Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 13 Dec 2006.

To cite this article: Steven D. Hudson , Edwin L. Thomas & Robert W. Lenz (1987): Imaging of Textures and Defects of Thermotropic Liquid Crystalline Polyesters by Electron Microscopy, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 63-72

To link to this article: http://dx.doi.org/10.1080/00268948708074525

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 63-72
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Printed in the United States of America

IMAGING OF TEXTURES AND DEFECTS OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS BY ELECTRON MICROSCOPY

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Introduction

There is strong interest in observing textures and defects in liquid crystalline polymers (LCP), because of their influences on the rheological and optical properties of these materials. The defects, called disclinations, are hypothesized to give rise to the non-Newtonian flow observed at low shear rates.[1] Disclinations are line singularities in the orientation of the molecular director ($\underline{n}(\underline{r})$). The orientation as a function of position following an imaginary loop around the disclination changes by $n\pi$. The strength of a disclination is defined as $n\pi/2\pi$. Disclinations of strength $\pm 1/2$ and ± 1 have been observed. The disclination line, or core as it is called, has a small but finite volume supposed to contain isotropic material.

While disclinations are singularities in the molecular director field $\underline{n}(\underline{r})$, the term texture refers to $\underline{n}(\underline{r})$ as a whole. A texture may contain many disclinations, or it may contain none at all, e.g. a monodomain texture. Disclinations may be arranged disorderly as in a Schlieren texture or organized as in a serrated wall texture. Banding is a type of texture which need not contain any disclinations. This texture is commonly observed upon relaxation of LCP's after shearing at moderately high rates.

Wood and Thomas[2,3] developed the technique of lamellar decoration which enables high resolution visualization of texture and disclinations. Our purpose is to demonstrate that this technique permits observation of various textures ranging from very high disclination density (50-100 $/\mu^2$) to that of a monodomain. We wish to exploit the technique as a diagnostic probe to investigate the relationship between textures and defects and the sample history (i.e. as a function of deformation rate, extent of deformation, relaxation time after deformation, and temperature).

Method

The polyesters formed from the condensation of 1,10 decanebisterephthaloyl chloride with various substituted

hydroquinones[4] were investigated. The chemical structure is shown in figure 1.

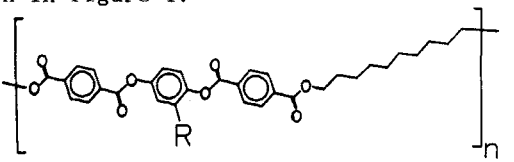


Figure 1. Chemical structure of the polyesters

The alkyl substituent group, R, may be hydrogen, methyl, ethyl, octyl, or decyl.[4] The methyl substituted polymer crystallizes readily and is therefore very useful for the lamellar decoration technique.

As a preliminary study, three different thin film preparation techniques were used to obtain a wide range of defect density. Very high defect density samples were prepared at room temperature by casting films of the polymer from isotropic 0.2% solutions in methylene chloride. As the solvent rapidly evaporates, the liquid crystalline state is nucleated in many sites at random orientations, much like when a LCP is cooled from an isotropic melt. By casting at room temperature, we hoped to capture a high disclination density. Intermediate defect density samples were prepared by spreading liquid crystalline films on hot phosphoric acid as previously done by Thomas and Wood.[2,3] Solid polymer was melted on a H_3PO_4 substrate at 170C, a temperature which the polymer is liquid crystalline (T_{LC}=154C for the methyl substituted polymer). After the polymer, which spreads due to the high surface tension of H_3PO_4, formed a thin film, the film was then immediately (within a few seconds) quenched on room temperature H_3PO_4. Subsequently, it was transferred to a room temperature H_2O substrate before placing on a microscope grid. In order to realize very low defect density, samples were prepared by spreading films on 170C mercury and annealing (relaxing) the polymer film, while in the liquid crystalline state, for 3 hours on the mercury substrate before quenching to room temperature.

