

Effect of branch content on the transition of crystalline structure and morphology of metallocene-catalyzed branched polyethylene

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Transition of crystalline structure and morphology of metallocene-catalyzed butyl branched polyethylene with branch content has been studied. It was found that the long periods of the branched polyethylene were controlled by crystallization conditions for the lower branch content samples and by branch contents for the higher branch content samples. When the branch content increased to a critical value the branched polyethylene had no long period because the crystalline morphology was changed from folded chain crystal to a bundled crystal. The TEM observations supported the results. The transition of the crystalline morphology resulted from the reduction of lamellar thickness with increasing of branch content since the branches were rejected from the lattice. The reduction of lamellar thickness with increasing of branch content also resulted in lattice expansion and decrease of melt temperature of the branched polyethylene. © 2001 Kluwer Academic Publishers

1. Introduction

Metallocene-catalyzed branched polyethylene, a copolymer of ethylene and α -olefin such as butene-1, hexene-1, or 4-methyl-pentene-1, has found a wide range of uses due to its enhanced thermal, optical and mechanical properties [1–4]. It was considered as a model compound to study crystalline structure and properties of crystalline polymer with branch chains due to its narrow molecular weight and strongly uniform comonomer sequence distributions. Although substantial progress has been made in almost every aspect of structure and property characterization [5–8], it is clear that the crystalline structure and morphology of these materials have not been fully understood because of their complexity of chemical microstructure [9].

The crystalline structure and morphology of branched polyethylene are dependent on the content, length and distribution of branches, together with the crystallization conditions. The content and length of branches formed from the copolymerization are related to the concentration and type of α -olefin while the distribution of branches is dependent on the polymerization conditions [10]. There is consensus that most short-chain branches, which accompany enchainment of α -olefin comonomers, are rejected from the polyethylene-like crystals [11, 12]. As branch content increases the lamellae first become thinner and eventually deteriorate into small crystallites. Therefore, the branch content is a predominant factor on

the crystalline structure and morphology of branched polyethylene.

Hitherto, there were many fractionation methods, such as solvent gradient fractionation, temperature raising elution fractionation and cross fractionation, to obtain homogeneous branched fractions. However, it must be recognized that it is impossible to obtain completely homogeneous fractions and there exist two kinds of heterogeneity in a branched polyethylene system: intra- and intermolecular heterogeneity in which the distribution of branches is not uniform along the chain backbone and among the molecules [13, 14]. The heterogeneity of distribution of branches results in the existence of many crystalline segments with various lengths, which makes the crystalline structure and morphology of branched polyethylene very complex with changing of branch content, especially for the high branch content fraction. In the work described in this paper, the crystalline structure and morphology of the butyl branched polyethylene (BBPE) with various branch contents were studied. The transition of crystalline structure and morphology with branch content was discussed.

2. Experimental procedure

Metallocene-catalyzed BBPE samples, with ethylene and 1-hexene as the comonomer, were provided by the Phillips Petroleum Company. The samples were

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TABLE I Molecular characteristics of butyl branched polyethylene samples

Samples	M_w	M_n	M_w/M_n	Branch contents (branches/1000C)
CF	5910	5160	1.14	3.4
C1	20600	18800	1.1	10.4
C2	31400	28100	1.12	10.6
C3	41400	36900	1.12	10.7
D1	19700	17500	1.13	40.2

fractionated by a cross fractionation method before they were used [15]. The fraction code D1 was just fractionated by solvent gradient fractionation. The molecular weight and polydispersity was measured by gel permeation chromatography (GPC). The branch content was measured by high temperature solution ^{13}C -NMR. The molecular parameters of these samples are listed in Table I. Note that the branch content only represents an average value.

The BBPE thin film samples with thickness of ~ 0.5 mm for small angle X-ray scattering (SAXS) experiments were melted at 160°C in a hot stage for five minutes, then they were shifted as quickly as possible to an oil bath at a preset crystallization temperature (T_c). The temperature fluctuation in the oil bath was controlled at $\pm 0.2^\circ\text{C}$. After a sufficiently long residence time of about three days the samples were quenched to room temperature in water. The SAXS experiments were carried out on a Philips PW1700 X-ray Diffractometer with Kraky small angle scatter system with $I = 40$ mA and $V = 45$ kV, Cu K_α ray ($\lambda = 0.1542$ nm). Wide angle X-ray diffraction (WAXD) experiments were also carried out on the Philips 1700 X-ray Diffractometer. The 2θ angle was scanned between 5° and 60° with scanning rate of $2^\circ/\text{min}$. The WAXD peak position and width were calibrated using a standard silicon crystal with known crystal sizes. The measurements of melt and crystallization temperature were carried out on a Perkin-Elmer DSC-7. To avoid influence of the transition of structure and morphology on the melt temperature, all samples were cooled rapidly from the melting state to room temperature.

