Melting behaviour of poly(phenylene sulphide): 2. Multiple stage melt crystallization

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Multiple stages of melt crystallization have been used in this study to investigate the origin of the multiple melting behaviour of poly(phenylene sulphide), PPS. In a companion study we reported results of single-stage melt crystallization of PPS and presented a model to explain the observation of multiple melting and crystallization temperature dependency of the melting peaks. In our model, the degree of undercooling determines whether the existence of preformed crystals or reorganization of imperfect crystals dominates the observed endothermic response. In this work, multiple sequences of crystallization and annealing from the melt have been used to vary the perfection of the crystals. At low crystallization temperature (high degree of undercooling), very imperfect crystals are formed which can reorganize during the d.s.c. scan. In Ryton V-1, triple melting peaks are observed, and the endothermic response depends strongly on annealing time and scan rate. Annealing at elevated temperature, which perfects the crystals, or increasing the scan rate, which reduces the chance for reorganization, both result in a decrease in the size of the uppermost endotherm. However, at high crystallization temperature (low degree of undercooling), the pre-existing crystals are much more perfect and less susceptible to reorganization. Studies of multiple stage crystallization indicate that it is possible to generate many distinct crystal populations by step-wise crystallization from the melt. The pre-existing crystals display their own melting points, each in response to a separate stage of crystallization. As many as seven melting points can be seen after five stages of melt crystallization, indicating that morphology (pre-existing crystals) dominates the appearance of the endothermic response after multiple stages of melt crystallization.

(Keywords: poly(phenylene sulphide); multiple stage; melt crystallization)

BACKGROUND

Poly(phenylene sulphide), PPS, is a high performance engineering thermoplastic which has been the subject of recent investigations into its crystallization and melting behaviour[1–9]. Because it is slow to crystallize, PPS exhibits two modes of crystallization: it can be melt crystallized over a wide range of undercooling conditions, and it can be quenched into the amorphous state, and then crystallized by heating above T_g (cold crystallization)[2]. PPS usually displays multiple melting peaks when scanned in a differential scanning calorimeter (d.s.c.) regardless of whether the crystallization occurred from the melt or from the rubbery amorphous state[1–3,6], similar to behaviour seen in other high performance polymers like PEEK[10–18] and PET[19–22]. In Part 1 of this research[1] we presented results of the melting behaviour of PPS which had been crystallized from the melt by a single stage crystallization treatment. This work is complementary to another study on the melting behaviour of PPS after cold crystallization[2]. The goal of our investigations is to explain the multiple melting behaviour, and the dependence of melting temperature on crystallization temperature, of polymers that are slow to crystallize, when these polymers are melt crystallized over a wide range of undercooling conditions.

In our previous studies of cold crystallization of PPS[2], and melt crystallization after a single stage treatment[1], we found that the observed behaviour could not be explained solely on the basis of preformed crystal populations. The idea that preformed crystal populations create the multiple endothermic response has been used previously to explain the melting behaviour of polyethylene[23,24] and PEEK[17], and PPS crystallized at high temperature[3]. However, depending upon the crystallization conditions (degree of undercooling), reorganization can also play a very significant role in determining the appearance of the d.s.c. thermograms in PPS, as it does in a variety of other polymers[19,22,25–31].

We presented a model in Part 1[1] in which reorganization and morphology (distinct preformed crystal populations) dominate in different crystallization temperature regions. Reorganization of very imperfect crystals dominates endothermic behaviour for crystallization at high degrees of undercooling, whether from the melt or from the rubbery amorphous state. By using variable crystallization time and temperature, we showed[1] that a portion of the high temperature endotherm can be attributed to reorganization. In this regime, the peak melting temperature of the uppermost endotherm is independent of the crystallization temperature. Then, as the melt crystallization temperature increases (degree of undercooling decreases), eventually distinct populations of crystals may be formed under conditions of slow growth and high chain mobility. Now the peak

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temperature of the uppermost endotherm increases linearly with the crystallization temperature.

In the present work, we report results of multiple stage crystallization of PPS from the melt. Multiple stage sequences of crystallization and annealing provide additional support for the model presented in Part 1[1]. These experiments reinforce the idea that morphology (pre-existing crystals) at low undercooling, and reorganization at high undercooling, must be used to explain multiple melting over the entire crystallization range in PPS. While our experimental studies have been performed on PPS, we expect this model to apply to other engineering polymers that crystallize slowly, such as PEEK and PET.

EXPERIMENTAL

In this work, multiple stages of crystallization/annealing have been employed to study the relative perfection of Phillips Petroleum Company. The commercial Ryton V-1 is a low molecular weight linear chain PPS (M_w about 15000) containing very low molecular weight oligomers. The experimental film grade is a medium molecular weight grade (M_w about 60000) of lightly branched PPS with melt index of 49 g (10 min)$^{-1}$. Details of the thermal analysis have been presented in Part 1.

In this work, multiple stages of crystallization/annealing have been employed to study the relative perfection of crystals formed from the melt at different degrees of undercooling. In one study, annealed samples of melt crystallized Ryton V-1 PPS were prepared in the d.s.c. by using a program mode. The samples were heated up to 310°C, and held for 3 min, to erase any crystals from the prior treatment, before cooling to 225°C. The crystallization took place rapidly at this low temperature and could be completed within 1 or 2 min. The samples were held for a period of time (t_c) at the crystallization temperature, 225°C, before being heated to the annealing temperature, 250°C. The samples were then held at this annealing temperature for another period of time (t_a) before being cooled to room temperature. All of the cooling and heating rates used between treatments were 200°C min^{-1}. Two kinds of experiment were performed: annealing time effect and crystallization time effect. First, crystallization time t_c was constant at 60 min, but the annealing time varied from 0 to 2000 min. Next t_c varied from 2 to 1000 min but the annealing time t_a was constant at 60 min. The effect of scan rate on the crystallized and annealed Ryton V-1 sample (crystallized at 225°C for 2 min and then annealed at 250°C for another 30 min) was also investigated from 1°C min^{-1} to 40°C min^{-1}.

