Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 45 (2004) 3967–3972

polymer

www.elsevier.com/locate/polymer

Ordering-induced micro-bands in thin films of a main-chain liquid crystalline chloro-poly(aryl ether ketone)☆

Shanju Zhang[a], Luxiang Fu[a], Jian Zhang[a], Jingjiang Liu[a], Decai Yang[a,*], Jason J. Ge[b], Christopher Y. Li[c], Stephen Z.D. Cheng[b*]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*
[b]*Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA*
[c]*Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA*

Received 13 June 2003; received in revised form 2 January 2004; accepted 2 January 2004

Abstract

Micro-banded textures developed from thin films of a main-chain thermotropic liquid crystalline chloro-poly(aryl ether ketone) in the melt were investigated using transmission electron microscopy (TEM), selective area electron diffraction, and atomic force microscopy techniques. The micro-banded textures were formed in the copolymer thin films after annealing at temperatures between 320 and 330 °C, where a highly ordered smectic crystalline phase is formed without mechanical shearing. The micro-banded textures displayed a sinusoidal-like periodicity with a spacing of 150 nm and an amplitude of 2 nm. The long axis of the banded texture was parallel to the *b*-axis of an orthorhombic unit cell. In the convex regions, the molecular chains exhibited a homeotropic alignment, i.e. the chain direction was parallel to the film normal. In the concave regions, the molecular chains possessed a tilted alignment. In addition to the effects of annealing temperatures and times, the thickness of the film played a vital role in the formation of the banded texture. A possible formation mechanism of this banded texture was also suggested and discussed. It was suggested that the micro-bands were formed during cooling.

Keywords: Chloro-poly(aryl ether ketone); Liquid crystalline polymer; Banded texture

1. Introduction

Control of molecular and supra-molecular ordering is of central significance in academic studies and some applications of small molecular liquid crystals and liquid crystalline (LC) polymers. For example, molecular alignment played an integral part in the development of liquid crystal devices, and the preferred molecular orientation is described as the director (or vector) [1]. Depending on the nature of the interactions of LC molecules in films with substrate surfaces, two limiting cases to describe the molecular alignment exist: homogeneous orientation with the chain molecules being perpendicular to the film normal, and homeotropic alignment with the director parallel to the film normal [2]. In most cases, a uniform orientation of the LC molecules can be induced via chemically or physically modifying surface, as well as, external mechanical, electric, or magnetic fields [3–7]. The resulting periodic banded structure, which shows an alternation in the molecular director, is commonly observed in lyotropic and thermotropic LC polymers.

During the past two decades, much attention has been paid to the banded structures formed in LC polymers by mechanical shearing [8–18]. It was shown that the banded textures were formed during the chains relaxation after the shear, and the bands were perpendicular to the shear direction in polarized light microscopy (PLM) and transmission electron microscopy (TEM). The bands had a periodicity ranging from 0.5 to 10 μm, depending on the nature of LC polymers and shearing rates. In general, it has been understood that the molecular and texture elasticity were the source of band formation [19,20].

Recently, it was reported that banded structures in LC

☆ For the occasion of the 75th birthday of Professor Richard Boyd for his pioneer contributions in polymer solid state physics.

* Corresponding authors.

E-mail addresses: dcyang@ns.ciac.jl.cn (D. Yang), scheng@uakron.edu (S.Z.D. Cheng).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.01.083

