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ARTICLE

A Study on the Epitaxial Ordering Process of the Polycaprolactone on the Highly Oriented Polyethylene Substrate

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ABSTRACT: Studies on the influence of foreign surfaces on the crystallization of polymers have demonstrated that the lamellae of the epitaxial polymer in the contact layer could be several times thicker than those produced by bulk crystallization under the same condition. It is, however, not clear that how far of the polymer melt from the interface can be affected by the foreign surface and how this effect propagates from the interface into the polymer melt. Therefore, the molecular dynamics of PCL during its epitaxy on an oriented PE substrate was studied. The obtained results show that keeping the samples at temperatures above the bulk melting temperature but below the equilibrium melting point of PCL for a period of time leads to the formation of unusual ordered PCL, which melts at much higher temperature than its bulk crystallized counterpart. It was demonstrated that the ordering process propagates from the interface into the PCL melt. For a sufficient time, all of the PCL chains can be organized into the similar ordered structure, which leads to the final epitaxial crystallization of PCL on the PE substrate with extremely broad lamellae thickness.

1. Introduction

Epitaxy is defined, most generally, as the crystals of one phase (guest crystals) grow on the surface of a crystal of another phase (host crystal) in one or more strictly defined crystallographic orientations.[1] Under this concept, it provides an effective way for fabricating well-defined polymer thin films with controlled crystalline structure and crystal organization. As examples, Lotz et al. have successfully modulated the melt-crystallization behavior of isotactic poly(1-butene) in different modifications through regulating the crystalline structure of the substrate polymers.[2,3] This leads to the polymer epitaxy being a very important research topic due to its theoretical and practical relevance. Therefore, since the early 1980s, epitaxial crystallization of polymers onto various polymeric substrates has been an extremely active subject in field of polymer science.[4−15]

It should be pointed out that the early studies on heteroepitaxy of polymers have mainly been focused on the origin and controlling factors of the polymer epitaxy. Through systematic studies on the epitaxial induced crystalline modifications of the epitaxial polymers and their unusual orientations with respect to the used substrates, e.g., molecular chain orientation and the contact planes of the involving polymer pairs, an understanding at the molecular level has been achieved.[16,17] It is now generally accepted that the occurrence of polymer epitaxy is based on some certain crystallographic matches, e.g., a coincidence of unit-cell dimensions, and a 15% mismatching is assumed to be the upper limit for the occurrence of the epitaxial growth.[18]

The polymer epitaxy follows actually the same two-step procedure including nucleation and crystal growth. The crystallographic matches influence essentially the nucleation stage of epitaxial crystallization. It reveals the special interactions between the epitaxial and substrate polymer chains in the contacting interface within a certain layer.[19,20] The evidence for this is twofold. First, it was confirmed that polymer epitaxy is a reversible process. For example, melt crystallization of polypropylene on oriented polyethylene substrate produces exactly the same mutual chain orientation as the polyethylene crystallized on the oriented polypropylene substrate.[21,22] Second, recent studies of the influence of foreign surfaces on the crystallization of polymers demonstrated that the lamellae of the epitaxial polymer in the contact layer could be several times thicker than those produced by bulk crystallization under the same condition.[23−25] This clearly discloses the importance of the surface interaction on the induced morphology of the epitaxial polymer. The things remain unclear are that (i) how far of the polymer melt from the interface can be affected by the existing interaction and (ii) how this effect propagates from the interface into the polymer melt. Therefore, the molecular dynamics during the epitaxial ordering process of polycaprolactone (PCL) on a highly oriented high-density polyethylene (PE) substrate at temperature above its nominal melting point has been studied. In the present work, we probed the crystallization dynamics of PCL on a highly oriented PE substrate by using DSC and AFM. The obtained results confirm the formation of ordered, unusual thick PCL lamellae in contact with the oriented PE substrate. The purpose of this paper is to provide the experimental details and the obtained results regarding the ordering dynamics of PCL chains on the highly oriented PE substrate.

