

Experiment to Teach Multiple Melting Phenomena in Semicrystalline Polymers Using Differential Scanning Calorimetry

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Abstract This article describes a laboratory experiment used to investigate the phenomenon of multiple melting in polymers. The experiment is aimed at the level of senior undergraduate chemistry students able to carry out the investigation in a research-style approach, working together in small groups. The experiment highlights characteristic thermal behavioral differences between polymers and small organic molecules. It demonstrates that shifts in observed melting temperature upon heating are typically due to inherent metastability of the polymer system and not to impurities in the sample, for example. Differential scanning calorimetry is used to demonstrate and explore this fundamental yet contemporary subject of polymer melting, using a well-known and commercially available polymer, isotactic polystyrene. Effects of thermal history of the sample, including crystallization temperature and crystallization time, as well as analysis conditions including heating rate, on the melting point of the polymer solid are each investigated. The experiment provides a hands-on example of structure-property relationships in polymer science.

Keywords: polymer, phase transitions, differential scanning calorimetry, isotactic polystyrene, multiple melting, upper-level undergraduate laboratory

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1. Introduction

Modern undergraduate degree programs in chemistry include learning outcomes in the areas of macromolecular systems, including polymer physical chemistry. Macromolecular systems include synthetic polymers, like isotactic polystyrene (i-PS). Some curriculum guidelines emphasize that such subject material should focus on the aspects that differentiate these large-scale systems from small molecule chemistry [1]. Polymer chemistry courses with lab components are increasingly being offered at the university undergraduate level as advanced physical chemistry electives for students majoring in chemistry. Guided inquiry-type practicums or laboratory components of lecture courses which offer more of a research-style experience are appropriate for and appealing to senior students, where enrolment numbers permit. A single research project lab experience can extend the full length of a traditional semester in which the course is offered. This paper describes a research project in which a small student research group of 3-4 students can investigate the thermal behavior of a semicrystalline polymer using differential scanning calorimetry (DSC). Specifically, DSC is used to investigate the multiple melting behaviour

of isotactic polystyrene (i-PS). Specific relevant background information for the instructor and for the student is also provided in the indicated sections below.

The project is an excellent extension of the theory of structure-property relationships typically presented in the lecture component of polymer physical chemistry content. It also helps to demonstrate the concept of non-equilibrium solids applied polymer materials. Students are very familiar with the equilibrium transitions of fusion and freezing for pure, small organic molecules and this experiment is an opportunity to compare and contrast the phase behaviour of the familiar small molecules with the long-chain linear polymer molecules. The level of instrumentation is appropriate for the students who have a fundamental understanding of calorimetry from previous and perhaps prerequisite physical chemistry course, so that the theory of DSC is a natural extension. Typically, institutions that would offer a course in polymer science would have instructors doing research in this area so that a DSC instrument would most likely be a standard part of the research instrumentation in the department and possibly could be used for these teaching purposes

Once students have prepared the samples by crimping known masses of polymer in the aluminum pans according to the manufacturer's instructions, there is no subsequent handling of chemicals. DSC experiments include

extended periods of time during which the students are not actively engaging with the instrument as it performs its programmed heating/cooling scans and collects data. During data collection, students only need to schedule time to load and unload samples. Once students meet the training requirements on the DSC instrument, students can perform DSC experiments safely according to a well-planned schedule. The project requires organization and teamwork from the students, skills which are very valuable. This design makes the term project both feasible and safe.

Students are encouraged to work in small research groups with 3 to 4 students, but the experiment can be accomplished with pairs too. Each group is given the investigation to do over a period of 4 to 5 weeks. Students at this level seem to enjoy the multiple-week, directed-study research project style of lab that is driven by an initial question and then continuously by subsequent results as they are obtained and discussed with the professor and group. During the scheduled weekly lab period, the students and professor participate in a group-meeting style discussion of the results to date. The discussion centers on the results of one series of DSC experiments that tests the effect of the first variable, and then on planning how to execute the next series of DSC experiments that will test the effect of the next variable. The DSC experiments are carefully planned and scheduled so that the total time per individual student spent over a single week does not exceed the expected lab time per week (e.g. 3 hours) and so that the tasks are divided evenly among the students in each group.

Group work often presents a challenge for assigning a grade to the individual student. To overcome this, each student in the group is required to process the group's acquired data individually, to produce the graphs like those included in the results section of this paper, and to submit their own responses to assigned questions on the concepts investigated and their interpretation of the results. Assigned questions are unique for each student in the group and are designed by the instructor so that the responses (after grading and corrections) provide the group what they need to easily collate and construct an Introduction and a Discussion with the necessary breadth and depth. The group works together to produce their own conclusion statements. Finally, with the components of a complete write-up available, the students of a single groups pool the information with the instructor's guidance and form a research-style poster for their group. The poster format requires the students to communicate very concisely and present interpretations and discussion points very logically and succinctly. In addition, the poster format requires the students to practice effective presentation and to incorporate large amounts of data on a single poster. The poster format is preferred over a digital slide presentation because it encourages more student engagement, and the posters can remain in an area for other students to browse, allowing for informal interaction among students.

