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Morphologies of metallocene-catalyzed short chain branched polyethylene single crystals formed from the melt at higher temperature

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Abstract

Metallocene-catalyzed short chain branched polyethylene single crystals, formed from the melt at a higher crystallization temperature of 114°C, were obtained. Highly elongated lamellae were formed, which are different from truncated lozenge or lenticular shaped single crystals formed at a lower crystallization temperature. It was found that there existed a definite line in the lamellae along the longitudinal growth direction and two regions were separated by the definite line. The lateral habits of both the regions were asymmetrical about the *b*-axis due to the chain tilting, which was the same as that at a lower crystallization temperature. Generally, the highly elongated lamellae were not straight, but curved towards the opposite direction with chain tilting direction due to a series of edge dislocation within a lamella. The inner side of a lamella was serrated and the outer side was smooth due to the lamellar curvature. The thickness of both regions of a lamella was different, the broader region was thicker than the narrower region, which was different from the uniform thickness of the lamellae formed at a lower crystallization temperature. The different thicknesses within a lamella were considered as the result of the initial thickness difference and the impact of isothermal thickening. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Short chain branched polyethylene; Single crystal; Elongated lamellae

1. Introduction

Recently, metallocene-catalyzed short chain branched polyethylene has received a lot of interest academically [1–4]. It has been regarded as the most popular model compound in the study of polymer crystallization due to its narrower molecular weight and more uniform comonomer sequence distributions. In our previous paper [5], it has been reported that butyl branched polyethylene thin film samples with low molecular weight can form single crystals from the melt at a lower crystallization temperature (102–106°C). The lateral habits of single crystals substantially changed from a truncated lozenge to a lenticular shape with the increasing of crystallization temperature. All lamellae were asymmetrical about the *b*-axis due to its chain tilting. However, the crystallization of this sample at a higher crystallization temperature has not been reported. It was expected that the structure and morphology of single crystals formed at a higher crystallization temperature would be changed due to the change of thermodynamic and kinetic behaviors.

On the other hand, spherulites can be grown from the melt by slowly decreasing the temperature through lamellae packing. The lamellae formed at a higher temperature are the foundation for forming spherulites. In general, the lamellar packing in thicker thin film has two manners [6]: (1) multilayer flat-on lamellae pile up, in which the spiral terrace can be produced between the lamellae and (2) many edge-on lamellae grow outward radially from a center nuclei to form banded spherulites. It has been suggested that the lamellae in polyethylene spherulites are often bent into S shapes [7]. This bending growth of lamellae in spherulites must be relevant to the structure and the morphology of free single lamellae. In this paper, the lateral habits of metallocene-catalyzed short chain branched polyethylene single crystals formed from the melt at a higher crystallization temperature were studied.

2. Experimental

2.1. Material

A metallocene-catalyzed low molecular weight single chain branched polyethylene, with 1-hexene as the

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comonomer, i.e. with butyl branches, was used in this work, which was kindly supplied by Phillips Petroleum Company. The molecular weight and polydispersity were measured by the GPC method. The weight average molecular weight was 5910 Da and polydispersity (Mw/Mn) of 1.1. Such narrow molecular weight distribution was obtained by a cross fractionation procedure [8]. A high temperature solution ^{13}C-NMR indicated average short chain branches of 3.4 per 1000 carbon atoms. Note that the branch content only represents an average value.

2.2. Single crystal growth

The thin film samples from a 0.1% dilute solution in xylene were deposited onto a freshly cleaved mica substrate coated with carbon. The films in a container were heated to 160°C on a hot stage for 30 min and then they were shifted to an oil bath as quickly as possible where the temperature was preset at 114°C. The temperature fluctuation in the oil bath was controlled at ±0.2°C. After a sufficiently long time of about 24 h for the single crystal growth, the samples were quenched to room temperature in the water.

2.3. Instruments and measurements

The single crystals formed were transferred on electron microscope grids and shadowed at about 20° with platinum. Morphological observations were performed in a JEOL 2010 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The gold was used as a calibration of the electron diffraction (ED) spacing. Atomic force microscope used was NanoScope III[a] with a standard silicon nitride cantilever, with a spring constant of 0.06 N/m and a resonance frequency of 5–50 kHz. The contact mode was used under ambient conditions.