2. Experimental Section

Commercial grade PCL, with molecular weight M_w 65 000 and polydispersity of 1.53, was purchased from Sigma-Aldrich Co.

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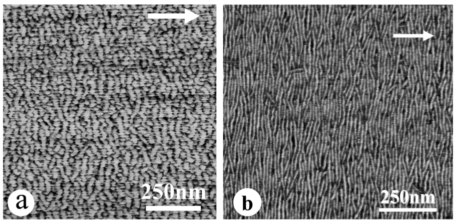

Figure 1. AFM phase images of (a) a highly oriented PE film and (b) a PCL layer crystallized on an oriented PE substrate from the melt. The PCL/PE double layer was heated treated first at 80 °C for 15 min and then cooled to room temperature on air. The arrows indicate the molecular chain directions of the PE substrate films.

PE used in this study was Lupolen 6021DX, produced by BASF AG Ludwigshafen, Germany. Uniaxially oriented thin PE films were prepared according to a melt-draw technique.[26] According to this method, a small amount of a 0.5 wt % solution of the PE in xylene was poured and uniformly spread on a preheated glass plate, where the solvent was allowed to evaporate at 125 °C. After evaporation of the solvent, the remaining PE thin molten layer was then drawn up by a motor-driven cylinder with a drawing speed of about 20 cm/s. The thickness of the obtained thin films ranges from 30 to 50 nm.

Samples for DSC measurements were prepared by sandwiching a solution cast PCL thin film of ca. 10 μm in thickness between two highly oriented ultrathin PE films with same chain orientation. Such a kind of configuration could enhance their contact areas as well as avoid dewetting of the PCL on PE surface. Samples for atomic force microscopy (AFM) were prepared by spin-coating a 1 wt % PCL chloroform solution on the highly oriented PE films supported by glass slides. The thickness of the PCL layer is about 100 nm. The samples were heat-treated at 85 °C (below the melting point of PE but well above that of PCL) for 15 min, then cooled to different temperatures for different periods of time, and finally cooled to room temperature.

Tapping-mode AFM images illustrating the morphology of PCL crystallized on PE substrate were obtained using a NanoScope III MultiMode AFM (Digital Instruments). Si cantilever tips (TESP) with a resonance frequency of ~300 kHz and a spring constant of about 40 N m^{-1} were used. The scan rate varied from 0.5 to 1.0 Hz. The set-point amplitude ratio (rsp) A_{sp}/A_0 was adjusted to 0.7−0.9, where A_{sp} was the set-point amplitude and A_0 was the amplitude of the free oscillation. The set-point ratio and amplitude were chosen as such that the surface was tracked while maintaining the necessary contrast in the phase images. To characterize the mutual orientation between PCL and PE, the samples were transferred onto TEM grids, and electron diffraction patterns were then obtained using a Hitachi H-800 transmission electron microscope operated at 100 kV.

DSC measurements were carried out by using a Perkin-Elmer Diamond DSC instrument with a liquid-nitrogen cooling accessory. Dry helium gas with a flow rate of 20 mL/min was purged through the DSC cell. The temperature and the heat flow of the equipment were calibrated with indium.

3. Results

It has been confirmed that epitaxial crystallization of PCL takes place whenever it grows on an oriented PE substrate, independent of its initial states, e.g., either from melt or from solution. Parts a and b of Figure 1 show the phase contrast AFM images of the highly oriented PE substrate and the PCL layer crystallized on the PE substrate from the melt, respectively. The arrows in the micrographs indicate the drawing directions of the PE substrate films. From Figure 1a, it can be clearly seen that the obtained PE substrate film consists of highly oriented lamellar structure with the lamellar long axes arranged perpendicular to the drawing direction. The average thickness of the PE lamellae is about 30 nm. The PCL crystallized on the PE substrate also shows highly oriented lamellar structure (Figure 1b). The PCL lamellae are much thinner than the PE lamellae: 6.5 nm for PCL vs 30 nm for PE. Nevertheless, they align in the same manner as the PE lamellae, i.e., perpendicular to the drawing direction of PE substrate film. This indicates the epitaxial growth of PCL on PE substrate.

