

SOLUTION CRYSTALLIZATION OF METALLOCENE SHORT CHAIN BRANCHED POLYETHYLENE: MORPHOLOGY AND MECHANISM*

Qiang Fu** and Rong-ni Du

*Department of Polymer Science & Materials, Sichuan University,
Chengdu, Sichuan 610065, China*

Fang-Chyou Chiu

Department of Chemical Engineering, Chang Gong University, Taoyun, Taiwan, China

Abstract Solution crystallization of metallocene short chain branched polyethylene (SCBPE) was carried out and very nice single crystals were obtained. Compared with single crystals grown from linear polyethylene, SCBPE single crystals are dirty due to intermolecular heterogeneity. The crystal morphology changes with crystallization temperatures. Lozenge, truncated lozenge, hexagonal, rounded and elongated crystal morphologies have been found at much lower crystallization temperature than in linear polyethylene. The electron diffraction shows there is a possibility that the single crystals may have hexagonal packing in a crystallization temperature range. The lateral habits of single crystal are discussed based on roughening theories.

Keywords Metallocene SCBPE, Single crystal, Roughening face, Growth mechanism

INTRODUCTION

Polyethylene (PE) with the repeating unit $-\text{CH}_2-\text{CH}_2-$ is one of the most utilized thermoplastic resins in the world. PE can be generally classified as three families: linear PE, long chain branched PE and short chain branched PE (SCBPE). Linear PE possesses linear structure without any branches, long chain branched PE represents the co-existence of long side chain branches and short side chain branches. SCBPE is a copolymer of ethylene and α -olefin such as 1-butene, 1-hexene and 1-octene. It consists of a linear backbone with short chain branches. Recently, metallocene SCBPE has received increasing interest in both academic and industrial circles due to its super thermal and mechanical properties. Compared with Ziegler-Natta copolymers, these SCBPEs set a new standard for polymer purity with narrower molecular weight and more uniform comonomer sequence distributions.

Solution crystallization of polyethylene is quite an old topic. A lot of work has been done on linear polyethylene single crystals grown from solution, covering the crystal structure, crystal morphology, growth kinetics and mechanism^[1-11]. The lamellar nature of polyethylene single crystals grown from dilute solution is well known. The well faceted lateral habits can be obtained from dilute solutions at relatively low crystallization temperature. The increasing curvature of nominally {100} faces can be seen as the crystallization temperature increases on or crystallization in a poorer solvent, such as dodecane or heptyl acetate. Two types of mechanism have been proposed for the rounding of habits. 1) thermally roughening, that is the growth face can be thermally roughened, namely, the free energy of a step vanishes at high temperature^[12]. Under such a condition, the crystal

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** Corresponding author: Qiang Fu (傅强), E-mail: qiangfu@pridns.scu.edu.cn

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growth front becomes rounded. 2) interrupted roughening, that is the advance of steps is interrupted by impurities^[13] or lattice strain^[14]. This effect results in the accumulation of steps on the growth face and the rounding of the growth front. The reason why a PE crystal has curvature at high temperature is still open to question.

So far almost all the solution crystallization is limited to linear PE, little has been reported on LDPE or SCBPE. It is hard to grow nice single crystal from branched PE, mainly because of the high heterogeneity among the molecules of LDPE or SCBPEs. Due to their narrower molecular weight and more uniform comonomer sequence distributions, metallocene SCBPEs make it possible for us to grow nice single crystal from solution.

The aim of this work is to extend solution crystallization from linear PE to SCBPE to obtain a broad base of quantitative data relating the lateral crystal habit to crystallization temperature and branching content. We will correlate these lateral habits and roughing theories of polymer to further clarify the mechanism.

EXPERIMENTAL SECTION

Materials

The hexyl-branched metallocene SCBPEs were provided by Phillips Petroleum Co. They had a weight average molecular weight (M_w) of 20,000 and a polydispersity(M_w/M_n) of 1.1. The branching content was 8.8 mol%.

p-Xylene and *n*-dodecane were chosen as the good and poor solvent for SCBPE, respectively as in the case of linear PE. The solvents were purified by distillation.

Sample Preparation

Suspensions of polymer crystals in a solvent were prepared as follows. An appropriate weight of SCBPE sample was first dissolved in the solvent by heating for 2 h at 100°C (xylene) or 130°C(dodecane). Then crystallization proceeded for 1000 min in an oil bath controlled to $\pm 0.3^\circ\text{C}$ at preset temperatures.

Electron Microscopy and Diffraction

Samples for electron microscopy and diffraction were deposited on carbon substrates before being shadowed and transferred to electron microscope grids.

