# Studies on the crystallization and melting of nylon 66: 2. Crystallization behaviour and spherulitic morphology by optical microscopy

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Negative spherulites and non-birefringent spherulites (the latter arising in two different temperature regions) and the so-called aggregates of nylon 66 have been reproduced and the conditions of their formation have been redefined. Growth rates were measured and the dependence on crystallization temperature ($T_c$) of both growth rates and spherulite forms were studied. Unusual effects were observed in the $T_c$ range where the growth of negative and positive spherulites compete. The most conspicuous, qualitatively new observations relate to crystallization memory effects arising from the presence of negative (and non-birefringent) spherulites. It is found that the localities of such spherulites retain a memory, i.e. they remain morphologically distinct after melting and recrystallization in specific ways, more precisely dependent on the highest melt temperature to which the sample had been exposed with conspicuous consequences for the final crystalline texture. The sum total of observations suggests a gradation of non-equilibrium melt states beyond the optical melting point (as opposed to residual seed crystals) which influences subsequent crystallization, with some suggestions with respect to this melt structure being made.

**(Keywords: nylon 66; crystallization; spherulites)**

## INTRODUCTION

In our previous publication[1] we studied the crystallization of nylon 66 by recording the X-ray pattern at the temperature of crystallization. We found, amongst other things, that crystallization, irrespective of the crystallization temperature, always occurs with hexagonally packed chains (the Brill structure) which then transform into the familiar triclinic structure during cooling. It has been known for a long time that nylons can display a range of spherulitic morphologies depending on growth conditions. The present paper will give renewed attention to these morphologies and to the way they arise.

Positively birefringent spherulites (positive spherulites) are the most common type occurring at all temperatures. Negatively birefringent spherulites (negative spherulites) form within the restricted temperature interval (255–265°C) after the polymer has melted[2]. In the same temperature region another species (spherulitic aggregates) also appears but with a higher growth rate. The morphology and growth behaviour of these different types of spherulite have been the focal point of several previous studies[2–9].

The orientation of the unit cell with respect to the radial direction within the spherulites is an important factor in determining the sign and morphology of the spherulites. This is assessed by microbeam X-ray diffraction[4,9]. For the positive spherulites the *a*-axis, and hence the hydrogen-bonded sheet, is found to be parallel to the radial direction with the chain direction perpendicular to the radius, i.e. tangential to the spherulite[8–10]. Within the limitations of this experimental technique one of us[9] could identify some orientation within the negative spherulites of nylon 6,10 and concluded that in the case of negative spherulites it is the *b*-axis which orients along the radial direction. In subsequent work, the absence of conventional fibrous sheaf-like structures in electron microscopic studies[7] and the lack of orientation in the X-ray patterns[4] led to the inference of a lower category of orientation within negative spherulites, with the chain (*c*-axis) tangential, but with no preferred crystallographic direction parallel to the spherulite radius.

Subsequently Lovinger[11] carried out an in-depth study on the morphology of positive and negative spherulites and on spherulitic aggregates of nylon 6,12, 6,10 and 66 using directionally solidified samples. From a detailed analysis he concludes that the negatively birefringent spherulitic fibrils are composed of short segments containing tangentially arranged stacks of hydrogen-bonded sheets, which is the arrangement proposed earlier by one of us[9]. In spherulitic aggregates the molecular chains are crystallized at 49° to the direction of solidification, making the assignment of the sign of the optical birefringence ambiguous[11].

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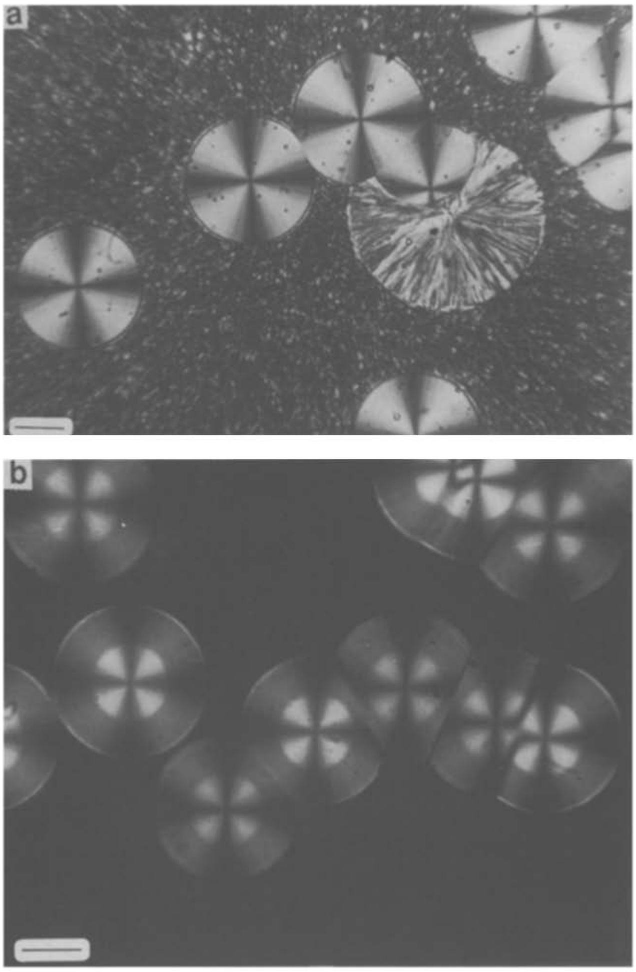

