Chinese Journal of Polymer Science Vol. 32, No. 9, (2014), 1253–1259

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2014

Thickness-dependent Orientation Structure in Poly(ethylene oxide) Multi-layer Crystals*

Yi-ning He[a], Xiao Liu[a], Qi Liao[b], Jian-jun Zhou[a**], Hong Huo[a] and Lin Li[a]

[a] *Beijing Key Laboratory of Energy Transition and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China*

[b] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Abstract Poly(ethylene oxide) multi-layer crystals were obtained and the re-crystallization behavior was studied to give insight into how melt thickness and temperature affect the lamellar orientation. For a special re-crystallization temperature, there exists a critical transition thickness range for the occurrence of edge-on lamellar orientation. Below the critical thickness, only flat-on lamellae were observed. While above the critical thickness, both flat-on and edge-on lamellae were found and the proportion of the edge-on lamellae increases with thickness. At low re-crystallization temperatures (below 30 °C), the critical transition thickness gradually increases from about 15 nm to 35 nm when the re-crystallization temperature was increased from 20 °C to 30 °C. However, when the re-crystallization temperature is above 30 °C, the critical transition thickness becomes constant. Our results demonstrated that the lamellar orientation could be specially modified by changing the melt thickness and re-crystallization temperature.

Keywords: PEO multi-layer crystal; Lamellar orientation; Re-crystallization temperature.

INTRODUCTION

Recently, polymer crystallization in thin (thickness less than 1000 nm) and ultrathin (thickness less than 100 nm) films has received considerable attention due to its different structures and properties with those in polymers[1–9]. In bulk, the anisotropic lamellae can isotropically distribute and the spherulite morphology is commonly observed in many crystalline materials[10]. However, for the thin and ultrathin films, the confined space prohibits the isotropic spherulitic growth of the lamellae crystals and can produce preferential lamellae orientation[11–13]. The preferential orientations of polymer crystals in thin and ultrathin films have been widely studied both experimentally and theoretically[14–18].

Film thickness and consequently the confinement effect is a very important factor that affects the preference of the lamellar orientation. Mellbring *et al.*[19] studied the crystallization of high-density polyethylene (HDPE) films with thickness ranging from 0.03 μm to 2 μm. Below a film thickness of 0.1 μm, the morphology was composed of the aggregation of edge-on oriented lamellae instead of the spherulitic structure as observed in thicker films. A similar morphological shift from band spherulite to sheaflike aggregates was observed in HDPE films at a critical thickness of 400 nm on calcite surface by Bartczak *et al*[20]. Schönherr and co-workers[17]

* This work was financially supported by the Natural Science Foundation of China (Nos. 20634050, 20804053 and 21074015), the Science Foundation of Beijing (No. 212030), the National Basic Research Program of China (973 Project No. 2011CB605605) and the Fundamental Research Funds for the Central Universities.

** Corresponding author: Jian-jun Zhou (周建军), E-mail: pla_zjj@bnu.edu.cn

Invited paper for the special issue of "Polymer Crystallization"

Received April 17, 2014; Revised May 12, 2014; Accepted May 16, 2014

doi: 10.1007/s10118-014-1504-z

observed poly(ethylene oxide) (PEO) ultrathin films crystallized on oxidized silicon substrates and imaged a preferred flat-on (*c*-axis perpendicular to the substrate) orientation of lamellar crystals in the films thinner than 300 nm. By contrast, the orientation of lamellar crystals is preferentially edge-on (*c*-axis parallel to the substrate) in the films thicker than 1 μm. Jeon and Krishnamoorti[21] carried out a systematic study on the film thickness dependence of lamellar orientation. The thin and ultrathin linear low density polyethylene films (20–800 nm) exhibited four distinct supermolecular morphologies: banded spherulite, sheaflike, and two intermediate morphologies. They believed that the mixed morphology was attributed to a combination of edge-on and flat-on lamellae. According to all the above experimental information, it is generally believed that the transition of lamellar orientation from edge-on to flat-on occurred with the decrease of film thickness.