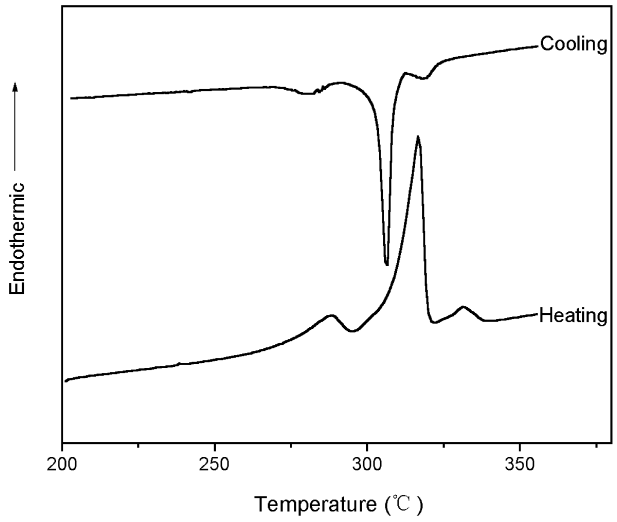


Fig. 1. DSC curves of Cl-*co*PEK during cooling and subsequent heating at scanning rates of 10 °C/min.

polymers were formed without mechanical shearing [21–25]. Therefore, the concept of crystallization-induced bands was introduced [21]; specifically, the bands arose from the volume change on the crystallization of sufficiently enlarged domains. In this case, the energy associated with excess free volume contributed to the buckling in forming the banded structures. Multiple banded textures on different length scales have also been observed in similar conditions [22]. Solidification-induced banded textures in non-crystallizable polymers have also been reported. The banded textures were generated during quenching from the oriented nematic phase to below the glass transition temperatures [23–25]. However, it is possible that the crystallization/solidification-induced banded textures possess different formation mechanisms, than those induced by mechanical shearing. Moreover, the molecular alignment of the banded textures reported thus far, irrespective of whether caused by the shearing-induced or the crystallization/solidification-induced, exhibit homogeneous orientation (the molecular chains are perpendicular to the film normal).

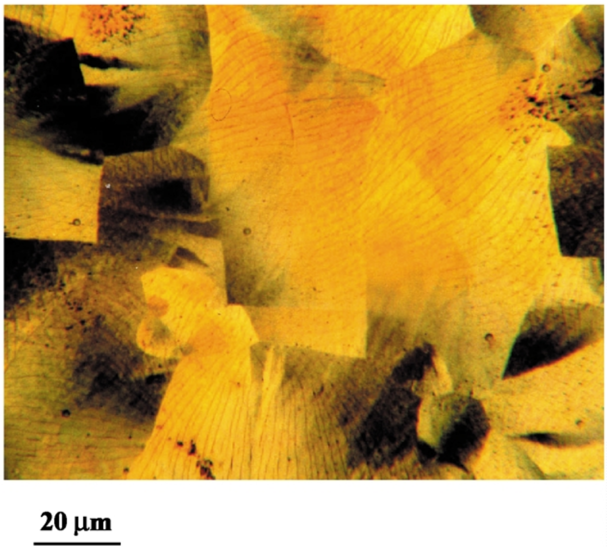


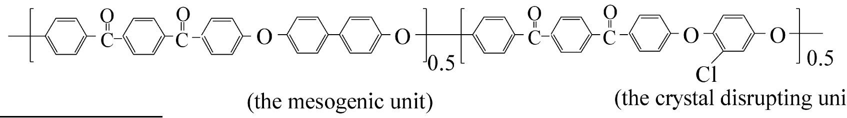
Fig. 2. PLM micrograph of the mosaic texture of Cl-*co*PEK in its highly ordered smectic crystal phase.

In our previous papers, we have reported that main-chain LC copoly(aryl ether ketone)s possessed highly ordered smectic LC phase behaviors and exhibited abundant LC textures in PLM such as schlieren, grainy, focal-conic, fan-shaped, mosaic, and spiral textures [26–28]. In particular, one of the copoly(aryl ether ketone)s that contained a chloro-pendent group, exhibited two main first order thermodynamic transitions: a crystal-to-highly ordered LC transition (T_m) at 318 °C, and a highly ordered LC-to-isotropic melt transition (T_i) at 333 °C measured by differential scanning calorimetry as shown in Fig. 1. The lower temperature transition at 285 °C might be associated with the existence of a crystal polymorphous. The highly ordered LC phase showed a mosaic optical texture between T_m and T_i as shown in Fig. 2 [26–28]. In this publication, we report our most recent study on the formation of ordered structures in inducing micro-bands in thin films of this copolymer. The molecular alignment in the banded region was homeotropic or tilted from the film normal direction as determined by TEM, selective area electron diffraction (SAED), and atomic force microscopy (AFM) techniques. A possible explanation for the formation of the micro-banded texture was also proposed.

