**Mechanical Properties of Polymers Exposed to a Low Earth Orbit**
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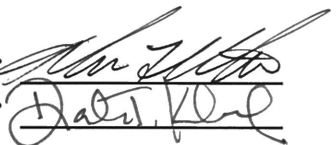
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## Abstract

Samples of 1.0 mil thick low density polyethylene, also known under the trade name Stratofilm®, were retrieved from the Long Duration Exposure Facility (LDEF) Satellite. These samples were exposed to diffuse atomic oxygen and ultraviolet radiation for a six year period before retrieval was possible. The fact that these samples survived is remarkable since ram atomic oxygen and UV radiation cause irreversible degradation of the polymer. However, these polymers were inadvertently protected from the effects of ram impact atomic oxygen and have thus survived.

These samples provide a singular opportunity to characterize polymeric properties under low earth orbit conditions. In order to characterize these polymeric films, it was necessary to determine the crystallinity of the exposed polymers. This is because the crystallinity is directly linked to the mechanical properties of the polymer and will serve to characterize them.

However, it is essential to characterize the crystalline properties of a control set of Stratofilm® first so as to provide a baseline reference. This enables the exposed polymers to be compared to the normal properties of Stratofilm®. Thus, the first phase of research undertaken is to characterize these control samples as well as begin characterizing the exposed polymeric materials.

the direction of the orbital vector. As a result, all polymers mounted on that side were all exposed to one hundred percent of ram atomic oxygen and were destroyed. In the same manner, all of the polymers on the opposite side of the satellite had only minimal exposure to ram atomic oxygen and were saved. Also, the test trays were partially sunken into the satellite. This further served to shield the test samples from the effects of ram atomic oxygen. Thus, the polymers were only exposed to diffuse atomic oxygen and UV radiation.

Also, it should be noted that these polymers were exposed to this low earth environment for a period of six years. This was due to the unfortunate Challenger Space Shuttle accident terminating the mission to retrieve the LDEF satellite. Thus, the originally planned one year experiment lengthened into a six year test.

These exposed polymers provide a singular opportunity to investigate the effects of low earth orbit environmental conditions on the mechanical properties of polymers. With the known exposure history of the polymers, it is now possible to characterize the effect of atomic oxygen and UV radiation upon them without the conditions that erosion bring. This research becomes increasingly important because it will allow a determination to be made as to how much polymeric degradation can be attributed to diffuse atomic oxygen and UV radiation as opposed to degradation caused by ram atomic oxygen. This determination can be done in part through studies of crystallinity. The percent crystallinity of the polymer is directly related to its mechanical properties, and thus it can be used to

## Introduction

With the increasing use of polymeric materials in orbiting spacecraft, it has become necessary to determine the effects of low earth orbit upon a polymers' mechanical properties. In a low earth orbital environment, atomic oxygen is the predominant element as opposed to nitrogen due to its heavier atomic weight. This causes atomic oxygen to settle at the low earth orbital level while atomic nitrogen seeks higher orbits to settle in. From past experience, it is known that polymers exposed to the direct ram impact of atomic oxygen undergo a serious and irreversible degradation. This is due to the erosion effect caused by the impact of ram atomic oxygen upon the polymer. By ram atomic oxygen, it is meant that particles of atomic oxygen actually impact the surface of the polymer. While a satellite travels in orbit around the earth, speeds average at about eight kilometers per second rendering impact on any scale a potential hazard, and with an impact energy equivalent to 5 eV, erosion effects are significant. This process is also known to be catalyzed by the presence of ultraviolet radiation. In low earth orbit, this environment prevails, and it has proven to be detrimental to the mechanical properties of polymeric materials.

In the case of the Long Duration Exposure Facility (LDEF) satellite, however, the effects of ram atomic oxygen were largely negated by the alignment of the satellite. Do to an error in the satellite alignment while being placed in orbit, the test tray was shielded from the effects of ram atomic oxygen by the satellite's body. More specifically, instead of rotating, the cylindrical shaped satellite orbited the earth with one side always pointed in

help define them. The polymers studied in this phase of research encompassed both control as well as exposed samples of 1.0 mil Stratofilm®, a low density polyethylene film manufactured for use in scientific balloons.

## Profile of Exposed Material Orbital Conditions

Normally, polymeric materials exposed to the low earth orbit environment suffer from disastrous degradation and weight loss due to the erosional effects of ram impact atomic oxygen. It is also known that diffuse atomic oxygen and UV radiation can alter the chemical structure of polymers, but the opportunity to determine the extent to which these chemical alterations effect mechanical properties has never been possible until now. The extended duration of polymer exposure to low earth orbit has enabled an opportunity to examine morphological and mechanical properties of exposed polymers to arise.

This long duration time was made possible by the fortuitous positioning of the test tray on the satellite as well as the satellite orientation itself. Together, these factors served to minimize exposure to ram atomic oxygen. Usually, spacecraft in LDEF orbit travel at a speed of 8 km/sec. This imparts an impact energy to atomic oxygen of approximately 5 eV. This condition, if present, is known to cause degradation and mass loss. However, if this condition is not present, as in this case, only diffuse atomic oxygen persists. Also, it should be noted that these samples received a minimum exposure to UV radiation as compared to other samples located on the LDEF. Hence, these samples were able to survive the extended time duration in low earth orbit.

However, it should be further noted that the LDEF samples were exposed to extreme thermal changes in addition to the diffuse atomic oxygen and UV radiation. These thermal changes were a result of heating periods when the LDEF was exposed to sunlight and cooling periods when the earth shielded the LDEF from the sun. As a result, the test samples experienced numerous melting and cooling cycles over a six year period. This thermal situation also cause simultaneous melting and crystallization to occur. As of yet, it is unknown to what extent this factor has influenced the mechanical properties of the Stratofilm®, but possible changes in the polymer could be the result of numerous anneals and/or in-situ crosslinking.

### Experimental Procedure

A Differential Scanning Calorimeter (DSC) model IIC was utilized in characterizing the crystallinity of the control as well as the exposed polymer samples. The basic principle behind the DSC is this. A test sample and a comparison sample are both heated at constant rates inside two separate chambers over a chosen temperature range. The test sample is contained in a small circular aluminum pan that has been crimped shut with a lid also made of aluminum. The comparison sample is simply an empty aluminum pan and lid that has been crimped shut. With both samples being heated at the same constant rate, the energy input needed to keep the temperature difference between the two samples at zero is measured. When the test sample reaches a phase change, for instance a melting point, more energy is input into heating the test sample (endothermic) so that its temperature remains consistent with that of the comparison sample. The opposite is also true. For

example, if a sample releases energy (exothermic) as in the case of crystallization, less energy will be put into that sample in order to keep consistent temperatures. The energy input into the test sample is measured as a function of energy input per unit time versus time or temperature. When this curve is integrated with respect to time in reference to a baseline, the energy input into the test system can be derived. This technique is also equally effective in determining the energy input required for recrystallization of a test sample. This is a direct measure of percent crystallinity and can therefore be used to help define mechanical properties.

However, in order for the experimental data to be useful, baseline plots needed to be made in order to provide a reference for integral calculations. These baseline plots were created by simply running a test with an empty aluminum pan and lid, un-crimped, under the same testing parameters. The resulting curves were then used as a basis for further integration of the various sample data curves.

Experiments were made on both a set of exposed samples as well as a set of control samples. The control samples were necessary so as to provide a reference to the normal characteristics of polyethylene. The set of exposed samples consisted of 6 samples of an average mass of 6 mg. This set of exposed materials were used for both melting point and crystallinity studies due to the limited quantities on hand. The set of control samples consisted of 23 samples, 14 of which were used for melting point studies. The remaining samples were utilized for crystallinity studies. All of these control samples had an average

mass of about 6.5 mg. It should be noted that the control samples and the exposed samples were created from the same original batch of raw material thus sharing the same origin.

The parameters varied in performing the melting point experiments were the heating rate in degrees Kelvin per minute, the temperature range in degrees Kelvin, the plotter speed in millimeters per minute, and the energy input in millicalories per second. In performing a series of experiments to determine the melting points of control and exposed samples, test samples were heated at chosen heating rates over a chosen temperature range thought to encompass the melting point temperature. Once reaching the final chosen temperature, the test was completed and a plot of millicalories per second versus temperature was recorded. On this plot, there would be a recorded peak in the energy reading which would represent the primary melting point. In conducting these melting point experiments, the parameters listed in Table 1 were used.

The purpose in conducting the melting point experiments was to determine if the test sample was actually melting or if the sample was crystallizing. If the sample was crystallizing, a step transition would be apparent in the data plot instead of the usual peak associated with a melting point. These tests would also reveal some more fundamental differences such as a change in melting temperature or if more energy per unit mass was required for melting. All these changes are symptomatic to morphological and chemical structural changes.

In conducting the crystallinity studies, the same parameters used in the melting point studies were varied. However, several differences should be noted. First, the temperature range used was much smaller. In fact, it was only from 340 K to 370 K. This was because the objective was only to heat the test sample so that recrystallization would occur. Thus, the temperature was kept deliberately well below the normal melting point of the material. Secondly, the heating rate was kept very high. This was to prevent the heating segment of the experiment from effecting the recrystallization process in any manner. Last of all, after the final temperature was reached (i.e. 370 K), the test sample was allowed to sit for 30 minutes in the test chamber at 370 K so that the recrystallization process was allowed ample time to be completed. In the crystallization studies, the parameters listed in Table 2 were used.

Specifically, the purpose in conducting the crystallinity studies was to determine the percent crystallinity of the test samples. This was accomplished by first integrating the resulting experimental curves. This gave a direct measure of the energy required for the recrystallization process. By taking this value and dividing it by the energy required for 100 percent crystallization, also known as the heat of fusion, a percent crystallinity of the sample is derived. The percent crystallinity is useful in predicting mechanical properties because of its direct involvement in determining these same properties.

The final experiment that was conducted on the control and exposed test samples was an annealing study. In this experiment, a test sample was placed in the DSC IIC and heated

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at 10 degrees per minute to 410K, a temperature well beyond its melting point. It was held at this temperature for a period of ten minutes in order to assure that all polymeric crystal structure was destroyed. This sample then underwent a controlled cooling at 10 degrees per minute to a temperature of 343K where it was held to anneal for a period of two hours. The length of this anneal period was chosen arbitrarily, but thought to be long enough to guarantee that the annealing process was complete. The sample was then cooled at 10 degrees per minute to 320K where it was then immediately heated again to 410K and held at this temperature for ten minutes. With its crystal history erased again, the sample underwent a controlled cooling to 363K where it annealed at this temperature for two hours. It was then cooled down to 320K and heated again to 410K. This concluded the experiment.

The purpose of this annealing study was to selectively grow crystals within the polymer. In doing this, it may be possible to characterize some of the effects that thermal cycling has had on the exposed samples in its six year exposure history. By selectively growing crystals, it may be possible to characterize the effects that those particular crystals have on mechanical properties.

In explanation, it is possible to selectively grow crystals due to the fact that this polymeric material has no true melting point. Crystals within the polymer structure have varying melting points. Thus, by holding the polymer at a high enough temperature, you may melt some crystalline material, but you will also encourage growth of the crystals whose

melting point is located in proximity to and above that temperature. By annealing at various temperatures, it is possible to selectively grow the crystals associated with those temperatures. The anneal temperatures chosen for this experiment were 343K and 363K. These temperatures were chosen arbitrarily, but do give representative data of crystal growth. Note that it was not possible to anneal at temperatures beyond 380K since total melt of all polymeric material occurred beyond this temperature.

### Results and Discussion

From the results of the melting point and crystallinity studies, some preliminary findings have been concluded. First, testing shows that the melting point of the exposed samples run an average of 5 degrees lower than the melting point of the control samples while keeping the amount of energy needed for melting about the same. This fact is correlated by the crystallinity studies which show that the percent crystallinity of the exposed samples run an average of 1.5 percentage points lower than the control samples. All these results are apparent from the data presented in Figures 1 through 8 and Tables 3 and 4. The correlation comes from the fact that less crystalline materials melt at lower temperatures due to their less organized structure. Together, these results suggest that the exposed samples have suffered a reduction in mechanical properties. This is because the general trend in polymer crystallinity is that the more crystalline a polymer, the higher the strength of the polymer.

Secondly, attention should be focused on another difference between the control melt samples and the exposed melt samples. From the results presented in Figures 9 through 34, there is a noticeable difference between the control and exposed samples. More specifically, the melt curve for the exposed samples is much broader and is not as well defined as compared to the control samples. Most likely, what this means for the exposed samples is that there is more crystalline material spread out over a larger melt range. As was stated earlier, most polymers do not have an precise melting point, but instead melt over a temperature range. It would seem that the exposed samples, even though they do exhibit less total percentage crystallinity, do have more of a crystalline distribution over melt temperatures. This would suggest some permanent change in the recrystallization process which tends to support the hypothesis that in-situ crosslinking has occurred. As for the typical characteristics of in-situ crosslinking, these will be discussed later in the paper.

However, in order to confirm that recrystallization of the Stratofilm® was complete, it became necessary to construct a graph known as an Avrami plot. This is a plot of the log of the mass fraction of spherulitic crystalline material versus the log of time. Theoretically, the beginning portion of this plot is linear in nature and represents the crystallization process. When this plot deviates and becomes non-linear, the crystallization process is generally complete. From Figures 52 and 53, we see that the recrystallization process for both the control as well as the exposed samples were well beyond completion. Of special note is the fact that both series of samples recrystallized at a surprisingly rapid

rate. In actuality, control and exposed samples only required about one minute to completely recrystallize. This may be due in part to the very low percentage of crystallinity seen in all of the polymeric test samples. These were significantly lower values than were expected. While values of percent crystallinity in the range of 20% were expected, experiments consistently showed a percentage crystallinity of between 2% and 5%. This is quite possible considering that this material is a specialized polymer. It has also been suggested that this polymer is actually a copolymer blend of polyethylene and polypropylene. If this is the case, then the presence of polypropylene could explain the low percentage of crystallinity.

