Switchable Nanostructures

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Springlike Nanohelical Structures in Chiral Block Copolymers**

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Helical structures are probably the most fascinating morphologies in nature, and they have been intensively studied as a result of their specific functions in the formation of biological architectures. Helical-chain conformations, such as single-strand α-helical peptides and double-stranded DNA, are regarded as the fundamental motifs for the hierarchical organization of proteins. A variety of origins for the formation of helical structures, such as hydrogen bonds,[1] solvophobic interactions,[2] π–π interactions,[3] cholesteric liquid crystal formation,[4] relative incompatibility,[5] and chirality,[6] have all been demonstrated. Biomimicking nature, helical morphologies have been obtained on different length scales by the interplay of noncovalent bonding interactions (that is, secondary forces). Block copolymers that consist of two chemically different components are able to self-assemble into various ordered nanostructures, such as spheres, cylinders, gyroids, and lamellae, as a consequence of the incompatibility of the constituent blocks.[7] Therefore, the self-assembled nanostructures in block copolymers appear promising in applications that employ the bottom-up approach.[8] In contrast to the helical superstructures in the hierarchical organization of chiral molecules, helical nanostructures have been obtained from the self-assembly of block copolymers that consist of achiral and chiral blocks, for example, polystyrene-*b*-poly(isocyanopeptide), in buffer solutions.[6a] However, a three-dimensionally packed nanohelical structure phase was found in the self-assembled chiral diblock copolymer, polystyrene-*b*-poly(L-lactide) (PS-PLLA), in the bulk.[9] Contrary to the conventional phase morphology of diblock copolymers, the formation of a nanohelical structure phase is attributed to the chirality of the constituent PLLA block.[9] Furthermore, a significant change, from long-pitch to short-pitch nanohelices, was found in the nanohelical phase upon annealing.[10] Thus, the structural geometries of the nanohelices might be strongly affected by applying stimulation. Herein, we report the internal and external stimuli, such as crystallization and shearing, respectively, which act on the nanohelical morphology so that the microphase-separated PLLA nanohelices exhibit springlike behavior in a PS matrix in response to the applied stimulus. Consequently, switchable nanostructures can be obtained by interplay of vitrification, crystallization, and microphase separation as well as shearing.

Bulk samples of block copolymers were prepared by solution casting of PS280-PLLA127 ($f^{v}_{\text{PLLA}} = 0.35$) in dichloromethane ($CH_2Cl_2$; 10 wt %) at room temperature. As evidenced by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS), a nanohelical structure phase quenched from microphase-separated melt at 165 °C (melting point of PLLA, ca. 160 °C) can be obtained from the self-assembly of PS-PLLA, and is packed in a hexagonal lattice.[9] In contrast to the racemic block copolymer, polystyrene-*b*-poly(D,L-lactide) (PS-PLA),[11] the formation of the nanohelical structures in PS-PLLA is attributed to the interplay of chirality and immiscibility of the constituent blocks.[9] As a result, the self-assembly of helical curvature is induced by the formation of specific conformations of PLLA chains arising from the interactions of chiral entities.

Considering their origin, the self-assembled nanohelical structures are expected to be affected by the changes of PLLA chain conformation. Notably, the PLLA component is intrinsically a crystallizable polymer as a result of the regularity of the chiral configuration. The crystallization of PLLA in PS-PLLA might give rise to significant changes in the self-assembly morphology and is thus considered as a driving force (namely, an internal stimulus) for manipulating the intrinsic nanohelical structure. The final morphology of crystalline block copolymers is strongly dependent on the experimental temperature, with respect to the order–disorder transition temperature (T_{ODT}), the crystallization temperature of the crystallizing block ($T_c^{\,c}$), the glass transition temperature of the amorphous block ($T_g^{\,a}$), and the crystallization rate.[12] Consequently, the microphase-separated morphology is determined by the crystallization temperature of PLLA that also justifies the degree of vitrification of the confined environment (that is, the PS matrix). The dividing confined environments—hard confinement ($T_c^{\,c} < T_g^{\,a}$) and soft confinement ($T_c^{\,c} \geq T_g^{\,a}$)—dictate the final morphology of crystallized PS-PLLA. For a system with $T_c^{\,c} < T_g^{\,a}$, the ordered nanostructure can be preserved because of the vitrified microdomains of the PS blocks. By contrast, if $T_c^{\,c} \geq T_g^{\,a}$, the effect of crystallization may lead to a change of microphase-separated morphology.