After the films were solidified, they were placed on electron microscope copper grids and then annealed in the solid state at 135C for 10 minutes to induce crystallinity. During annealing crystalline lamellae grow perpendicular to the chain direction (as shown schematically in figure 2). Because the final sample is semi-crystalline, it can be shown by electron diffraction that the c-axis in the crystal is

approximately parallel to the molecular director in the frozen nematic precursor.

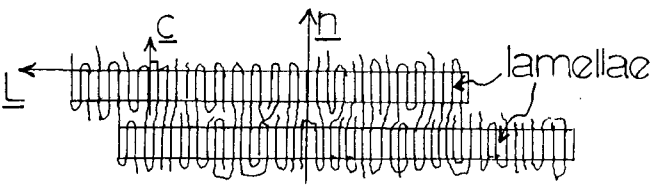


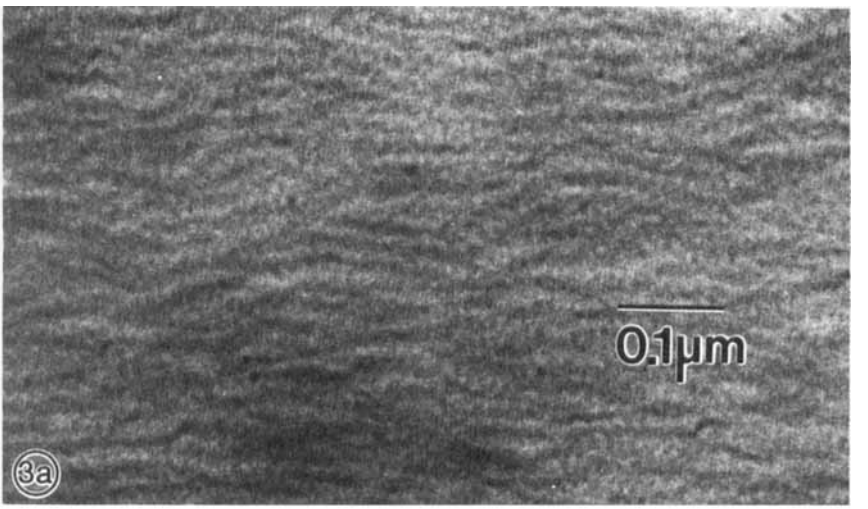
Figure 2. Schematic diagram showing the relationship between the molecular director, n, the chain axis, c, and the long dimension of the lamellae, L.

