2 -1 Chemical Science

Helicoidal Supramolecular Alternating Copolymers Formed by Barbiturate Naphthalene Molecules with Ether and Ester Linkages

We prepared novel supramolecular copolymers (noncovalent polymers) by mixing electron-rich and -poor hydrogenbonding supramolecular monomers through the formation of six-membered supramolecular complexes (rosettes). These monomers kinetically coassembled through a temperature-controlled protocol into amorphous coaggregates comprising a diverse mixture of rosettes. Over days, the electrostatic interaction between the two monomers induced an integrative self-sorting of rosettes. While the electron-rich monomer inherently forms toroidal homopolymers, the additional electrostatic interaction allowed helicoidal growth of supramolecular copolymers that are comprised of an alternating array of two monomers. These organization processes could be studied by small-angle X-ray scattering (SAXS).

We have been exploring the unprecedented selfassembly properties of a variety of barbiturated π -conjugated molecules [1]. These molecules organize into six-membered hydrogen-bonded complexes referred to as "rosettes" (Fig. 1a). The rosettes subsequently stack through $\pi - \pi$ interactions into a supramolecular polymer with an intrinsic radius of curvature of 7–15 nm. Extending this hierarchical process has also led to supramolecular polymers with unprecedented helicoidal higher-order structures [2, 3]. Herein, we focus on molecule 1 (Fig. 1b) [4, 5], which triggered the development of these unique supramolecular polymers. Molecule 1 mainly forms uniform toroidal fibers as closed nanostructures, rather than open-ended helicoidal structures (Fig. 1c). The efficient ring-closure during the continuous stacking of the rosette complex of 1 was attributed to its low aggregation tendency, which prevents the supramolecular polymer chains from elongating into helicoidal structures. Based on this molecular structure, we applied a small mutation by introducing a carbonyl group in the linker moiety to form 2 (Fig. 1b). It was predicted that enhancing the stacking force between

rosette complexes by admixing a monomer subunit with an electronically complementary π -conjugated core might realize alternating supramolecular copolymerization: due to its modification, the π -conjugated core of **2** is electron-deficient, and can thus interact with **1** via electrostatic interactions.

Atomic force microscopy (AFM) images of self-assembled 2 in methylcyclohexane (MCH) exhibited only indistinct linear fibrils (Fig. 1d). The very different spectroscopic outcome obtained upon introducing the ester group suggests that the lower electron density of the naphthalene core of 2 and/or dipole repulsion between the ester groups hamper the idiosyncratic stacking responsible for the formation of curved rosette aggregates [6]. Upon mixing 2 with 1, they kinetically coassembled into amorphous coaggregates when a 1:1 molar mixture of their monomers in MCH was cooled. Dynamic light scattering (DLS) measurements of the freshly cooled mixture showed small aggregates with size around 15 nm, which is far smaller than observed for toroids of 1 and linear fibrils of 2. In line with these observations, only amorphous coaggregates were observed in AFM images of the as-cooled fresh solution spin-coated onto highly oriented pyrolytic graphite (HOPG) (Fig. 2b).







Figure 2: a, Schematic representation of the supramolecular copolymerization of 1 and 2 into a helicoid and the thermal transition from the helicoid to an amorphous coaggregate. **b**, **c**, AFM images of the amorphous coaggregates (**b**: aged for 0 h) and helicoids (**c**: aged for 31 h) formed by a 1:1 mixture of 1 and 2 ($c_1 = 100 \mu$ M) at 20 °C. **d**, SAXS profiles of toroids of 1 (red), linear aggregates of 2 (green), amorphous coaggregates of 1/2 (light blue), and helicoidal aggregates of 1/2 (yellow, after 120-h aging). The white profile represents the simulation result that was most similar to the experimental data, which is based on the following parameters: pitch distance (p) = 5.5 nm, coil center-to-center distance (D) = 16 nm. The inset figure is a schematic representation of the helicoid with the parameters used for the model fitting.

resolution imaging revealed an outer helicoidal diameter of approximately 23 nm and pitch of approximately 5.7 nm (Fig. 2c). These results suggest that the topological extension from a toroidal to a helicoidal fiber was achieved, without synthetic extension of the aromatic core as we have done previously [2]. Based on IR studies, it can be concluded that the two monomer subunits kinetically coassemble by hydrogen-bonding to form various rosette complexes, and continuously dissociate and reassemble with rearrangement of the hydrogen bonds until the enthalpy gain of the system is maximized through the electrostatic interaction between 1 and 2. Upon heating, the helicoidal copolymers underwent a catastrophic transition into amorphous coaggregates via entropy-driven randomization of the monomers in the rosette (Fig. 2a).

The growth of the helicoidal supramolecular copolymers of 1 and 2 was studied by *in-situ* small-angle X-ray scattering (SAXS) measurements (Fig. 2d). Reflecting distinct differences in their nanostructures, individual assemblies formed by 1 and 2 displayed considerably different SAXS profiles. In contrast to a nonperiodic oscillatory feature at Q = 0.3-1 nm⁻¹ observed for the profile of 1 which is characteristic of our curved fibrous structures (red arrows), no such oscillatory feature was observed for 2 due to the absence of well-defined curvature in its nanostructure. The SAXS profiles of a 1:1 mixture of 1 and 2 measured after cooling showed a time-dependence. During the initial stages (0–2.5 h), the profiles correspond to small (< 10 nm) size-dispersed scatterers, with no visible oscillatory features. From 5 h onward, a nonperiodic oscillatory feature at Q = 0.3-1 nm⁻¹ can be observed (yellow curve). Although such features also appear in SAXS profiles arising from toroids of 1, the SAXS

from 1/2 exhibits an additional sharp scattering peak at $Q = 1.15 \text{ nm}^{-1}$ (d = 5.5 nm, yellow dotted arrow), which is likely to correspond to the helicoidal pitch (p) of the fibers as shown in Fig. 2d, which was estimated from AFM images to be ~5.7 nm (Fig. 2c). This assignment of the SAXS features could be verified by simulating the scattering of a model helicoid using SPONGE, a materials science-oriented scattering pattern calculator [7].

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