

Molecular ordering in a liquid crystalline material visualized by scanning electron microscopy

I. HEYNDERICKX, D. J. BROER

Philips Research Laboratories, PO Box 80000, NL-5600 J A Eindhoven, The Netherlands

Y. TERVOORT-ENGELEN

Centre for Polymers and Composites, Eindhoven University of Technology, PO Box 513, NL-5600 MB Eindhoven, The Netherlands

The molecular ordering in the bulk of a low molar mass-type liquid crystalline (LC) material is visualized by examining with scanning electron microscopy LC diacrylate films, in which the low molar mass-type LC ordering is fixed by UV polymerization. Micrographs of the fracture surfaces of these films exhibit a fine texture, illustrating the presence of a layered structure in the samples. This layered structure correlates with the director orientation in LC materials aligned by surface interaction.

1. Introduction

In the past, considerable effort has been devoted to the determination of the director profile in a macroscopically oriented low molar mass liquid crystalline (LC) material [1]. From a theoretical point of view, attempts were made to predict the profile of the molecular ordering within an LC sample by analytical calculations [2-5] or numerical simulations [6, 7]. Most of the experimental work was restricted to indirect observations of the molecular ordering, by e.g. polarizing microscopy [8, 9], polarized infrared [10] or Raman spectroscopy [11, 12], nuclear magnetic resonance [13] or X-ray diffraction (XRD) [14]. Some of these techniques provide a measure of the order parameter, when uniform alignment in the LC samples is assumed. Others are used to determine the molecular organization in non-uniformly aligned samples by comparing the predicted spectra based on a supposed model with the measured spectra. None of these, however, offers the possibility of a direct visualization of the molecular orientation in a non-uniformly aligned LC specimen.

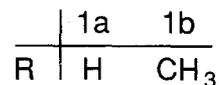
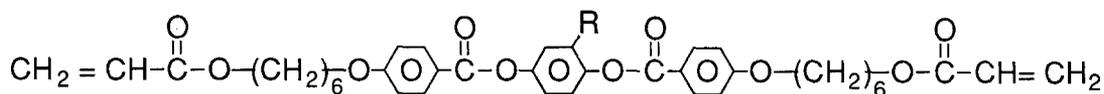
Recently, it has been demonstrated that the molecular organization within a monolayer LC material on an orienting substrate can be examined by using scanning tunneling microscopy (STM) [15]. This technique is very powerful in studying surfaces, but unfortunately gives no information on the director profile in the bulk of an LC sample. It may even be questioned whether the surface of a monolayer on top of a substrate possesses the same orientation as the surface of a bulk sample. In an attempt to visualize the molecular ordering in the bulk of an LC polymeric sample, scanning electron microscopy (SEM) [9, 16] or transmission electron microscopy (TEM) [9, 17, 18]

were used in combination with various decorating techniques. Recently, high-resolution electron microscope (HREM) photographs of the molecular ordering in nematic and smectic main-chain and side-chain LC polymers have been published [19, 20]. Because of the sample preparation methods, however, the use of SEM or TEM is limited to polymers and is not applicable to low molar mass LC materials.

This report describes a means of evaluating the molecular ordering in low molar mass-type LC materials with the SEM technique. It is based on the fixation of the director profile of an LC diacrylate by UV polymerization [21]. In the pre-polymerization state, the diacrylate molecules behave like ordinary low molar mass LC materials, possessing a nematic and smectic phase and being oriented by surface interaction or by an external electric or magnetic field. During the ultra-fast UV polymerization, the molecular organization hardly changes. No structural reorganization is observed in a polarizing microscope [22]. Dichroic measurements only reveal a small change in the order parameter, which even reduces to zero for a good choice of the polymerization temperature [21, 22]. The UV-polymerized LC diacrylate films have an optically clear appearance. Upon fracture, however, an alignment texture representing the profile of the molecular orientation across the cross-section of the film can be observed by SEM.

2. Experimental procedure

The synthesis and material properties of the mesogenic diacrylates 1a and 1b and their eutectic mixture 2 containing 80 wt % of 1b have been extensively described elsewhere [21]. The chemical structure of these materials is given in scheme 1.



