior of surfaces.

My research has focused on studying the synthesis and morphology of a MVE polymer in the solution phase. MVE polymers are synthesized by radical polymerization[8-14] using the radical initiator 2-2'-azobisisobutyronitrile (AIBN). In this scheme the AIBN is heated and splits into two radical initiators. The radical attacks one monomer at the double bond creating a monomer radical. The

monomer radical attacks another monomer and a polymer begins to form. This oligomer (which has a radical at the end of it) will then attack other monomers lengthening the polymer chain. This reaction continues, creating an alternating copolymer.

To better understand the polymer, it is necessary to understand what chemical reactions are contributing to the growth of the chain. The two main variables in a polymerization reaction are monomer and initiator concentration. The monomer concentration is important because there must be enough monomer units activated to avoid chain termination effects. For example, if in a solution 3 chains were activated then these may be terminated very quickly. Termination occurs when a radical is in solution and reacts with a monomer radical thereby making it unreactive in a radical polymerization or can occur if two monomer radicals react with one another. If there are many chains being activated these termination effects become negligible and polymers begin to form. The other factor, initiator concentration, works in much the same way. It activates the monomers for polymerization but it cannot be used in great excess if a long polymer is desired. If the mixture is thought of as a finite solution of monomers too much initiator will be detrimental to the polymerization process. This excess initiator concentration creates too many starting chains and will create polymers with weights smaller than if a lower concentration of initiator is used. A lower concentration will create fewer chains and they will grow using the stock monomers available to them. With the fewer chains the polymers can grow to longer lengths in the same amount of monomer stock solution. A balance is

necessary in choosing a starting initiator concentration. With a low concentration of initiator the time of polymerization will increase. Therefore the amount of initiator used must be small enough to make polymers of sufficient length but not so low the polymerization process cannot be completed in a reasonable time.

At this point the polymers have been created and it can now be thought of how to bond them to the surface of a substrate. There are two possible methods of bonding polymers to a surface; ionically[4-6,15-16] or covalently.[2-3,17] In an ionic bonding scheme zirconium phosphonate (ZP) chemistry is utilized. This chemistry, while beneficial, can lead to difficulties in the spectroscopic measurements we intend to do because the ZP layer can be subject to polarizability. This polarizability will interfere with interlayer excitation transport thereby precluding their use in certain applications. Thus a covalent bonding scheme is used.

The procedure for covalent bonding of our polymer layers onto a hydroxyl terminated surface has been reported elsewhere[3]. The silanol functionalities on a hydrolyzed silicon surface can be reacted with polymers combining selected vinyl ether or maleimide side group reactive functionalities. The surface is activated using a diacid chloride and the terminal acid chloride is reacted with the vinyl ether side group functionality to bond the polymer covalently to the surface which has been accomplished using ester and amide bonds.

This thesis does not report on measurements taken with polymer layers bonded to a silica surface, such studies will be referred to in the future work chapter. At this point we are attempting to understand the morphological and

compositional issues associated with a synthesis of MVE polymers using one type of vinyl ether and two different maleimides. The issues of interest here are 1) relative reactivity of the maleimides and 2) morphology of the polymers made in a series of solvents of varying polarity.

The long term goal of this work is to gain the ability to synthesize a wide range of MVE polymers and to control the conformation of these polymers in solution. To accomplish these goals we use a statistical model to understand solution phase emission spectra of the chromophores. The morphology of polymers in solution and on the surface is important to understanding interlayer interactions, coating uniformity and free volume. Interlayer interactions will be essential knowledge if we are to understand how to construct a multilayer system with a pre-determined chemical potential for a given analyte.

Free volume will also be important for understanding the porosity of these films. Understanding the morphology in solution is the first step in this process and we use steady state spectroscopy to investigate this. The morphology of the polymers in solution should be related to how they will be bound to the surface (Figure 1.1). That is, if a polymer is linear in solution it can be bound to the surface in a linear way which may not be the case if the polymer is in a coiled conformation. It is also possible that a coiled conformation may not absorb to the surface as well as a linear polymer may.

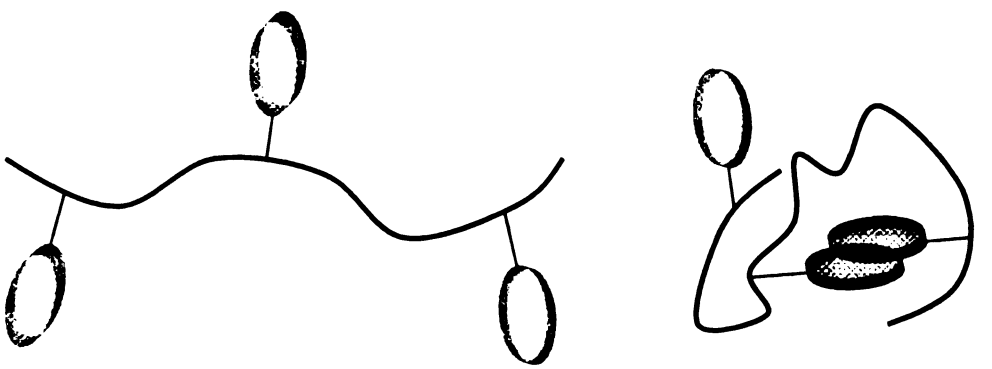

Figure 1.1 : Schematic drawing of a polymer in a linear (left) conformation and coiled (right) conformation. In a coiled conformation side groups may interact.

Adsorption to the surface is related to the availability of vinyl ether side groups to react with an activated surface. In a coiled conformation the chemically reactive side group could be sterically hindered and not available to react with the surface to the same extent as in a linear polymer. This information about the conformation is important knowledge when an attempt is made to build a structured chemical gradient system.

We probe polymer conformation in solution by monitoring the interactions between maleimide monomer side groups. Pyrene is useful because it easily forms excimers allowing facile examination of the interaction of our polymer chains. The spectroscopy of pyrene is well understood[18-29] and is easily integrated into our polymer synthesis using published reactions.[2] Pyrene readily forms excimers which prove very useful to this research.

Using pyrene as a fluorescent tag we can study the excimer properties of the polymer in solution. Excimers are useful because they describe the conformation of the polymer in solution based on the amount of excimer formed. Using pyrene as an example, an excimer is formed when a monomer of pyrene, M_1, is excited optically:

$$M_1 + h\nu \longrightarrow M^*$$

where M^* indicates a monomer in its first excited singlet state. The excited monomer can interact with another monomer, M_2, to form an excimer, D^*, as follows:

$$M^* + M_2 \longrightarrow D^*$$

The dimer signal is shifted strongly to the red portion of the spectrum. This shift is due to the different potential energy surface resulting from the interaction of the two monomers. This dimer then disassociates emitting a photon:

$$D^* \longrightarrow M_1 + M_2 + h\nu$$

The emitted photons are collected and the relative amounts of monomer and excimer are detected using emission spectroscopy. A monomer can absorb a photon and then emit the photon without forming a dimer. Thus, the concentration of monomer can have a direct effect on the amount of excimer formed in a fluorescence experiment.

Excimer formation is a diffusion controlled process. That is, a process by which the excimer formation is dependent upon the interaction between excited and ground state monomer units. Once a pyrene chromophore is excited it must find a ground state pyrene molecule within its fluorescent lifetime for an excimer to be formed. Thus, pyrene excimer formation is dependent on the concentration of pyrene in solution on a polymer chain.

Two limits can be identified for polymer morphology: linear (elongated) and coiled. This is pictured in Figure 1.2. If the polymer exists as a linear chain then the excimer concentration is predictable based on a statistical model. If it is a coiled system then the excimer concentration will be higher than predicted by the sample model. Due to the interaction of pyrenes that are not only adjacent to each other but nonadjacent pyrene as well because of the coiled conformation and the polymer bending into itself. This conformation allows for interaction

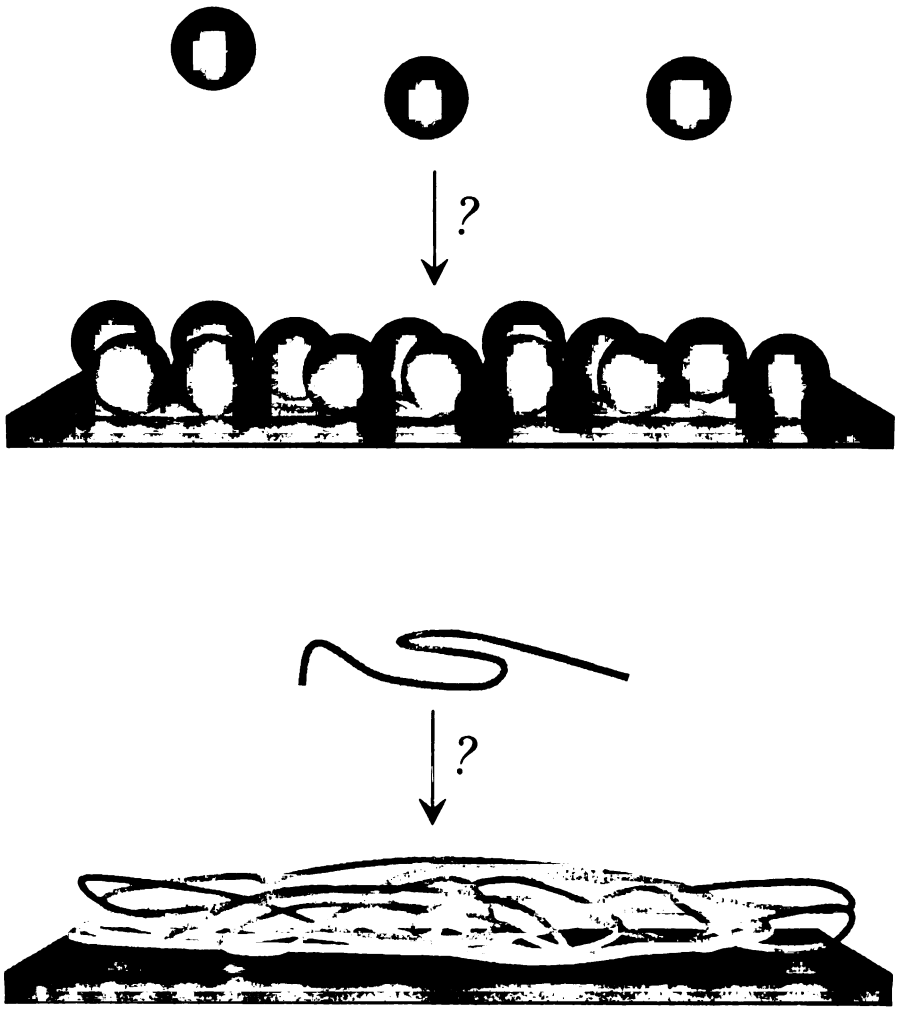

Figure 1.2: Representation of how polymers can be distributed on a silicon surface.

between pyrene functionalities not adjacent and an overall increase in the intensity of the excimer signal.

Using steady state fluorescence we can determine the amount of excimer relative to monomer. Excimer formation comes from pyrene chromophores interacting with each other. We would like to determine whether the polymers are straight chains in which there is a predictable excimer formation or whether they exist as coiled systems in which excimer formation is going to be higher than predicted by our statistical model.

In solution the coiled polymer conformation gives rise to excimer formation from interactions between adjacent pyrene side groups and non-adjacent pyrene side groups on the polymer chain. In a solvent that promotes "coiled" conformations excimer formation between non-adjacent pyrene side groups can occur. Excimer concentrations higher than what are predicted statistically can be attributed to coiled conformations of the polymer in solution.

