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# Investigation of crystal growth observed in crystallization in thin polyethylene terephthalate film

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**Abstract.** There was increasing evidence that the properties of polymer in thin polymer films differ to their bulk properties. This was represented by the discovery of substantial thickness dependent changes in mobility. In the present study, crystal morphology occurring during in the crystallisation of polyethylene terephthalate (PET) film has been investigated. It was found that the lamellar width was temperature and thickness dependence, and the structure having a diffusion-controlled nature grew in very thin regions ( $\sim 20$  Å in height) and at a very low temperature (65 °C) prepared from heating process but was not observed in thin films prepared from quenching process.

## 1. Introduction

In the past decade, there was increasing evidence that the physical properties of polymers in ultrathin films differed from those observed in the bulk due to the spatial confinement effects. In thin films, the phenomenon such as the chain orientation, segmental mobility, transporting process, and surface energy at the interface may become more dominant factors [1,2]. This requires a better understanding for scientific and technological viewpoints of thin polymer films. Thin polymer films have been applied as resist and interlayer dielectrics in microelectronics fabrications, as alignment layers in liquid crystal displays, and as lubricants in magnetic information storage devices. In each of these applications, the polymer chain orientation and state of organization played important role in determining the final properties [3,4].

The crystalline morphology has been shown considerably affected by film thickness in thin polymer films and fundamentally importance in the study of in thin films polymers [5-11]. In the present study, the thickness effect on crystal growth in thin poly(ethylene terephthalate) (PET) films has been investigated using atomic force microscopy (AFM) to obtain the nanoscale structural information. The aim is to extend to which the ordering properties in ultra-thin differ from bulk. Moreover, the growth process of the terrace of spherulite having a diffusion-controlled nature is quite interesting because it is in contrast to the case of the usual three-dimensional spherulites crystallized from the bulk state where the morphology is governed by surface nucleation process



## 2. Experimental Methods

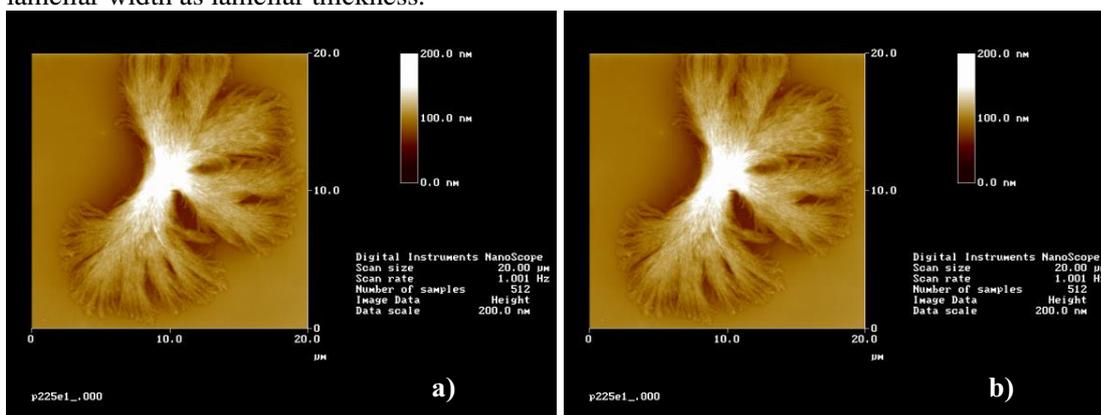
### 2.1. Sample Preparation

Polyethylene terephthalate) in the sheet form was dissolved by using 2- chlorophenol solvent. Concentration of solutions were in the range of 1 % - 10 %. The Polymer thin films were prepared by the spin-casting technique. This was done by placing a small quantity of polymer solution onto a 0.5 mm thick flat silicon substrate, which is held by a vacuum suction to a turntable. The substrate is then rotated at a particular angular rate for a specific time, usually between 1500–4000 rpm for 60 s. As a result, the polymer solution is spread onto its surface and so wets the entire wafer. Besides the solution concentration, varying the spinning rate also determines the film thickness. The resulting film is usually annealed to remove residual solvent and to relax internal stress at room temperature for two hours in vacuum. After the films were in left in vacuum, film thickness in this thesis are measured by using ellipsometry.