To examine the crystallization effect, the amorphous nanohelices (intrinsic nanohelices) of PS-PLLA were crystallized from hard ($T_{c,\text{PLLA}} < T_{g,\text{PS}} = 99.2\,°\text{C}$) to soft ($T_{c,\text{PLLA}} \geq T_{g,\text{PS}}$) confinement. The nanohelical morphology remained

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while PLLA crystallization was carried out under hard confinement (for instance, $T_{c,PLLA} = 80\,°C$; see Figure 1 a). The microdomains of the PS component became dark after staining with RuO_4, whereas those of the PLLA component appeared light. The crystallization of PLLA was restricted within confined microdomains because of the vitrification of the PS matrix, which preserved the helical morphology. Also, as evidenced by the one-dimensional (1D) SAXS profile (Figure 2 a and b), the diffraction peaks occurred at q^* ratios of $1{:}\sqrt{4}{:}\sqrt{7}{:}\sqrt{13}$, consistent with the hexagonally packed phase structure. As a result, the packing geometry of the crystalline nanohelices remained as a hexagonal lattice under hard confinement.

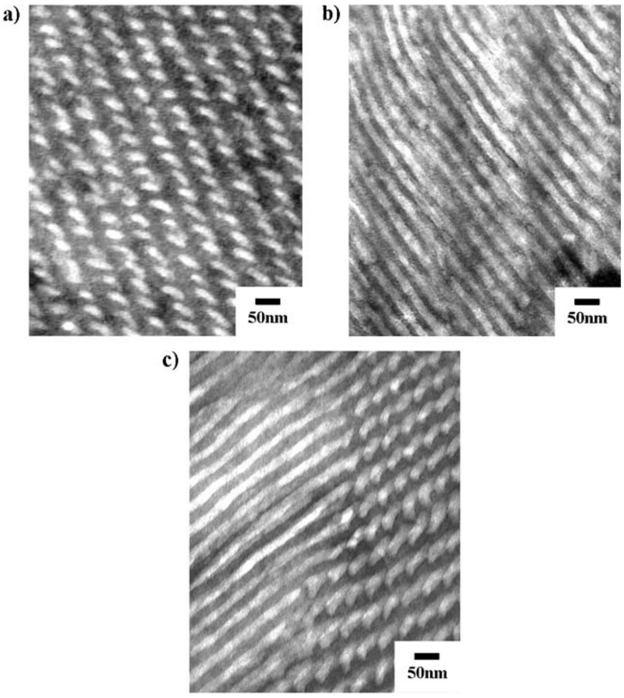

Figure 1. TEM micrographs of nanohelical structures in PS280-PLLA127 ($f^{v}_{PLLA} = 0.35$) bulk samples quenched from microphase-separated melt (165 °C), then a) crystallized at 80 °C for 120 min and b) crystallized at 110 °C for 120 min. c) TEM micrograph for phase transformation from helices to cylinders during crystallization at 110 °C.

By contrast, the nanohelices were transformed into a cylindrical phase when crystallization was carried out under soft confinement, while $T_{c,PLLA} > T_{g,PS}$ (for instance, $T_{c,PLLA} = 110\,°C$; see Figure 1 b). The developing stage of phase transformation can be clearly observed (Figure 1 c). The helical structure was stretched and transformed into a crystalline cylinder along the long axes of the helices (or cylinders), so that the hexagonal packing remained regardless of the transformation (Figure 2 c). The significant effect of crystallization on the microphase-separated phase is attributed to the stress-induced structural change when crystallization is carried out above $T_{g,PS}$.[12] As a result, the nanohelical structure behaves like a spring in response to a crystallization event, and the springlike PLLA microdomain can be modified as a crystalline spring under hard confinement, or a fully extended spring under soft confinement, by tuning the crystallization temperature.

