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A population distribution model for the alignment of nematic liquid crystals

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In polymer aligned liquid crystal cells, a surface layer exists. In this surface layer the in-plane distribution of the mesogens, the shape of the mesogens, and their average angle with the surface determine the pretilt angle in the bulk of the sample. A model to incorporate those effects has been proposed. This model gives quantitative agreement with a number of experiments for thick cells, where the optical effects of the surface layer can be neglected. By introducing a linear variation of the optical axis through the surface layer we get qualitative agreement between the model and the pretilt found in thin cells. The thickness of the surface layer is of the order 0·1–1·0 μm.

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1. Introduction

The crystal rotation method [1] is widely used to determine the pretilt angle for liquid crystals aligned on different surfaces. By this method we are determining the direction of the director in the bulk of the sample. In other words we are determining the direction of the symmetry axis of the liquid crystal [2].

By second harmonic generation (SHG), it is possible to determine the surface non-linear susceptibility tensor [3]. This tensor is related to the orientation of the optical axes of the liquid crystal molecules at the surface. By making some assumptions about the distribution function at the surface, information about the orientation of the mesogens can be obtained [3]. Usually, independent polar and azimuthal distributions are assumed. Mesogens are molecules of low symmetry. It is thus not possible a priori to know the orientation of the optical tensor in the molecular frame. Furthermore, even if the orientation of the optical tensor were known, there is no general procedure that can tell us the direction of the symmetry axis of a phase from the structure of the individual molecules that constitute this phase. Likewise, it is not possible from knowledge of the orientation of the symmetry axis to infer how the individual molecules are arranged on the surface. Therefore, we need a more detailed model which gives us information about the distribution of the optical axis in the sample.

When studying the relationship between the pretilt angle and mesogen or polymer properties, it is important to keep the distinction between molecular properties (as measured by SHG) and symmetry properties (as measured by the crystal rotation method). If this distinction is made it is no surprise that the angle between the molecules

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at the surface and the surface (as determined by SHG) is different from the angle between the optical axis of thick samples and the surface (from the crystal rotation method) [4–7]. These two experimental methods are probing two different properties of the nematic materials, and there is no general method for relating the two properties.

Due to the technological importance of the surface alignment of liquid crystals, it is of interest to find useful ways of describing the phenomenon. Those descriptions should explain how variations in polymer structure, mesogen composition or surface treatment change the observed orientation of the molecules at the surface and in the bulk, but still be simple enough to be handled easily.

Two different models have been proposed to link the high pretilt of the molecular optical axis at the surface with the lower pretilt of the symmetry axis in the bulk of the material. We [4, 7] have previously pointed out that due to the restricted rotation of the mesogens at the surface, the optical axis of the molecules and the mechanical axis will be different. The mechanical axis will be the axis around which the molecules rotate in the bulk of the material. A more complete discussion of the mechanical axis is given in § 2, while specifics on how to determine it are given in § 4.1.1.

In the bulk of the nematic phase there is free rotation of the molecules and all the different molecular axes coincide. The elastic forces act to avoid splay of the mechanical axis. Therefore, in the bulk of the material, the optical axis and mechanical axis coincide, while they do not at the surface. We will thus have a splay of the optical axis close to the surface. We have defined a surface region of thickness d^* where the optical axis shows a splay deformation. This model has been successful in accounting for the observed temperature variations of the pretilt, the observed variations in pretilt with cell gap, as well as, a slight asymmetry in the transmission versus angle of incidence during the measurements of pretilt by the crystal rotation method [4, 7].

If we assume a tilt of the optical axis on the surface of 9–19°, as reported from SHG measurements [3, 5, 6, 8, 9], our model predicts too high a bulk pretilt, compared to experimental results obtained with the crystal rotation method. The observed variations in pretilt with properties of the liquid crystal or alignment layer are not easily explained either [7]. Variations in the pretilt angles are too large to be explained by changes in the shape of the molecules (and thus the relative positions of the optical and mechanical axes) alone.

An alternative explanation has recently been given by the Philips group [5, 6]. From their SHG measurements, they find that all molecules point to the surface with an angle of about 13°. This angle is to a good approximation independent of the surface structure and treatment (only 8CB and 5CB have been investigated so far). However, the in-plane distribution varies. There is also a nearly linear correlation between the in-plane order, and the pretilt as measured for thick samples.

All molecules attach to the surface. The angle between the surface and the individual molecules is nearly constant, independent of surface structure and treatment. There is, however, an in-plane distribution of the molecules. This distribution has mirror symmetry relative to the plane defined by the rubbing direction and surface normal, but the mirror symmetry is broken for the plane perpendicular to the rubbing direction. More molecules are pointing along the rubbing direction than against the rubbing direction. The elastic forces will average the molecular tilt at the surface, to give a bulk pretilt. An in-plane distribution at the surface translates directly to a pretilt angle in the bulk. An increased in-plane order will give a higher pretilt [5, 6].

It is also easy to see how the more ordered crystalline polyimides should impart a higher in plane order, and thus give higher pretilt than the amorphous polyimides.

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This has recently been reported for the alkylene-biphenylimides [10]. It also neatly explains why an annealed polyimide, which is presumably more crystalline, should give higher pretilt than the unannealed, as found for the alkylene-pyromellitimides [11, 12]. This model, however, cannot explain that the pretilt angles measured by the crystal rotation method increase for thinner cells.

In § 2 we will show that a combination of our model and the model proposed by the Philips group is easily achieved, and that this combined model successfully explains a wide variety of observations.

2. Theory

The crucial assumption in our previous model [4, 7] is that the elastic forces do not act on the optical axis of the molecules, but on the mechanical axis. In the bulk of the sample there is free rotation and the direction of all long axes will coincide. As the molecules are fixed at the surface, the free rotation is suppressed, and the different long axes no longer coincide or, alternatively, the symmetry of the nematic phase is broken.

We define the mechanical axis as the molecular axis that the elastic forces appear to be acting on. As elasticity is a macroscopic property, while we are considering axis from a microscopic point of view, we cannot directly determine the mechanical axis. The mechanical axis will be the axis around which the molecules rotate in the bulk of the material. Although the axis of least inertia is one rotation axis in the gas phase, it might not be so in condensed phases. The axis perpendicular to the plane of least cross-section might be a more appropriate rotation axis. However, this axis will generally not coincide with the optical axis either. As the terms axis of least inertia or axis perpendicular to the plane of least cross-section are long and cumbersome, we prefer to use the shorter term, mechanical axis. Frank has pointed out that the elastic theory of liquid crystals relates to the director of the liquid crystal [2]. The director is the symmetry axis of the nematic phase. Exactly how this relates to the properties of individual molecules cannot be determined a priori.

It might seem a little unsatisfactory to build a model around an axis that is not well defined. The essential point of the model is that elastic forces do not act on the optical axis of the molecules. Due to the restricted rotation of the mesogens closest to the surface, we will thus have a layer close to the surface where there is a splay of the optical axis. Here, the existence of this surface layer has been taken explicitly into account, in contrast to the model of Barmentlo *et al.* [5, 6], where the first monolayer is fixed, and an undisturbed bulk layer exists on top of this monolayer.

