

Early stages of spherulite growth in melt-crystallized polystyrene*

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Samples of isotactic polystyrene were crystallized from the melt for short times (i.e. 1–10 min at 190°C, 17–81 min at 220°C), quenched and examined by transmission electron microscopy following permanganic etching and replication. Crystallization for the longest times resulted in the profuse nucleation of structures composed of hexagonal lamellae which splayed apart from one another at the edges. Such objects were similar to those previously identified in polystyrene crystallized at temperatures greater than 200°C. As the crystallization time was reduced, however, so the resulting structures became smaller and simpler until at the shortest times studied objects could be seen which consisted of a stack of lamellae connected together by a central thread or core, the length of which ranged from ~500 Å to several microns. It is therefore proposed that in these samples nucleation of chain folded crystals occurs about a backbone which includes some molecules in an extended configuration, the necessary local molecular extension being introduced, presumably, at some time during sample preparation and thereafter held in place such that relaxation is unable to occur prior to the onset of crystallization, despite heating to well above the polymer's equilibrium melting point. Reducing the molecular mass of the melt led to a dramatic reduction in the nucleation density. However, examination of sufficiently small objects again showed them to consist of stacks of lamellae, and as such, the nucleation process appeared qualitatively unchanged by the reduction in molecular mass.

(Keywords: isotactic polystyrene; crystallization; lamellae; nucleation)

INTRODUCTION

In many classes of materials electron microscopy has proved to be a key element in clarifying details of microstructure. However, the application of this to polymers, and melt-crystallized systems in particular, presents severe experimental problems which stem from the fundamental nature of the interaction of high energy electrons with these materials. Nevertheless, in recent years, following the introduction of etching and staining techniques^{1–4} a considerable body of information has been amassed concerning the complex arrangements of lamellar crystals present in melt-crystallized polymers. Much of this work has been aimed towards investigating the organization of lamellae within spherulites, which is frequently highly complex^{5–7}, together with gaining an understanding of the mechanisms by which these entities grow. Whilst the precise spherulitic architecture is found to be highly dependent on the particular polymer involved^{8–10}, in the systems so far studied the pattern of growth is seen to be the same. Spherulites develop through the initial formation of a framework of lamellae, termed dominant, which are composed of longer and more stereo-regular molecules selected from the melt. Subsequent crystallization then occurs between the established dominant lamellae to a degree dictated by the precise composition of the melt. Such later forming lamellae are termed subsidiary, and may themselves

exhibit a range of habits due to molecular fractionation effects. Nevertheless the important distinction is that dominant lamellae dictate the overall form of the structures observed, whilst subsidiary lamellae merely crystallize within a pre-established framework. One stage of the growth process not clarified by recent efforts in this area is that of nucleation and growth at the shortest times.

As part of a study of the crystallization of isotactic polystyrene, Edwards and Phillips¹¹ examined a range of samples crystallized in thin films, by direct imaging in the transmission electron microscope. One of these specimens, which was crystallized for just 1 min at 180°C contained simple sheaf-like entities composed of about four lamellae. As a result of these observations Edwards and Phillips proposed that the initial step in the growth of a spherulite involves the formation of a single lamellar crystal, the presence of which so perturbs the surrounding melt as to facilitate the nucleation of further lamellae such that a sheaf-like bundle is formed. However, even at the short crystallization time stated above the resultant objects are still fairly large, being ~0.5 μm in length. For this reason, and because crystallization in very thin films (~100 nm thick) often causes significant morphological changes^{12,13}, an investigation was undertaken to examine the earliest possible stages of spherulite growth in isotactic polystyrene in a range of samples crystallized for different times at different temperatures and from materials with different molecular mass distributions.

