Supporting Information:

Photo-controlled Water Gathering on Bio-inspired Fibers

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Supporting Information is included with Experimental Section, Supplementary Figure Legends (Fig. S1-S2), and Supplementary Table.

Experimental Section

Synthesis and photoisomerization of Azo polymer: The block copolymer (BCP) obtained via typical Atom Transfer Radical Polymerization (ATRP) method consists of poly(methyl methacrylate) (PMMA) and Azo unit (denoted as P(MMA-Azo)). 0.152 g of PMMA macroinitiator ($M_{n,\,GPC}$ = 28.7 k, PDI = 1.16) were dissolved in 2.6 g of DMF. Then CuCl (1.2 mg, 1.2×10^{-5} mol), tris(2-dimethylaminoethyl)amine (20 μL, mol), Azo monomer (0.161 g, 1.2×10^{-2} mol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and sealed under vacuum. The tube was placed in an oil bath at 90°C for 24 h to give a yellow powder. The product was continuously extracted with methanol in a Soxhlet apparatus overnight. The purified BCP was filtered and dried in vacuum, as light yellow powder (0.205 g). The resulting product had a M_n of 41.4 k, and a PDI of 1.38 by GPC (Figure S1). The Azo weight fraction is about 24% calculated from ^{1}H NMR. Photoisomerization of the samples was carried out by exposure to UV light (365 nm) and Vis light (436 nm) for 2.5 hours under ambient laboratory conditions of lighting and temperature.

Preparation of BCP Film: BCP film was prepared by solution casting of 1.0 g/mL of BCP solution in tetrahydrofuran (THF) on glass slide in a semi-closed box avoiding humidity. After casting, smooth film was prepared by putting the glass slide into an oven at 50°C for another day after solvent slowly evaporated, then in vacuum to remove the residual solvent. Rough BCP coated film was made by evaporating the solvent in the given condition (Temperature: 25°C, Humidity: 75 %).

Fabrication of bio-inspired fibers: The nylon fiber specimens were made by using an adhesive tape to fix a single nylon fiber with a diameter of ~18 μm (obtained from TaiZhou Feite Nylon Rope & Net & Belt CO., LTD, China) on a U-shaped holder with a certain amount of tension and the length of the fiber was about 2 cm. Bio-inspired fibers with

P(MMA-Azo) spindle-knots were prepared by immersing fiber specimens in the P(MMA-Azo)/(DMF+ethanol) solution (DMF：N,N-dimethylformamide) (1:10:1, P(MMA-Azo): DMF: ethanol, by weight) and drawing it out horizontally at 150 mm s^{-1}. A cylindrical film of polymer solution was then formed on the fiber surface and spontaneously broken up into polymer droplets along the fiber owing to the Rayleigh instability. After the fiber was dried completely in the given condition (Temperature: 30^{o}C, Humidity: 80%), periodic polymer spindle-knots formed. The surface roughness gradient of the spindle-knots was also designed through phase separation induced by the nonsolvent component in the polymer solution. Water vapour was condensed as droplets from the humid environment onto the polymer solution surface, caused by rapid solvent evaporation. After the solvent and water droplets evaporated completely, micropores were formed and elongated along generatrix and coalesced together due to the effect of surface tension. The roughness gradient is left due to the thickness gradient of the polymer on spindle-knots (more water droplets were formed on the center).

Characterization of microstructure: The structures of fiber and spindle-knots were observed by scanning electron microscope (SEM, Quanta FEG 250, FEI, America) at 25 kV with gold plating. In situ atomic force microscopy (AFM) measurement was performed using an Agilent AFM series 5500 (Agilent Technologies). Imaging was carried out in the AAC mode. The used cantilevers (Nanosensor) had frequencies within of 204–497 kHz and force constant values 10–130 N/m.

Water Collection and Observation: In order to clearly observe the behaviors of water droplets, the bio-inspired fibers placed on a small U-shaped holder were put in a chamber of sample. Fog generated by an YC-E350 ultrasonic humidifier (Beijing YADU Science and Technology Co., Ltd., China) was introduced into the sample chamber with a humidifying rate 50 ml h^{-1}. The behaviors of water droplets were recorded by the optical contact angle meter system (OCA40Micro, Dataphysics Instruments GmbH, Germany) with time scale. Time zero was chosen to be the frame in which gathered droplets began to visually appear.

Supplementary Figure Legends (Figs. S1-S2):

