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Lateral habits of single crystals of metallocene-catalyzed low molecular weight short chain branched polyethylene from the melt

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Abstract

The lateral habits of low molecular weight short chain branched polyethylene single crystals from the melt were studied. Three crystallization temperatures (102, 104 and 106°C) were selected for single crystal growth. It was found that the lateral habits of single crystals were asymmetric at all the crystallization temperatures selected. The electron diffraction patterns and tilting series experiments evidenced that there existed chain tilting in all the lamellae. It was the chain tilting that lead to the asymmetry of the growth rate and of lateral habits of the single crystals about the *b*-axis. The lateral habits substantially changed from the growth at 102°C where the truncated lozenge single crystals formed with straight (110) faces to the growth at 104°C where the lenticular single crystals appeared. This change occurred at 20°C lower than that in a low molecular weight linear polyethylene with the same molecular weight. Furthermore, kinetics theory analysis evidenced that the change of lateral habits from truncated lozenge to lenticular shape resulted from the transition of growth regime. The results were the same as that of high molecular weight linear polyethylene but different to that of low molecular weight linear polyethylene. It may be attributed by the existence of short branched chains. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Short chains branched polyethylene; Lateral habits; Asymmetry

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1. Introduction

It is well known that the lateral habits of linear polyethylene single crystals formed from a dilute solution depended on the crystallization condition used [1–3]. Kinetics theory has been widely employed to account for the change of the lateral habits [4–6]. As a function of crystallization temperature, the lateral habits of the single crystals obtained changed from a lozenge shape with straight (110) growth faces at lower temperature to a lenticular shape with curved (200) growth faces at higher temperature. The chains are tilted in linear polyethylene single crystals formed from a dilute solution [7]. It has been theoretically predicted that the growth regime of a single crystal changed from mono-nucleation (regime I) to multi-nucleation (regime II) with decreasing crystallization temperature [8].

The lateral habits of linear polyethylene single crystals formed from the melt have also been found to be crystallization temperature dependent, although it was difficult to establish a significant relationship between the crystal shapes and the crystallization temperature. It has been expected in general that a single crystal formed from the melt with chains entangled would be less ordered than that from a dilute solution with chains separated [9]. It has been reported that the folded chains in a linear polyethylene single crystal formed from the melt were inclined to the basal plane of lamellae and there was an inherent asymmetry of structure in the single crystal [10,11]. The fold surfaces were parallel to (*h*01) faces, usually to (201) faces, which corresponded to a chain tilting ~35° within (020) faces transverse to the long axis. Recently [12,13], a three-dimensional shape of linear polyethylene single crystal formed from the melt has been studied via the extraction method. The lateral habits of single crystals changed from a lenticular shape to a truncated lozenge shape with decreasing crystallization temperature. Kinetics theory and regime I–II transition have been used to explain this observation. It has been argued that the change of growth rates along the (110) and (200) faces resulted in the transition of the growth regime and the change in the lateral habit.

Compared with linear polyethylene, metallocene-catalyzed branched polyethylene possesses short chain branches. Although substantial progress has been made in almost every aspect to characterize the structure and

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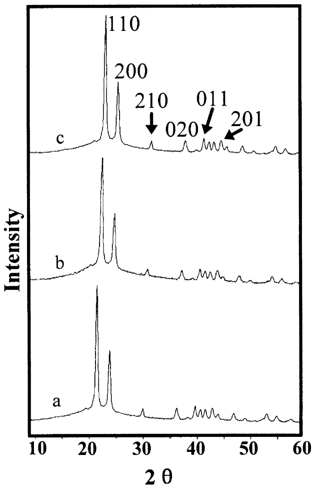

Fig. 1. Wide angle X-ray diffraction patterns of metallocene-catalyzed low molecular weight short chain branched polyethylene at variant crystallization temperatures of: (a) 102°C; (b) 104°C; and (c) 106°C.

property of linear polyethylene, it was less in the case of metallocene-catalyzed short chain branched polyethylene (SCBPE) [14]. It is speculated that the existence of branched chains makes branched polyethylene difficult to form single crystals from the melt and the lateral habits of branched polyethylene single crystals formed from the melt may be even more complex than that of linear polyethylene single crystals. In this paper, a metallocene-catalyzed low molecular weight short chain branched polyethylene single crystal formed from the melt was reported and its lateral habit was found to be crystallization temperature dependent.

