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Bilayers In Nanoparticle-Doped Polar Mesogens

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I. INTRODUCTION

Beneficial modifications of the structure and properties of functional soft organic materials such as liquid crystals (LCs) can be achieved by doping them with a small amount of inorganic nanoparticles. The effect of various types of nanoparticles on LCs has been investigated. The impact of solid nanoparticles on phases of soft materials depends greatly on the material and on the surface functionalization of nanoparticles [1,2]. New phenomena and material properties are observed if the surface functionalization consists of covalently bonded protomesogenic ligands. Such nanoparticles can self-assemble into nanoparticulate thermotropic liquid crystalline materials [3,4]. In contrast, silica nanoparticles with covalently bonded alkyl-type surface functionalization [5] can improve the electro-optical performance of LCs or lead to dual alignment effects [6]. Silica nanoparticles free of surface functionalization are suitable to fabricate bistable display devices with the capability of selective erase using optical fields [7,8]. Additionally, they create memory effects that are addressable by quasistatic electric or magnetic fields [9]. It was deduced that such permanent memory is very likely caused by a surface memory effect well known for planar substrates, where a surface-induced thin adsorbed layer of a lower-temperature nanostructure in nematic LCs [10–12] and smectic LCs due to purely sinusoidal density variation.

Surfactants, such as oleic acid, have been used for noncovalently bonded surface functionalization to obtain stable nanodispersions of inorganic nanoparticles in organic solvents. It is possible to prepare dispersions of BaTiO$_3$ nanoparticles by milling cubic BaTiO$_3$ in heptane in the presence of a small amount of oleic acid in a planetary ball mill [11,12]. From these dispersions, stressed BaTiO$_3$ nanoparticles, which possess permanent electric polarization, can be harvested [13]. Generally, doping of LCs with milled BaTiO$_3$ nanoparticles allows one to vary the structural properties of smectic LCs [14] and to enhance the performance of devices based on both the nematic LCs [15–20] and ferroelectric LCs [21].

Recent x-ray scattering experiments on BaTiO$_3$ nanoparticle dispersions showed that they induced a one-dimensional nanostructure in nematic LC 4-n-pentyl-4′-cyanobiphenyl that does not exhibit a smectic phase. Thus, BaTiO$_3$ nanoparticles in soft materials can cause the formation of novel soft phases. In rare cases, doped thermotropic LCs with n-alkyl solvents, such as n-heptane [22] or n-dodecane [23], exhibit additional liquid crystalline phases.

In this work, nanoparticle-induced smectic phases were obtained and studied in five homologues of the 4-alkyl-4′-cyanobiphenyl homologous series. The smectic phases were not observed in doped neat compounds, but in a gel formed when clear solutions of each compound in n-heptane were evaporated. X-ray diffraction patterns of these gels consisted of up to nine orders of diffraction peaks from a one-dimensional nanostructure. The electron density distribution along the layer normal was extracted from the scattering data, thereby providing insight into the molecular arrangement inside the induced phase. Usually, this is not possible in LC materials, because x-ray scattering only results in very few peaks in the case of nematic (absent a layer structure) and smectic LCs due to purely sinusoidal density variation.

II. EXPERIMENTAL PROCEDURE

The initial dispersion of BaTiO$_3$ nanoparticles was prepared by milling cubic (nonferroelectric) BaTiO$_3$ with a small portion of oleic acid and n-heptane for 25 h [11]. This well-known process resulted in a dispersion of nanoparticles that possessed an average diameter of 9 nm. The concentration of the initial dispersion was carefully adjusted to 45 mg of
BaTiO$_3$ nanoparticles per gram. The LCs were obtained from Merck [4-n-pentyl-4′-cyanobiphenyl (5CB) and 4-n-octyl-4′-cyanobiphenyl (8CB)] and from Synthon Chemicals [4-n-butyl-4′-cyanobiphenyl (4CB), 4-n-hexyl-4′-cyanobiphenyl (6CB), and 4-n-heptyl-4′-cyanobiphenyl (7CB)]. Clear solutions of each LC were prepared by dissolving 0.1 g of the LC in 0.2 g of $n$-heptane in Eppendorf Standard micro test tubes. Subsequently, 20 mg of the turbid turbid suspension was added to each test tube. The test tubes were sealed with Parafilm to prevent evaporation of heptane. These initially turbid mixtures were stored in sealed micro test tubes at room temperature. They transformed into white gels within $\approx 72$ h. Additional samples of doped 5CB and 8CB were prepared where the preparation method was varied in order to purify the gels and quantitatively study the yield. A solution of 0.1 g of the LC (5CB or 8CB) and 0.2 g of $n$-heptane was prepared in a centrifuge glass tube. In the next step, several samples were prepared while systematically varying the nanoparticle concentration, sealed with Parafilm, and stored for $\approx 72$ h at room temperature. The samples were then centrifuged, leading to a separation of LC-rich white gel in the lower part of the tube and a LC-poor clear solution in $n$-heptane in the upper part. These clear solutions were decanted to glass vessels. Both the glass vessels and the centrifuge glasses were placed in a fume hood to allow $n$-heptane to evaporate until they showed mass constancy. The final weights of doped LC (upside-down triangles) and the final weights of recovered neat LC (triangles) increased linearly with an increase in the concentration, sealed with Parafilm, and stored for $\approx 72$ h.

