Molecular, thermal and morphological characterization of narrowly branched fractions of 1-octene LLDPE: 2. Study of the lamellar morphology by transmission electron microscopy

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(Received 29 January 1992; accepted 17 March 1992)

The lamellar morphology of a linear low density ethylene/1-octene copolymer (LLDPE A), and its fractions with short chain branching contents ranging between 3 and 28 branches per 1000 C atoms, has been investigated using transmission electron microscopy. The weight average molecular weight of the samples studied decreases from 2.7×10^5 at the lowest branching content down to 4.9×10^4 at the highest branching content. The branching content is the major factor determining the lamellar thickness, while the morphological structure of the lamellae depends both on the branching content and the molecular weight. In contrast to the unfractionated copolymer LLDPE A, lamellar stacks were observed in all fractions.

(Keywords: LLDPE; TEM; lamellar morphology; quantitative analysis)

INTRODUCTION

The lamellar morphologies developed during crystallization from the melt of linear polyethylene are mainly determined by the molecular weight and the polydispersity of the samples[1–3]. Copolymerization of ethylene with an α-olefin introduces short chain branches in the polymer chain. Branches of sufficient size restrict the formation of thick lamellae. The comonomer content and the intra- and intermolecular distribution of the branches are, in combination with the crystallization conditions, the dominant factors controlling the thickness distribution of the lamellae[4,5]. The shape of the lamellae and the spherulitic morphology are also molecular weight dependent.

Ethylene/α-olefin copolymers (LLDPEs) are known to have a very heterogeneous chain microstructure, characterized by a broad distribution in molecular weight and ethylene sequence length[6–8]. A systematic study of the morphology of LLDPE is only possible through fractionation of the copolymer with respect to the short chain branching content and/or molecular weight. Different fractionation techniques have been used to elucidate the chain microstructure of LLDPE and its influence on the crystallization and melting behaviour[4–7,9–11].

In the first paper of this series[12], the preparative fractionation of a 1-octene LLDPE sample into eight fractions with a narrow short chain branching distribution has been presented. The chain microstructure has a strong influence on the thermal properties of the fractions. In the present paper the results of a quantitative study of the morphology of the fractions using transmission electron microscopy (TEM) are reported. The TEM technique, when used in combination with a statistical analysis, allows the determination of the complete lamellar and amorphous thickness distributions. Also, detailed information on the lamellar morphology of the fractions obtained in this study is of importance for correct interpretation of the diffraction experiments which will be presented in part 3[13].

EXPERIMENTAL

Materials

An ethylene/1-octene copolymer (LLDPE A), synthesized in a solution process has been fractionated with respect to the short chain branching content using a preparative temperature rising elution fractionation (TREF) technique. Eight fractions with a narrow short chain branching distribution were obtained. The average branching content of the samples ranges between 3 and 28 branches per 1000 C atoms. The sample with the lowest branching content has a weight average molecular weight of 2.5×10^5 which decreases to 4.9×10^4 at the highest comonomer content. The fractionation and molecular characterization have been reported in detail in part 1[12]. The molecular characteristics and crystallinity of the fractions and of the

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0032-3861/92/245186-05

Table 1 Average short chain branching content, weight average molecular weight, polydispersity and crystallinity of the fractions and the unfractionated LLDPE A

Fraction	SCB[a]	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	χ_c[b]
A1	39.6	19 100	3.98	11
A2	28.2	49 300	3.37	23
A3	20.4	94 000	2.86	34
A4	14.8	128 200	2.76	34
A5	11.5	146 200	2.75	41
A6	6.4	176 300	2.44	51
A7	3.2	252 000	2.20	48
A8	2.9	269 000	2.19	54
LLDPE A	9.7	114 000	3.67	37

[a] Number of branches per 1000 C atoms
[b] Calculated from the heat of fusion

unfractionated copolymer LLDPE A are given in *Table 1*. Fractions A1 and A8 will not be further considered on account of the very limited quantities obtained by fractionation.

