Near surface molecular orientation in polymeric alignment layers: a NEXAFS investigation

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ABSTRACT

Near-edge x-ray fine structure (NEXAFS) investigations were performed on buffed polyimide alignment layers for liquid crystal (LC) displays as well as on thin n-octyl-cyanobiphenyl (8CB) LC films evaporated in-situ onto the alignment layers. The full tensorial liquid crystal order parameter can be derived from the x-ray dichroism as a function of the substrate conditions, the layer thickness, and the thermal history. We compare a data set taken on poly-pyromellitimido-oxydianiline (PMDA-ODA) polyimide to a data set where highly oriented pyrolithic graphite (HOPG) was used as a substrate. While on graphite the aromatic rings are aligned parallel to the substrate, this is to a much lesser extent the case on polyimide. On polyimide, the LC molecular main axes are parallel to the substrate but the aromatic rings are about as often facing the substrate with the ring plane, as they do with the edge. During a brief heat treatment, most of the LC-material evaporates. On graphite, the remaining, rather tightly physisorbed layer is very well ordered, whereas on polyimide substrates the remaining layer is less ordered than thicker films.

Keywords: Liquid crystal surface anchoring, near-edge x-ray absorption fine structure, LC monolayers

1. INTRODUCTION

The orientation of nematic liquid crystals (LCs) close to solid surfaces is of high interest both for fundamental physics and for application in liquid crystal displays (LCDs). All liquid crystal cells used for displays are coated with polymeric alignment layers on their inside. Via an anisotropic surface–LC interaction the surface imposes a well-defined orientation onto the bulk material and thereby defines the ground (“off”) state of the cell. This phenomenon is often termed “surface orientational anchoring.”

Switching is achieved via a competition between an electric field and the orientating action of the cell surface. Alignment layers therefore are key components in LC displays. In the twisted nematic (TN) or the supertwisted nematic (STN) displays it does not suffice to provide a preferred in-plane axis, in addition there needs to be a specified pretilt angle of the orientation. The induction of a pretilt necessitates polar in-plane anisotropy (an “arrow”), which difficult to inscribe. Also, the high pretilt angles needed for STN displays are difficult to achieve.

In practice rubbed polyimide (PI) films still are the alignment layers dominating the market. “Optical buffing,” whereby an anisotropy is imprinted into the aligning surface with polarized UV light, is also intensely investigated but has not come to maturity yet. When mechanically buffing the polymer surface with a velvet cloth, the near-surface polymer chains undergo shear induced configurational rearrangements. The thus generated surface anisotropy in turn aligns the bulk LC. Importantly, a pretilt angle into the rubbing direction is achieved by the rubbing technique on many polymer surfaces including the widespread polyimides.

Despite the enormous practical relevance of surface anchoring, it is poorly understood in terms of the fundamental interactions. A wide variety of effects have been proposed which could potentially influence the surface anchoring mechanism. These include anisotropic LC orientational elasticity in connection with macroscopic grooves, quasi-

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epitaxial interactions on the molecular scale,\textsuperscript{6,7} surface electric fields,\textsuperscript{8} a near-surface order parameter different from the bulk (order electricity),\textsuperscript{9} and a coupling of a near-surface bending of the nematic director to surface electric fields (flexoelectricity).\textsuperscript{10} It is now generally agreed that molecular details matter. The most direct evidence comes from the experiments by the Shen group, who performed surface optical second harmonic generation (SHG) experiments on LC monolayers evaporated onto the alignment layers. These authors found not only a significant amount of anisotropy in the LC-monolayers – proving that the interaction has components acting on the molecular scale – but also a strong variation of anisotropy with the chemical nature of the substrate and the rubbing conditions.\textsuperscript{6,7} Given that molecular details are important, it seems highly desirable to gain the orientational information about the surface–LC interaction on the molecular level, as well. SHG has the sensitivity to measure orientation on the monolayer level. However, with regard to quantitative analysis, SHG entails complications insofar as it is highly biased towards the non-centrosymmetric part of the orientational distribution function (ODF). Whenever two molecules have exactly opposite orientation, the contributions of those two molecules to SHG cancel and they are therefore ignored. While it is certainly interesting that the members of the cyanobiphenyl family actually do display polar anisotropy close to polar surfaces, it is still unclear in quantitative terms how non-centrosymmetric the ODF is. All the molecules arranged in a pairwise antiparallel manner are missed by SHG.