The melting behaviour of the multiple stage crystallized PPS has been studied by performing the crystallization of both Ryton V-1 and film grade materials at five different temperatures and then rescanning at 20°C min^{-1}. Two kinds of multiple stage crystallization have been studied for Ryton V-1: (1) 10 min residence time at 265°C, 255°C, 245°C, 235°C and finally 225°C; and (2) 265°C (50 min), 255°C (17 min), 245°C (4 min), 235°C (3 min) and 225°C (2 min). However, for film grade material the treatments are: (1) 60 min crystallization time at five different temperatures, 265°C, 255°C, 245°C, 235°C and finally 225°C; and (2) 255°C (120 min), 245°C (60 min), 235°C (10 min), 225°C (6 min) and 215°C (4 min).

Two-stage crystallization of both grades of PPS has been studied by first melt crystallizing at 255°C for various times (10 min to 2000 min) and then jumping to 240°C for a fixed time (60 min for Ryton V-1 and 120 min for film grade PPS) before scanning. All of the heating and cooling rates used between stages of melting and crystallization and cooling were 200°C min^{-1}.

RESULTS

Annealing of melt crystallized PPS

Results of annealing Ryton V-1 PPS at 250°C after melt crystallization at 225°C are shown in *Figures 1–3*. In *Figure 1*, the first stage crystallization time was constant at 10 min, and the annealing time varied from 0 min (top left curve of *Figure 1A*, quenched after first stage) to 1998 min. Three endotherms are apparent in the material crystallized at 225°C and quenched. The third, middle endotherm, designated T_{m*}, is at first merely a shoulder on the low temperature side of the dominant endotherm, T_{m2}. The middle melting peak becomes a well resolved, isolated peak after 10 min annealing at 250°C, and becomes the dominant peak after annealing for 120 min at 250°C. Plots of the three endothermic melting peaks *versus* annealing time at 250°C are shown in *Figure 2A*. The lowest melting peak T_{m1} shifted to a higher temperature when the annealing time increased, and eventually merged into the middle melting peak when the annealing time was longer than 120 min. The upper melting peak temperature T_{m2} remains almost the same regardless of the annealing time. The middle melting peak temperature T_{m*} slightly increases as the annealing time increases.

The plot of the relative peak height (i.e., normalized to its value in the non-annealed sample) of the upper melting peak T_{m2} *versus* annealing time is shown in *Figure 2B*. The attempt to deconvolute the overlapped d.s.c. melting peak is difficult because no information is available about the real shape of the melting endotherms. But the relative height of the melting peaks provides information about the relative population of crystals at a particular melting region. By carefully inspecting the thermograms in *Figure 1*, we find the relative peak height of the upper melting peak T_{m2} decreases as the annealing time at 250°C increases.

Next, we tested the effect of the initial crystallization time. From the isothermal crystallization kinetics study (described in Part 1), the majority of crystals should be formed within 2 min when the Ryton V-1 is melt crystallized at 225°C. By fixing the annealing time, the effect of the time t_c at 225°C on the middle melting peak can be studied. *Figure 3A* shows the collective thermograms for various crystallization times from 2 to 999 min at 225°C, followed by a constant annealing time of 60 min at 250°C. The corresponding plots of the three melting peak temperatures *versus* the crystallization time at 250°C are shown in *Figure 3B*. The result shows that the effect of the initial crystallization time on the melting behaviour of the annealed PPS sample is very insignificant. The three melting peak temperatures only show very slight increases when the initial crystallization time at 225°C is longer than 600 min. The relative peak height of the upper melting peak slightly decreases, and the relative peak height of the middle melting peak slightly increases, as the initial crystallization time increases. In other words, the ratio of peak height of T_{m*} to that of T_{m2} increases from about 0.7 to 0.9 as the initial crystallization time at 225°C increases from 2 to 999 min.

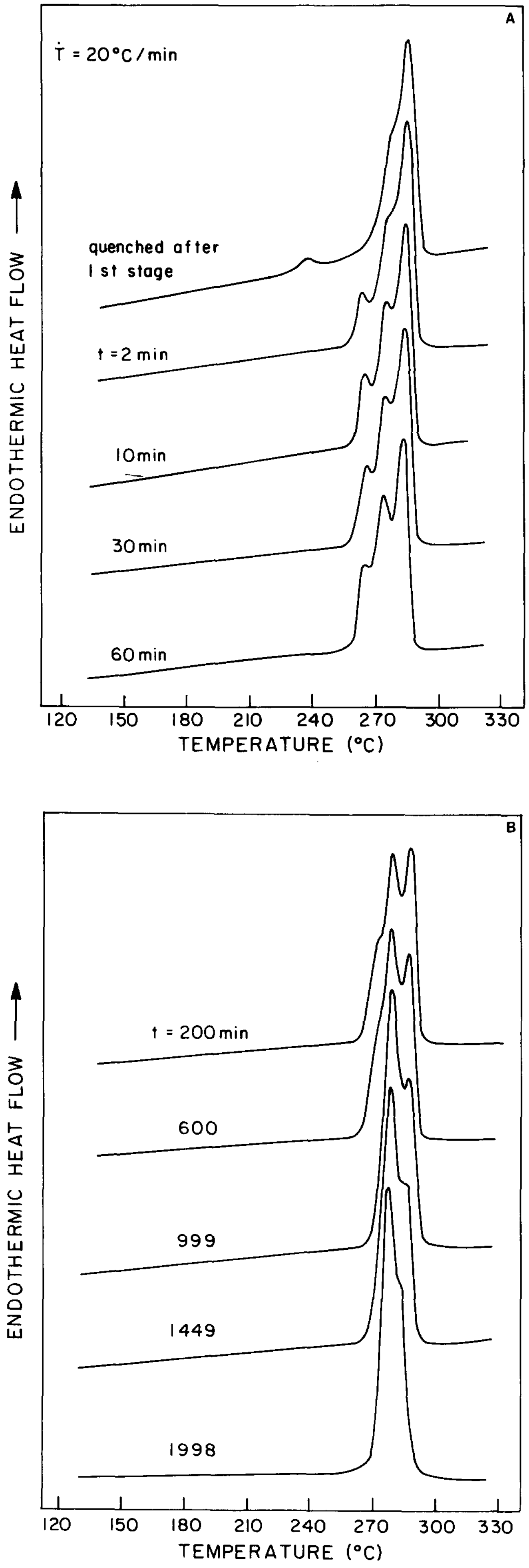

Figure 1 Collective melting endotherms of Ryton V-1 PPS melt crystallized at 225°C for 10 min, and immediately annealed at 250°C for the times indicated: (A) shorter annealing times, (B) longer annealing times

