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Chiral Smectic A and C phases with de Vries Characteristics

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Abstract

Infrared and dielectric spectroscopic techniques are used to investigate the characteristics of two chiral smectics namely: 1,1,3,3,5,5,5-Heptamethyltrisiloxane 1-[40-(undecyl-1-oxy)-4-biphenyl(S,S)-2-chloro-3-methylpentanoate] (MSi₃MR₁₁) and tricarbosilane-hexyloxybenzoic acid(s)-4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl ester (W599). The orientational features and the field dependencies of the apparent tilt angle and the dichroic ratio for homogeneous planar-aligned samples were calculated from the absorbance profiles obtained at different temperatures especially in the smectic A* phase of these liquid crystals. The dichroic ratios of the C-C phenyl ring stretching vibrations were considered for the determination of the tilt angle at different temperatures and different voltages. The low values of the order parameter obtained with and without electric field applied across the cell in SmA* phase for both smectics are consistent with the de Vries concept. The generalized Langevin-Debye model introduced in the literature for explaining the electro-optical response has been applied to the results from infra-red spectroscopy. The results show that the dipole moment of the tilt correlated domain diverges as the transition temperature from SmA* to SmC* is reached. The Debye-Langevin model is found to be extremely effective in confirming some of the conclusions of the de Vries chiral smectics and give additional results on the order parameter and the dichroic ratio as a function of the field across the cell. Dielectric spectroscopy finds large dipolar fluctuations in SmA* phase for both compounds and again these confirm their de Vries behavior.

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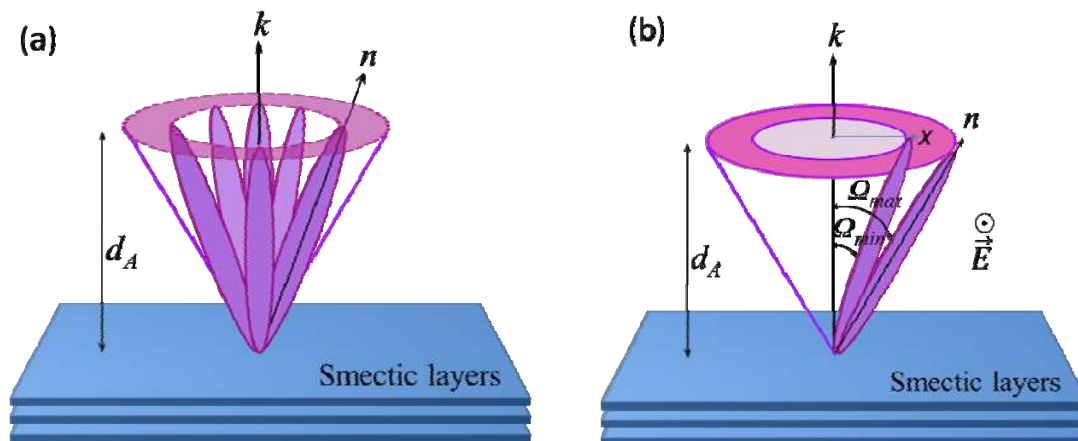
36 **1 Introduction**

