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Real-time observations of the kinetics and developing morphology of spherulites of a polyethylene copolymer

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Abstract

The morphology and kinetics of developing large spherulites of a metallocene-catalyzed linear-low-density polyethylene have been investigated in real time with polarizing optical microscopy. In contrast to the widely held view that lamellae advance smoothly into the melt, the isothermal growth rate of an individual radial unit fluctuates in space and time. There is also an overall continuing fall below the initial value with increasing radial distance as segregation proceeds and segregants accumulate. In the later stages of growth the morphology becomes increasingly irregular: some individual radial units may stop while others overtake them from the rear. Gross changes of direction occur to avoid certain regions which may be ~ 10 μm across, consistent with high concentrations of segregants, indicate that local conditions at the melt interface vary strongly even when growth is slow. © 2002 Published by Elsevier Science Ltd.

Keywords: Metallocene-catalyzed polyethylene; Spherulitic growth; Real-time observations

1. Introduction

Isolated polymer spherulites when observed growing isothermally with the polarizing microscope generally reveal a more or less circular and reasonably sharp envelope whose radius increases linearly with time. From this has come the widely held perception that the growth interface between spherulite and melt is rather uniform with arrays of radial lamellae advancing together as has been assumed in theories of the growth rate. In fact, neither of these conditions is true in general. Previous work has shown that the radial growth rate of spherulites of polyethylene copolymers declines monotonically towards a steady state as segregant concentration increases leading to cellulation with a smooth modulation of the growth envelope. However, as this paper now reports from real time observations, in such systems there can be strong variation in the rate and direction of advance of adjacent radial units. Depending upon local conditions and segregant concentration some are observed to slow and sometimes stop while others overtake them from the rear all the time avoiding large regions with high concentrations of segregants. This demonstration is similar to, and supports, contemporaneous observations on crystallizing copolymers using atomic force microscopy (AFM), but with simpler means of observation.

These observations were made in parallel with others on a range of polyethylene copolymers [1,2] which have shown how and when cellulation occurs during the growth of polymer spherulites, confirming that it is confined to circumstances of substantial segregation. Procedures to reduce primary nucleation have been used to allow the development of comparatively large objects to be observed continuously on the hot-stage polarizing microscope. Growth was monitored and recorded along different radii of the spherulites to see the actual behavior of spherulitic growth under segregating conditions rather than the average effect normally recorded. The growth rate of an individual radial unit fluctuates seemingly randomly with time, especially in the last stages of crystallization and is associated with a non-circular spherulitic envelope. The observations are given a consistent interpretation on the basis of an increasing concentration of segregated molecules and its distribution across the growth front. The work draws on data presented previously [3] and complements that made contemporaneously on other copolymers with atomic force instruments [4].

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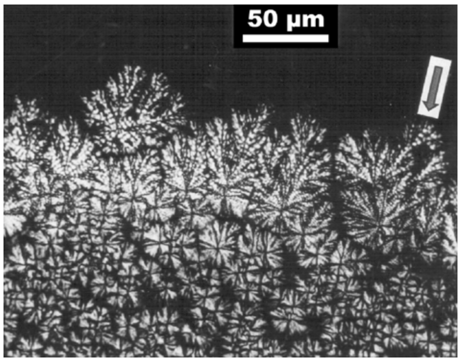


Fig. 1. A thin polyethylene film crystallized for 1.5 h at 93 °C and photographed between crossed polars. Note the larger spherulite size at the (upper) edge compared to the (lower) interior.