In addition, the lamellar orientation could also be controlled by crystallization temperature. Many studies have shown that with the increase of crystallization temperature the lamellar orientation gradually shifts from the favor of edge-on orientation to flat-on orientation. A three-layer glass transition temperature model was proposed to explain the predominance of edge-on lamellae observed at the surface of ultrathin films at low temperatures and the increase in the concentration of the flat-on lamellae as the temperature increases[15]. Furthermore, the interaction between polymer and substrate also effects the preferential orientation of lamellar polymer crystals. Ma and co-workers[22] performed dynamic Monte Carlo simulations to study the substrate effects. They found that for sticky walls, flat-on lamellae were dominantly formed at high temperature or at small thickness, on the contrary, edge-on lamellae was preferred on the slippery walls. Experimental observation has been confirmed by Yang *et al.*[14]. They proposed that the transition of lamellar orientation was determined by a critical surface free energy of the substrate which is equal to the surface tension of the polymer melt.

Researchers found that crystallization morphology and lamellar structure change with the film thickness. Generally they fabricated a series of thin films with different thickness by spin-coating method. From one thin film sample, they could only observe the morphology of polymer film with a specific film thickness rather than continuously changed film thickness. As a result, the exact transition thickness from flat-on to edge-on orientation was hard to be obtained because of the lack of enough quantitative description. A convenient and effective way to solve this problem is to use multi-layer crystals as template to study the thickness dependence of the lamellar orientation.

In this study, PEO multi-layer crystals with various thicknesses were obtained by self-seeding method and used to re-crystallize on polyvinylpyrrolidone (PVPY) substrates. We focus on the dependence of the lamellar orientation on the film thickness, and try to find the exact critical thickness range when flat-on lamellae turn to edge-on lamellae. For this purpose, lamellar orientation of re-crystallized PEO on PVPY substrate was characterized in detail by atomic force microscopy (AFM).

Materials and Sample Preparation

Poly(ethylene oxide) (PEO, $M_w = 1.0 \times 10^5$ g·mol^{-1}, $M_w/M_n = 1.4$) and polyvinylpyrrolidone (PVPY, $M_w = 5.8 \times 10^4$ g·mol^{-1}) were purchased from Sigma-Aldrich Chemicals and used without further purification. The melting point of PEO is 67 °C. Toluene was used as solvent after distillation. Silicon wafers were cleaned in a mixture of H_2SO_4 and H_2O_2 (70/30 vol%) for 30 min at 120 °C and then rinsed with abundant high-purity deionized water.

PEO multi-layer crystals were prepared by the self-seeding method from a 0.01 wt% toluene solution. The solution was first heated to 60 °C and maintained at this temperature for 30 min, then quenched to 0 °C and held for 2 h. The PEO solution was slowly heated (0.1 K·min^{-1}) to 34 °C and hold at 34 °C (seeding temperature) for 15 min, then quenched to 20 °C (crystallization temperature) and held for 7 days. PEO single crystal with screw dislocation prepared by increased the temperature difference between seeding temperature and crystallization temperature[23].

The samples for AFM studies were prepared as follows: PVPY film was used as substrate which was obtained by spin-coating its 1 wt% alcohol solution onto cleaned silicon wafers. The suspension containing PEO crystals was deposited onto the substrate and then the solvent was evaporated in a vacuum oven at 22 °C for 24 h. By using Linkam TMS 94 hot stage, the samples were first heated to 75 °C and annealed for 2 min to melt

the PEO crystals completely, then quenched at a rate of 100 K·min^{-1} to a selected crystallization temperature (T_c), and isothermally re-crystallized for 4 h. The melt and re-crystallization were processed in a nitrogen atmosphere.

The morphology of re-crystallized PEO samples was examined by a multi-mode atomic force microscope (Veeco Multi-Mode Ⅴ) using a tapping mode. AFM images were measured at a scan rate of 0.8 Hz, using etched silicon probes (Veeco Instruments) with a cantilever length of 125 μm, a resonant frequency of ~300 kHz, and a spring constant of ~40 N·m^{-1}. All AFM images were taken under ambient conditions at a resolution of 512 × 512 pixels. Height and phase images were simultaneously collected.

