ELSEVIER

Polymer 42 (2001) 6453–6461

polymer

www.elsevier.nl/locate/polymer

Multiple melting behavior in isothermally cold-crystallized isotactic polystyrene

T. Liu*, J. Petermann[1]

Department of Chemical Engineering, Institute of Materials Science, University of Dortmund, D-44221 Dortmund, Germany

Received 8 January 2001; received in revised form 13 February 2001; accepted 16 February 2001

Abstract

The multiple melting behavior and lamellar morphologies of isotactic polystyrene (iPS) isothermally crystallized from the glassy state have been investigated by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The influences of different experimental variables (such as crystallization temperature and time, heating rate) on the melting behavior of iPS are studied. The combination of thermal analysis and morphological results indicates that: (1) the 'annealing peak' is not associated with the melting of subsidiary crystals formed by secondary crystallization as often suggested in the literature; (2) two lamellar populations with different degrees of perfection within a single lamella are responsible for the so-called double melting behavior in iPS. The partial melting and repairing (via recrystallization) of iPS crystals are observed on lamellar level by TEM observations. From the obtained calorimetric and morphological results, the applicability of several crystallization and (subsequent) melting models is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Isotactic polystyrene; Annealing peak; Double melting behavior

1. Introduction

Many isothermally crystallized semicrystalline polymers exhibit double or multiple melting behavior upon heating in differential scanning calorimetry (DSC). However, there are considerable controversies in the literature concerning the origin of the multiple melting phenomenon [1–4], especially for the lowest-temperature endotherm (usually called the 'annealing peak') whose position is always only a few degrees above the annealing or crystallization temperatures [5]. This annealing-induced endotherm is the characteristic of many semicrystalline semistiff polymers, and as summarized in the literature, its origin can be ascribed to a variety of sources [1–5]: (1) melting, recrystallization and remelting during the DSC heating process, (2) the presence of more than one crystal modifications (polymorphism), (3) variation in morphology (such as lamellar thickness, distribution, perfection or stability), (4) physical aging or/and relaxation of the rigid amorphous fraction, (5) different molecular weight species and so on. Obviously, there exist more or less divergences among these different melting mechanisms, and up to now, no consensus has been reached as to the exact origin of multiple melting behavior of the semicrystalline polymers. A unique model that is reasonably compatible with all physical observations has not yet put forward. And the multiple melting behavior of polymers probably originates from very different reasons depending on the polymer and its crystallization condition. Therefore, a further understanding of the origin of double or multiple melting behavior is of great significance and should provide a new insight into the crystallization and melting process of crystalline polymers [2].

Regarding isotactic polystyrene (iPS), its multiple melting behavior has been extensively investigated as an example of an isotactic crystalline material [5]. The double melting peaks in iPS were first reported by Boon et al., who ascribed the lower-temperature melting peak to the original crystals formed upon crystallization, and the higher one to the recrystallized population during the heating process [6]. Later, an even lower endotherm about 10°C above the crystallization or annealing temperature (i.e. the annealing peak) was discovered in iPS by Pelzbauer and Manley, which was attributed to the melting of 'impurities' such as stereoblock or other sterically inhomogeneous molecular species [7]. Afterwards, the triple melting

---

* Corresponding author. Present address: Advanced Polymers and Chemicals Program, Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore. Tel.: +65-874-8384; fax: +65-872-7528.

E-mail addresses: liu-tx@imre.org.sg (T. Liu), peterman@ct.uni-dortmund.de (J. Petermann).

[1] Fax: +49-231-7552480.

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00173-2

behavior in iPS was thoroughly investigated by Lemstra et al. using the DSC [8,9]. They suggested that, the annealing peak originates from a secondary crystallization of the melt, trapped within the spherulites or intercrystalline links (for example, tie molecules). The next (second) melting endotherm was related to the normal primary crystallization process. The highest melting peak was attributed to the second one by continuous melting and recrystallization during the DSC scan. Although it was mainly based on thermal analysis results, in the past decades, this melting model for iPS was accepted by many authors [10–16].

On the other hand, it should be noted that Bell et al. proposed another melting mechanism to interpret the double-melting behavior in iPS by analogy with the investigations on nylon 66 [17,18]. They advocated that the two endotherms are neither caused by a bimodal crystal size distribution, nor by recrystallization, nor by orientational changes, nor by phase changes, but by the melting of two crystal forms: folded-chain crystals (related to the higher-temperature endotherm) and less perfect bundle crystals (associated with the lower). The same conclusion was also drawn by Lety and Noel [19]. Nevertheless, this dual-crystal-population model for iPS was thought erroneous owing to overlooking the recrystallization process on thermal analysis [5], and therefore, usually neglected by many researchers. As pointed out by Wunderlich in his review [5], a much more detailed structure analysis (especially on crystal morphology) is necessary before such assignment for multiple melting peaks can be made. And he further suspected that most likely both crystal types contain only minor variations in crystal morphology and molecular macroconformation. However, to our knowledge, no further morphological analysis has so far been carried out on the multiple melting behavior in iPS.

In addition, the extensive studies on multiple melting behavior are mainly focused on the melt-crystallized polymer samples, and less attention is paid to the cold-crystallized ones (i.e., crystallized from the glassy state). The melting process is usually studied on bulk materials by techniques such as DSC, X-ray (WAXS and SAXS) and density measurements. Since these techniques involve the study of bulk samples, normally no direct information can be obtained on the single lamellar level during the melting process. Especially, although the transmission electron microscopy (TEM) technique is a powerful tool that can provide confirmative evidence, the studies at this aspect are surprisingly scarce. Therefore, a more complete description and understanding on the multiple endothermic behavior require the direct confirmation by morphological observations using the microscopic techniques such as TEM.

In our present work, we mainly attempt to revisit the complex endothermic behavior of isothermally cold-crystallized iPS by combining the TEM technique with the calorimetry method. Here, it should be noted that the thermal treatment approach of isothermal crystallization is totally different from that of stepwise crystallization or annealing, which can also lead to multiple endothermic melting peaks. But the reasons of their occurrence can be definitely attributed to different crystal size populations [20,21]. And iPS is selected as the studied system based on the following considerations: (1) the characteristic slow crystallization rate of this polymer makes it an ideal subject for the study and refinement of multiple melting in polymers, due to the possibility of following the crystallization and melting processes in the DSC; (2) the absence of polymorphism makes it easier to investigate; (3) it has higher stability to electron irradiation than most other polymers [22,23].