Since quadrupolar anisotropy (as opposed to polar anisotropy) is the distinguishing feature of nematic LCs, second moments of the ODF are more important parameters than the third moments determined by SHG. In this communication we show that the quadrupolar anisotropy of thin LC layers can be obtained in molecular detail with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. These measurements are correlated with a determination of the same parameters on the underlying polyimide substrate. An implicit tenet underlying our investigations is that a thorough measurement of LC orientation – as opposed to positional order – as a function of film thickness, chemical nature of polymer surface, roughness, and temperature is key to an understanding of the surface–LC interaction. This assumption rests on the observation that a spontaneous net orientation makes liquid crystals special and peculiar materials, not positional order or crystallinity.

![NEXAFS principle](image1)

**Fig. 1:** Principle of near edge x-ray fine structure (NEXAFS) spectroscopy

The anti-bonding \(\pi^*\)-states correspond to maxima of absorption. The second moments of the orientation distribution function of the transition dipoles is determined from the x-ray dichroism. NEXAFS is surface-specific because of the finite escape depth of the secondary electrons.

![Chemical structure of 8CB](image2)

**Fig. 2:** Chemical structure of the liquid crystal molecule 8CB. The transition dipoles “1” and “2” correspond to the lower and the upper transition visible in the NEXAFS spectra (Fig. 3). They are oriented perpendicularly to the triple bond. Because the order parameters of both these transitions are known from experiment, the order parameter of the third direction, the *molecular main axis* (“3”), can be calculated as well.
In order to completely describe the LC-orientation, one would ideally want to measure the entire orientation distribution function (ODF) as a function of the distance from the aligning surface. However, to date no experimental technique exists which yields the entire distribution function with monolayer sensitivity. Only certain “moments” of the distribution like the ensemble average of $\cos \theta$ are available. Of particular importance in the context of the liquid crystal physics are the second moments like $<\cos^2 \theta>$. The reason is that the Landau-de Gennes nematic order parameter$^{11}$ is a second rank tensor based on just these second moments.$^{12}$ Any continuum theory trying to model the surface anchoring phenomenon will be based on the order parameter as the fundamental variable of state.$^{12}$ Continuum theories of surface anchoring will be inevitable in the foreseeable future because the problem of surface anchoring is too complex for ab-initio molecular dynamics (MD) calculations. Interestingly, realistic MD calculations can be done on LC-monolayers or even multilayers.$^{13,14,15,16}$ Understanding the orientation in LC-monolayers therefore is an intermediate step towards the full understanding of surface alignment which can be rigorously approached with both experiment and theory.

In principle, second moments of the orientation distribution function are easily measured via linear optical dichroism because the absorption depends on the $\cos^2$ of the angle between the polarization and the transition dipole moment. By rotating the sample with respect to the incident beam an equivalent absorption ellipsoid is determined which contains the second moments (“order parameters”) as its principal values. The nematic director is given by the orientation of the ellipsoid’s long axis. However, optical dichroism can not in practice be used on thin LC-layers in contact with alignment layers for two reasons. Firstly, the absorption bands of the conventional LC materials are located in the UV range, where the polyimide substrate absorbs, as well. The discrimination between the contributions from the substrate and the (very thin) LC layer is largely impossible. Secondly, in the optical range, the local field giving rise to the absorption does not equal the external optical field because the radiation of the neighboring oscillating dipoles may not be neglected. The local-field factors are in general anisotropic and difficult to obtain. Optical dichroism measurements are not usually employed to determine LC order parameters.