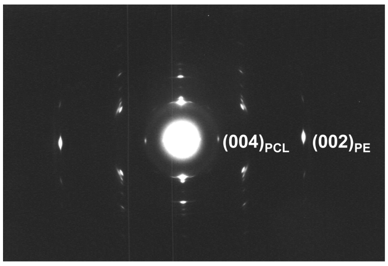

Figure 2. Electron diffraction pattern of a PCL/PE double-layered film, which has been heat-treated at 85 °C for 15 min and then cooled to room temperature on air.

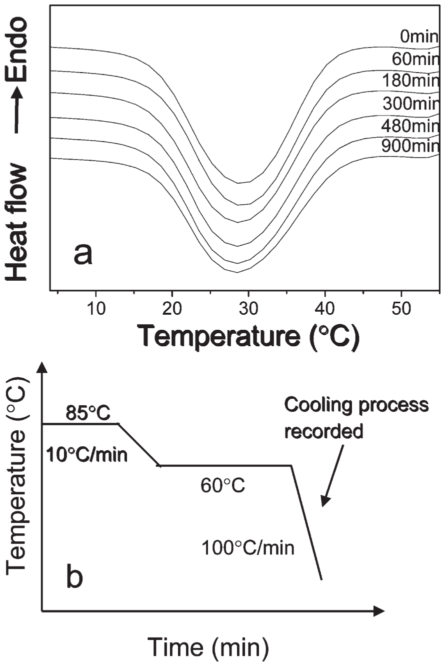

Figure 3. (a) DSC scans of the PCL/PE samples obtained during the cooling process as shown in (b). The cooling rate is 100 °C /min, and the isothermal times at 60 °C are indicated in the right side of (a).

Electron diffraction experiments have confirmed the occurrence of epitaxial crystallization of PCL on the oriented PE substrate and provided more detailed information about the mutual orientation relationship between the PCL and the PE substrate. As shown in Figure 2, the appearance of sharp and well-defined reflection spots confirms that both PE and PCL are highly oriented. The alignment of the $(004)_{PCL}$ diffraction spots in the same direction of the $(002)_{PE}$ reflections reflects a parallel alignment of both PE and PCL chains. The special parallel chain orientation of both polymers can be well explained in terms of a two-dimensional lattice matching based on the almost identical orthorhombic unit cells of them (PCL: $a = 0.747$, $b = 0.498$, and $c = 1.705$ nm; PE: $a = 0.74$, $b = 0.494$, and $c = 0.253$ nm).[27] For example, perfect matching exists between every (*hk*0) planes of both polymers and between the interatomic space along their chain axis (0.122 nm vs 0.123 nm for PCL and PE, respectively).

To obtain more information about the isothermal molecular dynamics of PCL on oriented PE substrate, further investigation

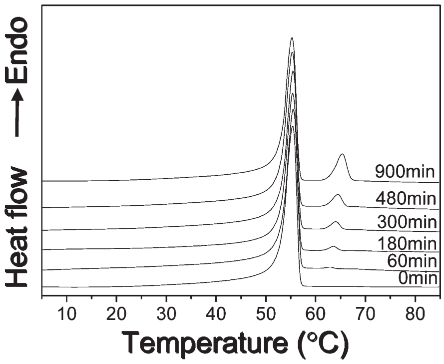

Figure 4. DSC heating scans of the PCL/PE samples after running the experimental protocols shown in Figure 3b. The heating rate is 10 °C/min, and the isothermal times at 60 °C are indicated on the right side.

