Growth Shape Observed in Two-Dimensional Poly(ethylene terephthalate) Spherulites

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ABSTRACT: We have investigated the growth shape of two-dimensional (2D) poly(ethylene terephthalate) spherulites using a transmission electron microscope technique in order to examine the role of a diffusion-controlled mechanism in the growth process. At the growth front of the 2D spherulites, we found a terrace-like morphology having a single crystal structure. The growth front of the terrace shows instabilities of periodic or groove patterns which can be explained by the diffusion-controlled theory for crystal growth.

Introduction

In general, when polymers are crystallized from the glassy or melt state, they show a higher order structure, so-called spherulites. The spherulites assume very complex morphology consisting of radially developed lamellar crystals with many branchings. A large number of investigations have been performed concerning the spherulite structure, but many unsolved problems still remain about the relationship between the morphology and the growth mechanism.[1,2] The crystal growth is governed by the following three processes:[3] (1) the incorporation process of molecules into crystals at the interface between crystal and liquid phases (interface growth kinetics), (2) molecular diffusion process from the liquid phase to the interface, and (3) diffusion process of latent heat at the interface. The pattern of crystal growth is determined by its rate-determining process. Keith, Padden,[4] and Goldenfeld[5] developed the spherulite growth theory from the view point of a molecular diffusion-controlled process, in which they considered that impurities are rejected from the growing crystal front. They accounted for the occurrence of spherulites with small-angle noncrystallographic branching of lamellar crystals using the diffusion-controlled growth theory. The important prediction of this theory is that the spherulitic morphology is scaled with a characteristic length determined by the ratio of diffusion constant and growth rate. Against this theory, Bassett and his group[6,7] claim that no characteristic length supporting the Keith and Padden theory was found in their electron microscopic studies and the spherulitic growth was not primarily a consequence of segregation of impurities. Recently, Toda and Keller[8] found the close relationship between spiral growth and the spherulite formation in the crystal growth of polyethylene from the melt. The formation mechanism of the spiral dislocation is based on a distortion caused by the three-dimensional shape of crystals. At present, it is considered that the formation of spherulites is governed by the interface growth kinetics and the spiral dislocation is responsible for the branching in the development of spherulites. However, is it true that the diffusion-controlled process really plays no important role in the spherulite formation? We believe this is not true because the segregation of impurities actually occurs during the crystallization process[9,10] and Tanaka and Nishi[11] observed the instability of the spherulite interface predicted by the diffusion-controlled theory in the polymer mixture system. These results indicate that under some special conditions the diffusion-controlled process might be dominant in the spherulite formation. In the case of two-dimensional spherulites (2D spherulites) grown from thin films on substrates, we can expect that the molecular diffusion processes probably play an important role because of the low dimensionality of the system or the interaction between a polymer chain and the substarate. In this study we have investigated the growth shape at the interface of the 2D spherulites because the interface varies its shape depending on the growth mechanism, which probably reveals the role of the diffusion process in the 2D spherulites formation.

Experimental Section

In this study, we employed poly(ethylene terephthalate) (PET) as the sample, because we can observe spherulites in a wide temperature range between the glass transition temperature (75 °C) and melting temperature (250 °C) and fix the spherulite structure by quenching to room temperature. The PET sample having a number-averaged molecular weight $M_n = 25\,000$ and polydispersity $M_w/M_n = 2.5$ was supplied from Toyobo Co. Ltd. This sample was dissolved in hexafluoro-2-propanol at a concentration of about 0.1 wt % and then cast on a cover glass for optical microscopy to make a thin film. The obtained films having about 100 nm thickness were used for transmission electron microscopic (TEM) observation. These thin films were melted at 290 °C for a few minutes and then crystallized isothermally at 220 °C, i.e. 30 °C of supercooling, for 2 h on a hot stage (Linkam 600T). This crystallization time is long enough compared to the crystallization half-time of 8 min at 220 °C of this sample. After the isothermal crystallization, they were immediately quenched into ice water. Because of slow crystallization rate of PET and the thin film thickness, the obtained spherulite structure can be frozen by thick quenching into ice water.[12] The films on a cover glass were shadowed with evaporated gold (Au) at an angle of $\tan^{-1}(1/4)$ and then coated with evaporated carbon to reinforce them. The crystallized films were removed from the cover glass using a dilute hydrofluoric acid solution and then mounted on specimen grids for TEM. The specimens without further treatments were examined by TEM using a JEOL JEM-200CS operated at an accelerating voltage of 200 kV. Selected-area electron diffraction experiments were carried out with the same instrument. Calibration of the diffraction spots