2. Background for Instructor

In this paper, the DSC output plot of heat flow against temperature is referred to as a DSC trace. Elsewhere, it may also be called a thermogram. Students are typically

introduced to phase behaviour in polymers by illustration of a generic heating trace showing the glass transition baseline shift, a broad exotherm showing in-situ crystallization during heating, and a final broad endotherm showing melting of the crystallized material, all in a single DSC trace. This is a good starting point. However, many synthetic semicrystalline polymers are processed in their melt state into useful objects after they solidify or crystallize in a mold. It is important for students to understand that the thermal history of the solid affects its formation, its degree of order, and consequently its melting temperature, thermal stability and ultimately its useful function. With an understanding of DSC, and knowledge of lamellar-level polymer solid-state structure like that given in the *Background for Students* section in this document, students are well prepared to discuss the results of this study.

2.1. Multiple Melting

It is important to note that there are at least two ways to isothermally crystallize a polymer sample. (i) The sample is melted to erase thermal history and quickly cooled directly to the desired crystallization temperature. This is referred to as melt-crystallization. (ii) The sample is melted to erase thermal history and then quickly cooled to below the glass transition temperature, and then finally quickly heated to the desired crystallization temperature. This is referred to as cold-crystallization.

When crystallized polymer samples are heated in the DSC, typically multiple (two or three) peaks are registered on the heating trace. The temperature position of the peaks, and their relative sizes and magnitudes, shift to smaller or greater values depending on the crystallization temperature at which the sample was formed, the time period during which it was permitted to crystallize at that temperature, and the rate at which the sample is heated in the DSC. This thermal behaviour is directly related to the structure of the semicrystalline polymer solid. The DSC heating trace thus provides an indication of the thermal response of the polymer solid to heating. Understanding this response necessarily involves a discussion of the microstructure of the polymer material.

Students discover that double or multiple peaks in the DSC heating trace are not necessarily due to the melting of two or more types of crystalline solids that are present in the sample before heating; that most semicrystalline polymers can effectively undergo a continuous process of partial melting and reorganizing into higher ordered and therefore higher melting material, during heating in the DSC. The DSC trace can indicate the melting not only of the material that was crystallized before heating, but also that which partially melts/recrystallizes and finally melts during the heating scan in the DSC.

While multiple melting in semicrystalline polymers is a fundamental phenomenon, the discussion of its elucidation has remained current over time in the polymer science research literature. This is because there is not just one reason for this behaviour in all polymers. There are other causes besides the partial melting/reorganization described above. A list of generally accepted possible reasons for the manifestation of multiple melting behaviour in semicrystalline polymers is standard text in the introduction section of all

relevant literature. For example, the introduction section of a paper by Liu and Petermann [2] on the multiple melting behaviour of cold-crystallized *i*-PS lists and references the possible reasons for multiple melting in semicrystalline polymers, so they are not repeated here.

2.2. Multiple Melting in *i*-PS

Isotactic polystyrene (*i*-PS) can be cold-crystallized or melt-crystallized, and both forms of isothermal crystallization can lead to very similar multiple melting behaviour in the sample upon subsequent heating in the DSC. Multiple melting in melt-crystallized *i*-PS has been investigated since the earliest reports by Boon et al. in 1968 [3] and Pelzbauer and Manley in 1970 [4]. Most of the relevant literature report that followed focus on cold-crystallized *i*-PS samples [2,5-11]. In the experiment described in this paper, students study only melt-crystallized samples.

2.2.1. Experimental Variables

Students investigate the effects of isothermal crystallization temperature, isothermal crystallization time, and DSC heating rate on the resultant multiple melting endotherm behaviour as manifest in the DSC heating trace. Students investigate the effects of these different variables in this order. The procedures given to the student can be those detailed in the Experimental section of this paper.

2.2.2. Choice of Polymer

Multiple melting endotherms are apparent in the DSC heating traces of most, if not all semicrystalline polymers, but the polymer selected for this study is *i*-PS. Polystyrene is extremely common, perhaps second only to polyethylene in its widespread use in our everyday lives. Students are very well acquainted with everyday materials made from polystyrene. However, most of the commercial polystyrene is atactic polystyrene (*a*-PS) and to a lesser extent syndiotactic polystyrene (*s*-PS). Structural formulas of the different polystyrene microstructures (atactic, syndiotactic, and isotactic) are given in the *Background for Students* section of this paper. Discussions surrounding the choice of polymer can therefore also tie into discussions in lecture about tacticity and chain configuration, and of course methods of polymerization and catalysis.

Isotactic polystyrene crystallizes isothermally relatively slowly. For this reason, *i*-PS is a good polymer to study in this experiment. Its characteristic slow rate of crystallization makes it very amenable to the study of its thermal behavior and multiple melting using standard heating and cooling rates in a DSC. It does not crystallize upon cooling from the melt state in the DSC at reasonable cooling rates (10°C/min) so that it is easy to make sure that all of the isothermal crystallization actually occurs at the desired temperature. To demonstrate this, a sample can be melted in the DSC by bringing it to 300°C for one minute and subsequently cooled in the DSC at a rate of 10°C/min to room temperature. This can be done, and the resultant cooling trace examined with the students to demonstrate the lack of any exothermic activity in the sample. It does not crystallize and there is only a baseline.