The BBPE thin film samples with thickness of about 100 nm for TEM observations were deposited from a 0.5% dilute solution in xylene onto a freshly cleaved mica substrate coated with carbon. The thin films were isothermally crystallized at 105°C for about 24 hours and then were transferred onto electron microscope grids and shadowed at about 20° with Pt. Morphological observations were performed in a JEOL 2010 TEM with an accelerating voltage 200 kV. Gold was used to calibrate the electron diffraction spacings.

3. Results and discussions

The influence of branch content on crystalline structure of the BBPE can be determined by SAXS experiments. Fig. 1 shows the Lorentz-corrected intensity functions of the BBPE samples crystallized isothermally at 102°C and 105°C . It is found that the long periods of C1, C2 and C3 are almost the same under the same crystalliza-

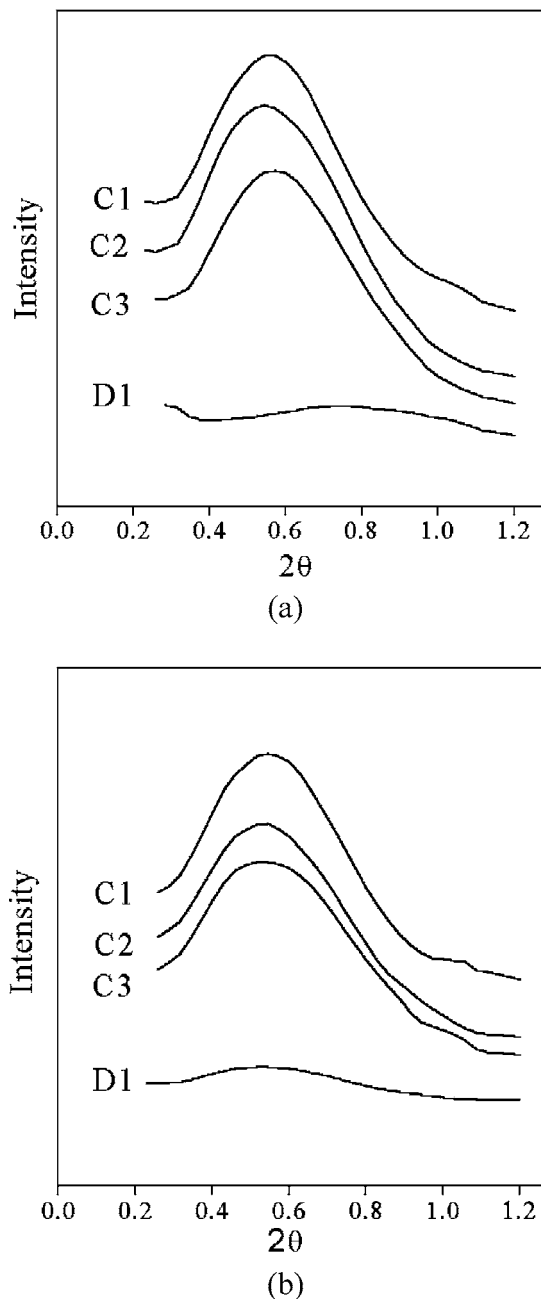


Figure 1 The Lorentz-corrected one-dimensional intensity function of the butyl branched polyethylene crystallized isothermally at (a) $T_c = 102^\circ\text{C}$ and (b) $T_c = 105^\circ\text{C}$.

tion temperature, which indicates that the molecular weight has no influence on the long period in the range of molecular weight used here. It is also found that the long periods of C1, C2 and C3 do not change with changing crystallization temperatures (see Table II). Nevertheless, as shown in Fig. 2, the long periods of CF with lower branch content are increased with increasing crystallization temperature. Generally, the long periods of crystalline polymers would increase with increasing crystallization temperature due to the thermodynamic effects. However, the long periods of the BBPE are dependent on both crystallization temperature and branch contents since the butyl branches are rejected from the crystals at normal isothermal crystallization conditions. With branched molecules the thickness of the crystal lamellae only can be smaller than the length between adjacent branch chains on the chain backbone. At lower

