

This article was downloaded by: [Moskow State Univ Bibliote]

On: 15 April 2012, At: 12:16

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Characterizing Two Methods for Achieving Intermediate Surface Pretilt

C. J. Holmes^a, T. S. Taphouse^b & J. R. Sambles^a

^a School of Physics, University of Exeter, Exeter, EX4 4QL, UK

^b HP Labs Bristol, Long Down Avenue, Stoke Gifford, Bristol, BS34 8QZ, UK

Available online: 11 Jan 2012

To cite this article: C. J. Holmes, T. S. Taphouse & J. R. Sambles (2012): Characterizing Two Methods for Achieving Intermediate Surface Pretilt, *Molecular Crystals and Liquid Crystals*, 553:1, 81-89

To link to this article: <http://dx.doi.org/10.1080/15421406.2011.609407>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Characterizing Two Methods for Achieving Intermediate Surface Pretilt

C. J. HOLMES,^{1,*} T. S. TAPHOUSE,² AND J. R. SAMBLES¹

¹School of Physics, University of Exeter, Exeter EX4 4QL, UK

²HP Labs Bristol, Long Down Avenue, Stoke Gifford, Bristol BS34 8QZ, UK

Two recipes for controlling the degree of surface pretilt exhibited by the director of the nematic liquid crystals 5CB and ZLI-2293 (Merck) are characterized. The first involves an “overbaked” and rubbed homeotropic aligning polyimide (Nissan SE-1211), and the second uses a rubbed layer of planar aligning polyimide (Nissan SE-130) on top of a homeotropic aligning polyimide (Nissan SE-4811). These allow the director pretilt to be controlled through a range of angles as measured here using the technique of an antiparallel aligned cell doped with a dichroic dye. Results for the “overbaked” Nissan SE-1211 suggest that the degree of pretilt obtained is strongly dependent on the surface upon which the aligning polymer is deposited. Measurements of surface energies using contact angles suggest they have little or no role in controlling the pretilt produced.

Introduction

For common nematic liquid crystals (LCs) consisting of calamitic or “rod shaped” molecules, the average orientation exhibited by the long molecular axis is described by a unit vector, \vec{n} , termed the director. Commercially available surface treatments for the alignment of nematic LCs tend to be restricted to homeotropic (alignment of the director normal to the surface) and near to planar (alignment of the director nearly parallel to the surface). However, there are cases where an intermediate director pretilt lying between homeotropic and planar is desirable, such as in the no-bias pi cell used for liquid crystal displays [1] where nanostructure alignment surfaces have been used to produce pretilt angles of over 45°.

Mechanically rubbed planar aligning polyimide films are widely used to control the alignment of the director in the vast field of flat screen display technology [2]. As such, much research has gone into developing an understanding of the mechanisms behind director alignment at boundaries, and several theories have been suggested to explain the phenomenon. One such explanation is that due to Berreman [3], where it is proposed that microgrooves and scratches caused by the rubbing process are elastically responsible for the alignment of the director parallel to the rubbing direction. An alternative proposal is that described by Geary et al. [4], where alignment is suggested to be caused by realignment of the polymer molecules at the surface, which in turn transfers alignment to the LC. In the case of planar aligning polyimides, it is interesting to note that the mechanical rubbing process can induce a small amount of pretilt away from the substrate, which is thought to

*Address correspondence to C. J. Holmes, School of Physics, University of Exeter, Exeter EX4 4QL, UK. E-mail: c.holmes@ex.ac.uk

be caused by a small inclination of the polymer elongation axis at the surface [4]. Other interesting work in this area by Rüetschi et al. [5] have shown that a surface patterned by scanning force microscopy can be used to align LC molecules in a manner indistinguishable from that of a rubbed polyimide layer.

As indicated, there are cases where near planar alignment or homeotropic alignment are not desirable, and large pretilt angles of the director at the bounding surface may be important for control of the optical and/or dynamic properties of a device. To this end, several methods for setting the degree of director pretilt at the bounding surface have been investigated. These include, but are not limited to, methods such as the mechanical rubbing of homeotropic aligning polyimides [6, 7], and the mixing of both homeotropic and planar aligning polyimides to produce intermediate pretilt angles [8–10]. Hwang et al. [11] have also investigated a method of using conventional planar polyimides doped with Polyhedral Oligomeric Silsequioxanes (POSS) nanoparticles, which alone give homeotropic alignment. The addition to the POSS nanoparticles in varying concentrations has been shown to tune the degree of pretilt, θ_0 (measured from the substrate) over the range $0^\circ \leq \theta_0 \leq 90^\circ$, it is suggested that this is through alteration of the surface energy of the alignment layer.

