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Crystal and multiple melting behaviors of PCL lamellae in ultrathin films

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ABSTRACT

In this paper, isothermal crystallization at different temperatures and multiple melting of four molecular weights (*MW*) PCL ultrathin films were investigated by using Atomic Force Microscopy (AFM). The results showed that: two different crystal structures, Flat-on and Edge-on lamellae, were simultaneously formed in PCL ultrathin films when the T_c lower than 30 °C. During the heating process, Edge-on lamellae was melted firstly. This demonstrated that the multiple melting behavior of PCL in ultrathin films was caused by the two different lamellar structures. With the increase of *MW*, or with the decrease of T_c, PCL chains in ultrathin films changed from Flat-on to Edge-on, and the controlled factors of growth process in ultrathin films transformed from surface nucleation-limited (NL) to melt diffusion-limited (DL).

1. Introduction

Crystallization of polymers is one of the most intriguing topics in macromolecular physics [1]. In recent years, polymer crystallization in thin and ultrathin films has attracted increasing interest in both practical applications and scientific importance [2–5]. Polymer ultrathin films belong to the quasi-two-dimensional nanoscale materials, and the films thickness is less than 100 nm. Polymer restricted in ultrathin films, due to the interfacial effect and the space effect between films and substrate, and the crystallization behaviors are different from bulk crystallization, such as polymer chain orientation, crystal growth rate, crystallinity, crystal morphology [6,7], and so on.

During the crystallization process of polymer in ultrathin films, there are some affinities between the molecular chain and the substrate surface. Due to the influence of geometric constraints, when the phase transformation occurs, polymer chains tend to oriented growth in the vertical direction of the substrate surface, i.e. the lamellae's *c* axis (unit cell) is perpendicular to the substrate surface [8], this ordered crystal structure is termed Flat-on lamellae. In addition, the interaction force between the substrate surface and the polymer chains in ultrathin films is mostly from the interaction of polymer end group and substrate. It leads to the mobility of polymer chains dropping, the polymer chains arranged in a preferred orientation during the crystallization process, are usually easier to growth Flat-on crystal. With the increase of the molecular weight, the proportion of polymer end group decreases, and the interaction between polymer chains and substrate also reduces, polymer chains incline to parallel to the substrate surface growth, now the growth of crystal is Edge-on, as shown in Fig. 1.

There are many influencing factors in the process of crystallization. It is generally thought that the growth kinetics of this system is usually controlled by two factors: nucleation-limited (NL) and diffusion-limited (DL). Each of these processes may be slower, with the variation of T_c, the processes compete with each other and ultimately affect the growth process and crystal morphology [9]. The two control processes depend largely on the T_c, when crystal at lower temperature, nucleation rate is quick and the segment movement ability is weak, so the nucleation rate is greater than the rate of diffusion, it is the melt diffusion controlled stage. With the increase of T_c, segment movement ability enhanced but the nucleation rate gradually decreased, the controlled factor of the crystal growth transition from DL to NL. When the T_c increases to a certain extent, melt diffusion become a faster process, the diffusion rate is larger than the nucleation rate, this moment is the surface nucleation controlled stage.

As we all know, a striking difference with respect to the behavior of a polymer and that of a low molecular compound concerns the melting process [10]. The compounds with low molecular weight have a well-defined melting temperature, while the polymer does not melt sharply at one particular temperature

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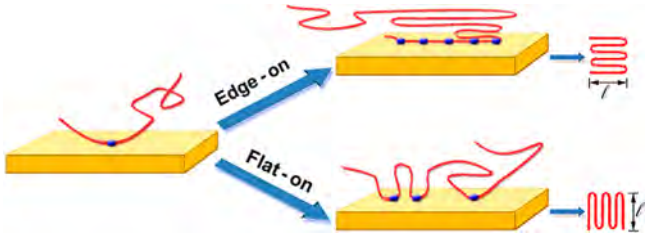

Fig. 1. The relationship between basement and molecular chain of polymer ultrathin film [8].

into clean liquid. Alternatively, it has a wide temperature range in the melting process. The appearance of multiple melting peaks is a long-standing phenomenon and still a controversial issue [11]. In particular, some semi-crystalline polymers often exhibit multiple melting behaviors during the heating process [12]. This interesting phenomenon, i.e. multiple melting transformation, has long been a hot spot in polymer physics, and in recent years, a large number of researches have appeared on the multiple melting transformation of various polymers, such as PA [11,13], PP [14], PET [15], PLLA [16–18], PEO [19] and so on. Chen et al. [19] used a low-molecular weight 4250 $gmol^{-1}$ PEO fraction to analyze multiple melting by Atomic Force Microscopy (AFM) and Differential Scanning Calorimetry (DSC). The results showed that the melting and recrystallization behaviors occurred during heating process and leaded to multiple melting.