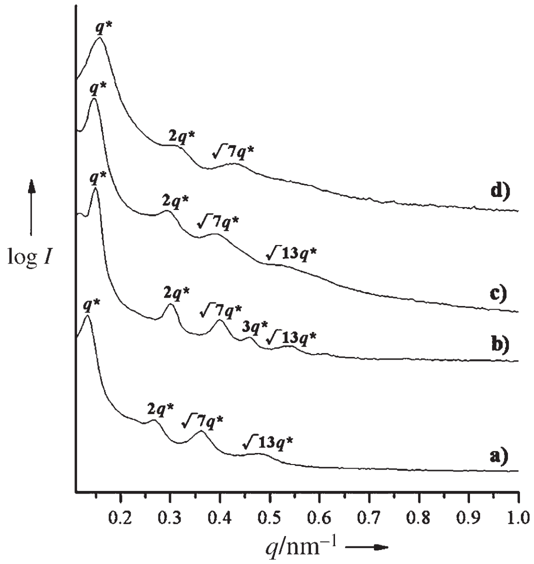

Figure 2. One-dimensional SAXS profiles for self-assembly of PS280-PLLA127 ($f^{v}_{PLLA} = 0.35$) with different geometries. a) Intrinsic nanohelices; b) crystalline nanohelices under hard confinement; c) stretched nanohelices (crystalline cylinders) under soft confinement; d) stretched nanohelices (amorphous cylinders) after shearing.

It is well-known that shear-induced orientation of block copolymers is one of the most convenient ways to generate a well-oriented morphology for bulk samples in practical applications.[13] Considering the springlike behavior of the nanohelical phase, shearing (an external stimulus as compared to crystallization) is expected to achieve the orientation of nanohelices and modify the morphology. Flow-induced alignment of the nanohelical phase was thus conducted by using a lubricated-channel die based on the design of Khan and Larson.[14] Molding and shearing of the intrinsic nanohelices were performed on a microphase-separated melt at 180 °C for 1 min, and then the processed strip was held in the die at the shearing temperature for 1 min before quenching with liquid nitrogen to eliminate the residual shear stress. The shear (velocity), vorticity, and velocity gradient directions were assigned as the *x*, *y*, and *z* directions, respectively. After quenching from the shearing melt, a hexagonally packed cylinder morphology was found in the *y*–*z* plane (Figure 3 a). Also, a longitudinal cylinder morphology was observed along the *y* direction (Figure 3 b), whereas the 2D SAXS pattern along the *y* direction appeared as a well-defined diffraction from oriented microdomains (inset of Figure 3 b). The 1D SAXS profile indicated the unchanged hexagonally packed structures after shearing (Figure 2 d). Thus, oriented cylinders were obtained, and the nanohelices also exhibited springlike behavior in response to shearing. Contrary to crystallization-induced cylinders, the shear-induced cylinders appeared as an amorphous entity.

The nanohelical phase with PLLA helices embedded in the PS matrix acted with springlike behavior upon internal and external stimulation. The stress-induced phase trans-

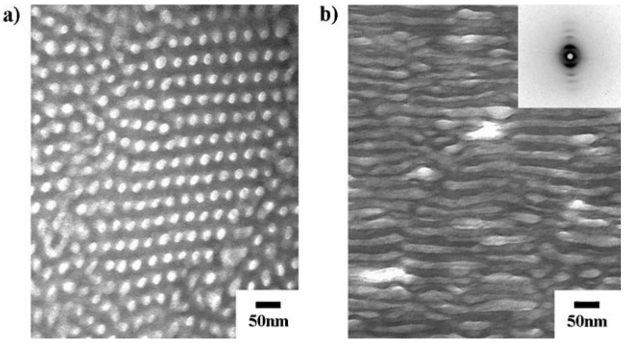

Figure 3. TEM micrographs of nanohelical structures in PS280-PLLA127 ($f^{v}_{\mathrm{PLLA}}=0.35$) bulk samples after shearing at 180 °C (above the m.p. of PLLA (≈160 °C) and $T_{\mathrm{g,PS}}$ (99.2 °C)) viewed a) parallel, and b) perpendicular to the shear axis. The inset shows the 2D SAXS pattern normal to the cylindrical axis.