RESULTS AND DISCUSSION

The multi-layer PEO single crystal could be obtained with self-seeding procedure. At a relatively high seeding temperature (T_s = 34 °C), multi-layer PEO crystals form through screw dislocation. The morphology of PEO single crystal is shown in Fig. 1(a). Here, the relatively large bottom layer is defined as the base layer and its boundary length is about 12 μm. The thickness of each layer is about 10 nm which was controlled by the crystallization temperature. The average layer number of screw dislocations in a PEO crystal is depended on the degree of super-cooling. Since the thickness of every layer is certain, more layers will result in thicker PEO crystals. The cross section result in Fig. 1(b) shows that the height of PEO crystal quantitatively increases with the layer number. The highest part of the PEO crystal is about 100 nm, which is about 10 layers of the PEO flat-on lamellae growing through the screw dislocation.

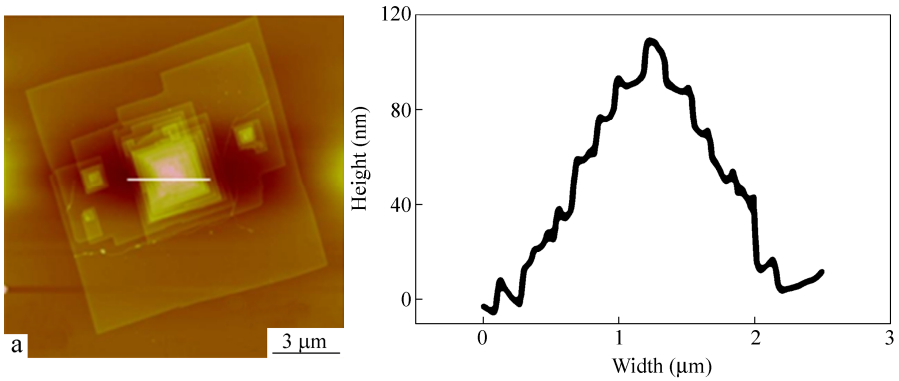


Fig. 1 The morphology of a PEO multi-layer crystal: (a) AFM height image and (b) the corresponding cross-section profile

PVPY film is a smooth, uniform and amorphous substrate. According to our previous work, the PVPY is chosen as the substrate to study the PEO multilayer crystals melting and re-crystallization morphology, since no apparent wetting or de-wetting behaviors were observed during melting within a short time. The melting process of the PEO crystals is *in situ* observed as shown in Fig. 2. The morphology of the multilayer PEO crystals is unchanged when the temperature is below 60 °C as shown in Fig. 2(a). When the temperature was increased to 63 °C, the crystals started to melt from both the edges of the base layer and the inside multilayer surrounding the screw dislocation points as shown in Fig. 2(b). Moreover, when the temperature is in the range of 63 °C to 68 °C, the melting and the re-crystallization processes can occur at the same time, as indicated by arrows in Figs. 2(b) and 2(c). Since the melting peak temperature of the PEO sample is 67 °C as measured by DSC, it is reasonable to observe that the partially melting and the thickening of the PEO multilayer crystal occurred at a temperature below the PEO melting point. When the temperature is increased above 70 °C, only the melting behavior can be observed. At 75 °C, PEO multilayer crystal melted completely and the melt kept the square shape. No obvious wetting or de-wetting behavior was observed, as shown in Fig. 2(d). Even though the whole thickness of PEO multilayer crystal melt, the relative height difference between each layer still exists. The

average thickness of the top layer surrounding the screw dislocation point is still much thicker than that of the base layer. The melted PEO cannot form a uniform thickness film in a short time on the PVPY substrate, which provides an ideal case to study the re-crystallization behaviors of the PEO melt with various thickness at the same experimental condition. The height difference of the PEO melts is ranging from 10 nm to 100 nm, which can be easily found and quantitatively determined by AFM in the same sample.

