

# Helical Microphase-Separated Structures formed from Multiblock Copolymers

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Hexagonally-packed double-stranded helical domain structure having a homochiral single row but with alternating chirality inversion was observed from a tetrablock terpolymer of the  $S_1IS_2P$  type, where S, I and P denote polystyrene, polyisoprene and poly(2-vinylpyridine), respectively.

SISP tetrablock terpolymer was synthesized by a living anionic polymerization.[1],[2] Molecular characteristics for the  $S_1IS_2P$  terpolymer are summarized in Table 1, and two kinds of structure parameter are used as  $\alpha (= \phi_{S1}/\phi_{S2})$  and  $\beta (= \phi_P/\phi_I)$ , where  $\phi_{S1}$ ,  $\phi_{S2}$ ,  $\phi_P$  and  $\phi_I$  are volume fractions of components  $S_1$ ,  $S_2$ , P and I, respectively.

Figure 1a and 1b show the 2D-TEM image and 3D-reconstructed image of I domains stained selectively by  $OsO_4$ , respectively, it has been confirmed that the I domains have double-stranded helical structure. While from the 2D-TEM image of P domains stained selectively by  $I_2$  as shown in Figure 1c, it has been confirmed that P domains have hexagonally-packed helical structure. Summarizing these experimental facts, it has been confirmed that the SISP terpolymer

shows hexagonally-packed structures having helical domains of P component surrounded with double-stranded helices of component I embedded in the matrices of component S as shown in Figure 1d. Figure 2 reveals a 3 dimensional reconstructed image of the SISP terpolymer by TEM tomography, in which the blue helices are right-handed double helix and the red helices are left-handed ones. This image clearly shows that helices in one row is homogeneous, however handedness is totally inverted in the adjacent row and so on.

## References

- [1] Y. Miyamori, et al., *ACS Macro Lett.* **2020**, 9, 32–37  
[2] Y. Miyamori, et al., *ACS Macro Lett.* **2021**, 10, 978–983

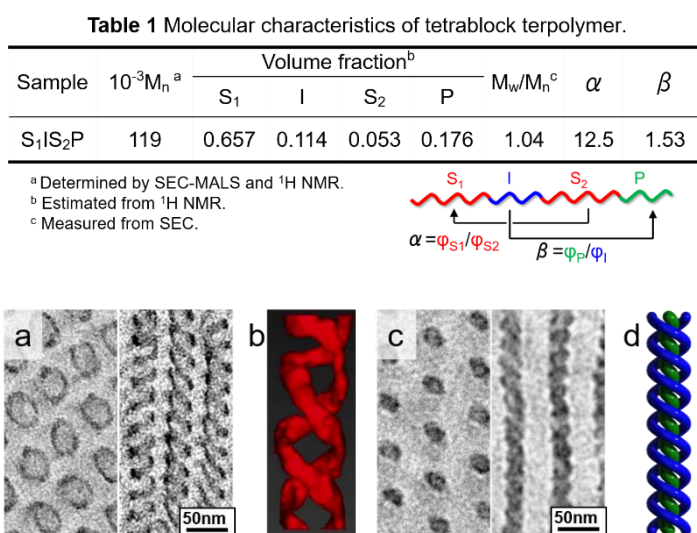


Figure 1. (a) TEM images of I domain stained by  $OsO_4$ , (b) 3D TEM images of I domain, (c) TEM images of P domain stained by  $I_2$ , (d) Schematic drawing of I/P domains.

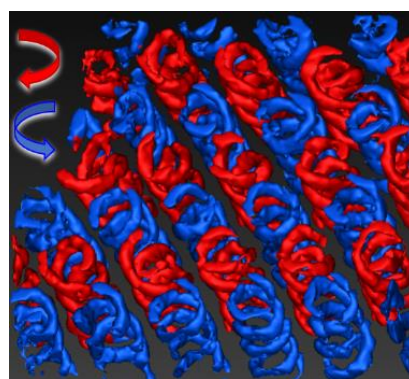


Figure 2. A projected view of a 3D-reconstructed image. The right-handed helices are painted with blue, while the left-handed helices are in red