Introduction

Spontaneously ordered fluids known as liquid crystals made their way from curious laboratory compounds to useful industrial materials with remarkable electro-optical and mechanical properties. Nowadays, these materials have been broadly applied in liquid crystalline displays and as ultra-strength fibers, which are prepared from liquid crystalline polymers. Optical and mechanical properties of liquid crystals arise from molecular self-organization into ordered structures of different types. Cholesteric liquid crystals exhibit helical supramolecular configuration that provides selective reflectivity at wavelength defined by helical pitch. A general understanding is that nematic layers are turning into helix by twisting relatively to each other (Figure 1a), and this order is strongly influenced by interfaces of liquid crystalline material on a substrate or in air. Therefore, the examination of surface assembly of liquid crystals can reveal important information of their behavior. Furthermore, studies of structural configuration of these ordered materials at small scales bring new insights into structure and properties of nanostructures, which has become essential players in technological developments.

Characterization of liquid crystals with atomic force microscopy (AFM) is not yet among the mainstream applications as the value of such studies is not well known. The situation may change when researchers are capable of mastering all capabilities of this method, which include measurements at different temperatures and in various environments. In this application note, we will present the studies of liquid crystalline oligomer with different sample preparations, which were performed at room and high temperatures, as well as in vapors of organic solvents using Keysight 9500 scanning probe microscope.
Experiments

Our examination was performed on a set of samples prepared with cholesteric cyclosiloxane oligomer SilGreen (“Wacker Chemie”), which contains biphenyl and cholesterol-based monomer units as the side chains, Figure 1b. SilGreen sample has been well studied by several research groups [1-3], and we want to expand these applications on a variety of samples in organic vapors. The oligomer is characterized at glass transition at ~50°C, and becomes isotropic above clearing temperature of 170°C.

Figure 1a-b. (a) Sketch of cholesteric nematic order. (b) Chemical structure of SilGreen oligomer.

Several oligomer samples were prepared for this study. When SilGreen powder was heated to 150°C, it spontaneously converted into green-color semi-spherical droplet with a height of around 2-3 millimeters. This order was frozen in the glassy state, and the top surface of the droplet has been examined. Another sample was prepared by placing the oligomer between two glass slides and heating to 140°C. The stack was held at this temperature for 30 minutes and glass slides were slightly sheared to enhance the material ordering. Afterwards, the stack was separated into two samples with the fractured oligomer surface open for AFM examination. Optical micrograph of the fractured surface is shown in Figure 2. The green and blue areas represent thick portions of the oligomer sample, and the dark circles of different size are actually the “wells” with thin layers of oligomer at the bottom. In addition, we have prepared oligomer films on Si and HOPG substrate using 1.5 mg/ml solution of SilGreen in chloroform. The thin film samples were made by placing a drop of the solution on the substrates. After drying the sample in air, thin film of oligomer (500 nm in thickness) was formed. Spin-casting of the same solution on both substrates was used for preparation of ultrathin oligomer films with thickness around 40 nm.

Figure 2. Optical micrograph of SilGreen sample prepared from a fracture of the glass/oligomer/glass stack after annealing at 140°C.

AFM studies of SilGreen samples were performed with Keysight 9500 scanning probe microscope, which has an environmental chamber for experiments in different vapors. The heating stage was used for temperature measurements. Oscillatory amplitude modulation (AM) mode and Quick Sense (QS) modes are applied for imaging. In AM mode, the measurements were performed at moderate force levels using Si probes with spring constants in the 2-40 N/m range and amplitudes in 10 nm – 30 nm range. For studies at elevated temperatures and in vapors of chloroform and methanol, the probe amplitude was increased to avoid tip adhesion to softening materials.
Results and Discussions

In this section, we will present the studies of thin oligomer films with data obtained on thick samples of fractured surface and large semi-spherical droplet. The results obtained on ultrathin films of SilGreen on HOPG and Si substrates have been reported in a previous application note [4]. Particularly, it was shown that the treatment of the ultrathin layer on HOPG in chloroform vapor has promoted the increase of nanoscale domains’ lateral dimensions. In contrast, the ultrathin film on Si substrate has lost its integrity by dewetting. In this condition, it is interesting to observe the chloroform vapor related changes of thin films on the same substrates.