Scheme 1

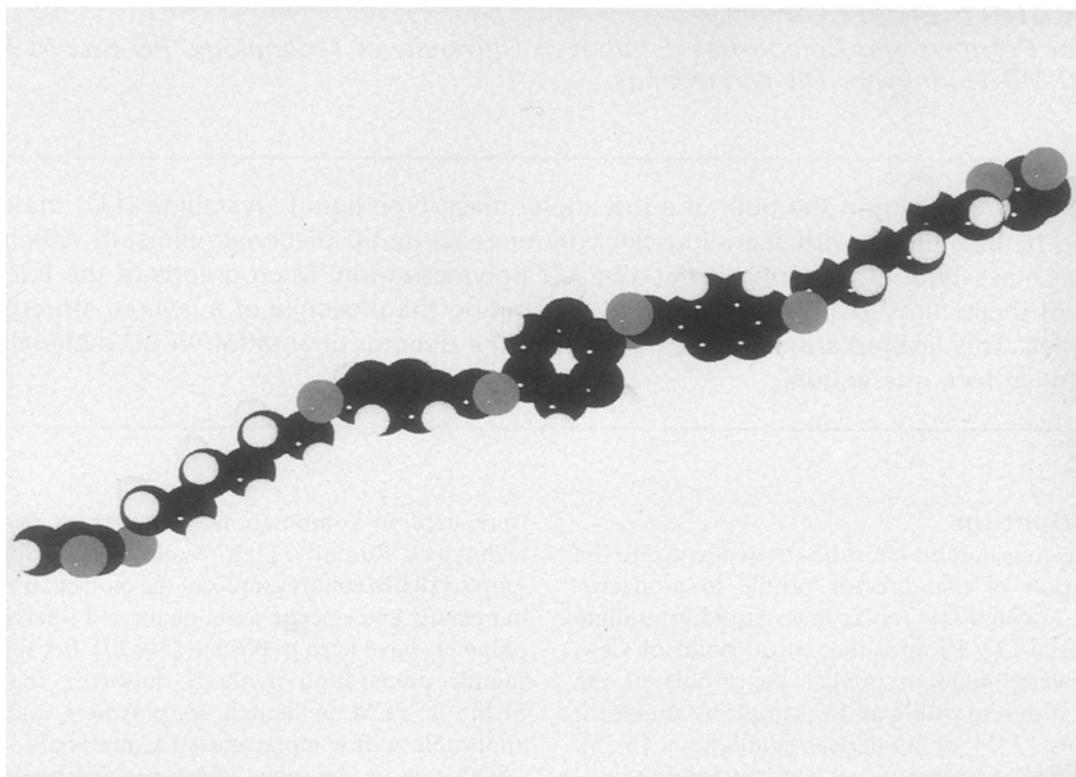


Figure 1 Conformation of the LC diacrylate 1a in its monomeric state as calculated by minimizing the free energy.

The transition temperatures are summarized in Table I, and Fig. 1 shows a model of a 1a diacrylate molecule as calculated by minimizing its free energy, using the software CHEMX (developed and distributed by Chemical Design Ltd, Oxford). According to this model, the length of the mesogenic unit is approximately 4.0 nm and the width about 0.5 nm. The conformation is not greatly affected by the substitution of a methyl group in the mesogenic unit, resulting in the 1b diacrylate. In a bulk sample the conformation may be influenced by the interaction with neighbouring molecules. This interaction, however, does not change the characteristic dimensions drastically [23].

The LC diacrylates are stabilized by the addition of 100 p.p.m. p-methoxyphenol and their UV photosensitivity is activated by the addition of 1 wt % 2,2-dimethoxy 2-phenylacetophenone (Irgacure 6M, Ciba Geigy). For the twisted nematic diacrylate samples, a small amount of the chiral material S811 (Merck) is added to the diacrylate monomer [24]. The influence of these amounts of additives on the transition temperatures of the diacrylates is negligible.

TABLE I Transition temperatures of the LC diacrylates 1a and 1b and their eutectic mixture 2 containing 80 wt% of 1b. The value between brackets indicates a monotropic transition.

Compound	LC transition temperatures (°C)						
1a	Cr	108	S _c	(86)	N	155	I
1b	Cr	86	N	116	I		
2	Cr	80	N	120	I		

Cr: crystalline,
S_c: smectic C
N: nematic
I: isotropic

In the monomeric phase, the LC diacrylate is aligned in a cell consisting of two glass plates, both at the inner side provided with an orienting layer and separated by a piece of foil with a thickness of about 60 μm. In order to obtain a planar alignment, a rubbed polyimide (JIB 1051, JSR) layer is used as an orienting medium. For realizing a homeotropic alignment, a layer of SiO₂ is evaporated on a glass

substrate and subsequently dipped in a dilute solution of the chromium complex Scotchban FC-805 [25].

The aligned samples are photopolymerized by means of a UV short-arc mercury lamp with a power output of 0.8 W cm^{-2} , illuminating the material for about 3 min. Subsequently, the diacrylate films are removed from the cell and plunged into liquid nitrogen for fracturing. The fracture surfaces are coated with a Au–Pd layer for examination by scanning electron microscopy (SEM). Micrographs were obtained with a Cambridge Stereoscan S200 operating at 20 kV.

