

How Temperatures Affect the Number of Dislocations in Polymer Single Crystals^{*}

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Abstract The influence of crystallization temperature (T_c) on the number of spiral growths on poly(butylene succinate) (PBS) single crystals, obtained by self-seeding method, was systematically studied. The studies show that the statistical average number of spiral growths formed on the PBS single crystals decays exponentially with respect to the T_c . Inspired by BCF (Bruton, Cabrera and Frank) theory and L-H (Lauritzen and Hoffman) theory, a thermodynamic model has been proposed, in which the origin of spiral growth was treated as a nucleation process. The model suggests that the nucleation rate of spiral growth depends on the inverse square of super-cooling degree, which predicted the density of spiral growth formed on lamellae, and was consistent with the experiments very well.

Keywords Dislocation; Spiral growth; Single crystal; Nucleation

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1872-2>.

INTRODUCTION

Real solids are generally not perfectly crystalline, as the dislocations exist in almost all kinds of crystals, such as inorganic, organic, polymer and bio-macromolecular crystals, *etc*^[1–6]. Since the theory of crystal growth was proposed by Bruton, Cabrera and Frank (BCF theory)^[7–9], it is generally accepted that both the spiral and terrace growths in crystal were originated from the dislocations and the spiral growth lamellae were formed by a pair of dislocations. However, even though the morphologies of spiral growth and terrace

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 21434003), the National High Technology Research and Development Program of China (No. 2015AA033801), the National Science and Technology Major Project of the Ministry of Science and Technology of China (No. 2013ZX09J13110-11B), the Fundamental Research Funds for the Central Universities, and the Program for Changjiang Scholars and Innovative Research Team in University. Jun Xu would like to thank the National Natural Science Foundation of China (No. 21374054) and the Sino-German Center for Research Promotion.

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Received June 20, 2016; Revised August 5, 2016; Accepted August 15, 2016

doi: 10.1007/s10118-017-1872-2

have been intensively studied^[10–18], and several studies suggest that the formation possibility of spiral growth in crystal is not random but shows a definite trend with temperature, it is hard to establish a quantitative relationship between the density of spiral growths and temperature.

According to BCF theory, if the crystal has a perfect surface which is terminated by molecularly smooth layer of atoms, it is generally not energetically favorable for further growth, and the key element for further growth is to achieve a two dimensional nucleus^[19]. Recently, dislocation-driven growth has been found to lead anisotropic growth of 1D nanowire, 2D nanoplates and 3D structures^[20–23], and the screw dislocations can promote bulk crystal growth at a significant rate under low supersaturation conditions^[22, 24]. Additionally, several physical properties of the crystal are affected by the presence of dislocation^[25]. Screw dislocation can influence the mechanical, thermal and electrical properties of the layered materials and potentially widen their application^[20, 21, 23, 26].

It is generally accepted that the adjacent crystal surfaces can slide over each other if tangential crystal growth is obstructed by defects, and this slide in turn forms a screw dislocation. From the perspective of defects, both dynamic and thermodynamic factors can be interpreted as the reasons for the formation of spiral growths. For the polymer crystals, the dynamic factors can be summed up to fast crystallization rate, irregularities in layer spreading of folded chain and non-planar stress^[13, 27–29]. The number of spiral growths increased under faster crystal growth rate or larger super-cooling temperature^[30], where rough growth front induced more number of screw dislocations. The special morphologies of lamellae were usually assumed to be the nucleation position of spiral growth and terrace, such as intersection of two single crystals, splitting of an existing lamellae, reentrant faces, depletion region and branch of stalk^[31–36]. These studies which were based on geometrical standpoint suggested that the formation of spiral growths were dependent on the irregularities of polymer chain arrangement.