Table 1. Characteristic Data Obtained from the Cooling Process of PCL after Melting at 85 °C and Kept at 60 °C for Certain Period of Times

time (min)	0	60	180	300	480	900
T_c (°C)	28.56	28.55	28.54	28.54	28.53	28.53
ΔH (mJ)	175.97	172.97	172.39	170.15	166.81	153.69

Table 2. Characteristic Data Obtained from the Heating Process of PCL after Melting at 85 °C for 15 min, Kept at 60 °C for a Certain Period of Times, and Then Cooled to Room Temperature

time (min)	0	60	180	300	480	900
T_{m1} (°C)	55.3	55.4	55.4	55.5	55.3	55.3
ΔH_1 (mJ)	178.4	176.2	174.5	174.2	171.2	158.6
T_{m2} (°C)		62.96	63.63	64	64.45	65.31
ΔH_2 (mJ)		0.93	3.23	6.22	10.42	25.45
total ΔH	178.4	177.13	177.73	180.42	181.62	184.05

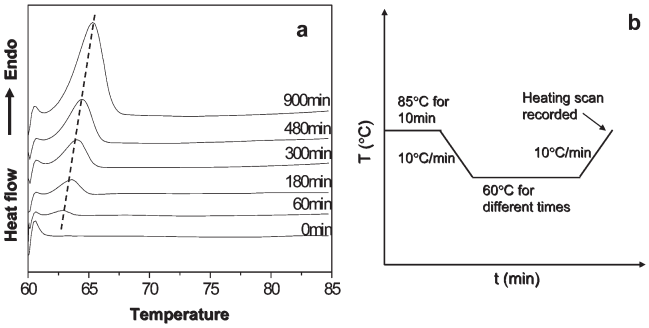

Figure 5. (a) DSC heating scans of the PCL/PE samples during the process as shown in (b). The heating rate is 10 °C/min, and the isothermal times at 60 °C are indicated on the right side of (a).

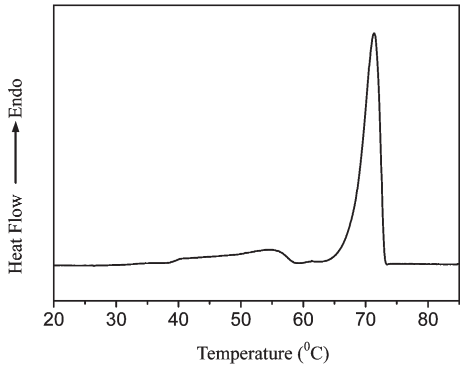

Figure 6. DSC heating scan of a PCL/PE sample, which has been heat-treated at 85 °C for 15 min, then kept at 60 °C for 14 days, and finally cooled to room temperature. The heating rate is 10 °C/min.

Table 3. Characteristic Data Obtained from the Direct Heating Process of PCL after Melting at 85 °C for 15 min and Kept at 60 °C for a Certain Period of Times

time (min)	0	60	180	300	480	900
T_m (°C)		62.81	63.48	63.99	64.47	65.32
ΔH (mJ)		0.54	2.54	4.95	8.92	22.96

has been carried out by using DSC. Figure 3a shows DSC cooling scans of the PCL/PE samples, which have been heat-treated at 85 °C for 15 min and then cooled to and kept at 60 °C for different times before cooling to room temperature, as indicated in Figure 3b. In Figure 3a, an exothermal peak appears in each of the cooling scan. These peaks locate at the same positions and exhibit similar shapes. Therefore, at a first glance, no effect of the isothermal process at 60 °C on the subsequent crystallization of PCL can be recognized. However, as summarized in Table 1, the value of the heat of fusion decreases remarkably with increasing keeping time at 60 °C. One may associate this with the decrease in crystallinity of PCL caused by thermal degradation when keeping the samples at 60 °C. The subsequent heating processes of these samples do not support this suggestion.

