Lamellar Materials

DOI: 10.1002/ange.200602541

Tailor-Made Onionlike Stereocomplex Crystals in Incompatible, Enantiomeric, Polylactide-Containing Block Copolymer Blends**

Lu Sun, Lei Zhu, Lixia Rong, and Benjamin S. Hsiao*

Self-assembled soft materials having curved lamellar structures include uni- and multilamellar vesicles (MLVs) and scrolled or curled tubules.[1] Due to their potential applications as chemical and biological microreactors, MLVs (or onions) have received much attention.[2] In concentrated

---

[*] L. Sun, Prof. L. Zhu
Polymer Program, Institute of Materials Science and
Department of Chemical, Materials, and Biomolecular Engineering
University of Connecticut
Storrs, CT 06269-3136 (USA)
Fax: (+1) 860-486-4745
E-mail: lei.zhu@uconn.edu
Homepage: http://www.ims.uconn.edu/~lzhu

Dr. L. Rong, Prof. B. S. Hsiao
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, NY 11794-3400 (USA)

[**] This work was supported by ACS PRF (41918-G7) and NSF CAREER Award DMR-0348724. The synchrotron X-ray experiments were carried out at the National Synchrotron Light Source in Brookhaven National Laboratory, supported by DoE.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

solutions of surfactants, monodisperse and closely packed onion phases were obtained under mechanical shear.[3] Occasionally, onionlike vesicles could be formed spontaneously, for example, cosurfactants were used to induce onion phases.[4] Multilamellar vesicles were also induced without shear by electrostatic interactions between cationic and anionic surfactants[5] or anionic macromolecules such as DNA.[6] The detailed formation mechanism for these surfactant onions is still under investigation.[7] Besides these lyotropic systems, thermotropic liquid crystals can also form onion defects in focal conic domains with positive Gaussian curvature.[8] The onionlike morphology was also predicted and reported in homopolymer/copolymer[9] and copolymer/copolymer[10] blends, where thermodynamic equilibrium played an important role. Contrary to the "soft" nature of the above materials, crystals cannot readily exhibit onionlike morphology due to their high bending moduli and symmetric structures. Indeed, in semicrystalline polymers only twisted and scrolled crystals with open structures have been reported.[11] Unbalanced stresses at folding surfaces were believed to be the origin of lamellar crystal curving. Direct evidence of this mechanical origin is still lacking.

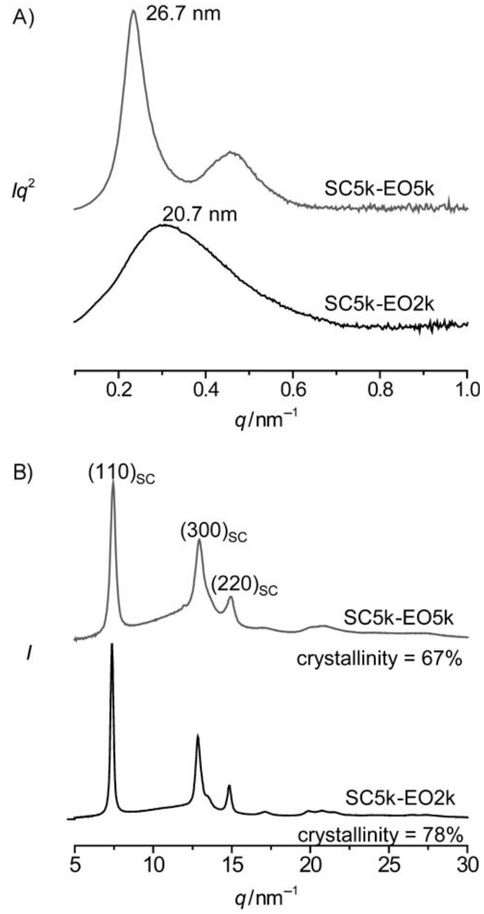

Figure 1. A) Small-angle X-ray scattering and B) wide-angle X-ray diffraction profiles for SC5k-EO5k and SC5k-EO2k at 50 °C. Curves are offset for clarity.

