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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(Received 11 June 1993)

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 (T_B) displays a hysteresis effect on heat cycling, with T_B being higher on heating than on cooling. These findings affirm the first-order transition character of T_B, 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 transition[1]. The room-temperature triclinic structure transforms into a pseudohexagonal structure at elevated temperatures, and the transition is reversible. Early workers[2,3] 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 proposed[4,5], 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 workers[6–11]. 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 (T_B) is considered to be the effect of conformational motion due to temperature and is associated with a packing change within the crystal[1].

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 transition[7,12].

Most existing studies[4–9] 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 (T_c) and transforms into the triclinic structure immediately below T_c on subsequent cooling[11].

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 T_c 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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0032-3861/94/12/2483–05

EXPERIMENTAL

The nylon-6,6 used in this study has a molecular weight of 49 kg mol^{-1}, determined by viscosimetry in H_2SO_4 (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 combintion 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 sample 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 T_B, where the crystalline peaks are well separated, and above T_B, where the crystalline and amorphous peaks are well separated (see *Figure 1*).

RESULTS

Demonstration of T_B *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 T_m. 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.*[8]. At room temperature the two strong $hk0$ reflections due to the triclinic structure are seen at diffracting angles 20.40 and 23.88°. With increasing temperature these two reflections converge and merge into one peak at the Brill temperature (T_B). 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 T_m it moves towards lower diffracting 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

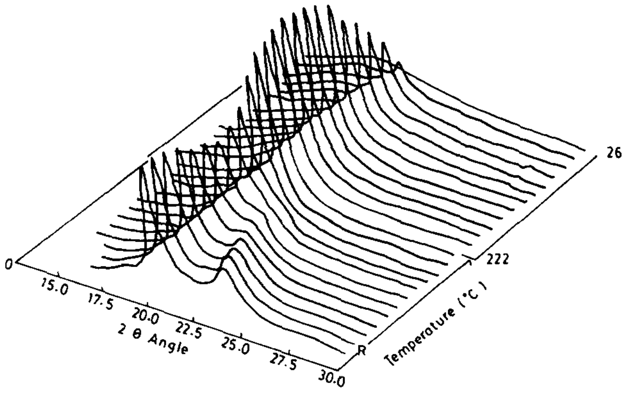

Figure 1 Three-dimensional view of the X-ray diffraction patterns of nylon-6,6 on heating from room temperature to melting

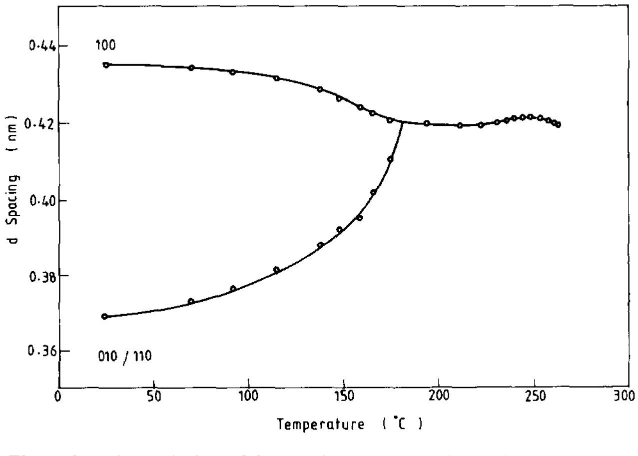

Figure 2 The variation of d_{100} and $d_{010/110}$ spacings with temperature on heating from room temperature to melting

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 at 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 drystallization, indicating the perfectioning of crystals with time.

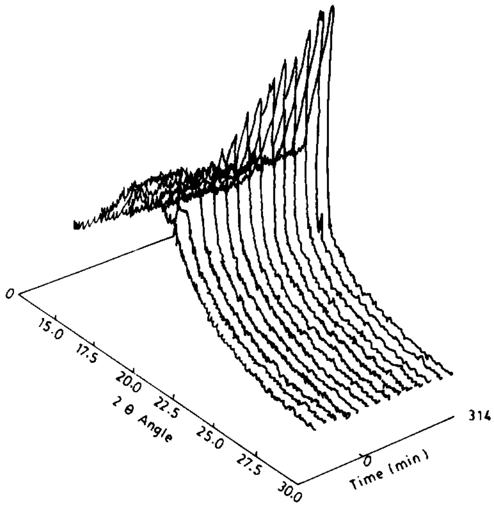

Figure 3 Three-dimensional view of the development of the X-ray diffraction pattern during isothermal crystallization at 260°C

