



## Surface reconstruction of chiral glassy oligomers under the action of volatile organic compounds (VOCs)

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### ABSTRACT

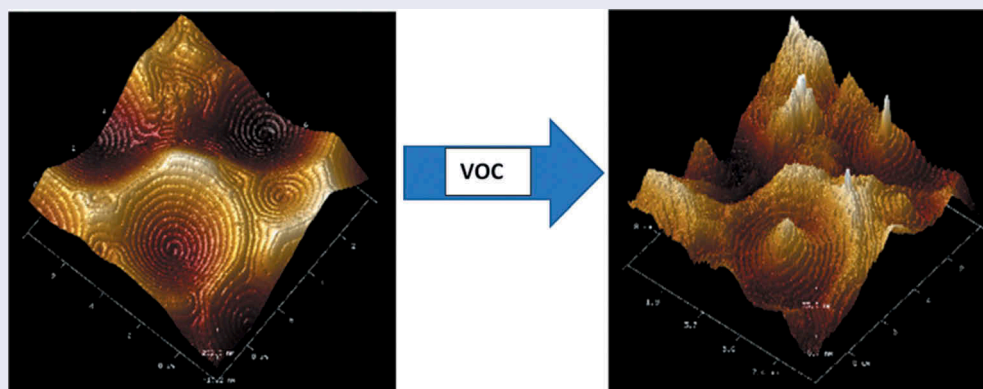
The response of chiral polymers to volatile organic compounds (VOCs) was studied by atomic force microscopy. It was found that under the influence of toluene vapour, the focal conic domains on the surface of chiral polymer undergo remarkable reconstruction that is at least partially reversible. This opens new ways for building VOC sensors and using surface reconstruction in creating new surface patterns for nanotechnology.

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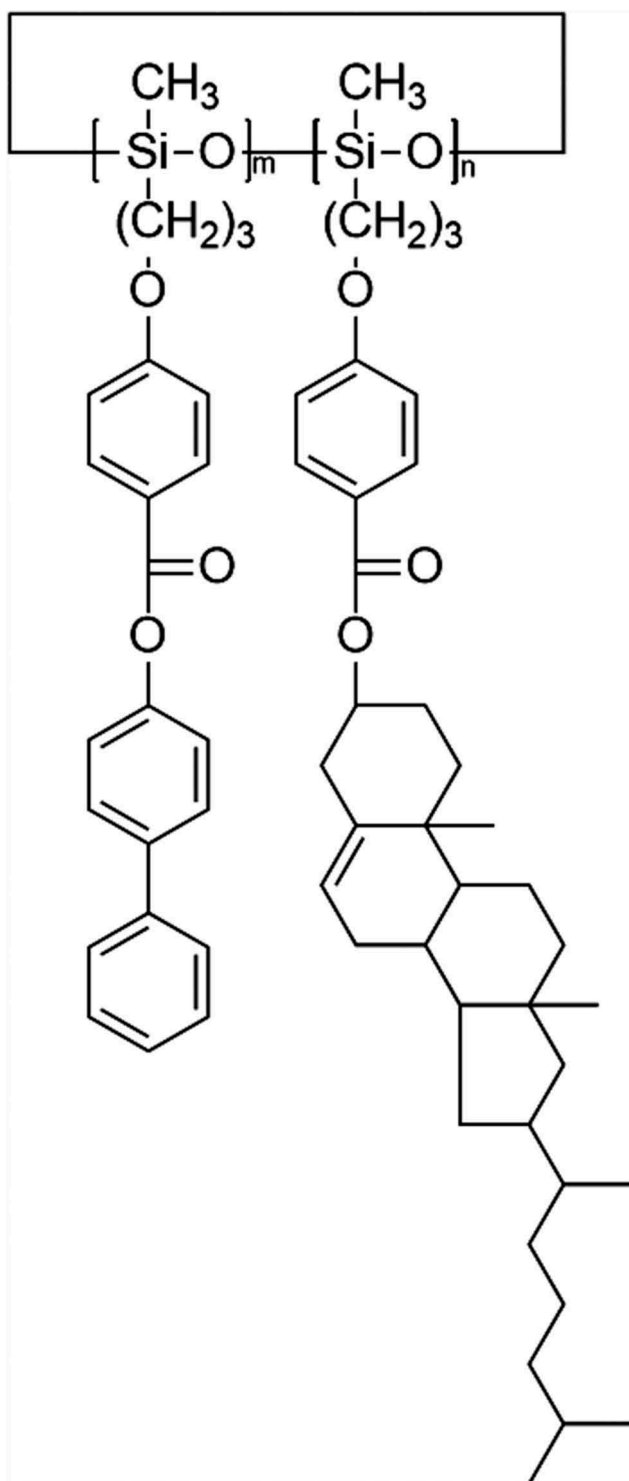


