

# Template induced chiral ordering in nematic liquid crystalline materials

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# Template induced chiral ordering in nematic liquid crystalline materials: A deuterium nuclear magnetic resonance study

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## Template induced chiral ordering in nematic liquid crystalline materials: A deuterium nuclear magnetic resonance study

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Glancing angle deposition is used to create porous liquid crystal alignment layers with high aspect-ratio, three-dimensional features. We use solid-state deuterium nuclear magnetic resonance to determine the alignment of alpha deuterated 4'-pentyl-4-cyanobiphenyl in a 3.2  $\mu\text{m}$  thick  $\text{SiO}_2$  film comprised of independent, helical structures. Comparing measured spectra with models, we determine that the liquid crystalline molecules exhibit chiral ordering dictated by the features of the template films. In the plane of deposition the liquid crystalline molecules tilt away from the substrate normal at an average angle of  $51^\circ$ , which is commensurate with the helical features of the chiral template. © 2006 American Institute of Physics. [DOI: 10.1063/1.2200882]

The director configuration of a liquid crystal in a confined environment depends on the delicate interplay between the elastic, surface, and external field forces.<sup>1</sup> Surface alignment approaches make use of materials such as rubbed polyimide layers,<sup>2</sup> self-assembled monolayers,<sup>3,4</sup> and thin films of obliquely evaporated  $\text{SiO}_x$ <sup>5,6</sup> to achieve a desired configuration. Molecular surface energies and surface pretilt angles tend to be radically different from material to material, depending on the nature of the interactions between the liquid crystalline molecule and the surface alignment layer. Confining liquid crystals to porous materials with large surface area to volume ratios results in complex and varied director profiles. The interaction of liquid crystals with a plethora of confining materials has been studied including Anopore and Nucleopore membranes,<sup>7</sup> and polymer dispersed liquid crystals (PDLCs).<sup>8,9</sup> The director profiles observed in these systems are influenced by a number of factors including cavity size, pore shape, and surface interactions.

Here we report the results of a solid-state deuterium nuclear magnetic resonance ( $^2\text{H-NMR}$ ) study in which liquid crystal confinement is provided by porous, chiral, microstructured thin films deposited by glancing angle deposition (GLAD).<sup>10</sup> Glancing angle deposition is a physical vapor deposition process in which the substrate is tilted such that the substrate normal forms a high angle of incidence with the source ( $>80^\circ$ ). This results in the growth of thin films—micrometers in thickness—comprised of independent, high aspect-ratio microstructures with tunable architectures and

large surface area to volume ratios. In-plane substrate motion during the deposition process can produce a wide range of geometries, including slanted posts, zigzags, and square spirals, which can be designed to have a three-dimensional photonic band gap.<sup>11</sup> The films used in this study are produced by continuously rotating the substrate during deposition, resulting in the growth of a chiral film; where the pitch and handedness of the helices are determined by the speed and direction of rotation, respectively. A scanning electron microscope (SEM) image of a helical film is shown in profile and from the top in Fig. 1.

It has been shown that helical GLAD films deposited from transparent materials, such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{MgF}_2$ , exhibit circular birefringence, which can be enhanced by the addition of liquid crystals.<sup>12,13</sup> However, the actual alignment of liquid crystals, which is a critical factor for the optimization of these systems, was only speculated.  $^2\text{H-NMR}$  provides an effective determination of liquid crystal molecular

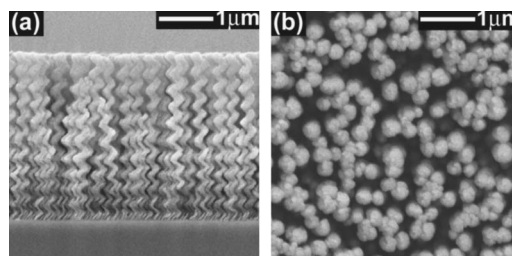


FIG. 1. SEM images of chiral structures with a pitch of  $\sim 320$  nm deposited on  $\text{SiO}_2$  films by glancing angle deposition shown in profile (a) and from the top (b).

