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RESEARCH ARTICLE

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Studies on confined crystallization behavior of polycaprolactone thin films

Abstract The confined crystallization behavior of polycaprolactone (PCL) in thin and ultrathin films was studied by AFM (atomic force microscopy). It was found that the crystalline morphology of PCL depended on the film's thickness. When the thickness is $d > 2\,R$g (radius of gyration), the polymer can crystallize into spherulites; when $R\text{g} < d < 2\,R$g, a dense-branch morphology and dendrites could be found; when $d < R$g, an "islands" structure could be obtained. Moreover, the effects of the crystallization temperature and the substrate and the molecular weight on the crystalline morphology were discussed. It was shown that the crystallization of PCL in thin films is a diffusion-controlled process, and it can be explained by diffusion-limited aggregation.

Keywords PCL ultrathin films, crystalline morphology, AFM, radius of gyration, diffusion-limited aggregation

1 Introduction

Recently, more and more efforts have been made on the study of polymer crystallization in a confined environment, especially in ultra-thin films ($d < 100$ nm). This is due to the fact that crystalline morphology and crystal growth of ultrathin polymer films are different from those of the bulk. Moreover, studies of polymer crystallization in thin films within lamellae scale can help in the understanding of the behavior of polymer crystallization in general. Some efforts have been made on this issue. For example, Frank and co-workers [1] examined the crystallization kinetics of poly (di-*n*-hexylsilane) in ultrathin films with AFM (atomic force microscopy). They found that there was a critical film thickness of 15 nm, necessary for crystallization, which was close to the typical lamellar thickness of crystalline polymer. Systematic work has been done by Reiter and Sommer [2] on diffusion-controlled crystallization behavior of poly(ethylene oxide). Sakai and co-workers [3] reported on the crystal growth process of poly (ethylene terephthalate) in thin films. The work by Miyamoto et al. [4] suggested that when isotactic polystyrene crystallized in ultrathin films, the crystal growth rate as well as the lamellar thickness depended on the crystallization temperature: $G(d)/G(\infty) = 1 - a/d$, where $G(d)$ is the growth rate of polymer crystal in thin film of thickness d, $G(\infty)$ is the bulk growth rate, a is a constant of about 6 nm independent on the crystallization temperature, molecular weight and substrate material. Magonov and Godovsky [5] studied the crystallization and melting behavior of low density polyethylene in ultrathin films and found that the quasi-2D spherulites were composed of sheaf-like aggregated lamellae with an edge-on mode respect to the substrate. Two types of branched patterns, i.e. dendrite and seaweed patterns were visualized by He et al. [6] with AFM and TEM (electron microscopy) for linear polyethylene crystallized in thin films. Kressler and Wang [7] studied the structure formation of poly (ε-caprolactone) thin films, during spin-casting and subsequent thermal annealing by scanning electron microscopy and atomic force microscopy. It was shown that film formation was ruled by dewetting and crystallization during the spin-casting, annealing and quenching processes. During the thermal annealing procedures, the rate of crystallization dominated the structure formation of polycaprolactone (PCL) thin films when the film thickness was large enough. However, the opposite was true for sufficiently small values of film thickness. Between these limits, the two processes could not be separated from each other. Xie and co-workers [8] investigated the crystalline morphology of PCL in ultrathin films and found the presence of dendrites.

These studies indicated that the mechanism of crystal growth of polymer varied in ultrathin films. The crystallization of polymers is governed by a surface nucleation process

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in bulk. However, the crystal growth in ultra-thin films is a diffusion-controlled growth process.

Polycaprolactone is a semi-crystalline and biodegradable polymer. It has been widely applied in the field of biomedicine with good results. However, the application is limited because the polymer is easy to crystallize at low temperatures. Therefore, it is very important to study its crystallization behavior.

In this paper, samples are prepared by spin-coating and isothermal crystallization. Then, the polymer crystallization behavior in thin films with different thickness is investigated. The effect of crystallization temperature, molecular weight and substrate on polymer morphology has been studied, and the main factors which affect polymer crystallization in thin films are also discussed.

2 Experiments

2.1 Sample preparation

Poly(ε-caprolactone) (PCL, $M_w = 22\,000$, $M_n = 11\,300$, was supplied by Polysciences; PCLs $M_w = 146\,000$ and $M_w = 65\,000$ were synthesized in our lab) films are prepared by spin-casting PCL-toluene solutions (the concentrations are from 4 to 0.05 wt%) on freshly cleaved mica substrates. The thickness of films obtained is from 120 to 4nm as determined by AFM. The radius of gyration of the Polyscience PCL is about 6 nm, and its melting temperature and glass transition temperature are 70 and −70°C respectively. Isothermal crystallization of these film samples are carried out at preset temperatures for a variable time on a hot stage and then cooled to room temperature for observation.