TABLE II Long periods and crystallinities of butyl branched polyethylene

Samples	Long periods (nm)		Crystallinity (%) ($T_c = 102^\circ\text{C}$)	Unit cell paraters		
	$T_c = 102^\circ\text{C}$	$T_c = 105^\circ\text{C}$		a (nm)	b (nm)	c (nm)
CF	19.53	20.61	89.6	0.751	0.505	0.251
C1	16.05	16.25	64.2	0.756	0.505	0.252
C2	16.12	16.30	63.8	0.755	0.505	0.251
C3	16.06	16.25	64.4	0.756	0.504	0.252
D1	—	—	32.4	0.764	0.506	0.252

crystallization temperature with long annealing time, the thickness of crystal lamellae of C1, C2 and C3 have approached the length between adjacent branch chains due to the higher branch contents and do not increase with increasing crystallization temperature. The thickness of crystal lamellae in CF is smaller than the length between adjacent branch chains at lower crystallization temperature, due to the lower branch contents, although the crystallization time is long enough. It would be increased through raising crystallization temperature until the crystal lamellae thickness approaches the length between adjacent branch chains. It is concluded that the long periods of the BBPE are controlled by branch content for the higher branch content samples and by crystallization temperature for the lower branch content samples.

It is found from Fig. 1 that the long periods of D1 can not be observed by SAXS at either of the two crystallization temperatures. It indicates that BBPE with very high branch content has no long period structure. The transition of the long period with branch content is related to the transition of crystalline morphology. According to the literature [16, 17], the crystalline morphology of branched polyethylene can be divided into four types with increasing of branch content: (1) lamellar morphology with well-developed spherulitic superstructure; (2) thinner lamellae and smaller spherulites;

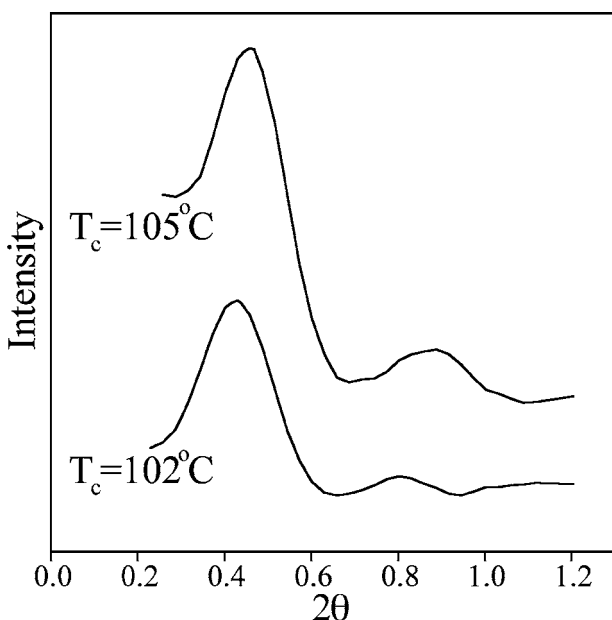


Figure 2 The Lorentz-corrected one-dimensional intensity function of C1 sample. It shows the increasing of long periods of C1 sample with increasing of crystallization temperature.

(3) a mixed morphology of small lamellae and bundled crystals; (4) no lamellae or spherulites. Thus, when the branch content is smaller, such as with CF, C1, C2 and C3, the BBPE can form regular folded crystals similar to linear polyethylene as shown in Fig. 3a. With the increasing branch content to the extent present in D1, the length between adjacent branch chains on the chain backbone is too short to form folded crystals and the bundled crystals with very small lamellar thickness through aggregation of molecular chains form instead as shown in Fig. 3b. In the bundled crystals the lamellae are less ordered and there does not exist regular alternation of crystalline layers and disordered amorphous regions, i.e. there is no long period in D1 crystals.

It can be seen that the crystalline morphology of the BBPE is changed from folded to bundled crystals when the branch content are increased to a certain level. The transition of morphology may be observed directly by TEM. Fig. 4 shows the TEM micrographs of C1 and D1 thin film samples crystallized isothermally at 105°C . It is found that large edge-on lamellae in the C1 sample aggregate to form large spherulites while thinner and smaller lamellae in the D1 sample are separated irregularly by a large amount of amorphous phase. The TEM observation results further evidenced the transition of morphology of the BBPE with branch content. On the other hand, it is also found from Fig. 4 that the crystallinity of the BBPE is changed due to the transition of morphology. It is clear that the amorphous phase content would be increased with increasing of branch

