A Twist Grain Boundary-like Twisted Smectic Phase in Monodisperse Poly(γ-benzyl α,L-glutamate) Produced by Recombinant DNA Techniques

Shi-Juang He, Chin Lee, Samuel P. Gido,*
Seungju M. Yu, and David A. Tirrell†

Polymer Science and Engineering Department,
University of Massachusetts, Amherst, Massachusetts 01003

Received August 13, 1998
Revised Manuscript Received October 26, 1998

Smectic ordering has been observed in perfectly monodisperse poly(γ-benzyl α,L-glutamate) (PBLG) which was synthesized using recombinant DNA technology.[1] These PBLG molecules form rigid α-helical rods 11.45 nm in length. In the present study, transmission electron microscopy (TEM) and electron diffraction reveals a banded morphology with an approximately 120 nm period which provides strong evidence for helical rotation of the director field as in a cholesteric or twisted smectic. Detailed examination of the relative orientation of the banding in the morphology images and the reflections in the electron diffraction patterns, indicating interchain and intrachain correlations, leads to the conclusion that the structure observed is a twisted smectic phase. The relationship between the twist and the layering is found to be that of the twist grain boundary (TGB) phase.[2,3] However, our data does not allow us to determine whether the monodisperse PBLG structure is blocky with discrete twist boundaries as in a true TGB or is a more continuously twisting structure. Thus, we will refer to the phase as TGB-like. Conventional, polydisperse PBLG is well-known to form cholesteric phases as a result of the chirality of the helical rod.[4] The formation of a TGB-like phase in monodisperse PBLG is consistent with the superposition of a smectic-A layering resulting from the uniform rod length on the twisted texture present in the cholesteric.

PBLG forms a cholesteric mesophase in a wide variety of organic solvents.[4] The cholesteric twist of PBLG is dictated by the chirality of the α-helical macromolecules and the dielectric properties of the medium,[5] and cholesteric order can be retained in solution-cast solid films.[6] There is no barrier preventing the transition from a cholesteric to a TGB-like smectic phase;[7] the phase thus formed would preserve the director twist characteristics of the cholesteric. However, formation of a twisted smectic mesophase for conventional PBLGs is hindered by the polydispersity of the chains. This polydispersity hinders the assembly of the structure into smectic layers.

A monodisperse derivative of PBLG, PBLG-1, was synthesized by recombinant DNA methods.[1,8] For this study, a PBLG-1 solid film, about 1 mm thick, was prepared from a 35 wt % PBLG-1 solution in a mixture of $CHCl_3$ (97%) and trifluoroacetic acid (3%) by slow evaporation on a Teflon plate.[1] X-ray scattering on this material yielded 2 orders of the 11.45 nm reflection corresponding to the smectic layer repeat.[1] The spacing of this repeat is commensurate with the chain length of PBLG-1, an α-helix with the degree of polymerization of 76. X-ray scattering in the previous study[1] on samples oriented in a 1.98 T magnetic field revealed a 1.26 nm reflection, attributed to lateral interchain correlations, oriented perpendicular to the lamellar sheet spacings. This indicates a chain orientation perpendicular to the sheets of the smectic phase (i.e., a smectic-A (more properly a smectic-A* since the rodlike units are chiral). The unoriented material used in the present study gave isotropic X-ray diffraction patterns,[1] indicating that the films produced for this study had no preferential chain orientation over length scales on the order of the sample dimensions.

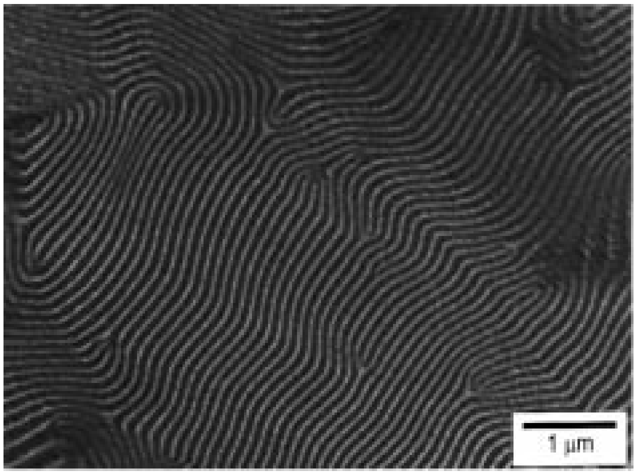

Figure 1. Bright-field TEM image of the banding in PBLG-1 with a repeat distance of about 120 nm. Disclinations and dislocations are apparent.

