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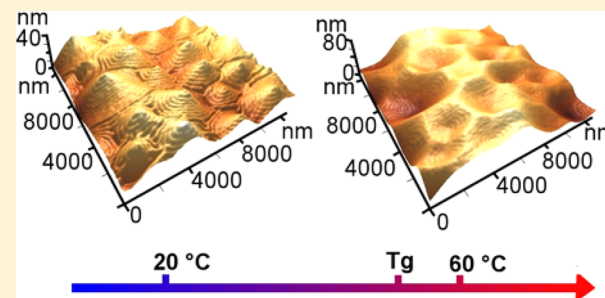
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S Supporting Information

ABSTRACT: The development of new approaches for the surface topography control is an important topic as the relief significantly affects physical and chemical properties of surfaces. We studied cholesteric cyclosiloxane oligomeric films on which surface focal conic domains with double-helix pattern were observed by means of AFM. In situ investigation of the dependence of the films topography on temperature showed that the surface relief formation can be effectively managed by varying conditions of thermal treatment. Obtained structures can be frozen by cooling the films below glass-transition temperature.



INTRODUCTION

Design and creation of nanostructured polymer films with a specific surface morphology is one of the most important problems of modern physical chemistry related to the study of surface phenomena, such as wetting, adsorption, adhesion, catalysis, and others.^{1–6} Of particular interest are the liquid crystalline (LC) oligomers and polymers having cholesteric order with a unique helical supramolecular structure, which can lead to the formation of nanorelief on the surface. This cholesteric structure of these compounds is able to be frozen in the form of a solid film by simple cooling of the LC mesophase below glass-transition temperature. Such cholesteric compounds are used as a matrix that guides the self-assembling of nanoparticles.^{7–9} Moreover, the cholesteric helix determines unique optical properties of these LC films;¹⁰ one of them is the selective reflection of light with a wavelength λ_{\max} depending on the helix pitch (P) according to the following equation

$$\lambda_{\max} = \langle n \rangle P \quad (1)$$

where $\langle n \rangle$ is the average refractive index of a liquid crystal. Recently we have demonstrated that a thermal prehistory may strongly affect the structure and properties of cholesteric films;¹¹ however, the evolution of surface topography upon temperature changes is still poorly understood. This knowledge will allow us to better control the processes of self-organization and the surface relief formation in cholesteric LC oligomers and polymers.

To explore the peculiarities of the topography changes in cholesteric films at different temperatures, we have selected an oligomeric cholesteric cyclosiloxane SilGreen (Figure 1). The cyclosiloxane SilGreen (“Wacker Chemie”) forms a left-handed cholesteric structure with a wide mesophase temperature range

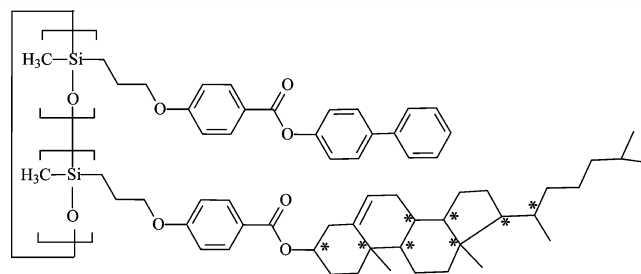


Figure 1. Chemical structure of cholesteric cyclosiloxane SilGreen.

(clearing temperature is 170 °C, glass transition $T_g = 48$ °C). The oligomer contains the definite ratio of biphenyl and chiral cholesterol-containing monomer units determining the wavelength of the selective reflection of light in the green spectral region ($\lambda_{\max} \approx 515$ nm).

It is significant that the properties of cholesteric films greatly depend on the alignment direction of the helix axis. We suppose that a cholesteric mesophase can be considered as a stack of nematic “layers” lying perpendicular to the helix axis and turning relative to each other. An intriguing case is cholesteric film forming two interfaces with different boundary conditions: planar and homeotropic. The latter is the case for the boundary between a cholesteric and air, where “layers”, aligned parallel to the substrate tend to curve perpendicular to the surface, forming focal conic domains (Figure 2).^{12–16} Their diameter is determined by the thickness of a cholesteric film, elastic constants of the cholesteric, and the difference in surface