RESULTS AND DISCUSSION

Crystal Habits

The electron micrographs of single crystals of SCBPE grown from 0.2% xylene and dodecane solution are shown in Fig. 1. Compared with single crystals grown from linear PE, it is interesting to note following features of SCBPE single crystals: 1) All the crystals are quite "dirty". The small crystals deposited on the main single crystal come from the molecules with relative high branching content, which can not crystallize at preset temperature, but crystallize during or after quenching to room temperature. As the crystallization temperature increases, the small aggregates become more dense, indicating that more and more molecules are excluded from the crystal at given temperatures. That means only molecules with less branching content can grow single crystals at higher temperature. Our result shows that even the metallocene SCBPEs possess at least macro-molecular heterogeneity, that is to say some molecules have higher branching content than the others. This conclusion coincides with our DSC stepwise crystallization data^[15]. 2) Single crystals with lozenge, truncated lozenge, hexagonal and elongated crystal morphologies are grown at much lower crystallization temperatures than in linear polyethylene, for example, the crystallization temperature will go to about 90°C for hexagonal shape in case of linear PE^[1], but only 80°C here. This is probably due to the limitation of crystal thickness. Due to the effect of branching, the crystal thickness can not grow to big size and the thin crystals will be dissolved at high temperature. It is surprising that the roughing face has not been found for the highly branched PE. If the interrupted roughing mechanism is correct, it should be easier for the highly branched SCBPE to be interrupted and rounded. 3) The electron diffraction of the crystals suggests that the single crystal with high chain branching may have hexagonal packing at high crystallization temperature (80°C and 82°C), as shown in Fig. 2a), but orthorhombic packing at low crystallization temperature ($< 78^\circ\text{C}$), as shown in Fig. 2b). The only explanation for

the hexagonal packing is that the side chain is included in the crystal lattice at high crystallization temperature.

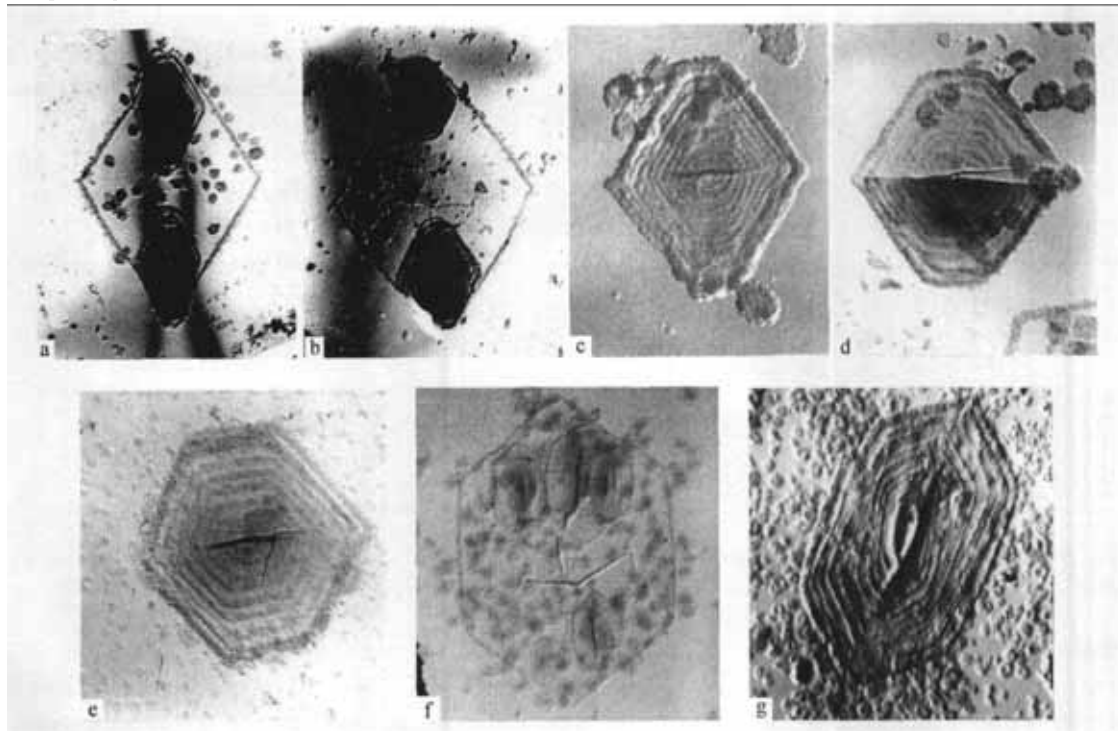


Fig. 1 Electron micrographs of single crystal grown from SCBPE, all the magnifications are 5000; crystallization temperature a) 70°C, b) 75°C, c) 78°C, d) 80°C e) 82°C, f) 86°C and g) 90°C a)–e) crystallized in xylene, f) and g) crystallized in dodecane