The crystal was grown undertaken by two different process; 1). by quenching process i.e. heating the sample above its melting point (260 °C), then subsequent undercooled to a desired crystallization temperature, 2). by heating process i.e. heating the sample to a desired crystallization temperature below the melting point

## 3. Results and Discussions

The qualitative insight into the effects of film thickness on crystallisation were obtained from atomic force microscopy (AFM) measurements. Typical data of the width of lamellar branches of the spherulite in a 465Å PET film by quenching process is shown in Figure 1. Section analysis showed that the width of lamellar branches of the spherulite was higher at high temperature than that at low temperature. The width of the lamellar branches at 225°C and 130°C were 107 nm and 76 nm, respectively. This implied that the mechanism controlling the growth of lamellae was similar than that in the bulk. According to Durell *et al* [12] the chains of thin PET films were aligned parallel to the surface, and hence it was considered the lamellar width as lamellar thickness.



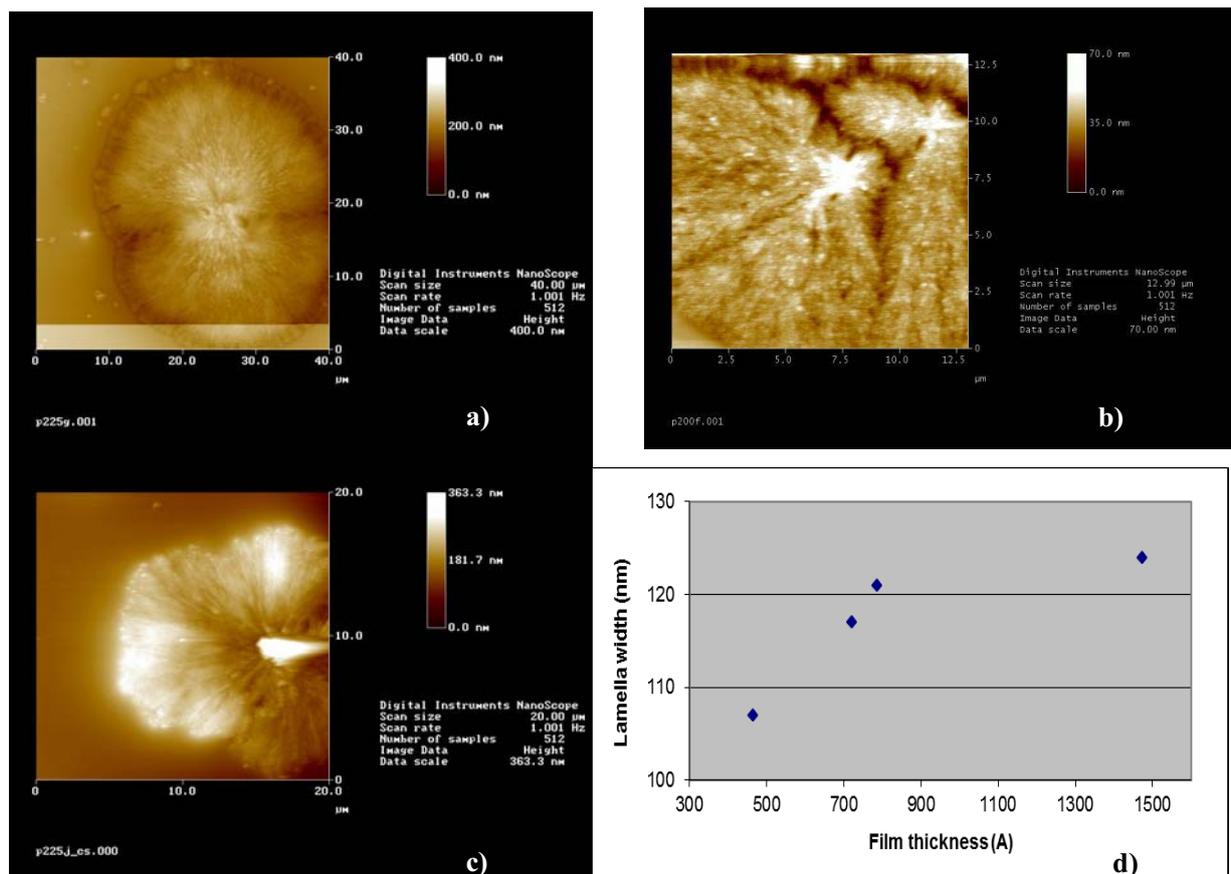
**Figure 1.** The lamella width decreases with decreasing temperature; comparison of a 465Å PET film crystallised at a). 225°C and b). 130°C observed by atomic force microscopy

