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Citation: AIP Advances 7, 075008 (2017); doi: 10.1063/1.4993455
View online: http://dx.doi.org/10.1063/1.4993455
View Table of Contents: http://aip.scitation.org/toc/adv/7/7
Published by the American Institute of Physics
Evidence of nanodiamond-self-assembly in a liquid crystal, and the consequent impacts on the liquid crystal properties

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(Received 8 May 2017; accepted 3 July 2017; published online 17 July 2017)

A small quantity of nanodiamonds (NDs) was dispersed in a nematic liquid crystal (LC), and the NDs were found to exhibit an anisotropic self-assembly along the nematic director. The anisotropic assembly of the NDs in the LC matrix was probed by measuring the dielectric anisotropy, $\Delta \varepsilon$, of the LC+ND system, which showed a significant increase in $\Delta \varepsilon$. Additional studies revealed that the presence of NDs reduced the rotational viscosity and the pretilt angle of the LC. The studies were carried out with several ND concentrations in the LC and the experimental results coherently suggest that there exists an optimal concentration of ND. Above this optimal ND concentration, the anisotropic assembly of the NDs was found to be not effective anymore. The rotational viscosity and the pretilt angle of the LC were found to increase above the optimal concentration of ND. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Controlled self-assembly of nanodiamonds (NDs) holds great promise for important applications, such as bio-imaging$^1$ and quantum computing.$^2$ NDs contain imperfections called nitrogen vacancy centers,$^3$ where a nitrogen atom replaces one of the carbon atoms. Electron spins in these nitrogen vacancy centers can be manipulated using magnetic fields to take advantage of properties, such as quantum entanglement.$^4$ Consequently, assembling NDs in large arrays is of great interest to quantum computing.$^5$ Therefore, finding ways to assemble NDs in arrays is an active area of both fundamental and applied research.$^6$–$^{11}$

In another direction, it is well established that the liquid crystal (LC) can be used to self-assemble various nanoparticles. For example, carbon nanotubes can be aligned in an LC media and an external field can be used to reorient them with the nematic director.$^{12}$–$^{24}$ Quantum dots can form chain-like one-dimensional arrays in an LC.$^{25}$–$^{28}$ Finally, the flat surface of graphene can couple to the nematic director.$^{29}$–$^{31}$ Here, we report that when a small amount of NDs are dispersed in an LC, the NDs form anisotropic array-like structures in the LC media.

Understanding the nanomaterial-self-assembly in the LC and the subsequent effects on the bulk LC properties is an important an active area of research. In this paper, we investigate the process of ND-self-assembly in the LC and its impact on the bulk properties of the LC.

It has been shown that LC molecules can anchor to the honeycomb pattern of graphene$^{32}$–$^{35}$ or carbon nanotubes, $^{36}$,$^{37}$ employing the $\pi-\pi$ electron stacking with a binding energy of -2 eV. A nanodiamond crystal possesses graphite-like surfaces$^{1}$,$^{38}$ and can promote $\pi-\pi$ stacking, as shown in Fig. 1(a) and (b). This graphite-like honeycomb faces on the ND crystals play an important role in organizing the NDs in the LC matrix. The presence of NDs subsequently alters some properties of the LC, such as rotational viscosity and electro-optical switching.

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II. EXPERIMENTS, RESULTS, AND DISCUSSIONS

The ND sample in ethanol solvent, obtained from Adamas Nanotechnologies, Inc., contained diamond crystals of an average diameter of 40 nm. The ethanol + ND solution was first remixed by sonication for 6 h. The liquid crystal E7 (obtained from EMD Millipore Corporation, $T_{NI} = 60.5^\circ C$) then was added to the ethanol + ND and sonicated for 6 h, allowing the LC to dissolve completely into the solution. The ethanol was evaporated slowly at an elevated temperature, leaving a pure LC+ND mixture. Finally, the LC+ND was degassed under a vacuum for 3 h. The process was repeated to produce five known concentrations of ND in the LC: E7+ND 1 = $0.94 \times 10^{-2}$, E7+ND 2 = $1.31 \times 10^{-2}$, E7+ND 3 = $1.68 \times 10^{-2}$, E7+ND 4 = $2.23 \times 10^{-2}$, and E7+ND 3 = $3.11 \times 10^{-2}$ wt%. The ND concentrations are kept low to prevent any large-scale aggregations. For consistency, the pure LC was also treated the same way, such as dissolving in ethanol followed by a slow evaporation and degassing. Commercially manufactured LC cells (LC2–5.0, planar antiparallel rubbed, from Instec, Inc.) with a $d = 5 \mu m$ spacing were used for our experiments. The cells were filled with the pure E7 or the E7+ND mixtures at temperature $T > 65^\circ C$ in the isotropic phase by capillary action and slowly cooled to room temperature.