Isotactic polystyrene however, is not a good polymer for widespread commercial use. Its crystallization rate is too slow under normal polymer processing conditions,

making it very difficult to use in injection molding or extrusion processes. Essentially the crystalline properties do not develop at a rate fast enough for practical use [12].

Isotactic polystyrene can in theory crystallize over a wide temperature range, approximately 130°C to approximately 220°C, but the rates of isothermal crystallization are more reasonable over a narrower range of 150°C to 190°C, still providing a wide range of crystallization temperatures for students to explore. It is thermally stable at temperatures needed to erase thermal history so there is no complication of degradation products forming. Finally, the melting behaviour is not complicated by polymorphism; it has only one crystal type.

3. Background for Students

A polymer is a linear, long-chain organic molecule with regular structural repeat units that are covalently linked through a process of polymerization of the original monomers. For most polymers the number of repeat units ranges from the order of 10^3 to 10^6 . Polymers used in everyday plastic items like polyethylene food containers can have a molecular weight near the high side of this range. Despite their exceptional length, many polymers form ordered solids via crystallization.

For small molecules, the same temperature is reported as both the crystallization (freezing) and melting (fusion) temperature. Indeed, at this equilibrium phase transition temperature, both the liquid and solid phases are present in equilibrium with each other. For crystallizable long-chain polymers, however, this is not the case. Polymer molecules need to be cooled significantly to temperatures well below their observed melting temperature for crystallization to occur at a reasonable rate. There is not one freezing temperature for a given polymer; crystallization can occur over a wide range of temperatures. The polymer melt needs to be cooled to a temperature at which nucleation can occur and at which temperature the chains retain enough thermal energy to move or diffuse through the melt to attach to a growing crystal, but not too much energy that the resultant structure is thermally unstable. It is not unusual to have measurable rates of crystallization occurring over as wide a range of temperatures as from 10 degrees below the melting temperature to 30 degrees above the glass transition temperature of the polymer. This is a range in which the thermal motion of the polymer chains is conducive to the formation of stable ordered regions [13]. Polymer crystallization is thus a kinetically controlled event in this case and not a purely thermodynamically controlled one.

Because of their sheer length, long-chain polymer molecules need to fold back and forth on each other in an accordion-like style in order to form ordered molecular solids. Once crystallization begins, this chain-folding creates ordered building blocks called lamellae. Crystallization continues with growth of these chain-folded lamellae in all radial directions from a common center, forming a spherical aggregate of the lamellar building blocks, called a spherulite. Neighbouring spherulites grow until they impinge upon each other forming the solid material. Figure 1 shows what a single spherulite looks like as observed using a polarized-light

optical microscope and the cartoon illustrates the mutual disposition of two lamellar building blocks with their constituent chain-folded structure.

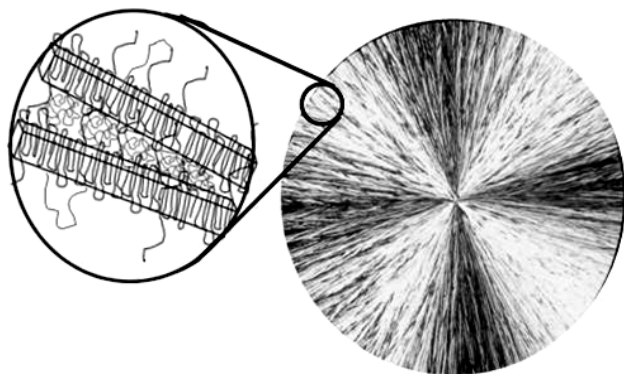


Figure 1. A polarized-light optical micrograph of a spherulite of *i*-PS grown in a thin film sandwiched between glass slides. The sample was melted at 300°C for one minute and then quickly cooled to a crystallization temperature of 170°C and held for 22 hours. The illustrated sketch shows the building blocks inside the spherulite, called lamellae, and their constituent chain-folded polymer molecules

The fundamentals of spherulite morphology as examined using this type of microscopy, and the general theory of polymer crystallization kinetics have been very well described previously in a series of two fundamental papers by Marentette and Brown [14,15].

Chain-folding requires structural regularity along the linear, polymer chain molecule in the form of identical or at least regular repeat units. A common crystallizable polymer with the simplest repeat unit is polyethylene which can be written as $\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_3$. Polystyrene is also a very common polymer used to make a large number of everyday items from drinking cups to computer casings. Depending on the type of polymerization reaction and conditions, the chain-linking reaction of styrene monomer repeat units can produce one of three different types of polystyrene chain configurations, described by the polymer tacticity, as illustrated in Figure 2.