2. Experimental

2.1. Materials and sample preparation

The powdery iPS sample ($M_w = 752{,}000$, isotacticity: 97%) was purchased from Polymer Laboratories. Here, it should be noted that the supplier was not able to further supply us with the detailed information for our investigation upon the kind of tacticity or the distribution of polymer chain sequences, although the tacticity may play an important role in the melting process due to the segregation of molecules in front of the growing tip during the lamellar crystallization. To obtain amorphous samples, the as-received iPS was heated to 250°C for 5 min, and subsequently quenched into ice water. Then, the amorphous samples were isothermally crystallized at different temperatures (T_c) for different times (t_c) followed by quenching to room temperature for the use of DSC measurements.

2.2. DSC measurements

DSC experiments were performed in a DSC-2920 from TA Instruments coupled with a TA-2000 control system. The temperature was accurately calibrated to be ±0.5°C in error, with gallium, indium and tin using the standard procedure. Most of the samples were heated with a scanning rate of 10°C/min from 50°C. In the present study, the isothermal cold-crystallization time is used as 6 h because the crystallization of iPS for this time is believed to be almost complete [24]. Therefore, for isothermally cold-crystallized iPS little change on DSC curves can be observed during the subsequent heating processes from room temperature or from the used T_c. For studying the effect of heating rate on the multiple melting behavior, the samples were scanned from 5 to 50°C/min. The weights of all the samples were in the range of 5 ± 0.1 mg. All crystallization and melting treatments were performed under nitrogen atmosphere in order to diminish oxidation.

2.3. TEM observations

Thin films for direct TEM observation were obtained by the following procedure: firstly, the dilute polymer-xylene solution (with concentration of 0.1%-w/v) was dropped onto mica covered with a carbon film, then the polymer films on the carbon-support film were floated onto the water surface and transferred onto electron microscope copper grids, finally the obtained thin films on the grids were melted at 250°C for 5 min and quenched into ice water. For the TEM observations, the amorphous thin films were crystallized at 160°C for 6 h, after which the resulting multiple melting peaks can be well separated in the DSC. The obtained crystalline thin film samples were further partially melted or annealed at different temperatures for different times.

For surface replica experiments, the bulk-crystallized samples were etched in 1% potassium permanganate in a mixture of sulphuric acid, phosphoric acid and water (5:2:2 v/v/v) for 2 h at room temperature. After subsequent washings, following the prescribed procedures by Olley and Bassett [25], the etched surfaces were examined under TEM using a standard one-stage replication process, i.e. making a first replicate in cellulose acetate, subsequently shadowing it with platinum, finally coating it with a carbon film. Morphological observations were performed using a Philips CM200 TEM operated at 200 kV, and the contrast in the bright-field (BF) electron micrographs of the thin films was obtained by defocusing the objective lens [26].

3. Results and discussion

3.1. DSC investigations on the multiple melting behavior in iPS

Influence of crystallization temperature. The effect of crystallization temperature (T_c) on the melting behavior of iPS (isothermally cold-crystallized at different temperatures for 6 h) at a constant heating rate of 10°C/min is illustrated in Fig. 1. It can be observed: (i) the DSC curves exhibit three endothermic peaks (labeled as T_a, $T_{m,1}$ and $T_{m,2}$ in the order of temperature from low to high) and one exothermic recrystallization peak (labelled as $T_{c,re}$, which is located between the last two melting peaks) for $T_c < 170°C$; for the case of $T_c > 170°C$, the recrystallization process is somewhat inhibited, therefore, the recrystallization exotherm can not be distinctly seen; when $T_c > 190°C$, only one melting peak ($T_{m,1}$) can be observed. (ii) The lowest-temperature endotherm, the so-called annealing peak (T_a), shifts to higher temperature with increasing T_c and appears always at ca. 10–15°C above the cold-crystallization or annealing temperature. Its magnitude also increases slightly with the increase of T_c. (iii) As increasing the T_c, the $T_{m,1}$ also shifts to higher temperatures, and finally merges into the highest endotherm ($T_{m,2}$). Its magnitude is strongly enhanced. (iv) With the increase of T_c, the $T_{m,2}$ almost remains constant around 220°C while its size gradually decreases. Accordingly, it is evident that the triple melting peaks are strongly undercooling dependent, especially for the intermediate melting peak, $T_{m,1}$. From Fig. 2, the equilibrium melting point of iPS can be approximately estimated to be 242°C by the Hoffman–Weeks extrapolation [27], which is well consistent with the values previously reported for the melt-crystallization studies in iPS [7].

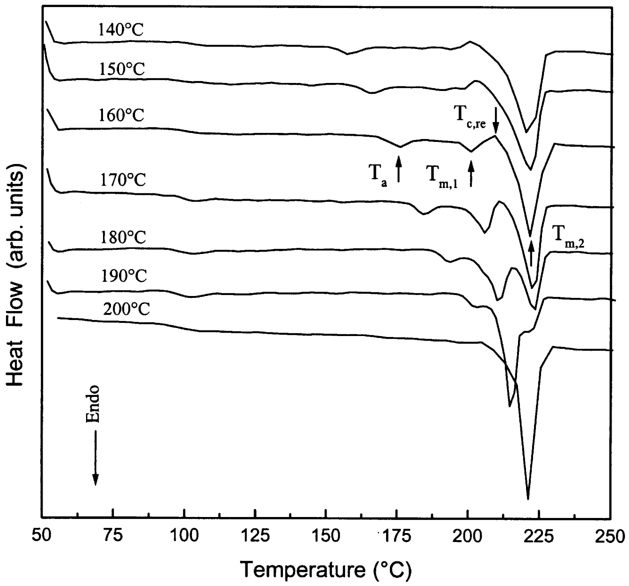

Fig. 1. DSC traces of iPS isothermally cold-crystallized at different temperatures for 6 h. The heating rate is 10°C/min.