2. Experimental section

2.1. Materials and sample preparation

The random chloro-copoly(aryl ether ketone) used in this investigation was synthesized by a nucleophilic substitution reaction based on 4,4′-biphenol and chlorohydroquinone with 1,4-bis(*p*-fluorobenzoyl)benzene [29–31], and abbreviated as Cl-*co*PEK. The chemical structure of the copolymer is



The number average molecular weight of this copolymer was about 5000.

Thin films of Cl-*co*PEK with a thickness between 20 and 50 nm were prepared for TEM and AFM experiments. The preparation of the thin films was done with a 0.1% solution of the copolymer in a 40/60 (w/w) mixed solvent

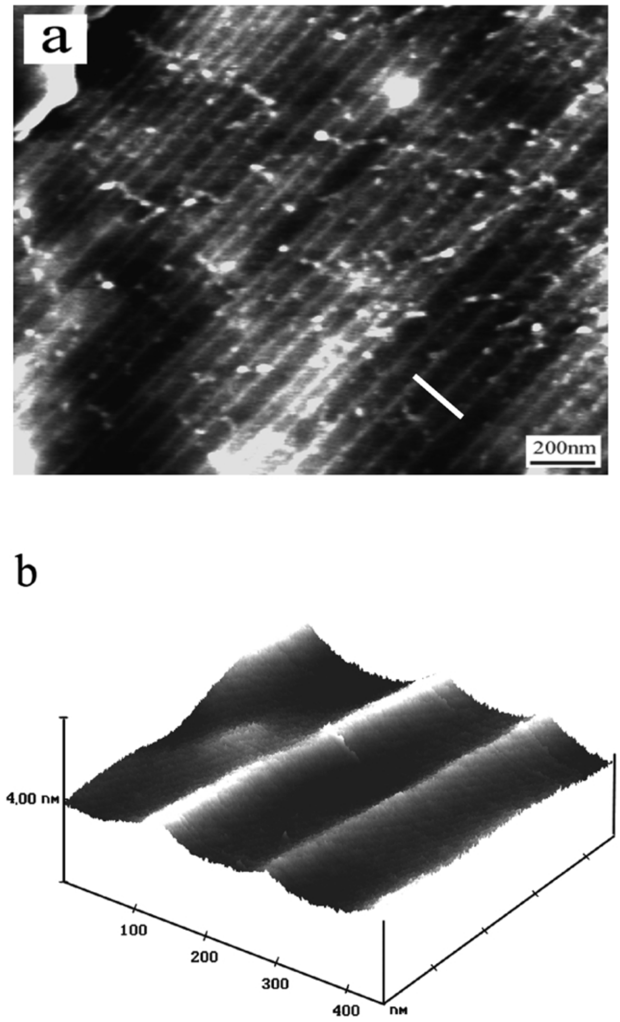


Fig. 3. (a) AFM height image of the thin film Cl-*co*PEK in a large area. The white solid line represents one periodicity of the micro-bands. (b) AFM height image in a local area of the micro-bands.

of *p*-chlorophenol/1,1,2,2-tetrachlorethane coated on carbon-coated cover glass slides, and the solvent was evaporated in a vacuum oven. After being heated above the T_i (360 °C) for 5 min, to eliminate previous thermal history, the films were rapidly cooled to a temperature between the T_m and T_i in the highly ordered LC phase temperature region (320–330 °C) for a preset period of time (usually 1–2 h). The thin film samples were then cooled to room temperature. The films were separated by etching glass slides using hydrofluoric acid. The thin films were then floated on the surface of water, and collected on copper grids for TEM and AFM observations.

