Studies on the crystallization and melting of nylon-6,6: 1. The dependence of the Brill transition on the crystallization temperature

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The isothermal crystallization process from the melt in nylon-6,6 was followed in situ by X-ray diffraction. At all the crystallization temperatures studied, the samples crystallized into the pseudohexagonal (hexagonally packed) Brill structure, which transformed into the triclinic structure on subsequent cooling to room temperature from the crystallization temperature. This transition occurs about 40°C lower than the respective crystallization temperature. Also the transformation temperature (TB) displays a hysteresis effect on heat cycling, with Ts being higher on heating than on cooling. These findings affirm the first-order transition character of TB, contrary to some previous suggestions. They also imply gradation in perfection and/or crystal size while in the Brill structure. It follows further that any difference in structure and property, as determined at room temperature, must reside in the Brill structure at the stage of formation and can only be reflected indirectly by the transformed structures observed at room temperature. With reference to spherulites, the latter has important implications for the arrangement of hydrogen bonding within the Brill structure. On the other hand, crystallization directly into the triclinic Bunn structure remains a possibility for crystallization from solution, awaiting confirmation by X-ray diffraction.

(Keywords: nylon-6,6; crystallization; Brill transition)

INTRODUCTION

Nylon-6,6, the commercially most successful polyamide, shows a crystal-to-crystal transition on heating, which is known as the Brill transition1. The room-temperature triclinic structure transforms into a pseudohexagonal structure at elevated temperatures, and the transition is reversible. Early workers2,3 suggested that the two-dimensional hydrogen-bonded sheets in the triclinic structure are changed to a three-dimensional hydrogen-bonded network between the chains. However, an alternative model has been proposed4,5, in which the high-temperature form is also triclinic with the hydrogen bonds arranged in sheets but the projection along the c axis has hexagonal symmetry. This model is accepted by many workers6-11. Irrespective of whether the structure is truly hexagonal or pseudohexagonal, the hexagonal packing of chains remains a common feature. We shall therefore adopt the term 'Brill structure' as a collective designation for the possible hexagonally packed high-temperature structures. The nature of the Brill transition (TB) is considered to be the effect of conformational motion due to temperature and is associated with a packing change within the crystal1.

The Brill transition is most clearly displayed in X-ray diffraction studies, as the two strongest reflections of nylon-6,6, the 100 and 010/110 reflections, merge into a single reflection at the transition. Other techniques such as d.s.c. are less sensitive, and in general do not show the Brill transition by way of a distinct endothermic peak. However, for solution-precipitated samples, a small endotherm around 200°C is identifiable with the Brill transition12.

Most existing studies4-9 that deal with the Brill transition have been carried out with precrystallized samples and look at the transformation from the triclinic to the hexagonally packed form during heating. At this stage the obvious question arises: Does nylon-6,6 crystallize directly into the triclinic structure or alternatively first, into the pseudohexagonal structure, which then transforms into a triclinic structure on cooling? Nylon-6,12 has been shown, when heated from the quenched amorphous state, to crystallize into the hexagonal structure for all crystallization temperatures (To) and transforms into the triclinic structure immediately below To on subsequent cooling12.

In the present work we studied the crystallization of nylon-6,6 at different temperatures and recorded the Brill transition on cooling from the respective To using a hot stage attached to an X-ray diffractometer. Subsequent parts of the series will deal with the spherulitic morphology (part 2) and with calorimetric effects associated with crystallization and melting (part 3).

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EXPERIMENTAL

The nylon-6,6 used in this study has a molecular weight of 49 kg mol⁻¹, determined by viscosimetry in H₂SO₄ (96%) at 25°C.

Sample preparation (melt crystallization)

The samples were prepared by pressing in a hot press at 285°C and then crystallized at 240°C for about 3 h under pressure. WAXS patterns of these samples showed no preferred orientation in the sample.

X-ray diffraction studies were carried out using a Philips diffractometer with Cu radiation (50 kV, 40 mA) in combination with an Anton Paar high-temperature X-ray cell. The cell was flushed with oxygen-free dry nitrogen to reduce sample degradation at high temperatures. To ensure that the sample temperature was accurately monitored, an extra-fine thermocouple was placed on the sample surface. The sample was placed in the sample holder and heated to the test temperature and held there for a minute to stabilize the temperature. The sample was then scanned from 15 to 30°C in the step scan mode with a step increment of 0.05°C. The time taken to complete a scan was about 5 min. After the scan the temperature was changed to the next test value.

