Full control of nematic pretilt angle using spatially homogeneous mixtures of two polyimide alignment materials

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A mixture of two polyamic acids, one having an alkyl side chain and ordinarily used for vertical liquid crystal alignment, and the other without a side chain and ordinarily used for planar alignment, is deposited on two substrates and baked. It is found that: i) the polymer alignment layer does not phase separate and ii) the pretilt angle $\theta_0$ of a cell filled with liquid crystal pentylcyanobiphenyl is a function of the relative polymer concentration and can be controlled continuously over the range $0^\circ \leq \theta_0 \lesssim 90^\circ$. A model is proposed in which quartic terms in the surface energy are responsible for the smooth variation of $\theta_0$ with concentration.

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Control of a liquid crystal’s polar “pretilt” angle for applications such as optical gratings, light valves, and birefringence-control devices is an active endeavor. Various approaches have been used to create a spatially uniform pretilt angle $\theta_0$ at a substrate, where we define $\theta_0 = 0$ for vertical alignment and $\theta_0 = 90^\circ$ for planar alignment. These include irradiating SiC layers of varying composition with an ion beam [1], rubbing a polyimide that has a relatively rigid backbone designed for homeotropic alignment [2–5], and the use of a side chain copolymer with appropriate ratios of vertical- and planar-aligning side chain moieties [6]. Microscopically inhomogeneous surfaces — with separate regions promoting vertical alignment and planar alignment — also can provide controlled polar tilt in the bulk [7–9]: As one transits into the bulk liquid crystal, the surface-imposed orientation homogenizes, with a spatially uniform tilt $\theta$ sufficiently deep into the bulk. For example, a homeotropic alignment agent (silane) was printed in a grating pattern with variable period onto a planar aligning substrate to control pretilt [10, 11]. Recently, Yeung, et al deposited a mixture of vertical and planar-aligning polyimide precursors onto a substrate [9, 12]. The two components phase separated, resulting in very small (a few hundred nm) patches of vertical and planar alignment regions at the surface with an average pretilt angle $\theta$ in the bulk.

Until recently our group has controlled $\theta_0$ by varying the rubbing strength or baking temperature of a single-component polymer (Nissan Chemical Industries SE-1211) alignment layer that has two moieties — an alkyl side chain that promotes vertical and a backbone that promotes planar alignment [3, 13, 14]. Recently we showed that the pretilt angle is a function of baking temperature for one particular mixture involving SE-1211 and a planar aligning polyimide without a side chain, Nissan Chemical Industries’ RN-1175 [15]. In this case there was no obvious sign of compositional inhomogeneities at the surface. Now, to achieve our ultimate goal of patterning a spatial pretilt profile over the surface, we prepared cells using different polyimide concentrations (baked at the same temperature) and measured the resulting pretilt angles. Concentration is an important control: Although baking individual pixels at different temperatures to achieve a spatially varying pretilt angle profile is not possible, and rubbing individual pixels at different strengths is at best extremely difficult, controlling the relative concentration of the polyimides (and therefore the pretilt angle) on a pixel-by-pixel basis can be accomplished, in principle, by ink-jet printing techniques. Moreover, the imposition of a spatially-varying pretilt profile — especially for small pixels
— requires that the pretilt angle within the small pixels be uniform. For appropriate concentrations of the polyimides SE-1211 and RN-1175, we find no indication of micro- or nanophase separation using phase sensitive atomic force microscopy. Although it has been suggested that individual vertically-aligning and planar-aligning regions of order a few hundred nanometers on a side are required to produce a spatially homogeneous angle (θ ≠ 0 and θ ≠ 90°) well into the bulk [12], we find that this need not be the case. Rather, for appropriate mixtures of materials a spatially-uniform alignment layer can produce a controlled pretilt, a result consistent with a simple Landau model.

