

This is the accepted manuscript made available via CHORUS. The article has been published as:

Phase behavior and characterization of
heptamethyltrisiloxane-based de Vries smectic liquid
crystal by electro-optics, x rays, and dielectric
spectroscopy

S. P. Sreenilayam, D. M. Agra-Kooijman, V. P. Panov, V. Swaminathan, J. K. Vij, Yu. P. Panarin, A. Kocot, A. Panov, D. Rodriguez-Lojo, P. J. Stevenson, Michael R. Fisch, and Satyendra Kumar

Phys. Rev. E **95**, 032701 — Published 10 March 2017

DOI: [10.1103/PhysRevE.95.032701](https://doi.org/10.1103/PhysRevE.95.032701)

1 The Phase behaviour and the characterization of heptamethyltrisiloxane
2 based de-Vries SmA* liquid crystal by electro-optics, x-rays and
3 dielectric spectroscopy

4
5 S. P. Sreenilayam^a, D. M. Agra-Kooijman^{b†}, V. P. Panov^a, V. Swaminathan^a, J. K. Vij^{a*}, Yu. P.
6 Panarin^{a, c}, A. Kocot^d, A. Panov^e, D. Rodriguez-Lojo^e, P. J. Stevenson^e, M. Fisch^{b§} and
7 Satyendra Kumar^{b,f}

8
9 ^aDepartment of Electronic and Electrical Engineering, Trinity College,-The University of Dublin,
10 Dublin 2, Ireland

11
12 ^{b†}Department of Physics and [§]College of Applied Engineering Sustainability and Technology
13 Kent State University, Kent, OH 44242

14
15 ^cSchool of Electrical and Electronic Engineering, Dublin Institute of Technology, Dublin 8,
16 Ireland

17 ^dInstitute of Physics, Silesian University, Katowice, Poland

18 ^eSchool of Chemistry and Chemical Engineering, Queens University, Belfast, BT7 1NN, U. K.

19
20
21 ^fDivision of Research and Department of Physics, University at Albany, Albany, NY 12222
22

23 A heptamethyltrisiloxane liquid crystal (LC) exhibiting Iso-SmA*- SmC*
24 phases has been characterized by calorimetry, polarizing microscopy, x-ray
25 diffraction, electro-optics and dielectric spectroscopy. Observations of a large
26 electro-clinic effect, a large increase in the birefringence (Δn) with electric field, a
27 low shrinkage in the layer thickness($\sim 1.75\%$) at 20 °C below the SmA* to SmC*
28 transition, and low values of the reduction factor (~ 0.40) suggest that SmA* phase
29 in this material is of the de-Vries type. The reduction factor is a measure of the
30 layer shrinkage in SmC* phase and it should be zero for an ideal de-Vries.
31 Moreover, a decrease in the magnitude of Δn with decreasing temperature
32 indicates the presence of the temperature-dependent tilt angle in the SmA* phase.
33 The electro-optic behavior is explained by the generalized Langevin-Debye model
34 as given by Shen et al. [Phys. Rev. E **88**, 062504 (2013)]. The soft mode dielectric
35 relaxation strength shows a critical behavior when the system goes from SmA* to
36 SmC* phase.

37 *Corresponding Author: jvij@tcd.ie

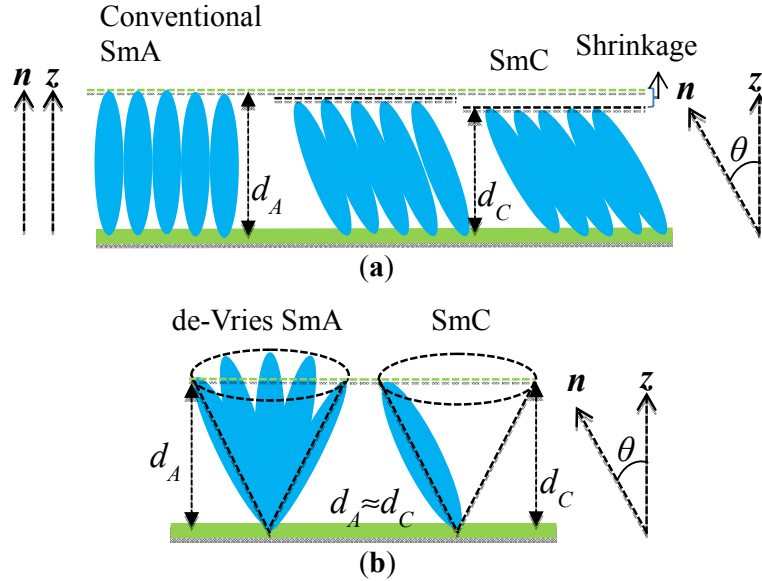
38 1. INTRODUCTION

39 In liquid crystalline (LC) compounds, the phase transition from the orthogonal (SmA) to
40 tilted (SmC) smectic phases is associated with an appearance of tilt (θ) between the molecular
41 long axis \mathbf{n} and layer normal z (Fig. 1a) Due to this tilt, the layer spacing in the SmC phase (d_C)
42 is smaller than in SmA (d_A). In the realm of the rigid-rod molecular model being valid (Fig. 1a),
43 the smectic layer thickness d_C is reduced from d_A by $\cos\theta$ [1-3]. In conventional SmC LCs, θ
44 varies from zero to $\sim 30^\circ$ depending on temperature. The large layer contraction in ferroelectric
45 SmC* induces chevron structures which in turn results into zigzag defects [4]. These defects
46 present a roadblock to a successful commercialization of the ferroelectric LC (FLC) devices. The
47 FLC devices intrinsically have faster switching modes [5] than their nematic counterparts that
48 are currently predominantly used in the industry. The objective is therefore to eliminate these
49 zigzag defects by making the smectic layer thickness almost independent of temperature so as to
50 have the most desirable features of FLCs in the next generation of displays.

51 In 1972, Diele et al. reported a non-chiral LC with the same layer spacing in the SmC and
52 SmA [6]. To explain it, de-Vries proposed a new type of SmA phase where the molecules are
53 tilted as in SmC with two possible structures. In one case [7,8], SmC-like layers are stacked in a
54 random fashion. In other words tilt directions with the same tilt angle in different layers are
55 randomly oriented. This implies that the azimuthal angle (φ) varies randomly from on layer to
56 next: no long range correlations in the azimuthal angle of the smectic layers was proposed to
57 exist in this case. In the second model of de-Vries [9], the molecules are tilted and the
58 correlation in the tilt direction exists within a single layer too, i.e. φ has a finite-correlation
59 length. If the correlation length is much smaller than wavelength of the visible light, then the
60 phase in optical experiments should behave as ‘a uniaxial SmA’. The results of both de-Vries
61 models should be that the directors in SmA phase would be distributed on to a cone as shown in
62 Fig. 1b.

63 The chiral de-Vries materials show electro-optic behavior due to the field-induced
64 azimuthal reorientation of the molecules on the cone and the apparent tilt angle measured by an
65 optical experiment in SmA thus increases with the field. They exhibit a significantly large
66 electroclinic effect due to the azimuthal reorientation and the induced tilt becomes saturated at
67 “high” electric fields once the degeneracy in the azimuthal angle is lost (the azimuthal angle is
68 condensed to values within narrow limits). For the zero external field, the maximum of the
69 molecular orientational distribution function is at the cone angle (volcano distribution) rather
70 than at the layer normal. The de-Vries behavior can be described by the reduction factor defined

71 as, $R = \frac{\delta(T)}{\theta_{opt}(T)} = \cos^{-1}[d_C(T)/d_{AC}] / \theta_{opt}(T)$; where $\delta(T)$ is the tilt angle for the layer shrinkage
 72 relative to layer thickness d_{AC} at the smectic A-C transition and θ_{opt} is the optical tilt angle
 73 determined by the polarizing optical microscopy [10, 11]. An ideal de-Vries material producing
 74 defect-free bookshelf geometry in SmC* phase will have the reduction factor $R=0$.

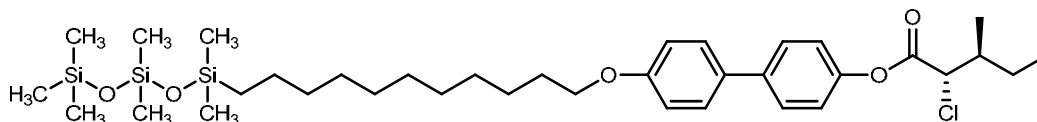


75
 76 **FIG. 1:** Schematic representation of (a) conventional SmA-SmC (rigid rod model) and
 77 (b) de-Vries SmA-SmC (diffuse cone model) phase transition. Here, z is the layer
 78 normal, n is the molecular long axis orientation, θ is the angle between n and z , d_C and
 79 d_A are the layer spacings in SmC and SmA phases, respectively.

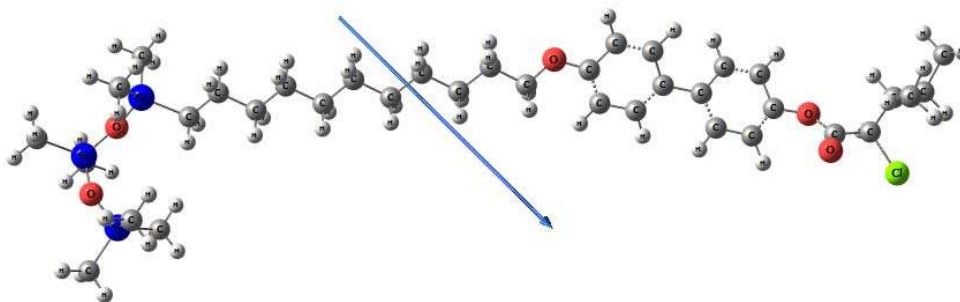
80 Several research groups reported de-Vries type behavior in smectic LCs composed of
 81 non-chiral [12-14] and chiral [15-19] molecules. LC materials that behave as ‘good de-Vries
 82 like’ so far are siloxane-terminated TSiKN65 compound [20], its carbosilane-terminated
 83 analogue W599 [21] and the 2-phenylpyrimidine derivative 8422[2F3] [22]. For these materials,
 84 the layer contraction at the smectic A*-C* transition lies in the range of 0.65 to 1%. In this
 85 paper, we present experimental results on the calorimetric, optical, polarization measurements,
 86 dielectric spectroscopy and x-ray diffraction on heptamethyl- trisiloxane derivative MSi₃MR11,
 87 which exhibits a strong electroclinic effect with birefringence strongly increasing at SmA* -
 88 SmC* phase transition. Experimental results suggest that the SmA* phase in this material is of
 89 de-Vries type. The reduction factor for this material is found to be ~ 0.40 . The electro-optic
 90 response and the induced polarization are found to be in agreement with the generalized
 91 Langevin-Debye model. The soft mode relaxation strength of de-Vries type SmA* phase as a
 92 function of temperature exhibits critical nature when the system undergoes a transition to SmC*
 93 phase.