Typical data of the thickness of a lamella branch for thin PET films crystallised at 225°C by quenching process of a 720Å, 786Å and a 1474Å is shown in Figure 2a, b, an d. Section analysis showed that the thickness of lamellar branches increased with increasing film thickness (Figure 2d). Similar results were

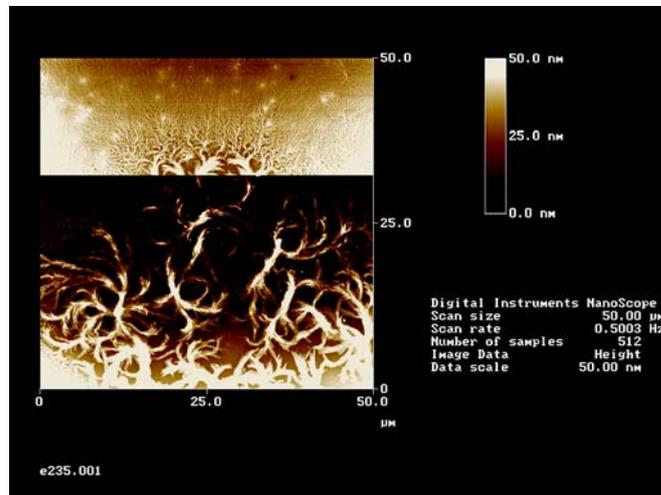
also observed by Wehrum [13] for the width of the main branches in thin PET film and also by Reiter *et al* [14] thin PEO film.

Sakai *et al* [11] observed that terraces appeared on the periphery of the final stage of spherulite growth in PET films (1000-2000 Å in thickness,  $M_n=25000$ ) crystallised at 220°C after melting at 290°C and were formed when the polymer crystallised from a very thin melt film. They confirmed the terraces to be inherent to the polymer itself and also an effect of film thickness. Sakai's results lead us to check their appearance in our PET film crystallised at 235°C by quenching process after melting at 280°C (Figure 3). It showed that the terraces did not appear on the periphery in our PET films (1474 Å in thickness), on the contrary with Sakai's result.

While Sakai *et al* considered that the terraces were an effect of film thickness, a similar thermal treatment (at 235°C) was given to a very thin film (465Å in thickness) to see the effect of the film thickness in our samples. It showed in Figure 4 branches of the spherulite on the periphery of the final stage still grew and filled the space outside the spherulite. It was interesting again that the terraces were not observed in our very thin PET film. While in the sample of Sakai *et al* the growth of the spherulite really stopped in a certain time of crystallisation and did not grow further to fill the space, our sample showed the contrary behaviour even at a thickness much smaller than that studied by Sakai *et al* [11].



**Figure 2.** The lamella thickness of a). 720 Å, b). 786 Å and c).1474Å PET film crystallised at 225°C observed by atomic force microscopy, d). The lamellar width increases with increasing film thickness



**Figure 3.** Spherulite of a 465 Å PET thin film after holding more than hour at 235 C° observed by atomic force microscopy.

There were some candidates causing the difference between our result and Sakai *et al*'s result;

- (1). Our measurement was conducted at room temperature on quenched samples, while Sakai *et al* conducted theirs in real time measurement using confocal scanning laser microscopy (CSLM).
- (2). Our PET films used silicon substrate, while Sakai *et al*'s film used glass and mica substrate
- (3). Our PET samples have very high nucleation density. This leads to the consequence that all the space was filled by the spherulites. As a result we could not observe the terraces or the terraces had no chance to grow, while the samples of Sakai *et al*'s showed the contrary behaviour in which the growth of the spherulites actually stopped in a certain time of crystallisation and did not proceed any further to fill the space.