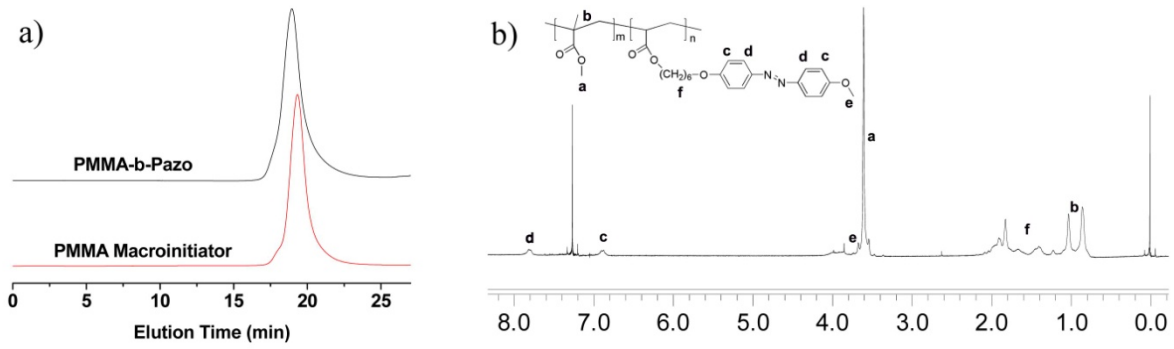

Fig. S1. The GPC curves of the original PMMA macroinitiator and block copolymer P(MMA-Azo). Compared to the starting PMMA macroinitiator, a visible unimodal shift to higher molecular weight is seen in the figure, which indicates that Azo is successfully introduced into PMMA. Number-average molecular weight (Mn) of P(MMA-Azo) block copolymer is 41,400 and the polydispersity index (PDI) is 1.38. b) The ^{1}H NMR curves of P(MMA-Azo) also indicates the successful introduction of Azo into PMMA.

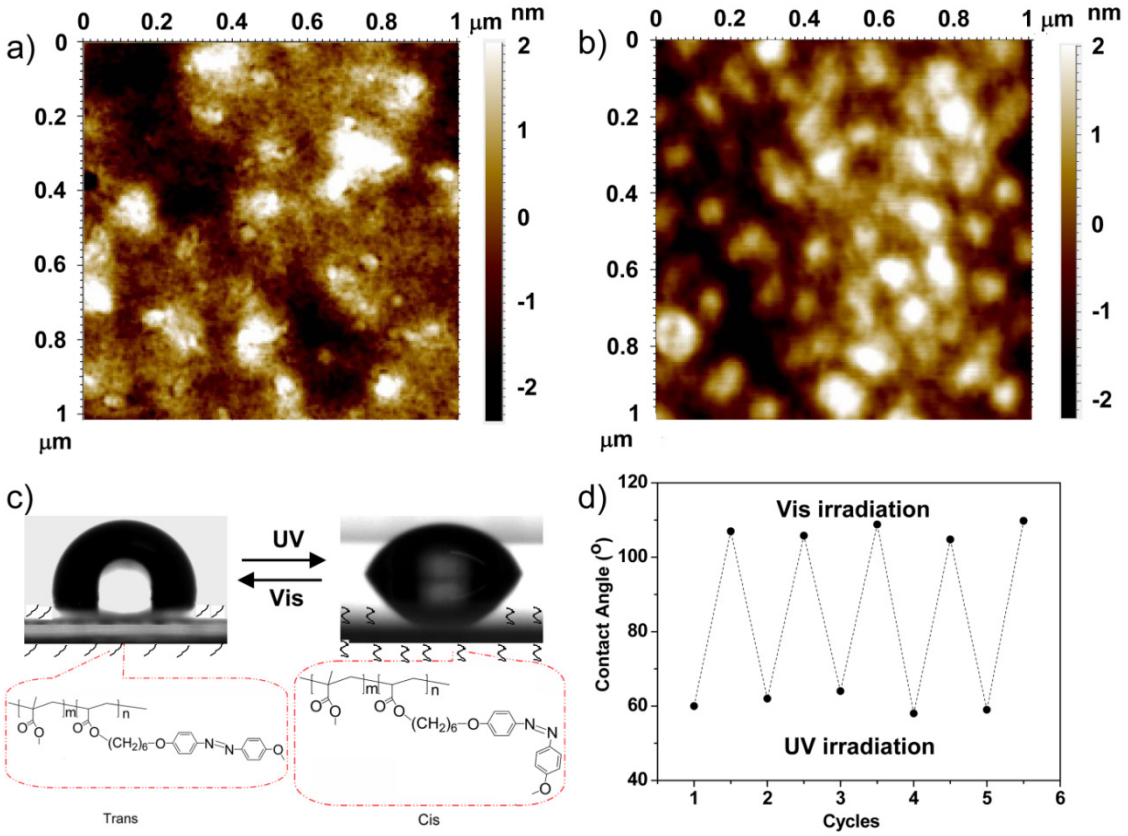

Fig. S2. AFM morphology images of smooth block copolymer (BCP) film after Vis (a) and UV irradiation (b). It is clear that the roughness increased obviously after UV irradiation. (c) CA at the rough BCP film, which shows a reversible change after Vis and UV irradiation (from 105^{o} to 62^{o}). (d) CA values of 5 cycle times after Vis and UV irradiation, indicating good reproducibility.

Supplementary Tables:

Table S1. Water static/dynamic contact angles (CAs) and RMS roughness on smooth / rough block copolymer (BCP) surface.

	Trans isomer					Cis isomer				
	CA (°)				RMS (nm)	CA (°)				RMS (nm)
	θ	θ_a	θ_r	$\Delta\theta$		θ	θ_a	θ_r	$\Delta\theta$	
Smooth	90	95	65	30	0.73	72	79	59	20	0.92
Rough	105	108	70	38	2.92	62	68	46	22	5.74

Note: The values are within experimental error of < ±2°. The CA hysteresis ($\Delta\theta$) related to hysteresis force (F_H) can be described with $\Delta\theta=\theta_a-\theta_r$, where θ_a, θ_r is the advancing and receding CA, respectively.