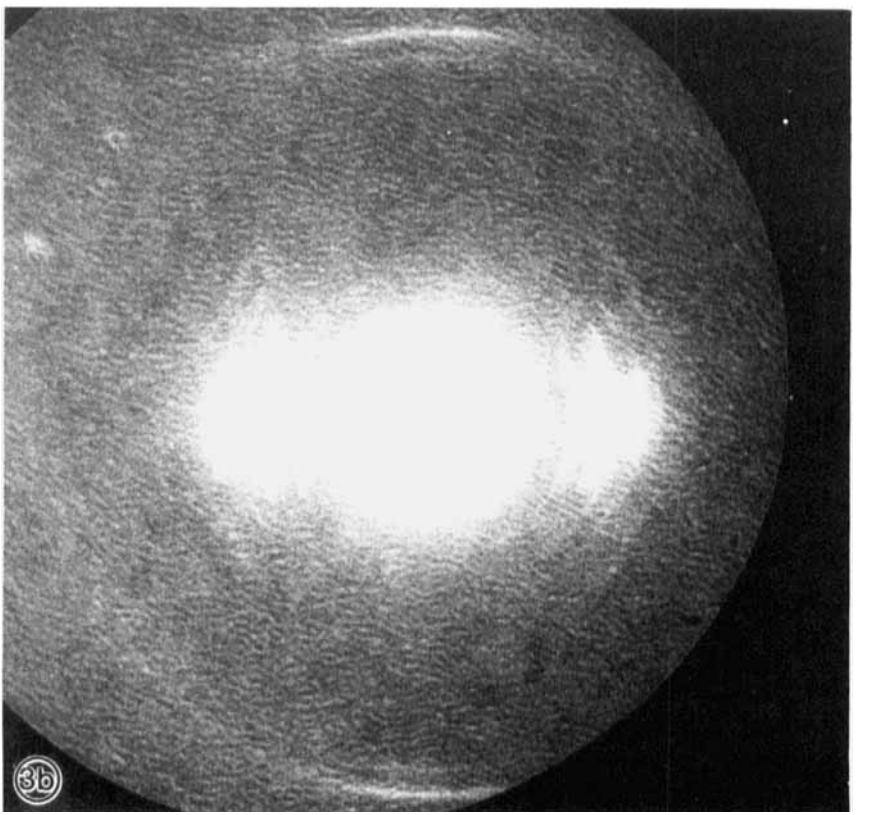
Results and Discussion

After crystallization, lamellae can be readily imaged with good contrast in thin films using bright field TEM. Figure 3a shows a high magnification bright field image showing the lamellae. The lamellar thickness is approximately 12nm. By superposing the diffraction pattern and the bright field image formed from the 000 spot (fig. 3b), it is shown that the chain direction, or molecular director, is perpendicular to the lamellae. Therefore upon crystallization, the frozen nematic precursor is effectively decorated with lamellae, revealing a map of the molecular director field. That the chain direction is perpendicular to the lamellae is further elucidated by figure 3c. This figure shows a crack which has grown following the chain direction in a sample with a banded texture. The director field here has a simple sinusoidal variation.

The images also reveal defects in the field of oriented lamellae (see fig. 4a). The lines drawn perpendicular to the lamellae on figure 4b correspond to the molecular director trajectories. It is observed that the same type of disclination occurs in the director field at the same location it does in the field of lamellae. The disclination in the director field is rotated in orientation with respect to that in the lamellar field. Figure 4 also shows a perspective view of the sample. The most common types of disclinations seen in these polyesters are those of strength, s, equal to +1/2 and -1/2.

Figure 5 shows a solution cast sample which has a very high defect density ($25/\mu^2$). Disclination densities up to 50-100 $/\mu^2$ have been observed; this density is at about the resolution limit of this decoration technique. Images at this density reveal interactions of disclinations. We hope to also determine a maximum disclination density above which the sample becomes effectively isotropic.





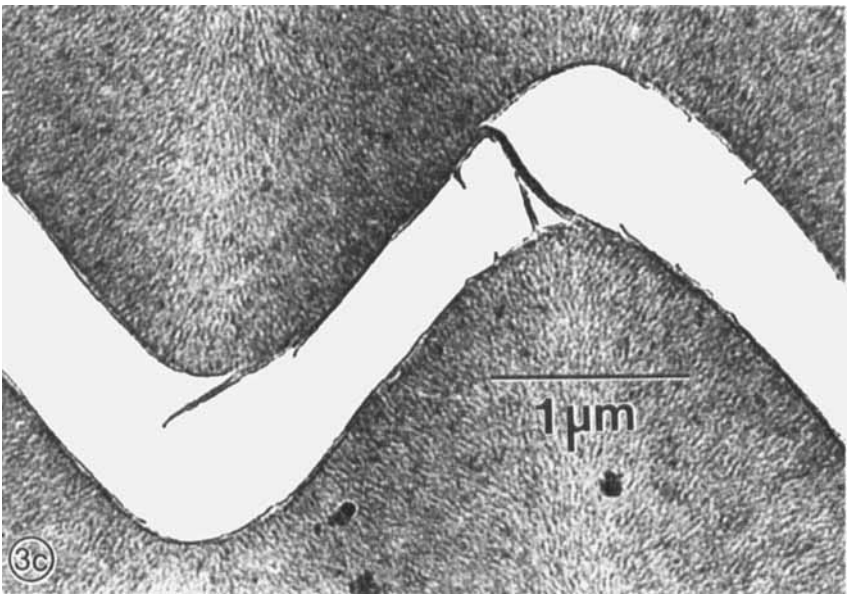


Figure 3. a.) High magnification micrograph showing the lamellar morphology. b.)Superposition of the diffraction pattern and the bright field image formed from the 000 spot establishing the orthogonal relation between the long dimension of the lamellae and the chain axis. c.) A banded texture in a thin film which has been subsequently subjected to stress. A crack has followed the sinusoidal trajectory of the molecules.

