

INDUCED CRYSTALLIZATION BEHAVIOR OF POLY(ETHYLENE ADIPATE) BY HIGHLY ORIENTED POLYETHYLENE*

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Abstract The crystallization behavior of poly(ethylene adipate) (PEA) on highly oriented high-density polyethylene (PE) substrate both from solution and isotropic melt was studied by means of optical microscopy, differential scanning calorimetry, atomic force microscopy and electron diffraction. The results show that the PE influences the crystallization of PEA strongly, which results in an epitaxial growth of PEA with well ordered structure. At the boundary of the PE substrate, a transcrystalline PEA layer is observed. Fine structural observation illustrates that the PEA grows on the PE substrate in edge-on lamellae with fixed orientation. Electron diffraction demonstrates that the epitaxial organization of PEA on PE occurs with both polymer chains parallel, which leads to the (00 l) PEA diffractions inclined $\pm 23.5^\circ$ to the chain direction of PE crystals. Combining the real space morphological observation and electron diffraction results, it is concluded that the epitaxial PEA edge-on lamellae are folded in the {00 l } lattice planes.

Keywords: Poly(ethylene adipate); Polyethylene; Epitaxy; Orientation.

INTRODUCTION

The structure and properties of a polymer at foreign surfaces are critical in many scientific and technical applications^[1–4]. It is known that the special interaction between the substrate and the polymer chain segments can strongly affect the physical properties of the polymer including glass transition temperature^[5–11], molecular mobility^[12–16], crystallization^[17–19] and melting behavior^[20]. This leads to increased interest in the structure and property characterization of polymer thin films contacted with a foreign surface. In particular, the crystallization behavior of polymers at interfaces has been extensively studied owing to the fact that over 2/3 synthetic polymers are crystallizable. The influence of a substrate on the crystallization of a polymer is most frequently displayed by the change in the crystallization kinetics. In some special cases, crystallization of a polymer on a substrate can also induce a unique oriented structure through epitaxial growth. This provides an effective pathway to manipulate the property and even the functionality of semicrystalline polymers^[21–30]. For example, poly(vinylidene fluoride) shows pronounced polymorphic crystalline forms^[31]. While its α -form is the most common one, its β -phase is the one that has attracted the widest interest due to the extensive piezo- and pyro-

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electric applications. It is well documented that crystallization on the surface of potassium bromide can successfully control the growth of it from melt at atmospheric pressure in its piezo- and pyro-electric β -form^[32]. As a consequence, the polymer epitaxy has been an extreme research theme since the early 1980s.

For polymer epitaxy, much attention has been paid to the systems with PE^[29, 30, 33–35]. In our previous work, we have studied the epitaxial crystallization of poly(butylenes adipate) (PBA), an aliphatic biodegradable polyester, on highly oriented PE substrate^[33]. As well documented, PBA exhibits two different modifications designated as α and β depending on the preparation conditions^[36–39]. While planar zigzag chains packed in an orthorhombic unit cell with dimensions $a = 0.506$, $b = 0.735$, and $c = 1.467$ nm was characterized for the β -form, the α -form was found to be packed with the planar zigzag PBA chains in a monoclinic unit cell with dimensions $a = 0.67$, $b = 0.80$, $c = 1.42$ nm, and $\beta = 45.5^\circ$. Our experimental results demonstrated that during crystallizing the PBA on oriented PE substrate, oriented β -form PBA lamellae arranged with their chain direction parallel to the chain direction of PE substrate crystals were always observed regardless of crystallization conditions^[33]. This has been well explained in terms of matching between the interchain distances when the almost identical ab projection of the crystalline structure of β -PBA and PE (orthorhombic unit cell with $a = 0.74$, $b = 0.494$, and $c = 0.2534$ nm^[40]) are considered. An additional aspect to be considered is associated with the similarity of crystalline unit cell, *i.e.* whether the same orthorhombic packing of both β -PBA and PE is an important factor in determining the epitaxial organization of PBA on oriented PE substrate. To clarify this, the crystallization behavior of poly(ethylene adipate) (PEA), which exhibits also the monoclinic and orthorhombic unit cells, on the highly oriented PE substrate was studied. The experimental results indicate that epitaxial crystallization of PEA on the oriented PE substrate takes place in its monoclinic form, indicating that the similarity in crystalline unit cell is not a crucial factor for determining the epitaxial growth.

The purpose of this paper is to present the detailed experimental results of PE induced PEA crystallization behavior. According to the obtained results, the origin of epitaxial crystallization of PEA on oriented PE substrate is discussed.