Both of the above problems can be overcome with NEXAFS spectroscopy.$^{17}$ Fig. 1 sketches the principle of measurement. The polarized photons from the synchrotron source excite a core-level electron to an unoccupied anti-bonding orbital state, from which it relaxes back to the ground state after about one femtosecond. Part of the energy is released via the emission of secondary electrons which are detected with a Channeltron detector. However, because of the electrons’ finite escape depth of about 2 nm, only the absorption spectrum of the near-surface molecules is probed. NEXAFS spectroscopy therefore is surface-specific. Different molecular building blocks can be identified by their absorption energy. The 1s-$\pi^*$-transitions are particularly useful because the corresponding absorption bands are narrower than the ones of the 1s-$\sigma^*$-transitions. Importantly, local-field factors are negligible in the x-ray domain because the absolute polarizabilities are very small, i.e. the dielectric constant $\varepsilon$’ is close to one. Finally, the absorption depends on the $\cos^2$ of the angle between the
electric field vector and the transition dipole just as in any other optical technique. From the analysis of the x-ray dichroism, the full tensorial nematic order parameter can be derived. Note, however, that the order parameter is associated with the transition dipole of the respective absorption band, which is in general different from the molecular main axis. For aromatic systems, the π*-transition dipole points perpendicular to the ring plane. The triple bond of cyano-biphenyls has two energetically separated transitions, the dipole moments of which are perpendicular to the bond direction and to each other.

NEXAFS spectroscopy has previously been used to study the orientation of polymeric alignment layers. Ouchi and co-workers proved for BPDA-Cn polyimide (poly-n-alkane-biphenyl-3,3,4,4'-tetracarboxylic dianhydride) that the pretilt angle seen in LC cells is already inscribed in the alignment layer. They observed a shift of the minimum of the angle dependent C1s–π* absorption (cf. Fig. 4) away from the 90° angle of incidence. Stöhr and co-workers have measured the rubbing dependence of the anisotropy and its dependence on thermal annealing in particular. Weiss and co-authors have described the quantitative analysis with regard to order parameters and also investigated the dependence on rubbing strength.

While the previous publications only cover investigations on the substrate, we for the first time report measurements on the substrates as well as on evaporated LC molecules. The line of reasoning is that the orientation of LC thin films will be similar to the orientation of the boundary layers in LC-cells. Since the LC–vacuum interface will have some influence on the orientation we can not claim that thin LC layers directly mirror the conditions found in boundary layers of bulk LCs. However, for the conditions of strong anchoring, it may be assumed that the influence of the substrate dominates. Also, knowing the orientation in thin films can help to elucidate the physics of the LC-boundary layer even if the LC–vacuum interface has to be included into modeling.

2. THEORY

The central variable of state in the physics of liquid crystals is the Landau-de Gennes nematic order parameter \( Q_{ij} \). The tensor order parameter \( Q_{ij} \) is defined as

\[
Q_{ij} = \frac{1}{2} \left( 3 n_i n_j - \delta_{ij} \right)
\]

where \( n_i \) is the direction cosine of the molecular main axis with the \( i \)-th laboratory axis. For example, the \( zz \)-component \( Q_{zz} \) is the second Legendre polynomial \( 1/3 \cos^2 \gamma - 1/3 \). Since \( Q_{ij} \) is symmetric, it becomes diagonal in the appropriate coordinate frame. The diagonal form is written as

\[
Q^{\text{dia}} = \begin{bmatrix}
- \frac{(S + P)}{2} & 0 & 0 \\
0 & - \frac{(S - P)}{2} & 0 \\
0 & 0 & S
\end{bmatrix}
\]

with \( S \) the uniaxial order parameter and \( P \) the biaxiality. Whereas LCs in the bulk have \( P = 0 \), this is not necessarily true close to surfaces. Also, note that for biaxial systems \( P \neq 0 \), the values of \( S \) and \( P \) depend on the choice of the \( z \)-axis. While in uniaxial systems the symmetry axis is defined as the \( z \)-axis, no such natural choice exists in the case of biaxiality. In this paper, the \( z \)-axis was taken as the surface normal, which will in general be different from the nematic director of the aligned bulk LC.
In experiment, one rotates the sample in the plane of the rubbing direction (θ) and perpendicular to it (φ). The band intensities \( A \) are fitted by functions of the form

\[
A(\theta) = A_0 [1 + \alpha \cos(2(\theta - \theta_0))] \\
A(\phi) = A_\phi [1 + \beta \cos(2\phi)]
\]

