Studies on the crystallization and melting of nylon 66: 3. Melting behaviour of negative spherulites by calorimetry

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(Received 18 June 1993; revised 31 March 1994)

The thermal behaviour of nylon 66, associated with the morphologies identified previously, has been examined. The thermograms for the crystallization temperatures (T_c), between 247°C and 265°C, were distinctly different from those at low T_c and from those given by samples crystallized non-isothermally on cooling. The endothermic peak could be identified with the melting of negative and zero birefringent spherulites (the latter of both kinds). On cooling, samples crystallized in the T_c range of 247–265°C, display certain characteristic exotherms indicating further crystallization. In view of the fact that 'morphologically' the preceding crystallization had been complete, such crystallization must take place within the appropriate morphological entities themselves, conforming to the particular morphology present already, or alternatively the effect may correspond to a solid–solid transformation. In addition to the above, a new high melting crystal form with T_m in the range of 280–285°C has become apparent forming under conditions corresponding to zero birefringent spherulites (high T_c) but distinct from the latter, not conforming to any morphology seen in our previous study. Finally, the new information and issues arising therefrom are summarized and placed in perspective.

(Keywords: nylon 66; spherulites; aggregate)

INTRODUCTION

In this paper we report thermal effects that relate to the formation and melting of the morphological features observed and studied in part 2[1]. Specifically, crystallization is conducted so as to produce selected morphological features identified previously under the polarizing microscope and the thermal behaviour, endotherms on heating and exotherms on cooling from the crystallization temperature (T_c) has been investigated.

EXPERIMENTAL

The thermal behaviour of the material was investigated in a Perkin–Elmer DSC 7 under nitrogen flow. A sample weight of 2–4 mg was used in all experiments. The temperature–time programme that was used is schematically represented in *Figure 1*. This programme is similar to the one used for the studies on the morphology of negative spherulites[1]. The sample was first heated to 300°C to remove the past thermal history. Then the sample was cooled to 100°C at 50°C min^{-1} during which the sample crystallized around 200°C into positively birefringent spherulites. The sample was subsequently heated at 10°C min^{-1} up to a temperature just above the melting peak of the material (~265°C) and was held at that temperature for 1 min. After this holding time the sample was cooled to the temperature interval between 247°C and 265°C to start the isothermal crystallization.

This procedure is slightly different from the one previously described[1], since the rapid cooling to 100°C results in a fine grained initial morphology and thus subsequently in a very high nucleation density of negative spherulites. This ensures that the entire material converts into negatively birefringent spherulites and into spherulitic aggregates within a limited period of time. From here on, negative spherulites will be the collective designation for spherulitic aggregates and negative spherulites where the fraction of such aggregates is very small.

Samples were kept at the various T_cs for time intervals between 15 min and 17 h to investigate how crystallization into negative spherulites affected the thermal behaviour. D.s.c. curves were recorded either by cooling and subsequent heating of the material or, in some experiments, by heating the sample directly from the T_c. Unless stated otherwise, experiments were carried out with a heating rate of 10°C min^{-1}.

RESULTS

Typical melting endotherm

A conventional thermogram as obtained after slow cooling is shown in *Figure 2a* and is used as a reference for all the new material to be presented. *Figure 2b* shows

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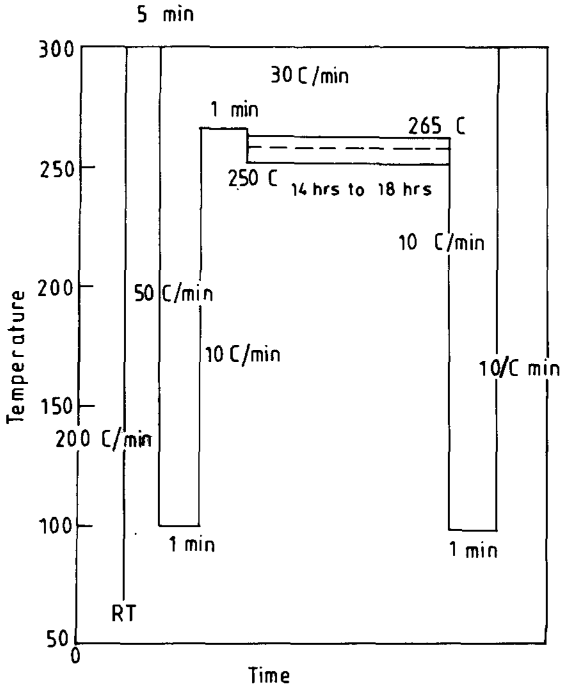

Figure 1 Temperature–time programme for the growth of negative spherulites in the differential scanning calorimeter

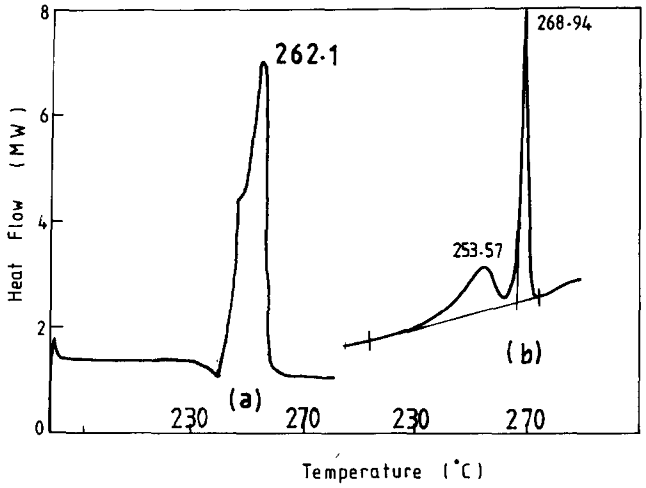

Figure 2 (a) D.s.c. heating curve of nylon 66 sample, crystallized by cooling at a rate of 10°C min^{-1} from the melt. (b) D.s.c. heating curve of nylon 66 after crystallization at 260°C (following *Figure 1*) for 90 min and cooling to 100°C at 10°C min^{-1}

