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Thermal analysis of poly(desamino arylates)

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ABSTRACT

THERMAL ANALYSIS OF POLY(DESAMINOTYROSYL ARYLATES)

by

Ali Cem Recber

The goal of this study is to better understand the thermal characteristics and molecular behavior of two poly(desaminotyrosyl arylates). These two polymers were chosen from a combinatorial library of polymers developed by changing the type and size of the two substitutable chain locations. TGA, DSC and TSC studies were conducted on Poly(12,10) and Poly(2,2) after the samples were exposed to various conditions. The TGA of Poly(12,10) shows low water uptake at 25°C, higher water uptake at 80°C. Water uptake for Poly(2,2) at 25°C is similar to Poly(12,10) at 80°C. The Thermally Stimulated Current analysis (TSC) results indicate a molecular mobile region for Poly(2,2) at 80°C and for Poly(12,10) at 40°C. An additional mobile region at 60°C for Poly(12,10) fibers is observed. DSC and TSC studies suggest that Poly(12,10) has two distinct modes of organization with a transition between these modes at about 60°C. The mode above 60°C has the higher water uptake than the mode below 60°C. Annealing at 70°C for 20 hours favors the high temperature mode. At room temperature, the material will relax to the low temperature mode. Previously published results indicate that these two modes of non-crystalline organization represent two different modes of hydrogen bonding.
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APPROVAL PAGE

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To my loved ones for their support and encouragement.
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CHAPTER 1
INTRODUCTION

1.1 Objective

Biomaterials are synthetic materials that are created in order to replace, support or heal tissue/organ. A biomaterials ability to achieve success depends on its properties and the body’s acceptance of the material. As the implant is placed in the body it must not invoke immunological and toxic responses. How the material is placed in the body and what its properties and functions are must be predetermined. Acceptance or rejection of the implant material is largely dependent on the bulk and surface properties of the implant. Thus before a material is implanted in the body, an extensive characterization of its properties must be done. These properties include mechanical, thermal, biodegradability and the changes of these properties as the material ages in the biological conditions. This characterization process is an important step in understanding the initial and long-term behavior of the material. This study involves the thermal characterization of two specific polymers created by Joachim Kohn for biomedical applications[1-3].

Tyrosine derived polycarbonates have been developed by Kohn at Rutgers University. The polymers are desaminotyrosyl monomers incorporated into a combinatorially designed library of polyarylates. These polymers achieve a wide range of thermal and mechanical properties by varying the length of the methylene groups. The library is created by varying the number of methylene groups in two different sites. One substitution site is in the side chain and the other site is in the backbone (Figure 1). The polymers studied will be referred as poly(R,Y). In this study, the two polymers chosen
were poly(DTE succinate) and poly(DTD decane). Poly(DTE succinate) will be referred as Poly(2,2) and poly(DTD decane) will be referred to as Poly(12,10). For Poly(2,2) the representations for R and Y are as follows Y: -(CH₂)₂ and R: -(CH₂)-(CH₃). For Poly(12,10) the R and Y representations are R: -(CH₂)₁₁-CH₃ and Y: -(CH₂)₁₀. The DT refers to the backbone composition that is desaminotyrosinetyrosyl based. The logic behind choosing these two polymers was to see the changes represented by these two extreme substitution conditions. Previous studies conducted on the combinatorial library have suggested a relationship between lengths of the methylene groups at these two locations to the molecular organization. These studies have shown that when the methylene groups at these substitution sites are short in length the material is amorphous. As the methylene groups at R and Y increase in length, the material is no longer amorphous and a certain organization is observed. This study is aimed at better understanding the nature of the bulk organization using these two polymers as representatives of short and long methylene chain length. Conventional and non-conventional thermal analysis techniques will be used to probe the behavior of these materials.
1.2 Background Information on Thermal Analysis

Thermal analysis of polymers is a common method for polymer characterization relevant to biomaterials. Using thermal analysis, it is possible to determine fundamental properties of a polymer such as phase transitions temperatures, rheology and molecular mobility. Different thermal analysis techniques give clues to different aspects of properties and behavior of polymers. It is the summation of these clues that enable us to determine whether a polymer is a good candidate as an implantable device. In this study three thermal analysis techniques were used. These techniques are Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Thermally Stimulated Current analysis (TSC).

Thermogravimetric Analysis and Differential Scanning Calorimetry are common

![Chemical structure of Poly(12,10) and Poly(2,2). Y: Number of methylene groups of the alkyl side chain. R: Number of methylene groups of the aliphatic diacid. Poly (R,Y): Poly (12,10) and Poly (2,2).]
methods used in polymer characterization. However TSC is a relatively unknown
technique. Aside from the thermal analysis of Poly(12,10) and Poly(2,2), the secondary
goal of this study is to introduce the TSC method as an important tool to supplement
other thermal analysis methods. Below is a brief description of each thermal analysis
 technique. Since TGA and DSC are common methods, the descriptions are not in detail.
However the description for the TSC is more detailed and other references will be
provided in the event the reader is interested in learning more about this technique.

1.2.1 Thermogravimetric Analysis (TGA)
This is a technique that measures the weight changes of a sample as a function of time
and/or temperature. Applications of TGA include determination of samples thermal
stability, amount of solvent remaining and amount of water absorbed. In TGA, a sample
is placed in an aluminum pan that has been tared previously. This aluminum pan is
attached to a balance that is very sensitive to any changes to weight. The sample and the
aluminum pan is placed inside a high temperature furnace. As the temperature is
increased inside the furnace, the balance measures the changes in the weight of the
sample. The instrument continuously compares the weight at room temperature to the
weight at the increased temperatures. The experimental output is the weight gained or
weight lost as a result of applying heat to the sample. The TGA is able to run at a specific
heating rate or isothermally. It is typically run in a controlled atmosphere. In the case of
this study, the heating rate was 5°C/min and the run was under constant nitrogen flow.
1.2.2 Differential Scanning Calorimetry (DSC)

Among the thermal analysis techniques, DSC is one of the most commonly used methods. Differential Scanning Calorimetry is used to examine the thermal transitions of a sample as a function of temperature. These transitions include glass transition, melting and crystallization. The sample is placed inside an aluminum pan and placed on one of two heating platforms inside a furnace. On the other heating platform, a second empty aluminum pan is placed as a reference. Both heating platforms are located in the same furnace. The instrument heats the two heating platforms at a specific heating rate. Both heating platforms are heated at the same heating rate. Since one heating platform has the sample and the other is empty, during a thermal event the temperature of each platform will be different. The difference in the temperature of the sample and the reference is the basis for the DSC. Typically, the output consists of the temperature on the x-axis and the difference in heat flow between the two platforms on the y-axis.

