Tunable quasi-homeotropic liquid crystal pretilt angle based on competing alignment layers

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The liquid crystal alignment properties of a spincoated mixture of two commercial homeotropic and planar aligning polyamic acids are investigated. Baking the coated substrates induces cleaving of the long alkyl side chains of the first polyamic acid which weakens the tendency for homeotropic alignment while the imidisation ratio of both polyamic acids changes in favour of planar alignment. By detailed measurement of the retardation induced by the liquid crystal, we show that the combination of these two mechanisms in the proposed mixture yields a spatially uniform liquid crystal pretilt angle that is tunable with the baking temperature in the quasi-homeotropic range 0–10°, which is important for the Vertically Aligned Nematic technology.

Keywords: liquid crystal alignment; quasi-homeotropic pretilt; competing alignment layers; Vertically Aligned Nematic (VAN) technology

1. Introduction

The alignment of liquid crystals near the substrate interfaces plays a crucial role in obtaining a well-defined switching behaviour in liquid crystal devices. A near-horizontal (planar) or near-vertical (homeotropic) alignment is desired in most applications. A small deviation (pretilt angle) from the planar or homeotropic alignment is often required to ensure a uniform switching of the liquid crystal when a voltage is applied. In this paper we focus on quasi-homeotropic liquid crystal alignment with pretilt $\theta \leq 10°$ (the tilt θ is defined here as the inclination angle of the liquid crystal director relative to the vertical direction), which is important for the Vertically Aligned Nematic (VAN) technology (*1–4*). The retardation induced by the liquid crystal for such a quasi-homeotropic orientation is very small. In order to determine the pretilt, we consider a relatively simple optical setup to measure small variations in retardation accurately.

Many techniques have been studied in literature to achieve a well-controllable liquid crystal alignment because of its important impact on the quality and performance of liquid crystal displays and devices. The classical approach as applied in the fabrication of liquid crystal displays (LCDs) is to mechanically rub a polyimide alignment layer deposited on the glass substrates to obtain a near-homeotropic or near-planar alignment. The oblique evaporation method (*5–7*) is an alternative approach to achieve a tunable near-homeotropic alignment. Typically, silicon dioxide (SiO$_2$) is evaporated on the substrate surface at a certain angle. The complex structure of the SiO$_2$ films and the azimuthal dependency leads to a pretilt in the alignment. This is a contactless method which poses no risk of damaging the substrate either mechanically or by electrostatic discharge. On the other hand, the cost of the vacuum equipment and the required angle of deposition are the disadvantages of this method.

More recently, new techniques that allow a continuous pretilt control over a wide range have been presented. In one approach, surface microtextures on silicon (*8*) are applied to obtain a pretilt angle that is tunable with the groove depth in the patterned substrates. A pretilt controllable over a wider range can be achieved with a double-layer alignment film (DLAF) (*9*) which is realised by coating the glass substrates first with a planar aligning polyimide and then coating the resulting film with a homeotropic aligning polyimide. Depending on the top alignment film structure and the concentration of the polyimides used in this technique, the pretilt can be controlled abruptly or continuously. In an alternative DLAF technique (*10*), the pretilt angle is determined by the thickness of the homeotropic aligning top layer. Another attractive approach to obtain a well-controllable liquid crystal pretilt is based on nano-structured alignment layers (*11, 12*). One technique (*13*) to obtain a suitable alignment layer is to spincoat the glass substrates with a mixture of homeotropic and planar-aligning polyimides dissolved in a common solvent, typically with a lower concentration of the homeotropic aligning polyimide. Upon drying, one of the polyimides will precipitate first because of the difference in solubility which will result in phase segregation and the formation of