2.2 Characterization

Polymer morphology of PCL thin films is obtained by AFM by using the apparatus SPA-300HV with a SPI 3800N controller (Seiko Instruments Industry Co. Ltd, Japan).

3 Results and discussion

3.1 Effect of film thickness on polymer morphology

It is known that film thickness plays an important role in crystallization of ultra-thin polymer films. Figure 1 shows the morphology of PCL films with different thickness.

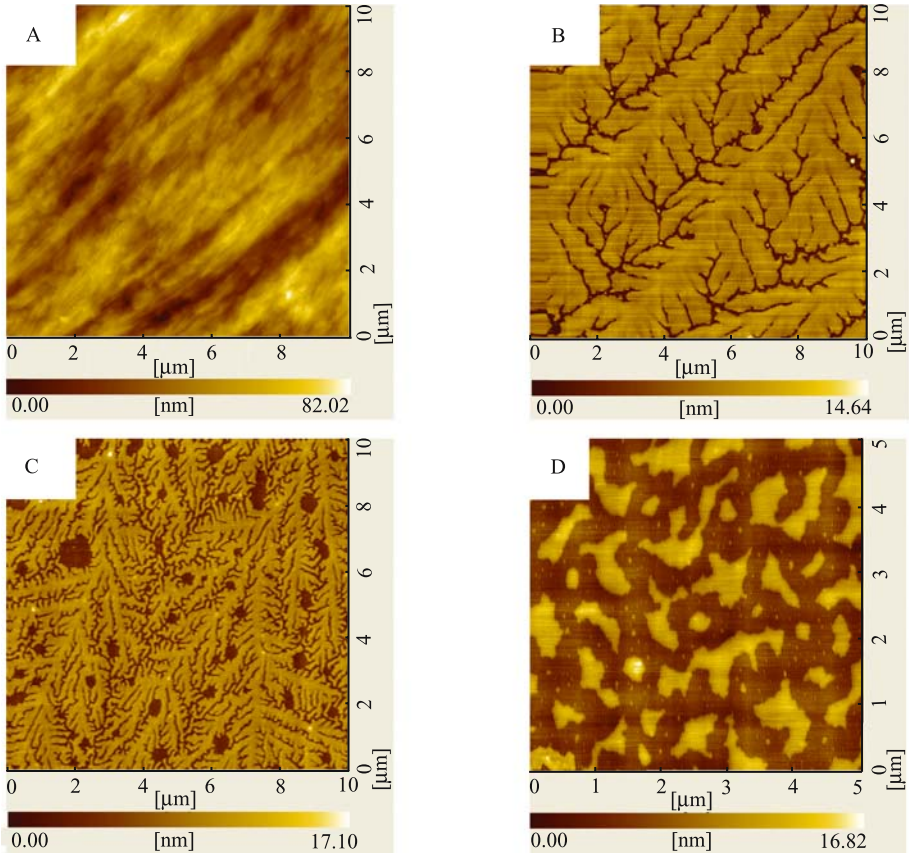

Fig. 1 AFM images of PCL ($M_w = 22{,}000$) with different film thickness (from (A) to (D), $d = 20, 12, 8, 5$ nm respectively) crystallized at 42°C for 30 min

When $d = 20$ nm, spherulites can be observed (Fig. 1(A)), a dense-branching morphology (DBM) appears when the film thickness decreases to 12 nm (Fig. 1(B)). A dendritic structure is found in the thin film with thickness of about 8 nm (Fig. 1(C)). For a 5 nm thin film, PCL cannot crystallize and dewetting process will take place (Fig. 1(D)). Generally, when $d > 20\ R$g, normal spherulites can be observed [9]. When $d > 2\ R$g, the spherulites become more and more diffusive. When $R\text{g} < d < 2\ R$g, a dendritic structure appears. It is the typical result of a diffusion-limited aggregation (DLA) growth [10] when $d < R$g, "islands" structure appears. Therefore, the morphology of PCL in thin films varies with changes in the film's thickness.

