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PRELIMINARY COMMUNICATIONS

Anchoring of 4-*n*-alkyl-4′-cyanobiphenyl liquid crystal molecules on rubbed polyimides

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In the literature it has been reported that the rigid cyanobiphenyl core of 4-*n*-alkyl-4′-cyanobiphenyl molecules deposited onto polyimide-coated substrates makes an average angle of ≈78° with respect to the surface normal, independent of the rubbing conditions applied and independent of the polyimide materials studied. A simple anchoring model based on a combination of dipole–dipole, van der Waals and steric interactions explains this angle.

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For most types of liquid crystal displays (LCDs) orientation control of the liquid crystal (LC) bulk layer is vital, since it affects the electro-optic performance of the display. A proper LC alignment is induced by orientation layers, directly contacting the LC within the LCD. At present, rubbed polymers are mostly used as orientation layers in industrial production, since they offer good alignment uniformity over a large area, high production speed and high reproducibility.

The nature of the interactions between the rubbed layer and the LC molecules is not yet fully understood. A better understanding is desirable, since it might help in optimizing the rubbing process, selecting better orientation layer materials, and finding alternatives to orient the LC bulk layer unidirectionally without rubbing. The latter is important, since the rubbing process can reduce the production yield by possible contamination of the orientation layer by the rubbing cloth, generation of dust particles and creation of electrostatic damage to the active switches that are used in active matrix addressed LCDs. Many techniques have been used in the past to establish a better understanding and of these the optical surface second-harmonic generation (SSHG) technique has been found to be quite useful.

Shen and co-workers [1–3] were the first to apply SSHG successfully to LC monolayers on polyimide-coated substrates. They used an LC compound of the 4-*n*-alkyl-4′-cyanobiphenyl series (*m*CB, where *m* corresponds to the number of carbon atoms of the *n*-alkyl group), more specifically 8CB. The transition moment that is probed in an SSHG experiment is directed along the rigid cyanobiphenyl core axis $\hat{\zeta}$ as is indicated in figure 1, showing the structure of an *m*CB molecule. SSHG enables the determination of the average polar and azimuthal molecular orientation distribution of *m*CB monolayers such as 5CB and 8CB deposited on to orientation layers.

By assuming a gaussian orientational distribution in the polar angle θ (which is defined as the angle between the cyanobiphenyl core axis $\hat{\zeta}$ of *m*CB and the surface normal of the substrate), a polar peak position θ_0 of 78° and a distribution width σ of approximately 10° were reported for an 8CB monolayer on both unrubbed and rubbed

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polyimide-coated substrates [1]. Further studies on the orientation behaviour of 8CB monolayers on polyimide-coated substrates with different rubbing treatments revealed a molecular polar angle θ_0 of approximately 76° and a width σ of 5–7°, independent of the rubbing conditions [2]. Similar results were obtained more recently for 8CB monolayers on rubbed JIB-1 polyimide-coated substrates, i.e. θ_0 of 78° independent of the rubbing conditions applied [4]. Apparently, the rubbing conditions do not affect the polar orientation θ_0 of 8CB molecules on the polyimide surface. This is in line with the finding that the polar anchoring energy of 5CB, which has a chemical structure similar to 8CB, on rubbed polyimide layers is independent of the rubbing conditions applied [5]. More recently, however, Seo *et al.* [6], showed that the polar anchoring energy of 5CB on polyimide Langmuir Blodgett (PI-LB) films is much weaker. It would be very interesting to compare SSHG data obtained for *m*CB monolayers deposited onto such PI-LB films, with monolayers deposited onto rubbed films of the same polyimide chemical structure.

Further studies have been performed on JIB-1 analogues. JIB-1 is a commercially available polyimide produced by Japan Synthetic Rubber Co., which is used as orientation layer material for active matrix addressed LCDs. It is synthesized by condensation of 2,3,5-tricarboxycyclopentylacetic acid dianhydride (TCA) and 4,4′-diaminodiphenylmethane (DDM) [7]. JIB-1 analogues were also produced by Japan Synthetic Rubber Co., using TCA in combination with a mixture of two diamines, one of which is DDM and the other is a diamine X containing a specific group that causes high LC bulk pretilt angles within the LC layer in LCDs [8].

SSHG experiments revealed an average polar angle θ_0 of 77° with a distribution width σ of 4° for 8CB monolayers on the rubbed layers of the various polyimides, independent of the concentration and composition of diamine X [9]. Similar results were obtained using 5CB monolayers [10]. Although θ_0 did not vary with the type of polyimide containing TCA units in combination with a mixture of DDM and diamine X, the LC bulk pretilt angle θ_p varied significantly [9, 10]. An explanation was given by a simple model in which the in-plane orientational distribution of the molecules of the monolayer plays an important role in controlling the LC bulk pretilt angle θ_p. This 'in-plane orientational distribution' model can be used to explain θ_p values of 5CB of up to 10–12° [9, 10].

In summary, an average polar angle θ_0 of $\approx 78°$ with a distribution width σ of 4° to 10° is observed for monolayers of 5CB and 8CB on rubbed polyimide-coated substrates, independent of the rubbing conditions applied and independent of the polyimide materials studied. In this article a possible explanation is given for these observations.

The anchoring model that is proposed considers the polyimide surface as a homogeneous and continuous surface. The SSHG data represent information about an ensemble of *m*CB monolayer molecules (actually an area of several mm^2 is probed in an SSHG experiment), resulting in an averaged polar angle θ_0 and a corresponding distribution width σ.