37 For successful applications of liquid crystals in devices, chiral smectics can play an important
38 role since they possess numerous desirable characteristics over nematics. The chiral smectics
39 in particular when sandwiched in cells have much higher operational speeds due to the
40 interaction of the electric field with the spontaneous polarization as opposed to a relatively
41 weak interaction with the dielectric anisotropy in nematics [1]. The spontaneous polarisation
42 arises from the lack of the mirror symmetry (due to chirality) in a plane at right angles to the
43 two-fold symmetry axis. The polarisation is parallel to this two fold axis and its direction
44 dependent on the applied electric field. The chirality also gives rise to a helical structure with
45 the helical axis being parallel to the layers-normal. The helix is unwound by the electric field
46 applied along the two-fold axis or by the surface interactions of molecules. In the smectic
47 phases, the rod shaped molecules exhibit positional order at least in one dimension apart from
48 the orientational order defined by de Gennes [2] in terms of a complex order parameter $\Phi e^{i\alpha}$.
49 This quasi-one dimensional translational order is a result of the Landau-Peierls instability
50 theorem [2] which states that the mean square displacement of the smectic layers diverges
51 logarithmically from their equilibrium position due to thermal fluctuations. The uniaxial
52 Smectic A (SmA) phase has an average orientation of the long molecular axes defined by the
53 director \vec{n} , which coincides with the perpendicular drawn to the smectic layers while in the
54 biaxial Smectic C (SmC) phase, the director \vec{n} is tilted by an angle dependent on temperature
55 with respect to the layer normal. If these molecules are chiral, then chiral phases denoted by
56 (*) are formed. In the SmA* phase, an electro-optical effect (known as the electro-clinic
57 effect) was first observed by Garoff and Meyer [3]. A uniform molecular tilt is induced in a
58 plane perpendicular to the applied electric field E. This plane coincides with the substrate's
59 plane for a planar-aligned cell, formed by the layer normal and the projection of the tilted
60 director onto this plane. The electro-clinic effect can be explained by a model deduced from
61 the Landau theory which predicts linearity between E and the induced tilt at low electric
62 fields. But the linear behaviour deviates as the temperature approaches the orthogonal SmA*
63 to tilted SmC* transition. This effect is accompanied by the contraction of the smectic layers
64 in magnitude by as large as 13% [4] scaled by the cosine of the tilt angle, resulting in their
65 buckling into first vertical and then horizontal chevron structures [5]. These are visible as
66 periodic stripe domains viewed under the crossed polarizers of a microscope. The chevron
67 structure leads to the appearance of the zig-zag defects in the cell. The striped domain

68 textures and the zig-zag defects do adversely affect the contrast ratio, acting as roadblocks to
69 the commercialization of smectics in devices.

70 The impetus to overcome the above problems in smectics led to finding materials with
71 minimal layer shrinkage in their titled phases. De Vries had reported a material which
72 showed only 1% layer contraction [6] deep in its SmC phase and had explained this feature
73 by the non-correlation model which assumed that stacks of smectic layers are formed in SmA
74 phase with molecules tilted permanently and uniformly in each layer [7]. The experimental
75 X-ray scattering results obtained by Adriaan de Vries and those of Leadbetter and Norris on
76 some new smectic liquid crystals [8] revealed that (a) the layer thickness in the SmA phase
77 is much lower than the molecular length and (b) the order parameter observed in the SmA
78 phase is much lower than unity. In order to explain these results de Vries proposed a diffuse-
79 cone model for SmA phase in which the azimuthal angle of the molecular directors are
80 distributed on to a cone, the axis of cone is directed along the layer normal with a finite cone
81 angle [9]. In the SmC* phase however, the azimuthal degeneracy in a layer is lifted as the
82 molecules are azimuthally ordered in a particular direction without affecting the magnitude of
83 the polar tilt angle. Due to the molecular chirality, the azimuthal angles in SmC* vary
84 systematically from layer to layer to form a macroscopic helical structure. The azimuthal
85 redistribution of directors takes place when an electric field is applied across a planar-aligned
86 cell in this phase. Some of the antiferroelectric liquid crystals that have been investigated
87 show characteristics of de Vries smectics [10,11].

88 Fig. 1 depicts the schematic representation of the diffuse-cone model in SmA* phase. Some
89 of the materials in SmA* called 'de Vries smectics' are known to exhibit large electroclinic
90 effect, a large increase in the birefringence with the field and a minimal layer shrinkage at the
91 SmA* to SmC* transition as well as in the SmC* phase [4]. In recent years a large number of
92 such mesogens have been synthesized [12, 13], with siloxane or perfluorinated segments at
93 the end of side chains (both of which are known to promote increased lamellar order), that
94 exhibit low orientational order due to nano-segregation of the constituents.



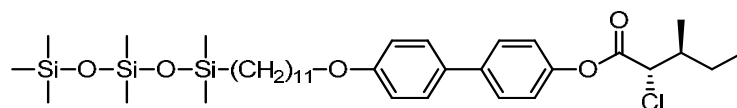
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96 **Fig. 1** (Color online) Schematic illustration of the de Vries diffuse-cone model in SmA*
 97 phase. Here \hat{k} is the layer normal, \hat{n} is the direction of long molecular axis, d_A is the layer
 98 spacing while Ω_{max} is the maximum tilt angle at a large field, Ω_{min} is evaluated from the
 99 experimental data on birefringence at zero field. The azimuthal angle is distributed on the
 100 cone at zero field. The apparent tilt angle is thus zero. For higher fields, the azimuthal angle
 101 condenses to an almost single value leading to the maximum apparent angle, Ω_{max} . The
 102 apparent tilt angle Ω_0 varies with the field.