For the numerical simulation of the director profile in an LC sample, the appropriate free energy expression is minimized with a home-developed computer program, based on the simulated-anneal method [6].

3. Results and discussion

3.1. Director profiles

In order to check the presence of texture on a cryo-fractured surface of a diacrylate foil, a 60- μm film of 1a was planarly oriented and polymerized in its nematic phase at a temperature of 130 °C. The film was quenched in liquid nitrogen and broken in directions both parallel with and perpendicular to the orientation axis. Fig. 2 shows a view of both fracture surfaces at once, where the surface at the right side lies perpendicular to the orientation direction, while the one at the left side lies parallel to it. Across the right surface, we observe a line texture in the direction from top to bottom. Further experiments confirmed that this texture is characteristic of a molecular alignment perpendicular to the fracture surface. From a more detailed micrograph, it can be deduced that an average distance between two lines is of the order of $\sim 100\text{--}150 \text{ nm}$. The nearest-neighbour distance, as determined by wide-angle X-ray scattering [23], is 0.50 nm, which implies that each “layer” corresponds to approximately 200–300 molecules. Occasionally, even finer lines are observed in between them. The fracture

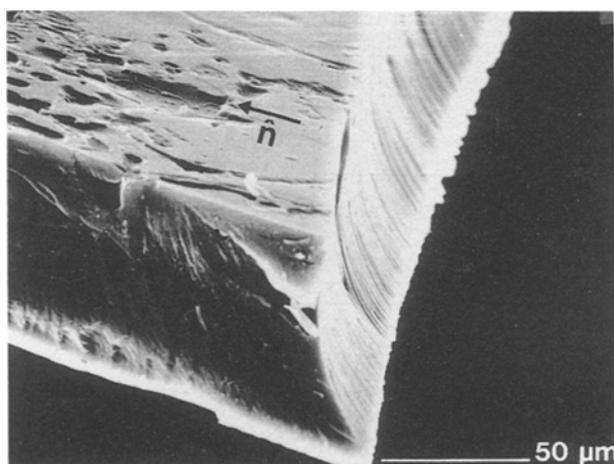


Figure 2 SEM photograph of an LC diacrylate foil UV polymerized in its nematic phase at 130 °C. The fracture surface at the right side lies perpendicular to the mean molecular orientation, while the one at the left side lies parallel to it.

surface along the orientation direction exhibits a scaly texture with terraces of about the same height as the line separation, i.e. 100–150 nm. On the top surface of the film some irregularities are observed, which are a kind of replica of the rubbed polyimide layer, which has been applied on the glass substrates as an orienting layer.

The experiments were repeated on a planar-oriented film of 1a, this time polymerized in its smectic phase at a temperature of 85 °C. A photograph (Fig. 3) of the sample in a polarizing microscope, with the orientation direction parallel to one of the polarizers of a crossed set, confirms the presence of a smectic ordering [8], which did not change on polymerization. The herring-bone texture observed in this figure is characteristic of a smectic C-phase ordering, and gives an indication of the cone angle between the actual molecular orientation and the surface-induced orientation direction. Fig. 4 demonstrates that in this case the surface, fractured along the orientation direction and lying in this micrograph from top to bottom, is more scaly than in the nematic case. Within the grooves we observe the layered texture characteristic of a fracture perpendicular to the orientation direction. Fig. 5 shows an example of a terrace structure,

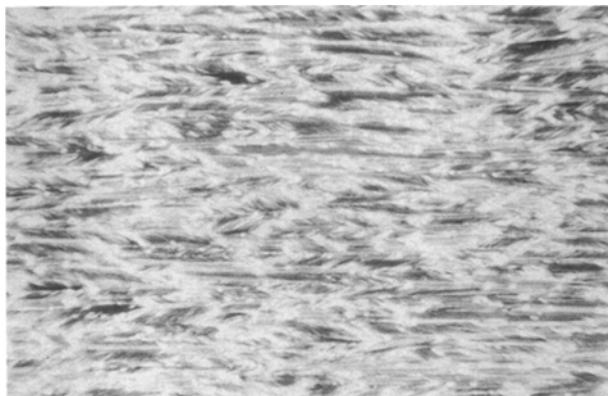


Figure 3 Image of a polymerized smectic diacrylate film in a polarizing microscope with the mean molecular orientation parallel to one of the polarizers of a crossed set. (Magnification = 500 \times)

