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Kinetic study of styrene/maleic anhydride copolymers using succine anhydride as the model compound

Barbara M. Jauch

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KINETIC STUDY OF STYRENE/MALEIC ANHYDRIDE COPOLYMERS USING SUCCINIC ANHYDRIDE AS THE MODEL COMPOUND

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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE

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ABSTRACT

The reaction of aniline with succinic anhydride, a low molecular weight poly[styrene-co-(maleic anhydride)], and a high molecular weight poly[styrene-co-(maleic anhydride)] were used to determine if these polymer reactions are diffusion- or reaction-controlled. Kinetic study protocols were developed to determine the rate constants for the succinic anhydride/aniline model reaction and for the 50/50 and 86/14 copolymers. These protocols were then used to gather kinetic data.

The succinic anhydride/aniline reaction was determined to be exothermic and to have an induction period. The succinic anhydride/aniline reaction was also determined to have an experimental rate constant of 13 L/mol min ± 25% at 67 ± 1.5 degrees Celsius. For the copolymer/aniline reactions, the experimental rate constants at 67 ± 1.5 degrees Celsius were determined to be .051 L/mol min ± 15% for the 50/50 polymer and .008 L/mol min ± 18% for the 86/14 polymer. The model reaction was found to be 250 times faster than the 50/50 polymer/aniline reaction and 1600 times faster than the 86/14 polymer/aniline reaction. The 50/50 polymer/aniline reaction was determined to be 6 times faster than the 86/14 polymer/aniline reaction. At 20 ± 1.5 degrees Celsius, the theoretical diffusion-controlled rate constant for the succinic anhydride/aniline reaction was determined to be 7.09 x 10^{11} L/mol min and the experimental rate of reaction was determined to be 0.72 L/mol min ± 25%. Thus, these reactions were determined to be reaction-controlled.
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INTRODUCTION

The modification of polymers is very important in polymer science. Three reasons for modifying polymers include: 1) to give the polymers new properties, 2) to combine the polymer with a nonpolymer in a composite, and 3) to probe molecular structure and dynamics. As mentioned above, new properties can be given to polymers through modification. Three properties which can be given to polymers via modification are interfacial, adhesion, and catalytic properties. Also, rigid thermoset materials can be formed via modification. Affinity supports which can be used in the isolation and purification of enzymes or immunodiagnostic systems can be made by modifying polymers. Finally, the strength of a polymeric material can also be enhanced by this process. (1)

Probes are compounds which possess a chemical trait that can be used to study a polymer's properties. There are four types of probes which can be used, including: 1) NMR, 2) ESR, 3) phosphorescent, and 4) fluorescent. These probes need to be added on to the polymer in order to study the properties of interest. One way to attach a fluorescent probe to a polymer is by chemically modifying a polymer using a nonpolymeric fluorescent compound.

There has been little research done on reacting amines with maleic anhydride containing polymers. Most of the work which has been done seems to concentrate on synthesizing poly(amic acids) and poly(imides) versus functionalizing the backbone of a polymer chain. For this study, the kinetic
parameters of the reactions of succinic anhydride, a low molecular weight poly[styrene-co-(maleic anhydride)], and a high molecular weight poly[styrene-co-(maleic anhydride)] with aniline will be analyzed. This kinetic data for the formation of amic acid will be compared and used to determine if these reactions are diffusion-controlled.

Organic polymers can be chemically manipulated in the same way as small organic molecules. They can be used as reactants in chemical reactions and they follow the same conventional functional group chemistry as small molecules.(1) These manipulations can also be considered chemical modifications of the polymer backbone. One way to chemically modify organic polymers is via nucleophilic attack of the polymer containing an appropriate functional group.

The presence of cyclic anhydride in a polymer structure enables attachment by primary amines to produce imides. The reaction of aniline with the backbone of poly[styrene-co-(maleic anhydride)] is an example of this type of reaction. This reaction occurs via acylation, or introduction of an acyl group (RC=O) into a compound.(2) Acylation can be accomplished by nucleophilic addition-elimination of aniline (amino group) on to the saturated maleic anhydride (carboxyl group) in the polymer backbone. It occurs by nucleophilic attack on the carbonyl of the substituted succinic anhydride by the amine of the aniline.(3,4) This reaction is the simplest homologue of a series of reactions
using aniline derivatives. The products can be used in fluorescence and fluorescence-quenching studies.

The acylation of anhydrides by amines has been carried out for different amines and anhydrides, including cyclic anhydrides. \(^{(2, 3, 4, 5, 6)}\) The reaction conditions for the reaction of aniline with succinic anhydride, based on Fieser's protocol \(^{(6)}\), are listed in Table I. Figure I contains the general reaction.

Table I: Reaction conditions for the reaction of aniline with succinic anhydride, according to Fieser's protocol \(^{(6)}\)

| Preparation of N-phenylsuccinamic acid: |
| Solvent:       | benzene       |
| Temperature:   | refluxing benzene |
| Reaction time: | immediate     |
| Stoichiometry: | 1:1 succinic anhydride:aniline |

| Preparation of N-phenylsuccinimide: |
| Solvent:       | benzene       |
| Temperature:   | refluxing benzene |
| Reaction time: | approximately 5 minutes |
| Stoichiometry: | 1:8 N-phenylsuccinamic acid:acetyl chloride |

The purpose of this study is to compare the reaction rate constants of succinic anhydride, low molecular weight poly[styrene-co-(maleic anhydride)], and high molecular weight poly[styrene-co-(maleic anhydride)] with aniline. These rate constants will be used to determine if the reaction is diffusion-controlled. The reaction of the succinic anhydride in the polymer backbone with aniline can be looked at in terms of small organic molecules or as a simple
Figure I: The general reaction for aniline with succinic anhydride. (6)

\[
\text{CH}_2\text{CO} + \text{H}_2\text{NC}_6\text{H}_5 \xrightarrow{\text{Refluxing Benzene}} \text{CH}_2\text{CONH}_6\text{H}_5
\]

N - phenylsuccinamic Acid

\[
\text{CH}_2\text{CONH}_6\text{H}_5 + \text{CH}_3\text{COCl} \xrightarrow{\text{Refluxing Benzene}} \text{CH}_2\text{CO} \text{NC}_6\text{H}_5 + \text{CH}_3\text{COOH} + \text{HCl}
\]

N - phenylsuccinimide
reaction of an amine with an anhydride. Thus, the reaction of succinic anhydride with aniline will be used as the model reaction for the reactions of poly[styrene-co-(maleic anhydride)] with aniline. Fieser's protocol for synthesizing N-phenylsuccinamic acid will be used to develop the model reaction for this study by modifying the reaction and reaction conditions. These modified reactions and conditions will be used in reaction kinetics studies.

Infrared spectroscopy (FTIR) is a technique which can be used to characterize all anhydrides, amic acids, and imides. It will be used to characterize the intermediate, N-phenylsuccinamic acid, and the product, N-phenylsuccinimide. For N-phenylsuccinamic acid, there are three characteristic peaks which must be identified. Table II contains these structures and peak regions(3).

Table II: Characteristic peaks of N-phenylsuccinamic acid.

<table>
<thead>
<tr>
<th>Type (structure)</th>
<th>Region (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>secondary amine (-NH-) and carboxylic acid (COH)</td>
<td>3500 - 3300 (two bands)</td>
</tr>
<tr>
<td>amide (RCONH-)</td>
<td>1700 - 1640</td>
</tr>
<tr>
<td>carboxylic acid (=C=O)</td>
<td>1725 - 1700</td>
</tr>
</tbody>
</table>

Also, the loss of the anhydride stretches (1840 - 1800 cm\(^{-1}\), usually two bands) can help to show that the anhydride has reacted.(3) For succinimides, "in the
infrared, an intense band is found between 1750 and 1700 cm\(^{-1}\) (antisymmetric) with a less intense band or shoulder between 1800 and 1750 cm\(^{-1}\) (symmetric).\(^{(7)}\) These peaks can also be seen for N-phenylmaleimide\(^{(8)}\) and should appear in the spectrum for N-phenylsuccinimide. These bands should be useful in identifying the intermediates and products for the polymer reactions.

Kinetic data is necessary to study the reactions of aniline with succinic anhydride and the polymeric anhydrides. This kinetic data can be used to determine if the reaction is exothermic or endothermic. Also, kinetic data can be used to determine the energy of activation of the reaction and the rate constants associated with the model and polymer reactions. The following discussion presents kinetic results gathered from the recent literature.

Acylation of amines by anhydrides have been shown to be both autocatalytic and exothermic.\(^{(5,9)}\) In a textbook on amide chemistry, edited by Zabicky, a chapter authored by A.L.J. Beckwith describes the synthesis of amides. Beckwith states that “acylation with anhydrides appears to be catalyzed by acid; in the absence of an excess of added acid the process is usually autocatalytic.”\(^{(5)}\) K.K. Kalnin'sh, a Russian researcher, studied the autocatalysis of phthalic anhydride with aniline derivatives. Research previous to this study showed that this reaction has an autocatalytic character. The results of the phthalic anhydride/p-toluidine reaction study showed that the kinetic curves produced the S - shape characteristic of autocatalytic reactions.\(^{(9)}\) Figure II gives a representation of this S - shaped curve. This reaction was performed in a solvent system of chloroform/acetonitrile. Heats of
Figure II: Kinetic curve for the reaction of phthalic anhydride with p-toluidine.(9)

"Kinetic curves for the reaction of phthalic anhydride with p-toluidine in CHCl₃ + 1 vol. % CH₃CN (1, 1') and in CH₃CN (2, 2'): A) direct reaction; B) reverse reaction; C) "oscillations" near equilibrium."(9)
reaction for different phthalic anhydride/aniline derivative reactions were all
determined to be negative by Kalnin'sh. (9) Table III presents the values
obtained by Kalnin'sh. et al.

Table III: Heats of reaction for the reactions of phthalic anhydride with different
amine derivatives in I) 4 Vol. % Acetonitrile and II) Acetonitrile.(9)
With relative errors of +/- 10 %.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Solvent</th>
<th>- ΔH (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Anisidine</td>
<td>I</td>
<td>52.3</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>57.7</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>I</td>
<td>49.7</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>55.6</td>
</tr>
<tr>
<td>Aniline</td>
<td>I</td>
<td>48.1</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>53.5</td>
</tr>
</tbody>
</table>

Thus, these reactions were all shown to be exothermic. The heat of reaction is
important in the analysis of kinetic data because if the reaction is performed in a
non-refluxing solvent, then the temperature of the reaction will actually change
over time. Whether a reaction is endothermic or exothermic can be determined
by recording the temperature of the reaction solution over time and graphing the
temperature versus time. If there is an increase in temperature over time then
the reaction is exothermic. If there is a decrease in temperature over time then
the reaction is endothermic.

Although aniline and succinic anhydride can be used as a model reaction,
the fact that the anhydride is actually part of the polymer must be considered.

By being part of a polymer, the anhydride has less ability to move around in
solution. Thus, this constraint can affect the reaction of the aniline with the anhydride group. The following three processes can also affect the overall reaction rate when one reactant is a polymer, compared to both reactants being small molecules:

1) mass transfer from the bulk liquid phase to the outer "surface" of the polymer.

2) diffusion of the reactant to the functional group within the polymer.

3) the intrinsic reaction itself at the site of the functional group.

Generally, small reactant molecules can freely penetrate into the polymer coils expanded in a good solvent. Under the condition of a freely penetrable polymer, the only role the polymer plays is in controlling the volume available for the functional group's movement. Thus, the reaction of the polymer's functional group with the small molecular reactant should act similarly to two free small molecules, and the polymer reaction should behave similarly to an appropriate small-molecule model reaction.(1)

In the above case, kinetic studies can be performed, but the constraint of the bound functional group must be kept in mind.(1) Rate constants can be deduced for the reaction within the polymer coils (local reactions) by experimental kinetic data and activation parameters can be determined through temperature dependence studies. These kinetic parameters can then be compared to the parameters found for the small molecule model reaction. Conclusions can then be drawn regarding the rate controlling reactions and
mechanisms. Most reactions are monitored by sampling the bulk solution, i.e. monitoring the disappearance of the reactant not bound to the polymer. Finally, if there is deviation from this simple situation, there can be difficulty in interpreting the kinetic data and in comparing it to the model reaction.(1)

Once the reactant has penetrated the polymer coil, diffusion to the functional group reaction site and the actual reaction must both take place. Both of these processes can exhibit complications. The first is the neighboring group effect; where neighboring groups on a macromolecule modify the reactivity of the functional group. This effect can be of either steric or electrostatic origin.(10) Neighboring groups can refer to both groups adjacent to the functional group on the polymer chain and groups near the functional group as a consequence of the polymer's conformation. Neighboring groups can either decrease or increase the reactivity of the bound functional group.(1) When neighboring groups decrease the reactivity of the bound functional group, low yields and conversions can result.(1,10) However, when the reactivity of the bound functional group is increased, higher yields and conversions are produced. There are only a few cases where the reactivity is increased.