94 **2. EXPERIMENTAL**

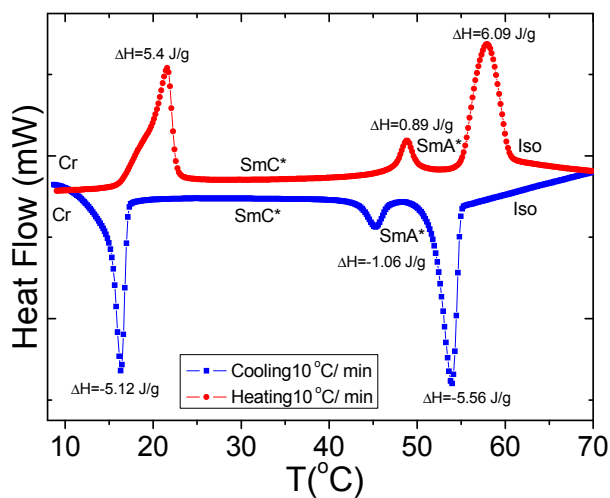
95 The molecular structure and the transition temperatures of the MSi₃MR11 are shown in
 96 Fig. 2a. This compound was resynthesized and it has two chiral centres. The synthetic procedure
 97 is given in the appendix A. One of the objectives here is to see whether two chiral centres give
 98 rise to a similar phenomenon as compounds with one chiral centre. The mesogenic core of MR11
 99 consists of a biphenyl 2-chloro-3-methylpentanoate unit. Here ‘M (mono-substituted)’ stands for
 100 the number of siloxane end groups attached to the mesogen MR11. The mesogen MR11 [23]
 101 with 11 methylene units is attached to a trisiloxane backbone. The purity of the sample was
 102 found to much higher through its analysis by NMR than for the previously synthesized sample
 103 [23]. An analysis for the purity of the sample is given in the appendix A. The transition
 104 temperatures (Fig. 2a) are obtained on cooling under quasi-equilibrium condition with a cooling
 105 rate of ~1°C min⁻¹ using polarizing microscopy.



107 (a)
 108 Cr 16°C [-5.12 J/g] SmC* 47°C [-1.06 J/g] SmA* 59°C [-5.56 J/g] Iso



110 (b)

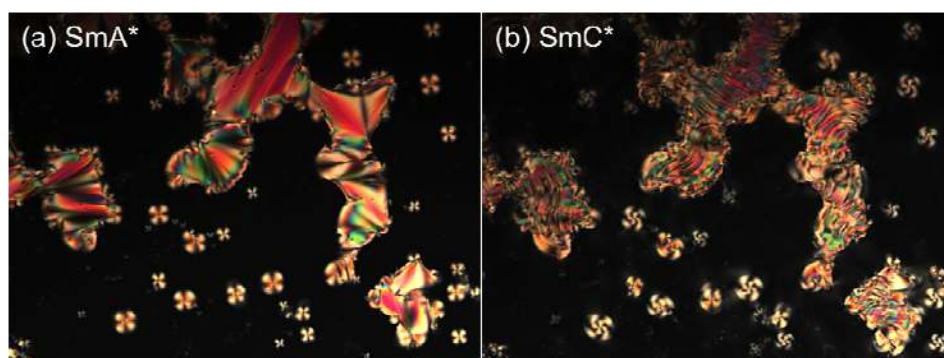


112 (c)

113 **FIG. 2** (color online) (a) Molecular structure of the LC material MSi₃MR11, phase
114 sequences and the transition temperatures (°C) with enthalpies (J/g, in square
115 brackets). (b) Optimized molecular geometry of MSi₃MR11. The arrow in Fig. 1b
116 shows the direction of the molecular dipole moment (3.562 D).(c) DSC cooling and
117 heating curves obtained at the rate of 10 °C min⁻¹. The transition temperatures are
118 obtained from the cooling cycle under the quasi-equilibrium condition at a rate of ~1
119 °C min⁻¹ using polarizing microscopy. Iso=isotropic state, Cr= crystalline state.

120 The optimized geometry of MSi₃MR11 (shown in Fig. 2b) is obtained by Density
121 Functional Theory (DFT) using B3LYP method with a 6-31G (d,p) level basis set. Optimized
122 geometry computations were carried out using Gaussian 09 software package [24]. The DSC
123 thermograms obtained for MSi₃MR11 are shown in Fig. 2c. In both heating and cooling cycles,
124 this material exhibits three transition peaks. The peaks in the DSC correspond to the phase
125 transitions I - SmA*, SmA* - SmC* and the crystalline state. These phases are additionally
126 characterized by polarizing optical microscopy. During the cooling cycle, enthalpy of the phase
127 transition Iso-SmA* is -5.56 J/g, whereas that of SmA*-SmC* is -1.06 J/g. The enthalpies
128 associated with the transition temperatures (first cooling and second heating rates of 10 °C min⁻¹)
129 show that the SmA*-SmC* phase transition is weakly of the first order [8,25].

130 The representative optical textures in the SmA* and SmC* phases (Fig. 3) were
131 recorded using the polarizing optical microscope (Olympus BX51) equipped with a CCD camera
132 (SPOT, Diagnostic Instruments, Inc.) on a non-oriented sample prepared between a glass slide
133 and cover slip placed in a Mettler Hotstage (FP82HT) with a thermal stability of ± 0.1°C.



134

135 **FIG. 3** (color online) Optical textures of MSi₃MR11 in (a) SmA*, 5 °C above
136 the SmA-SmC* transition, T_{AC}, and (b) SmC* (0.4 °C below T_{AC}), phases. The
137 dark regions in the texture correspond to homeotropically aligned LC
138 molecules.

139

140 The x-ray diffraction was studied on a sample contained in a flame sealed 1.0 mm quartz
141 capillary and placed inside a Linkam hotstage (HFSX350-CAP) with 0.05 °C precision

142 temperature controller (T95-HS) for a definitive identification of the smectic phases and for
143 temperature dependence studies of the structure parameters such as the layer spacing, tilt angle
144 and the orientational order parameters. The x-ray diffraction measurements were performed
145 using a microfocus Rigaku Screen Machine (Copper anode, $\lambda = 1.542 \text{ \AA}$) and the diffraction
146 patterns recorded by Mercury 3 CCD detector of resolution 1024×1024 pixels (size: 73.2×73.2
147 μm^2) placed ~ 73 mm from the sample. The data was calibrated against silver behenate standards
148 traceable to the National Institute of Standards and Technology. Data analyses were carried out
149 using FIT2D software [26] and Mathematica on the background corrected data (*i.e.* scattering
150 from an empty capillary was subtracted from the measured scattering data).

151 Electro-optic studies were made on planar cells filled with the material under study. The
152 planar alignment in this cell is achieved by coating the indium tin oxide glass substrates with a
153 RN1175 polymer alignment layer (Nissan Chemicals Japan) and baking the substrates at a
154 temperature of $250 \text{ }^\circ\text{C}$ for 30 minutes. The gap between the substrates is controlled by Mylar
155 spacers and the actual cell thickness is measured by the technique based on the optical
156 interference of reflected beams of light from the inner faces of the substrates of the cell. The
157 phases are characterized by using a polarizing optical microscope (Olympus BX 52) fitted with a
158 hot stage connected to a temperature controller (Eurotherm 2604). The electro-optic behavior of
159 the different phases is investigated by applying AC voltages of different amplitudes from a
160 signal generator (Agilent 33120A) amplified by a high voltage amplifier (TReK PZD700).
161 Dielectric spectroscopy over a frequency varying from 1 Hz-10 MHz is carried out using a
162 broadband Alpha High Resolution Dielectric Analyzer (Novocontrol GmbH, Germany) under
163 the application of a weak electric field of ($0.1 \text{ V}_{\text{rms}}$) applied across the cell with brass
164 electrodes. Temperature of the LC sample filled in the cell of gold coated brass electrodes is
165 stabilized to $\pm 0.05 \text{ }^\circ\text{C}$. The dielectric spectra are recorded during the cooling process from the
166 isotropic state.