Other characteristics that may be obtained from the Avrami plot are the type of crystalline geometry present in the polymer, the type of nucleation, and the growth control. This is determined from the slope of the linear portion of the plot. Depending on this slope, also known as the Avrami coefficient, there will be various characteristics present. These parameters are reiterated in Table 5. From the Avrami plot of the control samples, we see that the slope is approximately 3.88. From the Avrami parameters, we see that the nearest Avrami coefficient is four. This coefficient states that the control samples have underwent homogenous nucleation, have an interface growth control, and are spherulitic in geometry. For the exposed samples, we obtained an Avrami coefficient of approximately 3.40. Rounding down this coefficient and taking into account the typical characteristics of polyethylene, we obtain a polymer with all of the same characteristics as those realized by the control samples with one exception. The exposed samples have the characteristic of

instantaneous nucleation. This suggest some permanent morphology is present in the polymer. Again, this serves to substantiate the hypothesis of an in-situ crosslinked structure. However, as was stated in preceding paragraphs, this hypothesis will be discussed in further detail in the later on in this report.

Of some note are the melting plots of the exposed samples. From Figures 23, 24, 27, 28, 31, and 32; the melting plots of these exposed samples are shown to be ill-defined. This was due to the fact that the sample was made of a number of different exposed polymeric fragments. Thus, when testing occurred, the sample did not melt uniformly. It then became necessary to perform a re-melt of each of the exposed samples in order to insure that "clean" data was obtained. However, there is the question of whether this re-melt served to change the morphological properties of the polymer. This becomes a major issue since any change in morphology would result in tainted research data. Perhaps the answer lies in the in-situ crosslinked structure that the exposed polymers have retained.

From earlier work, there has been some implication that extensive in-situ cross-linking results from exposure to an atomic oxygen/UV environment. That is, the cross-linking process occurs simultaneously during a thermal cycling process which causes crystalline changes in the polymer. This has been supported by the fact that the crystalline melt temperature and the percent crystallinity of the exposed samples are relatively unchanged after repeated heating. This suggest a permanent morphology, a typical result of in-situ

crosslinking. Thus, re-melts should have little effect on the morphology of the exposed polymers.

From the annealing experiment, it was shown that anneals at various temperatures do in fact cause certain crystals to grow. The evidence of this can be seen from the DSC plots shown in Figures 50 and 51. As shown in these plots, there are two distinct peaks. Both of these represent large endothermic reactions, one of which is the main melting point. The other peak represents the energy required to melt the crystals that were selectively grown.

## Conclusions

Though these results show only preliminary findings, there can be derived a substantial conclusion. It would seem that even though the exposed samples of Stratofilm® survived the LDEF mission, they have lost some of their mechanical properties. This is apparent through the resulting changes in crystallinity percentages between the control samples and the exposed samples. This claim is further substantiated by the lower melting point temperature experienced by the exposed samples as compared to the control samples. While there is not a conclusive recrystallization kinetic theory to explain why this has happened, the fact still remains that there have been substantial changes in the crystalline structure of the exposed polymers. It is hoped that further testing on the DSC IIC and testing with X-ray diffraction techniques will further support this claim as well as reveal some of the underlying reasons as to why these changes have occurred. It was also

unfortunate that anneal studies on the exposed samples were not completed, but it is felt that this work will be completed sometime during the second phase of this experiment.

For the second phase of this experiment, these polymeric samples will undergo direct mechanical testing. This will be accomplished through the use of an instrument called the Rheometrics Solid Analyzer II (RSA II). Using this instrument, the test samples will be loaded at various frequencies and temperatures in order to determine its mechanical properties.

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# Tables and Figures

**Table 1: DSC Melting Point Experimental Parameters**

| Sample Type | Heating Rate | Temp. Range | Plotter Speed | Energy Input |
|---|---|---|---|---|
| Control | 5-10 deg K/min | 340K to 410K | 20 mm/min | 5-10 mcal/sec |
| Exposed | 5 deg K/min | 340K to 410K | 20 mm/min | 5 mcal/sec |

**Table 2: DSC Crystallinity Experimental Parameters**

| Sample Type | Heating Rate | Temp. Range | Plotter Speed | Energy Input |
|---|---|---|---|---|
| Control | 320 deg K/min | 340K to 370K | 10 mm/min | 0.5 mcal/sec |
| Exposed | 320 deg K/min | 340K to 370K | 10 mm/min | 0.5 mcal/sec |

**Table 3: Average Values of Energy and Melting Points**

| | Control Samples | Exposed Samples |
|---|---|---|
| **Average Melting Energy** | 132.08 mcal | 137.36 mcal |
| **Average Melting Temp.** | 377 K | 372.5 K |

**Table 4: Average Recrystallization Energies and Percentages**

| | Control Samples | Exposed Samples |
|---|---|---|
| **Avg. Recryst. Energy** | 15.58 mcal | 10.57 mcal |
| **Avg. Percent Crystallinity** | 3.654% | 2.470% |
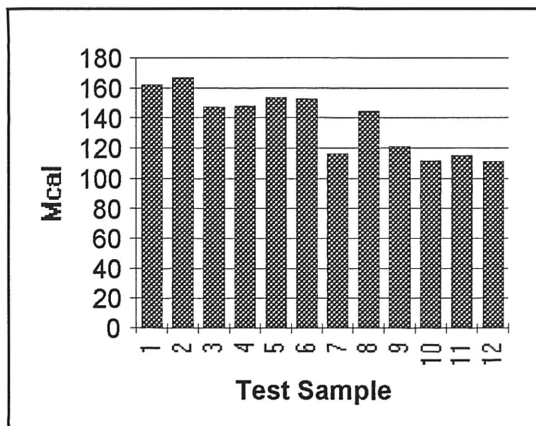
**Figure 1:  Melting Point Energy for Exposed Samples**
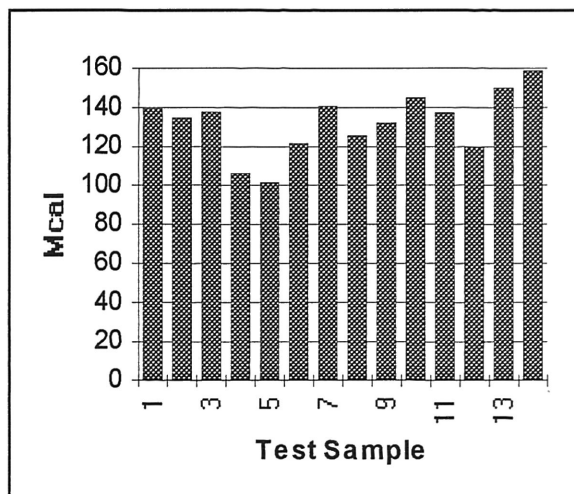


**Figure 2:  Melting Point Energy for Control Samples**
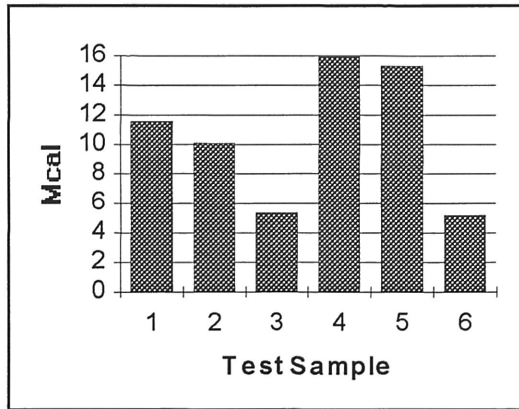
**Figure 3: Recrystallization Energy for Exposed Samples**
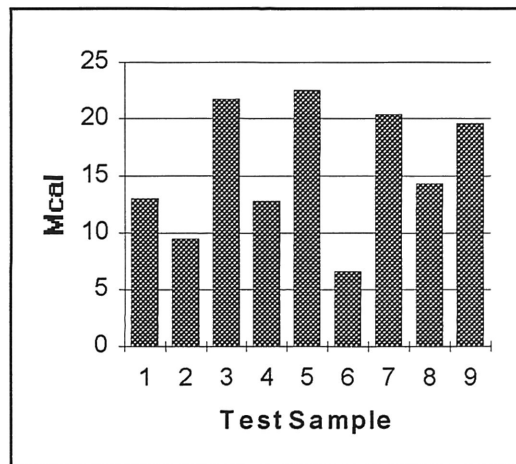


**Figure 4: Recrystallization Energy for Control Samples**
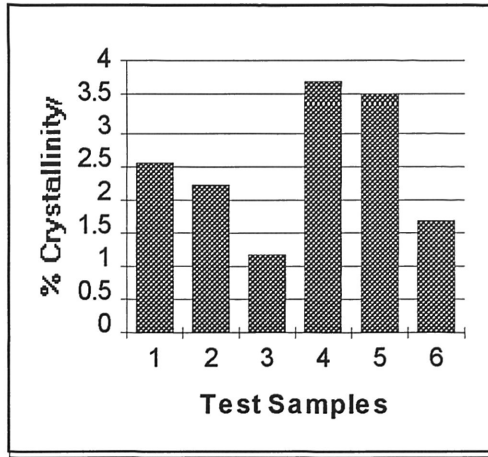
**Figure 5: Percent Crystallinity for Exposed Samples**
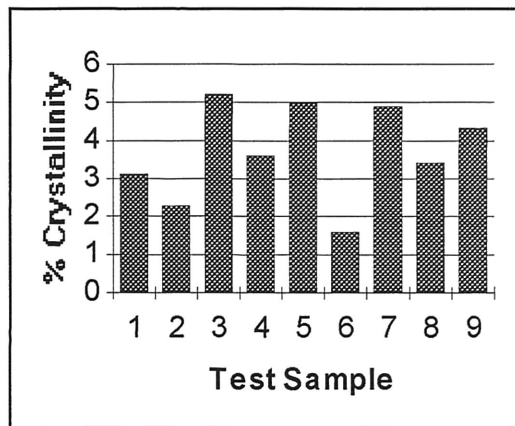


**Figure 6: Percent Crystallinity for Control Samples**
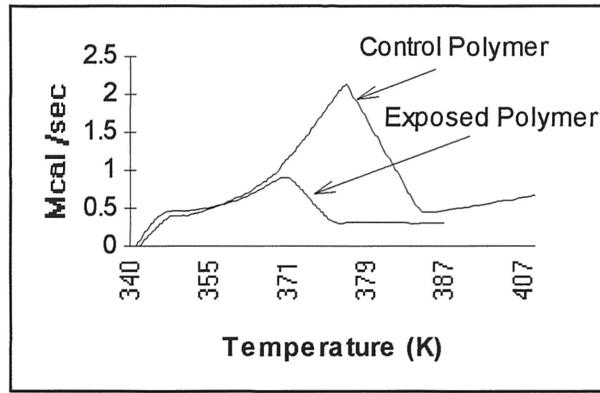
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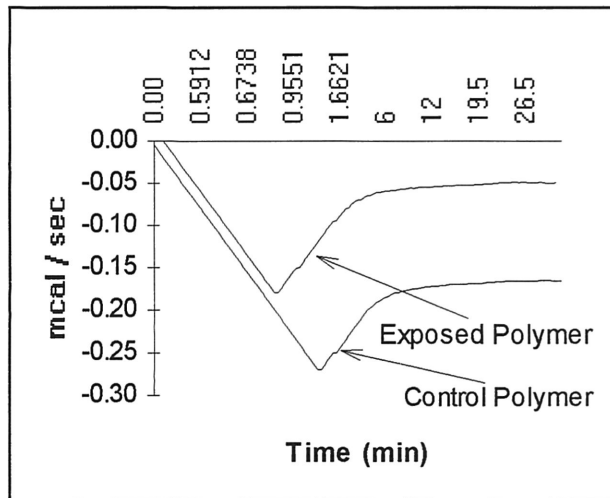


**Figure 8: Typical DSC Crystallinity Plots**
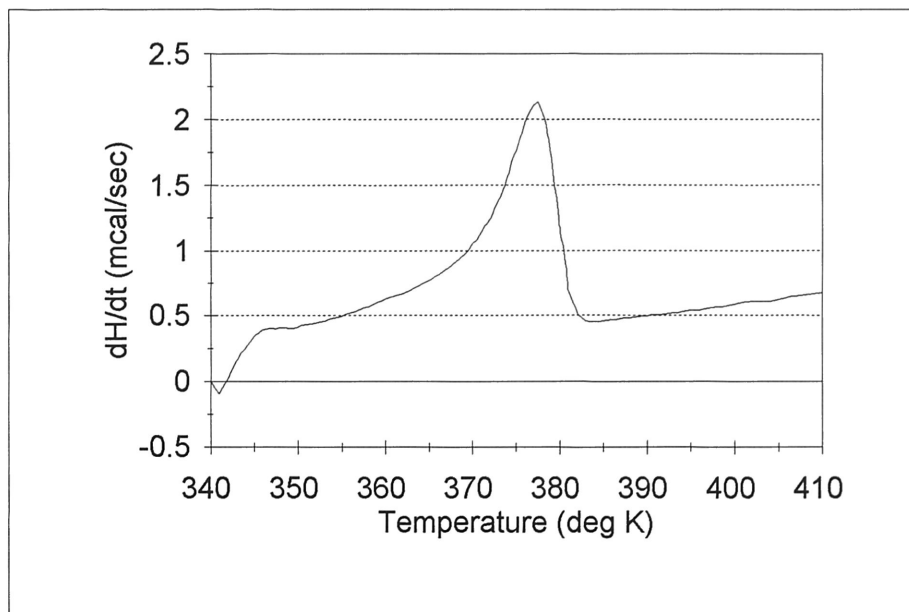
Figure 9: Control Sample Melt #1
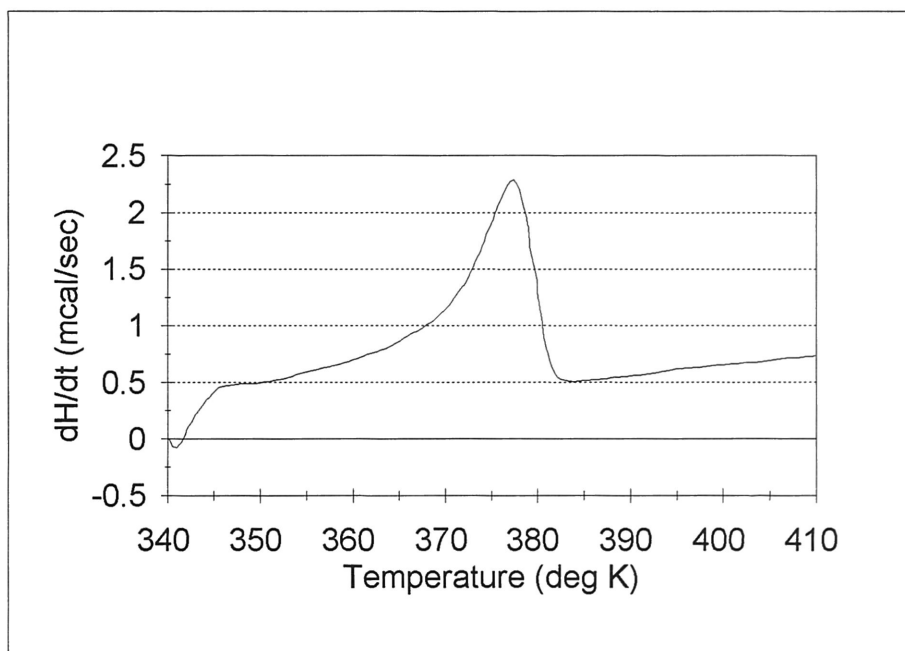


