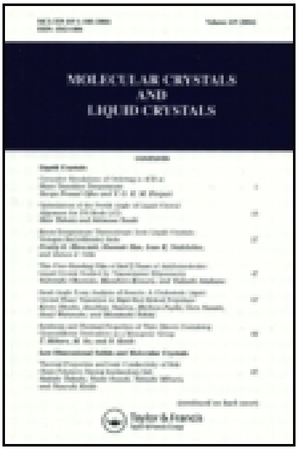

Molecular Crystals and Liquid Crystals

Nano-Structured Alignment Layers for Liquid Crystal Displays

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Version of record first published: 05 Oct 2009

To cite this article: H. S. Kwok, Y. W. Li & F. S. Yeung (2009): Nano-Structured Alignment Layers for Liquid Crystal Displays, Molecular Crystals and Liquid Crystals, 507:1, 26-40

To link to this article: http://dx.doi.org/10.1080/15421400903048040

Mol. Cryst. Liq. Cryst., Vol. 507, pp. 26–40, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903048040

Nano-Structured Alignment Layers for Liquid Crystal Displays

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The alignment of liquid crystal by nano-structured surfaces is investigated. Two methods of preparing the nano-structured inhomogeneous surfaces will be examined. It is shown that this type of surface can give excellent alignment properties. Reliable pretilt angles of any value between 0 and 9° can be obtained. Novel multi-domain structures can also be made in conjunction with photo-alignment. These nano-structured alignment layers are very useful for a variety of display applications.

Keywords: alignment; nanostructures

1. INTRODUCTION

The alignment of liquid crystal molecules is a critical step in the fabrication of liquid crystal displays. It is accomplished with an alignment layer on the glass substrate. Mechanically rubbed polyimide is used in most cases. Such alignment layers can provide pretilt angles of a few degrees from the surface normal or parallel to the surface and are deployed in a large scale commercially. There have also been several proposals to produce reliable high pretilt angles near 45° for various applications [1–14].

Recently we reported the application of nano-structured alignment layers for producing reliable pretilt angles of any value between 0° and 9° [15,16]. The idea is to allow two different alignment materials to form nano-domains on the alignment surface. If the domains are small enough, the alignment of the liquid crystal will be determined by the average

This project was financial support by the Hong Kong Research Grants Council contract number 614905.

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alignment action of the two kinds of materials. In particular, if one material gives a homogeneous alignment and the other one gives a homeotropic alignment, then any pretilt angle between 0° and 9° can be obtained.

In this paper, we present two approaches to the formation of such heterogeneous surfaces. Instead of trying to achieve a homogeneous uniform mixture of two different alignment materials, the alignment layer we produce is deliberately an inhomogeneous mixture of homogeneous and homeotropic materials. In fact, we shall show that nano-domains are necessary to achieve reliable high pretilt angles. Homogeneous mixture of two different materials will not work properly with reasonably large anchoring energies.

2. NANO-DOMAIN STRUCTURES

The central concept of the new alignment layer is to fabricate an inhomogeneous surface with nano-domains. If the domains are small enough, the alignment layer can also be very uniform. It is intuitively obvious that if there are two types of domains, one with homogeneous alignment and the other with homeotropic alignment, inside the liquid crystal cell, the liquid crystal molecules will tend to have an alignment direction that is in between these two extreme cases. So the important questions are how to produce the nano-domains reproducibly and how to predict the alignment of the LC molecules if one can achieve these nano-structures. The latter question is relatively easy to answer since it just involves the solution of the elastic energy minimization Euler-Lagrange equations. This issue will be examined first in this section.

