Supporting Information for

Confined Self-Assembly Enables Stabilization and Patterning of Nanostructures in Liquid-Crystalline Block Copolymers

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Experimental

Materials

The amphiphilic LCBC, poly(ethylene oxide)-block-poly(11-(4-(4-butyphenylazo)-phenoxy)-undecyl methacrylate, PEO\textsubscript{114}-b-P(M\textsubscript{n}AzC\textsubscript{4})\textsubscript{83} (Mn=46100, PDI=1.2), was prepared via a typical atom transfer radical polymerization (ATRP) method following our previously-reported way.\textsuperscript{1} For comparison, one azobenzene-containing homopolymer PM\textsubscript{n}AzC\textsubscript{4} was also synthesized (Mn=77300, PDI=1.22) by ATRP with ethyl 2-bromoisobutyrate (EBrIB) as initiator.\textsuperscript{2} The water-soluble ionic polymer, sodium polystyrenesulfonate (PSSNa) with weight-average molecular weight of 70000 was obtained from Aldrich and used as received. Unless otherwise indicated, all the other reagents and starting materials were purchased from TCI Co. and used without further purification.

Sample preparation

Fabrication of the pretreated films

The as-cast LCBC films were fabricated by spin-coating (1500 rpm for 2 s and 3500 rpm for 20 s) its toluene solutions (3-5 wt\%) on various clean substrates, such as glass or quartz slides, silicon wafers and rubbed polyimide (PI) films. The film thickness ranging from 120 nm to 200 nm was controlled by changing solution concentration and the rotation speed on spin-coating. After the solvent was evaporated at room temperature, a variety of well-defined MPS structures were acquired by annealing the LCBC films in vacuum at different temperatures from 45°C to
125°C for 24 h. The samples underwent the first annealing treatment are called the pretreated films.

**Fabrication of top-coated films**

To introduce the top coating layer, one PSSNa solution (8 wt%) in deionized water was spin-coated on the surface of as-cast or the pretreated LCBC films. To evaluate the thermal stability of the MPS nanostructures, the PSSNa-coated LCBC films were baked in a vacuum oven for 24 h at elevated temperatures until the damage to the nanostructures was observed. Then, the re-annealed PSSNa-coated films were immersed in deionized water to remove the water-soluble polymer.

**Characterizations**

$^1$H NMR spectra of compounds in deuterated chloroform were recorded on a Bruker AV500M by using tetramethylsilane as the internal standard. The number-average molecular weight (Mn) and polydispersity indexes of polymers were measured by gel permeation chromatography (GPC, Waters) with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. Thermodynamic properties of PEO, PSSNa, the PEO-PSSNa complex and the LCBC were measured with a differential scanning calorimeter (DSC, PerkinElmer DSC 8000) under nitrogen at a heating and cooling rate of 10°C/min. The UV-vis absorption spectra were carried out on a PerkinElmer Lambda 750. The birefringent characteristics of the LCBC films were performed by polarized optical microscopy (POM, Zeiss Scoper A1) equipped with a hot plate.
The thickness of polymer film was measured by one spectroscopic ellipsometer (J. A. Woollan Co., Inc., M-2000V). The coordination interaction between PEO and PSSNa was characterized by Fourier transform infrared spectroscopy (FTIR, Spectrum Two). The MPS nanostructures of the LCBC films were obtained by an atomic force microscopy (AFM, Bruker Multimode 8 in a tapping mode) and a field-emission scanning electron microscopy (FESEM, Nova NanoSEM430).

Results and Discussion

Figure S1. a) Differential scanning calorimetry (DSC) curve of the LCBC from the second heating and cooling scan (±10°C/min). b) UV-vis absorption spectra of the LCBC film annealed at different temperatures. c) AFM image of the as-cast LCBC film.
Figure S2. AFM phase images of the LCBC films upon secondary annealing at 125°C with or without a PSSNa surface covering layer: the as-cast films re-annealed without a), with b) a top coating and the 45°C-pretreated films re-annealed without c), with d) a top coating.

