Analysis of thickness dependent on crystallization kinetics in thin isotactic-polysterene films

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Abstract Crystallization kinetics of thin film of Isotactic Polysterene (it-PS) films has been studied. Thin PET films having thickness of 338, 533, 712, 1096, 1473, and 2185 Å were prepared by using spin-cast technique. The it-PS crystals were grown on Linkam-hostage in the temperature range 130-240°C with an interval of 10°C. The crystal growths are measured by optical microscopy in lateral direction. It was found that a substantial thickness dependence on crystallisation rate. The analysis using fitting technique based on theory crystal growth of Lauritzen-Hoffman showed that the fitting technique could not resolve to predict the mechanism controlling the thickness dependence on the rate of crystallisation. The possible reasons were due to the crystallisation rate varies with the type of crystals (smooth, rough, overgrowth terrace), and the crystallisation rate changes with the time of crystallisation.

1. Introduction
While mechanical applications of polymers took advantage of their bulk properties, there were many technologies in which ultra thin polymer films were used. For instance, they were applied as resist and interlayer dielectrics in microelectronics fabrications, as alignment layers in liquid crystal displays, and as lubricants in magnetic information storage devices [1]. In each of these applications, the polymer chain orientation and state of organization played an important role in determining the final properties [1,2]. There was increasing evidence that the properties of polymer in ultra thin may be different to their bulk properties [3]. This was represented by the recent discovery of substantial thickness dependent changes in mobility. Previous evidence about this was contradictory. Frank et al [1] suggested that in some polymers crystallisation may be completely hidden in ultrathin films i.e with the thickness of order 100 Å. In contrast, Wehrum [4] showed that crystallisation could occur in poly(ethylene terephthalate), albeit with kinetics reduced in speed over values for thicker films. Therefore, studies of polymer crystallization in thin films are of both scientific importance and practical significance.

Below Tg, polymers in the bulk are in the glassy state, where chains are frozen into position. Only recently has increasing experimental evidence been suggesting that near free surface polymer chains may be mobile, while the bulk is in the glassy state. Keddie et al [5] suggested the existence of such a mobility from observations of a decrease in Tg in ultra thin polymer films, without a variety of experiments, in effort to recognize the nature of enhanced surface mobility. The aim of this present studies is to extend to which the ordering properties in ultra-thin differ from bulk. Previous evidence about this is contradictory. This preliminary finding is expanded and undertaken a systematic study of the effect of thickness in crystallisation kinetics in ultra thin polymer films.
In order to understand the underlying molecular mechanism of thickness dependence of 
crystallization, very thin isotactic polystyrene films were chosen where homogeneous 
nucleation was extremely rare. The growth front nucleation did not represent a significant 
perturbation due to well-controlled perturbation [6] and large scale single crystals can be grown. Such crystals allow for an 
clear relation between crystal shape and orientation of all polymer chains within the lamellae. 
Moreover, crystal morphology can be directly related to the growth kinetics as there is no perturbation 
of growth front nucleation. As a result, the evolution of the crystal morphology can be followed in 
detail [3].

2. Experimental
In this study it-PS is supplied in the form of powder by Aldrich Chem. Co. with molecular weight 
$M_w$ of 400000, we use cyclohexanone as its solvent. Because it-PS powder is provided in the form of 
a crystal (not glassy), it is difficult to dissolved in cyclohexanone. To overcome this problem, it-PS 
powder is transformed to glassy state by melting it above its melting point. This is done by placing the 
it-PS powder onto the glass substrate and then melting it using a Linkam hot stage. Next, the melt it-
PS is quenched by removing quickly the glass substrate and putting it in water. The reason for this 
treatment is to ensure that the it-PS has not had time to form a crystalline state; instead glassy it-PS is 
obtained. This glassy it-PS can be easily be dissolved in cyclohexanone solvent to make a solution as 
a raw material to prepare thin films. In order to reduce impurities and filter un-dissolved (crystal) that 
may exist during preparation of the solution, the solutions are filtered.