Trapping reaction kinetics were used to study diffusion-controlled reactions in a study performed by Oshanin and associates.(11) The term “trap” is used to describe the functional group on the polymer chain which can react with another chemical compound. Thus, trapping involves the reaction of the functional group on the polymer chain with another chemical analogue.
Trapping kinetics were studied in systems in which traps were attached to segments of polymer chains having arbitrary conformations. These polymers were also randomly distributed in the solvent. They concluded that there is a correlation between trap placement and the rate at which particles react with a single chain. Thus trap placement can lead to strong screening effects and may suppress the rate constant. This “trap” can also be viewed as being the anhydride which is part of the polymer. The placement of this anhydride can affect the rate of the reaction and therefore the rate constant.

The second complication to the rate of the reaction is the actual collision of the reactants. When two species collide, they must be oriented correctly in order to react to form a product. In the case of the anhydride and aniline reaction, the amine must collide with the carbonyl of the anhydride from above or below the plane. If this specific collision does not occur the reaction cannot happen. Local geometries play a role in whether or not the orbitals of the reacting species overlap enough to form a new bond. Finally, steric hindrance is caused by the molecules surrounding the reactive site or, in this case, the neighboring phenyl groups. The species attached directly to the anhydride ring constitutes a primary hindrance. The secondary hindrance consists of the parts of the polymer chain not directly bound to the anhydride which can wrap around and still block the reaction site. Steric hindrance has already been discussed under the name of neighboring group effect.
The reaction of a polymer with a small molecule can be diffusion-controlled, reaction-controlled, or both. Recent research has shown that these kinds of reactions are not purely diffusion-controlled. Rather, once the molecule diffuses into the polymer the reactivity can be affected by neighboring groups and the placement of the neighboring groups. Chemical reactions which have rates of reaction that are influenced by the rate at which the reacting molecules diffuse towards each other are called diffusion-controlled reactions. This type of diffusion control is called microscopic or encounter control.

According to Stokes Law, a diffusion coefficient, D, can be defined by the relationship:

\[ D = \frac{kT}{6\pi\eta r} \]  

where \(k\) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ JK}^{-1})\), \(T\) is the temperature of the solution, \(\eta\) is the viscosity of the solution, and \(r\) is the radius of the molecules in solution. This equation can be used to determine the diffusion coefficient of a solution when the viscosity of the solvent is known. The average radius of an organic molecule, such as aniline, can be estimated to be 5 Angstroms, or 0.5 nm. In order to take into account the fact that there are two types of molecules in the solution, equation (1) can be used to determine the overall diffusion coefficient of the reaction mixture.

\[ D_A + D_B = \left[ \frac{(kT)}{(6\pi\eta)} \right] \times \left[ \frac{1}{r_A} + \frac{1}{r_B} \right] \]  

where \(A\) represents molecule \(A\) and \(B\) represents molecule \(B\). Full microscopic diffusion control introduces the concept that molecule \(A\) will immediately react
with molecule B when they reach a critical distance, $d_{AB}$. This full microscopic diffusion control can be represented by:

$$k_D = 4\pi(D_A + D_B) d_{AB}$$  \hspace{1cm} (3)

where $k_D$ is the reaction rate for diffusion control.(12) When $d_{AB}$ is set equal to $r_A + r_B$, and equation (2) is substituted into equation (3), the resulting equation is(12):

$$k_D = [(2kT)/(3\eta)] \times [(r_A + r_B)^2/r_Ar_B]$$  \hspace{1cm} (4)

When the radii of molecules A and B are equal, this equation becomes:

$$k_D = (8kT)/(3\eta)$$  \hspace{1cm} (5)

which can be used to determine the rate constant, $k_D$, of a fully diffusion-controlled reaction. Thus, this equation gives the rate at which the reaction will proceed for similar size molecules if the reaction is fully diffusion-controlled.(12)

Equation (5) can be very useful in determining reaction versus diffusion-controlled reactions. If the actual reaction between the two molecules, here succinic anhydride and aniline, is much slower than the rate of diffusion, then the rate of the reaction is reaction-controlled. However, if the rate of diffusion is slower than the rate of the actual chemical reaction, then the reaction is diffusion-controlled. If a reaction is diffusion-controlled, then the viscosity of the solution exerts an influence over the rate of the reaction.(12) In order to calculate the diffusion coefficient in the succinic anhydride/ aniline system it is necessary to know the viscosities of aniline and tetrahydrofuran. The viscosity of aniline and tetrahydrofuran at 20 degrees Celsius is 4.40 mPa's and
0.55 mPa's, respectively. As stated above, it has been found that reaction kinetics involving polymers are not always purely diffusion-controlled. The following discussion presents the analyses necessary to study the reaction of poly[styrene-co-(maleic anhydride)] with aniline and how to compare it to the model reaction of succinic anhydride and aniline.

The poly[styrene-co-(maleic anhydride)] and aniline reaction will be studied to determine the rate constants of the reaction and to see if this acylation reaction is purely diffusion-controlled. If the latter is not the case then the reaction will either be reaction-controlled or a combination of diffusion- and reaction-controlled. In a diffusion-controlled reaction, "the only obstacle is that of one reagent species finding the other." The rate is not dependent on local geometries or steric hindrances, whereas a reaction-controlled reaction depends on the local geometries and steric hindrances. One method for determining the kinetic parameters of a reaction is through the use of a fluorescent probe. The rates of reaction for succinic anhydride and poly[styrene-co-(maleic anhydride)] with aniline can be determined by monitoring the fluorescence of aniline. Once the rates of reaction have been determined for polymers with different molecular weights, the rates can then be compared to determine if they correspond to the equations for diffusion-controlled reactions.

Aniline has an inherent fluorescence which is due to its aromaticity and n to \( \pi^* \) transitions. Two maximum wavelengths for the absorption bands for aniline are listed in Skoog as being at 230 nm and 280 nm. Also, Skoog
states that the wavelength of fluorescence for aniline is 310 - 405 nm. The fluorescence of aniline can be used to monitor anhydride/aniline acylation reactions. The fluorescent intensity of aniline should decrease as these reactions proceed because "substitution of a carboxylic acid or carbonyl group on an aromatic ring generally inhibits fluorescence."(15) Different amines have been used to monitor the progress of reactions, as was reported in the recent literature.(16, 17) The use of fluorescence as a monitoring tool will be discussed in conjunction with recent literature in acylation kinetics.

Chong Sook Paik Sung from the University of Connecticut and associates (16, 17, 18) have done much work in the area of acylation reactions. This research has also contained a spectroscopic monitoring technique involving amines or diamines which exhibit fluorescence. In two articles by Sung and associates, diaminonaphthalene (DAN) is used to study the formation of polyamides and polyimides. DAN is similar to aniline in that it is an aromatic amine but it contains two amine groups instead of one. Phthalic anhydride is used as the acylating compound. From these compounds, six model compounds were synthesized. These model compounds consisted of: amic acid-amide, diamic acid, amine-imide, amic acid-imide, diimide, and diisoimide. These researchers produced model compounds which had mixed acid/amine groups because DAN has two NH₂ groups and each group can be reacted with the phthalic anhydride. Once the acid was formed, these compounds underwent imidization to form imides. This process gave a mixed amic acid/imide
compound. These six compounds were characterized by FTIR, DSC, UV/Vis, and fluorescence. DAN was the only compound found to exhibit a strong fluorescent intensity. Amic acid-amine, amine-imide, and diisoimide were found to be very weakly fluorescent.(18)

The next part of this article focuses on chemical imidization of a previously made poly(amic acid). Acetic anhydride and pyridine were used for the chemical imidization and UV/Vis was used to monitor the reaction. This monitoring of the reaction included taking an aliquot from the reaction vessel and diluting the aliquot in solvent, N-methyl-2-pyrrolidinone (NMP), in order to record the UV/Vis spectrum.(18) This monitoring procedure can be applied to other kinetic studies.

The second article, by Dickinson and Sung, analyzed the imidization and depolymerization reactions of DAN and partially fluorinated dianhydride (6FDA). Although this research was primarily a thermal imidization study, it is also an example of using fluorescent techniques for anhydride/amine reactions.(16)

Yoo and Sung also studied the model reactions of 1,5-naphthyene-diamine (NDA) and n-propionic acid (PA) and of NDA with benzoyl chloride.(17) Although these two reactions do not involve an anhydride, they are acylation reactions. The study of the NDA/n-propionic acid reaction involved characterization of the intermediates and products by IR, UV/Vis, and fluorescence. Kinetic studies were performed for the reaction between NDA and n-propionic acid at three different temperatures (95, 110, and 125 degrees
Celsius). Because NDA is a diamine, it has two amine groups which can react. Therefore, n-propionic acid can react at two spots on the NDA. This study showed that the first amine group in the NDA reacts faster than the second amine group in the NDA. The rate constant also increased for the reaction of n-propionic acid with the first amino group of the NDA as the reaction temperature was raised.(17)

Finally, the reaction of NDA with benzoyl chloride was analyzed in this study. Benzoyl chloride is a stronger acylating agent than anhydrides. This reaction occurred too fast at room temperature and had to be performed at 0 degrees Celsius. At this temperature, the reaction was slow enough to be studied. The fluorescence spectra showed a sharp decrease in intensity as the reaction proceeded. This was the same trend seen in the reaction with n-propionic acid.(17)

These studies are important because they show that 1) acylation reactions have been important in recent literature, 2) amine fluorescence can be used as a monitoring tool, and 3) kinetic parameters can be determined from fluorescence data. What these studies have not looked at is the application of these techniques to reactions between polymers containing anhydride groups and amino compounds. One study was performed that did react residual maleic anhydride groups on poly(vinyl alcohol)-g-[methyl methacrylate-co-maleic anhydride] with N-substituted amines. This reaction was followed by imidization of the N-substituted maleamic acid. One N-substituted amine studied was
aniline. In this study, the chemical and physical properties of the acylation and imidization products were of interest and the kinetics of these reactions were not examined. (19)

As cited in the literature review above, fluorescence studies can be used to determine the rate constants of reactions between aniline and anhydride species. However, adherence to Beer's Law must be determined in order to use fluorescence data. For Beer's Law to hold true, areas of the fluorescence signal must be proportional to the concentration of aniline. The following equation shows the general form of Beer's Law:

\[ A = \varepsilon bc \]  \hspace{1cm} (6)

where \( A \) is absorbance (area), \( \varepsilon b \) is the extinction coefficient of aniline times the path length, and \( c \) is the molar concentration of aniline. The full relationship for this expression is:

\[ A = A_\infty(1-e^{-bc}) + r \]  \hspace{1cm} (7)

Non-linear regression can be performed to determine \( A_\infty \), \( \varepsilon b \), and \( r \), where \( A_\infty \) is the area at saturation, or the maximum area, and \( r \) is the residual fluorescence due to the fluorescence of the solvent. This gives a final relationship of:

\[ A - r = A_\infty(1-e^{-(\varepsilon bc)}) \]  \hspace{1cm} (8)

This relationship is very important when using spectroscopic data such as fluorescence because this provides a way to convert absorbance (or area in this case) to concentration for a non-linear relationship.
Fluorescence data obtained from aliquots sampled from a reaction vessel can be used to determine the concentration of aniline in the reaction flask. Once fluorescence data has been collected, the areas received from the instrument can be converted to concentrations. This conversion can be done by rearranging equation (8).

\[
\frac{(A - r)}{A_\infty} = 1 - e^{(\pi bc)}
\] (9)

\[
1 - \frac{(A - r)}{A_\infty} = e^{(\pi bc)}
\] (10)

\[
\ln[1 - \frac{(A - r)}{A_\infty}] = \ln[e^{(\pi bc)}]
\] (11)

\[
\ln[1 - \frac{(A - r)}{A_\infty}] = -\pi bc
\] (12)

\[
c = -\ln[1 - \frac{(A - r)}{A_\infty}] / \pi b
\] (13)

Often aliquots taken from the reaction flask must be diluted to obtain an intensity which can be measured accurately. Thus, once the concentration of each aliquot from the kinetic study has been determined, it must then be divided by its dilution factor to obtain the original concentration of aniline present in the reaction vessel at the time the sample was taken.