As shown in Figure S2, both the spin-coating and the 45°C-pretreated LCBC films kept their previous nanostructures unchanged even after further annealing with a PSSNa top coat, while the uncoated films self-assembled into new MPS structures with stripe-like PEO nanocylinders, corresponding to the FESEM images shown in Figure 2. This top coating-caused stabilization of
MPS morphology occurred in three dimensions (3D), as confirmed by the cross-sectional AFM image of the PSSNa-coated LCBC film in Figure S3b.

Figure S3. Cross-sectional AFM images of the re-annealed LCBC films without a) or with b) a PSSNa surface covering layer.
Figure S4. The effect of a water-soluble PSSNa surface covering on the UV-vis absorption spectra of the as-cast films (upper) and the 45°C-pretreated films (lower) for the LCBC.

It is well known that the mesogenic alignment plays an important role in MPS nanostructures of LCBCs since the LC elastic deformation should interfere with the MPS process. Then, UV-vis absorption spectroscopy and polarizing optical microscopy (POM) were applied to investigate the mesogenic orientation in LCBC films. Figures S4a, S4b show a comparison of the absorption spectra of the as-cast films before and after annealing at 125°C with versus without
the surface covering layer, and a drastic decrease in the absorption peak at 337 nm was brought out after a high-temperature annealing whatever the film was coated or not.

Generally, the $\pi-\pi^*$ transition moment of the trans-AZ is directed along its long molecular axis, while the $\phi-\phi^*$ transition of the aromatic core does not possess any polarization dependence, enabling it to have nothing to do with isomerization and aggregation. Thus, the ratio of these two transitions is a powerful parameter to characterize the spatial orientation of chromophores.\textsuperscript{4,5} Almost identical change in the ratio was obtained from Figures S4a, S4b, indicating that the existence of PSSNa top coating makes no difference to the orientation of AZ mesogens in the LCBC film. Similarly, the same conclusion can be drawn for the 45°C-pretreated LCBC films (Figures S4c, S4d): whether it is coated with a top coat or not has no effect on the mesogenic alignment, which is also right for the homopolymer counterparts. Since there is no detectable difference of the change in the UV-vis absorption spectra between LCBC films and LC homopolymer films before and after reannealing process, it can be concluded that the mesogens in the continuous phase turned into out-of-plane orientation upon the secondary thermal treatment,\textsuperscript{4} which has nothing to do with the dispersed PEO phase domains in the LCBC film.
Figure S5. The effect of a water-soluble PSSNa surface covering on the POM images of the as-cast (upper) and the pretreated block copolymer films (lower): the as-cast films before annealing a) versus annealed at 125°C without b), with c) a top coating, and the 45°C-pretreated films before re-annealing d) versus re-annealed at 125°C without e), with f) a top coating.

POM observation showed that both as-cast and 45°C-pretreated LCBC films undergoing a reannealing process exhibited a typical birefringent texture of the smectic phase (Figures S5b, c, e, f), whereas the LCBC films without a high-temperature reannealing treatment showed a dark contrast (Figures S5a, d). Thus it can be concluded that whether the LCBC film is coated with PSSNa makes no difference in the orientation of LC microdomains.
Figure S6. The existence of coordination between PEO and PSSNa. a) DSC curves, and b) FT-IR spectra of pure PEO, PSSNa and their complex PEO-PSSNa (the mole ratio of polymer repeat unit is 4:1) with wavenumber range: 800-1500 cm\(^{-1}\).
**Figure S7.** The surface electric field distribution of the PSSNa-coated LCBC film. a) is the electric field distribution of the sample surface. b) is the experimental scheme. c) is the electric field distribution profile of the position marked by the blue line in a).

![Graphs showing the surface electric field distribution](image)

**Figure S8.** The complete removal of the PSSNa surface covering layer. UV-vis absorption spectra of a pure PSSNa thin film a), a LCBC film without a top coat b) versus a LCBC film with a top coat c).

![Graphs showing UV-vis absorption spectra](image)
**Figure S9.** The MPS nanostructures of the coated 45°C-pretreated films re-annealed at different temperatures: 140°C a), 160°C b), 180°C c) and 200°C d).