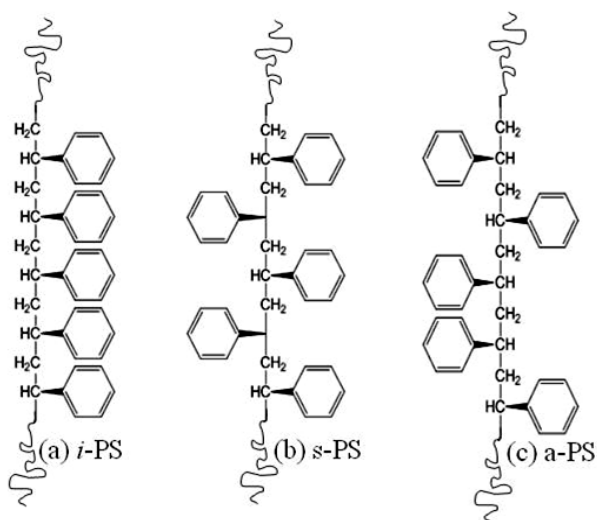


Figure 2. Structural formulas of polystyrene showing enough repeat units along the polymer chain backbone to illustrate the differences in tacticity: (a) isotactic polystyrene (*i*-PS) can crystallize; (b) syndiotactic polystyrene (*s*-PS) can crystallize; and (c) atactic polystyrene (*a*-PS) cannot crystallize.

Isotactic polystyrene (*i*-PS) has the pendant groups on one side of the backbone; syndiotactic polystyrene (*s*-PS) has them alternating from one to the other side and; atactic polystyrene (*a*-PS) has the pendant groups randomly appearing on either side of the backbone. As these are configurations and not conformations of the chain, they are not inter-convertible through simple free rotation of chain segments. Due to the regularity in their chain structures, both *i*-PS and *s*-PS can crystallize and are thus semicrystalline; *a*-PS is not crystallizable and forms an amorphous solid upon cooling; it does not display a melting temperature transition upon subsequent heating.

The process of lamella formation via chain-folding, and ultimately spherulite formation is not perfect. Polymers that crystallize from their melt (or glass) state do not form perfectly ordered crystals like small molecules. The resulting solid contains regions of disordered (amorphous) material and therefore crystallizable polymers are referred to as semicrystalline polymers. It can be seen in the illustrated sketch of the two lamellae in Figure 1 that the fold surfaces of the lamellae contain loose polymer chain ends and many polymer chain loops that have not chain-folded with perfect hairpin turns. In particular the inter-lamellar region is particularly disordered compared to the interior of the crystalline lamella. This is characteristic of crystallizable polymers. Regions and pockets of relative disorder can form between lamellae. Depending on many physical factors, and on the conditions of crystallization, varying relative amounts of crystalline and amorphous regions make up the solid material. The physical properties of materials made from semicrystalline polymers depend strongly on the relative amounts of amorphous (tougher, impact-resistant) and crystalline (more brittle) regions. Characterization and control of the polymer solid structure is essential to the design of materials for a particular function.

4. Experimental

4.1. Chemicals

Isotactic polystyrene (*i*-PS) was purchased from Aldrich Chemicals [cat.#45,038-3], with a molecular weight of 400,000 by gel permeation chromatography (gpc) as reported by the supplier.

4.2. Equipment

The differential scanning calorimeter used was a TA Instruments Q-100 instrument with a TA Instruments refrigerated cooling system (RCS). Polymer samples of known mass weighing in the range 1.50 to 2.00 mg were sealed in standard 40 microlitre size aluminum pans using the instrument press. The instrument was calibrated using an indium standard. A different sample was used for each DSC experiment.

4.3. Procedures

4.3.1. Effect of Crystallization Time

Thermal history and scanning conditions in the series of experiments to test the effect of crystallization time were as follows. Melt at 300 °C for 3 min to erase any thermal

history; Go to (rate ~ 80 °C/min) crystallization temperature of 170°C; hold at isothermal crystallization temperature for desired time; Go to (~ 80 °C/min) 80°C and equilibrate at temperature; heat at 10°C/min to 280°C. The five different crystallization times used are 240, 300, 360, 420, and 480 minutes.

4.3.2. Effect of Crystallization Temperature

Thermal history and scanning conditions in the series of experiments to test the effect of crystallization temperature were as follows. Melt at 300°C for 3 min to erase any thermal history; Go to (~ 80 °C/min) desired crystallization temperature; hold at isothermal crystallization temperature for 300 min; Go to (~ 80 °C/min) 80°C and equilibrate at temperature; heat at 10°C/min to 280°C. The five different crystallization temperatures used are 160, 170, 180, 185, and 190°C.

4.3.3. Effect of DSC Heating Rate

Thermal history and scanning conditions in the series of experiments to test the effect of heating rate were as follows. Melt at 300°C for 3 min to erase any thermal history; Go to (~ 80 °C/min) crystallization temperature of 170°C; hold at isothermal crystallization temperature for 300 min; Go to (~ 80 °C/min) 80°C and equilibrate at temperature; heat at desired heating rate to 280°C. The five different heating rates used are: 2.5, 5.0, 10 and 20°C/min.

