ORIGINAL CONTRIBUTION

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# A differential scanning calorimetry study on poly(ethylene terephthalate) isothermally crystallized at stepwise temperatures: multiple melting behavior re-investigated

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**Abstract** The multiple melting behavior of poly(ethylene terephthalate) (PET) was investigated with differential scanning calorimetry (DSC) by examining PET samples having been subjected to special schemes of crystallization and annealing treatment at multiple descending temperatures. Upon such step-wise annealing in decreasing temperatures, the existence of doublet melting peaks in addition to a series of multiple minor peaks in the PET has been demonstrated using carefully designed thermal schemes. Using the Hoffman theory, multiple lamellae populations, might be suggested to be simultaneously present in the PET subjected to such thermal treatments. However, direct experimental evidence has yet to be provided. The low-temperature minor crystals simply melt during normal scanning without having time enough to re-organize into higher-melt crystals. Nevertheless, the effect of scanning on non-isothermal crystallization does exist but is primarily confined to the temperature range much below the main melting region where the crystallization of polymer chains can progress at a reasonable rate. At higher temperatures near the main melting region, annealing for extended times is required in order to result in relative changes of the melting endotherms of the upper and lower peaks in the main melting doublet. In all we have shown that interpretations of the multiple melting phenomenon in semicrystalline polymers can be better refined.

**Key words** Multiple melting – DSC – crystallization – poly(ethylene terephthalate) – lamellar thickness

# Introduction

Widely used semicrystalline engineering polymers, such as aliphatic polyamides (nylons) [1–2] and poly(ethylene terephthalate) (PET) [3–8], have been reported to exhibit closely-spaced double-melting endotherms in the major melting region under certain crystallization/annealing conditions. Poly(butylene terephthalate) (PBT) was also reported [9–12] to exhibit similar behavior. Other polymers such as isotactic polystyrene [13], poly(1,4-isoprene) [14], isotactic polypropylene [15], and poly(vinylidene fluoride) (PVF$_2$) [16] are also known to show such behavior. The phenomenon of "double melting" in the major melting region should more appropriately be called "multiple melting" since semicrystalline polymers can actually develop a series of small endothermic peaks below the main melting temperature, when crystallized at multiple isothermal steps between $T_g$ and $T_m$ from high to low temperatures.

Two main mechanisms, dual morphology and melting–recrytallization–remelting, have been proposed for the

interpretation of double melting peaks. The dual morphology mechanism [10–12] claims that two melting peaks in polymers might be explained by two different spherulite structures. On the other hand, the recrystallization–remelt mechanism proposes that crystallization at lower temperatures can produce crystals that may have only a low degree of perfection and can melt and re-crystallize to yield crystals of better perfection or greater thickness upon a heating scan to a higher temperature during, for example, DSC thermal scanning [3–8]. Several investigators [17–20] claimed that the "dual melting peaks" were merely a "doublet appearance" of thermal behavior as a result of superposition of endothermic melting and exothermic recrystallization during DSC scanning. In other words, the crystals originally belong to a single population, but can undergo re-organization into a different population during normal DSC scanning (or equivalently, during regular heating processes). Lately, similar controversial arguments have also been debated concerning poly(phenylene sulfide) (PPS) [21, 22] and poly(ether ether ketone) (PEEK) [23–29]. By using PEEK and PPS as model systems in probing the multiple melting phenomenon and its relationships with observed crystallization kinetics, Woo et al., [30–32] also provided evidence for the postulation of simultaneously existing lamellae of multiple thicknesses as a result of crystallization and annealing at multiple decending temperature steps.

This study was motivated by a belief that interpretation from another view angle could be provided by realizing that each of the two mechanisms might have only described part of the factual observations. Only by a thorough thermal analysis scheme, a more complete insight can be achieved in explaining the phenomenon of the long controversial double (actually multiple) melting in semicrystalline polymers. In this study, we have tried to further clarify the related issues on multiple melting behavior by using the widely studied poly(ethylene terephthalate) (PET) as a convenient model system for semicrystalline polymers.