On the other hand, thermodynamic factors, such as the degree of super-cooling, character of polymer chains, number of defects and strain, *etc.* play a key role in the formation of screw dislocations. Schultz and Kinloch studied the energy barrier for the formation of screw dislocation in polymer crystals and predicted the temperature dependence of the degree of twist on crystalline polymer ribbons^[37]. The overall dislocation movement is treated as the cumulative effect of the nucleation, motion and annihilation of a larger number of individual kinks^[38]. Moreover, several studies suggest that screw dislocation density shows a definite trend with temperature^[28, 39–41]. Some semi-crystalline polymers tend to form multiple number of spiral growths in their single crystal, such as polyethylene, poly(ϵ -caprolactone) and poly(*p*-dioxanone)^[32, 42–46]. The possibility of spiral growth formation on their single crystals can be changed by modulating the crystallization conditions, in polymers such as poly(L-lactic acid), poly(butylene succinate) (PBS) and poly(ethylene oxide)^[47–52], which suggest that the crystalline habits of spiral growth in polymer single crystal is not only dependent on the dynamic factors, but also controlled by thermodynamic factors during the crystallization process. Although some studies suggest that there is intrinsic relationship between macroscopic morphology and defects in crystals, the quantitative relationship between the number of spiral growths and crystallization temperature has not yet been reported.

In the present paper, the self-seeding method was used to obtain a series of PBS single crystals, with T_c ranging from 65 °C to 52 °C, which with different number of spiral and terrace growth. A quantitative relationship between crystallization temperature and the number of spiral growths on polymer single crystals was established, and we showed a direct evidence that the formation of spiral growths on polymer single crystals could be well controlled.

EXPERIMENTAL

PBS $M_w = 6.3 \times 10^4$ g/mol and Lysozyme (LYSO) 14.3 kDa were purchased from Sigma-Aldrich Chemicals and used as received. The polydispersity and melting point of PBS is 1.7 and 114 °C, respectively. Silicon wafers were immersed in H₂O₂/H₂SO₄ (30/70, *V/V*) at 120 °C for 30 min and then rinsed with abundant high-purity

deionized water.

PBS single crystals were prepared by self-seeding method^[50] from a 0.01 wt% *o*-dichlorobenzene solution. First, the PBS solution was heated to 120 °C for 30 min to completely dissolve the PBS in *o*-dichlorobenzene. In the second step, the solution was quenched to 40 °C and held at this temperature for 2 h. Thirdly, the solution was slowly heated (0.2 K/min) to a suitable self-seeding temperature ($T_s = 80$ °C) to partially dissolve the crystals. In the fourth step, the surviving crystals were used as seeds to grow PBS single crystals at a specific isothermal crystallization temperature (T_c), ranging from 52 °C to 69 °C. After 96 h, a suspension containing PBS single crystals was prepared.

Atomic force microscopy (AFM) (Nanoscope V MultiMode III, Bruker) was utilized to observe the morphology and measure the size of PBS single crystals. The height images of PBS single crystals were captured with tapping mode. Silicon probes (TESP) with a resonance frequency of about 300 kHz and a spring constant of about 40 N/m were used. The samples were prepared by placing about 20 μ L of the preceding suspensions onto the cleaned silicon wafers, and dried in a vacuum oven at room temperature for 24 h.

Optical microscopy (OM) (Olympus, BX53F) was used to observe and count the number of spiral and terrace in the PBS single crystals. Samples were prepared by placing about 20 μ L of the preceding suspensions onto substrates (LYSO films). Here, the LYSO films were used to increase the contrast of the optical microscope. 1 wt% LYSO solution was spin-coated onto cleaned silicon wafers, and the thickness of LYSO films was controlled to about 50 nm by fixing the spin-coated rate (2000 r/min).

Electron diffraction (ED) was performed by using a JEM-2100 transmission electron microscopy (TEM) at an accelerating voltage of 100 kV. The preceding suspensions were directly deposited on carbon film supported cooper grids, and then the samples were dried in a vacuum oven at room temperature for 24 h.