Commercially available polyamic acid RN-1175 was mixed with SE-1211 in various ratios. The mixtures were spin coated at 2000 rpm for 9 s onto indium tin oxide coated glass substrates. The substrates first were prebaked at 110 °C for 3 min, and then fully baked at 255 °C for 25 min. This baking temperature is significantly higher than that prescribed by the manufacturer (180 °C for 50 min), sufficient to cleave off a fraction of the side chains of SE-1211 and further imidize the backbones of both materials. This results in a large and robust pretilt angle relative to the vertical direction [3].

Both substrates were rubbed with a cotton cloth using an Optron rubbing machine; details are identical to those in Ref. [16] except that the roller rotation rate was ν = 25 instead of ν = 10 rotations per second in Ref. [16]. Thus, the “rubbing strength” n_f, which is defined as the number of fibers passing a position of unit width [17], was n_f = 2.1 × 10^5 cm\(^{-1}\). This is considered to be very weak rubbing, and is weaker by an order of magnitude than the minimum rubbing strength n_f ≈ 2 × 10^6 cm\(^{-1}\) typically required to affect θ\(_0\) using SE-1211 [3]. Thus, no measurable change is expected in polar angle by the weak rubbing. Each pair of slides was placed together, separated by glass spacers dispersed in a UV curable epoxy, in an antiparallel configuration and the thickness was measured by interferometry. Typical thicknesses \(d\) were (10 ± 0.2) \(μm\). The cells then were filled with the liquid crystal pentylcyanobiphenyl ("5CB", Merck).

To determine the pretilt angle \(θ_0\) vs. weight ratio in the nematic phase, light from a He-Ne laser (wavelength \(λ = 633\) nm) passed consecutively through a polarizer, a Babinet-Soleil compensator, the cell, an analyzer, and into a detector. The polarizer and analyzer are at +45° and −45°, respectively, to the rubbed direction of the cell. A potential difference of 50 V at frequency 1000 Hz was applied across the cell thickness; this drives the liquid crystal director orientation in the bulk to be perpendicular to the substrates, except very close to
the surfaces. On reducing the voltage of the cell continuously to zero and simultaneously adjusting the compensator, we determined the optical retardation $\alpha = 2\pi \Delta n_{\text{eff}}(\theta_0) d/\lambda$ of the cell at zero voltage, where the effective birefringence $\Delta n_{\text{eff}}(\theta_0) = n_{\text{e eff}}(\theta_0) - n_o = \left[\cos^2 \theta_0/n_o^2 + \sin^2 \theta_0/n_e^2\right]^{-1/2} - n_o$. Here $n_e = 1.719$ and $n_o = 1.528$ are the extraordinary and ordinary refractive indices, respectively, of 5CB at room temperature [18]. Moreover, the bulk polar angle $\theta$ was spatially uniform across the cell thickness (and equal to $\theta_0$) because of the identical treatment of the two substrates comprising each cell and their antiparallel orientation. Thus the pretilt angles $\theta_0$ were deduced from measurements of $\alpha$.

Figure 1 shows $\theta_0$ vs. weight fraction $R$ of RN-1175, i.e., $R = [RN - 1175]/\{[RN - 1175] + [SE - 1211]\}$. The insets correspond to topographies for $R = 0.38$ (a) and $R = 0.95$ (b); these will be discussed below. For small $R$ the pretilt angle is near zero because the alignment layer is composed entirely or mostly of the vertically-orienting polyimide SE-1211. Vaughn, et al had examined a single concentration as a function of baking temperature, finding a minimum temperature $T_{\text{min}}$ below which the orientation remains vertical [15]. Based on that work, it is clear from Fig. 1 that the baking temperature of 255 $^\circ$C used in this experiment was very slightly above $T_{\text{min}}$, and thus a small nonzero pretilt angle obtains for pure SE-1211. At higher concentrations of RN-1175 the pretilt angle increases relatively smoothly to $\theta_0 \approx 70^\circ$ at $R = 0.67$. For $R < 0.67$ we observed a uniform texture using polarized optical microscopy, but for $1.00 > R > 0.70$ we observed homeotropic-like orientation but with tiny ($< 1 \mu$m) textures due to microphase separation of the polyimides, as will be discussed below. Then for the pure RN-1175 composition ($R = 1$) we observed a uniform texture with a pretilt angle $\theta_0 = 82^\circ$, i.e., nearly planar.