The basic idea of employing a nano-structured surface is as follows. Consider a surface consisting of domains of vertical (V) and horizontal (H) alignment materials. The liquid crystal molecules near the surface are aligned either vertically or horizontally. Away from the surface, however, the liquid crystal molecules will re-align themselves to minimize the elastic deformation energy. This re-alignment should give rise to a uniform tilt angle of the liquid crystal that can be very large. The situation can be simulated using the continuum theory of LC molecule alignment. Basically we minimize the total free energy in the bulk as well as on the surface of the alignment layer. The total energy per unit area is given by

$$\frac{F_{\mathrm{tot}}(\boldsymbol{n})}{\lambda^2} = \frac{K_{11}}{\lambda}\left\{ \int_0^1 \int_0^1 \int_0^1 \widetilde{\boldsymbol{F}}_e(\boldsymbol{n})\,dxdydz + \sum_{i=1}^{2} \int_0^1 \int_0^1 \frac{\lambda}{\ell_{ei}} f_i(x,y)\,\frac{\sin^2(\theta-\theta_{0i})}{2}\,dxdy \right\} \qquad (1)$$

where λ is the average size of the domains, K_{11} is the splay elastic constant, l_{ei} is the extrapolation length of domain i, $f_i(x,y)$ is unity if (x,y) is in domain i and zero otherwise. $l_{ei} = K_{11}/W_{\theta_i}$ where W_{θ_i} is the polar anchoring energy of domain i. $F_e(\boldsymbol{n})$ is the usual bulk Frank's free energy:

$$F_e(\boldsymbol{n}) = \frac{1}{2}\{K_{11}(\nabla \cdot \boldsymbol{n})^2 + K_{22}(\boldsymbol{n} \cdot \nabla \times \boldsymbol{n})^2 + K_{33}(\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2\} \tag{2}$$

Figure 1 shows the calculated director field as a function of cell distance (z-direction) along the surface (x-direction) for adjacent V and H domains for the case of strong anchoring. It is evident that the discontinuity in the director field near the alignment layer is relaxed rapidly due to elastic energy minimization. The director achieves a uniform pretilt angle in a critical distance of less than 0.25λ. This is called the relaxation length. The relaxation length should be larger that the extrapolation length in order for the elastic theory to work properly. It is easy to see that if the domains are randomly distributed, the same uniform pretilt angle will also be achieved. This final pretilt angle will depend on the area ratio of H and V domains, the relative anchoring strengths of the domains as

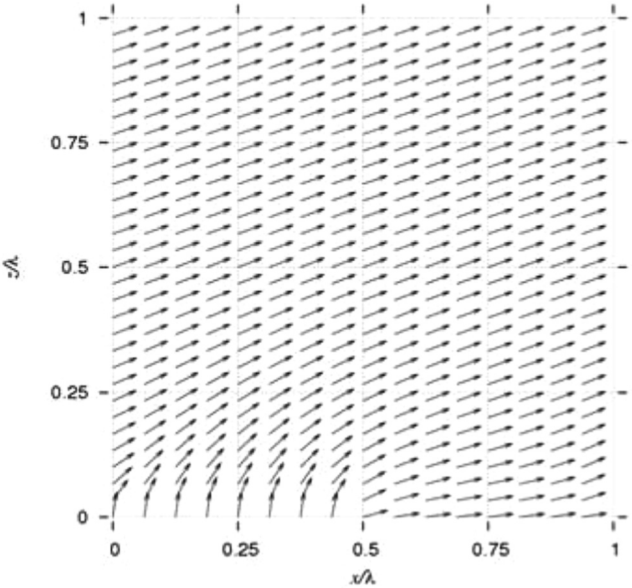

FIGURE 1 Director distribution for adjacent domains.

well as the elastic constants of the LC. Note that for the case of weak anchoring, this transition layer is absent and the LC has a uniform pretilt even on the alignment layer. It is straight forward to show that the average pretilt angle on the surface is given by

$$\theta_{av}(0) = \theta_1 + \frac{1}{2}\tan^{-1}\left(\frac{pW_{\theta 2}\ \sin 2(\theta_1 - \theta_2)}{pW_{\theta 2}\ \cos 2(\theta_1 - \theta_2) - (1-p)W_{\theta 1}}\right) \tag{3}$$

where p is the area fraction of vertical domains.