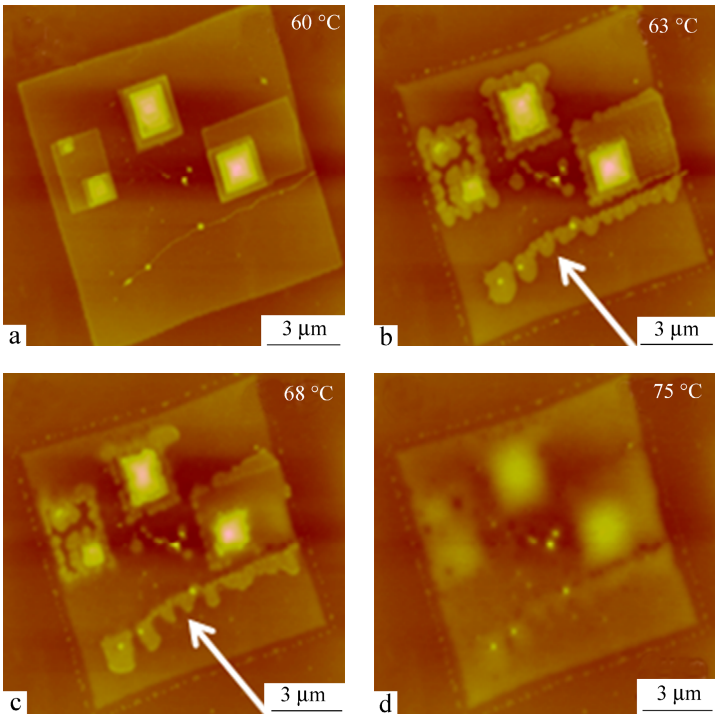


Fig. 2 AFM height images showing the morphologies of *in situ* melting behavior of a PEO multi-layer crystal on PVPY substrate at different temperatures: (a) 60 °C, (b) 63 °C, (c) 68 °C and (d) 75 °C (The height range is 180 nm for all images.)

Our previous works show that flat-on lamellae always form on the PVPY substrate during re-crystallization from single layer melt of PEO crystal if the crystallization temperature was above 15 °C[5]. In this work, in order to ensure the base layer re-crystallizing into flat-on lamellae, the re-crystallization temperature was chosen from 20 °C to 40 °C.

Figure 3(a) shows the morphology of PEO, which was re-crystallized at 30 °C on the PVPY substrate. There are three different height areas, as marked by (b), (c) and (d), which have different thickness on the PEO base layer. The height profiles are given by the corresponding cross-section analysis, and the detailed morphologies were shown in Figs. 3(b), 3(c) and 3(d) respectively. The average thickness of the base layer PEO lamellae is about 10 nm, and the dendritic growing lamella is the typical flat-on orientation. The highest area in Fig. 3(b) is about 30 nm as shown in the cross-section result. Lamellae with flat-on orientation form just as the flat-on lamellae from the base layer. It is suggested that the PEO lamellae should favor the flat-on over the edge-on orientations when the film thickness is lower than 30 nm at the selective crystallization temperature (T_c = 30 °C). The edge-on orientation lamellae can hardly be observed on the area of the thickness around 35 nm, as shown in Fig. 3(c). Some long and narrow lamellae appeared which are considered to be the edge-on orientation. Our observations suggested that the edge-on orientation can grow when the thickness of the PEO melt is in the range of 30 nm to 35 nm, which is designated as the critical transition thickness, though the proportion of the edge-on orientation is very low. The proportion of the edge-on orientation significantly increases at the 90 nm thick area on the same sample, as shown in Fig. 3(d). A detailed observation suggested that both flat-on and

edge-on lamellae coexist. Our primary results suggest that the proportion of edge-on orientation depends on the film thickness and the quantitative analysis will be presented in our forthcoming paper.