This research allows us to understand the solution phase conformation(s) of our polymers. In the future we would like to compare solution phase and substrate bound excimer formation and determine which model, a coiled or straight chain, best fits the experimental results. If the data show a statistical excimer concentration then it can be assumed there is very little self association and the polymer exists as a straight chain in solution. If our data indicate a higher than statistically predicted excimer concentration then there is self association in solution and we have a coiled system.

Doing these experiments has led to a wealth of knowledge on the functions that influence the relative reactivity of monomers and the functions of MVE polymers. This picture rests on a number of assumptions and we seek to evaluate them in this work.

We discuss in Chapter 2 of this thesis the synthesis of a series of maleimide-vinyl ether alternating copolymers where the relative reactivity of two maleimide monomers are determined from experimental conditions. In Chapter 3 the analysis of these polymers of variable pyrene loading is done by emission spectroscopy and the results are analyzed. These results are then compared to a theoretical model and conclusions are drawn. Chapter 4 discusses methods that will be implemented to examine relative reactivity ratios and how all of the data will be used to give an overall picture of the synthesis and morphology of these MVE polymers of varying pyrene loading density in various solvents.

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Chapter 2

EXPERIMENTAL

N-Pyrenemaleimide monomer was first synthesized by the procedure given below.[1,3-4] This compound was then polymerized with N-Phenylmaleimide and 1,4-butanediol vinyl ether according to a literature procedure.[2,5] To obtain relative reactivities of the monomers the polymerization solution was sampled at various time and analyzed by ^{1}H NMR.

Synthesis of N-Pyrenemaleimide monomer:

This reaction is represented in Figure 2.1. To a 100 mL round bottom flask 1-aminopyrene (Fluka, 98%) and maleic anhydride (Acros, 99%) were added in a 1:1 mol ratio in chloroform (EM Science, 99.8%). The reactants were sealed with a septum and stirred for 12 hours at room temperature to give the insoluble amic acid derivative. The product was then collected by suction filtration and added to a 50 mL round bottom flask with 30 mL of acetic anhydride (CCI, 97%). To this vessel a 1:1 mole ratio of sodium acetate (J.T. Baker, 99.3%) and the previous product were added. The contents were heated to 70°C in a oil bath for 2-3 hours. The resulting product solution was then added drop wise to 300 mL of stirring distilled water (distilled in house). The solid precipitate was then collected by suction filtration and allowed to dry in the air overnight.

The solid was then analyzed by ^{1}H NMR, confirming the absence of a carboxylic acid proton resonance. The resonances from 7.8- 8.5 ppm are attributed to the protons on the pyrene rings. At 7.2 ppm are the maleimide C=C

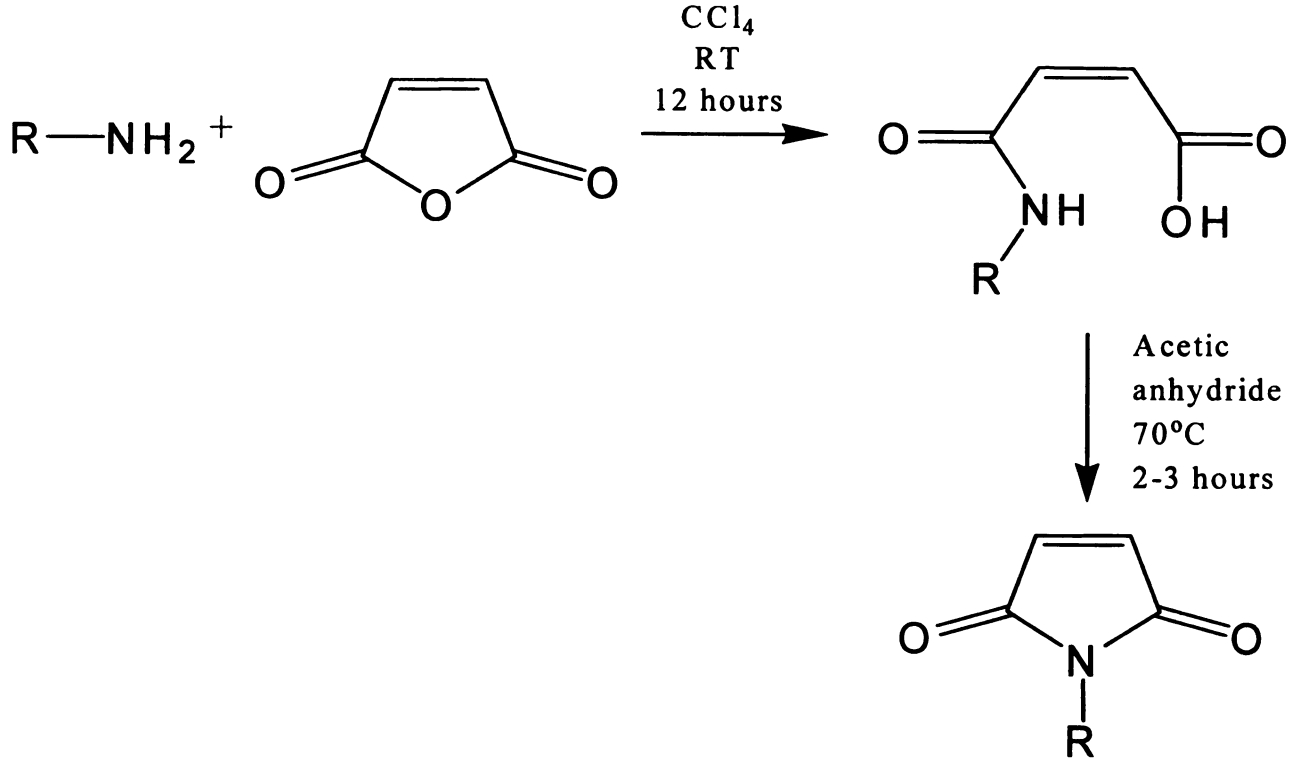

Figure 2.1 : Synthesis of substituted maleimide. R can be pyrene or another desired functionality.

allenyl protons and the large resonance at 3.25 ppm is water, a product of the amic acid ring closure dehydration reaction. At 2.5 ppm is the resonance for the reference solvent (DMSO)-d^6. This monomer was stored for later use in MVE polymer synthesis.

N-Pyrenemaleimide, AIBN (Aldrich, 98%) 1,4-butanediol vinyl ether (Aldrich, 99%) and chloroform were obtained from Aldrich and used as received. N-pyrenemaleimide was synthesized using the above procedure and used as is.

Polymerization of N-Pyrenemaleimide, N-Phenylmaleimide and 1-4-butanediol vinyl ether:

An MVE polymer was created using the monomers listed above. The reaction scheme is displayed in Figure 2.2. The monomer concentrations in solution were modified to create varied fractions of N-pyrenylmaleimide in the polymer.

To a 50 mL round bottom flask the monomers were added in 30 mL of chloroform and 1-2 mol % of AIBN was added as a radical initiator. The reactants were refluxed at 70°C for approximately 24 hours under an inert atmosphere of argon. The solution was then concentrated by rotary evaporation until approximately 5-10 mL of the solution remained. The resultant product was then added dropwise to hexanes (Jade Scientific, 98.5%) or diethyl ether (CCI, 99%) and the precipitant was collected by suction filtration.

This solid was analyzed by ^{1}H NMR (Figure 2.3) confirming the presence of both pyrene and phenyl chemical shifts. The protons due to the pyrene moiety. are found from 7.8 – 8.5 ppm. The phenyl resonances are

Maleimide Vinyl Ether Polymer Synthesis

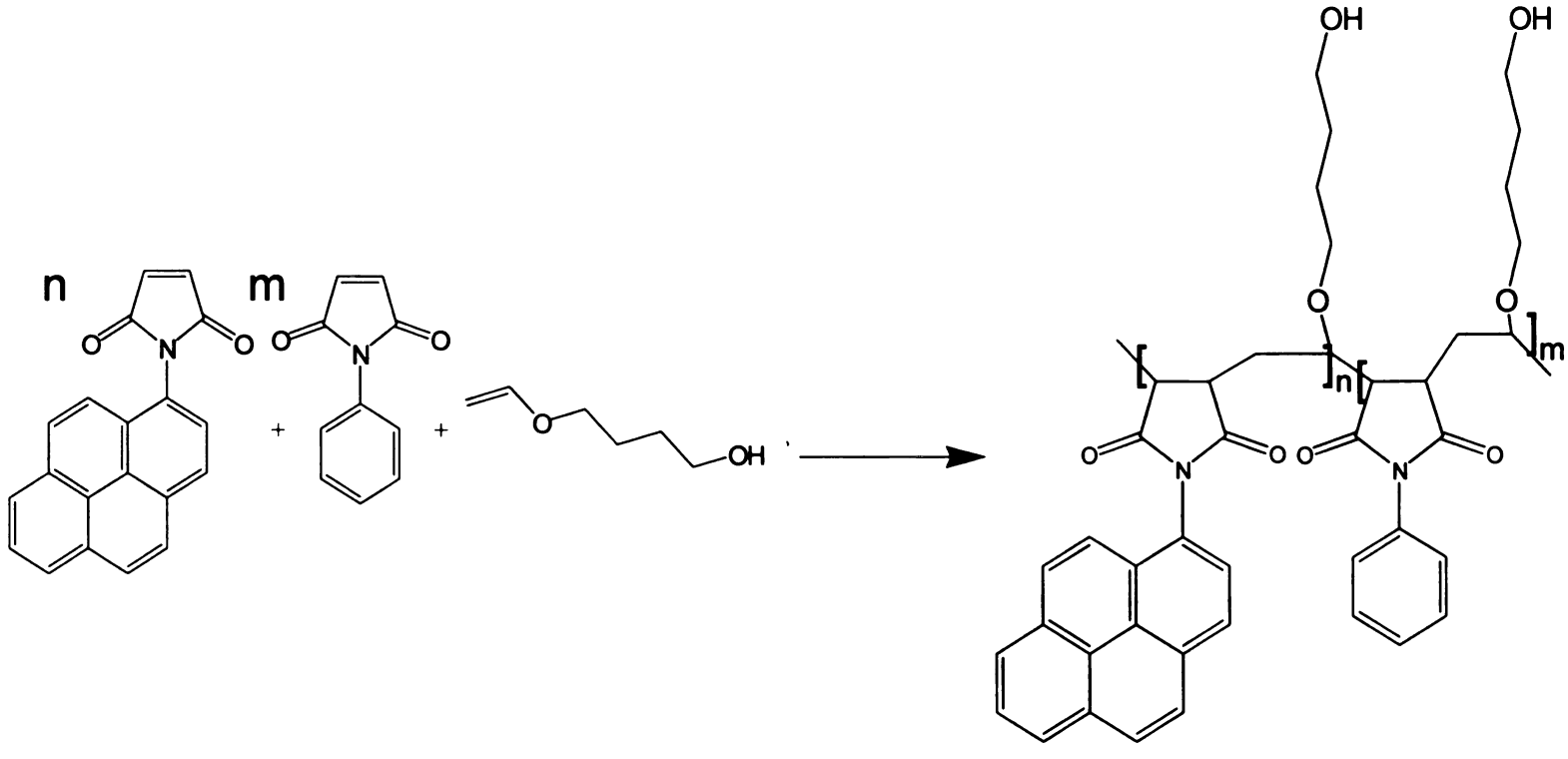

Figure 2.2: Synthesis of a maleimide vinyl ether polymer using a three monomer system. The coefficients n and m can vary based on solution stiochiometry.