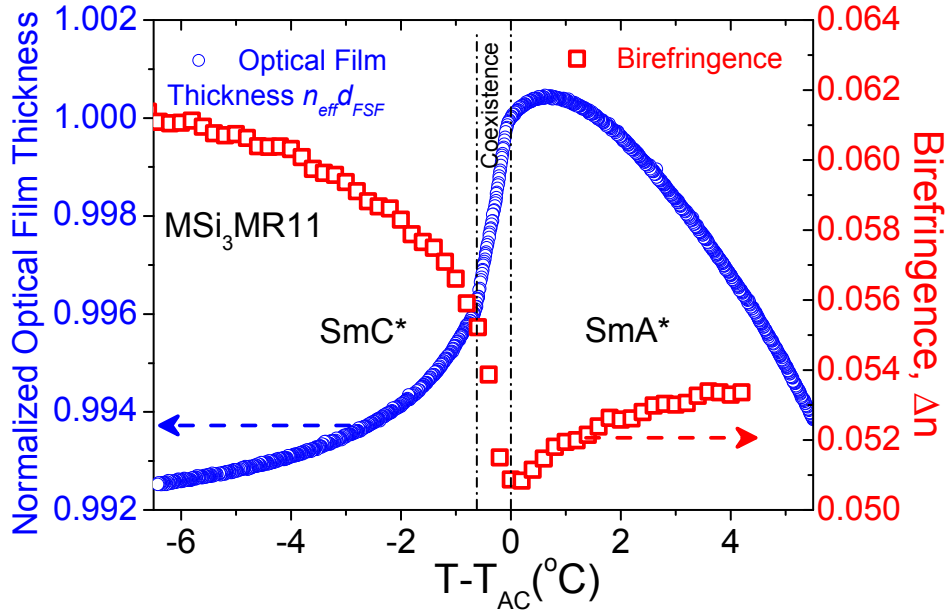
167 **3. RESULTS AND DISCUSSIONS**

168 **3.1 The Free-standing film thickness and Birefringence measurements**

169 The temperature dependence of the thickness of a free-standing film (FSF) is studied using a
170 high-resolution interferometric measurement technique [27]. A good quality homeotropic
171 alignment of LC molecules is achieved in the FSF of MSi₃MR11, the layer thickness covers
172 $\sim 10,000$ layers. An experimental measurement is carried out by shining an unpolarized beam
173 of light along the layer normal. Both heating and cooling cycles of the sample were carried

174 out with rates as low as $0.01^{\circ}\text{C}/\text{min}$ in order to avoid the change in the thickness that would
175 occur by a possible destruction of a few layers of the sample when the heating/cooling rates
176 were large enough. Figure 4 shows temperature dependence of the optical film thickness
177 normalized to the thickness at the SmA-SmC phase transition for the compound under study.
178 The optical film thickness is defined as its mechanical thickness multiplied by its effective
179 refractive index. The thickness is measured with a high resolution interferometric technique
180 to an accuracy better than 0.01%. If one simulates the refractive index with a change in the
181 tilt angle, then the normalized or the relative layer thickness can be obtained. Below the
182 isotropic temperature, the film thickness initially increases linearly but with a reduction in
183 temperature [28] and on approaching the smectic A* - SmC* transition, the film thickness
184 reverses its trend from increasing to decreasing with a reduction in temperature due to an
185 onset of the tilt. This trend characterizes SmA* - SmC* transition. For $(T-T_{AC})$ varying from
186 zero to -0.61°C , as seen in Fig. 4, a change in the normalized film thickness shows a sharp
187 decrease with a large drop-off in thickness. This anomalous drop is the characteristic
188 evidence for the first order SmA* - SmC* phase transition, labelled in Fig. 4 as the region
189 where SmA* and SmC* coexist. If all the layers in this narrow temperature range were to be
190 in the SmC* alone, the optical film thickness would have exhibited rather a linear low slope
191 drop-off with temperature; contrary to what is observed here. As already stated, the first-
192 order behavior is additionally corroborated by the DSC observations at the SmA* to SmC*
193 transition (Fig. 2b), which shows it to be a weak first-order transition. On further cooling the
194 film in the SmC* phase, its thickness continues to decrease only relatively slightly due to an
195 increase in the tilt angle. Finally the layer thickness reaches $d_C \approx 0.9925d_{AC}$ at 6.3°C below
196 T_{AC} . In this material, the layer shrinkage of 0.75% is found to be close to the reported values
197 of 0.73% and 0.65% for the other known de-Vries materials: W599 [21] and TSiKN65 [20],
198 respectively. This small layer shrinkage is due to an increase in the tilt angle with a
199 reduction in temperature; it is small because in going from SmA* to SmC*, the in-layer
200 directors with azimuthal angles degenerated and distributed on to a cone in SmA* condense
201 on to the azimuthal angles lying within narrower limits of the tilt in the SmC* phase (see
202 Fig. 1b); this process on its own requires no change in the layer thickness.

203

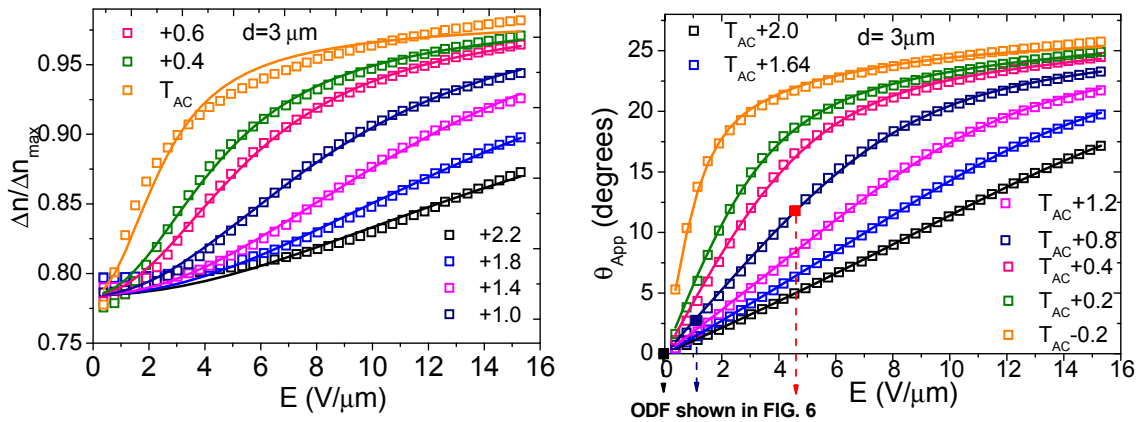


204

205 **FIG. 4:** (color online) Temperature dependence of the normalized optical film thickness;
 206 plotted as circles (\circ). Birefringence as squares, \square , plotted as a function of temperature on
 207 the right-hand side of Fig. 4. Measurements of the birefringence are carried out in the
 208 absence of external field on a 3 μm planar cell under cooling from the isotropic state. The
 209 coexistence region shown by two vertical dotted lines, where the two phases co-exist, is the
 210 signature of the first-order phase $\text{SmA}^* - \text{SmC}^*$ phase transition. In this narrow temperature
 211 range, if all the layers were to be in the SmC^* alone, the optical film thickness would have
 212 shown a small linear drop-off with temperature.

213 Figure 4 also shows the plots of the apparent birefringence Δn and the optical layer
 214 thickness as a function of $(T - T_{AC})$. The magnitude of Δn first decreases on cooling and then starts
 215 to increase after the $\text{SmA}^* - \text{SmC}^*$ phase transition has occurred [29]. The decrease in Δn is due
 216 to the de-Vries tilt appearing in the SmA^* phase where the in-layer directors are distributed on
 217 the cone. Values of the birefringence, Δn , and the apparent optical tilt angle, θ_{App} , are determined
 218 by recording the transmitted beam of light through the LC sample where a set of crossed
 219 polarizer and analyzer is rotated using a procedure similar to that described by Park et al. [30].
 220 Experiments were conducted by applying a triangular signal of frequency 46 Hz and an
 221 amplitude of 16 $\text{V}_{0\text{-pk}}/\mu\text{m}$. The frequency is so chosen as to allow sufficient time for switching to
 222 occur while avoiding the ionic conductivity from contributing to the switching current, and
 223 different from the mains frequency of 50 Hz to avoid interference from electrical noise to the
 224 output signal. Amplitude of the voltage applied should be large enough to saturate the tilt angle
 225 but at the same time it should be such be much lower than the dielectric breakdown of the
 226 sample by the electric field.

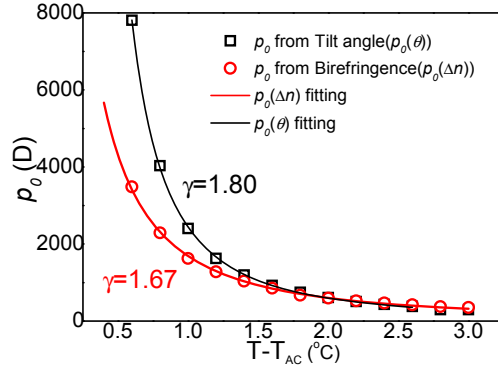
227 The field-induced tilt angle θ_{App} and Δn values for selected temperatures close to the SmA*
 228 - SmC* transition are plotted as a function of the applied field in Fig. 5. Magnitude of Δn
 229 increases with electric field (Fig. 5a) due to the lifting of degeneracy in azimuthal angle with the
 230 field. The behavior is typical of the diffuse-cone class of models for the SmA* phase. The tilt
 231 angle increases by the conventional electroclinic effect first and then finally it gets saturated
 232 with the field. This saturation in the tilt angle occurs in both SmC* and in the temperature range
 233 of SmA* closer to the SmA*-SmC* transition. At higher temperatures in the SmA* phase, the
 234 electroclinic effect itself is small and hence the electric fields applied are not large enough for
 235 the saturation in θ_{App} to show up; here θ_{App} shows almost linear response to the applied electric
 236 field [31] up to the value of $\theta_{\text{App}} \sim 15^\circ$. For temperatures closer to the SmC* - SmA* transition
 237 temperature, θ_{App} slightly deviates from the linear dependence on moderate values of the field,
 238 thus having a positive value of the second derivative with field. For large values of the electric
 239 field, θ_{App} continues to grow slowly and its second derivative becomes negative. Since the
 240 sigmoidal response of $\theta_{\text{App}}(E)$ and $\Delta n(E)$ could not be satisfactorily explained by Fukuda's
 241 Langevin-Debye approach [32], Shen et al. [21] proposed a modified model where they added
 242 additional term involving square of the electric field in the expression for the free energy.