2.2. Experiments and equipment

The highly ordered smectic crystal structure and micro-banded texture of the Cl-*co*PEK thin film samples were observed in TEM (JEOL 2010 TEM using a 200 kV accelerating voltage). In order to determine the chain direction in the micro-banded structure, a rotating–tilting stage for the specimen in SAED was used (with ±30° tilt and 360° rotation). Calibration of the camera length was carried out using Au as the standard material.

AFM measurements were performed using a Nanoscope III atomic force microscope (Digital Instruments) operated in the contact mode at ambient conditions. A Si_3N_4 tip attached to a 200 μm cantilever with a spring constant of 0.06 Nm^{-1}, was used with an applied force of 3 nN. Micrometer-scale and molecular lattice resolution images were obtained using 100 and 1 μm piezoelectric scanner heads, respectively. Scanning line frequencies were 1 Hz for large scale and up to 60 Hz for smaller areas. In most experiments, the samples were scanned or rotated in different directions and images were taken repeatedly. This technique provided an important approach in verifying the observed images.

3. Results and discussion

3.1. Observations of micro-bands

When a 20 nm thick Cl-*co*PEK film was annealed in the highly ordered smectic crystal phase at a temperature of 325 °C for 1.5 h and subsequently cooled to ambient temperature, micro-banded textures were observed at the film surface. Fig. 3(a) shows an AFM height image of the thin film surface. The periodicity of the micro-bands was around 150 nm. The overall shape of the micro-bands was sinusoidal-like at the top surface as shown in Fig. 3(b), which is an enlarged height image. It also contains alternative convex–concave parts, and the amplitude (the distance between maxima and minima) was around 2 nm. This banded texture was also observed in TEM bright field (BF) image as exhibited in Fig. 4. However, the less obvious bands in the TEM BF image resulted from the fact that, TEM observations only provide electron density difference of the sample. The alternative lighter and darker zones are representative of the micro-banded texture. When comparing the AFM image in Fig. 3(a) and (b) with the TEM BF image (Fig. 4), it seems that the convex–concave parts in AFM image correspond to the alternating electron density zones of the TEM image (see below).

It should be pointed out that the band observations were not related to the cooling rates used on the thin film samples. The banded texture was observed in both samples, that were quenched and cooled slowly to ambient temperature. However, the banded texture was strongly associated with the annealing process. Only the thin film samples annealed between the T_m and T_i for 1 or 2 h, showed the banded structure that was observed at ambient temperature. Direct cooling without annealing from temperatures either higher than the T_i or between the T_m and T_i did not yield the banded texture.

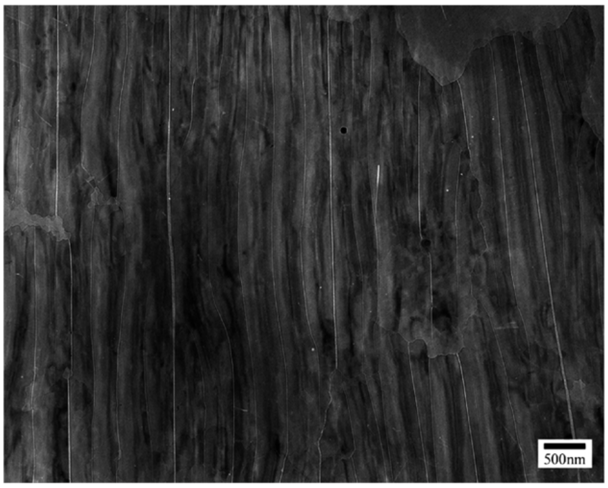


Fig. 4. BF TEM image of the Cl-*co*PEK thin film sample.

