

Hierarchical Superhelices from Achiral Polymers

Artificial periodic helical nanostructures on a sub-optical wavelength scale have been demonstrated to have prominent optical properties for application of metamaterials.

A helix is a fascinating structure in nature; from DNA to cell, tissues are related to the helical structure, but helical structures exist typically in a chiral system. Herein, Wei-Tsung Chuang (NSRRC), Yeo-Wan Chiang (National Sun Yat-sen University) and I-Ming Lin (National Sun Yat-sen University) proposed a novel concept of focal asymmetry to fabricate hierarchically helical structures from nanometer to submicrometer scale in the self-assembly of achiral dendron-jacketed block copolymers (DJBCP). As shown in **Fig. 1**, to create the focal asymmetry in dendrons, they synthesized two positional isomers of dendrons featuring two amphiphilic tails at the 3,4- and 3,5-positions of the benzoic acids, which behave as asymmetric and symmetric dendrons (denoted **aD** and **sD**), respectively. The ortho-position poly(2-vinylpyridine) (P2VP) in polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) and the para-position poly(4-vinylpyridine) (P4VP) in polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) respectively represent asymmetric and symmetric concepts in the supramolecular dendron-jacketed blocks. Through hydrogen-bonding interactions, **aD** and **sD** units can be grafted to the P4VP blocks and the P2VP blocks, resulting in DJBCP of four types with varied levels of asymmetry.

Figure 2 presents transmission-electron-microscope (TEM) images of the self-assembled nanostructures obtained from

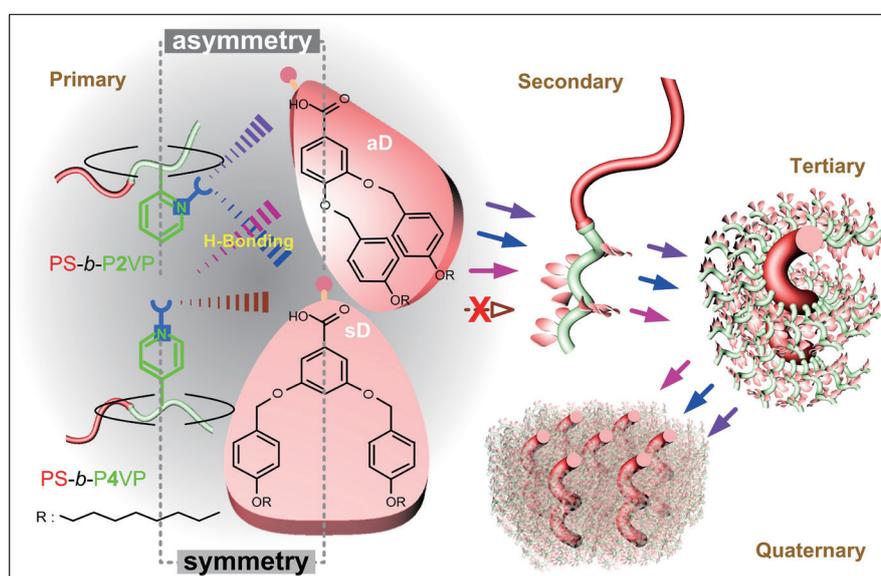


Fig. 1: Schematic representation of hierarchical helical assemblies of supramolecular DJBCP induced on controlling the asymmetric chemical structures of the dendrons and the interactive hydrogen-bonding (H-bonding) sites of the diblock copolymers. [Reproduced from Ref. 1]

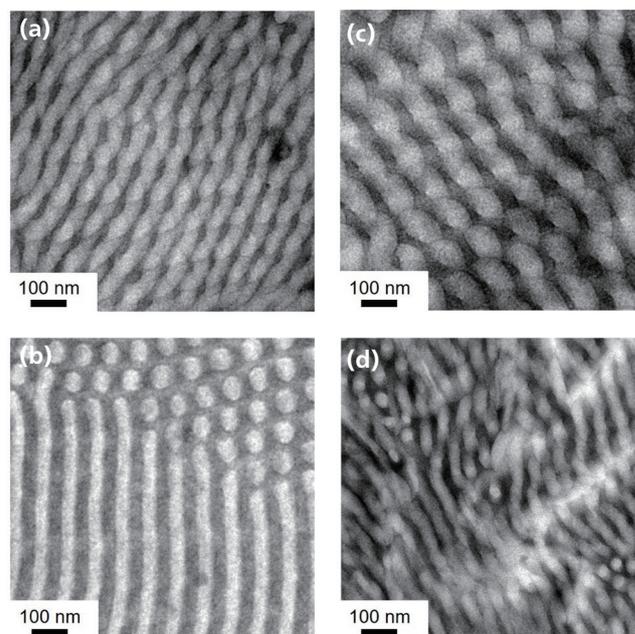


Fig. 2: TEM micrographs of films as cast of (a) PS-*b*-P4VP(**aD**)_{0.5}, (b) PS-*b*-P4VP(**sD**)_{0.5}, (c) PS-*b*-P2VP(**sD**)_{0.75} and (d) PS-*b*-P2VP(**aD**)_{0.3}. After staining with I₂, the dendron-jacketed blocks and PS blocks appear dark and bright, respectively. [Reproduced from Ref. 1]

the four types of DJBCP with a constant PS volume fraction, 0.23, so the PS domains (bright area in TEM images) are surrounded by dendron-jacketed blocks (dark area in TEM images). The helical structures appeared in the three types of DJBCP with asymmetric components, which are PS-*b*-P4VP(**aD**)_{0.5}, PS-*b*-P2VP(**aD**)_{0.3} and PS-*b*-P2VP(**sD**)_{0.75} (here, 0.5, 0.3 and 0.75 represent the molar fraction of **aD** or **sD** to P4VP or P2VP unit); PS-*b*-P4VP(**sD**)_{0.5} with both symmetrical components formed a cylindrical structure. Combining the above result, as long as it contains an asymmetric element, the helical structure can be produced.