Figure 10: Control Sample Melt #2
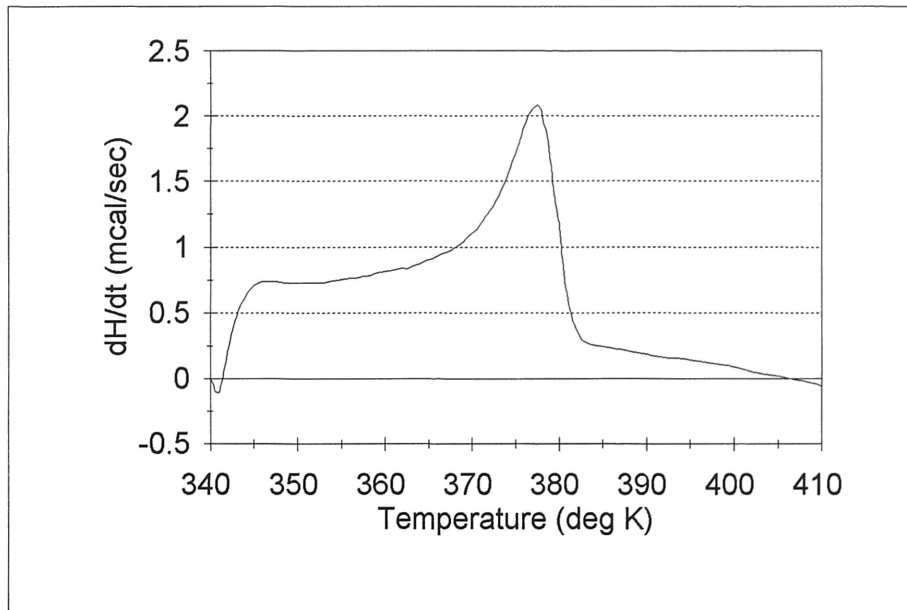
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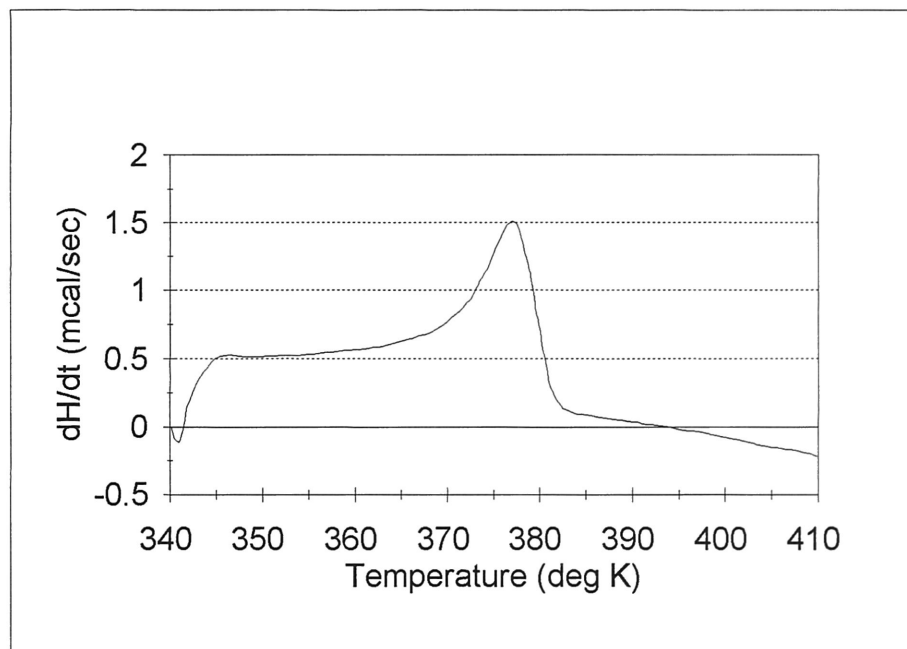


Figure 12:  Control Sample Melt #4
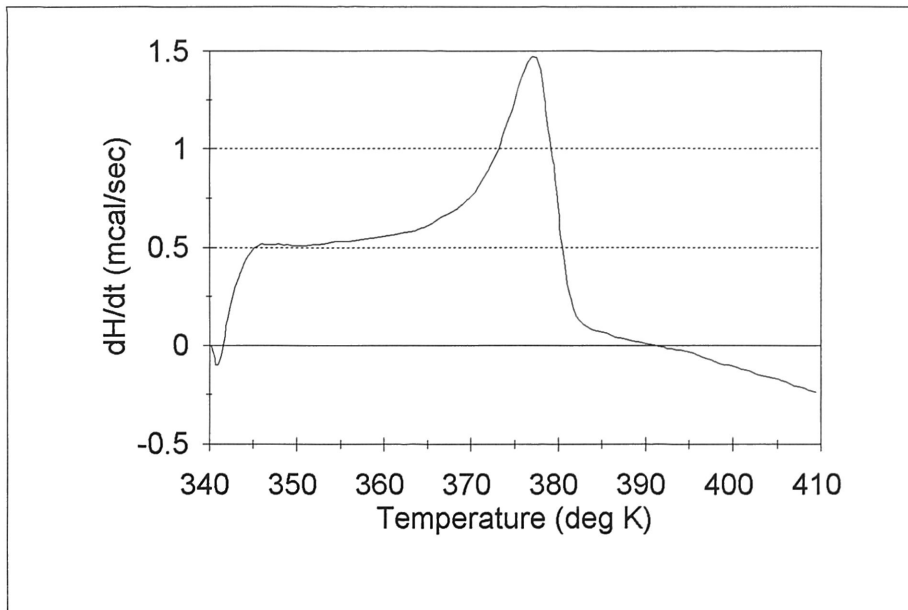
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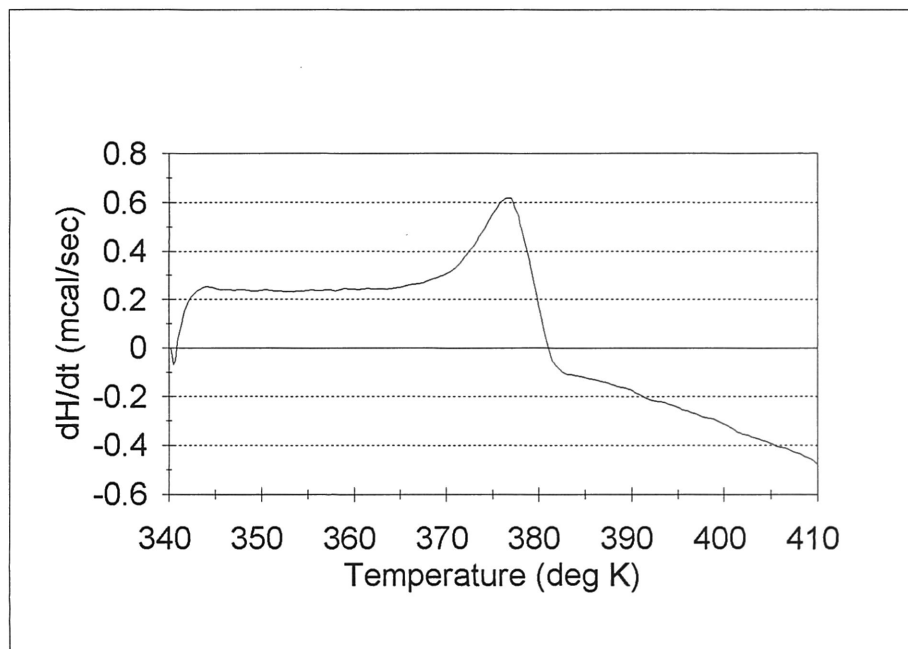


Figure 14: Control Sample Melt #6

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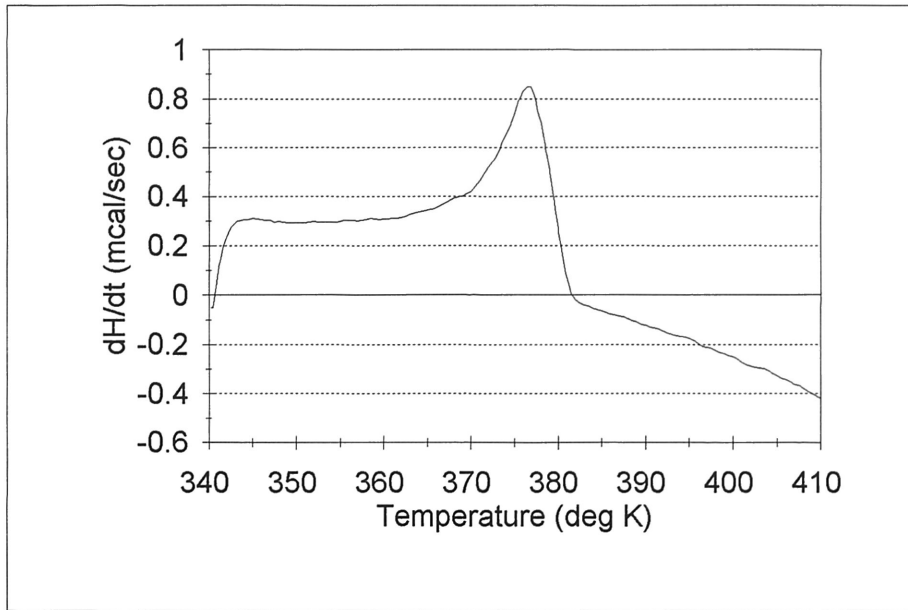
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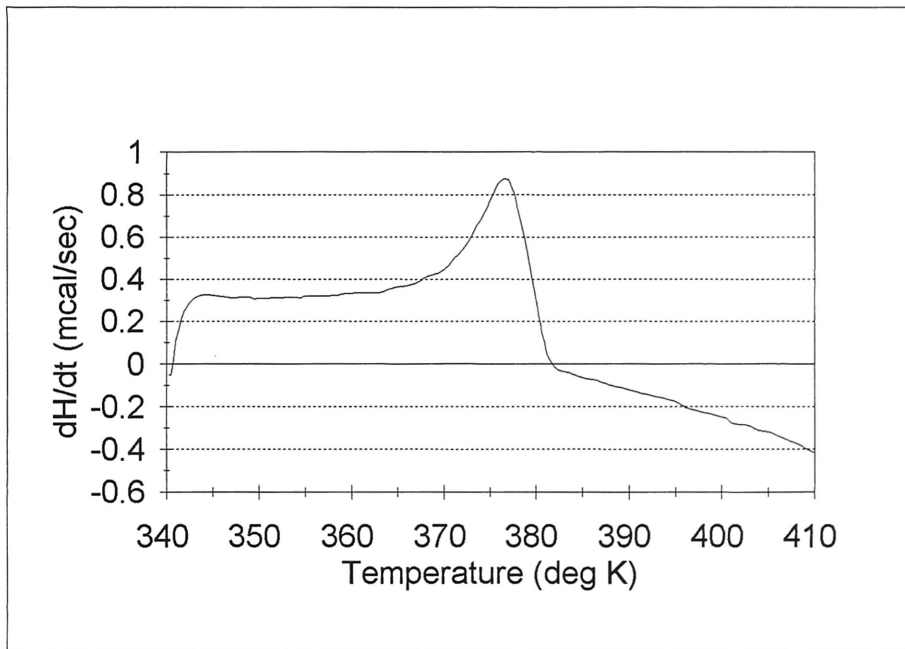