4.4. Hazards

According to the safety data sheet information from the supplier, the polystyrene chemical used has a WHMIS classification of 0 in each of the categories of health hazard, flammability, and physical hazards. Caution should be exercised when handling the polymer because it is a fine powder and may be harmful if inhaled. Tweezers or a small flat spatula can be used to safely transfer the powder to DSC pans on the balance before sealing the pans.

5. Results and Discussion

DSC heating traces are plots of the heat flow against the temperature over the temperature range scanned. In the figures containing DSC heating traces, the heat flow units are arbitrary and, more importantly, in a single figure the traces are plotted each on the same heat flow scale, but y-shifted for the sake of a clear overlay presentation. Endothermic transitions are indicated by peaks pointing upwards in these traces, and therefore exothermic transitions exhibit peak minima.

Figure 3 contains the DSC heating traces for samples crystallized at 170°C for the different time periods listed. This temperature was selected because the value falls in the middle of the range of theoretically possible crystallization temperatures for *i*-PS, spanning 120 to 220 °C. In each heating trace, the polymer melts with the characteristic triple peak endotherm under the conditions tested. For simplicity, the peaks of the triple endotherm, in order of increasing temperature, are referred to in this paper as pk1, pk2 and pk3, respectively. Varying the

crystallization time between 4 and 8 hours had no effect on the position of the peak temperatures in the heating traces recorded under the conditions employed. There is a slight increase in magnitude in the endotherms with increasing crystallization time, as expected since there is more material to melt after a longer time period of crystallization.

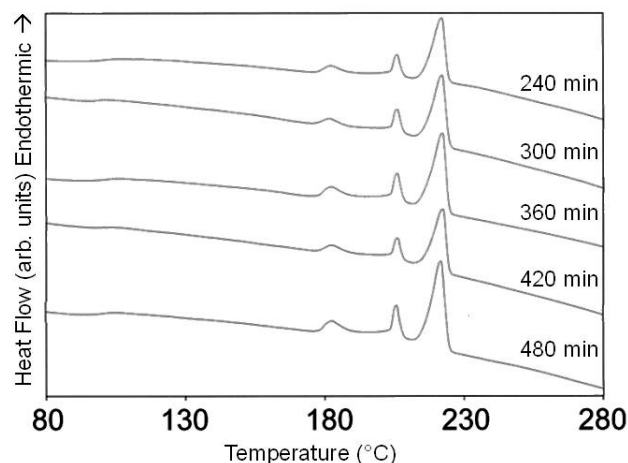


Figure 3. DSC heating traces of *i*-PS melt-crystallized at 170°C for the different times listed. Each sample quenched to 80°C following crystallization, and stabilized before scanning at 10°C/min. Each trace plotted on the same scale but y-shifted for presentation. Apparent baseline shift around 100 °C is the glass transition.

5.1. Explanation of pk1

Continuing with Figure 3, the lowest temperature peak (pk1) appears about 12 degrees above the crystallization temperature. It has been generally and commonly described in the relevant literature as the ‘anneal peak’. So-called anneal peaks are commonly observed in a DSC heating trace about 10 to 15 degrees above the crystallization or anneal temperature of many different semicrystalline polymers, regardless of the final melting temperatures. The reason for its appearance is therefore perhaps universal to semicrystalline polymers. It is generally accepted that the appearance of this peak is attributed to what is called the relaxation of the rigid amorphous fraction (RAF) [9]. The introduction section of a peer-reviewed paper explains it well and is paraphrased here below [11].

After a sample is allowed to solidify from the melt at a selected crystallization temperature for a given time period, crystallization may not be complete upon subsequent heating in the DSC. Some of the chains remain uncrystallized or amorphous and their relaxation is indicated by the familiar glass transition temperature upon subsequent heating. In the present context, this region is referred to as the mobile amorphous phase (MAF). The polymer chains that did manage to chain-fold completely and form lamellae will melt upon subsequent heating in the DSC and their phase transitions are seen in the middle and highest temperature endotherms, pk2 and pk3. Some chains however are part of an intermediate phase [16]. They are not part of the crystalline nor the amorphous phases just mentioned, and which are illustrated in the sketch included in Figure 1. They are constrained in an even smaller, continuous region between the amorphous

and crystalline regions. The chains of the RAF do not have enough mobility to register their relaxation at the glass transition temperature like those in the MAF. The chains of the RAF do not have enough order to register as a melting peak with the crystalline region. The RAF only needs to be heated by about 10 to 12 degrees above the temperature at which it was constrained (the crystallization temperature) for it to relax. Thus, the RAF manifests its relaxation with pk1, typically just degrees above the temperature at which the sample was crystallized.

The discussion of pk1 typically generates a lot of interest from the students, in part because students discover that peer reviewed research involves debate and conviction. It also piques student interest to see that the observation of pk1 behaviour is such a common occurrence in so many commercially important semicrystalline polymers. Discussion of pk1 phenomena also allows lecture concepts on non-equilibrium polymer solid state structure to come alive. Further discussion in this paper focuses on the appearance and significance of pk2 and pk3.