In the bulk of the nematic phase there is free rotation of the molecules and all the different axes coincide with the symmetry axis. The elastic forces act to avoid splay. In the bulk of the material the optical axis and mechanical axis coincide, while they do not at the surface. There is a short range bond order. At the surface the molecules are fixed. Due to the short range bond order, the neighbouring molecules are not entirely free to rotate either. The bond order decays rapidly, but until it is zero, the mechanical and optical axes do not coincide. We will thus have a splay of the optical axis close to the surface. We have defined a surface region of thickness d^*. In this layer the optical axis shows a splay. Alternatively we could call this the correlation length for the bond order.

Our recent model [4, 7] can directly be combined with the model of Barmentlo and co-workers [5, 6]. Instead of their molecules that are implicitly assumed to be rod-shaped, we introduce our bent molecules (see figure 1), and we now have a distribution of bent molecules. In all cases the optical axis makes an angle β_0 with the

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surface, while the mechanical axis makes a somewhat lower angle (β). How much lower will depend on the exact structure of the molecules. The average pretilt angle in the bulk will no longer be the average of the optical axes, but the lower average of the mechanical axes. In this model the pretilt will be a result of the in-plane order and the molecular shape which defines the relative position of the optical and mechanical axis.

Our model assumes that there are several different effects operating. The molecules have different shapes and charge distribution. They will be attached fairly strongly to the surface, making an angle β_0. So far this angle has only been determined directly by the SHG technique. We will thus use the angle between the optical axis of the molecule and the surface as β_0. As the molecules have a non-linear shape, this angle is different from the angle (β) that the mechanical axis makes with the surface. The latter depends on both β_0 and the structure of the mesogen. In our present derivation, it is sufficient to express the shape of the molecule with one simple number, α, defined as the angle between the optical axis and the mechanical axis of the individual molecules.

Our non-linear molecules can be modelled as consisting of two parts. The core which is usually aromatic, and often has a strongly polar group at one end, and the tail which is the alkyl chain. As the core contains all the π-electrons, the optical properties will be dominated by the core and it is the orientation of the core that we believe is probed by the SHG method.

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Both polar and dispersive forces play an important role in determining the angle β_0. We assume a simple shape of the molecules as shown in the insert in figure 3. The polar forces are in this model only due to the dipole (cyano in the compounds we will investigate here) at one end of the molecule, while the dispersive forces will act on the whole molecule. To minimize the polar part of the energy, the polar end group should point towards polar or charged groups at the surface, while the dispersive energy, which decreases rapidly with increased separation, will be minimized when the mesogen lies approximately flat on the surface. The exact angle β_0 will be the one that minimizes the total energy. The steric interactions are of course also important, but not easily modelled. This model can thus only be used as a crude approximation. It is however clear that to minimize the energy, β_0, α and the projection β_0 on to the surface should all be in the same plane. We can thus write

$$\beta = \beta_0 - \alpha \tag{1}$$

If the interaction between the alkyl tails of the mesogens are stronger than the interactions between the alkyl tail and the surface, the total energy will be minimized by pointing the alkyl tail into the bulk of the liquid crystal (in other words $+\alpha$ instead of $-\alpha$ in equation (1)). This seems to be the case on fluorinated surfaces, as we will discuss in § 4.2.

Next we have an in-plane distribution of the molecules. There is a mirror symmetry relative to the rubbing direction, but an asymmetry perpendicular to the rubbing direction. We will have more molecules pointing along the rubbing direction than against it. The parameter a_1 has been introduced to describe this asymmetry [5, 6].

We now need to find the average direction of the molecules. It is far from clear how to find the average of a direction [2], although most workers in the field of liquid crystals have some intuitive understanding of the concept.

For this work, we will adopt the following procedure for determining the average direction of the molecules. If any mirror planes are present, the average direction will be in this mirror plane, or perpendicular to it. We choose one direction along the surface as our positive direction (if a mirror plane is present this direction will be the intersection between the mirror plane and the surface). A molecule (i), whose projection is along the positive direction, will be given a positive direction, expressed by a positive angle β_i, while a molecule (j), whose projection is along the negative direction, will be given a negative angle $-\beta_j$. The average direction is then expressed by the numerical average of all directions. $\beta_{\text{average}} = \Sigma(\beta_i)/i$. If no mirror plane is present, we have to express the average direction by the two polar coordinates. The average direction will be the unit vector in the direction given by the polar coordinates (and any symmetry restrictions). This method gives an average direction in good agreement with intuitive understanding.

The next step is to relate this average direction of the surface molecules with the direction of the symmetry axis in the bulk of the phase. The symmetry direction in the bulk is related to the directions of the individual molecules by maximizing the expression

$$S = \langle 3\cos^2\theta - 1\rangle/2$$

for molecules that can be described by one single direction θ [2]. Thus we have the situation that the directions of the individual molecules, the order parameter (S), and the symmetry direction are all linked together.

Let us start with the somewhat unrealistic situation where we have perfect in-plane order, $a_1 = 1$. All molecules point along the rubbing direction. We might however still have a distribution of the polar angle β. We assume a gaussian distribution for this angle as is done for the SHG [3, 5, 6, 9, 13]. In this case, we see that the symmetry direction in the bulk is the same as the average direction of the molecules at the surface β.

The other case we will consider is for no in-plane order, $a_1 = 0$. This gives $\beta_{\text{average}} = 0°$, too. Experimentally it is found that this situation gives 0° pretilt of the symmetry axis in the bulk of the sample [5, 6]. Thus, for the cases of $a_1 = 1$ and $a_1 = 0$, we find that the symmetry direction in the bulk is the same as the average direction of the molecules at the surface. We assume, as an act of faith, that this is also the situation for the intermediate values of a_1.

The bulk pretilt is thus assumed to be an average of the in-plane distribution. With perfect in-plane order, the pretilt will be the angle between the mechanical axis and the surface (β). With molecules pointing both along the rubbing direction and against it, the bulk pretilt will be given by

$$\beta_{\text{obs}} = ((1 + a_1)\{\beta_0 - \alpha\} + (1 - a_1)(-\{\beta_0 - \alpha\}))/2 = a_1(\beta_0 - \alpha). \tag{2}$$

Furthermore, there might be a deformation of the polymer layer. The β_{obs} given in equation (2) will thus be relative to the polymer surface, while the pretilt measured by the crystal rotation method is relative to the glass surface. We call the angle between the polymer and glass surfaces τ.

We have previously found that there is a transition layer where the orientation of the optical axis gradually changes from the orientation at the surface (β_0) to the orientation in the bulk of thick samples (β_{obs}). For thinner samples the β_{obs} will thus depend on the thickness of the cells used for the measurement.

Introducing the thickness of the surface layer and the possible deformation of the surface, the observed pretilt can be written as

$$\beta_{\text{obs}} = \{(\beta_0 - \alpha) + (d^*/d)\alpha\}a_1 + \tau, \tag{3}$$

where d^* is the thickness of the transition layer. This equation is the same as that previously given [7], except for the introduction of the in-plane order a_1. We have also given the bulk pretilt (β_{bulk}) explicitly as $\beta_0 - \alpha$ this time, and introduced the shape of

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the surface (τ). A linear variation of the optical axis through the surface layer is assumed in deriving this equation.