Understanding or controlling lamellar curvature is thus an important research topic in the fields of biophysics and polymer science. In this study, we have designed a novel approach to tailor-make onionlike polymer crystals using the concept of unbalanced surface stresses. Crystalline stereocomplexes were obtained from enantiomeric polylactide (PLA) block copolymer blends, namely, poly(ethylene oxide)-*b*-poly(L-lactide) (PEO-*b*-PLLA) and poly(ethylene-*co*-1-butene)-*b*-poly(D-lactide) (PEB-*b*-PDLA). By biasing the PEO and PEB molecular weights (or volumes) to be unsymmetric, unbalanced stresses are generated on crystal basal planes and thus lamella curving is induced.

Three well-defined enantiomeric PLA block copolymer samples—two PEO-*b*-PLLA and a PEB-*b*-PDLA—were synthesized by controlled ring-opening polymerization of L- and D-lactides from monohydroxyl-terminated PEO-OH and PEB-OH prepolymers, respectively.[12] The number-average molecular weights M_n (k denotes thousands) and polydispersity indices (PDI) of these block copolymers were determined by ^{1}H NMR spectroscopy and size-exclusion chromatography (SEC): PEO-*b*-PLLA (5k–5.1k), PDI = 1.14; PEO-*b*-PLLA (2k–5.4k), PDI = 1.12; and PEB-*b*-PDLA (4.2k–5.4k), PDI = 1.09. Two stereocomplex samples were obtained by equimolar blending of PEB-*b*-PDLA (4.2k–5.4k) with PEO-*b*-PLLA (2k–5.4k) and PEO-*b*-PLLA (5k–5.1k), respectively, by using chloroform as a good solvent. They are denoted as SC5k-EO2k and SC5k-EO5k, respectively. The solution-cast samples were heated to 250 °C and held there for 15 min to melt stereocomplex crystals (melting temperatures ca. 195 °C), and stereocomplexes were crystallized by cooling at 1 °C min^{-1} under a dry N_2 atmosphere to room temperature.

Quantitative yields of stereocomplex crystals were confirmed by wide-angle X-ray diffraction (WAXD, Figure 1 B). Trigonal[13a] reflections for PLA stereocomplex (SC) crystals, $(110)_{SC}$, $(300)_{SC}$, $(220)_{SC}$, were seen at 8.4, 14.5, 16.9 nm^{-1} for both blends. No orthorhombic[13b] PLLA or PDLA crystal reflections were observed (e.g., the strong and overlapped $(110)_{LA}/(200)_{LA}$ reflections at 12.1 nm^{-1} were missing; LA = lactide). After peak deconvolution in Figure 1 B and normalization to the PLA weight percentages, the stereocomplex crystallinities for SC5k-EO5k and SC5k-EO2k were calculated to be 67 and 78 wt %, respectively.

Lamellar morphology of these stereocomplexes was studied by small-angle X-ray scattering (SAXS, Figure 1 A). SC5k-EO5k demonstrated the typical lamellar morphology with first- and second-order reflections at 0.23 and 0.46 nm^{-1}, respectively. The overall spacing was 26.7 nm. In contrast, a broader reflection with an average spacing of 20.7 nm was seen for SC5k-EO2k.

The difference in the SAXS profiles of SC5k-EO5k and SC5k-EO2k suggested different lamellar organizations inside the samples. Figure 2 A shows a typical transmission electron microscopy (TEM) image for SC5k-EO5k. Flat lamellar morphology with bright layers corresponding to PEB and stereocomplex crystals and dark layers corresponding to PEO and amorphous PLA was seen. This is because PEB and stereocomplex crystals resisted staining with RuO_4, but PEO and amorphous PLA did not.[12]

By decreasing the M_n of PEO from 5000 to 2000, the volume balance between PEB and PEO blocks was broken.

