Morphology and Structure of Single Crystals of Poly(ethylene glycol)−Poly(ϵ-caprolactone) Diblock Copolymers

Jingru Sun,† Xuesi Chen,† Chaoliang He,†,‡ and Xiabin Jing*,†

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, P. R. China, and Graduate School of Chinese Academy of Sciences, Beijing, 100039, P. R. China

Received February 9, 2006

Revised Manuscript Received April 21, 2006

In recent years, single crystals of block copolymers have been widely investigated to elucidate the effect of the second block on the crystallization of the first block. Most block copolymers investigated up to date are those consisting of a crystalline block and an amorphous block, such as poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS).[1−4] The block copolymers in which both blocks are crystalline have been studied rarely[5−10] because of the complexity in these systems. Take the copolymer poly(ethylene glycol)-*block*-poly(ϵ-caprolactone) (PEG-*b*-PCL) as an example. When it is allowed to crystallize, only the single crystals of either PEG or PCL are observed as if the other block is missing, although the wide-angle X-ray diffraction (WAXD) can provide powerful evidence for the presence of the crystals of the second block.[9] In one of our previous papers, the growth of concentric spherulites in PEG5000−PCL5000 (a block copolymer of PEG and PCL with block molecular weights of ∼5000) was observed and the evidence for cocrystallization of the PEG blocks and PCL blocks was obtained, but the apparent morphology of the concentric spherulites is still either of PEG or of PCL as if the crystals of the second block (crystallized later) are hidden in the first one (crystallized earlier).[9,10]

Recently, we examined the electron diffraction of PEG5000−PCL5000 in comparison with PEG5000 and PCL8000. By choosing proper operating parameters of electron diffraction (ED), we succeeded in observing the ED patternsof both PEG and PCL and in taking picture of the ED patterns. In this Communication, we report on the related results.

The single crystals of PCL, PEG, and PEG-*b*-PCL were grown from their dilute solutions in hexanol according to a method proposed by Iwata et al.[11] The solution was heated to 100 °C to eliminate its heat history and was isothermally crystallized at 40 °C. Then the solution was self-seeded by warming up to 90 °C and was isothermally crystallized again at 40 °C. After repeating this temperature cycle two or three times, slow cooling to room temperature was applied. Drops of the crystal suspension were deposited on clean Si wafers and TEM copper grids for AFM and TEM observations.

The AFM micrographs of PEG5000, PCL8000, and PEG5000−PCL5000 are collected in Figure 1. Measured in both height mode and phase mode, the three polymers all show lamellar single crystals with screw dislocations. Among them, PEG5000 is of square shape (Figure 1a)[12] and PCL8000 is of hexagonal shape (Figure 1b),[11] in agreement with the literature.[13−15] Differently from the two homopolymers, PEG5000−PCL5000 exhibits an elongated hexagonal shape (Figure 1c). The PEG5000−PCL5000 crystals are 20−30 μm in the length direction and 6−10 μm in the width direction, whereas the homopolymers only give their sizes of ca. 3 μm, although they are almost grown under the same conditions. Such results should be ascribed to the double effects of microphase separation and crystallization of two crystalline PCL and PEG blocks.

Table 1. Lamellar Thickness Data Evaluated by AFM

sample	lamellar thickness *L* (nm)
PEG5000	8.1 ± 1.2
PCL8000	17.0 ± 1.4
PEG5000−PCL5000	28.5 ± 3.0

The two angles in the length direction are ∼90°, and the other four are ∼135°. This morphology is never reported for PEG. It looks similar to some extent to the "truncated lozenge shape" observed by Beekmans et al.[13] in solution-grown PCL crystals and by Prud'homme et al.[14] in isothermally melt-grown PCL crystals. But its multilayer structure, perfect terrace surfaces, and screw dislocations are never reported.