However, its mechanisms are not completely clear even now. The behavior may result from the following [20]: (a) the presence of more than one crystal structure model, (b) variation in morphology (such as lamellar thickness, distribution, perfection or stability), (c) melting–recrystallization–melting mechanism during DSC heating process, (d) physical aging or/and relaxation of the rigid amorphous fraction, (e) different molecular weight species, (f) orientation effects and so forth.

Poly (ε-caprolactone) (PCL) is one of the most studied semi-crystalline thermoplastics due to its excellent biodegradability and biocompatibility. It has been widely used in many fileds, such as tissue engineering materials [21,22], drug delivery and controlled release carrier [23], surgery [24] and so on, it even has potential applications in the field of biodegradable materials.

Although theoretical studies have illustrated the mechanism of crystal and multiple melting in bulk polymer, the limited set of experimental data in ultrathin films is still insufficient to understand the origin of the evolution of lamellae. Also, it is a novel method to characterize the multiple melting in the ultrathin films. In this paper, we describe and analysis the crystal evolution and multiple melting in ultrathin films of PCL with four kinds of molecular weight (*MW*) by using AFM. The effect of isothermally crystallized temperature (T_c) and *MW* on the phenomenon of multiple melting were systematically discussed.

2. Experimental

2.1. Materials and sample preparation

PCL materials were supplied by JiNan Biochemical Co. Ltd. (China). Before the experiments, PCLs were carried out three times precipitation fractionations in order to get narrower the molecular weight distribution (*MWD*) of PCL (Solvent: Tetramethylene oxide (THF), Precipitating agent: petroleum benzin).

2.2. Characterization

2.2.1. Molecular weight characterize

The M_n and *MWD* (M_n/M_w) of fractionated samples were determined by GPC (Waters 2410) with Waters styragel column (The aperture is 10^3 Å, 10^4 Å and 10^5 Å, respectively). The M_n of samples is about 0.5×10^4, 0.8×10^4, 2.5×10^4 and 5.1×10^4, respectively. And all of the samples' *MWD* are less than 1.5.

2.2.2. Differential Scanning Calorimetry (DSC)

A TA Q2000 Differential Scanning Calorimetry (DSC) apparatus was used for the thermal analysis of Sapmles. The calibration of temperature scale and heat flow was carried out the melting scans of high-purity indium and zinc standard materials at the same heating rate (5 °C/min). In the experiment, about 3∼5 mg of the sample was weighed and sealed in an aluminum pan. By using DSC, the sealed sample was heated to 80 °C for eliminating the heat history completely, and it was quenched to T_cs (the isothermal crystallization temperature) for the complete crystallization. Finally, the heating curves were scanned by DSC at the heating rate of 5 °C/min.

2.2.3. Atomic Force Microscopy (AFM)

The model of AFM which was used in this experiment is BenYuan CSPM-5500, China Guangzhou BenYuan nanometer Instrument Company. The instrument is equipped with a hot stage, sample can be tested in situ heating and cooling, the accuracy is 0.1 °C. Moreover, the instrument includes software Imager 4.7 which can process data online and offline. In the experiments, Nano Devices RTESP tapping-mode silicon probe was used, all experiments were tested at the scanning range of 15 μm × 15 μm and 512 × 512 $pixel^2$, the scanning rate is 2 Hz.

Before the AFM testing, 0.25 mg mL^{-1} PCL solution was prepared, then dropped 1–2 drops of the solution on the mica surface, simultaneously dried 12 h under vacuum. Placed the prepared sample on the heating stage for 3–5 min at 80 °C to eliminate the thermal history thoroughly, then quenched to the setting temperature and isothermally crystallized for 30 min, finally investigated by AFM.

3. Results and discussion

3.1. The temperature dependence of PCL multiple melting

Fig. 2 was DSC heating curves of PCL-2.5×10^4 isothermally crystallized at T_cs (−30 °C to 40 °C). As shown in it, when the T_c was lower than 30 °C, all the curves had two melting peaks, in other words, multiple melting transformation took place. With the increasing of T_c, the lower T_m increased, and the higher T_m changed a little (shown in Fig. 3(a)). The peak height ratio of the lower to the higher decreased as the T_c increasing, as shown in Fig. 3(b). When the T_c was at or above 30 °C, the higher melting peak disappeared. In addition, the melting range decreased when the T_c increased. The results indicated that more perfect and uniform crystal could be got with the rise of temperature. Therefore, we might divide the PCL melting behaviors into two types, mono-melting and dual-melting, according to T_c.

3.2. Phase transition of PCL in ultrathin films during heating process

Based on the above DSC experimental results, we systematically investigated the heating process of PCL-2.5×10^4 ultrathin films isothermally crystallized at T_c lower than 30 °C. Here, we only analyzed the heating process of ultrathin films prepared at

20 °C. The sample morphology was in situ and real time scanning by AFM at a heating rate of 5 °C/min.

