Effect of smectic short-range order on the discontinuous anchoring transition in nematic liquid crystals

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We report studies on the temperature dependent alignment behavior of a homologous series of trans, trans-4,4′-dialkyl-(1α,1′α-bicyclohexyl)-4β-carbonitrile (CCNs) on a perfluoropolymer coated cells. Among six compounds in the series, one (CCN-35) has only nematic phase and the remaining five have either smectic-A or smectic-B in addition to the nematic phase. We simultaneously performed temperature dependent dielectric measurements and optical polarising microscope observation. It is found that except for CCN-35 and CCN-73, the remaining four compounds exhibit discontinuous anchoring transition from planar to homeotropic and vice versa with increasing thermal hysteresis. We developed a simple theory taking into account the effect of smectic short-range order at the substrates to explain the experimental observations. © 2014 AIP Publishing LLC.

I. INTRODUCTION

The molecules in liquid crystal displays (LCDs) are oriented in a particular direction with respect to the confining substrates. Generally, two types of orientations are preferred for both LCDs and for physical measurements, namely, planar and homeotropic. In the planar state, the director (the average direction of molecular orientation1) is parallel and in the homeotropic state the director is perpendicular to the substrates. There are various techniques for aligning liquid crystal molecules on the substrates. One common and inexpensive technique is coating of appropriate polyimides to get the desired alignments (planar or homeotropic). It is known that the alignment of liquid crystal molecules depend upon topography of the surfaces, chemistry of the liquid crystals, aligning agents, curing temperatures, and the rubbing strengths.2–4 The commercial aligning agents provide stable director alignment in the sense that it does not change the molecular orientation with temperature. However, there are some reports that on some unconventional alignment layers, the director can change its orientation from planar to homeotropic and vice versa continuously or discontinuously with temperature.9–12,14–22 Consequently, some theories are developed that shows the effect of various interactions on the alignment properties such as van der Waals interaction,23–25 short range dipole interaction, long range electrostatic interactions,26 and smectic short-range order effect.6,8 In the recent past, we have reported on the discontinuous anchoring transition of a nematic liquid crystal (CCN-47) from planar to homeotropic with a large thermal hysteresis on perfluoropolymer treated cells.27 We showed the possibility of various interesting applications, for example, rewritable memory device,28–30 bistable dielectric, and conductivity in this system.32 However, the reason for discontinuous anchoring transition in this system remained unexplored. In this paper, we studied the alignment properties of the homologous series of CCNs liquid crystals on perfluoropolymer. Interestingly, we found that two compounds do not show any anchoring transition. The remaining four compounds exhibit strong discontinuous anchoring transition in the nematic phase with increasing thermal hysteresis. Our experimental results suggest that the effect of smectic short-range order and the temperature range of nematic is important for the observed discontinuous anchoring transition. We developed a simple theory taking into account the short-range smectic order at the substrates that explains the experimental results.

II. EXPERIMENT

The chemical structure and the phase transition temperatures of compounds are shown in Fig. 1 and in Table I. The compound CCN-35 shows only one liquid crystalline phase, i.e., nematic (N). CCN-38 and CCN-47 show both nematic and smectic-A (SmA) phases. The remaining compounds CCN-46, CCN-55, and CCN-73 show both nematic and smectic-B (SmB) phases. Some physical characterizations such as X-ray, NMR, and dielectric relaxation studies have already reported.33–36 The molecules have transverse dipole moments (cyano group, -CN) and exhibits low birefringence and large negative dielectric anisotropy.37,38

The experimental cells were made of two indium tin oxide (ITO) coated glass plates with circularly patterned electrodes. These plates were spin coated with perfluoropolymer, poly [perfluoro (4-vinyloxy -1-butene)], known as CYTOP. A solution was prepared by adding 1 part of CTX-809A to 2 parts of CT-Solv.180 by weight and these were obtained...
from Asahi Glass Co., Ltd. Japan. The CYTOP coated glass plates were cured at 100 °C for 30 min. Cells were made by placing together such that their active areas overlapped. The typical cell thickness used in the experiment was ∼8 μm. The empty cell was heated and filled with the sample in the isotropic phase. The phase transitions and the anchoring transitions of the compounds were observed using a polarizing optical microscope (Nikon, LV100 POL) and a temperature controller (Instec, mk1000). The temperature dependent dielectric constant was measured by using a LCR meter (Agilent 4980) in cooling and heating at a temperature step of 0.1 °C/min. A sinusoidal voltage of frequency 1 kHz and an amplitude 0.2V was used for the dielectric measurements. The phase transition temperatures of the compounds and their anchoring transition temperatures were determined from the dielectric data.