2. Experimental

2.1. Material

A metallocene-catalyzed low molecular weight SCBPE, with 1-hexene as the 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 gel permeation chromatography (GPC). The weight average molecular weight (M_w) was 5910 Da and polydispersity (M_w/M_n) of 1.1. Such narrow molecular weight distribution was obtained by a cross fractionation procedure [15]. A high temperature solution carbon-13 nuclear magnetic resonance (NMR) indicated the 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 were deposited from a 0.1% dilute solution in xylene onto a freshly cleaved mica substrate coated with carbon. The films in a container were heated to 160°C in a hot stage for 30 min and then they were shifted as quickly as possible to an oil bath where its temperature was preset to a fixed crystallization temperature. The temperature fluctuation in the oil bath was controlled at ±0.2°C. Three crystallization temperatures (102, 104 and 106°C) were selected and a sufficiently long time of about 24 h was kept for the single crystal growth. The samples were quenched to room temperature in the water after single crystal growth.

2.3. Instruments and measurements

The powder samples for wide angle X-ray diffraction (WAXD) measurements were heated to above melting point on a glass substrate and then shifted as quickly as possible to an oil bath whose temperature was kept the same as that for single crystal growth. After the same crystallization time as that of the single crystal growth the samples were quenched to room temperature in the water. The WAXD experiments were carried out on a Philips 1700 X-ray Diffraction. The 2θ angle was scanned between 5 and 60° with a scanning rate of 2°/min. The WAXD peak position and width were calibrated using a standard silicon crystal with known crystal sizes.

The single crystals were transferred on electron microscope grids and shadowed at about 20° with Pt. Morphological observations were performed in a JEOL 2001 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Gold was used to calibrate the electron diffraction spacing.

Isothermal experiments were carried out in a differential scanning calorimeter of Perkin–Elmer DSC-7. The samples were heated to 160°C with a heating rate of 10°C/min for 10 min and then cooled to an appropriate crystallization temperature with a cooling rate of 320°C/min. The temperature was held constant until the crystallization was completed. The DSC measurements were calibrated by using standard indium and the experiments were performed under a flowing nitrogen atmosphere.

3. Results and discussion

Wide angle X-ray diffraction patterns of the powder sample of metallocene-catalyzed low molecular weight SCBPE at various crystallization temperatures are shown in Fig. 1. It is shown that the patterns at various temperatures are identical and the unit cell structure is not crystallization temperature dependent. Further analysis shows that the crystal lattice of low molecular weight SCBPE is orthorhombic with dimensions of $a = 0.751$ nm, $b = 0.505$ nm and $c = 0.251$ nm, which is the same as that of linear polyethylene.

Fig. 2a–c shows the lateral habits of metallocene-catalyzed low molecular weight SCBPE single crystals formed from the melt at temperatures of 102, 104 and 106°C, respectively. The lateral habits of the single crystals change with increasing crystallization temperature. The aspect ratio

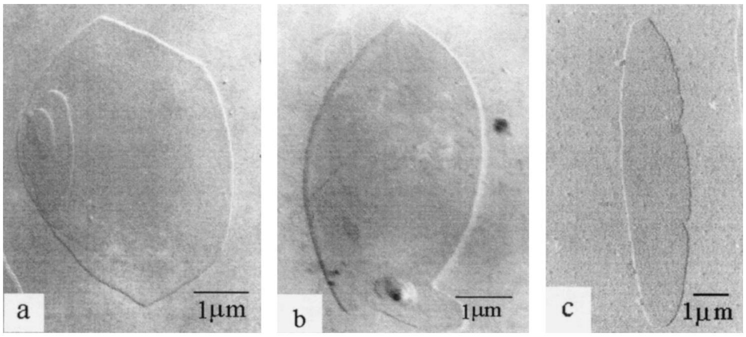

Fig. 2. Electron micrographs of bright field images of single crystals of metallocene-catalyzed low molecular weight short chain branched polyethylene formed from the melt with crystallization temperatures of: (a) 102°C; (b) 104°C; and (c) 106°C.

of lamellae formed at 102, 104 and 106°C are 1.39, 1.71 and 4.78, respectively, and all lamellae appear with curved (200) growth faces. It has been reported for curved lateral habits that the effects of a solvent is negligible for single crystals formed from the melt [9,16]. Defects appearing on the growth faces was the main reason for the curved lateral habits [17]. The lamellae with curved habits may be divided into small coherent domains several nanometres in width with distinct stacking and the boundaries of these domains formed stacking faults. The excess energy required for crossing the boundaries on a (200) faces is larger than the energy on a (110) faces, which cause curved (200) growth faces.

The lamellae (Fig. 2a–c) with the same electron diffraction pattern are shown in Fig. 3a. Table 1 lists the experimental and calculated d-spacing based on the orthorhombic unit cell parameters of low molecular weight SCBPE. The assignments of the reflections [the (020) and a series of (4k1) reflections] are also included. It indicates that the stems of folded chains are inclined ~35° around the b-axis and the fold surfaces of those lamellae are parallel to (201) faces in terms of the orthorhombic unit cell [18]. This result is supported by tilting series experiments in which the lamellae was tilted 35.3° about the b-axis (Fig. 3b). Three lamellae obtained at various crystallization temperatures have the same chain tilting. The reason for the chain tilting is that folds of chains are staggered which is a usual feature in polyethylene crystals [19]. The thermal motion of chain ends and the resultant defect structures in the plane of the end-group cause the chain tilting [17].