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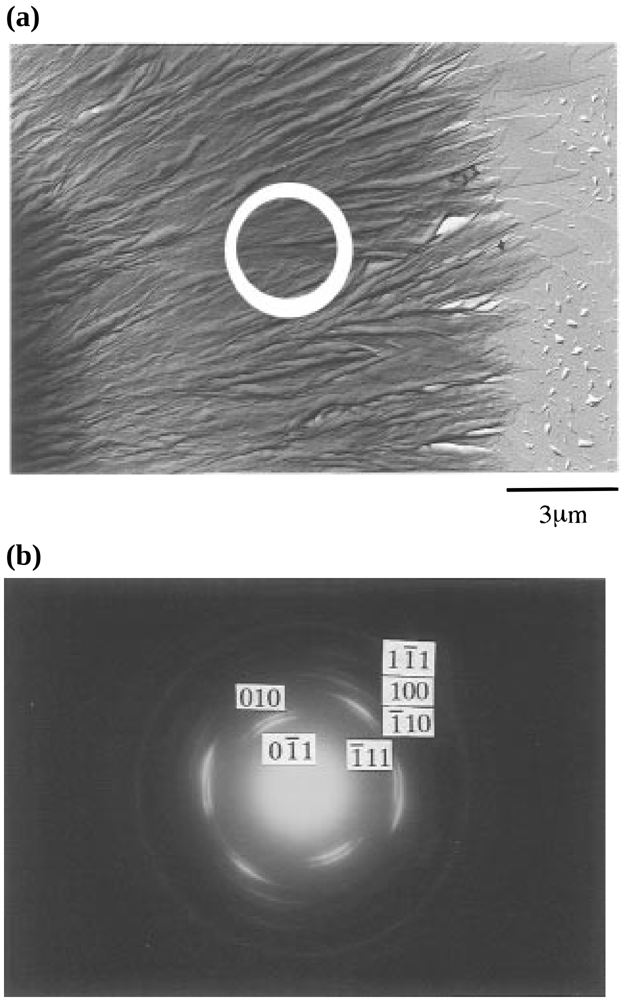

Figure 1. (a) TEM photograph for 2D PET spherulite. (b) Selected area electron diffraction pattern from the encircled region in part a. Rings are diffractions from evaporated Au for calibration.