In our theoretical model, there are thus five independent parameters. They are:

τ: the physical deformation of the polymer layer. τ will be a function of polymer treatment. We would expect different rubbing conditions to lead to different deformations. τ will also be a function of the polymer structure, with some polymers being more easily deformed than others. The permanent decrease in pretilt often found after heating the polymer can probably be explained by a decrease in τ.

a_l: the in-plane distribution of mesogens. This is a function of both liquid crystal structure, polymer structure and polymer treatment. It has been shown that longer alkyl chains in the liquid crystal will give a higher in-plane order [5]. We also expect more crystalline polymers to give a more regular structure and thus an increase in a_l. Before rubbing, a crystalline polymer will be polycrystalline, with randomly oriented crystallites. There will thus be no net order over macroscopic areas. On the other hand, it is not possible to measure the pretilt for these poorly oriented samples either. During the rubbing process, the surface is partly melted [14], stretched and cooled again. Stretching of polymers will give (partial) alignment of the crystallites [15], and evidence of this is also found from the induced birefringence in rubbed polymer layers [3, 16].

β_0: the angle between the optical axis of the mesogen and the surface. This will also depend on the structure of both the liquid crystal and the polymer. SHG evidence from a number of (unspecified) polyimides [3, 7–9, 13] shows a variation in β_0 from 9° to 19°. Part of these variations might be due to differences in analysing the data. When larger changes in polymer structure are made, the changes in β_0 will also be larger [3]. It has been concluded that stronger dipoles in the liquid crystal molecules might also increase β_0 [17].

α: the shape of the molecule. In our model it is sufficient to describe this by one parameter, the angle between the optical and mechanical axes.

d^*: the thickness of the surface layer. We have previously estimated this to be effectively 0·1–1·0 μm thick [4, 7].

Having split the contribution to the observed bulk pretilt into five different parts, we easily see one of the reasons for the bewildering array of sometimes contradictory results when trying to correlate the bulk pretilt angle with the bulk properties of liquid crystals. For example, will an increase in alkyl chain length of a mesogen give both an increase in a_l and an increase in α. As equation (3) shows, it is then far from clear what the changes in β_{obs} will be. Another example is changes in polymer structure which might give changes in both β_0 and a_l.

Any temperature dependence of the pretilt can be found from equation (3). We will assume that the in-plane distribution a_l is the only temperature dependent term. SHG measurements [3, 9] have found no temperature variation in β_0. As the shape of the surface will remain unchanged within the normal nematic temperature range, we assume τ to be temperature independent. The shape of the molecules will change slightly with temperature. The *trans–gauche* changes in the alkyl chain of nematic phases require around 9 kJ mol^{-1} [18], and the conformational distribution (and thus the average shape) will not change much. The only remaining factor is the thickness of the surface layer (d^*). Changes in this factor will only influence the observed pretilt for the thinnest cells.

Jerome [19] introduced the idea of sites at the surface where molecules will attach. She worked mostly with symmetric surfaces where the energy will therefore be the same

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for several sites. The idea of several randomly distributed sites has been applied to the surface memory effect on unrubbed polyimides [20]. The rubbing process breaks the symmetry of the surface, and the different sites are no longer equivalent. After rubbing, the SHG measurements reveal a large asymmetry in the distribution of molecules perpendicular to the rubbing and parallel to it [3, 5, 6, 9, 13, 21]. Nearly all the mesogens lie parallel or anti-parallel to the rubbing. There is also a slight asymmetry, with more mesogens lying parallel to the rubbing direction than anti-parallel to it. The number of mesogens perpendicular to the rubbing direction is small, and they do not contribute to the pretilt in our model. We will therefore neglect them. We will thus have a distribution of molecules parallel and anti-parallel to the rubbing direction. This distribution is given by a_l. We assume that this distribution is in thermodynamical equilibrium and follows a Boltzmann type distribution. With

$$a_l = 1 - \exp(-\Delta H/k_B T) \tag{4}$$

where ΔH is the enthalpy difference between the two orientations, T is the absolute temperature, and k_B is Boltzmann's constant ($1{\cdot}38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$). For the polymer aligned cells used in this study, we have found $\tau = 0$. The temperature dependence of the pretilt is normally determined in thick cells, $d^* \ll d$. We thus neglect the last two terms in equation (3). Combining equations (3) and (4) with the simplifications noted, and taking the logarithm for both sides, we obtain the following equation for the change in the bulk pretilt with temperature:

$$\ln(\beta_{\mathrm{obs1}}) - \ln(\beta_{\mathrm{obs2}}) = -(\Delta H/k_B)(1/T_1 - 1/T_2), \tag{5}$$

where the subscripts 1 and 2 refer to the two different temperatures.

It has been reported that SHG measurements show no significant [9] or only a small [3] temperature dependence for the distribution of molecules in the first monolayer. However, in both cases, surfaces with very low surface order were used. a_l was 0·06 in both cases. Thus the energy difference between the two orientational states will be small and the distribution should change very little with temperature. Over the temperature range 20 to 65°C, only a change in a_l of 0·008 would be expected according to equation (4). Even with the most careful corrections, it is difficult to achieve an accuracy better than 0·01 in the a_l value [20]. To measure the temperature variations of a_l on a surface with higher values of a, should be a good test of population distribution models for the surface pretilt.

We have previously given the relationship between the thickness of the surface layer and the deviation from symmetry for the transmission versus angle of incidence curve. During the derivation of that equation it was implicitly assumed that $a_l = 1$. Deriving the equation for any a_l is simple, and we will just write down the relationship between the asymmetry of the transmission versus angle of incidence as a function of the surface layer thickness

$$(2d^* a_l/d)\tan\phi = \sin(\theta - \theta_{\mathrm{bulk}}) \tag{6}$$

where ϕ is the angle of incidence, θ is the asymmetry, and $\theta(\beta_{\mathrm{bulk}})$ is the contribution to the asymmetry from the bulk [7]. The only change from before is that we now introduce an effective thickness of the surface layer $d^* a_l$ instead of d^*.

After a brief description of our experimental procedures (§ 3), we will give specific prediction from this model and show how they compare with experiments (§ 4).

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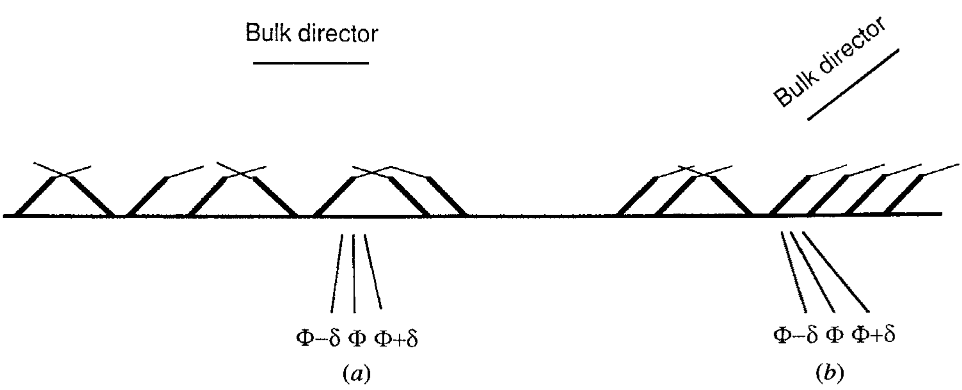

Figure 1. Illustration of how light incident from two different directions symmetric around the bulk pretilt angle will be affected by a slightly different retardation due to the surface layer. (*b*) for a well-ordered surface layer which gives a large change in retardation; (*a*) for a less ordered surface layer with a correspondingly smaller change in the retardation. The figure also illustrates the different pretilt of the bulk optical axis due to different population distributions at the surface.