5.2. Explanation of pk2 and pk3

Despite crystallization under isothermal conditions, the sample typically contains a spectrum of lamellar order, from relatively thin and disordered lamellae to the thickest, most ordered ones. The former begin to melt at relatively lower temperatures and the latter at higher temperatures. The crystallized sample is considered to exhibit a single but broad melting endotherm in the DSC trace between the pk2 onset and pk3 offset temperatures. This statement may seem to be in contradiction to what is seen in the DSC trace, but an explanation follows.

What is peculiar to semicrystalline polymers, including *i*-PS, is the potential for reorganization of partially melted chains of lower-temperature melting lamellae into more ordered, higher-temperature melting lamellae all while the sample is being heated in the DSC. While the phenomenon is common in polymer thermal behaviour, the concept of what is essentially an ordering event occurring while heating generates much discussion among students. In terms of the results presented in Figure 3, the thinnest and least ordered lamellae of the sample begin to melt at the onset of pk2. At the peak temperature of pk2 the sample has partially melted enough to permit the reordering process to begin. However, the reorganization, like crystallization, is an exothermic process. The net effect is demonstrated in the trace; a concurrent exotherm cuts into the otherwise single broad endotherm, creating a 'peak' at the peak temperature of pk2. At the minimum temperature between pk2 and pk3 the net transition being registered on the trace is once again endothermic and the signal rises again, creating a second 'peak' with the onset to pk3. The superposition of an exothermic trough on a broader endotherm can appear in the DSC trace as two peaks, namely pk2 and pk3 [17]. The sample thus undergoes a continuous process of melting and recrystallizing and/or lamellar thickening.

According to the results in Figure 3, increasing the crystallization time period from 4 hours to 8 hours does not produce a generally more highly-ordered and therefore

higher-melting material. This suggests that for each of the crystallization time periods investigated, the same range of lamellar order existed in the sample before heating because the DSC heating trace after reorganization appeared the same. Much shorter times (e.g., 1 hour) or much longer times (e.g., 24 hours) were not tested in the current investigation, but this is another parameter that instructors may choose to include. Perhaps the crystallization temperature would have a greater effect on the degree of crystallinity in the sample before heating and on its ability to reorganize during the heating scan.

A second series of DSC experiments was performed to investigate how increasing or decreasing the isothermal crystallization temperature might shift the temperature positions of specifically pk2 and pk3. A constant crystallization time of 5 hours was used. These are shown in Figure 4.

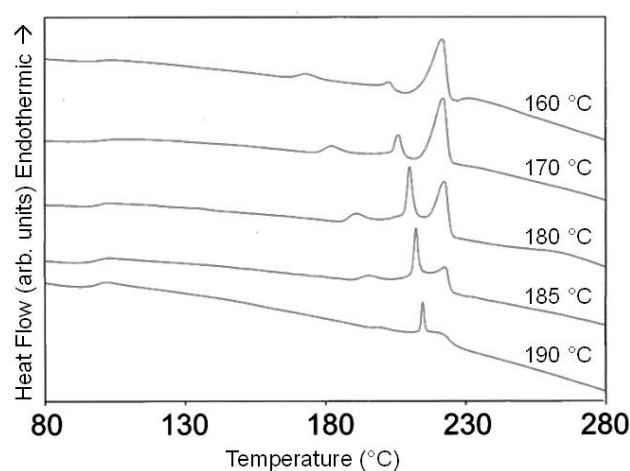


Figure 4. DSC heating traces of *i*-PS melt-crystallized for 5 hours at different temperatures listed. Each sample was quenched to 80°C and stabilized before scanning at 10°C/min. Each trace is plotted on the same scale but y-shifted for presentation. Apparent baseline shift around 100°C is the glass transition.

It is well known that polymers can form well-ordered, thick lamellae at high crystallization temperatures; relatively poor lamellae are formed at temperatures furthest removed from the melting temperature, that is, furthest away from equilibrium. At first glance it appears that the sample crystallized at the lowest temperature contains mostly well-ordered lamellae because it has the biggest pk3. However, this interpretation would be in contradiction to what is well known and stated above. A more careful interpretation is the following. The traces in Figure 4 show that with increasing isothermal crystallization temperature, the pk2 onset temperature increases, indicating that the quality of the poorest lamellae present before heating is increasing; and the pk3 offset temperature remains constant, indicating that the quality of the most ordered lamellae is not changing; the spectrum of lamellar order is narrowing.

The lamellae originally crystallized at the lowest temperature investigated (160 °C) are most susceptible to partial melting and reorganization into higher melting material during the scan and hence this trace shows the largest pk3 endotherm. It actually would have had the greatest amount of poorly crystallized lamellae before the heating scan, but the trace appearance indicates the largest

pk3 for melting of highly-ordered lamellae. The key is that these highly ordered lamellae were generated during the heating scan. With increasing crystallization temperature and therefore better lamellae in the sample before heating, a decreasing amount of lamellae is permitted to undergo partial melting and reorganization/lamellar thickening into higher-temperature melting material during the timeframe of the 10°C/min scan. The magnitude of the superimposed exotherm apparently decreases with increasing crystallization temperature and the resultant heating traces consequently have the appearance of a growing pk2 and a diminishing pk3.