EXPERIMENTAL

The PEA used in this study was purchased as a research-grade material from Aldrich Chem. Co. The weight-average molecular weight (M_w) determined by gel permeation chromatography (GPC) is *ca.* 10000 g/mol. The PE used in this study is Lupolen 6021DX, produced by BASF AG Ludwigshafen, Germany. Uniaxially oriented thin PE films were prepared according to a melt-draw technique introduced by Petermann and Gohil^[41]. According to this method, a small amount of a 0.5 wt% solution of PE in xylene was poured and uniformly spread on a preheated glass plate at *ca.* 125 °C, where the solvent was allowed to evaporate at the preparation temperature. After evaporation of the solvent, the molten thin PE layer was then drawn up by a motor-driven cylinder with a drawing speed of about 2 cm/s. The obtained thin films with thickness ranging from 30 nm to 50 nm are well suitable for TEM observation.

Samples for optical microscopy observation were prepared by dipping a glass slide, which was partially covered with highly oriented PE substrate thin film, into a 2 wt% chloroform solution of PEA. The obtained thin layer was then dried at room temperature for several days by evaporation of the chloroform. The dimensions of thus prepared samples can reach 2 cm $\times$ 2 cm. For melt crystallization of PEA, the sample was heat-treated at 75 °C (above the melting point of PEA but below the melting point of PE substrate) for 10 min and subsequently cooled to different temperatures for isothermal crystallization. Samples for atomic force microscopy (AFM) and electron diffraction studies were prepared by spin-coating 1 wt% chloroform solution of PEA on the mica surface covered with highly oriented PE film. Samples for differential scanning calorimetry (DSC) measurements were prepared by sandwiching a solution cast PEA film of *ca.* 10 μ m in thickness between two highly oriented ultrathin PE films with same chain orientation. Such a configuration could enhance their contact areas as well as avoid dewetting of the PEA on PE surface.

For optical microscopy observation, a Carl Zeiss Axioskop 40 optical microscope equipped with a hot stage was used in this study. All pictures presented in this paper were taken under crossed polarizers. Fine structure on lamellar scale was illustrated by Tapping-mode AFM images obtained using a Nano-Scope III MultiMode AFM (Digital Instruments). Si cantilever tips (TESP) with a resonance frequency of approximately 300 kHz and a spring constant of about 40 N m^{-1} were used. The scan rate varied from 0.5 Hz to 1.0 Hz. The set-point amplitude ratio A_{sp}/A_0 was adjusted to 0.7–0.9, where A_{sp} is the set-point amplitude and A_0 is the amplitude of the free oscillation. The set-point ratio and amplitude were chosen such that the surface was tracked while maintaining the necessary contrast in the phase images. Phase-contrast bright field transmission electron micrograph and electron diffraction pattern were taken with a Hitachi H-800 transmission electron microscopy operated at 100 kV.

DSC measurements were carried out by using a Mettler Toledo-822e DSC instrument with nitrogen gas purge at a flux of *ca.* 50 mL/min. The temperature and the heat flow of the equipment were calibrated with an indium standard.

RESULTS

Presented first in Fig. 1 is the representative phase-contrast bright field (BF) transmission electron micrograph and the corresponding electron diffraction pattern (inset) of the highly oriented PE substrate films. The arrow in the picture indicates the drawing direction during film preparation. In the BF image, the bright lines reflect the amorphous regions, while the dark areas between the bright lines display the high-density crystalline lamellar regions. It can be clearly seen that the obtained PE substrate film consists of highly oriented lamellar structure with the lamellae arranged perpendicular to the drawing direction. On the electron diffraction pattern, the appearance of well-defined sharp reflection spots confirms the high orientation of the PE films. All of the reflection spots shown in the diffraction pattern has been successfully accounted for by the orthorhombic unit cell with axes $a = 0.74$, $b = 0.494$, and $c = 0.2534 \text{ nm}$. The alignment of the (002) diffraction spots in the drawing direction demonstrates an orientation of the chain axes in the film plane and along the drawing direction. The coexistence of the (020) and (110) reflections indicates a fiber orientation, while the absence of the (200) reflections implies a preferred orientation of the a -axis more inclined in the film normal direction.

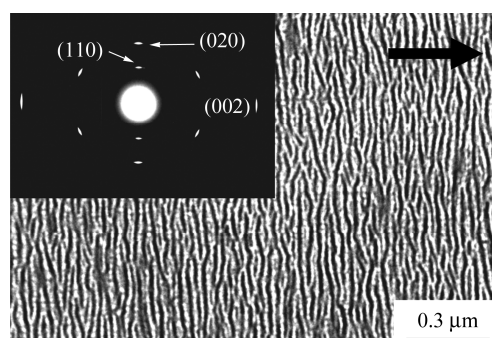


Fig. 1 A BF transmission electron micrograph and its corresponding electron diffraction pattern (inset) of a melt-drawn highly oriented PE film. The arrow indicates the drawing direction during film preparation.