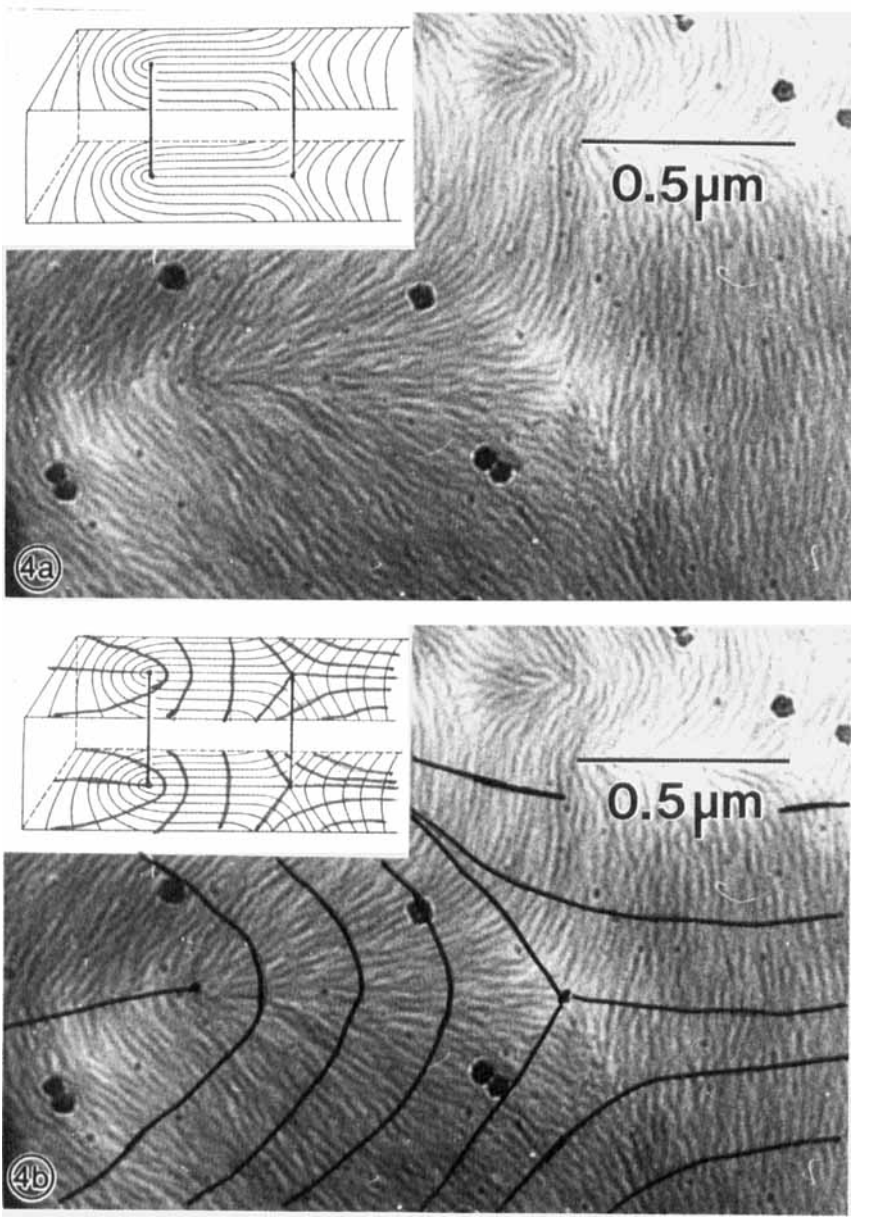


Figure 4. a.) A pair of +1/2 and -1/2 disclinations in the field of lamellae; a perspective view is in the inset. b.) The same pair but with lines drawn in pen perpendicular to the lamellae corresponding to the molecular director.

