Supporting information

Light Reversible Hierarchical Pattern by Photo-dimerization induced Wrinkles

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1. Materials

4-(chloromethyl) styrene (S-Cl) and n-butyl acrylate (BA) were provided by TCI Chemical CO., Ltd. Anthracene-9-methanol (AN-OH) was purchased from J&K Scientific Ltd. Other chemicals were obtained from China National Pharmaceutical Group (Shanghai, China). BA was washed for three times by 5 wt% sodium hydroxide solution and then dried in anhydrous magnesium sulfate. All other reagents were used as received.

2. Synthesis and Characterization of Materials

2.1 Synthesis of anthracene-containing styrene monomer (S-AN)

The procedure to synthesize the anthracene-containing styrene monomer (S-AN) used in this work as shown in Figure S1. A 150 mL 2-butanone solution of anthracene-9-methanol (AN-OH, 4.16 g, 20 mmol) was prepared and purged with highly pure N_2 gas for 30 min, to eliminate oxygen. To this stirred solution, a 2-butanone (7 mL) solution of potassium hydroxide (KOH, 5.6 g, 0.1 mol) and potassium iodide (KI, 16.7g, 0.1 mmol) was added as solids at ambient temperature. Then, the reaction system was cooled to 0 °C and added drop-wise with a 2-butanone (10 mL) solution of 4-(chloromethyl)styrene (S-Cl, 3.06g, 20 mmol) in 30 min. After

reacting for more than 1 day, the organic phase was collected, then precipitated in petroleum ether. After filtered and dried in vacuum oven at 70 °C overnight, the yellow power precursor S-AN (6.48 g) was obtained in quantitative yield. The structure of S-AN was verified by ¹H NMR spectrum in Figure S1.



Figure S1. Synthesis process and ¹H NMR spectrum of S-AN in CDCl₃ solution.

2.2 Synthesis of Poly (n-butylacrylate-co-anthracene-containing styrene) (PAN)

PAN series copolymer was synthesized as Figure S2: A set amount of monomers BA and S-AN at the feed mole ratio was dissolved in 5 mL of pre-dried 1, 4-dioxane. The total mass of monomers mixture is 2 grams, and the feed ratios of each monomer were listed in Table S1. Then 20 mg (1 wt % versus the total monomer weight) of 2,2-azobisisobutyronitrile (AIBN) was added, and the polymerization reactions were run at 70 °C for 24 h under nitrogen atmosphere. After cooling at room temperature, the

reaction mixture was precipitated for three times in 100 mL of cold hexane. Then the copolymer was obtained in the quantitative yield named PAN by filtration and dried at 80 °C for 24 h. The structure of final product was verified by ¹H NMR spectrum in Figure S2 and gel permeation chromatography (GPC) in Table S1. The different constituent ratio of the polymer is calculated by integrals in ¹H NMR spectra. The peak between above 6.0 was the signal of the proton connecting to anthracene and styrene. The signal below 1.0 belonged to the proton connecting to methyl of butyl-acrylate. And the result of actual constituent ratio in final copolymers can be found in Table S1.



Figure S2. Synthesis process and ¹H NMR spectrum of PAN-2 in DMSO-d₆ solution.

Sample	Mole ratio		Glass transition	GPC data		
	Feed	Actual*	temperature Tg (°C)	Mn(kDa)	Mw((kDa)	PDI
PAN-1	5:1	4.9:1	23.1	22.53	37.99	1.686
PAN-2	2:1	1.7:1	52.3	31.37	60.44	1.926

Table S1. Results of copolymers PAN-1and PAN-2 used in this work.

* Estimated from the integration of characteristic peak of aromatic hydrogen in anthracene and styrene at 6-9 PPM compared with the characteristic peak belonged to the proton connecting to methyl of BA below 1.0 PPM in DMSO-d₆ solution in NMR spectra.

2.3 Preparation of PDMS Substrate

Elastomeric PDMS sheets were prepared using silicone elastomer (Sylgard 184, Dow Corning). The base and curing agents were mixed at 10:1 ratio by weight and stirred at room temperature under reduced pressure. This precursor material was kept at 70 °C for 4 h to yield a cross-linked PDMS elastomer sheet (thickness approximately 400 μ m) and then divided into small square pieces with 1 centimeter long. The small square PDMS pieces were attached on the glass slide substrate using uncured Sylgard 184 as the adhesive.

3. Results



Figure S3. The dependence of wrinkle characteristic amplitude (A) and wavelength (λ) on the top-layer thickness. (a-f) 3D AFM images of the wrinkling PAN-1 coated PDMS sheet within different thickness of PAN-1 top-layer: (a) 40 nm, (b) 65 nm, (c) 90 nm, (d) 130 nm, (e) 160 nm, (f) 230 nm, respectively. (g) Amplitude value obtained from the AFM line analysis (black square, left vertical axis) and wavelength (hollow circle, right vertical axis) for typical bilayer system (blue triangle, right vertical axis) of the wrinkling PAN coated PDMS sheet fabricated at 70 °C for 4h within different concentration of PAN-1. (h) Wavelength (λ , right) and amplitude (A, left) of the wrinkling PAN-1 coated PDMS sheet as a function of the thickness of PAN top-layer. All the reaction time at 70 °C is set in 4h.



Figure S4. The effect of heating temperature on the wrinkle pattern. (a-e) AFM images and (f) characteristic amplitude and wavelength of wrinkle pattern dependent on the different heating temperatures.



Figure S5. Schematic illustration of the control experiments and (a-d) corresponding optical and AFM images showing the light dynamic photo-dimerization induced reversible wrinkle pattern. (a) the original wrinkle-free PAN coated PDMS sheet was subject to (step A) heating at 70 °C without 365 nm UV exposure to prescribed and (b) no wrinkle pattern was generated. (c) Then this bilayer was (step B) 365 nm UV exposed and subsequently heating to 70 °C or (step C) 365 nm UV exposed and synchronously heating to 70 °C, and (c) the same wrinkle pattern was obtained. (d) The wrinkled surface was fully eliminated by (step D) heating above 150 °C or (step E) 254 UV irradiation.



Figure S6. Typical force-distance curves recorded on the surface of wrinkled bilayers with different 365 nm light exposure time. The Young's modulus (E) of the film is calculated according to the retract force curve, and the pull-off peak force is regarded as the adhesion force.



Figure S7. The kinetics of reversible photo-dimerization. (a) Evolution of UV-Vis spectra of photo-dimerization reaction of PAN upon 365 nm UV exposure. (b-c) Evolution of UV-Vis spectra of depolymerization reaction (b) baking at 150 °C or (c) upon 254 nm UV exposure of PAN photo-dimers after exposed under 365 UV light for 110 min. The evolution of the characteristic ultraviolet absorption peak at around 370 nm was chosen for conversion calculations of the photo-dimerization conversion. For the convenience of statistical calculation, the photostationary state after sufficient time of 365 nm UV exposure is regarded as the complete photo-dimerization state. The intensity of 365 nm UV light and 254 nm light is approximately 20 mW/cm² and 3.5 mW/cm^2 .