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domains featuring planar or vertical alignment at the substrates (*12*). Well in agreement with theoretical considerations (*14*), it is shown that the inhomogeneous surface can induce a homogenised pretilt in the bulk that is controllable by the concentration of the homeotropic and planar-aligning polyimides in the mixture. It is observed for a similar approach (*15*, *16*) that a mixture containing about the same relative concentration of the Nissan Chemical Industries RN-1175 (planar alignment) and SE-1211 (vertical alignment) compounds does not undergo phase separation as the solvent evaporates and the resulting alignment layer leads to a virtually homogeneous composition across the surface. The pretilt angle is uniform throughout the entire cell and its value is determined by the baking temperature of the mixture. A very weak rubbing step is performed to promote a homogeneous azimuthal alignment. Baking the spincoated layer at high temperature induces chemical imidisation (*17*) of the backbones of the polyamic acids SE-1211 and RN-1175 which leads to the formation of a polyimide, thereby promoting a planar alignment. Furthermore, for higher baking temperatures a larger fraction of the side chains of SE-1211 are cleaved away which weakens the tendency for vertical alignment (*18*, *19*). Owing to these two mechanisms, the pretilt angle will increase for higher baking temperatures. It is shown (*20*) that a blend of homeotropic and planar-aligning HiPAL materials (*21*) yields a comparable continuous surface structure which induces a homogeneous pretilt angle that is controllable by the concentration of the two compounds. Furthermore, theoretical considerations (*20*) based on the Rapini–Papoular expression (*22*) for the surface energy of the liquid crystal at the interface with the alignment layer show that it is also possible to control the anchoring strength with this approach.

Using the techniques based on competing alignment layers as summarised above, the liquid crystal pretilt angle can be controlled continuously over a wide range. This approach is very attractive because the method is similar to the existing technology and there is no need for high-vacuum equipment. Up to now, the reported experimental results (*10*, *12*, *13*, *15*, *16*, *20*) on competing alignment layers typically yield a good tunability of the pretilt in the range 10–80°. We investigate whether a similar approach can be dedicated to induce a spatially uniform and controllable pretilt in the near-homeotropic range 0–10°, which is important for the VAN technology.

2. Pretilt technology

We consider a mixture of two commercially available polyamic acids (from Nissan Chemical Industries)

consisting of 40 wt% of SE-1211 (homeotropic alignment) and 60 wt% of RN-1286 (planar alignment), which is dissolved in solvent #26 or #23 from Nissan Chemical Industries, with the concentration of the polyamic acids about 8 wt% of the total solution. The solution is spincoated on the indium tin oxide (ITO)-coated glass substrates at 1800 rpm for 9 seconds. The solvent is evaporated by prebaking the samples at 80°C for 30 minutes. Next, the coated substrates are fully baked for 50 minutes at temperatures covering the range 155–315°C and the pretilt angle is induced during this step similarly as in the approach described by Vaughn *et al.* (*15*). After baking, a very weak rubbing step is performed by translating the samples under a rotating drum, covered with a velvet cloth. This weak rubbing is performed to promote a homogeneous azimuthal alignment while the pretilt angle induced during the baking remains unchanged. The two substrates are then assembled with antiparallel rubbing and the cell gap d is defined by using spacers in the glue. The thickness of the empty test cells is measured from the fringes of the Fabry–Pérot interference pattern recorded with a spectrophotometer. The commercial negative dielectric liquid crystalline material MLC-6610 from Merck with ordinary and extra-ordinary refractive indices $n_o = 1.4828$ and $n_e = 1.5824$, respectively, is inserted into the cell by vacuum or capillary filling.

3. Pretilt measurement

As the cells are assembled with antiparallel rubbing, the liquid crystal director is homogeneous throughout the layer and the birefringence Δn solely depends on the tilt θ of the liquid crystal director:

$$\Delta n = \frac{1}{\sqrt{cos^2\,\theta/n_o^2 + sin^2\,\theta/n_e^2}} - n_o. \qquad (1)$$

Therefore, the pretilt angle θ can be determined from the retardation Δnd of the liquid crystal device. We propose to extract this small retardation Δnd indirectly, by measuring the shift in retardation between a waveplate with well-known retardation R (expressed in nanometres) and the combination waveplate/liquid crystal sample, having retardation $R + \Delta nd$ assuming that the slow axes of the plate and the liquid crystal device are aligned. This shift in retardation can be determined from the transmission spectrum which is recorded between crossed polarisers (oriented at +45° and –45° relative to the slow axis, respectively) with a spectrophotometer. For the combination waveplate/liquid crystal cell, the transmission T between crossed polarisers can be calculated as

$$T = \frac{1}{2} sin^2 \left[\frac{\pi}{\lambda} (\Delta nd + R) \right]. \qquad (2)$$