RESULTS AND DISCUSSION

The AFM height images of PBS single crystals which grew from dilute solution by the self-seeding method are shown in Fig. 1. The PBS single crystals with various morphologies can be found even under the same seeding (80 °C) and crystallization (60 °C) temperature. The typical morphologies of the PBS single crystals appear as regular truncated lozenges with comparatively large truncating face, with mono-layer, two-layers and multi-layers as shown in Figs. 1(a), 1(b) and 1(c), respectively. The thickness of the mono-layer PBS crystals is about 10 nm and the size of the base layer almost remains the same when the seeding temperature is fixed. According to BCF theory and other studies, both spiral growth and island shape of multi-layers lamellae were thought to originate from dislocations^[53–56]. Island shape lamellae were formed by a single dislocation, while spiral growth lamellae by a pair of dislocations. When the number of spiral growth on the PBS crystals was counted, we consider the island shape and spiral growth multi-layer lamellae (in Figs. 1b and 1c) as the same due to the low resolution of optical microscope. When one spiral or terrace was observed in polymer single crystals, one dislocation was counted. The thickness of crystal boundary is about 6 nm, as indicated by the arrow in Fig. 1(a). The thickness difference between the central and boundary suggests that the boundary of the PBS crystal originates from the further growth at a lower temperature by secondary crystallization process (over growth) during the cooling of suspensions to room temperature. It is noted that the terrace lamellae which formed on the central area of PBS single crystal have the same thickness with the central area as shown by cross-section in Fig. 1(b). According to the lamellar thickness of the terrace and their growth region, it is reasonable to deduce that the terrace and spiral growth are originated during isothermal crystallization process instead of over growth during cooling. The typical morphology of PBS single crystal is shown in Fig. 1(a), and the corresponding electron diffraction pattern in Fig. 1(d). Four pairs of diffraction spots are observed, which could be attributed to the (020), (110) and (200) planes in the monoclinic unit cell^[57].

Even though the PBS crystals are obtained under the same crystallization conditions, there is a little morphological difference as shown in Figs. 1(b) and 1(c). The PBS crystal in Fig. 1(b) looks like a terrace and grows without handedness. While the PBS crystal in Fig. 1(c) shows a spiral growth of the successive lamella,

the corresponding electron diffraction results in Fig. 1(f) show that the diffraction pattern is superimposed of two lattice with slight rotation, which does not appear in Figs. 1(d) and 1(e). As the structure of PBS single crystals is too weak to finish the selected-area diffraction, therefore, the diffraction pattern was captured first, and then the corresponding morphology of sample was confirmed. The electron diffraction results in Figs. 1(d)–1(f) were obtained by the sample with same morphology corresponding in Figs. 1(a)–1(c), respectively. The multilayer lamellae and rotated diffraction pattern were frequently captured from the low T_c prepared samples, and were barely obtained by high T_c prepared crystals. According to our observation on PBS single crystal, the spiral growth does not always form on the center of the underlying layer or on any special positions, which means that it does not originate from the primary nucleus. Remarkably, most spiral growth and terrace were observed on the (020) sectors.