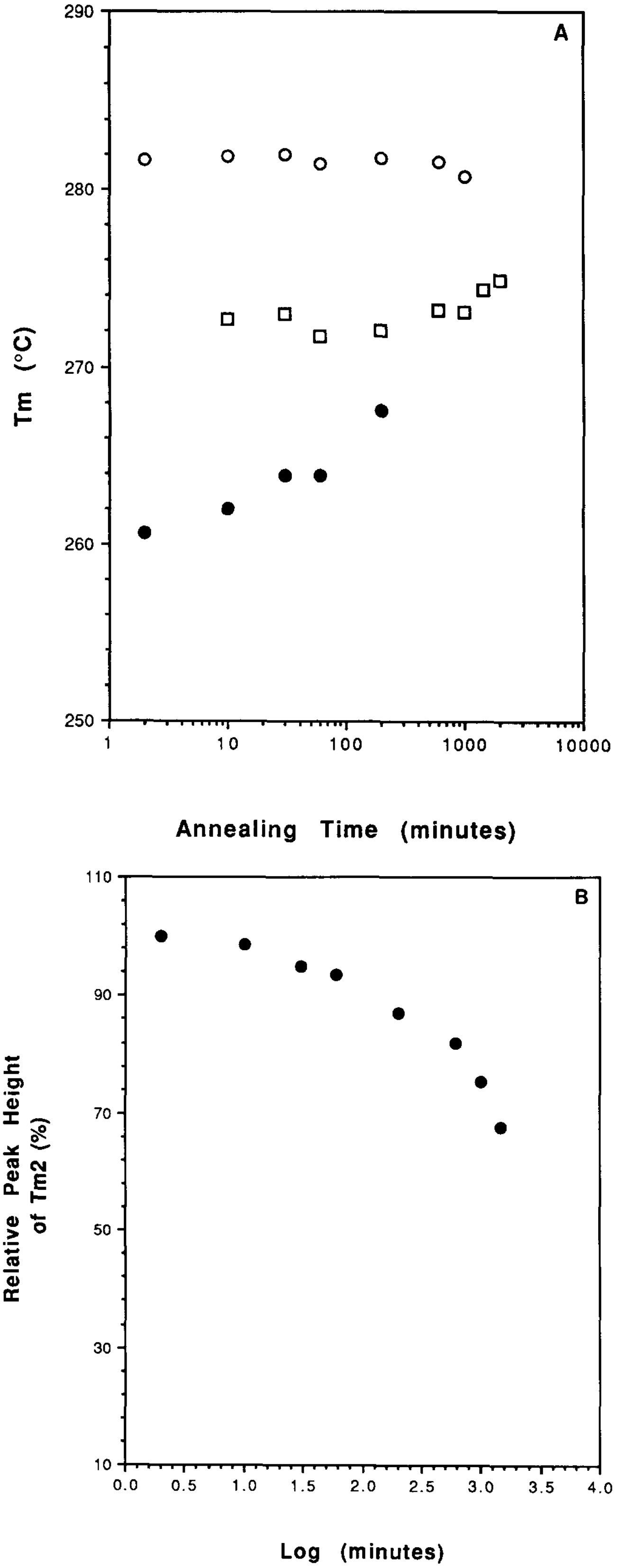

Figure 2 (A) Melting peak temperature *versus* annealing time: T_{m1} (●), T_{m*} (□), T_{m2} (○); and (B) relative peak height of T_{m2} *versus* log (annealing time), for Ryton PPS melt crystallized at 225°C for 10 min and immediately annealed at 250°C for various annealing times