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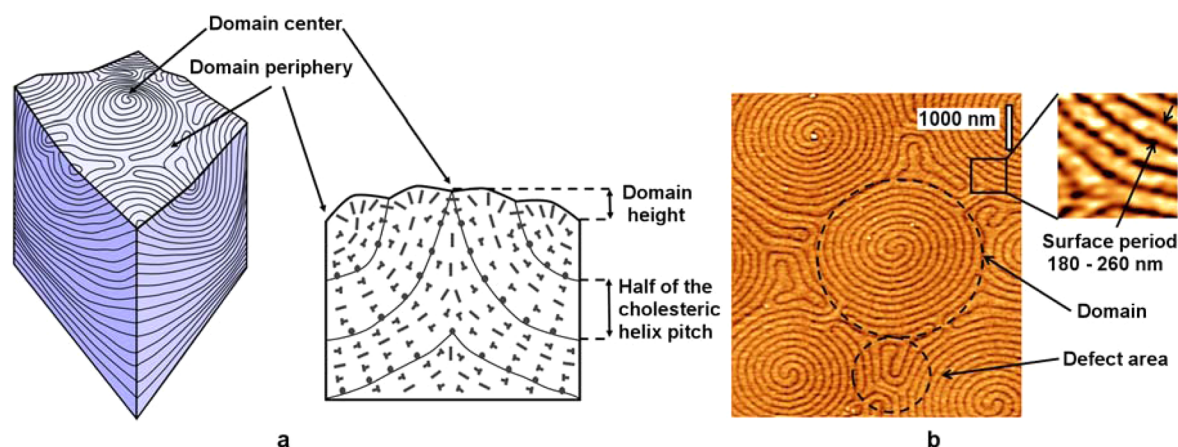


Figure 2. (a) Scheme of the focal conic domains structure in two projection. A perpendicular section of the cholesteric film through the domain center is shown to the right. The director distribution is drawn according to Meister et al.¹⁹ (b) AFM image of the double helix relief.

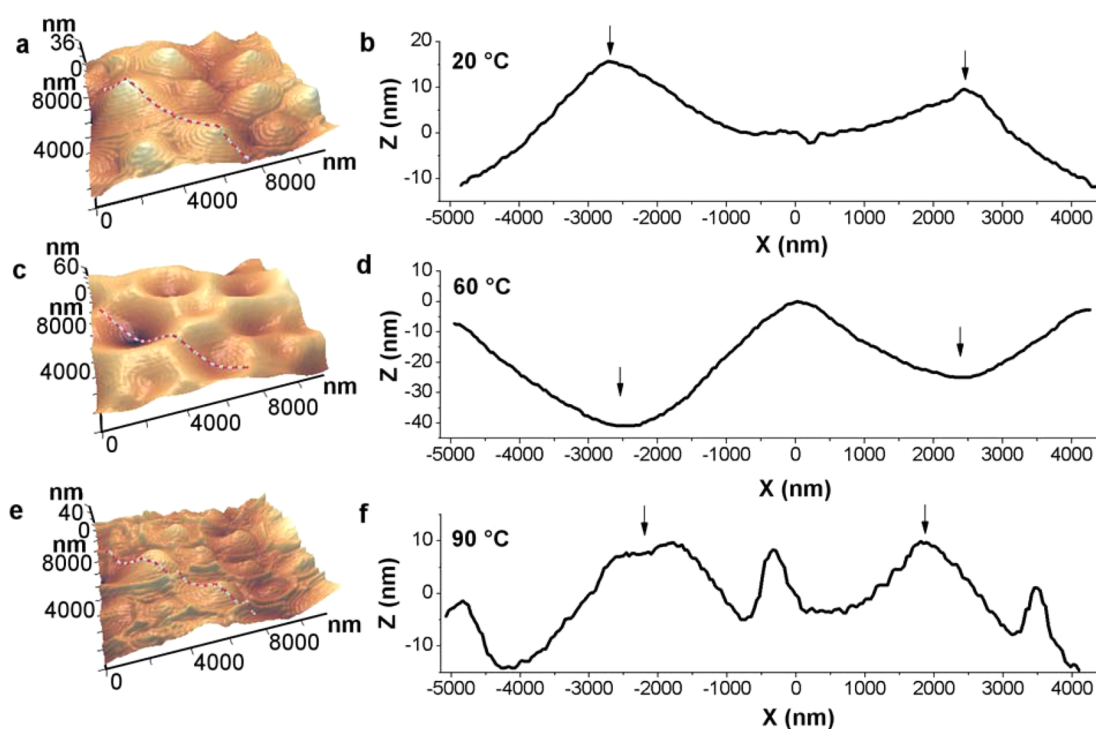


Figure 3. 3D AFM images of the quenched SilGreen film (left) and corresponding cross sections (right), whose positions are shown in dashed lines in the 3D images. The images were obtained at 20 (a,b), 60 (c,d), and 90 °C (e,f). Black arrows indicate the centers of the focal conic domains.