EXPERIMENTAL

In the course of this work, two fractions of polystyrene were examined. These materials were prepared by a two-

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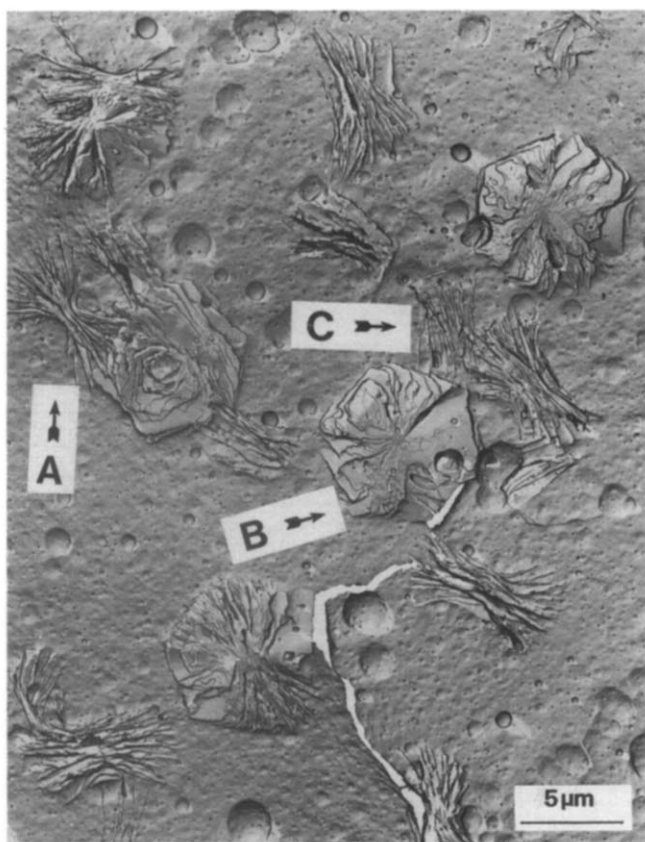


Figure 1 Transmission electron micrograph of a sample of isotactic polystyrene crystallized at 210°C for 8 h showing lamellar aggregates in random orientations intersecting the etched surface. A, B and C correspond to such structures viewed in three orthogonal planes, and these characteristic views are termed sheaf-like, hexagonal and edge-on, respectively

stage precipitation process based loosely on that of Tung¹⁴, from a sample of raw polymer purchased from Polymer Laboratories Ltd. Subsequent characterization by gel permeation chromatography gave values of $\bar{M}_m = 1.1 \times 10^6$, $\bar{M}_n = 3.9 \times 10^5$ for the high molecular mass material (fraction G) and $\bar{M}_m = 1.4 \times 10^5$, $\bar{M}_n = 7.9 \times 10^4$ for the lower molecular mass material (fraction B).

From these fractions samples were prepared by melting some of the polymer between a slide and a cover-slip, a slight pressure being applied both to force out any air and to give a film $\sim 50 \mu\text{m}$ in thickness. The resulting films were then crystallized as required after melting for 1 min at 260°C, before finally being quenched into cold water.

Following removal of the cover slip, the crystallized samples were etched in a 1% solution of potassium permanganate in a mixture of sulphuric acid, phosphoric acid and water (5:2:2 v/v/v). After recovery following prescribed procedures^{2,15}, the etched surfaces were prepared for electron microscopy by first shadowing with a platinum/palladium alloy, then coating with carbon and finally washing in a suitable solvent such that the clean replica was left on an electron microscope grid. By a suitable choice of solvent it was possible to remove either all the polystyrene or just the non-crystalline quenched regions. Alternatively by carefully selecting both the solvent and the extraction time, detachment replicas could be produced^{16,17}, where a thin crystalline layer suitable for study by electron diffraction was left adhered to the replica.

RESULTS AND DISCUSSION

The crystallization of polystyrene at high temperatures (greater than $\sim 200^\circ\text{C}$) generally results in entities of the type shown in *Figure 1*. Although the particular sample shown was crystallized for 8 h at 210°C, objects similar in both structure and size are also obtained after crystallization for 24 h at 220°C or 40 min at 200°C. The objects shown in this micrograph are sheaf-like arrays of lamellae which are hexagonal in shape and crystal structure. Such entities show characteristic appearances, corresponding to three orthogonal viewing directions of the structure in three orthogonal planes. These characteristic appearances are labelled A, B and C in *Figure 1* and have been termed sheaf-like, hexagonal and edge-on, respectively¹⁰. Comparison of the growth front with the interior structure nearer the centre of object A, for example, shows that growth proceeds by the initial formation of an array of dominant lamellae followed by subsequent subsidiary crystallization.

