Crystal Growth of Isotactic Polystyrene in Ultrathin Films: 
Film Thickness Dependence

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Abstract

The film thickness dependence of crystal growth is investigated for isotactic polystyrene (it-PS) in thin films, the thickness of which is from 20nm down to 4nm. The single crystals of it-PS grown at 180°C in the ultrathin films show the morphology typical in the diffusion-controlled growth: dense branching morphology (DBM), fractal seaweed (FS). The characteristic length of the morphology, i.e. the width of the branch, increases with decreasing film thickness. The thickness dependence of the growth rate of crystals shows a crossover around the lamellar thickness of the crystal, 8 nm. The thickness dependencies of the growth rate and morphology are discussed in terms of the diffusion of chain molecules in thin films.

Keywords: ultrathin film; isotactic polystyrene; crystal growth; diffusion controlled growth;

1 Introduction

Crystal growth of polymers in thin films has recently studied on morphology and growth rate [1, 2, 3, 4, 5, 6]. The crystal growth rate is reduced in thin films [7, 8, 1, 2, 4, 6]. For isotactic polystyrene (it-PS), the thickness dependence of the growth rate down to 20nm was found to be expressed as follows,

\[ G(d) = G(\infty)(1 - a/d), \] (1)

where \( G(d) \) is the growth rate in the film of thickness \( d \), \( G(\infty) \) is the growth rate in the bulk and \( a \) is a constant of about 6 nm independent of crystallization temperature, molecular weight and substrate materials. This decrease in growth rate was attributed to the reduction on mobility of chain molecules in thin films and proposed that the value of \( a \) corresponds to the tube diameter in the reptation model of polymer dynamics [2].

In a previous paper [6], we reported on morphological change with crystallization temperature for it-PS crystals in a ultrathin film, the thickness of which is 11nm; the crystal morphology changes from faceted to branched one with decreasing crystallization temperature. In the present paper we investigate the film thickness dependence of morphology and growth rate of it-PS crystals grown at 180°C in ultrathin films, the thickness of which is thinner than 20 nm, down to 4 nm. It is to be noted
that at 180°C in the bulk it-PS the growth rate is maximum and the morphology shows a circular disk. It is interesting to observe how the thickness dependence of growth rate, eq (1), together with morphology changes for \( d \leq a \). We will discuss the film thickness dependence of growth rate and morphology in terms of chain diffusion in thin films.

2 Experimental

The sample used was it-PS supplied by Polymer Laboratory (\( M_w = 590,000, \frac{M_w}{M_n} = 3.4 \), tacticity: 97% isotactic triad). This molecular weight corresponds to 22 nm in radius of gyration of a polystyrene molecule in the melt. Ultrathin films of the it-PS were prepared on a carbon-evaporated glass slide by spin-coating 0.3 to 1.0wt% cyclohexanone solution at 4000 rpm; amorphous it-PS films with uniform thickness of 4 - 20 nm were thereby obtained. The films were crystallized isothermally at several temperatures 180°C for a certain period of time in a hot stage (Mettler FP800). Before crystallization, the films were melted at 250°C for 3 minutes, quenched to room temperature much lower than the glass transition temperature \( T_g (\sim 90^\circ C) \), and immediately elevated to the crystallization temperature. The lateral growth rate was determined by in situ differential-contrast optical microscopy (Nikon Optiphoto-2). Detailed morphology and structure of the crystals were investigated by an atomic force microscope (AFM) (SHIMADZU SPM-9500J) and a transmission electron microscope (TEM) (JEOL 1200EX II) at room temperature after crystallization and quenching.