Aliquots taken from the reaction mixture at different times during the reaction can be used to determine the overall order of the reaction and the rate constant, \(k\). For a 1:1 stoichiometry, determination can be made by constructing a plot of log(concentration) versus time and a plot of 1/concentration versus time. If the slope of log(concentration) versus time is a straight line then the reaction is first order. If the slope of 1/concentration versus time is a straight line then the reaction is second order. The slope of the plot which gives a straight
line is the rate constant for the reaction.\(^{(20)}\) Sometimes the initial rate data can have a different slope than for the rest of the reaction. This could possibly be due to a catalysis effect or due to parts of the polymer chain reacting faster than other parts. The above process can be used to determine rate constants for the reactions in this study. One important concept to keep in mind is stoichiometric imbalance. If a second order reaction is close to being a 1:1 ratio, then the initial data should not be affected by stoichiometric imbalance. However, the data taken towards the end of the reaction may be affected due to the kinetics becoming pseudo first order.

The rate constant of a reaction is highly temperature dependent.\(^{(14)}\) This dependence on temperature must be determined and used to calculate the rate constant of the reaction at different temperatures. For this study, it is necessary to compare the rate constants of the reaction of aniline with succinic anhydride to the reactions of aniline with the polymers. To make these comparisons, all three reactions must have rate constants determined at the same temperature. The comparison of rate constants determined at different temperatures requires knowledge of the activation energy, \(E_a\), of the reaction. This activation energy can then be used to mathematically determine the rate constant for the reaction between succinic anhydride and aniline at the same temperature as that of the polymer reaction.

Fluorescence data can be obtained for this reaction at different temperatures. As stated above, this data can then be converted into
concentrations of aniline. The process for determining the rate constant can be used to determine the rate constant at each temperature. Once all the rate constants have been determined, they can be used to construct an Arrhenius Plot. The Arrhenius Law is:

\[
k = A e^{-\frac{E_a}{RT}}
\]  \hspace{1cm} (14)

where \( k \) is the rate constant, \( A \) is the frequency factor, \( E_a \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

When the natural log of both sides is taken, equation (14) becomes:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]  \hspace{1cm} (15)

or

\[
\ln k = \ln A - \frac{1000E_a}{RT}
\]  \hspace{1cm} (16)

The factor of 1000 is used if the activation energy is in units of kJ instead of J.

A plot of \( \ln k \) versus \( \frac{1000}{T} \) should be a straight line and the slope will be \(-\frac{E_a}{R} \), where \( E_a \) is in units kJ.\hspace{1cm} (21) \hspace{1cm} E_a \) and \( A \), which are empirical constants, can be determined from the slope and y-intercept, respectively, of this plot.\hspace{1cm} (14)

Using equation (16), the value for \(-\frac{E_a}{R} \) can be used in conjunction with the temperature of the polymer reactions and the frequency factor, \( A \), to determine the rate constant, \( k \), for the reaction at this temperature.

This study will cover the reactions of aniline with two poly[styrene-co-(maleic anhydride)] polymers, one having low molecular weight and one having high molecular weight. The low molecular weight polymer has a 50:50 styrene to maleic anhydride ratio; while the ratio for the high molecular weight polymer is
The first set of experiments to be performed consists of preparing the model compounds, N-phenylsuccinamic acid and N-phenylsuccinimide, and the polymer compounds, 50/50 poly[styrene-co-((N-phenyl)maleamic acid)], 50/50 poly[styrene-co-((N-phenyl) maleimide)], 86/14 poly[styrene-co-((N-phenyl) maleamic acid)], and 86/14 poly[styrene-co-((N-phenyl)maleimide)], and analyzing them using FTIR, UV/Vis, and fluorescence spectroscopy. Also the optimal reaction conditions for these reactions will be chosen. The next set of experiments will determine if the reaction of succinic anhydride with aniline is endothermic or exothermic. A temperature probe will be used to measure this relationship. The last set of experiments will provide the data to calculate the rate constants of the reaction of succinic anhydride, 50/50 poly[styrene-co-(maleic anhydride)], and 86/14 poly[styrene-co-(maleic anhydride)] with aniline. Rate constants for the succinic anhydride/aniline reaction will be calculated at five different temperatures to enable the determination of the activation energy. The rate constants for the two polymer reactions will be obtained in refluxing tetrahydrofuran. Finally, a conclusion will be drawn as to whether or not these reactions are diffusion-controlled by comparing the experimental rate constant, k, with the theoretical diffusion-controlled rate constant, kD, for the succinic anhydride/aniline reaction as previously discussed.
EXPERIMENTAL

Purification of Reactants and Solvent

_Tetrahydrofuran (THF)_

A distillation/reflux apparatus, Figure III, was set up to remove water from UV/Vis grade tetrahydrofuran, THF, (J.T. Baker, Inc.). A 5 ml pipette filled with drierite (with glass wool plugs) was placed in the N₂ line. All joints were sealed with Teflon tape. Grease could not be used because it is dissolved by THF. The UV/Vis grade THF was refluxed with sodium metal and benzophenone under N₂ until the solution turned navy blue. The navy blue solution was then refluxed for an additional 1-2 hours. The amount of THF needed for each reaction was distilled into an addition funnel.

_Aniline_

Aniline, 99.5 % (Aldrich Chemical Company, Inc., Lot# 00613AZ) was vacuum distilled using a vacuum pump, Figure IV. The first 20 ml was distilled into a receiving flask. The distillation apparatus was then wrapped with aluminum foil to protect the amine from decomposition due to light. Then the receiving flask was changed to a storage flask and the flask was wrapped with aluminum foil. The aniline was distilled over at approximately 39 degrees Celsius. Once the aniline was collected, a septum was put onto the neck of the
Figure III: Distillation/reflux apparatus used to purify THF.
Figure IV: Vacuum distillation apparatus used to purify aniline.
flask. A 5 ml pipette with drierite (with glass wool plugs) was inserted into the N₂ line. The stopcock on the flask was opened and a needle with N₂ blowing through it was inserted into the septum. N₂ was allowed to blow through the flask for a few minutes and then the stopcock was closed and the needle was removed. The aniline was stored wrapped in aluminum foil and in a refrigerator at approximately 4 degrees Celsius.

_Succinic anhydride_

The following procedure was designed by Shriner and Struck.(22) Ten grams of 99+ % pure succinic anhydride (Aldrich Chemical Company, Inc., Lot# 00708AY) was put into a one necked round bottom flask. Seven milliliters of acetic anhydride was added and heated until dissolved. Once dissolved, the flask was put into an ice bath. The crystals were suction filtered until dry and the crystals were rinsed twice with two 20 ml portions of cold ether. The above steps were repeated for a second time. The crystals were dried in an oven overnight at 46 degrees Celsius.

_50/50 and 86/14 poly[styrene-co-(maleic anhydride)]_

The two polymers used in this research were 50/50 and 86/14 poly[styrene-co-(maleic anhydride)]. The characteristics of these polymers are described in Table IV.
Table IV: Characteristics of 50/50 and 86/14 poly[styrene-co-(maleic anhydride)].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Units</th>
<th># of MA groups</th>
<th># of Styrene groups</th>
<th>Styrene : MA</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>15</td>
<td>7-8</td>
<td>7-8</td>
<td>1 : 1</td>
</tr>
<tr>
<td>86/14</td>
<td>150</td>
<td>21</td>
<td>129</td>
<td>6 : 1</td>
</tr>
</tbody>
</table>

These starting materials were not further purified.

Preparation of the Model Compounds

*N-phenylsuccinamic acid*

Approximately 1 g of recrystallized succinic anhydride was weighed out and placed in the reaction vessel with a stir bar, Figure V. The entire system was placed under N₂. Dried THF (30 ml) was added and the THF was refluxed to dissolve the succinic anhydride. Distilled aniline (2.7 ml) was added (1 mol succinic anhydride: 3 mol aniline) to push the reaction to completion. The reaction was run at reflux temperature for three hours.

Cyclohexane (50 ml) was chilled and added to the cold reaction flask to precipitate the white N-phenylsuccinamic acid. The product was collected by suction filtration using a Buchner funnel and then rinsed with 20 ml chilled cyclohexane. The product was dried in an oven overnight at 100-105 degrees Celsius. The product was stored in a capped vial, wrapped in aluminum foil. The pure product yield was 86.8 %. The FTIR spectrum is given in Figure VI.
Figure V: Apparatus used for the preparation of N-phenylsuccinamic acid, N-phenylsuccinimide, 50/50 poly [styrene-co-((N-phenyl) maleamic acid)], 50/50 poly [styrene-co-((N-phenyl) maleimide)], 86/14 poly [styrene-co-((N-phenyl) maleamic acid)], and 86/14 poly [styrene-co-((N-phenyl)maleimide)]. Also used for the polymer kinetic studies.
Figure VI: FTIR spectrum of N-phenylsuccinamic acid.
N-phenylsuccinimide

For a stoichiometric reaction, 1 g of succinic anhydride was dissolved into 30 ml of dry THF, Figure V. Once the succinic anhydride had dissolved and the solution had reached reflux temperature, 0.9 ml vacuum distilled aniline was added. The reaction proceeded at reflux temperature for three hours.

For the imidization reaction, 6.65 ml acetic anhydride (1.05 mol acetic anhydride per 1 mol of the ring open product) and 4.25 ml pyridine (.75 mol pyridine per 1 mol acetic anhydride) were added. The reaction mixture was refluxed for another three hours.

The N-phenylsuccinimide product was precipitated with 50 ml cold cyclohexane. The solution was placed in an ice bath for approximately 5 minutes and then suction filtered using a Buchner funnel. The product was rinsed with 20 ml of cold cyclohexane and dried in an oven for 30 minutes at 110 degrees Celsius. The pure product yield was 47.6 %. The FTIR for this product is given in Figure VII.

50/50 poly[styrene-co((N-phenyl)maleamic acid)]

Approximately 2 g of 50/50 poly[styrene-co-(maleic anhydride)] (Monomer-Polymer and Dajac Laboratories, Inc., Lot# 4-44-14) was dissolved in 75 ml dried THF under N₂ (Figure V). Once dissolved and refluxing, 2.7 ml distilled aniline (1 mol maleic anhydride: 3 mol aniline) was added to the reaction vessel. The reaction was refluxed for 10 hours. Chilled cyclohexane (125 ml) was
Figure VII: FTIR spectrum of N-phenylsuccinimide.
added to the warm reaction mixture which produced a white precipitate. Another 20 ml of cold cyclohexane was added to finish the precipitation. The product was suction filtered using a Buchner funnel and dried overnight in an oven at 100 - 107 degrees Celsius. The precipitate was a white powder. The FTIR is presented in Figure VIII.

50/50 poly[styrene-co-((N-phenyl)maleimide)]

Approximately 2 g of 50/50 poly[styrene-co-(maleic anhydride)] was dissolved in 100 ml refluxing dried THF under $N_2$ (Figure V). Then 0.9 ml aniline (1 mol maleic anhydride groups:1 mol aniline) was added to the reaction vessel. The reaction mixture was refluxed for 10 hours and then 4.25 ml pyridine and 6.64 ml acetic anhydride were added. The reaction was then refluxed for another 10 hours. The reaction mixture was allowed to cool down and 150 ml cold cyclohexane was added to the reaction mixture. This produced a white precipitate. The product was collected by suction filtration using a Buchner funnel and dried in an oven at 100 -120 degrees Celsius. The FTIR is given in Figure IX.