3. Results and discussions

Fig. 1 shows a TEM microphotograph of a lamellar single crystal grown from the melt at a higher crystallization temperature of 114°C for 24 h. It can be seen that the highly elongated lamellae were obtained with a length of several tens micrometers and usually limited in width to less than 1 μm. The longitudinal direction of a lamella is identified as *b*-axis by an ED pattern. It is found that, from ED patterns at various areas of a lamella, the direction of the *b*-axis changes throughout the entire lamella, which shows a very fast growth of lamellae along the *b*-axis at a higher crystallization temperature. All lamellae are not square-ended and the width of lamellae narrows down gradually to a leading tip at the growing end with the longitudinal growth.

It can be observed that there exists a definite line in a lamella along the *b*-axis, and two regions are separated by the definite line as shown in Fig. 2a One region is broader and another is narrower. It has been evidenced that, for polyethylene single crystal grown from the melt, stems of

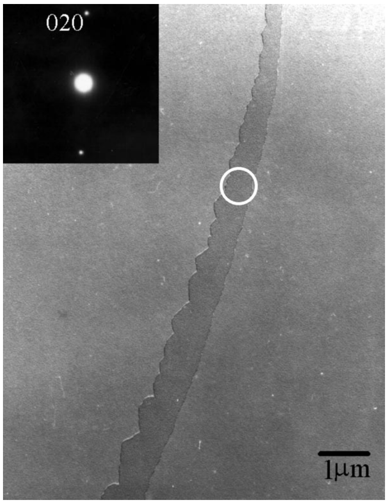

Fig. 1. TEM microphotograph of metallocene-catalyzed low molecular weight short chain branched polyethylene single crystal formed from the melt at 114°C.

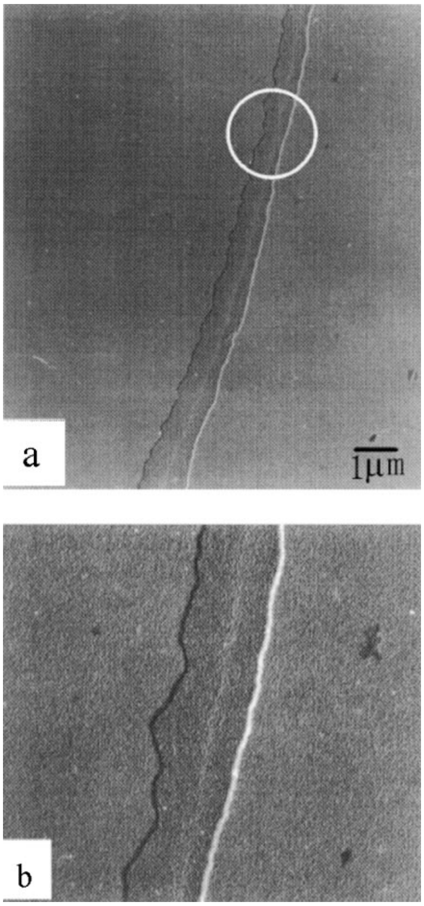

Fig. 2. (a) TEM microphotograph shows that the highly elongated lamellae with two regions separated by a definite line within a lamella, and the thickness and the width of both regions are different. (b) Part of an elongated lamella circled in (a).

folded chains are inclined with respect to the lamellar normal so that fold surfaces are parallel to (*h*01) planes [5,9,10]. They are usually parallel to (201), this corresponding to a chain tilt of ~35° within (020) plane transverse to the long axis. The chain tilt shows that the growth rate on opposite (200) growth faces is asymmetrical. A slower lateral growth occurs on faces that form an acute angle between the overhanging faces and the substrate. The conformational entropies of the coiled polymer molecules can be reduced, when molecules in the melting state deposit in the reentrant corner between the substrate and the overhanging growth faces [9]. This reduction of conformational entropies would retard the lamellar growth to form a narrower region. In general, the asymmetry in lateral growth is a common feature of lamellae grown in parallel contact with a substrate, whether growths are at lower crystallization temperatures or at higher crystallization temperatures.

