

Three-Dimensionally Packed Nanohelical Phase in Chiral Block Copolymers

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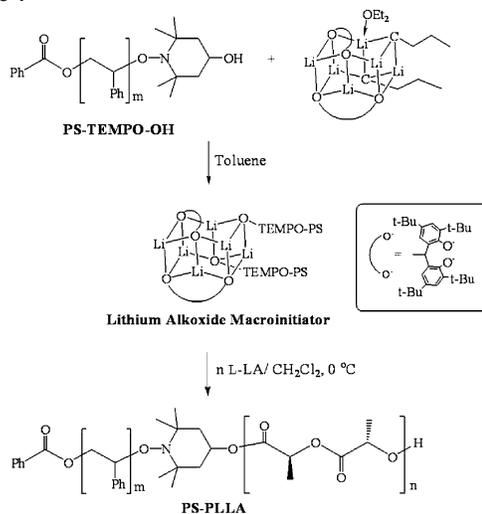
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The self-assembly of block copolymers has been extensively studied due to their abilities to self-assemble into one-, two-, or three-dimensional periodic nanostructures in the bulk with different compositions (i.e., volume fraction).¹ Defined structures can be easily tailored by molecular engineering of synthetic block copolymers, which is very appealing for the applications of nanotechnologies.² Biological architectures are formed by interplay among steric, hydrophobic, hydrogen-bonding, and electrostatic interactions to form hierarchical structures in different length scales. Since their early days, the self-assembly of synthetic supramolecules has been inspired by using similar interactions in biological matters and has already created a large number of nanostructures. Among them, helical morphologies in different length scales such as chiral centers, helical chain conformations, helical aggregations, and helical agglomerates have all been demonstrated.^{3–9}

The chirality of the chemical compounds remains to be one of the main driving forces for the formation of helical structures.⁴ Helical superstructures with a specific handedness have been obtained from buffer solutions of amphiphilic block copolymers containing charged helical blocks. The chiral entity of constituted block, aside from solvent, amphiphilicity, and electrostatic effects, plays an important role in the formation of helical superstructures in solution. In addition to the formation of helical superstructures from chiral block copolymers, an interesting nanohelical structure, helical ring on cylinder, has been observed from ternary triblock copolymers in the bulk, controlled by the relative incompatibilities of the three polymeric components in the block copolymers regardless of chirality.⁵ Here, we aim to examine the chirality effect on self-assembling structures in the bulk by using a diblock copolymer system constituting both achiral and chiral blocks, poly(styrene)-*b*-poly(L-lactide) (PS–PLLA). Well organized, hexagonally packed PLLA nanohelices with a left-handed helical sense were formed from the self-assembly of PS–PLLA in the bulk. This is perhaps the first time that the helical superstructures of chiral block copolymers were generated in the bulk and self-assembled to a 2D packed lattice.

A series of PS–PLLA copolymers with different volume ratios were prepared by a two-step “living” polymerization sequence (Scheme 1). On the basis of molecular weight and volume ratio, these PS–PLLAs were designated as PS_{*x*}-PLLA_{*y*} ($f_{\text{PLLA}}^v = z$), with *x* and *y* representing the numbers of the repeating unit for PS and PLLA blocks and *z* representing the volume fraction of PLLA (calculated by assuming that densities of PS and PLLA were 1.02 and 1.18 g/cm³, respectively). Bulk samples of the block copolymers were prepared by solution casting from dichloromethane (CH₂Cl₂) solution (10 wt % of PS–PLLA) at room temperature. After quenching from the microphase-separated melt,¹⁰ the thermally

Scheme 1



treated PS–PLLA samples were subsequently sectioned by ultramicrotome. A variety of self-assembling nanostructures, including spherical, hexagonally packed cylindrical, and lamellar structures, were identified by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Similar to the achiral block copolymer, poly(styrene)-*b*-poly(D,L-lactide) (PS–PLA),¹¹ most of the PS–PLLA samples exhibited typical phase structures as predicted by the theory based on block copolymer thermodynamics. Surprisingly, a nanohelical phase structure was observed for the PS280PLLA127 ($f_{\text{PLLA}}^v = 0.35$) sample, as shown by TEM in Figure 1. The pitch, projected diameter, and diameter of the nanohelices were determined as 43.8, 31.9, and 25.3 nm on average, respectively. Upon appropriate control of solvent evaporation rate, well-oriented microdomains consisting of 3D packed PLLA nanohelices in PS matrix were observed (Figure 2a). By examining the phase structure at different tilting angles in TEM, the nanohelices were found to be packed in a hexagonal lattice. The occupied volume fraction of PLLA blocks was calculated to be 31 vol %, which is approximately consistent with the estimated value from synthetic results ($f_{\text{PLLA}}^v = 0.35$). Corresponding 2D SAXS experiments using synchrotron radiations were performed to further identify the observed morphology. A well-defined scattering pattern having hexagonal-like diffraction was seen when the X-ray beam was aligned along the helical axis (Figure 2b). 1D SAXS profiles were extracted from 2D patterns by azimuthal integration as shown in Figure 2c. The diffraction peaks were found to occur at q^* ratios of $1:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{13}$. These results are consistent with the hexagonally packed phase structure of which the nanohelices can be treated as cylinder-like packing. However, even the reflections in Figure 2b indicate that the reflections possess almost identical spacing; the intensity of these reflections exhibits a 2-fold symmetry as shown