### III. RESULTS AND DISCUSSIONS

We present some representative textures of four compounds (CCN-35, CCN-38, CCN-55, and CCN-73) in un-rubbed CYTOP coated cells at various temperatures in Fig. 2. In CCN-35, below isotropic-nematic phase transition temperature a Schlieren texture with both half and integer strength disclinations are observed (Figs. 2(a)–2(b)). This suggests that the director is in the plane (planar anchoring), as any tilt of the director in this case is topologically not allowed.40, 41 It crystallizes at 38.4 °C without any smectic phase. The Schlieren texture remains the same in the entire nematic range suggesting no anchoring transition. CCN-38 exhibits similar

### TABLE I. Phase transition temperatures (°C) of the compounds. K → Crystal, SmB → Smectic-B, SmA → Smectic-A, I → Isotropic.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase transitions (°C)</th>
<th>Nematic range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN-35</td>
<td>K 38.4 N 49.3 I</td>
<td>10.9</td>
</tr>
<tr>
<td>CCN-38</td>
<td>K 41 SmA (23) N 49.5 I</td>
<td>26.5</td>
</tr>
<tr>
<td>CCN-46</td>
<td>K 30 SmB (26) N 54.7 I</td>
<td>28.7</td>
</tr>
<tr>
<td>CCN-47</td>
<td>K 25.6 SmA 28.2 N 57.3 I</td>
<td>29.1</td>
</tr>
<tr>
<td>CCN-55</td>
<td>K 25 SmB 30 N 66.4 I</td>
<td>30.4</td>
</tr>
<tr>
<td>CCN-73</td>
<td>K 38.6 SmB (38) N 50.2 I</td>
<td>12.2</td>
</tr>
</tbody>
</table>

![FIG. 1. Chemical structure of CCN-mn compounds.](image1)

![FIG. 2. Typical photomicrographs of four compounds at various temperatures during anchoring transition from planar to homeotropic while cooling.](image2)
texture in the nematic phase (Fig. 2(d)). On further cooling, it (CCN-38) shows appearance of small dark regions (Fig. 2(e)) at a particular temperature. These dark regions grow abruptly and randomly and finally the whole field of view becomes completely dark within a short temperature range (~1 °C (Fig. 2(f)). This means that the director orientation spontaneously changes from planar to homeotropic while cooling. The texture of CCN-55 in the nematic phase (Fig. 2(g)) is almost similar to that of CCN-38 (Fig. 2(d)). As the sample is cooled, the anchoring transition takes place by forming small dark regions just before the transition to SmB phase (Fig. 2(h)). Finally, the dark regions together with the typical SmB textures remain in the field of view (Fig. 2(i)). In CCN-73, the texture in the nematic phase (Fig. 2(j)) is similar to that of the previous compounds (Figs. 2(a), 2(d), and 2(g)). The N to SmB phase transition is observed around 37.8 °C and finally the whole field of view becomes texture in the nematic phase (Fig. 2(d)). On further cooling, it (CCN-38) shows appearance of small dark regions (Fig. 2(e)) at a particular temperature. These dark regions grow abruptly and randomly and finally the whole field of view becomes completely dark within a short temperature range (~1 °C (Fig. 2(f)). This means that the director orientation spontaneously changes from planar to homeotropic while cooling. The texture of CCN-55 in the nematic phase (Fig. 2(g)) is almost similar to that of CCN-38 (Fig. 2(d)). As the sample is cooled, the anchoring transition takes place by forming small dark regions just before the transition to SmB phase (Fig. 2(h)). Finally, the dark regions together with the typical SmB textures remain in the field of view (Fig. 2(i)). In CCN-73, the texture in the nematic phase (Fig. 2(j)) is similar to that of the previous compounds (Figs. 2(a), 2(d), and 2(g)).

