Morphology of Polyethylene Spherulite Crystallized from Melt

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ABSTRACT: The morphology of melt-crystallized polyethylene is reported. The samples were crystallized for different times at high temperature to produce early stages of spherulitic growth. Morphology studies using transmission electron microscopy showed that the largest proportion of the early objects was monolayers associated with a giant screw dislocation, and the remaining objects were multilayers. At the basal surfaces of these objects, the traces of the {1 0 0} planes were identified, and the angle between the different planes was found to be $67^{\circ}30'$. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1125–1129, 1999

Key words: polyethylene; crystal growth; screw dislocation

INTRODUCTION

The formation of spherulite in polymers is a feature of crystal growth that is still not well understood. That is reflected in the varying views as to what constitutes the essential nature of a spherulite.¹⁻⁷ In the past decade, however, following the introduction of etching techniques^{8,9} a wealth of information was introduced through the use of transmission electron microscopy concerning the complex structure of lamellar crystals present in melt-crystallized polymers.

Today, it is quite certain that spherulites develop through the initial formation of a framework of lamellae, termed dominant, and later formation of lamellae termed subsidiary, which are crystallized between the established dominant lamellae.^{2,4} This article considers two types of polyethylene: linear and branched. The former is highly crystallizable; the latter, less so. The aim of this work is to extend our study into a more general description of the lamellar structure in polyethylene.^{10,11} The investi-

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gation was carried out by crystallizing samples at high temperature from the melt to form the earliest possible stages of spherulitic growth. The crystallization at high temperatures generally produces immature spherulites. This involves interrupting the crystallization process at any stage, so that entities formed during crystallization are better demarcated with respect to their surrounding matrix.

EXPERIMENTAL

Materials

Two types of polyethylene were used: linear and branched. The linear polyethylene was supplied by Dupont Canada Commercial, Kingston, Ontario, and the branched polyethylene was supplied by B. P. Chemicals Ltd. (U.K.). Subsequent characterization by gel permeation chromatography performed by the Polymer Supply and Characterization Centre, RAPRA, Shrewsbury, U.K., gave values of $\bar{M}_m = 9.17 \times 10^4$, $\bar{M}_n = 1.41 \times 10^4$ for linear polyethylene, and $\bar{M}_m = 2.2 \times 10^5$, $\bar{M}_n = 8 \times 10^3$ for branched polyethylene.

Crystallization

A polarizing optical microscope was used in conjunction with Mettler hot-stage (FP-99). The speci-

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Figure 1 Transmission electron micrograph of a sample of branched polyethylene crystallized from the melt at 113° C for 1 h showing banded spherulite. Bar = 5 μ m.

mens were melted at 150°C, about 15°C above their equilibrium melting temperatures, on a hot stage under a dry nitrogen atmosphere and held there for 2 min to erase previous thermal history effects. Crystallization was then carried out by lowering the Mettler setting temperature to the required temperature. Following a predetermined crystallization time, the specimens were quenched into liquid nitrogen.

Transmission Electron Microscopy

The melt-crystallized samples were etched according to a method developed by Bassett's group.^{8,9,12} After etching, the samples were washed with water and left to dry. A standard two-stage replication was applied. A surface impression of the etched sample was obtained by softening a cellulose–acetate film with acetone. This was followed by shadowing the film with a platinum–palladium alloy, then coating it with carbon in a vacuum evaporator. The coated film was supported on TEM grids, and the celluloseacetate was dissolved away by extraction with acetone, leaving the coated replica intact. The replica examined in the TEM mode of a Philips 301 transmission electron microscope with 80-kV accelerated voltage.

RESULTS AND DISCUSSION

Figure 1 shows banded spherulites of branched polyethylene, consisting of polycrystals seen in various orientations around the radial b direction. In such a banded spherulite, continuity is often observable over 25 μ m. The defect at the bottom of the figure is due to cellulose–acetate film that did not completely dissolve in the extraction process. Closer inspection (Fig. 2) at the bands reveals local variations, between a few degrees to approximately 45°, in the orientations of lamellae. The implication is that some lamellae will be more favorably oriented for subsequent crystallization than others in their neighborhood, and in some regions one can see that the lamellae are doubled.



Figure 2 Details of Figure 1 revealing the lamellar branching at the bands. Bar = $0.5 \ \mu$ m.