Figure 16:  Control Sample Melt #8
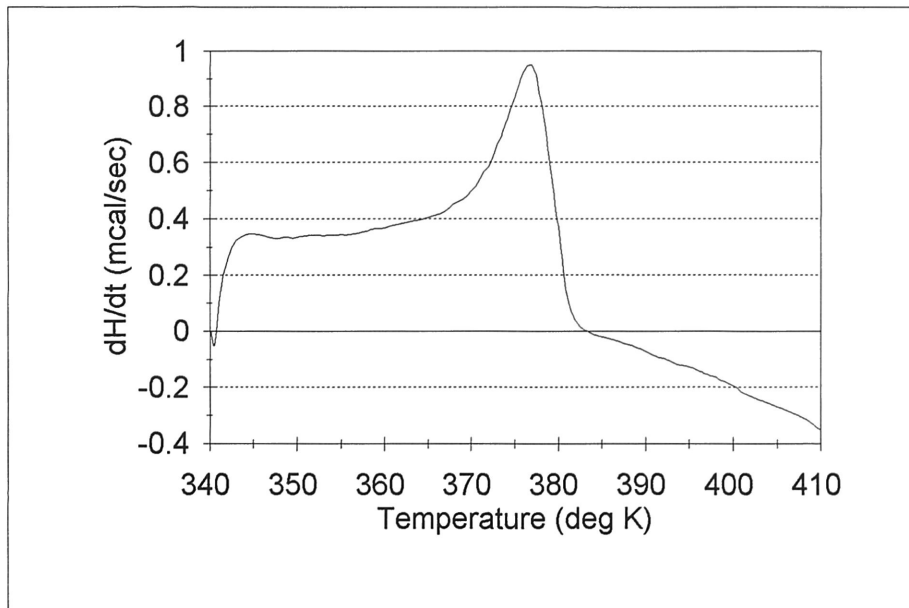
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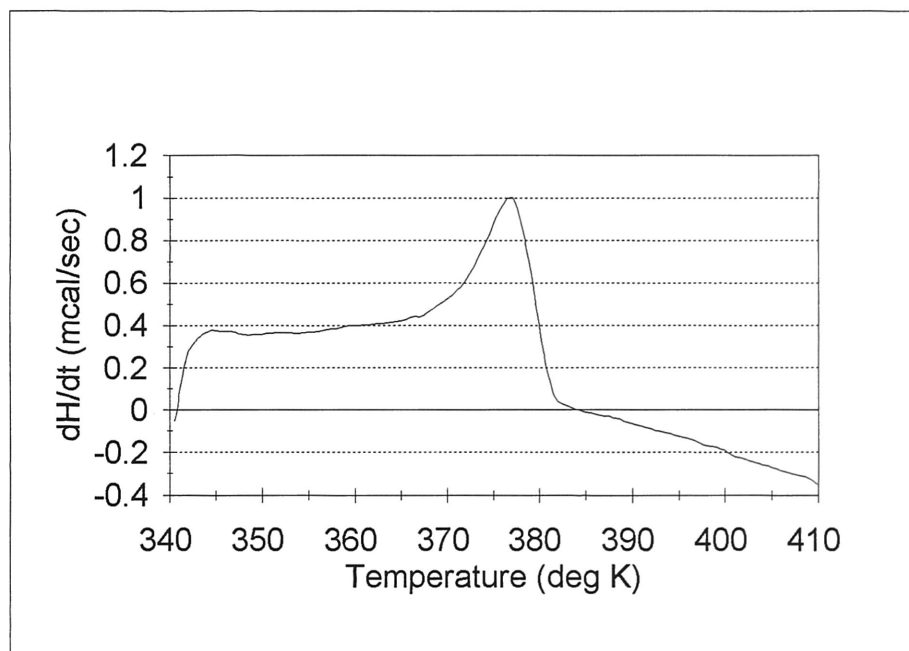


Figure 18:  Control Sample Melt #10
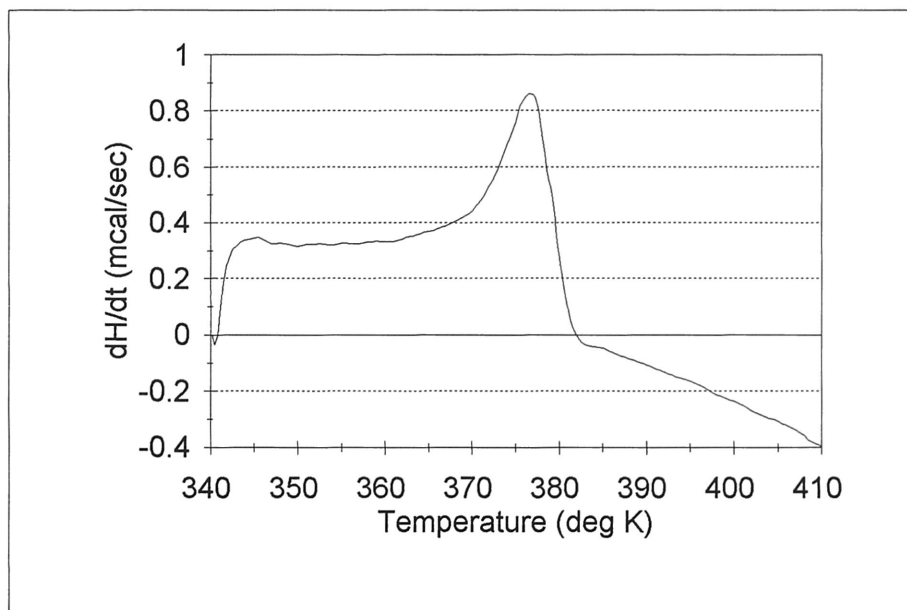
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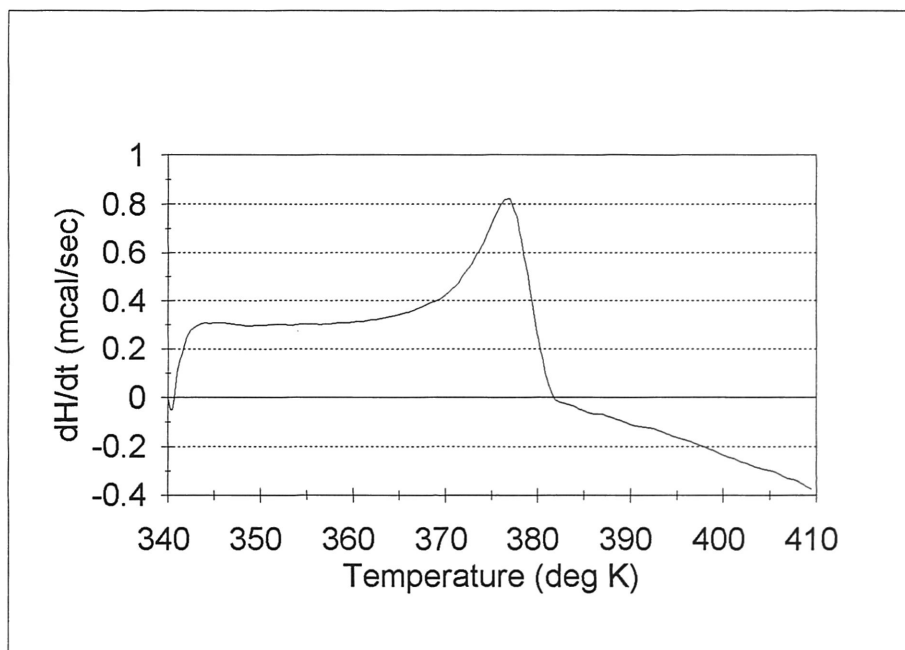


Figure 20: Control Sample Melt #12
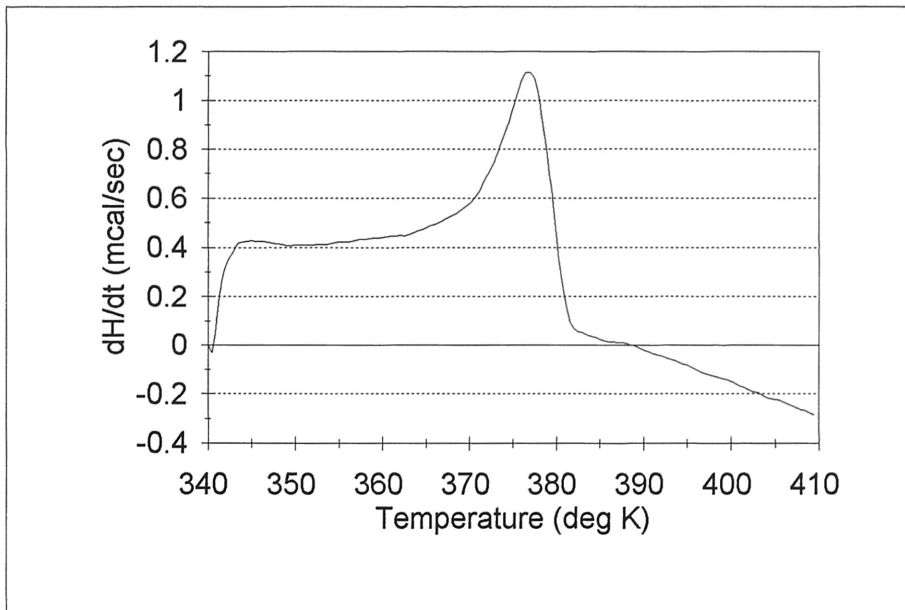
Figure 21:  Control Sample Melt #13
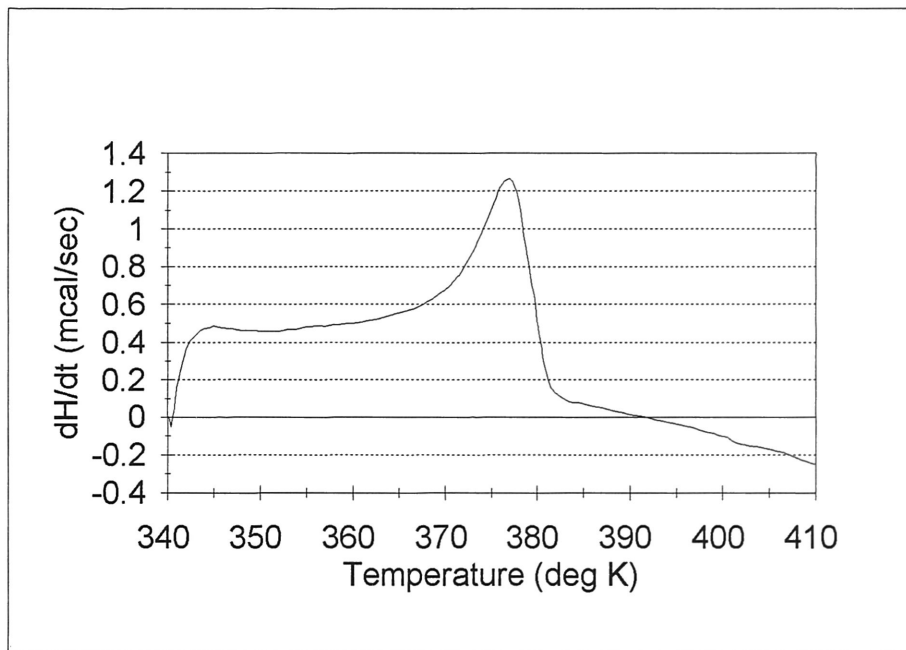


Figure 22:  Control Sample Melt #14
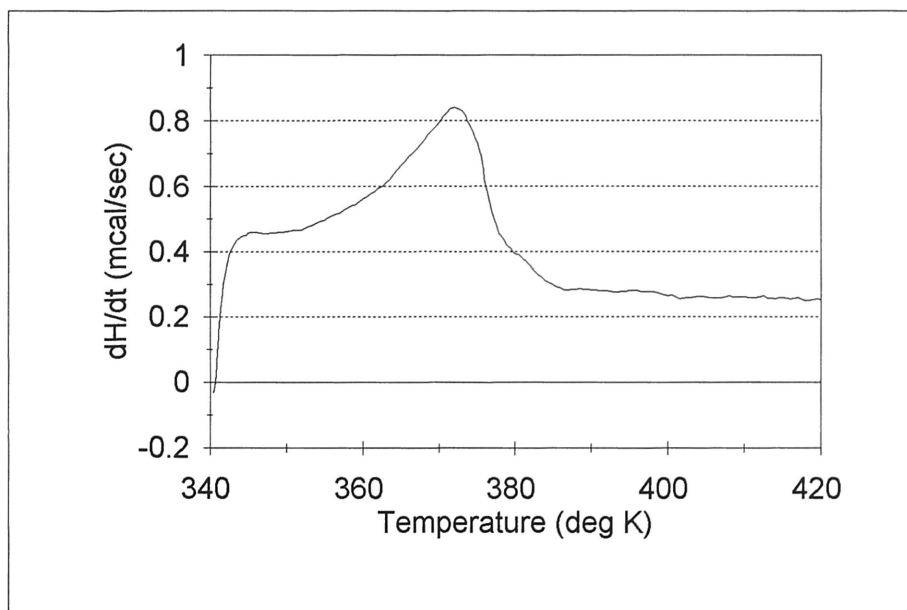
Figure 23: Exposed Sample
Melt #1
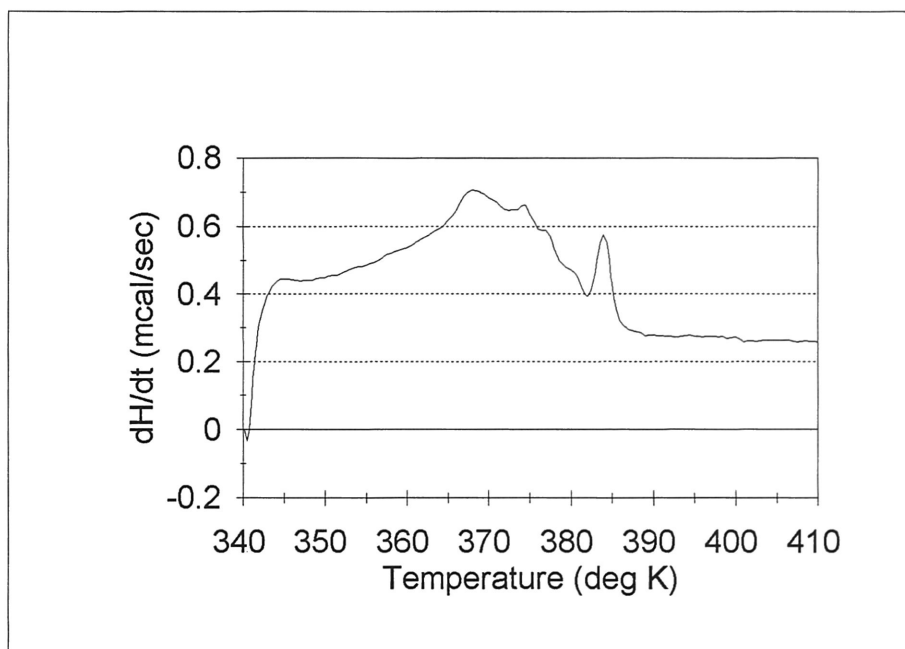