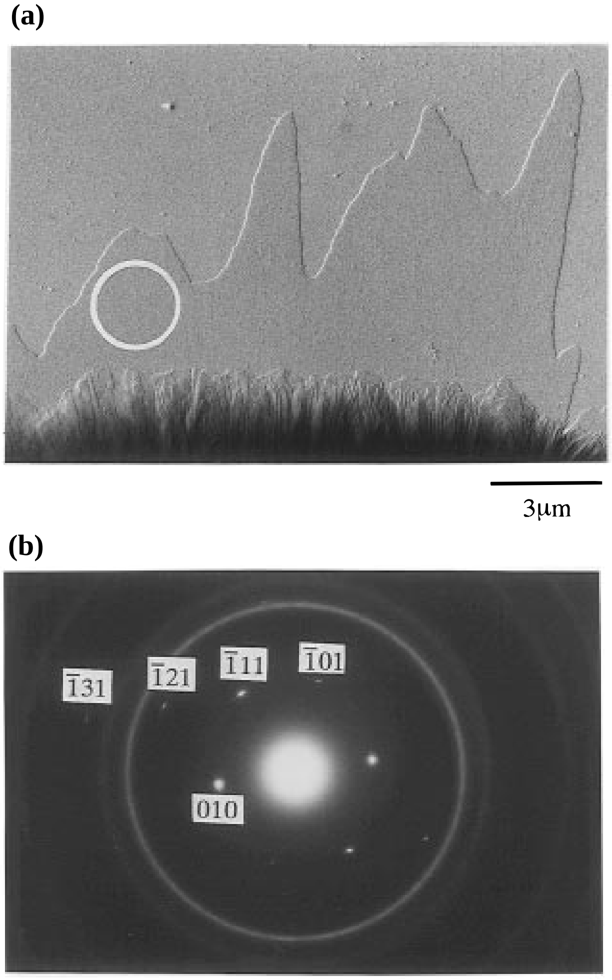

Figure 2. (a) TEM photograph for terrace structure observed at the growth front of the 2D PET spherulite. (b) Selected-area electron diffraction pattern from the encircled region of the terrace in part a. Rings are diffractions from evaporated Au for calibration.

was made using the Debye−Scherrer rings from the thin layer of gold evaporated on the same specimen.

Results and Discussion

2D spherulites grown from thin films show the extinction rings and Maltese cross patterns in polarized optical micrographs corresponding to the spherulites obtained from bulk crystallization. Figure 1a shows a TEM image for the boundary region of a 2D spherulite. In the inside of the 2D spherulite, stacked lamellar crystals parallel to the glass substrate plane are observed. Near the free surface of the spherulite, some ridge-like lamellae are developed in the radial direction with many branches. In the periphery of the spherulite, however, a terrace-like structure appears. The growth front of the terrace is several micrometers ahead from the edge of the stacked lamellae. There are some doubts as to whether the terrace is representative of the frozen-in stages in ongoing growth or artificial structure caused by a special substrate or experimental treatments for TEM observation. First, in order to check whether or not the terrace structure is affected by the substrate, the spherulites were formed on mica coated with evaporated carbon. The obtained spherulites also showed a very similar terrace structure. Second we tried to make in-situ observations of ongoing growth of 2D spherulites using a laser scanning confocal microscope (LSCM). We succeeded in the in-situ observation of ongoing growth of the terrace for the same sample and the same annealing conditions. Details of the in-situ observation of the terrace growth including its kinetics will be reported in a subsequent paper.[13] Then we concluded that the terrace is a structure inherent to 2D PET spherulites and independent of the kind of substrates or experimental treatments for TEM observation. Parts a and b of Figure 2 show an enlarged TEM image for the terrace and its electron diffraction pattern, respectively. The diffraction pattern from the terrace coincides with that from the single crystal of PET obtained by evaporating the solvent slowly from dilute solution at crystallization temperature.[14] This indicates that the growth front of the 2D spherulite or the terrace consists of single crystals several micrometers in size. The obtained diffraction spots correspond to the reflections from the (010), (020), $(\bar{1}01)$, $(\bar{1}11)$, $(\bar{1}21)$, and $(\bar{1}31)$ planes, as shown in Figure 2b. From this diffraction pattern, it is concluded that the [101] direction of the unit cell is perpendicular to the basal plane of the terrace,[15] that is, the PET chains are inclined about 25° from the normal of the basal plane. On the other hand, the diffraction pattern from the inner part to near the center of the spherulite shows arcs (Figure 1b), indicating that the stacked lamellae have an orientation distribution. Most of the arcs agree with the spots obtained from the terrace, which indicates a close