Figure 2 shows the calculated pretilt angle at large distances as a function of the area percentage p of the V domains. It is almost a straight line. The pretilt angle should depend on the ratio of the polar anchoring energies. However, it can be seen that for the range of ratios from 0.5 to 5.0, the calculated average pretilt angles are more or less the same. This is because of rather strong anchoring is used. For weak anchoring, the dependence on the ratio of $W_{\theta 1}/W_{\theta 2}$ will be stronger. It is also seen from Figure 2 that for small domain sizes, the uniform LC pretilt angle increases almost linearly with p. Since the result demonstrated no dependence on the finer details of the surface pattern such as the shape of the domains, it is expected that the result should be applicable to irregular surface patterns possessing a uniform length scale λ. For typical values of $W_{\theta i}$ ($\sim 10^{-4}$–$10^{-3}\,\mathrm{Jm}^{-2}$) and K_{11} ($\sim 10^{-11}$N), the strong anchoring limit ensues for $\lambda >> 0.01$–$0.1\,\mu$m.

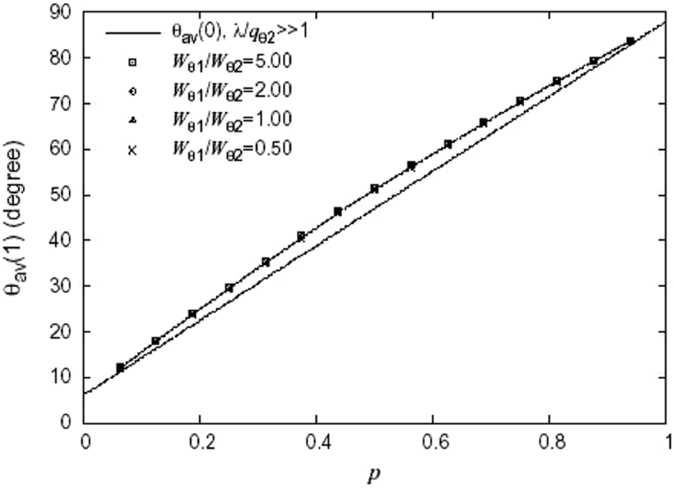

FIGURE 2 Calculated average pretilt angle as a function of area percentage of V domains.

If the domain distribution is random, then there will be a distribution of the pretilt angles at any distance. This distribution is more random near the surface and should be more uniform as z increases. Indeed, it is the case. The standard deviation of the distribution of θ can be half of the average value at $z = 0$, and decreases to near zero at $z = \lambda$.

3. ARE DOMAINS NECESSARY AND WHAT SIZE?

As mentioned in the Introduction, many attempts have been made to form a homogeneous uniform mixture of vertical and horizontal alignment materials in an attempt to get intermediate pretilt angles [3–12]. By and large, such attempts do not work too well. Actually one can use a simple physical argument to understand why such an approach should not give the desired results. Consider a uniform alignment layer consisting of both vertical and horizontal alignment materials in a ratio of A to B. Thus the surface energy density of the liquid crystal layer will show no spatial dependence and is simply given by

$$F_s = \iint (1-p)W_{\theta 1}\cos^2\theta + pW_{\theta 2}\sin^2\theta \, dS \tag{4}$$

where $W_{\theta 1,2}$ are the polar anchoring energies of the horizontal and vertical materials respectively. For reason of simplicity, we ignore the small pretilt angle that may be present for the vertical and horizontal materials. Obviously if p is zero, F_s is minimized at $\theta = 0$ and if $p = 1$, F_s is minimized at $\theta = 9^\circ$. This is intuitively obvious. Now for intermediate values of p, it is easy to see that F_s is minimized at either $\theta = 0$ or $\theta = 9^\circ$. The former solution is obtained if $(1-p)W_{\theta 1} < pW_{\theta 2}$ and vice versa. Intermediate solutions between 0 and 90° are not possible. This is a winner-takes-all situation for alignment. Thus for a uniform alignment layer without any domains, it is either vertical or horizontal alignment. Intermediate values are not achievable.