The AFM height images of PCL ultrathin films which were isothermally crystallized at 20 °C were shown in Fig. 4(a). As can be seen in Fig. 4(a), two different morphological lamellae, Flat-on (flake-like) and Edge-on (fiber-like), can be observed at the same time. Moreover, most of the Edge-on and Flat-on connected to each other. As shown in Fig. 4(b) (c) and (d), the Edge-on crystal gradually disappeared when the temperature increased. When the temperature reached 55 °C, the Edge-on crystal was completely melted, but the Flat-on did not show obvious collapsibility. When the temperature was increased to 57 °C, all the lamellae transformed into melting state and flocked together, and its periphery was smooth, as shown in Fig. 4(d). The similar report has been published [19], with the increase of the temperature, the edges of lamellae became smooth and the Flat-on lamellae was thickened which led to a later melting of the lamellae. In addition, the recrystallization probably occurred during the heating process, which also could exhibit multiple melting phenomenon.

In conclusion, there were two lamellar structures in the ultrathin films prepared at low temperature, and the lamellae had different T_m. Comparing the surface free energy of these two lamellae, the surface free energy of Edge-on crystal was obviously larger than that of the Flat-on ctystal [1,25,26], as shown in the Eqs. (2) and (3).

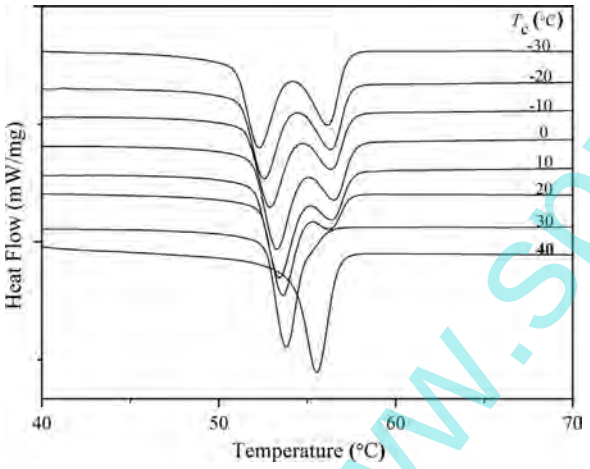

Fig. 2. DSC heating curves of PCL-2.5 × 10^4 isothermally crystallized at T_cs (−30 °C to 40 °C).

Edge-on:

$$\sigma_e(\text{Edge on}) = G_{\text{upper}} + G_{\text{lower}} + G_{\text{lateral}} \quad (1)$$

In this equation, G_{upper} is upper surface free energy; G_{lower} is lower surface free energy; G_{lateral} is lateral surface free energy.

Due to $G_{\text{upper}} = G_{\text{lower}} >> G_{\text{lateral}}$

Consequently

$$\sigma_e(\textit{Edge on}) = 2G_{\text{upper}} \quad (2)$$

The same to Flat-on:

$$\sigma_e(\text{Flat on}) = G_{\text{upper}} \quad (3)$$

This is because the Flat-on crystal is perpendicular to the substrate surface, it only has one surface; but the Edge-on crystal is parallel to the substrate surface, so it has two surfaces.

The effect of surface free energy on T_m is obvious, according to equation of Gibbs–Thomson [26]:

$$T_m = T_m^0(\infty)[1 - 2\sigma_e/(l\Delta h_f)] \quad (4)$$

The larger the lamellar thickness, the higher the T_m was, but the surface free energy was lower. Therefore, with the decrease of surface energy, the T_m progressively increased.

In summary, during the process of crystalline phase transition in the quasi two-dimensional space, there were multiple paths for the molecular chains to discharge into the crystal lattices, thus formed a variety of crystals, and these crystals had different physical properties. First of all, the molecular chains tended to grow relatively stable lamellae, i.e. Flat-on crystal. But at lower temperature, when the molecular chains discharged into the crystal lattice, the direction of chains could change easily because of the decline of molecular thermal movement. And it led to grow two kinds of lamellae with different surface free energy, i.e. these lamellae had different T_m. Obviously this is the internal reason which led to the multiple melting of PCL ultrathin films crystal. It supported that: when the lamellae was prepared at low temperature, it were easy for the molecular chains to grow imperfect crystal (the surface free energy is high) due to the grater driving force of crystallization and the weaker movement ability of segment. Ultimately, the imperfect crystal was melted first during the heating process, as the temperature increased, other perfect crystal was melted. Above all, this part of the experiment could support the multiple melting transformation mechanism from another perspective.