In order to find the anchoring transition temperatures and the range of thermal hysteresis, we measured the effective dielectric constant ($\epsilon_{\text{eff}}$) as a function of temperature in all the samples. The dielectric measurements were preferred than optical transmission measurements because it does not need rubbing which can modify the surface properties and hence can affect the anchoring transition temperatures. The temperature variation of $\epsilon_{\text{eff}}$ is shown in Fig. 3. The effective dielectric constant ($\epsilon_{\text{eff}}$) of all the compounds in the planar state (as observed under polarizing microscope) is higher than that of the isotropic phase. This shows that all the compounds have negative dielectric anisotropy, i.e., $\Delta \epsilon = (\epsilon_{||} - \epsilon_{\perp}) < 0$, where the subscripts refer to the direction in relation to the director. Thus, the dielectric constant of the planar state is $\epsilon_{\text{eff}} = \epsilon_{||}$ and in the homeotropic state $\epsilon_{\text{eff}} = \epsilon_{\perp}$. This was further confirmed by measuring the dielectric constants in independent planar and homeotropic cells (coated with AL-1254 and JALS-204), respectively. It is observed that in compound CCN-35, there is no noticeable change in dielectric constant during heating and cooling in the nematic phase. In case of CCN-38, CCN-46, and CCN-47, we notice an abrupt decrease of $\epsilon_{\text{eff}}$ in the nematic phase at a particular temperature ($T_{\text{ac}}$) (Fig. 3(a)). Similarly, again an abrupt increase in $\epsilon_{\text{eff}}$ is observed while heating at higher temperature ($T_{\text{ah}}$). For example, in CCN-38, we observe $\epsilon_{\text{eff}}$ decreases abruptly while cooling at about 41.4 °C ($= T_{\text{ac}}$). Similarly again an abrupt increase in $\epsilon_{\text{eff}}$ is observed while heating at about 43.7 °C ($= T_{\text{ah}}$). Thus the temperature range of thermal hysteresis ($\Delta T_h = T_{\text{ah}} - T_{\text{ac}}$) is 2.3 °C. The variation of $\epsilon_{\text{eff}}$ for both CCN-55 and CCN-73 is shown in Fig. 3(b) separately. In case of CCN-55, the planar to homeotropic transition occurs during cooling just before the SmB phase transition as discussed earlier (Fig. 2(h)). Surprisingly, there is no anchoring transition observed in CCN-73. The abrupt decrease of the dielectric constant in CCN-73 at 35 °C is due to the N-SmB phase transition (Fig. 2(k)). The anchoring transition temperatures and the thermal widths of the hysteresis are listed in Table II. It is observed that CCN-35 does not show any anchoring transition, CCN-38, CCN-46, CCN-47, and CCN-55 shows discontinuous anchoring transition in the nematic phase with increasing thermal hysteresis. The largest thermal hysteresis is observed in CCN-55 ($\Delta T_h = 9.5 °C$).

There are many experimental studies reported on the anchoring transition in nematic liquid crystals as mentioned in the Introduction. Various types of molecules such as polar, nonpolar, centrosymmetric with nematic or both nematic and smectic-A phases are chosen in various substrate conditions. Several theories were also developed to explain the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{ac}}$ (°C)</th>
<th>$T_{\text{ah}}$ (°C)</th>
<th>$\Delta T_h$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN-35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCN-38</td>
<td>41.4</td>
<td>43.7</td>
<td>2.3</td>
</tr>
<tr>
<td>CCN-46</td>
<td>44.7</td>
<td>47.8</td>
<td>3.1</td>
</tr>
<tr>
<td>CCN-47</td>
<td>44.5</td>
<td>49.8</td>
<td>5.3</td>
</tr>
<tr>
<td>CCN-55</td>
<td>27.3</td>
<td>36.8</td>
<td>9.5</td>
</tr>
<tr>
<td>CCN-73</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 3. (a) Temperature variation of dielectric constant of CCN-35, CCN-46, CCN-38, and CCN-47. (b) Temperature variation of dielectric constant of CCN-55 and CCN-73. The solid and open symbols correspond to the data while cooling and heating, respectively. The phase transition and anchoring transition temperatures during cooling and heating are indicated with arrows. Nematic-isotropic phase transition $T_{\text{NI}}$; Planar to homeotropic transition in cooling $T_{\text{ac}}$; Homeotropic to planar transition in heating $T_{\text{ah}}$.
experimental observations. For example, Parsons et al. have shown that the competition between dipole and quadrupole interaction can lead to the anchoring transition.\textsuperscript{16} Barbero et al. have shown that the competition between the nematic-nematic and nematic-substrate interaction leads to the anchoring transition.\textsuperscript{15} Komitov et al. reported on the anchoring transition in hybrid aligned cell and gave a model that accounts for the dependence of the elastic constants on the scalar order parameter. Zhang et al. had shown anchoring transition on micro-structured surface and suggested that it is due to the frustrated boundary condition in which the elastic energy due to spatial variation in the molecular orientation compromises an increase in the surface anchoring energy.\textsuperscript{17} From the above discussion it appears that there are various possible mechanisms for different types of the anchoring transitions in various experimental conditions. In the present system the molecules are highly polar and at a first glance Parsons model appears to be reasonable\textsuperscript{16} compared to the other model discussed. However, absence of anchoring transition in CCN-35 rules out the possibility that it is due to the competition between dipolar and quadrupolar interactions. Looking at Tables I and II, it appears that the presence of smectic phase and relatively wide temperature range of nematic is important for the occurrence of discontinuous anchoring transition in the CCNs homologue. In a computer simulation, Chakrabarti and Bagchi have shown that the onset of the growth of the orientational order in the nematic phase is found to induce a translational order, resulting in a smectic-like layer in the underlying inherent structures. Interestingly, they found that the inherent structures never seem to sustain orientational order alone if the parent nematic phase is sandwiched between the high-temperature isotropic phase and the low-temperature smectic phase.\textsuperscript{43} It has been shown by Shioda et al. that SmA short range order in the nematic phase can lead to continuous anchoring transition from tilted to homeotropic.\textsuperscript{6} However, discontinuous anchoring transition with a large thermal hysteresis so far has not been explained theoretically.