2. Materials and experimental

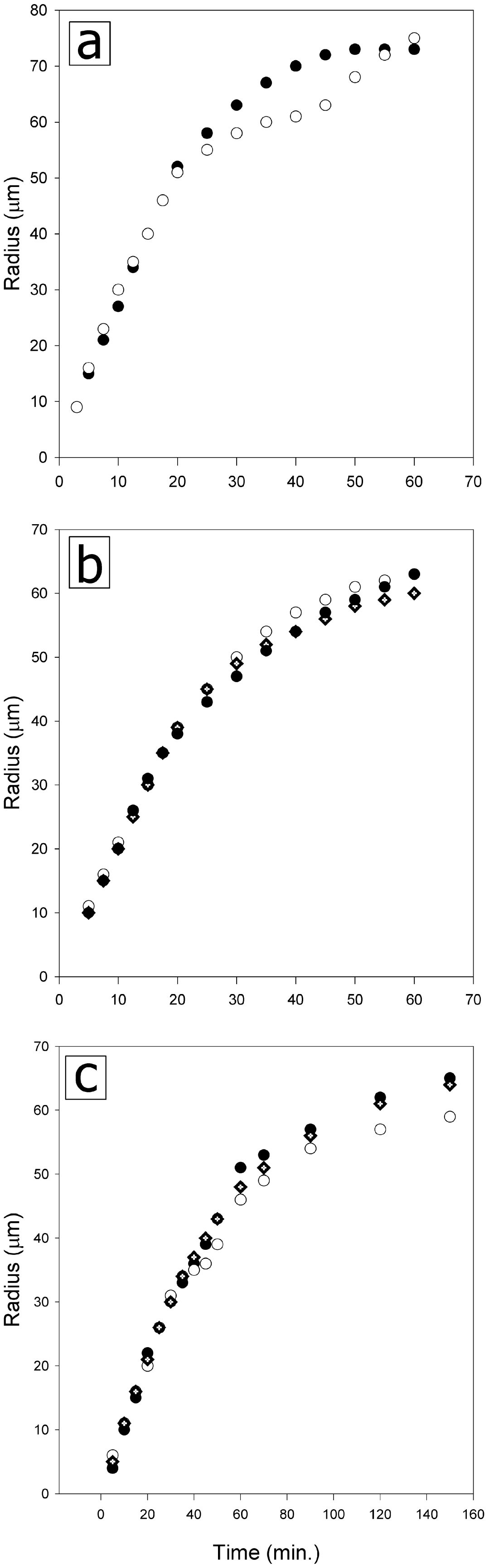
The metallocene-catalyzed polyethylene with butyl branches used in this work and previously [1] was kindly supplied by Dr P Jääskeläinen of Borealis Oy, Finland. The material has average molecular masses $M_w = 7.9 \times 10^4$ and $M_n = 4.0 \times 10^4$ with an average branch content of 28 branches per 1000 carbon atoms.

A thin film of around 15 mm in diameter was prepared between microscope slide and cover slip by melting the appropriate amount of material, using a Kofler hot bench at 140 °C. The slide, with the thin film and cover slip, was put afterwards into a Mettler FP82HT hot-stage. The specimen was then melted in the hot-stage with nitrogen flow and kept there for 3 h at 200 °C. At the end of this time, the temperature of the hot-stage was dropped to the required crystallization temperature using a Mettler FP90 central processor. During crystallization, the growth of spherulites was monitored and recorded by using a Hitachi Denshi CCD video camera and monitor screen. The video camera was connected with a Vickers Photoplan transmission polarizing microscope on which the hot-stage was standing. The changing positions of selected objects were marked directly on the video screen providing the input data of dimensions against time plots whose gradient is the radial growth rate.

Additionally, some selected specimens were examined subsequently in transmission between crossed polars using a Zeiss GFL polarizing microscope. For this purpose, some thin-film specimens of the material investigated were prepared and melted one by one at 200 °C for 3 h in the hot-stage. The temperature of the hot-stage is then dropped to that chosen for crystallization and, after the required crystallization time, each slide with the thin film and cover slip was quenched in an ice–water mixture. The slide was then carefully dried and taken for the investigation between crossed polars.

3. Results and discussion

Melting the thin film at high temperature, 200 °C with



nitrogen flow, for 3 h, is designed to reduce the density of primary nucleation and so increase spherulite size [5]. This is the case but, in practice, there are fewer nuclei towards the outside where the film has been pressed out during preparation with more in the central region of the film suggesting that heterogeneous nuclei have tended to remain in central regions. In consequence, near the edge of the thin film the diameter of spherulites reaches 70 μm while those grown far from the edge, impinged with up to 25 μm in radius as in Fig. 1.

Near the top of this figure, for a thin film after crystallization for 1.5 h at 93 °C, close to the edge of the film, spherulites have much longer radii, especially upwards towards the edge. For longer growth times, the changing morphology of spherulites and their kinetics can be detected clearly. Near the right of Fig. 1, there is a spherulite of non-identical branches. The branch to which the arrow points is longer than the others, especially those radii growing upwards. Although impingement is absent in this case, these differences in growth length reflect a difference in the kinetics of growth and thence the conditions at the crystal/melt interface.

The reason, following earlier work [1,2,6,7], is that the concentration of segregated molecules is varying across the growth front. This earlier work has shown that the kinetics of crystallization of branched polyethylene are sensitive to the concentration of segregated molecules across the growth front because of the depression of the local equilibrium melting point and isothermal supercooling which in turn depresses the growth rate. Previously, the average effect of segregation on the kinetics was studied in contrast to this paper which focuses on the actual localized kinetics along individual radii of the spherulites.