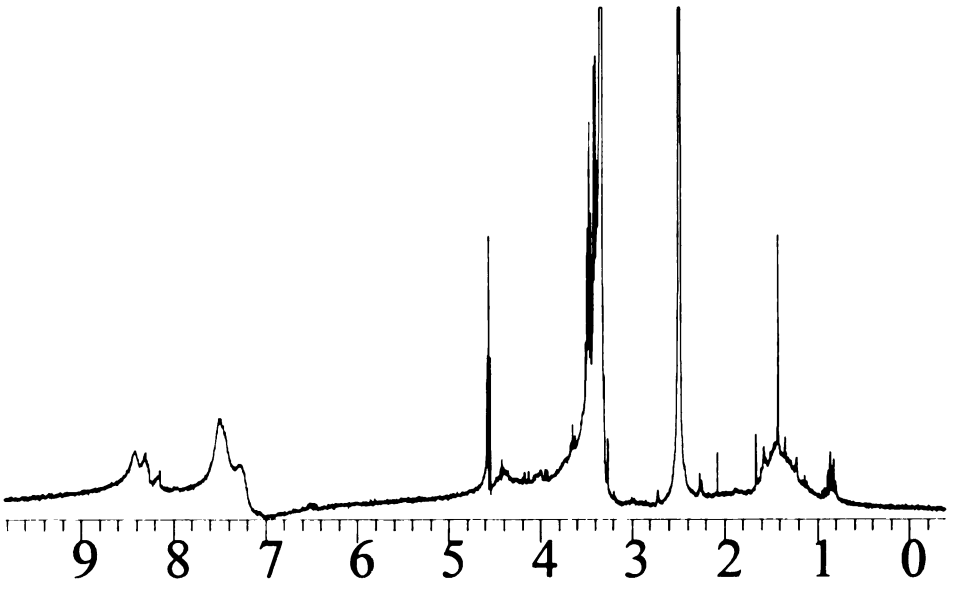

Figure 2.3: ^{1}H NMR of a MVE polymer synthesized with N-pyrenylmaleimide, N-phenylmaleimide and 1,4-butanediol vinyl ether

from 7.2 to 7.6 ppm. The large peak at 3.2 ppm is water from the solvent used in analysis by ^{1}H NMR From 1 to 2 ppm we see broad resonances due to the loss of vinyl character of the maleimide protons and the protons on the vinyl ether used.

Sampling of reaction mixture for NMR analysis:

During synthesis a polymerization reactions were sampled and analyzed by solution phase ^{1}H NMR spectroscopy. The measurements were performed according to the following procedure. The round bottom flask was disconnected from the reflux condenser column and a ~1 mL sample was removed using a Pasteur pipette. The reaction was continued following replacement of the reflux condenser column. The reaction aliquot was concentrated by rotary evaporation to ~0.5 mL and the resultant solution was added drop wise to ~30 mL of di-ethyl ether. This mixture was stirred for approximately 20 minutes and a portion, ~5 mL, was then added to a disposable glass test tube. The test tube was then centrifuged and the supernatant was removed. This was done to separate the polymer from the solution containing both monomer and polymer. The solid was allowed to air dry and was analyzed by ^{1}H NMR.

Gel Permeation Chromatography:

Gel Permeation Chromatography experiments were performed using a Waters Breeze GPC system. This system consists of a Waters 2414 Refractive Index Detector, Waters 2487 Dual wavelength absorbance detector, Waters 1515 Isocratic HPLC pump and Waters 717+ Autosampler. The wavelength of detection was 254 nm and the flow rate was 1mL/min. The analysis was done

using Breeze software provided by Waters. The column was Stragel HR 4E THF dimensions 7.8 X 300 mm (part# WATO44240). Samples were prepared by dissolving 1mg per mL of polymer in the mobile solvent, THF with BHT inhibitor.

Fluorescence Spectroscopy:

Fluorescence data were acquired using a Spex-J4 Flurolog3 fluorescence spectrophotometer with a slit width of 1 nm and an excitation beam of 317 nm. The data were collected and analyzed using SpectraAcq software.

Nuclear Magnetic Resonance:

NMR data were obtained using a 300 MHz Varian NMR. All samples were compared to a reference solvent, deuterated DMSO. All samples were scanned 64 times and a Fourier Transform was applied. Data were then transferred and analyzed using the computer program Mestrec.

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Chapter 3

RESULTS AND DISCUSSION

It is the intention of this research to demonstrate knowledge of the reaction conditions and an understanding of the properties of the polymers being synthesized. To achieve this goal, samples are analyzed by ^{1}H NMR and GPC. NMR will discern the relative concentrations of pyrenyl and phenyl side groups present in our polymers and can also be used to indicate how much of the polymer is forming. GPC will give an understanding of the polymer chain length.

The goal of this research is to examine the length and composition of the polymers being synthesized during the reaction and after completion. The length will give us an understanding of whether or not the polymer size fits our theoretical model which assumes each chain consists of about 10 monomer units. A value greater than 10 monomer units has little effect but a value smaller than this would create a highly variable distribution because one monomer unit would cause a large fractional change in the composition of the chain. Composition is important because we are studying the excimer formation of the polymer sidegroups in solution. We need an understanding of the order of the monomer units and whether or not there is a statistical distribution of monomer units on the polymer.

In an ideal situation the pyrenyl side group loading density would be directly proportional to the fractional concentration of pyrene monomer in solution. For example, if we added a 10% concentration of pyrene maleimide

relative to phenyl maleimide and we assume 10-unit chains the amount of pyrene on each chain would be 1 out of 10. If we were to change it to 20% then there would be 2 out of 10. Through ^{1}H NMR we intend to measure the relative concentrations of phenyl and pyrenyl side groups using procedures developed for other systems.[1-2]

GPC can be used to analyze the molecular weight and distribution of the polymers. The polymers should be of sufficient length so they can be compared to the theoretical model that has been constructed. Polymers of at least 10 monomer units should be sufficient for this comparison.

Analysis of polymers by NMR:

It is important to examine the reactivity of N-pyrenylmaleimde and N-phenylmaleimide during the reaction. This issue relates directly to the monomer reactivity ratios for each monomer unit. Equimolar amounts of N-pyrenylmaleimide and N-phenylmaleimide were reacted in solution with 1,4-butanediol vinyl ether. We wish to synthesize polymers where the concentration of each monomer unit on the polymer equals that which we add to solution. If this is not possible then we wish to know to what degree this deviates from a statistical distribution.

Polymers were analyzed by ^{1}H NMR and Figures 3.1, 3.2 and 3.3 show the pyrenyl and phenyl side groups present in the polymer. The signals were integrated and from these data the relative amounts of each side group were determined. The relative amounts of pyrene and phenyl signals are not equal to the amounts found in solution. ^{1}H NMR indicates there is more phenyl maleimide

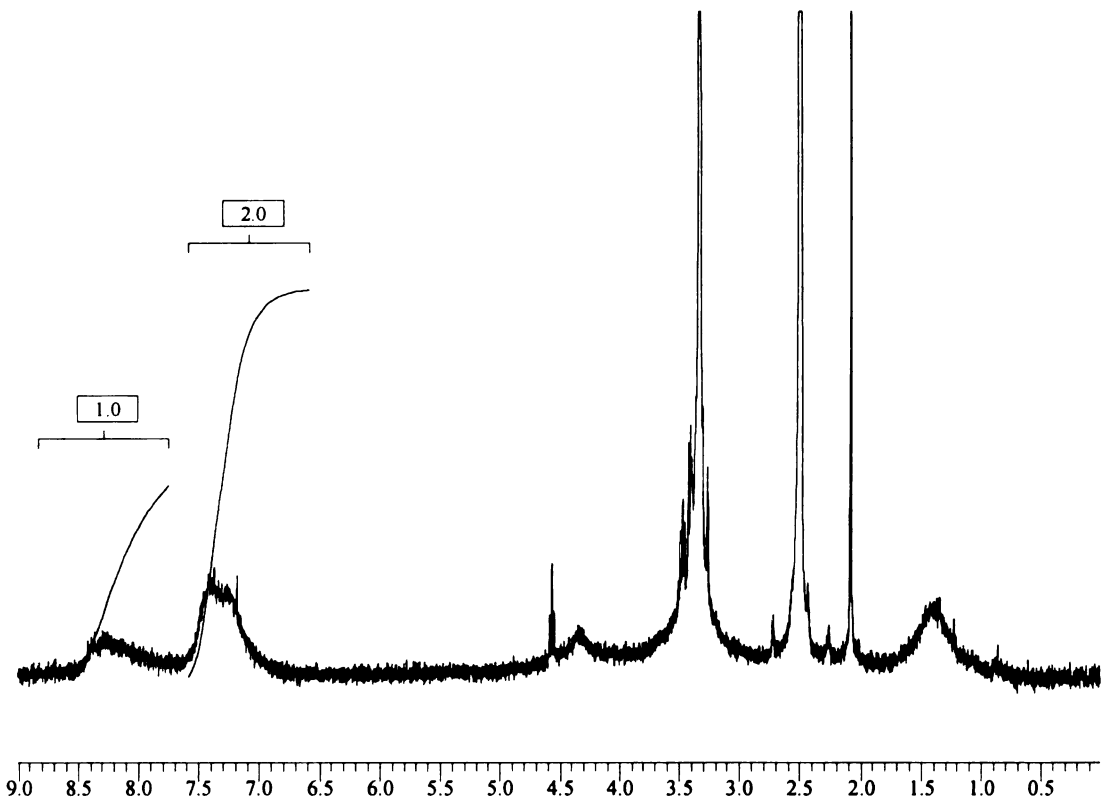

Figure 3.1: NMR spectrum of a polymer containing 3:1 phenyl:pyrene at 3hrs of reaction. Numbers above peaks are integrations

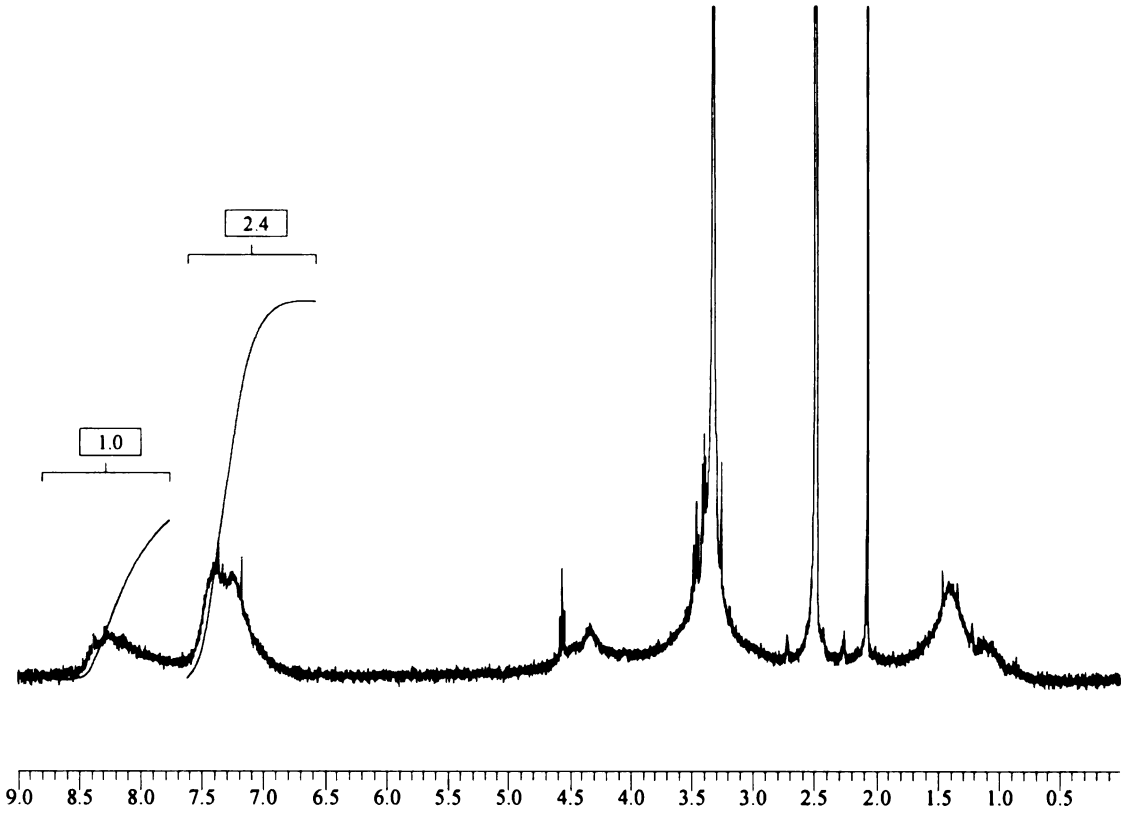

Figure 3.2: NMR spectrum of polymer containing 3:1 phenyl:pyrene at 6hrs of reaction. Numbers above peaks are integrations