Examination of micrographs such as *Figure 1* can give information on both the structural features present in a material and on their growth mechanism. However, due to the compact nature of even the comparatively simple entities so far considered, little can be deduced about the process of nucleation, and for this, smaller and even simpler objects must be examined.

The sample shown in *Figure 2* was crystallized at 220°C for 81 min and can again be seen to contain sheaf-like aggregates of hexagonal lamellae. However, comparison of these objects with more mature structures reveals a number of important differences. Whereas in the larger objects shown in *Figure 1* the edge structure consists of an open array of individual dominant lamellae which is only filled in nearer the centre by subsidiary crystallization, the entities of *Figure 2* show no such evidence of two-stage crystallization. Rather, all the lamellae appear equivalent, and all are reasonably termed dominant. Again unlike more mature structures, in many cases all the lamellae in a single entity are of comparable size, indicating that growth of each began at about the same time rather than one forming first followed by subsequent crystallization around it. However despite the simplicity of the objects in *Figure 2*, they are still sufficiently compact to prevent inspection of the initial nucleation. Thus it was necessary to examine still simpler objects.

Crystallization for just 17 min at 220°C gives rise to lamellar aggregates that are not merely smaller than those discussed already but which also have a significantly less compact interior morphology. Such structures are shown in *Figure 3*, i.e. groups of small lamellae $\sim 100 \text{ nm}$ in diameter which are connected together by a central thread. Such a structure which is highly reminiscent of shish kebab or row-nucleated morphologies^{18,19} suggests that the objects shown in *Figure 3* are composed of chain-folded lamellae growing about a core containing chains in an extended configuration. However, whereas shish kebabs and row nuclei result from crystallization in stirred solutions²⁰ or macroscopically strained melts²¹⁻²³, i.e. situations where molecules are extended through the deliberate application of external stresses, this is not the case in the samples considered here. Although in the preparation of the films some flow inevitably occurred, such ordered effects should have been eliminated by melting the samples at 260°C, approximately 20°C above the equilibrium melting point