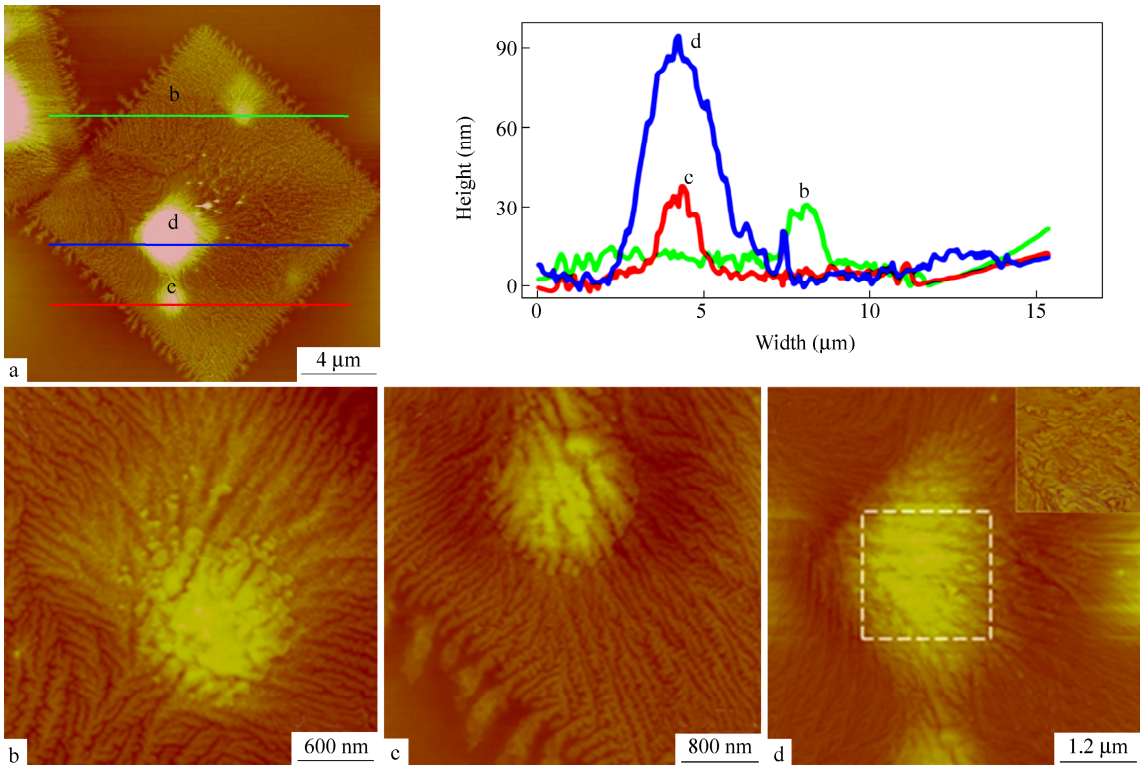


Fig. 3 AFM height images showing the orientation transition at 30 °C on PVPY substrate: (a) the re-crystallized PEO crystals with different thickness areas and the corresponding cross sections, (b) the thickness around 30 nm, (c) the thickness around 35 nm and (d) the thickness around 90 nm.

The thickness of the orientation transition from flat-on to edge-on is determined at different re-crystallization temperatures, and the morphologies are shown in Fig. 4. Only flat-on lamellae were found on the base layer at all temperatures. When the PEO melt was re-crystallized at 20 °C, flat-on lamellae dominated. However, edge-on lamellae can only be found at the area where the film thickness is about 15–20 nm as indicated by the arrow in Fig. 4(a). So 15–20 nm is considered to be the critical transition thickness from flat-on to edge-on orientation. At other temperatures, the minimum thicknesses for edge-on lamellae to grow are 30 nm, 40 nm, and 40 nm when the PEO melt was re-crystallized at 25 °C, 35 °C and 40 °C respectively. The morphologies are shown in Figs. 4(b)–4(d) and the edge-on lamellae are indicated by arrows.

The critical transition thickness and the corresponding re-crystallization temperature are summarized in Table 1. It can be clearly seen that the lamellar orientation transition depends on not only the re-crystallization temperature but also the thickness of the PEO melts. In the base layer of the PEO lamellae with a thickness around 10 nm, only the flat-on orientation can be developed in temperatures ranging from 20 °C to 40 °C. When the PEO melt is crystallized at 20 °C, the minimum thickness for the formation of edge-on orientation is around 20 nm (Fig. 4a). Since the thickness of each layer of the multi-layer PEO crystal is about 10 nm, it is suggested that the orientation transition can occur in the second layer of the PEO lamellae. Moreover, during crysatllization at a temperature above 30 °C, the minimum thickness that the edge-on lamellae can grow increases to 35–40 nm and tends to be constant (Figs. 3 and 4, Table 1), which means that the orientation transition may occur in the third to fourth layer of the PEO lamellae. Our results suggested that the temperature may only play a dominant role for very thin films in the transition of the lamellar orientation. If the film thickness is larger enough, the edge-on lamellar orientation prefers to grow.