In this study, we explore two recipes for controlling the surface pretilt exhibited by the liquid crystals 5CB and ZLI-2293. The first method involves the “overbaking” (baking at temperatures greater than the manufacturer’s guidelines) of the conventionally homeotropic aligning polyimide Nissan SE-1211. It has been reported in the literature [6, 7] that this method of overbaking has two effects on the aligning layer that help to promote planar alignment. The Nissan SE-1211 polyimide has a relatively rigid backbone that promotes planar alignment, as well as alkyl side chains which promote homeotropic alignment [6]. Firstly, the overbaking process weakens the molecular backbone, which in turn weakens the tendency for the Nissan SE-1211 layer to promote planar alignment, and secondly it cleaves away a fraction of the side chains, reducing the strength of the homeotropic alignment, leaving a controllable pretilt angle [6].

The second method investigated is that of a double layer polyimide. This technique involves the deposition of a base layer of the homeotropic aligning polyimide Nissan SE-4811. This layer is then baked and cured as per the manufacturer’s guidelines. On top of this homeotropic aligning surface is then deposited a layer of the planar aligning polyimide Nissan SE-130 which is then rub aligned. Varying the thickness of the Nissan SE-130 planar layer has been shown to control the level of pretilt exhibited in a cell [12]. A detailed description of the recipes and the techniques used to analyze them follows.

Experiment

Recipe 1—“Overbaked” Nissan SE-1211

3.2 cm by 2.5 cm glass slides with a conductive Indium Tin Oxide (ITO) coating on one side were spin coated at 4000 RPM for 40 seconds with the homeotropic aligning polyimide Nissan SE-1211. They were coated on either the plain glass side or on the ITO side, allowing cells to be made either with ITO or glass on the inner bounding surfaces.

After spinning, the slides were pre-baked at 95°C for 1 minute on a hotplate prior to being baked in an oven at 240°C for 60 minutes. This baking temperature is far above the manufacturer’s guidelines of 180°C for 50 minutes [6], hence the term “overbaked” polyimide. As suggested earlier, it is this overbaking that plays the important role in producing pretilt angles away from homeotropic. On removal from the oven, the slides

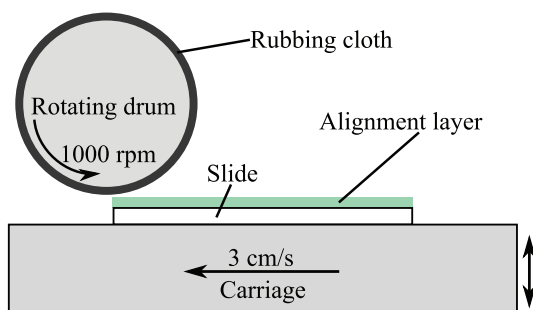


Figure 1. A schematic representation of the experimental rubbing machine set up. The moving carriage with sample attached is passed under the rotating drum and rubbing cloth at varying strengths of contact. To vary the rubbing strength, the carriage can be moved up or down.

were rubbed via a moving stage passing under a spinning drum with a rubbing cloth attached around the circumference (see Fig. 1). The rubbing system is set up so that the height of the stage can be varied from a level where the slides are made to pass under the drum barely touching the surface of the cloth, up to close contact between the slide and the cloth. Several authors have tried to quantify the strength of rubbing when referring to a rotating drum moving over the surface of a sample. In this case, we believe that the quantification of a rubbing strength parameter is dependent on too many variables and will be very difficult to reproduce exactly on another experimental setup. As we are showing here general trends in the degree of pretilt as function of this rubbing strength, we define simply a rubbing height, d , that can vary from 3.8 mm (strongest contact with the slide) to 4.5 mm (weakest contact with the slide). Experimental rubbing machine parameters are given in Fig. 1.

After both the plain glass and ITO coated glass slides are rubbed at varying values of d , LC cells were fabricated by aligning the top and bottom plates in an anti-parallel geometry (with no twist gradient across the cell), spaced with $5\ \mu\text{m}$ beads dispersed in a UV curing glue (Norland optical adhesive 73). This alignment of the slides leads to the creation of a uniformly tilted slab of LC between the top and bottom surfaces. The cells were then capillary filled in the isotropic phase with 5CB doped with 1% by weight of each of G472, G241 and G232 dichroic dyes from Hayashibara.