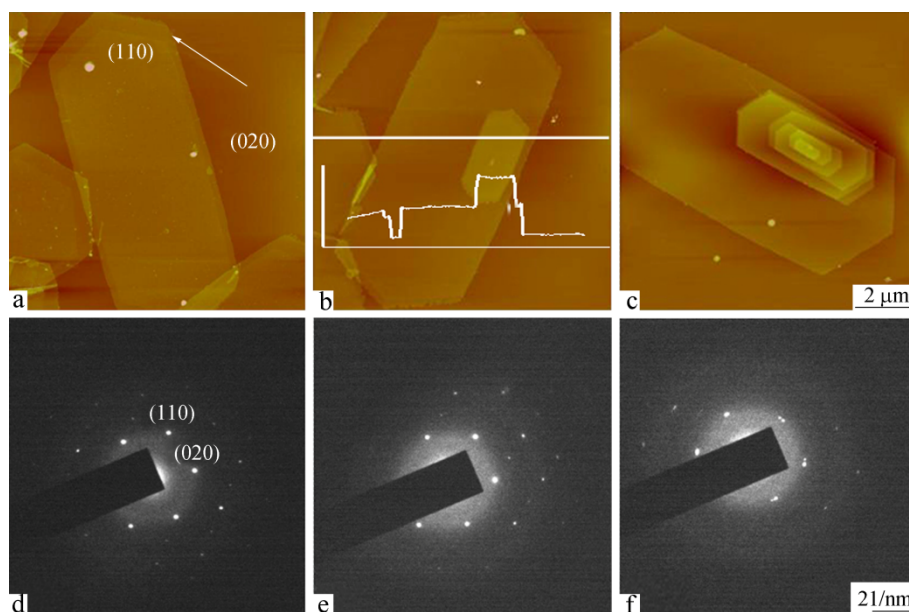


Fig. 1 AFM height images of PBS single crystals and the corresponding electron diffraction pattern: (a) a mono-layer single crystal, (b) a two-layers crystal with terrace, (c) a multi-layers crystal with spiral growth, (d), (e) and (f) the electron diffraction pattern of sample with morphology as (a), (b) and (c), respectively

Figure 2 shows the AFM height images of the PBS single crystals with different morphologies obtained by the self-seeding method under the same crystallization conditions (seeding at 80 °C and crystallizing at 52 °C for four days). The suspensions which were prepared by self-seeding method contain a large number of PBS single crystals. Six kinds of morphologies can be found in the suspensions: without or with up to five spiral and terrace growth in the PBS crystal, as shown in Figs. 2(a)–2(f). In order to obtain more morphological results, optical microscope was used to observe the statistical significant number of the PBS crystals. The number of the spiral and terrace in PBS crystals can be clearly distinguished from the optical images (see Fig. S1 in the supporting information). A series of suspensions containing PBS single crystals for each specific T_c ranging from 52 °C to 69 °C was prepared. For each T_c , about 200 to 300 PBS single crystals were observed by optical microscope and the number of spiral and terrace in each PBS crystal was also counted at the same time (see Fig. S2 in the supporting information). According to the BCF theory, the terrace and spiral growth originated from the dislocations, and one terrace was created by one dislocation. Here, the number of dislocations in PBS single crystals is equal to the number of terrace and spiral observed. We obtained screw dislocation number at various T_c , and the normalized results are shown in Fig. 3(a). At 52 °C, it can be seen that the maximum probability of screw dislocation number is around two. In the range of 60 °C to 69 °C, the maximum probability of screw dislocation number is zero.