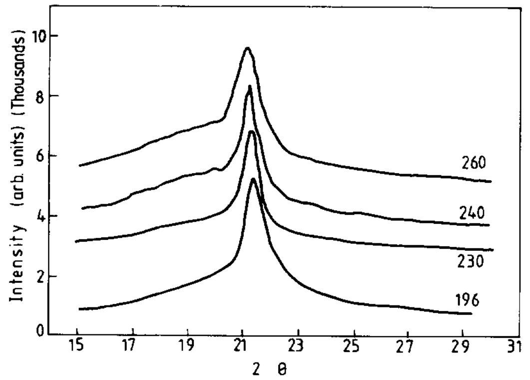

Figure 4 X-ray diffraction pattern at the end of crystallization for various crystallization temperatures (260, 240, 232 and 196°C)

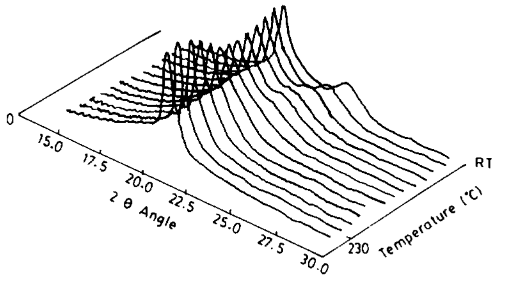

Figure 5 Three-dimensional picture of the X-ray patterns on cooling from T_c = 232°C to room temperature

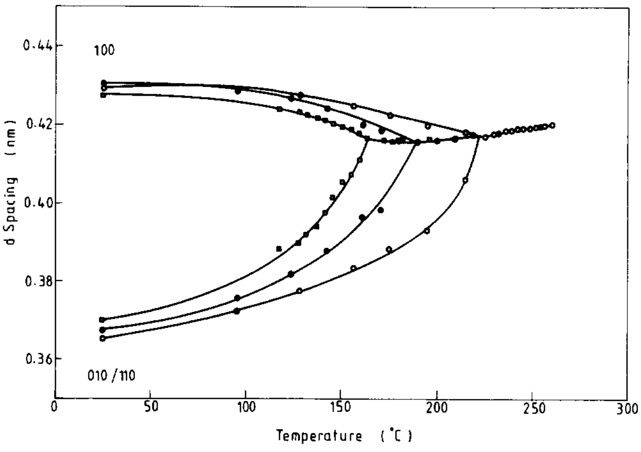

Figure 6 The variation of d_{100} and $d_{010/110}$ spacings with temperature on cooling to room temperature from T_c: (○) 260°C; (●) 232°C; (□) 196°C

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[11], 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

Table 1 Crystallization temperature (T_c) and Brill temperature (T_B) for melt-crystallized samples

T_c (°C)	T_B (°C)
196	160
232	190
260	225

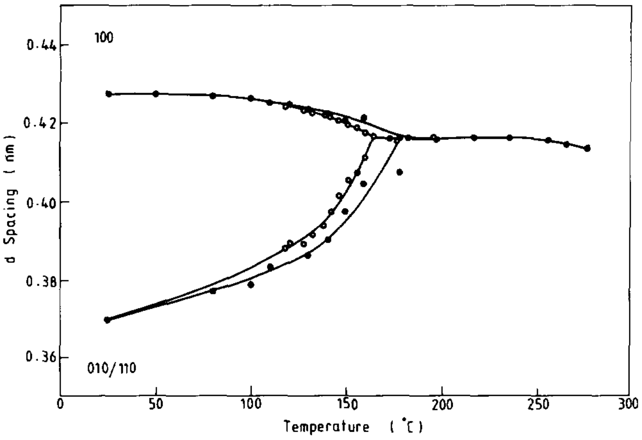

Figure 7 The variation of d_{100} and $d_{010/110}$ spacings with temperature on cooling to room temperature from $T_c = 196°C$ and on subsequent heating to melting point: (○) on cooling; (●) on heating

Figure 6 that T_B for nylon-6,6 depends on the crystallization temperature. *Table 1* gives values for T_c and the corresponding T_B. 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 of $d_{010/110}$ and a smaller increase in d_{100}. 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_c) 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.

T_B *of solution-crystallized samples*

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 peak). This peak was identified with the Brill transition[7,12]. The T_B values for the samples crystallized at 125 and 155°C, as measured by d.s.c., were 176.6 and 192.2°C, respectively. Owing to circumstances beyond our control, these d.s.c. runs could not be paralleled by X-ray diffraction experiments. They are quoted here merely for the record and for the possible differences compared to the melt-crystallized specimens (see below).

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. $T_c > (T_B)_{heat} > (T_B)_{cool}$), two important conclusions can be reached.