To give an overall inspection of the crystallization behavior of PEA on highly oriented PE substrate, the samples were observed by optical microscope under crossed polarizers. Figure 2 shows an optical micrograph of the layered PEA/PE sample as prepared, *i.e.* the PEA crystallized from solution after the evaporation of the solvent. For a direct comparison, the PEA is only partially supported by the PE oriented film, which is located in the lower left corner of the picture. The boundary line of the PE substrate film can be easily recognized. The arrow indicates the drawing direction of the highly oriented PE substrate during preparation, *i.e.* its chain

orientation, which is parallel to the boundary line. Considering that the PE film is too thin (less than 50 nm) to provide birefringence contribution at present condition, it is the PEA layer that contributes the birefringence in the optical micrograph. From Fig. 2, one can clearly see the different supermolecular structures of PEA crystallized on the glass and PE surfaces, respectively. On the glass substrate, the PEA crystallizes in spherulitic structure. This is typical for polymer crystallized from solution on glass slide. On the other hand, the PEA crystals on the PE substrate show much stronger birefringence with respect to the PEA spherulites formed on glass surface. Moreover, no individual PEA crystals can be identified. This implies unequivocally that the PE substrate exhibits strong nucleation ability toward PEA. The enhanced nucleation density of PEA results in the formation of abundant PEA microcrystallites that cannot be resolved individually under optical microscope. The strong nucleation ability of PE toward PEA is also demonstrated by the formation of the transcrystalline structure at the boundary of the PE substrate.

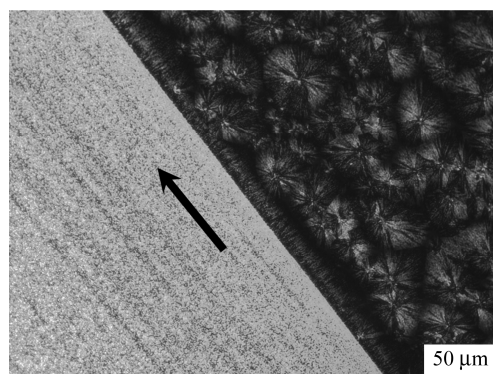


Fig. 2 An optical micrograph shows the morphologies of PEA crystallized from the solution on glass slide (upper right corner) and PE substrate (lower left corner). The boundary of PE substrate can be clearly identified and the molecular chain direction of PE is parallel to the boundary line as indicated by an arrow. The PE chain direction is 45° inclined to the polarizers.

Similar morphologies were also observed for the PEA melt crystallized on the highly oriented PE films. Figures 3(a) and 3(b) present the optical micrographs of the double-layered PEA/PE samples heat-treated at 75°C for 10 min and subsequently cooled to 27°C and 20°C for isothermal crystallization, respectively. In these pictures, the PE substrates are located at the lower left corners with the chain directions parallel to the boundary lines, as indicated by the arrows. The exact same thermal conditions provide us a reasonable comparison of the different crystallization behavior of PEA on glass slides and PE substrates. From Fig. 3(a), we see that crystallizing the PEA at 27°C on a glass slide (upper right corner) results in the formation of typical spherulites. The spherulites show clearly the banded structure caused by regular extinction phenomenon. Around the PE substrate boundary, a transcrystalline layer of PEA has been produced, indicating the high nucleation ability of PE towards PEA. It is interesting that extinction rings in the spherulites are straightened to parallel arranged linear extinction bands with same band periodicity as the spherulites. This means that the PE induced PEA crystals exhibit the same growth habit as bulk crystallized ones. The PEA crystals grown on the PE substrate (lower left corner) is, however, quite different. They grow in microcrystallites without extinction band. Actually, in the transcrystalline layer there exists also a non extinction thin layer, which is in direct contact with the PE boundary as indicated by the dash lines. When crystallizing the PEA at 20°C , except for the disappearance of the banded structures and the decrease in spherulite size, the morphologies of PEA on the neat glass, at the boundary of PE as well as on the PE substrate film do not change much. The disappearance of the banded structures is reasonable since they form only in the temperature window of $25\text{--}30^\circ\text{C}$ as reported in the literature^[42]. The decrease in spherulite size is caused by the enhanced nucleation density.