## 1. Introduction

Recently, chiral liquid crystalline glasses and elastomers have attracted a renewed attention in scientific community because of their ability to form peculiar surface patterns reflecting the arrangement of cholesteric layers beneath the surface and their unique optical properties [1–9]. Glass-forming chiral liquid crystals (CLCs) can be imagined as forming twisted nematic structure with each molecular plane twisted with respect to the adjacent plane by a small angle. A full rotation of these planes by 360 degrees defines the periodicity of the structure and its helical pitch  $P$  that also depends on the concentration of chiral units inside the molecule and the temperature. If incident light with the same sense of polarisation as cholesteric helix falls on planar CLC at zero angle then it undergoes selective reflection with a centre of the selective reflection band positioned at  $\lambda = nP$ , where  $n$  is an average refractive index of CLC. One

of the useful properties of Wacker CLC glasses (Figure 1) is their ability to be vitrified and form a planar cholesteric glass between two parallel substrates with the selective reflection band lying in the visible spectral range. The glass transition temperature of these compounds is about 50°C, but a dramatic decrease in viscosity occurs above 120°C. When the compounds are cooled from high temperature they become solid, and a spiral-like pattern is formed on the free surface above underlying focal conic domains. Wacker CLCs are also known for their ability to form blue phases discovered in pioneering work of Gilli et al. [1].

The surface patterns were studied by atomic force microscopy (AFM) for a number of glass-forming compounds. One of the first studies of glass-forming chiral compounds by means of AFM was published in 1996 [2,3]. The authors combined AFM and electron microscopy and showed that formation of focal conic domains in thick cholesteric films is responsible for the



**Figure 1.** Chemical structure of Wacker compound.

pattern appearing on the surface. They also used a theoretical approach in order to estimate the energies and stability of possible arrangements of cholesteric layers and focal conic domains below the surface. In recent publications [4,5], Mitov et al. studied the surface relief of the same compounds and created assemblies of gold nanoparticles by decorating cholesteric

surfaces. It was shown that nanoparticles can be organised along the spirals formed on the surface. Formation of surface relief and its change under light irradiation was also studied in cholesteric elastomers by Ma et al. [6].

The temperature was also shown to have a great effect on the formation of surface pattern and focal conic domains [7]. Moreover, it was demonstrated that surface relief undergoes significant transformations with dips and valleys becoming crests and hills under increasing temperature. In recent works [8], the light-sensitive chiral dopants were synthesised and blended with cholesterol-containing CLCs. It was shown that the addition of light-sensitive dopants with subsequent irradiation of the surface of CLC with laser induces *cis*- and *trans*-isomerisation of chiral dopants that changes their twisting power and leads to a shorter helical pitch.

Glass-forming CLC compounds are unique in a sense that their properties can be further fine-tuned for a number of novel applications. For example, the same glass-forming CLCs as ones used in the studies [1–8] were also used earlier in developing optically pumped lasing films [9] and sensors of mechanical deformations [10]. It was demonstrated in the study of Humar [11] that small glassy CLC spheres may potentially be used as lasers for liquid CLCs.