Sample preparation and the method of analysis of the micrographs

The samples were heated to 150°C during 10 min and subsequently crystallized from the melt on cooling at a rate of 5°C min^{-1}. Due to the identical thermal history, the same morphology is considered in the microscopic investigations as in the previous thermal study[12]. The staining and thin-section techniques used for the TEM study are essentially the method developed by Kanig[14]. The samples were treated at room temperature with chlorosulphonic acid for 12 h (A2), 1 day (A3), 2.5 days (A4, A5, A6 and LLDPE A), 4.5 days (A7), and subsequently stained with 2% uranyl acetate for 24 h. The low staining temperature and shorter staining times for the fractions with a high comonomer content are necessary to restrict staining damage[15]. Under such conditions, the staining medium only penetrates the amorphous zones, the crystalline core and the transition zones being unaffected[16,17].

The stained samples were sectioned into slices 30–50 nm thick at a temperature of −50°C using a glass-knife-equipped Reichart-Jung FC4 Ultracut E cryo-ultramicrotome. The low cutting temperature in combination with the increased mechanical resistance of the samples through staining, resulted in a low degree of cutting damage.

In order to obtain accurate values for the crystalline thickness, the samples were tilted until maximum contrast was obtained, indicating that the observed lamellae were parallel to the electron beam. The thickness of ~600 lamellae of each sample was measured and plotted into histograms with steps of 1 nm, which is about the accuracy of the readings. Within the regions where the lamellae were ordered in stacks, the amorphous thickness was determined in a similar way; ~150 values of the amorphous thickness could be measured for each sample.

RESULTS AND DISCUSSION

Crystalline lamellar thickness

The lamellar thickness frequency distributions of the fractions and LLDPE A are presented in *Figure 1*. The fractions A2, A3 and A4 with high comonomer contents, exhibit a comparable lamellar population with a narrow distribution. In the range of lower branching contents (A5, A6, A7), a gradual increase of the average lamellar thickness can be observed with decreasing branching content while the distributions become broader. The skewness of the histogram of fraction A7 towards higher values indicates the less pronounced influence of the branches on the lamellar thickness at low branching content.

The heterogeneous chain microstructure of the unfractionated copolymer LLDPE A results in a very complex crystallization exotherm and the double melting endotherm, as was shown in part 1[12]. The lamellar thickness distribution of LLDPE A as obtained by TEM consequently displays a broad lamellar thickness distribution. The thickest lamellae, which were present in fraction A7 are, however, absent in the unfractionated copolymer. The absence of the very thick lamellae confirms the lower final melting point of LLDPE A as compared to fraction A7, and arises from the cocrystallization of weakly branched molecules[12].

The lamellar thickness distributions have been fitted with a Gaussian function and good agreement was obtained, except for sample A7 which has a skewed distribution. The minimum and maximum observed thicknesses of the lamellae and the mean thickness are plotted as a function of the chain branching content in *Figure 2*.

The almost identical lamellar populations of fractions A2, A3 and A4 seemingly contradicts the further decrease of the melting point T_m with increasing branching

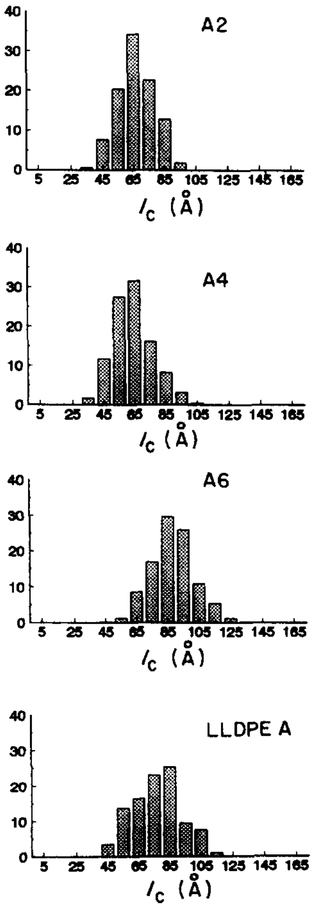

Figure 1 Lamellar thickness frequency histograms of the fractions and LLDPE A

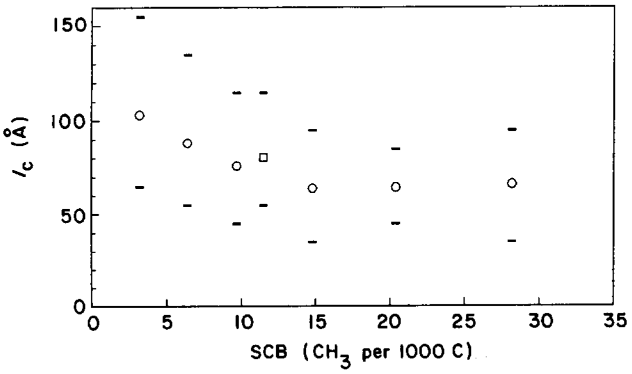

Figure 2 Upper and lower limits and mean values (○) of the lamellar thickness (l_c) as a function of the short chain branching (SCB) content of the fractions and LLDPE A (□)