a typical example of the melting endotherms of a sample that has been crystallized for 90 min at 260°C and was subsequently cooled to 100°C and then melted. Most striking in the melting behaviour is the unusually sharp peak near 270°C if compared to the normally observed melting endotherm of the material crystallized at much lower temperatures (*Figure 1*). Further extensive examination has shown that the peak position and area remained unaffected with heating rates between 10°C min^{-1} and 100°C min^{-1}. We could identify this peak with the melting of negative spherulites. This identification follows from the polarizing microscopy studies in part 2[1]. It could be ascertained, using a very thin slice of the above sample, that the entire material consisted of negative spherulites (70%) and spherulitic aggregates (30%). As is shown in *Figure 2b* the broader maximum would then correspond to the melting of material within the already crystallized structure that has crystallized further at lower temperatures during cooling (this material would otherwise not have crystallized at the intended T_c). As the sample volume is fully covered by the spherulites, it follows that the material crystallizing on cooling must be located within the geometrical boundaries of the spherulites.

Effect of crystallization time on thermal behaviour

The effect of crystallization time (t_c) at the given T_c on the thermal properties was established by holding the material at 260°C for various lengths of time between 15 min and 980 min. These experiments were all performed twice; in the first instance the heating curve was recorded (*Figure 3*) by heating the sample straight from T_c without previously cooling down to room temperature. In the second case the sample was cooled to room temperature after a predetermined t_c at T_c. In this case the cooling and subsequent heating curves were recorded as shown in *Figures 4* and *5*, respectively.

For $t_c = 15$ min at 260°C there was no endotherm on subsequent heating (*Figure 3*, top curve). This indicates that the spherulites have not yet formed to an extent sufficient to show up in the d.s.c. traces. The cooling curve in *Figure 4* (top curve) displays a sharp exotherm around 230°C. The crystallized material corresponding to this exotherm gives rise to positive spherulites. These spherulites melt at 250°C as seen in *Figure 5* (top curve) with a hint of a further endotherm at 270°C.

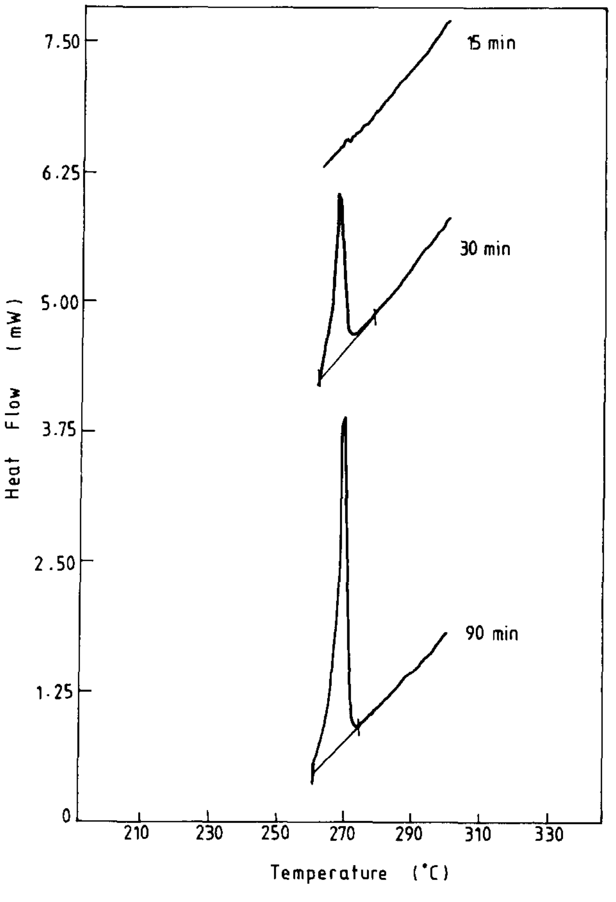

Figure 3 D.s.c. curves obtained during heating, without intervening cooling, directly from the isothermal crystallization temperature of 260°C after various time intervals

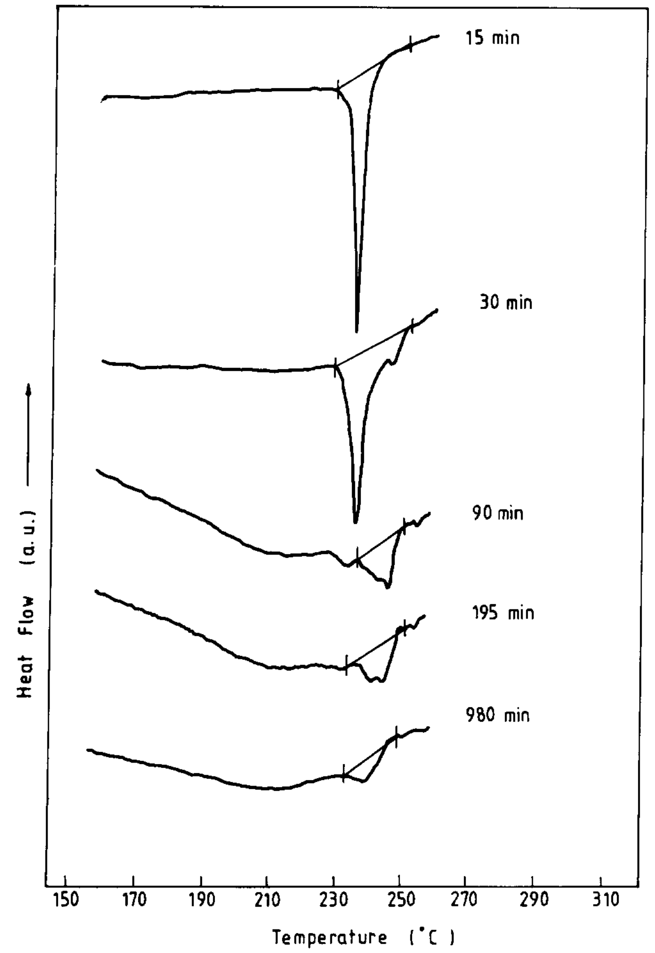

Figure 4 D.s.c. curves obtained during cooling following isothermal crystallization at 260°C for various time intervals