A residual concentration of $n$-heptane ($\approx 20\%$) was found to be present in the LC nanogels. Evidently, a small amount of $n$-heptane was stabilized and retained within the nanoparticle-induced phase.

For x-ray scattering experiments, the samples were filled in 1 mm quartz capillaries (Hilgenberg) and placed in a modified Instec (HCS402) hot stage with a temperature precision of $\pm 0.1$ °C. The hot stage was fitted with a pair of CoSm permanent magnets that produced a $\sim 2.5$ kG in situ magnetic field. Two sets of x-ray scattering experiments were conducted; first the gels of 4CB, 5CB, 6CB, and 7CB were investigated at ambient temperature in a Rigaku Screen Machine. These experiments were conducted with copper Kα radiation and a 75-mm-diam Mercury 3 CCD area detector positioned at a distance of $\approx 160$ mm from the sample. The second set of measurements were performed on centrifuged doped 5CB and 8CB gel samples at the Advanced Photon Source (beamline 6-ID-B) with 0.765 335 Å synchrotron radiation and a MAR345 image plate detector placed at a distance of $\approx 470$ mm.

The diffraction data were collected at 30 and 50 °C and analyzed with FIT2D [24] and MATLAB (Rev. R2012b).

III. RESULTS

A high-intensity small-angle peak was obtained for all samples as expected from the inorganic nanoparticles. The intensity versus scattering vector $q$ plots were generated by azimuthal integration of the two-dimensional patterns. The first set of results on gel samples is shown in Fig. 2 for the $q$ range of 0.5–6 nm$^{-1}$ peaks corresponding to the $d$ spacing 4.57 and 4.51 nm, respectively. A Bragg reflection at $q = 1.376$ nm$^{-1}$ (4CB, 6CB) or at 1.394 nm$^{-1}$ (5CB, 7CB) was observed along with two higher-order reflections.

The 4CB-gel sample had a waxy appearance while other gel samples were much softer. However, the diffraction pattern of the 7CB-gel sample differed from those of 4CB, 5CB, and 6CB samples. The latter three samples showed diffraction patterns similar to that from a powder sample. In contrast,

![Fig. 1](image1.png)

**FIG. 1.** The final weight of doped LC, for both 5CB (open symbols) and 8CB (filled symbols), is shown against the initial quantity of nanoparticles. Centrifugation of nanoparticle/$n$-heptane/LC gels and subsequent evaporation of $n$-heptane yielded (sedimented) doped LC (upside-down triangles) and a recovery of neat LC (triangles).

![Fig. 2](image2.png)