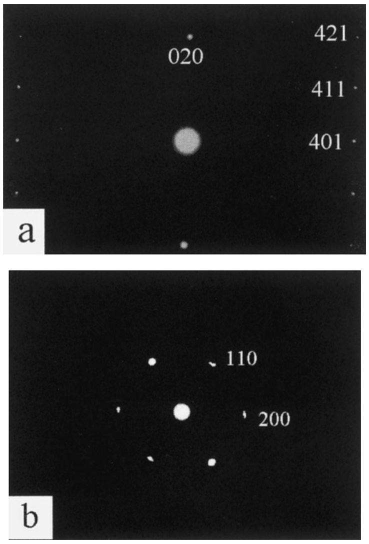

Fig. 3. (a) Electron diffraction pattern of three lamellae formed at all crystallization temperatures selected. (b) Electron diffraction pattern obtained by the lamellae tilting 35.3° about the b-axis.

The lateral habits of the single crystals in Fig. 2a–c are all asymmetric about the b-axis. The asymmetry of lateral habits undoubtedly results from the asymmetry of the lateral growth rate and of the inherent structure in the single crystals due to the chain tilting [11]. Along the chain tilting direction (the d_2 direction in Fig. 4) the angle between the substrate and overhanging growth faces is less than 90°. When molecules in the melt state deposit the reentrant corner between the substrate and the overhanging growth faces, the conformational entropies of the coiled polymer molecules could be reduced. This reduction of conformational entropies would retard lamellar growth [11]. On the other hand, according to the theory of Lauritzen and Hoffman [20] the crucial step of lamellar growth is the attachment of the first stem of a new molecule, an activated process opposed by a free energy barrier. Since the coiled molecules in question will not extend into the reentrant corner, the free energy barrier governing the nucleation rate will be higher and the effective driving force smaller. Both, conformational entropies reduction and higher free energy barrier, lead to the growth rate of the (200) growth faces towards the chain tilting direction slower than that towards another direction (d_1 direction), at which the angle is larger than 90°. This leads to the asymmetry of

Table 1
Experimental d-spacings of electron diffraction corresponding to calculated d-spacings from unit cell parameters obtained by X-ray diffraction in Fig. 1

	d_{020} (nm)	d_{401} (nm)	d_{411} (nm)	d_{421} (nm)
d (exp.)	0.250	0.154	0.147	0.134
d (cal.)	0.253	0.150	0.143	0.129

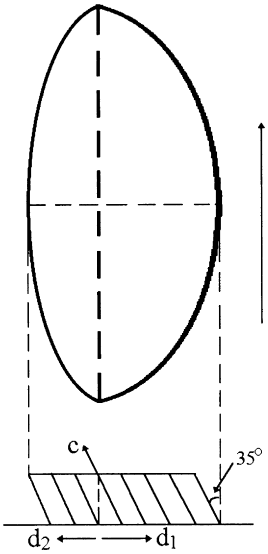

Fig. 4. Schematic representation of chain tilting in the lamellae. Chains tilting ~35° within (020) faces around the b-axis. The b-axis is vertical.

the lateral habits of the single crystals with respect to the b-axis. In general, the asymmetry in lateral growth is a common feature of lamellae grown in parallel contact with a substrate [11], and the asymmetric morphology of the lamellae must be due to the growth from thin films.

It is shown in Fig. 2a–c that the (110) growth faces of lamellae at 102°C are well developed, and those at 104 and 106°C, however, are not observed, and that the lateral habits of lamellae change from truncated lozenge to lenticular shape. This change of the lateral habits of lamellae is related to the formation mechanism of single crystals. For low molecular weight linear polyethylene, it has been reported that this change in lateral habits did not correspond to the regime transition, but due to a change in the folding behavior of the single crystals [21]. However, for linear polyethylene fractions with molecular weight ranging from 13 000 to 100 000 [12] it has been reported that the lateral habits of single crystals change in the vicinity of the transition temperature of the growth regime: lenticular shape elongated in the direction of the b-axis (type A) grown in regime I and truncated lozenge with curved (200) and straight (110) growth faces (type B) grown in regime II. The (110) growth faces were well developed in type B crystals while they were not observed in type A crystals [12]. The regime I–II transition in crystal growth rates can be used to explain the change in lateral habit.