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orientation in confined geometries with micrometer and nanometer length scales.<sup>7-9</sup> In  $^2\text{H-NMR}$  the host material is filled with liquid crystalline molecules deuterated at a specific site [in this case alpha deuterated 4'-pentyl-4-cyanobiphenyl (5CB- $\alpha d_2$ )], and the liquid crystal molecules tend to align along the direction of the magnetic field  $\mathbf{B}$ . Provided that the average pore size is considerably less than the characteristic diffusion length ( $\sim 10$  nm) and the magnetic coherence length ( $\xi_M = 1.6$   $\mu\text{m}$ ) is much larger than the cavity size, the alignment will be dominated by the surface of the pores.<sup>7-9</sup> Since here the average pore size is 30–300 nm these conditions are met. The  $^2\text{H-NMR}$  spectra therefore reflect the orientational distribution function of the director profile within the geometry, and are directly proportional to the orientational order parameter.<sup>7</sup>

For uniaxially aligned liquid crystals in the nematic phase, the resonance spectra consists of two peaks whose splitting is determined by two factors: the angle between the director and the external  $\mathbf{B}$ ,  $\theta_B$ , and the order of the system  $S$ . For a liquid crystal molecule at position  $r$ , the relationship between the resonance frequency  $\nu(r)$  and the angle between the local director and the  $\mathbf{B}$ ,  $\theta_B(r)$ , is  $\delta\nu(r) = \pm \delta\nu_B S(r) / 2S_B [3 \cos^2 \theta_B(r) - 1]$ , where  $\delta\nu_B$  and  $S_B$  are the splitting and order parameter of the bulk material.<sup>14</sup> The resulting spectrum is comprised of a superposition of the individual molecular spectra, and results in a measurement of the orientational distribution function.

To predict the alignment at the surface of the helices, we first evaporated 100 nm of  $\text{SiO}_2$  onto a glass substrate at normal incidence yielding a solid, nonporous film, and found that when 4'-pentyl-4-cyanobiphenyl (5CB) was applied to the sample, a multidomain planar orientation was observed between crossed polarizers suggesting that planar anchoring will also occur at the surface of the chiral structures. We therefore hypothesize three possible director configurations that may exist in the cavities between the helices. The first case is that of uniform alignment, in which the liquid crystalline molecules uniformly follow the chiral twist at a constant tilt angle (with respect to the substrate normal) dictated by the rise angle of the GLAD oriented pillars. The second possibility is the liquid crystalline molecules generally follow the chiral twist at a constant tilt angle, with a Gaussian distribution around this value that accounts for variations due to the thickening of the helical structures and local irregularities. The third possibility is inspired by the escaped radial and escaped twisted configuration observed in porous membranes,<sup>15</sup> and is characterized by an evolution of the tilt angle from the  $49^\circ$  rise angle at the surface of the helix to  $0^\circ$  midway between adjacent chiral pillars. For each hypothesized configuration, the angular distribution of liquid crystalline molecules was calculated, and used to generate the corresponding simulated  $^2\text{H-NMR}$  spectra for  $\mathbf{B}$  parallel and perpendicular to the substrate normal.

Samples were prepared for  $^2\text{H-NMR}$  measurements by filling a ten-turn helical GLAD film, 3.2  $\mu\text{m}$  in height, with 5CB- $\alpha d_2$  by spin-coating a solution of deuterated liquid crystal diluted with dichloromethane. The film was then cleaved into narrow strips approximately 25 mm in length, and nine strips were stacked in an NMR tube with a 1 cm

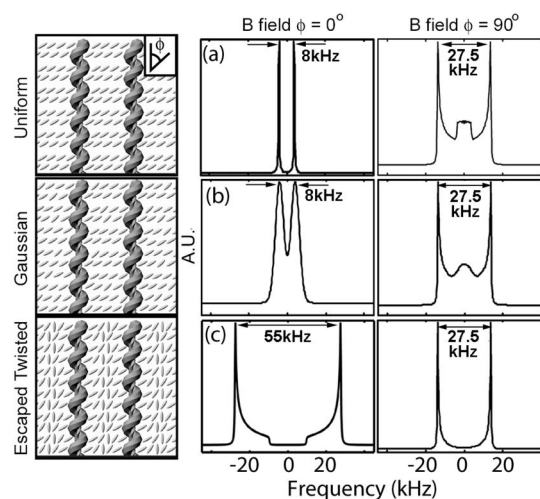


FIG. 2. Schematic diagrams and calculated spectra for three model director orientations: uniform ( $\theta = 49^\circ$ ) (a), Gaussian ( $\theta = 49^\circ$ ,  $\sigma = 3^\circ$ ) (b), and escaped twisted ( $\theta = 49^\circ$  at the surface of the structure, and linear evolution to  $\theta = 0^\circ$  at the center of the space between two structures) (c). Calculated spectra are shown for two orientations between  $\mathbf{B}$  and the substrate normal.