## Experimental section

The semicrystalline polymer samples used was poly(ethylene terephthalate) (PET, Shin-Kong Corp., Taiwan) in high-purity, additive-free forms. A power-compensated type of differential scanning calorimeter (Perkin–Elmer DSC 7, equipped with a cooling accessory) was used for various thermal treatments (quenching, annealing, or crystallization) of the samples and to observe the melting endothermic peaks. The temperature and heat of melting were calibrated with indium and zinc standards. Relatively small sample sizes (3–5 mg) were used to minimize the

effect of low thermal conductivities of the polymers. After designated thermal treatments, the polymer samples were scanned right from the crystallization temperature to approximately 50 °C above the respective melting temperature of each polymer. The newly improved capability of the DSC to heat and cool the polymer samples at extremely fast rates has helped to enhance the accuracy of the data by reaching and equilibrating at the targeted isothermal temperature quickly. Since all thermal treatments were conducted in the DSC, the temperature accuracy for annealing or crystallization of the polymer samples was excellent.

## Results and discussion

Minor crystals with sub-$T_m$ peak temperature

When crystallized at certain temperatures between the $T_g$ and $T_m$, PET has been known to exhibit two main doublet peaks (located at 250–260 °C) in addition to a minor endothermic peak further below the main melting doublets [18]. Under annealing or isothermal crystallization at multiple descending steps, it was further found that PET exhibited sub-$T_m$ multiple minor melting peaks in the low temperature range (between $T_g$ and $T_m$) in addition to the main doublet melting peaks. Figure 1 shows the DSC scan results demonstrating the melting behavior of the PET sample that had been crystallized at two descending isothermal steps: 210, and 190 °C for 60 min at each isothermal step. Two minor peaks are seen to be located at 239° and 203 °C; additionally, in the main melting region, double peaks at 246 and 258 °C are observed.

Fig. 1 Multiple melting endotherm peaks for PET step-crystallized at 210° and 190 °C for 60 min each
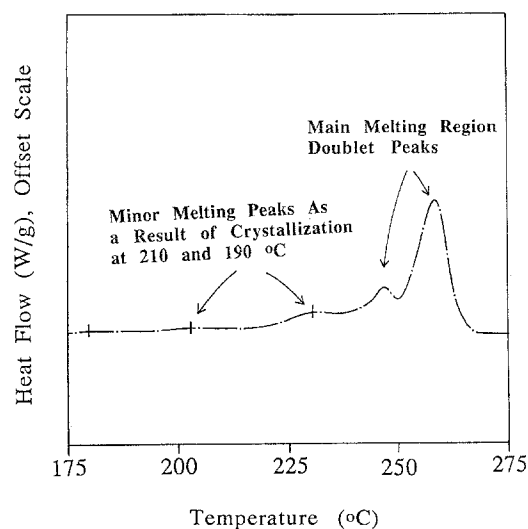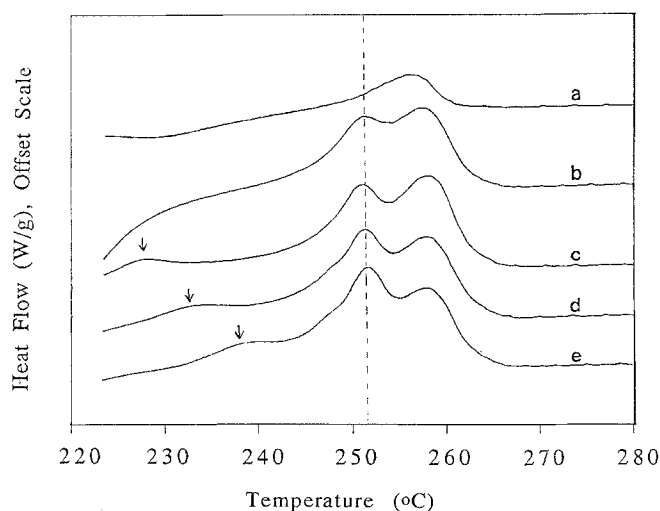
**Fig. 2** DSC melting thermograms of PET after crystallization at 220 °C for a) 0.5 min, b) 2 min, c) 5 min, d) 10 min, e) 60 min