The nematic phase shows dielectric anisotropy, $\Delta \varepsilon = \varepsilon_|| - \varepsilon_\perp$, where $\varepsilon_||$ and $\varepsilon_\perp$ are the dielectric components parallel and perpendicular to the nematic director, respectively. An LC’s $\Delta \varepsilon$ is proportional to the scalar nematic order parameter. It has been shown that when anisotropic nanomaterials, such as carbon nanotubes and graphene, are doped in a nematic LC, the LC’s $\Delta \varepsilon$ is enhanced because the anisotropic nanomaterials self-align themselves along the nematic director.\textsuperscript{14,16,17,20,29} When spherical nanomaterials, such as quantum dots (QDs), are dispersed in a nematic LC, the QDs are found to form anisotropic chain-like structures\textsuperscript{25} to reduce the elastic distortions in the LC, which is essential for minimizing the excluded volume. The anisotropic chain-like structure formation by the QDs leads to an enhancement in $\Delta \varepsilon$ of the LC.\textsuperscript{25} Therefore, an enhancement in $\Delta \varepsilon$ of an LC by
doping spherical nanomaterials indicates the formation of anisotropic self-assembled structures by the spherical nanomaterials in the LC media. In this paper, we experimentally demonstrate that the presence of NDs in E7 LC significantly enhances $\Delta \varepsilon$ of the LC.

The Fréedericksz transition (the re-orientation process of the director in the presence of an external field $E$), in the nematic LC, occurs because the director experiences a torque $\propto \Delta \varepsilon E^2$.\(^{39}\)

An Automatic Liquid Crystal Tester (Instec, Inc.)\(^{40}\) was employed to measure the dielectric constant $\varepsilon$ of the pure E7 and the E7+ND mixtures as a function of $E$, at 1000 Hz, in the nematic phase. The Automatic Liquid Crystal Tester (Instec, Inc.) has a built-in capacitance bridge, which can measure the capacitance of a sample as a function of the applied probing voltage in a wide frequency range from 1 Hz to 50 kHz. After measuring the capacitance, the dielectric constant $\varepsilon$ was extracted using $\varepsilon = \frac{C_{LC}}{C_{empty}}$, where $C_{LC}$ is the filled cell capacitance and $C_{empty}$ is the empty cell capacitance.

Figure 2 shows a typical Fréedericksz transition in the deep nematic phase at $T = 30^\circ C$, revealing that $\Delta \varepsilon$ increases when the LC is doped with NDs. The top inset in Fig. 2 represents $\Delta \varepsilon (= \varepsilon_\parallel - \varepsilon_\perp)$ as a function of temperature for E7 and E7+ND 3. Note that this 7\% increase in $\Delta \varepsilon$ is achieved by adding only $1.68 \times 10^{-2}$ wt\% of NDs in the LC. The bottom inset shows $\Delta \varepsilon$ as a function of ND concentration at $T = 30^\circ C$. Also, $\Delta \varepsilon$ increases monotonically with increasing ND concentration for the first three concentrations: E7+ND 1, E7+ND 2, and E7+ND 3. However, above E7+ND 3, $\Delta \varepsilon$ starts to decrease. This result depicts that there exists an optimal concentration, E7+ND 3, for which $\Delta \varepsilon$ reaches its maximum value. The schematic presentations show the formation of the ND-chains and their rotation in the LC matrix as $E$ is applied.