**Figure 1** (a) Negative spherulites and spherulitic aggregate (single fibrous entity), grown at 260°C and cooled to room temperature (scale bar = 30 $\mu$m). (b) Negative spherulite initially grown at 259°C and subsequently at 263°C, indicating the dependence of birefringence on crystallization temperature (scale bar = 30 $\mu$m)

It follows from previous work[1] that, all the above-mentioned spherulites have the Brill structure while growing and all previously determined texture arrangements refer to transformed structures rather than to structures in which the material has originally crystallized[1]. In this work we carried out an in-depth study of the growth and melting behaviour of negative spherulites using optical microscopy and d.s.c. Further, the detailed d.s.c. investigations will form the basis of a subsequent paper[12].

## EXPERIMENTAL

### *Materials*

Most of the work reported here was carried out using nylon 66 with a molecular weight of 24 kg mol$^{-1}$. Higher molecular weight nylon 66 (49 kg mol$^{-1}$) was also used. The samples were free from additives. The molecular weight was determined by viscosimetry in $H_2SO_4$ (96%) at 25°C.

A very thin section of a nylon 66 chip ($\sim$30–50 $\mu$m) was fused between clean microscope cover slips on a hot plate held at a temperature just above the melting point of nylon 66. This sample was then mounted in the Linkam hot stage under dry nitrogen flow. The hot stage was programmed to a specific temperature–time sequence. The crystallization of the sample was studied by polarized light microscopy using an Ultraphot microscope fitted with a high resolution video camera and video recorder to monitor the growth of the spherulites.

D.s.c. experiments were carried out under nitrogen with a Perkin–Elmer DSC 7. The samples were earlier prepared in a Linkam hot stage under identical conditions for the growth of negative spherulites with samples (4–6 mg) being sandwiched between cover slips. The samples were then recovered by breaking the glass cover slips. The heating rate was 10°C min$^{-1}$.

## RESULTS

### *Growth conditions*

The negative spherulites were grown as follows. The samples were initially melted and held at 300°C for 10 min to erase the unknown previous thermal history. The temperature was lowered to 250°C and maintained for 1 h while the material crystallized into positive spherulites. These positive spherulites were melted at 268°C for a variable time interval, of the order of 1–15 min and then lowered to the temperature range 255–265°C where the material crystallized into negative spherulites.

*Figure 1a* shows typical negative spherulites grown in the specified growth temperature interval. A less regular fibrous spherulite type entity is also seen. These, as seen from the interference colours on direct viewing, are much more highly birefringent (not readily observable in the black and white photograph). We shall refer to such entities as 'spherulitic aggregates' in keeping with their designation as 'aggregates' in the past literature[2–5]. Both the growth rate and the brightness of the spherulitic aggregates are higher than those of the negative spherulites. On cooling down to room temperature, as in the case of *Figure 1a*, the brightness of both the negative spherulites and spherulitic aggregates increases but otherwise the sign and overall character remain unchanged. The grainy background in *Figure 1a* is the product of crystallization during cooling of material, still uncrystallized at the initial crystallization temperature. It consists of small positive spherulites, as is the usual form of crystallization of nylon 66.

The birefringence of the negative spherulites varies with temperature. This is clearly seen in *Figure 1b*, where the growth temperature has been changed step wise in the course of the experiment. Accordingly the brightness of the spherulites also changed; increased brightness relates to higher birefringence obtained at lower growth temperature. *Figure 2* shows the temperature regions for the formation of the different spherulites. As can be seen,

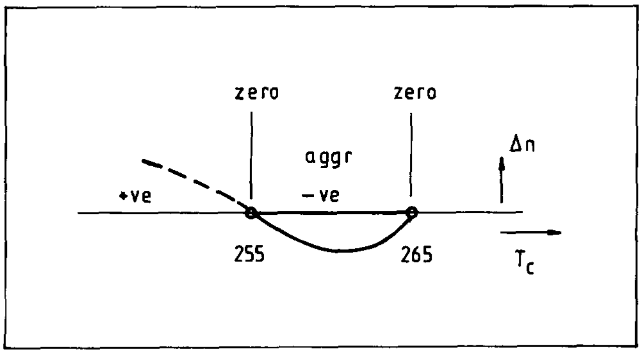

**Figure 2** Schematic representation of the dependence of spherulite birefringence on crystallization temperature ($T_c$)