86/14 poly[styrene-co-((N-phenyl)maleamic acid)]

Approximately 7.5 g of 86/14 poly[styrene-co-(maleic anhydride)] (Monomer-Polymer and Dajac Laboratories, Inc. Lot# 8097; Batch # 5-22-8) was dissolved by refluxing in 200 ml dried THF under $N_2$ (Figure V). Once dissolved,
Figure VIII: FTIR spectrum of 50/50 poly[styrene-co((N-phenyl)maleamic acid)].
Figure IX: FTIR spectrum of 50/50 poly(styrene-co-(N-phenylmaleimide)].
2.7 ml distilled aniline was added and the solution was refluxed for 12 hours. A 25 ml portion of the mixture was put into an evaporating dish and the solvent was removed. The evaporating dish was placed in the oven overnight at 65 degrees Celsius. The final weight was multiplied by 8 to determine the amount of product in solution because only 1/8 of the final solution was used to determine the amount of product. The FTIR spectrum is given in Figure X.

\[
86/14 \text{poly[styrene-co-}((N\text{-phenyl)maleimide})]}
\]

Approximately 7.5 g of 86/14 poly[styrene-co-(maleic anhydride)] was weighed out, recorded, and dissolved into 200 ml dried, refluxing THF under N₂ (Figure V). Once refluxing, 2.7 ml aniline (1 mol maleic anhydride groups:3 mol aniline) was added to the reaction vessel. The reaction was run for 12 hours at reflux temperature. Acetic anhydride (6.64 ml) and pyridine (4.25 ml) were then added and the mixture was refluxed for another 12 hours.

Temperature Studies of the Succinic Anhydride/Aniline Reaction

General Studies

Approximately 1 g of succinic anhydride was dissolved into 30 ml of UV/Vis grade THF using a sonicator to accelerate the dissolution. Aniline (0.9 ml) was pipetted into a 50 ml beaker. The succinic anhydride solution was
Figure X: FTIR spectrum of 86/14 poly[styrene-co-((N-phenyl)maleamic acid)].
added to the beaker with the aniline in it. A stopwatch was started when half of the succinic anhydride solution had been added. The tip of the thermal couple probe of the digital thermometer (Fluke 51 K/J thermometer) was placed approximately a quarter of an inch into the solution. The temperature was recorded every thirty seconds for 40 minutes. The same protocol was used for 25, 20, 15, 10, and 5 degrees Celsius, using a tall form beaker and an ice bath.

*Good reaction conditions*

Good reaction conditions were obtained by using twice recrystallized 99+ % succinic anhydride, distilled aniline, distilled THF, and a N₂ gas line. Approximately 1 g of twice recrystallized 99+ % succinic anhydride was dissolved into 30 ml of UV/Vis grade THF using a sonicator to accelerate the dissolution. N₂ gas was then bubbled into the solution for 5 minutes. Distilled aniline (0.9 ml) was pipetted into a tall form beaker and the beaker was placed into an ice bath set at 15 degrees Celsius. The needle for the N₂ gas line was then put into the long beaker. The succinic anhydride solution was cooled in an ice bath to 17 degrees Celsius and then added to the beaker with the aniline and N₂ line in it. A stopwatch was started when half of the succinic anhydride solution had been added. The tip of the thermal couple probe of the digital thermometer (Fluke 51 K/J thermometer) was placed approximately a quarter of an inch into the solution. The temperature was recorded every thirty seconds for 40 minutes.
Preliminary Ultraviolet/Visible Spectroscopy Studies

Dilutions of each reactant, intermediate, and product were analyzed on the Perkin Elmer 552A UV/Vis Spectrophotometer. The dilutions needed for measurable UV/Vis results were prepared by dissolving the compound into 10 ml of UV/Vis grade THF and then serially diluting to the listed concentration (g/ml). Table V shows the amounts of each compound dissolved in 10 ml UV/Vis grade THF along with the dilution factors, and final concentration.

For each compound 3 ml of solution was placed in a quartz cuvette and analyzed in the spectrophotometer versus a reference of 3 ml THF in another quartz cuvette. The operating procedure for the Perkin Elmer 552A UV/Vis Spectrophotometer can be found in Appendix A.
Table V: Dilution factors and concentrations for all compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>g compound per 10 ml THF</th>
<th>Dilution factors</th>
<th>g compound per ml THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>succinic anhydride</td>
<td>.3355</td>
<td>1/11 x 1/11</td>
<td>2.77 x 10^-4</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-</td>
<td>.2075</td>
<td>1/11 x 1/11</td>
<td>1.72 x 10^-4</td>
</tr>
<tr>
<td>(maleic anhydride)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86/14 poly[styrene-co-</td>
<td>.3708</td>
<td>1/11 x 1/11 x 1/6 x 1/6</td>
<td>8.51 x 10^-6</td>
</tr>
<tr>
<td>(maleic anhydride)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aniline (ml aniline/ml THF)</td>
<td>.68 ml</td>
<td>1/11 x 1/6 x 1/6 x 1/11</td>
<td>1.42 x 10^-6</td>
</tr>
<tr>
<td>aniline (ml aniline/ml THF)</td>
<td>.68 ml</td>
<td>1/11 x 1/6 x 1/6 x 1/11</td>
<td>1.56 x 10^-5</td>
</tr>
<tr>
<td>N-phenylsuccinamic acid</td>
<td>.2545</td>
<td>1/11 x 1/11 x 1/6 x 1/11</td>
<td>3.19 x 10^-6</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-</td>
<td>.2776</td>
<td>1/11 x 1/11 x 1/6 x 1/11</td>
<td>3.82 x 10^-4</td>
</tr>
<tr>
<td>((N-phenyl)maleamic acid)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86/14 poly[styrene-co-</td>
<td>.2961</td>
<td>1/11 x 1/11 x 1/6 x 1/11</td>
<td>4.08 x 10^-5</td>
</tr>
<tr>
<td>((N-phenyl)maleamic acid)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-phenylsuccinimide</td>
<td>.2743</td>
<td>1/5 x 1/5 x 1/5 x 1/5 x 1/5</td>
<td>8.78 x 10^-6</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-</td>
<td>.0727</td>
<td>1/11 x 1/11 x 1/6 x 1/11</td>
<td>1.00 x 10^-5</td>
</tr>
<tr>
<td>((N-phenyl)maleimide)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86/14 poly[styrene-co-</td>
<td>.0937</td>
<td>1/11 x 1/11 x 1/6 x 1/11</td>
<td>1.29 x 10^-5</td>
</tr>
<tr>
<td>((N-phenyl)maleimide)]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Preliminary Fluorescence Spectroscopy Studies

The 1.56 x 10^{-5} \text{ml} \text{aniline/ml THF}, the .0335 \text{g} \text{succinic anhydride/ml THF}, and the .02545 \text{g} \text{N-phenylsuccinamic acid/ml THF} solutions were used to receive preliminary fluorescence results using the Perkin Elmer MPF - 3L. A 3 \text{ml} sample of each solution was placed into a fluorescence cuvette. The emission spectra from 380 to 580 nm was recorded. Next, the excitation wavelength was changed to 289 nm which was determined from UV/Vis data for aniline, and the emission spectrum was recorded from 300 to 500 nm. For the succinic anhydride and the N-phenylsuccinamic acid solutions, the emission spectrum was recorded from 250 to 400 nm at excitations of 250 nm and 289 nm (determined from UV/Vis data of aniline). The operating procedure for using the Perkin Elmer MPF - 3L can be found in Appendix A.

Fluorescence Spectroscopy Studies

A Perkin Elmer Luminescence Spectrometer LS 50B was used to determine the fluorescence intensities of all reactants, intermediates, products, and solvents. It was also used in the kinetic studies to determine the decrease in aniline fluorescence intensity over time.
**Determination of variation between the four cuvette positions**

Quinine sulfate standard was prepared to a concentration of $7.2 \times 10^{-4}$ g quinine sulfate $[(C_{20}H_{24}N_2O_2)_{2}H_2SO_4\cdot2H_2O] / L$ water. The solution was sonicated for thirty minutes to accelerate dissolution. The quinine sulfate standard was run ten times in each cuvette position for ten days.

A fluorescence cuvette was filled with 3 ml of quinine sulfate standard. Cuvette number one was run ten times and the peaks and the intensities were recorded. Table VI contains the instrument parameters for the quinine sulfate standard.

<table>
<thead>
<tr>
<th>Table VI: Instrument parameters for the quinine sulfate standard.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Excitation wavelength:</strong> 200 - 370 nm</td>
</tr>
<tr>
<td><strong>Emission wavelength:</strong> 381 nm</td>
</tr>
<tr>
<td><strong>Excitation slit width:</strong> 2.5 nm</td>
</tr>
<tr>
<td><strong>Emission slit width:</strong> 2.5 nm</td>
</tr>
<tr>
<td><strong>Scan speed:</strong> 240 nm/min</td>
</tr>
<tr>
<td><strong>Number of scans:</strong> 1</td>
</tr>
</tbody>
</table>

The same procedure was performed for positions number two through four using the same cuvette and prepared quinine sulfate standard. This procedure was followed for 10 days. The following peaks were used to determine the fluctuation of intensity between cuvette positions over the 10 day period: 204 - 206 nm, 226 - 228 nm, 234 - 236 nm, and 279 - 283 nm. A representative spectrum for the quinine sulfate standard can be found in Figure XI. The average signal intensity variations were determined between each cuvette.
Figure XI: Excitation spectrum of the quinine sulfate standard at an emission wavelength of 381 nm.
Determination of instrument fluctuation

Quinine sulfate solution was prepared by dissolving 0.0331 g of quinine sulfate in 100 ml distilled water. A dilution factor of 1/1000 was used to prepare a quinine sulfate solution with a concentration of 3.31 x 10^{-4} g quinine sulfate/ L distilled water. The stock solution was degassed by sonicating for 20 minutes.

A 4.5 ml sample of quinine sulfate standard was sonicated for 5 minutes. N\textsubscript{2} gas was blown into a cuvette with a 5 ml pipette filled with drierite (with glass wool plug) in the line. The 4.5 ml sample was filtered into the N\textsubscript{2} dried cuvette using a 0.45 micrometer acrodisk.

The stock solution was run ten times under the same parameters as used in the determination of cuvette fluctuation (Table VI). This standard was run 10 times for 10 days in cuvette position number one.

Determination of emission of all compounds

The emission of the compounds were needed to determine the emission range which would be used to monitor the reactions. Thus, the emission spectrum of each compound was determined at different excitation wavelengths. A quinine sulfate standard was analyzed in position number two using the same protocol as above (Table VI). A cuvette was filled with THF and the emission spectrum was analyzed at excitations of 212, 289, and 299 nm. The cuvette was filled with aniline in UV/Vis grade THF at a concentration of 1.1 x 10^{-4} M aniline. The cuvette was placed in position number one. The aniline solution was
analyzed at an excitation of 300, 289, 240, 212, and 299 nm to determine if these excitations gave rise to an emission peak.

Solutions for the reactants, intermediates, and THF solvent were prepared and analyzed for the excitations of 220 nm, 240 nm, 260 nm, 280 nm, and 300 nm. Based on the data above, an excitation wavelength of 300 nm was chosen to run all of the kinetics experiments and all the compounds were analyzed at an excitation of 300 nm. Table VII lists the concentration of the compounds which were used to determine the fluorescence intensity, using an excitation wavelength of 300 nm. The concentrations of the polymers are based on the molarity of the anhydride groups.

Table VII: Concentrations of the compounds used for fluorescence determination.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>48.92</td>
</tr>
<tr>
<td>succinic anhydride</td>
<td>9.99 x 10^{-5}</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-(maleic anhydride)]</td>
<td>1.02 x 10^{-4}</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-(maleic anhydride)]</td>
<td>5.07 x 10^{-5}</td>
</tr>
<tr>
<td>aniline</td>
<td>1.01 x 10^{-4}</td>
</tr>
<tr>
<td>N-phenylsuccinamic acid</td>
<td>1.43 x 10^{-4}</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>2.59 x 10^{-4}</td>
</tr>
</tbody>
</table>
The fluorescence of 86/14 poly[styrene-co-((N-phenyl)maleamic acid)] was not determined.