Figure 24: Exposed Sample
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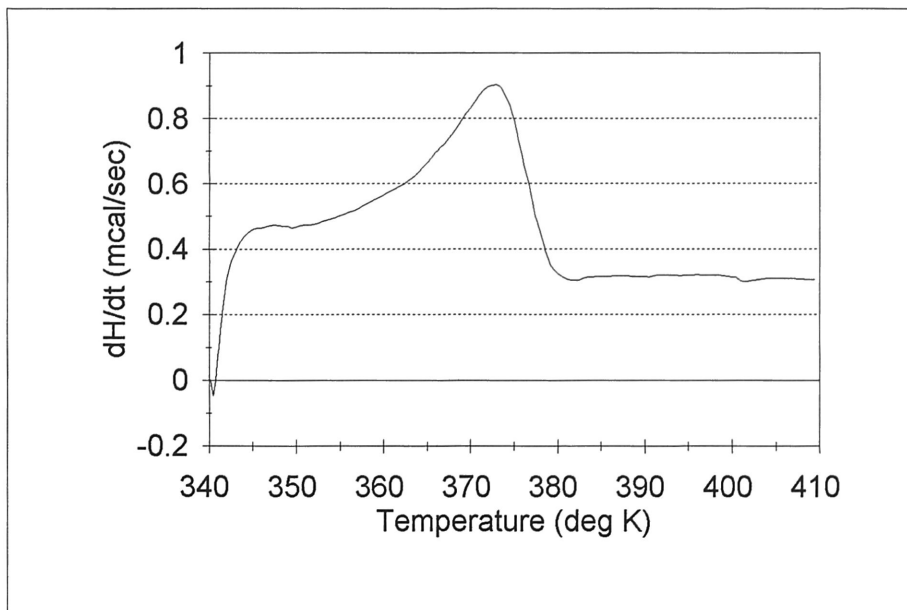
Figure 25:  Exposed Sample
Re-Melt of #1
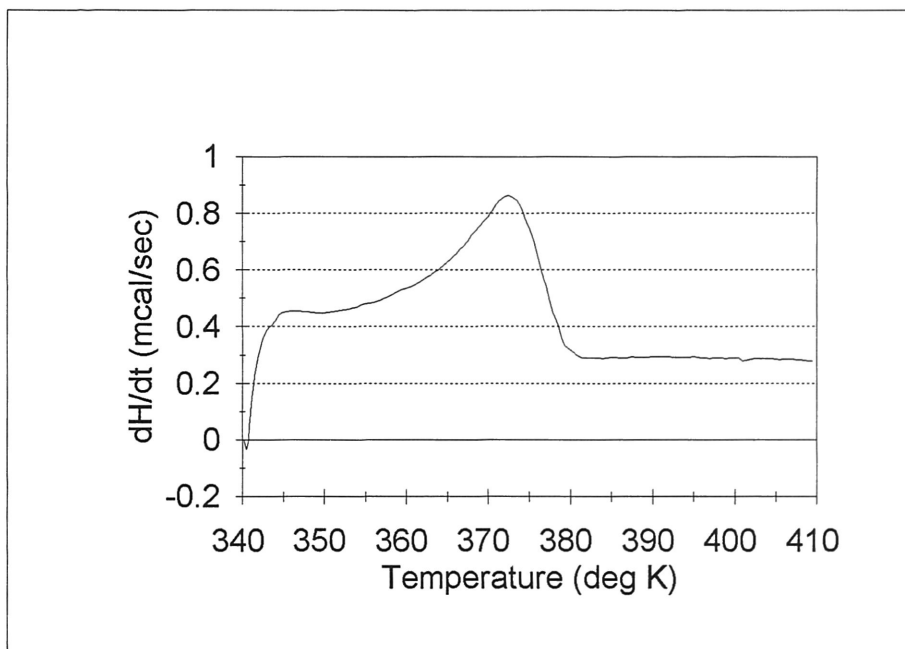


Figure 26:  Exposed Sample
Re-Melt of #2
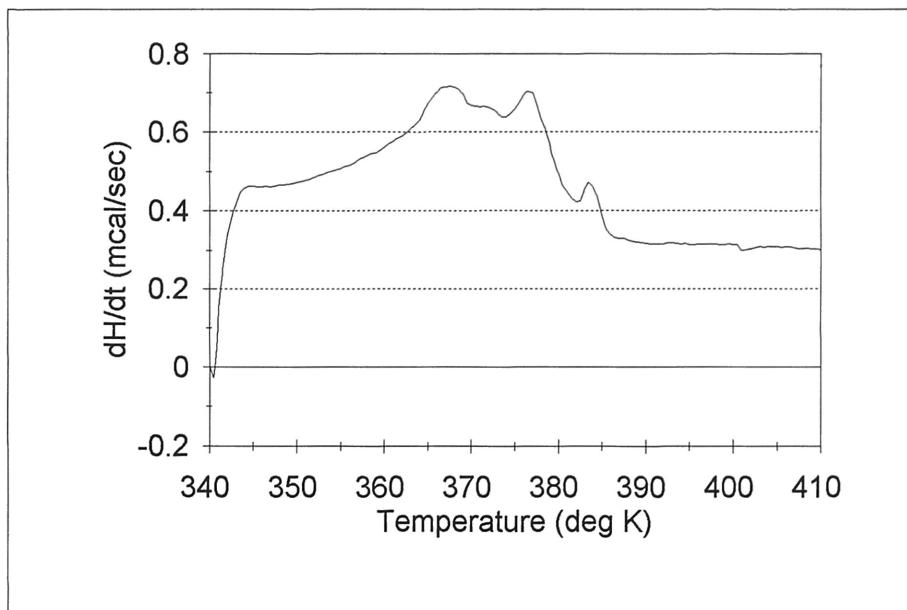
Figure 27:  Exposed Sample
Melt #3
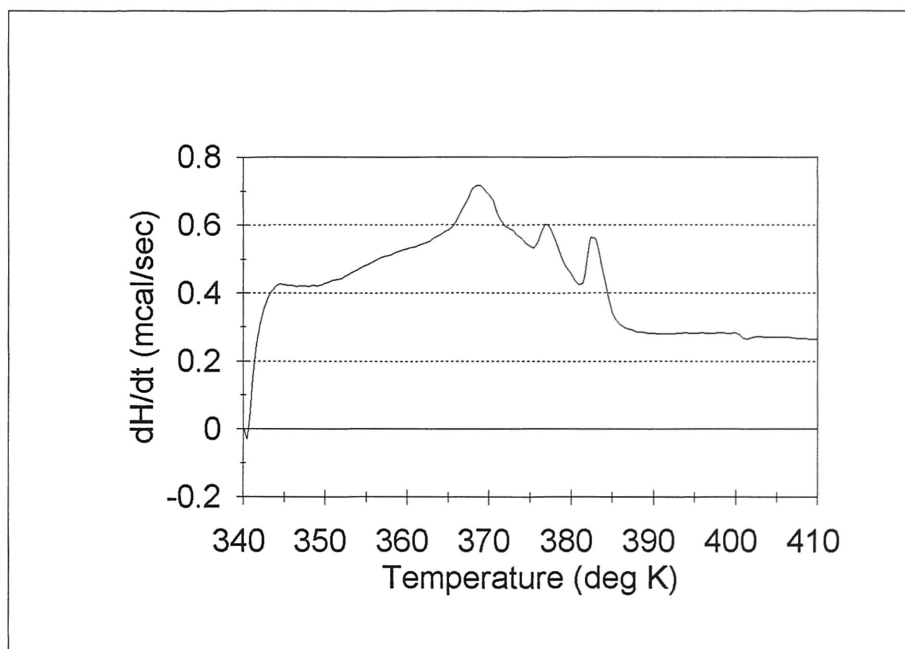


Figure 28:  Exposed Sample
Melt #4
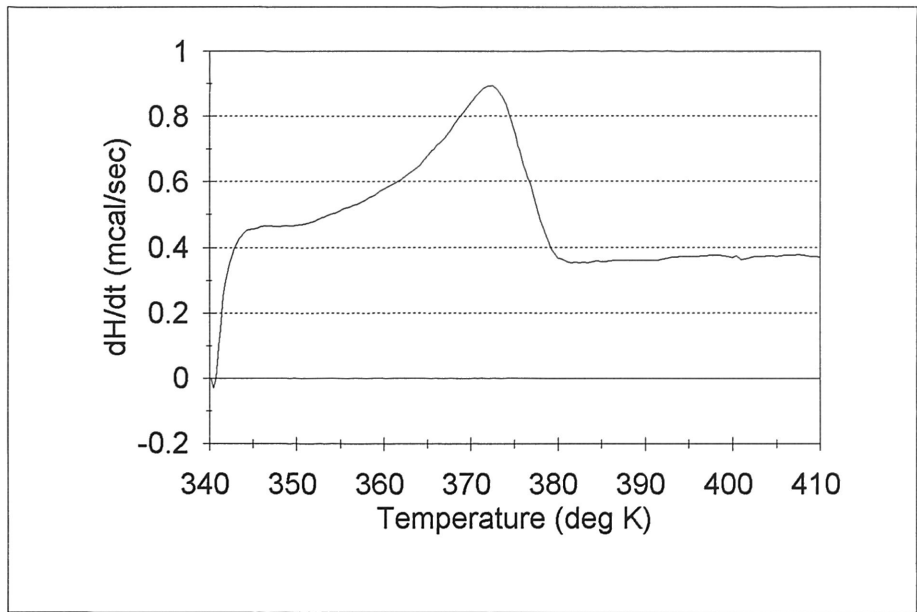
Figure 29:  Exposed Sample
Re-Melt of #3
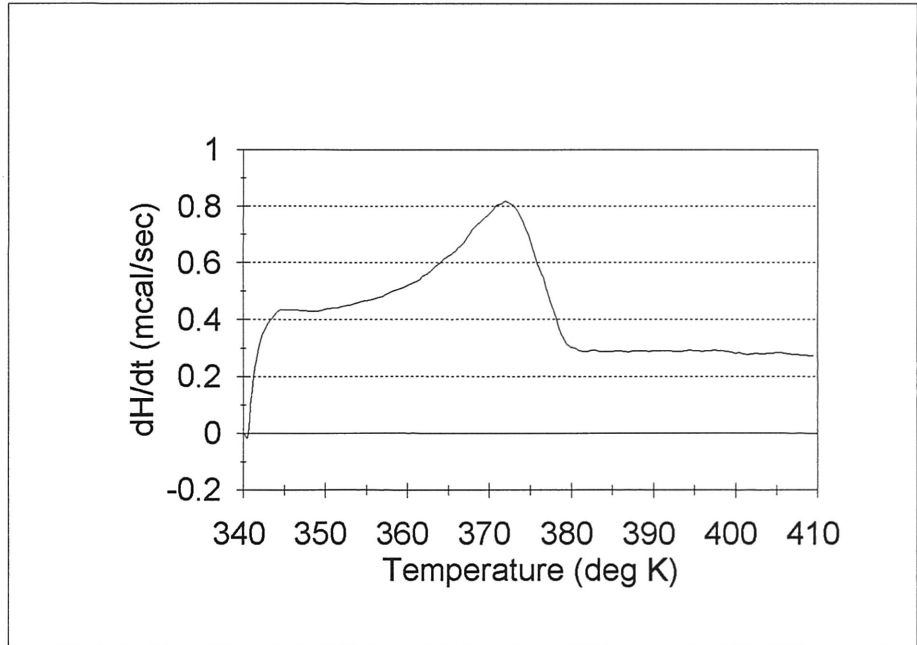


Figure 30:  Exposed Sample
Re-Melt of #4
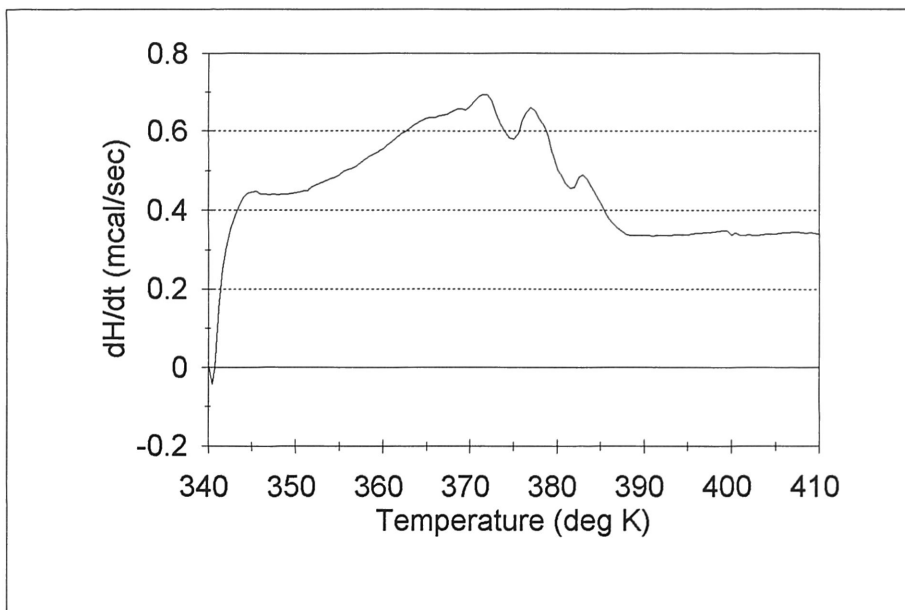
Figure 31:  Exposed Sample
Melt #5
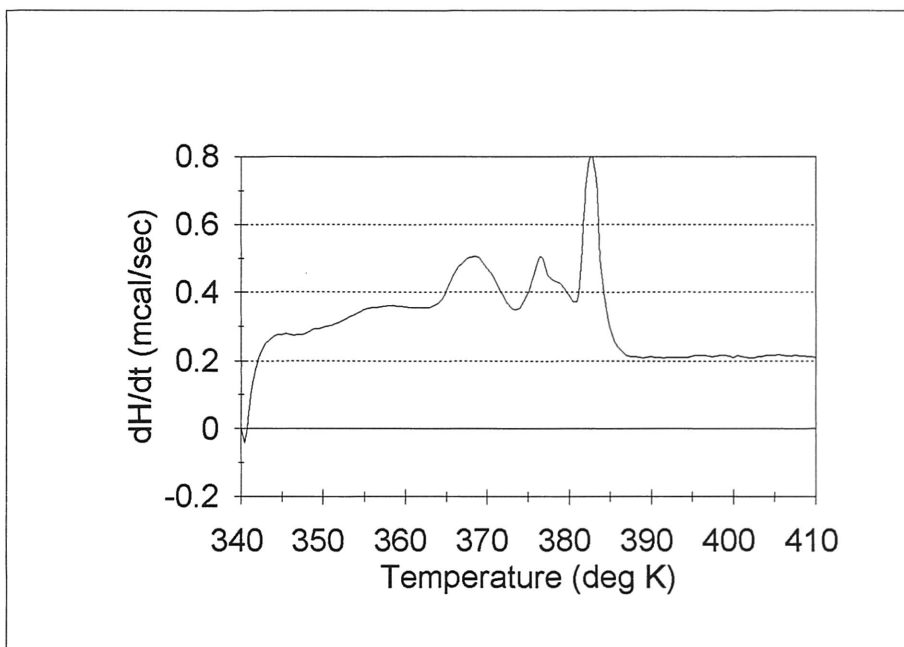