Using the difference in heat flow, it is possible to calculate heat capacity of a sample. Heat flow is units of heat (q) supplied per unit time (t). The heating rate is change in temperature (deltaT) per unit time (t). The ratio of heat flow to heating rate is the heat capacity (Equation 1.1).

\[
\frac{q}{t} \div \frac{\text{deltaT}}{t} = \frac{q}{\text{deltaT}} = \text{Cp(heat capacity)}
\]

During a DSC run, the changes in heat flow will give the changes in heat capacity as shown on Equation 1.1. On a DSC run, the thermal transitions a sample undergoes will be observed by the changes in the heat flow or heat capacity. For instance, a sample has a
higher heat capacity above its glass transition. During a DSC run, this is observed by the increase in heat absorption. Since more heat is absorbed, the heat capacity increases using Equation 1.1. Since \( T_g \) takes place over a temperature range, it is sometimes difficult to determine the exact temperature. Typically, \( T_g \) is taken as the temperature at which one half the change in heat capacity \( \Delta C_p \).

In the case of crystallization, the heat flow is in the opposite direction compared to glass transition. Thus, crystallization results in not absorption of heat but in dissipation of heat. This is observed in a DSC run as a big peak in the plot of heat flow versus temperature. In the case of melting, what is observed is the opposite of crystallization. During melting, absorption of heat is observed and it shows as a dip in the heat flow versus temperature plot (Figure 1.2).

![DSC plot showing thermal transitions](image)

**Figure 1.2** DSC plot showing thermal transitions.

Tg: Glass Transition.
Tc: Crystallization.
Tm: Melting.
1.2.3 Thermally Stimulated Current (TSC)

Thermally stimulated current (TSC) is a phenomenon in which a current is generated due to displacement of charges as a response to an applied electric field. When a material is placed under an electric field, the polar groups in the material align with respect to the electric field. The movement of these polar groups generates a current that is measured. TSC is the technique that is used to detect and analyze these currents. It is thermally stimulated because in this technique the current that is generated as a response to the electric field is analyzed as a function of temperature. This technique is sensitive to any molecular motion in the material. These molecular motions can be glass transitions and conformational motions. There are also motions due to enthalpic consideration such as crystal or liquid crystal transitions. It is expected that the movements due to Tg, conformational motions and dipole relaxations generate smooth polarization peaks compared to sharp polarization peaks observed in the type of movements due to enthalpic ordering.

Thermally Stimulated Current analysis can be performed by either thermally stimulated polarization current (TSPC) or by thermally stimulated depolarization current (TSDC). In TSDC, an electric field is applied to the material at a specific temperature in which there is enough energy for molecular motion. An electric field is applied so that the polar groups are aligned. After this, the material is brought to a lower temperature at a specific cooling rate, with the electric field still applied. At the lower temperature, the dipoles are no longer mobile and the orientation due to the polarization remains. Once the polar groups are frozen in the alignment, the electric field is turned off and the material is heated at a specific heating rate. As the material is heated, the oriented polar groups again
become mobile but this time without the electric field. This leads to the polar groups to reorganize in the more stable unaligned configuration. As the dipoles reorganize, the motion of the polar groups generates a current. This is the thermally stimulated depolarization current. Figure 1.3 below shows a description of a TSDC experiment.

![Diagram of TSDC experiment]

**Random molecular mobility.**

Temperature is increased and electric field is applied

Temperature is decreased while electric field is applied

Temperature is increased without the electric field

At low temperature molecules are immobile and remain aligned.

As molecules gain mobility, they align with respect to the E-filed.

As molecules become mobile, relaxation occur and random molecular mobility occur.

**Figure 1.3** Description of a TSDC experiment.

Thermally Stimulated Polarization Current is a method in which the material is brought to a lower temperature without the electric field. The material is then heated at a specific heating rate with the electric field on. The current that is generated as the polar groups align due to the electric field is called TSPC. Figure 1.4 on the next page describes a TSPC experiment.
In both cases the current measured is due to the displacement of charged groups within the material. The current is related to the number of charged groups present in the material. The relationship between polarization and the number of charged groups can be given by the equation derived from the Langevin analysis for thermal equilibrium during polarization.

\[ P_o = NpE / 3kT \]

\( N \) is the number of dipoles. \( E \) is the magnitude of the electric field. \( p \) is the dipole moment. \( k \) is the Boltzmann constant. \( T \) is the polarization temperature. The motion of the dipoles, as they move from the oriented to the unoriented position, generates an
experimentally detectable electric current. This process is called depolarization and the rate of depolarization, the loss of polarization per unit time, is the depolarization current.

\[ J(t) = \frac{dP(t)}{dt} \]  

In TSDC the current is the depolarization current and in TSPC the current is the polarization current. However in both cases the current is the change in polarization. The current is represented by \( J(t) \) and can be calculated by Equation 1.3.
CHAPTER 2
EXPERIMENTAL

2.1 Thermogravimetric Analysis (TGA)
Thermogravimetric analysis was conducted on Poly(12,10) and Poly(2,2) in order to study the amount of water absorption. TA instruments Q50 was used for TGA analysis. Initial experiments were conducted on samples that were taken from the desiccator. All the samples were in film form. The difference between the water absorption levels were then studied at various conditions. Initially, both samples were placed in deionized water for 24 hours in room temperature. Additional experiments were conducted in order to understand the effect of time and temperature on the extent of water absorption. These experiments were carried out by varying the time of immersion of the samples and the temperature of DI water. The heating rates for the experiments were 5°C/min.