Focal conic domains are formed when CLC is cooled from viscous liquid state, the slow rate of cooling results in the formation of well-defined surface pattern with valley and hills. The double spirals are formed either on the top of the hills or inside the valleys [7]. The typical distance between adjacent lines in a spiral-like surface pattern lies between 160 nm and 250 nm for CLC with a selective reflection band at 550 nm, i.e. this distance is often larger than half of helical pitch (c.a. 185 nm) in a planar state. It is well known that the formation of fingerprint structure in low molar mass liquid CLCs and focal conic domains is facilitated by homeotropic boundary conditions. Surface pattern similar to one observed in glass-forming CLCs is also formed in cholesteric elastomers [12]. The contact of many cholesteric liquid crystals with air promotes the homeotropic molecular orientation; however, the attribution of any anchoring energy to any free surface is questionable (it is more appropriate to consider surface energy and/or tension). It seems plausible to assume that the contact of free cholesteric surface with materials other than air or treated glass plates may result in the discovery of novel or appearance of better well-defined structures. To the

best of our knowledge, there are no studies on surface patterns formed by glass-forming CLCs under contacts with liquids. There are also no studies of surface patterns in glass-forming CLC under the contact with volatile organic compounds (VOCs) in the air.

We have previously shown that significant changes in cholesteric fingerprint structure may be observed when a cholesteric liquid crystal is placed in the atmosphere of VOCs [13]. In this article, we study the formation of surface pattern in glass-forming CLCs in different aqueous environments and the response of this pattern in CLCs placed in atmospheres of different VOCs.

## 2. Experimental

### 2.1. Materials and preparation

Glass-forming CLC with the molecular structure shown in Figure 1 was used in our experiments. The synthesis of this compound was first described by Bunning and Kreuzer [14]. The compounds were supplied by Wacker company. The groups containing biphenyl are mesogenic units that provide a formation of nematic structure if groups containing cholesterol are not present. Groups with cholesterol moieties provide a helical twist to the whole structure. The concentration of cholesterol groups in a molecule is responsible for the strength of the helical pitch. Ring-like siloxane backbone makes vitrification of these compounds possible. In addition, the computer simulations (to be published in a separate paper) show that mesogenic groups of molecules can penetrate through siloxane rings of other molecules that can provide additional conditions for vitrification and high viscosity.

Chiral compounds were dissolved in an organic solvent (toluene) and then deposited on small glass plates, heated up to 120°C and then kept at 90–95°C for a few hours. After that the hot plate was turned off and samples cooled to room temperature in about 1 hour in air. This procedure resulted in a very smooth surface with a number of different focal conic domains developed inside CLC. In order to study how formation of domains changes in different environments, the samples prepared in air were divided into four groups. The first group was heated again in the air, the second group was heated in pure water, the third and the fourth groups were heated in the solutions of polyacrylic acid in water (c.a. 1% weight solutions). All groups of samples were heated up to 90–95°C, kept at this temperature overnight and then cooled to room temperature in about 1 hour. The AFM experiments were performed using a

Bruker Multimode 8 AFM in a tapping mode with a stiff cantilever (the stiffness was in the range 10–70 N/m).

### 2.2. AFM studies and VOC treatment

Vapours of water, ethanol and toluene were used in the experiments. Toluene is a good solvent for CLC, while ethanol and water do not dissolve it at all. The vapours were produced in the plastic bottles by direct evaporation of solvents at room temperature. The vapours were squeezed out of the bottle and directed to the sample being scanned by AFM at a distance of about 10–15 cm from the sample. This geometry as well as the shape of the bottle's nozzle determine the pressure of VOCs at the surface of the sample. Separate measurements and calculations of the vapour flow has shown that concentration of toluene and other organic solvents was in the range  $(10^{-3} - 5 \times 10^{-3}) \times P_{\text{sat}}$ , where  $P_{\text{sat}}$  is saturated vapour pressure (for toluene at room temperature  $P_{\text{sat}} = 3.2 \times 10^{-2}$  bar [15]). It is important to underscore that the treatment in toluene was not continuous, but rather occurred in a series of concentration spikes ('puffs' created by bottle squeezes).