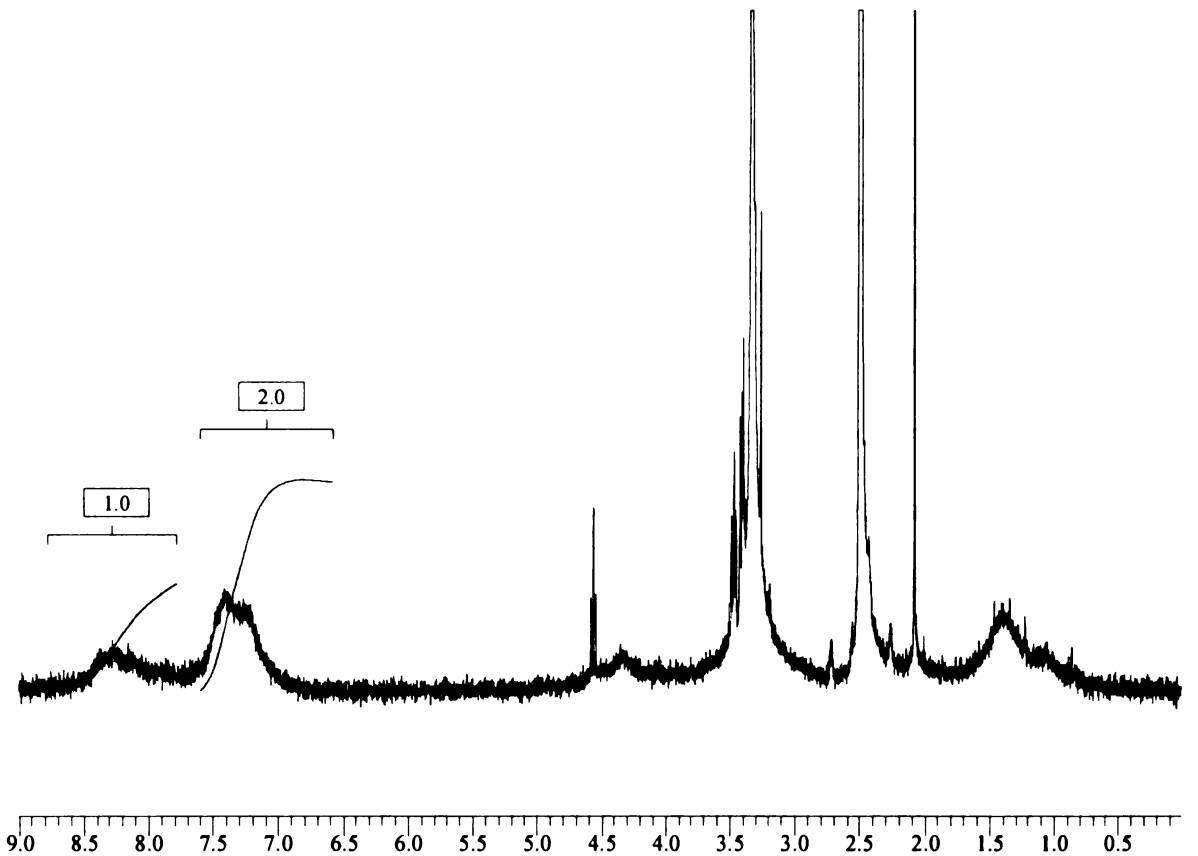

Figure 3.3: NMR spectrum of polymer containing 3:1 phenyl:pyrene at 9hrs of reaction. Numbers above peaks are integrations

incorporated into the polymer than would be expected from the solution phase stoichiometry. The N-phenylmaleimide monomer is more reactive toward vinyl ethers than N-pyrenylmaleimide. Monomer reactivity is influenced by a number of factors which may include differences in the polarity of the monomers or sterics of the monomers in the reaction. We can make simple arguments to analyze the significance of polarity and sterics.

These monomers would not differ significantly in polarity because the only difference between the two is the substitution, pyrene vs. phenyl, on the maleimide. One could argue the π electrons in the pyrene rings could cause a difference in the dipole moment of the N-pyrenylmaleimide in solution but such a difference would be negligible in importance. The position is also important in that the attack on the maleimide ring is of substantial distance from the substitution on the maleimide and would not be a large factor in the overall reactivity of the maleimdes in solution.

Steric issues are more likely to play a discernible role. The pyrenyl and phenyl maleimides are significantly different in size. The size of the maleimide monomers matters in the reaction because if the sterics are restricting on one monomer the other will be more reactive in solution. Using this argument one can see the phenyl ring is less restricting than the pyrene ring structure when compared with one another. Therefore the phenyl maleimide can be more reactive when compared to the pyrene maleimide in solution.

As figures 3.4 and 3.5 show the steric argument seems to explain our data. Throughout the reaction ^{1}H NMR spectra were taken and analyzed for pyrenyl and phenyl components of the polymer. The ratio of sidegroups incorporated should be the same as the solution phase reactant concentration ratio if the monomers are equally reactive. What we find is that the two maleimide monomers are not equally reactive, with the phenyl maleimide being the more reactive species. ^{1}H NMR analysis indicates for a reaction starting concentration ratio of 1:1 (phenyl:pyrene) maleimide side groups, the resulting polymer incorporation is ~ 1.5:1 (phenyl:pyrene). This difference can be attributed to the additional bulk of N-pyrenylmaleimide.

Based on this result we modified the reaction conditions in an attempt to compensate for the added bulk of the pyrenyl side group by reducing the amount of N-pyrenylmaleimide in solution and increasing the amount of phenyl maleimide. When the solution ratio of phenyl:pyrene was changed to 3:1 a ratio of 4:1 (phenyl:pyrene) on the polymer chain was found by ^{1}H NMR analysis. This ratio is more comparable to our initial concentrations of each monomer in solution. It also shows the monomer reactivity has changed and the difference in reactivity between the two monomers has been reduced. These results give us control of how much pyrenyl maleimide is incorporated in the polymer during polymerization.

The sterics of the reaction play a potentially important, if ill-defined role in controlling the distribution of pyrenyl and phenyl maleimides on the polymer chain. When equimolar amounts of pyrenyl and phenyl maleimide monomers are

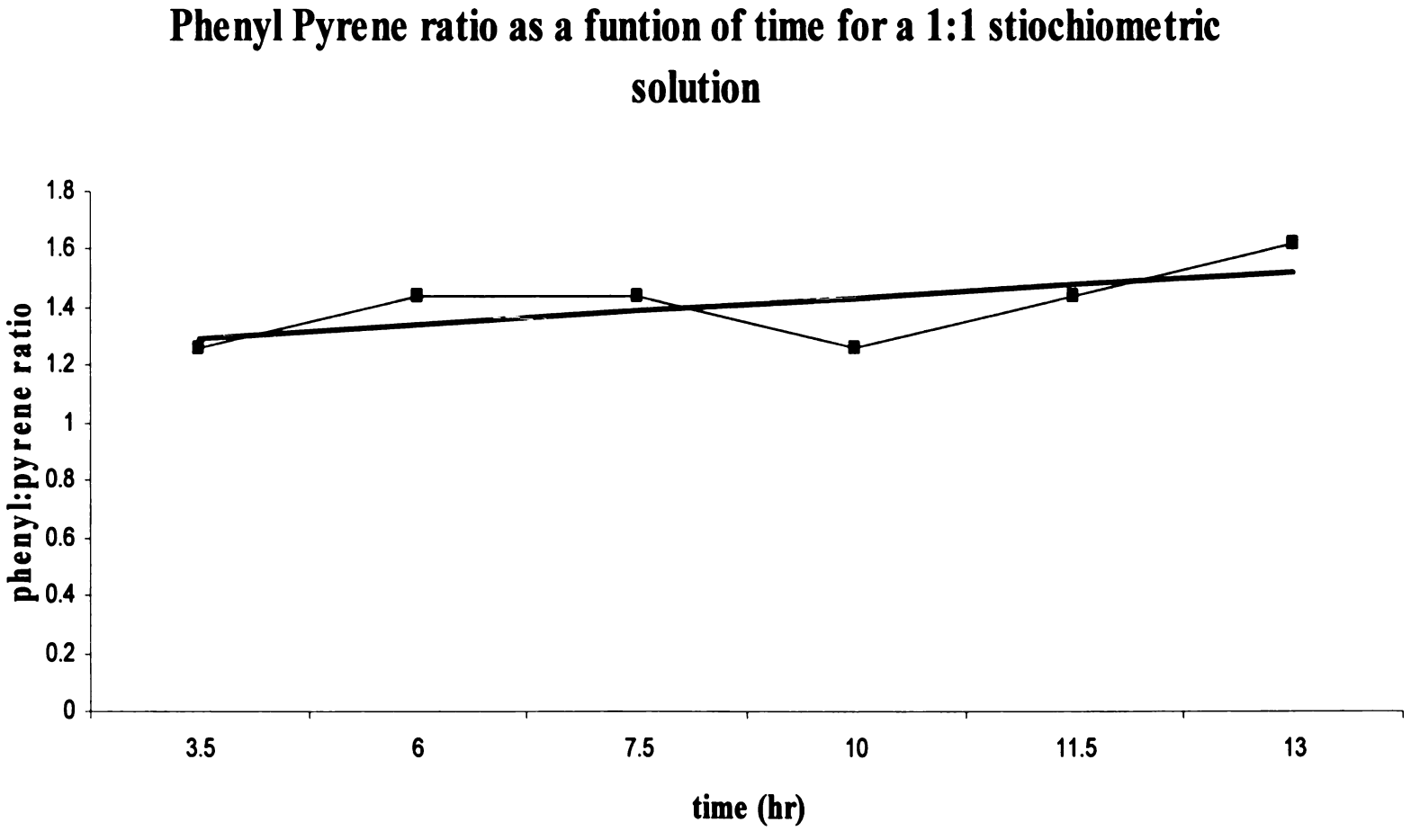

Figure 3.4: Phenyl:Pyrene ratios on MVE polymer chain as analyzed by NMR over time