The first candidate was most unlikely because the quenched spherulites observed at room temperature were the same as spherulite growing at isothermal crystallisation temperature. This was due to in a crystalline polymer re-growth of the spherulite (and the accompanying shape change of the boundaries) did not take place as we observed in the experiment. To ensure that secondary crystallisation did not take place, we quenched the sample very quickly to room temperature by purging it with liquid nitrogen. According to Stachurski [15], the spherulites did not re-grow at room temperature due to the free energy within the spherulite was no less and could be greater than that associated with the inter spherulitic boundary.

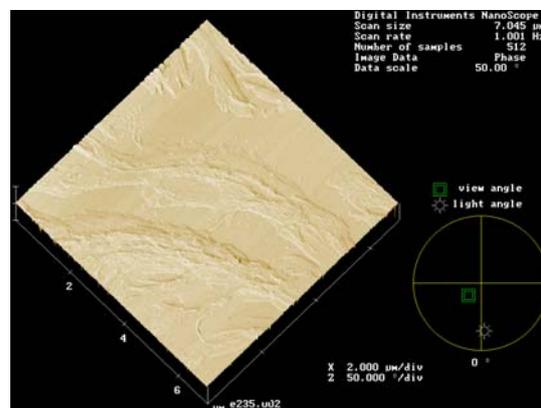
Although Sakai *et al* observed a similar terrace structure both on glass and mica substrates. They considered the formation of the terrace to be independent of the type of the substrates. The non-appearance of the terraces in our PET samples due to the effect of the silicon substrate was still possible. It was from the analogy of morphology dependence on the substrate type for a related system. Sutton *et al* [16] found that the morphology of the spherulites in thin it-polysterene films (500Å in thickness) to be dependent on the nature of the substrates. Moreover, we did not do the experiment on the same substrate as that used by Sakai *et al*.

The third candidate may be responsible for the disappearance in our studies, and this was a consequence of the existence of the impurities. In addition to the effect of high nucleation density in our PET sample, another difference between our sample and Sakai's samples was thermal treatment and solvent; our samples were isothermal crystallised at 235°C after melting at 280°C, while Samples of Sakai *et al* were

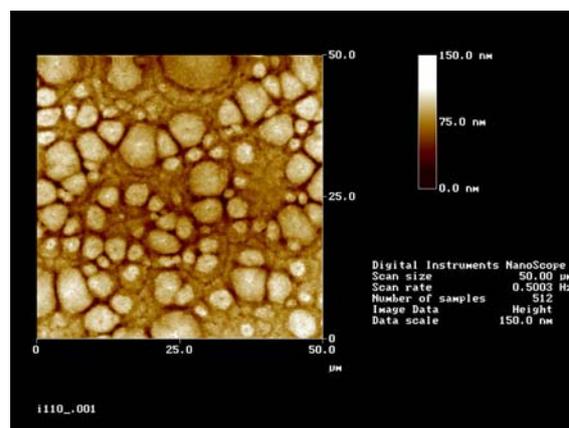
crystallised at 220°C after melting at 290°C. Our films were made from the PET sheet dissolved in 2-chlorophenol solvent, while Sakai *et al* 's samples from PET powder dissolved in a mixture of 95 % chloroform and 5 % trifluoroacid.

Another feature in Figure 4 seemed to be specific to lamellar growth of PET in thin films. It showed a wide spacing between adjacent lamellae. This was presumably a consequence of the relatively thin film. Although the spherulites had impinged on each other, the lamellae of one spherulite still continued to grow forward to penetrate into other adjacent spherulites in the thin PET film. It was interesting to compare this with the thick film (Figure 3) and also in the other samples where lamellae penetrating into the adjacent spherulite were not observed.

It showed also the image showing different contrast above and below (arrow in Figure 4). The difference in contrast was on account of the tip being too near to the surface.