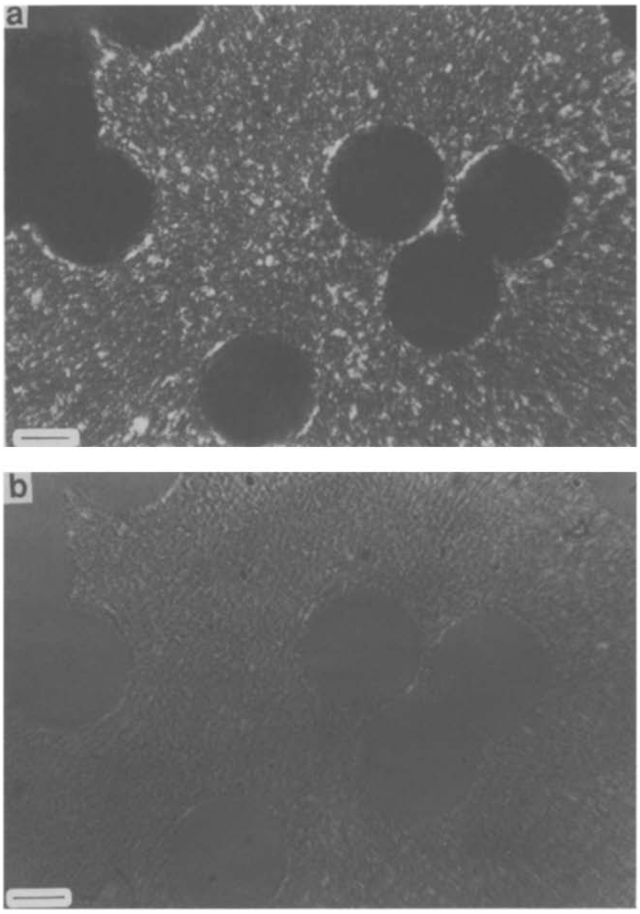

**Figure 3** (a) Non-birefringent spherulites of nylon 6,10 grown at 221°C under crossed polars (scale bar = 20 $\mu$m). (b) The spherulites in (a) under unpolarized light

they are in the order of zero, negative, zero, positive with descending crystallization temperature.

Nylon 66 spherulites formed at 255 and 265°C (the limiting temperatures of the interval) are non-birefringent. Between crossed polars they appear dark (*Figure 3a*) and in unpolarized light they are detected only by their outlines (*Figure 3b*)*.

Though most of the work was carried out using low molecular weight nylon 66, identical results were obtained for the high molecular weight nylon 66. However, we noticed that under identical experimental conditions high molecular weight nylon 66 gave at least twice as many spherulitic aggregates as the low molecular weight counterpart.

### *Growth rate*

*Figure 4* gives the growth rate of negative spherulites as a function of time at crystallization temperatures of 255, 262 and 264°C. The obvious feature is that the growth rate decreases with increasing growth temperature. A less obvious but important feature is the small but significant deviation of these lines from straight lines, indicating non-linear growth of the spherulites with time for all three samples. All measurements were based on isolated spherulites. The departure from linearity is at variance with the linear growth reported by Khoury[2] in the same crystallization temperature range. This could, however, arise due to the presence of shorter molecules in the molecular weight distribution[13].

At the lowest end of the above temperature range (255°C) the growth rate is the highest, but here the negative spherulites stop growing, when the dark background turns into a grainy structure which slowly transforms into positive spherulites. A close look at the periphery of the negative spherulite (*Figure 5*) reveals that the outer part of the spherulite had disintegrated and had transformed into positive spherulites as indicated by the arrows. Grainy structures in the course of crystallization of negative spherulites are not confined to the lower limit

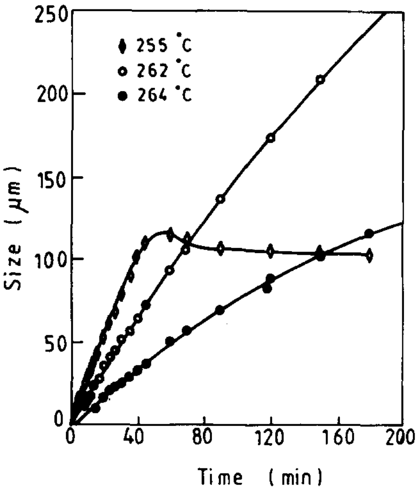

**Figure 4** Spherulite size as a function of crystallization time of negative spherulites for different crystallization temperatures. Growth at 255°C was stopped by the occurrence of a positively birefringent grainy background