First, the Brill transition must 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[5], 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[6], 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[7], an effect re-emerging also in the present work. Even so, there has been hesitancy in assigning T_B to a first-order transition[12]. 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

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_c, 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[13,14]. This seems to support the present findings of crystallization into the Brill structure, which is then quenched-in on rapid cooling. By the earlier alternative interpretation, given in ref. 14, the resulting crystals may just be too imperfect in such rapid crystallization to give rise to the fully developed lateral order, hence to the final three-dimensional lattice. The two fundamentally different cases, namely a quenched-in Brill structure, itself an equilibrium structure above T_B, or an imperfectly formed crystal, would not be distinguishable through $hk0$ reflections, a situation calling for renewed examination.

Having recognized the above, the question arises as to which features in structure and property, as observed at room temperature, are already present at T_c, i.e. in the primary Brill structure, and which arise during transformation on cooling. Foremost amongst these is the nature of the spherulites as identified by polarizing optics. Our recent studies on spherulites will be contained in separate papers[15,16]. Here it will merely be recalled that nylon spherulites are usually of positive birefringence. However, under special circumstances, negative and zero birefringent spherulites can also arise, together with entities of especially high birefringence of not readily identifiable sign (the so-called aggregates). By our findings all of these morphological features are associated with the Brill structure, in which they arise with their final birefringence characteristics, which do not change on subsequent cooling through T_B. This finding acquires particular importance for the most common positive spherulites, a point to which we shall return below.

All the above points referred to crystallization from the melt. The situation for solution crystallization seems to be different as to the structure into which nylon crystallizes. By our own fragmentary work briefly mentioned in this paper, and by information from the literature[7,12], it may appear that the crystals grow directly into the triclinic phase. Certainly, as registered by d.s.c. on solution-crystallized samples, which had been cooled from T_c and then dried in the course of heating, T_c is lower than T_B. This inference, however, need not be taken as conclusive, because here, in contrast to the melt case, the observation was not made *in situ* and the sample could have changed in the course of the treatment it had received before the registration of T_B. Even so, allowing for the above loophole, direct crystallization into the triclinic structure remains a strong possibility, which would clearly differentiate between melt and solution crystallization in a way not previously foreseen. Observations of lath-shaped crystals, elongated along the a direction with hydrogen-bonded planes running parallel to the long lath faces, are at least consistent with crystallization directly into the triclinic structure[17,18].

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 polarizating 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[19]. 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[20,21]. 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[22].

ACKNOWLEDGEMENTS

The authors wish to thank J. Moonen, W. Ramaekers, S. de Boer and W. Roovers from DSM Research for their help during the course of this work. Financial support by DSM Research, The Netherlands, is gratefully acknowledged.

REFERENCES

1 Brill, R. *J. Prakt. Chem.* 1942, **161**, 49

2 Brill, R. *Makromol. Chem.* 1956, **18/19**, 2940

3 Schmidt, G. F. and Stuart, H. A. *Z. Naturforsch.* 1958, **13a**, 222

4 Cannon, C. G., Chappel, F. P. and Tidmarsh, J. I. *J. Text. Inst.* 1963, **54**, T210

5 Colclough, M. L. and Baker, R. *J. Mater. Sci.* 1978, **13**, 2531

6 Itoh, T. *Japan J. Appl. Phys.* 1976, **15**, 2295

7 Starkweather, H. W., Jr and Jones, G. A. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 467

8 Hirschinger, J., Miura, H., Gardner, K. H. and English, A. D. *Macromolecules* 1990, **23**, 2153

9 Lovinger, A. J. *J. Appl. Phys.* 1978, **49**, 5003

10 Murthy, N. S., Curran, S. A., Aharoni, S. M. and Minor, H. *Macromolecules* 1991, **24**, 3215

11 Biangardi, H. J. *J. Macromol. Sci.-Phys. (B)* 1990, **29**(2/3), 139

12 Xenopoulos, A. and Wunderlich, B. *Colloid Polym. Sci.* 1990, **20**, 375

13 Starkweather, H. W. and Whitney, J. F. *J. Polym. Sci. (A)* 1963, **1**, 715

14 Sandeman, I. and Keller, A. *J. Polym. Sci.* 1956, **19**, 401

15 Ramesh, C., Keller, A. and Eltink, S. J. E. A. *Polymer* in press

16 Ramesh, C., Keller, A. and Eltink, S. J. E. A. *Polymer* in press

17 Dreyfuss, P. and Keller, A. *J. Macromol. Sci.-Phys. (B)* 1970, **4**, 811

18 Atkins, E. D. T., Hill, M., Hong, S. K., Keller, A. and Organ, S. *Macromolecules* 1992, **25**, 917

19 Bunn, C. W. and Garner, E. V. *Proc. R. Soc. (A)* 1947, **189**, 39

20 Herbst, M. *Z. Elektrochem.* 1950, **54**, 318

21 Keller, A. *J. Polym. Sci.* 1955, **17**, 351

22 Atkins, E. D. T. Macromolecules '92: Functional Polymers and Biopolymers, Canterbury, September 1992, Abstract, p. 10