

CRYSTALLIZATION BEHAVIOR OF POLYLACTIDE ON HIGHLY ORIENTED POLYETHYLENE THIN FILMS*

Yu-kuan An

Department of Physics, Binzhou Medical College, Yantai 264003, China

Shi-dong Jiang and Shou-ke Yan**

*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology,
Beijing 100029, China*

Jing-ru Sun and Xue-si Chen

*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China*

Abstract The crystalline structure and morphology of the PLA crystallized isothermally from the glassy state on highly oriented PE substrates at 130°C were investigated by means of optical microscopy, AFM and X-ray diffraction. The results indicate that the PE substrate influences the crystallization behavior of PLA remarkably, which leads to the growth of PLA crystals on PE substrate always in edge-on form rather than the twisted lamellar crystals from edge-on to flat-on when crystallizing the PLA on glass surface under the same condition. The edge-on PLA lamellae on the PE substrate are preferentially arranged with their long axes in the chain direction of the PE substrate crystals. It is further demonstrated that except for the different crystal orientation, the PE does not influence the crystalline modification and crystallinity of the PLA.

Keywords: Polyethylene; Poly(lactide); Induced crystallization; Morphology; Orientation.

INTRODUCTION

Poly(lactide) (PLA), as a biodegradable and biocompatible polymer, has attracted much attention. It is produced from renewable resources, such as corn starch, and exhibits comparable mechanical performance to those of petroleum-based traditional polymers^[1–7]. In the past decades, PLA has been successfully applied in the products of routine life, *e.g.* cups and packaging. Recently, this environmentally friendly polymer is under development for further more advantageous applications^[8–10]. To this end, controlled property tailoring is essentially required.

Generally, the mechanical and thermal properties of a semi-crystalline polymer depend strongly on its crystalline and phase morphologies. As an example, the mechanical and physical properties of the oriented polymeric materials may exceed those of their isotropic species by orders of magnitude and demonstrate an anisotropic feature^[11–15]. Moreover, the crystalline structure is another important factor, which influences the property even functionality of the polymeric materials. For example, the α -phase poly(vinylidene fluoride) with helical chain conformation can only be used as general plastics, while its β -counterpart has attracted the widest

* The work was financially supported by the National Natural Science Foundations of China (Nos. 50833006, 20634050 and 50973008) and the 47th postdoctoral granted financial support from China Postdoctoral Science Foundation (No. 20100470191).

** Corresponding author: Shou-ke Yan (闫寿科), E-mail: skyan@mail.buct.edu.cn

Received September 14, 2010; Revised September 29, 2010; Accepted October 11, 2010

doi: 10.1007/s10118-010-1028-0

interest due to its extensive piezo- and pyroelectric applications^[16–22]. This leads to the study on crystallization behavior and the resultant morphologies of semicrystalline polymers an everlasting research topic in the field of polymer physics. As a consequence, the crystallization and crystalline morphologies of PLA have also been extensively investigated in the past decades. Through systematic studies, it is now well known that the PLA can generate different crystalline structures, designated as α , α' , β and γ forms, depending on thermal and mechanical treatments^[23–29]. It should be pointed out that the early studies are mostly performed with PLA bulk materials. Crystallization of a polymer in contact with a heterogeneous surface can be quite different from that of bulk crystallization. The foreign surface may affect both the crystallization kinetics and the crystalline structure, and therefore influence the properties of the polymer material. A special case is known as polymer epitaxy^[30–32], which has already been widely employed for controlling the crystalline structure and orientation of a wide variety of crystallizable materials^[33–35]. Taking these into account, studies on the surface induced crystallization of PLA are of great significance for the aim of its structure regulation. To our best knowledge, there is, however, only one report dealing with the surface induced crystallization of PLA by hexamethylbenzene substrate^[26].