Figure 6 shows a sample made by spreading on H_3PO_4. Defect pairing and polygonalization are apparent in figure 6a. Banding, as seen in figure 6b, is evidence that some relaxation has occurred before quenching. It is evident that a band may end without any disclinations. Since banding may occur without the creation of any disclinations, this mechanism of relaxation can occur at short time scales.

Figure 7 shows a sample which had been annealed on 170C Hg for 3 hours. We see that during the annealing process, the disclinations of opposite sign have attracted each other and annihilated. Each disclination feels a force from all the other disclinations in the sample due to the distortional energy field around each disclination. The force on a disclination is, according to Nehring and Saupe[5], of the same form as the electrostatic force on charged particles:

$$F = k s_1 s_2 / r_{12}$$

where k is a constant proportional to the elastic constant (for the isotropic case when bend and splay constants are equal) and the length of the disclination line. r_{12} is the distance between disclinations of strength s_1 and s_2.

From these preliminary experiments, we conclude that the lamellar decoration technique can be used to analyze the effects of flow and thermal history on the texture. This technique permits visualization of the texture at high resolution. Disclination densities up to $50\text{-}100/\mu^2$ have been observed.

The support of the Materials Research Laboratory of the University of Massachusetts for financial aid and research facilities is appreciated. We also acknowledge the support of a NATO grant to E. L. Thomas.

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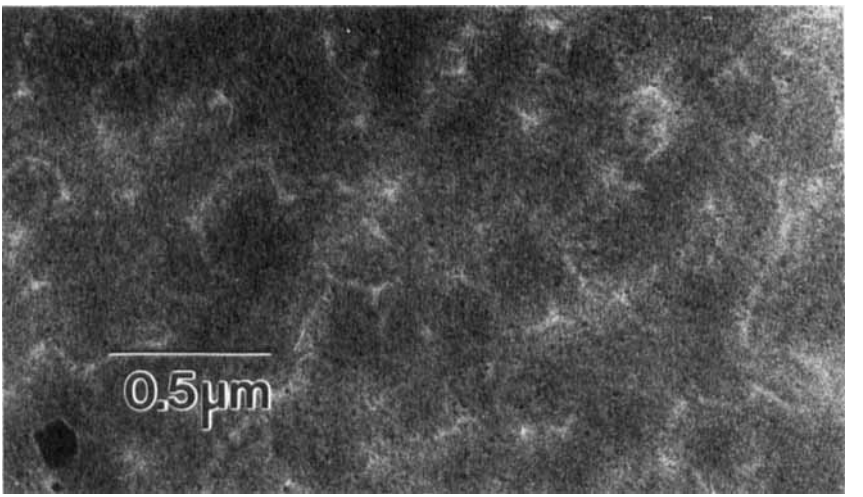

Figure 5. High defect density sample cast from dilute solution in methylene chloride.