To probe plausible explanations for the origin of these minor melting peaks, it was necessary to investigate how the minor peak temperatures changed as the annealing time was increased. Instead of trying to analyze the melting behavior of PET subjected to multiple isothermal crystallization temperatures, we first conducted experiments by subjecting the PET sample to a single isothermal temperature at a time for various duration of periods. Figure 2 shows the DSC thermograms (scanned at 10 °C min) of the PET samples that had been subjected to crystallization for various times at 220 °C. For the PET samples subjected to shorter crystallization times ( <1 min), only one peak (upper Peak) at 256 °C was observed in the major melting region (Curve-a). The first peak of the doublet (lower Peak) at 250 °C was apparently not observed yet. More notably, the minor melting peaks (between $T_c$ and $T_m$) were still absent in the PET sample after treatment of these short crystallization times. The lower peak (250°–251 °C) of the melting doublet started to appear in the PET samples subjected to crystallization times over 2 min, while the minor peak was still absent (Curve-b). The minor peak started to appear in the PET samples subjected to crystallization times over 5 min (Curve-c). Furthermore, the peak area and temperature of this "minor peak" were found to increase as a function of time.

The behavior of the main melting doublets however were quite different from the minor melting peaks. As the crystallization time was increased, the relative intensity of the main melting doublets shifted from the upper to lower peak. The total quantity of polymer chains available for forming crystals (lower and upper peaks) is a near constant

at a given condition. Therefore, when more polymer chains crystallize in forming thinner lamellae, there are less left to form thicker lamellae as the crystallization time is continually increased from 1 to 60 min. The temperatures of the main double melting peaks, however, stayed almost constant as the time was increased at the isothermal crystallization temperature of 220 °C. Similar melting behavior was also observed in the PET samples crystallized for various periods of time at two other temperatures of 210° and 230 °C, whose results are mostly similar to the 220 °C-crystallized sample and thus not shown here for brevity.

A closer inspection revealed that the 210 °C-crystallized PET exhibited a smaller lower peak compared to the PET samples crystallized at 220 °C for the same time. The lower peak intensity seemed to increase rapidly, and the magnitude of the upper peak decreased proportionally for the PET samples crystallized at higher temperatures. At a higher temperature of 230 °C, the progress of crystallization became slower, but the doublet peaks gradually merged with each other. The results suggested that an increase in the crystallization temperature resulted in more uniform thickness distribution of the crystals, as evidenced by observation of a sharper and higher melting single peak when the PET sample was crystallized at a higher temperature for longer time. There are differences in the melting endotherms observed among these PET samples crystallized at different temperatures. The 230 °C-crystallized PET exhibited only a single peak in the main melting region (250°–260 °C), while the 210° or 220 °C-crystallized PET displayed doublet peaks.

The above results suggested that there were at least three types of crystals growing at different initiation times in PET when crystallized at 220 °C for more than 5 min. These three included two different types of crystals which are responsible for the doublet peaks in the main melting region, and the crystal exhibiting the minor melting endotherm peaks belonged to the third type. The order of their appearance varied with the crystal sizes. Note that the upper peak always developed first, and the lower peak followed, with the minor crystal being the last. This fact indicates that the higher-melting crystals develop more quickly, while the crystal of the minor peak, being the lowest-melting crystals, generally takes a longer time to develop than the crystals of either lower peak or upper peak. The crystallization time dependence of the order of appearance of the peaks (upper and lower peaks, and sub-$T_m$ minor peaks) suggested that more than one type of crystals was present at various stages of time in the PET polymer crystallized at 220 °C. These results seem to demonstrate that crystalline lamellae of different thickness distributions can independently exist in PET when multiply annealed at descending temperature steps.
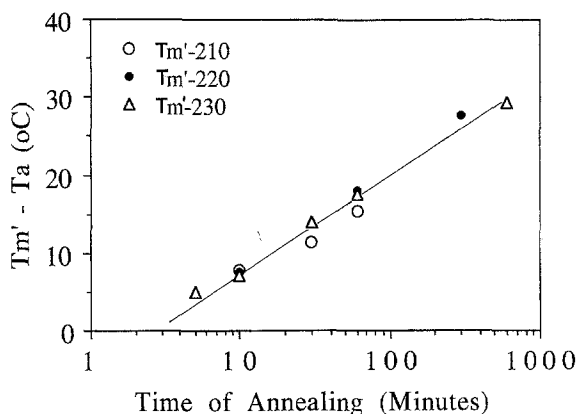
Fig. 3 Linear increase of temperature of the minor melting peaks with respect to isothermal crystallization temperature as a function of time