2.2 Differential Scanning Calorimetry (DSC)
Differential Scanning Calorimetry was conducted on Poly(12,10) and Poly(2,2) at 7°C/min for both heating and cooling rate. A TA instruments Q100 was used to conduct the experiments. For DSC experiments, the Heat/Cool/Heat method was used. In this method, the initial heating is done to erase possible thermal history of the sample. The cooling and second heating is used to determine thermal transitions of the polymers. DSC was used to determine phase transitions as a function of temperature. The melting and crystallization temperatures as well as enthalpic re-organizations were detected through the DSC method.
The DSC runs for Poly(12,10) were also used to understand how high temperatures affect the thermal transitions. Runs were conducted on the Poly(12,10) in which the same sample was heated from 0°C and the highest temperature varied from 70°C to 120°C. The changes in thermal transitions a sample undergoes as the sample is heated to different temperatures were observed.

Additional experiments for the Poly(12,10) were conducted to see the effect of multiple heatings by DSC. Heat/Cool/Heat cycle of Poly(12,10) was repeated five times consecutively with a heating and cooling rate of 7°C/min from 0°C to 120°C. Later, the same sample was run in a similar method of Heat/Cool/Heat cycle five consecutive times with a temperature range of 0°C to 90°C.

Annealing studies of the Poly(12,10) were also performed to examine the changes in thermal transitions. Sample of Poly(12,10) was placed in an oven for 75°C for 20hr. The sample was immediately placed in the DSC for analysis. The Heat/Cool/Heat cycle was conducted on the sample multiple times. Each run had the same heating and cooling rate. The only difference was the temperature the sample was heated to, which varied from 70°C to 120°C. The DSC run of the heat treated sample was compared to a non-heat treated Poly(12,10) run under same conditions. The purpose of the experiment was to better understand the changes in thermal transitions and the molecular organizations with respect to annealing. The DSC results were analyzed to understand the thermal transitions as well as the thermal stability of Poly(12,10) and Poly(2,2)
2.3 Thermally Stimulated Current (TSC)

Thermally stimulated current analysis was conducted in two different protocols. Thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC). Both modes were able to show the molecular mobility in both Poly(12,10) and Poly(2,2). In addition to the molecular mobility, modifications to the TSDC mode allowed the detection of enthalpic reorganizations that took place in Poly(12,10). For both Poly(12,10) and Poly(2,2), the heating and cooling rate was $7^\circ$C/min. The temperature range for Poly(12,10) was $0^\circ$C to $90^\circ$C and for Poly(2,2) it was $30^\circ$C to $110^\circ$C. Below is a brief description of the TSC experiment parameters.

**2.3.1 Thermally Stimulated Polarization Current (TSPC)**

In TSPC the temperature is brought down to a temperature at which the molecular motion is frozen. As the sample is heated at a rate of $7^\circ$C/min, an electric field with a specific voltage is applied. As the molecules gain mobility, the polar groups begin to align with respect to the electric field. It is the displacement of these polar groups as they align that is detected as current. Figure 2.1 below shows the profile of a TSPC run.

![Figure 2.1 Sample TSPC run.](image)

**Figure 2.1** Sample TSPC run. Ep: Applied voltage per mm thickness of sample. Current due to polarization of polar groups and current due to enthalpic organization is detected.
2.3.2 Thermally Stimulated Depolarization Current (TSDC)

Thermally Stimulated Depolarization Current probes the molecular mobility of the polar groups from the aligned confinement. Thus as TSPC measures the current as polar groups align, TSDC measures the polar groups as they relax from the aligned configuration. Generally, the sample is brought to a higher temperature where there is sufficient energy for the molecules to become mobile. The electric field is turned on to accomplish dipole alignment and the sample is brought to a lower temperature where the molecules are frozen in motion and remain aligned. While the sample is cooled, the electric field remains on. Once the sample is cooled, the electric field is turned off and the sample is re-heated. As the polar groups regain mobility, they begin to relax to a more stable unaligned configuration. This is called molecular relaxation. The TSDC mode can be run in a different way to detect molecular relaxations and also to detect current generated due to enthalpic re-organizations. Below are the different types of TSDC modes that were used to distinguish between these two types of current.

![Exp Params](image)

**Figure 2.2** Sample TSDC run I. Sample is polarized at first two segments. The current is read during the third segment when the sample is heated at a specified rate. Current is a result of polar relaxation and enthalpic organization.
Figure 2.3 Sample TSDC run II. Sample is polarized at all times. There is no dipolar relaxation since the electric field is on at all times. The current is measured at second and fourth segments. The current detected is due to enthalpic organizations only.

Figure 2.4 Sample TSDC run III. Sample is polarized during the first and second segments. The current is read during the second and fourth segments. The current detected at the second segment while cooling down is due to enthalpic re-organization. The current during the fourth segment is dipolar relaxation and enthalpic re-organization.

When a polar group begins to align with respect to the field during TSPC runs or begins to relax during a TSDC run, the current generated is due to dipole mobility. However, if a current is detected while the polar groups are not mobile due to
temperature or the electric field, the current is due to the re-organization of the polymer due to enthalpic considerations. By use of the various types of TSDC runs shown above it was possible to determine which of the current peaks are due to dipole mobility and which are due to enthalpic re-organization.

2.4 Sample Preparation

The polymers were received from Advanced Material Design, Piscataway, New Jersey. The samples were in powder form and were made into film by compression molding at 140°C using a Carver press. After compression molding, the samples were placed in a cooler. After this point the samples were stored in a desiccator. All the thermal analysis experiments were conducted on samples as films.

For TSC analysis previously made fibers were used. Fibers were spun with a James plunger fed micromelt spinner, fitted with a single hole 750 micron diameter spinnerette[4].
CHAPTER 3
RESULTS

3.1 Water Absorption

Thermogravimetric experiments were carried out on Poly(12,10) and Poly(2,2) in order to measure the extent of water absorption using TA Instruments Q50. Samples were in film form and immersed in a small jar containing deionized water. A water bath was used for samples that were immersed at temperatures higher than room temperature. The jar with the sample and DI water were placed inside the water bath and precautions were taken to prevent any of the bath water from getting inside the jar. The water absorption of Poly(12,10) and Poly(2,2) was measured for samples immersed in DI water at room temperature for 24 hours. Other TGA experiments were conducted in which the temperature and length of immersion time was varied. These experiments showed the effect the time and temperature of immersion has on the extent of water absorption for both Poly(12,10) and Poly(2,2).