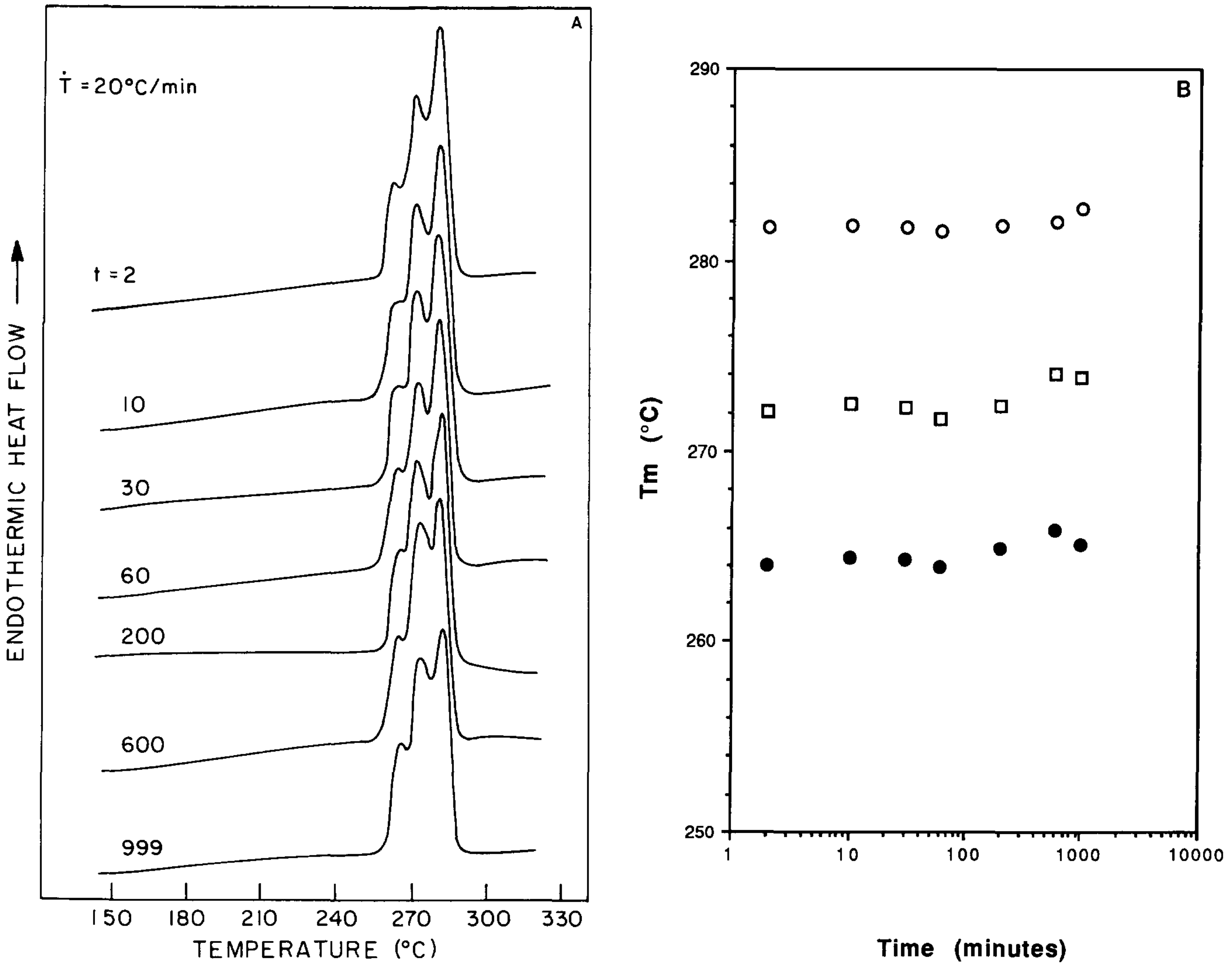

Figure 3 (A) Collective melting endotherms at different crystallization times, and (B) melting peak temperature *versus* crystallization time: T_{m1} (●), T_{m*} (□), T_{m2} (○), for Ryton V-1 PPS melt crystallized at 225°C and annealed at 250°C for 60 min

This is in contrast to the previous results shown in *Figure 1* in which the relative peak height ratio of T_{m*} to T_{m2} increases sharply when the crystallization time is fixed.

The scan rate dependency of the triple melting peaks of melt crystallized, annealed Ryton V-1 has also been investigated. The well defined triple melting peaks of Ryton V-1 PPS samples can be obtained by first crystallizing at 225°C for 2 min and then annealing at 250°C for 30 min. The collective d.s.c. thermograms of various scan rates of annealed, melt crystallized Ryton V-1 are shown in *Figure 4A*. The plots of the three melting peak temperatures *versus* scan rate are shown in *Figure 4B*. The vertical scale of the thermograms shown in *Figure 4A* is an arbitrary scale, and therefore no direct comparison between the heats of fusion of thermograms taken at different scan rates can be made. However, the relative peak heights of the upper and lower melting peaks within the same scan can be compared. The relative peak height of the lowest melting peak T_{m1} to that of the upper melting peak T_{m2} increases with the scan rate. The relative peak height of the middle melting peak T_{m*} to that of the upper melting peak T_{m2} also increases with increasing scan rate. With regard to the peak temperatures, as shown in *Figure 4B*, the middle melting peak temperature remains almost constant, changing only 1° as the scan rate varies from 1°C min^{-1} to 40°C min^{-1}. The upper melting peak temperature T_{m2} decreases significantly (11°) with an increase in scan rate, and the lowest melting peak temperature increases 6°.

Multiple-stage crystallization studies

The melting behaviour of the multiple-stage crystallized PPS, which has been exposed at several crystallization temperatures before completing crystallization, has been investigated. The resulting d.s.c. melting thermograms of samples exposed to five successive stages of melt crystallization are shown in *Figures 5* and *6* for Ryton V-1 and film grade PPS, respectively. By fixing the residence time at each stage of crystallization, 10 min for Ryton V-1 and 60 min for film grade, from 265°C to 225°C at 10°C intervals, the resulting melting endotherms (as shown in *Figure 5A* and *6A*) of both grades show four melting peaks. However, by carefully choosing the residence time in each stage, more than four melting peaks can be found. By using the time, t_m, required to reach the isothermal crystallization exotherm heat flow maximum (which we previously determined in Part 1) at each temperature as the residence time, we were able to identify seven melting peaks (as shown in *Figure 5B*) on the five-stage melt crystallized Ryton V-1, and six melting peaks on film grade. Comparing the melting endotherms of *Figure 5A* (constant time at each stage)