Recipe 2–Double Polyimide Layer

ITO coated glass slides were spin coated (on the ITO coated side) with the homeotropic aligning polyimide Nissan SE-4811 at 4000 rpm for 40 seconds. The samples were then prebaked on a hotplate at 100°C for 10 minutes, before being baked in an oven at 210°C for 40 minutes. After baking, the planar aligning polyimide Nissan SE-130 was spin coated on top of the homeotropic aligning layer at spin rates ranging from 3000 to 4000 rpm, prebaked on a hotplate at 100°C for 10 minutes and finally baked in an oven at 210°C for 40 minutes (two slides were not coated with the Nissan SE-130 layer, in order to build a control cell with just a homeotropic Nissan SE-4811 aligning layer).

The slides were then rubbed using various values of d (as per the overbaked Nissan SE-1211 recipe) and constructed into LC cells. The cells were again fabricated by aligning the top and bottom plates in an anti-parallel geometry, spaced with $5\ \mu\text{m}$ beads dispersed in

the UV curing glue. The cells were then capillary filled in the isotropic phase with ZLI-2293 (Merck) doped with the same dichroic dyes as the 5CB.

Camera Kit

In order to characterize the degree of pretilt obtained for each of the recipes described, the method developed by Edwards et al. [13] was used. Figure 2 shows the experimental set up. Firstly, the cell was placed upon a linearly polarized backlight and the intensity of the transmitted light was measured as the polarizer azimuth angle was rotated. Using a camera to measure the transmitted light allows many areas of interest to be characterized in one experiment. As the cell contains dichroic dye, the absorption—and therefore light transmitted—depends strongly on the input polarization and the director configuration. For example, a planar aligned cell will give a minimum in transmission when the input polarization is aligned with the director, and a maximum when the two are perpendicular. By contrast, in a homeotropic cell the transmission will be constant for all input polarizations. For cells with intermediate pretilt, the results will be somewhere between these two extremes.

In order to make the pretilt measurements, a reference cell is required with a known director orientation and filled with the same dye-doped liquid crystal as the cells to be tested. In this case, the reference cell was constructed with near planar alignment obtained from rubbed polyimide (Nissan SE-130). As the director orientation of the reference cell is known, this allows the absorption parameters for the dye to be calculated from the intensity

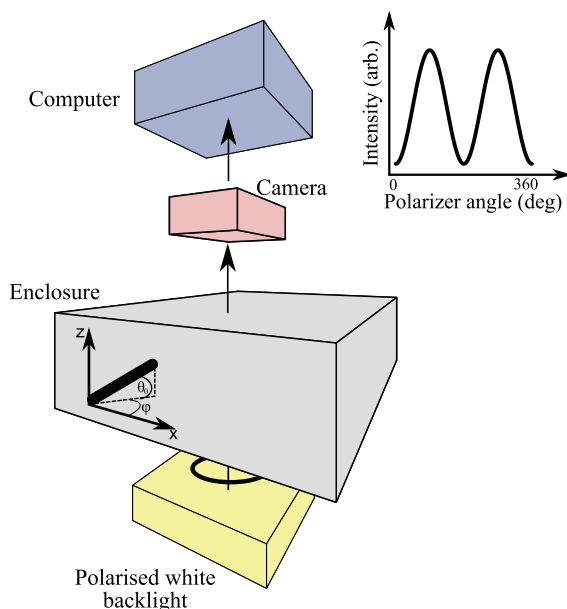


Figure 2. Schematic diagram of the machine vision technique of measuring surface pretilt. A polarized white back light is shone through the enclosure containing the antiparallel dye-doped cells, before passing into a camera and computer for analysis. The definition of the coordinate system and pretilt angle θ_0 is also shown. The figure inset shows the variation in the transmitted intensity as a function of the polarizer angle, with the minimum in transmission corresponding to the dye molecules being parallel to the polarization direction.

versus input polarization measurements. All the relevant parameters for the test cells are now known, except the liquid crystal orientation, which may be obtained by fitting the experimental data using an optical model of a tilted anisotropic slab [13].