103 In addition to the above model, other alternate models have been suggested in the
 104 literature for de Vries smectics. The conformational change model, also known as the zigzag
 105 model [14] assumes that the mesogens with tilted side chains and upright cores form a kinked
 106 conformation structure. The cluster diffuse cone model based on the results obtained from
 107 nuclear magnetic resonance spectroscopy considers the presence of tilted molecules in
 108 clusters. These are useful in explaining the magneto-clinic effect [15]. The inter-digitation
 109 model proposed by some authors [16, 17] states that the mesogens are interdigitated and this
 110 leads to low values of the orientational order parameter. The sugar-loaf model based on the
 111 Maier-Saupe orientational distribution function is predicted to be in close agreement with the
 112 experimental X-ray scattering results on de Vries smectics [18].

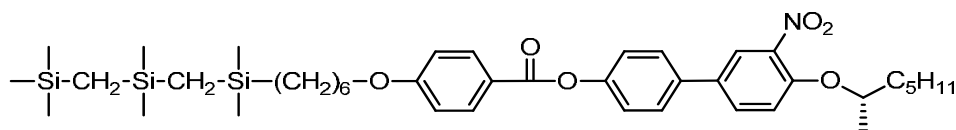
113 In this article, we report the infrared and dielectric studies carried out on two de Vries
 114 smectics in order to advance the understanding of deVriesness especially in the SmA* phase,
 115 which is not fully understood as yet. At present, a number of theoretical models are being
 116 tested for explaining an entire gamut of the experimental results. Additional testing of these
 117 models using data acquired by other techniques such as IR spectroscopy is timely and
 118 important. The two techniques of polarised IR and of dielectric spectroscopy are proven to

119 have yielded new results for the orientational order parameter and the tilt angle as a function
 120 of the bias field. The polarized IR technique provides a direct measurement of the dichroic
 121 ratio and the order parameters of the LC molecules as a function of the field rather easily
 122 which may not be the case with other techniques.



123

124 MSi₃MR₁₁: Cr 16°C-SmC* 47°C-SmA* 59°C-Iso



125

126 W599: SmC*29°C-SmA*43°C-Iso

126

127 **Fig. 2** The molecular structures of MSi₃MR₁₁ and W599 with their corresponding phase
 128 transition temperatures obtained by polarized optical microscopy at a cooling rate of 1 °C/min
 129 are specified.

130

131 2 Experimental Section

132 2.1 Materials

133 The chemical formulae of the two compounds, MSi₃MR₁₁ [19] and W599 [27], their phase
 134 sequences and transition temperatures are given in Fig. 2. These compounds were
 135 resynthesized by Stevenson group in Belfast, the synthesis of MSi₃MR₁₁ in particular is
 136 described in [26]. MSi₃MR₁₁ is made up of biphenyl 2-chloro-3-methylpentanoate core with a
 137 trisiloxane backbone while W599 has a tricarbosilane tail. The carbosilane tail can restrain
 138 the out of layer fluctuations and thus can lead to the formation of a better bookshelf smectic
 139 layer structure in SmA* phase.