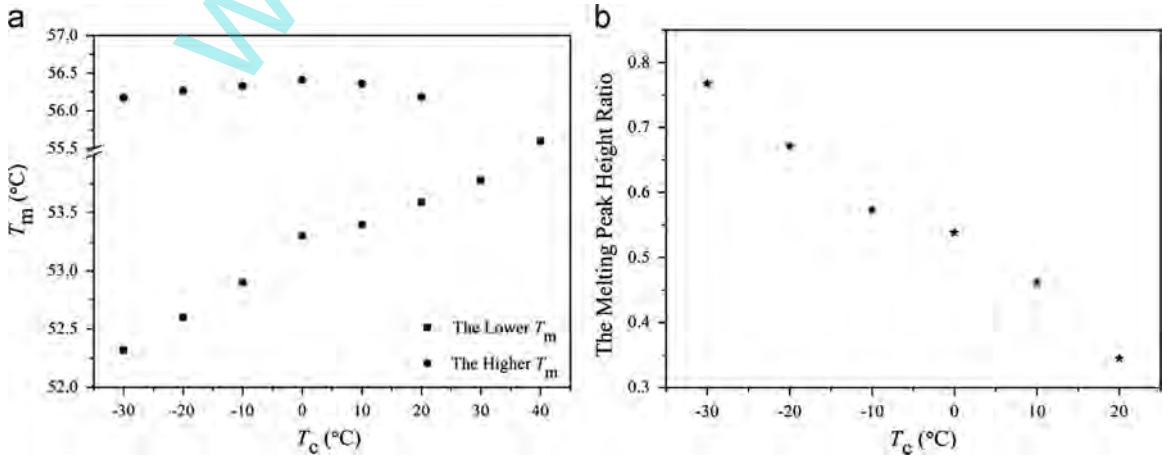

Fig. 3. (a) The relationship between T_c and (a) T_m; (b) the melting peak height ratio of the lower to the higher of PCL-2.5 × 10^4.

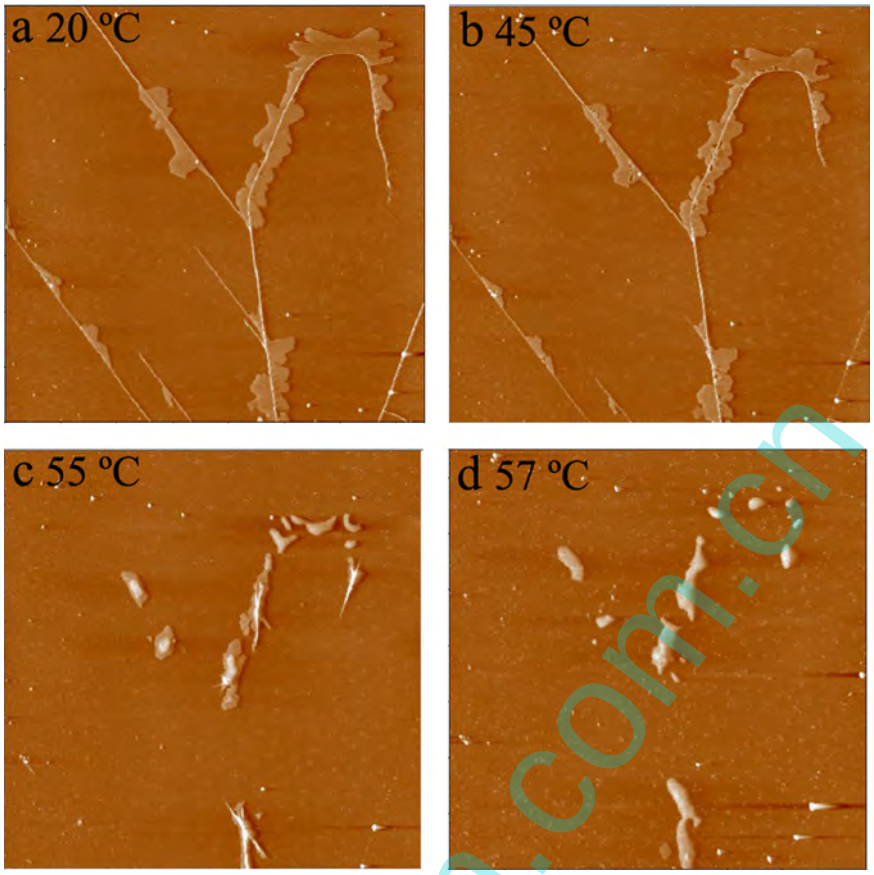

Fig. 4. AFM height images of PCL isothermally crystallized at 20 °C during heating process (15 μm × 15 μm).