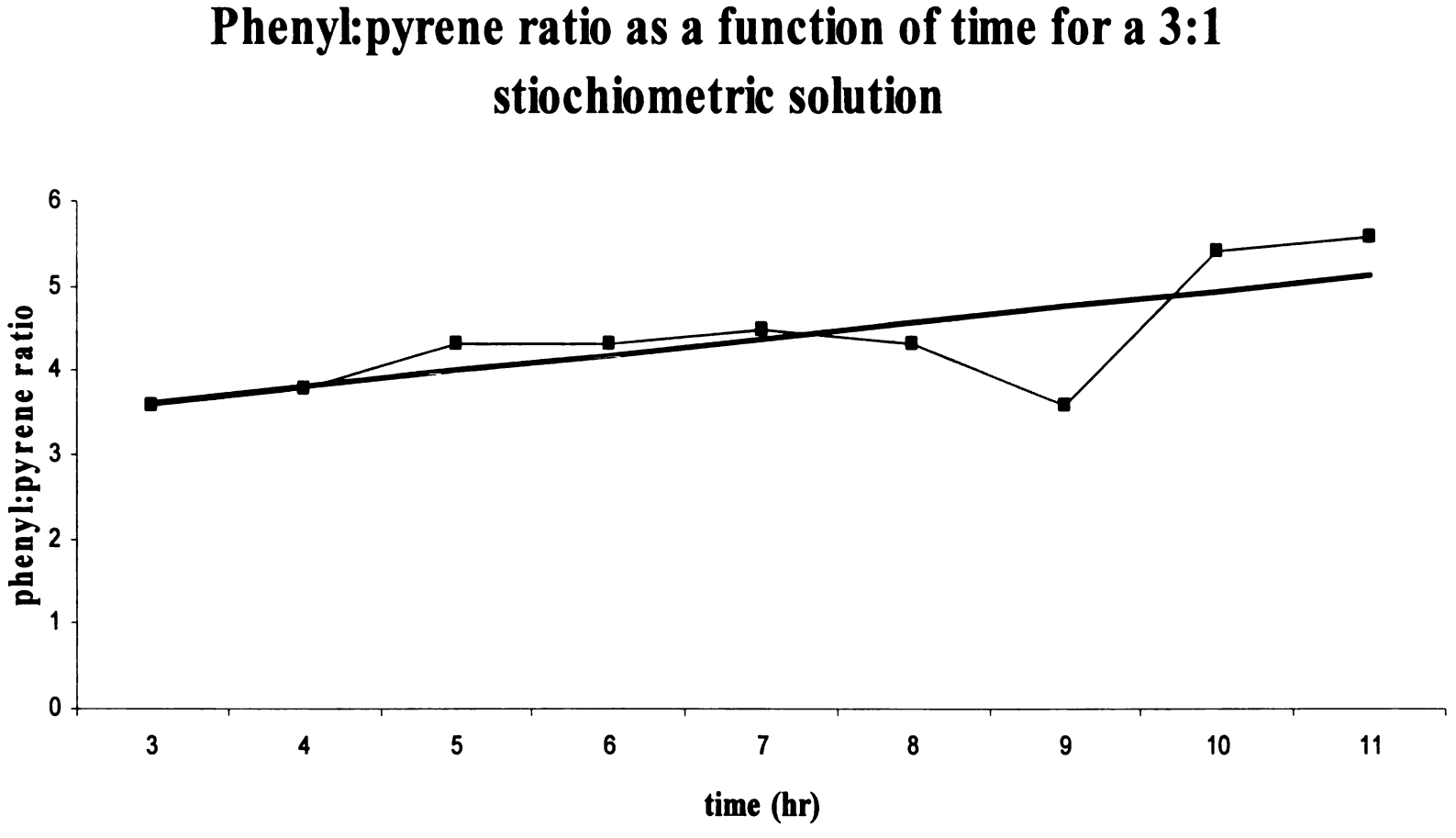

Figure 3.5: Phenyl:Pyrene ratios on MVE polymer chain as analyzed by NMR over time

added, the relative reactivity of the monomers is different. The mixture has been changed to reduce these steric influences by increasing the amount of N-phenylmaleimide in solution and this has had an effect on the selectivity of the monomers during polymerization. Our data indicate the phenyl:pyrenyl ratio does not change significantly with time. Future research will use N-pyrenylmaleimide in low concentrations to avoid these undesirable effects of having a nonstatistical amount of pyrenyl maleimide.

To this point the diffusion coefficients of each monomer have yet to be examined in this thesis. The hydrodynamic volume of each monomer can be calculated according to a method developed by Edward.[3] The hydrodynamic values of N-phenylmaleimide and N-pyrenemaleimide were found to be 150 $Å^3$ and 250 $Å^3$, respectively. If we apply these values to the Stokes-Einstein equation:

$$D^0 = kT/6\pi\eta r$$

where D^0 is the diffusion coefficient, k is the Boltzmann constant, T is temperature in K, η is the viscosity of the solvent and r is the Van der Waals radius of a sphere. Since both maleimides are in the same solution T and η are the same and the D^0 is proportional to 1/r. Using the r values found above we find D^0 is equal to 1.67×10^{-7} cm^2/s for N-phenylmaleimide and 1.0×10^{-7} cm^2/s for N-pyrenylmaleimide. Thus the diffusion coefficient for each maleimide is different from each other but not to the degree of what is found in the ^1H NMR data. We conclude that diffusion does play a role which may be comparable to the role

sterics play in the polymerization process. Future work will be dedicated to determining the degree diffusion plays in the polymerization process.

While NMR has been useful in determining the concentrations of pyrenyl and phenyl sidegroups on the polymers synthesized it can only be used to describe average concentrations in these polymers. It does not describe the position of these functionalities on the polymers. For example, NMR can be used to analyze a polymer of 10 monomer units at a concentration of 40% pyrene. NMR can indicate there are 4 pyrene units on the chain but it cannot tell us the position of these units. The difference between 4 units being adjacent to each other or being at other positions on the chain is indistinguishable by NMR. While this is true, the fact that the phenyl groups are more reactive than the pyrenyl precludes bonding or pre-aggregation of the monomers being incorporated and thus their distribution on the polymer chain. This point is important in our modeling of these polymers. To understand the excimer formation properties of the system we must have an understanding of the position of the monomer units on the polymer chain. It has been found the phenyl maleimide is incorporated into the chain more readily than the pyrenyl maleimide. This does not interfere with our statistical model in that we can adjust it to compensate for this.

At this point we are able to understand the relative concentrations of each of our monomer units on the polymer chains but not able to discern the position of these units. We consider the statistical model mentioned above following a discussion of the polymer M_w and M_n, because the results are relevant to determining the applicability of a statistical model. This information is important

when we compare our results and fluorescence measurements to our statistical model. If the polymer is of too few monomer units then the experimental data will not hold to the assumption the polymers follow a statistical distribution of monomer units.

GPC analysis of polymers:

GPC results indicate the polymers M_w values vary between 3000 and 16000 Daltons. This variation results from the reaction conditions used. Specifically, the concentration of monomer and the amount of initiator influence the M_w and M_n of the resulting polymers in predictable ways. Polydispersity Index (PDI) values have varied between 1.3 and 2 depending on reaction conditions. It has been found that the longer the chain, the more polydispersity in the polymer. For polymers with 16,000 (M_w) the PDI equals 2.

Initiator concentration has a substantial effect on the M_w of our polymers. Our initial experiments used 10 mol% of initiator. This initiator concentration resulted in polymers with a M_w of ~3000. Reduction of initiator concentration to 1 mol% resulted in a M_w of ~7000. To increase the M_w further the concentration of monomers was increased resulting in a M_w of ~16000 which is the highest value seen to date.

We have investigated the excimer properties of the polymers in various solutions using fluorescence spectroscopy. The excimer properties of pyrene containing polymers have been studied in the literature[4-7] and this method is used in determining whether the polymers exist as a straight chain or coiled conformation. We have examined our polymers in dilute solutions to reduce the

amount of intermolecular association between polymer chains and to compare these fluorescence measurements to a statistical model. If excess excimer fluorescence, above that predicted by a statistical model is seen, then it is attributed to intramolecular association of the pyrene on the polymers. This excess excimer formation leads to the conclusion the polymers exists in the coiled conformation. This experiment is done in several solutions where the solubility of the polymers varies to some degree. When the solubility of the polymer is low it will coil and intramolecular interactions will increase.

Figure 3.6 shows the fluorescence spectrum of pyrene at two concentrations, 0.06 μM and 0.05M. There are several features evident in these spectra. There are discreet vibronic transitions due to pyrene from ~370 to 400 nm. There is a broad featureless band between 425 and 500 nm due to excimer formation in solution.

Fluorescence measurements were made in three solutions, cyclohexane, acetonitrile and Dimethylsulfoxide (DMSO). The polymer solubility varies considerably in these solvents. The polymer is very soluble in DMSO, slightly less soluble in acetonitrile, and only slightly soluble in cyclohexane. This varying solubility gives us a model of what a coiled conformation may exhibit when excited. Figure 3.7 is an emission spectra of the polymers synthesized with differing concentrations of pyrene on the polymer. All spectra contain both monomeric and excimeric bands. As the pyrene loading on the polymer chains is increased, the amount of excimer observed in each spectrum also increases.

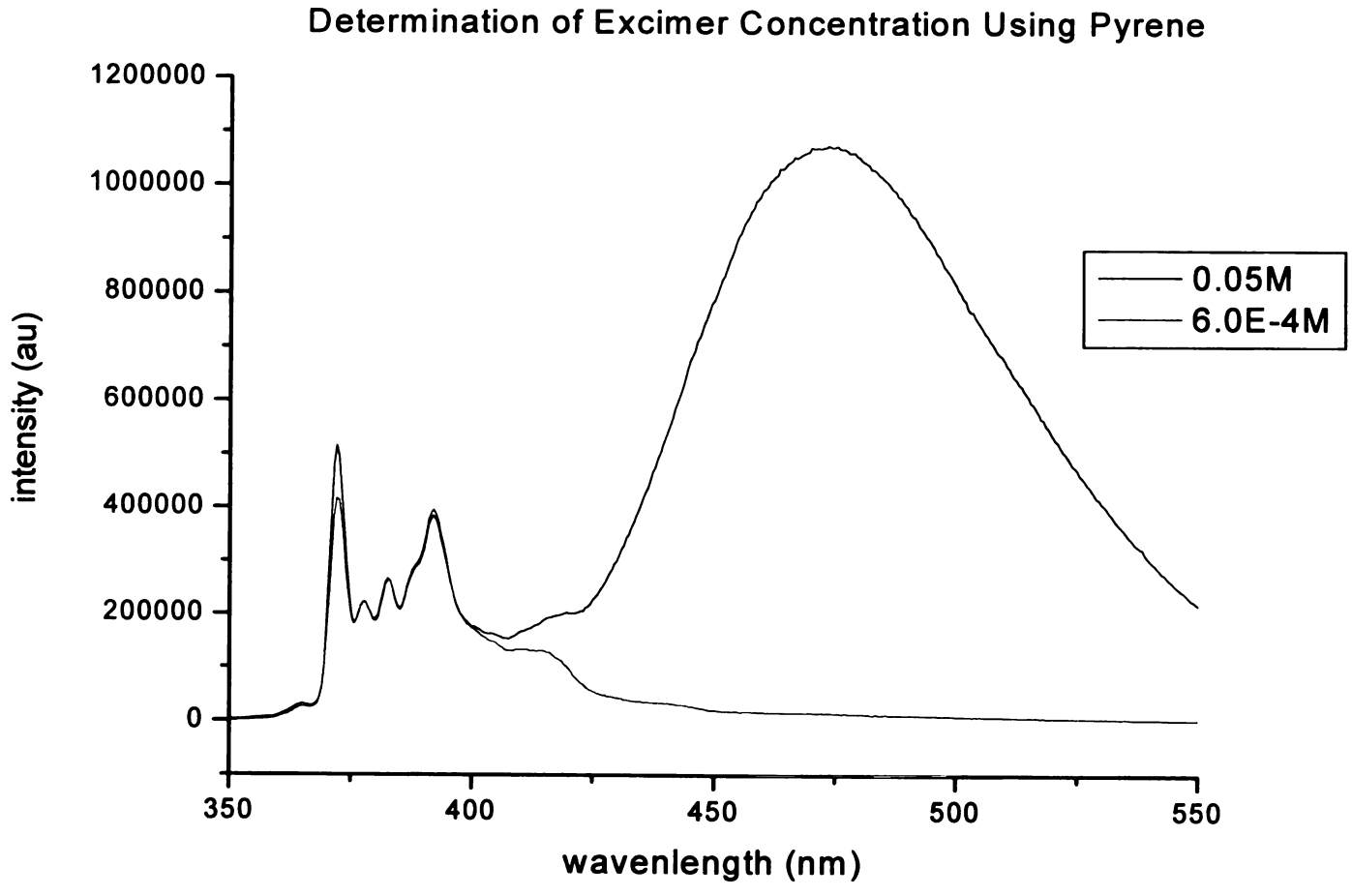

Figure 3.6: Fluorescence spectrum of pyrene at high (0.05M) and low (0.6uM) concentrations