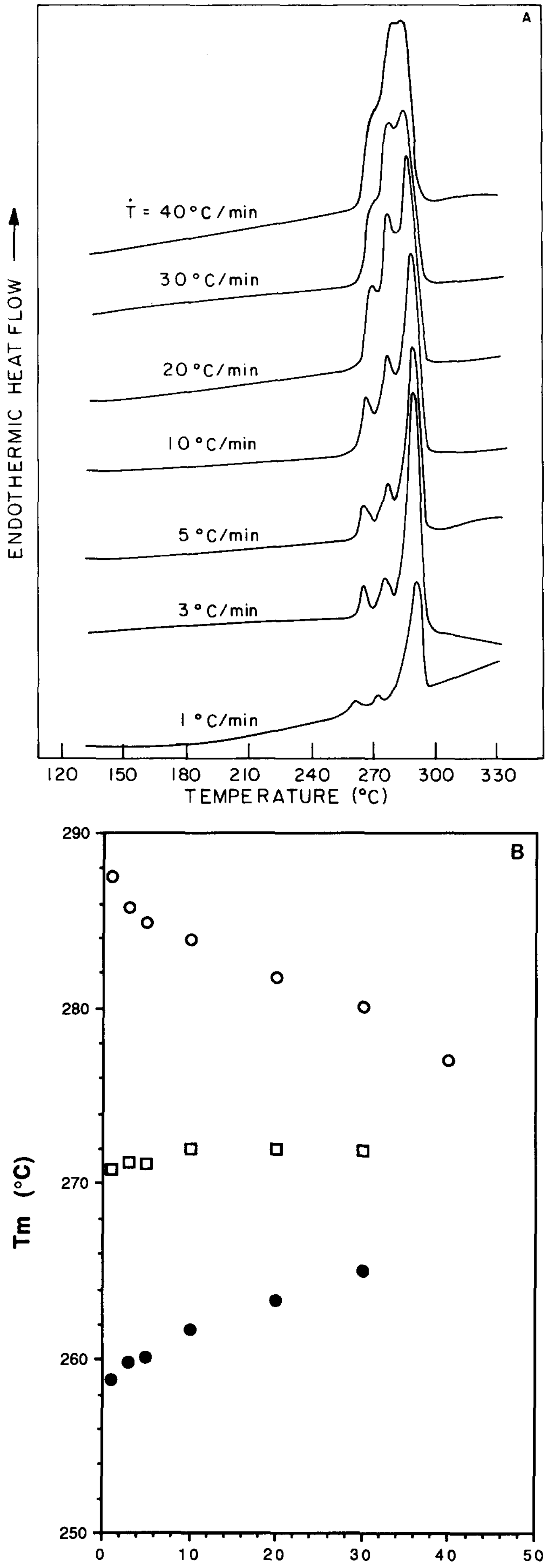

Figure 4 (A) Collective melting endotherms at different scan rates, and (B) melting peak temperatures *versus* scan rate: T_{m1} (●), T_{m*} (□), T_{m2} (○), for Ryton V-1 PPS melt crystallized at 225°C for 2 min and immediately annealed at 250°C for 30 min

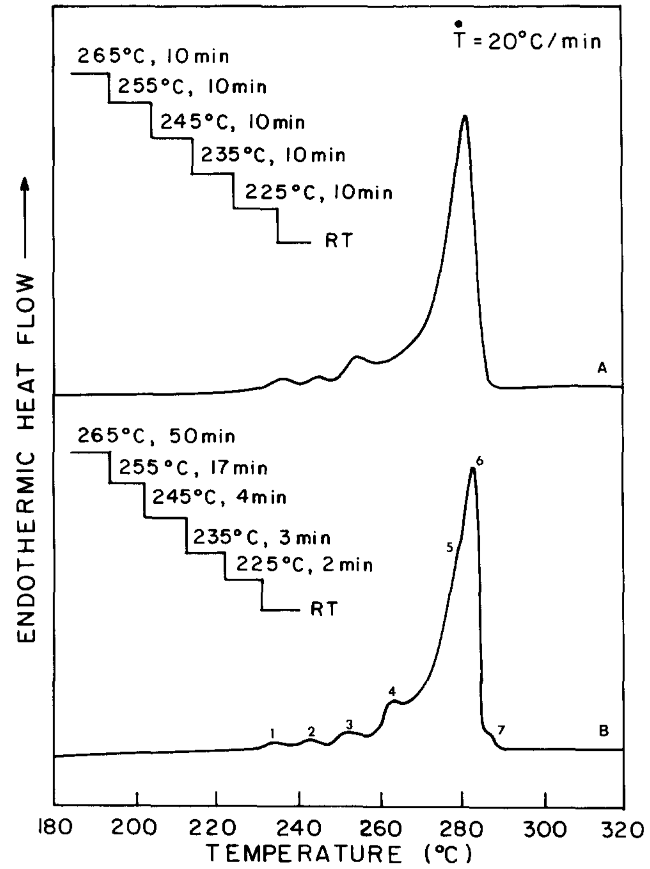

Figure 5 Melting endotherms of Ryton V-1 PPS exposed to five successive step crystallization temperatures from the melt: (A) constant residence time at each stage, (B) variable residence time at each stage

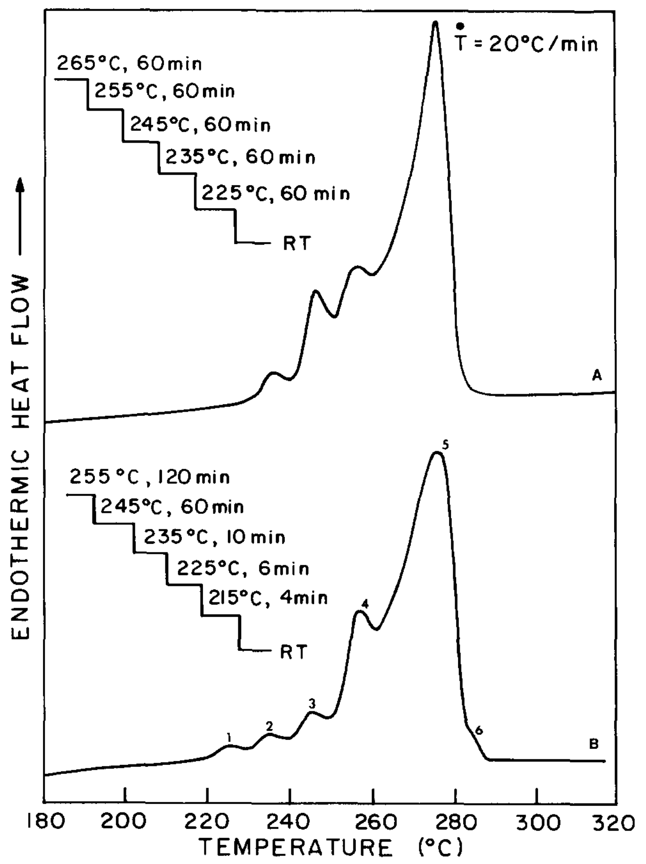

Figure 6 Melting endotherms of film grade PPS exposed to five successive step crystallization temperatures from the melt: (A) constant residence time at each stage, (B) variable residence time at each stage

and *Figure 5B* (varying time, t_m), not only have two additional peaks been observed at the temperatures between 260°C and 280°C, but also a small melting peak is found which is located just above the upper dominant peak (283°C) and has a melting peak temperature around 288°C. A similar result was also found in the multiple stage melt crystallized film grade PPS sample shown in *Figure 6B*.