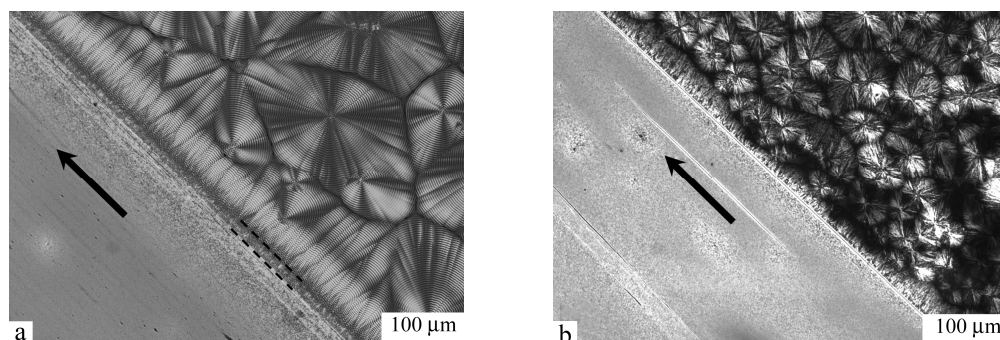


Fig. 3 Optical micrographs present the morphologies of PEA crystallized from melt on glass slide (upper right corner) and PE substrate (lower left corner) for 5 h at (a) 27 °C and (b) 20 °C, respectively. The boundary lines of the PE substrates can be clearly identified and the molecular chain directions are parallel to the boundary lines as indicated by the arrows. They are 45° inclined to the polarizers.

The above optical microscopic observations clearly indicate that the PE exhibits very strong nucleation ability toward PEA, resulting in the formation of microcrystallites. This has also been demonstrated by the elevated crystallization temperature of PEA in contact with the PE substrate during cooling from the melt. As shown in Fig. 4, the crystallization of PEA on the PE substrate starts at *ca.* 48 °C, which is about 25 K earlier than its bulk crystallization (at about 22 °C). It results from an early start of nucleation induced by PE. The peak crystallization temperature of PEA in contact with the PE is 32 °C, which is also much higher than its bulk peak crystallization temperature (at *ca.* 6 °C).

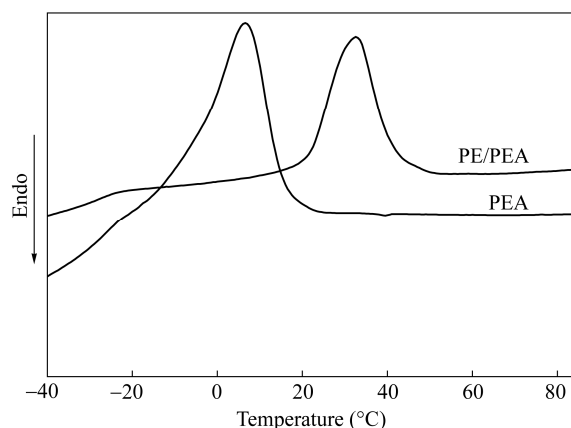


Fig. 4 DSC curves of the PEA/PE and pure PEA samples during the cooling process after heat-treated at 85 °C for 5 min to erase their thermal history. The cooling rate is 10 K/min.

It has frequently been reported that the specific nucleation capacity of PE on a series of materials results in the formation of oriented structures, namely, the occurrence of polymer epitaxy^[33–35, 43–45]. To find out whether the PEA grown on the PE oriented film also exhibits preferred orientation, fine structural features of PEA crystallized on the PE substrate surface has been revealed by AFM observation. Similar morphologies were always observed for the PEA crystallized on the PE substrate either from solution or from the melt at different temperatures^[46]. Figure 5 presents a representative AFM phase image of the PEA crystallized on highly oriented PE substrate. The arrow in the picture shows the drawing direction of the PE film during preparation. From Fig. 5, one can see a cross-hatched edge-on lamellar structure of PEA with its lamellae *ca.* $\pm 66.5^\circ$ apart from the chain direction of the PE substrate film. This indicates the occurrence of epitaxial crystallization of PEA on the PE substrate and has further been confirmed by electron diffraction.

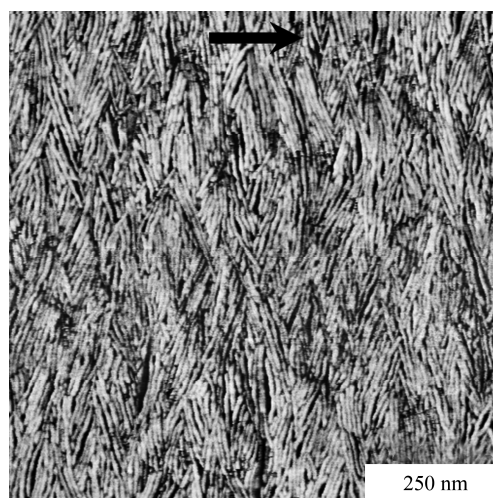


Fig. 5 An AFM phase image showing the fine structural feature of PEA crystallized from the solution on a highly oriented PE substrate. The molecular chain direction of PE is indicated by an arrow.