For the study, the heating rate was 5°C/min. Figure 3.1 illustrates the results of the TGA studies. For Poly(12,10) it was observed that the water loss was not significant after 100°C. The remainder of the studies were conducted so that the samples were heated to 100°C. The level of water absorption of Poly(2,2) agrees with previous studies which have shown that water plasticization of Poly(2,2) leads to rapid loss of mechanical properties and high levels of shrinkage [4]. Other water absorption experiments were conducted to determine the necessary conditions to increase the water absorption of Poly(12,10).
Figure 3.1 TGA analysis of Poly(12,10) and Poly(2,2) with samples placed in DI water at varying temperature and time.
3.2 Thermal Transition Experiments

Various DSC experiments were conducted to understand the thermal transitions of Poly(12,10) and Poly(2,2) using TA instruments Q100. Early into the study of Poly(2,2) it was realized that it did not undergo any significant thermal transitions other than the glass transition (Figure 3.2). These results were consistent with previous studies [5]. Most of the attention was given to Poly(12,10) and how the DSC results varied using different experimental conditions. Experiments were conducted as Heat/Cool/Heat cycles with heating and cooling rate of 7°C/min. The samples were all films but the treatments varied. Figure 3.3 shows an experiment in which the sample was heated five times with a temperature range of 0°C to 120°C. Figure 3.4 shows the same sample again heated five times at a different temperature range of 0°C to 90°C. In another experiment (Figure 3.5), the sample was heated six times. With each run, the sample was heated from 0°C to a different temperature with increments of 10°C. The starting temperature range was 0°C to 70°C and the final temperature range was 0°C-120°C. Figure 3.6 shows a similar run performed on Poly(12,10) annealed at 70°C for 20 hours.
Figure 3.2 Heat/Cool/Heat DSC run of Poly(2,2) showing only Tg and no other thermal transitions.
Figure 3.3 Heat/Cool/Heat cycle repeated five times Poly(12,10). Temperature range 0°C-120°C.
Figure 3.4 Heat/Cool/Heat cycle repeated five times Poly(12,10). Temperature range 0°C-90°C. Same Sample as Figure 3.3.
In another experiment (Figure 3.5), the sample was heated six times. With each run, the sample was heated from 0°C to a different temperature with increments of 10°C. The starting temperature range was 0°C to 70°C and the final temperature range was 0°C-120°C. Figure 3.6 shows a similar run performed on Poly(12,10) annealed at 70°C for 20 hours.
Figure 3.5 Heat/Cool/Heat cycle repeated six times with varying final temperature. Poly(12,10). Same sample in all runs.
Figure 3.6 Poly(12,10) annealed at 70°C for 20 hours. Heat/Cool/Heat cycle repeated four times with varying final temperature.
3.3 Molecular Mobility Experiments (TSC)

Thermally stimulated current analysis experiments were conducted on Poly(2,2) and Poly(12,10) to study the molecular mobility of the polymers. Similar to DSC experiments, the samples were in film form. In addition, Poly(12,10) fibers were also tested. Samples were placed between two electrodes. Before each experiment, the instrument undergoes an initialization procedure where the TSC cell is under vacuum and immediately flushed with helium. This removes any humidity and any other contaminants. This vacuum/flushing with helium is repeated three times and the remainder of the experiment is carried out under helium in 1100 mbar constant pressure. Samples were cooled using a constant flow of liquid nitrogen.

Figure 3.7 Schematic diagram showing the set up of the TSC/RMA 9000. Taken from the user manual of the instrument.
3.3.1 TSC Analysis of Films

The TSC analysis for Poly(2,2) and Poly(12,10) was conducted using different experimental parameters. Initial experiments were conducted on the polymers to examine the molecular mobility. For each sample TSDC and TSPC experiments were conducted at different applied electric voltage to analyze the dependence of current intensity on applied electric field. Figure 3.8 and Figure 3.9 below shows multiple TSPC and TSDC experiments for each sample. Positive peaks are the TSDC experiments. Negative peaks are the TSPC experiments. Since TSDC is depolarization and TSPC is polarization currents, the signals are mirror images of each other. Figure 3.8 shows the relationship of current intensity on applied electric field for a film sample of Poly(12,10). Figure 3.9 on the next page shows a similar run on a film sample of Poly(2,2).

![Graph showing TSPC and TSDC analysis](image.png)

**Figure 3.8** TSPC and TSDC analysis of Poly(12,10) Graph shows the relationship of current intensity and applied electric field.
Experiments were also conducted on Poly(12,10) and Poly(12,10) that had been immersed in deionized water. TGA analysis showed that Poly(2,2) absorbs water at room temperature and Poly(12,10) does not (Figure 3.1). TGA analysis also showed that Poly(12,10) absorbs water when immersed in deionized water at higher temperatures. TSC analysis was conducted on Poly(2,2) and Poly(12,10) immersed in DI water at room temperature and also at higher temperatures to observe any changes in the TSC spectra for both samples as a consequence of absorbed water. Figure 3.10 below shows the effect of water absorption on the TSC spectra for a film sample of Poly(2,2). The sample was immersed over night in deionized water at room temperature.

