Supplementary Information

Adsorption/desorption-induced phase transformation in the self-assembled monolayers of an amphiphilic rod-coil block copolymer

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1. Experiment section

Synthesis of Rod-Coil Block Copolymer. A PHIC-b-P2VP (Mw=120 kg mol^{-1},MWD=1.25, f_{P2VP}=0.3) rod-coil block copolymer was synthesized via living anionic polymerization. The P2VP homopolymer was first synthesized in THF at -78 ^{o}C by living anionic polymerization, using a potassium diphenyl methane (DPM-K) initiator. The copolymerization of P2VP and the PHIC block was carried out using sequential polymerization in the presence of sodiumtetraphenyl borate ($NaBPh_4$).

Preparation of Block Copolymer Solution. The PHIC-P2VP block copolymer powders were dissolved in anhydrous toluene (99.8%, Aldrich) in ambient conditions. In order to vary the surface coverage, the solution concentration was varied among 0.1, 0.05, 0.01, and 0.005 wt %. The solution was filtered through 0.2 μm Teflon membrane filter

before coating onto mica plates.

Coating Block Copolymer Films. Freshly cleaved mica substrates (Pelco, Ted pella Inc.) were obtained by carefully peeling off several layers using Scotch tape. Block copolymers were adsorbed from toluene solution onto mica plates by the immersion-coating method. In the immersion-coating method, mica plates were immersed in the copolymer solution for 1, 3, 6, and 15 h, removed from the solution, and then dried by exposure to the atmosphere.

Solvent Immersion Annealing of the Block Copolymer Film. The mica plates covered with block copolymer films were immersed in a clean anhydrous toluene or methanol for different periods of time. Then the plates were dried by exposure to the atmosphere.

Atomic Force Microscopy. Atomic force microscopy (AFM) was performed under a commercial scanning probe microscope (Digital Instruments Multimode SPM IIIa system). The AFM was equipped with a Quadrex for phase imaging and a Micro 40 active antivibration unit (Halcyonics). Tapping mode etched silicon probe (RTESP) (Veeco probe) was used for cantilever. These probes have force constant range of 20-80 N/m and resonance frequency of 276-303 kHz. The cantilever was forced to oscillate near its resonance frequency. The laser beam was centered on the tip of the cantilever and reflected on a photodiode. To minimize the surface deformation of the sample by the tip, the so-called light tapping was applied.

2. Film thickness measurement

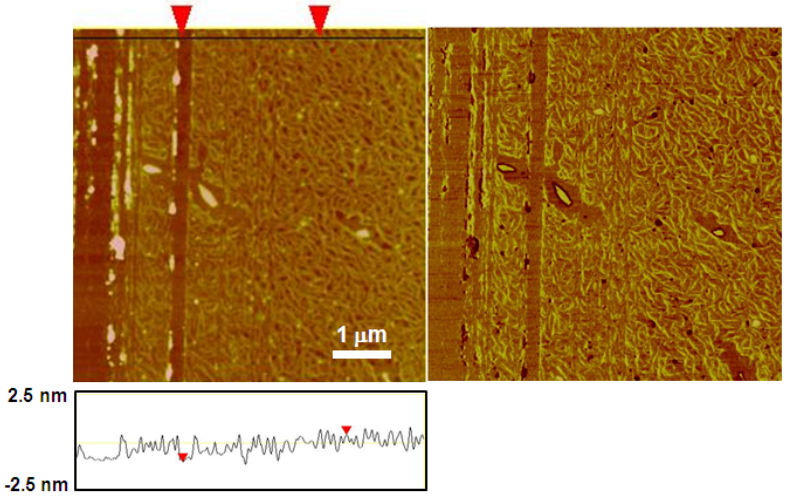

Fig. S1. Height contrast AFM image of a PHIC-b-P2VP monolayer film with a scratch.

3. AFM images of the films by immersion coating in higher concentions

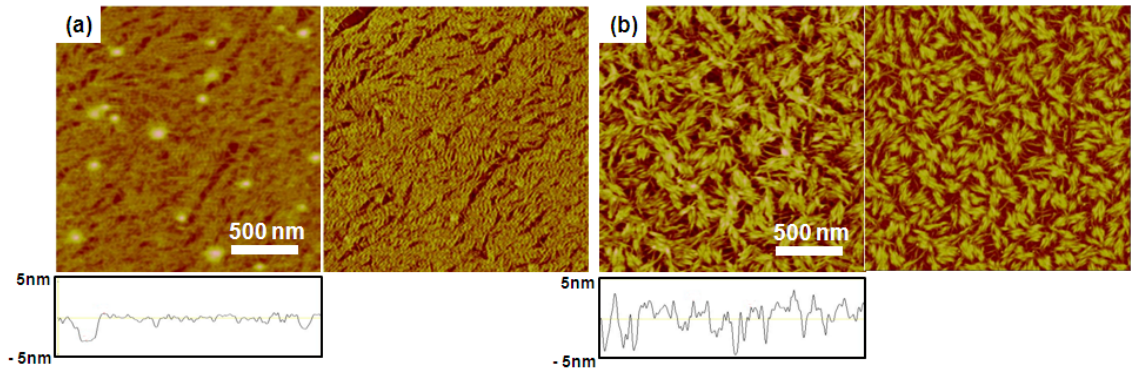

Fig. S2. Height contrast AFM images of dry rodlike PHIC chains tethered onto mica through adsorption of P2VP coils. The samples were obtained by the immersion coating of mica plates in toluene solution of PHIC-P2VP. (a) bilayer-thick (~3nm) film of the block copolymer by immersion in 0.05 w/v% for 15 h, (b) films with aggregates of the block copolymer by immersion in 0.1 w/v% for 15 h.