Monitoring the growth of spherulites along different radii gave the actual behavior of the localized growth rate. Fig. 2a shows the growth length along two different radii of one spherulite near the edge of the film. These were recorded during crystallization at 91 °C. The difference in behavior along the two radii is clear to see. Differentiation of this curve to yield the corresponding growth rate indicates some kind of random fluctuation superposed on a growth rate declining steadily from ~ 3 to <0.5 μm min^{-1}.

It should be pointed out that radii grow faster in these outer regions than was measured previously [1] and that the band period also increases compared to central regions where banding is present though barely resolved optically. Both factors point to a lower branch content in the outer regions, consistent with flow during film formation. This difference in composition does not, however, affect the validity of the conclusions to be drawn relating to the direct observation of variable rates of advance and directions of individual lamellae during their growth.

Fig. 2. (a) The length of two different radii of one spherulite near the edge of the film, plotted against crystallization time at 91 °C. (b) The increasing lengths against time of three different radii of another spherulite growing at 91 °C. (c) The length, of three different radii of a spherulite near the edge of the film, against crystallization time at 93 °C.

The lengths of three different radii in another spherulite, near the edge of the thin film and not far from the previous one, monitored and recorded at the same time during crystallization at 91 °C are plotted against time in Fig. 2b. There is a marked difference in kinetics between the objects recorded in Fig. 2a and b. For the latter, the growth rate declines, with apparently random spatial and temporal fluctuations, from ~ 2 to <0.5 μm min^{-1}. The kinetics of the former are always faster, by as much as 1 μm min^{-1}, approximately 30% of the average growth rate. The fluctuations in growth rate are an indication of the correspondingly varying distribution of the concentration of segregated more-branched molecules and sequences across the growth front. The concentration may also fluctuate with time due to a combination of the increase from advancing growth and the decrease due to diffusion. But the overall depression of growth rate points to a continuing increase in segregant concentration with crystallization time, consistent with the previous work [2,8].

Similar behavior has also been observed at different crystallization temperatures. Fig. 2c presents the growth lengths versus crystallization time at 93 °C for three different radii of one spherulite. The corresponding growth rate decreases from ~ 1 to ~ 0.1 μm min^{-1} with considerable fluctuation en route, confirming the same behavior found at 91 °C.

In the data of all three plots of Fig. 2, the variation in

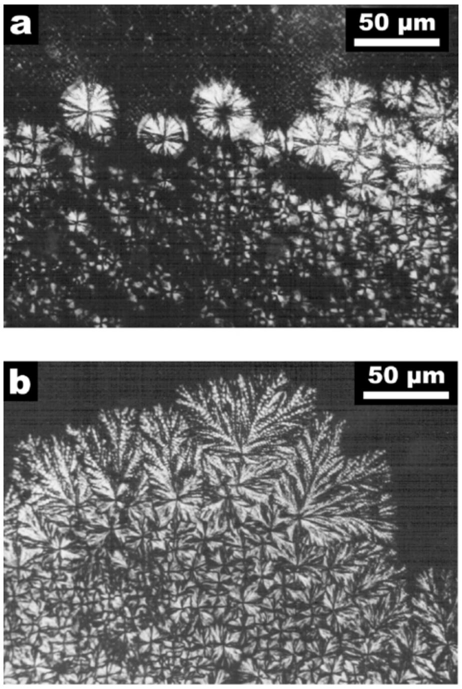


Fig. 3. Anisotropic spherulitic development in a thin polyethylene film at 91 °C observed between crossed polars after (a) 5 min and (b) 30 min crystallization.

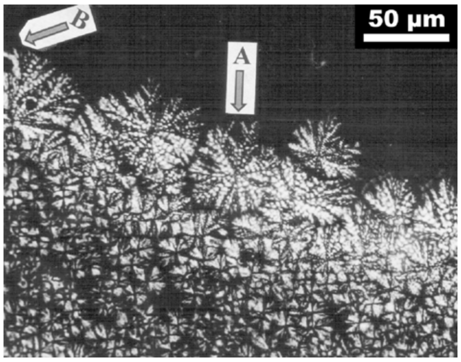


Fig. 4. An area of spherulites observed growing for 90 min at 93 °C between crossed polars.

growth rate for the radii of one spherulite is rather uniform in the early stage of growth, to around 10 min at 91 °C and around 20 min at 93 °C, after which deviations become more conspicuous. This is to be expected because the fluctuations in segregant concentration and thus in growth rate can only become larger when the concentration is itself high, i.e. in the later stages of growth as was shown in the previous work [2,6]. The more uniform, morphology in the earlier stages of growth is revealed directly in Fig. 3a for which the specimen was quenched after 5 min crystallization at 91 °C. This shows directly the nearly symmetrical circular growth found only in the beginning of crystallization.