If the observed lamellae are assigned to PCL, a natural question will be raised: where are the PEG blocks? To answer this question, electron diffraction (ED) was performed on the three single crystal samples (Figure 2). The ED pattern of PEG single crystal is characterized by two pairs of strong diffraction spots (Figure 2a), which are perpendicular to each other and are attributed to the (120) planes, indicating the monoclinic PEG crystals with the chain direction parallel to the electron beam. The PCL single crystals show strong (110) and (200) reflections (Figure 2b), implying an orthorhombic packing and a perfect crystallographic orientation with the *c* axis (the chain direction) perpendicular to the film plane. The ED pattern of PEG5000−PCL5000 single crystal (Figure 2c) is approximately the superposition of the ED patterns of both PEG and PCL single crystals. This superposition indicates that there are two separated single-crystal layers consisting of the PEG and PCL blocks, respectively. That is to say, two PEG lamellae grow on the upper and lower surfaces of a PCL lamella, respectively, if the PCL lamella is formed earlier. Therefore, the observed single crystal should be composed of three layers: one layer of PCL plus two layers of PEG. To confirm this conclusion, the lamellar thickness *L* is measured by AFM technique. As shown in Table 1, the *L* of PEG5000−PCL5000 is much larger than that of PEG or PCL single crystals and even larger than the sum of one layer of PCL plus one layer of PEG. This provides another piece of evidence for the coexistence of both PEG and PCL single crystals.

It is noticed in Figure 2c that the four ED spots of PEG are superposed on those of PCL in such a way that the line connecting the two opposite (120) spots of PEG and the line connecting the two opposite (110) spots of PCL make an angle of 7°−15°, implying that the *a* axes of PEG and PCL lattices make an angle of 22°−30°. This means that in addition to the parallel molecular chain direction the unit cell (*a* and *b* axes) of PEG single crystal has a narrow spatial orientation with respect to that of PCL single crystal. At the present stage, it cannot be considered as an epitaxial relation, but it implies that the PCL unit cells can determine the growth direction of the PEG single crystals to some extent.

* Corresponding author: Tel +86-431-5262112; Fax +86-431-5685653; e-mail xbjing@ciac.jl.cn.

† Changchun Institute of Applied Chemistry.

‡ Graduate School of Chinese Academy of Sciences.