energy between planar and homeotropic orientations of mesogens.^{17,18} Surface relief in the form of double helix corresponds to each domain. Its origin is the periodic changes of the mesogens orientation under the surface.¹⁹ The pitch of the double helix is greater than half the pitch of the cholesteric helix because “layers” approach the surface at an angle less than 90°. The height of the domains may change from the periphery to the center of the double helix depending on a thermal prehistory.¹¹

To reveal the origin of this phenomenon, we studied the evolution of cholesteric film topography at different temperatures, below and above glass transition point, using atomic force microscopy. This method has been successfully applied previously as a powerful tool for studying the structural changes caused by melting, crystallization, recrystallization, glass transition, and so on.^{20–25}

EXPERIMENTAL METHODS

Films Preparation. The cyclosiloxane SilGreen (“Wacker Chemie”) was used as received. Molecular mass and polydispersity of the cyclosiloxane were determined by GPC chromatography using instrument “Knauer” and polystyrene standard: $M_w = 2750$, $M_w/M_n = 1.1$.

For the investigations planarly oriented films of cyclosiloxane having free surface and different thermal prehistory were prepared as follows. A small amount of the substance was placed between two glass plates, heated to 140 °C, and subjected to shear deformation to obtain a good planar orientation. After 5 min of annealing at the same temperature two glass substrates were separated by shearing. As a result, two glass plates covered by cholesteric film were obtained and annealed additionally during ~30 min.

The thickness of the samples was $\sim 20\ \mu\text{m}$. This value is much higher than helix pitch, and thus a well-defined structure, consisting of focal conic domains, was formed.

In our experiments we have used two main types of samples:

- The first type is films annealed at $140\ ^\circ\text{C}$, followed by slowly cooling to room temperature at the rate of $1^\circ/\text{min}$ using a Mettler hot stage.
- The second type of samples (quenched films) was obtained by fast cooling of the films from $140\ ^\circ\text{C}$ to room temperature (20–30 s).

AFM Investigations. The investigation of the morphology of SilGreen films was conducted with the help of FemtoScan scanning probe microscope in semicontact mode of AFM in air. Cantilevers of series 15, produced by Mikromasch, with an average resonant frequency of 325 kHz were used. The sample was attached to a heating stage by means of a thermal paste. The surface temperature of the sample was varied in the range from room temperature ($20\ ^\circ\text{C}$) to $100\ ^\circ\text{C}$. The temperature changed with a step of $10\ ^\circ\text{C}$. The sample was kept at a constant temperature for 10 min before the scanning. Repetitive scans of the same region showed that the surface topography did not change under the probe action. The tuning of scan setting parameters (oscillation amplitude of a cantilever and set point) did not significantly influence the topographical images of the film, so image contrast was associated predominantly with the surface relief rather than the spatial variations of the mechanical properties of the surface.

AFM images were processed using FemtoScan Online program (<http://www.femtoscanonline.com>). To determine the height of a domain, we made a section along the fast scan direction through the domain center. The average linear slope of the surface was subtracted from the section. The height of the domain was calculated as the average of height differences measured between the domain center and its right and left edges.

RESULTS AND DISCUSSION

1. Topography Evolution of the Cholesteric Films at Different Temperatures. To determine the factors affecting the relief formation during cooling with different rates, we studied the surface topography of SilGreen films at different temperatures by means of AFM. We assumed that high surface tension of the oligomeric films allowed us to scan the surface at a temperature slightly above the glass-transition point. The material could flow under this condition to reduce any stress caused by thermal expansion or contraction. It was unexpected, but the periodic double-helix relief with the height of 1–4 nm was still observed at $100\ ^\circ\text{C}$ (Figure S1, Supporting Information).

