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Orientation in Nematic Liquid Crystals Doped with Orange Dyes and Effect of Carbon Nanoparticles

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Some properties of nematic liquid crystal E7 doped with two disperse orange dyes used together and effect of addition of carbon nanoparticles (single walled carbon nanotube or fullerene C60) on them were studied. Two dyes (disperse orange 11 and 13) having high solubility and order parameter were used as co-dopants. A notable increase in order parameter was obtained comparing to that of liquid crystal doped with single dye. When carbon nanoparticles were used as dopant, a decrease in order parameter was observed at low temperatures while it increased at high temperatures. When applied voltage changed, the order parameter abruptly increased in its threshold value and saturated in higher voltages as expected. An appreciable change in textures was not observed with addition of dopants. This addition gave rise to an increase in nematic-isotropic phase transition temperatures compared with that of pure liquid crystal.

Key words: Liquid crystal, Disperse orange dye, Carbon nanoparticle, Order parameter

I. INTRODUCTION

Guest-Host displays have attracted much attention because of their wide viewing angle, excellent hues, and high brightness levels. In order to realize bright and pure colors in these displays, the dyes having suitable characteristics must be used [1]. For this purpose, dyes having different structures have been studied as dopant. Two categories often used are azo and anthraquinone dyes. While azo dyes are usually characterized with high values of solubility and order parameter, the anthraquinone ones are preferred because of their high chemical, photo, and electrochemical stabilities [2].

Recently, new approaches were proposed to overcome limitations sourced from physical properties of liquid crystal, and different particles were added to liquid crystals [3–5]. Among several dopants, carbon nanotubes were found very interesting because of their anisotropic shape and strong interactions with liquid crystal [6, 7]. Their long axis aligns parallel to the LC director and with a bias voltage, the tubes also try to orient along the director [8–10]. The degree of alignment of nanotubes could be controlled in a liquid crystalline solvent and the ordered nanotube films could also enhance alignment in the nematic liquid crystal [11, 12].

In this work, the orientation in nematic liquid crystal doped with a couple of orange dyes and effect of carbon nanoparticles on it were studied. The results were discussed by comparing to each others.

II. EXPERIMENTS

Dyes (Fig.1) and carbon nanoparticles were supplied from Aldrich Chemical Company (Germany), nematic liquid crystal E7 (Fig.2) and organic solvents from Merck (Germany). They were used without further purification. Disperse orange 11, 13, and 37 are anthraquinone, bisazo, and monoazo structured dyes respectively. Liquid crystal E7 is an eutectic mixture of four different nematogens [13, 14].

Solutions were prepared by dissolving 0.5 mg of each of two dyes in 99 mg of the liquid crystal (i.e. 1%). In order to dissolve dyes in liquid crystal, the mixtures were heated and stirred in water bath. Dye/LC solutions were used after centrifugation at 14000 r/min and filtration. Single walled carbon nanotube or fullerene C60 in a small amount (0.05%) was added to these solutions. Sonication with an instrument Selecta (Unitronic OR) was employed to disperse the aggregated nanotube samples [15].

Isotropic-to-nematic phase transition temperatures were roughly determined by a polarising microscope Leica (DM2500 P) and the textures were photographed at various temperatures. Various magnifications of 4–50 times were employed by using an optical microscope equipped with a filtered halogen light source (12 V, 100 W) and digital pictures were acquired. A sample hot stage and cooling unit (Linkam Scientific Instruments, Model TS1500) connected to a programmable temperature controller (Linkam, Model THMS600) was
FIG. 1 Structures of disperse orange dyes. (a) Disperse orange 11, (b) disperse orange 13, and (c) disperse orange 37.

FIG. 2 Structures of nematic mixture E7.

utilized. The samples were heated at elevated temperature (∼75 °C) in glass-coated quartz cell until the nematic LC structure became optically isotropic, and then cooled to ambient temperature. The heating and cooling rate was 0.5 °C/min. Since the nematic-isotropic phase transition is thermally reversible, the clearing temperature was repeatedly determined by subsequent heating and cooling operations near transition point [16]. The clearing points were confirmed with thermograms obtained by using a differential scanning calorimeter from Shimadzu (Model DSC60). DSC experiments were carried out at the temperature range from −20 °C to 100 °C. Its scanning rate was 5 °C/min.