For a TEM observation, the solid sample was ultramicrotomed using a diamond knife at room temperature, producing sections about 50 nm thick. Electron diffraction coupled with TEM imaging was performed at 200 kV, and a cryogenic sample holder was used to reduce beam damage. Better imaging has been accomplished at 100 kV for improved contrast. Figure 1 shows a typical bright-field TEM image of PBLG-1. A banded texture was observed, arising because of mass-thickness variations of the sample. This morphology also displays disclinations of strength $s = +{}^1/_2$ and $s = -{}^1/_2$ as well as edge dislocations. A banding repeat distance of about 100−130 nm, which depends on the local contact angle between the knife and the sample, is observed by TEM. This length scale is an order of magnitude too large to be associated directly with the smectic layering previously reported for this material. There is, however, ample precedent for the TEM observation of banded textures in ultramicrotomed sections of glassy materials with liquid-crystalline symmetry when the director field is twisting, as in a cholesteric.[9,10] Cholesteric compounds when quenched into a solid state and sectioned with a diamond knife exhibit banding because of thickness variations; when the knife passes approximately in the plane of the helical axis, a sinusoidal surface topography is produced because of preferential crack propagation following the twist of the director field.[9−11] The thin microtomed sections are bounded by two sinusoidal fracture surfaces, and the phase relationship between these periodic topographies results in thickness varia-

---

* To whom correspondence should be addressed.

† Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

10.1021/ma981286j CCC: $15.00

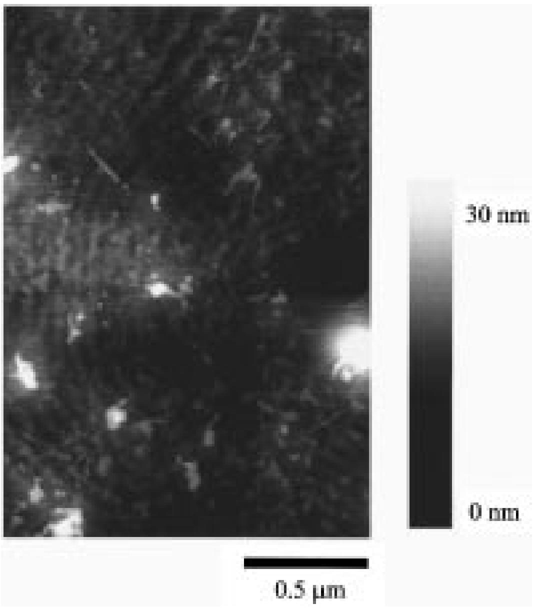

Figure 2. AFM image of a PBLG-1 microtomed surface. A banded texture with a 100−110 nm repeat is observed which arises from the sinusoidal surface topography.

tions which are maximized when the two surfaces are 180° out of phase. The sinusoidal fracture surface topography in PBLG-1 was imaged by atomic force microscopy (AFM), on the microtomed block face after thin sections had been cut. Figure 2 shows an AFM topography image of a PBLG-1 microtomed surface in which a repeat of the banding is confirmed to be about 100−110 nm, and the peak-to-valley distance (double the amplitude) of the banding is found to be 30 nm.

To correlate the chain orientation with the morphology, coupled electron diffraction and imaging experiments were conducted. Figure 3a shows a typical electron diffraction pattern of PBLG-1. The equatorial spots at a spacing of 1.26 nm correspond closely to the spacing of the 100 reflection from the hexagonal packing of helices previously reported for diffraction experiments on semicrystalline PBLG samples.[12,13] Thus, the equatorial spots are interpreted as arising because of correlations lateral to the PBLG-1 rods. At larger scattering angles, a faint and diffuse hexagonally shaped ring is observed. This distinctive pattern is consistent with the electron and X-ray diffraction patterns previously reported for oriented semicrystalline PBLG films.[12−14] Details of the indexing of these reflections are given in the references. The top and bottom of this hexagonal distribution of scattering intensity are horizontal streaks which result from the superposition of reflections on the fifth-layer line.[12,14] The horizontal streaking of these reflections in the present study is consistent with a less well-ordered liquid-crystalline arrangement with a suppression of registry in the chain direction between adjacent helical rods. The four faint reflections which form the sides of the hexagonal pattern are consistent in spacing and arrangement with the 0.45 nm 212 reflections of crystalline PBLG in the previously reported hexagonally shaped pattern.[12] The fact that these reflections are so faint and diffuse in our electron diffraction patterns is also consistent with a less well-ordered liquid-crystalline structure. This electron diffraction pattern provides a clear indication of the orientation of the PBLG-1 rods, which run parallel to the meridian of the diffraction pattern. The molecular orientation from the diffraction pattern can be mapped