IV. THEORETICAL

We present a simple theoretical model to account for the observed discontinuous anchoring transition in the nematic phase. We assume that the nematic liquid crystal (NLC) of thickness $d$ is bounded by two identical glass plates with the surface normals along the $z$-axis and there is no spatial variation of the orientational order parameter across the cell. The free energy of the sample per unit area can be written as\textsuperscript{12, 13}

$$ F = F_0 + 2[y_{11}v_iQ_{ij}v_j + y_{20}Q_{ij}Q_{ji} + y_{21}v_iQ_{ij}Q_{ji}v_j + y_{22}[v_iQ_{ij}v_j]^2] - D\int_0^d \psi(z)q^2(v_iQ_{ij}v_j)dz, \quad (1) $$

where $F_0$ is the free energy in the isotropic phase and $v$ denotes the outward normal at the two NLC-glass interfaces. The factor 2 in Eq. (1) is due to the contribution from the two surfaces. The nematic tensor order parameter is given by $Q_{ij} = \frac{1}{2}S(n_in_j - \frac{1}{3}\delta_{ij})$, where $S$ and $n$ being the scalar order parameter and the director in the nematic phase, respectively. In the above expansion of the free energy, we have considered only terms up to second order in $Q_{ij}$. For the samples studied in our experiments, the first order anchoring transition was observed only for samples which exhibit SmA or SmB phases below the nematic phase. The anchoring transition was not observed for the lower homologue of the compounds which do not exhibit any smectic phase (CCN-35). Therefore, it is reasonable to assume that the surface induced Smectic-like order plays a crucial role in the discontinuous anchoring transition. In fact, the effect of smectic short range order on the anchoring transition has been discussed previously.\textsuperscript{6, 8} For compounds exhibiting SmA phase, the glass-NLC interfaces tend to induce a SmA-like layer structure near the interfaces even in the nematic phase with layers parallel to the interface. The last term in Eq. (1) denotes the coupling of the surface induced SmA order with the orientational order parameter $Q_{ij}$. Substituting $Q_{ij}$ in Eq. (1), we obtain

$$ F = F_0 + \beta_{11}S((n \cdot v)^2 - 1/3) + \beta_{20}S^2 $$

$$ + \beta_{21}S^2((n \cdot v)^2 + 1/3) + \beta_{22}S^2((n \cdot v)^2 - 1/3)^2 $$

$$ - 3Dq^2S\int_0^d \psi(z)((n \cdot v)^2 - 1/3)dz, \quad (2) $$

where $\beta_{11} = 3y_{11}, \beta_{20} = 3y_{20}, \beta_{21} = 3y_{21}/2, \text{ and } \beta_{22} = 9y_{22}/2$. Assuming that the surface induced smectic order decays exponentially with a correlation length $\xi$ in the bulk of the nematic phase at temperatures above the nematic to smectic transition temperature ($T_{NA}$), the last integral term in Eq. (2) can be estimated as $-6Dq^2\xi^2\psi_0((n \cdot v)^2 - 1/3)$, and the free energy can be written as

$$ F[S, \xi, (n \cdot v)] = F_0 + F_1[S, \xi] + F_2[S, \xi, (n \cdot v)], \quad (3) $$

where

$$ F_1[S, \xi] = \left[2Dq^2\xi_0^2 - \frac{\beta_{11}}{3}\right]S + \left(\frac{\beta_{20}}{3} + \frac{\beta_{21}}{3} + \frac{\beta_{22}}{9}\right)S^2 \quad (4) $$

is the isotropic part of the surface free energy. The anisotropic part of the surface free energy (third term in Eq. (3)) is given by

$$ F_2[S, \xi, (n \cdot v)] = A(S, \xi)((n \cdot v)^2 + B(S)(n \cdot v)^4), \quad (5) $$

where the coefficients $A(S, \xi)$ and $B(S)$ are defined as

$$ A(S, \xi) = (\beta_{11} - 6Dq^2\psi_0^2)\xi + \left(\frac{\beta_{21}}{3} - \frac{2\beta_{22}}{3}\right)S^2 \quad (6) $$

$$ B(S) = \beta_{22}S^2. $$

The stable surface orientation, $\phi = \cos^{-1}(n \cdot v)$ can be obtained by minimizing the free energy in Eq. (5).