In the present work, the crystalline morphology of PLA induced by the oriented high-density polyethylene was studied in detail. Preferred orientation of the PLA crystals grown on highly oriented PE surface has been unambiguously demonstrated. It should be pointed out, however, unlike any other formerly studied systems, the PLA lamellae grow in the direction parallel to the chain direction of the PE substrate crystal. In other words, a perpendicular chain orientation of PLA and PE is obtained. This provides a first example of the perpendicular chain epitaxy and may improve the mechanical property of the system tremendously since the lamellae of one component bridging the crystalline and amorphous regions of the other component^[35, 36]. Here we describe the detailed experimental procedure and present the unusual crystallization behavior of PLA on highly oriented PE substrate.

EXPERIMENTAL

Materials and Sample Preparation

Commercial grade polylactide (PLA), Revode213H, with weight-average molecular weight (M_w) = 6.5×10^5 and polydispersity of 2.1 was obtained from Zhejiang Hisun Biomaterials Co., Ltd. The glass transition temperature of it was estimated by DSC as 60°C. High-density polyethylene (PE), Lupolen 6021DX, was obtained from BASF AG Ludwigshafen, Germany. The melting point of the used PE is measured by DSC to be 136°C. Highly oriented thin film of PE was prepared according to a melt-draw technique introduced by Petermann and Gohil^[30]. As illustrated in Fig. 1, a small amount of a 0.5 wt% solution of PE in xylene was dispersed uniformly on a preheated glass plate at 130°C. The xylene solvent was allowed to evaporate at this preparation temperature. After evaporation of the solvent, the thin molten PE layer of *ca.* 1 μm was then picked up by a motor-driven cylinder with a drawing speed of about 2 cm/s. In this way, we get highly oriented ultrathin PE films with thickness of *ca.* 50 nm.

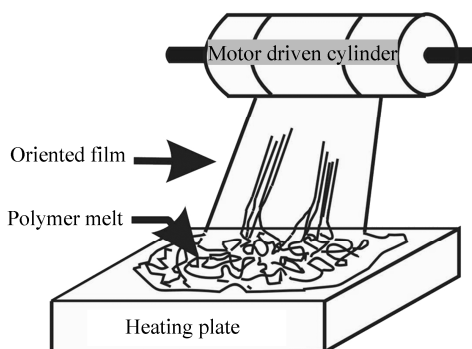


Fig. 1 A sketch for the preparation procedure of the highly oriented PE substrate films

Samples for optical microscopy and wide-angle X-ray diffraction (WAXD) observations were prepared by dipping glass slides covered with oriented PE thin films into a 2 wt% PLA/chloroform solution and then dried at room temperature for several days by evaporation of the chloroform. The obtained thin PLA layers of about 10 μm in thickness are initially in amorphous phase as reported in Ref. [37]. It has also been demonstrated by X-ray diffraction, which is not shown here since no any signals have been observed. Actually, the occurrence of epitaxial crystallization of it on the PE substrate already confirms its amorphous status unambiguously; otherwise it will remain in its initial crystalline state. The crystallization of PLA was realized by heating the as-prepared samples from room temperature to 130°C for 24 h, which enables an isothermal cold crystallization of PLA. For a direct comparison of the different crystallization behaviors of PLA on PE and glass surfaces, the glass slides were only partially covered by the oriented ultrathin PE films, which provide the possibility to put the PLA grown on PE and glass slide at exactly the same thermal conditions in the same view field. Samples for atomic force microscopy (AFM) observations were prepared by spin-coating a 1 wt% PLA/chloroform solution on the surface of mica supported PE oriented films. The PLA layers obtained in this way are about 100 nm in thickness. The AFM samples have subjected the same thermal treatment as the optical microscopy samples.

Characterization

For optical microscopy observation, an Axioskop40 optical microscope (Carl Zeiss, Germany) equipped with a Linkam THMS600 hot stage was used in this study. All pictures presented here were taken under crossed polarizers.

