

# Study on single crystals of butyl branched polyethylene in the presence of electric field

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## Abstract

Single crystal of butyl branched polyethylene with various molecular weight formed from the melt in the presence of electric field was studied. It was found that electric field influenced morphology and structure of the butyl branched polyethylene single crystals formed. The lateral habits of the single crystals were circular shape, which was different from truncated lozenge or lenticular shape single crystals formed from the melt in the absence of electric field. The stems in the single crystals formed in the presence of electric field were perpendicular to the basal plane of the single crystals, which was different from chain tilting in single crystals formed from the melt in the absence of electric field. The electron diffraction patterns showed that the structure of the circular single crystals was a quasi-hexagonal with looser chain packing. This looser chain packing was favorable to thickening growth of single crystals through chain sliding diffusion. The thickness of the single crystals was much larger and depended on molecular weight. It indicated that the single crystal in the presence of electric field should be an extended chain type single crystal. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Electric field; Single crystal; Branched polyethylene

## 1. Introduction

Recently there were a number of studies reporting the influence of electric field on liquid crystalline polymers [1–3] and diblock copolymers [4–6]. The electric field can induce alignment of liquid crystal molecules because of their dielectric anisotropy, and of block copolymer microstructure by deformation or flow caused by an electric field. However, few studies have been reported on the influence of electric field on crystalline polymers. The isothermal crystallization of poly(vinylidene fluoride) in the presence of high static electric field has been reported [7,8]. The primary nucleation, crystal structure and morphologies of a crystalline polymer were influenced through electric field induced orientation.

It is well known that morphologies and chain crystallization manners of polyethylene single crystals formed from the melt strongly depend on crystallization conditions. Normally, a folded chain crystal can be obtained through isothermal crystallization from the melt. And morphology of the single crystal was modulated as truncated lozenge or

lenticular shape by crystallization temperature [9–11]. When a high pressure field was added to the isothermal crystallization process the linear polyethylene single crystal with extended chain was found with morphology of circular shape [12]. By existing conceptions extended chain crystals was not realizable at normal conditions because of a high activation barrier to such an extended chain deposition [13]. Since electric field can overcome high activation barrier to form polyethylene extended chain single crystals similar to the elevated pressure, in this paper the formation of single crystals of butyl branched polyethylene thin film samples with various molecular weight under electric field was studied. Morphology and structure of the single crystals were discussed.

## 2. Experimental

### 2.1. Materials

Two metallocene-catalyzed short chains branched polyethylene samples with 1-hexene as comonomer, i.e. with butyl branches, were used in this work, which were produced by the Phillips Petroleum Company and kindly supplied by Professor S.Z.D. Cheng of the University of

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Table 1  
Molecular parameters of the butyl branched polyethylene samples

Samples	$M_w$	$M_w/M_n$	Branch content <sup>a</sup> (branches/1000C)	Average chain length (nm) <sup>b</sup>
F1	5910	1.12	3.4	53
C1	20,600	1.1	10.4	148

<sup>a</sup> The branch content only represents an average value.

<sup>b</sup> The calculation was conducted assuming the planar zigzag conformation.

Akron. After cross-fractionation [14] the fractions possess weight average molecular weight of 5910 and 20,600 Da and polydispersity of 1.12 and 1.1 respectively, which was measured by GPC. The branch content was measured by high temperature solution <sup>13</sup>C-NMR. The molecular parameters of these samples are listed in Table 1.

## 2.2. Instruments and measurements

An instrument to apply electric field to the thin film samples was made in this laboratory. An adjustable distance and voltage between top and bottom electrodes were used to control the electric field intensity applied on the samples. The bottom electrode was also used as a hot stage and its temperature was monitored within 30–500 °C with the temperature fluctuation of about 0.5 °C. In order to avoid the arc breakdown, the electrodes were under a high vacuum of above 10<sup>-3</sup> Pa.