The absorption spectra were scanned on a Perkin Elmer Lambda 900 UV-Vis-NIR double beam spectrophotometer equipped with the sheet polarizers. Liquid crystal cells were supplied from ForeSea Technologies (USA) and filled with mixtures by capillary action. The space between the electrodes was 5 μm. The samples with planar homogeneous orientation were mounted in a thermostat holder. After dichroic ratios \( N \) were determined, order parameters \( S \) were calculated using the following equation [2, 17]:

\[
S = \frac{N - 1}{N + 2}
\]

These experiments were repeated at various DC voltages and temperatures and in this way, effects of voltage and temperature on order parameter were tried to be determined [18].

### III. RESULTS AND DISCUSSION

In order to determine solubilities of dyes in the liquid crystal, saturated solutions were prepared by using an excess of dye and the amount of undissolved dye was calculated from the results of spectrophotometric analyses [19]. The solubilities determined in this manner were given in Table I.

The solubilities of two dyes in liquid crystal E7 are in high level. Especially for bisazo-structured orange 13 dye, this is an expected result [20]. The results of our studies performed with single dye were previously published. Both of solubility and order parameter obtained with orange 37 dye were very low [21]. Therefore, orange 11 and 13 dyes were used in subsequent studies. The liquid crystal was doped with mixtures containing these two dyes and carbon nanoparticles (nanotube or fullerene C60).

By using polarising microscope, textures were separately photographed for pure liquid crystal and mixtures at various temperatures. When adding dopants, an appreciable change in textures was not observed as seen from an example one given in Fig.3. During these studies, isotropic-to-nematic phase transition temperatures were also tried to be determined. The shifts in phase transition temperatures of mixtures are given in Table II. As seen from Table II, the nematic-isotropic phase transition temperatures \( (T_{NI}) \) of liquid crystal with additive were higher than that of pure LC. \( \Delta T_{NI} \) values denote the shifts with respect to the temperature of pure LC and stay within limitations required [22]. Moreover, the shifts have positive values. The addition of dopants give rise to an increase in liquid crystal temperature range, but not decrease.

Transition temperatures were also determined by differential scanning calorimetry (DSC) analysis and

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{\text{max}}/\text{nm} )</th>
<th>Solubility/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse orange 11</td>
<td>472</td>
<td>2.24</td>
</tr>
<tr>
<td>Disperse orange 13</td>
<td>428</td>
<td>2.60</td>
</tr>
<tr>
<td>Disperse orange 37</td>
<td>424</td>
<td>0.20</td>
</tr>
</tbody>
</table>

These experiments were repeated at various DC voltages and temperatures and in this way, effects of voltage and temperature on order parameter were tried to be determined [18].
FIG. 3 Textures of liquid crystal E7 at various temperatures with magnification of 40 times. (a) pure LC, (b) doped with carbon nanotube, orange 11 and 13 dyes. (a1) $T=25^\circ$C, (a2) $T=58.7^\circ$C, (a3) $T=60.7^\circ$C, (a4) $T=25^\circ$C, (b1) $T=58.8^\circ$C, (b3) $T=60.9^\circ$C, and (b4) $T=25^\circ$C.

TABLE II Phase transition temperatures determined by polarising microscope.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$T_I$</th>
<th>$T_N$</th>
<th>$T_I-T_N$</th>
<th>$\Delta T_I$</th>
<th>$\Delta T_N$</th>
<th>$T_{NI}$</th>
<th>$T_{NI}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E7</td>
<td>60.7</td>
<td>58.7</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>59.70</td>
<td>0.0</td>
</tr>
<tr>
<td>Disperse orange 11+disperse orange 13+E7</td>
<td>60.9</td>
<td>59.2</td>
<td>1.7</td>
<td>0.2</td>
<td>0.5</td>
<td>60.05</td>
<td>0.35</td>
</tr>
<tr>
<td>Disperse orange 11+disperse orange 13+E7+SWCNT</td>
<td>60.9</td>
<td>58.8</td>
<td>2.1</td>
<td>0.2</td>
<td>0.1</td>
<td>59.85</td>
<td>0.15</td>
</tr>
<tr>
<td>Disperse orange 11+disperse orange 13+E7+C60</td>
<td>61.3</td>
<td>59.1</td>
<td>2.2</td>
<td>0.6</td>
<td>0.4</td>
<td>60.20</td>
<td>0.50</td>
</tr>
</tbody>
</table>

TABLE III Phase transition temperatures and melting enthalpies determined by DSC.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$T_{NI}/^\circ$C</th>
<th>$\Delta H$/mW</th>
</tr>
</thead>
<tbody>
<tr>
<td>E7</td>
<td>59.33</td>
<td>5.91</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes</td>
<td>59.90</td>
<td>3.50</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+SWCNT</td>
<td>59.39</td>
<td>3.37</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+C60</td>
<td>59.29</td>
<td>4.36</td>
</tr>
</tbody>
</table>

the values close to the previous ones were obtained (Table III). An example thermogram is shown in Fig.4. In this stage, absorption spectra were scanned on a spectrophotometer equipped with the sheet polarizers and dichroic ratios were determined. Order parameters calculated from dichroic ratios are given in Table IV.