Generally, highly elongated lamellae are not straight but curved along the longitudinal growth direction. The lamellar bending moment should result from the edge dislocation. It is very interesting that all the lamellae bend towards the faster growth (200) planes, i.e. the opposite direction of chain tilting. It indicates that the edge dislocation motions are the same as shown in Fig. 3. The production of the same dislocation motion may be related to the difference of a surface folding structure at two (200) growth regions. Keith and Padden et al. have observed that the regularities of folding both narrower and broader regions of the highly elongated lamellae are different [9,11]. They have described that there existed a significant difference of folding the structure at opposite (200) growth regions due to the chain tilting. The larger stresses are considered to accompany less regular structure in fold surfaces formed at narrower region, i.e. the outer (200) growth region. For a flat-on lamella, it is impossible to release this stress through a lamellar twist because its lower surface is attached to the substrate. It is necessary to insert additional planes at outer (200) growth region, and a series of edge dislocation would be produced in a lamella, which results in the formation of a curved lamellae.

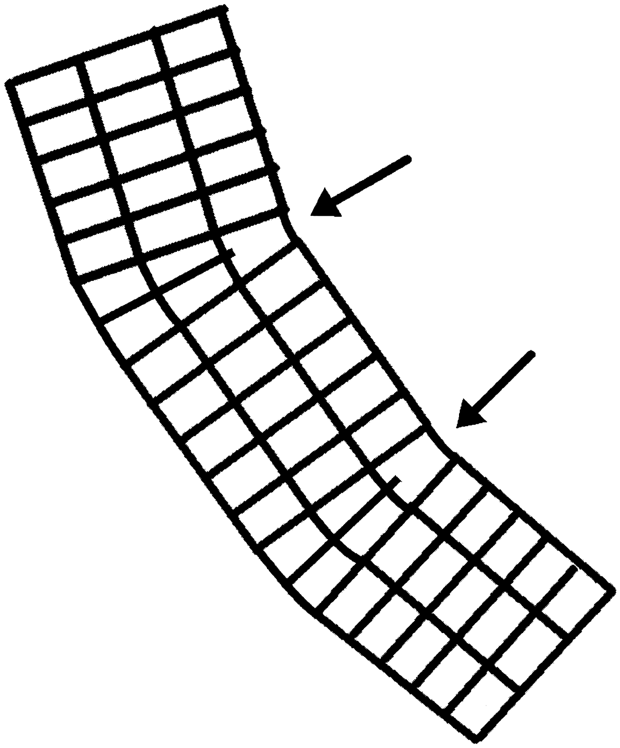

Fig. 3. Schematic representative of a series of edge dislocations in a lamella, which results in curved growth of lamella.

It can be seen that the outer side of curved lamellae is smooth and the inner side is serrated. Because of the edge dislocation and the bending moment of lamellae, the packing densities of chains near the inner dislocation point (arrows in Fig. 3) would be larger. The molecular rearrangement on the inner side of lamella would occur after the longitudinal growth, to attain tolerable packing densities, which result in an extension growth of the lamella and appearance of the serrated edge. Obviously, this tendency of outward growth after longitudinal growth would lead to lamellar branches, which is the foundation for forming spherulites. It shows that the tendency of lamellar branches always occurs at the inner edge of curved lamellae.

It shows that the thickness of the broader region of lamellae is thicker than that of the narrower region as shown in Fig. 2b. According to literature [12], the differences in lamellar thickness at opposite (200) growth regions arise from two different phenomena: the initial thickness differences and the impact of isothermal thickening. The initial thickness difference arises from the different energies of deposition of the incoming stems depending on the topology of the deposition site. Obviously, the inner (200) growth front of curved lamella is rougher than the outer (200) growth front, since the growth rate of inner (200) growth faces is faster than that of outer (200) growth faces [13]. The energy on the inner side can make a longer chain deposit. On the other hand, according to the above discussion, the folding surface of the outer (200) growth region (less regular folding) has a very rough folding surface. This region does not thicken (or thickens to a very limited extent) in the isothermal process, while the inner (200) growth region (more regular folding) thickens to a larger extent [12]. Therefore, the thickness of the inner (200) growth region is much thicker than that of the outer region of the lamella.