**FIG. 2.** Scattering profiles of gel samples of 4CB, 5CB, 6CB, and 7CB LCs. The inset shows the central region of the 2D scattering pattern in the 7CB-gel sample. The scattering pattern of 7CB is oriented: An intensity vs azimuthal angle scan is shown to quantify the orientation of the scattering pattern. The dashed secant is a guide to the eye and indicates the orientation of the scattering pattern; the orientation of the molecular long axis is perpendicular to it.
the three diffraction rings of the 7CB gel indicated a preferred orientation (indicated by an intensity versus azimuthal angle χ scan of the first diffraction ring in the inset in Fig. 2) of the molecules. Doped 5CB and 8CB samples were further investigated with synchrotron x-ray diffraction. Figures 3(a) and 3(b) represent diffraction patterns from oriented doped-5CB samples. The orientation (indicated by a dashed line) is pronounced and thus easily seen in the diffraction pattern recorded at 50 °C [Fig. 3(b)]. Intensity versus azimuthal angle χ scans of the first-order diffraction rings are shown in Fig. 4 as dashed lines. Intensity modulation of the first diffraction ring is more pronounced for doped 5CB at 50 °C than at 30 °C. Two reflections were seen in a diffraction pattern of doped 8CB at a temperature of 30 °C. Figure 3(c) shows a multiring pattern with an additional scattering signal indicated by the arrow which is characteristic of the partial bilayer smectic A_d phase (SmA_d) [25] of neat 8CB. Although the orientation of this SmA_d signal was not as pronounced as usually observed in neat 8CB, its orientation is approximately parallel to the magnetic field as in the neat 8CB. This SmA_d signal was not present in the diffraction pattern recorded at higher temperature 50 °C [Fig. 3(d)]. The χ scans of the first ring of the two multiring patterns and of the SmA_d signal at 30 °C are shown (Fig. 4). The χ scan of the SmA_d ring at 30 °C (marked as “Sm”) consists of two peaks. The maxima of both χ scans shown for a temperature of 30 °C in Fig. 4 appear at the same azimuthal angles. Accordingly, one cannot rule out the possibility of the coexistence of a nanoparticle-induced multilayer phase and the SmA_d phase of the neat LC.

The scattering curves (Fig. 5) were extracted by azimuthal integration of the diffraction patterns shown in Fig. 4 over a q range of 0.5–25 nm⁻¹. In the wide-angle range, a broad peak is present at approximately q = 22 nm⁻¹. To account for this peak, diffraction patterns of BaTiO₃ were simulated with POWDERCELL (Version 2.4). Cubic BaTiO₃ possesses a perovskite-type crystal lattice (space group Pm-3m) with a lattice constant of 0.4058 nm (JCPDS No. 75-0215 [26]), while tetragonal BaTiO₃ (space group P4mm) has a = 0.3992 nm and c = 0.4036 nm [27,28]. The calculated diffraction pattern yields the most intense (1 1 0) peak (d = 0.2869 nm) at q = 21.9 nm⁻¹. The (1 0 1) and (1 1 0) reflections are not degenerate in tetragonal BaTiO₃, where the (1 0 1) reflection (d = 0.2838 nm, q = 22.14 nm⁻¹) and the (1 1 0) reflection (d = 0.2823 nm, q = 22.26 nm⁻¹) had the highest and second highest peak intensities, respectively.
TABLE I. Position ($\mathbf{q}$), amplitude ($A$), full width at half-maximum (FWHM), and normalized scattering intensities ($I_{\text{norm}}$) obtained from Lorentzian fits to the nine multiples of the $d \approx 4.65$ nm peak for both 8CB and 5CB at 30 and 50 °C.