diameter; Teflon tape acted as a spacer between adjacent layers.  $^2\text{H-NMR}$  measurements were performed with a 7.05 T superconducting magnet and a solid-state spectrometer (AVANCE™ 300/Ultrashield™, 300 MHz, 89 mm, Bruker BioSpin GmbH). Due to the small volume of deuterated liquid crystalline material in the sample ( $< 100$   $\mu\text{L}$ ) considerable averaging was required to enhance the signal-to-noise ratio. Measurements were averaged over  $30 \times 10^6$  free induction decays (FID) signals, from which the Fourier spectra were calculated. The temperature of the sample was controlled at  $27^\circ\text{C}$ , well below the nematic-isotropic transition temperature of  $35^\circ\text{C}$ . Rotating the sample tube around its cylindrical axis varied the angle ( $\phi$ ) between the  $\mathbf{B}$  and the substrate normal; data were collected with the substrate normal parallel and perpendicular to the  $\mathbf{B}$ .

The rise angle of the helices used in this study was determined by examining the SEM image shown in Fig. 1. The angle formed between the arm of the helix and the substrate was measured at 15 arbitrary points, the average of which was  $49^\circ$ . The standard deviation of these measurements was  $3^\circ$ . The range of angles observed results, in part, from the broadening in the structure that occurs during growth.

Schematic diagrams for each model configuration are shown in Fig. 2, along with calculated  $^2\text{H-NMR}$  spectra. Figure 2(a) illustrates the simulated spectrum for a uniform configuration of liquid crystals oriented at  $49^\circ$  with respect to the substrate normal following the helical twist of the pillars. For  $\phi = 0^\circ$  ( $\mathbf{B}$  parallel to chiral pillars), the simulation yields two sharp peaks separated by 8 kHz; for  $\phi = 90^\circ$  ( $\mathbf{B}$  perpendicular to chiral pillars) a modified cylindrical distribution is simulated, with a uniform distribution of molecules from  $49^\circ$ – $90^\circ$ ,<sup>16</sup> resulting in two sharp peaks corresponding to the molecules oriented perpendicular to the  $\mathbf{B}$ , as well as a contribution from the molecules oriented near the magic angle ( $54.5^\circ$ ).<sup>9</sup> If a distribution function is added with a standard deviation of  $\sigma = 3^\circ$  to account for random variations within the sample, the spectra, as seen in Fig. 2(b), are broadened as



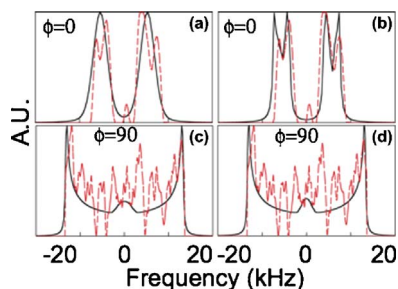


FIG. 3. (Color online) Measured  $^2\text{H}$ -NMR spectra for **B** parallel ( $\phi=0^\circ$ ) and perpendicular ( $\phi=90^\circ$ ) to the substrate normal, with theoretical Gaussian spectra overlaid. A single line splitting fit corresponding to  $50.8^\circ \pm 1.0^\circ$  is applied for the parallel (a) and perpendicular (c) cases; a double line splitting fit for  $49.6^\circ \pm 1.0^\circ$  and  $51.7^\circ \pm 1.0^\circ$  applied for the parallel (b) and perpendicular (d) cases. All fits contain a standard deviation of  $2^\circ$ .

expected, with peak spectral signatures matching those of Fig. 2(a). Figure 2(c) illustrates a schematic of the escaped-twisted configuration as well as the simulated spectra. The  $\phi=0^\circ$  case contains two peaks at the bulk splitting frequency as the majority of molecules in such a configuration are aligned in the field—the number of molecules contributing to the spectra in this configuration is proportional to the distance from the pillar. Since molecules at the magic angle are not represented in this configuration (as  $\phi$  ranges only from  $41^\circ$  to  $0^\circ$ ), there is no contribution in the center. When the sample is oriented at  $\phi=90^\circ$ , in Fig. 2(c), most molecules are now oriented  $90^\circ$  to the **B**, so the two lines are observed with a splitting of half the bulk.

