Reversible Folding/Unfolding of Diarylethene-Incorporated Supramolecular Polymers by Light

Helical folding of randomly coiled polymers is an essential organization process not only for natural protein but also for synthetic polymers, but realizing this dynamic process in supramolecular polymers (SPs) is a formidable challenge. Herein, we achieved photo-induced reversible folding/unfolding of SPs driven by photo-isomerization of diarylethene (DAE). A DAE-functionalized supramolecular monomer (open isomer) afforded randomly coiled SPs in a non-polar solvent. Irradiation of the solution with UV light causes ring-closure reaction of the DAE moieties, inducing helical folding of the SP chains. Subsequent visible-light irradiation to the resultant helical SPs induces their unfolding. These dynamic structural transition processes can be studied by in-situ small-angle X-ray scattering measurements.

We have been exploring unique self-assembling properties of a variety of barbiturated x-conjugated molecules [1, 2]. These molecules initially organize into six-membered cyclic hexamers referred to as rosettes by self-complementary hydrogen-bonding. The resulting rosettes subsequently stack with rotational and translational displacements to afford intrinsically curved supramolecular polymers (SPs) including toroids and catenanes [3, 4], random coils [5, 6], waves [7], spirals [8], and helicoids [5, 6]. Furthermore, incorporating a photochronic unit into the monomer allows us to control the higher-order structures of the corresponding SPs by light [5]. Herein, we studied the photosresponsive behavior of SPs formed by diarylethene (DAE)-incorporated molecules [1, 2]. These molecules initially organize into small-angle X-ray scattering (SAXS) revealed that ring-closure and ring-opening reactions of DAE units enable fine-tuning of curvature to the original random coils. SAXS gradually increased over a week and eventually reached 16.3 nm, which is comparable to that of the original random coils. AFM imaging after 10 days of aging showed that all SPs were unfolded to a similar degree as the original random coils [Fig. 2b]. When this photo-generated random coil solution was irradiated with UV light, we could again see helicoids by AFM, indicating the reversibility of the light-induced folding/unfolding processes [Fig. 2d]. The hysteresis between the folding and unfolding is presumably due to the interloop van der Waals interactions of the helicoidal structures that render the latter process slow.

References


Figure 1: a) Chemical structure of 1 (1o) and 1c. b-d) AFM images of random coils (b) and helicoids (c). d) Time-dependent SAXS profiles from random coils (orange line) to helicoids (blue line) in MCH upon UV irradiation. e) Schematic illustration of folding process by UV irradiation.

Figure 2: a) AFM images of photo-generated random coils with partial spiral domains (a) and photo-generated random coils after 10 days of aging (b). c) SAXS profiles of helicoids (blue), photo-generated random coils (brown) and 1-week aged photo-generated random coils (orange). d) Schematic representation of unfolding process of helicoids into random coils by visible-light irradiation.