The isothermal crystallization process was monitored by X-ray diffraction. The crystallization temperatures were 260, 240, 232 and 196°C. The samples were initially melted and then cooled at a rate of 50°C min⁻¹ to the respective crystallization temperatures. The development of the crystalline structure with time during isothermal crystallization was studied by scanning the sample at regular time intervals. After the crystallization the change in the crystal structure with temperature was monitored by scanning at different temperatures as the sample was cooled to room temperature.

Sample preparation (solution crystallization)

Solutions of nylon-6,6 in 1,4-butanediol (0.04% (w/v)) were prepared by dissolving at about 200°C. Crystals were grown isothermally at 120 and 155°C. The solution was hot filtered at the crystallization temperature after the completion of crystallization. The samples were washed in acetone and dried overnight in a vacuum oven at 65°C. A Perkin–Elmer DSC7 was used to characterize the samples. The samples were grown isothermally at 120 and 155°C. The solution was hot filtered at the crystallization temperature after the completion of crystallization. The samples were washed in acetone and dried overnight in a vacuum oven at 65°C. A Perkin–Elmer DSC7 was used to characterize the samples during heating. The heating rate was 10°C min⁻¹ and the experiments were carried out in a nitrogen environment.

Deconvolution procedure

It is apparent from the X-ray scans that in the transition regime the position of the 010/110 reflection can only be fixed by deconvoluting the 100 and 010/110 peaks. The diffraction profile is assumed to be the sum of three Pearson VII peaks (two crystalline peaks and an amorphous peak) and a linear background. In the fitting procedure it is assumed that the position of the amorphous peak depends only on temperature and not on the crystalline peak positions.

To increase the confidence of fitting, particularly in the temperature range where the crystalline peaks overlap, the amorphous peak position was fixed by interpolating the amorphous peak position obtained at temperatures well below Tₘ, where the crystalline peaks are well separated, and above Tₘ, where the crystalline and amorphous peaks are well separated (see Figure 1).

RESULTS

Demonstration of Tₘ on heating

First we will demonstrate the well documented effects of transformation and melting as a crystalline sample is heated to above the melting temperature Tₘ. The X-ray diffraction pattern during heating from room temperature to melting is shown in Figure 1. These patterns appear similar to those reported by Murthy et al.¹⁰ and Hirschinger et al.¹⁵. At room temperature the two strong hko reflections due to the triclinic structure are seen at diffraction angles 20.40° and 23.88°. With increasing temperature these two reflections converge and merge into one peak at the Brill temperature (T₀). From thereon only one reflection is seen at higher temperatures up to melting at 265°C. The peak intensity of the combined reflection of the new phase increases before decreasing due to the onset of melting. Another notable feature is the position of the amorphous peak. At room temperature it is between the two triclinic crystalline peaks, and at temperatures close to Tₘ it moves towards lower diffraction angles, indicating that the average distance between the chains in the amorphous phase has increased with increase in temperature.

The variation of the d-spacings with temperature is shown in Figure 2. The 100 spacing (d_{100}), the distance between the 100 planes, which is largely fixed by the hydrogen bonds and hence is less sensitive to temperature variation, shows an appreciable decrease close to the...
transition. On the other hand, \( d_{010/110} \) the spacing due to the doublet reflection of the 010 and 110 planes, shows a dramatic increase with temperature and equals the value of \( d_{100} \) at the transition. Above \( T_B \) the two spacings remain equal on further raising the temperature. The \( d \)-spacing of the combined reflections shows a slight increase with increase in temperature above \( T_B \) before decreasing very close to \( T_m \).

**Isothermal crystallization**

The course of isothermal crystallization at 260°C as followed by X-ray diffraction is shown in Figure 3. The crystalline peak slowly develops with time, as expected, because the supercooling is very low. The crystallization process at 240 and 230°C is very rapid but shows a similar trend. On the other hand, for the \( T_c \) of 196°C the sample displays appreciable crystallinity immediately after reaching 196°C from the melt. It will be shown below that here the sample has crystallized to a limited extent during cooling down to the intended \( T_c \) and that portion has already started transforming into the triclinic structure by the time \( T_c \) was reached.