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3. Experimental

The polyimides in this study were synthesized by reacting equimolar amounts of the alkylene diamines and aromatic dianhydrides in *N*-methylpyrrolidone (NMP) at room temperature. The resulting polyamic acids were spin coated on to clean indium–tin oxide (ITO) coated glass plates. The final ring closure was carried out by heating to 250°C for $\frac{1}{2}$ h for the s-BPDA derivatives and for 2 h at 300°C for the PMDA derivatives.

The resulting polyimide layers were rubbed in a FS-5JR-S rubbing machine from Fujioka MFG Co., Ltd. Different rubbing conditions were used to adjust the pretilt angles. Alternatively, different curing or annealing conditions were employed to achieve the same. Two rubbed glass plates were mounted together in an anti-parallel fashion. Mylar strips along two edges were used to keep a fixed distance between the two plates. The cells were assembled with a thermosetting, two-component epoxy glue.

The cells were vacuum filled with the different nematic liquid crystals, and the filling port sealed with Locktite 352 UV-curing glue. The liquid crystals used are all commercially available mixtures or single components and are given in the appropriate parts of § 4.

Pretilt angles were measured on an automated optical bench (all parts from Sigma Koki Co., Ltd), interfaced with a NEC-9801RA personal computer.

4. Results and discussion

4.1. *Effect of the liquid crystal*

4.1.1. *Calculating α*

The optical axis of the molecules is related to the π-electron system, and will to a large extent be fixed along any homologues series of liquid crystal materials. The mechanical axis will be a function of the shape of the molecule. For the cyanobiphenyls (*n*CBs), the optical axis will be fairly close to the symmetry axis of the two phenyl rings. For 4-methyl-4′-cyanobiphenyl, the symmetry of the molecules requires that any transitions are along the symmetry axis or perpendicular to this axis. Substituting one of the hydrogen atoms in the methyl group with an alkyl group will

Table 1. The angles between the mechanical axis and the optical axis for the various cyanobiphenyls adopted for this work.

Mesogen	$\alpha/°$
2CB	0·9
3CB	1·7
4CB	2·7
5CB	3·9
6CB	5·1
7CB	6·1
8CB	7·3
9CB	8·3
10CB	9·4
11CB	10·2
12CB	11·3

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hardly change the symmetry of the π-electron system. Thus there will be hardly any changes in the optical axis along this homologous series of mesogens. But the longer the alkyl chain is, the further the mechanical axis will be away from the optical axis. The angle between the optical axis and the mechanical axis increases as the alkyl chain becomes longer. We also see from the insert in figure 3 that there will be an odd–even effect. Adding an even methyl group will increase the weight of the alkyl chain, at a distance further removed from the optical axis than the previous methylene group. Adding an odd methyl group will increase the weight of the alkyl chain, but the added weight will be at the same distance from the optical axis as before. If we assume, that the angle between the cyanobiphenyl unit and the surface (β_0) is the same in all cases (as found by SHG [3, 5, 6, 8, 9]), we would thus expect a lower pretilt for the cyanobiphenyls with the longest alkyl chains. We would also expect the CBs with an even number of methylene groups in the alkyl chains to give slightly lower pretilt angles than those with an odd number. But it is also found that increased alkyl chain length increases the in-plane order [5, 6]. There will thus be two competing effects operating.

Frank [2] suggests that the mechanical axis of a mesogen can be approximated by the line joining the opposite ends of the rigid core. For the nCBs this would give $\alpha = 0°$ for all members. Completely ignoring the alkyl chain seems however, to be too crude an approximation. We adopted the following procedure for finding the mechanical axis. First we find the most extended conformation of the molecule, and find the centre of mass for this conformation. The mechanical axis was then placed through the centre of mass and the far end of the rigid part of the molecule; the cyano group is regarded as belonging to the rigid part of the molecule. This mechanical axis is closer to the core than the axis of least inertia for the most extended conformation. In the nematic phase we have a distribution of conformations, but there is also a coupling between conformations and order, giving a preference for the more linear conformations. Our procedure gives an *ad hoc* approximation to this coupling. As will be seen shortly it gives good agreement with other far more cumbersome procedures.

Table 1 gives the α values used when trying to fit the experimental data to equation (3). α itself has probable error of 1°, mostly due to the uncertainty in fixing the optical axis accurately. Due to the close similarity between the members of the homologues series, we expect the relative errors between the different *n*CBs to be about 0·5°.

The complete conformational distribution in the nematic phase has been determined

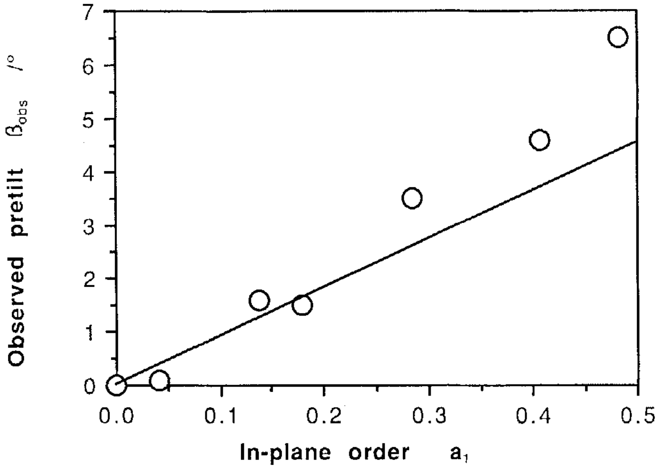

Figure 2. Pretilt (β_{obs}) as a function of in-plane order (a_1) for 5CB. Experimental data (open circles); theoretical curve calculated with the values $\beta_0 = 13°$ and $\alpha = 3{\cdot}9°$. Experimental values for a_1, β_{obs} and β_0 taken from [6].

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by a fit of NMR splittings to the rotameric state theory for CB and 8CB [22]. The individual orientations of all the possible conformations have also been calculated. They find angles of 6·2° (5CB) and 8·36° (8CB) between the symmetry axis of the biphenyl unit and the principal axis of the nematic phase. In other words, the 'average' molecule is not rotating around the symmetry axis of the biphenyl unit, but around an axis making an angle of 6·2° (5CB) or 8·36° (8CB) relative to this direction. Their values are slightly higher than ours of 3·9° and 7·3° for 5CB and 8CB, respectively.

Toriumi and Samulski [23] have used another set of approximations and found a stronger preference for the more linear conformations for the dialkyl compounds in the 4-alkoxybenzylidene-4′-alkylaniline series.

To check our estimates we also looked at the data from the Philips group [6]. Here, pairs of experimentally determined values for a_1 and β_{obs} are given, together with β_0 (= 13°) for 5CB. In figure 2, the solid line relates to our theoretical values for $\alpha = 3{\cdot}9°$, while the experimental values are from [6]. As can be seen, the agreement is excellent and well within the experimental errors in the determination of β_0 and a_1.

4.1.2 *Experimental results*

SEM micrographs of some of the rubbed polyimides reveal a few 3–4 μm wide grooves 15–20 μm apart. Along these grooves there are irregular structures. We cannot find any fish scale-like [24] or other tilted structures. As far as we can see from the micrographs, there is no asymmetry along the rubbing direction. As any tilting of the surface will thus be very small and only affect a small part of the total surface, we conclude that τ can be set to 0° for the rest of this work.