Fine structure on lamellar scale was obtained using an Agilent 5500 AFM (Agilent Technologies), which is specially designed for probing polymer materials. The AFM was operated in tapping mode using silicon cantilevers with spring constant of 20–30 N/m. The resonance frequencies were set as 140–160 kHz. The scan speed varied from 0.5 line/s to 1.0 line/s. The set-point ratio and amplitude were chosen such that the surface was tracked while maintaining the necessary contrast in the phase images.

Wide-angle X-ray diffraction experiments were carried out using a 12 kW rotating-anode generator (Cu K α) in combination with a Geigerflex D/max-RB diffractometer (Bruker AXS). The reflection peak positions and widths were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). Powder patterns were taken within the 2θ angle region of 5° – 30° at a scan rate of 10 ($^\circ$)/min. Background scattering was recorded and subtracted from the sample patterns.

RESULTS AND DISCUSSION

The surface morphology of the melt-drawn PE substrate films was first examined by AFM in tapping mode. Presented in Fig. 2 are the representative AFM height (part a) and phase (part b) images of the highly oriented PE films. The white arrow shows the drawing direction during film preparation. From both height and phase images, it can be clearly seen that the obtained PE substrate film consists of highly oriented lamellar structure with the closely packed crystalline lamellae arranged perpendicular to the drawing direction. This is in good accordance with the infra red spectroscopy and transmission electron microscopy results reported in Ref. [38]. The average thickness of the PE lamellae is measured to be about 20 nm. The lateral width of the highly oriented PE lamellae is estimated to be hundreds of nanometers. Moreover, the AFM results demonstrate that the melt-drawn PE films exhibit relatively smooth surfaces with height difference of only few nanometers, which is ideal for investigating the surface induced crystallization behavior of other polymers.

The morphology of PLA cold crystallized, *i.e.* crystallized from its amorphous state, on highly oriented PE substrate was first observed by optical microscope. Figure 3(a) presents an optical micrograph of the PLA isothermally crystallized at 130°C for 24 h. It presents the morphologies of PLA crystallized on both the PE oriented film and the glass surface, since the glass slide is only partially covered by the oriented PE film. The PE thin film locates at the upper left corner of Fig. 3(a). The boundary line of it can be recognized with careful inspection. The white arrow near and parallel to the boundary line indicates the drawing direction of the oriented PE thin film during preparation, *i.e.* the direction of its molecular chain orientation. The polarizer and analyzer

are aligned in the horizontal and vertical directions, respectively. Since the PE substrate film is too thin to give much birefringence contribution, the contrast of the optical micrograph comes from the PLA crystals, indicating the transition of PLA from amorphous state into crystalline phase. From Fig. 3(a), it can be seen that crystallization on the glass substrate, irregular spherulitic structure of PLA has been produced, see lower right corner of Fig. 3(a). The morphology of PLA crystallized on the PE surfaces is somewhat different from that on the glass slide. First of all, the PLA crystals created on the PE substrate exhibit a much stronger birefringence than that formed on the glass slide, as it can be observed by comparing the upper left with the lower right corners of the Fig. 3(a). This may be caused either by the different crystalline modification and crystallinity or the different spatial arrangement of the PLA crystals on the PE and glass substrates. With careful inspection, some domains of the PLA on the highly oriented PE substrate show lath-like structures, as indicated by the circles. They may be composed of PLA lamellar aggregates and imply some preferred orientation of the PLA crystals. This has been confirmed by the exceptional extinction phenomenon during the rotation of the sample around light beam axis. As illustrated in Fig. 3(b), a 45° anticlockwise rotation of the sample results in a remarkable birefringence reduction of the PLA crystals on PE substrate, while the contrast of the PLA crystals on the glass substrate does not change much. This indicates unambiguously that the PE substrate can induce the crystallization of PLA in an unusual way as compared with the glass substrate.