(3)

\( A_0 \) and \( A_\phi \) are prefactors allowing for an estimation of the layer thickness. The angle \( \theta_0 \) accounts for a possible ± \( \pi \) anisotropy along the rubbing direction. Perpendicular to the rubbing direction, any such offset is symmetry-forbidden. The parameters \( \alpha \) and \( \beta \) contain the information on anisotropy. Quantitatively, the order parameters \( S \) and \( P \) are related to \( \alpha \) and \( \beta \) by \(^{23}\)

\[
S = \frac{1}{3} \frac{3\alpha(\beta - 1) - 2\beta + \alpha(\beta + 1) \cos(2\theta_0)}{\beta - 3 + \alpha(\beta + 1) \cos(2\theta_0)} \\
P = \frac{3}{2} \frac{-\alpha(\beta - 1) - 2\beta + \alpha(\beta + 1) \cos(2\theta_0)}{\beta - 3 + \alpha(\beta + 1) \cos(2\theta_0)}
\]

(4)

For a triple bond, one can determine the order parameters of two separate transition dipoles, which are both perpendicular to the bond and perpendicular to each other. This is the situation with the LC-molecule 8CB shown in Fig. 2. The energetically lower band in Fig. 3 corresponds to the orbital which is perpendicular to the aromatic ring planes. It couples to the aromatic π-electron system and thereby lowers its energy relative to the other bond, which is in the ring plane. We denote the directions of those orbitals “1” and “2”. Interestingly, with the knowledge of the orientations of those two molecular axes, the orientation of the third axis (“3” in Fig. 2) can be derived as well. The three molecular axes form a rectangular tripod. With the directions of two members of a tripod fixed, the third axis is fixed as well. The third direction “3” is the *molecular main axis*, which is of fundamental importance in the LC-physics. One has

\[
S_3 = -(S_1 + S_2) \\
P_3 = -(P_1 + P_2)
\]

(5)

For display purposes, it is convenient to consider the matrix of orientation factors \( K = \langle n_i, n_j \rangle \). \(^{24}\) We denote its principal values \( f_x, f_y, \) and \( f_z \). \(^{25}\) One has

\[
f_x = \frac{-(S+P)+1}{3} \\
f_y = \frac{-(S-P)+1}{3} \\
f_z = \frac{2S+1}{3}
\]

(6)

The “equivalent” orientation distribution function (that is, the ODF Taylor-expanded to second order in the trigonometric functions) can be visualized as an ellipsoid, the principal axes of which are \( f_x, f_y, \) and \( f_z \) and which is rotated around the \( y \)-axis by the angle \( \theta_0 \) (Figs. 5 and 6). The outcome of each measurement are three such ellipsoids where the third one is calculated from the first two by use of eq. 5.

3. MATERIALS AND EXPERIMENTAL

For the present experiments PMDA-ODA polyimide (poly-pyromellitimido-oxydianiline) was used. Although this material is not specifically optimized for LC alignment, it is widely used for that purpose when the technical demands are not severe. The polymer was printed onto silicon wafers using an adhesion promoter (VM-651 from Dupont). Buffing was performed with a Yoshikawa YA-20-R cloth. We investigated different buffing strengths but report here only on “normal” buffing strength. The buffing distance, which is the integrated length of cloth in contact with any given spot on the sample, was 105 cm. The pile impression was 0.4 mm.

The LC used is the well-known substance n-octyl-cyanobiphenyl (8CB, see Fig. 2). It was purchased from BDH and used without further purification. In the bulk, 8CB has the phase sequence Cr \( 21.5 \) SmA \( 33.5 \) N \( 40.5 \) Is. \(^{26}\) In vacuum 8CB was found to sublime at temperatures above \(-50 \) °C. Therefore, the samples had to remain cooled during the entire
measurement process. We checked for a loss of material during the measurement by taking spectra at the same angle of incidence before and after a measurement and found no evidence for sublimation.