For the investigation of the effect of different liquid crystal materials, we are using thick cells with $d^* \ll d$, and we will thus neglect the contribution from the surface layer for the first part of the discussion.

Figure 3 shows the results of an experiment where different cyanobiphenyls have been added to the phenylcyclohexane mixture ZLI 1237. Here, as in the rest of the discussion in § 4.1, the pretilt (β_{obs}) is the pretilt measured by the crystal rotation method for thick samples. The pretilt we measure is the bulk value. We find that the observed

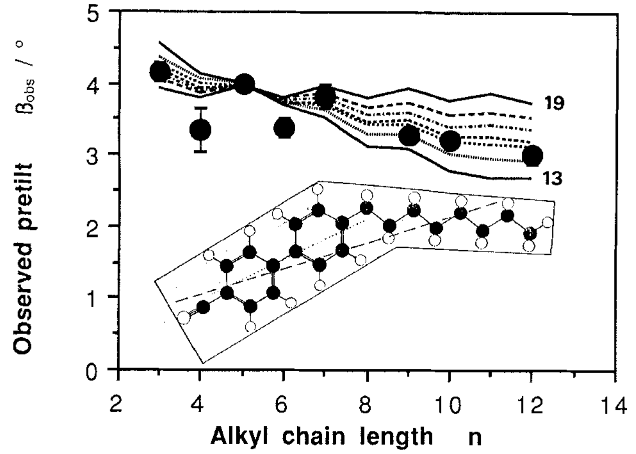

Figure 3. Pretilt as a function of the alkyl chain lengths for the addition of the *n*CBs to the cyanophenylcyclohexane mixture ZLI 1237. Approximately 50 per cent by weight of the additives. α values are given in table 1. Seven different values of β_0 are tried (19° top 13° bottom); the best fit is for $\beta_0 = 15°$. The insert shows the structure of the *n*CBs. The dotted line is the optical axis making an angle β_0 with the surface, while the dashed line is the mechanical axis making an angle β.

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pretilt angle decreases as the alkyl chain length increases. For the relatively high tilt s-BPDA-6 alignment layer, shown in figure 3, we can see a weak odd–even effect.

The pretilt angle found for undoped ZLI 1237 is 3·8° on s-BPDA-6. The α for this mixture of short chain cyanophenylcyclohexanes is 9°. We do not know β_0 or a_l. By choosing a value for β_0, we obtain a corresponding a_l value for undoped ZLI 1237 and for ZLI 1237 doped with 5CB. From the latter it is then possible to extract an a_l value for pure 5CB.

a_l increases with increasing chain length [5, 6]. The value for 8CB is 20 per cent higher than for 5CB. As the chain length increases, the attraction between the chains increases. There is also a steric effect operating. Adding a methyl group at an even numbered terminal position in the chain will lead to a methylene group pointing away from the long axis of the molecule. The packing will thus be more difficult than if we add a methylene group to an odd numbered position. In the latter case the group will be added, more or less, along the long axis of the molecule, and steric factors will be small. To take steric factors into account, we increase a_l by 20 per cent of the 5CB value for each additional methylene group in an odd-numbered position, that is, for carbon number (C_1, C_3, C_5 C_7...) in the chain. We do not change the a_l value for additional methylene groups in even numbered positions (C_2, C_4, C_6, C_8...). As figure 3 shows this still underestimates the odd–even effect. The 20 per cent odd-numbered methylene relative to 5CB is needed to have an increase in accordance with that found between 5CB and 8CB [5, 6].

From the data for undoped ZLI 1237 and ZLI 1237 doped with 5CB, we can find the a_l values for ZLI 1237 and 5CB. With a linear increase per odd-numbered methylene group, we can thus determine the a_l value for all the *n*CBs. For the different mixtures we assume that α and a_l will be a linear combination of the contribution from the two components. This allows us to calculate an expected observed pretilt for all the mixtures investigated; the a_l value for 5CB determines the 'slope' of the line for expected pretilt angles versus chain length. The theoretical lines for pretilt angles between 13° and 19°

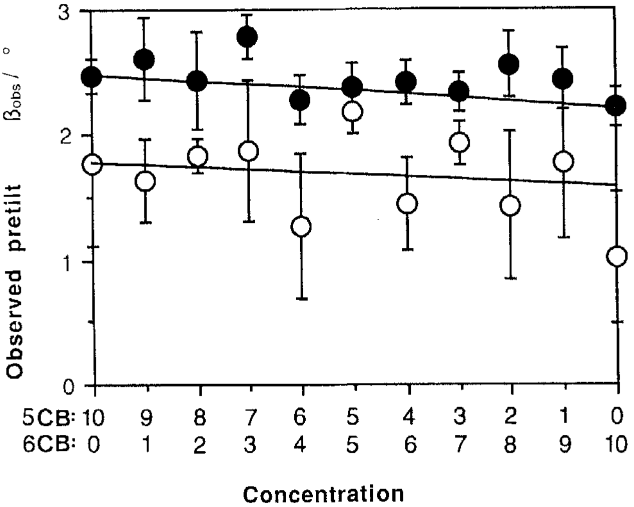

Figure 4. Pretilt as function of composition for mixtures of 5CB and 6CB. The surfaces used are PMDA-4 (filled) and PMDA-7 (open). $\beta_0 = 15°$; $\alpha = 3{\cdot}9°$ for 5CB and $5{\cdot}1°$ for 6CB. a_1 is 0·223 on the crystalline PMDA-4 and 0·160 on the amorphous PMDA-7.

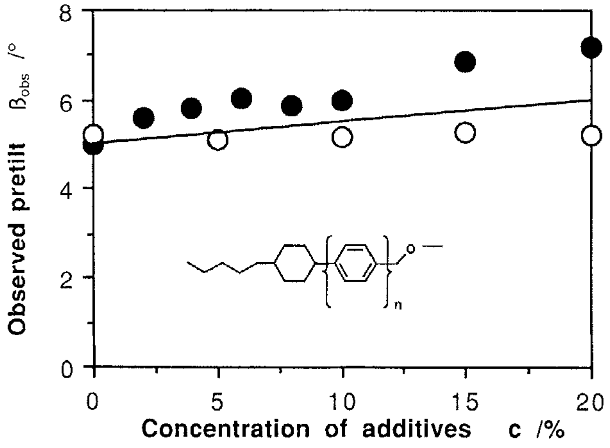

Figure 5. Pretilt as a function of the concentration of the additives to ZLI 1132. Filled circles, the three-ring compound. Open circles, the two-ring compound. The polyimide is RN-422 with $\beta_0 = 19°$; further details about the theoretical curve can be found in the text.

(taking into account a slightly varying concentration of the dopants) are shown in figure 3. The best fit of the data gives a pretilt of 15°.