Contact Angles

In order to measure the contact angles at the aligning surface, substrates were prepared identically to that of the overbaked Nissan SE-1211 recipe, but were not constructed into LC cells. The contact angles were then measured using a Cam 200 contact angle goniometer (KSV Instruments). Briefly, drops of water, ethylene glycol and di-iodomethene were dispensed onto the coated and rubbed substrate. A camera was used to image a drop on the surface a few seconds after it had been dispensed, allowing the contact angle between the drop and surface to be measured. These contact angles were then used to calculate the OWRK surface energies [14].

Results and Analysis

Figure 3 shows the pretilt angle, θ_0 , (measured from the substrate) as a function of the rubbing height for the overbaked Nissan SE-1211 recipe, as measured using the camera technique described. The two data sets correspond to the Nissan SE-1211 spun onto both the glass and ITO coated glass. For both cases, surface profiling measurements have shown that the polyimide layer thickness is very similar with a value of approximately 170 nm. Firstly, it is seen that for both surfaces there is the suggestion of a threshold, below which, any weaker rubbing results in little or no deformation away from the maximum pretilt

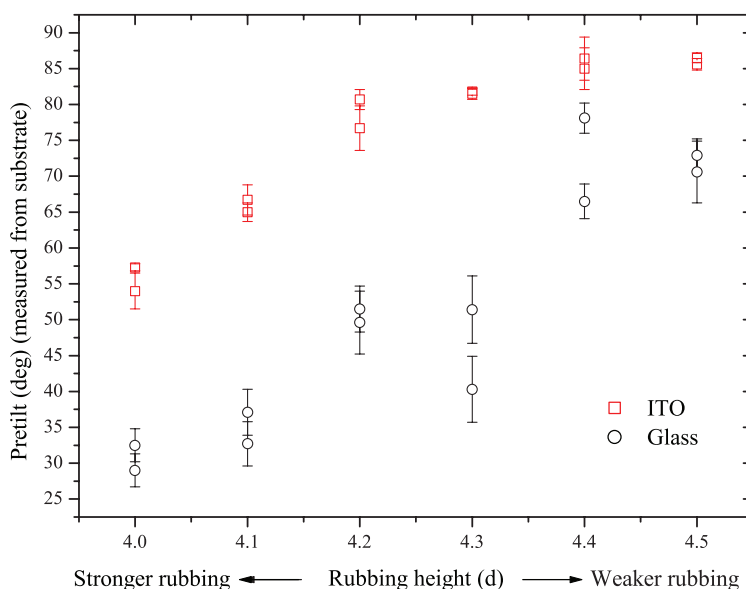


Figure 3. A plot of the measured pretilt angle as a function of the rubbing height and surface type for antiparallel dye-doped cells containing 5CB. The figure shows the much larger pretilt values for the case of Nissan SE-1211 spun onto ITO coated glass as opposed to plain glass for all values of the rubbing height.

angle measured (note that the maximum pretilt angle of $\theta_0 = 90^\circ$ would be achieved just by conventionally treated Nissan SE-1211, with no mechanical rubbing). This effect is shown by the saturation of the pretilt measurement when the surface is rubbed weakly. For Nissan SE-1211 spun onto the ITO coated surface, this value is approximately $\theta_0 = 85^\circ$ (or 5° tilted away from homeotropic) and for the case of Nissan SE-1211 coated on plain glass, the value is slightly lower (approximately $\theta_0 = 72^\circ$, or 18° away from homeotropic alignment). This result is not wholly unexpected, and shows that the largest value of θ_0 is not that of 90° (particularly in the case of Nissan SE-1211 spun onto plain glass), which we would expect for conventionally treated Nissan SE-1211 polyimide alignment layers. This result occurs at the weakest rubbing strength and therefore suggests that the overbaking process could be responsible for the small deviation of the director away from homeotropic alignment. It is likely that this pretilt occurs in randomly oriented domains, and in this case, the rubbing process gives an overall azimuthal alignment direction as well as further increasing the deformation of the director at the surface.