The material originally crystallized at the highest temperature investigated (190°C) would have the highest degree of original order in the sample before heating. However, pk3 is not the dominant feature of this trace so therefore the highest melting lamellae are mostly a product of in-situ partial melting and reorganization/thickening during the heating scan. The 190°C sample experienced the least amount of reordering during the heating scan.

Because this continuous process of partial melting/reorganization between pk2 onset and pk3 offset temperatures occurs during the heating scan, the extent to which it occurs should be greatly influenced by the rate at which the sample is heated through this temperature region. Keeping the crystallization temperature constant at 170°C and the crystallization time constant at 5 hours, the heating rate was varied over the range 2.5 to 20°C/min. The results of these five traces are in shown in Figure 5.

It is well known that faster heating rates in the DSC can increase sensitivity, and this is why the higher heating rate traces in Figure 5 show increasingly larger signals. Faster heating rates can also lead to superheating of the sample, and perhaps this is manifested in a slight shift in the position of the RAF relaxation (pk1) to slightly higher temperatures with increasing rate.

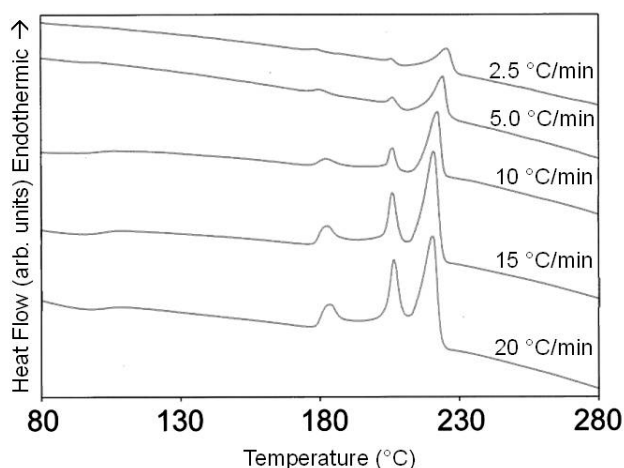


Figure 5. DSC heating traces of *i*-PS melt-crystallized at 170°C for 300 min and heated at the different rates listed. Each sample was quenched to 80°C and stabilized before scanning at 10°C/min. Each trace plotted on the same scale but y-shifted for presentation. Apparent baseline shift around 100°C is the glass transition.

Looking at the relative size of endotherm pk2 to pk3 in each of the traces, it is clear that at the slowest heating rate the sample has sufficient time to undergo the reordering process as pk3 is much larger than pk2. With increasing

heating rate, the sample has a decreasing amount of time to undergo the reordering process and the relative size of pk2 increases with respect to that of pk3. Finally, the offset temperature of pk3 shifts slightly to lower temperatures with increasing heating rate, supporting the idea that not only the amount of material undergoing reorganization is less, but also the quality of the highest-order lamellae formed decreases slightly, too.

As a final test to demonstrate that pk2 and pk3 are not due to a simple bimodal distribution of lamellae present in the sample before heating, but due to a continuous process of melting and recrystallization, the following heat-and-hold experiment was done. The experiment giving rise to the 10°/min trace in Figure 5 (also same as the 170°C trace in Figure 4) was repeated, but upon heating was halted at the temperature minimum between pk2 and pk3 (212°C) and held isothermally for 60 minutes. The sample was then quickly cooled to 170°C before reheating to 280 °C, this time without stopping.

Figure 6 contains (a) the original heating trace that shows the heating has stopped abruptly at 212°C; and (b) the subsequent heating trace that shows a baseline in the temperature region where pk2 had appeared in (a). The isothermal hold promotes the extent of the reorganization exothermic activity, with pk2 shifted to a higher temperature, effectively becoming a shoulder on pk3 in (b). The original pk2 material has partially melted and reorganized into higher-temperature melting material to the extent that it can at that temperature. However, when subsequently heated to higher temperatures during the recording of trace (b) it still has the potential to, once again, partially melt and reorganize, with the sample finally melting with a pk3 offset temperature the same as that in the Figure 5 traces.

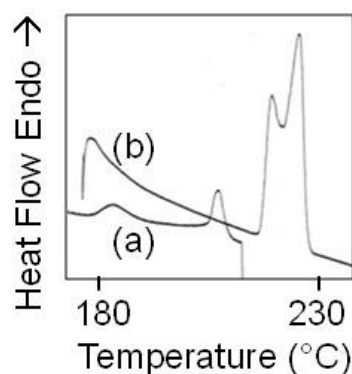


Figure 6. (a) DSC heating trace of *i*-PS melt-crystallized at 170°C for 300 min and heated at 10°C/min to 212°C. Sample then held isothermally for 60 min at 212°C and quenched back to 170°C (not shown). (b) Reheat of (a) at 10°/min. Scale is same as in Figure 1, Figure 2, and Figure 3. Initial bump in (b) is not sample related.