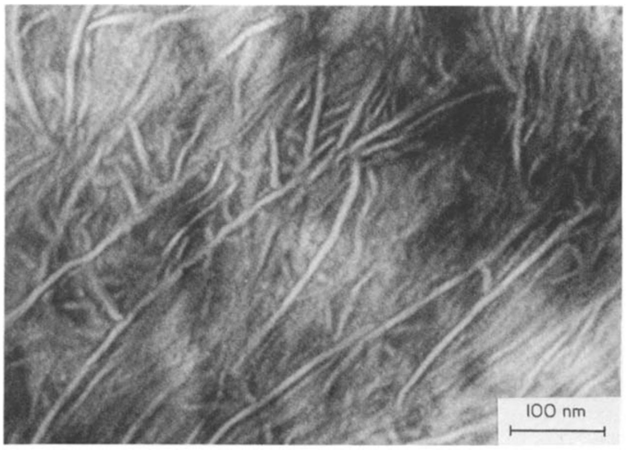

Figure 3 Electron micrograph of LLDPE A

content[12]. However, the lamellar thickness, as obtained with TEM measurements, includes the core of the crystals as well as the transition layer[18]. A decrease of the core thickness could therefore be masked by an increase in thickness of the transition layers. The results of the SAXS experiments, presented in part 3[13], indeed confirm a further decrease of the crystalline core and concomitant increase of the transition layer.

Lamellar morphology

Figure 3 shows the lamellar morphology of the unfractionated LLDPE A. The thickest lamellae develop during the onset of the crystallization process on cooling from high temperature and form the basis for the spherulitic morphology. At lower temperatures thinner lamellae fill up the space in between these thick lamellae. As a consequence no stacks of well ordered lamellae are formed.

The gradual change of lamellar morphology as a function of the chain branching content is illustrated in *Figure 4* for three different fractions. Fraction A7 consists of the thickest lamellae which are rather short and curved and exhibit a distortion in growth direction. Consequently the stacks formed by these lamellae have a restricted length. With increasing comonomer content (fraction A5) the lamellae become thinner, longer and exhibit a smoother curvature. This results in the formation of relatively well arranged, although unexpected, lamellar stacks, even at the highest short chain branching content (fraction A3).

The lamellar thickness of ethylene copolymers is primarily determined by the content and distribution of the short chain branches. The lamellar morphology, however, is not only influenced by the branching content but also by the molecular weight: high molecular weight molecules restrict the lateral growth of the lamellae. The correlation between the comonomer content and the molecular weight of the fractions used in this study, tentatively explains the morphological changes of the fractions, especially the presence of lamellar stacks even at high comonomer contents.

Amorphous thickness within the lamellar stacks

The thickness of the amorphous zones between crystalline lamellae was measured within the lamellar