Order parameters for liquid crystal doped with only orange 11 or 13 dye were determined as 0.62 and 0.59 respectively in our previous studies [21]. As seen from Table IV, the use of these two dyes as co-dopant resulted in an important increase in order parameter and the value of 0.84 was attained.

This increase may be attributed to hydrogen bonds formed between these two dyes. These bonds can form between the groups of amine (in orange 11 dye) and/or hydroxy (in orange 13 dye) with cyano moiety (of liquid crystal E7) [23]. This bonding enables the continuity of conjugate structure in the cell. As known, conjugate systems are widely used to improve charge injection/transport properties [24, 25]. The overall electrical conductivity enhanced in this way resulted in an increase in the value of order parameter.

In our previous studies performed with single dye, the value of order parameter was increased by addition of carbon nanoparticle. Surprisingly in this work, a decrease in value of order parameter was observed when adding the nanoparticle to the liquid crystal containing two dyes (Table IV).

FIG. 4 Thermogram of liquid crystal E7 doped with disperse orange 11 and 13 dyes.
TABLE IV Order parameters S obtained at various temperatures.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>T/°C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>E7+orange 11 and 13 dyes</td>
<td>18</td>
<td>0.84</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes</td>
<td>24</td>
<td>0.60</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes</td>
<td>30</td>
<td>0.51</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+SWCNT</td>
<td>18</td>
<td>0.79</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+SWCNT</td>
<td>24</td>
<td>0.60</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+SWCNT</td>
<td>30</td>
<td>0.55</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+C60</td>
<td>18</td>
<td>0.76</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+C60</td>
<td>24</td>
<td>0.61</td>
</tr>
<tr>
<td>E7+orange 11 and 13 dyes+C60</td>
<td>30</td>
<td>0.54</td>
</tr>
</tbody>
</table>

FIG. 5 Determination of saturation voltage for liquid crystal E7 doped with disperse orange 11 and 13 dyes.

It is not possible to explain this change with these results only. As a rough approximation, it may be said that while weak bonding between single dye and liquid crystal (OH···N≡C or NH₂···N≡C) is strengthened by carbon nanoparticles, they may give rise to the loss strength in strong mutual interactions between two dyes (OH···NH₂ plus OH···O=C). As a result, a decrease in high value of order parameter obtained with co-dopant two dyes is observed.

This effect is seen more dominantly in fullerene by comparing to carbon nanotube. Carbon nanotubes are nanoscale objects representing π-conjugated molecules. Single-walled nanotubes (SWNTs) show high conductivity along the tube length while they have very low conductivity across the diameter. However, the conductivity of fullerene C60 having spherical geometry is in high level in all of directions [26, 27].

Change in order parameter depending on voltage and temperature was also studied in this work. As seen from Fig.5, the order parameter increases when reaching a threshold value for voltage and saturates in higher voltages. Although increase in order parameter is in low scale, this change is an expected result [21, 28].

Order parameters obtained at various temperatures are given in Table IV. Its value for all mixtures decreases with an increasing temperature as expected [29]. While the addition of carbon nanoparticle give rise to a decrease in value of order parameter at low temperatures, an increase is observed at high temperatures. This result may be explained by increasing of electronic mobility at high temperatures.

IV. CONCLUSION

Some properties of nematic liquid crystal E7 doped with a couple of disperse orange dyes were studied. A notable increase in value of order parameter was observed comparing to the results obtained with single dye. This increase was attributed to hydrogen-bonding among dyes and liquid crystal as well as conjugate structure in cell. When carbon nanoparticles were added to these mixtures, a decrease in value of order parameter was observed at low temperatures. However, the order parameter showed an increase with this addition of carbon nanoparticle at high temperatures. An increase in temperature gave rise to a decrease in all of order parameters determined for liquid crystals with additive. However, this decrease was in narrower range for mixtures doped with carbon nanoparticles, especially fullerene C60. Although a remarkable change in texture was not observed with addition of dopants, they influenced the range of mesophase and caused an increase in the nematic-isotropic transition temperature of the pure host.