Figure 6(a) shows an electron diffraction pattern of a PEA/PE double layer, which has been heat-treated at 85 °C for 5 min and then cooled to 27 °C for isothermal crystallization. The appearance of well-defined reflection spots of both PEA and PE demonstrates that both the PEA and PE layers exhibit high degree of orientation, indicating the preferred orientation of PEA on oriented PE substrate, *i.e.* the occurrence of heteroepitaxy. All of the reflection spots contributed by PEA crystals can be accounted for by a monoclinic unit cell with parameters $a = 0.547$, $b = 0.724$, $c = 1.155$ nm, and $\beta = 113.5^\circ$ [42, 47, 48]. A sketch corresponding to the electron diffraction pattern of Fig. 6(a) with some reflections being indexed is shown in Fig. 6(c), in which the reflections coming from the PEA crystals are presented in short lines and those coming from PE substrate crystals are presented as solid ellipses. The angle between the $[00l]$ diffraction directions for PE and PEA crystals are measured to be $\pm 23.5^\circ$. Actually, the diffraction pattern contributed by the PEA crystals is somewhat similar to its fiber pattern, as presented in Fig. 6(b), simulated by using Cerius² program according to the same monoclinic unit cell. It should be pointed out that the strongest (110) and (020) diffractions in the fiber pattern are not observed for the epitaxially crystallized PEA, indicating that the (110) and (020) lattice planes of the epitaxially grown PEA crystals are out of Bragg diffraction condition. This suggests that the ac plane of the PEA is in contact with the PE substrate. In this case, as depicted in Fig. 7, a parallel chain alignment of both PEA and PE results in the location of (00 l) PEA diffractions in the direction exactly $\pm 23.5^\circ$ apart from the chain direction of both PE and PEA. According to the alignment shown in Fig. 7, the (200)_{PEA} diffraction spots of the PEA are expected to locate along the $[hk0]$ direction of PE. It is, however, not recognized in the electron diffraction pattern. This seems hard to be understood. But considering the almost identical lattice spaces of (200)_{PEA} and (020)_{PE} (0.25 versus 0.247 nm), overlapping of the (200)_{PEA} diffraction with the (020)_{PE} diffraction is highly possible. Taking all these into account, we speculate that the epitaxial crystallization of PEA on oriented PE substrate takes place with the (010)_{PEA} lattice plane in contact with the PE substrate and a parallel chain alignment of both polymers.

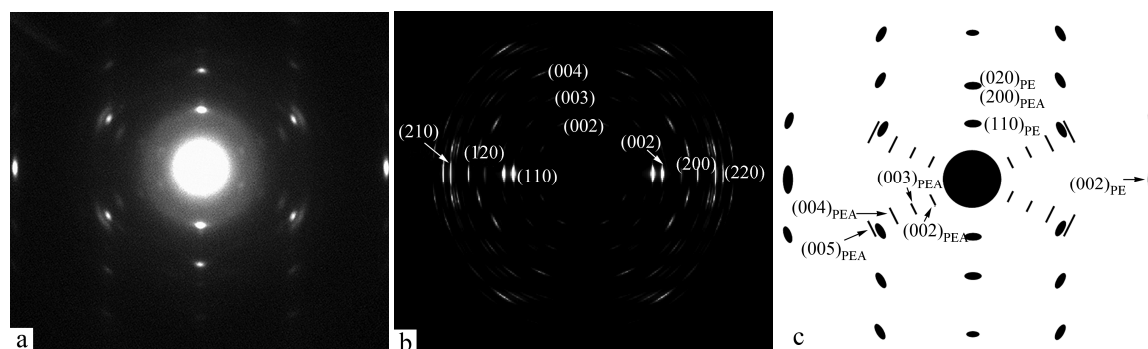


Fig. 6 (a) An electron diffraction pattern of a PEA/PE double layer, which has been heat-treated at 85 °C for 5 min and then cooled to 27 °C for isothermal crystallization; (b) A simulated diffraction pattern of the PEA with fiber orientation; and (c) a sketch of the electron diffraction pattern shown in Fig. 6(a)

The solid ellipses represent the reflection spots of PE, while the short lines represent the electron diffractions of PEA.

