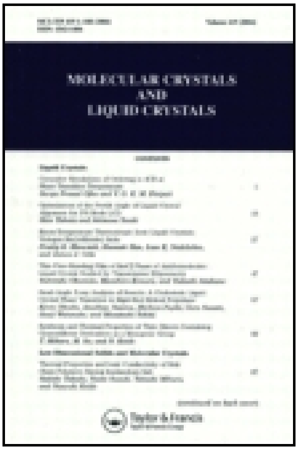

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Upon casting from dilute solution, liquid crystalline polyacetylenes and polyesters form mesoscopic dot and line patterns. After annealing in the liquid crystalline phase, the films dewet from the substrate and form isolated micronsize dots and line structures, which exhibit a peculiar surface structure as reveiled by polarizing microscopy and atomic force microscopy. The surface structure consists of micron-size shallow dimples that are a few nanometer in depth. The lateral spacing of the dimples, which arrange in a hexagonallattice, is directly proportional to the thickness of the dot. We propose that the dimple formation is due to a convective instability.

Keywords: polyacetylene; polyester; mesoscopic structure; droplet; dewetting; hierarchic structure; convection

INTRODUCTION

Due to their optical anisotropy liquid crystals find a wide variety of applications in the field of optics and electronics. For most applications the liquid crystalline compound is sandwiched between two surfaces and homogeneous and defect-free structures are needed. Thus considerable attention is paid to the research on liquid crystalline textures, dislocations and defects.

Here we report on the formation of a peculiar texture and surface structure of mesoscopic (i.e. micronsize) droplets of smectic liquid crystalline polymers that are formed on substrates. It is known that polymers cast from dilute solutions can form ordered mesoscopic dot and line structures [1-4]. The polymer structures have a lateral dimension of 200 nm to several 10 μm and a height of a few nm to a few hundred nm. The mechanism of pattern formation involves nonlinear dynamic processes during the casting process and a fingering instability at the edge of the solution droplet. A detailed description of the mechanism is already published and shall be referred to [2]. Since the mechanism is mainly dependent on the physical properties of the solvent and the substrate but not on the dissolved polymer, a wide variety of compounds can be used for pattern formation, including liquid crystalline polymers. .

EXPERIMENTAL

The synthesis of **1** is described elsewhere [5]. The polyester **2** was synthesized by an isopropyl-ortho-titanate-catalyzed trans-esterification reaction in the melt according to the literature [6].

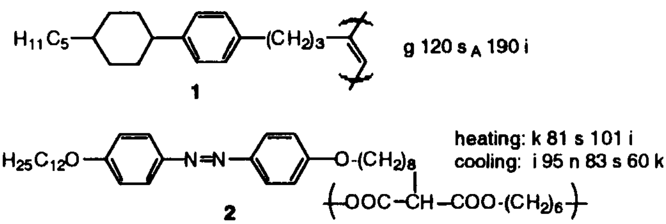

Figure 1: chemical formulae of the liquid crystalline polymers and their phase bahavior

Droplet samples were prepared by casting 40-100 μl of a $CHCl_3$ solution (c= 1 g/l) of the corresponding polymer onto a cleaned glass slide or a freshly cleaved mica substrate. After solvent evaporation at ambient conditions, the samples were annealed in a vacuum oven or under nitrogen in a hotstage (Japan Hightec 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 1-4 s/line, depending on the sample.

RESULTS AND DISCUSSIONS

After annealing in the isotropic phase 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. 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 (see Figure 2). Slow cooling (2°C/min) gives rise to a highly unusual texture in the center of the droplets. 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 at the rim of the droplet are smaller than those in the center. It has to be noted that the outer rim of the droplet shows only very weak and homogeneous birefringence (Figure 2). The same Maltese Cross texture is also observed when a quenched droplet sample is annealed in the mesophase, but the texture is not fully developed even after several hours of annealing.

By comparison with the polyester **2** it became clear that the Maltese Cross texture is specific for the smectic phase, since upon cooling from the isotropic phase the texture appears at the nematic-smectic phase transition temperature, but not in the nematic phase of **2**.

In order to get more detailed information on the texture, the samples were subjected to atomic force microscopy at room temperature. Since the polyester **2** crystallizes above room temperature, only the Maltese Cross texture of the glassy polyacetylene could be imaged. Figure 3 shows that the surface of the droplet exhibits hexagonally arranged indentations ("dimples"). Compared with the diameter of the dimple of around 1 μm, the depth is very shallow of around a few nm (see Figure 3 b).