3.3. *The effect of T_c on PCL ultrathin films morphologies*

As we all know, the crystallization temperature can affect the orientation of the lamellae formed in ultrathin film on solid substrates [27]. Fig. 5 is the AFM height images of PCL ultrathin films isothermally crystallized from −20 °C to 30 °C, the scanning range was 15 μm × 15 μm. As can be seen in Fig. 5, when T_c was low, a large number of Edge-on crystal existed, and along with the increase of T_c, the number of Flat-on crystal increased while the number of Edge-on crystal reduced, accompanying with the transformation of crystal surface from rough to smooth.

As we all know, the crystallization process requires a certain degree of crystallization driving force (undercooling, ΔT) to overcome the potential barrier of nucleation [28,29], and $\Delta T = T_m - T_c$, so T_c is an important factor to affect the crystal morphologies. With the increase of T_c, crystal growth was affected by two aspects, namely, the nucleation rate gradually decreased and the diffusion rate increased. During the nucleation process, Edge-on nucleus and Flat-on nucleus were both induced to grow, and Edge-on nucleus' dependence on supercooling was more obvious, i.e. with the increase of T_c, Edge-on crystal nucleus number decreased gradually, the number of the Edge-on crystal also reduced progressively. During the process of crystal growth, when the temperature rose, the molecular diffusion speed was accelerated, and spread to the Flat-on crystal nucleus whose thermo-dynamic properties were more stable. As shown in the images, with the increase of T_c, the number of Flat-on crystal had a gradual increase.

On the other hand, with the increase of T_c, the facet of Flat-on crystals turned from rough to smooth. The reason of this was the growth process of crystal had two main controlling factors: nucleation control (NL) and diffusion control (DL) [30]. The two processes might both be slow, with the variances of T_c, these processes competed with each other and finally the dominant process decided the growth process of crystal. When the crystallization temperature was very low, the fiber-like crystals (Edge-on) were formed, as shown in Fig. 5(a). When the T_c was 0 °C (Fig. 5 (c)), the number of fiber-like crystals decreased significantly. Especially, there was only one morphology lamellae (Flat-on) at 30 °C (Fig. 5(f)), so it had merely one T_m, which agreed with the result of DSC (see Section 3.1). This showed that: when T_c was lower, the crystal nucleation rate was fast, while the chain segment movement ability was so weak that the melt diffusion rate was too slow. Thus, this process controlled by the melt diffusion resulted in the asperities of lamellae's lateral surface. With the increase of T_c, the nucleation rate gradually decreased and the melt diffusion rate improved little by little. When the T_c was higher, the growth process of lamellae was completely controlled by nucleation, and the lamellae's periphery became smooth. The similar result has been reported by Zhang et al. [31].

Through the above analysis, T_c was a crucial factor in the PCL ultrathin films morphologies. Specifically, Flat-on and Edge-on lamellae grow simultaneously at lower T_c while only Flat-on at higher T_c. With the decrease of T_c, the segment movement ability was weaker, when the molecular chains discharged into the crystal lattice, the direction of chains could change easily, resulting in the gradually increased number of Edge-on crystal. Because of the difference in T_m between Edge-on and Flat-on, the multiple melting transition phenomenon became more and more obvious with the rise of T_c.

