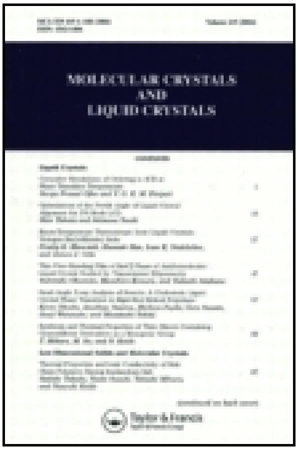

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Substrate Effect on the Surface Structures of Liquid Crystalline Polymers

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Annealing dewetted films of smectic polymers in their mesophase, a peculiar surface structure was observed by polarizing microscopy and atomic force microscopy. The surface structure, which develops independent from the substrate, consists of micron-size shallow dimples that are a few nanometer in depth. The lateral spacing of the dimples, which arrange in a hexagonal lattice, is directly proportional to the thickness of the dot. Based upon in situ video imaging of the dimple formation dynamics a mechanism is proposed.

Keywords polyacetylene; smectic polymer; mesoscopic structure; dewetting; substrate effect

INTRODUCTION

Upon casting from dilute solution, many different types of polymers form micronsize dewetted structures on substrates [1-4]. One interesting aspect is that the dewetted films show a high degree of in-plane order on the micrometer-size scale. This makes these mesoscopic structures interesting for electronic or photonic applications. Since the formation process involves non-linear dynamic processes during the evaporation of the solvent, the chemical nature of the polymer itself is not important for structure formation. Among others, also liquid crystalline polymers can be used to form mesoscopic patterns. In addition to the micrometer-size dewetting and pattern formation, liquid crystalline materials show a long range ordering with a repeat unit in the nanometer-size range. Thus an interplay between the liquid crystalline order on the nanometer-scale and the film dewetting on a micrometer-scale exists.

Recently we reported the formation of a novel "dimple structure" on top of dewetted droplets of liquid crystalline smectic polymers [5]. The dimple structure, as shown in Fig. 1, consists of micrometer-size indentations in the surface, which are a few nanometer deep. Since the diameter of the dimple corresponds to the height of the liquid crystalline droplet at that location, we proposed a model in which the smectic layers form torus like structures that extend throughout the whole thickness of the material, i.e. from the substrate to the top surface.

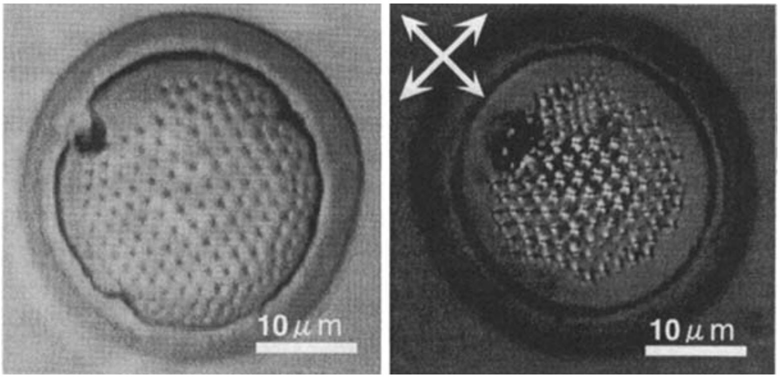
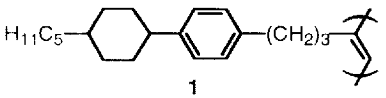


Figure 1: optical (a) and polarizing (b) micrograph of a micrometer-size droplet of **1** on glass. The white arrows indicate the orientation of polarizer and analyzer.



1

g 120 s_A 190 i

Figure 2: chemical formulae of the liquid crystalline polymers and their phase behavior

EXPERIMENTAL

The synthesis of **1** is described elsewhere [6].

Before casting, clean substrates were obtained as follows. Mica and HOPG were freshly cleaved. Glass slides were washed with detergent (decon) and with aqueous KOH/ethanol. These glass slides were hydrophilic. Immersion in a 10% dichloromethane solution of chlorotrimethylsilane gave hydrophobic glass slides.

Samples were prepared by casting 40-100 µl of a $CHCl_3$ solution (c=1 g/l) of the corresponding polymer onto the substrate. After solvent evaporation at ambient conditions, the samples were annealed in a vacuum oven or under nitrogen in a hotstage (Linkam RH600). Polarizing micrographs were taken with an Olympus BH-70 microscope equipped with a Sony video system. Phase transition temperatures were determined by DSC (Seiko Instruments DSC 22C). Atomic force images were taken by an Olympus NV 2500 microscope in the AC mode, in which a vibrating tip is scanned over the surface at a resonance frequency of ca 70 kHz. The scanning speed was 15-60 µm/s, which corresponds to 1-4 s/line, depending on the sample.

RESULTS AND DISCUSSIONS

Nonlinear dynamic and non-linear dynamic processes during the casting and the evaporation of the solvent lead to micrometer-size variations of the film thickness [2]. Thus, directly after the casting, a film with heterogeneous thickness was formed. After annealing at elevated temperatures a dewetting of the initially formed cast film takes place. Optical microscopy reveals that, during the heating, the reduction in viscosity at the clearing point leads to an abrupt rupture of the film and droplet formation (Figure 3). A sample prepared by this method consists of droplets of various size. The smallest droplets have a diameter of 1 µm or below, whereas larger droplets can have diameters of several 100 µm.