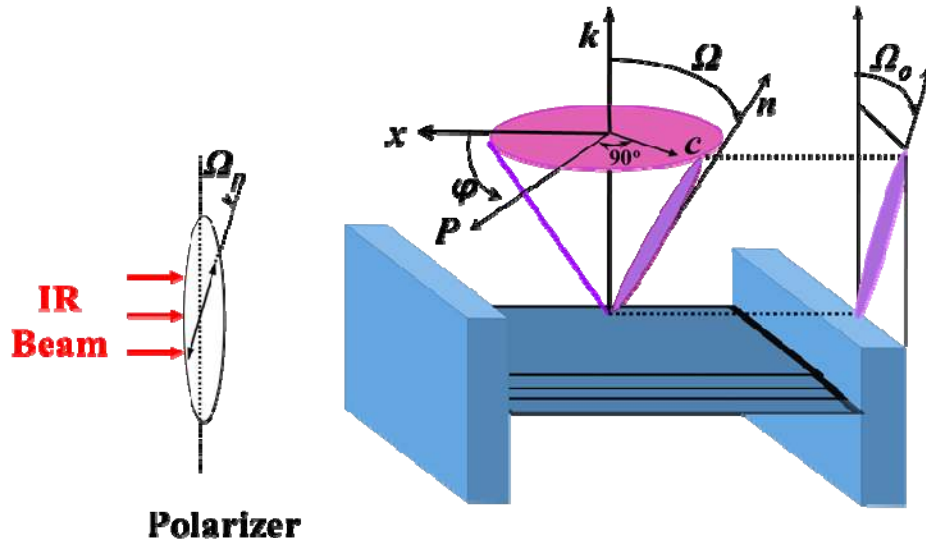
140 2.2 Measurements

141 The polarized IR measurements were performed on MSi₃MR₁₁ and W599 compounds, using
 142 a Bio-Rad FTS-6000 spectrometer in the 450 to 4000 cm⁻¹ wave number range. The
 143 spectrometer is equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT)
 144 detector, a computer controlled wire grid rotation polarizer and a hot stage where a
 145 temperature stability to within ± 0.1 °C can be attained for these investigations. A total of 64
 146 experimental scans are averaged to make the signal to noise ratio get above 2000 for a 2 cm⁻¹

147 spectral resolution. The planar alignment of LC molecules is achieved as follows: two Zinc
148 Selenide (ZnSe) windows covered with a thin layer of indium tin oxide (ITO) are used to
149 make a sandwich type LC cell. The Mylar spacers of 5 μm thickness are used to separate
150 these two overlapping windows. Both windows are coated with a polymer solution RN1175
151 (Nissan Chemicals), following which the windows are kept in an oven at 250 $^{\circ}\text{C}$ for one hour.
152 The windows are rubbed and rubbing directions are antiparallel to each other. The IR spectra
153 are recorded in both SmA* and SmC* phases with a greater emphasis laid on the detailed
154 measurements being carried out in the former. DC bias voltages of both polarities (positive
155 and negative) are applied to cells. The polarizer is rotated from an angle of 0° to 180° in steps
156 of 20° for each applied voltage. For each of its positions, the IR spectra are recorded. The
157 Perkin Elmer Grams Research (PEGR) program is used to analyse the intensity and the width
158 of each measured spectral line while the origin 7.5 program is used to fit each absorbance
159 profile. Dielectric measurements are carried out using a Novocontrol impedance analyser in
160 the frequency range of 0.1 Hz to 10 MHz with an alternating RMS voltage of 0.1 V applied
161 across the cell. For dielectric experiments, ITO coated glass substrates are used and treated in
162 the same way as were the ZnSe windows, to order to obtain the planar alignment of the LC
163 molecules. The sheet resistance of the ITO coated glass substrate, R is ($\sim 20 \Omega/$). This
164 resistance is in series with the cell capacitance, C. The time constant of the combination, RC,
165 shifts the peak frequency, $f = 1/ (2\pi RC)$, of this parasitic RC arrangement beyond 1 MHz
166 (highest frequency in the experimental window). The experimental results of the
167 measurements are free from the ITO parasitic effect.