**Beer's Law Study**

A Beer's Law study was conducted using different concentrations of aniline in THF solutions. A set of 10 ml volumetric flasks were calibrated using deionized water as a standard. Each was weighed and then filled with water until the meniscus was on the line and then the flasks were reweighed and the temperature of the water was taken. The empty flasks were then placed in an oven set at 104 degrees Celsius, cooled at room temperature, and then the procedure above was repeated two more times.

The aniline solutions were prepared by making the solutions given in Table VIII and then serially diluting them. Table VIII displays the amounts of aniline used, the dilution factor, and the final concentrations of each aniline solution used to construct the Beer's Law plot.

**Table VIII: Solutions of aniline prepared for the Beer’s Law plot.**

<table>
<thead>
<tr>
<th>Amount aniline (ml) per 10 ml THF</th>
<th>Dilution factor</th>
<th>Concentration(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.014</td>
<td>.1/10 x .1/10 x 1/10 x 1/10</td>
<td>1.55 x 10^{-7}</td>
</tr>
<tr>
<td>0.027</td>
<td>.1/10 x .1/10 x 1/10 x 1/10</td>
<td>2.99 x 10^{-7}</td>
</tr>
<tr>
<td>0.014</td>
<td>.1/10 x .1/10 x 1/10</td>
<td>1.55 x 10^{-6}</td>
</tr>
<tr>
<td>0.027</td>
<td>.1/10 x .1/10 x 5/10</td>
<td>2.99 x 10^{-6}</td>
</tr>
<tr>
<td>0.019</td>
<td>.1/10 x .1/10 x 5/10</td>
<td>1.05 x 10^{-5}</td>
</tr>
<tr>
<td>0.027</td>
<td>.1/10 x .1/10</td>
<td>1.54 x 10^{-5}</td>
</tr>
<tr>
<td>0.019</td>
<td>.1/10 x .1/10</td>
<td>2.1 x 10^{-5}</td>
</tr>
<tr>
<td>0.027</td>
<td>.1/10 x .1/10</td>
<td>2.98 x 10^{-5}</td>
</tr>
</tbody>
</table>
The aniline solutions were analyzed in the PE Luminescence Spectrometer at the parameters listed in Table IX.

Table IX: Optimal instrument parameters determined for the Beer’s Law Plot data and for the kinetic studies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation wavelength</td>
<td>300 nm</td>
</tr>
<tr>
<td>Emission wavelength</td>
<td>300 - 500 nm</td>
</tr>
<tr>
<td>Excitation slit width</td>
<td>2.5 nm</td>
</tr>
<tr>
<td>Emission slit width</td>
<td>2.5 nm</td>
</tr>
<tr>
<td>Scan speed</td>
<td>240 nm/min</td>
</tr>
<tr>
<td>Number of scans</td>
<td>1</td>
</tr>
</tbody>
</table>

The area under the peak from 306.5 - 500 nm was calculated by the instrument and standardized to the quinine sulfate solution. The areas were then plotted versus concentration. A representative spectrum of aniline can be found in Figure XII.

Kinetic Studies

The excitation wavelength of 300 nm and the emission range of 300 - 500 nm were chosen for the kinetic studies. The samples from the kinetic studies needed to be filtered to remove dust and other particles which could affect the fluorescence results. Swinney holders and filter disks made of PTFE were chosen because PTFE is not dissolved by THF and aniline. It was also
Figure XII: Emission spectrum of aniline at an excitation wavelength of 300 nm.
determined that the best parameters for the kinetic experiments for aniline are those parameters listed in Table IX.

Succinic Anhydride

The procedure for conducting the succinic anhydride and aniline kinetic studies was as follows. In a beaker at room temperature, approximately .5 g of succinic anhydride was dissolved into 15 ml THF with the aid of a sonicator bath. Then .45 ml aniline was added to a 50 ml beaker. The succinic anhydride/THF solution was then added to the aniline in the 50 ml beaker. Once half had been added, a stopwatch was started. An initial aliquot of .15 ml was taken at 30 seconds and was added to 9.85 ml THF. This solution was serially diluted to a dilution factor of .15/1000. An aliquot was then taken every 3 minutes for thirty minutes. The diluted samples were then analyzed in the fluorescence spectrophotometer.

A 4.5 ml portion of quinine sulfate standard was sonicated for 5 minutes and put into N₂ dried fluorescence cuvette via a .45 micrometer acrodisk. It was put into position 2 of the instrument and analyzed at the parameters stated in Table IV. The areas were recorded for the ranges 200 - 255 nm, 255 - 300 nm, and 300 - 370 nm as well as the baseline for the spectrum. Then the samples from the kinetic study had to be analyzed. Each sample was sonicated for 2 minutes and filtered into a N₂ dried cuvette using the PTFE disk. The samples were analyzed in position 1 and the area of the peak from 306.5 - 500 nm was
recorded. The area was recorded from 306.5 - 500 nm to avoid interference from the reflection of the excitation wavelength where the excitation wavelength (300 nm) was so close to the emission spectrum being analyzed (300 - 500 nm).

Once all samples were analyzed, they were standardized according to the quinine sulfate analysis of the day. A ratio was determined by dividing the areas of the quinine sulfate standard of the day by the quinine sulfate areas recorded when the solution was first made. These three ratios were then averaged and the peak from the kinetic run was then divided by this ratio. In this way the peaks from day to day could be standardized.

After these runs were completed at room temperature, it was determined that more data was needed at the beginning of the reaction. Therefore, three more runs at room temperature were performed with smaller time intervals between aliquots. The same protocol was used for both the 45 minute and the 10 minute runs.

This procedure was also followed for performing the reaction in a 5, 10, 16, and 20 degrees Celsius cold bath. Aliquots were taken every minute for the first 5 minutes and one aliquot was taken at 7 minutes. Then, one aliquot was taken every 5 minutes from 10 to 45 minutes. These aliquots were analyzed in the same manner as above, except the dilution factors had to be changed due to the instrument fluctuations being very high. The new aliquot size and dilution factors were .1 ml aliquot being taken and diluted with 9.9 ml THF and then
serial diluting to a dilution factor of .1/1000. The final areas then had to be multiplied by 1.5 to take into consideration the change in dilution factors.

50/50 poly[styrene-co-(maleic anhydride)]

For 50/50 poly[styrene-co-(maleic anhydride)], the same protocol as for the succinic anhydride/aniline reaction was followed in refluxing THF. A reflux apparatus was set up and the polymer was dissolved in 100 ml of THF. Aniline (0.9 ml) was added to the reaction mixture and an aliquot (.5 ml) was taken every 10 minutes for two hours. Each sample was diluted with 9.5 ml THF, serially diluted to a dilution factor of .5/1000, and then analyzed as above.

86/14 poly[styrene-co-(maleic anhydride)]

The procedure for the kinetic studies of 86/14 poly[styrene-co-(maleic anhydride)] was also similar to the succinic anhydride/aniline reaction. A THF still was set up and connected to an addition funnel which was further attached to the kinetic study reaction vessel (see Figure V). THF was refluxed under nitrogen gas with sodium metal and benzophenone until the solution turned navy blue. Then 86/14 poly[styrene-co-(maleic anhydride)] and a stir bar were added to the reaction vessel and 100 ml of THF was distilled and collected in the addition funnel. The THF was then added to the reaction vessel and heated to reflux temperature. Once all of the polymer had been dissolved, previously distilled aniline was added in a stoichiometric fashion (.45 ml) by a syringe
through a septum on the reaction vessel. Aliquots (.5 ml) were taken approximately every 4 - 5 hours for 36 hours using a syringe. These samples were serially diluted to a dilution factor of .5/1000 and analyzed in the same manner as for the above reactions.
RESULTS

The reaction conditions for the succinic anhydride and aniline reaction was modified from Fieser's conditions(6) discussed in the introduction. These modifications include the use of acetic anhydride instead of acetyl chloride in the cyclization reaction. The solvent system was also modified to use THF instead of benzene. These changes were necessary to study the 50/50 and 86/14 poly[styrene-co-(maleic anhydride)] reactions with aniline. These modified reactions were used as the model reactions for this study and are represented in Figure XIII. Table X contains the reaction conditions for the synthesis of the model reactions.

Table X: Conditions for the acylation and imidization reactions used to synthesize N-phenylsuccinamic acid and N-phenylsuccinimide.

Preparation of N-phenylsuccinamic acid:

<table>
<thead>
<tr>
<th>Solvent:</th>
<th>tetrahydrofuran (THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>refluxing THF</td>
</tr>
<tr>
<td>Reaction time:</td>
<td>3 hours</td>
</tr>
<tr>
<td>Stoichiometry:</td>
<td>1:3 succinic anhydride:aniline</td>
</tr>
</tbody>
</table>

Preparation of N-phenylsuccinimide

<table>
<thead>
<tr>
<th>Solvent:</th>
<th>tetrahydrofuran (THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>refluxing THF</td>
</tr>
<tr>
<td>Reaction time:</td>
<td>3 hours</td>
</tr>
<tr>
<td>Stoichiometry:</td>
<td>1:3 succinic anhydride:aniline</td>
</tr>
<tr>
<td></td>
<td>1.05:1 acetic anhydride:N-phenyl-</td>
</tr>
<tr>
<td></td>
<td>succinamic acid</td>
</tr>
<tr>
<td></td>
<td>0.75:1 pyridine:acetic anhydride</td>
</tr>
</tbody>
</table>
Figure XIII: Succinic anhydride/aniline model reaction.
FTIR was used to characterize the intermediates and products of the acylation and imidization reactions. Table XI contains the characteristic peaks displayed by the intermediates and products.

Table XI: Characteristic IR bands. Each band represents one peak.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>Band (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-phenylsuccinamic acid</td>
<td>amine</td>
<td>3500 - 3300 (sharp)</td>
</tr>
<tr>
<td></td>
<td>amide</td>
<td>1700 - 1640 (sharp)</td>
</tr>
<tr>
<td></td>
<td>carboxylic acid</td>
<td>1725 - 1700 (sharp)</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>amide</td>
<td>1700 - 1640 (small)</td>
</tr>
<tr>
<td></td>
<td>anhydride</td>
<td>1840 - 1800 (small)</td>
</tr>
<tr>
<td></td>
<td>carboxylic acid</td>
<td>1725 - 1700 (small)</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>amide</td>
<td>1700 - 1640 (small)</td>
</tr>
<tr>
<td></td>
<td>anhydride</td>
<td>1840 - 1800 (small)</td>
</tr>
<tr>
<td></td>
<td>carboxylic acid</td>
<td>1725 - 1700 (small)</td>
</tr>
<tr>
<td>N-phenylsuccinimide</td>
<td>imide</td>
<td>1705 (strong)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1777 (shoulder)</td>
</tr>
<tr>
<td></td>
<td>anhydride</td>
<td>1850 (very small)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1821 (very small)</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleimide)]</td>
<td>imide</td>
<td>1705 (medium)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1777 (medium)</td>
</tr>
<tr>
<td></td>
<td>anhydride</td>
<td>1850 (small)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1821 (small)</td>
</tr>
</tbody>
</table>

Comparisons of these IR spectra will be presented in the Discussion Section.

UV/Vis spectra of these compounds were used to determine the maximum wavelength of absorption for each compound. The UV/Vis spectra were recorded with UV/Vis grade THF as the reference. Before each spectrum was
recorded, the instrument was set back to a zero baseline. The maximum wavelengths are recorded in Table XII and were needed to determine the optimal excitation wavelength. It was determined that the reactions should be monitored at a wavelength of 300 nm.