243 **5(a)**

244 **5(b)**

245
 246



5(c)

247
248

249 **FIG. 5:** (color online) (a) Measured values of the birefringence as a function of the electric field
250 are fitted to the generalized Langevin-Debye model (solid lines) [21], (b) the field induced
251 optical tilt (experimental values in symbols) are fitted to this model (solid lines). Data points for
252 the Orientational distribution function (ODF) to be shown in Fig. 6 are marked in Fig. 5b. (c)
253 The local dipole moment p_0 obtained from (Δn and θ_{App} fits) as a function of the reduced
254 temperature. The solid lines are the best fits to the power law equation for the total dipole
255 moment $p_0(T) = A/(T-T_{AC})^\gamma$; γ is the power law exponent.

256 In spite of the several approaches [32-36] that exist for modeling the unusual electro-optic
257 characteristics of the de-Vries compounds; we choose the generalized Langevin-Debye model
258 that was recently proposed by Shen et al. [21] for the better analysis of our data for the reasons
259 given above. Fit of the data to the model leads to the orientational distribution function (ODF),
260 with a complete azimuthal degree of freedom but the tilt θ is allowed to vary by the applied field
261 within a certain range of values. A quadratic term in the electric field in the expression of free
262 energy has been found to have significantly improved the fit of the experimental data to the
263 model. According to this model the free energy, U , is expressed as:

$$264 \quad U = -\mathbf{p} \left(1 + \alpha \frac{\mathbf{p}}{|\mathbf{p}|} \cdot \mathbf{E} \right) \cdot \mathbf{E} = -p_0 E \sin \theta \cos \varphi (1 + \alpha E \cos \varphi) \quad (1)$$

265 Here $p = p_0 \sin \theta$ is the dipole moment of the domain correlated in the tilt brought about by
266 the condensation of the azimuthal angle. The first term ($-p_0 E \sin \theta \cos \varphi$) given in Eqn. 1
267 describes the dipole interaction energy and the second term ($-p_0 E^2 \sin \theta \cos^2 \varphi$) includes the tilt
268 susceptibility that increases with the square of the electric field. This term leads to the sigmoidal
269 response in both Δn and θ_{App} with applied field. α is the phenomenological scaling factor. The
270 tilt angle θ_{App} and the birefringence Δn as functions of the applied field become:

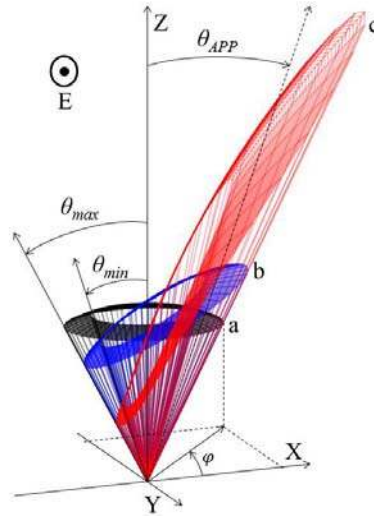
271
272

$$\tan 2\theta_{App} = \frac{\langle \sin 2\theta \cos \varphi \rangle}{\langle \cos^2 \theta - \sin^2 \theta \cos^2 \varphi \rangle} \quad (2)$$

273
$$\frac{\Delta n}{\Delta n_{max}} = \frac{\langle \cos^2 \theta - \sin^2 \theta \cos^2 \varphi \rangle}{\cos 2\theta_{App}} \quad (3)$$

274 An average $\langle Y \rangle$ is estimated over the orientational distribution of molecules according to
 275 the formula $\langle Y \rangle = \int_{\theta_{min}}^{\theta_{max}} \int_0^{2\pi} Y(\theta, \varphi) f(\theta, \varphi) \sin \theta d\theta d\varphi$, where the mean field orientational
 276 distribution function $f(\theta, \varphi)$ is expressed as $f(\theta, \varphi) = \exp[-U/k_B T] / \int_{\theta_{min}}^{\theta_{max}} \int_0^{2\pi} \exp[-U/
 277 $k_B T \sin \theta d\theta d\varphi$ [21]. In this model, the field induced angle varies between the values inferred
 278 from the birefringence at zero electric field (θ_{min}) to the maximum field (θ_{max}). For the latter Δn
 279 is assumed to be saturated by the field. Here, for MSi3MR11, the limiting values of the induced
 280 angle are found to be $\theta_{min} = 16.93^\circ$ and $\theta_{max} = 26.63^\circ$ (Fig. 5a, b). These limiting values of θ
 281 themselves are temperature independent but the actual value within these limits is nevertheless
 282 temperature dependent. Datasets obtained for both $\Delta n(E)$ and $\theta_{App}(E)$ are fitted by the model
 283 [21]. However in contrast to the procedure used in [21], the fitting is carried out separately for
 284 both $\Delta n(E)$ and $\theta_{App}(E)$. Though better fits for both (a) and (b) are obtained, however the fits
 285 with different power law exponents do reveal short-comings of the model. However both
 286 exponents are in the “de Vries - range” and outcome of the ODF is clearly “diffused-cone”. If
 287 such a limitation is material independent then this issue needs to be addressed in future.$

288 Figure 6 shows the ‘orientation distribution function’ (ODF), $f(\theta, \varphi)$, for MSi₃MR11 at a
 289 temperature of $T = (T_{AC} + 0.8)^\circ\text{C}$ for different strengths of the electric field. The simulated ODF is
 290 rather close to a corresponding result demonstrated earlier for a different material (Fig. 5 (a,b) in
 291 ref [21]). One can see that the model enforces a clear diffused cone distribution – by confining
 292 the cone angle between the limits of θ_{min} and θ_{max} . In this case, the re-distribution of the
 293 azimuthal angles of molecules caused by the electric field generates a finite apparent optical tilt
 294 angle very close to the one found in the experiment (Fig. 5b). For the higher field strengths,
 295 nearly all of the molecules are aligned along a single direction on the outer (θ_{max}) cone. Note that
 296 the modelled ODF shown in Fig. 6 corresponds to the aromatic core part of the molecule that
 297 exhibits birefringence in the visible range of wavelengths.



298

299 **FIG. 6** (color online): The Orientation Distribution Function $f(\theta, \varphi)$ of MSi₃MR11 at a
 300 temperature of $T = (T_{AC} + 0.8) \text{ }^\circ\text{C}$ for various values of electric field strengths – (a) 0 V/ μm
 301 (black); (b) 1.14 V/ μm (blue); and (c) 4.17 V/ μm (red). X - Y is the smectic layer plane and Z is
 302 directed along the layer normal. Electric field is applied along the Y direction which lies in the
 303 smectic layer.

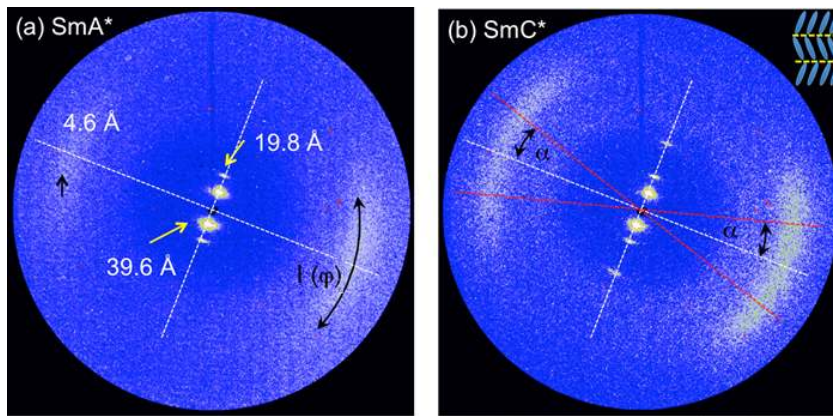
304 The local dipole moment p_0 , (Fig. 5c), determined as a fitting parameter increases with
 305 decreasing temperature in the SmA* phase. On approaching the SmA* - SmC* transition from
 306 the high temperature side, the magnitude of p_0 in the generalized Langevin-Debye model
 307 diverges corresponding to the correlation length of the tilt domain where the azimuthal angle is
 308 condensed to values within narrow limits. Here the magnitudes of p_0 obtained from the fitting of
 309 the birefringence and the tilt data are somewhat different in the vicinity of the smectic SmA* -
 310 SmC* transition. Also, the scaling parameter α of the electric field varies from 0.017 to 0.023
 311 $\mu\text{m}/\text{V}$ for birefringence and ~ 0.024 to 0.11 for data on the tilt angle. This clearly indicates that
 312 the system is more complex than the simple assumptions made in this model despite the quality
 313 of the individual fits of Δn and the apparent tilt angle to the model. One of the main reasons for
 314 this discrepancy could be that the model assumes constant values of θ_{\min} and θ_{\max} independent of
 315 temperature. But measurements on the layer thickness and on temperature dependence of the
 316 zero-field birefringence reveal that θ_{\min} does at least vary with temperature. The second reason
 317 could be that the molecular biaxiality that is neglected in the model so far has to be taken into
 318 account [33].

319 To analyze the temperature dependence of the correlated dipole moment, p_0 , we fit the
 320 data to the power law equation, $p_0(T) = A / (T - T_{AC})^\gamma$ (Fig. 5c), γ is the power law exponent. The
 321 fit is found to be excellent but temperature dependencies of the local dipole moment are

322 different for the birefringence and the apparent tilt angle. Exponents for d_C and d_L are found
 323 to be 1.67 and 1.80, respectively. These fits lead to the conclusion that the correlated tilt (or the
 324 correlation length) increases with a reduction in temperature in the SmA* phase [37], this is
 325 reminiscent of the de-Vries behavior [9,18].