AFM images were obtained at different temperatures for the two types of SilGreen films, quenched, and slowly cooled. As an example, images of the quenched film are shown in Figure 3. It was found for both types of films that the shape of the focal conic domains changed from convex to concave at $60\ ^\circ\text{C}$ (Figure 3a–d). Upon further heating, the surface relief at first became smoother. Then, at $90\ ^\circ\text{C}$, folds with height of $\sim 10\ \text{nm}$ appeared between the focal conic domains, and the domain centers rose above the surface (Figure 3e,f). The comparison of cross sections in Figure 3 shows that the distance between the centers of the domains reduced at $90\ ^\circ\text{C}$, which may be due to the shrinkage of the material in the surface plane. A temperature gradient may occur near the surface of the films

because of the intense heat outflow from the surface. As a result, the shrinkage of the material below the surface was larger than along the surface. According to our assumption, it may lead to the folds formation on the surface, as seen in Figure 3e,f.

Some differences between the two types of the films should be pointed out. First, the height of the focal conic domains was greater for the quenched films (15–30 nm) than for the slow cooled films (5–20 nm). Any changes in the pattern of double helix relief were not observed for the slow-cooled films at heating to $100\ ^\circ\text{C}$, as opposed to the quenched films, for which some minor changes occurred already at $80\ ^\circ\text{C}$. At $90\ ^\circ\text{C}$, the double-spiral relief significantly anisotropically deformed. As a result, some large focal conic domains changed their size, and small focal conic domains with diameter of $\sim 1000\ \text{nm}$ could form or disappear in defective areas.

2. Dependence of the Domains Height on the Temperature. Two typical domains were selected in the quenched and slow-cooled films to plot the dependence of the height of the domains on the temperature (Figure 4).

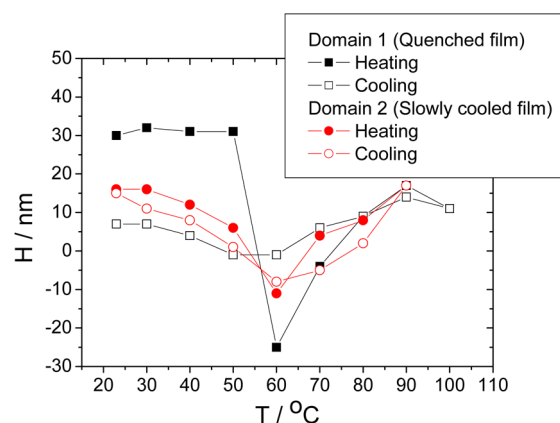


Figure 4. Dependence of the domains height (H) on the temperature. Squares and circles denote the data for the quenched (domain 1) and the slow-cooled (domain 2) samples, respectively. Error in height determination is $\sim 2\ \text{nm}$.

For all domains there is a minimum height at $60\ ^\circ\text{C}$, which corresponds to their shape switching. This effect is especially strong for the quenched film. Upon cooling the surface changes in the quenched film were negligible different from the dependences obtained for the slow-cooled film. It can be supposed that a decrease in the domains height, when the temperature rises below glass transition (flow of the material is frozen), is explained by the thermal deformation of the sample, assuming that the film shrinks more in the perpendicular direction to the “layers” than along the “layers”. Above the glass-transition temperature, increase in the molecular mobility takes place and the material can flow. This allows the surface to get the shape that corresponds to the minimum of the free energy. It is interesting to note that at $60\ ^\circ\text{C}$ the concave shape of the domains instead of a flat shape leads to an increase in the surface area and hence to the growth of its energy; however, the angle at which the “layers” approach the surface becomes higher that reduces the deformation energy of the liquid crystal near the surface. From this point of view, if the cholesteric “layers” come to the surface at an angle of 90° , the effects of the domain shape switching should completely disappear.

The observed dependence of the domain height on the temperature is probably associated with the temperature

dependence of liquid crystalline elastic constants and helix pitch in the studied cholesteric films. In particular, we may assume a significant increase in twist elastic constant under the cooling of the samples. This effect is associated with an appearance of the fluctuation of the layered order (elements of smectic phase). This assumption is supported by X-ray investigation of cholesteric cyclosiloxanes, revealing the small-angle scattering related to these smectic fluctuations.²⁶ The growth of the twist elastic constant results in helix untwisting under the cooling (see Section 6 of this paper) and, as consequence, in strong modification of surface topography.

