Abstract—The issue of long term stability of polymer stabilized blue phase liquid crystals was investigated. It was found that for certain liquid crystals and commonly used chiral dopant combinations, polymer stabilized blue phase liquid crystals develop dendrite-like structures. These features are highly scattering and are detrimental to the uniformity of texture. Various possible causes were looked into and it was identified that crystallization of the chiral dopant leads to dendrites and a possible remedy is proposed.

Index Terms—Chiral dopants, dendrites, long term stability, polymer stabilized blue phase liquid crystals (BPLCs).

I. INTRODUCTION

Blue phases (BPs) are thermodynamically frustrated phases existing in highly chiral liquid crystals (LCs) between cholesteric and isotropic phases. BPs are widely believed to be of three types namely, BPI, BPII, and BPIII in the order of increasing temperatures at which they exist. BPI and BPII have body centered and simple cubic lattice structures in their director fields, respectively [1], [2]. BPIII is amorphous with randomly distributed double twisted cylinders [3]. Inherent periodicity in BPI and BPII leads to the presence of Bragg reflection in these crystals. Colorful platelets of BPs are due to different crystallographic domains selectivity Bragg reflecting in different regions of the visible spectrum. The peak Bragg reflection wavelength can be tuned by an electric field over the entire visible spectrum, opening the possibility of reflective displays without color filters [4]. In nature they exist only in a very small temperature interval, typically 1°C to 2°C. Various techniques viz. doping with nano-particles [5], [6], doping with dendron shaped molecules [7], addition of short-chain polystyrene [8], synthesis of bimesogenic compounds [9], polymer stabilization [10], [11], etc., have been applied to broaden the temperature range. Out of these techniques, polymer stabilization is the most convenient and successfully increases the temperature range by tens of degree Celsius [10], including room temperature. With the most severe limitation of narrow temperature range solved, this phase of LCs has become a promising material for future displays and myriad non-display photonic components [12]–[16].

With sub-millisecond switching times, polymer-stabilized blue phase liquid crystals (PSBP-LC) are at least one order of magnitude faster than their nematic counterparts. Non-requirement of alignment layers and polarization independent characteristics further increase their appeal. Previously researchers have also investigated other interesting aspects viz. the effect of polymer network on electro-optical properties [17] and the means of reducing operating voltages [18].

Polymer stabilization does enhance the temperature range of BP, however in some cases long term stability of PSBP-LC remains a problem. In this paper, we report a thorough study on appearance of highly scattering crystalline structures, which are undesirable as they compromise the long term stability of PSBP. Its root cause is identified and a possible remedy is proposed.

II. EXPERIMENTS

We prepared various BPLC samples using different base nematic liquid crystals JC-1041XX (Chisso Corporation, Japan), 5CB (Sytchon Chemicals, Germany), HTG135400 (HCCH, China), HBG980000 (HCCH, China); two types of chiral dopants (CD) ZLI-4572 (Merck, Germany), R5011 (HCCH, China); monomer 2-Ethylhexyl Acrylate (EHA, Sigma Aldrich, Belgium); cross linker RM257 (Sython Chemicals, Germany) and photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPAP, Sigma Aldrich, Belgium). The compositions for difference mixtures in weight percentages are listed in Table I. LC cells were assembled by using 0.7 mm thick white float glass and 1.1 mm thick ITO coated glass, Corning 1737F with sheet resistance of 20 Ω/sq (both from PGO, Germany). Prior to cell fabrication glass plates were thoroughly rinsed in a sequence of steps involving overnight soaking in a RBS deter-
**TABLE I**