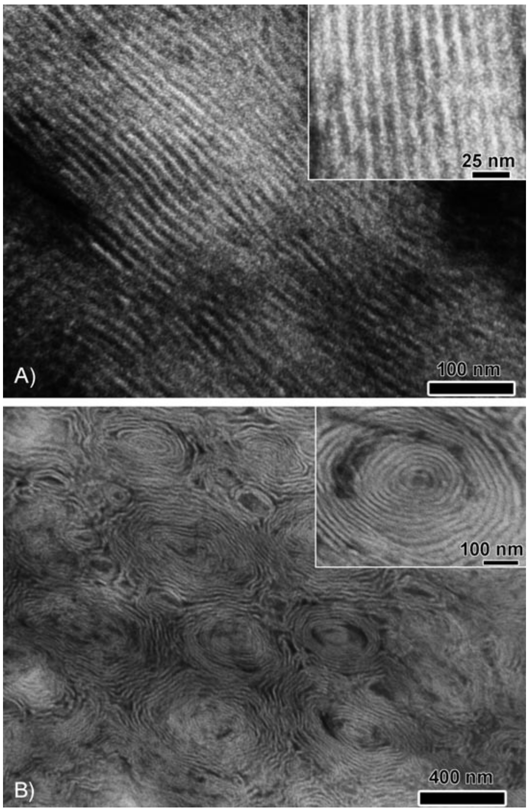

Figure 2. Bright-field TEM images of A) SC5k-EO5k and B) SC5k-EO2k crystallized from the melt during cooling at 1 °C min^{-1}.

Figure 2B shows the typical morphology of SC5k-EO2k. Intriguingly, concentric microdomains were seen throughout the sample. We concluded that onion crystals, instead of scrolled lamellar crystals,[11] were obtained. A closer view of the onion structure is shown in the inset of Figure 2B. The central dark microdomain represents amorphous PEO and PLAs (the sectioning happened to cut through the center of the onion). The lamellar stacking near the center seemed tighter than that at the periphery. Again, the bright layers are PEB and crystalline stereocomplexes, and the dark layers amorphous PEO and PLAs. The overall diameter and shape of the onions seemed to be variable. However, since the sample was sectioned (ca. 70 nm) at various portions of the onions, the actual onion sizes were not equal to those observed in TEM, and will be studied in the future by small-angle light scattering. The slightly elliptical shape of the onions may result from film compression during cutting.

Based on the above results, we propose a possible molecular model for the onionlike stereocomplex crystals (Figure 3). Curved PEB, PLA stereocomplex, and PEO-rich microdomains arrange into a noncentrosymmetric multilamellar structure in which PEB and PEO are always at the outside and the inside of a curved PLA stereocomplex lamellar crystal, respectively. This is reminiscent of the noncentrosymmetric scrolled crystals of chrysotile asbestos.[11] We performed a quantitative thickness analysis of the PEO-rich, PEB, and PLA stereocomplex layers for both samples using the thicknesses of the dark and bright layers in the TEM images (Figure 2). Detailed calculations are described in the

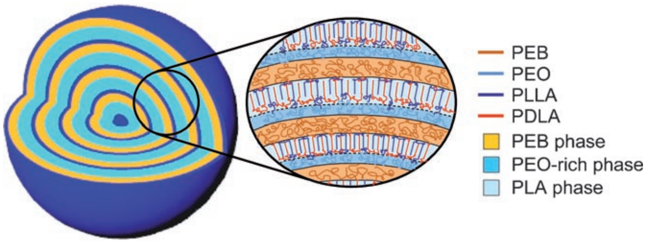

Figure 3. Molecular schemes of a SC5k-EO2k onionlike crystal with a curved noncentrosymmetric lamellar structure.