The ND crystal possesses graphite-like surfaces as shown in Fig. 1(a). On the honeycomb-like hexagonal pattern, the LC molecules can form short-range order due to $\pi-\pi$ stacking, by matching the LC’s benzene rings on the honeycomb structure.\(^{32–37}\) See Fig. 1(b). When NDs are doped in an LC, the short-range LC orders at the ND’s graphite-like surfaces align with the global nematic director of the LC to minimize the elastic distortions. The minimization of the elastic distortions leads to the minimization of the excluded volume, and therefore, the NDs form anisotropic arrays in the LC, as schematically represented in Fig. 1(c). As the NDs form these anisotropic arrays, the LC+ND system gains additional structural anisotropy from the ND arrays — hence the observed increase in $\Delta \varepsilon$. If the NDs were to stay individually without forming the

![Fig. 2. Dielectric constant $\varepsilon$ as a function of applied rms field $\vec{E}$ ($f = 1000$ Hz) in the nematic phase ($T = 30^\circ C$) for E7 and the optimal concentration E7+ND 3, listed in the legend. This shows a typical Fréedericksz transition and an increase in the dielectric anisotropy $\Delta \varepsilon$ for the optimal concentration E7+ND 3 sample. Top inset: Dielectric anisotropy $\Delta \varepsilon$ as a function of temperature for E7 and the optimal concentration E7+ND 3, listed in the legend. Bottom Inset: The dielectric anisotropy $\Delta \varepsilon$ as a function of nanodiamond concentration in the nematic phase at $T = 30^\circ C$. The dashed-line is a guide to the eye. Schematic illustrations show the rotation of nanodiamond assemblies in the LC matrix as the field is applied. Schematics are not to scale.](image-url)
anisotropic arrays, $\Delta \epsilon$ would not increase as the system would not gain any anisotropy. Presumably, with increasing ND concentration, more ND arrays are formed, and therefore, $\Delta \epsilon$ increases monotonically with increasing ND concentration. However, we believe that above E7+ND 3 concentration, the NDs start to aggregate and no longer effectively form the anisotropic arrays. Consequently, $\Delta \epsilon$ decreases for E7+ND 4 and E7+ND 5.

It can be noticed in Fig. 2 that $\epsilon_\perp$ for the E7+ND sample is smaller than that of the pure E7. Our further investigations show that the presence of NDs reduces the pretilt angle of the LC in the cell, which plays a role in decreasing $\epsilon_\perp$ of the E7+ND system.

We performed experiments to study the rotational viscosity $\gamma_1$ and the pretilt angle $\theta_o$ for the pure E7 and the E7+ND mixtures. The rotational viscosity for the nematic samples was obtained by measuring the transient current induced by a DC field across the planar-aligned cell configuration.\textsuperscript{41–43} When a DC field (much higher than the threshold field) is applied across a planar LC cell, the induced transient current $I(t)$ through the cell shows a time response as the nematic director undergoes planar to homeotropic orientational transition. The transient current response is given by\textsuperscript{41–43}

\[ I(t) = \frac{A(\Delta \epsilon \epsilon_o)^2 E^3}{\gamma_1} \sin^2[2\theta(t)] \]  

where $A$ is the area of the cell, $E$ is the electric field, and $\theta$ is the angle the director makes with the electrodes at a given time. At $\theta = 45^\circ$, $I(t)$ reaches its peak, $I_p = \frac{A(\Delta \epsilon \epsilon_o)^2 E^3}{\gamma_1}$ at the peak time,

\[ t_p = \left[ \frac{\gamma_1(-\ln\tan \theta_o))}{\Delta \epsilon \epsilon_o} \right] \frac{1}{E^2} \]

where $\theta_o$ is the pretilt angle. A DC field pulse of 1 V/µm with a pulse interval of 1 Hz was applied across the cell to generate $I(t)$. Then, $I(t)$ in the cell was detected as a function of time through a load resistor in series by a digital storage oscilloscope. The peak current, $I_p$, was detected from the $I(t)$ vs. time graph (see the bottom-left inset in Fig. 3(a)) to extract $\gamma_1$ from the known values of $E$, $\Delta \epsilon$, and $A$. After extracting $\gamma_1$ from the peak transient current, Eq. 2 was used to find $\theta_o$ from the peak time for the LC samples. This method is one of the most accurate methods to measure $\gamma_1$ and $\theta_o$.\textsuperscript{43} Figure 3(a) represents $\gamma_1$ as a function of temperature for pure E7 and E7+ND hybrids, listed in the legend. Similarly, Figure 3(b) shows $\theta_o$ as a function of temperature for pure E7 and E7+ND hybrids.