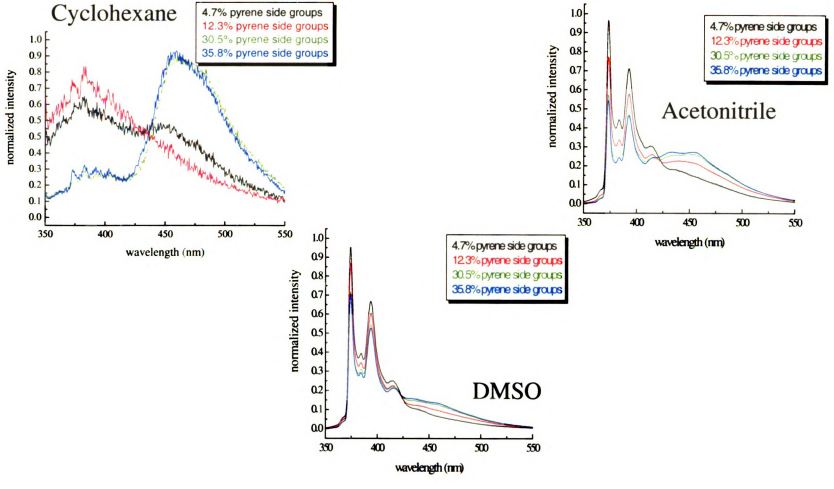

Figure 3.7: Fluorescence spectra of pyrene containing MVE polymers with various pyrene loading density in various solvents

This is expected as an increase in the concentration of pyrene on the polymer will lead to increase of the probability of adjacent pyrenes forming excimers. The issue at hand is the comparison of the experimental data to our model.

Acetonitrile is a "good" solvent, meaning the polymer is soluble in it. A "poor" solvent is one in which the polymer is insoluble. The solvent used to determine an insoluble conformation is cyclohexane. Figure 3.8 exhibits the polymer emission response in cyclohexane for X% pyrene loading. It can be seen that the excimer band is more intense than the monomer bands in contrast to the acetonitrile spectrum (Figure 3.9) where the monomer bands are more intense than the excimer bands under conditions of similar pyrene loading density and polymer concentration.

The intensification of the excimer band relative to the monomer band is due to the polymer being in a coiled conformation because of the insolubility of the polymer. The excimer band is more intense because there is more interaction between the pyrenyl side groups. The interaction is not only from adjacent side groups but also from nonadjacent pyrenyl groups on the same polymer chains. With the polymer in a coiled conformation this interaction is possible, if the polymer is in a more linear conformation this interaction is less frequent. This difference is evident in the acetonitrile spectrum where the excimer band is much less intense when compared with the monomer band. The polymer is more soluble in acetonitrile so it will exist in a more predominately linear conformation and there will be fewer interactions between nonadjacent pyrenyl sidegroups giving rise to a less intense excimer band.

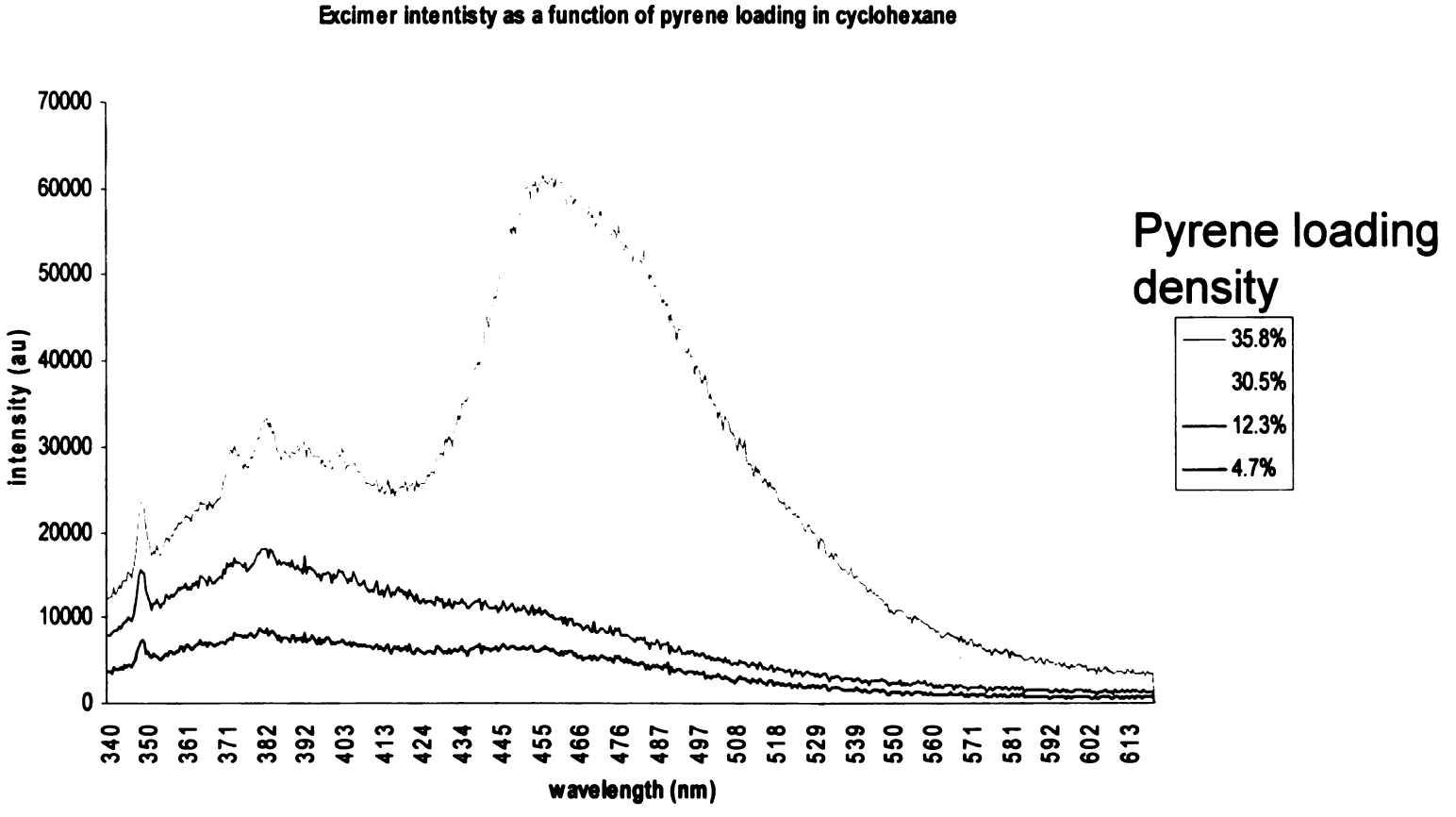

Figure 3.8: Excimer intensity of pyrene containing polymers in cyclohexane

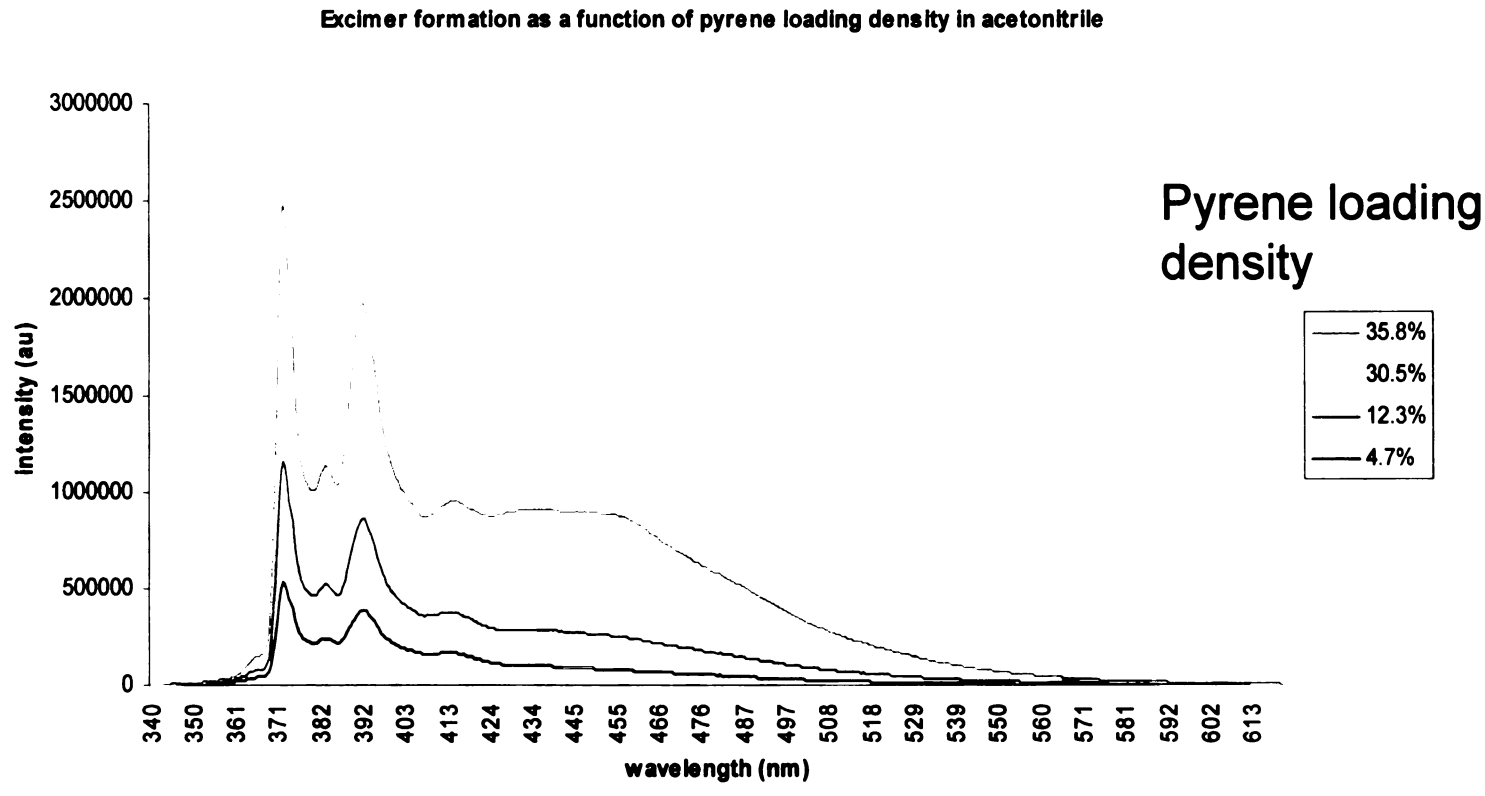

Figure 3.9: Excimer intensity of pyrene containing polymers in acetonitrile

These experimental results have been compared to a theoretical model. The polymer has been assumed to be linear and the theoretical model predicts the probability of excimer formation found as a function of loading density on the polymer chain.