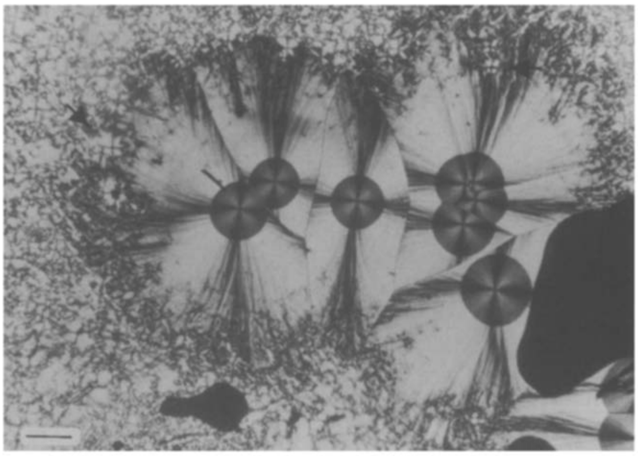

**Figure 5** Partially disintegrated boundary of negative spherulite. Initially grown at 262°C (inner weakly birefringent region) and subsequently at 257°C. The arrows indicate the positive spherulites which appear within the boundary of negative spherulite in the later stages at 257°C when the uncrystallized melt turned into a grainy background (scale bar = 30 $\mu$m)

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* The micrographs (*Figures 3a* and *b*) are added for completeness so as to convey the pronounced visual impressions through which the sequence in *Figure 2* is established and identified throughout the work. They are from a parallel but otherwise less complete study on nylon 6,10, as no photographs were available, or could be obtained, of the zero birefringent spherulites of nylon 66 at the time of the writing of the papers. We also performed tilting tests with a Fedorow Universal stage on samples such as in *Figure 3a* and found that they stayed dark up to the maximum tilt angle of 50°, demonstrating that they are genuinely non-birefringent and not merely in an orientation that produces extinction

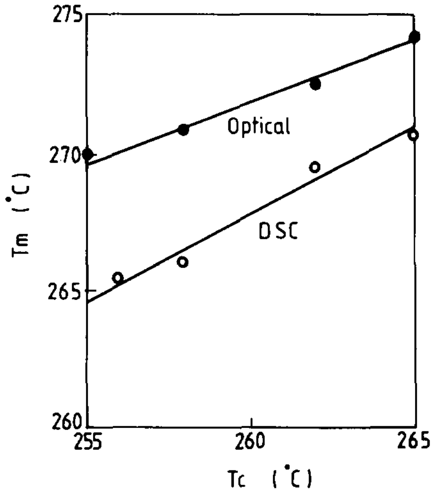

**Figure 6** Dependence of optical and d.s.c. melting point as a function of crystallization temperature ($T_c$)

of the boundary for the temperature range for negative spherulites. The formation of a grainy background also occurs at higher temperatures, but there it takes much longer, and it may not interfere with the growth of negative spherulites, which may have enough time to grow steadily until they impinge, covering most of the field of view. The situation will be different for the lower temperatures where the development of the grainy background could disrupt the growth of the negative spherulites. This is evident from the growth curve of *Figure 4*. The spherulites were grown at 255°C, the growth then stopped after 50 min and the size of the spherulites was reduced when the positive spherulites appeared. In contrast, at higher growth temperatures negative spherulites continue growing even though their growth rate steadily decreases.

### *Melting behaviour of negative spherulites*

The melting point of negative spherulites is measured by two different techniques, optical microscopy (optical melting point, $T_m$) and d.s.c. (calorimetric melting point). The $T_m$ is taken as the temperature where the Maltese cross under crossed polars disappears, i.e. merges with the background. Both the optical and calorimetric melting points show a systematic increase with increasing crystallization temperature, as seen from *Figure 6*. The $T_m$ is in close agreement with a previously reported value[5].

As seen optically, the spherulitic aggregates melt at ~1°C higher than the negative spherulites. D.s.c. heating traces do not resolve the individual melting peaks of negative spherulites and those of the spherulitic aggregates.

### *Memory effects due to negative spherulites*

Memory effects in the crystallization of nylons are receiving increasing attention[14,15]. This is partly because of their pronounced influence on the crystallization behaviour with all its implications for processing, where it can be utilized favourably to yield products with advantageous properties. In addition to memory effects in general, the negative spherulites of nylon 66 exhibit their own memory effect. Such memory, while gradually diminishing with regards to the strength of the effects they give rise to, can persist up to 15°C beyond the $T_m$ and become erased only by heating the melt to still higher temperatures.