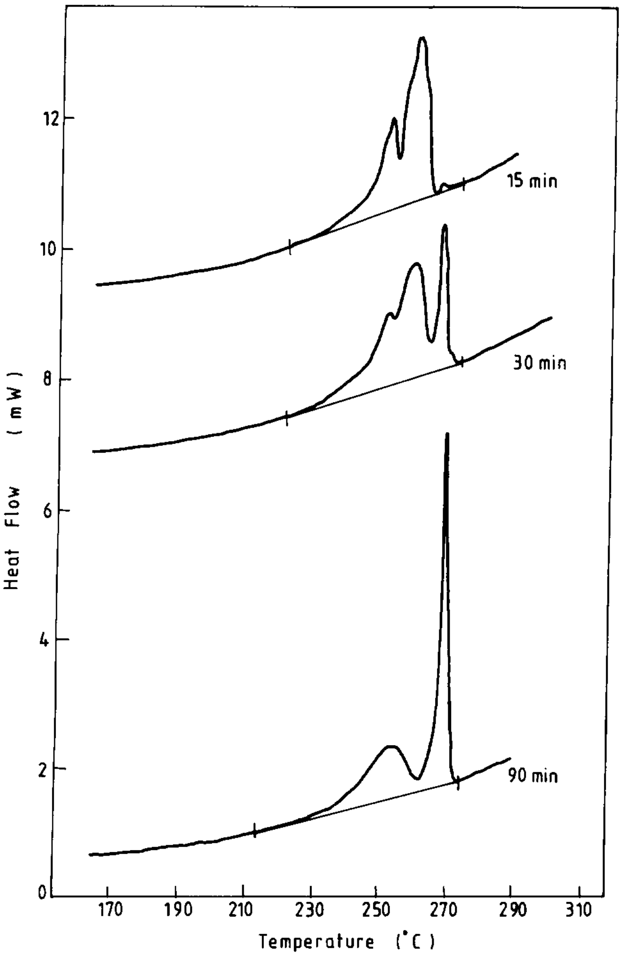

Figure 5 D.s.c. curves obtained during heating following isothermal crystallization and subsequent cooling to room temperature

After a $t_c = 30$ min the heating curve (directly from T_c) shows a sharp endotherm at 270°C (*Figure 3*, middle curve). In the cooling experiment a new exotherm starts developing at 243°C in addition to the prominent one at 230°C (*Figure 4*, second curve from top). In the subsequent melting curve (*Figure 5*) the sharp high temperature peak is identical to that in *Figure 3* and the contribution arising from material which has crystallized on cooling, while still prominent, has decreased.

After 90 min the crystallization of negative spherulites is complete (the whole field is covered by negative spherulites) and direct heating displays an unusually sharp melting peak at ~270°C (*Figure 3*, bottom curve); an increase of t_c induces no significant changes in the curves. On cooling such a sample from the T_c the sharp exotherm is no longer observed (cf. the top and bottom exotherms in *Figure 4*). However, the small exotherm at 243°C is now the only one present; it has developed more or less simultaneously with the amount of material crystallized at the T_c.

In *Figure 6* the melting enthalpies of both endotherms are plotted as a function of time, which summarizes the above-mentioned behaviour. As can be seen, the peak areas of the sharp peaks in both *Figures 3* and *5* are almost identical, i.e. the peak area is not affected by cooling. This also applies to the peak temperature of the sharp endotherm (*Figure 7*).

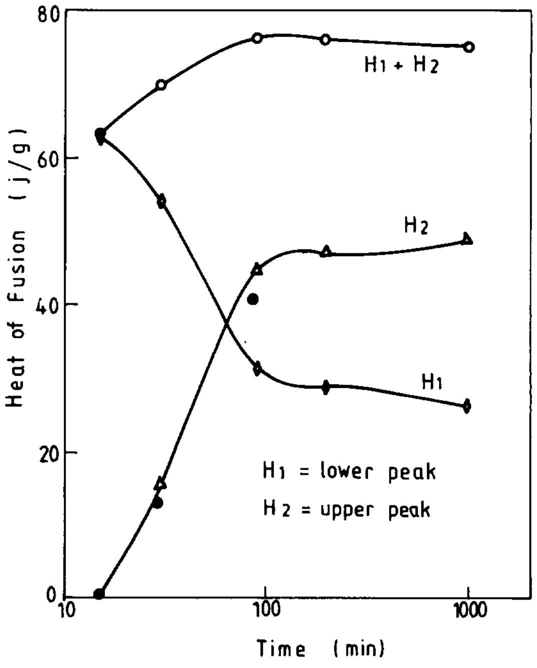

Figure 6 Heat of fusion as a function of crystallization time: (◇) heat of fusion of low temperature peak (H_1); (△) heat of fusion of the high temperature peak (H_2); (●) heat of fusion of high temperature peak, during heating, without intervening cooling; (○) total heat of fusion (H_1+H_2)

Dependence on T_c

For a more detailed investigation, samples were crystallized with the above-mentioned temperature programme at various T_cs between 247°C and 263°C. Crystallization took place overnight to ensure that all the material was fully converted into a crystalline structure, both as assessed by d.s.c. (ΔH reaches a constant value) and by optical microscopy examination of the sample, consisting entirely of negative spherulites. The subsequent exotherms on cooling are plotted in *Figure 8*, whereas the endotherms on reheating the corresponding sample after cooling are shown in *Figure 9*. From *Figure 8* the T_cs can be divided into two distinct regions according to the type of exotherms they yield on cooling. In between these regions an intermediate region can be found, in which no distinct exotherms are observed.