To account for the experimentally observed first order anchoring transitions, we assume that the coefficients
$\beta_{11}, \beta_{21} > 0$ but the coefficient $\beta_{22} < 0$. Then the stability conditions for the surface tilt angle $\phi$ are given by $\phi = \pi/2$ if $A(S, \xi) > 0$ and $\phi = 0$ if $A(S, \xi) + 2B(S) < 0$. In the mean field approximation, the smectic correlation length $\xi$ depends on temperature as $\xi = \xi_0(T - T_{N\alpha}/T_{N\alpha})^{-1/2}$ for $T > T_{N\alpha}$. As the anchoring transition in our samples occur at temperature far below the isotropic to nematic transition temperature $T_{N\beta}$, we assume that the orientational order parameter $S$ saturates to a constant value and is independent of temperature during the anchoring transition. This is reasonable because those four compounds which showed anchoring transition have relatively large nematic temperature range (Table I). Then minimization of Eq. (5) and the stability conditions predict a first order anchoring transition from $\phi = \pi/2$ at temperature $T > T_{ah}$ to $\phi = 0$ at temperature $T < T_{ac}$ with thermal hysteresis between $T_{ah}$ and $T_{ac}$ as observed experimentally, where

$$T_{ah} = T_{N\alpha} + T_{N\alpha} \frac{36D^2q^4\psi_0^2\xi_0^2}{\left[\beta_{11} + (\beta_{21} - 4(\beta_{22}/3)S)\right]^2},$$

$$T_{ac} = T_{N\alpha} + T_{N\alpha} \frac{36D^2q^4\psi_0^2\xi_0^2}{\left[\beta_{11} + (\beta_{21} + 2(\beta_{22}/3)S)\right]^2}. 
(7)$$

We now estimate $T_{ah}, T_{ac}$, and $\Delta T_{h}$ from Eq. (7). Considering the case of the compound CCN-47, the layer spacing in the smectic phase is $\sim 20 \times 10^{-8} \text{cm}$ giving $q \sim 3 \times 10^4 \text{cm}^{-1}$. We assume that the bare smectic correlation length $\xi_0 \sim 5 \times 10^{-8} \text{cm}$ and $D \sim 3.9 \times 10^{-6} \text{erg/cm}$. The anchoring coefficients $\beta_{11}$ and $\beta_{21}$ are expected to be of similar magnitudes. We assume $\beta_{11} \sim 2 \text{erg/cm}^2$ and $\beta_{21} = 0.9\beta_{11}$. The magnitude of the higher order anchoring coefficient $\beta_{22}$ is expected to be relatively smaller than $\beta_{11}$ and we assume that $|\beta_{22}| \sim 0.15|\beta_{11}|$. At temperatures corresponding to anchoring transition in our samples, we assume that the nematic order parameter $S \sim 0.6$ and the surface induced smectic order parameter $\psi_0 \sim 0.005$. Using the above parameters, $T_{ah}, T_{ac}$, and $\Delta T_{h}$ are estimated to be $323^\circ \text{K}, 318^\circ \text{K},$ and $5^\circ \text{K}$, respectively, which agree very well with our experimental observations. As reported earlier by Rosenblatt et al., the surface induced smectic order in the nematic phase can drive an anchoring transition from the planar to homeotropic orientation which is continuous in nature. Here, we demonstrated both experimentally and theoretically that such transition can be of first order with the discontinuous jump in the surface orientation from planar to homeotropic orientation with a thermal hysteresis.

V. CONCLUSIONS

In conclusion, we studied the anchoring transition of a homologous series of a liquid crystal (CCNs) on fluoropolymer treated cells. CCN-38, CCN-46, CCN-47, and CCN-55 exhibits discontinuous anchoring transitions with increasing thermal hysteresis. We found that the compound CCN-35 which has no SmA or SmB phase does not show any anchoring transition. CCN-73 has SmB phase but the nematic temperature range is short and does not also show any anchoring transition. Our experimental results show that the smectic short-range order and the wide temperature range of nematic is important for discontinuous anchoring transition. We developed a simple theory considering the experimental observations and showed the discontinuous anchoring transition with a finite thermal hysteresis.

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