The memory effects have different manifestations, according to whether the melt, which originally contained negative spherulites and aggregates, is crystallized below ~250°C, including the most common case of cooling to room temperature, or whether it is first held above 255°C in the temperature range ($\Delta T_{neg}$) where negative spherulites normally grow. We shall take these two situations in turn. The negative spherulites used in the experiments to follow have formed at 261°C.

*Cooling to room temperature.* Here, the imprint of the original negative spherulites (and spherulitic aggregates) is preserved in the final field of view, consisting of the usual positive spherulites. An example is shown in *Figure 7*. Here the continuous background is constituted by fine scale spherulites, identified as positive by the first-order red plate test. The isolated, or partially overlapping, dark areas are the sites of the original negative spherulites. These have lost the spherulitic appearance and contain a fine, grainy texture. In some instances they are surrounded by a transcrystalline rim, which has a positive sign of birefringence. The origin of the overall dark contrast is not known; it is not due to looking along the optic axis of an otherwise overall uniformly birefringent object, as no noticeable brightening has occurred on tilting the slide. Even so, we can say that the pre-existing negative spherulite (and aggregate) has noticeably affected the subsequent crystallization and the resulting texture. *Figure 8* is particularly revealing. Here the negative spherulite regions must have become deformed at some stage of sample handling. We see that the whole comet-shaped deformed region appears darker, which indicates that the portion of the material, originally constituting the negative spherulites, is distinct from the rest even in its deformed state.

In the case of *Figure 7*, the melt temperature was 5°C above $T_m$. On raising the melt temperature, the contrast between the initial negative spherulite area and the surroundings is reduced and at $T_m + 10°C$ only the outlines remain distinct, which gradually fade away as the holding temperature above $T_m$ is raised further.

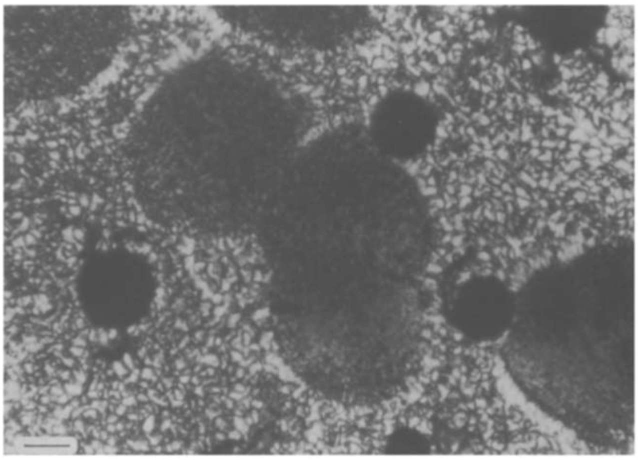

**Figure 7** Sample displaying 'memory effect' associated with negative spherulites. The sample contained originally negative spherulites, that were melted at 273°C for 1 min and subsequently cooled to room temperature. The darker circular regions correspond to the locations of the original negative spherulites (scale bar = 10 $\mu$m).

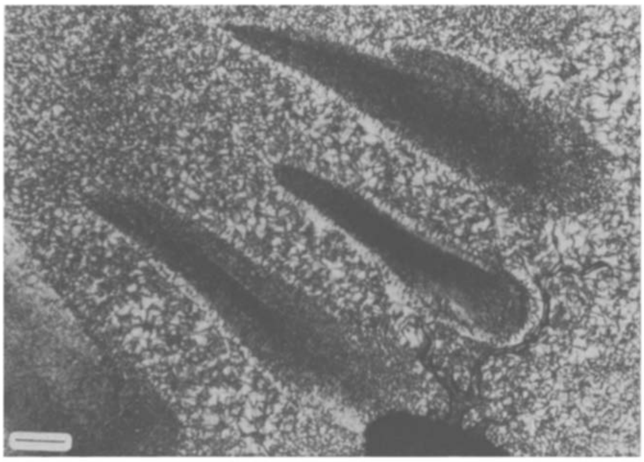

**Figure 8** Area of the same sample as in *Figure 7*, which was deformed during melting

*Holding in the temperature range of the initial negative spherulite growth* ($\Delta T_{neg}$). Here, a variety of effects were observed, all reflecting the memory of the initial negative spherulite (and spherulitic aggregate) state, as manifest by the appearance of the entities arising at the sites of the initial negative spherulites (and spherulitic aggregates). The effects depended very sensitively on the melt temperature and thus were affected by temperature variations across a given sample. Also, there were variations from one experiment to the next, no doubt due to the usual vagaries of nucleation-induced effects. Even so, a trend could be identified, which will be presented here with some selected examples.