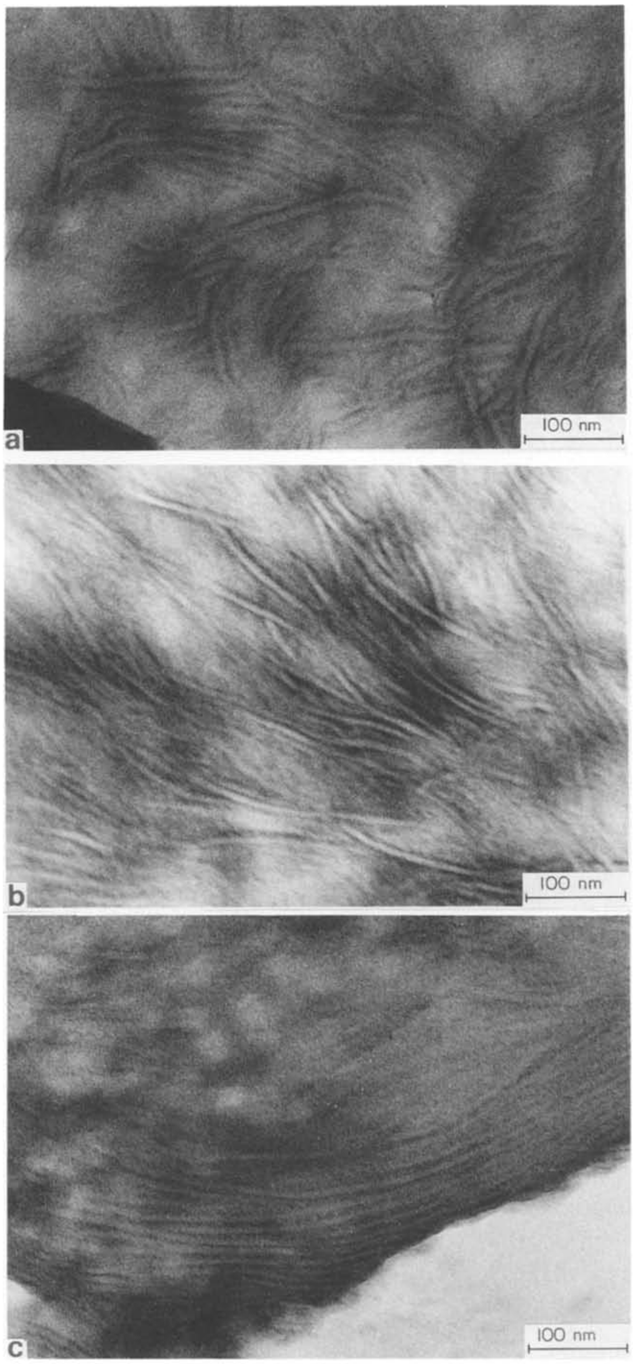

Figure 4 Electron micrographs of the lamellar morphology of fractions (a) A7, (b) A5 and (c) A3

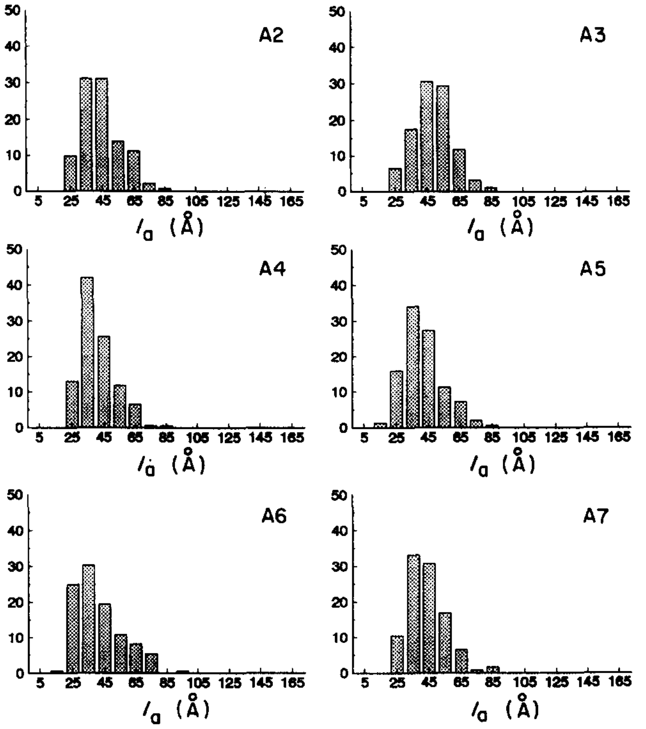

Figure 5 Thickness distribution histograms of the amorphous zones within the lamellar stacks of the different fractions

stacks. The histograms in *Figure 5* show that the amorphous thickness distributions are asymmetric and involve a skewness towards higher values. For fractions A7, A6, A5 and A4 the minimal thickness is between 2 nm and 3 nm, with a most probable thickness around 3.5 nm; <5% of the amorphous layers in the stacks have a thickness >7 nm. For fractions A3 and A2, which have a higher short chain branching content, these values increase by ~1 nm.