3.2 Effect of crystallization temperature on polymer morphology

It is well known that supercooling plays an important role in polymer crystallization in ultrathin films. Normally, supercooling can affect the growth rate and polymer morphology. Brener et al. [11] gave a morphology diagram of possible structures in two-dimensional growth and suggested that the seaweed pattern was favorable for the higher degree of supercooling, while the fractal one was favorable for the lower degree of supercooling. These results are consistent with the data we obtained (Fig. 2).

In the process of dendrite growth, there is a characteristic width. It has been reported that the characteristic width of branches depends on the crystallization temperature. The height and phase images of PCL dendrites at different crystallization temperature are shown in Fig. 3, and it can be found that the width of the branch varies with the crystallization temperature. Moreover, the characteristic width also depends on the molecular weight. The dendrites of PCL in ultrathin films of the same thickness but with different molecular weight of 146 000 and 22 000 can be found in Fig. 4 (the samples were crystallized at the same temperature). It is shown that the characteristic width of PCL with high molecular weight is less than that of PCL with low molecular weight. It indicates that molecular motion plays an important role in the diffusion-controlled process. The molecular motion becomes more active with the decreasing of molecular weight. Therefore, the diffusion process is strengthened, and the characteristic width is increased.

3.3 Effect of molecular weight on polymer morphology

The AFM images of PCL ultrathin films of the same thickness, with different molecular weight of 146 000 and 65 000 are shown in Fig. 5(A) and (B), respectively. It was found that the branches of dendrites become irregular with the increasing of molecular weight. This resulted from the decreasing of diffusion due to the increasing of molecular weight. However, the effect of the molecular weight on the polymer morphology is not so essential.

3.4 Effect of substrate on polymer morphology

Different crystalline morphologies of PCL with different substrates are shown in Fig. 6. Substrates play an important role in the crystallization of thin polymer films because of the presence of an interaction between the substrates and the polymer, and this effect was notable. A fractal structure is found for PCL on carbon substrate and spherulites are obtained for samples on silicon and glass. For graphite substrates, kneel crystals are observed for PCL ultrathin films. These results may be caused by the differences in the interaction between PCL and substrates.

From these results it is found that the polymer crystallization in ultrathin films is a diffusion-controlled process, which is far from equilibrium. The crystalline morphology of PCL depends on the film's thickness. When the thickness $d > 2\ R$g (radius of gyration), the polymer can crystallize into spherulites; when $R\text{g} < d < 2\ R$g, the dense branch morphology and

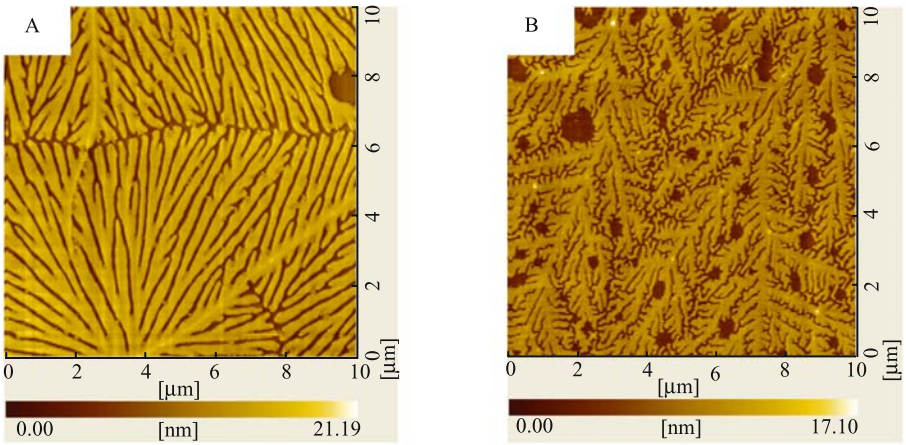

Fig. 2 AFM height and phase images of PCL crystallized at different temperature
(A) Room temperature; (B) 42°C ($M_w = 22\ 000$)