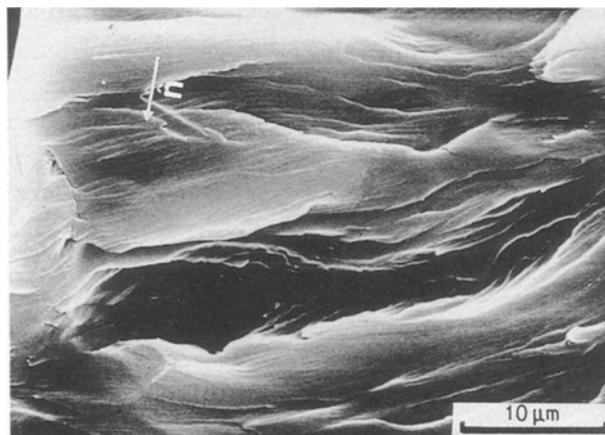


Figure 4 SEM image of a diacrylate film UV polymerized in its smectic phase at 85 °C and fractured along the orientation direction.

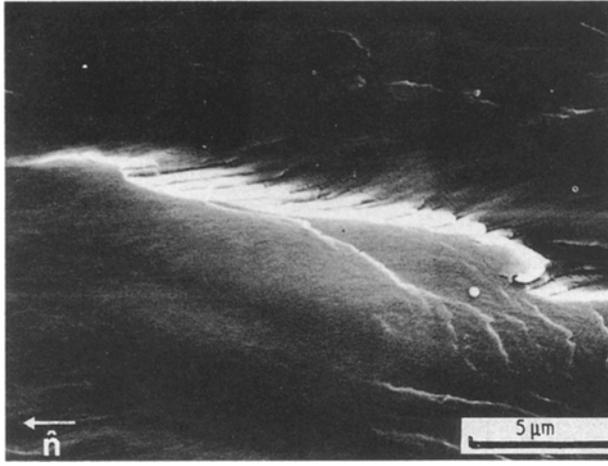


Figure 5 SEM image of a diacrylate film UV polymerized in its smectic phase at 85 °C and fractured along the orientation direction.

consisting of steps parallel to the film surface, and consequently perpendicular to the layered structure observed in the previous photograph. The average height of these steps is again ~ 100 nm. The experimental situation of the smectic diacrylate film is sketched in Fig. 6 with the fracture surface in front of the figure. It shows a layered structure in the depth, as observed in Fig. 4, and a stepwise texture parallel to the film surfaces, as observed in Fig. 5. The mean molecular ordering coincides with the direction defined by the cross-section of the plane parallel to the steps and the plane parallel to the layers, being parallel to the fracture surface. It means that by breaking a smectic diacrylate film, the fracture surface peels off in layers parallel to the mean molecular orientation.

The texture found in a homeotropically aligned film of 1a polymerized at 116 °C is shown in Fig. 7. The existence of a macroscopic homeotropic molecular ordering is demonstrated by conoscopy, which yields the image in Fig. 8, possessing the characteristic shape of a uniaxial optical medium with the indicatrix along the optical axis of the conoscope [26]. In Fig. 7 the small part of the actual fracture surface in front of the picture is too dark to show any substructure here, but a closer investigation reveals a line texture across the surface from right to left. An accidental burst of the film in the direction perpendicular to the actual frac-

ture surface exhibits the same layered structure. The secant of both layered structures leads to a molecular orientation perpendicular to the plane of the film (at the left side of the micrograph) and confirms the homeotropic orientation.

The idea postulated above, suggesting that the direction of the molecular orientation is given by the secant of layered textures observed on different fracture surfaces, is examined further on samples possessing a homeoplanar or twisted alignment.

The texture observed on a surface fractured along the planar orientation direction of a homeoplanarly aligned film of 1a polymerized at 120 °C is shown in Fig. 9. The substrate at the bottom of the photograph has been provided with a homeotropically aligning layer, while the substrate at the top contains a rubbed polyimide layer for planar orientation. The scaly structure of the surface is evidence of the molecular ordering: at the bottom the lines clearly lie perpendicular to the substrate, while the lines run more or less parallel to the substrate at the top. An important observation is that there seems to be quite a drastic change from planar to homeotropic orientation near the middle of the sample. This is supported by Fig. 10, demonstrating for the same sample the surface fractured perpendicular to the planar orientation axis, again with the homeotropic alignment at the bottom and the planar alignment at the top. The lower half of the fracture surface exhibits a layered texture, which near the substrate more or less follows the direction of the homeotropic orientation. In a relatively narrow region near the middle of the sample, these layers are strongly curved towards the depth. Analogous to earlier findings, one would expect near the top substrate a line texture characteristic of a fracture surface perpendicular to the molecular ordering. However, on the upper half of the fracture surface almost no texture is observed across the whole length of the sample. The absence of any texture there, is not understood. The director profile near the middle of the cell changes more drastically than predicted by numerical simulations. Fig. 11 shows the result of such a simulation for the tilt profile $\theta(z)$ across a homeoplanarly aligned LC cell with a thickness of 60 μm. According to the experimental results, an s-shaped curve with a steep change of θ around $z = d/2$ is expected. The numerical simulation, however, yields a convex curved