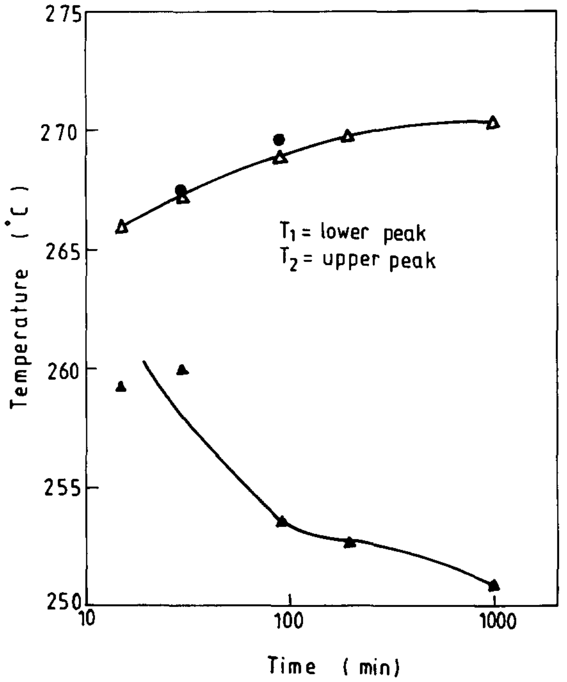

Figure 7 Peak temperature position as a function of crystallization time: (▲) position of low temperature peak (T_1); (△) position of high temperature peak (T_2); (●) position of high temperature peak, during heating, without intervening cooling

Region I. The first region corresponds to temperatures between 255°C and 265°C, where negative spherulites are grown in accordance to the temperature programme employed. In this temperature range a distinct exotherm is observed around 243°C which is consistently present for all T_c in this region. A further, less pronounced and broad exotherm is observed at lower temperatures. Upon reheating the material (*Figure 9*) two endotherms are observed: a broad melting peak around 250°C and a very sharp melting peak at around 270°C, which is clearly identical to the one seen on direct heating. An additional endotherm at around 280°C is found for samples crystallized above 263°C and will be discussed in detail later.

Considering all the results together, the observations can be rationalized as follows. If the material is immediately heated after holding at the T_c, only the sharp melting peak at the high temperature is observed. The size of the peak is similar to that of the high temperature melting peak in the heating experiment after prior cooling. This shows that it is caused by the melting of structures, in this case negative spherulites, formed at the storage temperature (T_c) itself. The broad endotherm on the other hand is related to the melting of crystals that have formed upon cooling. Since the material is fully converted into negative spherulites before cooling, the material that crystallizes on cooling is interfibrillar (or interlamellar) within the negative spherulites. We shall return to this point in the discussion below.

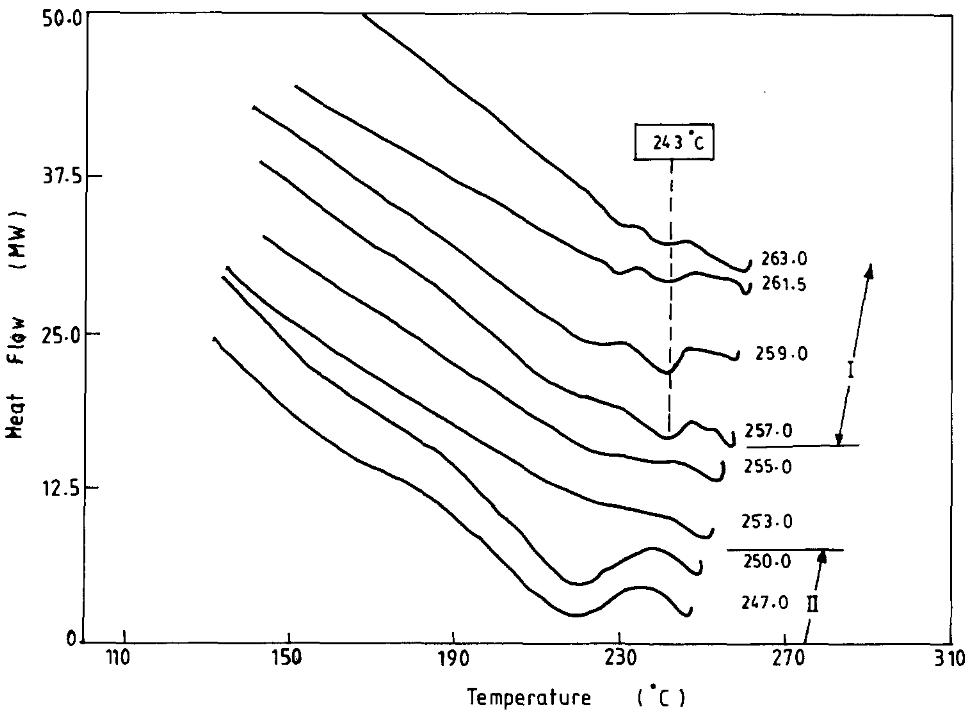

Figure 8 D.s.c. cooling curves of nylon 66 following crystallization for ~15 h at various temperatures