DISCUSSION

Heteroepitaxies of PE on an oriented substrate or other polymers on the oriented PE substrate have been frequently studied. In most cases, a parallel chain alignment of the epitaxial pairs has been obtained^[33, 34, 49–52]. Up to date, only three exceptions have been reported in the literatures. One is the epitaxial crystallization of PE with isotactic polypropylene (*i*PP)^[20, 29–31]. It was found that, either PE crystallized on oriented *i*PP substrate^[43, 53, 54] or *i*PP grown on the oriented PE substrate^[55], an alignment of both polymer chains $\pm 50^\circ$ apart from each other was always observed. Another one is the epitaxial crystallization of PE with syndiotactic polypropylene (*s*PP), for which a 37° inclination of both polymer chains has been observed whenever epitaxial crystallization between these two polymers takes place^[56, 57]. The third one is the epitaxial crystallization of PLLA on highly oriented PE substrate, which results in an arrangement of PLLA with molecular chains perpendicular to the chain direction of the PE substrate^[35]. These different mutual chain orientations are associated with the different matching geometries of the involved polymers. We here present another case of the parallel chain epitaxy with PE. In the present case, even though the chains of both polymers are parallel aligned, the lamellar orientation of the PEA with respect to the PE substrate is quite different from the parallel chain epitaxy reported previously. For a fully understanding of the obtained mutual orientation feature, the crystalline structures of PE and PEA have to be compared.

Similar to the PBA, it was reported that the PEA exhibits also two different crystalline forms^[42, 47, 48, 58, 59]. One of them is characterized by the aforementioned monoclinic unit cell, while the other one is reported to be the type of an orthorhombic unit cell with the dimensions of $a = 0.512$, $b = 0.841$, and $c = 1.228$ nm^[58, 59]. In our previous study about the epitaxial crystallization of PBA on highly oriented PE substrate, we found that in all cases the PBA crystallizes in its orthorhombic form with the chain axes of the PBA crystals parallel to the chain direction of the PE crystals. This has been well explained in terms of interchain distance matching between both polymers. However, we do not know whether the same orthorhombic unit cells of both PEA and PE plays also an important role in governing the epitaxial growth of PEA. For the present case, one can find excellent matching of both kinds of PEA with PE substrate. For example, the interchain distance of PEA in its orthorhombic form along a -axis matches very well with the interchain distance of PE along b -axes. The mismatching is 3.5%, well below the upper limit (15%) for the occurrence of polymer epitaxy as proposed by Lotz and Wittmann *et al*^[29]. On the other hand, even excellent matching is found between the interchain distances of PEA in its monoclinic form along the $[100]$ direction and PE along its b -axis direction. The discrepancy is only 1.2%. It is this better matching that results in the epitaxial growth of PEA on the PE substrate in its monoclinic form. This implies that crystallographic matching is more important for polymer epitaxy than the molecular chain packing way in the unit cell.

Another thing to be addressed is the lamellar arrangement of PEA grown on the PE substrate. The electron diffraction result clearly indicates a simple parallel chain alignment of both polymer chains. The AFM image shows, however, a crosshatched lamellar structure with the PEA lamellae *ca.* $\pm 66.5^\circ$ apart from the chain direction of the PE substrate crystals. This indicates a $\pm 23.5^\circ$ inclination of the PEA chains with respect to lamellar normal direction. It is actually reasonable when the lamellae with $\{00l\}$ fold surfaces is considered. As illustrated in the right part of Fig. 7, a chain folding in the $\{00l\}$ surface leads exactly to the formation of PEA lamellae 66.5° apart from the chain direction of the PE substrate crystals. This crosshatched structure should take the response for a remarkable property improvement of the PE/PEA system reported in Ref. [60], as also found for the PE/*i*PP system^[61, 62].

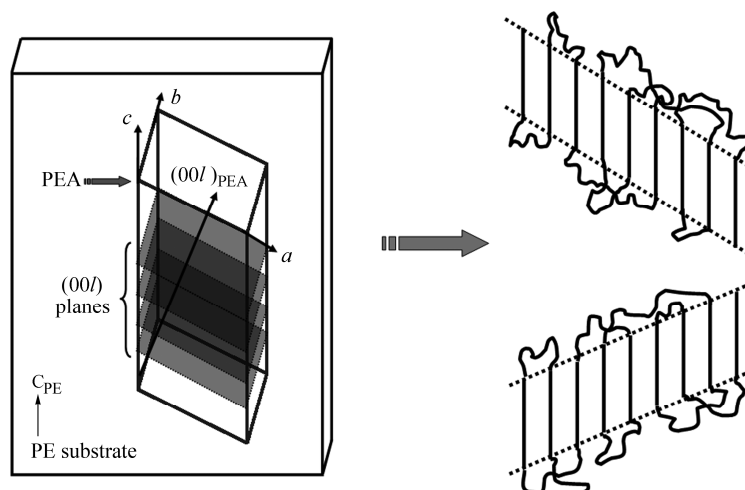


Fig. 7 A sketch of the crystal orientation of PEA with respect to the PE substrate and the chain folding way in the lamellar crystals