Figure 3 Transmission electron micrograph of a sample of linear polyethylene crystallized from the melt at 130°C for 23 h showing dominant lamellae. Bar = 1 μ m.

The first-forming lamellae are called dominant; such lamellae can be seen alone by crystallizing linear polyethylene from the melt at 130°C for 30 h (Fig. 3). It can also be seen that the edge of the lamella at the arrowed region is eroded during the etching process, so that the traces of the chain molecule can be seen to be inclined to the lamellar normal. The splaying apart of adjacent dominant lamellae from a common axis, as shown in Figure 4, is rather regular and at approximately constant angles. A strong candidate for the origin of this splaying is the defects inside the lamellae on the atomic scale. These defects cause screw dislocation, as can be seen in Figure 4. At the screw dislocation the lamellae are usually doubled; this gives a hint to understanding how the new lamellae form in a process that is likely to proceed in the same direction depending on the crystallization time.

Figure 5 shows an early stage in the crystallization. The embyonic spherulite shown is surrounded by materials solidified during the quenched process. At the arrowed region A the layer is bent, which may be attributed to the stresses on the surface from the quenched material. This material usually contains short molecules, which cannot crystallize isothermally but can do so at lower temperatures.^{13,14} This type of structure was identified in other polymers, such as isotactic polypropylene¹⁵ and isotactic polystyrene.¹⁶ Closer inspection of Figure 5 reveals that behind the growth fronts is the emergence of subsidiary lamellae at arrow B. Accordingly, two types of lamellae may be distinguished, so that wide lamellae advance into the melt, leaving the regions between them to be filled in by later-forming platelets. The



Figure 4 Transmission electron micrograph of a sample of linear polyethylene crystallized from the melt at 130°C for 23 h showing splaying apart of the dominant lamellae from screw dislocation. Bar = 1 μ m.

former are termed dominant lamellae; the latter, subsidiary lamellae.

Figure 6 shows an early stage of spherulite formation. The point of contact between two lamellae becomes the locking site, from which screw dislocation begins. The object shown in Figure 6 supports the mechanism of the spiral growth when two lamellae are met proposed by Keith and Padden.¹⁷ The assumption about screw dislocation formed at a locking site is not always true, however, as in the early stages of growth when lamellae are separated from each other by several tens of microns, and the likelihood of these lamellae touching each other is small.

Figure 7 shows that the origin of screw dislocation is different from what was shown in Figure 6. The growth of the object in Figure 7 is started



Figure 5 Transmission electron micrograph of a sample of linear polyethylene crystallized from the melt at 130°C for 23 h showing an early stage of embryonic spherulite. Bar = 1 μ m.



Figure 6 Transmission electron micrograph of a sample of linear polyethylene crystallized from the melt at 130°C for 23 h showing two lamellae connected by a central screw dislocation. Bar = 2 μ m.

by one lamella, which then splits to form another lamella splayed apart from screw dislocation. Accordingly, Figure 7 confirms that the dislocations exist within the lamellae from the beginning. Such dislocation results from defects inside lamella on the atomic scale. The lamellar habit in Figure 7 is elliptic and elongated along the *b*-axis. A similar habit was seen in polyethylene from poor solvents at high temperatures by Organ and Keller, $^{18-20}$ who demonstrated that the *b*-axis always extends along the length of the lamella. Closer inspection of Figures 6 and 7 reveals crossed lines at the basal surfaces of the lamellae. The angle between the crossed lines was measured at 67°30' for many lamellae. Accordingly, these lines indicate the directions of the $\{1 \ 1 \ 0\}$ planes. This result can be compared to results for the single crystals grown from dilute solutions, where a similar angle between {1 1 0} planes was found.¹²



Figure 7 Transmission electron micrograph of a sample of linear polyethylene crystallized from the melt at 130°C for 23 h showing splitting of the dominant lamellae from a central screw dislocation. Bar = $2 \mu m$.

CONCLUSIONS

The following conclusions can be stated:

- 1. The lamella always extends along the *b*-axis.
- 2. Screw dislocation usually forms either

when two lamellae touch each other or from defects inside the crystal itself.

- 3. The lamellar habit at high-crystallization temperatures is elliptic, which is in agreement with the result obtained by Organ and Keller^{18–20} at high temperature from poor solvents.
- 4. The traces of the {1 1 0} planes were identified, and the angle between the different planes is 67°30'.

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