3.2. Molecular orientation in the ordered structure of the micro-bands

When SAED experiments were conducted on the thin film as shown in Fig. 4, a SAED pattern was obtained as shown in Fig. 5. Based on previously reported results in determining the crystal structures in poly(aryl ether ketone)s [32–34], this SAED pattern with strong and sharp diffraction spots, likely represented a [001] zone SAED pattern, and it should provide information on the molecular lateral packing structure in the thin films. The measured dimensions of the unit cell based on this SAED pattern were $a = 0.77 \pm 0.02$ nm and $b = 0.61 \pm 0.02$ nm, and it was a rectangular lattice. Assuming that the chain direction was to be parallel to the film normal in the convex regions, the three-dimensional structure should be orthorhombic. The long axis of the micro-bands was determined to be parallel to the *b*-axis direction. However, if the chains were tilted in the concave regions, the three-dimensional structure should be monoclinic.

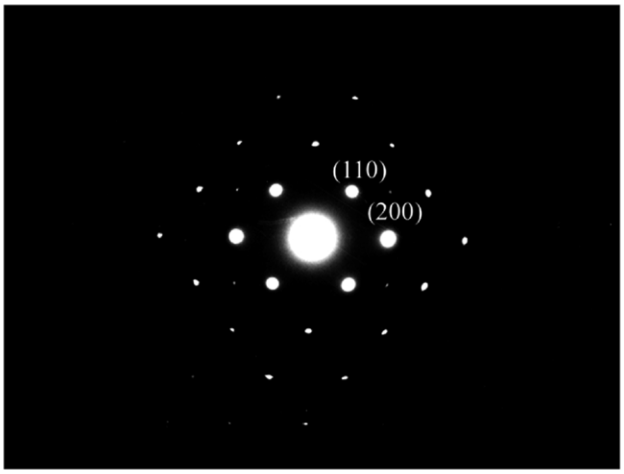


Fig. 5. SAED pattern of the Cl-*co*PEK thin film sample.

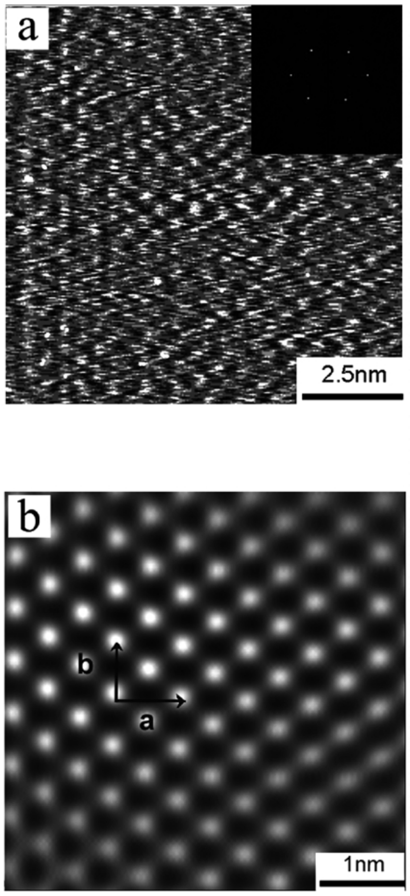


Fig. 6. Unfiltered AFM high-resolution image of the thin film and the Fourier transformed diffraction pattern as inserted (a); and the Fourier filtered image of Fig. 5(a) (b).

When the scan resolution was increased in AFM, a molecular lattice resolution image could be obtained. Fig. 6(a) shows the lattice image of the convex regions selected from the height image of Fig. 3(b). A two-dimensional Fourier transformation generated a diffraction pattern which is inserted in Fig. 6(a). From this, a rectangular lattice for the lateral chain packing could be obtained. After Fourier filtering, a two-chain lateral packing model was clearly observed in Fig. 6(b), where the bright spots were representatives of chains projected in a head-on direction. The two-dimensional lateral dimensions were $a = 0.79 \pm 0.02$ nm and $b = 0.63 \pm 0.01$ nm, which corresponded well to the dimension parameters obtained using SAED technique in Fig. 5.