The measured spectra are presented in Fig. 3 and overlaid with fitted spectra following the model above. By inspecting our simulated spectra in Fig. 2, we can immediately rule out the escaped-twisted structure as the experimental  $\phi=0^\circ$  spectrum in Fig. 3(a) has a narrow splitting of 5.4 kHz, a feature not present in the simulated escaped-twisted spectrum. The spectrum in Fig. 3(a) is fit with a Gaussian distribution of molecules following the chiral pillars oriented at  $50.8^\circ$  with respect to the **B**, which agrees well with the measured rise angle of the helices of  $49^\circ \pm 3^\circ$ . The Gaussian distribution used a  $\sigma=2.0^\circ$  to broaden the lineshapes as discussed earlier. Although we do not expect diffusion to influence our spectral shape, it should be noted that for a uniform distribution, such as the data and fit in Fig. 3(a), diffusion will never modify the lineshape as the molecules are at a constant angle with the **B** even in the fast diffusion regime. The 5.4 kHz splitting matches well with the simulated fit. Rather than fitting with a single angle broadened by a Gaussian distribution it is also possible to fit the data with a spectra corresponding to contributions from two fixed angles. This is shown in Fig. 3(b), with splittings corresponding to  $49.6^\circ \pm 1.0^\circ$  and  $51.7^\circ \pm 1.0^\circ$ . The  $^2\text{H}$ -NMR technique is extraordinarily sensitive to angles in this region because of the slope of  $\delta\nu$ . This fit is in excellent agreement with the observed spectra; however, we expect that variations

in angle are dictated by inhomogeneities in the helical film itself, which should evolve gradually rather than at two discrete angles. The presence of these two peaks may simply reflect the sensitivity of this method at these angles. Alternatively, uneven stacking of the substrate layers in the NMR tube cannot be ruled out.

We also rotated the sample to  $90^\circ$  with respect to the **B**. With such little material, we expected an extremely low signal spectrum, which is clearly the case. However, it does provide an additional check to our model and the more convincing  $\phi=0^\circ$  spectrum. Although the spectra in Figs. 3(c) and 3(d) exhibit poor signal-to-noise ratios, the same distributions used to fit the spectra in Figs. 3(a) and 3(b), respectively, correspond well with observed splittings for the  $\phi=0^\circ$  case. Due to the low signal-to-noise ratio, we could only match the splitting, not the details of the center portion of the spectra.

In conclusion, we have shown that  $^2\text{H}$ -NMR is a highly useful tool to determine the alignment of liquid crystalline molecules in a chiral GLAD template. This approach paves the way towards deciphering the interaction of liquid crystals in three-dimensional photonic crystals, for which index matching could potentially be used to make photonic devices and optical switches.

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<sup>1</sup>K. Miyano, Phys. Rev. Lett. **43**, 51 (1979).

<sup>2</sup>S. Ishihara, H. Wakemoto, and K. Nakazima, Liq. Cryst. **4**, 669 (1989).

<sup>3</sup>V. K. Gupta and N. L. Abbott, Science **276**, 1533 (1997).

<sup>4</sup>H. T. A. Wilderbeek, J. P. Teunissen, C. W. M. Bastiaansen, and D. J. Broer, Adv. Mater. (Weinheim, Ger.) **15**, 985 (2003).

<sup>5</sup>J. L. Janning, Appl. Phys. Lett. **21**, 173 (1972).

<sup>6</sup>T. Motohiro and Y. Taga, Thin Solid Films **185**, 137 (1990).

<sup>7</sup>G. P. Crawford, M. Vilfan, J. W. Doane, and I. Vilfan, Phys. Rev. A **43**, 835 (1991).

<sup>8</sup>I. Amimori, J. N. Eakin, J. Qi, G. Skacej, S. Zumer, and G. P. Crawford, Phys. Rev. E **71**, 031702 (2005).

<sup>9</sup>A. Golemme, S. Zumer, D. W. Allender, and J. W. Doane, Phys. Rev. Lett. **61**, 2937 (1988).

<sup>10</sup>K. Robbie, M. J. Brett, and A. Lakhtakia, Nature (London) **384**, 616 (1996).

<sup>11</sup>S. R. Kennedy, M. J. Brett, H. Míguez, O. Toader, and S. John, Photonics Nanostruct. Fundam. Appl. **1**, 37 (2003).

<sup>12</sup>A. C. van Popta, J. C. Sit, and M. J. Brett, Appl. Opt. **43**, 3632 (2004).

<sup>13</sup>J. C. Sit, D. J. Broer, and M. J. Brett, Adv. Mater. (Weinheim, Ger.) **12**, 371 (2000).

<sup>14</sup>G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991).

<sup>15</sup>D. W. Allender, G. P. Crawford, and J. W. Doane, Phys. Rev. Lett. **67**, 1442 (1991).

<sup>16</sup>G. Chidichimo, Z. Yaniv, N. A. P. Vaz, and J. W. Doane, Phys. Rev. A **25**, 1077 (1982).