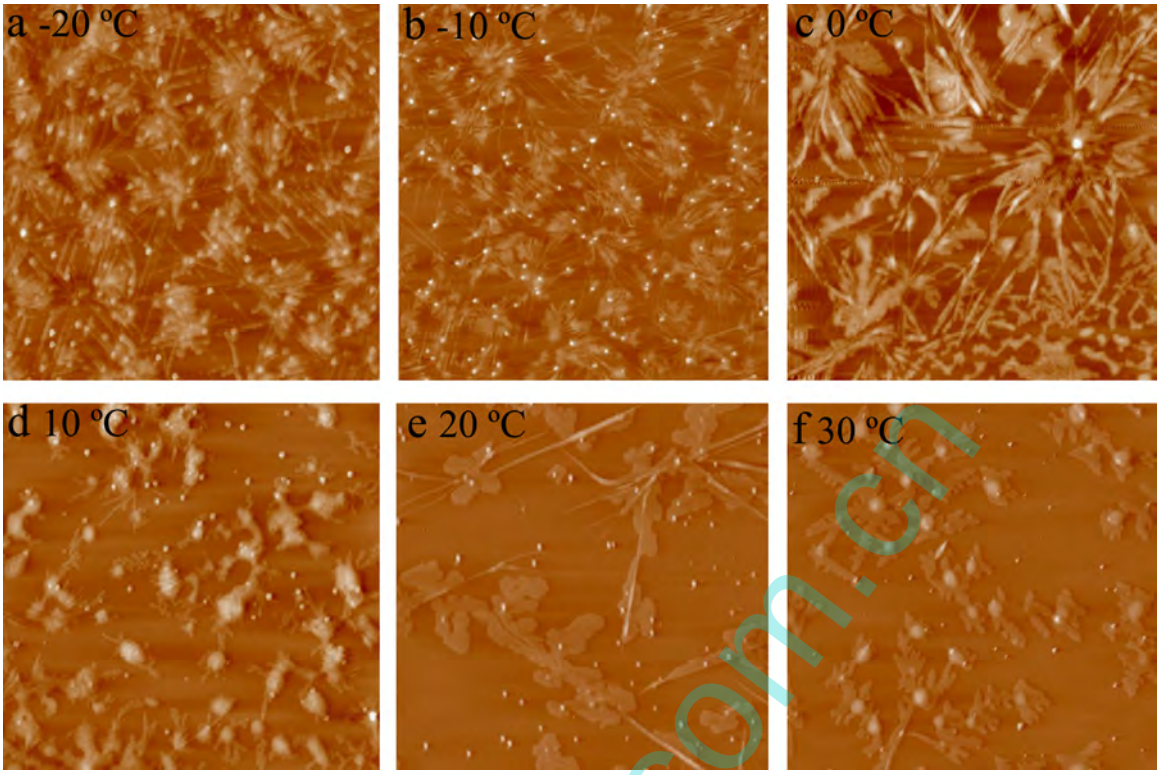

Fig. 5. AFM height images of PCL isothermally crystallized at different T_c (15 μm × 15 μm).

3.4. The effect of molecular weight (the same T_c) on PCL ultrathin film morphologies

PCL ultrathin films with four different molecular weights prepared at 0 °C were studied as an example, the surface morphology was observed by AFM (scanning range is 15 μm × 15 μm), as shown in Fig. 6. As can be seen in Fig. 6(a), (b) and (c), there were two kinds of structures (some flake-like crystal (Flat-on) and some straight fiber-like crystal (Edge-on)) existed in the morphologies. In addition, the shape of Flat-on was irregular and the color was similar. Moreover, most of Flat-on lamellae and Edge-on lamellae connected and influenced with each other, reflecting that the direction of molecular chains changed when the lamellae formed.

With the increase of *MW*, the number of Edge-on gradually increased. This can be attributed to the orientation mechanism and segment movement ability in the ultrathin films. The orientation direction of lamellae was related to the interaction force between the interface of ultrathin films and the molecular chains. When the force was strong, it was favorable for the growth of Flat-on crystal. It can be explained as follows: the molecular chains movement ability was weak on the interface, only leading to the formation of Flat-on lamellae, on which inhibited effect was weak, rather than that of Edge-on crystal nucleus. The most induced effect of interface came from end-group. When the molecular weight was smaller, the proportion of end-group was larger, and the interfacial effect was more obvious. Therefore, Flat-on nucleus could form alone and induced smooth lamellae. As the molecular weight increased, the proportion of end-group declined gradually, the interfacial effect also decreased, it could form both Edge-on nucleus and Flat-on nucleus, and with the increase of molecular weight, Edge-on crystal nucleus increased gradually, leading to the increase of Edge-on crystal. When the molecular weight increased to 51,000, most of the crystal was Edge-on, showing that most molecular chains of PCL lamellae were growing parallel to the mica substrate surface, as shown in Fig. 6(d). At the same time, due to the high molecular weight, the chains were so strongly intertwined and entangled that the segment mobility decreased, molecular chains could not discharge into the lattice regularly. During the phase transition process, the direction of molecular chains changed easily. Thus, both sides of the Edge-on could induce to grow Flat-on lamellae, and when the Flat-on grew to a certain extent, the direction of molecular chains changed on its boundary again, resulting in growing Edge-on lamellae.

In addition, as shown in the Fig. 6(d), many adjacent bunch of Edge-on lamellae could grow parallel to each other. This was because the lamellae had shearing functions to the adjacent melt, namely the melt surrounding the lamellae was pre-orientation state, so both sides of the lamellar were more likely to induce a new nucleation and crystal growth. Generally speaking, when isothermally crystallized at low temperature, the crystals were irregular. The possible reason was that the nucleation speed was fast at low temperature, resulting in forming numerous nuclei, including the Edge-on nuclei and the Flat-on nuclei, and molecular chains motion ability was low, it was unable to form perfect lamellae. To sum up, with the increase of molecular weight, the number of Edge-on crystal was also on the rise, more unstable crystal existed in the system, the multiple melting transition phenomenon was more easily to take place.

3.5. The relationship between the thickness and T_c

Lamellar thickness was one of the most direct parameters that reflect the polymer crystal properties, especially thermal stability. Moreover, different thickness and thickness distribution of the lamellae were formed at different T_c. In this part, the multiple melting transformation was illustrated by the thickness and thickness distribution of Flat-on crystal in other way. In general, when the distribution of thickness was wider, the melting range was wider and the multiple melting transition was more obvious.