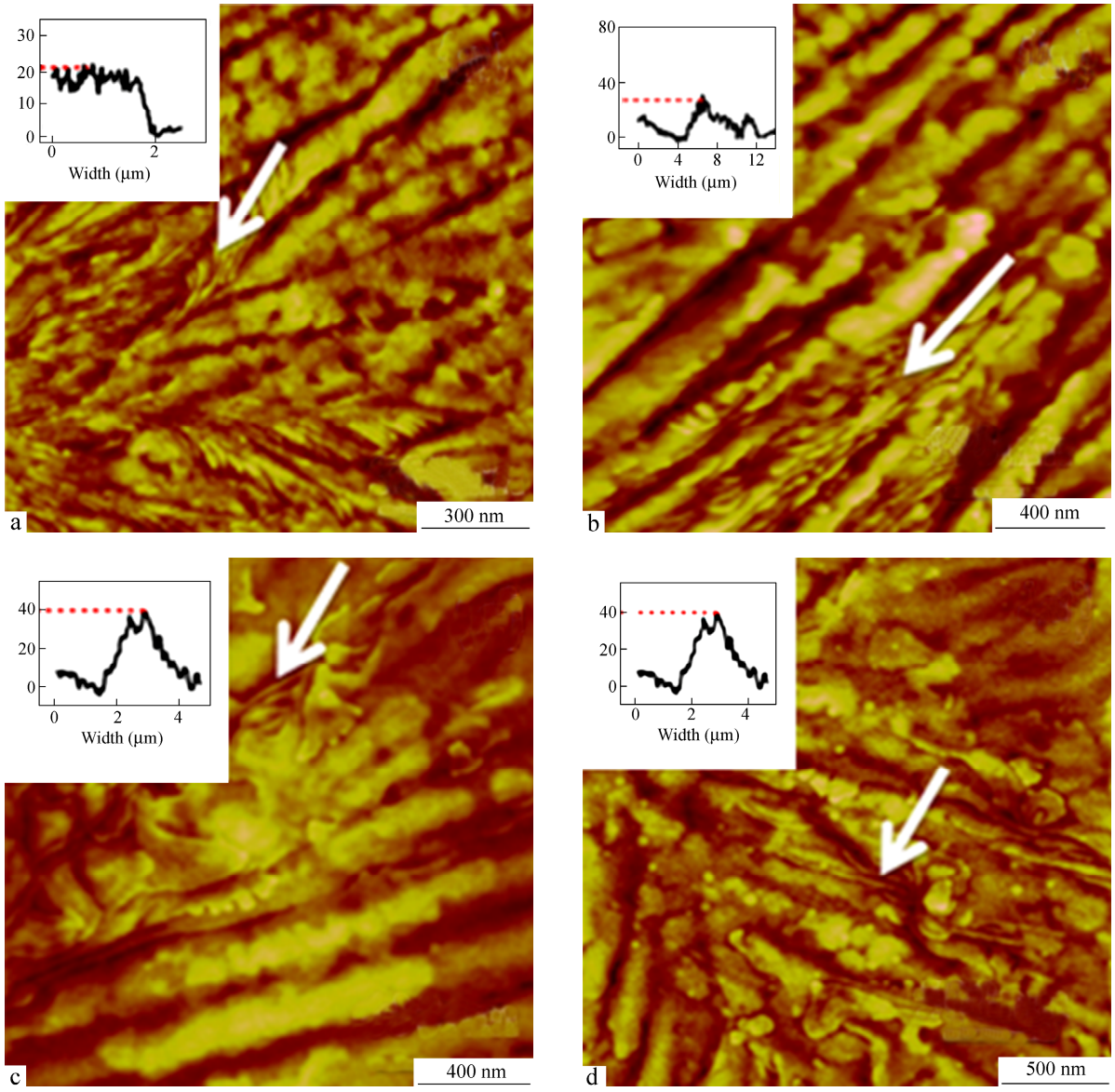


Fig. 4 AFM height images and corresponding cross sections on PVPY films at different temperatures: (a) 20 °C, (b) 25 °C, (c) 35 °C and (d) 40 °C (The arrows indicated the edge-on lamellae.)