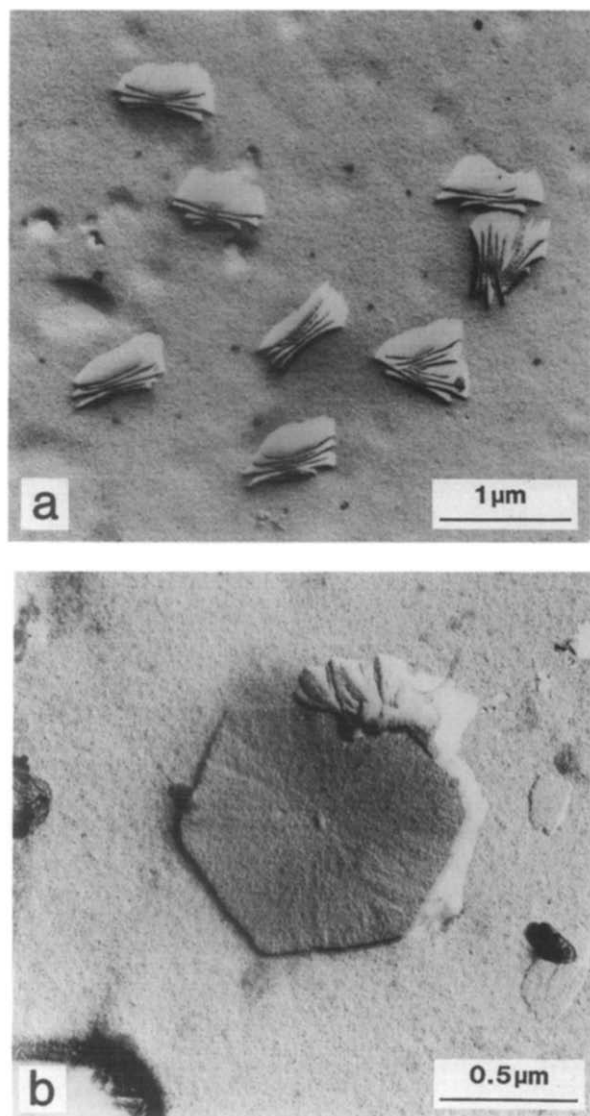


Figure 2 Transmission electron micrographs of a sample of isotactic polystyrene (fraction G) crystallized at 220°C for 81 min showing (a) sheaf-like aggregates of (b) hexagonal lamellae

the longer molecules which are most likely to become entangled, nucleation as described above should be very sensitive to changes in the molecular mass distribution of the melt. For this reason the early stages of spherulite growth were investigated in the lowest available molecular mass fraction of polystyrene, where the value of \bar{M}_n was nearly an order of magnitude lower than that in the material described above.

The most marked change observed following the

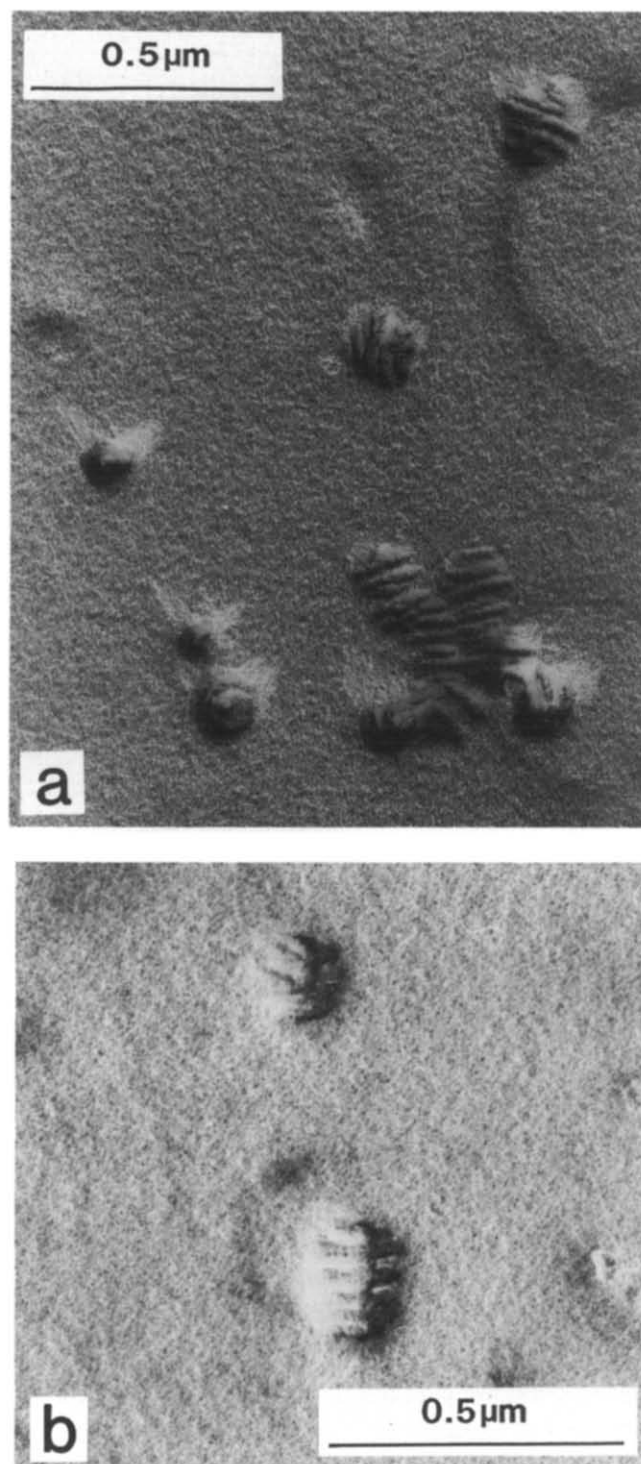


Figure 3 Transmission electron micrographs of two separate areas (a) and (b) of a sample of isotactic polystyrene (fraction G) crystallized at 220°C for 17 min. Structures are shown which consist of a number of lamellae connected together by a central thread