## 3. Results and discussion

The typical AFM image of CLC surfaces formed in the air is shown in Figure 2. It can be seen that spiral-like structures representing focal conic domains formed beneath the surface are formed in valleys and on hills. It can also be seen from AFM images that some spirals do not have uniform height. The average distance between the lines is about 250 nm, but the surface of the spiral is not very uniform.

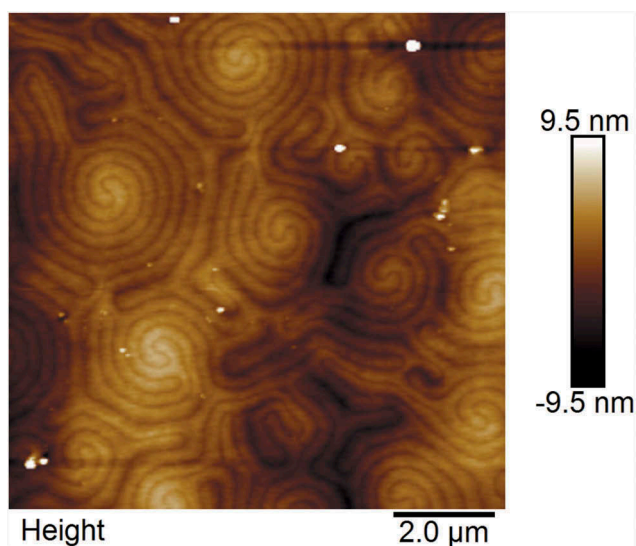
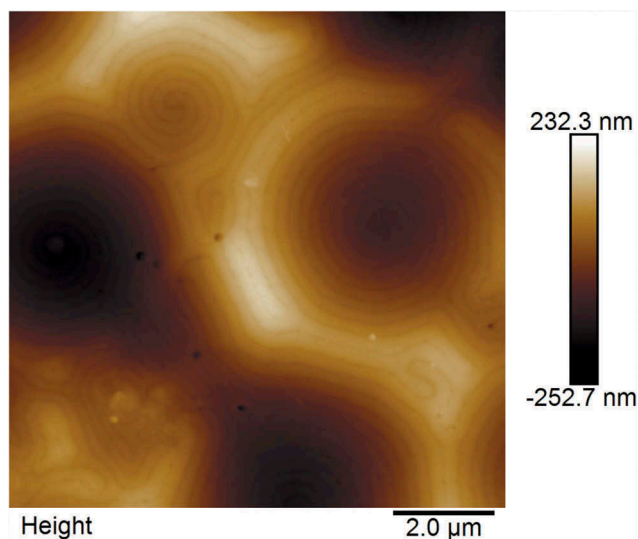


Figure 2. Typical AFM image of surface pattern formed in air.



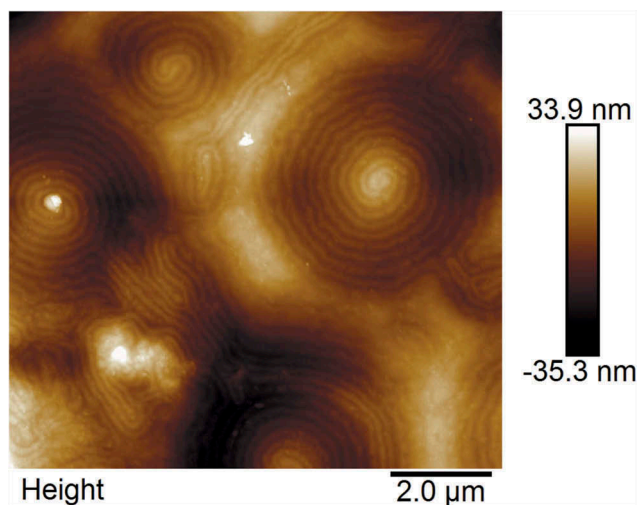
**Figure 3.** Typical surface image formed in water solution of polyacrylic acid.