It is worthwhile to point out two additional experimental results to support the above statement. First of all, our DSC results of the PET samples subjected to various periods of isothermal crystallization showed that it was the upper Peak (higher-melt crystals) that appeared first, and this was found to be true for the samples crystallized at all three isothermal temperatures: 210°, 220°, and 230 °C. This would contrast the recrystallization/remelting mechanism, which explicitly expresses that in the beginning there exist only lower-melt crystals, which can melt, recrystallize, and finally remelt at a higher temperature during temperature scanning. It is re-melting of the recrystallized crystals that is responsible for the observed higher-melt peak. Second of all, the results also showed that once the crystals melt, it would take anywhere from 1 to 5 min to develop a higher-melt peak of significant magnitude. For example, at temperatures higher than 230 °C, it would take times longer than 5 min to develop a detectable higher-melt peak. Therefore, in the short temperature span (242–248 °C) within which the lower-melt crystals supposedly would melt during scanning, there would not be time enough (only 0.6 min) for the melted polymer chains to recrystallize into higher-melt crystals. The reason is that the temperature is too high and the time too short for the polymer chains to reorganize into crystals of a higher melting peak.

As stated, the temperatures of the sub-$T_m$ minor peaks increased as the isothermal crystallization time was increased. This was observed in all the PET samples crystallized for various periods of time at 210°, 220°, and 230 °C, respectively. Figure 3 shows the temperature increase of the minor peak from the annealing temperature $(T'_m - T_a)$ plotted as a logarithmic function of crystallization time, $\log(t)$. The temperature of the melting of the minor crystals are seen to increase linearly with $\log(t)$ for all the three isothermal crystallization temperatures investigated. After

an extended long time of crystallization, say 10 h, the minor melting peak eventually moved up high enough to merge within the main melting peak. At this time, the originally thin lamellae of the minor crystal are thickened and no longer distinguishable from the normal lamellae of the major crystal.

The DSC results so far have shown that the melting peak temperatures of the minor crystal entities in PET increase with log(time). Can this increase be related to any physical phenomenon in the polymer crystal morphology? Bassett and Patel [33] have done a transmission electron microscopy study on isotactic poly(4-methylpentene-1) and found that the measured average lamellar thickness of the polymer increases logarithmically with the time of annealing at the temperature of 241 °C. The Hoffman's equation [34] provides a correlation between the observed increase of the peak melting temperatures, from which the lamellar thickening can be easily understood. The theory states that $T'_m = T^0_m(1 - 2\sigma_e/\Delta H_f \cdot L)$, where $T^0_m$ is the melting point of an infinite perfect crystal, $\sigma_e$ is the surface energy of the crystals, $\Delta H_f$ the heat of fusion, and $L$ the lamellar crystal thickness. From the above equation, if a PET sample displays multiple melting peaks, a multiple lamellae population might likely exist in it. Additionally, if held at an annealing temperature, the melting temperature of a low-melt crystal $(T'_m)$ would increase with an increase in lamellar thickness $L$. Consequently, if the thickness of a low-melt crystal lamella increases with log(time), so would the peak melting temperature of this corresponding crystal since the melting temperature of the lamellae is long known to be proportional to the thickness [33, 34].