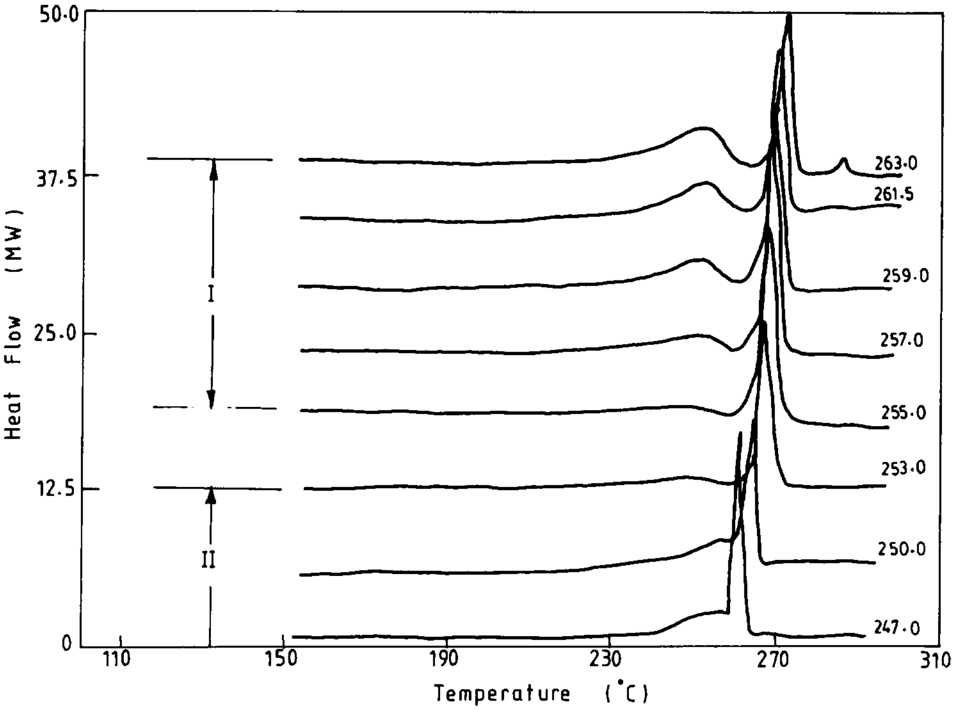

Figure 9 D.s.c. heating curves of nylon 66 after cooling to room temperature and subsequent heating (as illustrated in *Figure 1*)

Region II. In region II ($T_c < 253$°C) a crystallization exotherm around 220°C is observed, which corresponds to the additional crystallization of still amorphous material (*Figure 8*). After heating a similar behaviour is observed as in region I, except that both melting peaks have come closer together (*Figure 9*) with the high temperature peak having shifted slightly towards lower temperatures. The changing position, specifically the upward shift of the low temperature peak, we attribute to the variation of the morphological environment in which the additional crystallization has taken place (not pursued further here). Also upon heating immediately after crystallization at T_c only a sharp endotherm is found. This would suggest that the observed high temperature melting peak in all experiments (both regions I and II) results from the melting of crystals formed at the chosen T_c itself. As the spherulites grown at the low T_cs (within region II) are positive[1] it follows that the unusually sharp high temperature endotherm is not exclusive to negative spherulites but to the high T_c range in question (as compared to the usual crystallization on cooling, *Figure 1*). In fact there seems to be a cut off in T_c by this d.s.c. criterion: the sharp high temperature endotherm appears when T_c is >245°C.

The intermediate region between regions I and II encompasses a very narrow temperature range (253–255°C) and represents the lower limit of the temperature interval where, as reported in part 2, the spherulites grow as non-birefringent spherical (or circular) entities[1]. Samples crystallized in this region do not show any distinct exotherm on cooling.

The endotherm around 280°C (*Figure 9*) appears for samples crystallized at the highest temperatures where, as reported in part 2, the spherulites grow as non-birefringent spherulites (Figure 3 in ref. 1). However, the amount of material that melts at 280°C is small. Conversion of material into these high melting crystals is very slow. The observed melting point is dependent on T_c. The highest value achievable is 285°C obtained for a T_c value of 265°C.

Since crystallization can be promoted by orientation, we investigated the crystallization under shear in the temperature region 263–270°C using a Rheometrics instrument and studied the thermal behaviour of the sheared sample by d.s.c. The d.s.c. trace of the sample sheared in the Rheometrics instrument using a parallel plate cell is shown in *Figure 10* for $T_c = 265$°C. For the present purpose the salient feature of *Figure 10* is the peak at 281.7°C. This peak is still present but less well developed for the lower shear temperatures of 263 and 264°C. Under static conditions in the differential scanning calorimeter it took >20 h to develop this peak; under shear conditions it develops in <15 min. It is also interesting to note that once the melt temperature of 270°C is exceeded this peak does not appear at any T_c, not even under shear. This clearly indicates that this high temperature peak develops only in a very narrow temperature range around 265°C, i.e. the range where the zero birefringent spherulites grow and under the same conditions as required by these spherulites.

Figure 11 is a plot of the melting temperature (T_m) *versus* T_c for all isothermal crystallization experiments performed. In addition to providing an overview it clearly demonstrates that there are two distinct ranges in the T_c, one below and one above the discontinuity around 247°C.