3. Influence of Thermal Prehistory on Topography of the Films. Obtained data explain the dependence of the surface relief on the thermal prehistory of the sample. As an example, we compare the topography of the film cooled in two ways (Table 1). During the cooling from 100 °C to room

Table 1. Dependence of the Height of Three Adjacent Domains 1-3^a and Root-Mean-Square Roughness (R_q) of the Surface on the Thermal Prehistory of a SilGreen Film

temperature ^b	domains height (nm)			R_q (nm) ^c
	1	2	3	
100 → 20 °C	33 ± 1	37 ± 1	36 ± 1	10.5 ± 0.1
60 → 20 °C	20 ± 2	15 ± 1	12 ± 2	5.9 ± 0.1

^aDomains are shown in Figure S2, Supporting Information. ^bCooling from 100 °C to room temperature occurred for 11 min after switching off the heating stage. ^c R_q was measured for AFM scans with the area of $20 \times 20 \mu\text{m}^2$.

temperature, the sample quickly passed a temperature region around 60 °C where the height of the domains became negative. As a result, the domain height and root-mean-square roughness of the surface is approximately twice as large as in the case of the cooling from 60 °C to room temperature.

4. Thermoinduced Changes of Interdomain Distances. Now, let us discuss the details of interdomain distance changes. The heating of the slow-cooled film to 90 °C resulted in a decrease in distance between domains by ~20%. After cooling, the distance increased again, but its value remained 10% smaller than the initial one. An example of the dependence of interdomain distance on temperature is shown in Figure 5. Further heating and cooling cycles also caused a decrease in the distance between the centers of domains, but the amplitude of these changes became smaller from cycle to cycle (Figure S4).

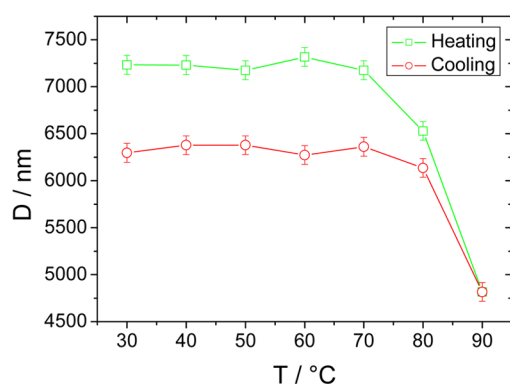


Figure 5. Dependence of distance between two domains (D) in the slow-cooled film on temperature.

Taking into account the fact that the double-helix pattern did not change for slow-cooling films, that is, the domains contained the same number of helix turns as before the heating, this effect can be explained by the rearrangement of the domains in the bulk of the film and the increase in the turning angle of the cholesteric “layers” near the surface. (See the scheme in Figure 6.) According to the proposed scheme, the

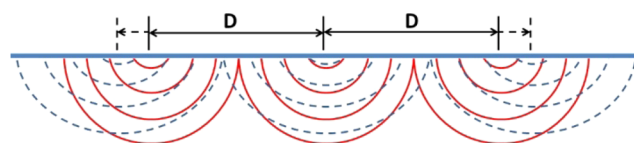


Figure 6. Scheme showing the changes of the distance (D) between the domains centers after a heating. Dashed and solid lines denoted the “layers” before and after the heating, respectively.

distance between the turnings of the double helix (period of double-helix relief) should decrease. The distribution of the period values was sufficiently wide; however, the average values of the period slightly shifted. It decreased from 247 (standard deviation of 10 nm) to 244 nm (standard deviation of 13 nm) for the quenched sample and from 203 (standard deviation of 15 nm) to 195 nm (standard deviation of 16 nm) for the slow-cooled sample.

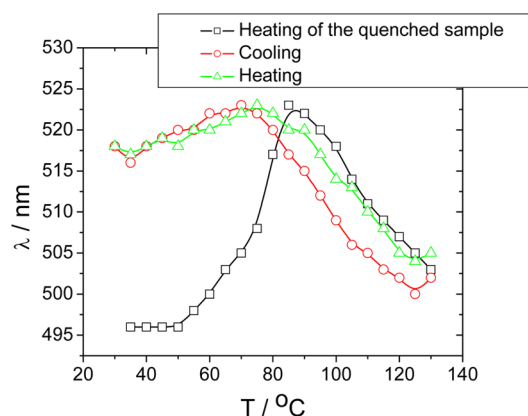
5. Effect of Long-Term Heating on Surface Topography of the Films. The changes of the film microstructure in the bulk should be associated with a high cost of energy because of a huge size of the domains. So the domain's reorganization should also be observed at a temperature slightly higher the glass-transition point, however, over a long time scale. It was found that the distance between the domains centers shortened after 66 h heating at 60 °C (Table 2), presumably due to further rotation of cholesteric “layers” near the surface according to the scheme in Figure 6. Moreover, the domain's depth significantly decreased. It approved our previous suggestion: The higher the angle of the cholesteric “layers” approaching the surface, the smaller the domain height changes upon heating or cooling.