Sequence of crystallization. In order to explore the sequence of crystal formation during cold crystallization, the amorphous iPS samples were isothermally crystallized at 160°C for various times (from 10 min to 48 h) followed by quenching to room temperature and heating to complete melting (250°C) at 10°C/min in the DSC. The collective thermographs are presented in Fig. 3. It can be observed that: (i) when the crystallization time (t_c) is less than

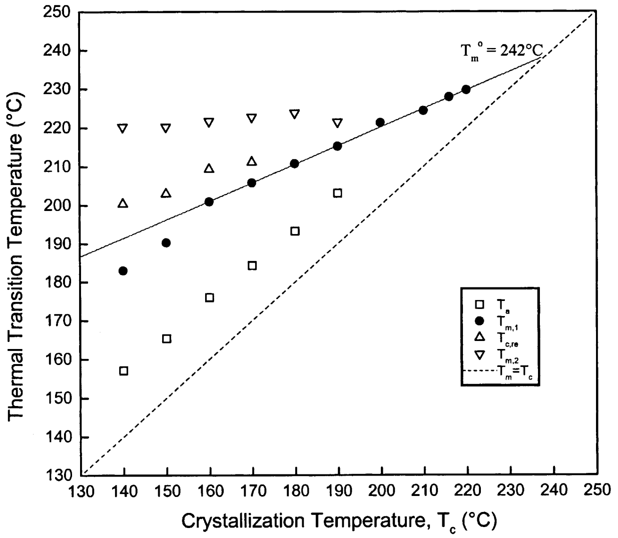

Fig. 2. Thermal transition temperatures vs crystallization temperature for iPS isothermally cold-crystallized at different temperatures for 6 h.

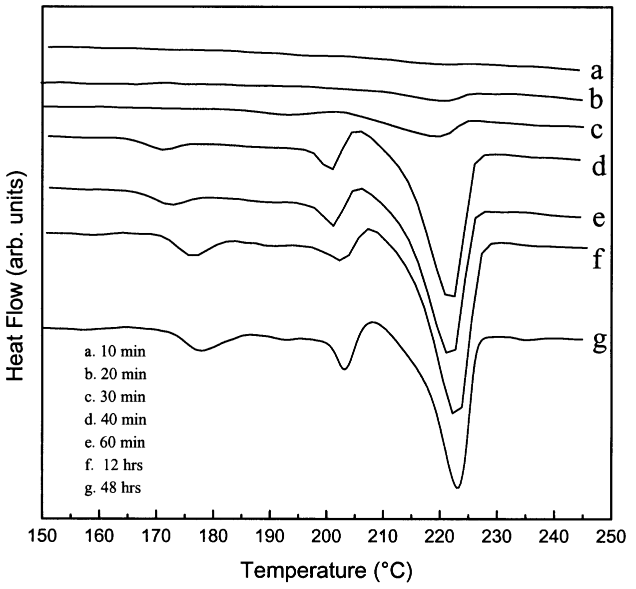

Fig. 3. DSC traces of iPS isothermally cold-crystallized at 160°C (A) and 190°C (B) for different periods of time. The heating rate is 10°C/min.

10 min, no appreciable crystallization has taken place; (ii) for the case of $t_c = 20$ min, only a very small and broad upper endotherm ($T_{m,2}$) is observed around 220°C; (iii) when the isothermal treatment at 160°C is further prolonged (e.g. $t_c = 30$ min), an even smaller lower melting peak ($T_{m,1}$) can be seen with careful inspection at about 195°C, in addition to the further developed upper melting peak ($T_{m,2}$); (iv) when $t_c = 40$ min, the $T_{m,1}$ becomes apparent and the $T_{m,2}$ is well developed, and additionally, the annealing peak (T_a) is now beginning to form with a small endotherm at about 170°C; (v) the triple endotherms slightly move to higher temperatures as crystallization proceeds. It indicates that as increasing the t_c, the perfection of pre-existing crystals related to the $T_{m,1}$ is significantly enhanced. The three endothermic peaks may develop simultaneously, but the strongest being identified first. Similar observations, which are strong evidences against the melting-recrystallization explanation, have been reported by Cheng et al. [28] and Bassett et al. [29] in poly(aryl ether ether ketone) (PEEK), by Cheng et al. [30] and Cebe et al. [31] in poly(phenylene sulfide) (PPS).

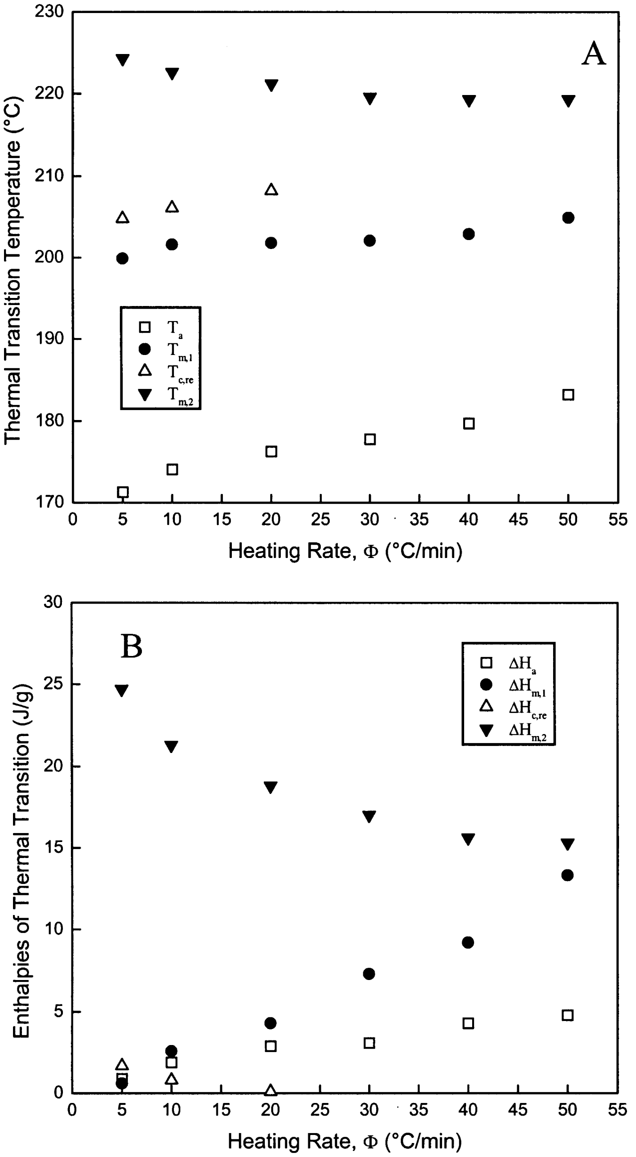

Fig. 4. (A) Thermal transition temperatures and (B) their corresponding enthalpies for iPS isothermally cold-crystallized at 160°C for 6 h when performed at different heating rates in DSC.