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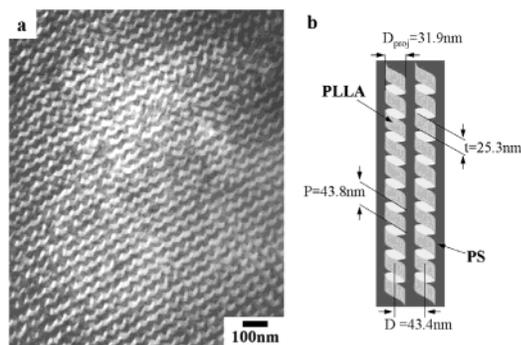


Figure 1. (a) TEM micrograph of PS280PLLA127 ($f_{\text{PLLA}}^v = 0.35$). (b) Schematic representation of nanohelical morphology.

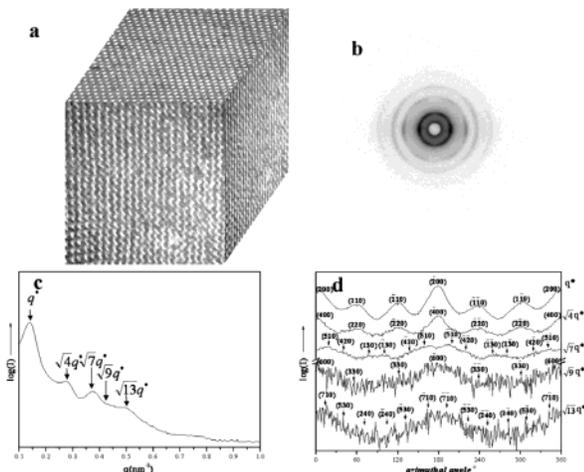


Figure 2. (a) 3D TEM micrograph. (b) 2D SAXS diffraction pattern along the direction of helical axes. (c) 1D SAXS profile for PS280PLLA127 ($f_{\text{PLLA}}^v = 0.35$) solution-cast sample. (d) Azimuthally scanning SAXS profile of Figure 2b.

in Figure 2d. Consequently, these results suggest a pseudo-orthorhombic structure for the packing of nanohelices (because the ratio of the a -axis and b -axis unit cell dimensions is nearly equal to $\sqrt{3}$) instead of a true hexagonal (it is probably orthorhombic). We speculate that the 2-fold symmetry in the intensity for an almost hexagonally packed structure is attributed to the deformation of nanohelix in uniaxial direction, in a way similar to the α -helical conformation of poly(L-alanine)¹² and the α -form crystal of PLLA.¹³ In Figure 1, it was found that the nanohelix adopted a left-handed helical sense, which is consistent with the fact that the PLLA blocks also possess an L chiral center. The formation of nanohelical phase structure has never been reported in PS-PLA block copolymers¹¹ and PLLA homopolymers before.¹⁴ We speculate that the appearance of the nanohelical structure in the PS-PLLA may be attributed to the effect of chirality interacting with the immiscibility of constituted blocks, unlike noncentrosymmetric phase structures in achiral triblock copolymers or their blends.¹⁵ Instead of the interplay in the elastic potential and interfacial energy, the self-assembly of helical curvature is induced by the formation of specific configurations of PLLA chains due to the interactions of chiral entities. Similar to the formation of helical crystals from chiral liquid crystalline polymers,⁶ the chirality strength is strong enough to compete with self-ordering processes and to stabilize the helical morphology when the phase structures possess the specific configurations (for instance, low liquid crystalline order). The studies of detailed mechanisms are still in process.

It is known that aliphatic polyesters can be hydrolytically degraded because of the unstable character of the ester group.¹⁶ For potential applications of these materials, the nanohelical phase

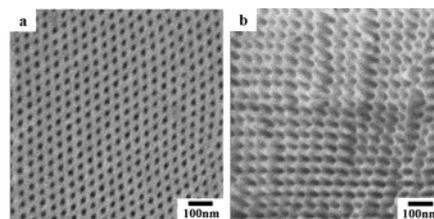


Figure 3. FESEM micrographs of hydrolyzed PS280PLLA127 ($f_{\text{PLLA}}^v = 0.35$) solution-cast samples by viewing (a) parallel to the helical axes and (b) perpendicular to the helical axes.

can be hydrolyzed to eliminate PLLA. Field emission scanning electron microscopy (FESEM) was used to observe such hydrolyzed samples from different views (Figure 3).¹⁷ The ordered nanohole arrays parallel to the helical axes in the hydrolyzed samples were confirmed by FESEM, and results were similar to those observed by scanning probe microscopy. The orderly packed nanohelical structure perpendicular to the helical axes from the fractured cross section was also verified. In conclusion, we demonstrated a new material system with helical nanostructures that may provide new opportunities for block copolymer applications in the field of nanotechnologies.

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Supporting Information Available: Detailed synthetic procedures, characterization, thermal analyses, and tilting images of TEM (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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