<table>
<thead>
<tr>
<th>Mixture name</th>
<th>LC</th>
<th>Concentration</th>
<th>CD</th>
<th>CD Concentration</th>
<th>EHA</th>
<th>RM257</th>
<th>DMPAP</th>
<th>Sample name</th>
<th>Polymerization state</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>LC1&lt;sup&gt;a&lt;/sup&gt; + LC2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>44.2 + 34.1</td>
<td>ZLI-4572</td>
<td>10.1</td>
<td>4.2</td>
<td>7.0</td>
<td>0.4</td>
<td>I</td>
<td>polymerized</td>
</tr>
<tr>
<td>A2</td>
<td>LC3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>77.3</td>
<td>ZLI-4572</td>
<td>9.9</td>
<td>4.6</td>
<td>7.2</td>
<td>1.0</td>
<td>III</td>
<td>polymerized</td>
</tr>
<tr>
<td>A3</td>
<td>LC&lt;sup&gt;d&lt;/sup&gt;</td>
<td>79.0</td>
<td>ZLI-4572</td>
<td>10.2</td>
<td>3.3</td>
<td>6.8</td>
<td>0.6</td>
<td>V</td>
<td>polymerized</td>
</tr>
<tr>
<td>B1</td>
<td>LC1 + LC2</td>
<td>47.9 + 38.9</td>
<td>R5011</td>
<td>2.9</td>
<td>3.3</td>
<td>6.4</td>
<td>0.5</td>
<td>VII</td>
<td>polymerized</td>
</tr>
<tr>
<td>B2</td>
<td>LC3</td>
<td>88.0</td>
<td>R5011</td>
<td>3.1</td>
<td>4.1</td>
<td>4.4</td>
<td>0.4</td>
<td>IX</td>
<td>polymerized</td>
</tr>
<tr>
<td>B3</td>
<td>LC4</td>
<td>88.4</td>
<td>R5011</td>
<td>3.0</td>
<td>3.5</td>
<td>4.5</td>
<td>0.5</td>
<td>X</td>
<td>polymerized</td>
</tr>
</tbody>
</table>

<sup>a</sup> is JC1041-xx; <sup>b</sup> is 5CB; <sup>c</sup> is HTG135400 and <sup>d</sup> is HBG980000

* Concentration: A1 is adopted from [10] and rest are optimized in our lab

Fig. 1. Experimental setup for the measurement of transmission spectra of PSBP-LC. White light is converted to circularly polarized light by a polarizer (P) with pass axis at 45° with respect to the c-axis of subsequent Quarter Wave Plate (QWP). L1 focuses the beam to a small spot on the LC cell and L2 focuses the beam onto the integrating sphere which collects the light to the USB spectrometer.

Taking cue from literature on concentration we prepared sample I. On gradual cooling from isotropic state as the characteristic texture of BP appeared, UV polymerization was used to stabilize the phase. Response times were measured to be in the sub-millisecond range and the results from tuning the Bragg reflection peak with an electric field were found to be in tune with literature, for PSBP. However, it was found that after a period of roughly 24 hours, the uniform BP texture was disturbed by the presence of dendritic structures as can be seen from Fig. 2(a). The samples were stored in darkness at a constant temperature of 21 °C and humidity controlled at 40% in the clean room. Such features are highly undesirable as they defeat the purpose of polymer stabilization. In order to eliminate the hypothesis of the polymerization process itself being a cause; we prepared sample II, an unpolymerized version of I. In due course of time this cell also developed undesired defects as can be seen from Fig. 2(b), which compromised the uniformity of texture. Although the physical appearance of the latter differed greatly from its polymerized counterpart, this observation absolves the polymerization process. The reason behind the difference in appearance is discussed later. These
structures invariably start from the filling end of the LC cell and continue to grow till they cover the entire cell.

To understand the dendrite-like structures better and to identify the mechanism responsible for their appearance, we studied their response to an electric field. The dendrites were found to be uninfluenced by the presence of an electric field. In Fig. 3(a) the characteristic platelet texture of BP can be clearly seen surrounding the dendrites. The cell is mounted between crossed polarizers. When a high DC voltage (140 V) was applied, regions with dendrites remained highly scattering while the rest of the cell turned dark as the liquid crystals switched, Fig. 3(b). From this observation, it can be safely inferred that molecules in liquid crystalline state are not present in the dendritic regions. However their mere absence from the region is not enough evidence to conclude that liquid crystals have no role to play in the manifestation of this phenomenon. It is worth noting that properties of PSBP in regions free from dendrites remain unchanged. The reason for this explained later. Fig. 4 shows transmission versus voltage curve and Bragg reflection before and after appearance of defects. The switching on and off times (10%–90% of transmission), before (after) were 668 μs (645 μs) and ~950 μs (759 μs) respectively.

We next prepared a sample without monomers, cross-linker or photoinitiator. The concentration of ZLI-4572 (9.87%) and the ratio of concentrations of JC-1041XX (50.07%) to 5CB (40.06%) are kept the same as in the LC mixture A1. A POM of these samples, Fig. 5(b) taken roughly 24 hours after filling, reveals the presence of dendrites in the region close to the hole used for capillary filling, whereas the central portion of LC cell, Fig. 5(a) remains uniform and devoid of these defects. The whole cell gets covered by dendrites in due course of time. The presence of dendritic structures in these samples exonerates monomers, cross-linker and photoinitiator from having any role in dendrite formation. Normally the openings for capillary filling are left open after carrying out the polymer stabilization. In order to preclude external influences such as dust, atmospheric gases and moisture from interacting with liquid crystals, openings were hermetically sealed. This did not have any influence on the formation of crystals either. Clearly, this leaves us with, either liquid crystals or chiral dopant or a combination of both being the cause of dendrites.