Figure 4 shows the corresponding DSC heating scans of the samples after running the experimental protocol shown in Figure 3b. It is clear from Figure 4 that all of the samples exhibit a lower temperature endothermic peak at about 55 °C. These peaks are unambiguously contributed by the melting of the crystals formed at ca. 29 °C during cooling of the sample. For the sample kept at 60 °C for more than 3 h, extra melting peaks can be clearly seen at relatively higher temperatures. These high temperature peaks become larger and shift to higher temperature with increasing time at 60 °C. They are certainly attributed to the isothermal process. The characteristic data listed in Table 2 support the above reasoning. The decrease in the ΔH_1 value for the low-temperature melting peak with time is in reasonable agreement with the data listed in Table 1 when the annealing effect during the reheating is considered. The enhancement of the ΔH_2 value for the high-temperature melting peak with time illustrates the influence of isothermal process on the crystallization of the PCL. On the other hand, the slight increase in the total enthalpy value indicates an increment in crystallinity of PCL with increasing time at 60 °C. To distinguish the contribution of the isothermal process at 60 °C from the part caused by subsequent cooling, heating scan direct after annealing has been performed.

Figure 5a shows DSC heating scans of the samples subjected to a thermal treatment as shown in Figure 5b. From Figure 5a, one can clearly see that the DSC curve for the sample did not subject an isothermal process at 60 °C exhibits only a linear baseline without any endothermic peak. For the samples kept at 60 °C for some time, even for only 60 min, an endothermic peak appears in the subsequent heating process of each sample. The characteristic data corresponding to these endothermic peaks are presented in Table 3. As in the case of Figure 4, these peaks shift to high temperature and become larger and larger with time. For the sample held at 60 °C for 2 weeks, as shown in Figure 6, almost all of the PCL melts at ca. 70 °C.

The above phenomenon has also been observed when the samples were isothermally treated at higher temperatures. As shown in Figure 7a, the DSC curves of the samples kept at 63 °C from the melt for a period of time exhibit also two endothermic peaks. The lower temperature ones, originating from the subsequent cooling to room temperature, locate at the same position as that shown in Figure 4. The higher temperature ones are, however, somewhat different from those observed in Figure 4. They can be clearly identified only when the samples were kept at 63 °C from the melt longer than 40 h. Moreover, the

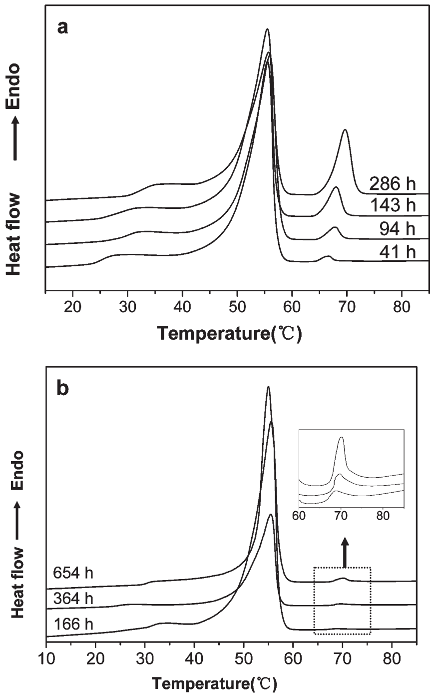

Figure 7. DSC heating scans of the PCL/PE samples which have been heat-treated at 85 °C for 15 min and then cooled to and kept at (a) 63 °C and (b) 65 °C for different times as indicated.

high-temperature peaks shift to even higher temperatures. It reaches 70 °C after the sample being kept at 63 °C from the melt for 286 h. At even higher temperatures, e.g., 65 °C, as shown in Figure 7b, the annealing time needed to produce the higher temperature peak is longer than 160 h. Now, the peak temperature is already around 70 °C as it can be first recognized. This phenomenon disappears only when the isothermal treatment temperature is over 70 °C. For example, no high-temperature melting peak was observed for the samples held at 70 °C for more than 25 days.