10.1021/ma0603074 CCC: $33.50
Published on Web 05/02/2006

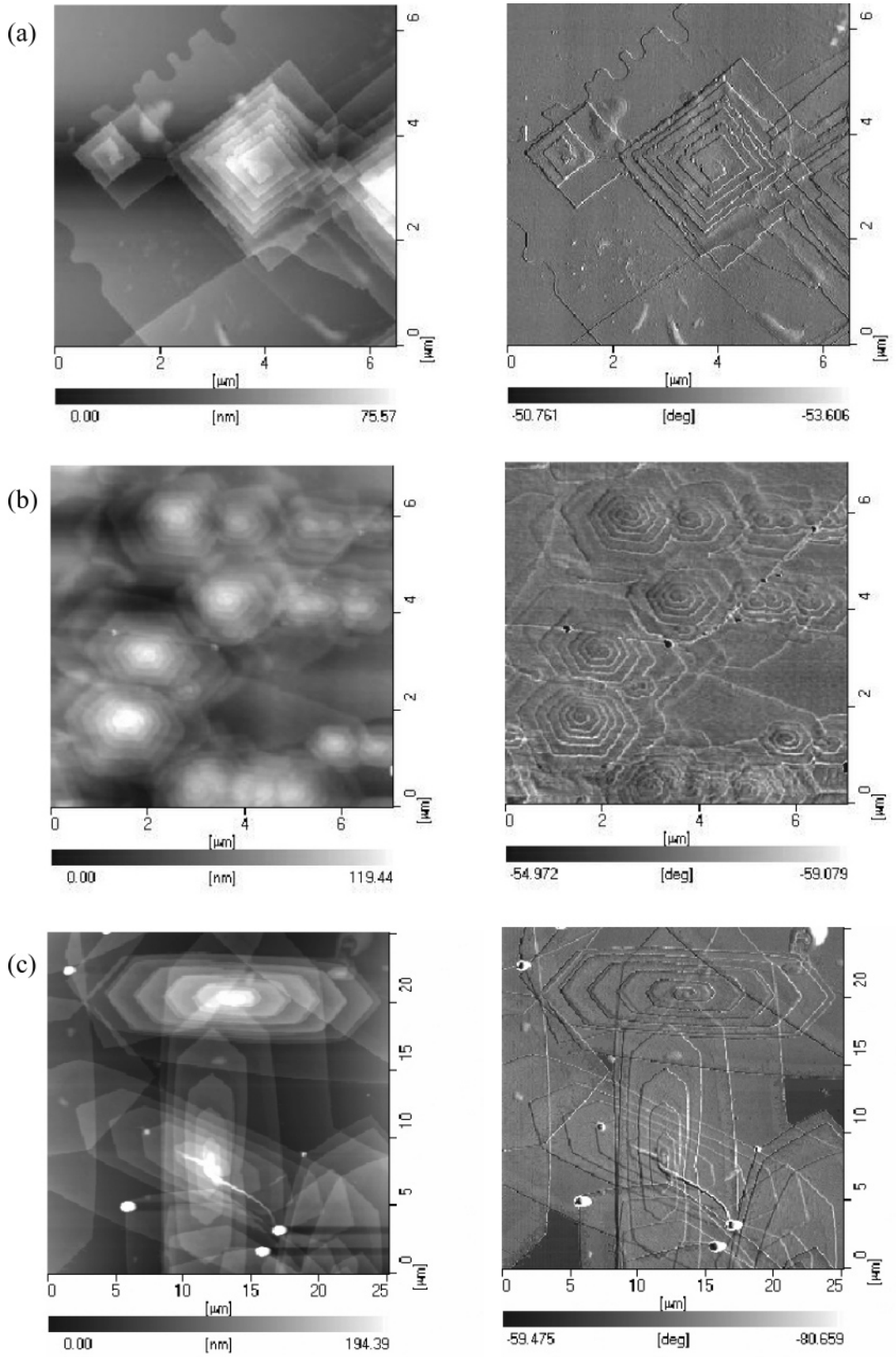

Figure 1. AFM height (left) images and phase (right) images of (a) PEG5000, (b) PCL8000, and (c) PEG5000−PCL5000.

According to ref 9, PCL is assumed to crystallize first and PEG chains are excluded from the PCL lamella onto the upper and lower surfaces. After the chain folding of PEG, the total thickness should be the sum of one layer of PCL plus two layers of PEG. In the present study, equal block molecular weights (5000) are used. At the experimental temperature, the lamellar thickness of PEG is a half of PCL (Table 1). Consequently, the PEG chains can achieve a close packing in the lamellae without free space or crowding. That is why the measured lamellar thickness is larger than the sum of one layer of PCL and one layer of PEG and why the perfect screw-dislocated large single crystals are obtained (less inner stress).

In summary, the concurrence of the ED patterns of PEG and PCL single crystals in that of PEG-*b*-PCL single crystals and