326 3.2 X-ray Diffraction

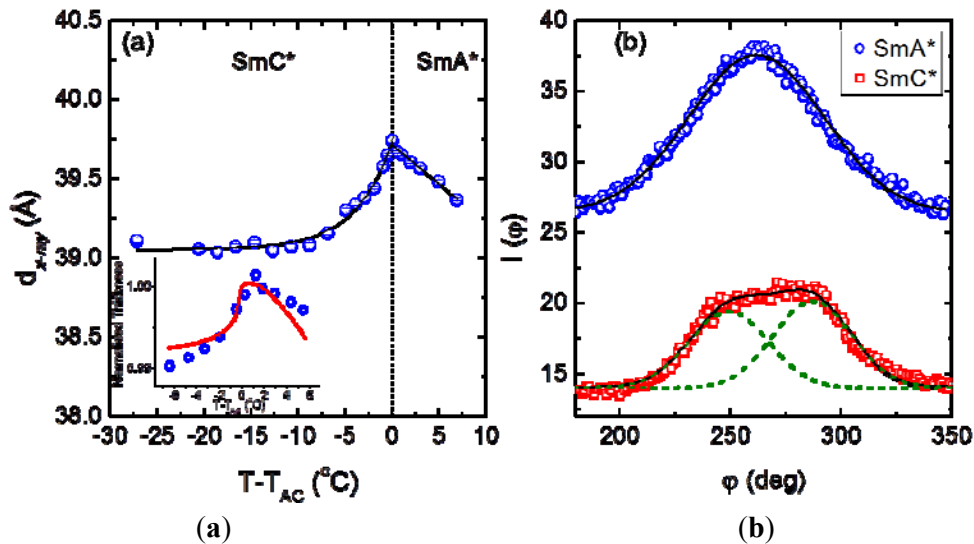
327 The x-ray diffraction pattern for the SmA* shows sharp Bragg layer reflection peaks in the
 328 small angle region centered at $\sim 39.6 \text{ \AA}$ and the 2nd order reflection centred at $\sim 19.8 \text{ \AA}$, shown in
 329 Fig. 7a. A pair of diffuse crescents in the wide-angle region perpendicular to the layer peak
 330 located at $\sim 4.6 \text{ \AA}$ confirm the orthogonal smectic (SmA) nature of this phase. In the SmC* phase
 331 (Fig. 7b), the 3rd order smectic reflections appear at $\sim 13.4 \text{ \AA}$ and the crescents are centered at 4.6 \AA
 332 \AA perpendicular to the layer peaks, this seems to be indistinguishable from the SmA* phase.
 333 However, the pair of wide-angle crescents are more diffuse in the SmC* phase, than in SmA*,
 334 where each crescent can be approximated as a sum of the two crescents separated by an angle 2α ,
 335 α being the molecular tilt angle with respect to the layer normal. This corresponds to the domain
 336 structure with the opposite tilts, as illustrated in the inset of Fig. 7b.



337
 338 **Fig. 7:** Representative x-ray diffractions patterns of MSi3MR11 in (a) SmA* phase
 339 (1.2 °C above the T_{AC}) and (b) SmC* phase (17.5 °C below the T_{AC}). Inset of (b)
 340 depicts the SmC* structure.
 341

342 The temperature dependence of the smectic layer spacing (Fig. 8a), determined from the
 343 Lorentzian fits to the first small-angle peak reveals 1.75% maximum layer shrinkage in the
 344 SmC* phase, approximately 20 degrees below the smectic A* to C* transition. Note that the
 345 optical layershrinkage of 0.75% mentioned above is based on the smallest d_C spacing, obtained
 346 approximately 6 degrees below the smectic AC transition. The inset in Fig. 8a shows a
 347 comparison between the layer thickness measured by x-ray with the optical FSF thickness, the

348 latter is normalized by the value at the SmA* to SmC* transition temperature. A different trend
 349 in between the two is due to a change in the refractive index tensor by the molecular tilt angle θ
 350 [27]. On cooling the cell in SmC* this deviation reaches $\sim 20\%$ of the total shrinkage which can
 351 be explained by a larger value of the tilt at the phase transition point as compared to the material
 352 described in [27]. The tilt angle, α in the SmC* phase was calculated as half the angle of
 353 separation between the centers of the two Gaussian fits to the azimuthal intensity distribution,
 354 $I(\varphi)$ of the wide angle reflection at 4.6 \AA , Fig. 8b. Owing to the difficulty in obtaining a single
 355 domain sample, a reasonable temperature dependence of the tilt angle in the SmC* phase
 356 specifically close to the SmA* - SmC* transition was difficult to determine. Nonetheless, the
 357 maximum calculated tilt angle α_{\max} is $\sim 20^\circ$ in the lower SmC* phase.

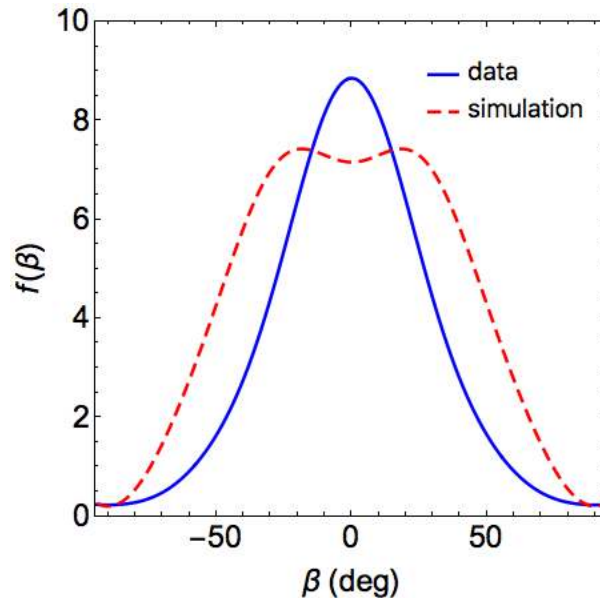


358
 359
 360 **FIG. 8.** (color online): (a) Temperature dependence of the layer spacing determined
 361 from the x-ray diffraction. A comparison of the results of the layer thickness from the
 362 free standing film experiment (red [solid line](#)) and the layer thickness from the x-ray
 363 results as discrete points (circles) given in the inset. Both curves in the inset are
 364 normalized (b) The representative azimuthal intensity distribution $I(\varphi)$ of the wide-
 365 angle reflection centered at 4.6 \AA in the SmA* (open circles) and in the SmC* (open
 366 squares) phases. The solid black line in SmA* is a single Gaussian fit (FWHM=64),
 367 while in SmC*, it is the sum of two Gaussian fits (dashed-lines) with FWHM = 36.

368 The orientational order parameter, $\langle P_2(\cos\beta) \rangle$ from the azimuthal intensity distribution $I(\varphi)$
 369 of the wide angle reflection centered at $\sim 4.6 \text{ \AA}$ (Fig. 7b) is determined using the method of
 370 Davidson et al. [38], numerical inversion method increased the value from 0.41 ± 0.01 (SmA*) to
 371 0.58 ± 0.01 (SmC*). Here, β corresponds to the angle between the director and the long axis of
 372 the molecule. The low values of $\langle P_2 \rangle$ obtained here are the typical ones for the de-Vries
 373 compounds with chiral components, as compared to the $\langle P_2 \rangle$ for de-Vries without chiral
 374 components [12,13], however these low values are also partly attributed to the presence of multi

375 domains in the scanned sample volume. Correspondingly, the average molecular fluctuation [13]
 376 $\langle\beta\rangle$, decreased from $35.8^\circ \pm 0.2$ (SmA*) to $31.6^\circ \pm 0.2$ (SmC*). The extent of molecular
 377 fluctuations in SmA* is much larger than the measured maximum apparent tilt, $\theta_{\text{App}} \sim 25^\circ$ which
 378 obscures the dip in the expected volcano-shaped ODF for de-Vries compounds and effectively
 379 appears as sugarloaf distribution shown in Fig. 9 as a solid line. To illustrate this, a simulated
 380 orientational distribution function ODF with respect to the layer normal in de-Vries SmA phase
 381 with a polar tilt angle $\alpha = 25^\circ$ and the molecular fluctuations $\langle\beta\rangle \sim 23^\circ$ is also shown in Fig. 9 (red
 382 dashed line). Note that the x-ray diffraction probes the electron density related to the overall
 383 molecular length, thus the sugarloaf-shaped ODF obtained from the x-ray experiment does not
 384 rule out the diffuse-cone distribution obtained from the visible light optical parameters of the
 385 same compound.

386

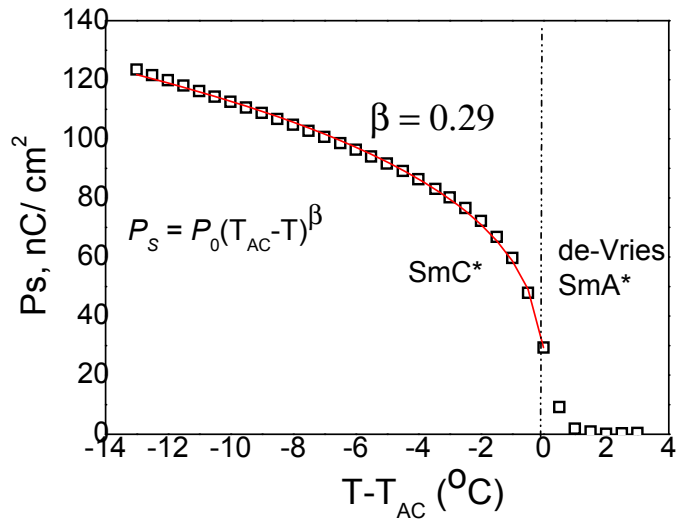


387

388 FIG. 9. (color online) The orientational distribution functions in the SmA* phase
 389 determined from the experimentally measured $I(\varphi)$ (solid line) and the simulation
 390 (red dashed line).using molecular fluctuations $\langle\beta\rangle = 23^\circ$ and the tilt angle $\alpha = 25^\circ$

391 3.3 Spontaneous Polarization Measurement

392 The spontaneous polarization P_S is measured using a planar cell of thickness $4 \mu\text{m}$ as a function
 393 of temperature and the results are shown in Fig. 10. For conducting the experiment, an external
 394 triangular wave ac voltage of $50 \text{ V}_{\text{pk-pk}}$ of frequency 152 Hz is applied across the planarly
 395 aligned cell using the method reported previously [39]. Measured value of P_S corresponds to its
 396 saturated value by the external field at the temperature of interest. The LC under study gives P_S
 397 $\sim 124 \text{ nC cm}^{-2}$ for a temperature of $T=(T_{\text{AC}} - 13.5)^\circ\text{C}$.