The lowest concentration, E7+ND 1, does not show any significant change in $\gamma_1$ and $\theta_o$. However, E7+ND 2 and E7+ND 3 exhibit a significant decrease in $\gamma_1$ and $\theta_o$. The top insets in Fig. 3(a) and (b) show $\gamma_1$ and $\theta_o$, respectively, as a function of ND concentration at $T = 30$ °C. Interestingly, above E7+ND 3, $\gamma_1$ and $\theta_o$ do not show any further decrease, verifying the existence of the optimal concentration at E7+ND 3.

The pretilt angle $\theta_o$ is the initial slant angle of the LC molecules from the aligning substrate, as schematically shown in Fig. 3(c). Therefore, when $\theta_o$ decreases, $\epsilon_\perp$ (perpendicular component of the dielectric constant) also decreases. In Fig. 2, $\epsilon_\perp$ for E7+ND 3 clearly shows a smaller value than pure E7, indicating a significant decrease in $\theta_o$ for the E7+ND sample. We believe that during the filling process of the LC cells, possibly some NDs sediment down and/or get stuck to the substrates from the LC+ND mixture, and align themselves with their graphite-like surfaces exposed to the LC. These graphite-like surfaces promote planar anchoring due to $\pi-\pi$ stacking, as shown in Fig. 1(b), and presumably reduce the average pretilt angle on the substrate. Fig. 3(d) schematically illustrates the reduced pretilt angle at the graphite-like surface and LC interface.

Now, we show that the reduction in $\gamma_1$ has a significant effect in the LC’s switching times. The two characteristic times,\textsuperscript{44} rise (voltage on) and decay (voltage off), of the nematic director can be described as

\[ \tau_{\text{rise}} = \frac{\gamma_1 d^2}{\Delta \epsilon \epsilon_o V^2 - K_{11} \pi^2}, \tau_{\text{decay}} = \frac{\gamma_1 d^2}{K_{11} \pi^2}, \]

where $d$ is the cell thickness, $\epsilon_0$ is the free space permittivity, $K_{11}$ is the splay elastic constant, and $V$ is the applied voltage. $\tau_{\text{rise}}$ is the time the nematic director takes to rotate from planar to homeotropic configuration, when the voltage is turned on across a planar aligned cell. Similarly, $\tau_{\text{decay}}$ is the time
FIG. 3. (a) Rotational viscosity, $\gamma_1$, for E7 and E7+ND samples as a function of temperature. Inset: $\gamma_1$ as a function of nanodiamond concentration in the nematic phase at $T = 30^\circ$ C. The dashed-line is a guide to the eye. (b) Pretilt angle, $\theta_0$, for E7 and E7+ND samples as a function of temperature. Inset: $\theta_0$ as a function of nanodiamond concentration in the nematic phase at $T = 30^\circ$ C. The dashed-line is a guide to the eye. (c) Schematic representation of the natural pretilt of the LC molecules on an aligning substrate. (d) Schematic representation of the reduced average pretilt angle of the LC molecules in the presence of the graphite-like surface of a nanodiamond.

the director takes to rotate back from homeotropic to planar configuration after the voltage is turned off. Since $\gamma_1$ is linearly proportional to the two characteristic times, a reduction in $\gamma_1$ should result in an accelerated switching response.

The field-induced nematic switching times were studied from the electro-optic responses of the pure E7 and E7+ND 3 samples. The optical setup consisted of a beam from a 5-mW He-Ne laser (continues wave) at wavelength 633 nm that passed through a polarizer, the LC cell, a crossed analyzer, and into a Newport photodetector (Newport Model 1621, nanosecond photodetector, wavelength 350-1000 nm, Silicon Detector, 0.8 mm Diameter, 1 ns rise time). The beam was polarized at an angle of $45^\circ$ with respect to the nematic director. The output of the detector was fed into a digital storage oscilloscope. A dc voltage pulse at a pulse interval of 20 Hz was applied across the cell and the change in transmitted intensity as a function of time (both when the voltage was turned on and off) was detected by the oscilloscope. Transmittance responses for voltage on and off for several applied voltages (much higher than the threshold switching voltage) were studied for pure LC and LC+ND 3. The setup was computer-controlled and data acquisition was performed using LabVIEW® software.