Table XII: UV/Vis results (maximum wavelengths and Absorbance) for all reactants, intermediates, and products.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lambda max (nm)</th>
<th>Abs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>succinic anhydride</td>
<td>227.5</td>
<td>.291</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-(maleic anhydride)]</td>
<td>223-224</td>
<td>.550</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-(maleic anhydride)]</td>
<td>211.8</td>
<td>.610</td>
</tr>
<tr>
<td>aniline</td>
<td>240</td>
<td>.220</td>
</tr>
<tr>
<td>aniline</td>
<td>289</td>
<td>.357</td>
</tr>
<tr>
<td></td>
<td>239.2</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>.810</td>
</tr>
<tr>
<td>N-phenylsuccinamic acid</td>
<td>240</td>
<td>.417</td>
</tr>
<tr>
<td></td>
<td>210.5</td>
<td>.343</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>213</td>
<td>1.51</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>244.2</td>
<td>.804</td>
</tr>
<tr>
<td></td>
<td>214.5</td>
<td>1.58</td>
</tr>
<tr>
<td>N-phenylsuccinimide</td>
<td>228.5</td>
<td>.636</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleimide)]</td>
<td>227.5</td>
<td>.329</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-((N-phenyl)maleimide)]</td>
<td>210</td>
<td>.531</td>
</tr>
</tbody>
</table>
Confirmation of the use of 300 nm as the excitation wavelength was performed by actually determining the fluorescence of the starting materials and the intermediates at an excitation wavelength of 300 nm. The emission coefficients ($A_{em}$) calculated for these compounds are listed in Table XIII and it is assumed that the relationship between area and concentration is linear. This assumption was used because in this research it was only necessary to determine if aniline had a much stronger fluorescence intensity than the other compounds. The equation: $A = A_0(1-e^{(-\varepsilon bc)})$ was used. Because of the low concentrations of the solutions, the $e^{(-\varepsilon bc)}$ part of the equation was assumed to be equal to 1 - $\varepsilon bc$. Thus, this equation was reduced to $A = A_{em}bc$, where $A_{em}b$ is the slope and the emission coefficient for the compound when absorbance is proportional to concentration. The emission of the polymers are based on anhydride groups.

Table XIII: Emission coefficients for starting materials and amic acid compounds by linear regression.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission coefficient (Emission/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>2.29</td>
</tr>
<tr>
<td>succinic anhydride</td>
<td>$6.72 \times 10^6$</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-(maleic anhydride)]</td>
<td>$6.82 \times 10^6$</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-(maleic anhydride)]</td>
<td>$1.46 \times 10^7$</td>
</tr>
<tr>
<td>aniline</td>
<td>$1.91 \times 10^8$</td>
</tr>
<tr>
<td>N-phenylsuccinamic acid</td>
<td>$2.75 \times 10^6$</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-((N-phenyl)maleamic acid)]</td>
<td>$1.17 \times 10^7$</td>
</tr>
</tbody>
</table>
The emission coefficient was not determined for 86/14 poly[styrene-co-(N-phenyl)maleamic acid]. Because the maximum wavelength for the emission peak for aniline was observed at 334.5 nm, the emission spectrum was monitored at 300 - 500 nm and areas were calculated between 306.5 - 500 nm.

As stated above, the relationship used to determine the emission coefficients in Table XIII assumes that the plot of area versus concentration is linear. However, it is not entirely wise to make this assumption because often the relationship between area and concentration is not linear. Therefore the emission coefficient for aniline was determined using non-linear regression. A plot of signal versus concentration was constructed from the data in Table VIII. From this data, Sigma Plot was used to obtain the emission coefficient, maximum area, and residual area using equation (7). The corresponding plot is given in Figure XIV. For Figure XIV, the R-fit is the regression line for the data, C.I. are the lines for the confidence interval. Also, the black boxes represent the original experimental data and the clear boxes designate the data which was obtained on 8/12/94. The results from this plot can be found in Table XIV.

Table XIV: Non-linear regression data for aniline.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission coefficient ($A_{obs}$)</td>
<td>$7.985 \times 10^8$</td>
<td>$\pm 450.2$</td>
</tr>
<tr>
<td>Residual ($r$)</td>
<td>750.5</td>
<td>$\pm 377$</td>
</tr>
<tr>
<td>Maximum area ($A_*$)</td>
<td>61900</td>
<td></td>
</tr>
</tbody>
</table>
Figure XIV: Plot of signal versus concentration for aniline using Sigma Plot.

Beer's Law Plot for Aniline

- Experiment
- R-Fit
- C.I.
- Data(8/12/94)
From the data in Table XIV, the areas obtained from the Perkin Elmer Spectrophotometer were converted to concentrations. The following equation was used to determine the concentration of aniline for each aliquot:

\[
c = \frac{-\ln[1-((A - r)/A_m)]}{eb}
\]  

(13)

where \(c\) is concentration, \(A\) is the area, \(r\) is the residual, \(eb\) is the extinction coefficient, and \(A_m\) is the maximum area. The concentrations then had to be divided by the dilution factors to determine the original concentration in the reaction vessel. The dilution factors which were used for each reaction are described in the Kinetic Studies section of the Experimental Section. Once the rate constant was determined for the two polymers, each rate constant had to be divided by a final dilution factor to adjust for the fact that the concentration in the reaction vessel was different for the succinic anhydride/aniline reactions.

For each kinetic run, the rate constants were determined for the polymers and succinic anhydride with aniline at 67 degrees Celsius from the concentrations of aniline determined from equation (13). The plots of 1/undiluted concentration versus time in seconds for the reaction between succinic anhydride and aniline at 5, 10, 16, 20, and 25 degrees Celsius can be found in Figures XV through XIX, respectively. Because the beginning of these reactions showed a lag in slope at the early sampling times compared to the latter times, Figures XX through XXIV contain these plots without the first 800 seconds. These plots also show the regression for each kinetic run at the five different temperatures. The activation energy for the reaction between succinic
Figure XV: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 5 degrees Celsius.
Figure XVI: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 10 degrees Celsius.
Figure XVII: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 16 degrees Celsius.
Figure XVIII: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 20 degrees Celsius.
Figure XIX: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at room temperature (25 degrees Celsius).
Figure XX: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 5 degrees Celsius without the first 800 seconds. (Rate constant, k, determination)
Figure XXI: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 10 degrees Celsius without the first 800 seconds. (Rate constant, k, determination)
Figure XXII: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 16 degrees Celsius without the first 800 seconds. (Rate constant, k, determination)
Figure XXIII: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at 20 degrees Celsius without the first 800 seconds. (Rate constant, k, determination)
Figure XXIV: Plot of 1/undiluted concentration aniline versus time for the succinic anhydride/aniline reaction at room temperature (25 degrees Celsius) without the first 800 seconds. (Rate constant, k, determination)
anhydride and aniline was required in order to convert the rate constant to 67 degrees Celsius. Figure XXV displays an Arrhenius plot of ln(rate constant) versus 1000/temperature (in Kelvins). A second Arrhenius plot (Figure XXVI) was constructed to account for outlier points for one of the kinetic runs at room temperature. The outlier point was determined visually. This figure also contains the linear regression used to determine the slope, or \(-E_a/R\), for this plot. 

\(E_a\) was determined to be \(47.3 \pm 14\) kJ/mole for the succinic anhydride/aniline reaction. The value of the activation energy/universal gas constant was used to determine the rate constant for the succinic anhydride/aniline reaction at 67 degrees Celsius. The rate constant is given in Table XV. Table XV also contains the rate constants determined for the two polymer reactions.

Table XV: Rate constants determined for the succinic anhydride and polymer reactions with aniline at 67 degrees Celsius.

<table>
<thead>
<tr>
<th>Compound reacted with aniline</th>
<th>Rate Constant ((\text{L/mol min}))</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic anhydride</td>
<td>13</td>
<td>(\pm 25%)</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-(maleic anhydride)]</td>
<td>.051</td>
<td>(\pm 15%)</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-(maleic anhydride)]</td>
<td>.008</td>
<td>(\pm 18%)</td>
</tr>
</tbody>
</table>

The rate constants for the polymers were obtained from their corresponding plots. Figures XXVII and XXVIII display the plots of 1/undiluted concentration versus time for the polymer reactions. Figures XXIX and XXX contain these plots without the first few data points since the slope of the first few data points
Figure XXV: Arrhenius Plot of \( \ln(\text{rate constant}) \) versus \( 1000/\text{Temperature} \).

**Succinic anhydride and aniline reaction**

*Activation energy determination*
Figure XXVI: Arrhenius Plot of ln(rate constant) versus 1000/Temperature, accounting for outlier points.
Figure XXVII: Plot of 1/undiluted concentration aniline versus time for the 50/50 poly [styrene-co-(maleic anhydride)]/aniline reaction.
Figure XXVIII: Plot of 1/undiluted concentration aniline versus time for the 86/14 poly [styrene-co-(maleic anhydride)]/aniline reaction.

86/14 polymer with aniline
Reflux THF

![Graph showing the plot of 1/undiluted concentration aniline versus time for the 86/14 poly [styrene-co-(maleic anhydride)]/aniline reaction.](image)
Figure XXIX: Plot of 1/undiluted concentration aniline versus time for the 50/50 poly [styrene-co-(maleic anhydride)]/aniline reaction without the first few data points. (Rate constant, k, determination)

50/50 polymer with aniline
k determination at reflux THF

![Graph showing the plot of 1/undiluted concentration aniline versus time for the 50/50 poly [styrene-co-(maleic anhydride)]/aniline reaction without the first few data points. The graph includes data points for Run I, Run II, and Run III, with regression lines for each run marked as 'Regress I', 'Regress II', and 'Regress III'.]
Figure XXX: Plot of 1/ undiluted concentration aniline versus time for the 86/14 poly [styrene-co-(maleic anhydride)]/aniline reaction without the first few data points. (Rate constant, $k$, determination)
are different from the rest of the data. This behavior will be addressed in the Discussion Section.

The theoretical rate constant determined for the succinic anhydride/aniline reaction at 20 degrees Celsius was calculated using equation (5). The viscosity of tetrahydrofuran (0.55 mPa's) was converted to Pa's, which is equivalent to kg m$^{-1}$s$^{-1}$. Once $k_D$ was found to be $1.963 \times 10^{-17}$ m$^3$s$^{-1}$, this value was multiplied by $6.022 \times 10^{26}$ dm$^3$m$^{-3}$mol$^{-1}$ to determine the diffusion rate constant in L·mol$^{-1}$s$^{-1}$. The final conversion was from seconds to minutes. This theoretical value can be found in Table XVI, in addition to the experimental rate constant for the succinic anhydride with aniline reaction at 20 degrees Celsius and the calculated experimental rate constant at 67 degrees Celsius.

Table XVI: Experimental rate constants, $k$, and the theoretical diffusion rate constant, $k_D$ for the succinic anhydride/aniline reaction.

<table>
<thead>
<tr>
<th>$k$ (L/mol·min)</th>
<th>$k_D$ (L/mol·min)</th>
<th>Temperature (Celsius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>0.72</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>7.09 x 10$^{11}$</td>
<td>20</td>
</tr>
</tbody>
</table>

The rate constants in Table XV were then used to determine the ratios of the rate constants. Table XVII contains the calculated molecular weight ratio and experimental rate constant ratio determined for these reactions. These ratios will be analyzed in the Discussion Section.
Table XVII: Calculated molecular weight ratio and experimental rate constant ratios for the succinic anhydride and polymer reactions.

<table>
<thead>
<tr>
<th>Species</th>
<th>MW Ratio</th>
<th>Experimental k ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 polymer: succinic anhydride</td>
<td>15:1</td>
<td>1:250</td>
</tr>
<tr>
<td>86/14 polymer: 50/50 polymer</td>
<td>100:1</td>
<td>1:6</td>
</tr>
<tr>
<td>86/14 polymer: succinic anhydride</td>
<td>1500:1</td>
<td>1:1600</td>
</tr>
</tbody>
</table>

Data for the temperature studies is the final set of data which needs to be presented. The succinic anhydride/aniline reaction was performed at five different temperatures (5, 10, 15, 20, 25 degrees Celsius). The reaction was monitored over time using a temperature probe and plots of solution temperature versus time were produced for three runs at the five different temperatures. These plots can be found in Figures XXXI through XXXV. The temperature variance for these temperature studies and the kinetic studies was determined to be ± 1.5 degrees Celsius from the temperature study data.
Figure XXXI: Solution temperature versus time for the succinic anhydride/aniline reaction at 5 degrees Celsius.
Figure XXXII: Solution temperature versus time for the succinic anhydride/aniline reaction at 10 degrees Celsius.
Figure XXXIII: Solution temperature versus time for the succinic anhydride/aniline reaction at 15 degrees Celsius.
Figure XXXIV: Solution temperature versus time for the succinic anhydride/aniline reaction at 20 degrees Celsius.