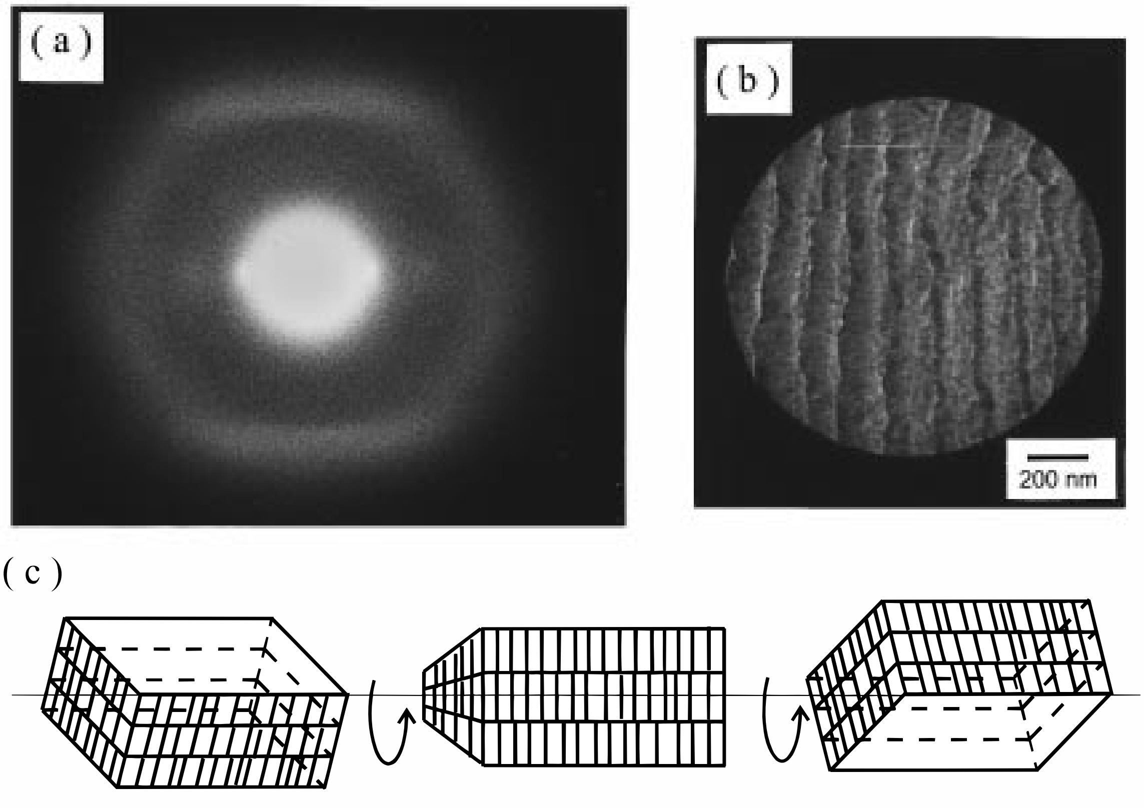

Figure 3. Coupled diffraction and TEM imaging. (a) Electron diffraction pattern of PBLG-1. The characteristic equatorial reflection at $d = 1.26$ nm represents the lateral packing distance between helical rods. A second-order reflection is also visible. (b) Defocused image; banding is parallel to the helical rods. (c) Schematic representation of the geometrical arrangement of the PBLG-1 molecules consistent with the diffraction pattern and the image in (a) and (b) (i.e., TGB structure).

to the image of the banded morphology shown in Figure 3b. This TEM image was obtained by defocusing the central spot of the diffraction pattern (Figure 3a). It shows only the material contributing to the diffraction and preserves the rotational orientation between the pattern and image.

Electron diffraction coupled with the morphology image establishes that the chain axes of the PBLG-1 rods lie parallel to the 120 nm bands in the image. These bands necessitate a twisting director perpendicular to this rod direction, as in a cholesteric. The X-ray diffraction data simultaneously requires layering with a 11.45 nm repeat, and a chain axis normal to these smectic layers (i.e., smectic-A). These geometrical requirements can only be satisfied by the TGB structure,[2,15] which is illustrated in Figure 3c and which is shown in the correct orientation with respect to the diffraction pattern and image. The geometrical requirements are inconsistent with other twisted liquid-crystal structures such as the smectic-C*.

The twist grain boundary phase was first predicted by Renn and Lubensky[16] between cholesteric and smectic A phases. Their TGB model[3,16] proposed that grain boundaries of screw dislocations account for rotation of blocks of smectic-A layers, as drawn in Figure 3c. Experimental observation of the TGB structure was first reported by Goodby et al.,[2] and subsequently by other investigators.[17–19] To date, this structure has been found in several chiral thermotropic liquid crystals in different sequences such as isotropic–TGB–smectic-C*,[2] cholesteric–TGB–smectic-A,[17] and cholesteric–TGB–smectic-C*.[18] To the best of our knowledge, the present study of PBLG-1 is the first report of a TGB-like structure in a lyotropic liquid crystal.