Figure 4 shows the observed pretilt for a series of mixtures of 5CB and 6CB. As the proportion of 6CB increases, the pretilt decreases, both on the crystalline PMDA-4 and on the amorphous PMDA-7. It seems that the effect of increasing the angle between the optical and mechanical axis is stronger than the increase in in-plane order. The thickness of all these cells is 120 μm. We can thus neglect the surface layer thickness. The theoretical curves are calculated based on equation (3). For the calculation, we have used the following parameters: $\beta_0 = 15°$, which is the value found on the structurally similar s-BPDA-6, and $\alpha = 3{\cdot}9°$ for 5CB and $5{\cdot}1°$ for 6CB (table 1

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gives list of α values for all the *n*CBs). a_1 is found to increase 20 per cent between 5CB and 8CB [5], we assume that this increase is linear in odd-numbered methylene groups. Both 5CB and 6CB contain three odd-numbered methylene groups, and will thus have the same a_1. For the different mixtures we assume that α and a_1 will be a linear combination of the contributions from the two components. Using the pretilt observed for pure 5CB then gives us an a_1 of 0·223 for 5CB on crystalline PMDA-4 and of 0·160 for 5CB on amorphous PMDA-7. These values will be the same for 6CB and all the mixtures. The pretilt angles will thus decrease due to the larger value of α for the 6CB than for 5CB. We see that there is good agreement between theory and experiment.

The values obtained here agree well with direct determinations by SHG [21] for 8CB on PMDA-4, whereby $\beta_0 = 14°$ and $a_1 = 0{\cdot}23$ are found. The latter value is sensitive to rubbing conditions and is difficult to compare directly for different experimental set-ups.

In figure 5 the results for a complementary experiment are shown. Two different compounds are added to ZLI 1132. Here one of the dopants will make the core of the molecule larger by introducing an extra phenyl ring. This will make the molecular shape more linear, for example, decrease α. Decreasing α will increase the term $\beta_0 - \alpha$ and thus increase the pretilt. We see that for the three ring compound, there is an increase in the pretilt with increasing concentration. Doping with the similar two ring compound gives no change in the pretilt. The change in pretilt found is thus not the result of changed interactions with the surface.

The theoretical curve is calculated by assuming $\beta_0 = 19°$—a value found for several commercially available polyimides [3, 9]. α is set equal 9° for the cyanophenylcyclohexane mixture. 9° is half the angle between the axes of the 1,4-positions in the two rings. For the dopant, we have assumed $\alpha = 1°$. We see that the calculated pretilt given by the full line is a little too low.

There might be an accompanying increase in a_1 with this dopant. As an increase in the length of the flexible alkyl chain gives an increase in a_1, increasing the length of the more rigid core would probably be even more effective. A rough estimate of the increase in a_1 due to the increased length of the core can be given as follows. With a 20 per cent contribution from each odd-numbered methylene group, we find that 60 per cent of the total contribution is due to the alkyl chain, and thus 40 per cent is due to the two rings of the aromatic core for 5CB. Adding another ring should thus increase a_1 by about 20 per cent, if the increase is linear in number of aromatic groups, as well as methylene groups. However, to reproduce the experimental data we must increase a_1 by 100 per cent for the three-ring compound relative to the two-ring compound. This seems too large a change. These data were obtained for 20 μm thick cells and we might here approach cell thicknesses where changes in the surface layer thickness will also influence the observed pretilt. The effect of the surface layer thickness will be discussed further in § 4.2.

From the results in figures 3–5, it is clear that changes in the structure of the liquid crystal material influence the pretilt. Changes that reduce the angle between the optical and mechanical axes increase the pretilt, while changes in structure that increase the angle reduce the pretilt. More specifically, a longer (or heavier) alkyl chain will reduce the pretilt, while a heavier core will increase the pretilt. Qualitatively, the results are just as the theory predicts. Using values from the literature, together with reasonable choices of the unknown constants, we also obtain satisfactory quantitative agreement.

The in-plane order is also found to depend on the structure of the liquid crystal material. Increasing the length of the molecule increases a_1. If the increase is in the core

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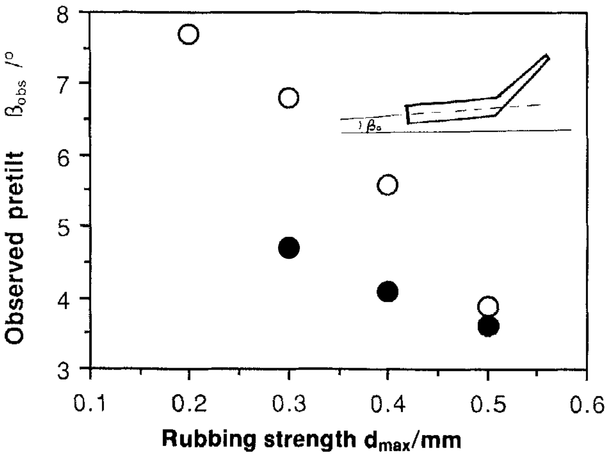

Figure 6. Observed pretilt as a function of rubbing and cell gap for ZLI 1132 with RN-422 as the alignment layer. $\beta_0 = 19°$; $\alpha = 10°$. Open circles, 6 μm cell gap; filled circles, 25 μm cell gap.

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of the molecule, the two effects cooperate, and we find a strong increase in the observed pretilt angle. If the increase in length of the molecule is due to the alkyl chain, the two effects will oppose each other. For the systems we have studied here, the effect of a more bent structure has been the stronger one, and there has been a small net decrease in the observed pretilt.

4.2. *Effect of the cell thickness*

The surface layer will give an extra retardation. Thus thin cells will give a larger pretilt angle than thicker cells, as the relative importance of the surface layer increases; this is expressed in equation (3).

We have previously shown that for the Schiff's base mixture RO-TN-200, the observed pretilt increases as the cell thickness decreases [7].

In figure 6, a new set of measurements is shown. Here the pretilt is changed by changing the rubbing conditions. We see that in all cases, 6 μm cells yield a higher pretilt than 25 μm cells. The difference is, however, smaller for a higher degree of rubbing, when the pretilt decreases. The polyimide used here is the commercially available RN-422, as in figure 5. This is a fluorine containing polymide. It has been found [25] that when a fluorine containing polyimide was rubbed, there was an increased concentration of fluorine containing groups in the surface layer, together with a decreasing bulk pretilt. The same has been found for RN-422. It seems likely that the changed surface composition has led to a change in angle at the surface (β_0).

We fixed the surface layer thickness at 0·5 μm, and tried to calculate β_0 and a_1 from the pairs of values for 6 and 25 μm thick cells. In all cases, this approach yielded a_1 values much above 1. This is of course clearly impossible. Instead we have assumed that the alkyl chain points out of the surface, as shown in the insert of figure 6. We then found that β_0 decreased from 8·8 to 2·6°. a_1 was also found to decrease from about 0·4 to 0·2.

Rubbing the fluorine containing polyimide brings more fluorinated groups to the top surface [25]. The cyano groups of the mesogens are repelled by the partly negatively charged fluorine. the mesogen will thus show a smaller tendency to attach to the surface,

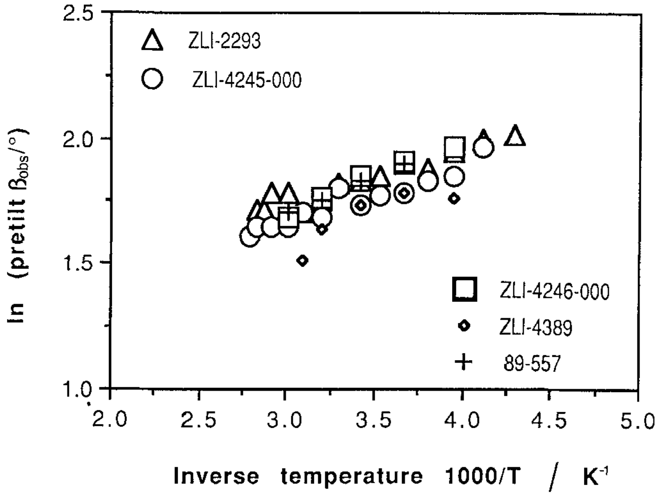

Figure 7. The temperature dependence of the observed pretilt angles. Data taken from [26]. In accordance with equation (5) we have a linear fit over a wide temperature range. The cell gap is 50 μm [27].