The butyl branched polyethylene thin film samples were deposited from a 0.05% dilute xylene solution onto a freshly cleaved mica substrate coated with evaporated carbon. After evaporation of solvent the thin film samples were transferred on the bottom electrode and heated to 160 °C under vacuum, and the electric field perpendicular to the thin film surface was applied on and kept constantly for 2 h. Then the bottom electrode was quickly cooled to the various crystallization temperatures and the thin film samples started to crystallize. After the crystallization was completed the power was shut down and thin film samples were taken out and quenched in water. Then the thin film samples were transferred on grids and shadowed at tan<sup>-1</sup>(1/2) with platinum for transmission electron microscope observation. The transmission electron microscope was a model of JEOL 2010 TEM with an accelerating voltage 200 kV. The gold was used as calibration of the electron diffraction spacing. Atomic force microscope used in this work was NanoScope III<sup>a</sup> with a standard silicon nitride cantilever with a spring constant of 0.06 N/m and resonance frequency of 5–50 kHz. The contact mode was used under ambient conditions.

## 3. Results and discussions

When butyl branched polyethylene thin film samples with molecular weight of  $M_w = 5910$  Da crystallized iso-

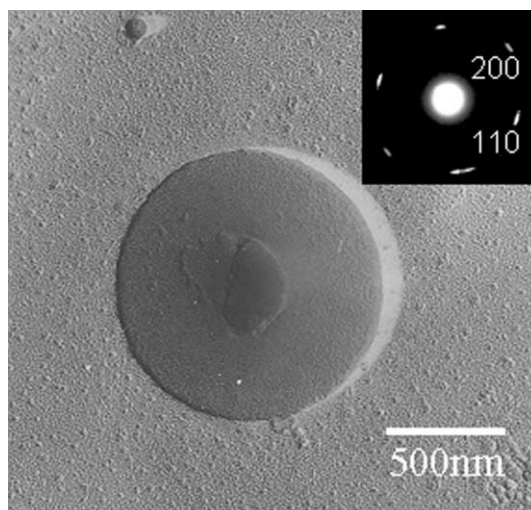


Fig. 1. TEM micrographs and electron diffraction patterns of the single crystals of butyl branched polyethylene with  $M_w = 5910$  Da formed under  $E = 12$  kV/cm and  $T_c = 125$  °C.

thermally from the melt at  $T_c = 125$  °C and  $E = 12$  kV/cm, the lateral habits of the electric field induced single crystals are circular shape as shown in Fig. 1. It can be seen that the lateral habits of single crystals in the presence of electric field for the butyl branched polyethylene are different from truncated lozenge or lenticular shape single crystals formed in the absence of electric field [11]. From TEM observation, the nucleation density of the circular single crystals is much larger, and the radius of the single crystal is much smaller, commonly about 1–1.5 μm. It indicates that the external electric field can induce nucleation of the single crystals. Generally, for a critically stable nucleus with gathering  $N$  strands with length  $L$  and cross-sectional area  $A$ , the free energy of formation of nucleus in the absence of an electric field can be expressed as follows [7]

$$\Delta F_0 = -NLA\Delta f + 2NA\sigma_e + 2L\sqrt{NA}\pi\sigma \quad (1)$$

where  $\sigma_e$  and  $\sigma$  are the end-surface and side-surface free energies of the nucleus and  $\Delta f$  the free energy of melting of a boundless unit volume of crystal. When an electric field was applied in nucleation, the expression for the free energy of formation of nucleus in the presence of electric field ( $\vec{E}$ ) can be written as

$$\Delta F_e = -NLA(\Delta f + \vec{p}\cdot\vec{E}) + 2NA\sigma_e + 2L\sqrt{NA}\pi\sigma \quad (2)$$

Since polarization ( $\vec{p}$ ) and electric field ( $\vec{E}$ ) point to the same direction, the item of  $\vec{p}\cdot\vec{E}$  in Eq. (2) is always positive. Comparing Eq. (1) with Eq. (2) it is shown that the existence of electric field decreases the free energy of nucleation, which makes it easier to form large numbers of nucleus.

It is found that the electron diffraction patterns of the circular single crystals are more surprising as shown in Fig. 1. The existence of (110) and (200) reflection indicates

that the stems in both circular single crystals are almost perpendicular to the basal plane, which is different from chain tilting in single crystals of both linear and butyl branched polyethylene formed in the absence of electric field [11,15]. On the other hand, the structure of the circular single crystals is not typically orthorhombic or hexagonal but quasi-hexagonal structure. The parameters of unit cell are  $a = 0.828$  nm and  $b = 0.487$  nm, which shows cross-sectional area per chain of  $0.202$  nm<sup>2</sup>. According to literature [16] the hexagonal cell of polyethylene crystals formed at elevated pressure referred to orthohexagonal axes are  $a = 0.846$  nm and  $b = 0.488$  nm, which showed cross-sectional area per chain of  $0.206$  nm<sup>2</sup>, and the parameters of a orthorhombic cell are  $a = 0.751$  nm and  $b = 0.505$  nm with cross-sectional area per chain of  $0.190$  nm. It indicates that the chain packing density of the quasi-hexagonal phase in the presence of electric field is lower than that of equilibrium orthorhombic but higher than that of hexagonal phase [2].