6. Optical Properties of the Cholesteric Films. Finally, let us consider how the thermal treatment affects the optical properties of the cholesteric films. Selective light reflection increases slightly to the temperature of 80 °C, which can be connected to an extension of the film in the direction perpendicular to the cholesteric layers. Then, the twisting of the cholesteric helix begins and λ_{max} is starting to decrease. In this temperature range, it is possible to set the desired values of λ_{max} , which can be retained at room temperature by quenching. As an example, consider the black curve in Figure 7. After quenching the film from 140 °C, λ_{max} had a value of ~496 nm at room temperature, which was ~20 nm less than for the slow-cooled film. Upon further heating of the quenched film, its λ_{max} was starting to growth at a temperature range above the glass-transition point (48 °C) until it reached an equilibrium value. Strong increase in λ_{max} under cooling in the range of ca. 120–170 °C could be explained by the growth of smectic order elements previously discussed. (See Section 2.)

It is interesting to compare these data with the dependence of the distance between the centers of the domains on the temperature (Figure 5). It is worth noting that the beginning of the interdomain distance reduction coincides with the decrease in λ_{max} . Error in wavelength determination is ~2 nm.

Table 2. Parameters of Three Adjacent Domains (1–3)^a before and after Long Heating

temperature (°C)	domain height (<i>H</i>) (nm)			distance between the domains centers (nm)		
	1	2	3	1 and 2	2 and 3	3 and 1
20	14 ± 1	11 ± 1	5 ± 1	3700 ± 25	3700 ± 20	3800 ± 40
60	−22 ± 1	−23 ± 1	−33 ± 1	3800 ± 80	3700 ± 40	3800 ± 15
60 (after 66 h of heating)	−5 ± 1	−8 ± 1	−15 ± 1	3600 ± 50	3500 ± 70	3600 ± 80
20 (after 66 h of heating)	7 ± 1	5 ± 1	−2 ± 1	3600 ± 15	3300 ± 40	3700 ± 20

^aSee Figure S3, Supporting Information.Figure 7. Dependencies of wavelength of selective light reflection (λ_{max}) on temperature.

CONCLUSIONS

The influence of temperature on the structural processes and surface relief formation in the thin-cholesteric cyclosiloxane films was studied. It was shown that the initial films are characterized by focal conic domain structure. At high temperatures (above 80 °C), the twisting of the cholesteric helix occurs and the effective domain rearrangement is possible in the bulk of the film. At lower temperatures, but above the glass transition point, the processes of the domain restructuring significantly slow down, and the existing stress in the films relaxes by the changing of their surface shape. Finally, below the glass-transition temperature, the preformed structure can be frozen. Our findings help us to better understand the influence of the thermal prehistory on the structure of the oligomeric cyclosiloxane LC films and recognize the possible ways to control the surface relief formation. Obtained results demonstrate great possibilities of the manipulation of optical properties of cholesteric systems and their surface structure by temperature changing.

The present paper has a pure fundamental interest; however, the possibility of preparing the cholesteric films with exotic domain surface relief structures with controllable domain sizes is of a great practical importance for creation of the materials with the controllable thermoregulated degree of wettability. This is now one of the centers of attention in nanotechnology and nanoscience studies. This is the basis of the self-cleaning action of ultrahydrophobic surfaces such as the “lotus blossom”, which gave the effect its name.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b06643.

AFM image, obtained at 100 °C, of a slow-cooled SilGreen film (Figure S1). AFM images of domains whose parameters are given in Table 1 (Figure S2) and Table 2 (Figure S3). Changes of distance between two domains in a slow-cooled film measured in successive cycles of heating and cooling (Figure S4). (PDF)

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Notes

The authors declare no competing financial interest.

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