3 Results

Figure 1 shows the AFM images (height mode) of it-PS lamellar crystals grown at 180°C in ultrathin films below 20 nm in thickness. Amorphous regions around the crystals close to the growth interface is always thinner by several nanometers than the region far from the interface (original thickness); we call hereafter this region “halo”, named after the bright region in TEM images \( \text{(2)} \). A few nm-thick amorphous layer covers the surface of these lamellae, including lateral growth surface \( \text{(4)} \). In 17 nm-thick films Fig.\( \text{1a} \), the crystal shows a rounded shape with an undulated growth interface and a few small overgrowth lamellae is on its surface. It is observed that the top surface of the lamellar crystal is also undulated a few nm in height as indicated by the radial stripes. In films thinner than 15nm, the crystal morphology changes to that observed in the diffusion-controlled growth \( \text{(3)} \), as shown in Fig\( \text{1b to f} \). In 14 nm thick films, the crystal shows the splitting of growth face to have many irregular branches typical in the dense branching morphology (DBM) or compact seaweed (CS) \( \text{(6)} \). The envelope of this branching structure is nearly circular; we call hereafter this envelope “average front” in contrast to the local growth interface of its branch \( \text{(7)} \). The crystal grown in 11nm-thick films (Fig\( \text{1c} \)), also consists of many branches, however it has an almost hexagonal average front similar to the compact dendrite (CD) \( \text{(8)} \). Below about 8 nm, the average front is triangular rather than hexagonal; it is to be noted that it-PS has the trigonal crystal structure \( \text{(9)} \). There is little material left between the branches developed.

It is clearly shown in Fig\( \text{1d-f} \) that for films thinner than 10nm the mean width of the branches increases as the film thickness decreases. While the branched structures are compact in films thicker than 10nm, those in film thinner than 10nm are rather open structure similar to the fractal dendrite (FD) or seaweed (FS) \( \text{(10)} \). Figure 2 shows the dependence of the mean width of branches, \( w \), in CS or side branches in dendritic structure on the inverse of film thickness, \( d \); the value of \( w \) remains constant down to the film thickness of 10nm and becomes larger and larger with decreasing film thickness.

Although the top surface of the lamellar crystal grown in films thicker than 11 nm is at almost the same level as that of surrounding melt, the crystals in films thinner than 10 nm protrudes from the surrounding amorphous surface. The regions of “halo” extend over a few hundreds nm radially in the thicker films and are observed in the AFM images as dark contrast in front of the growth face of a crystal. In films thinner than 10 nm, the width of the “halo” becomes larger with decreasing film thickness and eventually no “halo” is observed. Figure 3 shows the TEM bright field images of it-PS crystals grown in ultrathin films at 180°C with the diffraction patterns. The diffraction patterns prove that all the branching crystals have a sin-
Figure 1: AFM images of it-PS crystals grown at 180°C in ultrathin films. Each crystal is grown (a) in a film 17 nm thick for 30 min, (b) 14 nm, 1 hr, (c) 11 nm, 1 hr 30 min (d) 9.7 nm, 3 hr 15 min, (e) 8.7 nm, 3 hr 15 min (f) 6.2 nm, 8 hr 30 min. Scale bars represent 5 µm.

Figure 2: The mean width of branches $w$ vs. inverse of film thickness $1/d$ of it-PS crystals grown at 180°C.

Figure 4 shows the time evolution of the farthest tips from the center of crystals, $r_{tip}$, measured by in-situ optical microscopy. All the growth rates of farthest tips in ultrathin films down to 5 nm-thick were found to be constant during growth (linear growth); it is to be noted that the growth rates of reentrant sites between the farthest tips decreased during growth. The growth rates of farthest tips determined from the data in Fig. 4 are plotted against the inverse of film thickness, $1/d$, as shown in Fig. 5. The growth rates of it-PS grown at 180°C in ultrathin films also decrease with decreasing film thickness according to the Eq. (1) with $a \sim 7.2$ nm. However below about 9 nm, the Eq. (1) can not hold any longer and a crossover of the film thickness dependence is observed; the decreasing rate of $G$ with $1/d$ becomes much lower, and in 5 nm-thick films the growth rate reduces to 1/20 of that in the bulk. It is very interesting that the thickness of 9 nm is that of crystal lamellar thickness grown at 180°C.
Figure 3: Electron micrographs and diffraction patterns of it-PS crystals grown at 180°C in (a) 11 nm-thick films, (b) 8 nm and (c) 6 nm respectively. Scale bars represent 2 µm.