In fact this result has been obtained before [17]. In that experiment, a uniform layer of vertical alignment material is coated on a homogeneous alignment surface. It was shown that as the thickness of the second layer was increased, the tilt angle of the LC changed from horizontal to vertical alignment abruptly. More recently, Bos *et al* demonstrated the same result using a second alignment layer that either wet or unwet the first layer [18]. It was shown that if complete wetting occurred, then the dependence of tilt angle on the average thickness of the second layer was very abrupt. However if incomplete wetting occurred, then the dependence was more gentle, allowing all values of pretilt between 0 and 90° to be achievable. Thus domains are needed in order to have reliable intermediate pretilt angles by elastic energy minimization. It is not a good idea to form spatially homogenous mixture for the purpose of achieving a large pretilt angle. Presumably, if the second order term in the anchoring energy is used in Eq. (4), an intermediate pretilt angle may be possible. But the anchoring energy will be weak. It should also be noted that the nano-domains are difficult to observe. Thus there may be domain formation which can be mistaken as a homogeneous composition of two different materials.

Thus nano-domains are the best way to achieve an intermediate pretilt angle as shown in Figures 1 and 2. Spatially separated vertical and horizontal alignment domains will allow the liquid crystal molecules to relax to an intermediate tilt angle to minimize the total free energy. The question is what should be the optimal size of the domains? Since the relaxation length is about 0.25λ, and we would like to have a cell gap of at least 2 μm, λ should be about 100–500 nm. This will ensure that the relaxation length is at most 125 nm which is still much smaller than the cell gap. Note that the extrapolation length $l_{ei} = K_{11}/W_{\theta_l}$ is about 15 nm, thus the relaxation length is larger than the extrapolation length as required by elastic theory.

4. NANO-DOMAINS BY PRECIPITATION

The most difficult issue is how to obtain the nano-domains reliably without resorting to microfabrication techniques and photolithography. Phase segregation during the drying process can be used to achieve the random nano-domains [19]. The H and V alignment polyimides are first dissolved in a common solvent. They are then coated onto the substrate. Upon drying, because of the difference in solubility, one of the polyimides will precipitate first, to be followed by the remaining one. Thus phase segregation and domain formation will result.

Experimentally, commercial V and H-polyimides were dissolved and diluted in the standard solvent provided by the company. The resulting solution was used to form the alignment film on ITO coated glass by spin coating or printing. The coating technique is important as it determines also the rate of solvent evaporation. The liquid film is then allowed to solidify under a controlled environment. The solid film formation process is the crucial step in determining the structure of the resultant film. Essentially, since the H and V-polyimides are generally not miscible in the solid form, a segregation process occurs during drying of the liquid film. The rate of precipitation, the relative solubilities in the solvent, the surface wetting properties of the polyimides all play an important role in determining the final structure of the film.

The film was first preannealed at 90°C for 5 minutes followed by hard baking at 230°C for 90 minutes to allow imidization. During this heating process, the polyimide precursors phase separate into nano-domains rich in either polyimide or polyimide precursor before imidization completes. To produce azimuthal alignment in the polyimide film, the film surface was rubbed with a rayon cloth as in standard industrial processing. The rubbing direction defines the LC pretilt direction in the individual polyimide domains.

Figure 3 shows examples of such a nano-structured surface. It was taken with an AFM with a maximum scale of 5 µm. In that picture, the light colored domains correspond to the V-polyimide while the darker background is composed of the H-polyimide. It can be seen that the V-polyimide forms a Voronoi network in the latter case.

Cross-sectional AFM profiles of the 1.4 and 2.7 wt% samples show the V regions to be elevated by ~2.3 nm from the H regions, whereas the overall thickness of the film is ~7 nm according to ellipsoimetry.