<table>
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<tr>
<th>Diff. Order</th>
<th>0th</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
<th>7th</th>
<th>8th</th>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ (nm$^{-1}$)</td>
<td>1.345</td>
<td>2.681</td>
<td>4.021</td>
<td>5.365</td>
<td>6.717</td>
<td>8.074</td>
<td>9.438</td>
<td>10.813</td>
<td>12.190</td>
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<tr>
<td>$A$ (arb. units)</td>
<td>520.00</td>
<td>37.76</td>
<td>36.78</td>
<td>7.77</td>
<td>10.06</td>
<td>2.63</td>
<td>3.63</td>
<td>0.75</td>
<td>1.44</td>
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<tr>
<td>FWHM (nm$^{-1}$)</td>
<td>0.077</td>
<td>0.068</td>
<td>0.072</td>
<td>0.073</td>
<td>0.076</td>
<td>0.077</td>
<td>0.078</td>
<td>0.067</td>
<td>0.091</td>
</tr>
<tr>
<td>$I_{\text{norm}}$</td>
<td>1.000</td>
<td>0.289</td>
<td>0.632</td>
<td>0.238</td>
<td>0.482</td>
<td>0.182</td>
<td>0.344</td>
<td>0.094</td>
<td>0.227</td>
</tr>
<tr>
<td>8CB, 50 °C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ (nm$^{-1}$)</td>
<td>1.345</td>
<td>2.681</td>
<td>4.021</td>
<td>5.363</td>
<td>6.715</td>
<td>8.072</td>
<td>9.433</td>
<td>10.804</td>
<td>12.185</td>
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<td>$A$ (arb. units)</td>
<td>701.300</td>
<td>49.205</td>
<td>45.151</td>
<td>9.639</td>
<td>11.683</td>
<td>3.136</td>
<td>4.266</td>
<td>1.211</td>
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<tr>
<td>FWHM (nm$^{-1}$)</td>
<td>0.133</td>
<td>0.118</td>
<td>0.119</td>
<td>0.117</td>
<td>0.114</td>
<td>0.118</td>
<td>0.112</td>
<td>0.128</td>
<td>0.104</td>
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<td>$I_{\text{norm}}$</td>
<td>1.000</td>
<td>0.376</td>
<td>0.776</td>
<td>0.295</td>
<td>0.560</td>
<td>0.217</td>
<td>0.404</td>
<td>0.150</td>
<td>0.237</td>
</tr>
<tr>
<td>5CB, 30 °C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$ (arb. units)</td>
<td>591.60</td>
<td>55.98</td>
<td>47.30</td>
<td>9.17</td>
<td>11.82</td>
<td>3.16</td>
<td>4.30</td>
<td>0.91</td>
<td>1.51</td>
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<tr>
<td>FWHM (nm$^{-1}$)</td>
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<td>0.107</td>
<td>0.102</td>
<td>0.094</td>
<td>0.095</td>
<td>0.097</td>
<td>0.092</td>
<td>0.086</td>
<td>0.090</td>
</tr>
<tr>
<td>$I_{\text{norm}}$</td>
<td>1.000</td>
<td>0.375</td>
<td>0.712</td>
<td>0.246</td>
<td>0.497</td>
<td>0.192</td>
<td>0.357</td>
<td>0.099</td>
<td>0.207</td>
</tr>
<tr>
<td>5CB, 50 °C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ (nm$^{-1}$)</td>
<td>1.344</td>
<td>2.675</td>
<td>4.012</td>
<td>5.354</td>
<td>6.703</td>
<td>8.055</td>
<td>9.417</td>
<td>10.783</td>
<td>12.164</td>
</tr>
<tr>
<td>$A$ (arb. units)</td>
<td>253.671</td>
<td>21.296</td>
<td>19.328</td>
<td>3.941</td>
<td>4.866</td>
<td>1.310</td>
<td>4.30</td>
<td>0.406</td>
<td>0.770</td>
</tr>
<tr>
<td>FWHM (nm$^{-1}$)</td>
<td>0.111</td>
<td>0.109</td>
<td>0.109</td>
<td>0.104</td>
<td>0.103</td>
<td>0.105</td>
<td>0.100</td>
<td>0.096</td>
<td>0.107</td>
</tr>
<tr>
<td>$I_{\text{norm}}$</td>
<td>1.000</td>
<td>0.332</td>
<td>0.679</td>
<td>0.246</td>
<td>0.477</td>
<td>0.185</td>
<td>0.354</td>
<td>0.103</td>
<td>0.249</td>
</tr>
</tbody>
</table>

In contrast to the simulated powder diffraction patterns, no sharp wide-angle scattering peaks were expected, because a system of BaTiO$_3$ nanoparticles was studied. Specifically, both the cubic and the stressed tetragonal nanoparticles were present in these samples, and the (1 1 0) and (1 0 1) reflections are broadened due to the finite-size effect. This leads to the composite broad peak observed at $q \approx 22$ nm$^{-1}$.

Due to short-range lateral positional order correlations (SRC), a broad scattering peak centered at $q \approx 14$–$15$ nm$^{-1}$ is usually observed in soft phases of the calamitic mesogens 5CB and 8CB. Such a liquidlike peak is also observed at $q \approx 4.65$ nm in cyanobiphenyls. Surprisingly, nine orders of a Bragg reflection with $d \approx 4.65$ (±0.025) nm were observed and are marked from 1 to 9 in Fig. 5. Their width for doped 5CB is much larger than that in neat 8CB (inset). The smectic peak at $q \approx 1.9$ nm$^{-1}$ is seen in scattering curves of doped 8CB at 30 °C. The calculated $d \approx 4.3$ Å is characteristic for the average transverse intermolecular separation $d_L$ in cyanobiphenyls. The calculated $d \approx 4.3$ Å corresponds to smectic layer spacing of the stable Sm$A_d$ phase of the neat 8CB at 30 °C.

