One-Shot Preparation of Topologically Chimeric Supramolecular Copolymers with Segregated Secondary Structures

Supramolecular polymers are promising next-generation polymeric materials with versatile functions. The important step is the construction of segregated supramolecular structures that can realize synergetic combinations of different polymeric properties. Here, we report an example of one-shot preparation of topologically chimeric supramolecular copolymers. When cooling non-polar solutions of two different monomers that individually form linearly extended and helically folded fibers, we obtain nanofibers with helical–linear segments. Mechanistic insights revealed the formation of heteromeric hydrogen-bonded intermediates during the polymerization, and this allowed gradual variation of the monomer composition. We further demonstrate that deformation of the linear segments by photoirradiation induces the higher-order folding of the chimeric fibers.

Self-assembled one-dimensional (1D) nanostructures consisting of segregated supramolecular domains of multiple components can exhibit sophisticated functions due to the synergetic combinations of different molecular properties [1]. In self-assembly phenomena, however, molecular components associate through reversible intermolecular interactions to form polymeric arrays, and this allows self-recognition of the individual molecular components to afford self-sorted nanostructures (narcissistic self-sorting). Accordingly, in most cases, seeded growth approaches are used to prepare multicomponent 1D nanostructures (i.e., block supramolecular copolymers) [1–5]. However, even by using the seeded growth approach, attaining the heterojunction of nanostructures with dramatically different morphologies is challenging because the structures of those molecular components are also dissimilar. Here, we report the first example of one-shot preparation of topologically chimeric supramolecular copolymers with helical–linear structures [6].

We previously found that cooling (1.0 K min^{-1}) of a hot methylcyclohexane (MCH) solution of diphenylnaphthalene-based barbiturate **Nap** resulted in the formation of helically folded fibers [**Fig. 1(A)**, **(C)**] [7]. The continuously curved structure originates from intrinsic curvature upon stacking of hydrogen-bonded hexamers (rosettes) due to the rotational and translational offsets [7, 8]. Atomic force microscopy (AFM) measurement revealed that **Ant** monomer having an anthracene unit instead of the naphthalene unit on **Nap** self-assembled into linearly extended fibers [**Fig. 1(B)**, **(D)**]. A major cause of the loss of intrinsic curvature of **Ant** is that the degree of translational/rotational displacement becomes smaller by strong π–π stacking interaction. The

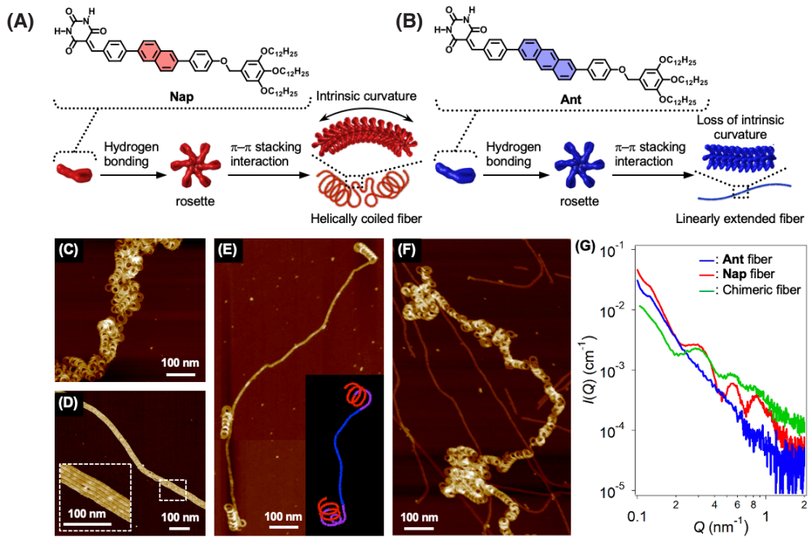

Figure 1: (A, B) Molecular structure and schematic representation of the supramolecular polymerization of **Nap** **(A)** and **Ant** **(B)**. **(C, D)** AFM images of supramolecular polymers of **Nap** **(C)** and **Ant** **(D)** prepared by cooling a hot MCH solution of each molecule (c = 1.0 × 10^{-5} M) using a cooling rate of 1.0 K min^{-1}. **(E, F)** AFM images of supramolecular (co)polymers prepared by cooling a hot MCH solution of a 1:1.3 mixture of **Ant** and **Nap** using a cooling rate of 1.0 K min^{-1} **(E)** and a 1:1.5 mixture of **Ant** and **Nap** using a cooling rate of 0.1 K min^{-1} **(F)**. **(G)** SAXS profiles of MCH solution of **Nap** (red line), **Ant** (blue line), and a 1:1.5 mixture of **Ant** and **Nap** (green line) prepared at a cooling rate of 1.0 K min^{-1}.