Figure 4: Time evolutions of $r_{tip}$ of it-PS crystals grown at 180°C in each film thickness. The upper abscissa is for the data of 30 nm and 15 nm thick films and the lower abscissa for 6.4 nm and 4.8 nm.

Figure 5: Growth rate $G(d)$ vs. inverse of film thickness $1/d$ for it-PS crystals grown at 180°C in ultrathin films. The dotted line shows $G(d) = G(\infty)(1 - a/d)$ with fitting parameters $a = 7.2$ nm and $G(\infty) = 21$ µm/hr.
4 Discussion

The experimental results on the morphology and growth rates indicate that the diffusion process of chain molecules begins to control the crystal growth in ultrathin films [14]. The morphological instability in ultrathin films was considered to be caused by the gradients of film thickness in the “halo” region, which could make a self diffusion field of polymer molecules [8]. When the film thickness is much thicker than the depletion of “halo” of several nanometers, the effect of the gradient on instability is so small that the crystal remains a circular disk as schematically shown in Fig. 6 a. However, when the film thickness becomes thinner than the lamellar thickness (∼ 9 nm), the growth of crystal requires diffusion of molecules in the melt further from growth front in order to supply crystallizing materials for the thicker crystals (Fig. 6 b,c). Hence, the growth rate in films thinner than lamellar thickness also decreases with decreasing film thickness. This film thickness dependence of the growth rates is different from that in films thicker than lamellar thickness caused by reduction of chain mobility in thin films due to entanglement effect [4], and hence the crossover is observed at lamellar thickness. A morphological instability appears by the gradient of film thickness around a crystal; the characteristic length of the diffusion controlled growth, such as the width of branches, is generally scaled by the diffusion length \( l_D \) given by \( 2D/G(d) \) where \( D \) is the diffusion constant of chain molecules [15, 16, 6]. For the film thinner than the entanglement distance, i.e. the diameter of the tube in the reptation model (∼ 7 nm [17]), entanglement effect on diffusion constant is small; the diffusion constant \( D \) should remain almost constant with film thickness [3]. Still the \( G(d) \) decreases with decreasing film thickness. Consequently \( l_D \) increases as denoted in Fig. 6 b,c and hence the width of branch \( w \) accordingly increases with decreasing film thickness. When \( l_D \) becomes very large and then “halo” is hardly observed as in Fig. 6 f in very thin films, the situation looks similar to the DLA growth: the crystal structure hence should become open fractal aggregates. In fact, this has been demonstrated in the Monte Carlo simulation [4, 5] on crystallization of adsorbed polymer monolayers, where the thicker the lamellar thickness becomes, the wider the width of branches.
and more open the structure becomes. It is worth noting that the dendritic tip can grow steadily even in the diffusion controlled growth as in Fig. 4, while the steady growth of a spherical interface is impossible; its growth rate decreases with time as $G \propto t^{-1/2}$.

5 Conclusion

In this paper we have reported the film thickness dependence of morphology and growth rates of i-PS crystals grown at 180°C in ultrathin films thinner than 20 nm down to 4 nm. It is clearly shown that in films thinner than 15 nm, the crystal morphology typical in the diffusion-controlled growth appeared and the morphology varied with decreasing film thickness from dense branching morphology (DBM) to diffusion-limited aggregates (DLA). In particular, it is found that in films thinner than the lamellar crystal, the structure becomes more open and characteristic length of the structure becomes larger and larger with decreasing film thickness. The dependence of the growth rates on film thickness also changed in the vicinity of the lamellar thickness.

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