Two-stage crystallization studies

The collective thermograms of the two-stage crystallization experiment of film grade and Ryton V-1 are shown in *Figures 7* and *8*, respectively. The first stage crystallization temperature is 255°C and the second stage is 240°C. When the residence time at the higher first-stage crystallization temperature is not long enough for crystal growth to be initiated (ca. 5 min for Ryton V-1 or 60 min for film grade), the subsequent melting endotherms are exactly the same as the endotherm of single-stage crystallization at 240°C. However, if the PPS samples stay at the first stage crystallization temperature for a longer time so that crystals are generated at 255°C, then four melting peaks can be observed. In *Figure 8* four endotherms begin to emerge after about 120 min residence time at 255°C for film grade PPS. For Ryton V-1, the four endotherms can be seen in *Figure 7* to emerge after 15 min at 255°C. The four melting peaks are not very easy to identify from the melting endotherm of Ryton V-1 PPS due to the overlap of the two upper peaks, but four clearly separate peaks can be easily identified for the film grade. By using an assumption that the endothermic melting peak shape of the crystals generated at 240°C will be the same regardless of time at 255°C, we are able to separate the two endotherms which were formed at the two separate crystallization conditions (dashed lines). We do not imply that the ratio of the crystal populations generated at both stage crystallization temperatures can be calculated by directly comparing the areas underneath the two deconvoluted endotherms from *Figure 7* or *8*. The purpose of this peak separation is to explore the possible cause of the multiple melting peaks and provide a qualitative comparison of the relative crystal distribution corresponding to the two separated melting endotherms. As the residence time t_1 at 255°C increases, the fraction of the endotherm produced at this first stage crystallization also increases. The result from two-stage crystallization indicates that the melting processes of the two categories of crystals generated from two different crystallization temperatures are independent. Each category of crystal melts without interfering with the other category of crystal.

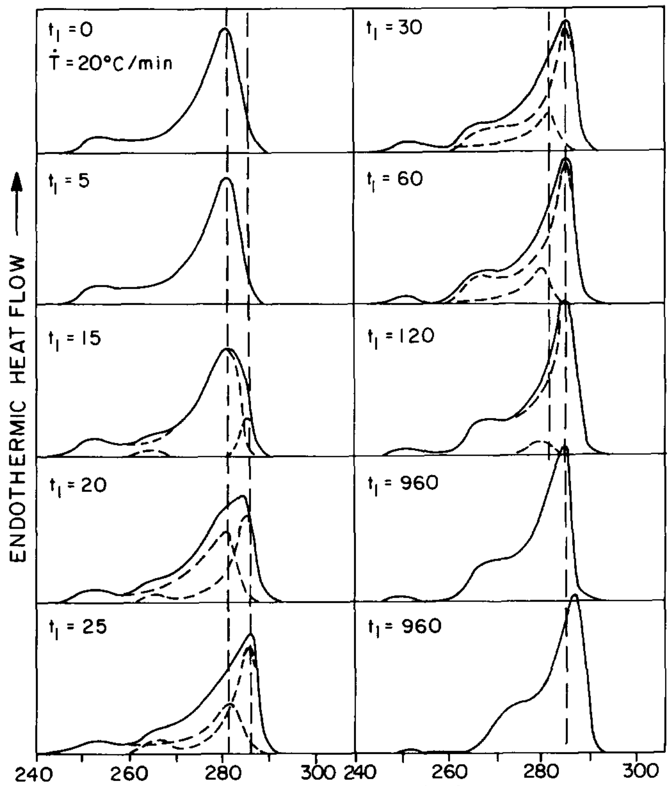

Figure 7 Collective melting endotherms of two-stage melt crystallized Ryton V-1 PPS, crystallized from the melt at 255°C for the times indicated, and then further crystallized at 240°C for 60 min

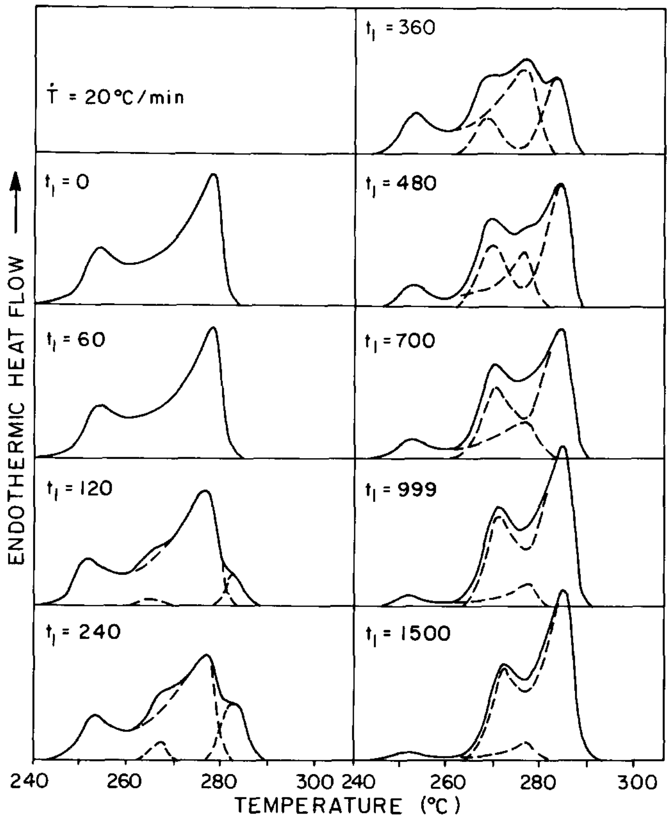

Figure 8 Collective melting endotherms of two-stage melt crystallized film grade PPS, crystallized from the melt at 255°C for the times indicated, and then further crystallized at 240°C for 120 min