Although the AFM results seemed to indicate that the molecular chains in the convex regions were parallel to the film normal, Figs. 3–6 do not directly provide any structural relationships between the chain orientation and the micro-bands. In order to establish this relationship and understand the formation mechanism of the micro-bands, DF experiments in TEM were carried out. Fig. 7 shows the SADF image of the banded texture taken from the (200) reflection. The bright zones in this figure indicated that the molecular chains obey the (200) Bragg reflection in the SADF image

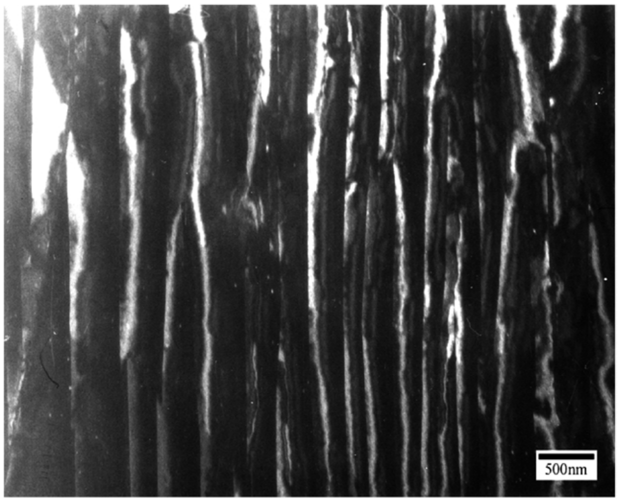


Fig. 7. (200)-DF TEM image of the Cl-*co*PEK thin film sample where the bright and dark zones correspond to the micro-bands.

and, therefore, were homeotropically aligned. Note that only the chain molecules located in these banded regions contributed to the ED pattern shown in Fig. 5. It is also important to note that these alternating bright and dark zones also corresponded to the BF TEM micrograph in Fig. 4 and the convex–concave regions of the AFM in Fig. 3.

The remaining question was, how are the molecules in the concave region of the micro-bands as seen in the AFM images in Fig. 3 (as well as the bright regions of the BF image of TEM in Fig. 4) aligned? Since the thin film thickness was around 20 nm, which is roughly similar to the extended chain length, it was speculated that only a single layer of chain molecules was involved in the thin films. When the band height changed with a magnitude of about 2 nm, one would expect that the molecules in these bands to periodically change their orientations. We tried to find which direction the chain molecules were tilted using a tilting stage in SAED experiments. After tilting the film around both the a-and the b-axes determined in Fig. 5, the tilted SAED results indicated that the chain molecules in the concave regions in the thin film were indeed tilted. However, the tilt directions and tilt angles were not fixed with respect to the film normal. Therefore, a more precise description of the chain direction should be that molecules are staggered along the *b*-axis.

3.3. Origin in the formation of the micro-bands

In the past, crystallization and structural ordering induced micro-banded textures have been reported. In those cases, the molecular orientation was homogenous, similar to the case under mechanical shearing [8–18]. Homeotropic orientation of chain molecules with micro-banded texture was first reported in LC polyethers via thermal annealing on carbon-coated cover glass slides. It was also noted that this micro-banded texture did not appear when the polyether was deposited on silane-grafted substrate surfaces [5]. In the case reported here, both the annealing process on the thin film samples, as well as the film surface chemistry resulted in micro-bands only being formed in samples having a thickness in the vicinity of 20 nm. Fig. 8 shows a sample with a variable thickness. In the right part of Fig. 8, the film thickness was close to 20 nm, and the micro-banded texture can be found. In the left part of Fig. 8, the sample was thicker than 20 nm, and no banded texture was observed.