If only the waveplate is inserted between crossed polarisers, the term Δnd vanishes in Equation (2). In this case, the transmission reaches its kth maximum value at wavelength λ_1 while this maximum is shifted to wavelength λ_2 if both the liquid crystal sample and waveplate are inserted between the crossed polarisers:

$$\lambda_1 = \frac{2R}{1 + 2k}, \qquad (3)$$

$$\lambda_2 = \frac{2(\Delta nd + R)}{1 + 2k}. \qquad (4)$$

If the cell thickness d is known, the birefringence Δn can be calculated from the shift in wavelength $\Delta \lambda = \lambda_2 - \lambda_1$ where the kth transmission maximum occurs:

$$\Delta n = \frac{(1 + 2k)\Delta \lambda}{2d}. \qquad (5)$$

Assuming a constant tilt θ of the liquid crystal director across the cell, θ can be calculated numerically from the measured wavelength shift $\Delta \lambda$ by combining Equations (1) and (5). For near-homeotropic alignment, a small-angle approximation of Equation (1) can be used as a good approximation to calculate the pretilt:

$$\theta \approx \sqrt{\frac{n_e^2}{n_o(n_e^2 - n_o^2)} \frac{(1 + 2k)\Delta \lambda}{d}}. \qquad (6)$$

As an illustration, Figure 1 shows the transmission spectrum of the waveplate in combination with or without the liquid crystal sample as recorded between crossed polarisers in the 620–670 nm range. The waveplate used is a Newport 10RP22-06 multi-order waveplate (order $m = 25$, $R = 16{,}136.4$ nm) that acts as a half wavelength plate for 632.8nm.

The liquid crystal sample considered in Figure 1 has a cell gap $d = 108.65$ μm and was fully baked at $T_b = 185°C$. A large cell gap was chosen in order to perform an accurate measurement of the pretilt. Without the liquid crystal sample, the transmission reaches a maximum value in Figure 1 at 632.8 nm, as for this wavelength the waveplate acts as a $\lambda/2$-plate ($k = m = 25$). Inserting the liquid crystal cell increases the retardation by Δnd which leads to a shift in wavelength $\Delta \lambda = 0.5$ nm where the 25th transmission maximum occurs, as shown in Figure 1. Using $d = 108.65$ μm, the tilt angle of the liquid crystal director is calculated from Equation (6) or by using Equations (1) and
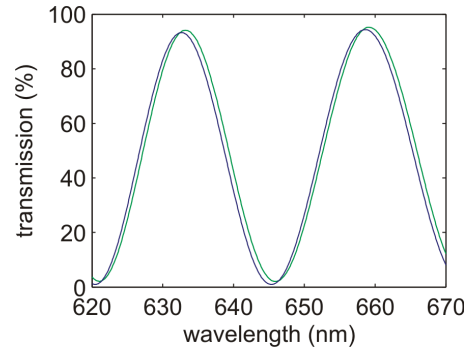

Figure 1. Experimental transmission spectrum recorded between crossed polarisers of the wave plate (blue) and of the combination wave plate/liquid crystal sample (green). (Colour refers to the online version.)

(5) to be $\theta = 2.1°$. Taking into account the accuracy ± 0.05 nm of the spectrophotometer, Equations (1) and (5) can be used to evaluate the maximum error on the extracted pretilt angle as of the order of $0.1°$. The periodic nature of the spectrum of the multi-order waveplate can be used to carry out multiple measurements at different peaks to further increase the accuracy of this method.

4. Experimental results

The pretilt angle of the samples baked at temperatures in the range 155–315°C is measured at room temperature using the experimental setup described above. Figure 2 shows the extracted pretilt values as a function of the baking temperature T_b for the considered temperature range. As expected, the pretilt angle increases with the baking temperature T_b in Figure 2.