The nine harmonics of the $d \approx 4.65$ nm peaks were fitted to the Lorentzian line shape to estimate the scattering amplitudes. Initially, each of the peaks was fitted individually. One Lorentzian function and a straight line as background were fitted to the second- to ninth-order peaks. For the first- and second-order peaks, a second Lorentzian centered at $q < 0.3$ nm$^{-1}$ was added to model the intense small-angle scattering caused by the inorganic nanoparticles. The results are summarized in Table I. For 5CB at 30 °C, the full width at half-maximum (FWHM) of the Lorentzian fit to the first-order peak was fixed at 0.1 nm$^{-1}$ and a second peak function was added. From its comparison with doped 8CB, where a small amount of smectic-like material was present in the sample, we infer that a small amount of nematic-like component was present in 5CB which contributed to the scattering near $q \approx 1.4$ nm$^{-1}$ at 30 °C (see also the inset in Fig. 5). The Lorentz-corrected and normalized scattering intensities are listed in Table I. Additionally, a schematic of the Bragg scattering observed at the small angles is shown (Fig. 6) for both doped 5CB and 8CB at 30 °C.

The nine harmonics of the Bragg reflection arose from a multilayer structure of $d = 4.65$ nm. Similar multilayer structures with far fewer diffraction orders have been observed and analyzed in LC side chain polymers [30]. The scattering

FIG. 6. Schematic scattering intensities of nine multiples of the $d \approx 4.65$ nm Bragg peak observed in doped 5CB and doped 8CB (black lines) and the residual LC (gray lines) present in doped 5CB (neat nematic phase) and doped 8CB (neat Sm$A_d$ phase) at 30 °C.
amplitudes \( A_{\text{scat}}(q) \) of such structures can be expressed as a Fourier transform of the electron density profile \( \rho(z) \) in the \( z \) direction perpendicular to the layers:

\[
A_{\text{scat}}(q) = \int_{-d/2}^{d/2} \rho(z)e^{-iqz}dz. \tag{1}
\]

The electron density profile can be extracted from the measured scattering amplitudes from the inverse Fourier transform in terms of cosine functions when a symmetric electron density profile is expected:

\[
\rho(z) = \sum_n A_n \cos\left(\frac{n2\pi z}{d}\right). \tag{2}
\]

The modulus of the scattering amplitudes \( |I_0|^{0.5} \) can be directly calculated since the intensities were recorded. However, their signs remain indeterminate (the phase problem). A common method to obtain the sign is to calculate the \( 2^n \) electron density profiles described by Eq. (2) and compare them to what sign one should expect from a possible molecular arrangement [30]. Accordingly, the 5CB molecule was visualized using the open-source software Avogadro [31,32] in order to estimate the size of the characteristic molecular building blocks (Fig. 7). The molecular model clearly shows that the terminal cyanophenyl moiety is twisted with respect to the central phenyl moiety of the molecule. Each of these resonance-stabilized building blocks possesses a relatively high and delocalized electron density which is higher than the average electron density in the alkyl chain.

After careful examination of the calculated electron density profiles, the phase combination \([+ - - + - - + -]\) was selected. To show the accuracy of this phase combination, molecular models of 5CB and 8CB were scaled and their relative electron density versus layer spacing (Fig. 8) plotted. It should be noted that Fig. 8 represents the average relative electron density distributions inside the soft phases and not the electron density of a single molecule. Nevertheless, superposition of the molecular model over the electron density profile is instructive and shows that the cyanobiphenyl group leaves a footprint on the shown relative electron density profiles. The two peaks observed in the electron density profiles fit the characteristic spacing of the electron-rich moieties of the cyanobiphenyl group. A drop in the electron density is observed at the position of the alkyl chain. The layer spacing is equal to twice the molecular length in both phases. Thus, the molecular arrangement in the present phase is comparable to the bilayer SmA\( _2 \) phase [25]. However, in contrast to the present nanoparticle-induced phase, such a large number of higher orders of the small-angle peak are never observed in neat thermotropic systems. The molecular arrangement in thermotropic phases of \( n \)-alkyl-cyanobiphenyls can be very well understood in atomistic simulations under the assumption that the alkyl tails favor an all-trans conformation [33]. A schematic of the molecular arrangement is shown (Fig. 9) for the 5CB and \( n \)-heptane molecules. The molecules are
found to possess a short-range positional order within the bilayers, and the alkyl chains are allowed to move freely in the nanoparticle-induced phase.