Effect of scanning rate on non-isothermal crystallization

How do we then explain the dependence of the number of peaks on the scanning rate, or more specifically, peak splitting as the DSC scanning rate is reduced? To answer this question, we conducted further experiments on PET samples subjected to various pre-scan thermal treatments to be described as following. One PET sample was quenched from the melt state at 280° to 210 °C. DSC was performed on the sample immediately after an isothermal hold for 0.5 min at 210 °C. The result is shown in Fig. 4, Thermogram (a). Quite pronounced melting doublet peaks are observed in the PET sample, with the peak temperatures at 247.7° and 258 °C. As will be pointed out, this pronounced melting endotherm should not be mistaken as a result of only isothermal crystallization at 210 °C for 0.5 min. Other influences have to be considered as well. Further non-isothermal crystallization (not re-crystallization/re-melting) took place during heating scan. Notice in Thermogram (a) that an apparent downward exotherm

Fig. 4 Comparison of DSC thermograms of two PET samples a) PET crystallized at 210 °C for 0.5 min then scanned 10 °C/min; b) PET crystallized at 210 °C for 0.5 min, scanned 500 °C/min up to 235 °C, then scanned 10 °C/min up to 280 °C
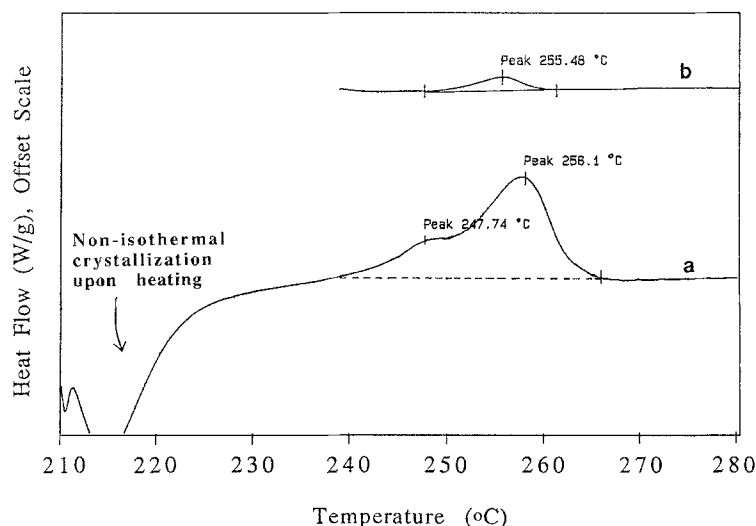


was observed immediately after the scan was started at 210 °C, indicating that further crystallization took place during the early stage of scanning at 10 °C/min. For close comparison, another PET sample was subjected to a different pre-scan thermal treatment prior to being scanned at the same 10 °C/min rate. The PET sample was similarly quenched from 280° to 210 °C and held for 0.5 min. However, instead of scanning up from 210 °C at 10 °C/min, the sample was first scanned at the highest rate of 500 °C/min from 210° to 235 °C to allow no time for any possible non-isothermal crystallization between 210° and 235 °C. The heating scan was programmed in such a way that once the temperature reached 235 °C at this high scanning rate, the DSC scanning rate was reverted back to 10 °C/min and scanning was continued from 235 to 280 °C. Thermogram (b) of the same figure shows that the sample that had been treated with 500 °C/min heating from 210 to 235 °C exhibited a single peak with a much smaller melting endotherm and a peak temperature of 255.5 °C. Note also that these two PET samples were both scanned at the same 10 °C/min rate between 235 and 280 °C to generate the melting endotherms, but one, Thermogram (a), exhibited doublet melting peaks and the other, Thermogram (b), exhibited a smaller single peak. We believe that the doublet peaks indeed represent crystal lamellae of two thickness distributions. Furthermore, the distributions can be narrowed, uniformed, or changed by the thermal treatments performed on the polymer prior to melting.

In order to evaluate the effect of different heating rates on inducing crystallization of the PET samples during heating prior to reaching the melting region, a series of PET samples subjected to various pre-scan thermal treatments were prepared. PET samples were first quenched (fast-cooled) from the melt state at 280 °C quickly at − 320 °C/min to 220 °C. Thus, no crystals formed at time
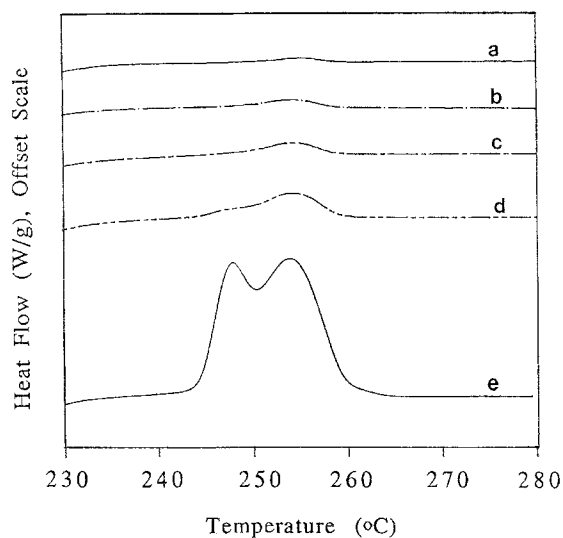