Influence of heating rate. It is well known that the heating rate dependence on the multiple melting behavior is often cited as evidence in favor of the 'melting-recrystallization' model [32–39]. The iPS samples, cold-crystallized at 160°C for 6 h, were heated at different rates (Φ), and the DSC results (the thermal transition temperatures and their apparent enthalpies) are presented in Fig. 4A and B, respectively. It can be seen that, with increasing the heating rate the T_a and $T_{m,1}$ shift toward higher temperatures (with an increase in the heats of fusion) probably due to the superheating effect caused by a low thermal conductivity of the samples (i.e. the instrumental factor) [38,39], while the $T_{m,2}$ slightly shifts to the opposite direction accompanied with a decrease in its magnitude. Therefore, it is evident that some recrystallization does take place during the heating process in the DSC. At higher heating rates, the sample passes through the recrystallization temperature region so rapidly that there is insufficient time for the melted materials to reorganize into new crystals. Hence, the reorganization process (i.e. partial melting and recrystallization) is largely inhibited, and can even hardly be observed in the DSC curves (for example, when the heating rate is higher than 20°C/min, as shown in Fig. 4B). The amount and perfection of the recrystallized materials decrease with increasing the heating rate. The consequence is that the parts of reorganized crystals, which contribute to the highest melting peak, decrease.

In summary, the following conclusions can be drawn based on the above thermal analysis experiments: (i) from the fact that the $T_{m,2}$ develops rather simultaneously to the $T_{m,1}$, it is reasonable that the double melting peaks are assigned to the coexistence of two lamellar populations with different perfection; (ii) the experiments of heating rate dependence on the double melting behavior, especially the presence of an exothermic crystallization peak just below the $T_{m,2}$, indicate that a recrystallization does occur during a heating process in the DSC; (iii) a surprising observation from DSC is that the high melting material ($T_{m,2}$) is formed preferably at higher undercooling. A reasonable explanation is as follows. When the samples were crystallized at lower T_c, the formed crystals are less perfect and therefore are relatively prone to be annealed during heating to a crystal population with a higher thermodynamic stability. However, at higher T_c the formed crystals are relatively more perfect and therefore are difficult to be further annealed. In addition, it should be noted that there is no drastic difference in the shapes of electron diffraction patterns from iPS crystallized at lower and higher T_c except for the intensity, therefore, a crystal perfectioning during heating is possible.

3.2. Morphological evidence from TEM observations and on the origins of the multiple melting peaks in iPS

The proposed mechanisms on the multiple melting behavior for iPS in the literature were more or less deduced from thermal analysis results, and only few morphological investigations were carried out. In this section, the morphological observations are made to investigate the origins of the multiple melting behavior in iPS using the TEM.

The DSC trace of iPS isothermally cold-crystallized at 160°C for 6 h is presented in Fig. 5. Isothermal crystallization (arrow a) and partial melting experiments (arrow b–f) are performed at several distinct temperatures as indicated on the heat flow curve. Fig. 6A and B show the TEM micrographs of an iPS thin film and an etched bulk sample cold-crystallized at 160°C for 6 h (arrow a in Fig. 5), respectively. It can be seen from Fig. 6A that, the well-developed spherulitic structures consisting of closely packed edge-on lamellae are the main characteristic morphology for this crystallization temperature. A number of lamellar stacks continuously grow outward from the central regions by splaying and branching. Close inspection of the micrograph indicates that the shapes, sizes and contrast of the individual lamellae vary over the spherulite, but no systematic clarification into different categories of lamellae can be seen. However, we do not rule out the possibility of existence of secondary crystals which are probably formed in-between the framework of primary crystals due to the confined growth space (see below). Additionally, in the open regions of the micrograph, flat-on crystals can be observed, particularly within the spherulitic 'eyes' on either side of the nuclei. Examination of replica surface of bulk-crystallized iPS samples also revealed the similar morphologies in continuous stacked-up lamellar form as shown in Fig. 6B.

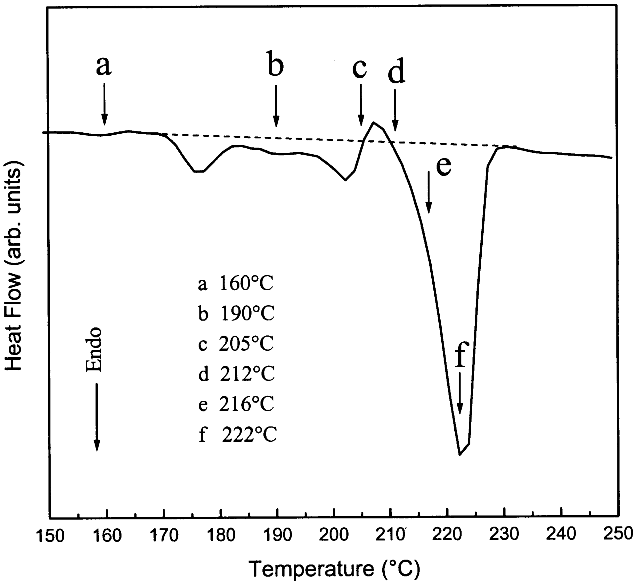

Fig. 5. DSC trace for iPS isothermally cold-crystallized at 160°C for 6 h. The temperatures where the partial melting experiments are performed are indicated by arrows.