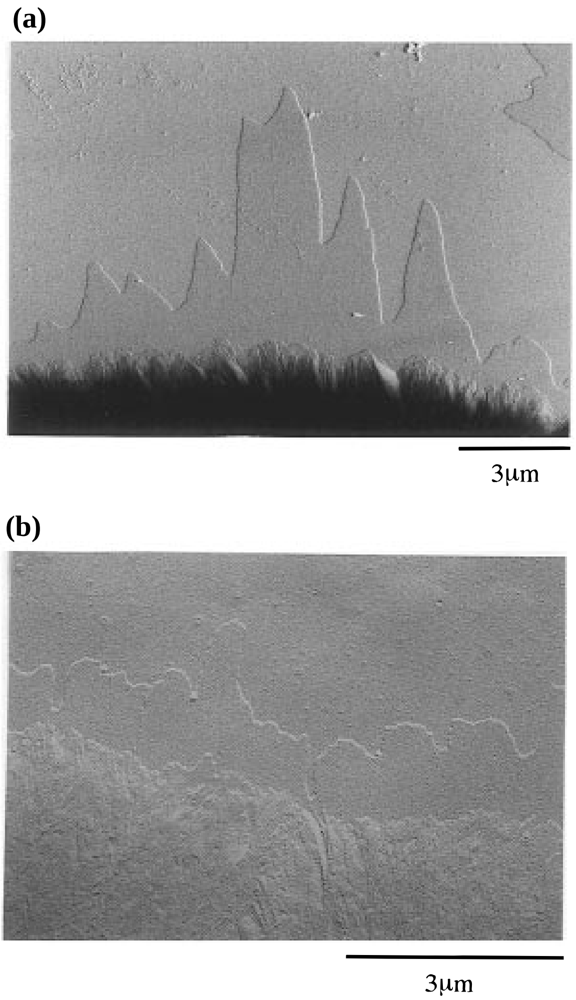

Figure 3. (a) Periodic shape interface of the terrace. (b) Groove shape interface of the terrace.

relationship between the terrace and the stacked lamellae, but some additional diffraction peaks are obtained from the stacked lamellar part. These additional peaks are attributed to the reflections from $(0\bar{1}1)$, (100), $(\bar{1}10)$, and $(1\bar{1}1)$ planes, as shown in Figure 1b, and the additional diffraction pattern is very similar to the X-ray diffraction pattern with the beam parallel to the basal plane of the lamellar crystals. This indicates the existence of lamellae having edge-on orientation. The edge-on lamellar crystals may therefore be in the ridge structure because the orientation of the PET molecules in the stacked lamellae parallel to the substarate is considered to be identical to that in the terrace.

In this study we focus our attention on the shape of the growth front of the terrace, which is hereafter called the step. If the growth of the step follows the interfacial growth kinetics, the shape of the step should be determined by stable crystal faces having minimum growth rates. However, the shape of the growing step does not show the stable facets but serious instability, as shown in Figure 2a. The shape observed at the step is fairly complex, but we may classify the following two categories: (1) the interface having a periodic shape, as shown in Figure 3a, and (2) the interface having a groove shape, as shown in Figure 3b. In the following we discuss each growth shape from a diffusion-controlled process point of view.

(a) Periodic Pattern. In order to show the periodic feature of the interface, we carried out the Fourier analysis of the interface profile.[16] First, from the TEM images we extracted the shape of the step and the boundary between the stacked lamellae and the terrace. Then the interface coordinates were expressed by the radial distance from the boundary to the step as a function of periphery distance on the boundary. The obtained interface profiles were smoothed by fitting with a least-squares cubic B-spline. The spline-fitted interface functions were then Fourier transformed to get the power spectra of the interface profiles. The obtained power spectrum is shown in Figure 4. The important Fourier components lie within a limited range of the wave vactor k. This indicates the existence of the characteristic growth modes; the characteristic size of the main mode is about 3 μm, which is consistent with the interface profile of the terrace in TEM images (Figures 2a and 3a). Similar results were obtained by Chou and Cummins[17] for solidifying succinonitrile and by Dougherty et al.[18] for the launching of side branches in fully developed dendrites.

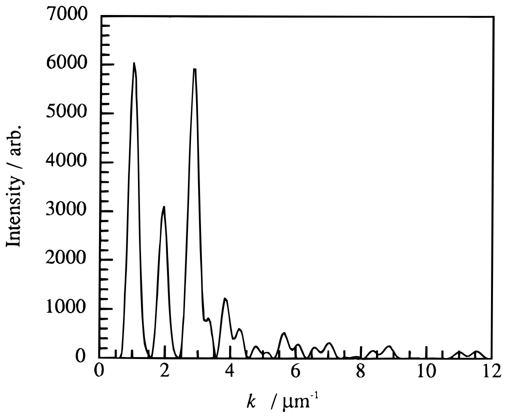

Figure 4. Power spectrum obtained for the periodic shape interface.