Figure 3.9 TSPC and TSDD analysis of Poly(2,2) Graph shows the relationship of current intensity and applied electric field.
Figure 3.10 shows that there is a shift in peak intensity to a lower temperature due to water absorption. With every consecutive run, the polymer dries and the peak intensity is shifted to the right. After about the 3\textsuperscript{rd} to 4\textsuperscript{th} run, most of the water has evaporated and the shift in the peak intensity is no longer seen. Previous studies on Poly(2,2) has shown that when a sample is wet the Tg is shifted to a lower temperature. With every consecutive run the sample dries and the shifting is no longer seen and the Tg remains at around 80°C. The data in Figure 3.10 show similar results conducted through TSC analysis. The Tg values and its behavior agrees with the previous study [5].
Thermally Stimulated Current experiments were also conducted on Poly(12,10) samples immersed in deionized water overnight at room temperature. When sample of Poly(12,10) is immersed in water overnight at room temperature the TGA analysis showed very little water absorption. As a result it was expected that the TSC results would be the same compared to a TSC result of a dry Poly(12,10) sample. Figure 3.11 shows the result of the TSC experiment in which a film sample of Poly(12,10) was immersed in deionized water at room temperature overnight. When compared to Figure 3.8 (TSC of a dry Poly(12,10)), the results are very similar.

![Figure 3.11 TSC analysis of Poly(12,10) immersed in deionized water at room temperature overnight.](image-url)
Since TGA analysis showed that Poly(12,10) absorbs water at higher temperature, additional TSC experiments were conducted in which film samples of both Poly(12,10) and Poly(2,2) were immersed in 80°C deionized water for a period of 2 hours. Figure 3.12 and Figure 3.13 show that the water absorption in both samples lead to plastization and a shift of the peak to lower temperatures. With every consecutive run, water is released and the samples dry. This results in the peaks to shift to higher temperature until it reaches the expected values of 40°C of for Poly(12,10) and 80°C for Poly(2,2). The shifting to lower temperatures are consistent with the amount of water each sample absorbs. Poly(2,2) absorbs greater amount of water and as a result has a greater shift to lower temperatures.

![Graph](image.png)

**Figure 3.12** TSPC analysis of Poly(12,10) immersed in deionized water at 80°C for a period of 2 hours.
The experiments on Poly(12,10) showed that the major peak at around 40°C is linearly related to the applied field (Figure 3.8). However the smaller peak at around 60°C was not. Experiments were conducted using a modified TSDC run as discussed in section 2.3.2. In a typical TSDC experiment (Figure 2.2. Sample TSDC Run I), the current is measured only during heating in which the field is off. In the modified TSDC experiment (Figure 2.4 Sample TSDC Run III) the current is measured during cooling when the field is on and also during heating when the field is off. After the initial polarization, the current detected during cooling can not be due to dipolar relaxations since the dipoles are immobilized as a result of the applied field. The current detected while cooling is due to

Figure 3.13 TSPC analysis of Poly(2,2) immersed in deionized water at 80°C for a period of 2 hours.
enthalpic re-organization and the current during heating is depolarization and enthalpic re-organization. The goal of the experiment was to point out that if the current measured at 60C is enthalpic re-organization, then it should remain during the cooling phase in which polar groups are immobilized. The experiment was run on the same sample twice (Figure 3.14). The first run is at an applied electric field of 200V and the second run at 400V.

![Graph](https://via.placeholder.com/150)

**Figure 3.14** Modified TSDC Run III of Poly(12,10). Graphs shows the depolarization current (40C) and enthalpic organization (60C) upon heating and enthalpic organization only during cooling.

Figure 3.15 shows the same two experiments as Figure 3.14. However, the signal for 200V is multiplied by 2 through the software in order to directly compare the
intensity of the two peaks at two different voltages. The runs are made consecutively with
the same sample to point out the direct dependence of current intensity on the applied
electric field for dipolar relaxation and the lack of direct dependence of current intensity
on the applied electric field in the case of enthalpic re-organization. The direct
relationship is due to the linear relationship that exists between the number of dipoles
aligned and the amount of voltage applied as mentioned in Section 1.2.3.

![Graph showing TSDC runs at 200V and 400V](image)

**Figure 3.15** Modified TSDC Run III of Poly(12,10) with the signal at 200V multiplied by 2.

Modified TSDC runs and TSPC run were conducted on Poly(2,2). In all the runs
there was only one peak observed at around 80°C (Figure 3.16). This is the peak
associated with the glass transition of the polymer.
3.3.2 TSC Analysis of Poly(2,2) Fibers

From the TSC studies conducted on the Poly(2,2) and Poly(2,2) film, it was seen that the Poly(2,2) had only one peak associated with the glass transition. Poly(2,2) showed two distinct peaks, one associated with molecular relaxation and the other enthalpic reorganization. Additional TSC studies were conducted on Poly(2,2) fibers to see the effect of processing on the molecular relaxation and enthalpic re-organization. The TSDC, TSPC and modified TSDC experiments carried out for the Poly(12,10) film were repeated for the Poly(12,10) fiber.

**Figure 3.16** TSDC runs and TSPC run of Poly(2,2). In the modified TSDC Run II (Figure 2.3) Light Blue, the polarization is on at all times and there is no current measured. This suggest an absence of enthalpic re-organization and only the peak due to Tg is observed.

3.3.2 TSC Analysis of Poly(12,10) Fibers

From the TSC studies conducted on the Poly(12,10) and Poly(2,2) film, it was seen that the Poly(2,2) had only one peak associated with the glass transition. Poly(12,10) showed two distinct peaks, one associated with molecular relaxation and the other enthalpic re-organization. Additional TSC studies were conducted on Poly(12,10) fibers to see the effect of processing on the molecular relaxation and enthalpic re-organization. The TSDC, TSPC and modified TSDC experiments carried out for the Poly(12,10) film were repeated for the Poly(12,10) fiber.
Figure 3.17 TSDC Run I analysis of Poly(12,10) fibers. Graph shows an extra peak around 60°C that is linearly related to the applied electric field suggestive of an additional mode of molecular relaxation in Poly(12,10) fibers.