Depending on the value of the pretilt angle, three zones can be distinguished as indicated in Figure 2. The first zone covers the broad 155–215°C interval in which the near-homeotropic pretilt angle changes gradually with the baking temperature. Table 1 lists the
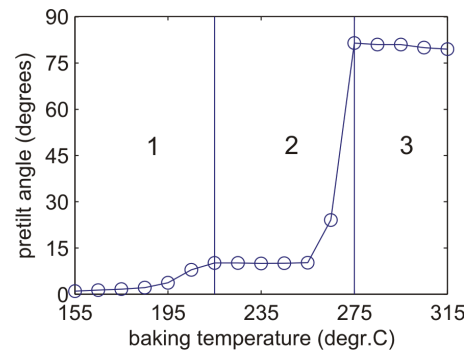

Figure 2. Pretilt angle as a function of the baking temperature T_b.

Table 1. Near-homeotropic pretilt angles θ as a function of the baking temperature. T_b. The maximum error on the extracted pretilt angle is of the order of 0.1°.

T_b	155°C	165°C	175°C	185°C	195°C	205°C	215°C
θ	0.9°	1.3°	1.6°	2.1°	3.7°	7.9°	10.1°

measured near-homeotropic pretilt angles as a function of the baking temperature T_b within this range. For increasing temperatures in this range, the imidisation ratio of the polyamic acids increases and a larger portion of the long alkyl side chains of SE-1211 are cleaved. Owing to these two mechanisms, the pretilt angle increases gradually with temperature in this range. Compared with earlier reported experimental results (*10*, *12*, *13*, *15*, *16*, *20*), the pretilt angle in this quasi-homeotropic range can be realised with very high accuracy because the variation in pretilt is only $\Delta\theta = 10°$ over a wide $\Delta T = 60°$C temperature interval. The desired near-homeotropic pretilt angle can be obtained using the proposed alignment RN-1286/SE-1211 mixture by choosing the appropriate baking temperature according to Table 1. Optical inspection of the samples between crossed polarisers shows that the pretilt angle is spatially uniform over the sample. To check the temperature behaviour of the liquid crystal alignment, the pretilt measurements have been repeated at different temperatures by inserting the samples in a hot stage and using the setup described in Section 3. In agreement with the observations reported by Kwok and Yeung (*12*), the pretilt angle remains the same for all temperatures throughout the test and the temperature behaviour of the alignment mixture is found to be similar to the behaviour of the individual compounds. The stability of the pretilt angle in time has been checked by monitoring the samples over a period covering several months. No deviation of the values listed in Table 1 has been measured.

The pretilt angle remains nearly constant in the second zone in Figure 2 for curing temperatures $215°C < T_b \leq 255°C$. This indicates that the imidisation ratio is saturated and no additional portion of the alkyl side chains of SE-1211 is cleaved. There is an abrupt transition to a near-planar alignment in the second zone for curing temperatures in the range 255–275°C. A very similar transition from homeotropic to planar alignment is also observed within the same temperature interval when only SE-1211 is used as the alignment layer. This shows that the 255–275° C range is the critical temperature interval where all long alkyl side chains of SE-1211 that induce the vertical alignment are broken. This explains the abrupt transition to a near-planar pretilt in Figure 2. In the third

zone of Figure 2, a constant near-planar pretilt angle $\theta \geq 80°$ is obtained. For such high curing temperatures $T_b \geq 275°C$, the long alkyl side chains of SE-1211 are cleaved and the backbones of the polyamic acids are fully imidised, resulting in a planar alignment.