398

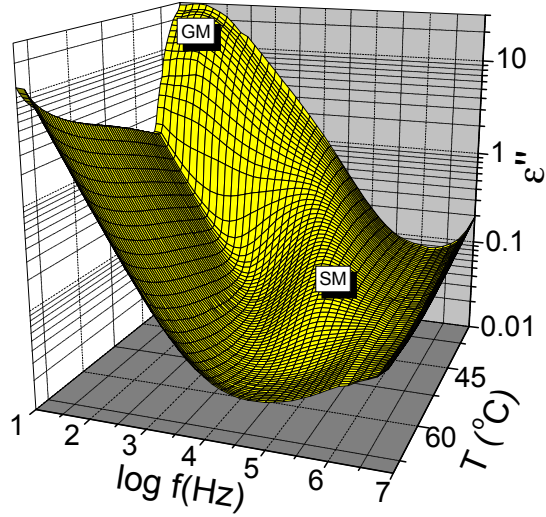
399 FIG. 10. (color online) Spontaneous polarization P_S vs $(T-T_{AC})$ measured on $4\ \mu\text{m}$ planar cell
 400 under cooling from the isotropic state. A triangular-waveform voltage of 50 Vpk to pk at a
 401 frequency of 152 Hz is used in the experiment. $P_0 = 56.9\ \text{nC}\cdot\text{cm}^{-2}$.
 402

403 P_S values are fitted to the power law equation $P_S = P_0 (T_{AC} - T)^\beta$. In the fitting, it is not
 404 possible to include the values P_S in the SmA phase. The power law exponent, $\beta = 0.29$, is
 405 found from the fitting. This value so determined is close to that for the tricritical behavior; i.e.
 406 the point where the first and second order transitions meet with each other. The transition can
 407 then be described as ‘a weakly first order transition’.

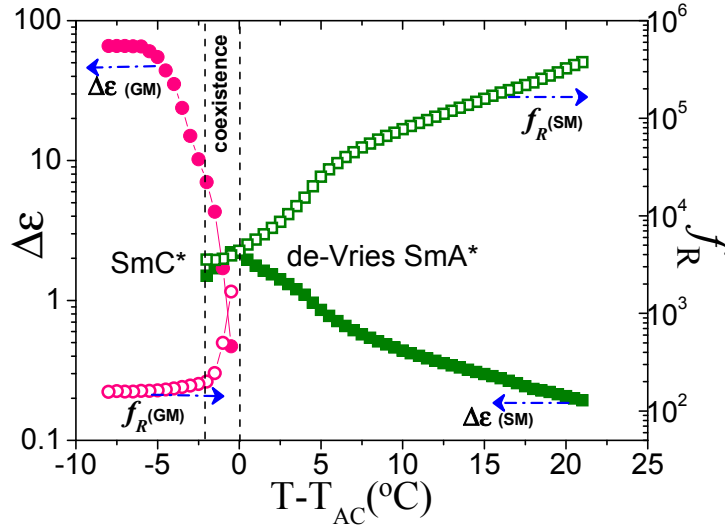
408 3.4 Dielectric Spectroscopy

409 Figure 11a shows the three dimensional plot of temperature dependent dielectric loss
 410 spectra (ϵ'') of a planarly-aligned cell filled with MSi₃MR11. The electrodes are made up of
 411 brass, these are gold-plated so as to have almost zero contact resistance. This is done to avoid the
 412 parasitic effects of the finite resistance of ITO electrodes acting in series with the cell-
 413 capacitance on the dielectric spectra.

414



(a)



(b)

415
416
417

418
419

420 FIG. 11. (color online) (a) The three dimensional (3D) plot of temperature dependent
421 dielectric loss spectra (ϵ'') for a 10 μm planarly aligned cell in the frequency range 1 Hz -
422 10 MHz. The dielectric measurements are carried out on the sample under cooling from
423 the isotropic state. Temperature is stabilized to ± 0.05 $^{\circ}\text{C}$ and the applied voltage in the
424 experiment is fixed as 0.1 V_{rms} . (b) The dielectric relaxation strength $\Delta\epsilon$ and the
425 relaxation frequency f_R for both the Goldstone (GM) and soft (SM) modes are plotted as
426 a function of the reduced temperature. The temperature range where the two phases co-
427 exist is shown by a set of vertical dotted lines close to the transition temperature.

428 The dielectric measurements are carried out over a frequency range of 1 Hz to 10 MHz
429 using a broadband Alpha High resolution Dielectric analyser (Novocontrol GmbH, Germany),
430 measurement made under a weak applied voltage of 0.1 V_{rms} . Temperature of the cell is
431 controlled to within ± 0.05 $^{\circ}\text{C}$. The temperature dependencies of the dielectric strength ($\Delta\epsilon$) and

432 the relaxation frequency (f_R), are obtained by fitting the dielectric spectra to the Havriliak -
 433 Negami equation [40] :

$$434 \quad \varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \sum_{j=1}^n \frac{\Delta\varepsilon_j}{[1 + (i\omega\tau_j)^{\alpha_j}]^{\beta_j}} - \frac{i\sigma_{dc}}{\varepsilon_0\omega} \quad (4)$$

435 Here, ε_∞ is the high frequency permittivity that includes the atomic and electronic
 436 polarizabilities, j is the number of relaxation processes and it varies from 1 to n , $\omega=2\pi f$ is the
 437 angular frequency, ε_0 is the permittivity of free space, $\Delta\varepsilon_j$ refers to the dielectric relaxation
 438 strength of the j th mode. α_j ($0 \ll \alpha_j \leq 1$) and β_j ($0 \ll \beta_j \leq 1$) are the symmetric and asymmetric
 439 broadening parameters of the complex dielectric function of the j^{th} relaxation process. The
 440 $\sigma_{dc}/\varepsilon_0\omega$ is contribution of the dc conductivity to ε'' . The relaxation frequency, f_j , of the j^{th}
 441 relaxation process is related to its relaxation time τ_j as [41]:

$$442 \quad f_j = \frac{1}{2\pi\tau_j} \left[\frac{\sin(\alpha_j\pi)}{2+2\beta_j} \right]^{1/\alpha_j} \left[\frac{\sin(\alpha_j\beta_j\pi)}{2+2\beta_j} \right]^{-1/\alpha_j} \quad (5)$$

443 In this case we fix $j = 2$ as we focus on to the two predominant modes: Goldstone mode
 444 (GM) and the soft mode (SM) over a restricted range of frequencies; inspite of the fact that many
 445 additional modes can possibly exist in a FLC cell [42]. The dielectric spectra are analysed using
 446 WINFIT programme purchased from Novocontrol GmbH. Temperature dependencis of the
 447 dielectric strength ($\Delta\varepsilon$) and relaxation frequency (f_R) for the two modes are shown in Fig. 11b.
 448 On cooling the cell from the isotropic state, the amplitude of the $\Delta\varepsilon$ increases and reaches a
 449 maximum value at the SmA* - SmC* phase transition. The corresponding f_R decreases on
 450 cooling over a broad temperature range of SmA* phase but with a sharper trend in its lower
 451 temperature range. In the studied chiral MSi3MR11 material, the soft mode fluctuation is
 452 dielectrically active in the SmA* phase due to the component of the dipole moment parallel to
 453 the probe field fluctuating with the applied electric field. Remarkably strong soft mode
 454 absorption is found in the dielectric spectra of de-Vries materials over a broader temperature
 455 range in comparison to the materials that exhibit a conventional SmA phase. For example the
 456 dielectric strength rises continuously with a reduction in temperature in this sample as opposed
 457 to a sudden rise of $\Delta\varepsilon$ in a conventional SmA phase, [compare Fig. 11b with Fig. 1b of Ref. 43]
 458 and Fig. 11b with Fig. 8a and 8b of [44]. Similarly the soft-mode relaxation frequency
 459 continuously decreases over a very wide temperature range in SmA* in this sample as opposed
 460 to conventional SmA in which a sudden change in the frequency occurs over a very narrow

461 range of temperatures close to the SmA* - SmC* transition [compare Fig. 11b with Fig 1b of
462 [43]] for the relaxation frequency.

463

464 **4. CONCLUSIONS**

465 The siloxane liquid crystalline compound exhibiting de-Vries SmA* phase was studied by DSC,
466 polarizing optical microscopy, XRD, FSF, electro-optics and dielectric spectroscopy. MSi₃MR11
467 shows a direct transition to SmA* phase on cooling from the isotropic state. Calorimetric studies
468 confirm earlier works on the LC thermograms that report first order SmA*-SmC* phase
469 transition in de-Vries LCs. Based on the results of Δn and θ_{App} measurements, together with the
470 minimum layer shrinkage ($\sim 1.75\%$) obtained in this case, we characterize SmA* of the studied
471 material to be of the de-Vries type, since an increase in the tilt angle with reducing temperature
472 leads to decrease in magnitude of the birefringence. An increasing Δn with applied field was
473 found in the vicinity of SmA*-SmC* transition. The generalised Langevin-Debye model as
474 proposed by Shen et al. [21] is used to explain the electro-optical effects observed
475 experimentally in the de-Vries SmA* phase of this material. While retaining power law
476 dependencies of the optical parameters (Δn , θ_{App}) on temperature with slightly different
477 exponents, the observed phenomena are well described by this model. The critical exponents
478 indicate that dimension of the system is greater than unity in agreement with the de-Vries nature
479 of the material. The soft mode relaxation strength from dielectric spectroscopy shows a critical
480 behavior when the LC system approaches SmA* to SmC* phase transition. The future
481 development of the de-Vries model should include temperature dependencies of the minima and
482 maxima of cone angles and the molecular biaxiality must be included in the model parameters.
483 X-ray scattering gives rise to sugar-loaf orientational distribution function but it does not exclude
484 the observation of the diffused cone model for the electro-optical effects (birefringence and the
485 tilt angle) as explained in the text. It would also appear that the presence of the two chiral centres
486 in the molecule does not prevent this material from exhibiting the de Vries behaviour.