Under the same crystallization conditions, this difference in lamellar thickness indicates a conformational change. AFM measurement shows that the thickness of the broader region is 12.9 nm and the narrower region is 8.6 nm as shown in Fig.4. For this low molecular weight branched polyethylene samples (the length of a chain with full extended and zigzag conformation is about 53 nm), the chain folding in the broader region should be a non-integral folded conformation and a one- or two-folded conformation at the narrower region of lamellae [14].

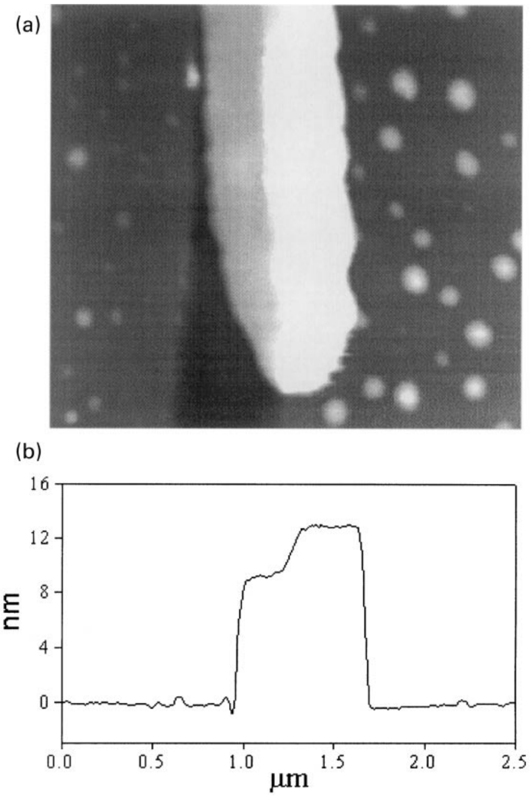

Fig. 4. AFM height image of an elongated lamella. The curve shows that the thickness of the broader region is 12.9 nm and the narrower region is 8.6 nm.

According to the above discussion, this difference in the folded length of chains within a lamella is relevant to chain tilting. However, this phenomenon has not been observed in the lamellae formed at a lower crystallization temperature though the chains have the same tilting as at a higher temperature [5]. It is well known that the flexible polymer chains in a chain-folded manner do not correspond to the thermodynamically stablest form but occur due to kinetic reasons [11]. At a lower crystallization temperature, the lamellar growth is controlled completely by kinetic factors due to a fast growth rate. The difference in the folding structure and the surface free energy at two regions of the lamellae (along opposite (200) planes) cannot cause change in thickness within a lamella. However, at a higher crystallization temperature, the thermodynamic factors play an essential role in the lamellar growth due to the slower growth rate of lamellae, and the lamellar growth is more close to the thermodynamic equilibrium growth. Therefore the difference in the folding structure and the surface free energy within a lamella causes change in the folded length of chains.

4. Conclusions

When metallocene-catalyzed short chain branched polyethylene thin film samples crystallized isothermally from the melt at a higher crystallization temperature, highly elongated lamellae were obtained, which was different from the truncated lozenge or lenticular shape single crystals formed at lower crystallization temperatures. The lateral habits of the lamellae on opposite (200) growth faces were asymmetrical due to the chain tilting. The highly elongated lamellae are curved due to a series of edge dislocations, and the lamellae bent towards the opposite direction with a chain tilting direction. It was found that the inner side of the curved lamella was serrated and the outer side was smooth. The morphological difference of growth front arose from the lamellar curvature. The thickness of the lamellae formed at a higher crystallization temperature was not uniform, which was different from that formed at lower crystallization temperatures. It was considered that the differences in lamellar thickness arose from the initial thickness difference and the impact of isothermal thickening.

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