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and also a lesser tendency to break up the dimeric pairs. In a dimeric pair, there is no dipole to attach to the surface, and hence β_0 will be small. At the same time, the two molecules forming the dimeric pair will normally do so in a head-to-tail fashion, thus giving one molecule parallel and one anti-parallel to the rubbing direction. This will also lower the in-plane order a_1.

4.3. *The temperature dependence of the pretilt*

In equation (5), we gave an expression for the temperature dependence of the pretilt angle. In our model, the pretilt is a result of a temperature dependent change in the population distribution on the surface. This averages to a change in the optical axis in the bulk of the sample. In figure 7, we have plotted the data from [26]. The cell gap for these measurements is 50 μm [27]. As can be seen, the data for all five compounds fall on straight lines over a very wide temperature range. The new model is in excellent agreement with the experimental results.

4.4. *Effect of the polymer surface*

As crystalline polyimides are more ordered than amorphous polyimides, we would expect crystalline polyimides to give higher in-plane order than amorphous polyimides, and thus also a higher pretilt angle. This has indeed been found for a homologues series of alkylene-biphenylimides [10], although the effect seems to be less regular in the closely related alkylene-pyromellitimides [11].

Recently, some of the alkylene-pyromellitimides have been studied by SHG [21], and a higher in-plane order a_1 has been found for the crystalline PMDA-4 and PMDA-6 than for the amorphous PMDA-3 and PMDA-5. There is also a very pronounced odd–even effect for the second moment of the distribution (a_2).

For the surfaces used in this study, we find a higher pretilt on the crystalline surfaces than on the amorphous ones. This can easily be explained by assuming that the more regular crystalline surfaces will also give a more regular surface layer with a higher in-plane order (larger a_1). However, changes in the surface will also lead to changes in β_0. This change might be large enough to overcome the effect of increased in-plane order. On increasing the crystallinity of the surface, we assume that a_1 always increases, while β_0 might increase or decrease. The total effect on the pretilt is thus not easily predicted. The pretilt might increase, decrease or stay constant.

SHG measurements [3, 5, 6, 8, 9, 13] have found β_0 varying from 9° ± 5° to 19° ± 5° depending on the polymer surface used. Unfortunately, no details have been given about the surfaces. There have also been variation in the signal intensity, signifying a variable amount of monomeric 8CB attached to the surface. For silane covered surfaces, β_0 values have been found between 23° and 51°, depending on the amount of bare glass (polar sites) for attachment [28].

4.5. *Some remarks regarding* a_1

So far, we have implicitly treated a_1 as a product of two factors, one entirely due to the surface and one due to the liquid crystal. Fitting the data in figure 4, we implicitly assumed that the relative increase per odd-numbered methylene group was the same irrespective of the surface used. In other words, a_1 was treated as a simple product of contributions from the surface and the liquid crystal. This assumption is probably quite good when we look at the *n*CBs, or other homologous series of strongly polar mesogens, where the part of the mesogen interacting with the surface is unchanged. But as the data in table 2 show this effect is not generally true. Here, we have looked at several liquid crystals in cells with PMDA-7 as alignment layer. Some of the cells have been left unannealed, while others have been annealed at 285°C for one hour. This procedure has previously been found to increase the pretilt angle for the liquid crystalline mixture ZLI 1132 [12]. For the liquid crystals ZLI 1275, ZLI 1132, ZLI 1800-000 and ZLI 3700-000, which all contain materials having the strongly polar cyano group, there is also a clear increase in the pretilt. For the ester based ZLI 1081 and RO-TN-103, and the dialkyl-phenylcyclohexane mixture ZLI 1602, there is no such effect, however. The latter three mixtures do not have components with strong terminal polar groups that can attach to the surface. Thus they do not show any higher pretilt, even if the order of the surface itself has been improved. On the other hand, β_0 is lower for these compounds. RO-TN-619 contains both esters and cyano-compounds, and the mixture behaves like the other ester mixtures.

4.6. *Some qualitative effects*

Some effects already described in the literature can easily be explained through our model for surface alignment.

Long alkyl chains at the surface will often give homeotropic alignment. However, SHG measurement find no differences in the distribution of the optical axis between the surfactants that give homeotropic alignment and those that give planar alignment [28]. In figure 8 we have sketched one solution to this problem. The optical axis, or aromatic core, of the molecules make the same angle with the surface in both cases. In the absence of alkyl chains from the surface, the alkyl chains of the liquid crystals will prefer the orientation shown to the left. We have planar alignment. With long alkyl chains from the surface, there will be interactions between the alkyl chains from the surface and those belonging to the liquid crystal. The liquid crystal molecules adopt the orientation shown on the right. We obtain the homeotropic alignment [29].

With unrubbed surfaces, the in-plane distribution will be symmetric; a_1 is identical to zero. In this case there are two possible orientations of the director in the bulk. It can be parallel to the surface (giving a pretilt of exactly 0°) or it can be perpendicular to

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Table 2. Comparison of pretilt angles for different nematic fluids on annealed and unannealed PMDA-7.

Liquid crystal	Pretilt angles on PMDA-7/° Unannealed	Pretilt angles on PMDA-7/° Annealed 285°C (1 h)	Change/per cent
Terminal cyano group			
ZLI 1275	1·5 ± 0·4	2·0 ± 0·3	+ 33
ZLI 1132	2·3 ± 0·1	2·7 ± 0·2	+ 18
ZLI 3700-000	3·1 ± 0·3	3·8 ± 0·2	+ 23
ZLI 1800-000	2·4 ± 0·1	3·1 ± 0·1	+ 32
			Average + 27
Two terminal alkyl chains			
ZLI 1081	1·5 ± 0·3	1·2 ± 0·1	− 20
RO-TN-103	2·4 ± 0·4	2·7 ± 0·1	+ 12
ZLI 1602	1·5 ± 0·2	1·5 ± 0·2	− 1
RO-TN-619†	3·0 ± 0·1	2·9 ± 0·1	− 3
			Average − 3

† Also contains cyano compounds.

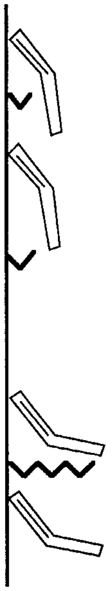

Figure 8. A sketch explaining how different surfactants might give planar or homeotropic alignment while all showing the same β_0.

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the surface (giving homeotropic alignment with exactly 90° pretilt). It has recently been found that a surfactant treated surface gives a distinct transition, with surfactants with six or fewer carbon atoms giving planar alignment, and those with seven or more giving homeotropic alignment [30, 31]. No intermediate alignment was found. This is in agreement with our model which predicts that for symmetry reasons, only planar or homeotropic alignment is allowed on unrubbed surfaces.