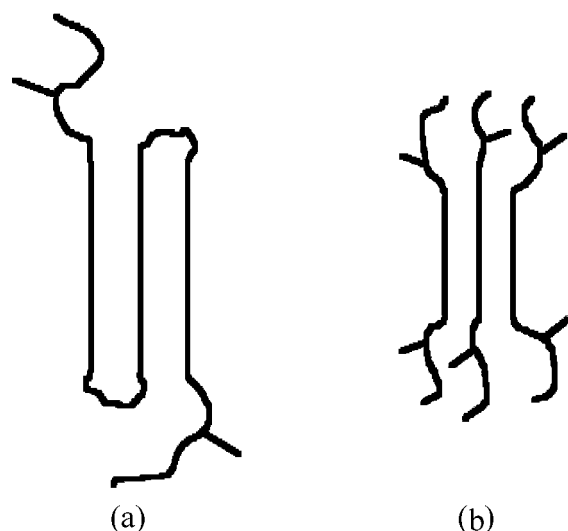
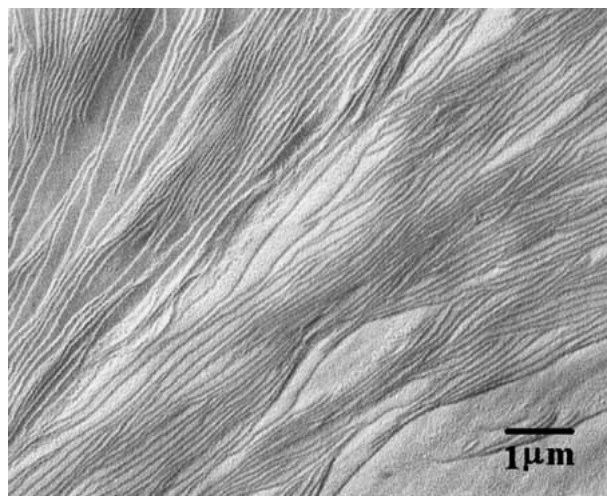
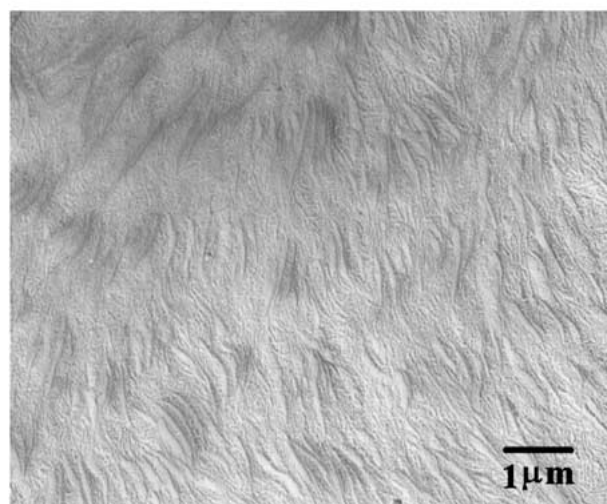


Figure 3 Schematic representation of the transition of crystalline morphology of the branched polyethylene from (a) folded chain crystals to (b) bundled crystals with increasing of branch contents.



(a)



(b)

Figure 4 TEM micrographs of (a) C1 and (b) D1 thin film samples crystallized isothermally at 105°C.

content because the branches are rejected from the lattice and exist in the amorphous region. The WAXD results show that the crystallinity of the BBPE is decreased with increasing of branch content as shown in Fig. 5. As shown in Table II the crystallinity in the

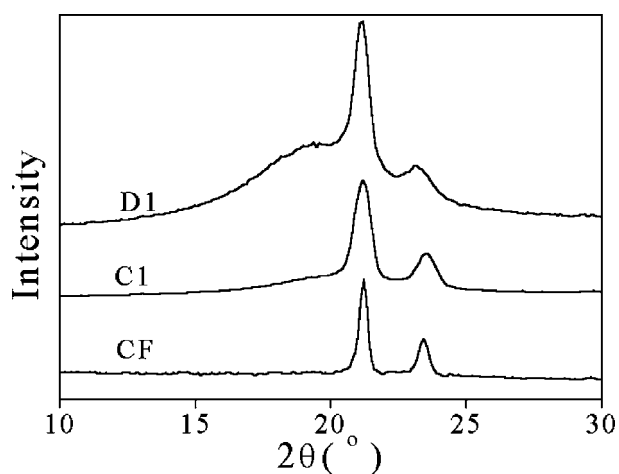


Figure 5 WAXD pattern of the butyl branched polyethylene with various branch contents crystallized isothermally at 105°C.