Figure 4 represents the normalized transmitted intensity response as a function of time for voltage (12V) on and voltage (12V) off for E7 and E7+GP 3 at $T = 30^\circ$C. Figure 4(a) shows that when the applied voltage is turned on at $t = 0$, the transmitted intensity drops as a function of time for E7 and E7+ND 3. The time the transmitted intensity takes to drop from 90% to 10% of the maximum intensity, after the voltage is turned on, is defined as the optical switching on, $\tau_{on}$. Figure 4(b) shows that the transmitted intensity increases as a function of time for E7 and E7+ND 3, after the applied voltage is turned off. The time the transmitted intensity takes to rise from 10% to 90% of the maximum intensity, after the voltage is turned off, is defined as the optical switching off, $\tau_{off}$. Note that $\tau_{rise}$ and
\[ \tau_{\text{decay}} \] from Eq. 3 are not equal to the electro-optical responses – \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \), respectively. However, the optical response is mainly due to the director’s rotation after the voltage is turned on or off. Therefore, neglecting the backflow in the cell, one can write \( \tau_{\text{rise}} \propto \tau_{\text{on}} \) and \( \tau_{\text{decay}} \propto \tau_{\text{off}} \).

It is apparent that E7+GP 3 sample responses faster than pure E7 when the voltage is turned on and off. Figure 5(a) and (b) show \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \), respectively, as a function of applied voltage for E7 and E7+ND 3. The results depict that at the optimal ND concentration, the LC switches significantly faster than the pure LC. Since \( K_{11} \) is not changed in E7+ND, the faster response is attributed to the reduction in \( \gamma_1 \). Note that the driving voltage, \( V \) is the dominating factor for \( \tau_{\text{rise}} \); see Eq. 3. Therefore, when \( V \gg V_{\text{th}} \), the effect of any change in \( \gamma_1 \) on \( \tau_{\text{rise}} \) is very small. In Fig. 5(a), the difference in \( \tau_{\text{on}} \) (\( \propto \tau_{\text{rise}} \)) between E7 and E7+ND 3 is more prominent in the low applied voltage regime. As \( V \) increases, the difference in \( \tau_{\text{on}} \) between E7 and E7+ND 3 is reduced.

According to several reports in the literature, the presence of carbon nanomaterials (such as carbon nanotubes, graphene flakes, fullerenes) in liquid crystals can significantly reduce the free-ion concentration in the LC media\(^{19,20,45}\) by the ion-trapping process. The diminished presence of free-ions can reduce the internal friction, resulting in a decrease in the rotational viscosity \( \gamma_1 \), of the LC media\(^{29-31,34,35}\). A reduction in \( \gamma_1 \), therefore, causes a faster rotation of the LC molecules. It is possible that NDs, being a carbon allotrope, also trap some ions and reduce the free-ion concentration in LC, decreasing \( \gamma_1 \) — hence the observed accelerated responses for \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) in the E7+ND sample.
As discussed before, we believe that above the optimal concentration E7+ND 3, the NDs start to aggregate. In aggregated forms, the NDs’ exposed surfaces to the LC are reduced greatly and the NDs no longer effectively interact with the LC. Consequently, $\gamma_1$ and $\theta_0$ do not show any further decrease for E7+ND 4 and E7+ND 5. Also note that two independent measurements, i.e., $\Delta \varepsilon$ and $\gamma_1$ indicate the same optimal ND concentration — E7+ND 3.

III. CONCLUSIONS

The enhancement in $\Delta \varepsilon$ for the LC+ND samples suggests that the NDs form anisotropic assemblies, which can be reoriented using the LC platform by applying an external electric field. The presence of NDs has a favorable impact on the LC’s rotational viscosity and pretilt angle. The reduction in rotational viscosity results in a faster electro-optic response of the LC, which could have potential applications in faster electro-optic devices. The reduction in pretilt angle also has applications in viewing angles. For in-plane-switching (IPS) LC displays, the viewing angle characteristics strongly depend on the pretilt angle. It has been theoretically predicted and experimentally observed that the smaller the pretilt angle of the liquid crystal, the wider the viewing angle characteristics of the IPS panel. Therefore, our results on the reduction of the LC pretilt angle by incorporating NDs is important and relevant for developing LCDs with wider viewing angles.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (Award No. N0001417WX01519) and the investment grant at the U.S. Naval Academy.