Replacing the base nematic JC-1041XX with HTG135400 and HBG980000, we prepared samples III, IV, V and VI. As can be seen from Figs. 6(a) and 7(a), dendrites start to appear roughly after 24 hours of polymer stabilization and affect the complete cell in samples III, IV, V, and VI respectively. The same behavior is observed in their respective unpolymerized counterparts, Figs. 6(b) and 7(b), respectively.

Form these experiments it can be concluded that dendrite formation is not linked to a particular liquid crystal mixture or their interactions with a specific chiral dopant.

In the samples with slightly lower concentration of chiral dopant, ZLI-4572 (9.0%) with JC-1041XX (51.4%) and 5CB (39.6%), BP was not found to be present. On cooling from isotropic phase at the cooling rate of 0.1 °C/min, the LC directly transformed to cholesteric droplets [22] shown in Fig. 8(a). However, these samples did not develop any dendritic structures. Hence the concentration of chiral dopant is suspected to be a crucial parameter. The concentration dependence of the phenomenon points towards crystallization being involved.

Although LC mixture is composed of components which are solid at room temperature, the probability of their crystallization is rather low. This leaves us with chiral dopant, which is also a solid at room temperature with limited solubility in LC mixture. This hypothesis is further supported by the shape of dendrites in polymer stabilized and non-polymer stabilized samples. In the case of unobstructed growth, crystals prefer to grow in a highly directional fashion. However the polymer network of PSBP presents an obstruction and forces them to bend, resulting in a branch like texture. This experiment also reveals that the minimum concentrations required to achieve critical chirality, for the BPs to be established, happens to be close to the solubility limit of chiral dopant in the nematic base.

Having established that the dendrite formation is a result of crystallization of chiral dopant we can explain, why properties of PSBP in regions free from them remains unaltered. Crystallization proceeds with local phase separation of chiral dopant. In regions free from it the concentrations remain unchanged so do optical and electro-optical properties. Also, it was recently reported that the polymer network in itself is capable of preserving and inducing chirality to achiral molecules. This capability of polymer networks has been demonstrated by using them as a template to induce BP in achiral liquid crystals [23].

Having arrived at this conclusion, the obvious step was to replace the chiral dopant. Knowing that the critical concentration of chiral dopant required to induce BP is inversely proportional to its HTP, we chose R5011, a chiral dopant with an HTP value greater than 100 μm⁻¹ [24]. The HTP of ZLI-4572 is reported to be 37.6 μm⁻¹ [25]. Samples VII to XII were prepared...
Fig. 4. (a) Transmission versus Voltage through the PSBP and (b) Bragg reflection in Sample B2 before and after appearance of dendrites.

Fig. 5. POM of the sample without monomer, crosslinker and photoinitiator after 24 h of filling (a) central region of the cell and (b) region near the filling end.

Fig. 6. POM showing dendritic structures in liquid crystal cells between crossed polarizers of LC mixture A2 at room temperature. (a) Sample III and (b) Sample IV.

Fig. 7. POM showing dendritic structures in liquid crystal cells between crossed polarizers of LC mixture A3 at room temperature. (a) Sample V and (b) Sample VI.

Fig. 8. (a) POM of a sample with low chiral dopant concentration (b) POM of a sample without dendrites days after polymerization.

Fig. 9. Chemical structures of the two chiral dopants involved in this study. (a) R5011 and (b) ZLI-4572.

Chiral dopants can be broadly classified in two categories: asymmetric center and axially asymmetric chiral compounds. R5011 belongs to axially asymmetric chiral binaphthyl derivatives which are typical atropisomeric chiral dopants [26]. Being conformationally rigid these chiral dopants manifest high HTP with R5011 with concentrations listed in Table I. The difference between the molecular structures of the two chiral dopants is shown in Fig. 9.
values [27], which results in appearance of BP with lower concentrations of chiral dopants. Samples VII, IX and XI then resulted in PSBP which were stable in true sense, by remaining devoid of any undesired manifestations for months. No such defect appeared in their unpolymerized counterparts, samples VIII, X and XII either. The POM manifestations formonths. Nosuchdefectappearedintheirunpolymer-
stable intruesense, by remaining devoid of any undesiredman-
centrationsofchiraldopants.

values [27], which results in appearance of BP with lower con-

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Geert Van Steenberge, photograph and biography not available at time of publication.

Olga Chojnowska, photograph and biography not available at time of publication.

Przemysław Kula, photograph and biography not available at time of publication.

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