CONCLUSIONS

The crystallization behavior of PEA on highly oriented PE substrate both from solution and isotropic melt was investigated by means of optical microscopy, DSC, AFM and electron microscopy. The results clearly indicate that the PE substrate has strong nucleation ability toward PEA as revealed by the appearance of PEA transcrystalline layer at the PE boundary as well as the heteroepitaxy of PEA on the PE surface. The epitaxial crystallization of PEA on the PE substrate results in the formation of PEA edge-on lamellae with the long axes *ca.* $\pm 66.5^\circ$ apart from the chain direction of PE crystals. Electron diffraction result shows that PEA grows epitaxially on the PE substrate in its monoclinic form with its *ac* plane as the contact plane. The PEA molecular chains are aligned parallel to the chain direction of the PE substrate, which leads to the $(00l)$ diffractions of the PEA $\pm 23.5^\circ$ apart from the chain direction of PE substrate crystals. The combined AFM and electron diffraction results indicate that folding of the PEA chains in the lamellar crystals takes place in the $\{00l\}$ surfaces. Moreover, the epitaxy of PEA in its monoclinic form rather than orthorhombic form originates from a better matching and indicates that the similarity in the unit cell systems is not so important as the matching between the involving polymer pairs in governing the polymer epitaxy.

REFERENCES

- 1 Liu, F.P., Gardner, D.J. and Wolcot, M.P., *Langmuir*, 1995, 11: 2674
- 2 Brown, H.R., Char, K., Deline, V.R. and Green, P.F., *Macromolecules*, 1993, 26: 4155
- 3 Green, P.F., Palmström, C.J., Mayer, J.W. and Kramer, E.J., *Macromolecules*, 1985, 18: 501

- 4 Klein, J., *Science*, 1990, 250: 640
- 5 Frank, C.W., Rao, V., Despotopoulou, M.M., Rease, R.F.W., Hinsberg, W.D., Miller, R.D. and Rabolt, J.F., *Science*, 1996, 273: 912
- 6 Forrest, J.A., Dalnoki-Veress, K. and Dutcher, J.R., *Phys. Rev. E*, 1997, 56: 5705
- 7 Forrest, J.A. and Mattson, J., *Phys. Rev. E*, 2000, 61: R53
- 8 DeMaggio, G.B., Frieze, W.E., Gidley, D.W., Zhu, M., Hristov, H.A. and Yee, A.F., *Phys. Rev. Lett.*, 1997, 78: 1524
- 9 Kim, J.H., Jang, J. and Zin, W.C., *Langmuir*, 2001, 17: 2703
- 10 Fryer, D.S., Nealey, P.F. and de Pablo, J.J., *Macromolecules*, 2000, 33: 6439
- 11 Torres, J.A., Nealey, P.F. and de Pablo, J.J., *Phys. Rev. Lett.*, 2000, 85: 3221
- 12 Frank, B., Gast, A.P., Russell, T.P., Brown, H.R. and Hawker, C., *Macromolecules*, 1996, 29: 6531
- 13 Zheng, X., Rafailovich, M.H., Sokolov, J., Strzhemechny, Y., Schwarz, S.A., Sauer, B.B. and Rubinstein, M., *Phys. Rev. Lett.*, 1997, 79: 241
- 14 Zheng, X., Sauer, B.B., van Alsten, J.G., Schwarz, S.A., Rafailovich, M.H., Sokolov, J. and Rubinstein, M., *Phys. Rev. Lett.*, 1995, 74: 407
- 15 Russell, T.P. and Kumar, S.K., *Nature*, 1997, 386: 771
- 16 Lin, E.K., Kolb, R., Satija, S.K. and Wu, W.L., *Macromolecules*, 1999, 32: 3753
- 17 Reiter, G. and Sommer, J.U., *Phys. Rev. Lett.*, 1998, 80: 3771
- 18 Schönherr, H. and Frank, C.W., *Macromolecules*, 2003, 36: 1199
- 19 Despotopoulou, M.M., Frank, C.W., Miller, R.D. and Rabolt, J.F., *Macromolecules*, 1996, 29: 5797
- 20 Chai, L.G., Li, L., Liao, Q. and Yan, S.K., *Acta Polym. Sin. (in Chinese)*, 2012, (11): 1342
- 21 Seifert, H., "In Structure and properties of solid surfaces", University of Chicago Press, Chicago, 1953, p. 318
- 22 Bonev, I., *Acta Crystallogr., Sect. A*, 1972, 28: 508
- 23 Zhang, J., Yang, D., Thierry, A., Wittmann, J.C. dan Lotz, B., *Macromolecules*, 2001, 34: 6261
- 24 Wittmann, J.C. and Lotz, B., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, 19: 1837
- 25 Wittmann, J.C. and Lotz, B., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, 19: 1853
- 26 Kopp, S., Wittmann, J.C. and Lotz, B., *Polymer*, 1994, 35: 908
- 27 Kopp, S., Wittmann, J.C. and Lotz, B., *Polymer*, 1994, 35: 916
- 28 Wittmann, J.C. and Lotz, B., *Prog. Polym. Sci.*, 1990, 15: 909
- 29 Jiang, S., Qian, H., Liu, W., Wang, C., Wang, Z., Yan, S. and Zhu, D., *Macromolecules*, 2009, 42: 9321
- 30 Dong, H., Li, H., Wang, E., Wei, Z., Xu, W., Hu, W. and Yan, S., *Langmuir*, 2008, 24: 13241
- 31 Wang, T.C., Li, H.H. and Yan, S.K., *Chinese J. Polym. Sci.*, 2012, 30(2): 269
- 32 Lovinger, A.J., *Polymer*, 1981, 22: 412
- 33 Sun, Y., Li, H., Huang, Y., Chen, E., Zhao, L., Gan, Z. and Yan, S., *Macromolecules*, 2005, 38: 2739
- 34 Yan, C., Li, H., Zhang, J., Ozaki, Y., Shen, D., Yan, D., Shi, A. and Yan, S., *Macromolecules*, 2006, 39: 8041
- 35 An, Y.K., Jiang, S.D., Yan, S.K., Sun J.R. and Chen, X.S., *Chinese J. Polym. Sci.*, 2011, 29(4): 513
- 36 Fuller, C.S. and Erickson, C.L., *J. Am. Chem. Soc.*, 1937, 59: 344
- 37 Fuller, C.S. and Erickson, C.L., *J. Am. Chem. Soc.*, 1939, 61: 2575
- 38 Fuller, C.S. and Erickson, C.L., *J. Phys. Chem.*, 1939, 43: 323
- 39 Minke, R. and Blackwell, J., *J. Macromol. Sci. Phys.*, 1979, B16: 407
- 40 Minke, R. and Blackwell, J., *J. Macromol. Sci. Phys.*, 1980, B18: 233
- 41 Petermann, J. and Gohil, R.M., *J. Mater. Sci.*, 1979, 14: 2260
- 42 Woo, E.M., Wu, P.L., Wu, M.C. and Yan, K.C., *Macromol. Chem. Phys.*, 2006, 207: 2232
- 43 Wittmann, J.C. and Lotz, B., *J. Polym. Sci., Polym. Phys. Ed.*, 1985, 23: 205
- 44 Yan, S. and Petermann, J., *Polym. Bull.*, 1999, 43:75
- 45 Yan, S., Späth, T. and Petermann, J., *Polymer*, 2000, 41: 4863
- 46 Wu, J., Zhou, H.X., Liu, Q. and Yan S.K., *Chinese J. Polym. Sci.*, 2013, 31(6): 841
- 47 Hobbs, S.Y. and Billmeyer Jr, F.W., *J. Polym. Sci.*, 1969, A-2: 1119
- 48 Turner-Jones, A. and Bunn, C.W., *Acta Cryst.*, 1962, 15: 105