Based on the mean thickness of the crystalline lamellae $\langle l_c \rangle$ and the amorphous layers $\langle l_a \rangle$, and assuming a two-phase model, the volume crystallinity V_c of the lamellar stacks can be estimated from equation (1)[19]. The weight crystallinity W_c of the stacks can then be calculated from equation (2) using the amorphous density ρ_a and crystalline density ρ_c. The values of ρ_c were calculated from WAXS experiments[13], while a value of 0.85 was used for ρ_a.

$$V_c = \frac{\langle l_c \rangle}{\langle l_c \rangle + \langle l_a \rangle} \qquad (1)$$

$$W_c = \frac{1}{1 + \dfrac{\rho_a}{\rho_c}\dfrac{(1 - V_c)}{V_c}} \times 100 \qquad (2)$$

In *Figure 6* the W_c of the lamellar stacks is plotted as a function of the degree of crystallinity, χ_c, determined from the heat of fusion using d.s.c.[12]. The W_c is ~20% higher than χ_c for fractions with a low comonomer content (high crystallinity). This discrepancy increases up to 35% at higher comonomer contents.

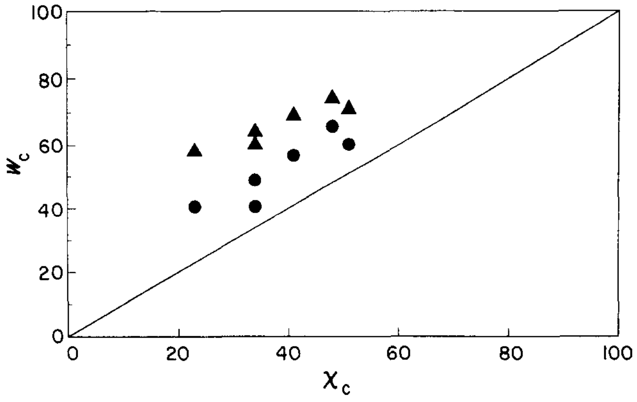

Figure 6 Crystallinity of the lamellar stacks (W_c) as a function of the degree of crystallinity (χ_c) of the fractions as determined from the heat of fusion, without (▲) and with (●) correction for the transition layers

The observed deviation is the result of the presence of a transition layer between the crystalline core and the amorphous layers. The transition layer is included in the lamellar thickness for the TEM measurements, and thus in the value for W_c. However, it is only the core of the lamellae that contributes to the heat of fusion[5] and consequently to χ_c.

The contribution of the transition layer to the average distance between neighbouring lamellae in the stacks increases from ~5 to 20% with increasing chain branching content[13] for the samples studied. After correction for the transition layer, W_c is still higher than χ_c. Consequently, a part of the amorphous material must be located in zones outside of the lamellar stacks.

CONCLUSIONS

The lamellar morphology of eight fractions of an ethylene/1-octene copolymer (LLDPE A) with a narrow branching distribution was studied in a quantitative manner by TEM. The average branching content of the fractions increases from 3 up to 28 branches per 1000 C atoms while the weight average molecular weight decreases from 2.5×10^5 at the lowest branching content down to 4.9×10^4 at the highest.

The heterogeneous LLDPE A sample is characterized by a complex chain microstructure and consequently displays a broad lamellar thickness distribution. The thick lamellae form the basis of the spherulitic morphology while the thinner lamellae fill up the space in between the thick lamellae. As a consequence regular lamellar stacks are absent. The short chain branching content strongly affects the lamellar thickness of the fractions. With increasing branching content, the lamellae become thinner, exhibit a smoother curvature and longer lateral dimensions. The thickness distributions are Gaussian and broaden with decreasing comonomer content. The chain microstructure – comonomer content and molecular weight – controls the lamellar morphology. The concomitant decrease in molecular weight with increasing comonomer content results in the formation of lamellar stacks even at high short chain branching contents. The W_c of the stacks is significantly higher than the χ_c of the samples. Therefore, a considerable part of the amorphous material must be located outside of the lamellar stacks.

ACKNOWLEDGEMENTS

The authors feel highly indebted to Dr I. G. Voigt-Martin and co-workers of the Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, Germany, for the very interesting and valuable discussions, and the opportunity to make use of the local experimental facilities. The authors (FD and GG) are indebted to the Belgian National Science Foundation for financial support.

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