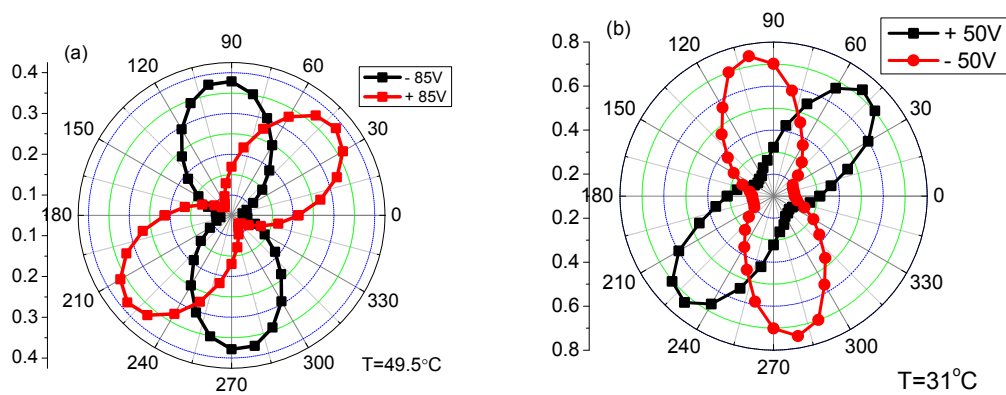
168 **3. Results and Discussion**

169 **3.1 Polarized IR spectroscopy:**



170

171 **Fig. 3** A schematic representation of the measurement system for de Vries SmA* phase.
 172 ZnSe windows coated with ITO containing the sample are mounted on the hot stage. The
 173 polarizer can be automatically rotated by an angle Ω_p . The constituent molecules are tilted by
 174 Ω from the layer normal n . The polarization P is normal to the c -director (projection of the
 175 molecular director on the smectic plane) makes an angle ϕ with the normal drawn to the cell.
 176 While Ω_o is the angle between the layer normal and the projection of the effective optic axis
 177 onto the plane of the cells windows.



178

179

180 **Fig. 4** (color online) Polar plots of the absorbance profiles for the C-C phenyl ring stretching
 181 vibrational band for both negative and positive fields at temperatures of (a) 49.5°C for
 182 MSi₃MR₁₁ and (b) 31°C for W599. These temperatures correspond to the SmA* phase of
 183 these materials at zero field.

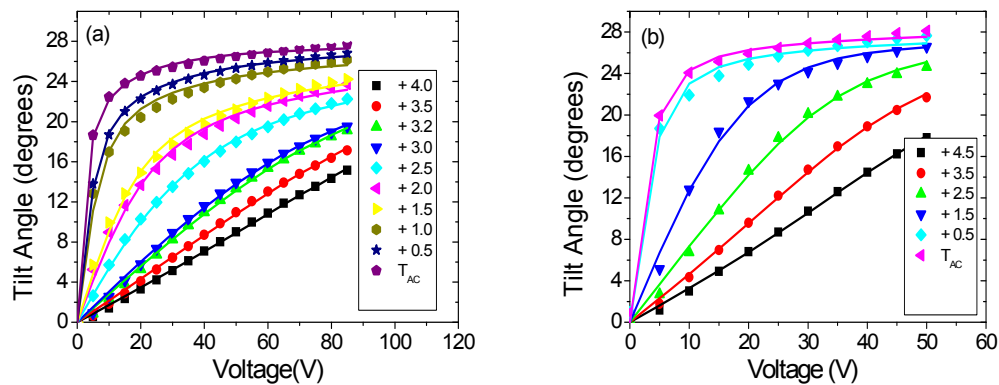
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185 The infrared studies are performed on cells with ITO coated ZnSe windows as illustrated in
 186 Fig. 3. The infrared spectra of the sample cell consists of several absorption bands, these
 187 pertain to the different molecular groups of the constituent molecules of the system. From
 188 these spectra, the C-C phenyl ring stretching vibration is chosen to carry out a detailed
 189 analysis of the LC system since the transition dipole moment of these vibrations, positioned
 190 at 1608 cm^{-1} for $\text{MSi}_3\text{MR}_{11}$ and 1605 cm^{-1} for W599, is approximately parallel to the long
 191 molecular axis in each of these compounds. The absorbance profiles $A(\Omega)$ for this C-C band
 192 is a function of the angle by which the polarizer is rotated under the application of negative
 193 and positive DC voltages across a planar-aligned cell. The experimental data as a polar plot
 194 of A vs Ω_p are presented in Figs. 4(a) and 4(b), for different values of the applied DC voltage.
 195 A unique absorbance profile is constructed for each applied voltage and is fitted to the
 196 equation [20-22]

$$A(\Omega_p) = -\log_{10}[10^{-A_{\parallel}} + (10^{-A_{\perp}} - 10^{-A_{\parallel}})\sin^2(\Omega_p - \Omega_o)] \quad (1)$$

197 where the polarizer angle is denoted by Ω_p , minimum and maximum values of the absorbance
 198 at different polariser angle ($A(\Omega_p)$) are given by A_{\perp} and A_{\parallel} while the polarizer angle at
 199 which absorbance for the phenyl stretching vibration is maximum is represented by Ω_o (the
 200 apparent tilt angle). The dichroic ratio R is defined as A_{\parallel}/A_{\perp} while the orientational order
 201 parameter S is calculated using equation derived in reference [23]