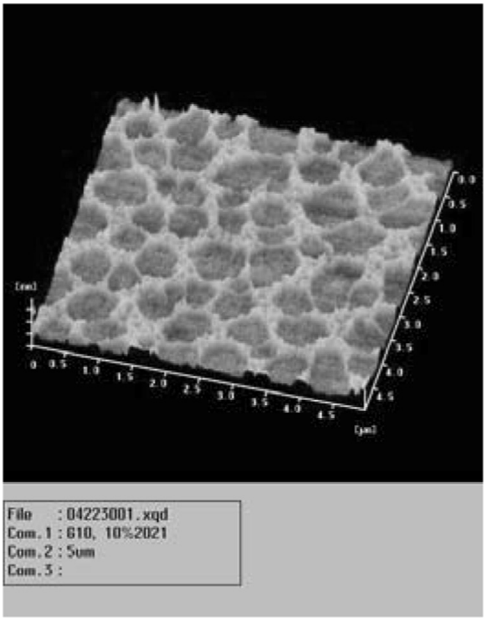

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FIGURE 3 Atomic force micrograph of the nano-structured surface. Light colored region corresponds to vertical polyimide.

Given the surface V domains to be only 2.3 nm thick, lying on top of a continuous layer of H-polyimide with thickness of approximately 10 nm, the observed initial rise in p can be very well accounted for.

It should also be noted that the value of p and the wt% are not proportional to each other from the AFM pictures. It is because that due to the difference in precipitation rate, the H-polyimide is always near the glass substrate. The area ratio of the V-polyimide is always larger than the volume ratio. In fact, if the V-polyimide precipitates at a later stage after the H-polyimide has all precipitated, then it is possible that the film will be entirely covered by the V-polyimide and the area ratio becomes unity no matter what the original volume ratio in the liquid film. This is in fact the case for V concentration of higher than 25% as shall be seen in Figure 4.

Many combinations of commercially available H and V-polyimides are tried in the experiment. By varying the volume ratio of the H and V-polyimides, the area ratio of V:H can be changed. Thus various pretilt angles can be obtained. Figure 4 shows the measured pretilt angle as a function of the volume ratio of the V material for the particular condition used. The results reported were obtained with JALS9203 and JALS2021 from Japan Synthetic Rubber Company. Other materials show similar results. It should be noted that even though the pretilt angles depend on the processing parameters and the materials used, the results are reproducible once the processing conditions are fixed.

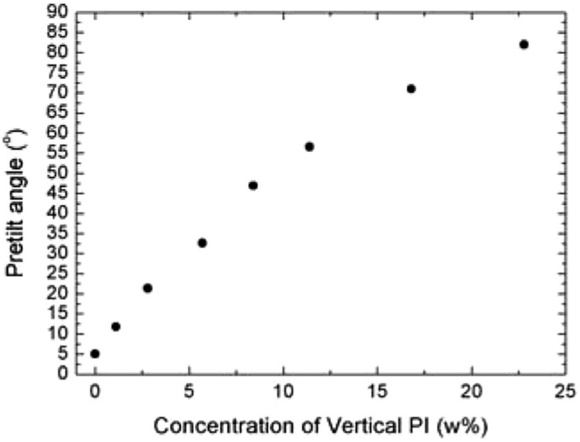

FIGURE 4 Measured pretilt angle as a function of concentration of the vertical polyimide.

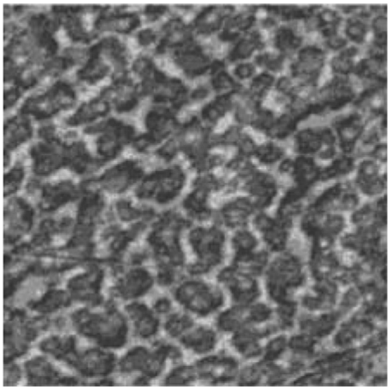

FIGURE 5 Morphology of the two-step surface.