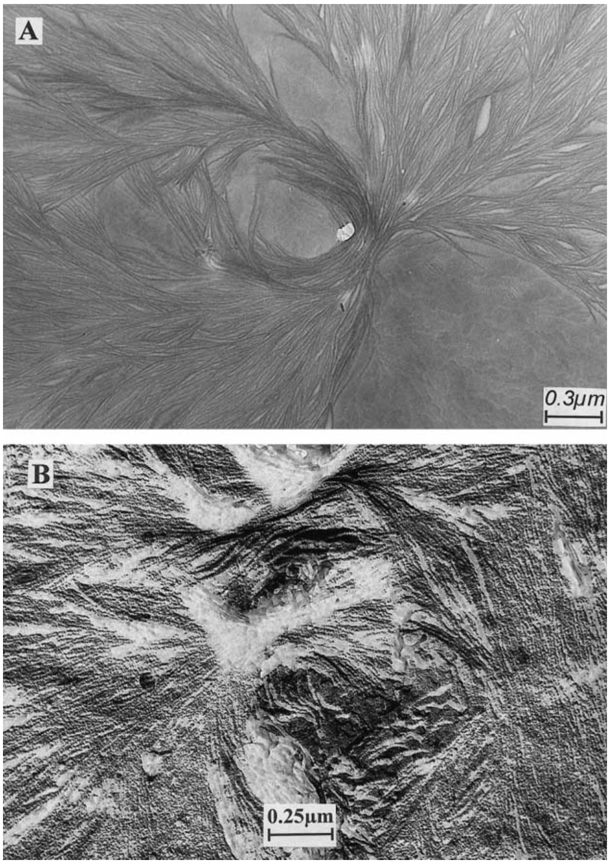

Fig. 6. (A) Bright field (BF) electron micrograph of an iPS thin film sample cold-crystallized isothermally at 160°C for 6 h; (B) lamellar morphology of a bulky iPS sample having the same thermal history as in (A). Replica of an etched surface.

The annealing peak in iPS. In order to investigate the origin of the annealing peak (T_a) for iPS from the point of morphological view, partial melting experiments are performed. Typically, the sample is thermally treated at a temperature just above the T_a for a short time (e.g. 1 min), then quenched to room temperature for TEM observations. If the annealing peak results from the melting of material formed by a secondary crystallization, as suggested in the literature, then such a change (i.e. the disappearance of these secondary crystals) is expected to be observed upon TEM observations. For this purpose, the thermal treatment temperature, 190°C, which is just above the annealing peak ($T_a = 175$°C) but below the intermediate endotherm ($T_{m,1} = 202$°C), is chosen for the crystallization temperature of 160°C. Fig. 7 shows the BF electron micrograph of the iPS sample as in Fig. 6, which was further thermally treated at 190°C for 1 min (arrow b in Fig. 5) and quenched to room temperature. No clear evidence can be seen in the lamellar morphology from that observed in Fig. 6. Also, there is almost no morphological changes even for longer annealing times at 190°C (for example, 1 h). Therefore, it is likely that the annealing peak is not associated with a melting of subsidiary crystal populations, as suggested by many other authors [6,8–16]. Combining this observation with the temperature-modulated DSC (TMDSC) results in which a relaxation transition (on the non-reversing heat flow) and a melting event (on the reversing heat flow) were observed at ca. 15°C above the T_c, we believe that a constrained interphase between the amorphous and crystalline phases plays a role which may not be ignored for the origin of this annealing- or crystallization-induced endothermic peak, as observed in the other polymeric systems, such as PPS, poly(ethylene terephthalate) (PET) and syndiotactic polypropylene (sPP) [3,40].

The double melting peaks in iPS. Similarly, the partial melting experiments were also performed in order to investigate the origins of the double melting peaks ($T_{m,1}$ and $T_{m,2}$) in iPS. The initially crystallized sample was thermally treated at the endothermic peak of the $T_{m,1}$ for 1 min, and quenched to room temperature for subsequent TEM observations. If the double endothermic behavior results from the melting of different crystal populations, the less perfect (less stable) crystals should disappear (be melted), and only the more stable (or perfect) ones are expected to remain upon the subsequent TEM observations.

Fig. 7. BF electron micrograph of an iPS sample as in Fig. 6, which was further treated at 190°C (above the annealing peak, 175°C) for 1 min and then quenched to room temperature.

The BF electron micrograph of such a partial melting experiment performed at 205°C (arrow c in Fig. 5) for 1 min (which is approaching to $T_{m,1}$), using an iPS sample which has the same thermal history as that in Fig. 6, is depicted in Fig. 8A. Note that this thermal treatment temperature (205°C) is located at the intersection of the baseline (the dash line in Fig. 5) with the heat flow trace. From Fig. 8A, most interestingly it can be seen that many intact lamellae seen in Fig. 6 become segmented and disconnected (partially melted). Therefore, it indicates that the thermal stability along a single lamella is not uniform. Within an individual lamella, some parts are more stable or perfect than the others. Hence, the double melting peaks in iPS are, to a much extent, associated with a distribution of lamellar perfection. In fact, over 20 years ago,

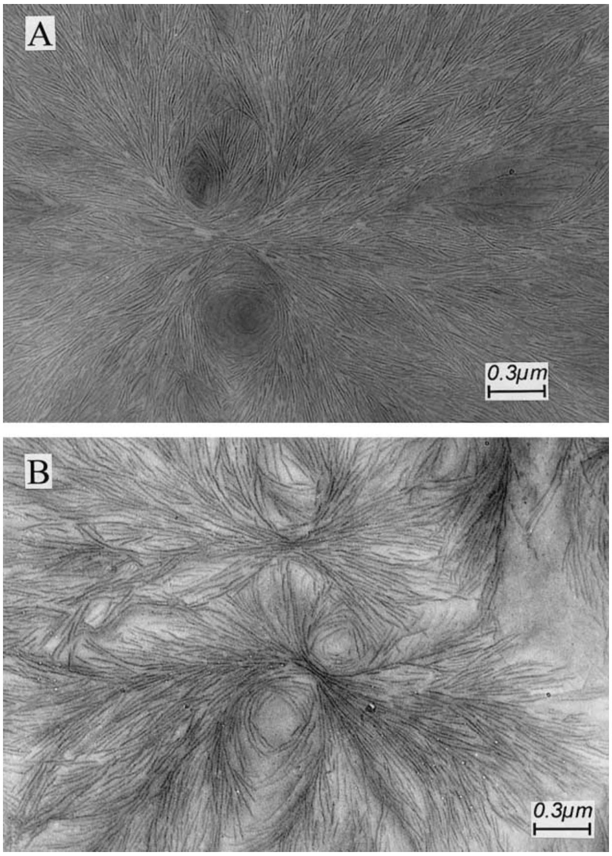

Fig. 8. (A) BF electron micrograph of an iPS sample having the same thermal history as in Fig. 6, and subsequently treated at 205°C for 1 min and then quenched to room temperature; (B) BF electron micrograph of an iPS sample isothermally cold-crystallized at 170°C for 6 h, which was subsequently treated at 211°C for 1 min and then quenched to room temperature.