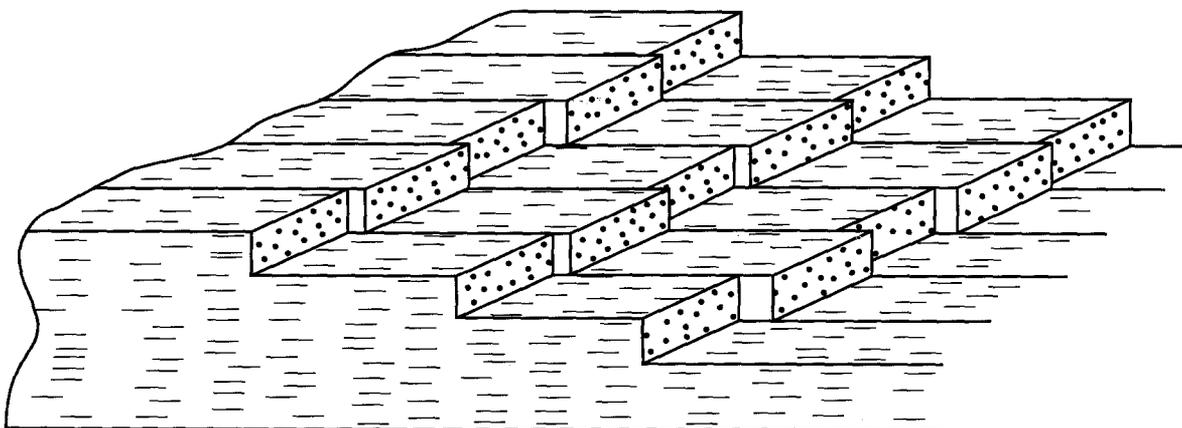


Figure 6 Sketch of the structure occurring in a smectic diacrylate film as interpreted from SEM photographs.

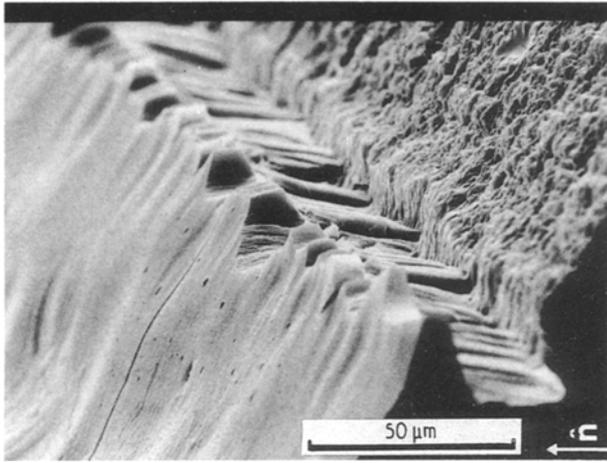


Figure 7 SEM photograph of a broken homeotropically aligned diacrylate film UV polymerized at 116 °C.

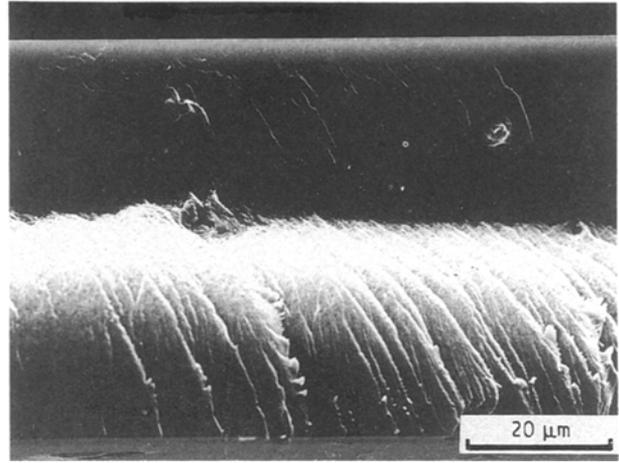


Figure 10 SEM image of a fracture surface perpendicular to the planar orientation of a homeoplanarly aligned diacrylate film UV polymerized at 120 °C.