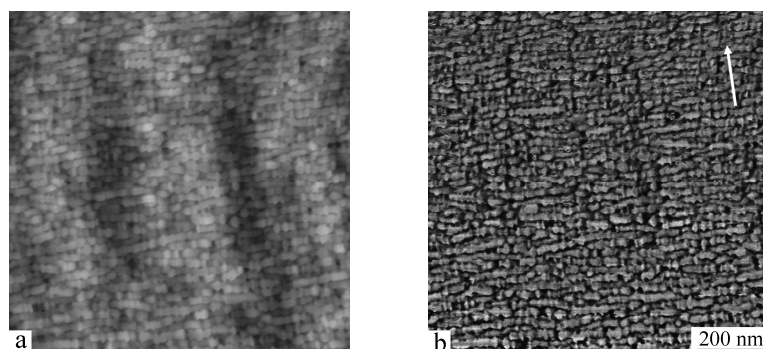


Fig. 2 Height (a) and phase (b) AFM images of the melt-drawn PE ultrathin films. The white arrow represents the drawing direction during film preparation.

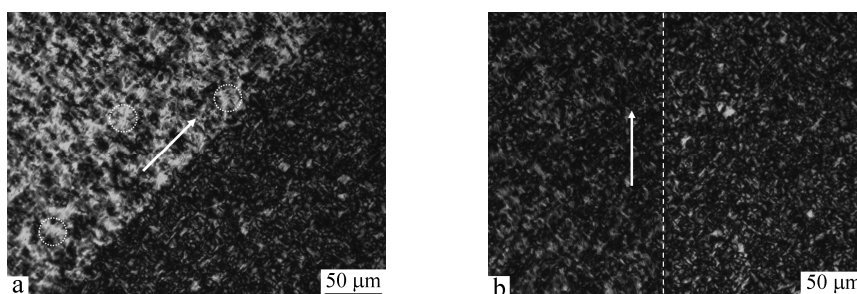


Fig. 3 (a) An optical micrograph of PLA cold crystallized on the PE and glass substrates at a boundary region (The PE substrate is located in the upper left corner of the picture. The arrow indicates the molecular chain direction of PE substrate); (b) Another optical micrograph taken from the same area as part (a) but rotated 45° anticlockwise about the light beam.

The polarizer and analyzer are aligned in the horizontal and vertical directions, respectively.

It should be pointed out that a 45° anticlockwise rotation of the sample shown in Fig. 3(a), which produces a status of the sample as shown in Fig. 3(b), leads to a parallel alignment of the PE chain direction in the analyzer direction. According to the extinction rule of the optical microscope under crossed-polarizers, a reduction of the birefringence of the PLA crystals on the PE substrate indicates that the PLA crystals created on

the PE substrate are oriented with their molecular chains either parallel or perpendicular to the chain direction of the PE substrate. To find out the mutual orientation relationship between PLA and PE, fine structures of PLA crystallized on the PE and glass substrates are monitored by AFM at a lamellar scale. As presented in Fig. 4, the morphologies of PLA crystallized on highly oriented PE and glass substrates are quite different. On the glass slide, see Figs. 4(a) (height image) and 4(b) (phase image), the PLA grows in spherulitic structure. At the centre of the spherulite, *i.e.* the crystalline nucleus, edge-on crystalline lamellae are observed. As the edge-on lamellae splay outward, lamellar twisting takes place, which leads to the transition from edge-on to flat-on lamellae of PLA. At the boundary region of the PLA spherulite, flat-on lamellar crystals with smooth surface are the solely observed morphology. This is the reason why the PLA crystals grown on glass slide display relatively weaker birefringence as compared with that on PE substrate. Moreover, the lamellar thickness measured from the flat-on PLA crystals is approximately 15 nm. On the contrary, the PLA crystallized on the oriented PE substrate possesses completely different morphology. First, as illustrated in Figs. 4(c) and 4(d), the PLA crystallizes always in edge-on lamellae at any place. These edge-on lamellae are thicker than the flat-on lamellae formed on glass slide, 20 nm *vis* 15 nm. Second, the edge-on PLA lamellae are preferentially parallel aligned rather than compose a spherulitic structure. Third, the parallel aligned PLA lamellae are mostly oriented with the long axis in the chain direction of the PE substrate crystals. This indicates the existence of special interaction between the PLA and PE molecules, which results in an epitaxial crystallization of PLA with chain axis perpendicular to the chain direction of the PE substrate crystals, if a {001} fold surface of PLA crystals is accepted. For this kind of orientation, a complete extinction of the PLA crystals under crossed-polarizers with the chain direction along either the polarizer or analyzer is expected. This is actually not the case. As can be seen from Fig. 3(b), there are still some birefringence of the PLA crystals grown on PE substrate even when the PE molecular chains are aligned in the analyzer direction, which corresponds to a parallel alignment of the PLA chains with the polarizer.