In Figure 3.17 an additional peak at 60°C is observed. This is the temperature where the peak for the enthalpic re-organization was previously observed. A modified TSDC Run II (Figure 2.3) was conducted to single out the peak due to enthalpic re-organization to make sure that it was still present. The current was measured during the cooling stage. This allows the detection of enthalpic re-organization only as discussed in sub-section 1.2.3. The result of this experiment is illustrated in Figure 3.18.
The TSDC experiments clearly show an additional peak at 60°C not present in film samples. The linear relationship of this peak to the applied electric field and the absence of the peak during modified TSDC experiments strongly suggests that this peak is an additional molecular relaxation peak that is not seen or not detected in the film form of Poly(12,10). If the peak is associated with fibers and not films, then the peak should decrease or disappear with consecutive runs of the fiber at higher temperature. Additional
TSDC experiments were conducted on the fiber where multiple runs of conventional TSDC (TSDC Run I) experiments were performed consecutively. The temperature range was changed from 0°C-90°C to 0°C-120°C. Figure 3.16 shows the results of this experiment. Since the temperature range is increased, the sample will lose its fibrous structure and with every consecutive heating to 120°C it will resemble more of a film structure. It is expected then, that the second peak associated with the fibrous peak will decrease. Inspection of the samples after the experiments showed that the samples were no longer fibrous but were fused together into a film. As Figure 3.19 shows, the additional peak associated with fibrous structure, decreases with each consecutive run.

![Figure 3.19](image)

*Figure 3.19* Multiple TSDC Run I experiments on Poly(12,10) fiber. With every consecutive run, the extra peak associated with molecular relaxation decreases and the enthalpic peak becomes more apparent.
CHAPTER 4
DISCUSSION

4.1 Water Absorption

Thermogravimetric Analysis of Poly(12,10) and Poly(2,2) has shown the distinct differences between the two polymers in their ability to absorb water. In Figure 3.1, Poly(2,2) shows a water absorption of 3.2% when placed in DI water at room temperature overnight. Previous studies have shown similar water absorption levels. These studies also pointed out the rapid plasticization of water resulting in quick loss of mechanical properties and high levels of shrinkage[5].

Thermogravimetric Analysis experiments on Poly(12,10) have shown that the level of water absorption varies and it depends on the thermal history of the polymer. When Poly(12,10) is placed in water at room temperature overnight, there is only 0.56% water absorption compared to 3.2% for Poly(2,2). Additionally, when Poly(12,10) is placed in water at room temperature for two weeks there is only a small increase in water absorption to about 0.85%. However, the water absorption characteristics of Poly(12,10) significantly change when the polymer is placed in DI water at higher temperature. In fact the absorption levels become very comparable to Poly(2,2) when the sample is placed in 80°C water for two hours. Figure 3.1 shows that the water absorption of Poly(12,10) at 80°C for 2 hours is 2.11%. This is a significant increase compared to 0.85% at room temperature for 2 weeks. The significant difference in water absorption is an important indication of the difference in the mode of organization between the two polymers which will be discussed in the following section.
4.2 Structural Organization in Poly(2,2) and Poly(12,10)

4.2.1 Poly(2,2)

Differential Scanning Calorimetry and Thermally Stimulated Current Analysis experiments were conducted on Poly(2,2) to understand the nature of organization and molecular mobility of the polymer over a temperature range of 30°C-110°C. Through the DSC and TSC experiments it was observed that the polymer has a glass transition at around 80°C. The DSC and TSC analysis of the polymer shows the glass transition and no other phase transitions. The TSC agrees with the DSC results showing a molecularly mobile region around the glass transition (Figure 3.2). The TSC and DSC results agree with other studies pointing out the amorphous character of the polymer [4-6]. Additional modified TSC experiments support the absence of any other phase transitions or relaxations of the polymer over the temperature range studied (Figure 3.13).

Thermally Stimulated Current experiments were also conducted on water treated Poly(2,2) (Figure 3.10 and Figure 3.13). It has already been shown in the TGA experiments that the polymer absorption level was 3.2% at room temperature when placed in DI water overnight. The experiments were conducted on wet samples immediately after they were taken out of the water treatment. The TSC experiments show that the molecular mobility of the polymer is significantly affected by the presence of water. Figure 3.10 shows the TSDC and TSPC experiments of water treated Poly(2,2). The experiment was conducted so that consecutive runs were performed. On each consecutive run water is driven off the polymer by the increase in temperature. Thus, the level of water in the sample progressively decreased and the effect is seen by the shifting of the peak to higher temperatures. Figure 3.10 shows that initially the sample has high
levels of water and the peak appears at 60°C. After the sixth cycle of heating to 110°C the water is completely removed and the peak returns to the expected temperature of around 80°C. The shift of this peaks agrees with previous DSC studies conducted on the water treated Poly(2,2) showing a decrease in temperature of the glass transition. Similar to the experiment conducted on TSC runs, the previous report indicates a return to the normal glass transition of 80°C as the polymer dries[5]. The TSC results of Poly(2,2) on both dry and wet samples agree with the DSC results in this study (Figure 3.2) as well as other studies indicating a plasticization of the sample by water [5].

4.2.2 Poly(12,10)

The structural organization of Poly(12,10) is considerably more complicated than Poly(2,2). The TGA analysis of Poly(12,10) has shown two distinct water absorption characteristics of the polymer (Figure 3.1). At lower temperatures, the water absorption is very low and at higher temperature it is comparable to the water absorption levels of Poly(2,2) at room temperature. Thermal analysis experiments were conducted on the Poly(12,10) as films, fibers, water treated films and annealed films. All these experiments showed a significant variation of phase transitions and molecular relaxations suggestive of a dependence of structure and property on the process history of the polymer.

In the case of a film form of Poly(12,10) the TSC analysis shows a molecular relaxation at 40°C. TSC analysis conducted on the polymer by varying the electric field have shown that the intensity of the peak is linearly related to the applied field following the equation mentioned in sub-section 1.2.3 (Equation 1.2). Additional to the molecular relaxation at 40°C, there is a peak at 60°C. The lack of direct dependence of this peak to the applied field is indicative of this peak being the result of enthalpic re-organization and
not molecular relaxation. This was further supported by modified TSDC experiments (Figures 3.14-3.16). Water treated samples were placed for TSC analysis and for the samples that did not absorb water there was no difference in the TSC spectra (Figure 3.11). Samples that did absorb water showed TSC spectra similar to wet Poly(2,2) samples. The water absorption of Poly(12,10) lead to the shifting of the peak to lower temperatures (Figure 3.12). Similar to Poly(2,2), when Poly(12,10) absorbs water, it results in plasticization and a shift in the peak to lower temperatures. This is a similar process as Poly(2,2) in which water absorption leads to plastization of the polymer. This suggest that although it was not seen in the DSC experiments, the transition at 40°C is a glass transition. The DSC runs in this study and previous studies have not been able to detect any glass transitions of Poly(12,10). Only the water plastization effects in the TSC runs have been able to point to a glass transition at 40°C.