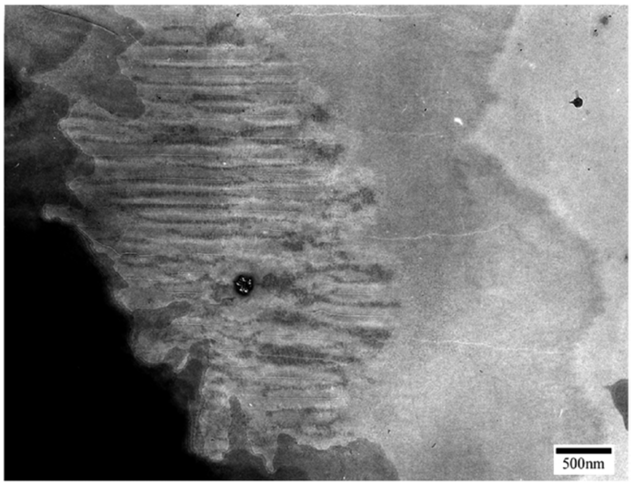


Fig. 8. BF TEM image of the Cl-*co*PEK thin film with different thickness in different areas. In the left part of this figure, the film thickness is around 20 nm, and in the right part of this figure, the film thickness is substantially thicker than 20 nm.

A possible explanation for the formation of this banded texture involves the effects of the substrate, and the energy associated with excess free volume. The copolymer film was initially cooled from the isotropic melt to the LC transition temperature (320–330 °C) thereby forming a highly ordered LC phase as shown in Fig. 1. This phase transformation process was accompanied with a decrease in volume due to the first-order thermodynamic transition. During the annealing process, the poly-domain sample gradually became mono-domain via annihilation of disclinations, and unifying the chain orientation. Both processes produce contractions perpendicular to the chain direction and expansions along the chain direction. These two processes also contributed to the energy associated with excess free volume due to the texture elasticity and lateral close packing. Under an assumption that all the molecules in the thin film 'participate' in these processes, and no new materials become available, the overall sample area must contract.

It was reported that Helfrich–Hurault undulations were found in a smectic A phase [35]. The principle of this finding was that, when a homeotropic sample was heated slightly, and then cooled, the smectic layers contracted. When the sample thickness was fixed, this contraction could be achieved through undulations [36,37] in the sample, and resulting in banded texture. We believe that the micro-banded texture found in our case should possess a similar mechanism. Therefore, the banded texture was formed in this manner on cooling the annealed Cl-*co*PEK thin film to ambient temperature.

4. Conclusion

Ordering induced formation of a micro-banded texture in the Cl-*co*PEK thin film mono-domain was experimentally observed in TEM and AFM images after thin films were annealed in the highly ordered smectic crystal region of 320–330 °C, and subsequently cooled to ambient temperature. The banded texture was sinusoidal-like with an amplitude of ~2 nm and periodicity of 150 nm. Based on SAED results, the band-long direction was along b-axis of the smectic crystals, which possessed an orthorhombic packing. In the convex regions, the chain molecules exhibited homeotropic alignment with the chain direction parallel to the film normal. In the concave regions, the chain molecules were tilted. The thickness of the thin films also served as one of the controlling factors for the formation of the banded texture. Only when the thickness of the film was comparable to, or a little larger than the extended chain length (~20 nm) of the copolymer, could the regular single crystal-like banded texture be formed. A possible mechanism for the banded texture formation may be similar to that seen in Helfrich–Hurault undulations.

Acknowledgements

DCY acknowledges the support from NNSF of China; SZDC acknowledges the support from NSF (DMR-0203994).