The Lauritzen–Hoffman secondary nucleation theory has predicted the regime I–II transition [8]. The general form of the secondary nucleation theory rate equation is

$$G = G_0 \exp\left[-\frac{U^*}{\mathrm{R}(T - T_\infty)}\right]\exp\left[\frac{K_g}{T\Delta Tf}\right] \qquad (1)$$

where G is the linear growth rate, U^* the activation energy and T_∞ the temperature at which all motions are associated with viscous flow cease, f a factor which corrects for variation in the heat of fusion with temperature below the equilibrium melt point and taken as $2T/(T_m^0 + T)$. T is crystallization temperature and ΔT is supercooling. T_m^0 the equilibrium melting point is 144.5°C [22]. Ross and Frolen [23] have used reciprocal halftime data to give a reasonable indication of the growth rate of crystals. Though bulk crystallization rates are not simple to interpret because they do not provide information on the individual contributions of the nucleation rates, growth rates, and secondary crystallization rates involved, it is possible to determine the number of regimes existing over the crystallization temperature range and also the regime transition temperature [24]. It has been found previously that the actual values

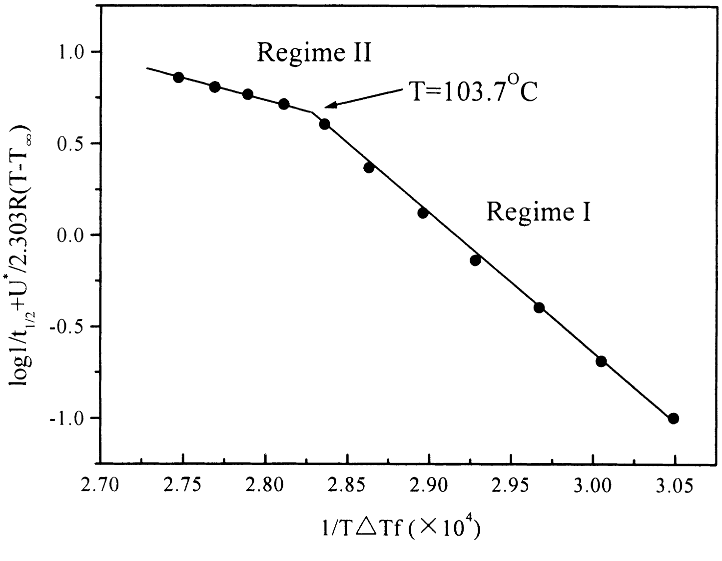

Fig. 5. Kinetic behavior of metallocene-catalyzed low molecular weight short chain branched polyethylene assuming heterogeneous nucleation. The regime I–II transition temperature is 103.7°C.

used for U^* and T_∞ are of little significance in the kinetic analysis of polyethylene. $U^* = 1500$ cal/mol and $T_\infty = T_g - 30°C$ [25].

Fig. 5 shows a plot of $\log(t_{1/2})^{-1} + U^*/2.303R(T - T_\infty)$ versus $1/T(\Delta T)f$ for the low molecular weight SCBPE. It is found that the growth regime of the crystal at lower crystallization temperatures is regime II. When the crystallization temperature closes to 104°C, the growth regime changes to regime I. The transition of the growth regime corresponds to the change in the lateral habits of lamellae from truncated lozenge to lenticular shape for low molecular weight SCBPE. It is expected that the regime I–II transition results in the change in the lateral habits of single crystals, which is the same as that of higher molecular weight linear polyethylene but different to that of lower molecular weight linear polyethylene [12,21]. The change in temperature of the lateral habits of the low molecular weight linear polyethylene ($M_n = 5800$, $M_w/M_n = 1.1$) single crystals formed from the melt was 124°C [21] which is 20°C higher than the SCBPE with almost the same molecular weight. This may be attributed to the existence of branched chains. The existence of branched chains decreases the rate of secondary nucleation relative to the rate of surface spreading [25] and causes the regime I–regime II transition to translate to lower temperature.

4. Conclusion

1. The lateral habits of metallocene-catalyzed low molecular weight SCBPE single crystals from the melt are found to be crystallization temperature dependent, and they appear as curved (200) growth faces at all the crystallization temperatures selected. The curved lateral habits of the single crystals result from the defects' structure appearing on the growth faces of the single crystals.
2. The lateral habits of the single crystals are asymmetric about the *b*-axis at all the crystallization temperatures studied. The asymmetric lateral habits result from the chain tilting in the single crystals.
3. Kinetic theory analysis indicates that regime I–II transition causes a change in the lateral habits of the single crystals from lenticular shape to truncated lozenge, which is the same as that of higher molecular weight linear polyethylene but different to that of lower molecular weight linear polyethylene. It may be attributed by the existence of branched chains.

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