formation from nanohelices to cylinders was driven either by crystallization or shearing. Considering the springlike behavior, a reversible process comprising transformation from stretched nanohelices (that is, cylinders) to intrinsic nanohelices would be expected once the stress-induced morphology was thermally treated to release the built-in stress. Figure 4 shows the reversible morphology at which the crystalline cylinders gradually revert to the original nanohelical structures through undulation, once the crystallized samples are remelted (at 165 °C) and then annealed at a temperature (130 °C) above the glass transition temperature of PS ($T_{\mathrm{g,PS}}=99.2$ °C). Similar results can also be obtained in shear-induced, amorphous cylinders, which progressively transform into an intrinsic structure once the shearing samples are annealed at a temperature (130 °C) above the glass transition temperature of PS (see the Supporting Information).

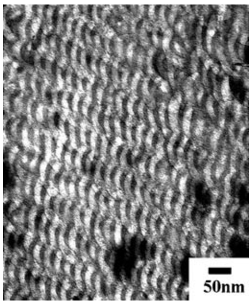

Figure 4. TEM micrograph of crystalline cylinders of PS280-PLLA127 ($f^{v}_{\mathrm{PLLA}}=0.35$) bulk samples after annealing at 130 °C for 60 min from 165 °C (microphase-separated melt).

In conclusion, a variety of self-assembled nanohelices in chiral block copolymers were observed by applying internal and external stimuli (that is, crystallization and shearing). The amorphous nanohelices in the bulk transform into crystalline nanohelices and cylinders by crystallization, and into amorphous cylinders by shearing. The crystallization-induced cylinders were thermally reversible, and able to revert to the original nanohelices upon remelting and annealing. In contrast to crystallized nanohelices, the reversible phase behavior can also be found in shear-induced cylinders by simple thermal annealing. As a result, the hexagonally packed nanohelical structure of the PLLA in the PS matrix of chiral PS-PLLA block copolymers has springlike behavior in response to the applied stimulus. This unique phase behavior thus might provide a technique for manipulating tunable nanohelical structures in practical applications. Consequently, switchable nanohelices from chiral block copolymers can be manipulated by the interplay of vitrification, crystallization, and microphase separation as well as shearing.

Experimental Section

PS-PLLA samples were prepared by using living free radical and ring-opening polymerizations in sequence. Detailed synthetic routes were described in our previous paper.[9]

The number-average molecular weight of PS and polydispersity index (PDI) of PS-PLLA were obtained by gel permeation chromatography. The molecular weight of the PLLA block was measured by ^{1}H NMR analysis. On the basis of molecular weight and volume ratio, the PS-PLLA is designated as PSx-PLLAy ($f^{v}_{\mathrm{PLLA}}=z$); x and y represent the numbers of repeating units of PS and PLLA, respectively, and z indicates the volume fraction of PLLA calculated by assuming that the densities of PS and PLLA are 1.02 and 1.18 g cm^{-3}, respectively. The number-average molecular weights of PS and PLLA and the PDI of PS280-PLLA127 ($f^{v}_{\mathrm{PLLA}}=0.35$) were 29400 g mol^{-1}, 18300 g mol^{-1}, and 1.21, respectively.

The thermal behavior of PS-PLLA was examined by differential scanning calorimetry (DSC). The sample was first heated to 165 °C and then cooled to −50 °C at a rate of 150 K min^{-1}. The glass transition temperatures of the PLLA and PS blocks were clearly identified as 51.4 and 99.2 °C, respectively.

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