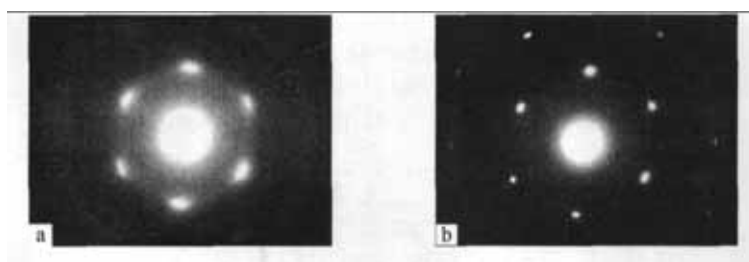


Fig. 2 Examples of electron diffraction of single crystal showing the hexagonal packing a) and orthorhombic packing b)

Growth Mechanism

For linear polyethylene, the lozenge and truncated lozenge are the typical habits at lower crystallization temperature as shown in Fig. 3. Lenticular (type a) and truncated lozenge with curved edges of the $\{100\}$ growth faces (type b) at high crystallization temperature are the two typical habits. The three dimensional structures of polyethylene crystals have been well documented. Truncated hollow pyramid, chair crystal and hollow pyramid are reported. Our result shows SCBPE single crystals have the same morphologies of the linear polyethylene.

The most successful theory of polymer crystal growth has been the kinetic theory developed mainly by Hoffman *et al*^[16]. Depending on the competition between nucleation rate and the lateral spreading rate, Hoffman and his co-workers were the first ones to introduce the concept of regime transitions into the crystallization of polymer after an investigation on linear PE fractions. Three regimes were established as shown in Fig. 4. In Regime I the growth front is smooth and all folds are parallel to the edge of crystal. In Regime II the surface becomes rougher and in Regime III a rough growth front is produced. According to Hoffman's theory, crystals

formed at lower supercooling would be expected to grow slowly and have well-defined facets and more regular fold surface structure. So Hoffman's theory and the experimental observation are not compatible. On the other hand, the thermally roughening mechanism, can not explain the strong anisotropy of single crystals either. When the growth face is thermally roughened, the face can grow without secondary nucleation and growth should be enhanced and isotropic.

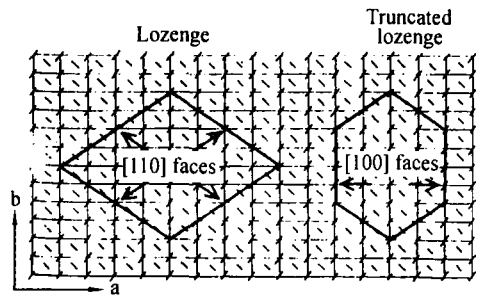


Fig. 3 Typical morphologies of PE single crystals at low crystallization temperature

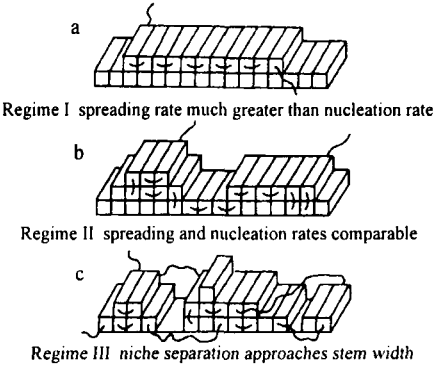


Fig. 4 Schematic representation of Hoffman's three regimes theory

With the assumption of interrupted crystallization, it is expected that single crystals grown from SCBPE, which has side groups on the backbone, will be easier to be roughened. There are two factors, which may retard the growth. First, metallocene SCBPES possess at least molecular heterogeneity, only molecules with less branching content can be crystallized at high temperature. So the higher the temperature, the less the molecules can be crystallized, hence the more the impurities will be in the solution. Secondly, after the side groups are rejected from the crystal lattice, they will locate on crystal surface instead. So the lattice strain will be stronger compared with crystal grown from linear polyethylene. If the growth steps can be treated as kinks on one dimensional substrate (Fig. 5), these two factors will seriously interrupt the advance of a step, and make the single crystal be rounded easier. However, the roughening face of single crystals with high branching has not been seen at the temperature studied. The reason is not clear so far, and warrants further study. Inclusion of the side chain in the crystal lattice is a good explanation for the present observation.

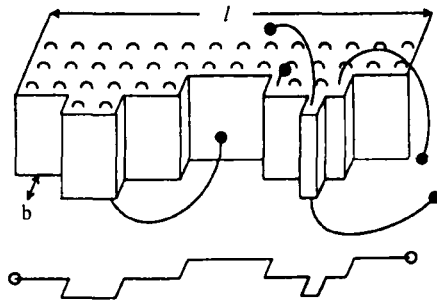


Fig. 5 Correspondence between steps on growth face and kinks on one-dimensional substrate

CONCLUSION

We have succeeded in growing single crystals from metallocene SCBPE samples. The branching and crystallization temperatures have a large effect on the lateral habits. Lozenge, truncated lozenge, hexagonal, rounded and elongated crystal morphologies have been found at much lower crystallization temperature than in

linear polyethylene. The roughening face has not been seen for the highly branched SCBPE. Future work is needed to make more clean and nice single crystals, and to clarify further their morphologies and mechanism.

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