5. NANO-DOMAINS BY TWO-STEP PROCESS

An alternative to the precipitation process is a two-step process [20]. In this technique, the horizontal and vertical alignment materials are deposited on the substrate separately. For example, the vertical alignment polyimide can be deposited, cured, before the second layer of horizontal alignment layer is deposited. The requirement for the second layer is that it should not wet the first layer. Thus domains are formed. One advantage of this method is that the requirement for the two materials to be miscible in a common solvent is no longer needed. Thus a wider range of materials can be used for form the

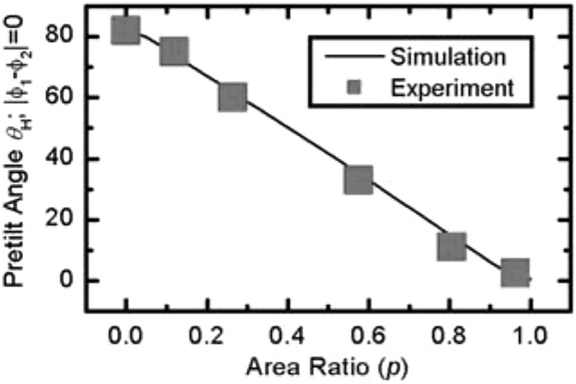

FIGURE 6 Dependence of the pretilt angle on the area ratio of the horizontal photoaligned surface.

nano-domains. In particular, photoalignment materials can be used for the second layer, adding to the flexibility and usefulness of the nano-structured surface.

Figures 5 and 6 show the result with a photoalignment layer as the second overcoat. Since the second layer does not wet the first layer, nano-domains are formed by Marangoni convection. Figure 5 shows the surface morphology for the two step process. Clearly, domains of the second layer are observed. Figure 6 shows the measured pretilt angle as a function of the average thickness of the second layer. The average thickness can be correlated to the area percentage of the second horizontal alignment layer.

6. PROPERTIES OF THE ALIGNMENT LAYER

The anchoring strength and the temperature stability of the new alignment surface have been studied and reported previously. Basically the anchoring energy is strong and similar to the original polyimides as expected. The temperature stability in terms of storage and operating temperature are also similar to the original polyimide as well. Here we report the dependence of the pretilt angle on some processing parameters.

6.1. Dependence on Baking Temperatures

Different baking condition of polyimides results in different pretilt angles. We have studied the dependence of curing temperature against pretilt angles. Three samples with the same concentration of vertical polyimide are coated on the glass substrates. They were then put into an oven in vacuum and hard-baked under different temperature. The samples were then taken out and assembled into test cells.

Figure 7 shows the result of the studies. The pretilt angles increase with decreasing hard-baking temperature. As the curing temperature for horizontal polyimides and vertical polyimides is around 230°C and 180°C respectively, for a hard-baking temperature below 230°C, most of the horizontal polyimides are not yet polymerized. Therefore, the pretilt angles and the alignment are not stable. In order to obtain a stable and repeatable result of pretilt angles, the curing temperature of 230°C is fixed to use as the hard-baking temperature.

6.2. Dependence on Hard-Baking Medium

In order to check the stability of the nano-structured alignment layer, hard-baking under different medium is studied. Five samples with

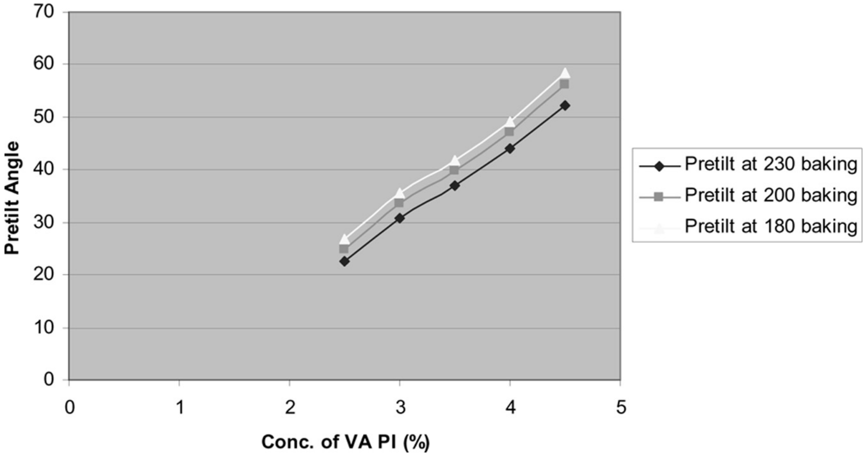

FIGURE 7 Dependence on hard-baking temperature.

different pretilt angles as shown in Figure 8 were put into three different 230°C oven in vacuum, filled with nitrogen and filled with air respectively. It was found that the pretilt angles remained almost unchanged under three different conditions as shown in Figure 8. It clearly shows that the pretilt angle is stable on different baking environment.