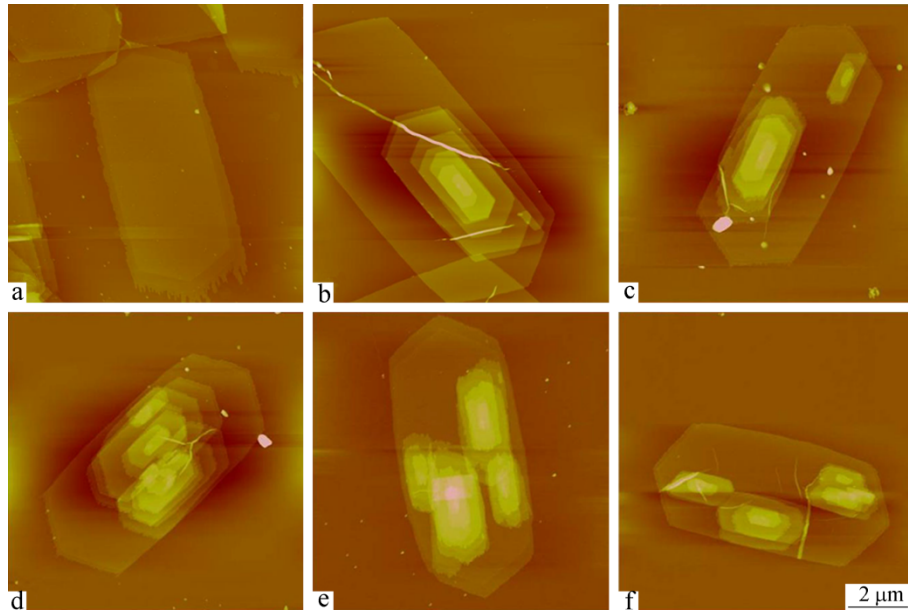


Fig. 2 AFM height images of PBS crystals with different number of spiral and terrace growth: (a) no spiral and terrace, with (b) one, (c) two, (d) three, (e) four and (f) five spiral or terrace growths

Here, we define the proportion of PBS single crystals with n screw dislocations at a certain T_c as $P_n = N_n/N$, where the N_n is the number of PBS crystals with n screw dislocations and N is the total crystal number counted. As shown in Fig. 3(a), the P_0 (the proportion of PBS crystals without any screw dislocation) decreases from 100% at 69 °C to around 5% at 52 °C. The P_1 (the proportion of PBS crystals with only one screw dislocation) gradually increases from 0% at 69 °C with the maximum around 50% at 58 °C, and then it decreases to around 16% at 52 °C. The proportions of PBS crystals with several screw dislocations (P_2 to P_5) are all increased when the T_c is decreased from 69 °C to 52 °C. Our observations clearly indicate that the screw dislocations in PBS crystal tend to occur at a lower T_c . The mono-layer PBS single crystals could only be prepared at a relatively higher T_c . We chose the proportion of the PBS crystals with different number of screw dislocations as weight factors to calculate the statistical average number of screw dislocations, and obtain the expected value of screw dislocations at each T_c , as shown in Fig. 3(b). The number of screw dislocations, on average, decays exponentially with respect to the T_c . Since the number of spiral growth in PBS single crystals for a fixed T_c is not a certain value during observation, the “ n ” is a statistical average value, and the error bars represent the distribution condition of the number of spiral growth instead of the precision of the measurement.

Traditionally, the formation of screw dislocations is associated with the number of defects in the crystals. However, the statistical significance number of defects in the crystals is difficult to be directly measured or counted by experiments. In order to establish the relationship between the number of screw dislocations and the number of defects, it is necessary to identify the characteristic parameter for defects. During polymer crystallization, the T_c is regarded as the key parameter to introduce defects^[40, 41]. On the basis of our experiments, we infer that the number of screw dislocations is also directly related to T_c , so we try to use T_c as a bridge to connect the defects and screw dislocations. According to the classical nucleation theory, the number of defects determines the nucleation rate and has to obey the Boltzmann distribution at different T_c . So it is reasonable to deduce that the screw dislocation process will also obey the Boltzmann distribution, follow the classical nucleation theory, and can be treated as a nucleation process induced by the defects.