Fig. 5 Effects of scanning rate on further crystallization leading to different development of lower vs. upper crystals

equal to 0. Then, immediately the samples were heated up from 210° to 242 °C by using various heating rates of 500°, 20°, 10°, 5°, and 1 °C/min, respectively. After the treatments, the samples were quenched back to 210 °C and immediately scanned uniformly at 10 °C/min to 280 °C for all the samples. Since the heating scan to observe the melting endotherm of the PET samples are all 10 °C/min, any observed differences in the melting behavior of these PET samples are not caused by the DSC heating rate, but rather caused by the difference in the pre-scan thermal treatments between 210° and 242 °C.

Figure 5 shows the DSC thermograms of these PET samples. Thermograms (a)–(e) represent the results of DSC heating scans of the PET samples subjected to pre-scan

heating at 500°, 20°, 10°, 5°, and 1 °C/min, respectively, between 210° and 242 °C prior to being scanned all uniformly at 10 °C/min to generate the melting endotherm. As the heating rates used in the pre-scan treatments between 220° and 240 °C were decreased from 500° to 1 °C/min, the melting endotherms of the PET samples increased. The sample subjected to pre-scan treatment of 500 °C/min heating between 220° and 242 °C revealed no melting endotherm at all upon DSC scanning between 220° and 280 °C at 10 °C/min scanning rate. The most pronounced increase in the melting endotherm was observed in the sample subjected to pre-scan thermal treatment at the lowest heating rate 1 °C/min. This fact suggests that pre-scan heating rates changed the time duration within which the polymer could further crystallize. The induction of crystallization, however, mostly occurred at the beginning of the scanning where the temperature was lower. The slower the heating rates, the longer the time duration spent in the low-temperature range, and the more the polymer can further crystallize during the heating scan. When the PET was scanned to temperatures close to the main melting region, the recrystallization rate would become so slow that no crystallization could be observed during the scanning time span in which a normal scanning rate was used.

To investigate how annealing of PET at temperatures close to the main melting region could affect the melting peak temperatures, a series of PET samples was prepared by subjecting the samples to thermal treatments described as following. PET samples were first quenched from the melt state at 280° down to 220 °C, and isothermal crystallization was allowed to progress for 10 min. According to our previously discussed results, crystallization at 220 °C for 10 min was close to completion and the sample so crystallized upon DSC scanning would reveal doublet melting peaks (see Fig. 2, Thermogram (d)). The 220 °C-crystallized samples were then heated to 257 °C and held (annealed) at this temperature for various lengths of time ranging from 1 to 60 min before being quenched back to 235 °C. Note that the annealing temperature of 257 °C was used since this was the peak temperature of the upper peak of the main melting doublet of a PET sample having been crystallized at 220 °C. A DSC scan at 10 °C/min was then performed immediately on all samples from 235° to 280 °C after the prescribed thermal treatments.

Figure 6 shows the DSC thermograms of the 220 °C-crystallized PET samples having been subjected to post annealing at 257 °C for 1, 5, 10, and 60 min, respectively, as Curves (a) to (d). There are several interesting features in the figures. The melting endotherm of the 220 °C-crystallized/257 °C-annealed PET shows a doublet-peak feature. The peak temperature of the lower peak remained unchanged while the temperature of the upper peak in the
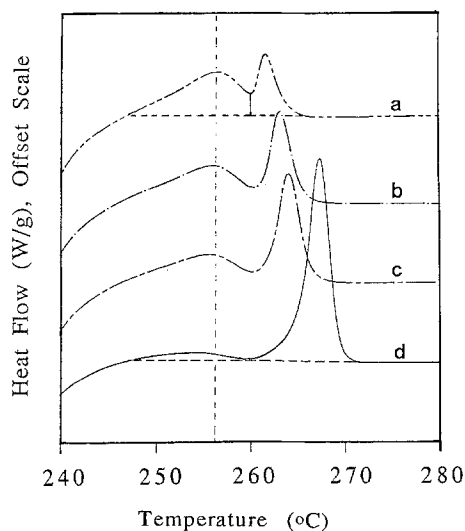