When the negative spherulites (*Figure 9a*) were melted and $T_m$ was only slightly exceeded (by ~1°C), then the negative spherulites reappeared in their entirety on subsequent holding at $\Delta T_{neg}$, with the whole field lightening up (*Figure 9b*), i.e. without growing from a centre. In such case, however, the brightness is much lower and the birefringent field appears grainy as compared to the initial negative spherulite (*Figure 9a*). This type of memory effect termed 'enhanced self nucleation'[16], has also been found in polyethylene, but in the present nylons occurs only in the negative spherulites.

The region which originally comprised the negative spherulite (and spherulitic aggregate) remained distinct after exposure of the sample to higher melt temperatures, even if the spherulite itself was not reconstituted as such on holding at $\Delta T_{neg}$. There could be two kinds of departure from the initial negative spherulite. One was the successively increasing multinucleation of negative spherulites with increasing temperature in the melt. This is seen from *Figures 10–12*, which show samples held at $\Delta T_{neg}$, with subsequent cooling to room temperature (the fine grained background can be identified as small positive spherulites, which arose on cooling). Here we see a single spherulite and a multiplicity of spherulites (in both cases negative) in two different localities (*Figure 10*), a fine grained structure, still identifiable as consisting of negative spherulites (*Figure 11*) and an apparently dark area, consisting of fine birefringent grains of unidentifiable sign (*Figure 12*). The sequence corresponds to an increasing density of nucleating centres, all within the area of the original negative spherulite. The second departure was the appearance of a transcrystalline rim along the boundary of what had been the initial single negative spherulite or spherulitic aggregate (an example of the latter is shown in *Figure 13*). By the first-order red plate test this transcrystalline structure was also of negative character. It appears therefore, that the boundary can nucleate new negative spherulitic growth into the virgin melt at $T_{neg}$, but not into the molten material

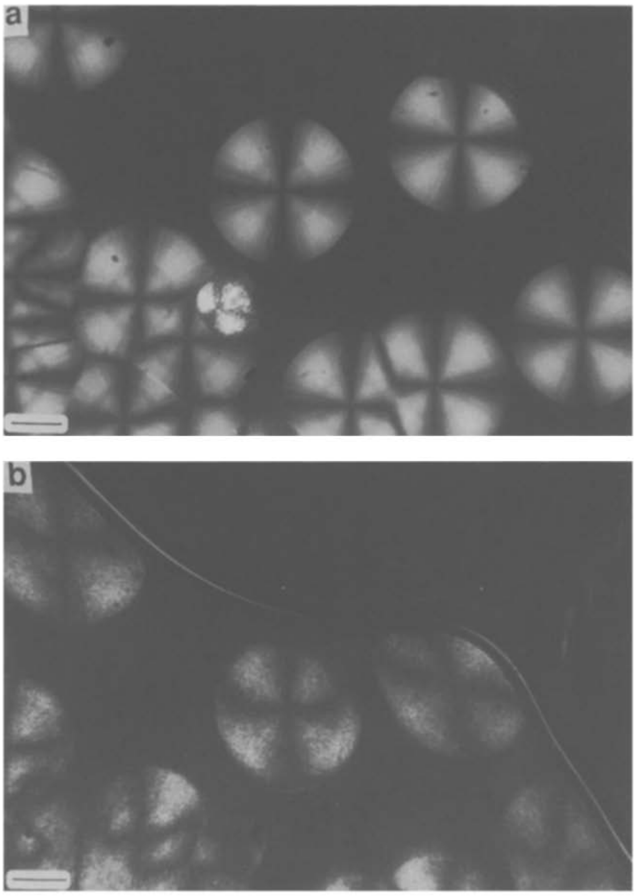

**Figure 9** (a) Negative spherulites growing at 261°C. *In situ* micrograph at 261°C (scale bar = 25 μm). (b) Negative spherulites in (a) after melting just above the optical melting point and reappearance on holding between 255°C and 265°C. Note the deformation of the spherulite boundaries by the meniscus of the melt. *In situ* micrograph at 260°C

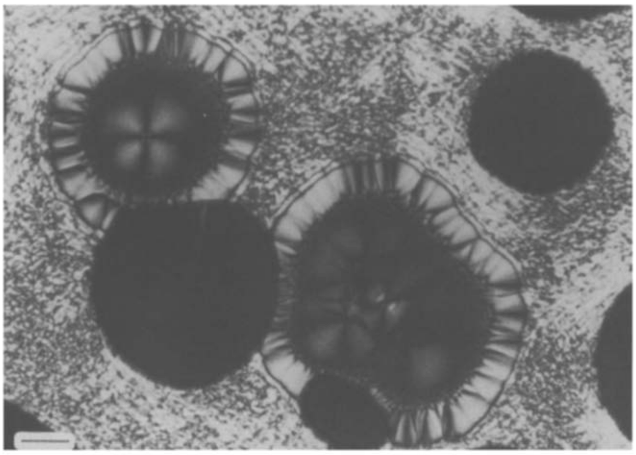

**Figure 10** Negative spherulites that were molten for ~1 min at 1°C above their optical melting point (268°C in this case) and subsequently stored at 257°C. The transcrystalline overgrowth layer displays negative birefringence (scale bar = 15 μm)