- 49 Takahashi, T. and Ogata, N., *J. Polym. Sci., Polym. Phys. Ed.*, 1971, 9: 895
- 50 Takahashi, T., Inamura, M. and Tsujimoto, I., *J. Polym. Sci., Polym. Phys. Ed.*, 1970, 8: 651
- 51 Fenwick, D., Smith, P. and Wittmann, J.C., *J. Mater. Sci.*, 1996, 31: 128
- 52 Richards, R.B., *J. Polym. Sci.*, 1951, 6: 397
- 53 Yan, S., Yang, D. and Petermann, J., *Polymer*, 1998, 39: 4569
- 54 Yan, S., Yang, D. and Petermann, J., *J. Polym. Sci., Polym. Phys. Ed.*, 1997, 35: 1415
- 55 Yan, S., *Macromolecules*, 2003, 36: 339
- 56 Petermann, J., Xu, Y., Loos, J. and Yang, D., *Polymer*, 1992, 33: 1096
- 57 Schumacher, M., Lovinger, A.J., Agarwal, P., Wittmann, J.C. and Lotz, B., *Macromolecules*, 1994, 27: 6956
- 58 Yang, J., Pan, P., Dong, T. and Inoue, Y., *Polymer*, 2010, 51: 807
- 59 Satoh, M., *Polym. Prepr. Jpn.*, 2008, 57: 460
- 60 Im, S.S., Kim, T.J., Han, S., Moon, T.J. and Bae, Y.C., *J. Appl. Polym. Sci.*, 1997, 65: 1745
- 61 Gross, B. and Petermann, J., *J. Mater. Sci.*, 1984, 19: 105
- 62 Petermann, J., Broza, G., Rieck, U. and Kawaguchi, A., *J. Mater. Sci.*, 1987, 22: 1477