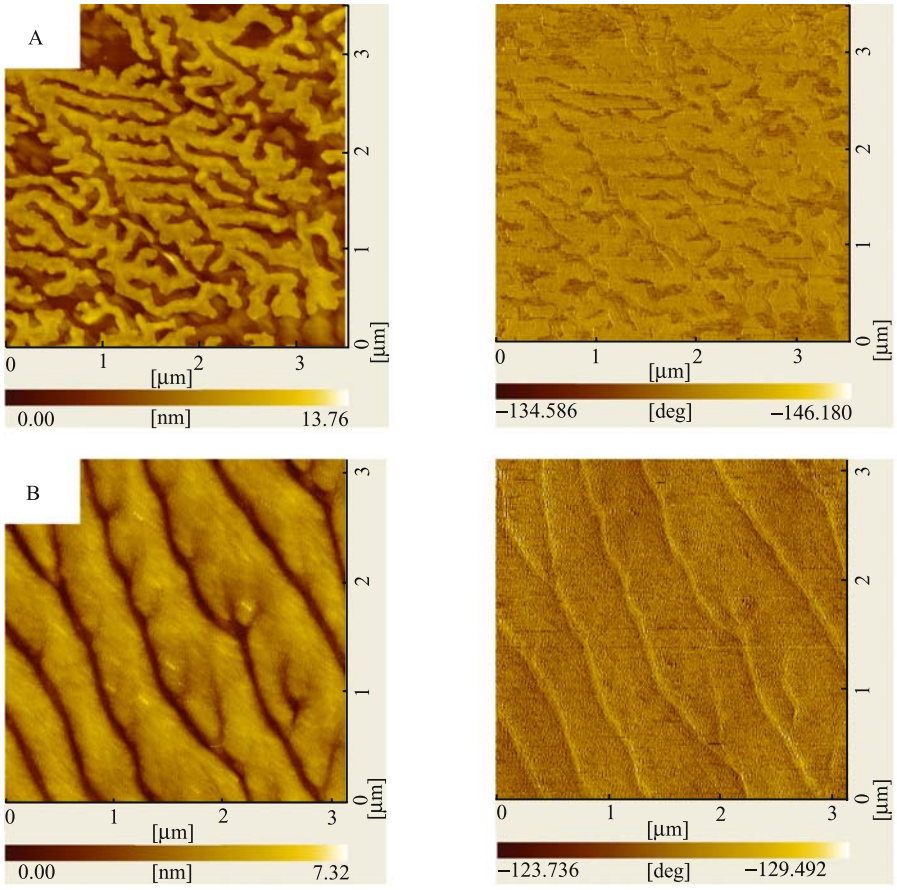

Fig. 3 AFM height and phase images of PCL crystallized at different temperature
(A) 40°C; (B) 50°C (M_w = 22 000)

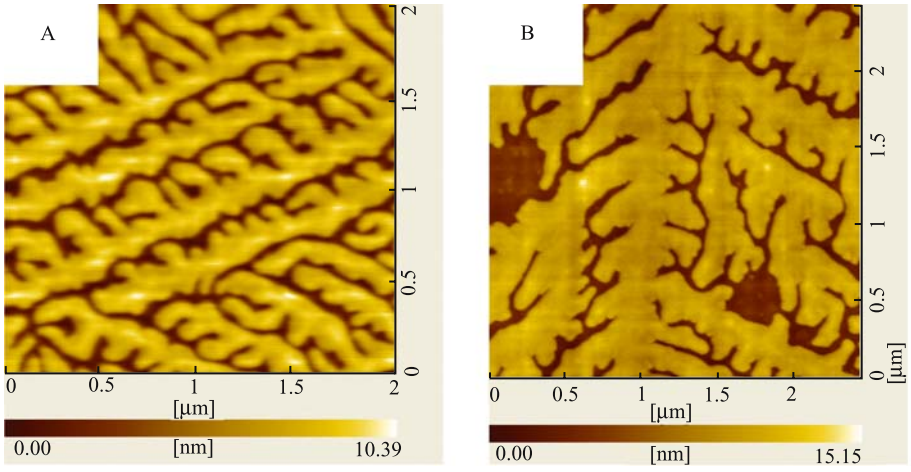

Fig. 4 Effect of molecular weight on polymer morphology
(A) M_w = 146 000; (B) M_w = 22 000 (crystallized at 42°C, d = 9 nm)

dendrites could be found; when $d < Rg$, the "islands" structure could be obtained. Moreover, the crystalline morphology of PCL depends on the crystallization temperature. When thickness $d < 2\,Rg$, the seaweed pattern is favorable for low temperature, while the dendrites is favorable for high temperature. The effect of the molecular weight on polymer morphology is not very essential, while the substrates play an important role in the crystallization of thin polymer films.