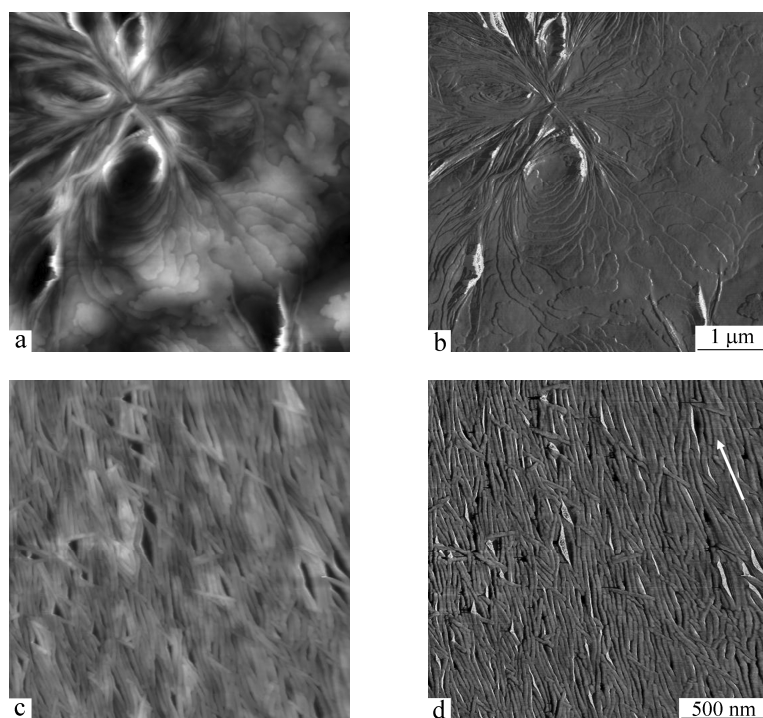


Fig. 4 AFM height (a, c) and phase (b, d) images showing the different morphologies of PLA crystallized on glass (a, b) and PE (c, d) substrates

The molecular chain direction of the PE crystals is indicated by a white arrow; The thermal history of the sample is the same as that of Fig. 3.

This should be caused by the large film thickness for optical microscopy observation. Considering that the epitaxial crystallization takes place in a thin layer directly in contact with the substrate^[39, 40], the top layer of the PLA could be unaffected by the PE substrate and crystallized in a random oriented way. Actually, even in the thin film used for AFM study, there are already some lamellae being deviated from the chain direction of the PE substrate, see Figs. 4(c) and 4(d).

The above experimental results indicate that the PE can induced epitaxial crystallization of PLA, which leads to the PLA lamellar crystals oriented preferentially with the lamellar long axis parallel to the chain direction of the PE substrate crystals. This causes the PLA crystals with different birefringence under optical microscope depending on sample orientation with respect to the polarizer. It is also different from the PLA crystals grown on glass substrate. Possibilities relating to the contrast difference of the PLA crystals grown on PE and glass substrates may also rest on the different crystallinity or/and crystalline modification. To clarify this, X-ray diffractions of the PLA crystals crystallized on the PE and glass substrates were performed. Figure 5 shows the X-ray diffraction profiles corresponding to the PLA crystals formed on PE and glass substrates, respectively. The diffraction peaks are contributed by the PLA crystals since the used PE substrate film is too thin (*ca.* 50 nm in thickness) to give any diffractions at present condition. From Fig. 5, it is clear that the PLA crystallized on PE and glass surface from the glassy state exhibits exactly the same crystalline structure also with similar crystallinity. The diffraction peaks at $2\theta = 14.8^\circ$, 16.7° , 19.1° ascribed to the (010), (200 or 110), (203) lattice planes of α -PLA crystals indicate that the PLA crystallizes both on glass and PE substrates in its α -form^[6]. This demonstrates that the morphological differences viewed by optical microscope are solely caused by different spatial arrangement of the produced PLA crystals.