The TSC analysis of the polymer in fiber form on the other hand showed an additional peak associated with molecular relaxation at 60°C. At first it was believed that this peak was again due to enthalpic re-organization that is seen at 60°C for films. However, as Figure 3.17 points out both peaks that are seen, one at 40°C and the other at 60°C, are linearly related to the applied field. This suggests that both peaks are due to molecular relaxation. Experiments were conducted on the fiber samples to see whether the enthalpic peak at 60°C seen on films still remained for fiber. The modified TSDC experiments shown on Figure 3.18 point out the presence of a small enthalpic peak at 60°C. Thus, there are two peaks at about 60°C for fibers. One is linearly related to the electric field, meaning it is an additional mode of molecular relaxation and the other is the peak that is also seen in films associated with enthalpic re-organization. Because the
second molecular relaxation is at 60°C and is greater than the enthalpic peak, modified TSDC runs are necessary to observe the enthalpic peak. During the TSC analysis of fiber it was observed that the repeatability seen in TSC runs of films was not observed in fibers. This is due to the difficulty in preparing uniform fiber samples. The last TSDC experiment was to see the effect of high temperatures on the fiber TSDC spectra. If the additional relaxation peak is associated with the fiber orientation, then increasing the sample to higher temperatures should melt the fiber with the loss of orientation and the spectra should look more like the film form of Poly(12,10). Figure 3.19 shows consecutive TSDC experiments conducted on Poly(12,10) fiber with the final temperature at 120°C. With each consecutive run the second peak decreases. It is also interesting to point out that the enthalpic peak is becoming more apparent as the second relaxation peak decreases.

The DSC analysis of Poly(12,10) also supports the complicated behavior of the polymer. DSC analysis of the polymer was carried out at different temperature ranges. DSC analysis was also carried out for the samples of films annealed for 20 hours at 75°C. Each different DSC experiment showed a complicated aspect of the behavior of the polymer. Initial experiments were conducted with a heat/cool/heat cycle. Initial heating cycle erases the thermal memory of the polymer and the second heating cycle is examined more closely. Figure 3.3 shows a heat/cool/heat cycle with a temperature range of 0°C-120°C repeated five times. It shows one distinct peak at around 41°C on cooling and another peak at around 56°C on heating and a smaller one at 68°C. These major peaks seem to stay at the same temperature range and have the same intensity. Figure 3.4 shows the same experiment repeated with the same sample with the exception of the
heating range of 0°C-90°C. At this temperature range the experiments are not repeatable. With every consecutive run, the peak intensities upon cooling and upon heat decrease and a temperature shift is observed. Upon looking closely at the peak during cooling a second peak appears (Figure 3.4). As one peak decreases, the second peak increases in intensity. This suggests a conversion of one form to another form.

Additional DSC experiments were conducted in which the sample was heated multiple times at different temperature ranges. During the initial run, the sample was heated to 70°C starting from 0°C. With each consecutive run, the sample was heated to a higher temperature in increments of 10°C. The sixth and final experiment had a temperature range of 0°C-120°C (Figure 3.5). During this experiment, it was observed that when the temperature range is 0°C-100°C or higher, a single sharp peak is observed and the peak intensity remains the same. If the temperature range is below 0°C-100°C the double peaks with varying intensities are observed. Additional DSC experiments were carried out where the Poly(12,10) was annealed at 75°C for 20 hours. Again heat/cool/heat cycles with varying temperature ranges were performed. Figure 3.6 shows the DSC analysis of the annealed sample. It is seen that when the final temperature is only 70°C the peak observed on cooling is very low intensity. As the final temperature is increased, the peak on cooling returns back to the values similar to samples that were not annealed. This is indicative of a polymer with different modes of organization where one is more stable than the other depending on the temperature and process history. Figure 4.1 below shows a phase transition diagram that models the phase transitions as observed by DSC and TSC.
The graph above shows the proposed model for the Poly(12,10) where there are multiple modes of organization that the polymer can achieve depending on the temperature. The mode of organization that has the lowest Gibbs free energy at any particular temperature is favored. This is commonly seen in crystals and is called polymorphism. It is the phenomenon where the same chemical substance is able to crystallize in more than one structure. In the case of enantiotropic polymorphism,

**Figure 4.1** Phase transition diagram of Poly(12,10). Graph shows the different modes of organization of Poly(12,10) that are stable at different temperatures with respect to free energy.  
A: Low-temperature mode of aggregation.  
B: High-temperature mode of aggregation.  
U: Unorganized (Possibly Amorphous).
illustrated in Figure 4.1, the substance transforms from mode A to B when heated and the reverse change taking place upon cooling. The DSC and TSC results suggest that the Poly(12,10) has behavior that is similar to an enantiotropic polymorphism. Poly(12,10) is able to undergo different modes of organization depending on the temperature. The DSC and TSC analyses have shown that these transformations are reversible as seen in enantiotropic polymorphism. Although Poly(12,10) is not a crystalline polymer it has been suggested of its liquid crystalline properties and behavior [4-6]. It has been shown that the x-ray diffraction pattern of Poly(12,10) and additional thermal analysis results have supported the idea of Poly(12,10) being highly layered mesogenic structure with layering similar to that of a smectic or discotic liquid crystal[5]. This supports the idea of the polymer having multiple modes of aggregation and one type being favored over the other at different temperatures.