An important issue is whether our surface is composed of a spatially uniform concentration of the two polyimides, or whether micro- or nanophase segregation is occurring, as observed by Yeung, et al [12]. To address this issue we performed tapping mode atomic force microscopy (AFM) using a Bioscope BS3-N (Veeco) scanning probe microscope to obtain topographical and phase images of the surfaces coated with the mixtures of RN1175 and SE1211. Phase detection is particularly sensitive to compositional variations at the surface, as it reflects the viscoelastic properties of the materials, and provides contrast between micro- or nanophase species far superior to topographical measurements [19, 20]. To exclude topographical effects from the phase images, the AFM double-scanned each line, such that
topography was obtained from the first scan (see insets in Fig. 1). This information was used in feedback to control the probe during the second line scan to obtain 5 μm × 5 μm phase images, with a resolution of 9.8 nm. The scan speed was 10 μm s⁻¹, and a silicon cantilever stylus with spring constant 42 N m⁻¹ was oscillated at the fundamental resonance frequency of 310 kHz.

Figure 2 shows four phase mode images for weight fractions \( R = 0.38 \) (a), \( R = 0.67 \) (b), \( R = 0.95 \) (c), and \( R = 1.00 \) (d). [Note the difference in the vertical scales]. The two lowest RN-1175 concentrations (a,b) and the pure RN-1175 (d) show a virtually homogeneous composition across the surface, with phase variations under 0.1° (a) and 1° (b,d). This is not the case for Fig. 2c, corresponding to \( R = 0.95 \), which shows significant phase structure, with variations of order 40° from one region of size several hundred nm to the next. This also corresponds to the concentration region that showed microscopic domains using optical micrography. In Fig. 3 we show the phase variation for a single slice along the x-axis for the four concentrations, all using a common vertical scale. Relative to the large phase variations associated with weight fraction \( R = 0.95 \), the other three show virtually no structure, indicating a high level of compositional uniformity. These are the same concentrations for which the polarized optical micrographs show no domain structure. Based upon the results of Figs. 1 through 3 it is clear that uniform mixtures of appropriate vertical- and planar-aligning polyimide can result in a continuum of pretilt angles over almost the entire range \( 0° < \theta_0 < 90° \).

As an aside, we note the extremely rough topography for \( R = 0.95 \) in Fig. 1, inset (b). Here we believe that the more hydrophobic SE-1211 preferentially segregates to the free surface, promoting vertical alignment of the 5CB. Owing to the much deeper topography in Fig. 1 inset (b) as compared to inset (a), the crenellations of the rubbing fibers [having radius of curvature \( r = (700 ± 70) \) nm as measured by AFM] cannot reach into the deep troughs. Thus the troughs produce a random azimuthal orientation on length scales \( \lesssim 0.5 \) μm, and are responsible for the tiny optical domains in the otherwise homeotropic bulk. This will be the subject of future investigation.