of isotactic polystyrene^{24,25} immediately prior to crystallization. In agreement with this, the objects discussed here differ from row-nuclei in that there is no preferred orientation of the core structure throughout the film, rather the direction of the core varies from place to place, as shown in *Figure 4*. It seems more likely that the core crystals in *Figure 3* result from molecules being drawn out between entanglements and held in a sufficiently extended configuration during preparation of the sample. The extended molecular conformations must then be held in place, such that relaxation is unable to occur despite heating to 260°C which again points to the influence of entanglements at these molecular lengths.

Other samples crystallized for various times at 200 and 190°C appeared identical to similarly sized objects crystallized at 220°C and will not be discussed further here.

In the above discussion it is proposed that crystallization occurs about a core which contains molecules in a partly extended conformation, and that this non-equilibrium state is maintained as a result of molecular entanglements. If this is the case then, since it is

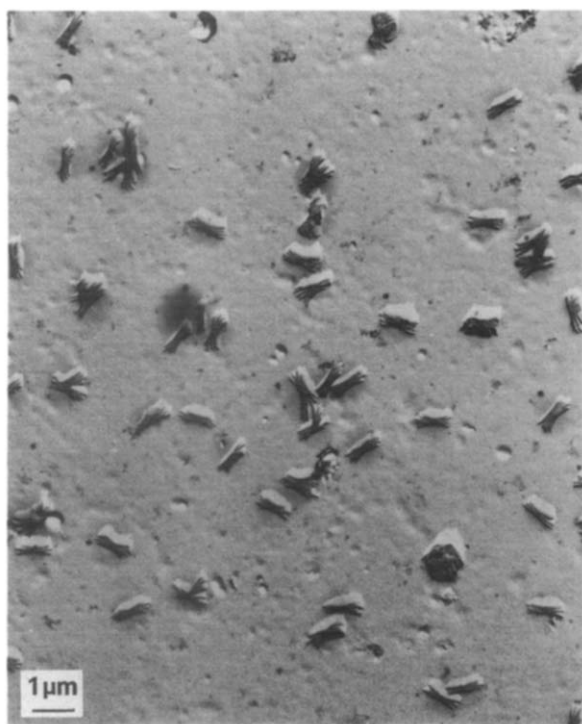


Figure 4 Transmission electron micrograph of a sample of isotactic polystyrene (fraction G) crystallized at 220°C for 81 min showing a large number of sheaf-like structures in random orientations

nucleation occurs through the formation of small stacks of lamellar crystals which are connected together by a central thread. By comparison with shish kebab structures, it is proposed that the above morphology