The experiments show that the circular single crystals of linear polyethylene in the presence of electric field cannot be formed. It is considered that the branched polyethylene has certain polarities due to the asymmetry of molecular chain, even though the molecular polarities are very weak (the molecular modulation shows that the dipole moment of a branched polyethylene molecular chain is about 0.03 Dby). The experiments also evidenced that, when the strength of electric field is lower, the circular single crystals cannot be formed. Perhaps the branched polyethylene molecular chains respond to the external electric field and change their crystallization growth mechanism. The single crystals do not grow as their crystal faces. For the single crystal growth, the external electric field is a uniform and spherulitically symmetrical field, and the circular single crystals can be formed.

Another feature of the circular single crystal is that its thickness is very large. According to literature [13], the thickness of polyethylene single crystal formed in the absence of electric field and elevated pressure is about 10–20 nm, and increases with increasing crystallization temperature but is almost independent of the molecular weight. However, AFM experiments show that the thickness of the circular single crystal with molecular weight of 5910 Da is about 50–60 nm as shown in Fig. 2, which is much larger than that of single crystal formed in the absence of electric field. For the sample of molecular weight of 20,600 Da, the thickness of the circular single crystals formed in the presence of electric field is about 145–155 nm as shown in Fig. 2. It indicates that the thickness of single crystal in the presence of electric field is molecular weight dependent. This single crystal in the presence of electric field should be extended chain type single crystal.

Maybe the structural analyses can help us to understand the reason of the extended chain type single crystal formation. It has been reported that a single crystal tended to grow two-dimensionally, i.e. lateral growth and thickening

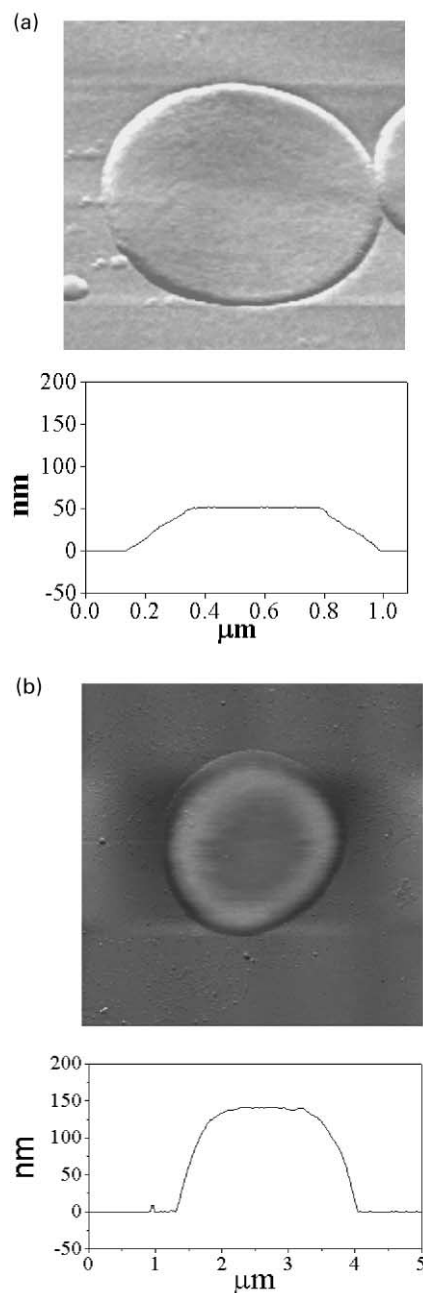


Fig. 2. AFM images of (a) circular single crystals of lower molecular weight sample formed under electric field with  $E = 12$  kV/cm and  $T_c = 125$  °C and (b) that of higher molecular weight sample with  $E = 12$  kV/cm and  $T_c = 120$  °C. The curves show that the thickness of the single crystals are 50–60 nm for lower molecular weight sample and 145–155 nm for higher molecular weight sample.

growth, because the thermodynamic driving force and the sliding diffusion of chains within the single crystal played essential roles [17,18]. The thickening growth of a single crystal depended on chain packing density. The looser the chain packing, the easier was the thickening growth. According to earlier discussions, the cell density of single crystals formed in the presence of electric field is much smaller and the chain packing is much looser. Therefore,

under the electric field the thickening growth rate of the single crystal was larger and sliding diffusion of chains occurred easily, which is similar to the conditions of elevated pressure, and an extended chain type single crystal can be formed.