Petermann et al. have reported upon TEM observations that the melting of a single lamella in iPS starts at various areas [41]. They suggested that the occurrence of melting in the various parts is due to structural variations along the surfaces of lamellae resulting in a hindrance of the lamellar thickening process. Nevertheless, in that report the investigations on the lamellar morphologies for iPS was not related to the multiple melting behavior.

Moreover, from Fig. 1 it can be seen that the amount of the crystals melted at $T_{m,1}$ (crystallized at 160°C) is much smaller than that at $T_{m,2}$. This is consistent with the TEM observations (Fig. 8A), in which only a small fraction of crystals are melted when the partial melting temperature approaches to $T_{m,1}$ (e.g. 205°C for 1 min). In order to further confirm it, an iPS film sample was isothermally crystallized at a higher temperature (170°C) for 6 h (see Fig. 1), since at this crystallization temperature the magnitude of the $T_{m,1}$ is comparable to that of the $T_{m,2}$. As a comparison, when this sample was treated at a temperature just between the double melting peaks (211°C for 1 min), it can be clearly observed that much more lamellar fractions are melted (Fig. 8B). Additionally, besides the fragmentation of single lamella, the distance between neighboring lamellae also increases. This probably indicates the existence of secondary crystals with lower thermodynamic stability [42,43]. Therefore, from our DSC measurements and the TEM observations we have to conclude that two distinct thermally stable fractions along a *single* lamella exist. The relative amount of them in a single lamella mainly depends on the tacticity and the thermal history (e.g. crystallization temperature). A preliminary result also supports our suggestions: when using iPS with low tacticity, the amount of less stable part increases (for the same crystallization temperature and time). Very interestingly, similar observations were also performed most recently in sPP lamellar single crystals by Cheng and his coworkers using TEM and atomic force microscopy (AFM) coupled with hot stage [44]. Accordingly, this is probably a common observation in semicrystalline vinyl polymers. The cause of such an observation is due to uneven distribution of tacticity along polymer chains, which leads to one domain with relatively lower tacticity and other locations with higher tacticity. In the beginning of crystallization, the molecules with higher tacticity will crystallize first, and those molecules with lower tacticity will be first rejected and accumulated in the front of crystal growth. Later on, as soon as these enriched molecules are too many and cannot diffuse away quickly enough, they have to crystallize to form less perfect crystals. These defective or less perfect crystals accumulated in certain locations possess relatively high free energies (that destabilize the crystals) and provide nuclei for the crystal melting event [44]. Therefore, it is segregation during crystallization process that would be responsible for the melting of lamellar domains with different thermodynamic stability.

It should also be noted that Marand and his coworkers recently reported the crystallization, melting and morphology of random ethylene/1-octene copolymers via a combination of DSC and AFM [45]. They tentatively associate two different crystallization mechanisms (prevalent in separate temperature ranges) with the coexistence of two distinct crystalline superstructures (i.e. lamellae and fringed-micellar or chain cluster structures). They further suggest that the multiple melting behavior of these copolymers is associated with the existence of separate morphological entities and is not explained by a mechanism of melting–recrystallization–remelting. In fact, the molecular chain structures of isotactic polystyrene (for instance, here with tacticity of 97%) can also be considered as a random copolymer of 'pure' iPS (with tacticity of 100%) and 'defective' atactic polystyrene (aPS). Then, the present situation in iPS is very similar to that in the random ethylene/1-octene copolymers.

When further increasing the temperature of the partial melting experiment (for example, 212°C for 1 min, indicated by the arrow d in Fig. 5), it is seen that the degree of the disconnection becomes more apparent and only a few lamellar fractions are left (Fig. 9A). However, the lamellar fractions grow laterally with increasing annealing time (212°C for 30 min) as shown in Fig. 9B. The 'destroyed' disconnected lamellae are 'repaired' due to the recrystallization/reorganization process, finally become a nearly

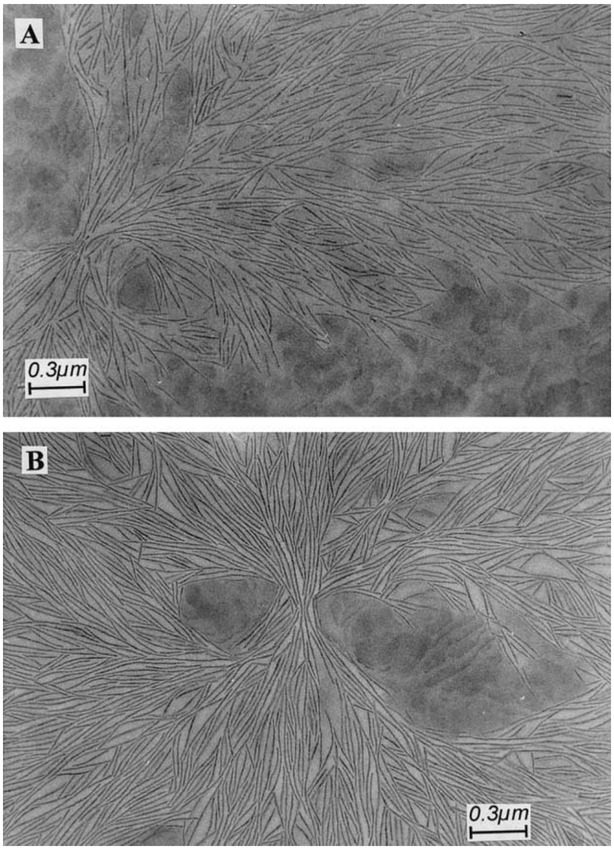

Fig. 9. BF electron micrograph of an iPS sample having the same thermal history as in Fig. 6, which was further treated at 212°C for 1 min (A) and for 30 min (B) and then quenched to room temperature.