References

[1] Wood BA, Thomas EL. Nature 1986;324:18.
[2] Donald AM, Windle AH. Liquid crystalline polymers. New York: Cambridge; 1992. p. 48.
[3] Uchida T, Ishikawa K, Wada M. Mol Cryst Liq Cryst 1980;60:37.
[4] Donald AM, Windle AH. J Mater Sci 1984;19:2085.
[5] Ho RM, Yoon Y, Leland M, Cheng SZD, Yang D, Percec V, Chu P. Macromolecules 1996;29:4528.
[6] Dean D, Geil P. Acta Polym 1997;48:149.
[7] Xie F, Hu Z, Liu J, Yan D, He T, Wang B, Zheng R, Cheng SZD. Macromol Rapid Commun 2001;22:396.
[8] Kiss G, Porter RS. Mol Cryst Liq Cryst 1980;60:267.
[9] Viney C, Donald AM, Windle AH. J Mater Sci 1983;18:1136.
[10] Donald AM, Windle AH. Polymer 1984;25:1235.
[11] Donald AM, Viney C, Windle AH. Polymer 1985;26:870.
[12] Marsano E, Carpaneto L, Ciferri A. Mol Cryst Liq Cryst 1988;155:267.
[13] Chen S, Qian R. Makromol Chem 1990;191:2475.
[14] Pardey R, Zhang A, Gabori PA, Harris FW, Cheng SZD, Adduci J, Facinelli JV, Lenz RW. Macromolecules 1992;25:5060.
[15] Pardey R, Shen D, Gabori P, Harris HW, Cheng SZD, Adduci J, Facinelli J, Lenz R. Macromolecules 1993;26:3687.
[16] Chen JT, Thomas EL, Ober K, Mao G. Science 1996;273:343.
[17] Yoon Y, Zhang A, Ho RM, Cheng SZD, Percec V, Chu P. Macromolecules 1996;29:294.
[18] Hou J, Wu W, Xu M, Li Z. Polymer 1996;37:5205.
[19] Picken SJ, Moldenaers P, Berghmans S, Mewis J. Macromolecules 1992;25:4759.
[20] Gleeson JT, Larson RG, Mead DW, Cladis PE. Liq Cryst 1992;11:341.
[21] Hoff M, Keller A, Odell JA, Percec V. Polymer 1993;34:1800.
[22] Ge JJ, Zhang JZ, Zhou W, Jin S, Li CY, Wang SY, Harris FW, Cheng ZSD. J Mater Sci 2000;35:5215.
[23] Song W, Chen S, Jin Y, Qian R. Liq Cryst 1995;19:549.
[24] Chen S, Song W, Jin Y, Qian R. Liq Cryst 1993;15:247.
[25] Chen S, Song W, Jin Y, Qian R, Zhou Q. Mol Cryst Liq Cryst 1990;188:197.
[26] Yang D, Tian M, Zhang S. Inter Microsymp Polym Phys, Guilin PRC 1997;64.
[27] Zhang S, Zheng Y, Wu Z, Tian M, Yang D, Yosomiya R. Macromol Rapid Commun 1997;18:729.
[28] Zhang S, Yang D, Cheng SZD, Zheng Y, Wu Z, Yosomiya R. Acta Polym 1998;49:198.
[29] Zhang S, Zheng Y, Wu Z, Tian M, Yang D, Yosomiya R. Polym Bull 1997;38:621.
[30] Zhang S, Zheng Y, Wu Z, Tian M, Yang D, Yosomiya R. Liq Cryst 1998;24:311.
[31] Zhang S, Fu L, Liu J, Yang D, Gao Z, Jia M, Zheng Y, Wu Z. Macromol Chem Phys 2000;201:649.
[32] Ho RM, Cheng SZD, Hsiao BS, Gardner KH. Macromolecules 1994;27:2136.
[33] Ho RM, Cheng SZD, Fisher HP, Eby RK, Benjamin S, Hsiao BS, Gardner KH. Macromolecules 1994;27:5787.
[34] Ho RM, Cheng SZD, Hsiao BS, Gardner KH. Macromolecules 1995;28:1938.
[35] Kahn F. Appl Phys Lett 1973;22:111.
[36] de Gennes PG, Prost P. The physics of liquid crystals, 2nd ed. Oxford: Claredon Press; 1993.
[37] Kleman M. Points, lines and walls. New York: Wiley; 1983.