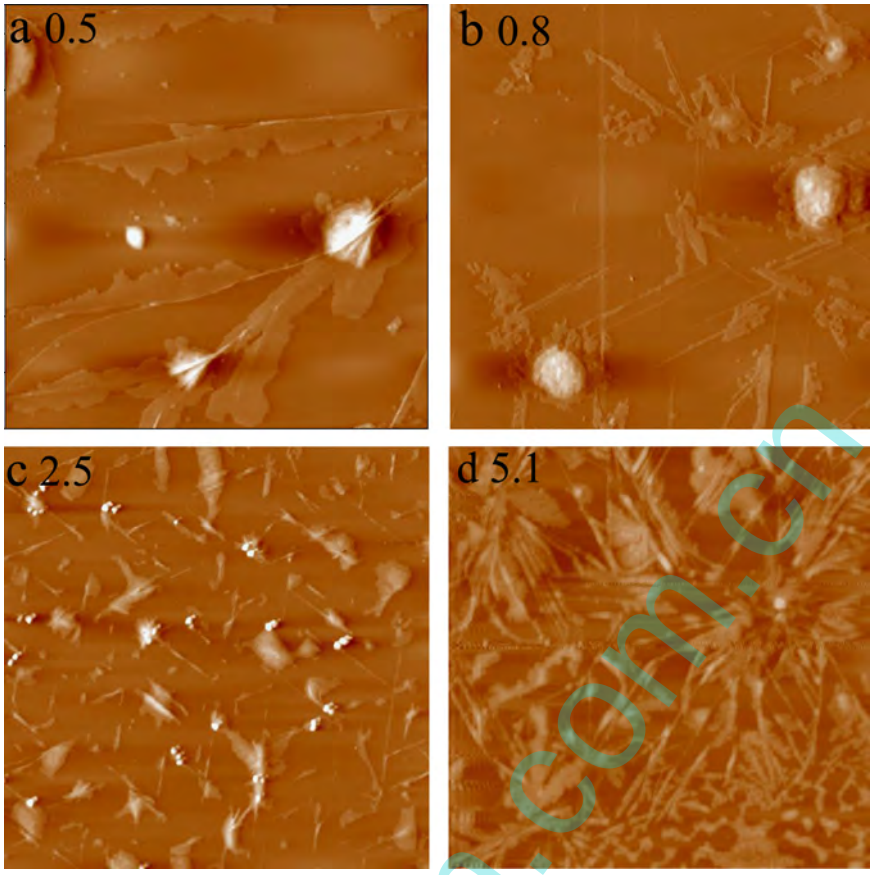

Fig. 6. AFM height images of PCL with different molecular weight (10^4) isothermally crystallized at 0 °C (15 μm × 15 μm).

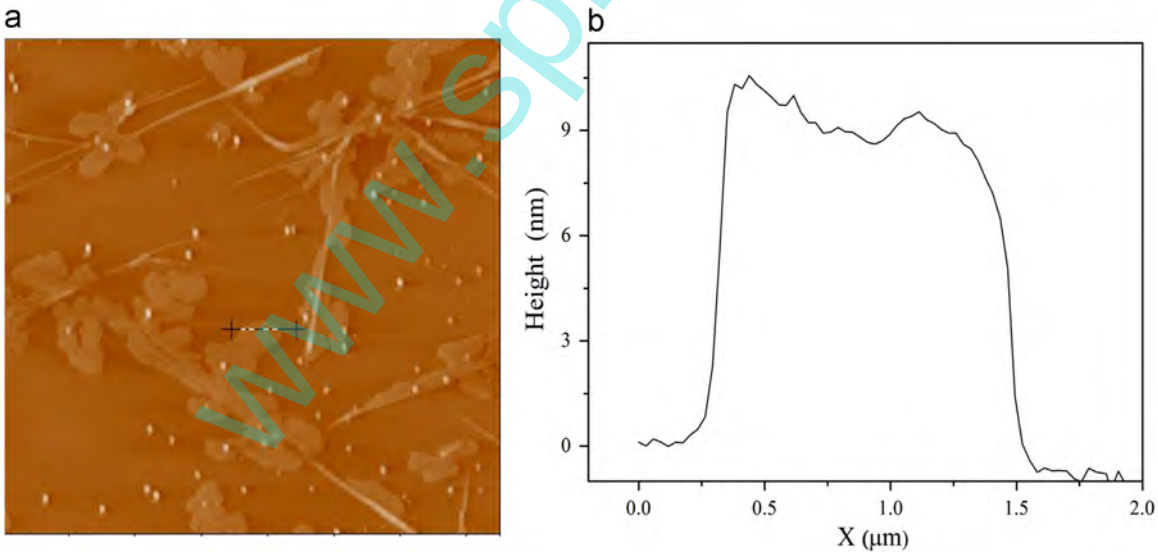

Fig. 7. (a) AFM height image of PCL-2.5 × 10^4 isothermally crystallized at 20 °C (15 μm × 15 μm); (b) The relationship between height and AFM scanning hatched line of Fig. 7 (a).