DISCUSSION

General characteristics of the thermograms

In the present paper we have examined the heat effects associated with the formation and melting of morphologies discussed and characterized previously[1] with the aid of polarizing microscopy. First, however, we invoke the principal findings of part 1[2], where it was established by *in situ* X-ray diffraction, that all crystalline structures, at least within melt crystallized material, arise

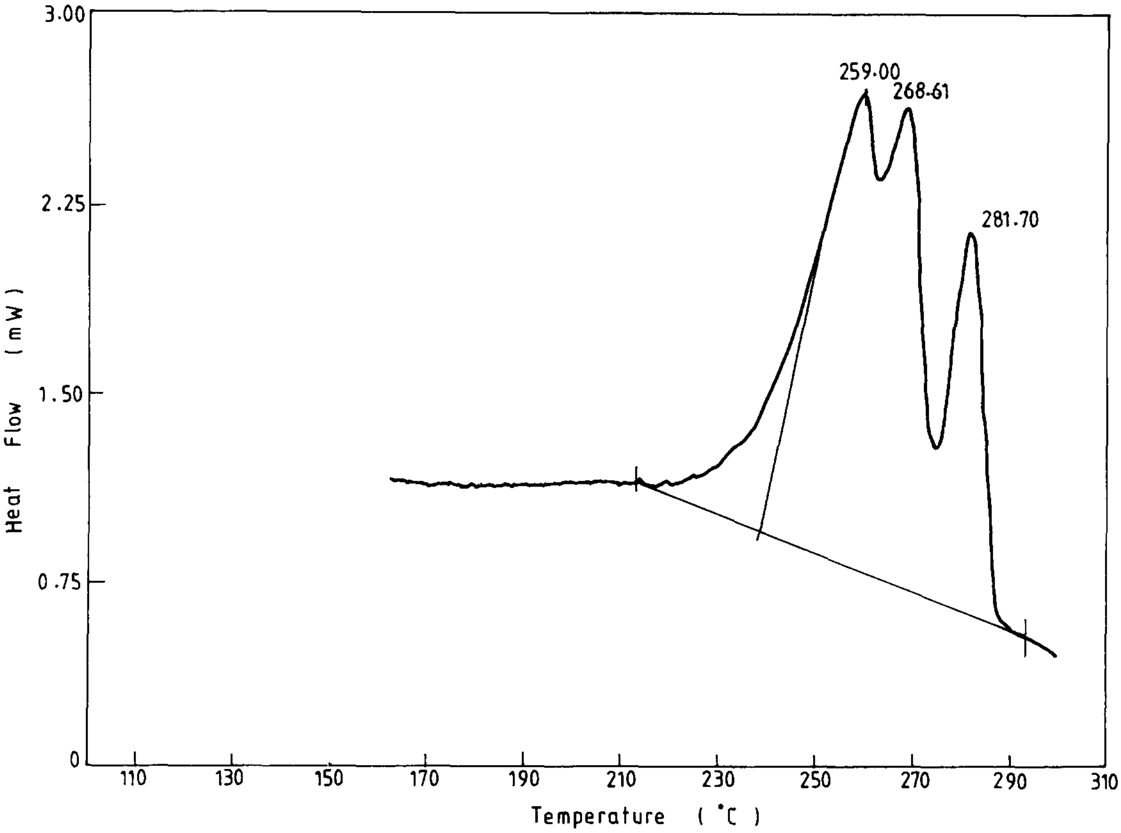

Figure 10 D.s.c. heating curve of material crystallized under shear in the Rheometrics instrument at 265°C

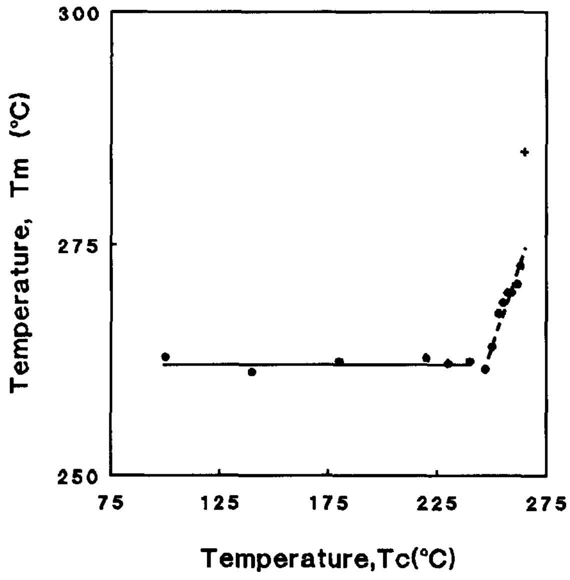

Figure 11 Dependence of the melting temperature on crystallization temperature for nylon 66 [+ refers to high melting endotherm in *Figures 9* (top curve) and *10*]

in the hexagonally packed Brill structure and not in the familiar Bunn and Garner structure. The latter structure was shown to be the result of subsequent first-order phase transformation on cooling to room temperature. This transition temperature itself is found to be related to the preceding T_c and occurs ~40°C below this temperature. It follows therefore that all the heat effects reported in the present paper correspond to the formation (exotherms) or melting (endotherms) of crystals having the Brill structure, and hence all melting points and heats of fusion relate to such a structure. It follows that all the usually reported solid state reorganizations and perfections induced by heat treatment should occur while in the Brill structure. It should be noted that the usual multiple peak thermograms in polymers are attributable to structure rearrangements (e.g. lamellar thickening, refolding) on heating. In the present work we are practically free from such effects: at least those structures which formed at the high temperatures, the focus of our attention, seem by the present results to be immune to such rearrangements. It follows that the thermal peaks in our thermograms relate to structural elements which are primary products of crystallization. Further, except for cases where we were deliberately following the development of structures, we always ensured that the specific morphologies we were to explore calorimetrically were representative of the sample as a whole, in fact the only morphological type present, which enabled a one-to-one correlation between thermal behaviour and morphology. This may not hold for structures that form non-isothermally during cooling. In this case rearrangement could well occur during subsequent heating, which could lead to multiple peak thermograms in d.s.c. as observed previously[3,4]. The top curve in *Figure 5* corresponds to such a case.