Upon heating the samples from 30 to 50 °C, the FWHM of the fitted Lorentzian peaks of doped 5CB increased only slightly from \( \approx 0.10 \) to \( \approx 0.11 \) nm\(^{-1}\). The correlation length (2\( \pi \)/FWHM) of the multilayers was \( \approx 60 \) nm, or 12–13 layers at the higher temperature. Heating the doped 8CB sample led to an increase of the FWHM from \( \approx 0.07 \) to \( \approx 0.12 \) nm\(^{-1}\). Accordingly, the correlation length in doped 8CB decreased from 90 to 52 nm (from 19 to 11 layers).

The relative electron density profiles along the z direction are presented for both doped 5CB and doped 8CB in Fig. 9. Near the center, these profiles show a variation of the relative electron density that is characteristic for a head-to-head arrangement of cyanobiphenyl groups. The variation of electron density is much smaller in the aliphatic region and plays a relatively insignificant role in x-ray diffraction from multilayer structures. Nevertheless, one can speculate that the aliphatic chains of the 4-\( n \)-alkyl-4′-cyanobiphenyl molecules are stabilized by London interactions. The multilayer phase shows a general layer spacing of 4.5 nm for all studied homologues, and \( \approx 20\% \) of \( n \)-heptane are stabilized in the nanostructure. The remainder of \( n \)-heptane appears to be stabilized in the aliphatic part of the 4-\( n \)-alkyl-4′-cyanobiphenyl bilayers. Using the concentration of approximately 15% of nanoparticles in the systems investigated, a density of BaTiO\(_3\) of 6 g/cm\(^3\), and 1 g/cm\(^3\) for the density of the organic materials, we estimate that the nanoparticles will comprise about 2.5% of the sample volume. Therefore, eight nanoparticles may be present in a 9-nm-thick layer with a size of \( \approx 160 \) nm \( \times \) 160 nm. Based on this assumption, a two-dimensional schematic of a thin layer of a nanoparticle-doped sample is shown (Fig. 10). Both polar nanoparticles (gradient filled) and nonpolar nanoparticles (uniformly filled) are shown. A monolayer of 5CB is grafted onto the surface of these inorganic nanoparticles. The nanoparticles are surrounded by multilayer shells of \( n \)-heptane-stabilized 4-\( n \)-alkyl-4′-cyanobiphenyl bilayers. The aliphatic bilayer interfaces are indicated by black lines. Due to the irregular shape of nanoparticles, these shells are most likely elliptical rather than perfectly spherical. A phase that consists of nonoriented, elliptically shaped multishells would lead to powder (nonoriented) x-ray diffraction patterns. In addition, samples may also appear to be weakly oriented because the ellipses may become oriented in the magnetic field. Alternatively, pairing or formation of strings (or chains) of polar nanoparticles may also lead to cigar-shaped multishells more prone to orient in an external field. Oriented scattering patterns were observed in 7CB gel (with an unknown heptane content), doped 5CB, and doped 8CB. The orientation effects in 5CB and 8CB were more pronounced at higher temperature. One can speculate whether the higher chain length of 7CB and 8CB leads to more stable cigar-shaped multishells and thus to a more pronounced orientation observed in the scattering patterns. Presumably, repeated heating and cooling in a magnetic field could also generate the higher degree of orientation as observed at higher temperatures.

IV. CONCLUSIONS

In conclusion, evidence presented here clearly shows the impact of nanoparticle doping on the phase behavior and molecular organization of small mesogenic polar molecules in which the rigid part of the molecule, and not the overall molecular length, determines the layer spacing of the induced self-assembled nanostructure. These investigations of one-dimensional soft nanostructures are very useful as they reveal detailed information about the molecular arrangement in the multilayers. The results also provide evidence for a preferred orientation of soft modified phases in an external field. The technique employed in this study is suitable to test other mesogens and presumably even nonmesogens in order to study the nature of molecular associations induced by the presence of nanoparticle in soft phases. This method has great potential to produce alignment layers for use in LC devices, to achieve memory effects, and as a method to induce and investigate novel phases in other self-assembling photonic structures, such as chiral nematic and chiral smectic LCs.

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