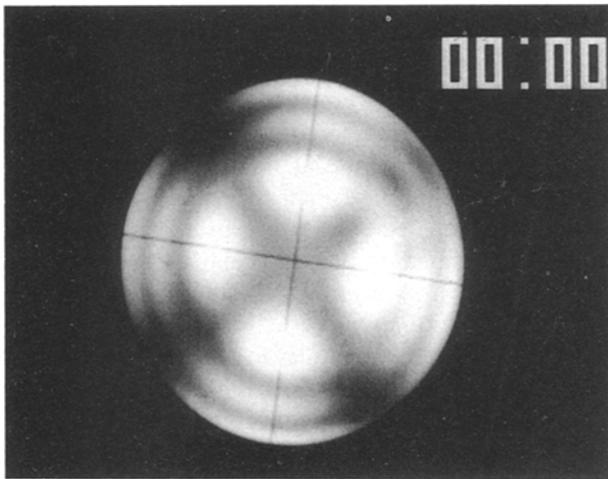


Figure 8 Conoscopic image of the macroscopic homeotropic molecular ordering in a diacrylate film UV polymerized at 116 °C.

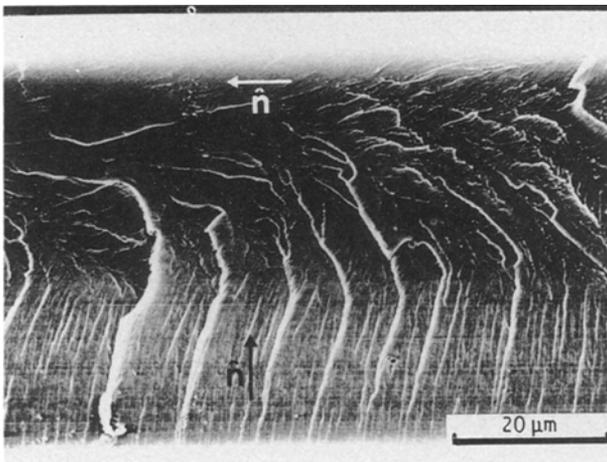


Figure 9 SEM image of a fracture surface parallel to the planar orientation of a homeoplanarly aligned diacrylate film UV polymerized at 120 °C.

dependence of $\theta(z)$ such that at any height in the cell θ is somewhat larger than its value obtained in the case of a linear dependence. The amount of curvature predicted by the simulation is affected by the ratio K_{33}/K_{11} of the bend to splay elastic constant, and by

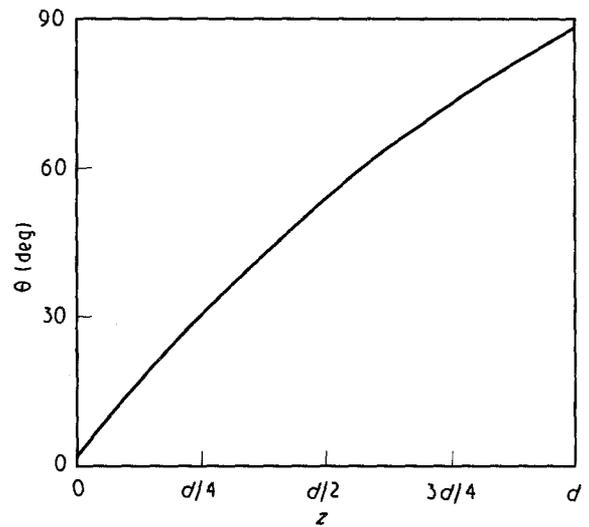


Figure 11 Tilt profile as a function of the height in a homeoplanarly aligned LC sample with a thickness of 60 μm, as obtained from a numerical simulation.

the anchoring constants inserted in the model to describe the interaction of the LC molecules with the orientation layer near each of the substrates. For realistic values of the parameters, however, their effect on the $\theta(z)$ curve, however, is not large enough to reproduce the experimental observations.

A twisted nematic diacrylate film with a natural pitch of 25 μm is prepared from the addition of 0.5 wt% S811 to the eutectic mixture 2 [24]. The mixture is melted between two planarly orienting substrates rubbed in parallel directions and subsequently polymerized at 113 °C. The film is broken along and subsequently across the rubbing axis. Fig. 12 shows the texture observed on a surface parallel to the rubbing direction. Near the edges a scaly structure characteristic of a fracture parallel to the molecular orientation is observed. Scanning the surface from top to bottom, one finds four bands exhibiting a somewhat vertically lined texture, suggesting that the fracture surface now lies perpendicular to the molecular ordering. These bands are interlaced with much darker, slightly scaled regions. The mean