Schadt and co-workers [32] obtained good alignment by irradiating a UV-curable polymer with polarized UV light. The irradiation will break the circular symmetry of the untreated polymer. Irradiation with linearly polarized light will leave two mirror symmetries. One is parallel to the polarization direction, and of little concern to us. The other mirror plane is perpendicular to the polarization. This mirror plane will result in $a_1 = 0$. In other words, the pretilt should be 0° in this case. This is also what was observed [32]. Generally, any treatment which leaves a mirror plane perpendicular to the preferred director of the mesogens will give $a_1 = 0$, and thus give 0° pretilt.

This is also found with the recently introduced stamped alignment [33]. In this case, τ is non-zero, but there is no order induced by the epoxy polymer used. It is found that β_{obs} equals τ [33], as equation (3) predicts for $a_1 = 0$.

It is found that the distribution of the molecules at the surface is fixed fairly strongly [3, 5, 6, 8, 9]. The distribution is symmetric with respect to the rubbing direction. This symmetry direction is imposed on the rather fluid nematic phase. On cooling down into a crystalline or highly ordered smectic phase, the alignment is often destroyed. Instead, a new alignment is imprinted on to the surface. This is the so called surface memory effect [34]. In our mode this is easily explained. The forces between the molecules in the crystalline or highly ordered smectic phase mechanically force a reorientation of (some of) the molecules at the surface. On heating the material back into the nematic phase, the same mechanism operates as described before. But in this case, the rubbing process is not the process that has destroyed the symmetry of the in-plane order. The crystallites of the crystalline (or highly ordered smectic) phase have imposed their preferred orientation on the surface. In the nematic phase formed upon subsequent heating, we will thus have an average orientation along the preferred directions of the different crystallites.

The same explanation has already been given to account for the surface memory effect found when a smectic A phase has been magnetically reoriented on an unrubbed surface [20].

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5. Conclusions

We have developed a population distribution model for the surface alignment of the nematic phase. The model only contains parameters that can be measured or calculated directly from knowledge of the liquid crystal structure. The model is in good agreement with experimental data, and can explain a large number of observations and measurements.

For polymer surfaces, the three most important factors determining the pretilt are the angle between the optical axis of the mesogens and the surface, the angle between the optical and mechanical axis of the mesogens and the in-plane distribution of the mesogens at the surface.

The in-plane order of the mesogens seems to be governed both by the long range order (crystallinity) of the surface, and dispersive interactions between the mesogens. The first effect appears stronger for the systems tested so far.

References

[1] Baur, G., Wittwer, V., and Berreman, D. W., 1976, *Physics Lett.* A, **56,** 142.

[2] Frank, F. C., 1980, *Liquid Crystals*, edited by S. Chandrasekhar (Heyden), 1.

[3] Feller, M. B., Chen, W., and Shen, Y. R., 1991, *Phys. Rev.* A, **43,** 6778.

[4] Myrvold, B. O., 1993, *Polymer Preprint*, **34,** 758.

[5] Barmentlo, M., Hollering. R. W. J., and van Aerle, N. A. J. M., 1992, *Phys. Rev.* A, **46,** R4490.

[6] Barmentlo, M., Hollering, R. W. J., and van Aerle, N. A. J. M., 1993, *Liq. Crystals*, **14,** 475.

[7] Myrvold, B. O., Kondo, K., and Oh-hara, S., 1994, *JSID* (in the press).

[8] Guyot-Sionnest, P., Hsiung, H., and Shen, Y. R., 1986, *Phys. Rev. Lett.*, **57,** 2963.

[9] Chen, W., Feller, M. B., and Shen, Y. R., 1989, *Phys. Rev. Lett.*, **63,** 2665.

[10] Yokokura, H., Oh-e, M., Kondo, K., and Oh-hara, S., 1993, *Molec. Crystals liq. Crystals*, **225,** 253.

[11] Myrvold, B. O., Yokokura, H., Iwakabe, Y., Kondo, K., and Oh-hara, S., 1992, *Proc. Japan Display '92*, p. 827.

[12] Myrvold, B. O., Kondo, K., and Oh-hara, S., 1993, *Jap. J. appl. Phys.*, **32,** 5052.

[13] Barmentlo, M., van Aerle, N. A. J. M., Hollering, R. J. W., and Damen, J. P. M., 1992, *J. appl. Phys.*, **71,** 4799.

[14] Becker, M. E., Kilian, R. A., Kosmowski, B. B., and Mlynski, D. A., 1986, *Molec. Crystals liq. Crystals*, **132,** 167.

[15] For example, Michl, J., and Thulstrup, E. W., 1986, *Spectroscopy with Polarized Light*: Partially Aligned Solutes (VCH Publishers).

[16] Geary, J. M., Goodby, J. W., Kmetz, A. R., and Patel, J. S., 1987, *J. appl. Phys.*, **62,** 4100.

[17] Myrvold, B. O., Kondo, K., and Oh-hara, S., 1994, *Liq. Crystals* (submitted).

[18] Myrvold, B. O., and Klaeboe, P., 1986, *Spectrochim. Acta* A, **42,** 1035.

[19] Jerome, B., 1992, *Molec. Crystals liq. Crystals*, **212,** 21.

[20] Ouchi, Y., Feller, M. B., Moses, T., and Shen, Y. R., 1992, *Phys. Rev. Lett.*, **68,** 3040.

[21] Johannsmann, D., Zhou, H., Sonderkaer, P., Wierenga, H., Myrvold, B. O., and Shen, Y. R., 1993, *Phys. Rev.* (in the press).

[22] Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1982, *Proc. R. Soc.* A, **381,** 117.

[23] Toriumi, H., and Samulski, E. T., 1985, *Proceedings of the 10th Liquid Crystal Conference*, Japan, p. 82.

[24] Nakamura, M., 1981, *J. appl. Phys.*, **52,** 456.

[25] Seo, D.-S., Kobayashi, S., and Nishikawa, M., 1992, *Appl. Phys. Lett.*, **61,** 2392.

[26] Weber, G., Plach, H. J., Naemura, S., and Scheuble, B., 1989, *Proc. Japan Display '89*, p. 532.

[27] Naemura, S. (personal communication).

[28] Barmentlo, M., Hoekstra, F. R., Willard, N. P., and Hollering, R. W. J., 1991, *Phys. Rev.* A, **43,** 5740.

[29] Shen, Y. R., 1989, *Liq. Crystals*, **5,** 635.

[30] Crawford, G. P., Ondris-Crawford, R., Zumer, S., and Doane, J. W., 1993, *Phys. Rev. Lett.*, **70,** 1838.

[31] Crawford, G. P., Ondris-Crawford, R., Zumer, S., Keast, S., Neubert, M., and Doane, J. W., 1993, *Liq. Crystals*, **14,** 1573.

[32] Schadt, M., Schmitt, K., Kozinkov, V., and Chigrinov, V., 1992, *Jap. J. appl. Phys.*, **31,** 2155.

[33] Sugawara, K., Ishitaka, Y., Abe, M., Seino, K., Kano, M., and Nakamura, T., 1992, *Proc. Japan Display '92*, p. 815.

[34] Clark, N. A., 1985, *Phys. Rev. Lett.*, **55,** 292.

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