Figure 32:  Exposed Sample
Melt #6
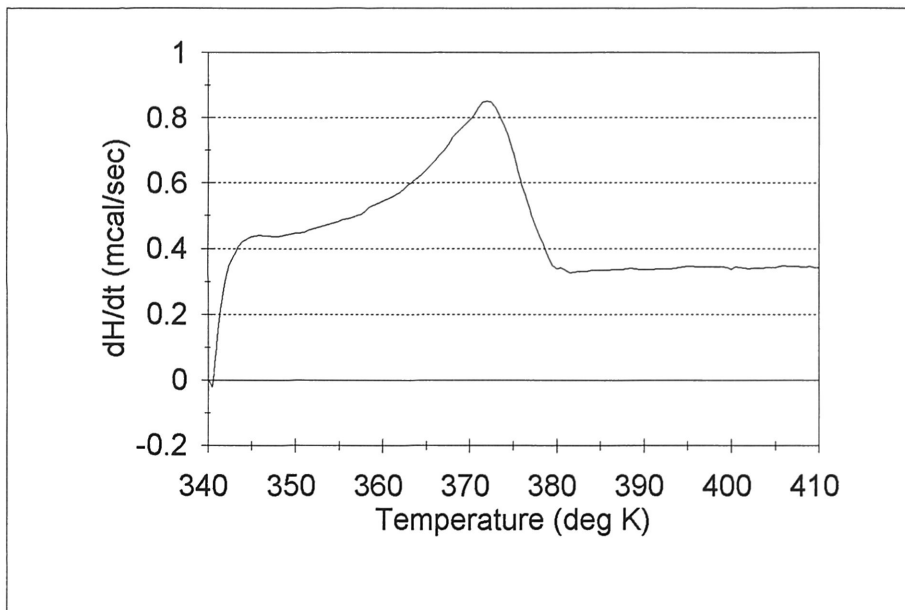
Figure 33:  Exposed Sample
Re-Melt of #5
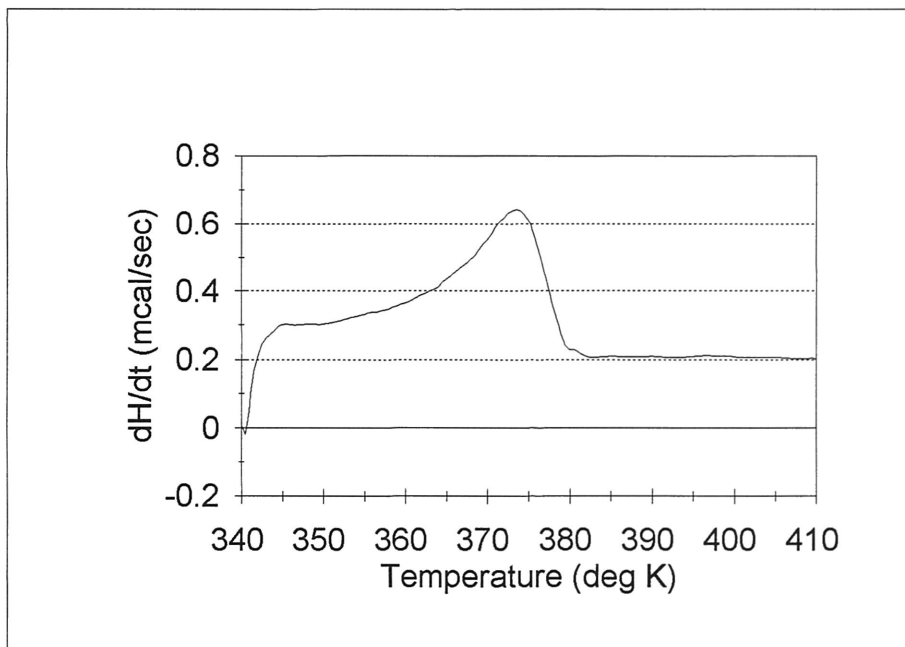


Figure 34:  Exposed Sample
Re-Melt of #6
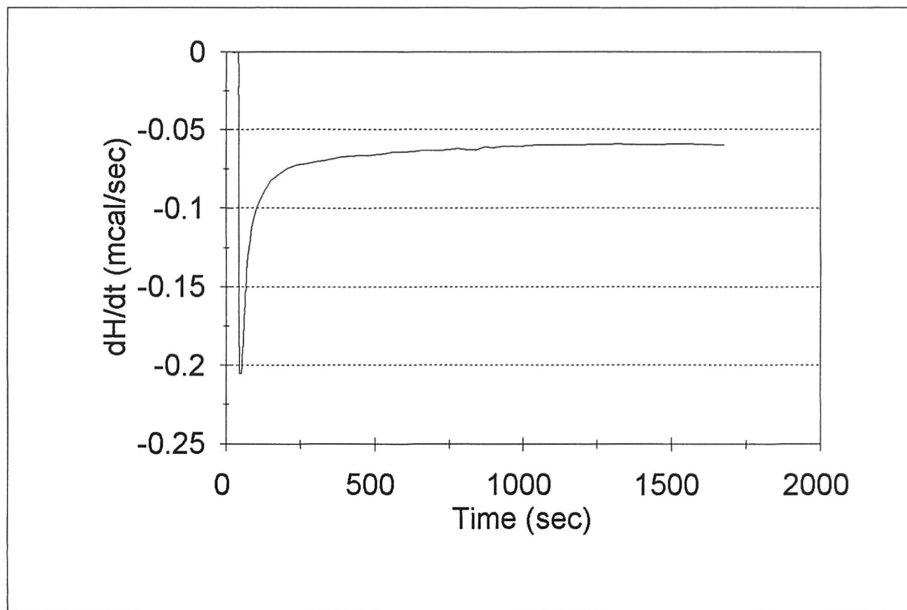
Figure 35: Control Sample
Cystallization #1
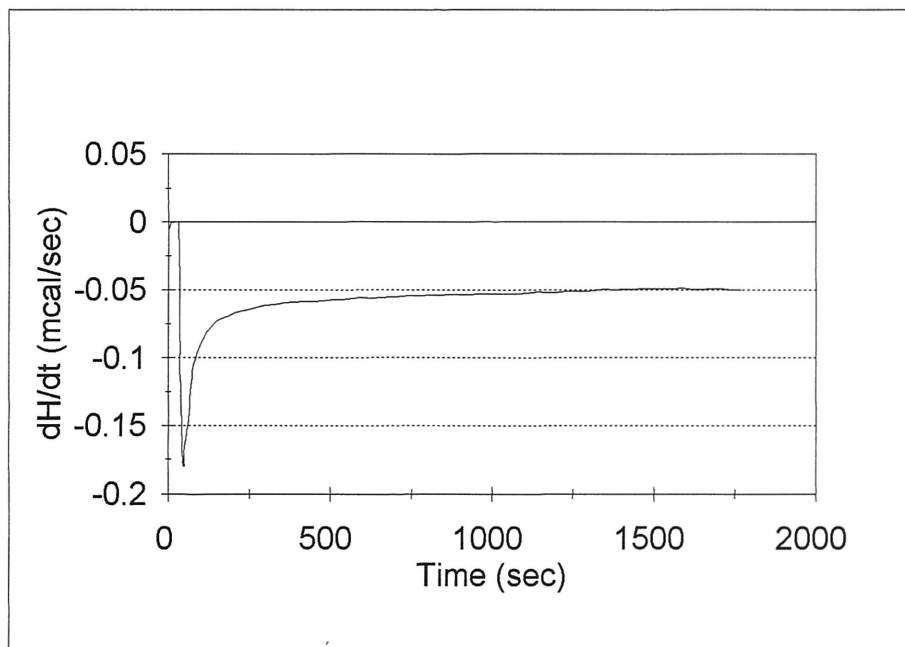


Figure 36: Control Sample
Crystallization #2
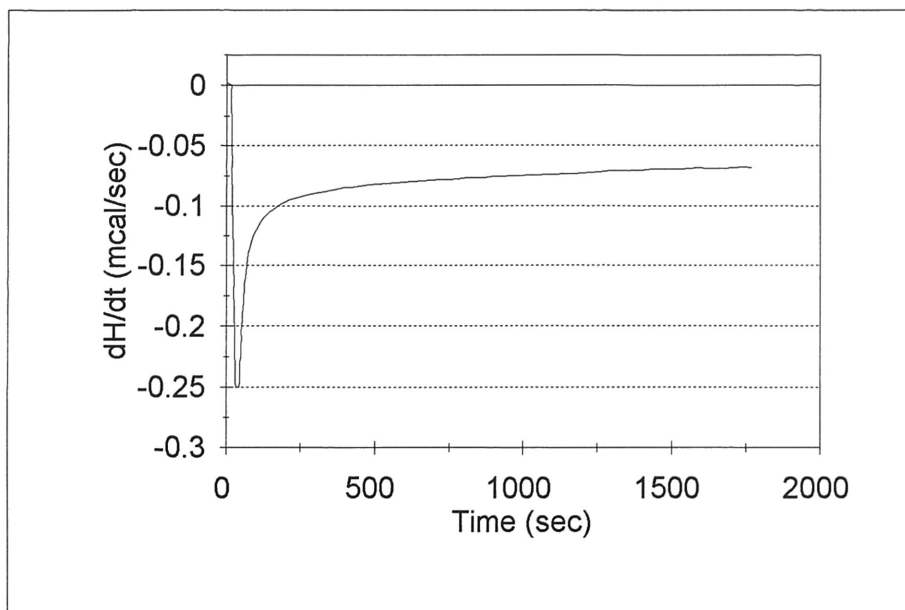
Figure 37: Control Sample
Cystallization #3
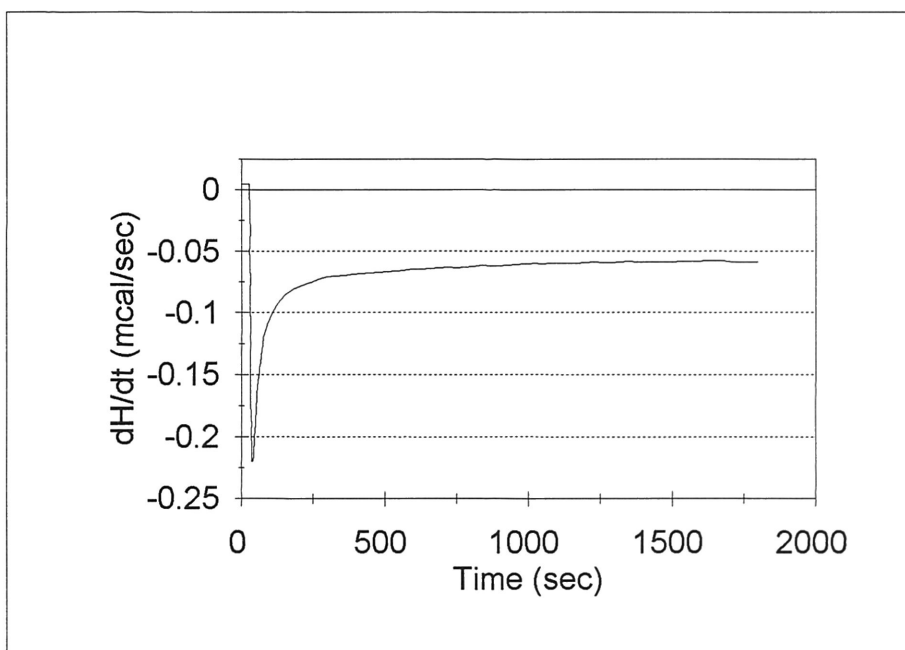