Perhaps most strikingly, the trend that the measured pretilt angle is lower in the case of the plain glass surface than for the ITO coated surface is retained over all rubbing strengths. It is clear that director is closer to homeotropic for the samples prepared on ITO coated glass, rather than that of plain glass for any given value of the rubbing height. In the case of samples prepared on glass, the pretilt angle is shown to be controllable from approximately 30° to 70° , whereas for samples prepared on ITO, the pretilt angle is tuned from 55° to 85° for the same values of the rubbing height. The error bars in Fig. 3 are calculated from the standard deviation in measurements across several areas of the cell and give a measure for the magnitude of the spatial variability in pretilt produced by this recipe. Some preliminary experiments have also shown that the same trend of harder rubbing producing a more planar alignment is also observed for overbaked Nissan SE-1211 cells filled with the liquid crystal ZLI-2293.

Figure 4 shows the contact angle, ψ and surface free energies for the overbaked Nissan SE-1211 recipe. Contact angles are shown as a function of the rubbing height and the liquid used to make the droplet, along with the calculated OWRK surface energies [14]. Figure 4a shows how the contact angles measured for overbaked Nissan SE-1211 on the plain glass substrate vary as a function of the rubbing height and liquid drop (water, ethylene glycol and di-iodomethane). It is seen that the contact angles vary very little, except for at the highest rubbing strengths, possibly due to damage to the aligning layer caused by the strong rubbing (scratches can be seen on the aligning layer at particularly hard rubbing values). Figure 4b shows how the values of the surface energies also vary little across the range of rubbing strengths used, unsurprisingly since they are related to the contact angles. Figures 4c and 4d depict the same information for the Nissan SE-1211 on the ITO coated surface. Here we see a similar trend as before, with very little difference in the contact angles and surface energies as a function of the rubbing strength. Importantly, the surface energies vary very little between both the plain glass surface and the ITO coated surface, leading to the conclusion that the surface energies give little information as regards the manner in which the surface treatment controls pretilt.

Figure 5 shows the measured pretilt angle for the double polyimide recipe as a function of both rubbing height and Nissan SE-130 spin rate for cells filled with ZLI-2293. Firstly, we see that for the control sample (circles) for which no planar aligning layer has been coated onto the base homeotropic layer, the measured pretilt value is close to homeotropic, $\theta_0 = 86^\circ$ (as expected from a conventional Nissan SE-4811 aligning layer) even though it has been rubbed moderately hard. For the case of a planar aligning layer of Nissan SE-130 spun at 3500 rpm on top of the Nissan SE-4811 layer (squares), there is a clear trend with