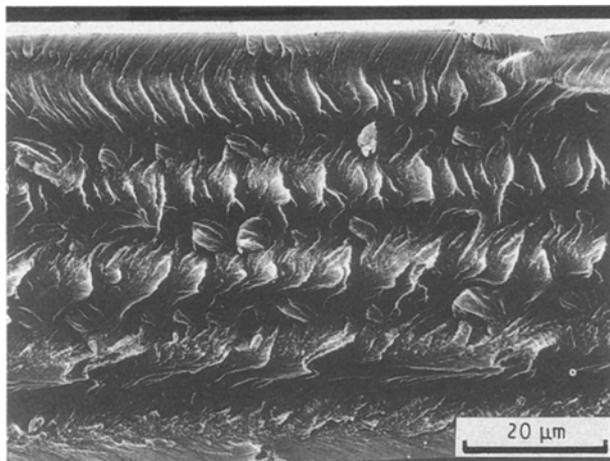


Figure 12 SEM photograph of a twisted nematic diacrylate film with a natural pitch of 25 μm , UV polymerized at 113 $^{\circ}\text{C}$ and broken along the rubbing direction at the substrates.

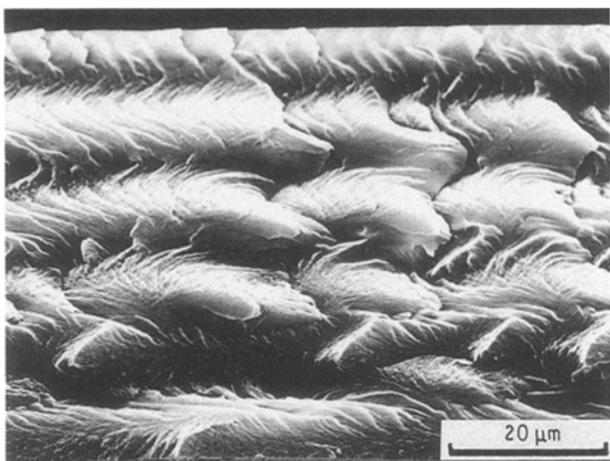


Figure 13 SEM photograph of a twisted nematic diacrylate film with a natural pitch of 25 μm , UV polymerized at 113 $^{\circ}\text{C}$ and broken perpendicular to the rubbing direction at the substrates.

distance between the bands in the bulk of the sample is about 12 μm , which means half the value of the natural pitch or, in other words, the distance over which the molecules rotate through an angle π . So the texture across this surface suggests that the molecules describe a rotation of 4π around an axis perpendicular to the molecular axis over the thickness of the film. The texture of Fig. 13 found on a surface perpendicular to the rubbing direction leads to the same conclusion. Near the substrates at the top and bottom of the photograph, a more or less vertically aligned texture is visible. In between we find three bright bumps which, however, exhibit no clear vertical line structure. The mean distance between these bumps is again 12 μm , and they are separated by darker, more scaly regions. Interpreting the bright bands as regions in which the director lies perpendicular to the surface confirms the conclusion that the molecular ordering describes a helix of 4π across the film thickness. But as the molecular orientation rotates through an angle of π over a distance of approximately 12 μm , one would expect that the molecular ordering describes a helix of 5π across the thickness of a 60 μm foil instead of the

observed helix of 4π . Near the substrates, however, the periodicity in the director orientation of about 12 μm seems to be disturbed. Especially near the substrate at the bottom of both micrographs, the distance needed to change the molecular orientation is significantly larger than in the bulk of the sample. A possible explanation of this observation may be the interaction of the molecules with the alignment layer applied on the substrates. It would suggest that in the case of surface induced alignment dilation of the helix from the expected 5π to the observed 4π may occur near the substrates.

Fig. 14 shows a photograph of a fracture surface of a 90 $^{\circ}$ twisted nematic diacrylate film made by UV polymerizing at 120 $^{\circ}\text{C}$ material 1a, to which 0.01 wt % S811 has been added. The film is broken such that the molecular orientation at the top of the picture lies parallel to the surface, whereas it lies perpendicular to it at the bottom of the picture. From theoretical calculations, a continuous rotation of the mean molecular ordering through an angle of $\pi/2$ is expected between top and bottom [27]. In Fig. 14 we observe a somewhat scaly structure at the top substrate, changing into a much rougher structure towards the bottom. The scaly structure at the top agrees with previous findings. Only a small region near the bottom exhibits the layered structure expected for a surface broken in a direction perpendicular to the molecular orientation. These layers are gradually slanting towards a direction parallel with the fracture surface such that they become scales in the upper half of the picture. The slanting behaviour of the layers correlates with the continuous rotation of the molecular ordering from perpendicular to parallel to the fracture surface. On the scales a fine texture is visible, consisting of lines parallel to the film surface. This fine texture becomes more pronounced as the layer is less tilted with respect to the perpendicular position. It reflects the planar molecular alignment occurring during the uniform twist through an angle of $\pi/2$.