These phenomena were qualitatively explained by the framework of the Mulins–Sekerka theory.[19] Langer[20] developed this theory into the thermal and chemical models. The chemical model means the diffusion of the impurities as mentioned in the Keith, Padden, and Goldenfeld theory. The motion of the solid–liquid interface is governed by three equations:[20,21] (1) the diffusion equation, (2) energy conservation at the interface, and (3) the Gibbs–Thomson condition. These equations were linearlized and solved for the interface advancing at a constant velocity (v_0) which has a superposed sinusoidal perturbation. The resulting linearlized solution for the growth rate [$\omega(k)$] is given by

$$\omega(k) = v_0 k(1 - d_0 l k^2)$$

where $l = 2D/v_0$ is the diffusion length and d_0 is the capillary length. The planar growth front is always unstable ($\omega(k) > 0$) against small fluctuations for wave vectors $0 < k < k_c = (d_0 l)^{-1/2}$, with the maxmum instability at $k_{max} = (3d_0 l)^{-1/2}$ which establishes the length scale $\lambda_{\max} = 2\pi/k_{\max}$ of the initial pattern. This $\lambda_{\max}$ corresponds to the so-called characteristic length introduced by Keith and Padden.[4] The result of Figure 4 can be explained by this characteristic mode.

In order to confirm the diffusion-controlled growth of the terrace, we examined the growth rate of the terrace by LSCM observation and obtained a $t^{1/2}$ growth law for the step.[13] From these experimental results, we concluded that the terrace growth is governed by the diffusion-controlled model.

There are some candidates to explain the cause of the diffusion-controlled growth of the terrace: (1) thermal diffusion, (2) impurity diffusion, and (3) low dimensionality effect. The thermal diffusion model is inadequate to explain the observed phenomenon because the thermal diffusion length of this system becomes $l = 2D/v_0 \cong 200$ cm using the thermal diffusion constant[22] $D = 8.7 \times 10^{-4}$ cm^2 s^{-1} and the growth rate of the spherulite at 220 °C $v_0 = 0.09\ \mu$m s^{-1}. The value of v_0 was obtained from in-situ observation of the growing 2D spherulites using an optical microscope.

It is well-known that segregation of molecules according to their molecular weight takes place during the crystallization, so-called fractionation.[9] The noncrystallized excluded molecules (low molecular weight component) are stored at the growth front of the spherulite, resulting in a region where the concentration of low molecular weight component is higher than its average concentration. Such component inhomogeneity at the periphery of spherulites affects the crystallization and causes nonlinear growth and shape instability of spherulites because the low molecular weight components act as impurities. Then the fractionation is considered as a kind of the impurity diffusion model.

The meaning of the low dimensionality effect is that the diffusion of each polymer chain may be restricted by the direct interaction to the substrate in the very thin region of the sample. From an experimental point of view, it is very difficult to distinguish the fractionation effect and the low dimensionality effect in the spherulitic growth of PET. Then our standing point is as follows. If the low dimensionality effect is dominant, the terrace will appear only in the very thin region. On the other hand, if the fractionation is dominant for the terrace growth, the terrace will appear independent of the sample thickness, but according to the LSCM observation, the terrace could be grown in the very thin region (<1000 Å) and in the thick region the normal spherulites grew. From these results we considered that the low dimensionality effect is probably responsible for the terrace growth. However, we cannot eliminate the possibility of the fractionation effect because the fractionation is a general phenomenon during crystallization and it is very difficult to examine the fractionation effect directly.

(b) Groove Structure of Terrace. As shown in Figure 3b, we find the interface with deep grooves, which are distinctly different from the periodic structure described above. To our knowledge, the morphology of the interface having the grooves is quite unique and has not yet been reported experimentally. Recently Saito and Uwaha[23,24] showed very similar interface profiles for the steps in a surface diffusion field using Monte Carlo simulation for crystal growth from vapor. In their simulation, a gas atom impinges on the top of a crystal with a frequency f and is adsorbed on it. An adatom (adsorbed atom) is desorbed into the ambient with a certain lifetime. During the diffusion, an adatom performs a random walk on the crystal surface (Burton–Cabrera-Frank model[25]), and when the adatom touches a step from the lower terrace, it is solidified with a certain probability (Schwoebel effect[26]). According to their simulation, the morphological instability of the step takes place when an impingement rate f of atom on a substrate surface exceeds a critical value, f_c. The instabilized morphology is characterized by many grooves between the almost flat fronts. This feature of instability shows a good agreement with the interface profile in Figure 3b, although the correspondence between this simulation and 2D spherulite growth has not been clarified.