4. Discussion

The above experimental results clearly indicate that the appearance of the high-temperature melting peaks is associated with isothermal process. Hereafter we first discuss the origin of the high-temperature peaks. It was reported that ordered stable layer of alkanes could form above their melting points of bulk crystal on flat solid substrates.[28] Our previous FTIR study on the same system also indicates that the PCL chains get gradually oriented along the chain direction of the oriented PE substrate at temperatures above its bulk melting point.[29] Therefore, the high-temperature melting peaks should be associated with the substrate-induced ordered structure of PCL during the isothermal process. Through AFM observation on the structure of the epitaxial polymer in the contact plane with the substrate, Tracz et al. have demonstrated that the epitaxial PE crystalline lamellae in the contact layer with the substrate could be several times thicker than those produced by bulk crystallization.[23−25] Taking into account that the melting point of a polymer is proportional to its lamellar thickness,[30] the melting temperature of the ordered PCL on the oriented PE substrate should be much higher than that of the bulk PCL.

On the basis of the above discussion, the present results indicate that the induction time of ordering process of PCL on PE substrate increases with increasing temperature. This ordering process is even prohibited at temperatures above 70 °C. Considering that the equilibrium melting temperature of PCL estimated by the Hoffman−Weeks plot is around 70 °C (see Figure 8), it is concluded that the organization of PCL into an ordered structure following the chain orientation of PE can take place only below its equilibrium melting point.

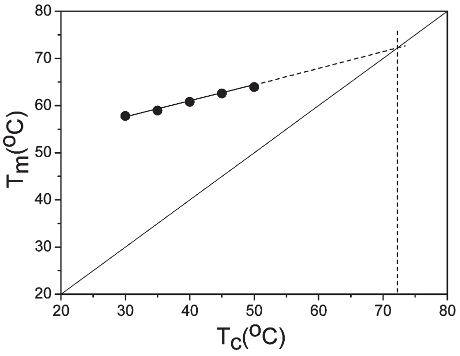

Figure 8. T_m vs T_c plot of the used PCL sample.

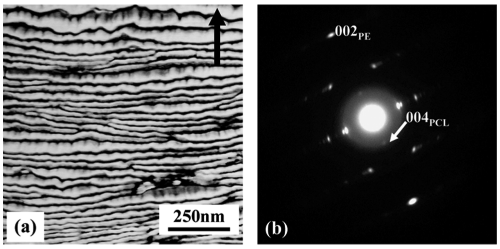

Figure 9. (a) AFM phase image of a PCL/PE double layer, which has been heat-treated at 85 °C for 15 min, cooled to and kept at 60 °C for 6 days, and finally cooled to room temperature. The arrow in the picture shows the chain direction of the PE substrate. (b) Corresponding electron diffraction pattern of the above used double layer.

Moreover, the facts that (i) the high-temperature peaks get larger and larger and (ii) they shift also to high temperature with time provide us more information about the ordering process of PCL chains on the oriented PE substrate during the isothermal process. First of all, the increase in enthalpy, leading to a gradual increase in height of the high-temperature melting peak, may reflect an increment of the amount of the ordered PCL chains or/and a perfection process of the ordered structure. One may suggest that this process happens only in the contact plane. However, from Figure 6, we can see that the sample held at 60 °C for 2 weeks shown mainly the high-temperature peak. This clearly indicates that almost all of the PCL has been ordered into the same state, giving rise the high-temperature melting peak. Considering that bulk crystallization of PCL cannot take place at 60 °C, we conclude that the alignment of more and more PCL molecular chains into an ordered structure with time during the isothermal process takes the main responsibility of the increase in enthalpy. In other words, the ordering of PCL chains does not only occur in the interface contacting with PE substrate. It propagates also from the interface into the bulk away from the contact surface. AFM observation and electron diffraction confirm that the PCL lamellae get thicker and thicker with isothermal time at 60 °C. As shown in Figure 9, after 6 days at 60 °C, the PCL grows still epitaxially on the PE substrate and forms edge-on lamellae with molecular chains in film plane and parallel to the chain direction of PE substrate crystal (Figure 9b). The lamellar thickness of PCL, i.e., the fold chain stem length, can reach ca. 55 nm (see Figure 9a). It is about 8 times thicker than those shown in Figure 1b (55 vs 6.5 nm). This is somewhat larger that the reported values of PE organized on talc, MoS_2, and freshly cleaved highly oriented pyrolitic graphite. It is reasonable since isothermal process at higher temperature was