The thin it-PS films are prepared by using spin casting. Varying concentration of the solution or speed 
of the spin controls the thickness of the films. Variation of concentration of the solution produces 
greater variation of film thickness than variation of speed of the spin. Their thickness is characterised 
by ellipsometry. Theoretical explanation of the ellipsometry method is given elsewhere [7].
The thermal treatments of thin it-PS films were also similar to the thermal treatment of thin PET 
films. Under reflected light microscopy, the film was placed onto a Linkam hostage and heated at 
250°C (the melting point of it-PS powder is 215°C) for 3 minutes to melt the film and remove any 
differences in thermal and mechanical history of the film prior crystallisation. The melt film then was 
under cooled to a constant crystallisation temperature in range 200 – 130°C (with intervals of 10°C). 
In these studies, the Linkam hot stage was not needed to be purged with liquid nitrogen. This was the 
case as the thin it-PS film took a long time to crystallise (on average 30 minutes) after it had reached a 
constant crystallisation temperature.

3. Results and Discussions
The crystals seen in thin it-PS films were different from those of thin PET films [8]. Thin it-PS films 
formed crystals of hexagonal plates, hexagonal crystal having re-entrant corners to form a star-like 
shape or sunflower crystal, rounded hexagonal and circular discs rather than the circular discs seen in 
the thin PET films. The form of crystals produced in thin it-PS films depend on the crystallisation 
temperature. In other words, the crystals in it-PS films show a morphological transition with 
crystallisation temperature. Moreover the growth rate of crystals in the same film thickness and 
crystallisation temperature also shows variation with the type of crystal.

This is illustrated in Figure 1, which shows morphologies of crystals an annealing a 2185Å° film for 6 
hours at different temperatures. Note the series of qualitatively different morphologies. We also find 
that the morphologies depend on temperature. It can be seen in the figure that the morphological 
transition occurs from sunflower-like shape crystal with many re-entrants (190°C), sunflower-like 
shape crystal with many re-entrants and hexagonal with re-entrants to form star-like shape (180°C), 
banded circular (170°C), banded and dual circular (160°C), dual circular (150°C) and finally smoothed 
circular (130°C).
Figure 1. A morphological transition in the 2185Å film it-PS film from high temperature to low temperature.

Figure 2 shows the data of crystallisation rate of crystal for all film thickness crystallised in the temperature range of 130-190°C normalised to the thickest film (2185Å in thickness). The growth rate, which was measured, was the growth rate of crystals crystallised for less than 1 hour as displayed in the graph in Figure 3. It can be seen that the rate of crystallisation still depends on film thickness in thin it-PS films, but the thickness dependence on the rate of crystallisation is very complicated. Therefore, it cannot establish a generalised behavioural trend of the thickness dependence on the rate of crystallisation as thin PET films [8].

Figure 2. Thickness dependence on crystallisation rate of crystal in thin it-PS films normalised to the thickest one (2185Å in thickness). The data are from measurement of crystal growth for holding less than 1 hour.
PS. \( R_{tc} = \text{rounded hexagonal thin crystal}, \ C_{stc} = \text{circular smooth thin crystal}, \ C_{rtc} = \text{circular thin crystal}, \ C_{sTc} = \text{circular smooth thick crystal}, \ C_{rTc} = \text{circular thick crystal} \)

**Figure 3.** morphological transition as a function of crystallisation temperature and film thickness in it-PS films after holding about hour. PS. HP = hexagonal plate, RH = rounded hexagonal, C = circular, re= re-entrant, s= smooth, r= rough, and d= dual