6.3. Dependence on Baking Time

The high-temperature stability of the nano-structured alignment layers was checked. A LC test cell was placed in an oven at 100°C for 24 hours. The pretilt angles did not change. Table 1 shows the

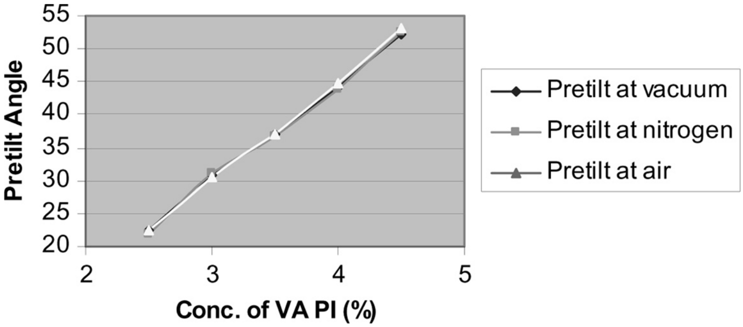

FIGURE 8 Dependence of hard-baking environment towards pretilt angles.

TABLE 1 Measured Pretilt Angles Before and After Baking for 24 Hours

	Before Baking	After Baking
Test Sample 1	32.3°	32.3°
Test Sample 2	44.9°	44.9°
Test Sample 3	58.6°	58.6°

measured pretilt angles before and after baking. In fact, the temperature stability is expected to be good since the components of the polyimides are commercially available and demonstrated well for LCD applications.

Three different samples with different pretilt angles as shown were put into an 180°C oven. The samples were taken out and their pretilt angles are checked at 2-hour intervals. The results are shown in Figure 9. It was found that the pretilt angles remained almost unchanged throughout the experiment. In fact, this temperature stability is to be expected since the individual polyimide is stable against temperature cycling. There is no reason for the nano-structured layer to be unstable against temperature cycling.

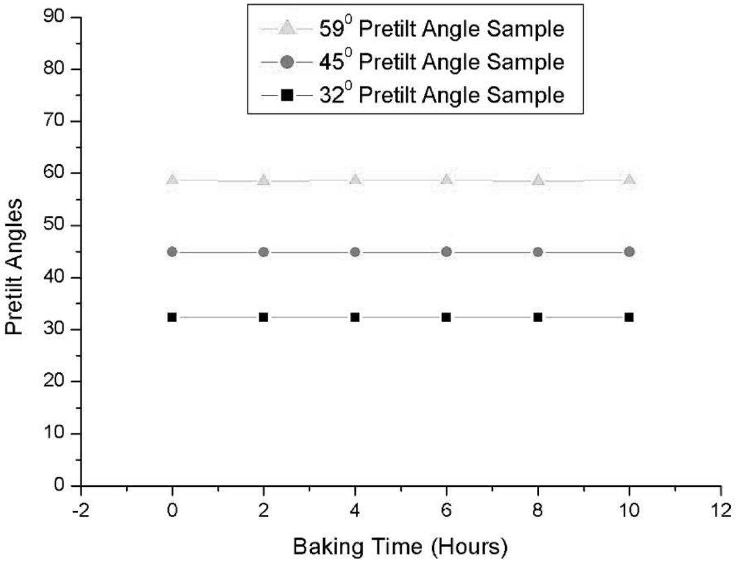

FIGURE 9 Stability of the pretilt angle as a function of baking time.