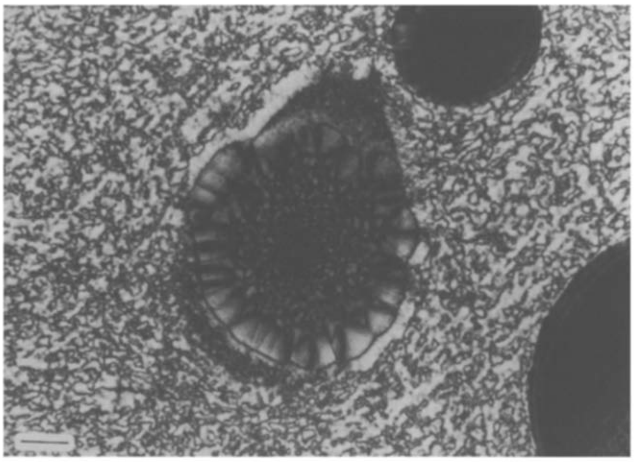

**Figure 11** As in *Figure 10*; the sample has experienced a slightly higher melt temperature (≈272°C)

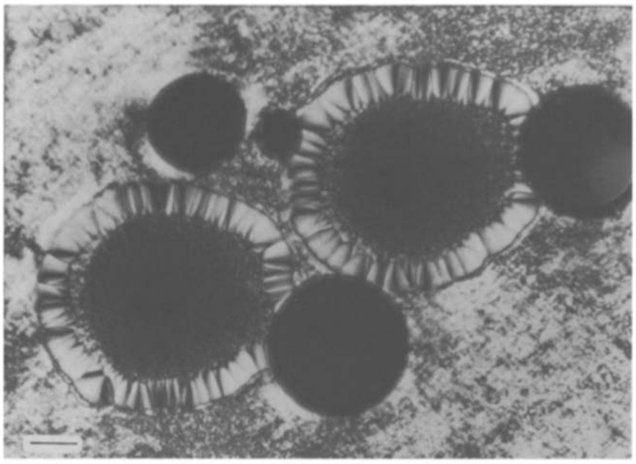

**Figure 12** As in *Figure 11*; the sample has experienced an even higher melt temperature (≈276°C)

inside the original boundary of the negative spherulite. Crystallization within the boundary is occurring by reappearance of new spherulites within the interior (*Figures 10–12*). Note that the negatively birefringent transcrystalline region itself can nucleate a second transcrystalline zone on cooling to room temperature, which has positive birefringence (the second, narrower rim in *Figure 10*).

Previously identified memory effects in nylon 6[14], nylon 66 and nylon 46[16] are related to the enhancement of the nucleation rate and to the crystallization temperature for a given cooling rate. The memory effect displayed by the present negative spherulites is in fact much more basic. As was shown above, it is due to the inability of the melt, arising from the preceding negative spherulite region, to crystallize into the usual positive spherulites on cooling below 250°C, where the positive spherulites normally grow. A further feature in *Figure 9* deserves attention. Here the initial spherulites (*Figure 9a*), which reappear after melting, are distorted (*Figure 9b*), apparently due to pressure by the fluid meniscus nearby. Clearly this indicates deformable fluid-like character. We do not know at what stage the deformation has taken place. Even so, the observation indicates that either the negative spherulite itself or at least the corresponding region has remained distinct in the melt. This effect is additionally illustrated by *Figure 8*.

## DISCUSSION

The present work has revived the long standing largely unresolved topic of optically distinct spherulites in nylons. As apparent from the photographs, the effects are unusually striking. They should be highly relevant, not only to our understanding of nylons, but also to practical aspects such as solidification memory and ultimately to mechanical properties. It is certainly reassuring that all the effects found decades ago can be re-established so readily.

The most salient new features found presently are the crystallization memory effects associated with the negative spherulites. Clearly, where there has once been a negative spherulite the melt has become permanently affected. This is revealed by the distinctly different crystalline textures forming in the particular localities and holds as long as a specific melt temperature is not exceeded.