In the samples formed in pure water under conditions specified above the spiral-like structures do not easily form. The AFM scans show a rather uniform flat surface with traces of poorly visible spiral pattern.

However, the presence of about 1% of polyacrylic acid in water results in the formation of fine structures shown in Figure 3. The centres of the spirals are almost always located in valleys and dips. These structures are also characterised by uniform changes in heights of spirals with well-defined steps and almost ideal Archimedes-like spiral structures. The distance between lines is about 260 nm and is very uniform. The structures formed in aqueous environments with dissolved polyacrylic acid and/or surfactants were chosen for further experiments with VOCs.

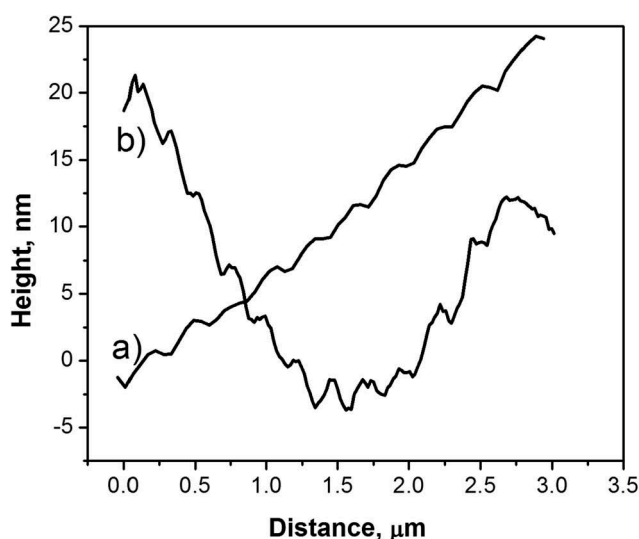
In experiments with VOCs, it was found that the better metrics to quantify the exposure of surface to vapours of VOC may be the dose rather than the time of exposure at certain vapour concentration. The dose can be simply defined as concentration multiplied by time of exposure. In a wide concentration range of VOC the use of this variable instead of concentration or time of exposure alone allows for more universal explanation of experiments.

The surface structure of glass-forming CLC did not respond to the vapour of alcohol but did so vigorously to the presence of toluene vapour. It is not surprising that the CLC surface responded to the presence of a good solvent in air, but it was found to be very surprising the manner in which it responded. Two effects were observed. First, the surface pattern started to change substantially even at low doses. The spiral started to wobble and became less 'ideal' with significant

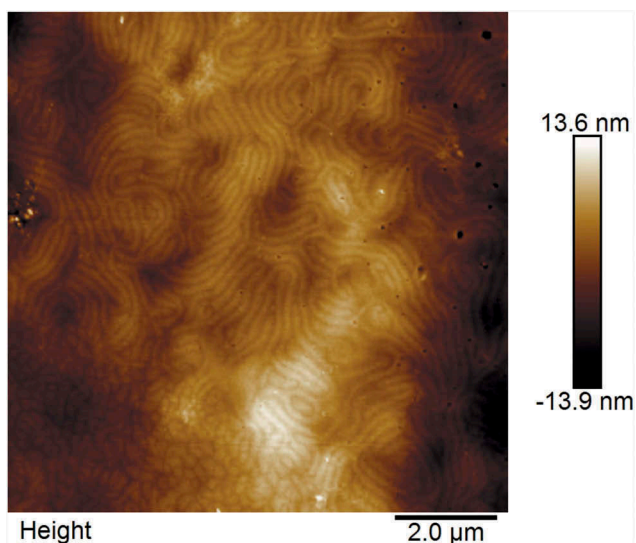


**Figure 4.** Surface image changes under exposure to toluene.

derivations from Archimedes shape. Moreover, the central part of each spiral started to grow, so that each centre actually popped out of the valley of a spiral (Figure 4). The only possibility of such behaviour is the change of focal conic domain beneath the surface and the upward motion of its centre. The degree of wobbling and structural changes increase with increasing dose. However, it seems that some of these changes at these levels of dose are still fully reversible: if the vapour is removed, the wobbling relaxes back to its initial form. This relaxation, however, takes much longer time. The typical surface profile of a spiral is shown in Figure 5 where it is compared to the profile of the same spiral before any exposure to toluene. It can



**Figure 5.** Surface profile along the radius of the spirals shown in Figures 3 and 4, distance is measured from the bottom of the spiral: (a) before exposure to toluene, (b) after exposure to toluene. The growth of central peak is seen at smaller distances.