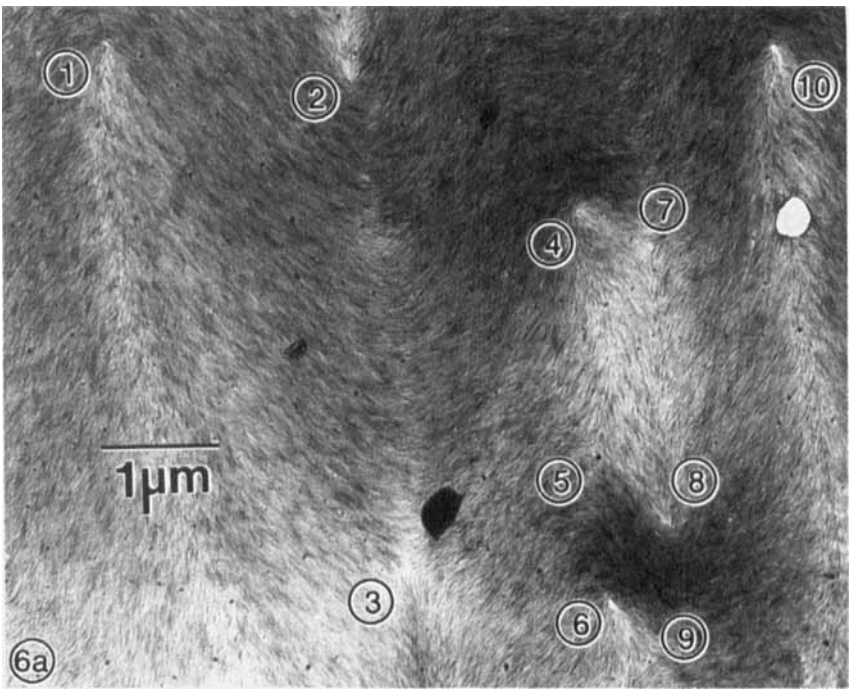

Figure 6a.

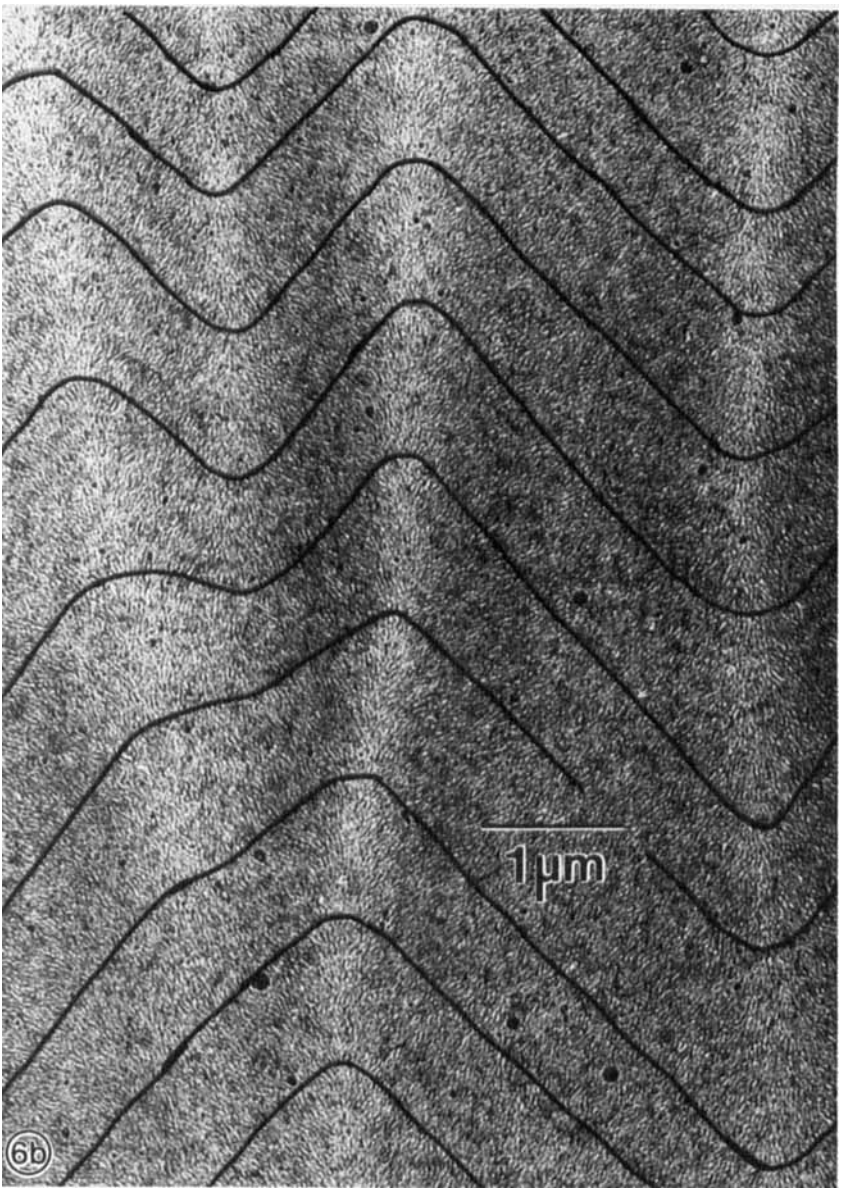

Figure 6. Intermediate defect density sample melt spread on H_3PO_4 (dark spots are bits of dust). a.) Pairing of defects and polygonalization. Disclinations marked 1,2,4,6,8,10 are +1/2 and those marked 3,5,7,9 are -1/2. b.) Banded texture.