As shown in **Fig. 3**, PS-*b*-P4VP(**aD**)_{0.5} was selected for small-angle X-ray scattering (SAXS) with oscillatory-shearing alignment *in situ* at **TLS 23A1**. A highly ordered SAXS pattern reveals a highly oriented and ordered

structure. The distance between two helices and a pitch length estimated from the diffraction positions are ca. 140 and 125 nm, respectively, which are consistent with the TEM image. In Fig. 3(d), the azimuthal scan of the first-order diffraction of the cross pattern reveals that the helical angle (twisting power) of the PS helix is approximately 50° , as estimated from the angle enclosed between the arms of the cross. The twisting power of the PS helices becomes adjustable on controlling the grafting ratio (x

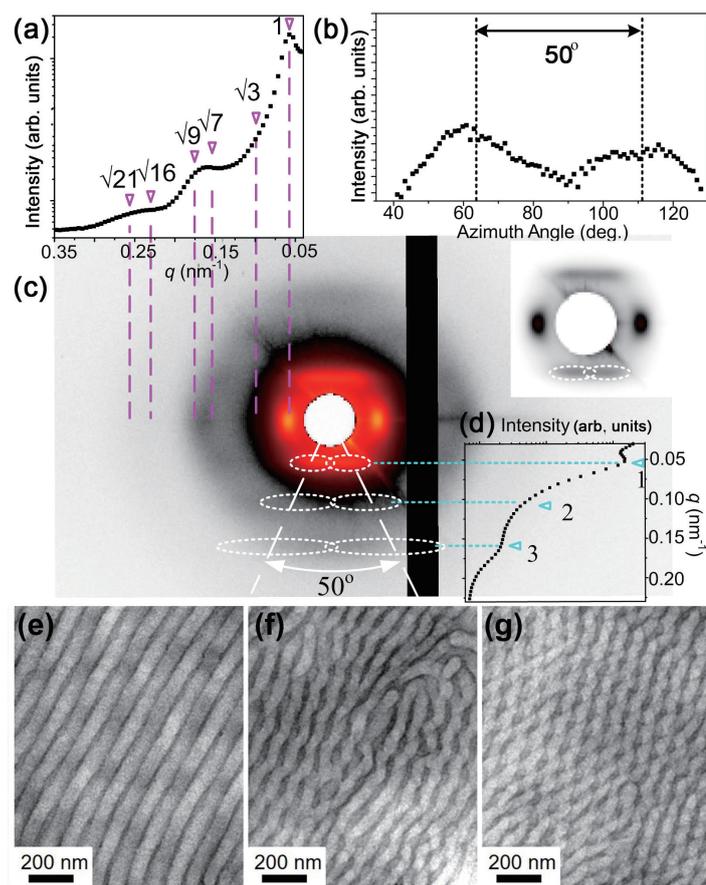


Fig. 3: (a) 2D SAXS pattern of PS-*b*-P4VP(aD)_{0.5}, recorded under shear alignment *in situ* using a rheometer; the inset in the upper-right corner is a selected magnified zone. (b) 1D SAXS profile integrated along the equatorial direction of the 2D SAXS pattern in (a). (c) 1D SAXS profile integrated from the cross pattern in (a). (d) Azimuthal angle scan from first-order diffraction of the cross pattern. (e–g) TEM images of PS helices with adjustable curliness, obtained at grafting ratios $x =$ (e) 0.3, (f) 0.4 and (g) 0.5 in PS-*b*-P4VP(aD) _{x} . [Reproduced from Ref. 1]

$= 0.3–0.5$) in PS-*b*-P4VP(aD) _{x} . Upon increasing the grafting ratio, the corresponding apparent curliness was increased, as evident in the TEM micrographs (Figs. 3(e)–3(g)). This effect means that the degree of helical curliness can be hierarchically transmitted across various length scales in the DJBCP system. Notably, such adjustable curliness is rarely observed in BCP-based helical structures.

In summary, this work shows the first discovery of helical structures with tunable curliness triggered from the focal asymmetry in an entirely achiral system of DJBCP through hydrogen-bonding interactions. (Reported by I-Ming Lin, National Sun Yat-sen University and Wei-Tsung Chuang)

This report features the work of Wei-Tsung Chuang, Yeo-Wan Chiang and their coworkers published in J. Mater. Chem. C **8**, 1923 (2020). This paper was selected as the inside front cover of Issue 6. [Cover image reproduced by permission of Wei-Tsung Chuang and The Royal Society of Chemistry from *J. Mater. Chem. C*, 2020, **8**, 1923, <https://doi.org/10.1039/C9TC06135E>.]

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- SAXS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

Reference

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