**Figure 4.** Three dimension figure of small size of spherulite as a part of branching of big spherulite of a 237 A° PET thin film at 235 C° observed by atomic force microscopy

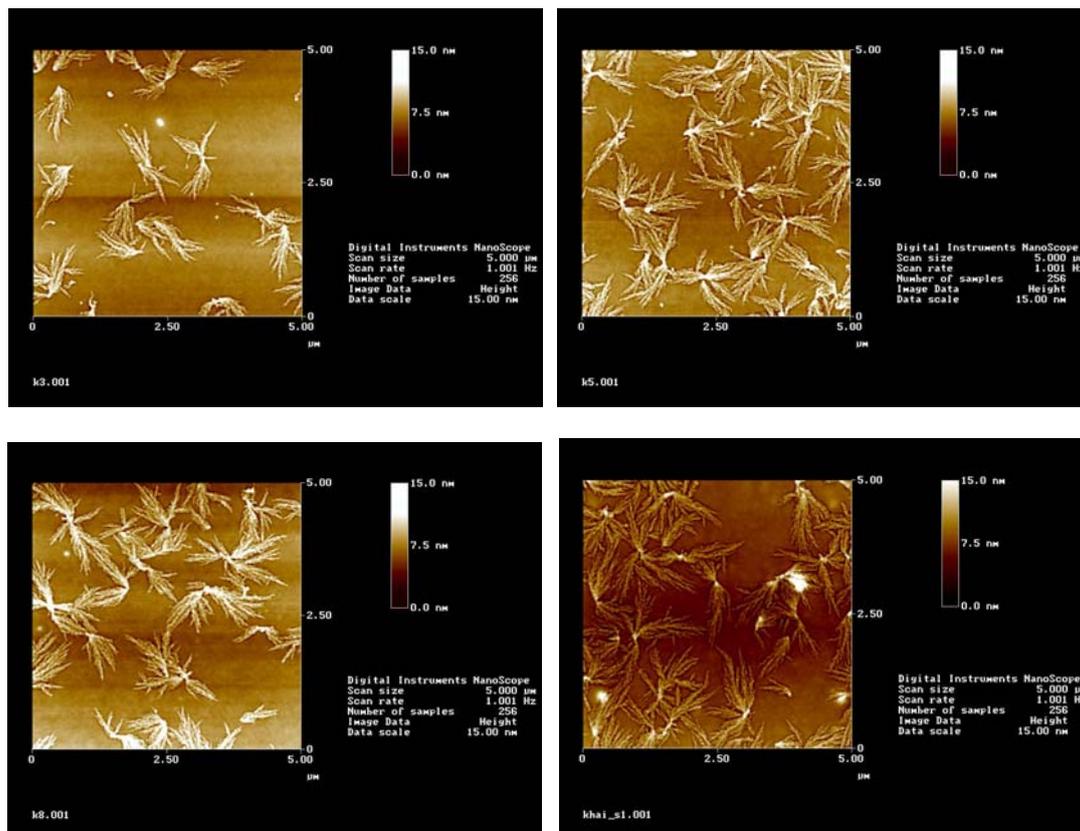


**Figure 5.** a 1474A PET at 110°C observed by atomic force force microscopy

Figure 5 displays a section of the spherulite in Figure 4. A dendritic structure can be seen (arrow) growing from the main lamellar branch. Section analysis shows that the thickness of this dendritic structure is about 2 nm. Frank *et al* [4] found that when the thickness of films is larger than 22nm, crystal growth is three dimensional as in the bulk state, but when it is thinner than 15 nm, the growth become one

dimensional. Hence, we can consider that the growth of the dendritic structure in figure 5 was one dimensional

The dendritic structure in Figure 5 showed similarities with fingerlike branched structure having diffusion-controlled nature observed by Reiter *et al* [17]. Reiter *et al* have observed that a finger-like branched pattern appears when poly(ethylene oxide) is crystallised in quasi-2-D geometry. Therefore, the mechanism that controls the growth of the dendritic structure in our sample was probably similar with the fingerlike branched structures of Reiter's film