487 **ACKNOWLEDGEMENTS**

488 This work was supported by 13/US/I2866 from the Science Foundation of Ireland as
489 part of the US–Ireland Research and Development Partnership program jointly administered with
490 the United States National Science Foundation under grant number NSF-DMR-1410649 and by
491 the DFG (Grant TS 39/24-1). A. Kocot thanks National Science Centre Poland for grant
492 2011/03/B/ST3/03369.

493 **Appendix A:**

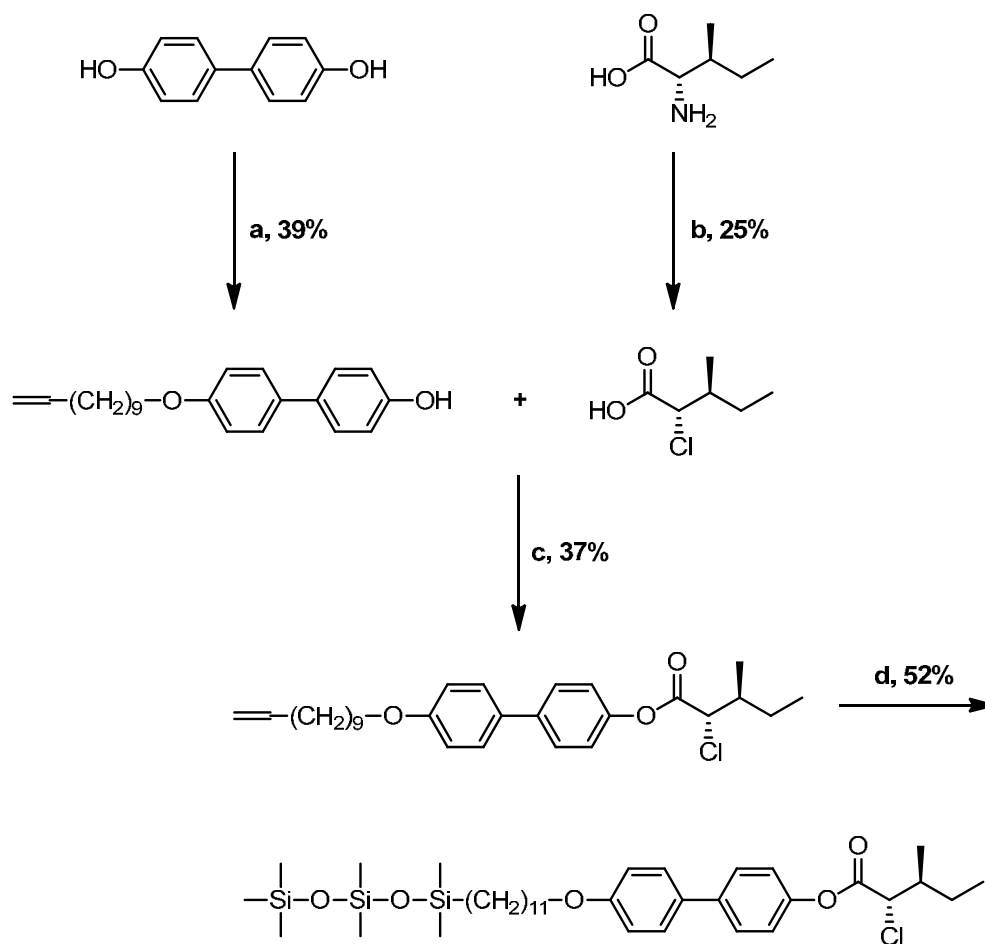
494 **Synthetic Procedure**

495 All reagents were purchased from Sigma Aldrich, Fluorochem, Alfa Aesar, ABCR and used
496 without any further purification. Solvents were purchased from Sigma Aldrich, DMF was
497 purchased pre-dried, THF was dried using a sodium/benzophenone still under N₂. All reactions
498 were generally carried out under argon using oven-dried glassware. TLC plates were performed
499 on Merck silica gel 60 F₂₅₄ and were visualized using a 254 nm light source. Flash column
500 chromatography was performed on Fluorochem silica gel 60 (40-63 micron).

501 ¹H and ¹³C spectra were recorded at 25°C (CDCl₃ as solvent and TMS as reference) using a
502 Bruker 400 MHz Ultrashield (Avance 400). HRMS spectra were recorded using a Waters – TOF
503 Electrospray micromass LCT premier.

504 Procedures for each reaction are provided below.

505



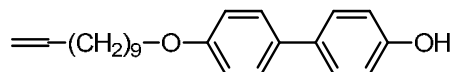
506

507 **Fig. 12.** Reagents and conditions: a) 11-bromo-1-undecene, K₂CO₃, DMF; b) NaNO₂, HCl, H₂O,
508 0 °C; c) DMAP, DCC, THF; d) 1,1,1,3,3,5,5-heptamethyltrisiloxane, Karstedt's catalyst, THF.

509

510

511 4'-(undec-10-en-1-yloxy)-[1,1'-biphenyl]-4-ol (T1)



512

513

514

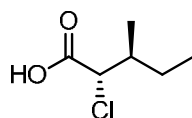
FIG. 13, T1

515

516 4,4'-dihydroxybiphenyl (5.00 g, 26.85 mmol), 11-bromo-1-undecene (6.26 g, 26.85 mmol) and
517 potassium carbonate (3.72 g, 26.92 mmol) were dissolved in dry DMF (25 mL) under nitrogen
518 and stirred at room temperature overnight. Water (25 mL) was added, the solution was
519 neutralised with HCl (1M) and the precipitate was filtered. The solid was dissolved in hot
520 ethanol and any insoluble particles were filtered. The suspension which formed is then filtered a
521 second time to yield a white powder (3.40 g, 10.04 mmol, 37%).

522 ¹H NMR (400 MHz, CDCl₃) δ: 7.45 (d, *J* = 6.7, 2H), 7.42 (d, *J* = 6.6, 2H), 6.94 (d, *J* = 8.7, 2H),
523 6.88 (d, *J* = 8.6, 2H), 5.82 (m, 1H), 4.98 (m, 2H), 4.72 (m, 1H), 3.98 (t, *J* = 6.6, 2H), 2.04 (m,
524 2H), 1.78 (m, 2H), 1.65-1.2 (m, 12H).

525 (2S,3S)-2-chloro-3-methylpentanoic acid (T2)



526

527

FIG. 14, T2

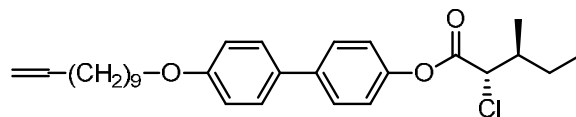
528 A suspension of L-isoleucine (5.00 g, 38.12 mmol) in 6M HCl (40 mL) was cooled to 0 °C. A
529 solution of sodium nitrite (2.63 g, 38.12 mmol) in water (15 mL) was added drop-wise. Solution
530 was stirred for 4 hours at 0 °C and 1 hour at room temperature. The compound was extracted
531 with ethyl acetate and dried with magnesium sulphate. The solvent was evaporated and the oil
532 distilled to give a light yellow oil (1.43 g, 9.50 mmol, 25%).

533 ¹H NMR (400 MHz, CDCl₃) δ: 9.28 (s, 1H), 4.22 (d, *J* = 6.5, 1H), 2.10 (m, 1H), 1.65 (m, 1H),
534 1.34 (m, 1H), 1.05 (d, *J* = 6.8, 3H), 0.92 (t, *J* = 7.4, 3H).

535 (2S,3S)-4'-(undec-10-en-1-yloxy)-[1,1'-biphenyl]-4-yl 2-chloro-3-methylpentanoate T3

536

537



538

539

(FIG. 15, T3)

540

541 A solution of T1 (1.00 g, 2.95 mmol), T2 (0.44 g, 2.95 mmol), DMAP (0.04 g, 0.33 mmol) and
 542 N,N'- Dicyclohexylcarbodiimide (0.61 g, 2.96 mmol) in dry THF (30 mL) were sealed under
 543 nitrogen and stirred overnight at room temperature. The precipitate was filtered and solvent
 544 evaporated. Crude was purified using column chromatography (ethyl acetate/hexane, 1:1, R_f =
 545 0.63). The compound was then dissolved in hot petroleum ether and any precipitate was filtered
 546 away to give a yellow wax (0.52 g, 1.10 mmol, 37%).

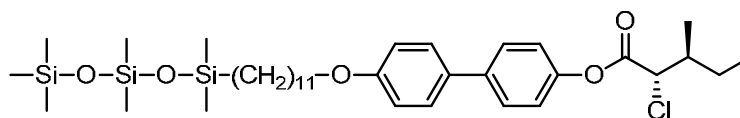
547 ^1H NMR (400 MHz, CDCl_3) δ : 7.56 (d, J = 8.6, 2H), 7.48 (d, J = 8.7, 2H), 7.16 (d, J = 8.6, 2H),
 548 6.96 (d, J = 8.7, 2H), 5.82 (m, 1H), 4.97 (m, 2H), 4.40 (d, J = 7.1, 1H), 3.99 (t, J = 6.5, 2H), 2.24
 549 (m, 1H), 2.05 (m, 2H), 1.80 (m, 3H), 1.70-1.16 (m, 14H), 1.15 (d, J = 6.7, 3H), 1.00 (t, J = 7.4,
 550 3H).