**Figure 6.** 'Random pattern', a surface image of the same area as in Figures 3 and 4 after higher doses of toluene exposure.

easily be seen that the central part of the spiral raises and the overall depth of the spiral decreases.

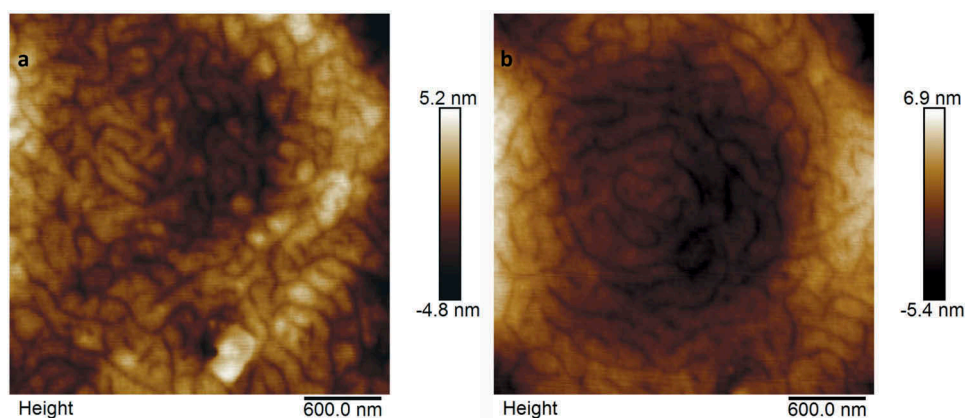
If the treatment continues for a longer time or the pressure of toluene rises (larger VOC exposure dose that can be roughly estimated as 20 s exposure to  $10^{-3} P_{\text{sat}}$ ) a sudden transition in the CLC structures is observed (see Figure 6). At certain critical dose, the surface pattern changes at once, many visibly random defects appear on the surface. The later pattern is at least partially reversible as shown in Figure 7(a) for a single spiral that existed at place of this visibly disordered pattern before treatment in toluene. The defects on the surface start to organise themselves in a spiral-like pattern after removal of toluene (Figure 7(b)). It takes a few hours without any

presence of toluene for this organisation to show. Unfortunately, due to time constraints, it was impossible to use longer times to follow the reversible structural changes occurring after removal of vapour in the same spiral.

Interestingly, the effects of transforming valleys into hills were previously observed [4] under increasing temperature. Obviously, increasing temperature results in higher molecular mobility, the effect also caused by diffusion of toluene molecules inside CLC. Regarding the nature of transformation, most likely the surface tension and mechanical stress stored in vitrified glass cause the raise of the central part of the valleys. Indeed, the rough estimations of pressure due to the negative slope of focal conic domains with the radius  $R < 1 \mu\text{m}$  in accordance with Young–Laplace equation produces an upward pressure of about few atmospheres that is more than enough to produce such transformations. The detailed analysis of transformations will be published elsewhere.

#### 4. Conclusions

It was observed that formation of chiral pattern with focal conic domains located in the valleys on chiral surface of glass-forming polymers is facilitated by treatment of polymers in water solution of surfactants and polyacrylic acid. The surfaces of chiral polymers become sensitive to vapours of toluene and undergo spectacular reconstruction with valleys transforming into hills. The discovered effect can be used in building sensors of VOCs and creating novel surface patterns.



**Figure 7.** Partial reversal of 'random pattern' back to spiral pattern after removal of toluene from (a) to (b).

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## Disclosure statement

No potential conflict of interests is reported by the authors.

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