The anchoring of the 8CB molecules of the monolayer on the polyimide-coated substrates is determined by a combination of dipole–dipole interactions, van der Waals (dispersive) interactions, and steric interactions. SSHG experiments have shown that the 8CB molecules of the monolayer are adsorbed with the cyano end group towards the polyimide surface [1]. This indicates a strong dipole–dipole interaction between the polar polyimide surface and the cyano group of 8CB. In addition, the relatively large θ_0 indicates that the 8CB molecules favour an interaction in which the biphenyl unit is as

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close as possible to the polyimide surface. In this way the dipole–dipole interactions between the polar cyano end groups of neighbouring 8CB molecules, attached to the surface, are reduced.

From the literature, it is well-known that the biphenyl unit of many *m*CB molecules and 4-*n*-alkyloxy-4′-cyanobiphenyl (*m*OCB) molecules is not planar, and that the two phenyl rings are twisted to a certain extent. This is due to a competition between π-conjugation between the phenyl rings stabilizing a non-twisted biphenyl conformer, and steric repulsion between *ortho*-hydrogen atoms favouring the twisted structure. For many *m*CB and *m*OCB molecules, either in the solid or in the liquid crystalline state, a twist angle between 36° and 43° has been reported (see [11, 12] and the references therein).

Assuming the biphenyl twist angle of $\approx 40°$ is not affected by the anchoring of the 5CB and 8CB molecules onto the surface, steric interactions between hydrogen atom H2 of the biphenyl unit (indicated in figure 1) and the polyimide surface will determine the closest contact between the cyanobiphenyl core and the surface. In that case, the vector through atoms H3′ and H5′, indicated in figure 1, will be parallel to the substrate surface. In other words, the distance from hydrogen atoms H3′ and H5′ to the substrate surface is identical, as is the case for the distance from H6′ and H2′ to the substrate surface. The proposed anchoring model is shown in figure 2. A simple calculation reveals that, under given circumstances, the angle between the surface normal and $\hat{\zeta}$ will be 78–79°. This corresponds very well with the θ_0 values that have been determined by SSHG for 5CB and 8CB on various polyimide layers, prepared from TCA as tetracarboxylic unit and a mixture of two diamines.

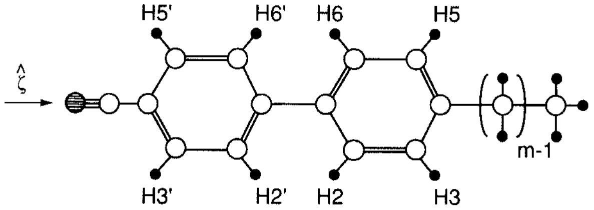

Figure 1. Structure of a 4-*n*-alkyl-4′-cyanobiphenyl (*m*CB) molecule, including some atomic labelling and the axis $\hat{\zeta}$ referred to in the text. *m* indicates the length of the *n*-alkyl unit, being 5 and 8 for 5CB and 8CB, respectively. The open circles represent carbon atoms, the filled circles hydrogen and the shaded circle nitrogen.

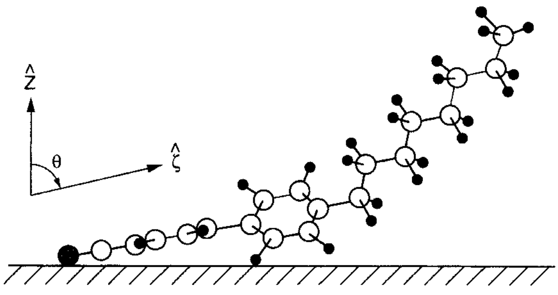

Figure 2. Proposed model of anchoring of a 4-*n*-octyl-4′-cyanobiphenyl (8CB) molecule on a polyimide-coated substrate. The molecule is attached by the polar cyano end group to the polyimide surface. In this drawing $\hat{z}$ indicates the surface normal. The open circles represent carbon atoms, the filled circles hydrogen and the shaded circle nitrogen.

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Before concluding, it must be mentioned, however, that the observed θ_0 of $\approx 78°$ is not a universal value for 8CB. When a glass substrate is modified by surfactants such as octadecyl-trichlorosilane (OTS), θ_0 can range between $\approx 70°$ and $\approx 36°$, depending on the packing density of the OTS monolayer [13]. In this situation the 8CB molecules are again anchored quite strongly with their polar cyano end group towards the glass substrate. Due to the high density of octadecyl chains of OTS on the substrate surface, steric interactions between the 8CB molecules and the octadecyl chain force the cyanobiphenyl core to stand more upright [13].

In the literature, results are reported on the temperature dependence of the bulk pretilt angle θ_p (for example, see [14]). In order to understand these results in terms of the anchoring model presented in this article, more information is needed. For example, information on the temperature dependence of the SSHG data is needed. In addition, the effect of temperature on the twist angle within the biphenyl core of the *m*CB molecules must be known.

In conclusion, a simple anchoring model is presented which explains the averaged polar angle θ_0 of $\approx 78°$ that is observed for monolayers of 5CB and 8CB on rubbed polyimide-coated substrates, independent of the rubbing conditions applied and the polyimide composition. The model is based on the strong anchoring between the polar cyano end group of the *m*CB molecules and the polyimide surface, in combination with the tendency of the biphenyl core to align as much as possible along the surface. Assuming the two phenyl units of the biphenyl show a twist angle of $\approx 40°$, a maximum polar angle θ_0 of 78–79° can be derived. The model presented earlier [9, 10], explaining the relation between the orientational distribution of the *m*CB molecules of the monolayer and the LC bulk pretilt angle θ_p is still valid.

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