The theoretical model was obtained by assuming our polymers consist of linear chains. We assume these are 10-monomer chains for convenience. We further assume if pyrenes are adjacent to one another on the polymer chain they will form an excimer upon excitation with a probability equal to unity. Finding the distribution of pyrene on the polymer chain is calculated by:

$$\text{Combinations} = n!/x!(n-x)!$$

where n the number of monomer units possible on the chain and x is the number of pyrene units possible on the chain. For example, if we use a 10 monomer unit chain and a concentration of 20% pyrene in solution then n equals 10 and x equals 2. Combinations refer to the number of ways the phenyl and pyrenyl side groups can be arranged. This calculation tells us the number of combinations a pyrene can occupy based on concentration and length of chain. What must be found is the degeneracy of the combinations because one pyrene is no different from another. For example if pyrene A occupies position 3 and pyrene B occupies position 6 for our experiment it is no different than if pyrene A occupied position 6 and pyrene B occupied position 3. When this is taken into account we can find the number of unique combinations of monomers adjacent to one another and divide this by the total number of combinations to find the probability

of excimer forming. We can assume the probability upon excitation of a pyrene molecule is either going to form a monomer or excimer:

$$P(m) + P(x) = 1$$

where P(m) is the probability of monomer and P(x) is the probability of excimer upon excitation. We can find the probability of monomer using the above method to find the probability of excimer formation, P(x). We can determine the probability for a variety of pyrene loading densities and determine the amount of excimer we would expect based on this statistical model (Figure 3.10). Note the excimer probability is unity at 60% pyrene loading concentration since there is no way to add 6 pyrenes to a 10 unit chain without at least two of the pyrenes being next to each other.

Also displayed in Figure 3.10 is how ± 1 pyrene per chain, relative to the expected loading will affect the probability of excimer forming. For example, a pyrene loading concentration of 10% predicts that one pyrene will be found on each 10 unit chain. While this is the most likely possibility there will be some chains that will have 2 pyrenes and some will have no pyrene. This probability may be small but it can occur and if the 2 pyrenes are adjacent then excimer can form. This uncertainty will affect the measurement and has been factored into the model when comparing the experimental data to it. The uncertainty will allow a small amount of excimer to be found for chain loading concentrations where it may not be obviously possible. This uncertainty has been determined by assuming the pyrene distribution on the polymer chain will follow a Gaussian function. If this is the case the error will be $\pm 1\sigma$. The deviation in a 20%

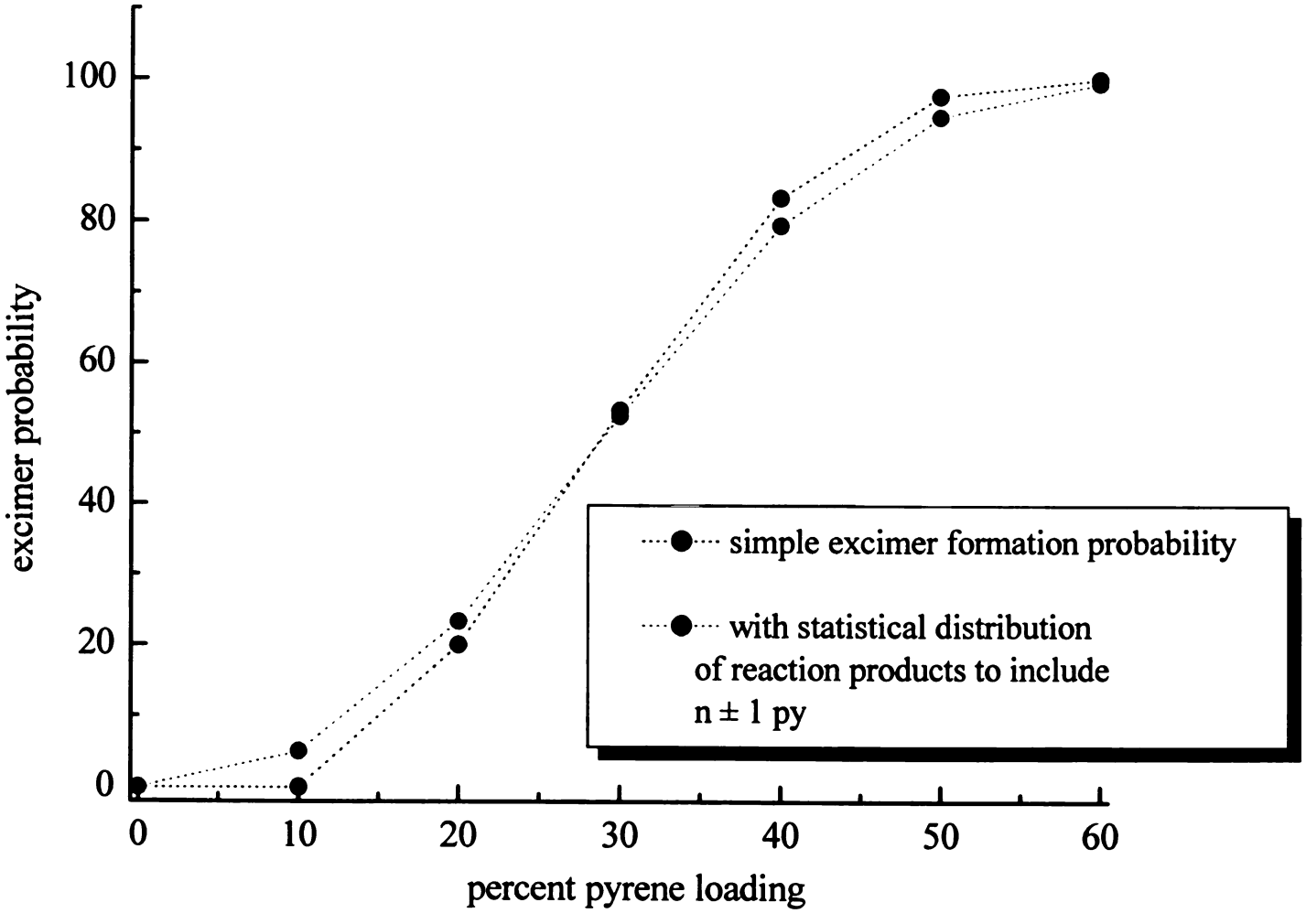

Figure 3.10: Excimer probability as a function of pyrene loading

measurement would therefore contain 10% and 30% pyrene possibilities. This has been factored into the curve and displayed in the figure. This model assumes polymer forms linear chains and tells us any deviations that appear will manifest as more excimer formation than the model predicts because of intramolecular association of nonadjacent pyrenes.

The experimental data were determined by obtaining fluorescence spectra of the polymers in various solvents. By knowing a particular pyrene concentration will give a certain fluorescence we determined the amount of excimer formed in each of these solvents. This was done for polymers of various pyrene loading densities and compared to our statistical model.

A comparison of the experimental data to the theoretical model is shown in Figure 3.11. Experiments have shown the polymers exhibit excimer intensity above what is predicted statistically. This is due primarily to the conformation of the polymers in these solutions. The polymer is least soluble in cyclohexane and, as expected, the excimer to monomer intensity ratio is highest in this solvent. The polymer exhibits less excimer formation for acetonitrile and DMSO. This is also expected as it is more soluble in each of these solvents. Overall the polymers seem to extend but some amount of coiling in all of these solvents due to the much higher than statistically predicted excimer intensity. This comparison of experimental data to the theoretical model leads us to conclude the polymers exist in a coiled conformation and not the linear chain that was expected.

It is important to understand these polymers were not created using the experimental condition as described above. The initiator level used was much

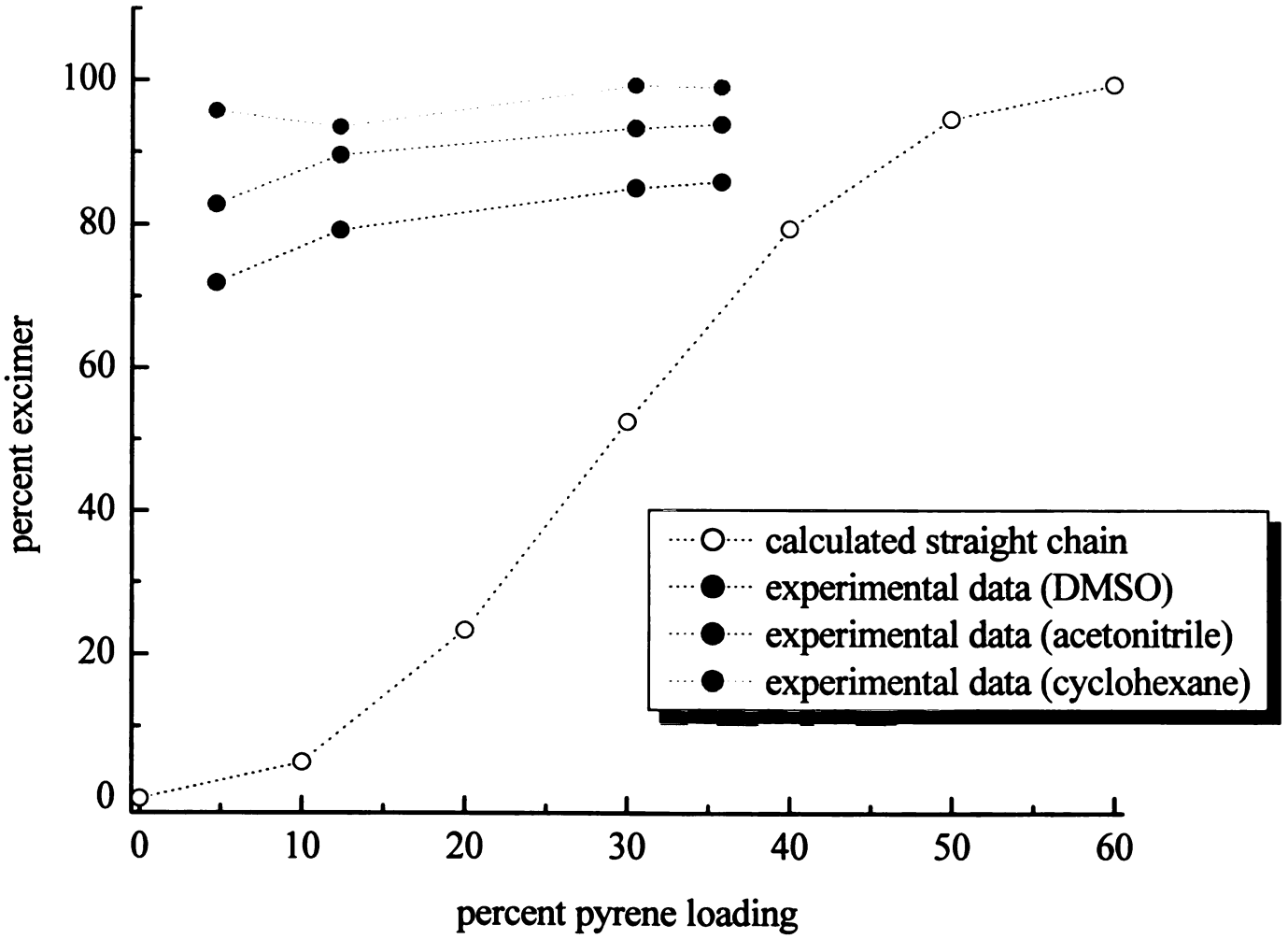

Figure 3.11: Comparison of experimental and statistical results

higher than what we have used recently and this will affect the amount of pyrene on the polymer to a large degree. It is expected that these polymers that were formed early on vary greatly in the amount of pyrene on the polymer chain. This variation is due to the polymers being less than 10 monomer units in length. Pyrene addition to a polymer of small length will dramatically change the concentration on the polymer as opposed to a longer chain polymer. These polymers might vary a great deal when being compared to our model system and could lead to erroneous results. Work is now being done to understand the consumption of the monomers involved in the polymerization and to repeat the experiments. These polymers may have a more statistical distribution of pyrene on the chain and will exhibit less excimer which will affect the comparison. For this reason the results here should be interpreted as illustrative rather than indicative of a polymer created under more controlled conditions.