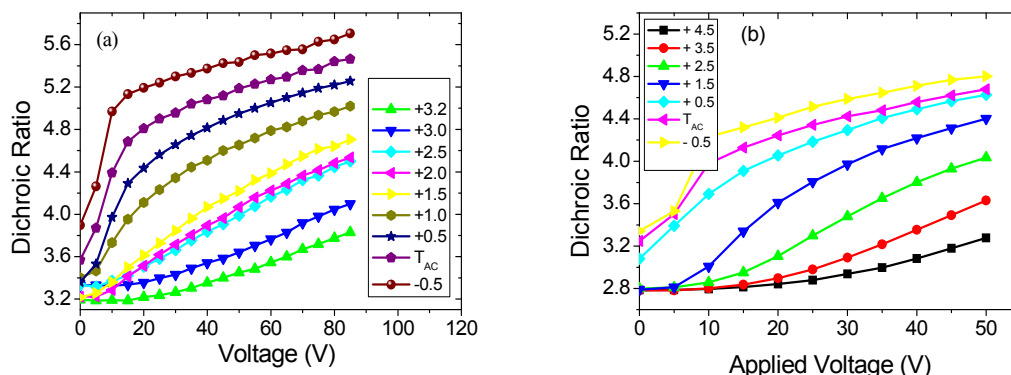
$$S = \frac{R - 1}{R + 2} \quad (2)$$



202

203 **Fig. 5** (color online) Voltage dependence of the molecular tilt angle (Ω_0), determined from
 204 the absorbance profiles of the C-C phenyl ring stretching vibration at various temperatures in
 205 SmA^* phase but close to the $\text{SmA}^* - \text{SmC}^*$ transition for (a) $\text{MSi}_3\text{MR}_{11}$ at 1608 cm^{-1} and (b)
 206 W599 at 1605 cm^{-1} . The symbols correspond to the experimental data, while the solid lines

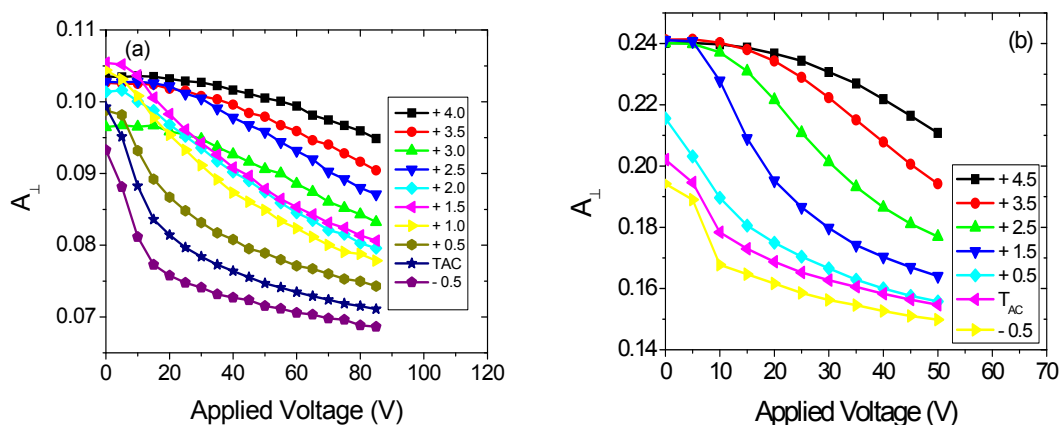
207 are fits to the generalized Langevin-Debye model given in section 3.2. The thickness of the
 208 sample is 5 μm .