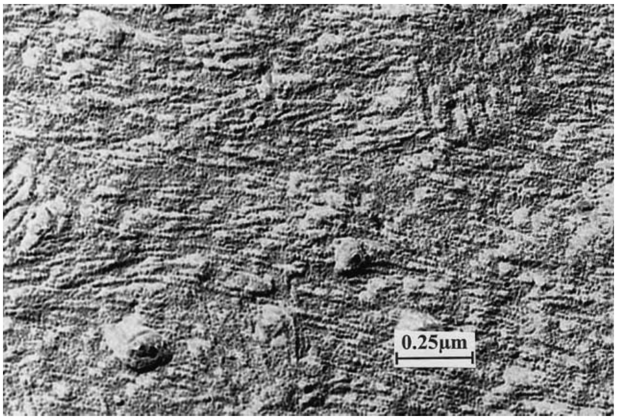

Fig. 10. Surface replica of an etched iPS bulky sample having the same thermal history as in Fig. 6, which was further treated at 216°C for 1 min and then quenched to room temperature.

'connected' lamellar structure again. Such a repairing phenomena of the molten domains (via a recrystallization process while annealing at higher temperature for an extended period of time) was also observed in sPP by Cheng and his coworkers [44]. These fragmentation processes can also be observed from the surface replica electron micrograph (Fig. 10) for the etched bulk iPS sample having the same thermal history as in Fig. 6 but further treated at 216°C for 1 min (arrow e in Fig. 5). When the partial melting experiment is carried out at an even higher temperature, for example, 222°C (arrow f in Fig. 5, the peak temperature of the $T_{m,2}$) for 1 min, most of the lamellae are melted and only a small fraction of them remains (Fig. 11).

3.3. Discussion on several crystallization and melting models

According to the melting-recrystallization model [6,8–16,32–39], all lamellae melt at $T_{m,1}$ and give rise to the lower-temperature endotherm. The melted material undergoes a continuous recrystallization process into thicker lamellae which subsequently melt at higher temperature, $T_{m,2}$. This model is based mainly on the observations, that the higher melting peak is also heating rate dependent, but shifts to lower temperatures and decreases in magnitude at higher heating rates (Fig. 4). However, it neglects the observations on the sequence of the crystallization (Fig. 3), which was also previously pointed out by several authors in other semicrystalline polymers [28–31,46]. While we question the melting–recrystallization model for the only explanation in the double melting behavior of the iPS, we do not dispute and rule out this phenomena of melting-recrystallization in general. The appearance of the exothermic crystallization peak $T_{c,re}$ just below the high melting endotherm $T_{m,2}$ is a direct indication that a melting–recrystallization does take place during the heating process in the DSC. It is even confirmed by our morphological observations (Fig. 9B).

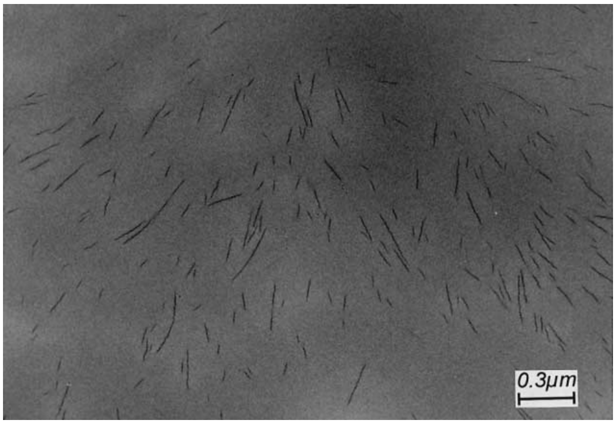

Fig. 11. BF electron micrograph of an iPS sample having the same thermal history as in Fig. 6, which was further treated at 222°C for 1 min and then quenched to room temperature.

According to the dual lamellar stack model, which was originally proposed by Cebe et al. [31,47,48] and by Bassett et al. [29], and was subsequently extended by other authors [49–53], there exists a bimodal distribution of lamellar *thicknesses* within the semicrystalline polymers, with the melting of thinner and thicker lamellae associated with the low and high endotherms, respectively. This is definitely true when crystallizing at two distinct temperatures. For the case of isothermal crystallization, two different models were proposed [54]: the dual lamellar stack model (with the thick and thin lamellae in separate stacks) [50,55] and the lamellar insertion model (with the thin lamellae inserted between thicker lamellae in the same stack) [51–55]. The lamellar stack model was based on the morphological observations of two distinctly different types of lamellar populations revealed by TEM [49]. The primary argument in favor of the lamellar insertion model comes from observations using time-resolved small angle X-ray scattering (SAXS) techniques [51–53]. However recently, using real-time SAXS, Verma et al. have reported the morphological changes during long time melt crystallization and subsequent melting in PEEK [54,55], in which the SAXS data are incompatible with the lamellar insertion model and therefore this model was discarded by them.

According to the dual lamellar stack model, the subsidiary (or secondary) lamellae are often regarded as the crystallites that were formed between the dominant lamellae during the secondary crystallization process. However, from our studies on iPS an impingement was not observed for the presence of the less perfect lamellae. From our morphological observations in iPS (for example, Fig. 8), a crystal model with the alternating (perfect and less perfect) domains along an individual lamella is concluded. A similar hypothesis has recently emerged from the investigations of sPP lamellar single crystals based on TEM and AFM observations [44]. But care should be taken to generalize our observations from the iPS to other polymers. Due to different segmental mobility, chain conformational defects and diffusive processes, different crystallization and melting events may occur in different polymers.

4. Conclusions

The triple melting behavior and lamellar morphologies of isothermally cold-crystallized iPS have been investigated by combining DSC and TEM techniques. The thermal analysis results indicate that the appearance of the multiple melting peaks (consequently the crystalline morphologies) in iPS is strongly dependent on the thermal history. By combining the DSC measurements with TEM morphological observations, it is concluded that: (1) the annealing peak is not related to the melting of the subsidiary crystals formed by secondary crystallization; (2) two lamellar components with different thermodynamic stability within a single lamella exist, and they are associated with the double melting behavior in isothermally crystallized iPS. The lower melting peak is mainly due to the melting of less perfect lamellar domain (which serve as melting nuclei), while the higher melting peak is mainly due to the melting of more perfect part within the same lamella, and to some less extent, to the melting of a recrystallized population during heating process. The occurrence of repairing of molten lamellar domain via recrystallization is confirmed by morphological evidence from the TEM observations.