Figure 38: Control Sample
Crystallization #4
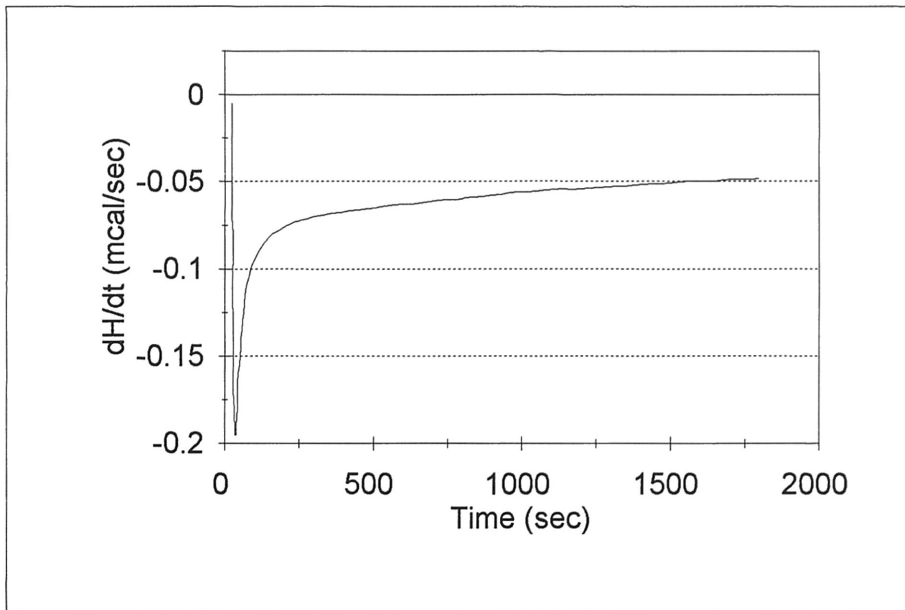
Figure 39:  Control Sample
Cystallization #5
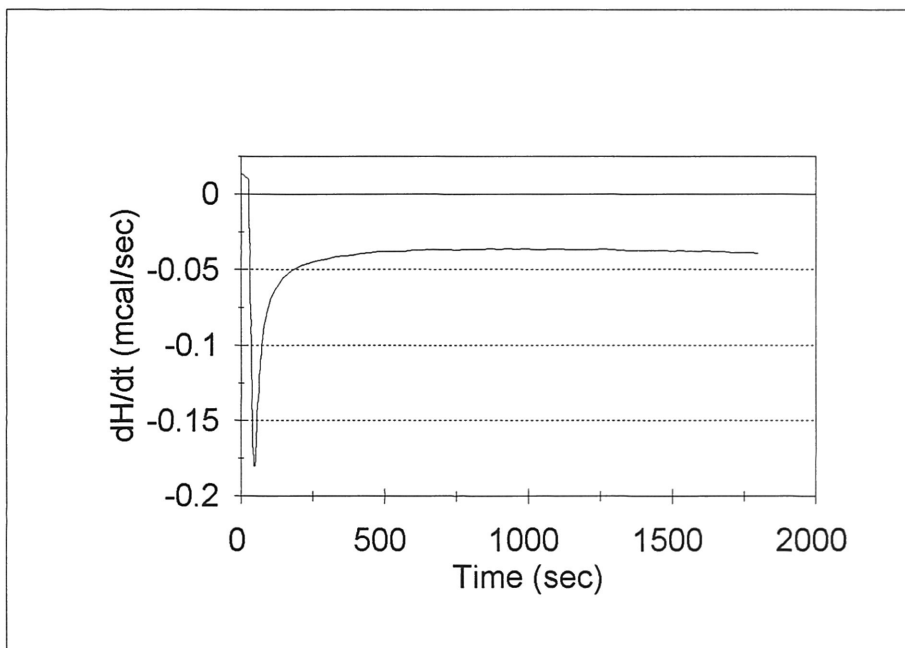


Figure 40:  Control Sample
Crystallization #6
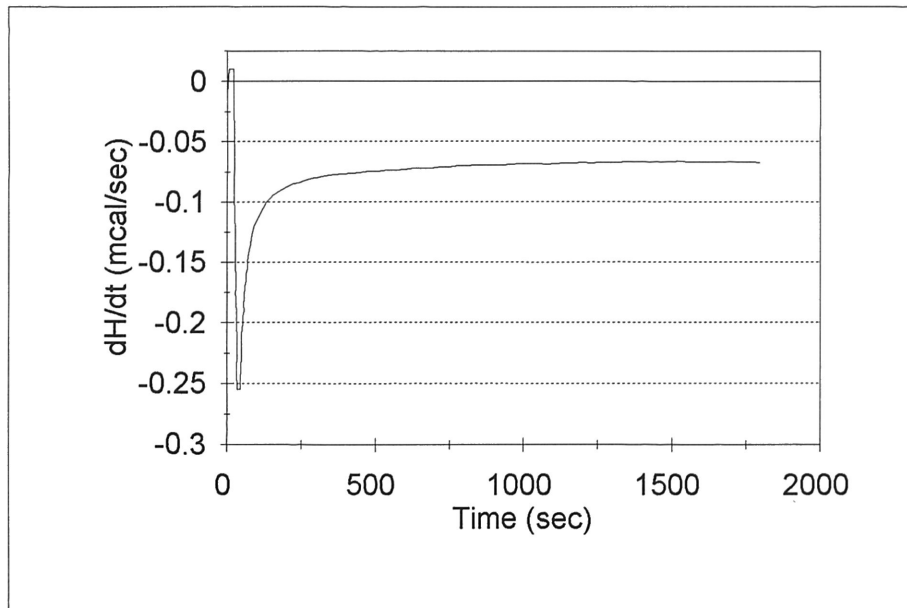
Figure 41: Control Sample
Cystallization #7
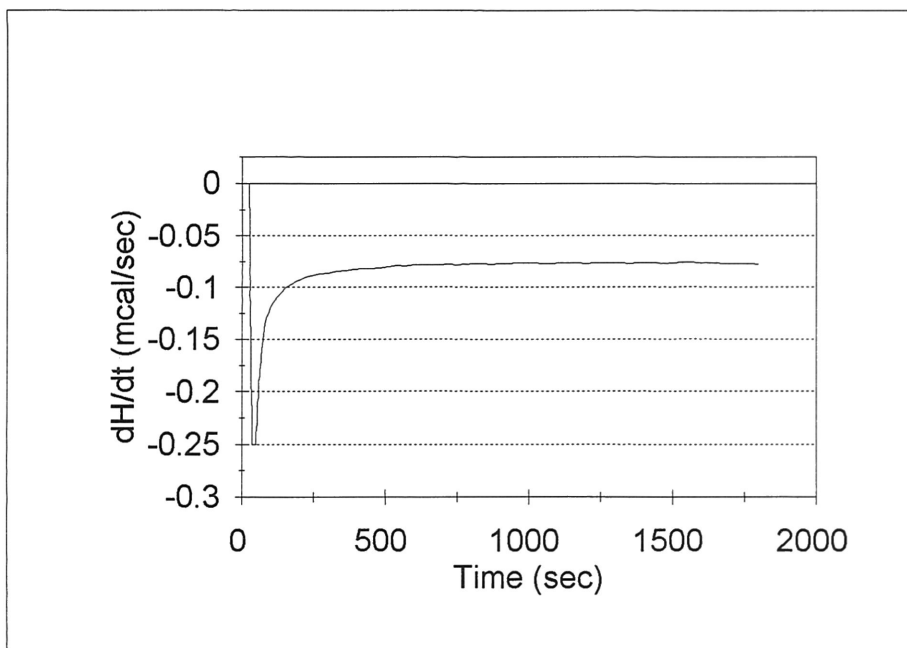


Figure 42: Control Sample
Crystallization #8
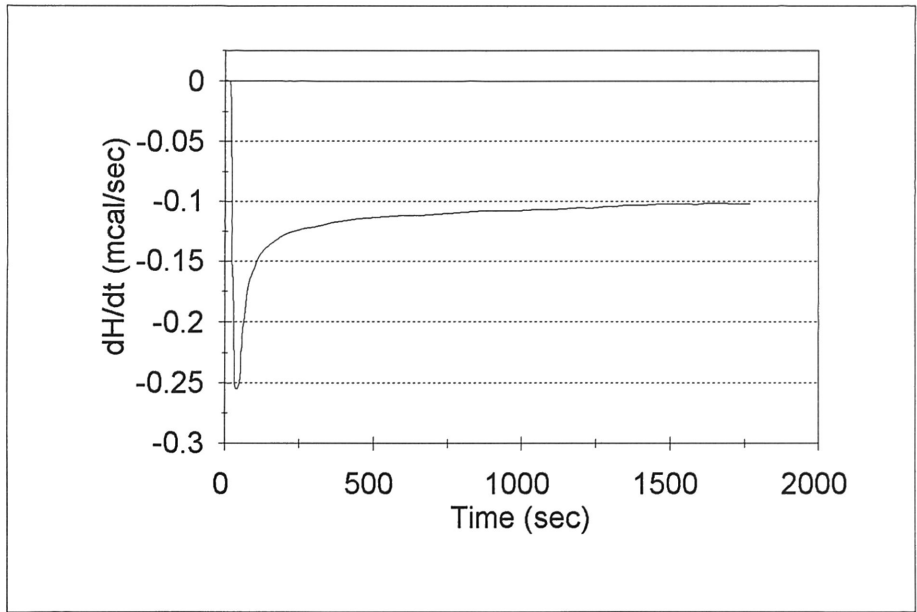
Figure 43:  Control Sample
Cystallization #9
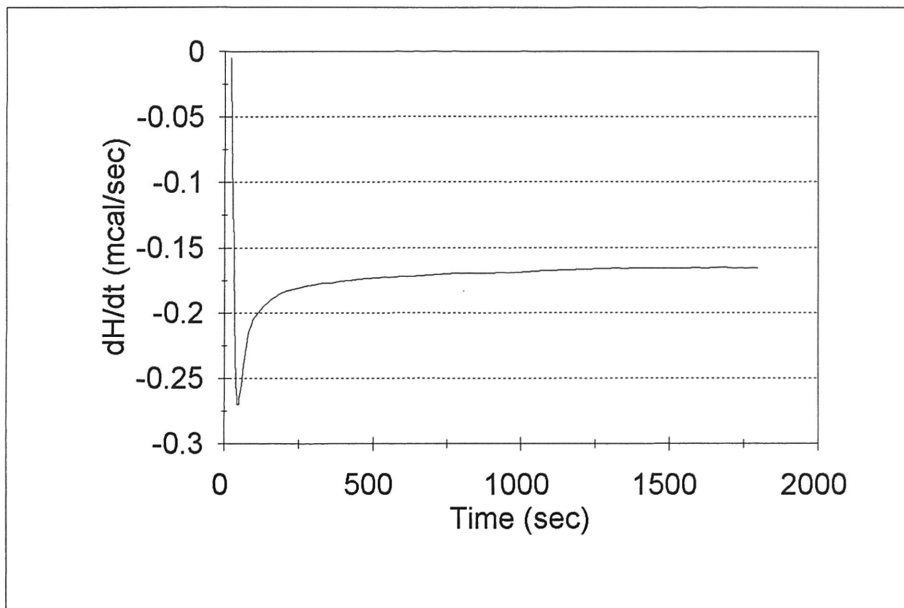
Figure 44:  Exposed Sample
Crystallization #1
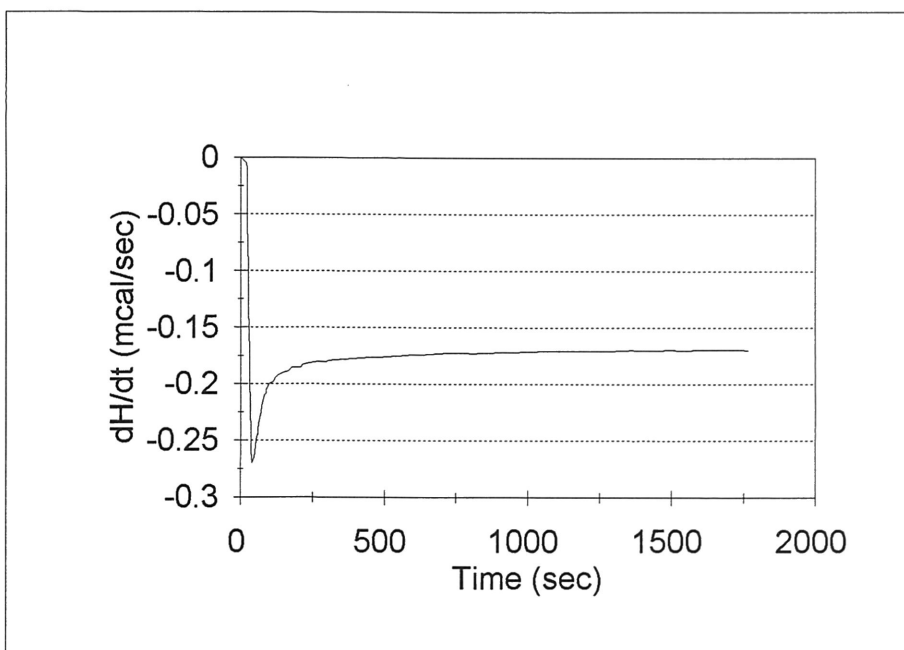