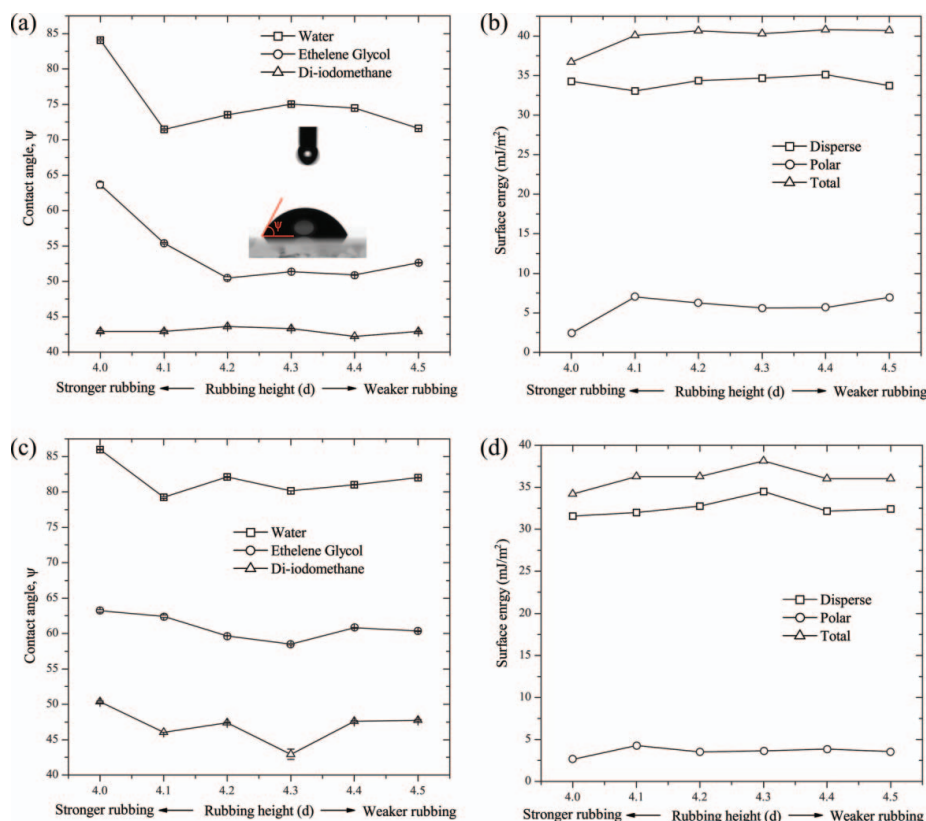


Figure 4. The contact angle and surface energies for droplets of water, ethylene glycol and diiodomethane on overbaked Nissan SE-1211 polyimide layers coated on the plain glass surface (a,b) and for the ITO coated surface (c,d). Figure 4a inset shows the definition on the contact angle ψ .

respect to the rubbing strength. We see an almost linear dependence through all rubbing strengths, with the value of pretilt being controlled from 66° to 87° . It is worth noting that although these samples are rubbed over a similar range of strengths, the variability of pretilt angles achieved is much smaller than that of the overbaked Nissan SE-1211 case. This difference could well be due to the use of ZLI-2293 as opposed to 5CB, as well as the difference in the recipe used. Figure 5 also shows data for Nissan SE-130 layers spun at rates of 3000 and 4000 rpm, which, within error, give very similar pretilt values close to $\theta_0 = 80^\circ$. The lack of clear trend in pretilt angle as a function of Nissan SE-130 spin rate is in contradiction with results from Zheng et al. [12], where it is shown that the degree of pretilt can be tuned from $0^\circ \leq \theta_0 \leq 90^\circ$ for cells filled with E7, using the Nissan SE-130 spin rate and subsequent layer thickness as the controlling variable.

Our measurements on cells filled with E7 or 5CB showed that alignment of the LC was very near homeotropic for all Nissan SE-130 spin rates used. However it is worth noting that spin coating the Nissan SE-130 on top of baked Nissan SE-4811 can sometimes lead to non-uniform coverage of the Nissan SE-4811 surface. Some preliminary experiments show that an oxygen plasma ash treatment of the baked Nissan SE-4811 layer before applying the Nissan SE-130 layer can significantly reduce this effect, presumably because the Nissan SE-130 is better able to wet the Nissan SE-4811. For cells where the Nissan SE-4811 layer

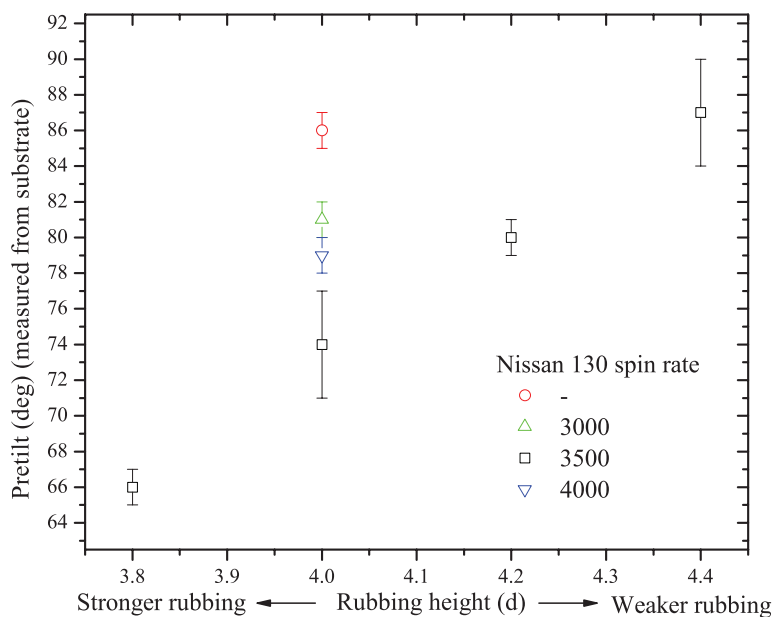


Figure 5. A plot of the measured pretilt angle as a function of both rubbing height and Nissan SE130 spin rate for anti-parallel dye-doped cells containing ZLI-2293. The figure shows how the pretilt angle appears to vary linearly with rubbing strength, but shows no trend with respect to the Nissan SE130 spin rate.

is given the oxygen plasma ash treatment, we see some moderate pretilt for 5CB ($\theta \sim 60^\circ$), but it still does not appear to be dependent on the Nissan SE-130 spin rate. This may be due to the difficulty in reproducing the experimental rubbing conditions of Zheng et al. [12].