Acknowledgements

We are grateful to the Alexander von Humboldt-Stiftung for granting a stipend to T. Liu and to the Fonds der Chemischen Industrie for their financial support. Also, we thank Dr Shouke Yan for his excellent assistance in the TEM experiments.

References

[1] Hobbs SY, Pratt CF. Polymer 1975;16:462.
[2] Verma RK, Hsiao BS. Trends Polym Sci 1996;4:312.
[3] Bonnet M, Rogausch KD, Petermann J. Colloid Polym Sci 1999;277:513.
[4] Liu T, Yan S, Bonnet M, Lieberwirth I, Rogausch KD, Petermann J. J Mater Sci 2000;35:5047.
[5] Wunderlich B. Macromolecular physics, vol. 3. New York: Academic Press, 1980. p. 1.
[6] Boon J, Challa G, Van Krevelen DW. J Polym Sci 1968;A2(6):1791.
[7] Pelzbauer Z, Manley RStJ. J Polym Sci 1970;A2(8):649.
[8] Lemstra PJ, Kooistra T, Challa G. J Polym Sci 1972;A2(10):823.
[9] Lemstra PJ, Schouten AJ, Challa G. J Polym Sci Polym Phys 1974;12:1565.
[10] Overbergh N, Berghmans H, Reynaers H. J Polym Sci Polym Phys 1976;14:1177.
[11] Overbergh N, Girolamo M, Keller A. J Polym Sci Polym Phys 1977;15:1475.
[12] Berghmans H, Overbergh N. J Polym Sci Polym Phys 1977;15:1757.
[13] Overbergh N, Berghmans H, Smets G. J Polym Sci 1972;C38:237.
[14] Plans J, MacKnight WJ, Karasz FE. Macromolecules 1984;17:810.
[15] Silvestre C, Cimmino S, Karasz FE, MacKnight WJ. J Polym Sci Polym Phys 1987;25:2531.
[16] Petrillo E, Russo R, D'Aniello C, Vittoria V. J Macromol Sci Phys 1998;B37(1):15.
[17] Bell JP, Dumbleton JH. J Polym Sci 1969;A2(7):1033.
[18] Bell JP, Slade PE, Dumbleton JH. J Polym Sci 1968;A2(6):1773.
[19] Lety A, Noel C. J Chim Phys Physicochim Biol 1974;69:875.
[20] Chung JS, Cebe P. Polymer 1992;33:2325.
[21] Ko TY, Woo EM. Polymer 1996;37:1167.
[22] Petermann J, Gohil RM. J Macromol Sci Phys 1979;B16(2):177.
[23] Bu HS, Cao J, Zhang Z, Zhang Z, Festag R, Joy DC, Kwon YK, Wunderlich B. J Polym Sci Polym Phys 1998;36:105.
[24] Moll C. Diploma Thesis, University of Dortmund, 1999.
[25] Olley RH, Bassett DC. Polymer 1982;23:1707.
[26] Petermann J, Gleiter H. Phil Mag 1975;31:929.
[27] Hoffman JD, Weeks JJ. J Res Natl Bur Stand 1962;A66:13.
[28] Cheng SZD, Cao MY, Wunderlich B. Macromolecules 1986;19:1868.
[29] Bassett DC, Olley RH, Raheil IAM. Polymer 1988;29:1745.
[30] Cheng SZD, Wu ZQ, Wunderlich B. Macromolecules 1987;20:2802.
[31] Chung JS, Cebe P. Polymer 1992;33:2312.
[32] Holdsworth PJ, Turner-Jones A. Polymer 1971;12:195.
[33] Blundell DJ, Osborn BN. Polymer 1983;24:953.
[34] Blundell DJ. Polymer 1987;28:2248.
[35] Groeninkx G, Reyaners H. J Polym Sci Polym Phys 1980;18:1325.
[36] Jonas A, Legras R. Macromolecules 1993;26:813.
[37] Jonas A, Russell TP, Yoon D. Macromolecules 1995;28:8491.
[38] Lee Y, Porter RS. Macromolecules 1987;20:1336.
[39] Lee Y, Porter RS, Lin JS. Macromolecules 1989;22:1756.
[40] Stranz M. Diploma Thesis, University of Dortmund, 1999.
[41] Petermann J, Gohil RMJ. Macromol Sci Phys 1979;B16(2):177.
[42] Keller A, Cheng SZD. Polymer 1998;39:4461.
[43] Cheng SZD, Keller A. Annu Rev Mater Sci 1998;28:533.
[44] Zhou W, Cheng SZD, Putthanarat S, Eby RK, Reneker DH, Lotz B, Magonov S, Hsieh ET, Geerts RG, Palackal SJ, Hawley GR, Welch MB. Macromolecules 2000;33:6861.
[45] Alizadeh A, Richardson L, Xu J, McCartney S, Marand H, Cheung YW, Chum S. Macromolecules 1999;32:6221.
[46] Velikov V, Vivirto J, Marand H. ACS Polym Prepr 1993;34(2):835.
[47] Cebe P, Hong SD. Polymer 1986;27:1183.
[48] Cebe P, Chung S. Polym Compos 1990;11:265.
[49] Lattimer MP, Hobbs JK, Hill MJ, Barham PJ. Polymer 1992;33:3971.
[50] Wang J, Alvarz M, Zhang W, Wu Z, Li Y, Chu B. Macromolecules 1992;25:6943.
[51] Krüger KN, Zachmann HG. Macromolecules 1993;26:5205.
[52] Hsiao BS, Gardner KH, Wu DQ, Chu B. Polymer 1993;34:3986.
[53] Hsiao BS, Gardner KH, Wu DQ, Chu B. Polymer 1993;34:3996.
[54] Verma RK, Hsiao BS. Trends Polym Sci 1996;4:312.
[55] Verma RK, Marand H, Hsiao BS. Macromolecules 1996;29:7767.