Figure 3a-d. AFM images of thin film of SilGreen on Si substrate recorded at different temperatures.
Thin films of SilGreen on Si and HOPG

By analogy with the images of ultrathin film of SilGreen on Si, surface topography of the thin oligomer film does not exhibit any particular pattern, and its overall relaxation is characterized by roughness $S_a = 0.7$ nm, Figure 3a. Small nanoparticles are scattered among the smooth patches of the material. The surface changes are not very pronounced as the sample temperature was raised to 70°C, Figure 3b. The overall roughness has slightly increased to 0.9 nm. Slight traces of surface fragmentation were observed at some locations, and they became more noticeable at sample temperature of 80°C, Figure 3c. Further increase of temperature to 100°C has led to a decrease in contrast. When the sample was cooled down to room temperature, its surface exhibited the ordered focal-conical pattern, Figure 3d. The averaged relaxation roughness ($S_a = 0.8$ nm) did not change much and the width of fine extended features was in the 300 - 350 nm range. This surface transformation might already happen at 80°C as tiny features of Figure 3c resemble with the high-contrast details of Figure 3d. In contrast to the behavior of ultrathin film, the chloroform vapor has not influenced the focal-conical order of SilGreen thin film on Si.

The sets of images in Figures 4a-f and 5a-f illustrate the surface structural transformations of thin film of the oligomer on HOPG at different temperatures and in chloroform vapor. Morphology of spin-cast film is characterized by grainy structures with lateral dimensions of ~100 nm, Figure 4a. These structures, which are still seen at 90°C (Figure 4b), have transformed into large domains as the sample temperature was raised to 110°C, Figure 4c. These domains are best resolved in the phase image in Figure 4d. Chilling of the sample did not change this morphology and the images at room temperature provide well-resolved patterns, Figure 4e-f. Most clearly resolved domains have the extended structures. Their length is up to 1 µm with width in the 200 nm – 380 nm range.

![Figure 4a-f. AFM images of thin film of SilGreen on HOPG substrate recorded at different temperatures.](image)

![Figure 5a-f. AFM images of thin film of SilGreen on HOPG substrate recorded in dry air (a, d, e, f) and in chloroform vapor (b, c).](image)
The thin SilGreen film annealed at 110°C has been subjected to chloroform vapor. The initial domain structure of the film (Figure 5a) has changed after the injection of the solvent into the microscope chamber. This is seen at the top part of the image in Figure 5b, where the surface structure has disappeared. The vapor effect has further developed and the image in Figure 5c shows a blurry contrast with multiple dark spots. They hint on the morphology changes, which became more obvious after the chloroform vapor was substituted with dry air, Figure 5d. The grainy morphology, which was again observed in dry air, is similar to the one that commonly seen on the spin-cast sample, Figure 4a. In other words, the temperature-induced domain order of SilGreen film has been destroyed by chloroform vapor. The domains have been restored in the second heating of this sample to 110°C. This is obvious from the images, which were obtained after cooling the sample to room temperature, Figures 5e-f. Newly formed domains are slightly larger in size and more extended compared to those formed during the previous high-temperature treatment.