Temperature Study
20 degrees Celsius

- ■ Run II
- + Run I
- * Run III
Figure XXXV: Solution temperature versus time for the succinic anhydride/aniline reaction at 25 degrees Celsius.
DISCUSSION

The primary goals of this project were 1) to study how primary amines react with polymers with maleic anhydride in their backbone, 2) to determine the experimental rate constants for succinic anhydride, 50/50 poly[styrene-co-(maleic anhydride)], and 86/14 poly[styrene-co-(maleic anhydride)] with aniline, and 3) to determine if these reactions are diffusion-controlled by comparing the experimental rate constant, $k$, with the theoretical diffusion rate constant, $k_D$, for the succinic anhydride/aniline reaction. All three of these goals were met by this project.

Much of this research project had to do with determining the actual conditions and protocol for the reactions and kinetic studies of succinic anhydride and poly[styrene-co-(maleic anhydride)] with aniline. The following discussion illustrates what conditions and protocol were used and why they had to be employed.

The reaction conditions for the succinic anhydride and aniline reaction were modified from Fieser’s original protocol (6), see Table X and Figure XIII, which are located in the Results Section. These modified reactions were used as the model reactions. Also, reaction conditions were determined for the 50/50 and 86/14 poly[styrene-co-(maleic anhydride)] reactions. These experimental conditions were presented in the Experimental Section. These procedures were found to produce the best conversion to product, based on the following
experimental conditions: dry conditions, 3:1 aniline to succinic anhydride ratio, three hour reaction time, distilled aniline and THF, and twice recrystallized succinic anhydride. One important aspect of these reactions is that the succinic anhydride/aniline reaction and the polymer/aniline reactions had to be performed at different temperatures. The succinic anhydride/aniline reaction could not be performed above room temperature because the reaction happened too quickly to be measured. This observation corresponds with Fieser's protocol because this protocol uses refluxing benzene (80 degrees Celsius) as a solvent and the reaction product forms practically immediately. (6) The polymer/aniline reactions had to be performed in refluxing THF because below that temperature these reactions occurred too slowly. Another important condition for these reactions was the drying of the solvent, THF, and the use of nitrogen gas. Water had to be eliminated from the reaction vessel in order to have the best conversion possible and also to prevent any possible side reactions.

Although these conditions were used to synthesize the intermediates and products for spectral analysis, these conditions were not conducive for the fluorescence kinetic studies. An open vessel was used to perform these kinetic studies. This change in protocol was necessary for the succinic anhydride/aniline reaction because this reaction happened so quickly that good, precise data was impossible to obtain with a syringe technique in a closed system. With dry conditions, it would have been necessary to completely clean and dry the syringe between samples. Because samples were taken every one
to two minutes, the procedure of cleaning, drying, and re-assembling the syringes proved to be an impossible task. The error produced from this procedure caused inconsistency in results from aliquot to aliquot and thus was not pursued any further.

Dry conditions were important for the polymer reactions due to the long reaction times, which lasted over 24 hours. In addition, the sampling protocol was possible for the polymer reactions because there was enough time in between samples to properly clean, dry, and re-assemble the syringe being used to draw the aliquots. Thus, the dry conditions using a syringe for sampling was deemed very useful for the polymer reactions.

Conditions and protocol were then determined for the kinetic monitoring of these reactions. Because amines have been used in recent literature as monitoring tools(16, 17, 18), it was thought that aniline could be used to monitor these reactions. Chong Sook Paik Sung from the University of Connecticut and associates (16, 17, 18) have used spectroscopic monitoring techniques involving amines or diamines which exhibit fluorescence. In some of their research (16, 18), diaminonaphthalene (DAN) was used to study the formation of polyamides and polyimides. In another study, by Dickinson and Sung, the imidization reaction of DAN and partially fluorinated dianhydride (6FDA) were analyzed.(16) Although this research was primarily a thermal imidization study, it is an example of fluorescent techniques used to monitor and study anhydride/amine reactions.(16) Finally, Yoo and Sung also studied the model reactions of
1,5-naphthyenediamine (NDA) and n-propionic acid (PA) and of NDA with benzoyl chloride. (17) These two reactions do not involve an anhydride but they are acylation reactions and are thus examples of using an amine as a monitoring tool. (17)

In order to use aniline as the monitoring tool in this project, several experimental parameters had to be determined. First, the absorption and emission spectra for the compounds were obtained. The determination of these spectra was also performed in the above cited literature. UV/Vis spectroscopy was used to determine the wavelength of maximum absorption for each compound. These wavelengths are located in Table XII. The two maximum wavelengths for the absorption bands listed in Skoog for aniline are at 230 nm and 280 nm. (15) These wavelengths are similar to two of the maximum wavelengths found experimentally for aniline. It was determined from the wavelengths of the compounds to monitor the reactions at 300 nm. The wavelength of 300 nm was selected because one of aniline’s maximum wavelength of absorption was at 289 nm. This wavelength was not very close to the wavelength of maximum absorption of the other compounds. Also, by actually using 300 nm as the excitation wavelength, a shoulder of this peak could be used and this wavelength is even further away from the absorption bands of the other compounds. This determination was important because an excitation wavelength must be chosen that only excites the aniline. Otherwise, other compounds besides aniline could be detected and contaminate the results.
Confirmation of the use of 300 nm as the excitation wavelength was performed by actually determining the fluorescence of the starting materials and the intermediates at an excitation wavelength of 300 nm. The emission coefficients calculated for these compounds are listed in Table XII. It must be kept in mind that the calculation of these emission coefficients assume that the relationship between area and concentration is linear. The wavelength of 300 nm was used to monitor aniline during the kinetic studies because the extinction coefficient is at least 10 times greater for aniline than for the other compounds. The reaction concentration of aniline to anhydride was 1:1 for all of the reactions, including the polymer reactions. Because the maximum wavelength for the emission peak for aniline was observed at 334.5 nm, the emission spectrum was monitored between 300 and 500 nm. This range is also supported by Skoog(15) who states that the wavelength of fluorescence for aniline is 310 to 405 nm.

Once these optimum absorption and emission bands were determined, a protocol for the actual sampling of the reaction solution had to be determined. The succinic anhydride/aniline reaction was performed under nitrogen gas to obtain products which were not exposed to water. For the kinetic studies, however, it was determined that accurate aliquots could not be obtained for the reaction if it was performed under nitrogen gas. The reasons for this difficulty were explained earlier in this discussion. Thus the succinic anhydride/aniline kinetic studies were not performed under nitrogen gas. For the polymer/aniline
reactions it was necessary to perform the reaction under nitrogen gas. This difference in the reaction procedures is due to the length of time the polymer reactions take. The longer the reaction time, the more likely that water can enter the system. Water can react with the maleic anhydride in the polymer backbone and cause side products. The main side reaction is the production of a carboxylic acid via the nucleophilic addition of water to the carbonyl. Thus, the polymers were reacted under nitrogen flow and in an “air free environment” to prevent reactions with water from the air.

Glass pipettes (1 ml) were used to sample from the succinic anhydride/aniline reaction vessel, where as a needle and syringe had to be used to take samples for the polymer reactions. It was determined that samples taken right from the reaction flask and diluted once (1 ml/100 ml THF) were still too concentrated for the fluorimeter. Therefore, serial dilutions of the samples were made using 1 ml pipettes. To determine the accuracy of these serial dilutions, three samples were made by dissolving succinic anhydride in THF and then adding aniline. After 30 seconds, a sample was taken and diluted two times. The area data obtained from these samples were used to determine that the serial dilution process has a deviation of 2.2%, as compared to each other. The above dilution technique is seen elsewhere in the literature where UV/Vis or fluorescence is used to monitor acylation reactions. These studies also use amines as the monitoring compound.
There were a few reaction conditions that were deemed necessary throughout this research. The first was the use of PTFE filter holders and filters. Through Gelman labs, who makes these PTFE filter set ups, it was determined that PTFE was a compound that would not be dissolved by either THF or aniline. The same is true for glass pipettes. Thus, this equipment was used so the kinetic data would not be affected by contaminants.

There were three other important techniques that were used as precautionary measures. These include: sonicating and filtering the diluted samples, chilling the vials of THF before adding a sample, and storing the diluted samples in a refrigerator (at 4 degrees Celsius) until it was possible to run the fluorescence spectroscopy. However, the samples were returned to room temperature before they were analyzed. The processes of sonication and filtration are important to obtain true, reproducible kinetic data. These techniques help to reduce light scattering. Sonication dissipates air which could otherwise cause bubbles in the fluorescence cuvette and cause erroneous results. Filtration using the PTFE disk and holder is needed to filter out any kind of solid contaminants, for example dust, that could affect the fluorescence readings. As with sonication, this technique also helps to provide true, reproducible results. The other two experimental aspects are important to stop the reaction in the samples at the time the sample is taken. The reaction occurring in the sample is stopped when the sample mixes with the chilled solvent (THF). Based on the rate data, the reaction has been slowed by a factor
of 40 million, therefore it was assumed that the reaction was stopped until the samples could be analyzed. This result was determined by the fact that only a very slight increase in area was shown between the samples taken the day that the reaction was run versus storing the samples overnight. Also, this slight increase should be similar across all of the stored samples, thus not affecting the final results because time from sampling to measurement was consistent for each run. However, across runs there were different time frames between sampling and measurement. Again, the above techniques helped to obtain good, reproducible results.

The use of the Perkin Elmer Spectrophotometer had to be taken into consideration. Once the optimal settings (Table IX) were determined for the instrument, other possible causes of data collection error had to be determined and taken into account. The PE Fluorescence Spectrophotometer has an inherent fluctuation due to power surges, etc. Scans which were run one after another of the same quinine sulfate sample produced results with only a small amount of fluctuation. However, the fluctuation of the instrument from day to day could be fairly large. These fluctuations could cause the areas to be larger or smaller than the previous day. Thus, fluctuations were important to take into account. They were taken into account by running a quinine sulfate standard every day the instrument was used. Fluctuations were also taken into account by subtracting the area below the baseline of the aniline fluorescence spectrum from the area of the peak obtained from the instrument. This calculation takes
the area off of the peak that could change from day to day due to daily, random fluctuation of the instrument. To further ensure confidence in the area readings, the same cuvette position in the instrument was used for all samples. Taking into account the use of a quinine sulfate standard, the same cuvette position, and subtracting the area of the baseline from the aniline peak, I would estimate the confidence in the data to be approximately ± 5 %. However, it is also important to note that the aliquots taken for each kinetic run were analyzed one after another. Thus, for each kinetic run there was not the large fluctuation problems of analyzing some samples from a kinetic run on one day and the rest of the samples from the same run on another day.

This research produced other outcomes besides the experimental protocol for these reactions. FTIR was used to characterize the intermediates and products of the acylation and imidization reactions. Table XI contains the characteristic bands for the intermediates and products. The intermediate, N-phenylsuccinamic acid, was determined to have both the secondary amine band (3500 - 3300 cm\(^{-1}\)) and amide band (1700 - 1640 cm\(^{-1}\)). There was also a carboxylic acid band at approximately 1700 cm\(^{-1}\). These bands correspond well to the spectra found in the literature (see Table II). Also, the loss of the anhydride stretches (1840 - 1800 cm\(^{-1}\)) was observed. Thus, it was shown that practically all of the succinic anhydride was reacted to form the amic acid. For the polymers, however, there was less conversion to the amic acid. This conclusion can be drawn because the bands for the anhydride are stronger for
the polymer amic acid intermediates than for the model reaction. This result can also be seen in the results from the kinetic studies, where aniline is used up at a greater rate and at greater amounts for the succinic anhydride reaction versus the polymer reactions, see Figures XV - XXIV and XXVII - XXX.