Fast cooling (ca 10°C/min) from the isotropic phase to room temperature leads to an unspecific texture. Slow cooling (2°C/min) gives rise to a highly unusual texture in the center of the droplets (Figure 1). It consists of circular domains of a few micrometer diameter with a dark center and a 'Maltese Cross', where the arms are parallel to the polarizer and analyzer position. The circular domains form a hexagonal lattice and the domains closer to the edge of the droplet are smaller than those in the center. Each droplet also shows a non-structured rim.

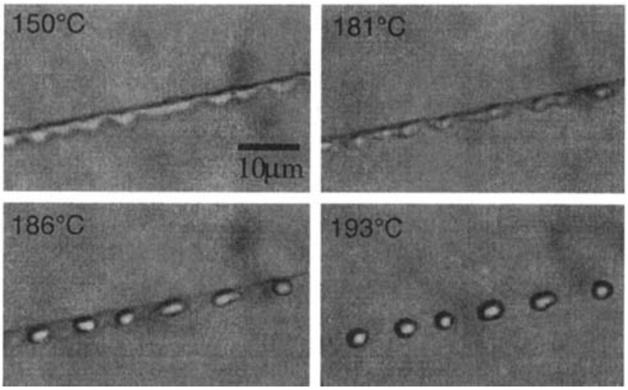


Figure 3: optical micrographs of the dewetting process in a film of **1**. The film was heated with a rate of 10°C/min.

Atomic force microscopy at room temperature showed that the surface of the droplet exhibits hexagonal arranged indentations ("dimples") [4]. The dimple diameter and droplet height have a linear correlation, but dots with a height of less than 650 nm do not exhibit a dimple structure. Below this sharp threshold height the droplets have a regular spherical shape, like droplets of amorphous polymers [1]. In a previous paper, we proposed a model for the pattern formation, which is based on the formation of a torus-like defect structure in the liquid crystalline phase.

Since the structure is dependent of the droplet height, it can be speculated that the substrate depresses dimple formation. Thus by tuning the chemical nature of the substrates (crystallinity, hydrophilicity, etc) dimple formation can be controlled. For each kind of substrate characteristic (crystalline - amorphous, hydrophilic - hydrophobic) one example was chosen and dewetted films were prepared. It turned out that on three of the investigated substrates, hydrophilic glass, silanized hydrophobic glass, and mica, droplets of **1** exhibited a non-birefringent rim and a central dimple structure (Figure 4 a-c). Films prepared on the fourth substrate, highly oriented pyrolytic graphite (HOPG), did not dewet. Reflectance microscopy showed that a continuous film was formed, which is due to the strong interaction of the hydrophobic polymer with the hydrophobic substrate. The thickness of this film is not constant, and micrometer-size spherical protrusions can be seen (Figure 4 d).

The hydrophilicity of the substrate does not influence the dimple structure, but the different interaction with **1** manifested in the contact angle. Hydrophilic substrates had a higher contact angle (mica: 10°; hydrophilic glass: 12°) than silanized hydrophobic glass (4°). Since polymer **1** did not dewet from the most hydrophobic substrate, HOPG, it has a contact angle of 0°.

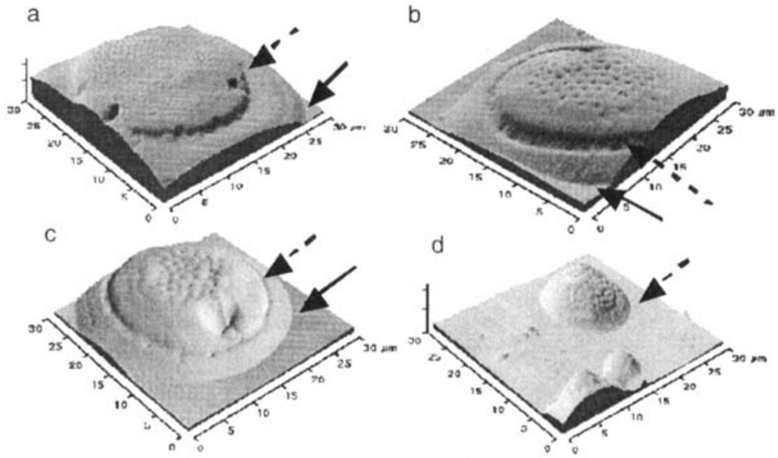


Figure 4: Atomic Force Images of droplets of **1** on different substrates.
a: hydrophobic glass, b: mica, c: hydrophilic glass, d: HOPG. The solid arrow indicates the contact angle with the substrate, the broken arrows the contact angle of the dimple area.

Despite the fact that the contact angles with the substrate (solid arrows in Figure 4) depend on the substrate, the angle that is formed between the non-structured rim and the dimple area (broken arrows in Figure 4) is 10°-12° on all substrates, including HOPG. This shows that the dimple structure is independent on the chemical nature of the substrate.

SUMMARY

We have found a new type of texture and surface structure in micrometer-sized droplets of smectic liquid crystals that formed after dewetting of a film on a solid substrate. This dimple structure is independent of the substrate and occurs in droplets on various substrates, independent on their crystallinity or hydrophilicity. This is further evidence that the dimple structure is formed by a process within the droplets and is not a substrate-induced effect, like epitaxy.

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