5.3. Ideas for Further Investigation

There may be an opportunity to further explore the relationship between crystallization temperature and observed melting behaviour using the DSC data already collected. In Figure 7, the peak temperatures of each of pk2 and pk3 from Figure 4 are plotted against their corresponding crystallization temperature and a linear regression is performed on each of the two plots. It is

interesting to then have students ponder the implication of the extrapolation of these lines to their point of intersection and predict the melting behaviour that might be manifest in the DSC trace of a sample crystallized at the crystallization temperature associated with this point of intersection. Students tend to predict that a sample crystallized at this temperature will melt with a single peak endotherm, and this can be tested. In Figure 7, the x-axis variable for the point of intersection is a crystallization temperature of 212°C.

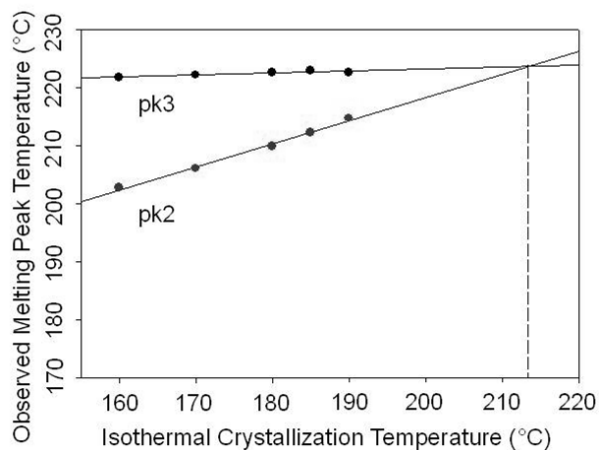


Figure 7. Plots of observed pk2 and pk3 peak temperatures against isothermal crystallization temperature for DSC heating traces presented in Figure 4. Samples were isothermally crystallized for 300 min and subsequently heated at 10 °C/min. Dashed line is added to indicate intersection of plots at isothermal crystallization temperature of 212°C

Figure 8 is a reprint of Figure 4 with the added DSC heating trace of a sample crystallized at 212°C for 24 hours.

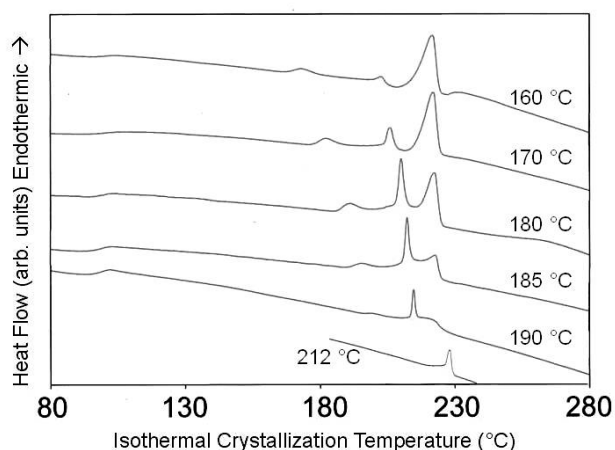


Figure 8. DSC heating traces (10°C/min) of *i*-PS isothermally crystallized at the temperatures listed for 5 hours (except for the 212°C trace where sample was crystallized for 24 hours). Samples were cooled quickly to 80°C after crystallization before being scanned from 80°C to 280°C. All traces same scale, but y-shifted for presentation

The isothermally crystallized sample at 212°C is observed to melt with one small and narrow endotherm, the peak temperature of which is 228°C. Students can discover through trial and error that if crystallized for just 5 hours at this high temperature, not enough material has crystallized to give a measurable signal in the subsequent heating trace. A time of 24 hours was selected to make

sure that it would be crystallized. There is no sign of partial melting and reorganization during the heating scan, leading to the conclusion that high melting material is present before heating.

6. Conclusion

DSC is a very powerful tool in thermal analysis and an essential one in polymer science. The understanding of structure-property relationships in polymer science is extremely important. This laboratory exercise on multiple melting is a straightforward investigation of a contemporary and complex problem. It is an excellent way for students to compare the familiar concept of melting point in small organic molecule solids to thermal behaviour in polymer solids. The results of a series of systematic experiments can combine to tell a story that helps students understand the idea of non-equilibrium structures in polymer science.

This laboratory exercise works very well with a small group of senior students working as a team on a research project. The production of the research poster is a good way to help students develop their scientific writing and presentation skills. Instructors can point students to Information for Presenters sites of conferences or professional organizations to reinforce the importance of format in science communication. From a student point of view, the poster is a fresh change from the traditional formal written lab report. Resources typically exist in Earth Science Departments or other departments on campus where posters can be printed for the purpose of presenting.

DSC provides the calorimetry tool that allows students to test ideas by planning experiments involving the control and thoughtful variation of variables that include crystallization temperature, crystallization time, and heating rate. The programmable heating scans allow for the addition of annealing, too, if desired. The ability to program precise thermal treatments of samples and control multiple variables, allows for instructors to choose their own desired focus of the experiment and its related curriculum. Multiple series of experiments can be assigned to each student group, or each student group can investigate the effect of a single variable and perform a single series of experiments. In the latter approach, students pool and share their data as a class to obtain the full scope of the investigation. This form of collaboration promotes a strong sense of responsibility from the students in acquiring reproducible results.

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