Although there is some suggestion of a finer scale structure, the detail revealed by the TEM images of the present study is not sufficient to allow the assessment of whether the helical rotation of the smectic layers actually occurs in the blocky manner predicted by theory or whether the deformation is more continuous. Previous results on monodisperse PBLG-1, which had been oriented in a 1.98 T magnetic field, showed a focal conic texture. A focal conic is not observed for the TGB structure.[3] Additionally, the X-ray scattering from the oriented sample indicated a smectic-A structure. Unoriented samples of this material show a fan-like optical texture which does allow for the possibility of a twisting director, as in a cholesteric or a TGB phase.[7] We are led to the conclusion that the magnetic alignment of PBLG-1 untwists the material, producing a smectic-A. In the absence of the aligning field, the chirality of the rods produces a twisted TGB-like structure. Clearly, however, the TGB-like phase observed in monodisperse PBLG results from the superposition of the cholesteric twist observed in conventional polydisperse PBLG (as a result of the chirality of the helical rod) and a drive to form a layered structure brought about by the monodisperse chain length.

Acknowledgment. Funding from the NSF Division of Materials Research, Polymers Program (S. P. Gido CAREER award, DMR-9624306) is gratefully acknowledged. Funding was also provided by the NSF Material Research Science and Engineering Center (MRSEC) at the University of Massachusetts Amherst. We would like to thank E. D. T. Atkins and R. Valluzzi for useful discussions.

References and Notes

(1) Yu, S. M.; Conticello, V. P.; Zhang, G.; Kayser, C.; Fournier, M. J.; Mason, T. L.; Tirrell, D. A. *Nature* **1997**, *389*, 167.
(2) Goodby, J. W.; Waugh, M. A.; Stein, S. M.; Chin, E.; Pindak, R.; Patel, J. S. *Nature* **1989**, *337*, 449.
(3) Renn, S. R.; Lubensky, T. C. *Phys. Rev. A* **1988**, *38*, 2132.
(4) Block, H. *Poly(g-benzyl-L-glutamate) and Other Glutamic Acid Containing Polymers*; Gordon & Breach: New York, 1993.
(5) Samulski, E. T.; Tobolsky, A. V. In *Liquid Crystals & Plastic Crystals* Gray, G. W., Winsor, P. A., Eds.; Ellis Horwood Limited: Chichester, 1974.
(6) Samulski, E. T.; Tobolsky, A. V. *Nature* **1967**, *216*, 997.
(7) Kleman, M. *Points, Lines, and Walls. In Liquid Crystals, Magnetic Systems and Various Ordered Media*; John Wiley & Sons Ltd.: New York, 1983.
(8) Zhang, G.; Fournier, M. J.; Mason, T. L.; Tirrell, D. A. *Macromolecules* **1992**, *25*, 3601.
(9) Berreman, D. W.; Meiboom, S.; Zasadzinski, J. A.; Sammon, M. J. *Phys. Rev. Lett.* **1986**, *57*, 1737.
(10) Willcox, P. J.; Gido, S. P.; Muller, W.; Kaplan, D. L. *Macromolecules* **1996**, *29*, 5106.
(11) Bunning, T. J.; Vezie, D. L.; Lioyd, P. F.; Haaland, P. D.; Thomas, E. L.; Adams, W. W. *Liq. Cryst.* **1994**, *16*, 769.
(12) Parsons, D. F.; Martius, U. *J. Mol. Biol.* **1964**, *10*, 530.
(13) Bamford, C. H.; Elliott, A.; Hanby, W. E. *Synthetic Polypeptides*; Academic Press Inc.: New York, 1956.
(14) Vainshtein, B. K.; Tatarinova, L. I. *Conform. Biopolym. Pap. Int. Symp. Madras* **1967**, *2*, 569.
(15) Goodby, J. W.; Waugh, M. A.; Stein, S. A.; Chin, E.; Pindak, R.; Patel, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 8119.
(16) Lubensky, T. C.; Renn, S. R. *Phys. Rev. A* **1990**, *41*, 4392.
(17) Lavrentovich, O. D.; Nastishin, Yu. A.; Kulishov, V. I.; Narkevich, Yu. S.; Tolochko, A. S.; Shiyanovskii, S. V. *Europhys. Lett.* **1990**, *13*, 313.
(18) Nguyen, H. T.; Bouchta, A.; Navailles, L.; Barois, P.; Isaert, N.; Twieg, R. J.; Maaroufi, A.; Destrade, C. *J. Phys. II (France)* **1992**, *2*, 1889.
(19) Anakkar, A.; Daoudi, A.; Buisine, J.-M.; Isaert, N.; Bougrioua, F.; Ngyyen, H. T. *Liq. Cryst.* **1996**, *20*, 411.

MA981286J