D1 sample is half of that in the C1 sample under the same crystallization condition although their molecular weights are almost the same.

It is also found from Table II that the lattice expands in the a direction with increasing branch content. The lattice expansion results are more confusing. The initial interpretation is that the branches may be accommodated within the lattice through the conformational defects of molecules [18]. However, the conformational defect does not provide enough volume to accommodate ethyl and alkyl branches. The main reason of the lattice expansion should be the reduction of lamellar thickness with the increasing branch content. It is well documented that the unit cell of the thinner crystal lamellae may be altered by the local stress exerted at the basal planes, and the lattice expansion can be occur due to the strain at the interphase. This phenomenon is also observed in linear polyethylene both solution and melt crystallized and in the n -alkanes. Davis and coworkers [19] ascertained that the unit cell dimensions of linear polyethylene are functions of the lamellar thickness, i.e. the thinner the lamellae, the larger the unit cell dimensions. Thus, it is demonstrated that the lattice expansion with increasing branch content results from the formation of thinner crystal lamellae controlled by the length between adjacent branch chains although no branch chains are included within the lattice.

The reduction of the lamellar thickness with increasing of branch content is also evidenced through analysis of the melt temperature. To avoid structural and morphological complications present after isothermal or slow crystallization the rapidly crystallized samples were analyzed through DSC melting thermograms. This crystallization procedure is quite satisfactory for comparative purposes although it is far from equilibrium. Fig. 6 shows the melt temperature of the rapidly crystallized BBPE samples. It indicates that the melt temperature decreases with increasing branch content. Obviously, decreasing the melt temperature results from decreasing the lamellar thickness. On the other hand, it is worthy to note that D1 has two peak melt temperature. Because D1 is a fraction of solvent gradient fractionation, so that there exists intra-molecular

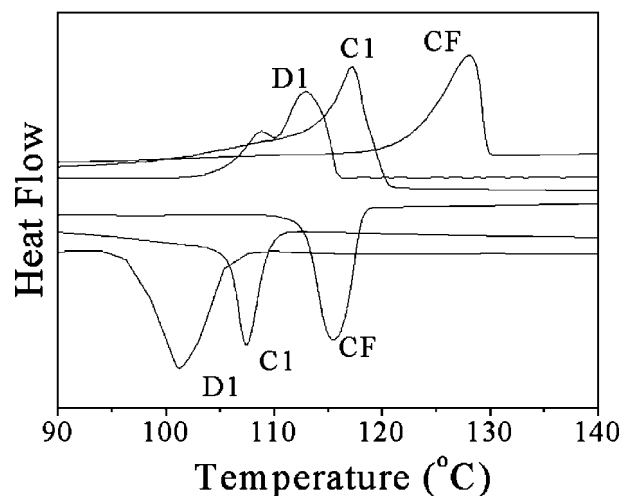


Figure 6 DSC heating and cooling traces of rapidly cooled CF, C1 and D1 samples. The heating and cooling rates are 10°C/min.

heterogeneity in a branched polyethylene. The distribution of branches is not uniform along the chain backbone, i.e. the length between adjacent branch chains at the same backbone is not the same. Since the D1 sample contains a type of bundled crystals in which the lamellar thicknesses are controlled by the length between adjacent branch chains, lamellae with various thicknesses would be formed in D1 crystals. Thus, the thinner crystal lamellae would melt first, then the thicker, and two peak melt temperatures would appear in the melting thermograms. For the samples with lower branch content such as CF and C1, because the length between adjacent branch chains is long enough and the lamellar thickness is almost uniform, only one peak melt temperature appears in the melting thermograms.

4. Conclusions

(1) When the branch content of the butyl branched polyethylene are low, it can form regular folded chain crystals with regular alternation of crystalline layers and disordered amorphous regions. However, when the branch content of the butyl branched polyethylene are high, it only can form a bundled crystal, because the crystallization segments are too short to fold, with the thinner and smaller lamellae less regularly separated by the amount of amorphous phase. The long periods of the branched polyethylene were controlled by crystallization conditions for the lower branch content samples and by branch content for the higher branch content samples.

(2) With limitation of branches the lamellar thickness of branched polyethylene would decrease with increasing branch content. The reduction of the lamellar thickness resulted in the decreasing of crystallinity and melt temperature and lattice expansion of the branched polyethylene with increasing branch content.

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