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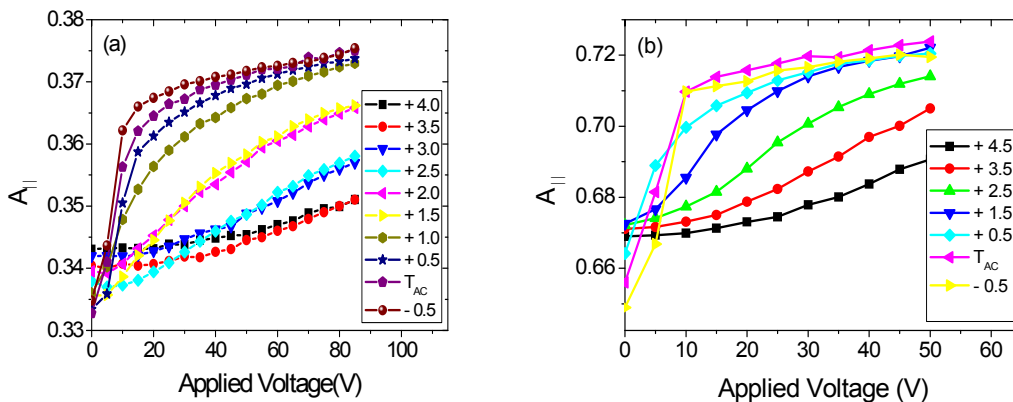
210 **Fig. 6** (color online) Dichroic Ratio ($R=A_{\parallel}/A_{\perp}$) versus the applied DC voltage for the phenyl
 211 band 1608 cm^{-1} at different temperatures for a homogeneously planar-aligned cell of $5\mu\text{m}$
 212 thickness for (a) MSi₃MR₁₁ and (b) W599.

213 The tilt angle R , A_{\perp} and A_{\parallel} and S for the phenyl band are plotted as a function of the electric
 214 field for both MSi₃MR₁₁ and W599 in Figs. 5 to 9. The dependencies of the above parameters
 215 on the applied field for various temperatures is intriguing. In the SmA* at 52.5°C for
 216 MSi₃MR₁₁ and 34°C for W599, an increase in the applied voltage (field = voltage/cell
 217 thickness), the tilt angle shows a linear behaviour which is due to the electro-clinic effect.
 218 The shape of the curves starts changing as the LC cell approaches the transition temperature
 219 from SmA* to SmC* phase.



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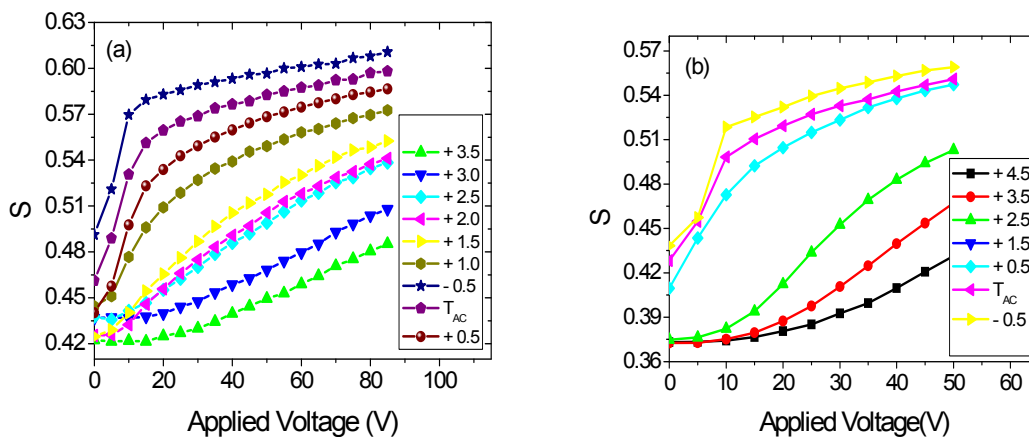
221 **Fig. 7** (color online) Variation of A_{\perp} with voltage for a homogeneous planar-aligned cell of 5
 222 μm thickness (a) MSi₃MR₁₁ and (b) W599.



223

224 **Fig. 8** (color online) Voltage dependence of A_{\parallel} at different temperatures for (a) MSi_3MR_{11}

225 and (b) W599 for a homogeneous planar-aligned cell of $5 \mu m$ thickness.



226

227 **Fig. 9** (color online) Dependence of S on applied voltage for a homogeneous planar-aligned

228 cell of $5 \mu m$ thickness (a) MSi_3MR_{11} and (b) W599.