DISCUSSION

During the crystallization process, polymer chain segments pack together to form crystal seeds and then proceed with crystal growth from the seeds. The perfection of crystals which can be formed will be strongly controlled by the crystallization conditions, and will then affect the subsequent melting behaviour. We have reported[32] that the crystal perfection, which is in terms of crystal density and average lattice dimensions, of the cold crystallized PPS increases as the crystallization temperature and the residence time increase. Similar results have been reported for PEEK[33,34]. In order to understand the relationship of the melting temperature of the preformed crystals with the crystal perfection, the multiple stage crystallization experiments were studied.

Annealing effect of melt crystallized PPS

From *Figure 1* we see that there is a third middle melting peak occurring in the front shoulder of the upper melting peak when the Ryton V-1 was melt crystallized at a temperature below 230°C[1]. From the annealing treatment of Ryton V-1 melt crystallized at large undercooling we observed that the peak height of the upper melting endotherm T_{m2} decreases as the annealing time at 250°C increases. This annealing time dependency of the upper T_{m2} melting peak height strongly indicates that at least a fraction of the upper melting peak does not represent the real melting of pre-existing crystals. If the upper melting peak T_{m2} of the Ryton V-1 which crystallized at 225°C were solely due to melting of pre-existing crystals, we would expect the crystal population of the upper melting endotherm to increase when the polymer crystals are made more perfect by annealing at 30°C below their upper melting peak temperature. Therefore, the related melting peak height should increase as the annealing time increases. The observed decrease of the upper melting peak height upon annealing suggests that a large part of endotherm T_{m2} is due to remelting of crystals formed from reorganization of crystals melting originally at T_{m1} and T_{m*}. The fraction of crystals able to be reorganized is subsequently suppressed by annealing at a higher temperature to form the more perfect crystals. These more perfect crystals, after long time annealing at 250°C, will melt at a relatively higher temperature, and the chance of reorganization will be reduced, because the reorganization rate is slower at a higher temperature.

Evidence of multiple crystal perfections

From the previous study[1] we found the third middle melting peak is not found when Ryton V-1 is fast cooled at the same rate of 200°C min^{-1} directly from its melt to room temperature. This means that the observation of triple melting peaks is related to the crystallization history at 225°C. The third middle melting peak of Ryton V-1 PPS is not due to the formation of a population of crystals during cooling to 225°C. We suggest that the third middle melting peak is due to the melting of a population of pre-existing crystals which is formed at 225°C (large undercooling condition). Therefore at least two kinds of crystal perfections can be identified when the Ryton V-1 PPS is crystallized isothermally at large undercooling. These two distributions of crystal perfection melt at the lower melting temperature T_{m1} and at the middle melting temperature T_{m*}. The reason for the triple melting peak is that one of the crystal populations melts at relative low temperature (T_{m1}), then reorganizes and subsequently melts at a higher temperature (T_{m2}). The second population of crystals melts at a temperature, T_{m*}, between T_{m1} and T_{m2}. One key reason that the third middle melting peak can be seen is because the crystal perfection of the second kind of crystals (melting at T_{m*}) is much less perfect than that of reorganized crystals, and therefore the two melting endotherms, T_{m*} and T_{m2}, are not completely overlapped and can be separately identified.

The scan rate study, *Figure 4*, provides further evidence that T_{m1} and T_{m*} represent melting of preformed crystals, while T_{m2} is largely due to reorganization. As the scan rate increases, the temperature of T_{m1} increases and T_{m2} decreases. The relative peak height ratio of T_{m1} and T_{m2} goes up with scan rate. Thus, under conditions which are unfavourable to reorganization, the relative population of crystals melting at T_{m1} increases with respect to those melting at T_{m2}. A similar relation holds for T_{m*}. The relative peak height ratio of T_{m*} to T_{m2} increases as scan rate increases. This suggests that there are different levels of crystal perfection existing prior to the scan; each type of crystal is subject to reorganization at low scan rates. A large portion of endotherm T_{m2} results from the melting of reorganized material.

Multiple stage crystallization

The multiple melting peaks of semicrystalline polymers, such as PPS[3] and PEEK[18], can be generated by using the multiple stage crystallization technique. We have previously reported[3] that five melting peaks can be observed when the Ryton V-1 PPS has been crystallized for 2 h at 270°C, 230°C, 190°C and finally 150°C. From the multiple stage crystallization investigation, shown in *Figures 5* and *6*, we observe as many as seven melting peaks from a five-stage crystallization treatment. Similar results have also been reported by Chang[18] on PEEK. Chang reported that more than ten melting peaks can be seen if the PEEK was crystallized for 20 min at every 20°C interval from its melt. The formation of the multiple melting peaks indicates that multiple distributions of crystal perfection are able to be formed by using a multiple stage crystallization. At least one crystal population having a certain crystal perfection can be formed at each individual stage of crystallization. Therefore at least one of the multiple melting peaks is associated with the melting of each of the populations of crystals. Based on a w.a.x.s. study of cold crystallized PPS[32] and the multiple stage crystallization studies, we observe that the less perfect crystals, which have a smaller crystal lattice density and a lower melting peak temperature, will be formed at lower crystallization temperature. The crystal perfection can be improved by increasing the crystallization temperature or residing a longer time at a high temperature (annealing effect).