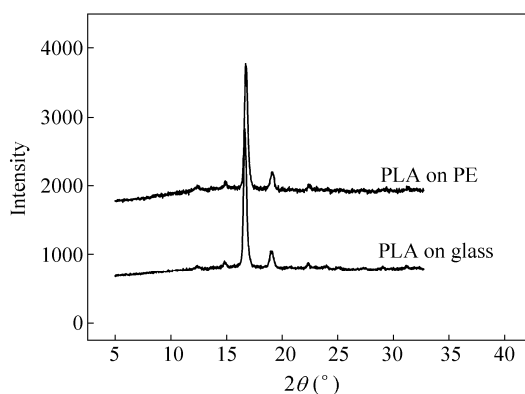


Fig. 5 X-ray diffraction profiles of the PLA crystals formed on PE and glass substrates, respectively. The thermal history of the samples is the same as that of Fig. 3.

CONCLUSIONS

The crystalline structures and morphologies of the PLA crystallized isothermally on glass and highly oriented PE substrates at 130°C were investigated by means of optical microscopy, AFM and X-ray diffraction. The optical microscopy observation shows that the PE substrate exhibits special effect on the crystallization of PLA as revealed by the oriented crystallization of PLA on the PE substrate. This leads to the crystallization of PLA on PE substrate always in edge-on structure, while lamellar twisting from edge-on to flat-on takes place when crystallizing the PLA on glass surface under the same condition. The edge-on PLA lamellae on the PE substrate are preferentially arranged in the chain direction of the PE substrate crystals with only a few exceptions. The X-ray diffraction results indicate that, except for the different crystal orientation, the PLA grown on the two different substrates exhibits the same crystalline modification with similar crystallinity. The origin of the unusual alignment of PLA on PE substrate is not clear at present. Detailed electron microscopy studies on the exact mutual crystalline orientation relationship and its formation mechanism are now under way.