The comparison with the polarizing microscope shows that the center of a Maltese Cross corresponds to the center of a dimple. The distance between two dimples corresponds to the height of the droplet at that position, thus the dimples get smaller towards the edge of the droplet, where the droplet is less high. By collecting data from many droplets of different size, it is possible to show that a linear correlation between dimple diameter and droplet height exists, as shown in Figure 4. In addition, optical as well as atomic force microscopy show that droplets 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].

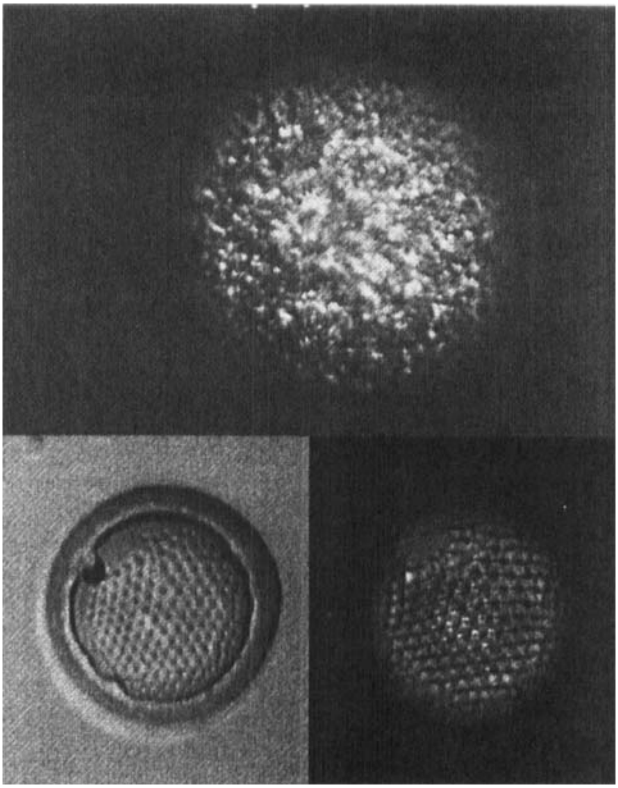

Figure 2: : Micrographs of the liquid crystal textures in mesoscopic droplets of the polyacetylene **1**. Top: polarizing micrograph of a droplet after rapid quenching from the isotropic phase. Bottom: optical- and polarizing- micrograph of a droplet after 2°C/min cooling from the isotropic phase. The diameter of the droplets is approx. 25 μm in both cases.

Both the small droplets as well as the non-birefringent edge of the droplet show no particular surface structure and they are very smooth. Thus only indirect evidence on the aggregate state of the mesogens (amorphous or liquid crystalline) can be made. In Figure 3c a part of the non-birefringent rim (between 2 and 4 μm on the lateral scale) shows a smooth surface with a roughness of less than 1 nm and no curvature. It can be assumed that in this region the smectic lamellae are parallel to the surface, which explains the smoothness. Together with the polarizing microscopy we conclude that the mesogens in the rim are aligned homeotropically.

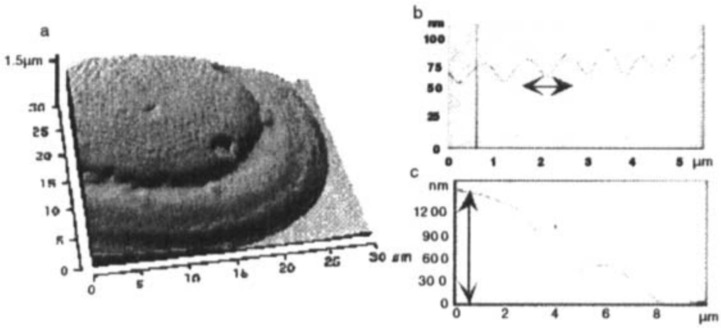

Figure 3: AFM image and cross section of a droplet of **1**. a: AFM image. b: cross section at the center of the droplet in a. The arrow indicates the diameter of a dimplec: cross section of a different droplet. The arrow indicates the total height of the droplet. Note the different z scale in b and c.

In order to get a more detailed insight into the origin of the dimple structure, droplet samples were prepared on various substrates. On all investigated substrates, hydrophilic glass, silanized hydrophobic glass, mica and highly oriented pyrolytic graphite (HOPG), a non-birefringent rim and a central dimple structure were observed. These results show that the dimple structure is not surface-induced, since it is independent on the crystallinity and hydrophilicity of the substrate.