Since the crystal lamellar thickness and the perfection of polymer chain packing in the crystal lattice are strongly related to the crystallization kinetics[19,33,34], the melting point of a lamella will be affected by the crystallization temperature. When the crystallization takes place at a higher temperature, the chain mobility is higher and the nucleation and crystal growth rates are slower; the perfection of the crystal and the lamellar thickness are higher. Subsequently the melting point of the crystals will be higher. In assigning the origin of the individual endotherms in *Figures 5* and *6*, we must consider the residence time at each crystallization stage. For Ryton V-1 (*Figure 5A*) the residence time of 10 min was not long enough to generate crystals at 265°C or 255°C. The first three observed endotherms (from low to high temperature) come from the 225°C, 235°C and 245°C stages and represent the T_{m1} endotherms. The fourth highest endotherm is the superposition of the T_{m2}s, and is dominated by the T_{m2} from the 245°C stage.

In *Figure 5B*, crystallization time was chosen as the time to reach the exothermic heat flow maximum, and was long enough at each stage to generate crystals. The first three endotherms (from low temperature to high) are the same as observed in *Figure 5A*. The fourth endotherm comes from the 255°C T_{m1} endotherm. The fifth and sixth endotherms have contributions from the T_{m2}s of all stages, and include the T_{m1} from the 265°C stage. The smallest, and highest temperature, endotherm is due to the formation of a small population of very perfect crystals, perhaps more like extended chain crystals.

Similar interpretation can be made for the film grade PPS shown in *Figure 6*. At first we chose a constant residence time of 60 min, which was too short to generate crystals at 255°C or 265°C. Using the same approach as in the Ryton material, we then selected the crystallization time to be the time to reach the exothermic peak maximum. However, we eliminated the 265°C step because of the very long residence time that would have been required. The major difference between the scans in *Figure 6A* and *6B* is that the largest endotherm in the scan of *Figure 6B* is very broad compared to its shape in *6A*. The reason is that it contains contributions from melting of crystal populations crystallized at lower temperatures than in *Figure 6A*.

Based on the results from the multiple stage crystallization studies, we have designed a two-stage isothermal crystallization experiment to explore the effect of preformed crystals, which are formed at a higher temperature for a short time, on the subsequent melting behaviour after completing the crystallization at a lower temperature. The PPS specimen was first isothermally crystallized from the melt at a higher temperature, 255°C, for various times and then jumped to a lower temperature, 240°C, to proceed with the second stage crystallization. The purpose of the first-stage crystallization is to generate relatively perfect crystals at the higher first-stage crystallization temperature, and the amount of crystals will depend on the residence time at the first stage. If the residence time at the first stage crystallization temperature is not long enough for spherulites to fill the space completely, then a certain fraction of the polymer melt will coexist with the preformed crystals. It is not possible to separate the melt from the preformed crystals by quenching or fast cooling due to the fact that the imperfect crystals formed would be subject to reorganization. Therefore, the purpose of the second-stage crystallization is to fix the melt by further crystallization at a relatively low temperature. Crystals formed at this lower temperature have melting endotherms that will not overlap with the melting endotherm of crystals generated after the first-stage crystallization. From the isothermal melt crystallization kinetics study[1], we found the crystallization will be complete within 100 min for film grade and 30 min for Ryton V-1 at 240°C. Also, from our previous work[3], we know that the dual melting peaks formed at 255°C do not completely overlap with the dual melting peaks formed at 240°C for both materials. Hence, we should be able to observe clearly the two kinds of endotherms after subjecting the polymer to the two-stage crystallization, and three or four melting peaks should be able to be identified.

By varying the residence time at the first stage, the ratio of the crystal populations formed at these two crystallization temperatures can be varied. From *Figures 7* and *8*, we find that if the residence time at the first stage is very short (less than 60 min for film grade and 10 min for Ryton V-1), two melting peaks resulted from the second stage crystallization. When the first stage residence time of Ryton V-1 is longer than 10 min but shorter than 30 min (within 60 min to 700 min for film grade), then four endothermic peaks are observed: two melting peaks from each stage of crystallization. When the first stage residence times of both grades of PPS are long enough (more than 700 min for film grade and 30 min for Ryton V-1), three melting peaks result from the two-stage crystallization, similar to the results we have reported previously[3].

After the deconvolution of the overlapped peaks, dual melting behaviour is observed for crystals formed at the first stage melt crystallization even at a very short residence time at the first stage. For example, dual endotherms were observed from the crystal fraction generated at 255°C for 15 min for Ryton V-1 and 120 min for film grade. By using the momentary annealing technique[1], i.e., by heating the amorphous PPS to an annealing temperature instantaneously and then cooling down, we have suggested that the dual melting behaviour of cold crystallized PPS is due to reorganization, and the melting-reorganization phenomenon is a continuous process. If the reorganization takes place continuously during the d.s.c. scan, then there should be only three melting peaks observed from two-stage crystallized samples, two melting peaks referring to the melting of two kinds of crystals, and the third due to the melting of the reorganized crystals. Therefore, we suggest that the existence of the four melting peaks, even when the crystal fraction from the first-stage melt crystallization is small, provides evidence of double morphologies which exist at the first stage crystallization temperature.

CONCLUSION

We have proposed a model based on crystallization kinetics considerations to explain the multiple melting behaviour of PPS melt crystallized over a wide range of undercooling conditions. When PPS is crystallized by multiple stages of heat treatment from the melt, the distribution of crystals forms in response to each temperature stage. The multiple endotherms are due to the melting of the different crystal perfection distributions. A two-stage crystallization sequence of high crystallization temperature followed by low crystallization temperature results in very distinct crystal populations which develop and melt independently.

For PPS melt crystallized at large undercooling, there is a broad distribution of crystal perfection. For Ryton V-1, a triple endothermic response was observed after melt crystallization at high degree of undercooling, and this triple endotherm allowed us to explore the ability of the imperfect crystals to reorganize during the d.s.c. scan. Annealing at elevated temperatures results in improvement in the perfection of the crystals, and a decrease in the relative size of the uppermost endotherm. These results, and the scan rate dependency of the upper endotherm, suggest that crystals formed at high undercooling are subject to reorganization. The melting behaviour of PPS melt crystallized over a wide range of undercooling conditions can be explained by including effects of both morphology (i.e., pre-existing crystals) and reorganization.

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