The DSC results showing the loss of signal intensity in Figure 3.4 suggest that the polymer favors the lower-temperature mode below 42°C. However, the loss of signal suggests that less of the lower mode (Mode A) is being formed. This would mean that with every consecutive run the higher temperature mode (Mode B) is forming and it is in a metastable state at below 42°C. This is supported by the fact that if the sample is placed in room temperature, the original intensity comes back. Thus, over time the metastable state has transformed to the lower-temperature mode. Based on Figure 3.4 and the proposed model, the transformation observed at 42°C is the transformation between modes A and B. When the sample is heated multiple times at higher temperature ranges as in Figure (0-120), the signal is very repeatable. Thus the samples is undergoing complete transformation. Based on the model, at 120°C the sample is in the U mode and
the transformation observed upon cooling can be transformation from U to B or from U to A. Further studies are needed to determine the transformation.

During the annealing experiments in Figure 3.6, it was observed that there is a single peak at 80°C. This peak is only seen in the case of annealed samples at 75°C for 20 hours. Annealing studies have also shown that during a heat/cool/heat cycle with upper temperature of 70°C, the peak upon cooling is not seen. This is suggestive that the peak seen at around 80°C is the formation of the higher temperature modification (Mode B). When an annealed sample is placed in room temperature, the expected peak during cooling returns. This supports the idea that the higher temperature mode (Mode B) is formed during annealing and when left at room temperature it returns back to the lower temperature mode (Mode A).

The DSC analysis of Poly(12,10) has also shown that while conducting a heat/cool/heat cycle multiple times at temperature range of 0°C-120°C, the signal during cooling is considerably different than the peak seen while cooling from 90°C. This suggests that the organization taking place when cooling from 120°C is different then the organization observed when cooling from 90°C. Looking at the proposed model on Figure 4.1 it is hypothesized that the peak seen when cooling from 90°C is a transition from mode B to mode A. With every consecutive run, less of the A is being formed. There is only a partial conversion from mode B to mode A. This is the reason for the decrease of signal. When the sample is left at room temperature, the metastable state of B changes back to mode A. This is supported by the return of the peak over time. The peak that is seen upon cooling from 120°C is the transformation of the unorganized or melt
mode directly to the A mode. This is consistent with the behaviour depicted in Figure 3.3 where there is no loss of peak intensity.

Previous FTIR studies have shown that Poly(12,10) has two modes of hydrogen bonding, one at low temperatures and one at high temperatures [8]. The hydrogen bonding associated with the low temperature bonding has been associated with the forming of long range order and the high temperature hydrogen bonding has been linked with the amorphous phase. This is suggestive that the modes of aggregations that are seen in Figure 4.1 are a consequence of the type and magnitude of the two hydrogen bonding. Where Mode A consists of the hydrogen bonding associated with the lower temperature hydrogen bonding and Mode B consist of the hydrogen bonding associated with the higher hydrogen bonding.
CHAPTER 5
CONCLUSION

The thermal analysis of Poly(12,10) and Poly(2,2) were performed to better understand the thermal behavior, chemical behavior, stability and phase transitions of the polymer. This is a necessary step for determining the polymers potential use as an implant. The study has shown that Poly(2,2) is an amorphous polymer that has high rate of water absorption. The glass transition at around 80°C is highly effected by amount of water present in polymer. The water content leads to the decrease of the glass transition with the end result of loss of mechanical properties and shrinkage. At biological conditions this is what should be expected.

Poly(12,10) shows a more complicated behavior. There are two modes of organization seen at different temperatures. Higher temperature mode is able to exist at lower temperature in the metastable state. The thermal transitions of the polymer are greatly effected by the process history of the polymer. Water absorption studies have shown that the lower temperature mode does not absorb water and it is associated with ordered hydrogen bonding in the N-H region [6]. When the sample is heated to higher temperatures, the water absorption of Poly(12,10) is very similar to Poly(2,2). When water is absorbed, TSC studies have shown the shift of 40°C peak to lower temperatures similar to Poly(2,2). This shift suggest a plastization by water and possibly indicating that the peak at 40°C is associated with glass transition. The FTIR studies have shown that the disordered hydrogen bonding seen in Poly(2,2) is similar to the disordered hydrogen bonding seen in Poly(12,10) at higher temperatures[6]. Since the higher temperature
mode of Poly(12,10) has the same water absorption characteristics as Poly(2,2) and has the same type of amorphous hydrogen bonding, the higher temperature mode of Poly(12,10) is also amorphous.

The TSC analysis of Poly(12,10) have shown that there is molecular mobility of the polymer at 40°C in films and with fibers there is an additional mobile region at 60°C. This points out the importance of processing history to the structure and performance of the polymer. Film form of Poly(12,10) has and ordering that results in the trapping of the mobile groups seen at 60°C. Only when it is in the fiber form that these mobile regions at 60°C are able to move. This could have important implications with respect to the samples application as an implant and differences in aging between the film and fiber forms of Poly(12,10).

Through TGA, DSC and TSC it has been shown that Poly(12,10) has two modes of non-crystalline organization. These organizations have different water absorption characteristics. A potentially important consequence of this study is that the degradation rate of Poly(12,10) may be varied. It may be controlled simply by changing the temperature. This implies that the degradation of the polymer may be switched on from low degradation rate to high degradation rate depending on the temperature. This suggest that it may be possible to have the ability to control the kinetics and mechanism of degradation in the body.
FUTURE WORK

Future work will be conducted on the complicated phase transitions of Poly(12,10). Further studies are needed to better understand the proposed model in Figure 4.1. Modulated DSC analysis might be necessary to confirm that the TSC peak at 40°C is associated with the glass transition. Similar work conducted on Poly(2,2) and Poly(12,10) will be performed on the other polymers of the combinatorial library. This will be done on the combinatorial library of the tyrosine based polymers as well as for the other combinatorial libraries. Whether or not there are other polymers with multiple modes of non-crystalline organization will be determined. Lastly, the relationship of these thermal properties with biological responses will be formed. Cell attachment and migration with respect to the combinatorial library will be determined. Studies on the biological response to the different modes of organization of the polymers will be determined. Through characterization of the polymers, it will be possible to determine which polymer is the best candidate as a specific implant. Through the characterization of water absorption, it will also be possible to determine which polymer will be used among the combinatorial library for a specific degradation rate.
REFERENCES