On the other hand, according to literatures [15,19], the surface folding of a folded chain single crystal formed from the melt is non-adjacent re-entry and the folding surface is less regular compared to that of single crystals formed from solution. The surface alignment of the circular single crystals in the presence of electric field was determined by AFM in the range of  $\sim 5$  nm as shown in Fig. 3. It shows that the surface alignment is very regular. The surface point packing is in agreement with electron diffraction results with  $a = 0.822$  nm and  $b = 0.494$  nm. It once more

suggests that the circular single crystal with truncated tapered cross-section should be an extended chain type single crystal and the extended chains are packed side-by-side in the single crystals.

#### 4. Conclusions

Morphology of the butyl branched polyethylene single crystals was circular shape when melt crystallization was carried out isothermally in the presence of electric field. The chain orientation in the circular single crystals was almost perpendicular to the basal plane, which was different from chain tilting in single crystals formed in the absence of electric field. The structure of the circular single crystal was a quasi-hexagonal structure and chain packing density in the circular single crystals was lower. The thickness of the single crystal was much larger and depended on molecular weight. It implied that the single crystal in the presence of electric field was an extended chain type single crystal.

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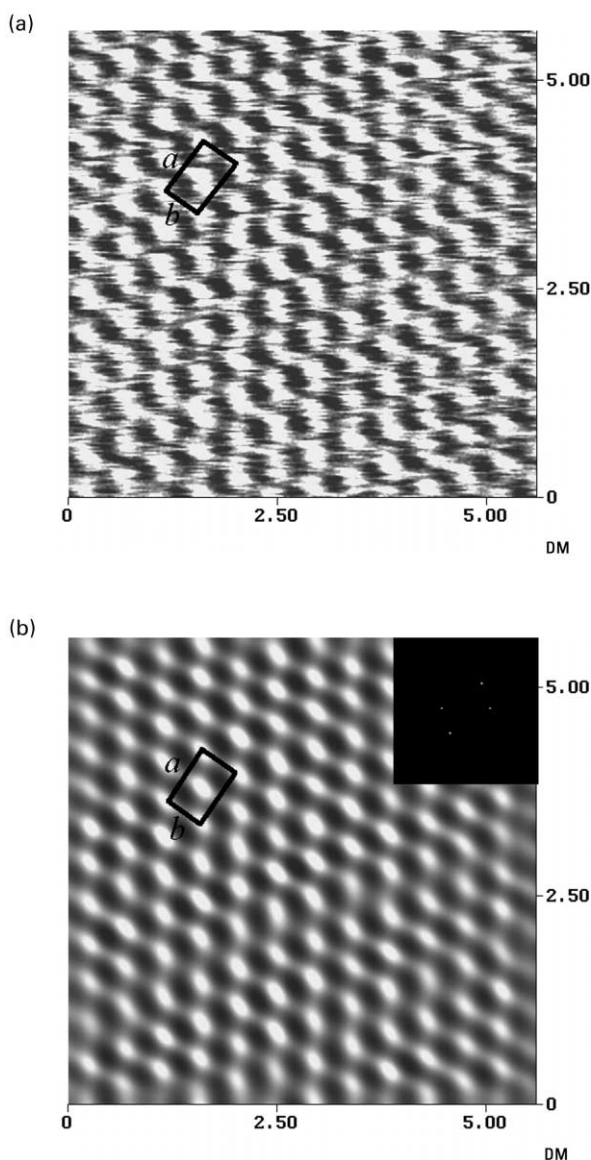


Fig. 3. High-resolution AFM image at surface of the circular single crystal with truncated tapered cross-section. (a) Original image and (b) image after Fourier transmission. The insert indicates a quasi-hexagonal cell (as ortho-hexagonal axes).