551

552 (2S,3S)-4'-((11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyl)oxy)-[1,1'-biphenyl]-4-yl 2-
 553 chloro-3-methylpentanoate MSi3-MR11

554

555



556

557

FIG. 16, MSi3-MR11

558

559 A solution of T3 (0.20 g, 0.42 mmol) in dry THF (10 mL) was put under nitrogen. 1,1,1,3,3,5,5-
 560 heptamethyltrisiloxane (0.14 g, 0.63 mmol) and platinum(0)-1,3-divinyl-1,1,3,3-
 561 tetramethyldisiloxane (0.021 mmol, 420 μL of 0.05 M solution) were added to the solution
 562 which was stirred for ~4 hours until the double bond was fully reduced. Solvent was evaporated
 563 and compound purified using column chromatography (DCM/Hexane, 2: 8, where R_f = 0.76 in
 564 ethyl acetate: hexane, 1:9), to give a white wax (0.15 g, 0.22 mmol, 52%).

565 ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (d, J = 8.8, 2H), 7.48 (d, J = 8.8, 2H), 7.16 (d, J = 8.8, 2H),
 566 6.96 (d, J = 8.8, 2H), 4.39 (d, J = 7.1, 1H), 3.99 (t, J = 6.6, 2H), 2.23 (m, 1H), 1.80 (m, 3H),
 567 1.52-1.22 (m, 17H), 1.15 (d, J = 6.8, 3H), 0.99 (t, J = 7.5, 3H), 0.53 (m, 2H), 0.09 (s, 9H), 0.06
 568 (s, 6H), 0.02 (s, 6H).

569 ¹³C NMR (101 MHz, CDCl₃) δ: 168.29 (C), 159.12 (C), 149.49 (C), 139.42 (C), 132.72 (C),
570 128.33 (CH), 128.00 (CH), 121.58 (CH), 115.07 (CH), 68.36 (CH₂), 62.88 (CH), 39.31 (CH),
571 33.68 (CH₂), 29.87 (CH₂), 29.82 (2CH₂), 29.64 (CH₂), 29.62 (CH₂), 29.52 (CH₂), 26.29
572 (CH₂), 25.39 (CH₂), 23.45 (CH₂), 18.52 (CH₂), 16.22 (CH₃), 11.11 (CH₃), 2.04 (3CH₃), 1.50
573 (2CH₃), 0.43 (2CH₃).

574 HRMS (EI): calcd for C₃₆H₆₁ClO₅Si₃Na [M + Na⁺] 715.3413, found: 715.3438.

575

576

577

578

579

580

581

582

583

584

585

586

587

588

589

590

591

592

593

594

595 **REFERENCES**

- 596 [1] S. Kumar, Phys. Rev. A **23**, 3207 (1981).
- 597 [2] C. R. Safinya, R. J. Birgeneau, J. D. Litster, and M. E. Neubert, Phys. Rev. Lett. **47**, 668
598 (1981).
- 599 [3] J. P. Lagerwall and F. Giesselmann, Chem. Phys. Chem. **7**, 20 (2006).
- 600 [4] T. P. Rieker, N. A. Clark, G. S. Smith, D. S. Parmar, E. B. Sirota, and C. R. Safinya,
601 Phys. Rev. Lett. **59**, 2658 (1987).
- 602 [5] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).
- 603 [6] S. Diele, P. Brand, and H. Sackmann, Mol. Cryst. Liq. Cryst. **16**, 105 (1972).
- 604 [7] A. de Vries, Abstracts Book of the 5th International Liquid Crystal Conference, 150,
605 Stockholm, (1974).
- 606 [8] A. de Vries, Mol. Cryst. Liq. Cryst. **41**, 27 (1977).
- 607 [9] A. de Vries, A. Ekachai, and N. Spielberg, Mol. Cryst. Liq. Cryst. Lett. **49**, 143 (1979).
- 608 [10] Y. Takanishi, Y. Ouchi, H. Takezoe, A. Fukuda, A. Mochizuki, M. Nakatsuka, Jpn. J. Appl.
609 Phys. **29**, L984 (1990).
- 610 [11] M. D. Radcliffe, M. L. Brostrom, K. A. Epstein, A. G. Rappaport, B. N. Thomas, R. Shao,
611 and N. A. Clark, Liq. Cryst. **26**, 789 (1999).
- 612 [12]. H. G. Yoon, D. M. Agra-Kooijman, K. Ayub, R. P. Lemieux, and S. Kumar, Phys. Rev.
613 Lett. **106**, 087801 (2011).
- 614 [13] D. M. Agra-Kooijman, H. G. Yoon, S. Dey, and S. Kumar, Phys. Rev. E **89**, 032506 (2014).
- 615 [14] K. Merkel, A. Kocot, J. K. Vij, P. J. Stevenson, A. Panov, and D. Rodriguez, Appl. Phys.
616 Lett. **108**, 243301 (2016).
- 617 [15] N. Hayashi, T. Kato, A. Fukuda, J. K. Vij, Yu. P. Panarin, J. Naciri, R. Shashidhar, S.
618 Kawada and Sh. Kondoh, Phys. Rev. E **71**, 041705 (2005).
- 619 [16] Ch. Bahr and G. Heppke, Phys. Rev. A **41**, 4335 (1990).
- 620 [17] U. Manna, J. -K. Song, Yu. P. Panarin, A. Fukuda and J. K. Vij, Phys. Rev. E **77**, 041707
621 (2008).
- 622 [18] O. E. Panarina, Yu. P. Panarin, J. K. Vij, M. S. Spector, and R. Shashidhar, Phys. Rev. E **67**,
623 051709 (2003).
- 624 [19] O. E. Panarina, Yu. P. Panarin, F. Antonelli, M. Reihmann, and G. Galli, J. Mater. Chem.
625 **16**, 842 (2006).
- 626 [20] M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt and R. Shashidhar,
627 Phys. Rev. E **61**, 1579–1584 (2000).

- 628 [21] Y. Shen, L. Wang, R. Shao, T. Gong, C. Zhu, H. Yang, J. E. MacLennan, D. M. Walba, and
629 N. A. Clark, *Phys. Rev. E* **88**, 062504 (2013).
- 630 [22] J. P. F. Lagerwall, F. Giesselmann and M. D. Radcliffe, *Phys. Rev. E* **66**, 031703 (2002).
- 631 [23] G. Galli, M. Reihmann, A. Crudeli, E. Chiellini, Yu. P. Panarin, J. K. Vij, C. Blanc, V.
632 Lorman, and N. Olsson, *Mol. Cryst. Liq. Cryst.* **439**, 2111 (2005).
- 633 [24] M. J. Frisch et al.; Gaussian 09, Revision E.01 Gaussian, Inc., Wallingford CT, (2009).
- 634 [25] A. Mchisuki, and S. Kobayashi, *Mol. Cryst. Liq. Cryst.* **243**, 77 (1994).
- 635 [26] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann,
636 *High Pressure Research* **14**, 235. 1996
- 637 [27] V. P. Panov, J.K. Vij, Yu. P. Panarin, C. Blanc, V. Lorman, J. W. Goodby, *Phys. Rev. E* **75**,
638 042701 (2007).
- 639 [28] K. L. Sandhya, Yu. P. Panarin, V. P. Panov, J. K. Vij and R. Dabrowski, *Eur. Phys. J. E* **27**,
640 397 (2008).
- 641 [29] K. Saunders, D. Hernandez, S. Pearson, and J. Toner, *Phys. Rev. Lett.* **98**, 197801 (2007).
- 642 [30] B. Park, S. -S. Seomun, M. Nakata, M. Takahashi, *Jpn. J. Appl. Phys.* **38**, 1474-1481
643 (1999).
- 644 [31] S. Garoff and R. B. Meyer, *Phys. Rev. Lett.* **38**, 848 (1977); *Phys. Rev. A* **19**, 338 (1979).
- 645 [32] A. Fukuda, Proceedings of the 15th International Display Research Conference of the SID
646 (Society for Information Display, San Jose, California, 1995), p. 61; S. Inui, N. Iimura, T.
647 Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, and A. Fukuda, *J. Mater. Chem.* **6**, 671 (1996).
- 648 [33] J. V. Selinger, P. J. Collings, and R. Shashidhar, *Phys. Rev. E* **64**, 061705 (2001).
- 649 [34] N. A. Clark, T. Bellini, R. Shao, D. Coleman, S. Bardon, D. R. Link, J. E. MacLennan, X.
650 Chen, M. D. Wand, D. M. Walba, P. Rudquist, and S. T. Lagerwall, *Appl. Phys. Lett.* **80**,
651 4097 (2002).
- 652 [35] P. J. Collings, B. R. Ratna, and R. Shashidhar, *Phys. Rev. E* **67**, 021705 (2003).
- 653 [36] Z. V. Kost-Smith, P. D. Beale, N. A. Clark, and M. A. Glaser, *Phys. Rev. E* **87**, 050502(R)
654 (2013).
- 655 [37] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press,
656 Oxford, 1993), Sec. 10.2.1.
- 657 [38] P. Davidson, D. Petermann, and A. M. Levelut, *J. Phys. II* **5**, 113 (1995).
- 658 [39] V. M. Vaksman and Yu. P. Panarin, *Molecular Materials*, **1**, 147 (1992); V. Panov, J. K.
659 Vij, and N. M. Shtykov, *Liquid Crystals*, **28**, 615 (2001).
- 660 [40] S. Havriliak (Jr.) and S. Negami, *Polymer*, **8**, 161 (1967).
- 661 [41] O. E. Kalinovskaya and J. K. Vij, *J. Chem. Phys.* **111**, 10979 (1999).

- 662 [42] Yu. P. Panarin, H. Xu, S. T. Mac Lughadha, and J. K. Vij, *Jpn. J. Applied Phys. (Part 1)*, **33**,
663 2648 (1994).
- 664 [43] H. Xu, J. K. Vij, A. Rappaport and N. A. Clark, *Phys. Rev. Lett.* **79**, 249 (1997).
- 665 [44] A. Kocot, R. Wrzalik, J. K. Vij, M. Brehmer and R. Zentel, *Phys. Rev B* **50**, 16346 (1994).