REFERENCES

- 1 Ikada, Y. and Tsuji, H., *Macromol. Rapid Commun.*, 2000, 21: 117
- 2 He, Y., Fan, Z.Y., Hu, Y.F., Wu, T., Wei, J. and Li, S.M., *Eur. Polym. J.*, 2007, 43: 443
- 3 Zhao, Y.A., Li, X.R. and Yuan, X.Y., *Acta Polymerica Sinica*(in Chinese), 2008, (2): 405
- 4 Yao, J.Y., Yang, Q.F., Shu, X.J., Zhang, A.J. and Du, J.H., *Acta Polymerica Sinica*(in Chinese), 2008, (10): 929
- 5 Zhang, J.M., Tashiro, K., Tsuji, H. and Domb, A.J., *Macromolecules*, 2008, 41: 1352
- 6 Li, X.J., Zhong, G.J. and Li, Z.M., *Chinese J. Polym. Sci.*, 2010, 28(3): 357
- 7 Lu, Y., Wei, R.Q. and Liu, X.N., *Acta Polymerica Sinica*(in Chinese), 2009, (1): 66
- 8 Zhang, W.X. and Wang, Y.Z., *Chinese J. Polym. Sci.*, 2008, 26(4): 425
- 9 Yuan, X.B., Kang, C.S., Zhao, Y.H., Gu, M.Q., Pu, P.Y., Tian, N.J. and Sheng, J., *Chinese J. Polym. Sci.*, 2009, 27(2): 231
- 10 Liu, A.X., Wei, J.C., Chen, X.S. and Jing, X.B., *Chinese J. Polym. Sci.*, 2009, 27(3): 415
- 11 Smith, P. and Lemstra, P., *J. Mater. Sci.*, 1980, 15: 505
- 12 Oh, S.Y., Akagi, K. and Shirakawa H., *Synth. Met.*, 1989, 32: 245
- 13 Gagnon, D.R., Karasz, F.E., Thomas, E.L. and Lenz, R.W., *Synth. Met.*, 1987, 20: 245
- 14 Andreatta, A., Tokito, S., Smith, P. and Heeger, A., *J. Molec. Cryst. Liq. Cryst.*, 1990, 189: 169
- 15 Lovinger, A.J., *Science*, 1983, 220: 1115
- 16 Prest, J.W.M. and Luca, D.J., *J. Appl. Phys.*, 1978, 49: 5042
- 17 Matsushige, K., Nagata, K. and Takemura, T., *Japan. J. Appl. Phys.*, 1978, 17: 467
- 18 Lovinger, A.J., *Polymer*, 1980, 21: 1317
- 19 Lovinger, A.J., *J. Appl. Phys.*, 1981, 52: 5934
- 20 Lovinger, A.J., *Macromolecules*, 1981, 14: 322
- 21 Takahashi, Y., Matsubara, Y. and Tadokoro, H., *Macromolecules*, 1982, 15: 334
- 22 Lovinger, A.J., *Polymer*, 1987, 28: 617
- 23 De Santis, P. and Kovacs, J., *Biopolymers*, 1968, 6: 299
- 24 Hoogsteen, W., Postema, A.R., Pennings, A.J., Ten Brinke, G. and Zugenmaier, P., *Macromolecules*, 1990, 23: 634
- 25 Kalb, B. and Pennings, A.J., *Polymer*, 1980, 21: 607
- 26 Cartier, L., Okihara, T., Ikada, Y., Tsuji, H., Puiggali, J. and Lotz, B., *Polymer*, 2000, 41: 8909
- 27 Puiggali, J., Ikada, Y., Tsuji, H., Cartier, L., Okinara, T. and Lotz, B., *Polymer*, 2000, 41: 8921
- 28 Zhang, J.M., Duan, Y.X., Sato, H., Tsuji, H., Noda, I., Yan, S.K. and Ozaki, Y., *Macromolecules*, 2005, 38: 8012
- 29 Cho, T.Y. and Strobl, G., *Polymer*, 2006, 47: 1036
- 30 Peterman, J. and Gohil, R.M., *J. Mater. Sci.*, 1979, 14: 2260
- 31 Seifert, H., "Structure and properties of solid surfaces", University of Chicago Press, Chicago, 1953
- 32 Bonev, I., *Acta Crystallogr, Sect A*, 1972, 28: 508
- 33 Lovinger, A.J., *Polymer*, 1981, 22: 412
- 34 Wittmann, J.C. and Lotz, B., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, 19: 1853
- 35 Sun, Y.J., Li, H.H., Huang, Y., Chen, E.Q., Zhao, L.F., Gan, Z.H. and Yan, S.K., *Macromolecules*, 2005, 38: 2739
- 36 Chang, H., Zhang, J., Li, L., Wang, Z., Yang, C., Takahashi, I., Ozaki, Y. and Yan, S., *Macromolecules*, 2010, 43: 362
- 37 Zhang, J.M., Tsuji, H., Noda, I. and Ozaki, Y., *Macromolecules*, 2004, 37: 643
- 38 Yan, C., Zhang, J.M. and Yan, S.K., *Chinese Science Bulletin*, 2006, 51: 1751
- 39 Yan, S.K., Lin, J., Yang, D.C. and Petermann, J., *J. Mater. Sci.*, 1994, 29: 1773
- 40 Yan, S.K., Lin, J., Yang, D.C. and Petermann, J., *Macromol. Chem. Phys.*, 1994, 195(1): 195