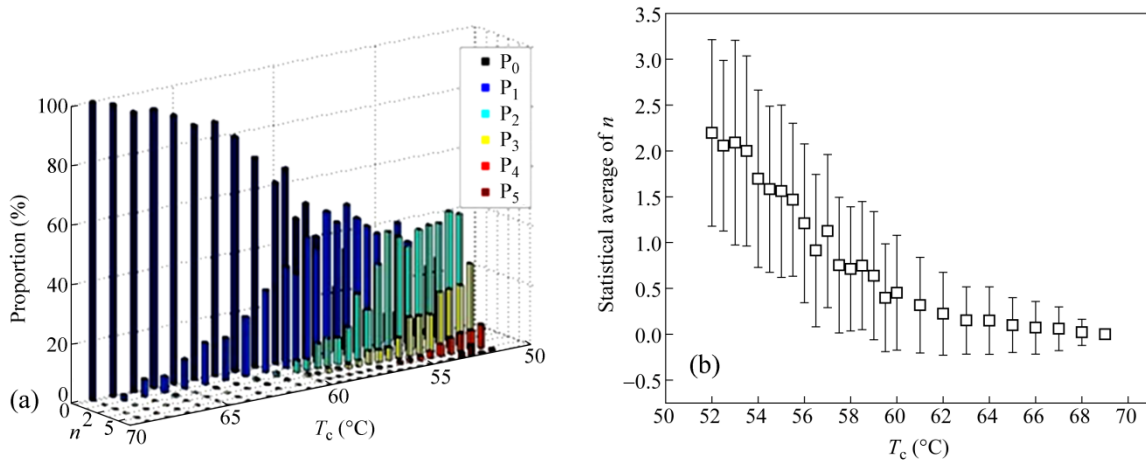


Fig. 3 The relation between the number of screw dislocation and crystallization temperature: (a) the proportion of PBS crystals with different number of screw dislocations against the crystallization temperature and (b) the statistical average number of screw dislocations as a function of the crystallization temperature

Since several studies showed that the screw dislocation was associated with step on crystal surface^[58–61], it was suggested that irregular arrangement or chain thickening may promote screw dislocation formation in polymer crystals. The nucleus of spiral growth induced by steps and kinks in BCF theory is similar to secondary nucleus in L-H theory^[62]. Here, we try to use a model to simulate the screw dislocation nucleation process. We assume that the stems at the growth front have lateral dimension a and thickness l as shown in Fig. 4(a). Lindenmeyer^[63] and Holland^[64] suggested that dislocation might be produced by strains or chain thickening. Further, Lauritzen and Hoffman^[65] proposed that the thickening might be nucleated at chain end. As a few segments thickening, several new surfaces are generated to form a thickening nucleus. According to previous literatures and the experiment fact of screw dislocation with multi-layer lamellae, we assume that the stems in the screw dislocation nucleus slide along the dislocation direction for a few segments. The slide distance is nl , and n should range from 0 to 1. When $n = 0$, there is no slide between stems. When the nucleus is equal to secondary nucleus in L-H theory, no screw dislocation is formed. When $n > 0$, the stem slides for a few segments, which may induce the formation of screw dislocation. Thus, for a screw dislocation nucleus composed of v_1 columns and v_2 rows stems, the free energy to nucleate a screw dislocation can be expressed as:

$$\Delta G = 2v_1v_2a^2\sigma_e + 2v_2al\sigma + 2nv_1al\sigma - v_1v_2a^2l\Delta f \quad (1)$$

where σ_e and σ are the free energies per unit area for fold surface and lateral surface, respectively, and Δf is the free energy of fusion per unit volume of the macroscopic crystal. The free energy ΔG have a saddle point at which the partial derivatives $\partial\Delta G/\partial v_1$, $\partial\Delta G/\partial v_2$ and $\partial\Delta G/\partial l$ simultaneously vanish. Similar to the L-H theory, the critical free energy of dislocation nucleation could be expressed as the following:

$$\Delta G^* = 32n\sigma^2\sigma_e \frac{(T_m^0)^2}{\Delta T^2\Delta h_f^2} \quad (2)$$

where Δh_f is the heat of fusion per unit volume of the crystal, T_m^0 is the equilibrium melting point of the macroscopic crystal, and ΔT is the degree of super-cooling. According to the classic nucleation theory^[30], the nucleus formation rate can be expressed as the following:

$$S = \frac{NkT}{h} \exp\left(-\frac{\Delta\phi^*}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (3)$$

where N is the number of molecules, kT/h is the frequency of thermally activated vibrations (k is Boltzmann's