Let us turn to a Landau model to understand why a spatially homogeneous alignment layer can produce a surface orientation \( \theta_0 \) different from \( 0° \) and \( 90° \). We assume that for a fully-mixed alignment layer the \( \theta_0 \)-dependent surface free energy \( f_{\theta_0} = \)
\[ \frac{1}{2} \left( A \sin^2 \theta_0 + B \cos^2 \theta_0 + C \sin^4 \theta_0 + D \cos^4 \theta_0 \right), \]

where the coefficients \( A \) and \( B \) are the quadratic anchoring strength coefficients in the Rapini-Papoular approximation [21], and \( C \) and \( D \) are quartic coefficients [23, 24]. This form for \( f_\theta \) assumes a pair of orthogonal easy axes, one vertical (\( \theta_0 = 0 \)) due to the side chains and one planar (\( \theta_0 = 90^\circ \)) due to the backbone, which has been shown experimentally to be appropriate [13, 14]. \( f_\theta \) represents only the initial few terms in the expansion. First keeping only the quadratic terms, \( f_\theta = \frac{1}{2}B + \frac{1}{2}(A - B) \sin^2 \theta_0 \), which is minimum at \( \sin \theta_0 = 0 \) for \( A > B \) and at \( \sin \theta_0 = 1 \) for \( A < B \). Such a free energy would suggest that the equilibrium orientation could be only vertical or planar if only the quadratic terms were retained; this corresponds to a two-state system suggested by Kwok [25]. However, it is well known that for large deviations from the easy axis it is necessary to retain higher order terms in \( f_\theta \). [23, 24, 27, 28]. This certainly is the case here as any significant pretilt would correspond to large deviations from the easy axes. Now keeping both the quadratic and quartic terms, we find that

\[ f_\theta = \frac{1}{2}(B + D) + \frac{1}{2}(A - B - 2D) \sin^2 \theta_0 + \frac{1}{2}(C + D) \sin^4 \theta_0; \]

thus \( f_\theta \) can be minimized for \( \sin \theta_0 = 0 \), \( \sin \theta_0 = 1 \), or for some intermediate value of \( \sin \theta_0 \) depending upon the relative magnitudes of the coefficients and the signs of \( C \) and \( D \), which can be positive or negative [24, 27, 28]. It is clear that the extended free energy, which includes beyond-quadratic terms, admits a continuum of solutions for \( \theta_0 \). Moreover, for our materials the quartic coefficients apparently are sufficiently large to provide a smooth variation in \( \theta_0 \) vs. \( R \).

To be sure, rubbing of the alignment layer could have resulted in a pair of not-quite-orthogonal easy axes, and thus in pretilt angles different from 0 and 90° [26]. However, our very soft rubbing strength is much weaker than the minimum required to induce a nonzero pretilt in previous experiments using pure SE-1211 [3]. Moreover, by means of optical microscopy we examined an unrubbed sample using a mixture \( R = 0.38 \), and found that \( \theta_0 \) is consistent with that of the weakly rubbed cell (Fig. 1). Thus, the observed pretilts are due to higher order contributions to \( f_\theta \) rather than to non-orthogonal easy axes.

To summarize, we have demonstrated that controlled pretilt of the liquid crystal can be achieved by a homogeneous mixture of two appropriate polyimides. Because the pretilt angle \( \theta_0 \) can be a sufficiently weak function of relative concentration \( R \), it becomes possible to micropattern a \( \theta_0 \) vs. \( x,y \) profile on a substrate.

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FIG. 1: Pretilt angle $\theta_0$ vs. $R$, the weight fraction of RN-1175. Insets show topography for $R = 0.38$ (a) and $R = 0.95$ (b).

FIG. 2: Phase mode AFM images for RN-1175 concentrations $R = 0.38$ (a), $R = 0.67$ (b), $R = 0.95$ (c), and $R = 1.00$ (d). Note the different vertical axes in each panel.

FIG. 3: Typical phase difference vs. $x$ for a single slice in each panel in Fig. 2. Here a common vertical axis scale is used. $R = 0.38$ (Fig. 2a) corresponds to the nearly flat trace near $\Delta \varphi = 0$. 
Pretilt angle $\theta_0$ (degrees)

Weight ratio $R \ RN-1175 : SE-1211$
Phase difference $\Delta \varphi$ (degrees)

- $R = 0.67$ (b)
- $R = 0.95$ (c)
- $R = 1.00$ (d)

X Position (nm)