3.2. Interpretation of layered structure

SEM micrographs of a fracture surface of a UV-polymerized LC diacrylate film exhibit a pronounced layered texture. The mean distance between the layers is estimated to be about 100–150 nm, corresponding to a layer of approximately 200–300 molecules. The occurrence of a layered texture parallel to the molecular orientation and perpendicular to the film surface, as observed in uniaxially ordered samples polymerized in the nematic and smectic phase, might be explained as follows.

1. Due to the anisotropic distribution of covalent bonds, the oriented polymer networks show an anisotropic mechanical behaviour with the room temperature (RT) tensile strength being a factor of two, and the RT tensile modulus a factor of three lower in the direction perpendicular than parallel to the director [28]. During brittle fracture of the sample at liquid nitrogen temperature, where the mechanical anisotropy even is somewhat enhanced, local delamination

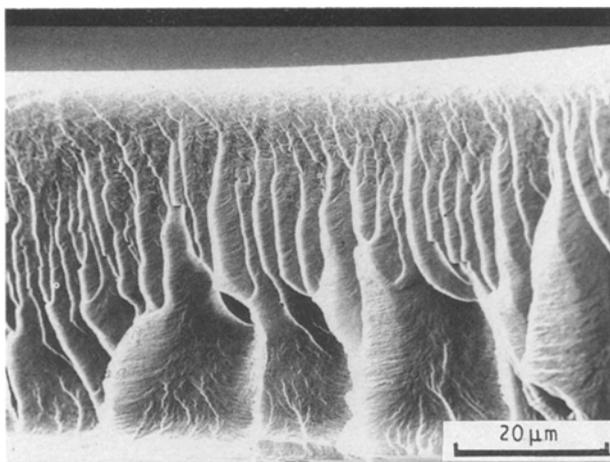


Figure 14 SEM photograph of a fracture surface of a 90° twisted nematic diacrylate film UV polymerized at 120°C. The mean molecular orientation at the top of the picture lies parallel to the fracture surface and at the bottom perpendicular to it.

or inelastic deformation is most likely to occur in a direction perpendicular to the director, which indeed explains why the layered texture is formed parallel to it. However, assuming a purely uniaxial molecular orientation, there is no immediate cause for the layers to be formed exclusively perpendicular to the film surface.

2. During polymerization of the LC acrylates and subsequent cooling to RT or the temperature of fracture, there is a considerable shrinkage due to a change in the Van der Waals volume during polymerization, the closer molecular packing being a result of a decreased entropy of the polymerized system and the thermal expansion [29, 30]. However, due to the highly asymmetrical sample geometry which allows the shrinkage to occur freely in the direction perpendicular to, but not in the plane of the film, stresses are expected to manifest themselves mainly in the latter directions. This means that delamination or strain would be propagated in planes perpendicular to the film surface.

It is the combined action of both effects that determines the direction of the layers formed during fracture. This, of course, is hypothetical and also some counter arguments can be made. Anisotropic volume relaxation studies [30] revealed that the volume relaxation for the $-(\text{CH}_2)_6$ -spaced samples is somewhat higher along the director than perpendicular to it, which would propagate the formation of layers perpendicular to the director. Apparently, this effect is dominated by the anisotropic mechanical properties, such that layers containing the direction of the mean molecular ordering result.

4. Conclusions

In general, we can conclude that for the geometries discussed above the director orientation corresponds to the secant of the two planes defined by the layered texture on mutually perpendicular fracture surfaces, which is most clearly illustrated by Fig. 6. This way of interpreting SEM images can also be applied to a large extent to samples with a more complicated

surface-induced alignment. For almost all the samples described in this study, the observations can be correlated to the expected director profile. One exception is the homeoplanarly aligned sample, which exhibits a sharp change in tilt angle near the mid-height of the sample instead of a more gradual change of $\theta(z)$ as predicted by numerical simulations. Another interesting observation is that SEM micrographs of twisted nematic samples seem to suggest that, in the case of surface-induced alignment, an eventual dilation of the pitch is probably located near the substrates. Unfortunately, the information obtained from the SEM photographs is not always detailed enough to provide an accurate visualization of the director profile in the bulk of an LC sample. Nevertheless, the SEM study of UV-polymerizable LC diacrylates has been shown to be a valuable technique for understanding the molecular ordering in low molar mass-type LC materials.

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