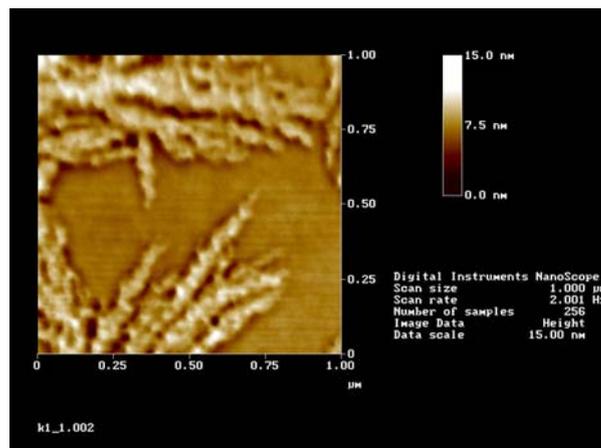


**Figure 6.** The petal structures of a 100A (a), a 223A (b), a 510A (c), and 1358A(d) heated at 65°C for 3 days observed by atomic force microscopy

The cause of the dendritic structure becoming very thin was explained by Sakai *et al*. Sakai *et al* (1999) proposed that the level of the melt surface decreases with the passage of time due to the consumption of the molten PET molecules by crystallisation to form the main lamellar branches. As a result, the thickness of the layer surrounding the dendritic structure became very thin.

The roughness analysis was done for a 1474Å film crystallised at 235°C (Figure 3) and crystallised at 110°C by quenching process (Figure 6) to see any correlation between the roughness and crystallisation temperature. At 235°C, the average roughness was 0.0375 μm, whereas at 110°C, the average roughness was 0.0123 μm. These results implied that high temperature promoted a roughening of the surface and low temperature resulted in smoothing of crystal faces. Roughening at high temperature as observed by atomic force microscopy was due to a wide spacing between adjacent lamellae and thick lamellae. Smoothing at low temperature was a result of small spacing between adjacent lamellae and thin lamellae.

Finally we consider the morphologies obtained by crystallisation at very low temperature by heating process. At very low temperature, the morphology of the spherulites is very different (Figure 7 and 8). We can see the structures of the ‘spherulite’, consisting of petals radiating from the centre. We called it a petal structure (Figure 7) rather than ‘spherulite’ because of the uncommon morphology. The petal structures show similarities with the terraces having long needle crystals as observed by Sakai *et al.* From the argument that the structures of sample in the figure 7 show similarities with the terraces of Sakai’s samples, we may then consider that the petal structures in Figure 7 are governed by the diffusion.



**Figure 7.** Long needle-like crystals observed in a 1358A PET at 65°C heated for 3 days

From foregoing discussion relating to the appearance of terraces in our PET thin films, we may give an impression of the terraces in our PET samples,

- (1). We did not observe the terraces in our PET thin films at high temperature as observed by Sakai *et al.*, but we observed the dendritic structures in the very thin region in the PET thin film crystallised at high temperature showing similarities with the finger-like branched structures of Reiter’s films having a diffusion controlled-growth nature.
- (2). We observed that all crystals with petal structures in PET thin films (100-1400Å in thickness) grow at a very low temperature and showed similarities with the terraces as observed by Sakai *et al* having diffusion controlled-growth nature.

Figure 7 displayed a comparison of the morphology of spherulites crystallised at crystallisation temperature of 200°C produced by quenching the sample from the melt (Figure 7a) and by heating the sample from the glass (Figure 7b). It can be seen that the quenching process creates a low nucleation density (and so large crystals grow), whereas the heating process creates a high nucleation density (and so small crystals grow). The difference of the number and size of crystals is probably caused by the different of the mechanism of the phase separation as an initiation stage of crystallisation. While the crystals by a quenching process grew from nucleus as a result of activated process, the crystals by a heating process grow from well-ordered region in the glass state. The existence of the well-ordered in the glassy state in PET was observed by Kaji *et al* [18] using  $^{13}\text{C}$  spin diffusion nuclear magnetic resonance spectroscopy.

#### 4. Conclusion

The nanostructural of crystals in thin PET film was temperature and dependence thickness as shown by lamellar width was higher at high temperature than that at low temperature, and the lamellar width increased with increasing films thickness. The nucleation density may affect the nonexistence of terraces of spherulite having diffusion-controlled nature in these thin PET film studies prepared by quenching

process. However, those crystals were observed in PET thin films (100-1400Å in thickness) grow at a very low temperature by heating process.

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