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Chapter 4

CONCLUSIONS AND FUTURE WORK

This thesis has described the synthesis of MVE polymers and the morphology of the polymers in various solvents. Using a published synthesis N-pyrenylmaleimide was synthesized and then integrated into a radical-initiated polymer synthesis. The polymers were then added to several different solvents in which the solubility of the polymer varied. Solutions in which the polymer was insoluble exhibit high excimer fluorescence. When the polymer was soluble in a solvent the excimer intensity decreased. This was then compared to a theoretical model in which two assumptions were made. Excimer intensity is due to adjacent interactions of pyrene on the polymer chain and the chain is linear as to not have any interaction between nonadjacent pyrene. Comparison of the experimental results to the theoretical model indicates the polymer is in a coiled conformation in solvents such as cyclohexane and intramolecular interactions are occurring. In solvents such as DMSO where the solubility is higher intramolecular interactions are not as dominant and excimer formation follows a more statistical or linear trend.

Future work is being focused on finding the monomer reactivity ratios to find if the polymer is statistical or blocky in nature. This work is important to the model because if we attribute excimer fluorescence to adjacent pyrenes on a polymer there must be a statistical distribution of these pyrene units on the chain. If the polymer is blocky then the pyrene will not follow a statistical distribution.

This will lead to excimer formation from effects that are not due to the polymer morphology. Excimer will form due to polymer morphology and from the blocky nature of the polymer. If these polymers form in a blocky nature comparison to a statistical model will be difficult.

Work has begun to describe whether or not these polymers formed are blocky or statistical. In order to do this we must study how the monomers are consumed in the reaction as it proceeds. Thus, the reaction must be sampled and analyzed at points in the reaction to understand how the monomers are consumed during the polymerization process.

Absorbance spectroscopy is the method of monomer analysis we are using presently. Absorbance spectroscopy could prove useful because each monomer could be resolved using this technique. The N-phenylmaleimide can be resolved from the N-pyrenylmaleimide based on the different absorbance of the phenyl and pyrene functionalities. What would be needed are the extinction coefficients of each monomer.

The extinction coefficients can be found using Beer's Law:

$$A=\epsilon bc$$

Where A is absorbance, ϵ is extinction coefficient, b is the path length of the cell in cm and c is concentration in mol/liter. A plot of absorbance as a function of concentration will yield a slope equal to the extinction coefficient. The plots for each monomer are shown in Figure 4.1 and 4.2. The extinction coefficient for N-phenylmaleimide was found to be 17200 L/mol-cm at 220 nm, and the extinction

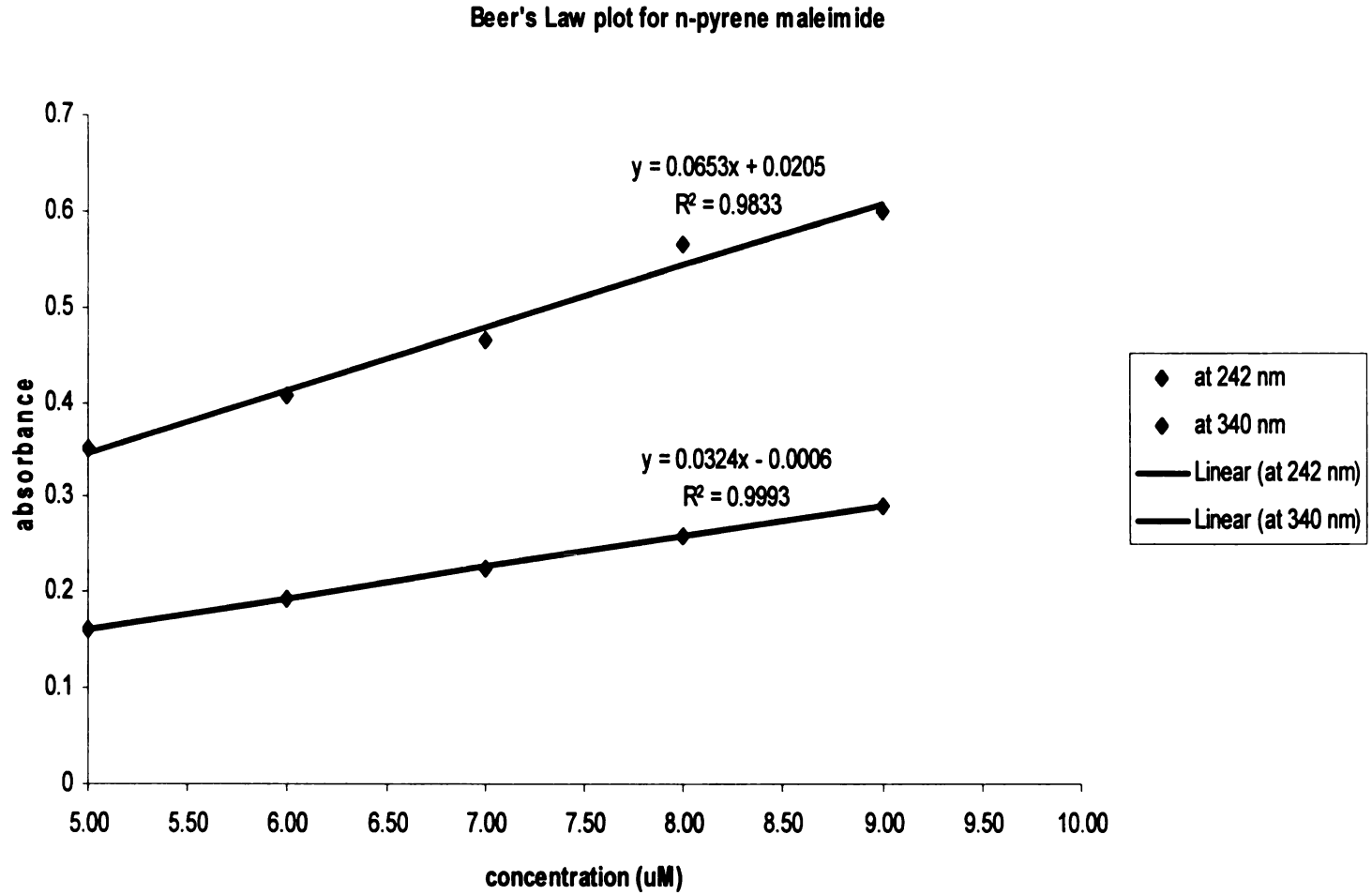

Figure 4.1: Beer's law plot for n-pyrene maleimide. Extinction coefficient is equal to slope

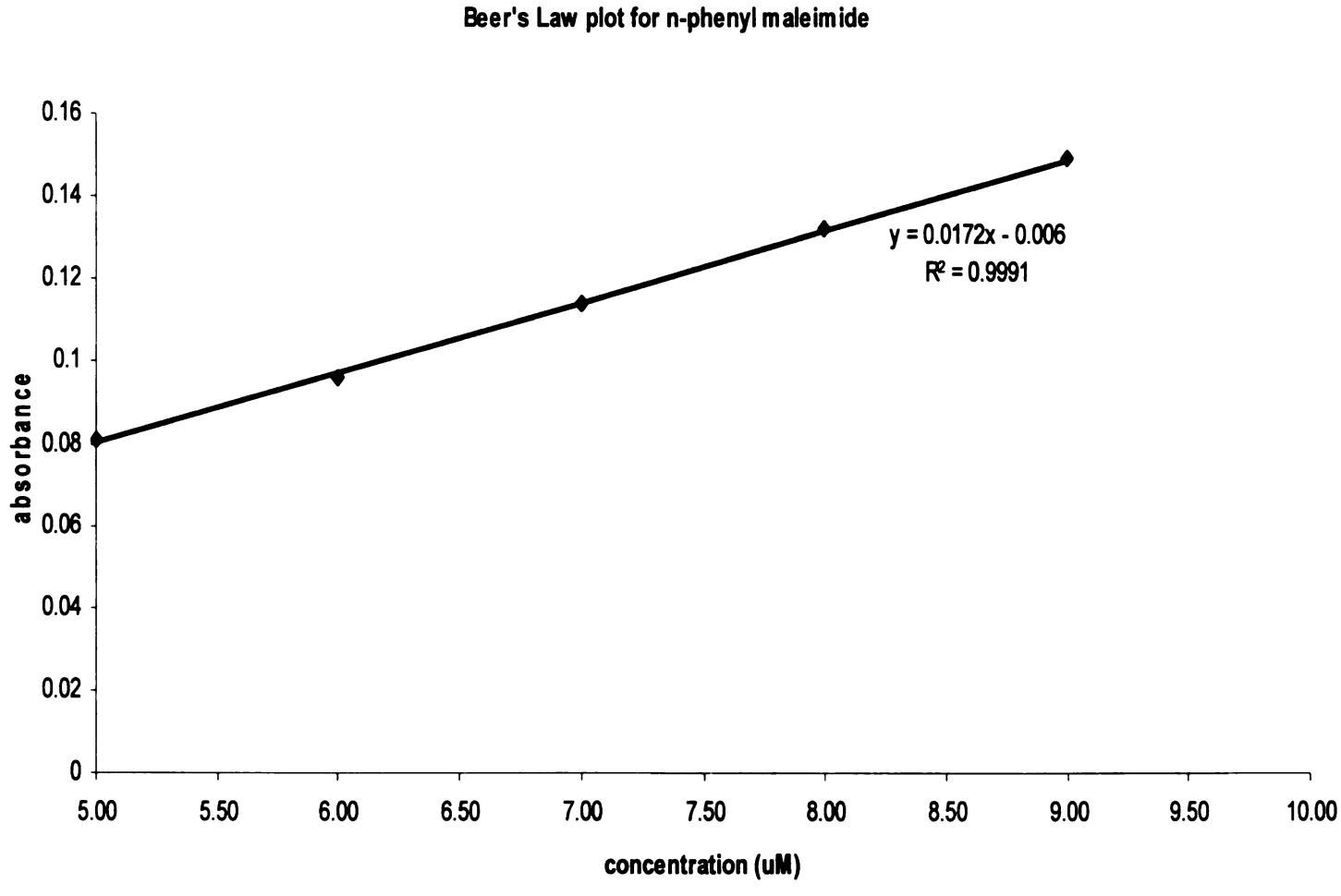

Figure 4.2: Beer's law plot for n-phenyl maleimide. Extinction coefficient is equal to slope

coefficient for N-pyrenylmaleimide was found to be 65300 L/mol-cm at 242 nm and 32400 L/mol-cm at 340 nm.

What we intend to do now is to sample the reaction mixture and to analyze the samples by absorbance spectroscopy. By finding the absorbance at specific wavelengths and using Beer's Law the concentrations of each monomer can be found in solution. These concentrations will be examined if each monomer is being reacted at the same rate. The monomer reactivity information can be used to find if the polymer forming is blocky or statistical.

After this aspect has been examined the polymers will be adsorbed to a silica surface using the chemistry described previously. The excimer to monomer ratio for bound polymer on the surface will be examined and this information will allow evaluation of whether or not the morphology of the polymer on the silica surface is related to that in solution.