Supporting Information. The respective thicknesses of the PEO-rich, PEB, and PLA stereocomplex microdomains were 7.02, 9.18, and 4.50 nm for SC5k-EO2k, and 10.85, 7.22, and 8.66 nm for SC5k-EO5k. Since differential scanning calorimetry showed similar melting temperatures (193 °C for SC5k-EO2k and 199 °C for SC5k-EO5k), the thicknesses of the stereocomplex-crystal lamellae in both samples should be similar. It is reasonable to assume that SC5k-EO2k has a noncentrosymmetric structure with a single layer of PLA stereocomplex crystal (thickness ca. 4.5 nm), whereas SC5k-EO5k has a centrosymmetric structure with two layers of PLA stereocomplex crystals, each about 4.3 nm thick, within a long period. Note that the immiscible PEO-rich and PEB layers thus have direct contact, as shown in Figure 3. We speculate that the energy penalty from direct contacts between PEB and PEO could be compensated by lamella bending induced by unbalanced surface stresses. Experimental studies are currently underway to further prove this noncentrosymmetric structure.

Before stereocomplex growth, a honeycomb rather than onion structure was seen in molten SC5k-EO2k at 205 °C.[12] We speculate that formation of the onion structure is closely related to the crystallization process. During crystal growth, screw dislocations might often occur, and they could force a PLA stereocomplex crystal (PEB and PEO at each side of a PLA crystal) to stack into a noncentrosymmetric structure. Detailed stereocomplex crystallization pathways are currently under study.

The maximum and minimum curvature in the onion crystals should be determined by the bending rigidity of stereocomplex crystals, similar to the situation in chrysotile asbestos.[11] From the TEM image in Figure 2B, the inner and outer onion diameters are 40–50 and 500–700 nm, respectively.

In conclusion, using SAXS and TEM techniques we compared crystalline morphologies in stereocomplexes SC5k-EO5k and SC5k-EO2k. In SC5k-EO5k, PEO and PEB have similar molecular weights (or volumes), and flat lamellar crystals were obtained. In contrast, since PEO had a much smaller molecular weight (or volume) than PEB in SC5k-EO2k, unbalanced surface stresses from the stretching of PEB brushes induced onionlike crystals.

Experimental Section

Model PEO-*b*-PLLA and PEB-*b*-PDLA diblock copolymers were prepared by controlled ring-opening polymerization of L- and D-lactides from PEO-OH ($M_n = 2000\,\text{g}\,\text{mol}^{-1}$ with PDI = 1.07 and $M_n = 5000\,\text{g}\,\text{mol}^{-1}$ with PDI = 1.08, Aldrich) and PEB-OH ($M_n = 4200\,\text{g}\,\text{mol}^{-1}$, 67 % ethylene and 33 % 1-butene, PDI = 1.06, Aldrich), respectively, in toluene with 0.5 equiv $AlEt_3$ as catalyst.[12] PLA molecular weight was controlled by conversion and determined by ^{1}H NMR spectroscopy on a Bruker DMX 500 spectrometer. To remove unconverted monomers and impurities, crude products were dissolved in chloroform and precipitated in hexanes for PEO-*b*-PLLA (in methanol for PEB-*b*-PDLA). PEO-*b*-PLLA was further washed with methanol (PEB-*b*-PDLA with hexane) twice to remove unconverted PEO-OH (PEB-OH) homopolymer. The PDIs for all samples were determined by SEC with THF as solvent and polystyrene as standard on a Viscotek GPCmax system. To prepare the stereocomplex, PEO-*b*-PLLA (2k–5.4k) and PEO-*b*-PLLA (5k–5.1k) were blended with PEB-*b*-PDLA (4.2k–5.4k) in chloroform at a concentration of 10 wt %. After drying in a vacuum oven at 50 °C for 3 d, stereocomplexes were stored in a desiccator. SAXS and WAXD experiments were performed at the X27C beamline in the National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength of the X-ray beam was 0.137 nm. TEM experiments were performed on a Philips EM300 at an accelerating voltage of 80 kV. Thin sections with a thicknesses of about 75 nm were obtained by using a Leica Ultracut UCT microtome equipped with a diamond knife at −30 °C. Thin sections were collected on 400-mesh TEM grids, freeze-dried, and stained in RuO_4 vapor at room temperature for 30–60 min.