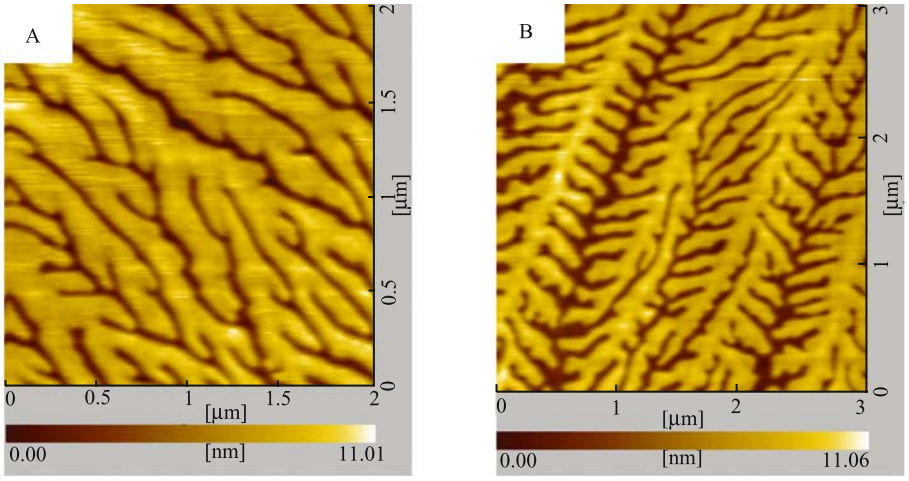

Fig. 5 Effect of molecular weight on polymer morphology
(A) $M_w = 146\ 000$; (B) $M_w = 65\ 000$ (crystallized at room temperature, $d = 8$ nm)

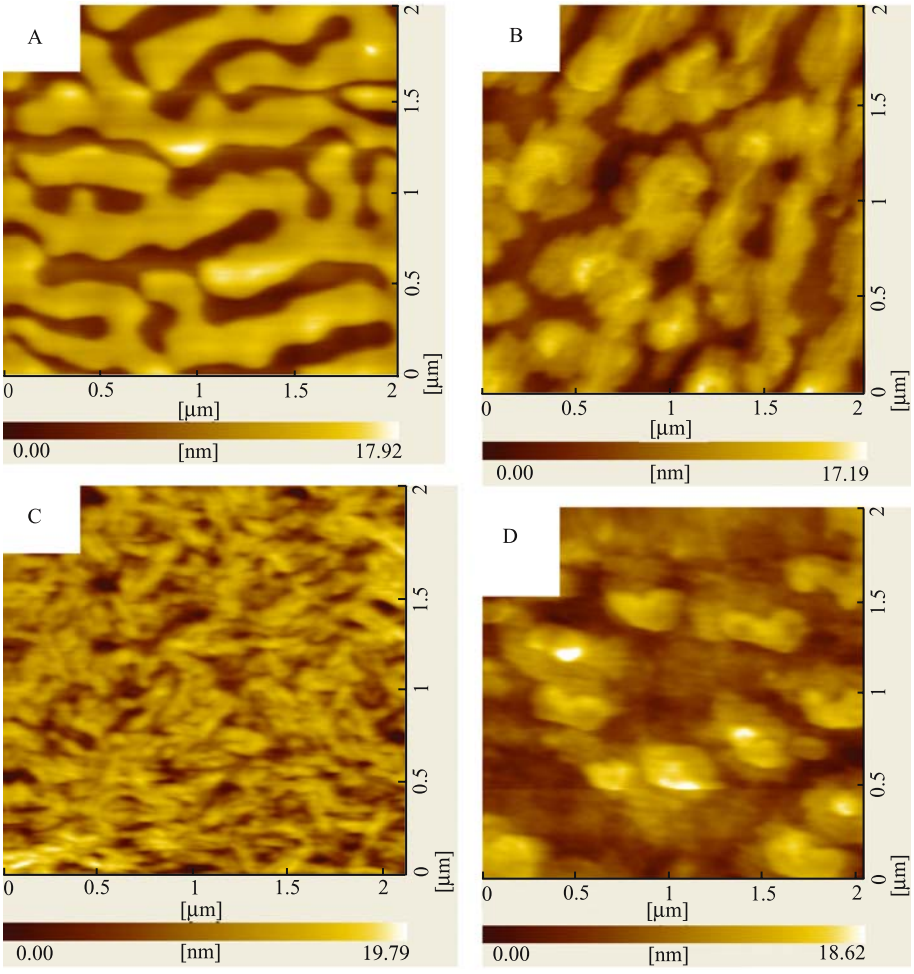

Fig. 6 Effect of substrate on polymer morphology
(A) Carbon film; (B) Silicon; (C) Graphite; (D) Glass (crystallized at room temperature, $d = 10$ nm)

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