Table 1. The critical thickness of the orientation transition at different temperatures

Recrystallization temperature (°C)	20	25	30	35	40
Lamellar transition thickness (nm)	15–20	25–30	35–40	35–40	35–40

CONCLUSIONS

Poly(ethylene oxide) multi-layer crystals were obtained and the re-crystallization behavior was studied with AFM. Our results demonstrated that the transition of lamellar orientation from flat-on to edge-on occurred in a narrow thickness range. For a special re-crystallization temperature, there exists a critical lamellar transition thickness range. Below the critical thickness, only flat-on lamellae were observed. While above the critical thickness, both flat-on and edge-on lamellae were found and the proportion of the edge-on lamellae increases with thickness. At low re-crystallization temperatures (below 30 °C), the critical transition thickness gradually

increases from about 15 nm to 35 nm when the re-crystallization temperature was increased from 20 °C to 30 °C. However, when the re-crystallization temperature is above 30 °C, the critical transition thickness becomes constant. Our results demonstrated that the lamellar orientation could be specially modified by changing the melt thickness and re-crystallization temperature.

REFERENCES

1 Liu, Y.X. and Chen, E.Q., Coord. Chem. Rev., 2010, 254: 1011
2 Wang, Y., Ge, S. and Rafailovich, M., Macromolecules, 2004, 37: 3319
3 Li, L., Chan, C. and Yeung, K.L., Macromolecules, 2001, 34: 316
4 Mareau, V.H., and Peudhomme, R.H., Macromolecules, 2005, 38: 398
5 Grozev, N., Botiz, I. and Reiter, G., Eur. Phys. J. E, 2008, 27: 63
6 Zhai, X.M., Wang, W., Zhang, G.L. and He, B.L., Macromolecules, 2006, 39: 324
7 Zhang, G.L., Jin, L.X., Ma, Z.P., Zhai, X.M., Yang, M., Zheng, P., Wang, W. and Wegner, G., J. Chem. Phys., 2008, 129: 224708
8 Liu, Y.X., Zhong, L.W., Su, S.Z. and Chen, E.Q., Macromolecules, 2011, 44: 8819
9 Zhang, G.L., Jin, L.X., Zheng, P. and Wang, W., Chinese J. Polym. Sci., 2013, 31(4): 798
10 Kawashima, K., Kawano, R., Miyagi, T., Umemoto, S. and Okui, N., J. Macromol. Sci., Part B: Phys., 2003, B42: 889
11 Wang, Y., Sokolov, J., Gersappe, D., Araki, T., Zhou, Y. Kilcoyne, Ade, H., Marom, G. and Lustiger, A., Phys. Rev. Lett., 2006, 96: 028303
12 Ponting, M., Lin, Y.J., Keum, J.K., Hiltner, A. and Baer, E., Macromolecules, 2010, 42: 8619
13 Chai, L.G., Li, L., Liao, Q. and Yan, S.K., Acta Polymerica Sinica (in Chinese), 2012, (11): 1342
14 Yang, J.P., Liao, Q., Zhou, J.J., Jiang, X., Wang, X.H., Zhang, Y. Jiang, S.D., Yan, S.K. and Li, L., Macromolecules, 2011, 44: 3511
15 Wang, Y., Chan, C.M. and Ng, K.M., Macromolecules, 2008, 41: 2548
16 Jeon, K. and Krishnamoorti, R., Macromolecules, 2008, 41: 7131
17 Schönherr, H. and Frank, C.W., Macromolecules, 2003, 36: 1188
18 Yang, P. and Han, P.Y., Langmuir, 2009, 25: 9960
19 Mellbring, O., Kihlman, Ø.S., Krozer, A., Lausmaa, J. and Hjertberg, T., Macromolecules, 2001, 34: 7496
20 Bartczak, Z., Argona, A.S., Cohena, R.E. and Kowalewski, T., Polymer, 1999, 40: 2367
21 Jeon, K. and Krishnamoorti, R., Macromolecules, 2008, 41: 7131
22 Ma, Y., Hu, W.B. and Reiter, G., Macromolecules, 2006, 39: 5159
23 Liu, X., Wei, Q.S., Chai, L.G., Zhou, J.J., Yan, D.D., Yan, S.K. and Li, L., Acta Polymerica Sinica (in Chinese), 2013, (5): 654