**Fractured SilGreen sample**

For environmental studies of thicker SilGreen samples such as the fractured surface (Figure 2) and macroscopic semi-spherical droplet, we have tried methanol and chloroform vapors. The surface modifications in methanol vapor were minor, and most of the work has been done in chloroform environment. It has been shown that focal-conical morphology and furrowed pattern with linear domains are common for free surfaces of SilGreen material [1]. Morphology of both types was observed on top surfaces of thick patches of the fractured surface, whereas the furrowed morphology has dominated inside the “wells”, while the oligomer layer is much thinner, Figure 6a. The extended strips, which are 200 - 240 nm in width, occupy a larger part of the area shown in this image. The injection of 1 ml of chloroform turns out to be excessive as it has been followed by substantial change of surface morphology, Figure 6b. The surface layer became enriched in multiple voids with lateral size of several micrometers, which formed the 10-nm steps on the top surface. At higher magnification, one can see that in many locations, smooth linear strips became grainy, Figure 6c-d. One part of the top structure near the “etched” regions sustained its integrity, where the other parts exhibit fine grainy sub-structure, Figure 6d. The grainy structures also dominate on the bottom surface.
The effect of chloroform vapor has preserved in the sample after opening the chamber to dry air. The top area of the thick regions of the fractured sample have completely converted to the grainy morphology. On thinner regions, the effect was less substantial and the linear strips were modified only in a few locations. One of the areas with a partial transition to the grainy structures is shown in Figure 7a. This was monitored after the secondary but small-volume (0.3 ml) injection of chloroform. The surface changes, which have followed this change of environment, are recorded in Figures 7b-c. In the downward scan (Figure 7b), the chloroform vapor has induced the contrast loss. In the following upward scan (Figure 7c), it has partially restored yet the structural changes (if any) cannot be distinguished. The situation has been further clarified after the chamber was opened. The image in dry air (Figure 7d) shows the healing effect of the latest vapor treatment. The surface pattern is identical to the previously treated one (Figure 7a), and the grainy sub-structure has vanished.

The surprising action of chloroform vapor on SilGreen morphology is further presented in Figure 8a - 8f. The 10-µm thin oligomer region exhibits familiar surface morphology (Figure 8a), and a smaller area, which is marked with a red square, was monitored following the chloroform injection. The vapor presence has been noticed at the bottom of the downward scan in Figure 8b. The alternation of the contrast, that the bright strips were converted to dark and vice versa, was one of the effects, Figure 8c (upward scan). In the next step, the spiral pattern at the top of the image, which is marked with a red star, has changed its orientation, Figure 8d. Furthermore, the whole morphology pattern changed, with much larger spacing (700 nm - 800 nm), Figure 8e. The optical reflectivity of SilGreen material with such order should be shifted to IR region. The observed morphology transformation was not preserved when the sample was subjected to dry air, Figure 8f. The final structure is quite similar to the original one (Figure 8a), but the spiral domain has reoriented.

Figure 8a-f. AFM images of the fractured SilGreen sample recorded in dry air (a, f) and in chloroform vapor (b-e).
Taking a step aside from the environmental studies, we would like to discuss several images, which open a question about possible visualization of molecular structure of SilGreen oligomer and other liquid crystalline oligomers/polymers. In this respect, studies of the samples, in which single macromolecules are spread on substrate, can be informative. In the examination of macroscopic semi-spherical droplet of the oligomer on HOPG, several images have been recorded, as shown in Figure 9a-d. The image, which was obtained on the top of the droplet, shows typical morphology of cholesteric liquid crystal, Figure 9a. Close to the droplet edge, the surface morphology has changed to a relatively smooth pattern and, finally, the arrays of tiny features were seen close to the substrate, Figure 9b. In these regions at a smaller scale (Figure 9c-d), the ribbons with a cross-section profile of 50 -60 nm in width and 6-7 nm in height are major nanoscale structures, which are surrounded by multiple grains with similar dimensions. Based on the size of these objects, which are much smaller than the characteristic liquid crystalline spacings, one can tell that they are composed of only a few oligomer molecules. Therefore, the search for proper sample preparations that facilitate visualization of single molecules and macromolecules is highly desired.

Figure 9a-d. AFM images of a semi-spherical SilGreen droplet on HOPG. The images were obtained in dry air at the top of the droplet (a) and at the droplet edge (b-d).
Conclusions

In expanding AFM applications, the use of the microscope capabilities of operating at different temperatures and in various environments is rather essential for the extraction of comprehensive information regarding surface morphology, nanoscale structures and local material properties. The elements of such approach have been implemented in our studies of liquid crystalline material - SilGreen. The data has provided new insights on structural configuration and behavior of this compound. Further efforts are needed to address mechanism of vapor-induced structural transformations and to visualize the molecular order of SilGreen on different substrates.

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References

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