Conclusions

We have characterized two existing methods for varying the degree of surface pretilt exhibited at the bounding surface of an LC cell. The first overbaked Nissan SE-1211 recipe gives results that demonstrate a similar trend to that of Rosenblatt et al. [6, 7], but here we also observe that the surface upon which the aligning polyimide is deposited plays an important role. We have seen that the pretilt angles are consistently lower for cells where the Nissan SE-1211 is spun onto the plain glass side rather than onto the ITO coated side. The reason for this is still unclear. Surface profiling experiments have shown that the polyimide layer thicknesses are similar, and the degree of pretilt is uniform over the majority of the cell. One possible suggestion is that the conductive nature of the ITO surface plays a role in removing static charge from the surface, or at least modifies the local electric field, which is without doubt present in the rubbing process. On both surfaces, we also see that there is a threshold for the onset of pretilt away from the homeotropic (or close to homeotropic) starting condition, and that the overbaking process itself possibly plays a role in tilting the director away from homeotropic.

An analysis of the contact angles and surface energies for both the glass and ITO surfaces as a function of the rubbing strength also gives an interesting result. It is seen that the rubbing parameter seems to have little effect on the surface energy of the sample and

the surface energy does not appear to be a good measure of the LC alignment properties of the surface in this case. In other systems, surface energy does appear to be correlated with LC alignment [11, 15], although there are examples where the correlation is not clear [15].

We have also shown control of pretilt using a double polyimide layer of Nissan SE-130 on top of Nissan SE-4811, following the work of Zheng et al. [12]. We have shown that the pretilt can be tuned through a smaller range of angles (compared to the overbaked Nissan SE-1211) as a function of the rubbing strength (at one spin rate) for cells filled with ZLI-2293. Crucially, we did not observe a reproducible trend in the pretilt angle as a function of the Nissan SE130 spin rate, and subsequent layer thickness for either of the LCs 5CB and ZLI-2293.

Acknowledgments

The authors would like to thank the EPSRC and Hewlett Packard for funding this work.

References

- [1] Yeung, F. S.-Y., & Kwok, H.-S. (2006). *Appl. Phys. Lett.*, 88, 063505.
- [2] Toney, M. F., Russell, T. P., Logan, J. A., Kikuchi, H., Sands, J. M., & Kumar, S. K. (1995). *Nature*, 374, 709.
- [3] Berreman, D. W. (1972). *Phys. Rev. Lett.*, 28, 1683.
- [4] Geary, J. M., Goodby, J. W., Kmetz, A. R., & Patel, J. S. (1987). *J. Appl. Phys.*, 62, 4100.
- [5] Rüetschi, M., Grütter, P., Fünfschilling, J., & Güntherodt, H.-J. (1994). *Science*, 265, 512.
- [6] Wang, R., Atherton, T., Zhu, M., Petschek, R., & Rosenblatt, C. (2007). *Phys. Rev. E.*, 76, 021702.
- [7] Huang, Z., & Rosenblatt, C. (2005). *Appl. Phys. Lett.*, 86, 011908.
- [8] Yeung, F. S., Ho, J. Y., Li, Y. W., Xie, F. C., Tsui, O. K., Sheng, P., & Kwok, H. S. (2006). *Appl. Phys. Lett.*, 88, 051910.
- [9] Vaughn, K. E., Sousa, M., Kang, D., & Rosenblatt, C. (2007). *Appl. Phys. Lett.*, 90, 194102.
- [10] Wu, W. Y., Wang, C. C., & Fuh, A. Y. G. (2008). *Opt. Express*, 16, 17131.
- [11] Hwang, S. J., Jeng, S. C., & Hsieh, I. M. (2010). *Opt. Express*, 18, 16507.
- [12] Zheng, B., Zheng, W., Lin, B., Wang, J., & Yu, S. (2007). Annual Meeting of ROC TLCS (P 43).
- [13] Edwards, E. G., Taphouse, T. S., Cornford, S. L., & Kitson, S. C. (2010). *Appl. Phys. Lett.*, 96, 021104.
- [14] Operation Manual, CAM Contact angle and surface tension meter, version 1.32, KSV Instruments.
- [15] Cognard, J. (1982). *Mol. Cryst. Liq. Cryst. Suppl.*, 1 1.