In further investigate any relation between the thickness dependence and crystallisation rate, it used the equation (1) of spherulite growth rate of Lauritzen-Hofman [9] for fitting to find out the activation temperature \( (T_A) \), Vogel temperature \( (T_V) \), constant \( B_o \), and equilibrium melting point \( (T_f^\infty) \). The result of spherulite growth of different thickness informs us directly whether the crystallisation rate was a function of film thickness. An analysis of data using the equation (1) for the spherulite growth rate \( (G) \), with the dependence of \( G \) on the segmental mobility, given by the ‘Vogel Fulcher law’ represented by the first term and the undercooling ‘driving force’ represented by the second term of the equation gives us more information which term is affected by thickness of the thin polymer films. An attempt was made to do the non-linear to get \( T_A, T_V \) and \( B_o \) with \( T_f^\infty \) fixed at 513\(^\circ\)K for it-PS thick film, but the software could not resolve this. This was probably because either the crystallisation temperature range of these studies was too short to be fitted by the program or the data was complicated. This procedure was done because the value of parameter \( B_o \) when fitting was done using equation (2), was required. To overcome this problem a trial and error approach was taken. Finally it used a 465 as a value for constant geometry for bulk system.

\[
G = \exp\left(-\frac{T_A}{T-T_V}\right) \cdot \exp\left(-\frac{B_o}{T_f^\infty - T}\right) \tag{1}
\]

\[
\left(\ln G + \frac{B_o}{T_f^\infty - T}\right)^{-1} = \frac{T}{T_A} + \frac{T_V}{T_A} \tag{2}
\]


\[
\left[ \ln(G) + \left( \frac{T_A}{T - T_V} \right) \right]^{-1} = \frac{T}{B_o} - \frac{T_V^\infty}{B_o} \tag{3}
\]

Table 1

| Thickness (Å) | \(T_A\) (K) | \(T_V\) (K) |
|---------------|-------------|-------------|
| 338           | 1406.3±     | 327±8.45    |
| 533           | 1352.7±     | 330±9.67    |
| 712           | 1511.7±     | 322±6.87    |
| 1095          | 1661±       | 311.5±2.98  |
| 1473          | 1468.67±    | 323.44±6.3  |
| 2185          | 1666±84.2   | 309±6       |

The deduced activation temperature \(T_A\) and deduced Vogel temperature \(T_V\) by the fitting procedure by using equation (2) is shown in table 1. In the fitting, the equilibrium melting point \(T_f^\infty\) and constant geometry \(B_o\) were assumed to be 513K and 465, respectively. The equilibrium melting point \(T_f^\infty\) and the constant geometry \(B_o\) were obtained using fitting procedure in the opposite way that is by assuming that the activation and Vogel temperature are constant for the bulk system stating equation (1) in the form of equation (3) that was by assuming that the activation and Vogel temperature were constant for the bulk system. Table 2 displays the value of the equilibrium melting point \(T_f^\infty\) and the constant geometry \(B_o\) obtained from fitting by assuming the activation temperature \(T_A\) and the Vogel temperature \(T_V\) of the bulk are constant i.e. 1666 and 309, respectively.

Table 2

| Thickness (Å) | \(B_o\)     | \(T_f^\infty\) (K) |
|---------------|-------------|---------------------|
| 338           | 456.9±26    | 512.6±5             |
| 533           | 432.6±34    | 510.2±6             |
| 712           | 480.4±50    | 505.81±4.4          |
| 1095          | 494.7±32    | 514.5±6             |
| 1473          | 461.35±36   | 512±6               |
| 2185          | 410.5±25    | 508.5±7             |
Figure 4. Temperature dependence of crystallisation rate for various it-PS film thickness of experimental data (D) and expected (F).

Figure 4 displays the deducted crystallisation (line) and the experimental crystallisation rate. It can be seen that the fitting technique cannot resolve the thickness dependence on the rate of crystallisation. This was because the deducted crystallisation rate is very spread with the behaviour of the experimental crystallisation rate, especially in the temperature range of 150-180°C and also at low temperature.

4. Conclusion
To conclude therefore, the fitting technique could not resolve to predict the mechanism controlling the thickness dependence on the rate of crystallisation. It was because the rate of crystallisation in it-PS films was complicated due to the following factors; first: the crystallisation rate varied with the type of crystals (smooth, rough, overgrowth terrace). Second: the crystallisation rate changed with the time of crystallisation. It was evidenced by the morphology of crystals dependant on the time of crystallisation, especially in thick films. In other word, the crystallisation rate in it-PS thick films was non-linear.

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