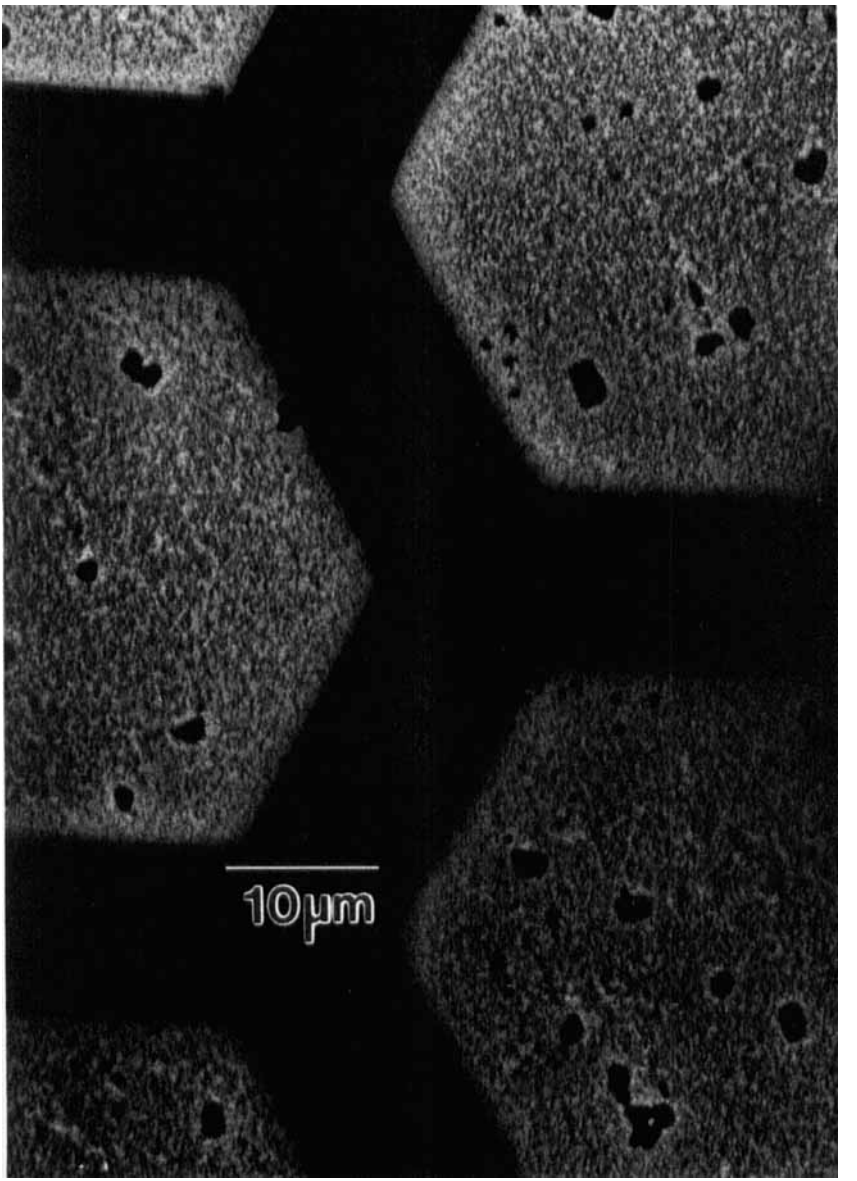

Figure 7. Zero defect sample annealed in the liquid crystalline state on 170C mercury for 3 hours (hexagonal grid is the microscope grid).