Received: June 25, 2006
Revised: August 9, 2006

Keywords: block copolymers · crystal engineering · phase transitions · self-assembly · stereocomplexes

---

[1] a) M.-E. Meyre, C. Faure, *Recent Res. Dev. Phys. Chem.* **2004**, *7*, 321 – 338; b) S. Zhang, D. M. Marini, W. Hwang, S. Santoso, *Curr. Opin. Chem. Biol.* **2002**, *6*, 865 – 871; c) J. M. Schnur, *Science* **1993**, *262*, 1669 – 1676.

[2] a) F. Gauffre, D. Roux, *Langmuir* **1999**, *15*, 3738 – 3747; b) O. Regev, R. Backov, C. Faure, *Chem. Mater.* **2004**, *16*, 5280 – 5285; c) P. Chenevier, L. Bourel-Bonnet, D. Roux, *J. Am. Chem. Soc.* **2003**, *125*, 16261 – 16270.

[3] a) P. Sierro, D. Roux, *Phys. Rev. Lett.* **1997**, *78*, 1496 – 1499; b) P. Versluis, J. C. van de Pas, J. Mellema, *Langmuir* **2001**, *17*, 4825 – 4835; c) C. Oliviero, L. Coppola, R. Gianferri, I. Nicotera, U. Olsson, *Colloids Surf. A* **2003**, *228*, 85 – 90.

[4] a) H. Hoffmann, U. Munker, C. Thunig, M. Valiente, *J. Colloid Interface Sci.* **1994**, *163*, 217 – 228; b) J. Oerdisse, C. Couve, J. Appell, J. F. Berret, C. Ligoure, G. Porte, *Langmuir* **1996**, *12*, 1212 – 1218.

[5] a) J. Hao, H. Hoffmann, K. Horbaschek, *J. Phys. Chem. B* **2000**, *104*, 10144 – 10153; b) A. Song, S. Dong, X. Jia, J. Hao, W. Liu, T. Liu, *Angew. Chem.* **2005**, *117*, 4086 – 4089; *Angew. Chem. Int. Ed.* **2005**, *44*, 4018 – 4021.

[6] a) B. J. Battersby, R. Grimm, S. Huebner, G. Cevc, *Biochim. Biophys. Acta* **1998**, *1372*, 379 – 383; b) S. Hubner, B. J. Battersby, R. Grimm, G. Cevc, *Biophys. J.* **1999**, *76*, 3158 – 3166.

[7] L. Ramos, D. Roux, P. D. Olmsted, M. E. Cates, *Europhys. Lett.* **2004**, *66*, 888 – 894.

[8] a) P. Boltenhagen, O. D. Lavrentovich, M. Kléman, *Phys. Rev. A* **1992**, *46*, R1743 – R1746; b) M. C. Choi, T. Pfohl, Z. Wen, Y. Li, M. W. Kim, J. N. Israelachvili, C. R. Safinya, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 17340 – 17344.

[9] a) K. M. Hong, J. Noolandi, *Macromolecules* **1983**, *16*, 1083 – 1093; b) S. Koizumi, H. Hasegawa, T. Hashimoto, *Macromolecules* **1994**, *27*, 6532 – 6540.

[10] J.-J. Zhang, G. Jin, Y. Ma, *J. Phys. Condens. Matter* **2006**, *18*, 837 – 845.

[11] B. Lotz, S. Z. D. Cheng, *Polymer* **2005**, *46*, 577 – 610, and references therein.

[12] L. Sun, J. E. Ginorio, L. Zhu, I. Sics, L. Rong, B. S. Hsiao, *Macromolecules*, submitted.

[13] a) L. Cartier, T. Okihara, B. Lotz, *Macromolecules* **1997**, *30*, 6313 – 6322; b) L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, B. Lotz, *Polymer* **2000**, *41*, 8909 – 8919.