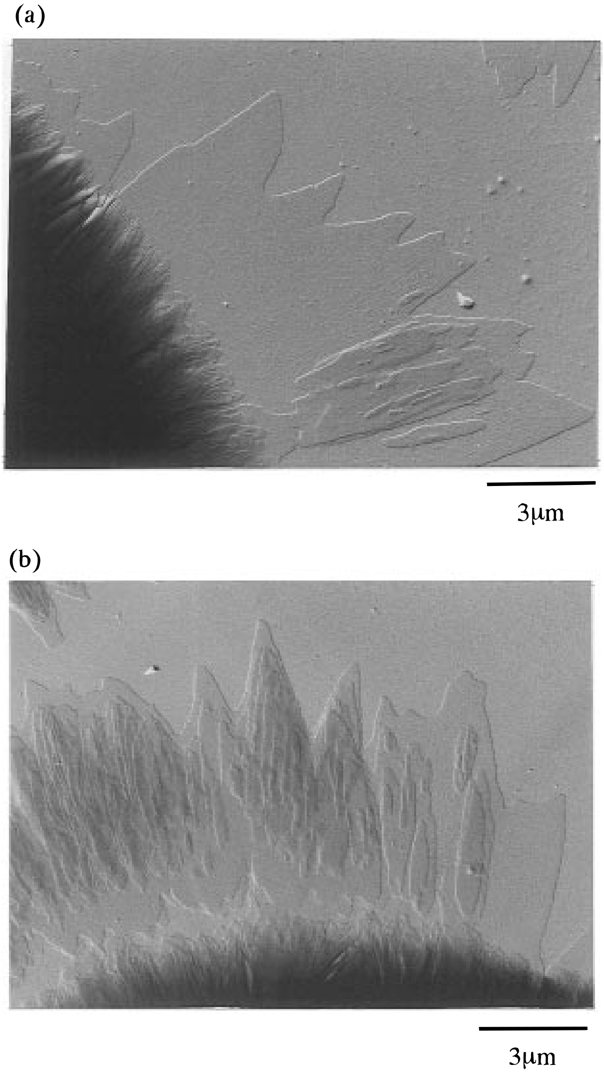

Figure 5. (a) The initial stage of lamellar overgrowth on the terrace. (b) A new spherulitic band on the terrace made of overgrown lamellae.

Finally, we pointed out the relationship between the terrace and the 2D spherulite using TEM images. Sometimes we found overgrown lamellae on the terrace as shown in Figure 5a,b. The electron diffraction patterns of the overgrown lamellae are identical with that from the terrace, and their morphology is a spindle-like shape and indicates multistep edges. It is considered that the overgrowth is due to the spiral growth as observed in the crystal growth of polyethylene and polystyrene.[27] The spiral dislocation is probably introduced by distortion arisen from the three-dimensional shape of the terrace and the chain-packing manner in the terrace. The morphology of well-developed overgrown lamellae is identical to that of the 2D spherulite, as shown in Figures 1a and 5b.

The terrace having a single crystal structure was found at the growth front of the 2D spherulite. We confirmed that the terrace is not an artificial structure caused by a special substrate or experimental treatments for TEM observation but the structure inherent to 2D PET spherulites. The interface profiles of the terrace show instabilities having periodic or groove patterns, which can be explained by the diffusion-controlled theory for crystal growth. Concerning the diffusion-controlled spherulite growth, some models have been presented, but no characteristic length supporting the diffusion-controlled model was found in electron microscopic studies for 3D spherulites. Our observation shows that in the case of 2D spherulites the diffusion field in the thin film plays an important role in the pattern formation of the terrace, although at present we cannot make clear the growth mechanism of the terrace quantitatively.

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