Figure 45:  Exposed Sample
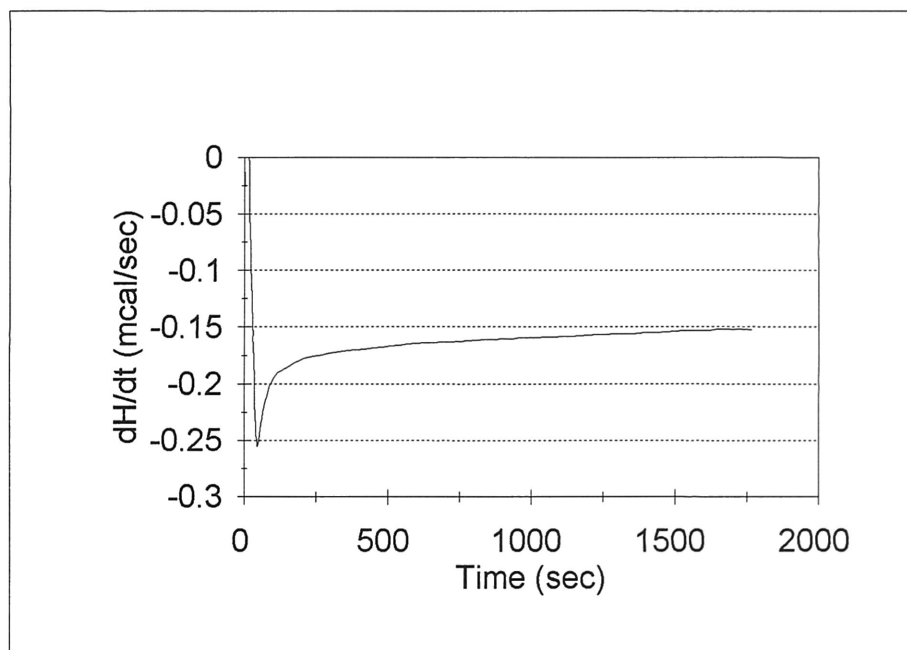Crystallization #2
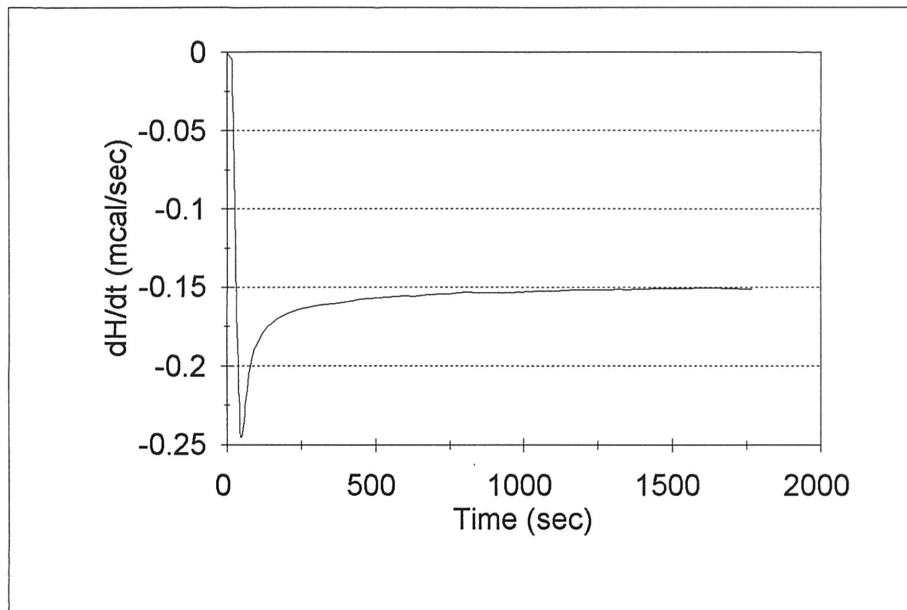
Figure 46: Exposed Sample
Crystallization #3
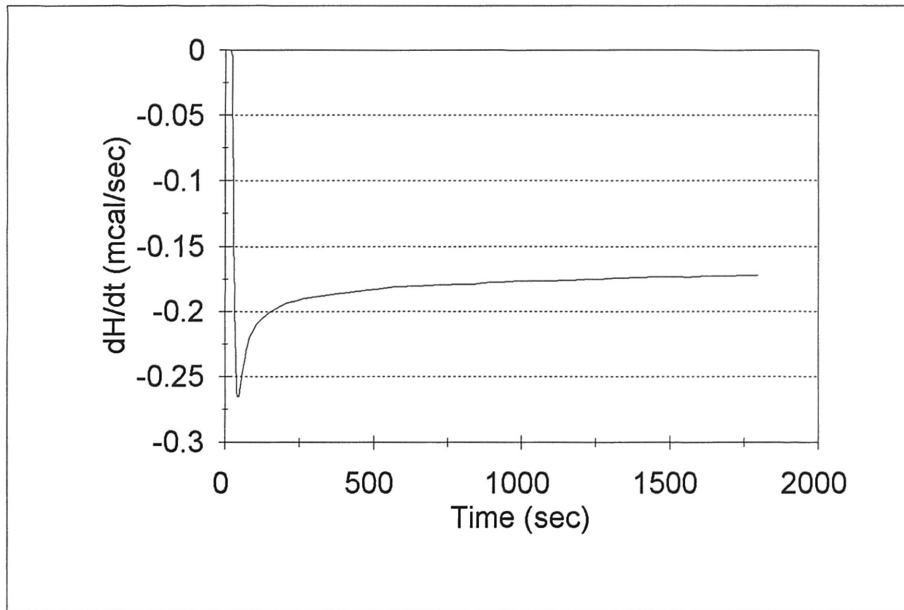


Figure 47: Exposed Sample
Crystallization #4
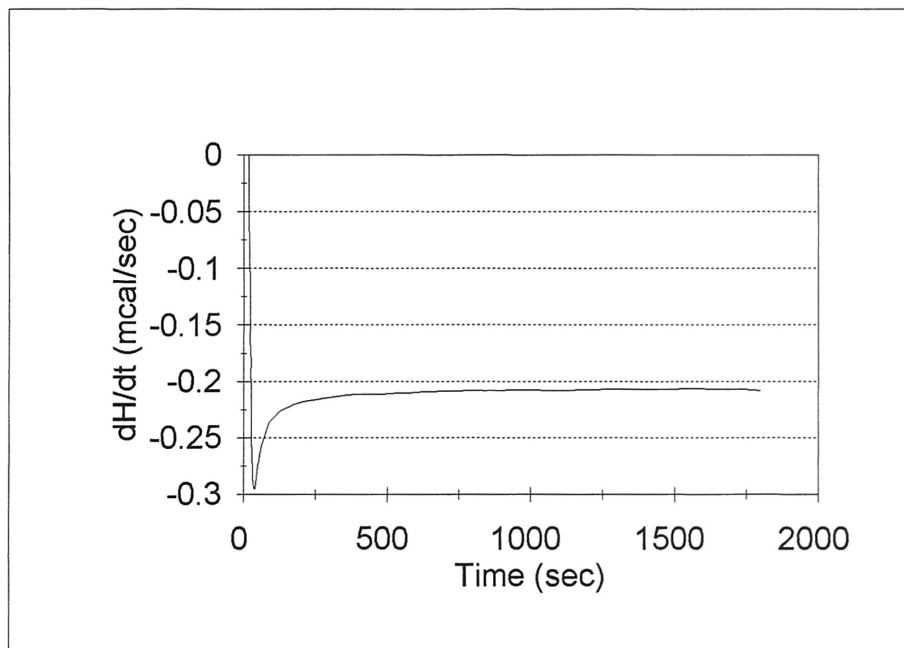
Figure 48: Exposed Sample
Crystallization #5


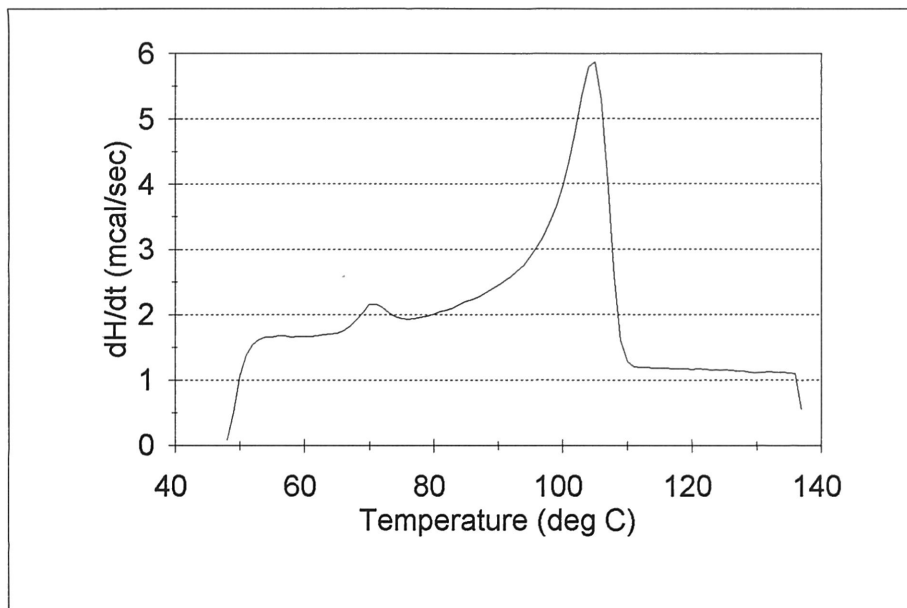
Figure 49: Exposed Sample
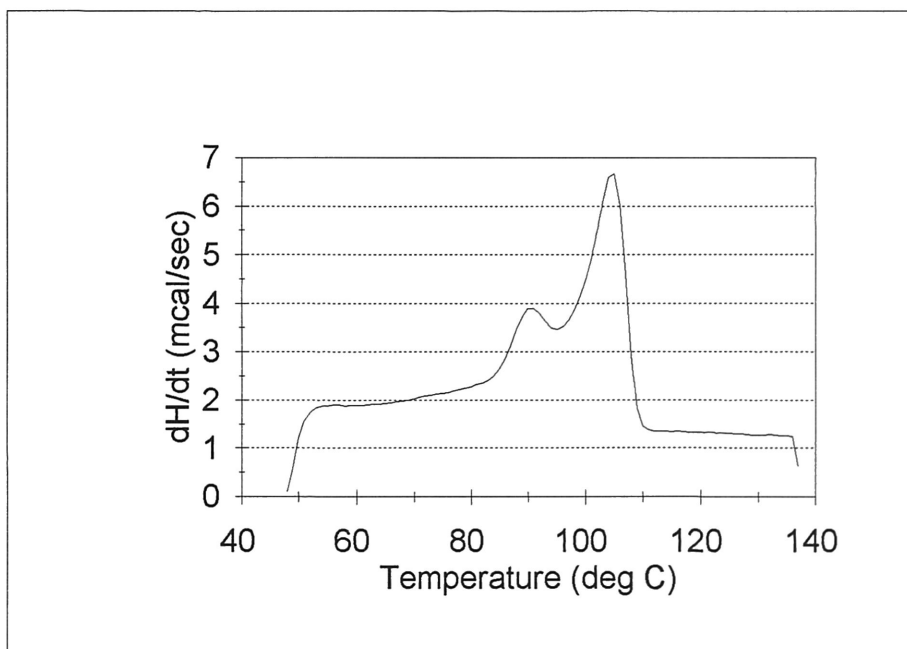Crystallization #6

Figure 50: Control Anneal
at 70 deg C



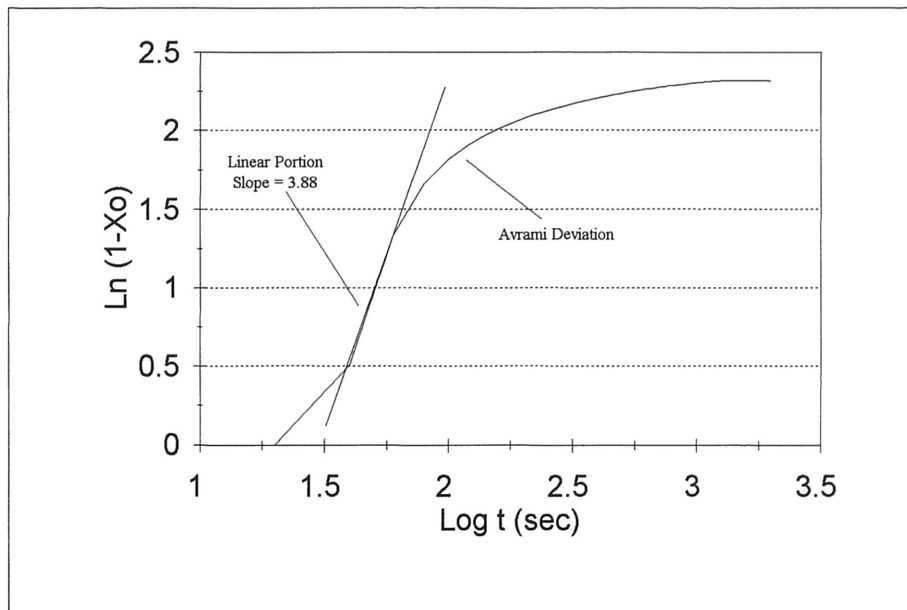Figure 51: Control Anneal
at 90 deg C

Figure 52: Control Avrami Plot
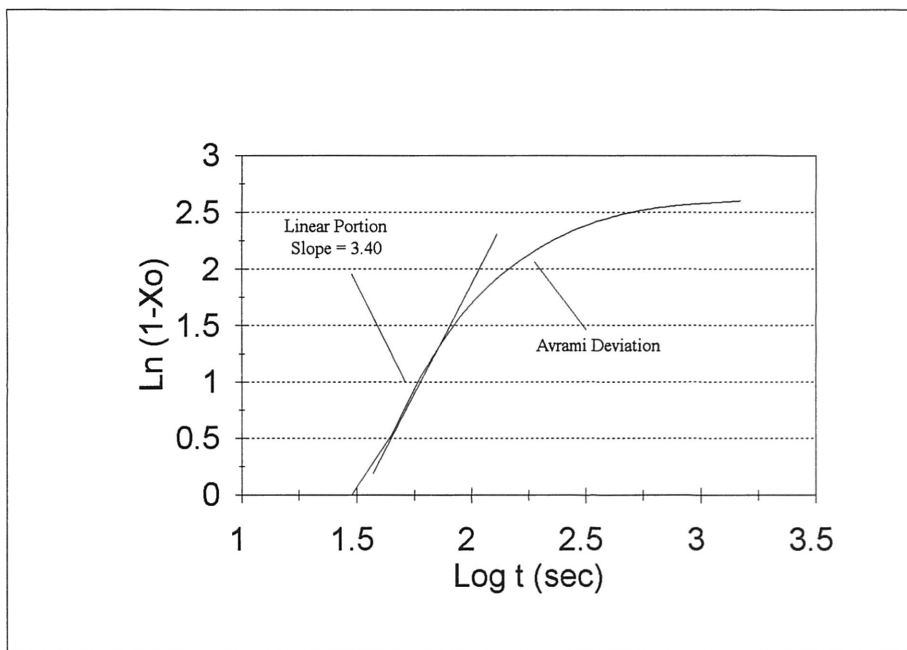


Figure 53: Exposed Avrami Plot

**Table 5: Avrami Parameters \***

| Coefficient | Nucleation | Growth Geometry | Growth Control |
|---|---|---|---|
| | | | |
| 0.5 | Instantaneous | rod | diffusion |
| 1 | Instantaneous | rod | interface |
| 1 | Instantaneous | disc | diffusion |
| 1.5 | Instantaneous | sphere | diffusion |
| 1.5 | Homogeneous | rod | diffusion |
| 2 | Instantaneous | disc | interface |
| 2 | Homogeneous | disc | diffusion |
| 2 | Homogeneous | rod | interface |
| 2.5 | Homogeneous | sphere | diffusion |
| 3 | Instantaneous | sphere | interface |
| 3 | Homogeneous | disc | interface |
| 3.5 | - | - | - |
| 4 | Homogeneous | sphere | interface |

\* Taken from reference 4- Polymer Materials Science