Fig. 7 was the AFM height images of PCL-2.5 × 10^4 ultrathin films isothermally crystallized at 20 °C and the lamellar thickness measured by AFM software. Fig. 7(b) was the relationship between the absolute height and scanning range of the position which was marked by vernier in Fig. 7(a). The lamellar thickness was 9.29 nm which was calculated based on the height average of Flat-on lamellae according to Fig. 7(b).

The distribution pattern showed in Fig. 8(a) was the nonlinear fitting of height distribution histogram which was gotten by the statistic of all lamellar thickness in Fig. 7(b). The lamellar thickness distribution could be reflected by K which was the ratio of peak height and half peak width in Fig. 8(a), and $K=18.75$. Fig. 8 (b) was obtained by the same data processing of samples prepared at other T_c.

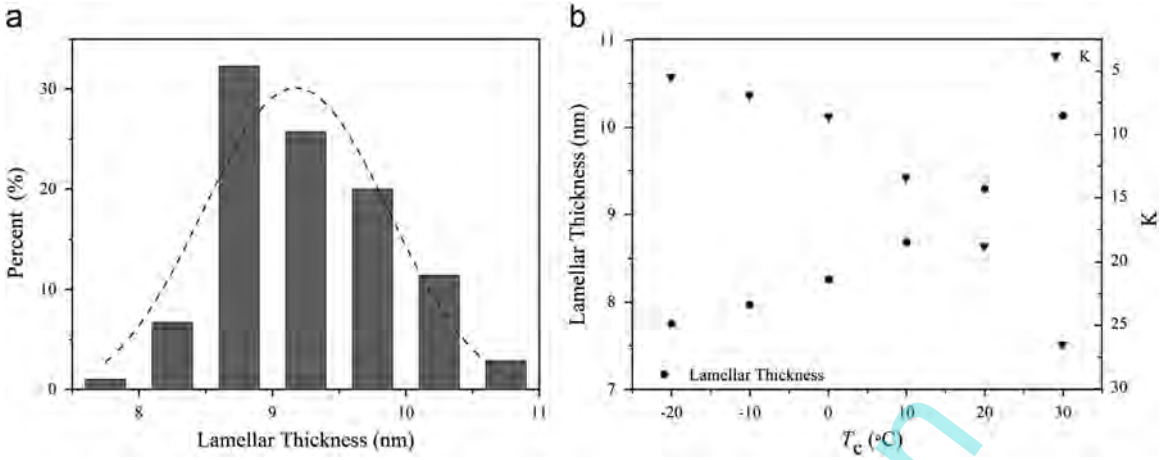

Fig. 8. (a) The lamellae thickness distribution; (b) The lamellar thickness and K as a function of T_c (K is the ratio of peak height and half peak width in Fig. 8(a)).

As shown in Fig. 8(b), the lamellar thickness and K all increased with T_c. On the one hand, it reflected the relationship between T_c and lamellar thickness. And the lamellar thickness increased from 7.75 nm to 10.13 nm. On the other hand, it demonstrated the regularity of lamellar thickness according to K value. The lamellar thickness had a decisive influence on its T_m. When the crystal was prepared at low temperature, the undercooling was high, so it was easy to form a variety of crystal nucleus with different sizes which would lead to forming different structures and thicknesses of lamellae. What's more, the chains movement ability was so weaker at lower T_c that a variety of lamellae with different structures and regularity formed when the molecular chains discharge into the crystalline region. All of those may lead to the multiple melting transformation.

4. Conclusions

The melting process of PCLs prepared at lower T_c was in-situ researched by AFM. And the dependence of the multiple melting of PCL on T_c and MW was systematically investigated by using DSC and AFM. In ultrathin films, there were two different morphologies, Flat-on lamellae and Edge-on lamellae, when PCLs were prepared at T_c lower than 30 °C. And during the melting process, the Edge-on lamellae melt first, and then the Flat-on lamellae disappear gradually. It showed that the multiple melting behavior in PCL ultrathin films took place due to the two different structures, Flat-on lamellae and Edge-on lamellae. With the decrease of T_c, or with the increase of MW, the amount of Edge-on lamellae increased, and the multiple melting behavior became more obvious. Furthermore, the multiple melting phenomenon was illustrated according to the regularity of lamellae thickness from another point view. With the rise of T_c, the regularity of lamellar thickness increased. In conclusion, with the decrease of T_c, or with the increase of MW, nucleation process should be fast, and molecular movement should be limited to diffuse slowly. In this condition, there were many different paths of phase transition to form a variety of lamellae with different morphologies and different thickness, which were significant influencing factors on polymer multiple melting transformation.

Acknowledgments

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