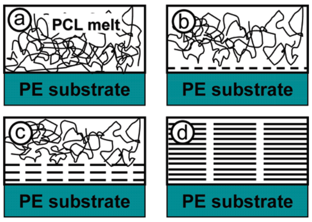

Figure 10. Sketches describing the induced ordering process of PCL on highly oriented PE substrate during the isothermal process at temperatures above the bulk melting point but below the equilibrium melting point of PCL.

used here rather than a cooling process with different cooling rates used by Tracz et al.[23−25]

Second, during the above-mentioned ordering process, if the ordered PCL chain sequence length was fixed, the peak temperature should keep unchanged. The shift of peak position to high temperature with time implies an increment in the stem length of the ordered PCL chain as well. This is understandable since thickening of the polymer crystalline lamellae, even unfolding of the polymer chain, takes place during the annealing of existing polymer crystals at high temperatures.[31−33] This is also supported by the increase in high-temperature melting with increasing isothermal temperature when the dependence of the lamellar thickness on bulk crystallization of a polymer is considered.

According to the above discussion, the ordering process of PCL from melt on the PE substrate at temperatures higher than its bulk melting temperature can be schematically presented in Figure 10. At the initial stage, the PCL is in a random coil molten state (Figure 10a). With the passage of time, the PCL starts to organize into an ordered structure following the orientation of the substrate crystals. The organization process may first take place in a monolayer contacted directly with the PE substrate (Figure 10b). With increasing time, the ordered PCL chain sequence length increases. At the same time, the ordered layer propagates from the interface into the PCL bulk (Figure 10c). The increase in the ordered PCL chain sequence length results in the shift of the melting temperature toward high temperature, while the increase in the layer thickness contributes to the increment of the enthalpy. For sufficient time, all of the PCL chains can be organized into an ordered structure (Figure 10d). Meanwhile, the ordered PCL segments get a maximum length or even possibly form fully extend chains.

5. Conclusions

The structure and structure evolution of PCL on highly oriented PE substrate were investigated by DSC and AFM combined with electron diffraction. AFM and electron diffraction results clearly indicate that PCL can grow epitaxially on the oriented PE substrate with both polymer chain axes parallel owing to a two-dimensional lattice matching. DSC measurement shows that keeping the samples at temperatures above the bulk melting temperature but below the equilibrium melting point of PCL for a period of time leads to the appearance of a high-temperature melting peak on the subsequent DSC heating process. This high-temperature peak is associated with an ordered unusual broad PCL chain sequence caused by strong interaction between both polymers. The high-temperature peak shifts to high temperature and becomes larger and larger with isothermal time, indicating an increase in the ordered PCL phase and ordered PCL chain sequence length. This clearly demonstrates that the surface-induced unusual structure not only occurs in the contact layer but also propagates from the interface into the PCL melt. Combining all these experimental results, the molecular dynamics of PCL melt on the PE substrate at high temperature can be described as follows: Keeping the PCL melt on the PE substrate at high temperature, a monolayer PCL contacted directly with the PE substrate has been first arranged into an ordered structure. This ordered layer becomes thicker while the ordered chain sequence length becomes longer with time. With sufficient time, all of the PCL chains can be organized into the ordered structure well above the melting point. This will lower the nucleation barrier by prealigning the polymer chains already in the melt. Thus, when lowering the temperature below the melting point, these prealigned chains can easily form a nucleus and crystals will grow even at high temperatures, which leads to the epitaxial crystallization of PCL on the PE substrate with extremely broad lamellae.

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