Thermal effects for isothermal crystallization at high T_c

It is apparent by comparison of *Figure 2a* with the rest of the thermograms that isothermal crystallization at elevated T_c induces thermal effects which are distinct from those encountered in nylon 66 subjected to more conventional thermal histories. The principal feature is a very sharp endothermic peak at 270°C, lying slightly but consistently above the conventional melting range of nylon 66 (*Figure 11*). The sharpness observed is unusual for a crystalline thermoplastic and is more reminiscent of an isotropization peak in a liquid crystal polymer. The calorimetrically distinct T_c regime is closely defined by the T_m *versus* T_c curve in *Figure 11*. This curve is well approximated by two straight lines, one nearly horizontal (lower T_c) (which almost certainly includes perfection of the less perfect crystals forming at the lower temperatures during the heating run), the other with a steep slope (higher T_c), where the latter comprises the T_c region giving rise to the unusually sharp endotherm of our present concern, extending down to the break in the curve at 247°C.

While it is certainly the case that the melting of all the 'optically unusual' morphological entities, the negative and zero birefringent spherulites and spherulitic aggregates are always associated with such a very sharply peaked endotherm, this attribution is not unique. Namely, the positively birefringent spherulites, such as arise in the high T_c region in question (above the break in the T_m *versus* T_c curve in *Figure 11*) display a very similar feature on melting. Structures formed at high T_c are thus distinct by two criteria: anomalous morphology and associated birefringence; and melting endotherms distinct by sharpness and position where the two criteria are not quite equivalent. The morphological divide (Figure 2 in ref. 1) is at $T_c = 255°C$ and relies on the melt not having exceeded 270°C while the calorimetric divide is at $T_c = 247°C$, i.e. at the break in the T_m *versus* T_c curve in *Figure 11* with no condition regards the preceding melt history.

Effects on cooling from T_c

A further interesting issue is the crystallization and the nature of crystals which form after a sample which had crystallized in the T_c range considered (247–265°C) is being cooled. Here we leave out of consideration experiments such as in *Figures 3* and *4* (except for the bottom curves) where the material has not yet achieved its final crystallinity at the intended T_c: clearly the material which has not been given time to crystallize at T_c will do so on cooling in the conventional manner. Instead we shall focus our attention on cases where crystallization is allowed to go to completion at the intended T_c. We know from the preceding morphological work[1] that here the appropriate spherulite type is occupying the full sample volume, hence 'morphologically' the material is fully crystallized. Any change that is taking place on cooling registered calorimetrically must therefore occur within the spherulites already present. Such is the case for the smaller exothermic peaks in *Figure 8*, the peak around 243°C in region I and the larger but broader peak around 220°C in region II. One may surmise that they correspond to crystallization of the melt which became trapped within the expanding spherulite. However, at least for the range where negative spherulites form, this cannot be the usual crystallization of the melt which at these lower temperatures, corresponding to the cooling exotherms in *Figure 8*, would give positive spherulites on its own. This is because the visual image of the negative spherulites does not change on cooling: the negative spherulites stay negative and in fact become brighter, hence even more negatively birefringent. This means that the newly crystallizing material conforms to the texture already present, thus enhancing it, even under conditions where it would form different morphology if it crystallized on its own. (The same applies for the zero birefringent spherulites which stay unaltered even on cooling, but in view of the fact that there is no or little additional crystallization on cooling the issue does not forcefully arise.)

Further, for the 243°C exotherm at least, even more basic factors seem to be involved. It is seen from cases such as in *Figure 4* that the exotherm peak at 243°C actually develops together with the source of the main endothermic peak (which arises on melting the same sample). It follows that the exotherm at 243°C must be intrinsically and exclusively associated with such spherulites. Unless it is due to some uncrystallized material specially constrained by such spherulites the observation suggests a transformation within crystals already constituting such spherulites, which would occur on cooling. Whatever the source of the effects, they are bound to have an influence on the final structure and properties of such materials at room temperature in which respect the differences between those obeying regions I and II must also be of consequence.

Most intriguing is the situation for the intermediate region around $T_c = 253°C$. Here in this range, morphologically corresponding to the low T_c version of zero birefringent spherulites[1], there is no exotherm on cooling, as if there was no uncrystallized material present in those zero birefringent spherulites and/or as if no subsequent transformation took place within them. Besides placing these observations on record we have no explanation to offer at this stage.

Clearly *Figures 8* and *9* raise several further questions. Foremost amongst them is the balance between exotherms and endotherms and the overall degrees of crystallinity in the final stage and at the different stages along a given thermogram. For example, by inspection there seems to be more material crystallizing on cooling the morphologically fully crystallized sample from a lower T_c (lying in region II) than from the higher T_c (region I) and practically none crystallizing on cooling from T_c in the intermediate region. By conventional argument this would imply that the latter sample is the most crystalline. While this seems to go against conventional credibility, this and similar other possibilities clearly invite further investigation. Whatever the uncertainties may be at the present stage, the systematic differences between the samples crystallized at different T_c are firmly established by the present experiments.

The melting peak at 280–285°C

The highest temperature endotherm (above 280°C, with a maximum attainable value of 285°C) deserves special comment. First, this melting point is distinct as there is nothing between 273°C and 280°C. There is no gradual shift of the melting point in the upward direction. With regards to its origin there seems to be a correlation with the conditions giving rise to the higher temperature version of zero birefringent spherulites (Figure 2 in ref. 1): it arises at the same T_c where those zero birefringent spherulites also form and requires the same restrictions on melt history, namely that the melt should not have reached temperatures above 270°C. The structures melting at 282°C are not identical to those constituting the zero birefringent spherulites, but develop very slowly after the above spherulites have already formed. (The 270°C peak has already developed when the 280–285°C peak starts to appear — see top curve in *Figure 9*). The above points to the possibility that the