Fig. 6 DSC thermograms showing the relative magnitudes of lower and upper peaks and location of peak temperatures of PET samples annealed for various times at 257 °C. The samples had been subjected to post annealing at 257 °C for a) 1, b) 5, c) 10, and d) 60 min, respectively

doublet is enhanced due to annealing at 257 °C. Furthermore, the intensity of the lower peak decreases but the magnitude of the upper peak increases as the annealing time is increased. It would be difficult to use the postulation of remelting/recrystallization during scanning to explain the results shown in this figure. For example, Curve (d) shows that there is almost no amount of low-temperature crystal to remelt and re-crystallize, but a large high-melt peak results. Curve (a) shows that there is proportionally more of low-temperature crystal entities to remelt and recrystallize, but only a relatively smaller high-melt peak is observed in the DSC thermogram. Re-organization of crystals might be achieved by extended holding (for example, in this case, 60 min of annealing), but re-organization (i.e., re-melt/re-crystallization) cannot be achieved during a normal scanning time, for example, at 10 °C/min or so.

To quantitatively compare how the relative magnitudes of lower peak versus upper peak changed with annealing time at 257 °C, the areas under the doublet peaks were integrated. Figure 7 shows the ratio $r =$ (melting enthalpy of upper peak)/(melting enthalpy of lower peak) as a function of annealing time. A linear relationship is observed within the range of annealing time studied, indicating that the melting enthalpy of upper peak increases at the expense of the decrease in that of lower peak. Again, the peak temperature of the upper peak was found to increase almost linearly as a logarithmic function of annealing time at 257 °C. This result further suggests not only that there might be multiple crystalline lamellar entities
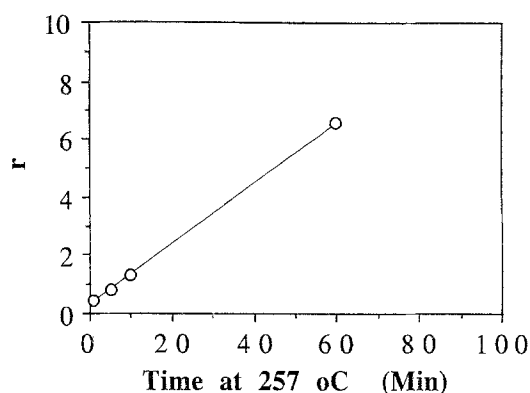
**Fig. 7** Changes of relative magnitudes of melting enthalpy of lower and upper peaks as a function of annealing time at 257 °C

co-existing with different distributions of lamellar thickness but also that the relative magnitudes of these populations of crystals can change as a result of extended sample annealing.

## Conclusion

From the Hoffman's theory and the demonstrated multiple melting peaks in step-wise annealed PET in this study,

if a sample displays multiple melting peaks, a multiple lamellae population might likely exist in it. Additionally, these lamellae can grow sequentially and independently as the PET is isothermally crystallized and annealed at multiple descending temperatures. When a semicrystalline polymer such as PET is crystallized under such conditions, these independent lamellae display multiple melting peaks upon a thermal scan. The low-temperature minor crystals simply melt but do not re-organize into higher-melt crystals during normal scanning. However, when it is not sufficiently crystallized at an isothermal temperature or at several multiple temperatures after quenching from the melt state, the semicrystalline polymer can undergo further crystallization upon heating or extended isothermal holding in DSC. It is important to note that the effect of scanning and its rate on non-isothermal crystallization is primarily confined to the temperature range further below the melting region where the crystallization kinetics progress at a reasonable rate. In addition, explanations and mechanisms have been also proposed for the minor melting endotherms observed further below the temperatures of the main melting doublets.

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