It is seen from Figure 4 that during isothermal crystallization the sample always crystallized in the Brill structure. Indeed, this is the case for all \( T_c \) values investigated. A closer look at the pattern of the sample crystallized at 196°C will show that the tail on the higher-angle side of the single peak has more intensity than in the patterns for higher \( T_c \). In fact, the deconvolution procedure showed the presence of a small peak due to the 010/110 reflection. At first sight one may conclude at this stage that at 196°C a small portion of the sample crystallizes into the triclinic structure. However, on cooling a clear Brill transition becomes apparent (indicated by the relatively small but abrupt change in \( d_{100} \) around 160°C, indicating that the sample had crystallized into the hexagonally packed structure at 196°C. The small peak is due to material that has crystallized before reaching the intended \( T_c \) and has started transforming into the triclinic structure by the time \( T_c \) (for discussion on \( T_c \) dependence of \( T_B \), see below). Nevertheless, the amount of material transformed is rather small and the Brill structure still characterizes the bulk of the material. The \( d \)-spacing in the Brill structure shows a small decrease with time during crystallization, indicating the perfectioning of crystals with time.

**Cooling following isothermal crystallization**

On cooling from \( T_c \) at some stage the Brill structure formed initially transforms into the triclinic structure by the appearance of a new peak corresponding to the 010/110 reflection as seen in Figure 5. However, unlike nylon-6,12, which shows the transformation immediately at the start of cooling, for nylon-6,6 it occurs at temperatures considerably lower than the corresponding \( T_c \). This can be seen more clearly from Figure 6, which shows \( d \)-spacing as a function of temperature during cooling for all the \( T_c \) values examined. It is apparent from...
The present experiments thus lend further support to past data which are all confined to extensive past literature on the subject, to which they are quoted here merely for these d.s.c. runs could not be paralleled by X-ray diffraction experiments. They are quoted here merely for the melt-crystallized specimens (see below).

A small endothermic peak around 200°C in the d.s.c. trace was observed on heating the solution-crystallized sample (melt-crystallized samples do not display this effect). This peak was identified with the Brill transition \( \Delta T \). As seen, \( T_c - T_b \) is roughly constant in the range of 35-40°C for different \( T_c \) values. On cooling below \( T_b \) the split between the 100 and 010/110 reflections increases owing to a large decrease in \( d_{1010/110} \) and a smaller increase in \( d_{1100} \). We note that these effects depend on \( T_c \), and through it on \( T_b \).

It is of interest to compare the transition from the Brill structure to the triclinic structure (during cooling from \( T_b \)) with the reverse transition from the triclinic to the Brill structure on heating (from room temperature to the melting point). Such a study was carried out for the sample crystallized at 196°C, and Figure 7 shows the d-spacings during both a cooling and a heating cycle. As seen, the d-spacings do not show appreciable differences up to quite elevated temperatures, where they start to diverge, leading to a \( T_b \) that is 20°C higher for heating than for cooling from the crystallization temperature.

**Table 1** Crystallization temperature \( (T_c) \) and Brill temperature \( (T_b) \) for melt-crystallized samples

<table>
<thead>
<tr>
<th>( T_c ) (°C)</th>
<th>( T_b ) (°C)</th>
</tr>
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<tbody>
<tr>
<td>196</td>
<td>160</td>
</tr>
<tr>
<td>222</td>
<td>190</td>
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<td>260</td>
<td>225</td>
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![Figure 7](image-url) The variation of \( d_{100} \) and \( d_{010/110} \) spacings with temperature on cooling to room temperature from \( T_c = 196°C \) and on subsequent heating to melting point \( (\circ) \) on cooling; \( (\bullet) \) on heating.

**DISCUSSION**

While some of the findings here are contained in the extensive past literature on the subject, to which they thus lend further support, past data are all confined to effects observed on heating. The present experiments represent a new departure involving in situ isothermal crystallization from the melt with emphasis on the crystallization process itself not previously considered in the context of the crystal structure. It has emerged as a principal conclusion that crystallization from the melt takes place directly into the Brill structure, which then transforms at \( T_b \) into the triclinic structure on cooling to room temperature.

In the course of the experiments establishing the above fact, it emerged that the value of \( T_b \) which according to the above is necessarily lower than \( T_c \) is dependent on \( T_c \) with \( T_c - T_b \) being approximately constant, i.e. essentially independent of \( T_c \). This gives rise to a substantial temperature interval roughly 40°C below \( T_c \) where the Brill structure can exist as a stable modification.