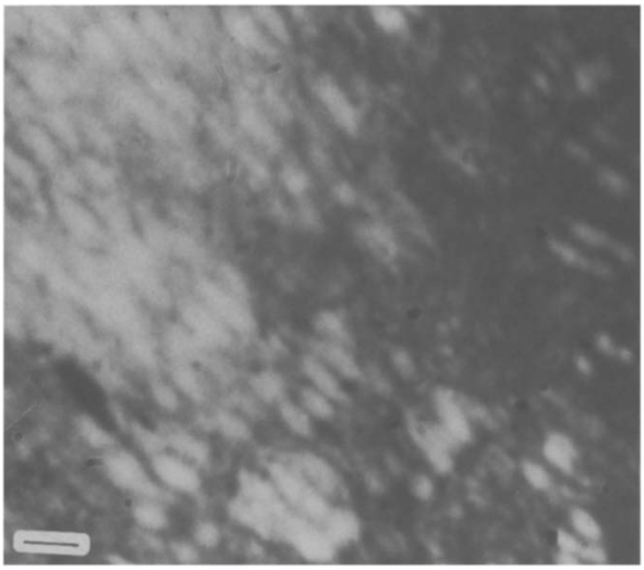

Figure 12 Polarized light micrograph of disc-shaped crystals, obtained during crystallization at 265°C under shear flow. The photograph was taken at 282°C (scale bar = 20 μm)

high melting crystals originate from the (high temperature variant) zero birefringent spherulites themselves, e.g. through a large discontinuous increase in lamellar thickness.

The promotion of the crystals with $T_m > 280°C$ by shear flow is certainly most notable and provides a good means for further study without requiring excessive storage times at elevated temperature with the associated hazard of degradation. It is to be noted that here we are not dealing with chain extension induced crystallization as in the familiar shish-kebab formation of polyethylene. First, even a cursory examination under the polarizing microscope revealed that shear flow also promoted all other kinds of crystallization, including that of negative spherulites, by reducing their time of formation. Second, the same scouting tests with the polarizing microscope showed no evidence of the well known shish-kebab or row-type structures or any fibrosity appearing. The field of view is essentially spherulitic with small patchy and elongated disc-shaped birefringent regions which are aligned in a given direction and persisted to the highest temperatures (284°C) when heated on the microscope hot stage (*Figure 12*). The latter are almost certainly the high melting crystals in question which we had no opportunity to explore further. With regards to the effect of the shear flow, this is likely to be merely through the raising of the stored energy which can influence phase transitions by raising the transition temperatures, analogously to the well documented case of producing liquid–liquid phase separation in solutions through shear flow in a rheometer[5], rather than through the direct molecular effect of chain stretching. However, whatever the origin and structure, it represents a more stable thermodynamic state than either the positive or negative or non-birefringent spherulites or the spherulitic aggregates, if not the state of ultimate stability itself. Looking at it from another way, in view of the recognition of the existence of this high temperature form, all the other forms just listed must necessarily be classified as corresponding to metastable states. There are precedents of high melting nylon crystals in the literature; the ones appearing closest to the present work are those reported by Starkweather and Jones[6], who also found an endotherm at 282°C on samples extruded between 260°C and 270°C.

Some general issues on melt history

It will be recalled that all the thermal effects referred to in this paper, together with the underlying morphologies[1], have arisen from the Brill structure[2] and hence are characteristic of this latter structure. As discussed in part 2, the unusual structures in question are dependent on melt history, which, by the arguments in part 2, implies differences in melt states, most plausibly related to the degree and geometry of hydrogen bonding corresponding to both equilibrium and non-equilibrium states[1]. Clearly the same should apply to the associated thermal effects explored in the present paper. In addition to the structures explored morphologically in part 2 and studied further for thermal effects in the present paper, the thermal studies revealed a further structure with a high melting point (>280°C), which has previously escaped our attention[1]. Reverting to a morphological exploration of this newly indicated structure, beyond the cursory observations quoted above, is clearly called for, but this lies beyond the practical possibilities of the present programme. It is clear even at this stage, that this new structure also relies on melt history, hence on the existence of some kind of melt structure indicated throughout this programme of work. Following up the nature of melt structures, most obviously through systematic recording of hydrogen bonding, in the light of the various crystal varieties arising from the assumedly different melt states, would clearly be the next step forward.

CONCLUSIONS

The first most salient conclusion which arises[2] is the fact that all crystallization (and melting) takes place in a high temperature crystal structure (the Brill structure) which is different from the structure registered by usual investigations at ambient temperature. It follows that for a meaningful interpretation of the crystallization process, and for an understanding of the resulting structures and properties one needs to relate these to the Brill structure and not to the transformed structure at room temperature as usually implied in such works. It is then a further matter as to what the Brill structure really is, particularly in terms of hydrogen bond content and geometry. One of the most important questions, which arises in polyamides, is in fact whether there is a single unique high temperature structure with associated hydrogen bonding at all, or whether there is instead a more or less continuous gradation of such structures within a broader range which we here term Brill structure. The present work provides at least a few pointers in this direction.

In continuity with previous works a puzzling wealth of features, on the level of the polarizing microscope, are apparent[1]. These are forming in the temperature range which is straddling the conventional melting region of nylon 66, and are often of striking visual appearance. Conditions of their formation have now been more closely defined with some new features added, possibly the most important of which is their effect on melt memory with ensuing influence on subsequent crystallization. In molecular terms these structures are still inadequately characterized, let alone understood, but some of the effects associated with them (e.g. the overall appearance of negative spherulites, the occasionally observed deformability and the presently investigated sharp melting endotherms) give the impression of a distinct state of matter, intermediate between crystal and melt, rather than that of a conventional crystal. This last issue, together with the nature of the melt state from which such structures arise, calls for further examination.

Finally, the thermal effects associated with the above structures display a wealth of features matching those displayed by the morphology. In addition to providing much more information on those structures they are indicative of the varied richness of effects which characterize the high temperature behaviour of polyamides.

ACKNOWLEDGEMENT

Financial support by DSM Research, The Netherlands, is gratefully acknowledged.

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