Of course, the appearance of the negative spherulites themselves is due to some memory effect, as negative spherulites do not arise at all once the melt has exceeded a certain limiting temperature (~270°C for nylon 66). Persistence of seeds has been suspected to enable crystallization at temperatures which are too high for positive spherulites to form and grow readily. In this case, such spherulites would be of different structure displaying negative birefringence, but at these high temperatures requiring pre-existing nuclei to form at observable rates. Our present observations refute this previously held inference. By first heating the melt up to 280–300°C the formation of negative spherulites is suppressed. In this case, positive spherulites do appear in the temperature range, where for lower preceding melt temperatures negative spherulites would have grown. Thus, positive spherulites can and do appear and grow in the temperature range, where for lower melt temperatures the negative spherulite dominates. However, the growth of positive spherulites is much slower and sets in after a long induction time. This means that persistence of seeds cannot be the sole factor responsible for negative spherulites and that there must be some residual structure throughout the melt as a whole at these lower melt temperatures. This residual structure would be responsible for the formation of negative spherulites and is lost irreversibly with further increase in temperature. Nevertheless, the positive spherulites obtained at these higher temperatures seem to have some common feature

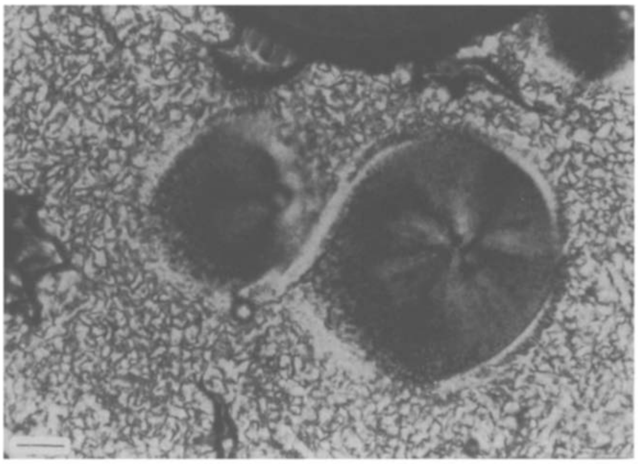

**Figure 13** Remains of aggregates after melting for 1 min at 269°C and subsequent storage at 257°C (scale bar = 12 $\mu$m)

with the negative spherulites, as can be shown by d.s.c. criteria[12].

At this point we may speculate on the nature of the possible organization within the melt. The most likely feature is the retention of hydrogen bonds. It is known that nylon 66 melts at 270°C and retains almost 25% of the hydrogen bonds originally present in the crystal[17]. This alone would represent a 'structure' within the melt, which, as far as hydrogen bonds tend to form sheets, could also impart local anisotropy to such a 'structure'. It would be expected that the number of hydrogen bonds is increasingly reduced on further increase in melt temperature and thus the corresponding structure and associated local anisotropy becomes progressively obliterated with increasing temperature. It follows from our observations, that such organizations would represent non-equilibrium structures, which cannot be reconstituted on cooling. On the above basis, our observations would require that the positive spherulites form from the 'structure free' melt, i.e. from a melt with no hydrogen bonds in excess of those which are in statistical equilibrium at the corresponding melt temperature. Conversely, the negative spherulites, which after initiation grow at much faster rates, would require such pre-existing structures for their formation. Clearly, this hypothesis calls for testing by direct spectroscopic determination of the hydrogen bond content. This, however, lies beyond the scope of the present investigation.

## ACKNOWLEDGEMENT

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## REFERENCES

1 Ramesh, C., Keller, A. and Eltink, S. J. E. A. *Polymer* 1994, **35**, 2483

2 Khoury, F. *J. Polym. Sci.* 1958, **333**, 389

3 Lindegren, C. R. *J. Polym. Sci.* 1961, **1**, 181

4 Mann, J. and Roldan-Gonzalez, L. *J. Polym. Sci.* 1962, **60**, 1

5 Magill, J. H. *J. Polym. Sci.* 1966, **4**, 243

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

7 Cannon, C. G. and Harris, P. H. *J. Macromol. Sci. B* 1969, **3**, 357

8 Keller, A. *J. Polym. Sci.* 1955, **17**, 291

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

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

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

12 Ramesh, C., Keller, A. and Eltink, S. J. E. A. *Polymer* 1994, **35**, 5300

13 Keith, H. D. and Padden Jr, F. J. *J. Appl. Phys.* 1964, **35**, 1270

14 Khanna, Y. P. and Reimschuessel, A. C. *J. Appl. Polym. Sci.* 1988, **35**, 2259

15 Derks, W. H. P. DSM internal report, 1990

16 Chivers, R. A., Barham, P. J., Martinez-Salazar, J. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 1717

17 Garcia, D. and Starkweather, H. *J. Polym. Sci., Polym. Phys. Edn* 1985, **32**, 537