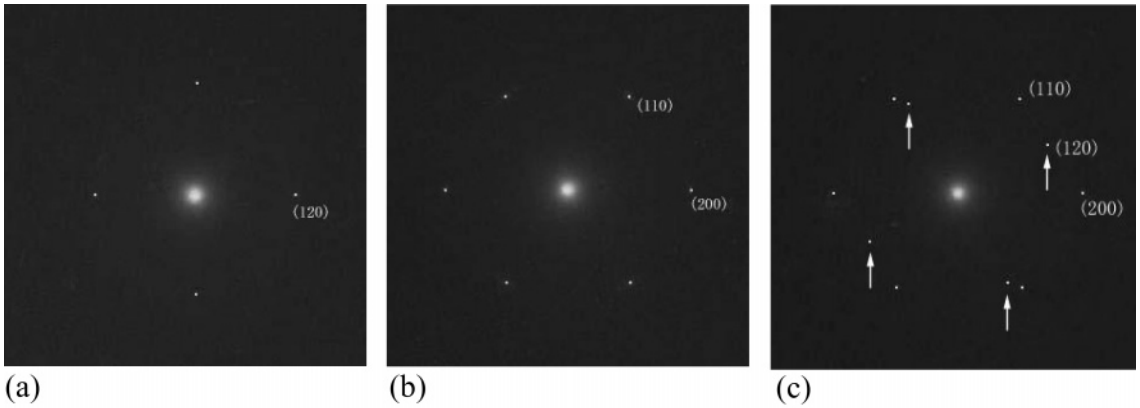

Figure 2. Electron diffraction patterns of single crystals of (a) PEG5000, (b) PCL8000, and (c) PEG5000−PCL5000. The ED spots of PEG single crystal are indicated by the arrows.

the larger lamellar thickness in PEG-*b*-PCL provide convincing evidence for the coexistence of the two single-crystal layers formed from the two blocks. The PCL blocks crystallize first to form a screw-dislocated lamella with a shape of truncated lozenge and to exclude the PEG blocks. The PEG chains fold themselves on the two surfaces of the PCL lamella to achieve a three-layer structure. That is why the block copolymer assumes the apparent morphology of PCL but can form much thicker and larger single crystals. Further investigation is in progress, and the results will be published elsewhere.

Acknowledgment. Financial support was provided by the National Natural Science Foundation of China (Project No. 20274048 and 50373043), by the National Fund for the Distinguished Young Scholars (No. 50425309), and by Chinese Academy of Sciences (Project No. KJCX2-SW-H07).

References and Notes

(1) Huang, P.; Zhu, L.; Cheng, S. Z. D.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Liu, L.; Yeh, F. *Macromolecules* **2001**, *34*, 6649.
(2) Lee, S.-W.; Chen, E.; Zhang, A.; Yoon, Y.; Moon, B. S.; Lee, S.; Harris, F. W.; Cheng, S. Z. D.; von Meerwall, E. D.; Hsiao, B. S.; Verma, R.; Lando, J. B. *Macromolecules* **1996**, *29*, 8816.
(3) Chen, W. Y.; Li, C. Y.; Zheng, J. X.; Huang, P.; Zhu, L.; Ge, Q.; Quirk, R. P.; Lotz, B.; Deng, L.; Wu, C.; Thomas, E. L.; Cheng, S. Z. D. *Macromolecules* **2004**, *37*, 5292.
(4) Zhu, L.; Huang, P.; Chen, W. Y.; Ge, Q.; Quirk, R. P.; Cheng, S. Z. D.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Yeh, F.; Liu, L. *Macromolecules* **2002**, *35*, 3553.
(5) Bogdanov, B.; Vidts, A.; Schacht, E. *Macromolecules* **1999**, *32*, 726.
(6) Shiomi, T.; Imai, K.; Takenaka, K. *Polymer* **2001**, *42*, 3233.
(7) Piao, L. H.; Dai, Z. L.; Deng, M. X.; Chen, X. S.; Jing, X. B. *Polymer* **2003**, *44*, 2025.
(8) Piao, L. H.; Deng, M. X.; Chen, X. S.; Jiang, L. S.; Jing, X. B. *Polymer* **2003**, *44*, 2331.
(9) He, C. L.; Sun, J. R.; Deng, C.; Zhao, T.; Deng, M. X.; Chen, X. S.; Jing, X. B. *Biomacromolecules* **2004**, *5*, 2042.
(10) He, C. L.; Sun, J. R.; Zhao, T.; Chen, X. S.; Jing, X. B. *Biomacromolecules* **2006**, *7*, 252.
(11) Iwata, T.; Doi, Y. *Polym. Int.* **2002**, *51*, 852.
(12) Snetivy, D.; Vancso, G. J. *Polymer* **1992**, *33*, 432.
(13) Beekmans, L. G. M.; Vancso, G. J. *Polymer* **2000**, *41*, 8975.
(14) Mareau, V. H.; Prud'homme, R. E. *Macromolecules* **2005**, *38*, 398.
(15) Núñez, E.; Gedde, U. W. *Polymer* **2005**, *46*, 5992.

MA0603074