The product, N-phenylsuccinimide, displayed a strong band at 1705 cm\(^{-1}\) and a shoulder at 1777 cm\(^{-1}\). These bands are characteristic of succinimides\(^{(7)}\) and for N-phenylmaleimide\(^{(8)}\). Also, only a very small anhydride band was seen. Thus, the reaction had high conversion to product. These characteristic bands were also found for the polymer products. However, the bands were not as strong or sharp for the polymers compared to N-phenylsuccinimide. The anhydride bands were slightly stronger in the IR spectra of the polymer products. Therefore, the conversion for these reactions were not as high as for the model reaction. For the succinic anhydride/aniline reaction, the activation energy, \(E_a\), was determined to be 47.3 kJ/mole. The work performed by Kalnin'sh and associates\(^{(9)}\) determined the heat of reaction (-\(\Delta H\)) for the reaction of aniline with phthalic anhydride was approximately 48 to 53 kJ/mole, depending on the solvent system. From \(E_a\) and -\(\Delta H\), it can be determined that the activation energy is approximately equal to -\(\Delta H\) and that the forward reaction has approximately half the activation energy as the reverse reaction.

Another finding determined from this research project is that the succinic anhydride/aniline reaction is exothermic. This trend was observed and studied at five different temperatures (5, 10, 15, 20, 25 degrees Celsius) and plots of
temperature versus time were constructed, which can be found in Figures XXXI through XXXV. These plots show the general trend of this reaction to produce heat. The beginning of these curves are S-shaped and then reach a maximum. Finally, these curves tend to slope down to just about baseline. The data received for the lower temperatures, 5, 10, and 15, had results which were more spurious as compared to the 20 and 25 degree runs. These more spurious results could be due to the difficulty in keeping these solutions at the appropriate temperature for the 40 minute reaction time. It could also be due to the production of heat by the reaction itself. However, the general trend of these curves show an increase of solution temperature over the 40 minute reaction time and thus an exothermic reaction. Kalnin'sh observed the heats of reaction for the phthalic anhydride/aniline derivative reactions to be exothermic. Values for these heats of reaction were determined to be -48.1 kJ/mole in CHCl₃ + 4 Vol. % acetonitrile and -53.5 kJ/mole in acetonitrile. Thus, the exothermic nature of the succinic anhydride/aniline reaction correlates with the exothermic nature of the phthalic anhydride/aniline reactions.

Finally, there are a few trends that appeared from the kinetic studies that must be addressed. First, there tends to be an induction period during the first ten minutes of the reaction of succinic anhydride with aniline. This result agrees with the results found for the phthalic anhydride/aniline reaction performed by Kalnin'sh. Also, this result is supported by Beckwith's description that, in the absence of added excess acid, the reaction is usually autocatalytic. Thus,
this induction period could be due to an autocatalytic effect of the amic acid groups being produced as the reaction proceeds. The amic acid groups therefore act as an acid catalyst for the reaction.

Another possibility is that the aniline is complexing with the amic acids to form a complex which fluoresces more intensely than aniline alone. "It has been found empirically that fluorescence is particularly favored in molecules that possess rigid structures." (15) Thus, enhanced emission can be due to increased rigidity in a structure. (15) However, the trends in the data show that the initial readings for the reactions are not low. If there was a trend for the initial readings to be low and then for the readings to increase, and finally for the readings to decrease, then complexation could possibly be occurring. However this trend is not seen in the data, therefore it does not appear that complexation is an important factor under these experimental conditions.

There is also a general trend for 50/50 poly[styrene-co-(maleic anhydride)] which must be addressed. There is a twenty minute period for the 50/50 polymer where there is a faster reaction than for the rest of the reaction. Because the 50/50 polymer has more maleic anhydride groups than the 86/14 polymer, it is more likely that there are maleic anhydrides on the ends of the 50/50 polymer chain. The period of increased rate for the 50/50 polymer could be due to the maleic anhydrides on the end of the polymer chain reacting more quickly than those further in on the chain. For the 86/14 polymer there are less maleic anhydride groups per unit then for the 50/50 polymer. This creates a
much smaller chance that there are maleic anhydride groups on the ends of the 86/14 polymer chains. The plot of the kinetic data for the 86/14 polymer does not show a faster rate at the beginning times of the reaction which could be due to there being very few, if any, maleic anhydride groups at the ends of the polymer chains. The lag at the beginning of the 86/14 polymer reaction could also be due to an induction period. This result would correspond with the induction period found for the succinic anhydride model reaction.

The hypothesis that the reaction of aniline with 50/50 poly[styrene-co-(maleic anhydride)] and with 86/14 poly[styrene-co-(maleic anhydride)] are not totally diffusion-controlled has been demonstrated by this project. This result corroborates with the statistical data determined by Oshanin and associates(11) by using trapping kinetics. The data to support this conclusion can be found in the following discussion.

The rate constants determined for the polymers and succinic anhydride with aniline at 67 degrees Celsius are as follows (from Table XV):

<table>
<thead>
<tr>
<th>Compound reacted with aniline</th>
<th>Rate Constant (L/mol min)</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic anhydride</td>
<td>13</td>
<td>± 25 %</td>
</tr>
<tr>
<td>50/50 poly[styrene-co-(maleic anhydride)]</td>
<td>.051</td>
<td>± 15 %</td>
</tr>
<tr>
<td>86/14 poly[styrene-co-(maleic anhydride)]</td>
<td>.008</td>
<td>± 18 %</td>
</tr>
</tbody>
</table>

The polymers and succinic anhydride reactions had to be performed at different temperatures due to the polymers reacting slowly at room temperature and succinic anhydride reacting too quickly to monitor at 67 degrees Celsius. By
performing the succinic anhydride reaction at five different temperatures, it was possible to obtain an activation energy, 47.3 kJ/mole, and thus determine the rate constant at 67 degrees Celsius to be 13 L/mol\text{min}. The plots used to determine the rate constants for succinic anhydride can be found in Figures XX through XXIV and for the polymers in Figures XXIX and XXX.

The rate constant data above can be analyzed to show that the reaction of the 50/50 and 86/14 polymers is not diffusion-controlled. If a reaction is purely diffusion-controlled, then the rate constant of the actual chemical reaction, k, will be larger than the rate constant for diffusion, k_0, of the reactants. The viscosity of the aniline-THF system was estimated to be 0.55 mPa\text{s}, which is the viscosity of the solvent, THF. As can be seen from Table XVI, the rate constant for diffusion (7.09 \times 10^{11} \text{L/mol\text{min}}) is much greater than the rate constant for the succinic anhydride/aniline reaction (.72 \text{L/mol\text{min}}) at 20 degrees Celsius. The rate of this reaction is limited by the rate at which succinic anhydride and aniline can chemically react and not by how quickly they diffuse together. Therefore, this chemical reaction is reaction-controlled.

The molecular weight ratio and experimental rate constant ratios for the succinic anhydride and polymer reactions were presented in Table XVII in the Results Section. From the values in this table it was determined that the succinic anhydride reaction with aniline was 250 times faster than the 50/50 polymer reaction and 1600 times faster than the 86/14 polymer reaction. Because these reactions proceeded even slower than the succinic
anhydride/aniline reaction, then they, too, must be reaction-controlled. This
deduction was made because the rates of reaction for these polymers are even
slower than the theoretical rate constant for diffusion for succinic anhydride and
aniline in THF. Therefore, these polymer reactions are also reaction-controlled
and the rate of these reactions depend on the mechanism by which the species
react (local geometries, etc.). It is also important to note that the rate of reaction
for the 86/14 polymer is 6 times slower than the 50/50 polymer reaction. This
difference in reaction rate could be due to a difference in the level of steric
hindrance between the 50/50 and 86/14 polymers.

There are 15 units in the 50/50 polymer and approximately seven to eight
of these units are maleic anhydride groups. For the 86/14 polymer, there are
150 units and of these units approximately 21 are maleic anhydride groups. The
86/14 polymer has more maleic anhydride groups per chain but also more
styrene groups causing more steric hindrance in the 86/14 polymer than in the
50/50 polymer. Also, the polymer chain in both the 50/50 polymer and the
86/14 polymer can prevent the reaction site from being accessible to the aniline.
The succinic anhydride model compound does not have this problem of steric
hindrance. The 50/50 polymer possesses primary hindrance from the species
attached directly on the anhydride ring causing the reaction to be about 250
times slower. In addition to primary hindrance, the 86/14 polymer may also
possess secondary hindrance due to parts of the chain not directly bound to the
anhydride being able to wrap around and still get in the way of the reaction site, causing the reaction to be 6 times slower than the 50/50 polymer.

For the 86/14 polymer there are 6.1 times more styrene groups than maleic anhydride groups. The 50/50 polymer has a 1:1 ratio of styrene groups to maleic anhydride groups. Therefore, there is a 6 times greater chance of an aniline bumping into a styrene group instead of a maleic anhydride group in the 86/14 polymer than in the 50/50 polymer. Thus there are six times more styrene to hit before reaching a maleic anhydride to react with in the 86/14 polymer compared to the 50/50 polymer. As can be seen from the ratio of the rate constants for the 86/14 polymer: 50/50 polymer, the rate constants of the 50/50 polymer is 6 times larger than the 86/14 polymer. This value corresponds to the fact that there are 6.1 times more styrene groups in the 86/14 polymer compared to the 50/50 polymer. Thus, the fact that the 86/14 polymer reaction is 6 times slower than the 50/50 polymer is more than likely caused by there being more styrene groups, or primary hindrance, instead of being caused by secondary hindrance due to the “wrapping” of the polymer chain.

In summary, these acylation reactions were determined to be exothermic and reaction-controlled. There were a few conditions necessary for the kinetic studies which must be reiterated. They are: 1) dry reaction conditions for the polymers, 2) consistent and accurate aliquot protocol and sample preparation, 3) use of a quinine sulfate standard to compare kinetic runs performed on
different days, and 4) consistent temperature for the reaction vessel, i.e. use of ice bath or reflux to maintain vessel temperature.

There are two possible directions that this project could take from here. The first would be to use a model compound which may better represent the primary hindrance found in the styrene/maleic anhydride polymers, such as 2, 3-t-butylbutanedioic anhydride:

![Chemical Structure](image)

The other possible direction for this project would be to use larger rings with amino substituents, for example 1-aminonaphthalene or 1-amino-pyrene to determine the effect of the number of rings on the rate constants. Another important step for this project would be determining the concentrations of the samples used for the kinetic experiments by another instrument, such as HPLC. This experiment would help to determine the validity of the fluorescence results. In order to accomplish the above tasks, reaction conditions and mathematical ways to compare data between each amine would need to be determined. The above experiments are needed to more fully understand the kinetics of these type of polymer reactions.
APPENDIX A

The following appendix contains procedures specific to two of the instruments used for experimentation.

**Perkin Elmer UV/Vis Spectrophotometer**

Let the UV/Vis lamps and recorder warm up for approximately one half hour. The instrument parameters should be set as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mode</strong>:</td>
<td>Absorbance</td>
</tr>
<tr>
<td><strong>Scan speed</strong>:</td>
<td>20 nm/min</td>
</tr>
<tr>
<td><strong>Format time</strong>:</td>
<td>5 nm/cm</td>
</tr>
<tr>
<td><strong>Response time</strong>:</td>
<td>2 sec</td>
</tr>
<tr>
<td><strong>Slit width</strong>:</td>
<td>2.0 nm</td>
</tr>
<tr>
<td><strong>Lambda minimum</strong>:</td>
<td>191 nm</td>
</tr>
<tr>
<td><strong>Lambda maximum</strong>:</td>
<td>500 nm</td>
</tr>
<tr>
<td><strong>Ordinate minimum</strong>:</td>
<td>0.000</td>
</tr>
<tr>
<td><strong>Ordinate maximum</strong>:</td>
<td>2.000</td>
</tr>
</tbody>
</table>

Set the recorder on remote and set the chart at 480.

**Perkin Elmer MPF - 3L**

Adjust the meter needle to approximately five by using the sample zero percent adjust knob. Then set the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample sensitivity</strong>:</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>Excitation slit</strong>:</td>
<td>7 nm</td>
</tr>
<tr>
<td><strong>Emission slit</strong>:</td>
<td>7 nm</td>
</tr>
<tr>
<td><strong>Scan speed</strong>:</td>
<td>3</td>
</tr>
<tr>
<td><strong>Excitation wavelength</strong>: (from UV/Vis data for aniline)</td>
<td>239 nm</td>
</tr>
<tr>
<td><strong>Emission dial</strong>:</td>
<td>380 nm</td>
</tr>
</tbody>
</table>

Turn the recorder to 12 and set to record in cm/min.
REFERENCES