5. Conclusion

In conclusion, the alignment properties of a spin-coated mixture of two commercial homeotropic and planar aligning polyamic acids have been investigated here. Baking the coated substrates induces cleaving of the long alkyl side chains of the first polyamic acid which weakens the tendency for vertical alignment while the imidisation ratio of both polyamic acids changes in favour of planar alignment. The combination of these two mechanisms in the proposed mixture yields a spatially uniform, quasi-homeotropic liquid crystal pretilt angle which is well controllable by the baking temperature. An experimental setup is proposed to measure the small retardation induced by the near-homeotropic orientation of the liquid crystal. It is shown experimentally that for the proposed mixture the liquid crystal pretilt angle can be accurately controlled in the range from 0.9° to 10.1° by adjusting the baking temperature of the spincoated mixture in the range 155–215°C. Therefore, the proposed method is an attractive approach for the realisation of a spatially uniform small liquid crystal pretilt in, e.g., VAN cells.

References

(1) Schiekel, M.F. *Appl. Phys. Lett.* **1971**, *19*, 391–393.
(2) Kahn, F.J. *Appl. Phys. Lett.* **1972**, *20*, 199–201.
(3) Vanbrabant, P.J.M.; Dessaud, N.; Strömer, J.F. *Appl. Phys. Lett.* **2008**, *92*, 091101.
(4) Vanbrabant, P.J.M.; Dessaud-Velthoven, N.; Strömer, J.F.; Neyts, K. *Appl. Phys. Lett.* **2008**, *93*, 261112.
(5) Janning, J.L. *Appl. Phys. Lett.* **1972**, *21*, 173–175.
(6) Armitage, D. *J. Appl. Phys.* **1980**, *51*, 2552–2555.
(7) Son, P.K.; Park, J.H.; Cha, S.S; Kim, J.C.; Yoon, T.H.; Rho, S.J.; Jeon, B.K.; Kim, J.S.; Lim, S.K. *Appl. Phys. Lett.* **2006**, *88*, 263512.
(8) Lee, F.K.; Zhang, B.; Sheng, P.; Kwok, H.S.; Tsui, O.K. *Appl. Phys. Lett.* **2004**, *85*, 5556–5558.

(9) Zhang, K.; Liu, N.; Twieg, R.J.; Auman, B.C.; Bos, P.J. *Liq. Cryst.* **2008**, *35*, 1191–1197.

(10) Lee, Y.J.; Gwag, J.S.; Kim, Y.K.; Jo, S.I.; Kang, S.G.; Park, Y.R; Kim, J.H. *Appl. Phys. Lett.* **2009**, *94*, 041113.

(11) Komitov, L. *J. Soc. Inf. Disp.* **2008**, *16*, 919–925.

(12) Kwok, H.S.; Yeung, F.S. *J. Soc. Inf. Disp.* **2008**, *16*, 911–918.

(13) Yeung, F.S.; Ho, J.Y.; Li, Y.W.; Xie, F.C.; Tsui O.K.; Sheng, P.; Kwok, H.S. *Appl. Phys. Lett.* **2006**, *88*, 051910.

(14) Wan, J.T.K.; Tsui, O.K.C.; Kwok, H.S.; Sheng, P. *Phys. Rev. E* **2005**, *72*, 021711.

(15) Vaughn, K.E.; Sousa, M.; Kang, D.; Rosenblatt, C. *Appl. Phys. Lett.* **2007**, *90*, 194102.

(16) Lee, J.H.; Kang, D.; Clarke, C.M.; Rosenblatt, C. *J. Appl. Phys.* **2009**, *105*, 023508.

(17) Bessonov, M.I.; Zubkov V.A. *Polyamic Acids and Polyimides*; CRC Press: Boca Raton, FL, 1993.

(18) Shioda, T.; Wen, B.; Rosenblatt, C. *Phys. Rev. E* **2003**, *67*, 041706.

(19) Huang, Z.; Rosenblatt, C. *Appl. Phys. Lett.* **2005**, *86*, 011908.

(20) Komitov, L.; Barbero, G.; Dahl, I.; Helgee B.; Olsson, N. *Liq. Cryst.* **2009**, *36*, 747–753.

(21) Komitov, L. *Thin Solid Films* **2008**, *516*, 2639–2644.

(22) Rapini, A.; Papoular, M. *J. Phys. Colloq. (France)* **1969**, *30*, 54–58.