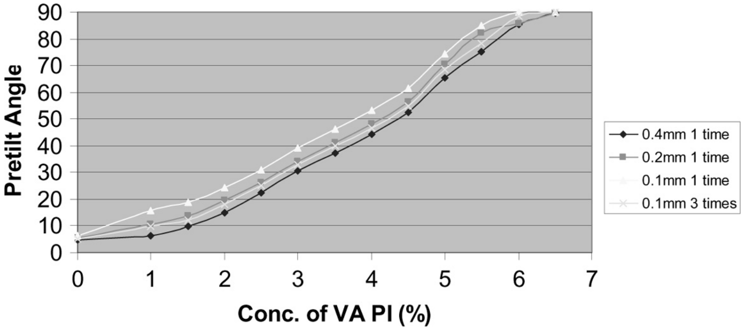

FIGURE 10 Measured pretilt angles under different rubbing strength.

6.4. Dependence on Rubbing Strength

The pretilt angles of the nano-structured alignment layer are directly proportional to the Rubbing Strength (RS) [21], where RS is defined as

$$\mathrm{RS} = NM(2\pi rn/V - 1) \tag{5}$$

Here N is the number of the repeated rubbing times, M is the depth of the deformed fibers of the cloth due to pressing (mm), n is the rotation rate of the drum (1500/60 s), V is the speed of the substrate (15.0 mm/s) and r is the radius of the drum (100 mm).

The polyimide film is rubbed using a drum which wrapped with a nylon cloth (Y-15) provided by Yoshikawa Chemical Industries Co. Ltd. Different combination of rubbing times and the rubbing depth of the rubbing cloth are studied. The result is shown in Figure 10. It can be seen that when RS increases, the pretilt angles decreases. As the number of repeated times for the rubbing process increases, damage to the coated polyimides occurs. Therefore, the best way to obtain a good alignment layer is to rub the alignment layer for one time only.

7. CONCLUSIONS

In summary, we have studied the properties and process conditions of the new nano-structured alignment layer. By forming nano-domains of two different kinds of polyimide, it is possible to obtain any pretilt angle from 0 to 9°. These nano-structured alignment layers are robust, resilient and reproducible. Even though the pretilt angle depends on many parameters, once these parameters are fixed, the pretilt angle produced is uniquely determined. The process window is very wide according to our study. The only issue is the large area uniformity of such surfaces. Presumably this is simply an equipment issue. Better processing equipment should produce uniform alignment layers over a large area.

The new alignment layer consists of nano-structures of two different polyimide materials, one for vertical alignment and the other for horizontal alignment. In fact, the same concept can be extended to any pair of alignment materials. For example, we have discovered that the combination of a non-aligning polymer and a conventional homogeneous polyimide can give homogeneous alignment with adjustable anchoring energies. This is due to the averaging effect of strong and no anchoring of the two individual components. The concept of nano-domains of different materials can also be extended to the case of photoalignment. It may be possible to use photoalignment techniques to create nano-domains as demonstrated in this paper [20]. The advantage of the photoalignment layer is that further multi domain structures can be achieved by selected area exposure. Such multi domains are useful for wide viewing angles and other bistable applications.

In fact, the concept of the nano-domains can be used to explain some of the earlier results as well. For example, it was found that the pretilt angle in vertical alignment polyimides becomes smaller as the rubbing strength increases [5]. We hypothesize that this is due to nano-domain formation as a result of damage to the polyimide layer. It is well known that vertical alignment polyimides will lose its alignment properties due to damage by strong visible light or ultraviolet light. It is believed that strong rubbing produces random domains of damaged non-aligning polyimide amidst a background of the vertical alignment polyimide. This nano-structure will result in a pretilt angle that is between 9° and 0. Thus the earlier result can be explained using the multi-domain argument.

The concept of a nano-structured alignment layer depends critically of course on the availability of nano-structures. Thus the fabrication technique of the nano-structure is of paramount importance. In the present study, we explored the use of differential precipitation for the formation of the nano-domains. Presumably, microfabrication techniques can also be used. Perhaps the new nano printing or inkjet printing technology can also be employed as well. We expect progress in this direction to be made as the demand for high pretilt angle increases. High pretilt angles are of course needed in the no-bias bend LCD cells and in bistable twisted nematic LCD.

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