constant and h is Planck's constant), while $\Delta\phi^*$ is the activation energy of a molecule transporting across the phase boundary. In Eq. (3), the nucleus formation rate is determined by two parts: $\exp(-\Delta\phi^*/kT)$ and $\exp(-\Delta G^*/kT)$, corresponding to nucleation barrier contribution of chain diffusion, adhesion and folding process respectively. For polymer crystallizing from melt and solution, it differs mainly in the ability of chain motion. In our self-seeding solution system, since the nucleation barrier ΔG^* is overwhelmingly greater than $\Delta\phi^*$ at small $\Delta T^{[30]}$, the nucleation rate should be proportional to $\exp(-\Delta G^*/kT)$. According to Eq. (2), ΔG^* is inversely proportional to ΔT^2 , so the nucleation rate should show dependence on $\exp(-1/\Delta T^2)$. A linear relationship between the logarithm of nucleation rate and inverse square of super-cooling degree could be expected.

As directed by the nucleation model, we transform the exponential decay data in Fig. 3(b). Since the number of screw dislocations is an indication for the nucleation rate, we plotted the logarithm of screw dislocation numbers against the inverse square of super-cooling degree. The results are shown in Fig. 4(b). An approximately linear relationship between $1/\Delta T^2$ and $\ln n$ is found in our tested temperature range. The linear relationship demonstrates that our experimental results agree well with the established model. It is suggested that the formation of screw dislocations need to overcome the nucleation barriers, which is controlled by the super-cooling degree.

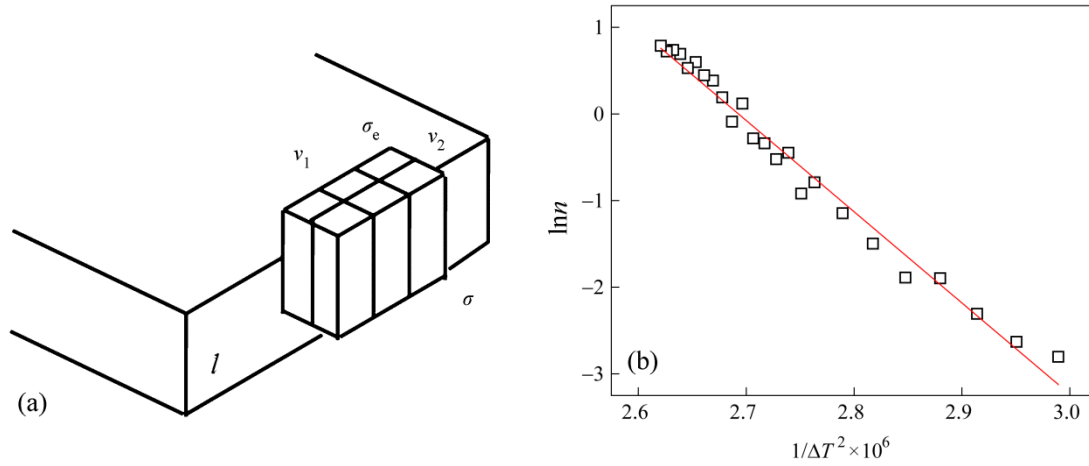


Fig. 4 The screw dislocation formation mechanism in the crystal: (a) a schematic diagram to show the nucleation of a screw dislocation and (b) the logarithmic statistical average number of screw dislocations as a function of the inverse square super-cooling degree

CONCLUSIONS

PBS single crystal, which was prepared by self-seeding method, has been studied with AFM, TEM and OM. The results indicate that the number of spiral growths in PBS single crystal depends on the degree of super-cooling. The statistical average number of spiral growths decay exponentially with respect to the T_c . A thermodynamic model inspired by BCF theory and L-H theory was proposed to establish the relationship between the degree of super-cooling and nucleation rate of screw dislocations in crystal. The deduction of the model indicates that the logarithm of screw dislocation number is inversely proportional to the square of super-cooling degree, which agrees well with the experimental observation. This model establishes the relationship between spiral growth (macro morphologies) and defect number (micro structures), which should be helpful for the morphological control of the polymer single crystals.

ACKNOWLEDGMENTS We are grateful for helpful advice and discussions from Professor Bernard Lotz.

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