When adding to the above the hysteresis effect observed, namely that for a given \( T_c \) the Brill transition is attained only at a higher \( T \) on heating than observed on preceding cooling (i.e. \( T_c > (T_b)_\text{heat} > (T_b)_\text{cool} \)), two important conclusions can be reached. Firstly, the Brill transition may be a first-order transition. This point has been an issue of uncertainty and debate. Mainly because of the absence of a clear endotherm in the pertinent thermograms, the first-order transition character of the structure change, as registered by X-ray diffraction, has been queried, suggesting anisotropic thermal expansion as the only process taking place without any discontinuity (larger increase in \( d_{010/110} \) than in \( d_{100} \) on heating until the two merge; in fact, crossing of the two spacings has also been reported, but in the light of the present work, and also of that in ref. 7, this can be discarded). Later a small endotherm corresponding to \( T_b \) has been observed on material crystallized from solution, an effect re-emerging also in the present work. Even so, there has been hesitancy in assigning \( T_b \) to a first-order transition. The presently observed hysteresis on cooling and heating, however, conclusively favours the attribution of a first-order transition to \( T_b \). In fact, such a hysteresis would be inconceivable for mere thermal expansion.

Secondly, the dependence of \( T_b \) on \( T_c \) implies a gradation of order in the perfection of the Brill structure, determined by the crystallization temperature. Higher perfection may represent a better ordered lattice, e.g. with fewer defects, or larger crystal size, or both factors together. Of course, larger lamellar thickness for higher \( T_c \) is the well documented situation in chain-folded crystals, but so far we do not have sufficient information on the lamellar thickness of our present system to allow correlation with \( T_b \).

In view of the newly established fact that crystallization always occurs in the Brill structure, it follows that any structural feature or property, such as we may observe at room temperature, relates not directly to the crystal structure in which the sample initially solidified, but to one that is the product of transformation. It follows further that, as far as there are features at room temperature that are affected by \( T_c \), these do not relate directly to the primary crystallization process itself. Thus spacings \( d_{100} \) and \( d_{010/110} \) are known to depend on \( T_c \) but by the present findings (Figure 6) this dependence seems to relate more directly to \( T_b \). As seen from Figure 6, changes in spacing on cooling (decrease in \( d_{010/110} \) and a smaller increase in \( d_{100} \)) appear to be the same function of \( T \) in the course of cooling, but are displaced along the \( T \) axis for different \( T_c \) values, the appropriate

**Figure 6** The variation of \( d_{100} \) and \( d_{010/110} \) spacings with temperature on cooling to room temperature from \( T_c = 196°C \) and on subsequent heating to melting point \( (\circ) \) on cooling; \( (\bullet) \) on heating.

**Figure 7** The variation of \( d_{100} \) and \( d_{010/110} \) spacings with temperature on cooling to room temperature from \( T_c = 196°C \) and on subsequent heating to melting point \( (\circ) \) on cooling; \( (\bullet) \) on heating.
$T_B$ being the starting point in each case. Thus the variation in spacing with $T_c$ at an appropriately lowered temperature does not establish itself at $T_B$, where all the relevant spacings are equal, but through the differences in the process of transformation. Clearly, the source of the difference must reside already at $T_c$ (within the Brill structure) where so far no difference has been seen, at least not by the methods employed.

It is known from past works that a hexagonally packed structure can be preserved on rapid quenching from the melt.

The last points, those relating to solution crystallization, bring in the issue of the growth direction in the course of crystallization. In melt crystallization, on the level of polarizing microscopy, this corresponds to the radial direction of the spherulite. In the case of the most common positive spherulites, this corresponds, by definition, to the direction of highest polarizability in terms of the optics of the spherulites. In view of the fact that the chains are tangentially oriented, the positive birefringence can only arise by a direction of high polarizability being radial, more than compensating for the overall highest polarizability along the chain direction as averaged with the direction of least lateral polarizability, a situation recognized early by Bunn and Garner. In terms of the triclinic structure, this condition is fulfilled by the 010 planes lying parallel to the radius, which has in fact been verified by X-ray diffraction.

The fact brought in focus by the present work, that the same positive birefringence applies even in the Brill structure, means that the same directional preference of groups of high polarizability must be present also in this case, i.e. that all lateral directions are not equivalent despite the hexagonal packing of the chains, specifically that the distinctness of the 010 planes is retained. This in turn implies the retention of at least a sizeable portion of the hydrogen-bonded sheet structure of the low-temperature triclinic phase (Bunn structure) within the Brill structure. The fact that this applies not only for heating but also for the spherulites formed in situ at $T_c > T_B$ means that it is not a memory effect but an effect associated with the Brill structure as in equilibrium. Clearly this point leads to the all-important issue of existence, or otherwise, of the preferential hydrogen-bond directions within the Brill structure, which, however, will not be further pursued at this stage: it is the subject of modelling work being pursued by Atkins et al. in the Bristol laboratory.

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