8CB was evaporated from a Knudsen cell at a distance of 100 mm to the sample. The thickness of the 8CB layer was estimated from the ratio of the peak intensities of the 8CB and the PI peaks (see Fig. 3). We estimate the typical thicknesses to be in the range of 0.3 to 5 monolayers.

The NEXAFS measurements were performed at the beamline HE-TGM2 of the synchrotron radiation facility BESSY (Berlin, Germany). The spectra were recorded at the N1s absorption edge with an energy resolution of better than 800 meV. X-ray absorption was measured in partial electron yield (PEY) detection mode with a retarding voltage of –150 V. A background originating from C photoelectron yield was subtracted from the spectra before further processing. The polarization of the synchrotron beam is better than 90%. Angle calibration was done by taking C1s spectra from highly oriented pyrolytic graphite and identifying the angle of minimum absorption with the angle of vertical incidence. The escape depth of the secondary electron amounts to about 2 nm and exhibits a weak dependence on the angle between surface normal and photon angle of incidence.

After a certain number of evaporations the sample underwent a heat treatment. The temperature was raised to +50 °C for about 2 seconds and then lowered back to the standard temperature of measurement, which was -110 °C. The heat treatment has two effects. Firstly, all but the most tightly physisorbed molecules evaporate. It is generally believed that
those tightly bound units play a dominating role in surface anchoring. For example, they are believed to be responsible for the "surface-memory effect."28-29 With the heat treatment we zoom-in onto this sub-ensemble of LC molecules. A second effect of the heat treatment is that the LC film goes through a condition where the bulk material would be in its nematic state. We think that by going through this stage, the LC monolayer can undergo orientational relaxations and thereby come closer to the state of a hypothetical LC interfacial layer as present in LC displays.

4. RESULTS AND DISCUSSION

We here show a selection of a larger number of experiments, which will be presented in more detail in a later communication. The results obtained on graphite and on rubbed polyimide are graphically displayed in Figs. 5 and 6. The columns correspond to the transitions as indicated in Fig. 2. The graphite sample underwent three subsequent evaporation steps before it was heated. For the polyimide sample, we show data sets taken before and after a heat treatment. The outcome of the experiments is summarized as follows:

• Thin LC layers adsorbed on graphite have the aromatic rings aligned parallel to the substrate. Band “1” is essentially lined up parallel to the surface normal. This agrees with the results of detailed MD simulations13,14,15 as well as with images taken in the liquid phase with the scanning tunneling microscope.30

• In contrast, no preferential alignment of the ring planes with the substrate is found on the polyimide surfaces. Band “1” and band “2” have about the same order parameters. The molecular main axis is largely parallel to the surface as evidenced by the pancake-like shape of the ODF of band “3” (right-hand-side in Fig. 6). However, the molecules appear to have cylindrical symmetry around this axis.

• As the films on graphite become thicker they are progressively more disordered. For polyimide substrates, this effect is less evident. However, very thin layers on PI are less ordered from the start-out.

• After the heat treatment, the orientational order on graphite has even increased. The cigar-shaped ODF of band “1” has become narrower. In contrast, after heating the polyimide sample, the remaining LC-layer has about the same amount of order as the thicker layers.

• The inclination of the ellipses with respect to the surface normal behaves somewhat irregularly. The substrate displays a tilt into the rubbing direction, as reported previously.23 The adsorbed LC molecules show a tilt in the same order of magnitude, but the direction of tilt is not always the same as the one in the substrate. This point needs further clarification.

• On rubbed polyimides the pancakes representing the main chain orientation become laterally squished at high LC coverage. This corresponds to an LC-director parallel to the rubbing direction. Quantitatively, the in-plane anisotropy is smaller than for the bulk LC in contact with the alignment layer.

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