As shown in Figure S9a, when the re-annealing temperature was 140°C, the unambiguous dotted nanostructure was obtained after the removal of PSSNa. The original MPS structures were still clearly visible in Figures S9b, c when the temperature was raised to 160°C or 180°C. Further increasing the re-annealing temperature to 200°C, the film on the whole preserved the dot-like morphology, but its nanostructure was partly damaged in Figure S9d. So the threshold value of the efficient nanostructure stabilization should be just below 200°C. Obviously, with the increase of the re-annealing temperature, the thermal stability of nanostructure gradually
decreased, which could be attributed to the increased activity of PSSNa for interfering with the MPS of LCBC.

**Figure S10.** The effect of surface coating thickness on thermal stabilization of the MPS structures. The coating layer thickness measured by ellipsometer is proportional to the concentration of PSSNa aqueous solution: 1% a), 2% b), 3% c), 5% d), 8% e) and 10% f).

The effect of surface coating thickness on the thermal stabilization of the MPS structure was studied, as shown in **Figure S10.** It was demonstrated that the concentration of PSSNa aqueous solution was proportional to the thickness of the resulting coating film. With the increase in the
PSSNa film thickness, the top coating plays a more remarkable role in the thermal stability of nanostructure just as expected.

**Figure S11.** The thermal stabilization of the MPS structure when rubbing polyimide film was used as the substrate. AFM phase-shift images of the 45°C-pretreated film a) and its re-annealed film with a top coating b), POM images of the re-annealed film with the rubbing direction along the polarizer (top) and rotated by 45° (down) c), polarized UV-vis spectra of the re-annealed film.
d). When the sample was rotated by 45 degrees, there was an obvious contrast, suggesting that the mesogens in the film had been oriented along the rubbing direction successfully.

Figure S12. Long-term preservation of LCBC thin films with versus without a PSSNa surface covering layer. The nanostructures of the 45°C-annealed films freshly prepared a), stored for 6 months with a top coating b), stored for 3 months c) and 6 months d) without a top coating.
The coated film preserved its nanostructure clear and nondestructive after being kept at room temperature for 6 months, different from the uncoated one whose nanostructure was full of defects and impurities.

**Figure S13.** The controllable complex nanostructure generated by a brand-new mask: selected-area PSSNa top coat. a) The photomicrograph, c) the large-area AFM phase image of
the border region between with (top-right) and without a top coat (bottom-left), b) the enlarged view of the selected area in figure c).

A dotted morphology was first obtained upon annealing at 45°C, then applying the PSSNa top coating to the selectively patterned areas. The re-annealing treatment of the patterned film was performed at 125°C, and a controllable complex nanostructure was obtained after the removal of the stable layer: the uncoated areas transformed into a striped nano-pattern with an in-plane arrangement, while the PSSNa-covered regions maintained the previous dot-like nano-pattern due to the stabilizing effect.
**Figure S14.** Fabrication of a hierarchical nano-pattern by combination of the confined self-assembly and nanoscale inkjet printing, that is, by multi-repeat of the following operations: selected-area coating, re-annealing, removing the surface covering layer. Insets are the diverse MPS structures before coating in different areas of the same LCBC film: the as-cast part a) and the 45°C-pretreated b), 75°C-pretreated c), 95°C-pretreated d) and 125°C-pretreated e) parts, respectively.

The complicated nanostructure shown here can be prepared by multi-repeating of the following simple steps: selected-area casting of PSSNa, re-annealing, eliminating the top coating.
In other words, compared to previous reports,\textsuperscript{6,7} the hierarchical nanostructures will be effortlessly manufactured by a combination of the confined self-assembly with nanoscale inkjet printing and be conserved for a long time with little disruption, which is crucial for the wider application of MPS structures.

\textbf{Figure S15.} Photocontrol of MPS structures in LCBC thin films with PSSNa coating. As-cast films a), b) and 125°C-annealed films c), d) before (left) versus after (right) UV irradiation. The UV
light wavelength, power density and irradiation time were 365 nm, 134 mW/cm$^2$, 30 s, respectively.

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