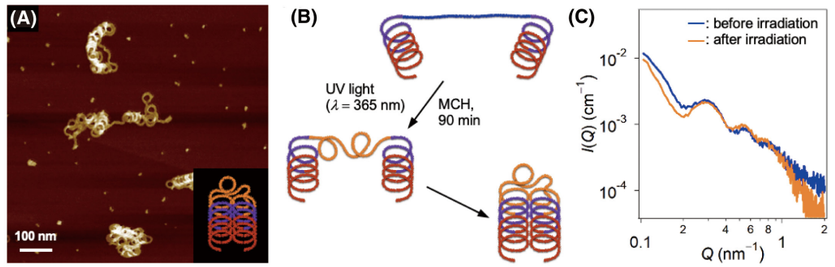

Figure 2: (A) AFM images of chimeric fibers after irradiation with UV light (λ= 365 nm) in MCH at 293 K for 90 min. **(B)** Schematic representation of the topology changes upon UV irradiation of chimeric fibers. **(C)** SAXS profiles of MCH solutions of the 1:1.5 mixture of **Ant** and **Nap** before (blue line) and after irradiation (orange line) with UV light (λ = 365 nm) at 293 K for 90 min.

dramatically different homopolymer topologies (helically folded and linearly extended fibers) arising from very similar monomer structures inspired us to explore supramolecular copolymerization that could afford helical–linear fibers. To our surprise, cooling a MCH solution of monomeric 1:1.3 mixture of **Ant** and **Nap** at a cooling rate of 1.0 K min^{-1} afforded nanofibers comprising helically coiled and linearly extended segments [**Fig. 1(E)**]. We refer to these unique fibers as “chimeric fibers”. On the other hand, under kinetic conditions by fast cooling (0.1 K min^{-1}), the two monomers self-sorted to afford simple mixtures of linearly extended and helically coiled fibers [**Fig. 1(F)**]. The temperature-dependent UV-vis absorption and fluorescence spectra of the mixture solution revealed an interplay of the supramolecular copolymerization processes of the **Ant** and **Nap** [9]. Upon cooling a monomeric solution of the mixture by slow cooling (0.1 K min^{-1}), the **Ant** rosette, which is highly aggregative via π–π stacking interactions, primarily self-nucleates through a self-recognition process of the acene moieties and elongates into linearly extended fibers. Upon further cooling under thermodynamic conditions, the **Nap** rosette self-recognizes by the π–π stacking interactions and elongates into helically coiled fibers. In contrast, under kinetic conditions (1.0 K min^{-1}), a small amount of **Nap** monomers can be already incorporated into the **Ant** rosettes and assemble to the elongating linear segments. Upon further cooling, the **Nap** content of the rosettes gradually increases, and eventually **Nap**-rich rosettes form helically coiled segments to afford helical–linear chimeric nanofibers. Accordingly, we succeeded in one-shot preparation of topologically chimeric fibers via a gradient supramolecular copolymerization.

The chimeric fibers exhibited photoinduced folding by segment-selective topological change. Photodimerization of anthracene moieties in **Ant** homopolymers induced an attenuation of the stiffness of the main chain [**Fig. 2(A)**]. A similar change in the linear segments in chimeric fibers allowed cohesion of helical segments, thus leading to higher-order folding of chimeric fibers [**Fig. 2(B)**].

These characteristic secondary structures of supramolecular polymers were also studied in solution using small-angle X-ray scattering (SAXS). In our previous study, the MCH solution of helically folded homopolymers of **Nap** displayed scattering peaks within the range of Q= 0.3–0.9 nm^{-1} that were attributed to the intrinsic curvature [**Fig. 1(G)**] [7]. In contrast, the homopolymer solution of **Ant** with linearly extended topology exhibited only fractal-like scattering, which is in good agreement with intrinsically uncurved fibers. The solution of chimeric nanofibers within the same range of **Nap** homopolymers also displayed the identical scattering peaks characteristic of intrinsic curvature of helical segments. The SAXS profile of the solution containing compactly folded fibers did not show new peaks in the measured region [**Fig. 2(C)**], thus demonstrating that an intrinsic curvature could not be generated by the photodimerization of **Ant** due to the inhomogeneity of the curvature in the **Ant** segments.

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[9] Schematic representation of the plausible process is shown in ref. [6].

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