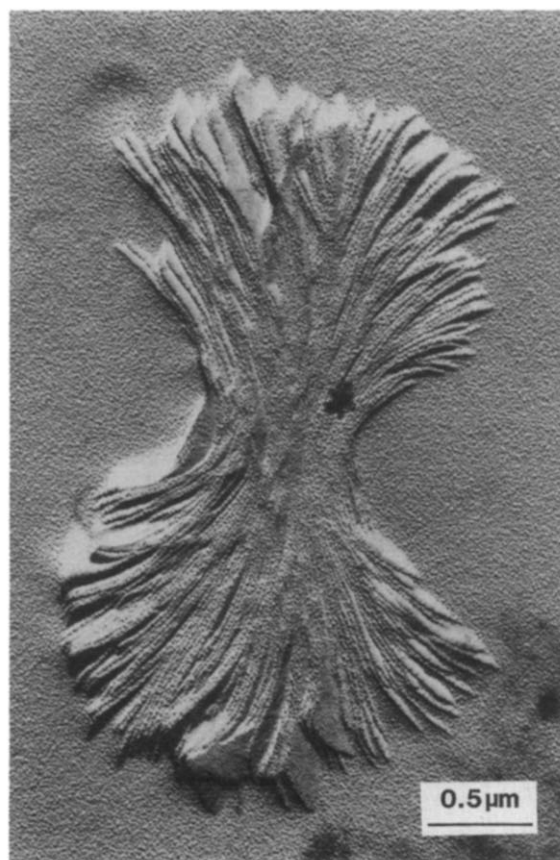


Figure 5 Transmission electron micrograph of a sample of lower molecular mass isotactic polystyrene (fraction B) crystallized at 190°C for 10 min. Complex sheaf-like aggregate

reduction in molecular mass was in the nucleation density. Whereas in fraction G nucleation densities of the order of 10^5 objects per square millimetre were observed, crystallization of the lower molecular mass material for short times (~ 1 min at 190°C) appeared to result in no crystalline aggregates. Crystallization times were then extended to about 10 min, again at 190°C (equivalent to ~ 5 h for fraction G at 220°C). An example of the structures produced is shown in *Figure 5*. Whilst this and similar objects are of great interest in clarifying details of the mechanism by which spherulites grow, they are too well developed to be informative on nucleation. Further attention was thus given to considerably reduced crystallization times.

Eventually detailed examination of a sample crystallized for 1 min at 190°C revealed a small number of structures, such as shown in *Figure 6*. Although no connecting thread can be seen in this object (it could lie above or below the etched surface), the similarity between the appearance of this and the other objects already discussed suggests that they all have similar origins. In addition the fact that reducing \bar{M}_m from $\sim 10^6$ to $\sim 10^5$ leads to a reduction in nucleation density from $\sim 10^5$ to $\sim 1 \text{ mm}^{-2}$ is clearly indicative of the importance of the molecular mass distribution and the long molecules in particular in the nucleation process observed in these systems. Although there is no suggestion of qualitative change in nucleation, the number of nuclei would fall with molecular length because it is the longer molecules which will entangle more and so be liable to create extended nuclei.

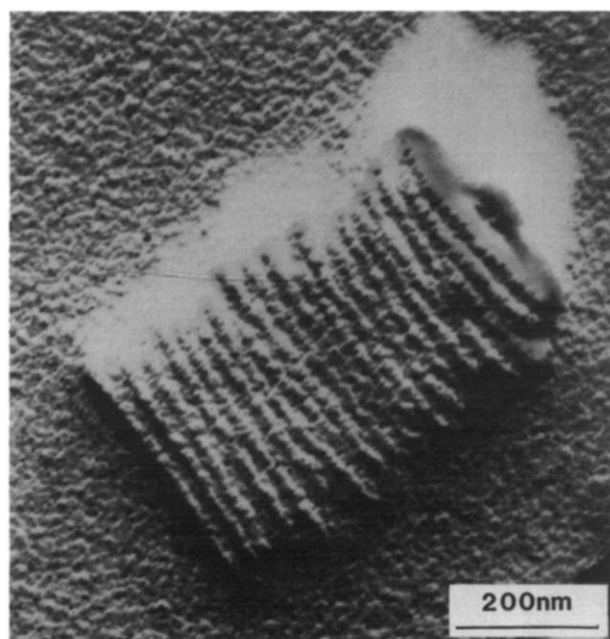


Figure 6 Transmission electron micrograph of a sample of lower molecular mass isotactic polystyrene (fraction B) crystallized at 190°C for 1 min. Small stack of lamellae similar to those observed in fraction G but with less direct evidence of connectivity

CONCLUSIONS

From the results presented here, it can be concluded that in high molecular mass isotactic polystyrene copious

results from the presence within the melt of molecular portions which become extended during sample preparation, and which are unable to relax prior to the initiation of crystallization, presumably through the action of entanglements. Subsequently, chain-folded lamellar overgrowth occurs. Reducing the molecular mass of the melt leads to a dramatic reduction in nucleation density, consistent with entanglement of the longer molecules being the root cause of the formation of extended nuclei.

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