The intriguing fact that the dimple diameter directly correlates to the height of the droplet at that point and that the dimple formation is suppressed in thin areas leads us to the conclusion that the dimple formation is due to a convective motion during annealing. This convection can be caused either by a temperature gradient in the droplet or by local differences in the surface tension that leads to the so-called Marangoni-effect [7].

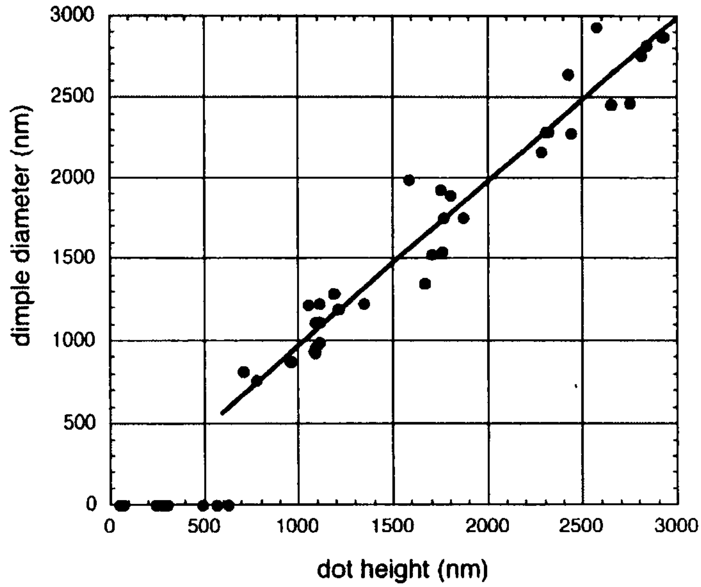

Figure 4: Graph of dimple diameter versus droplet height. The straight line with the slope = 1 is a guide for the eye. Below 650 nm droplet height, no dimple structure was found. In order to indicate that droplets existed with certain diameters they were assigned a zero dimple diameter.

The convection cells are circular, thus the distance between the cells is equal to their height. Since the anisotropic viscosity in the smectic phase favors the sliding of the smectic layers along the flow direction, the smectic layers form torus-like structures. This then explains both the indentation in the center of the droplet, as well as the Maltese-Cross birefringence, as can be seen in the model in Figure 5. Below the threshold height of 650 nm this convection current does not develop, either because of the sufficient thermal conductance, or due to friction with the substrate.

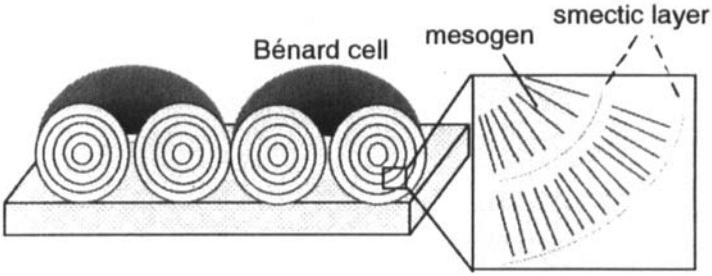

Figure 5: model of the dimple formation. Bénard-type convection leads to the formation of circular domains, in which the mesogens and the smectic layers arrange according to the anisotropic viscosity .

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 flim on a solid substrate. The hexagonal arrangement of dimples on the droplet surface is independent on the substrate, but the size of the dimples correlates directly with the height of the droplet. Furthermore, below a threshold height of 650 nm no dimple formation occurs. Thus these results we conclude that a convective instability during sample annealing is the reason for dimple formation.

References

[1] O. Karthaus, K. Ijiro, M. Shimomura, *Chem. Lett.*, **1996**, 821 (1996).
[2] O. Karthaus, L. Grasjo, N. Maruyama, M. Shimomura, *Chaos*, **9**, 308 (1999).
[3] O. Karthaus, L. Grasjo, N. Maruyama, M. Shimomura, *Thin Solid Films*, **327–329**, 829 (1998).
[4] O. Karthaus, T. Koito, N. Maruyama, M. Shimomura, *Mol. Cryst. Liq. Cryst.*, **327**, 253 (1999).
[5] S.-Y. Oh, K. Akagi, H. Shirakawa, *Macromolecules*, **26**, 6203 (1993).
[6] B. Reck, H. Ringsdorf, *Macromol. Chem., Rapid. Commun.*, **6**, 291 (1985).
[7] L.E. Scriven, C.V. Sterling, *Nature (London)*, **187**, 186 (1960).