Non-symmetrical spherulitic morphologies are obtained with longer crystallization time. Fig. 3b shows such spherulites after 30 min crystallization at 91 °C. The irregular growth appears also in the form of deviation from the usual growth direction, by as much as 90° from the initial radius. This gives the spherulites a pseudo-dendritic appearance not dissimilar to that found during crystallization of blends of poly(vinylidene fluoride) and poly(ethyl acrylate) [9].

The reason why there is a deviation of growth direction is that crystal growth always tends to take the faster route, in this case of lower segregant concentration, and avoids those of higher concentration. Fig. 4 shows two clear examples of how deviations in growth can occur as a result of existence of some regions with higher segregant concentration. In Fig. 4 the arrow, A, points to a region sketched in detail in Fig. 5a. The three directions O–A, O–F and O–H are originally radial from O, the spherulite center, and represent the regular growth during the first stages of crystallization. But as can be seen, O–A deviates to A–B and then to both B–C–D and B–E, avoiding the shaded area S ~ 10 μm across. The branch O–F deviated to F–G and then stopped before reaching the location H–I when it was overtaken by its neighbors to right and left. Hence, the growth directions O–A–B–E, O–F–G and H–I–J are seen to be avoiding the shaded area S which is left uncrystallized. As crystal growth always favors the fastest available route, S can only be a region of slow growth and high segregant concentration. The second example is shown in Fig. 5b, which illustrates area B in Fig. 4. Here the original growth direction P–Q does not continue but is succeeded by deviations close to 90° to reach R and eventually V. The selection of sideways, rather than continued radial, growth has to reflect slower growth conditions and higher segregant concentrations immediately ahead.

These and other [4] experiments have been on copolymers whose segregated molecules' slow growth and, in sufficient concentration, lead to morphological instability and cellulation, often with lamellae contained within rather smooth envelopes indicating a correspondingly smooth variation of segregant concentration [1,2,10]. While it is to be expected that lamellar advance should reflect local changes in segregant concentration, the strong variations in space and time observed here show that segregant concentration can vary considerably on a small scale, from radial unit to radial unit. Whether the growth rate also fluctuates for linear homopolymers is less clear. Linear polyethylene, for example, does cellulate when crystallizing at high temperatures, ~128 °C, but without morphological instability, when shorter molecules are unable to crystallize [11]. Then the growth envelope resembles a square wave with lamellae advancing smoothly outside regions where segregated shorter molecules are presumed to have concentrated. When crystallization is carried out at such high temperatures [12] it is necessary to exclude the role of segregation before concluding that the isothermal advance of an individual lamella is an inherently fluctuating quantity.

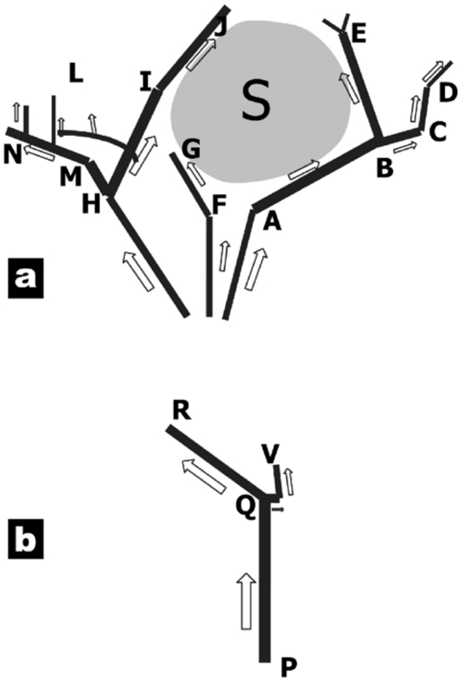


Fig. 5. (a) Sketch of area A in Fig. 4. (b) Sketch of area B in Fig. 4.

4. Conclusions

The important observation here is the random fluctuation, superposed on a continuing decline, in the rate of advance of an individual radial unit recorded during crystallization of a polyethylene copolymer. This develops most strongly in the last stages of crystallization and is associated with a non-symmetrical morphology in which there are sudden changes of direction to avoid non-crystallizing regions. The underlying reason is that the concentration of segregated molecules while increasing during crystallization is not uniformly distributed across the growth front but, can as here, show a strong local variation.

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