229 The dependence of the tilt angle, the dichroic ratio R and the order parameter S show non-
 230 linearity, and eventual saturation, with applied voltage close to the $SmA^* - SmC^*$ transition
 231 temperature. A sigmoidal type response is seen close to this transition temperature. In the
 232 SmC^* phase, the tilt angle, the ratio R , and the order parameter S increase rapidly with
 233 voltage but are saturated at relatively low voltages. An unwinding of the helical structure
 234 leads to a large increase in R for both compounds studied here. This increment can be
 235 attributed to a decrease in A_{\perp} and increase in A_{\parallel} (see Figs. 7 and 8). Minimum absorbance
 236 (A_{\perp}) is proportional to the average value of the squares of the projections of transition dipole
 237 moments of the phenyl ring in a direction perpendicular to the directors in the tilt plane. The
 238 direction of tilt angle (Ω_o) starts moving to the direction of the molecular tilt with the

239 unwinding of the helix leads to a decrease in A_{\perp} and consequent increase in R . This is quite
 240 contrary to the normal SmA*-SmC* transition where the values of R and S especially in the
 241 SmA* do not depend on voltage and stay almost constant with field [24]. A simple
 242 simulation was performed using Maple software to elucidate our experimental results. The
 243 value of R should be less in the de Vries phase than in the unwound state when no voltage is
 244 applied to it. R can be calculated from the absorbance profile obtained in the unwound state
 245 and integrating it over ψ so that a fictitious distribution of molecular tilt directions is
 246 introduced according to the equation given below [25]:

$$247 \quad A(\Omega_p) = \frac{1}{2\pi} \int_0^{2\pi} -\log_{10} \left[10^{-A_{\parallel}} + (10^{-A_{\perp}} - 10^{-A_{\parallel}}) \sin^2 \left[\left[\Omega_p - \Omega_0 \times \cos(\psi) \right] \frac{\pi}{180} \right] \right] d\psi \quad (3)$$

248 On inserting the experimental parameters, A_{\perp} and A_{\parallel} , R and Ω_0 obtained for the unwound
 249 state in the above equation, the dichroic ratio at the various temperatures in SmC* and SmA*
 250 phase for the random undisturbed state is calculated. Since the helical pitch of the samples is
 251 less than the aperture of the infrared beam passing through them, equation 3 is applicable for
 252 both phases. The value of R in the undisturbed state comes out to be 3.2 for MSi₃MR₁₁ at
 253 50.5°C and 2.8 for W599 at 31°C. The results obtained are in accordance with the
 254 experimental values. R is found equal to 4 for MSi₃MR₁₁ and 3.5 for W599 in the SmC*
 255 phase. For the SmC* phase, the simulated values slightly deviate those from experiments. A
 256 plausible explanation for the discrepancy between the two is as follows: surfaces in a planar-
 257 aligned cell tend to distort the helical structure of the SmC* phase.

258 Values of the tilt angle with the applied voltage obtained by us show striking similarities in
 259 magnitude and response to the tilt angles measured by the electro-optical method [26, 27] for
 260 both samples. For W599, Shen *et al.* [27] found the tilt angle saturated at an angle as large as
 261 $\sim 33^\circ$ [27]; they applied higher electric fields upto 35 V/ μm , while in our case the maximum
 262 field applied was 10 V/ μm resulting into to a lower tilt angle, fully saturated at 28° . It has also
 263 been proven in the literature that both W599 and MSi₃MR₁₁ are de Vries smectics and they
 264 satisfy the criterion of the lower layer-shrinkages of 0.73 % and 1.75 % at 10 °C and 20 °C,
 265 respectively below the SmA*-SmC* transition temperature. The orientational order
 266 parameters for both materials are found to be low under zero electric field. The order
 267 parameter increases with the field, consistent with the de Vries scenario. In the SmA* phase,
 268 azimuthal angles of the molecular directors of calamitic mesogens are disordered. It is natural
 269 that for a disordered arrangement, the orientational order parameter is low for a wider

270 distribution of the director orientations. Whereas on the application of an electric field in
 271 SmC* phase, the azimuths get aligned in a particular direction and sense. While the layer
 272 spacing remains almost constant, the average local directors tilt with respect to the layer
 273 normal. Hence the measured orientational ordering of the molecular directors in SmC* phase
 274 along the optical axis is higher than in the SmA* phase.

275 **3.2 Recent models of de Vries Smectics:**

276 Several theoretical models have been suggested to explain the unusual electro-optical
 277 response of de Vries smectics, the first being that of the Langevin-Debye model that had
 278 originally been proposed by Fukuda [28] to explain the thresholdless switching in tilted chiral
 279 smectics. This model was used by Clark *et al.* [29] to explain the electro-optical properties of
 280 de Vries materials; C4 and C6. This model assumes that in the absence of electric field in
 281 SmA* phase at a fixed temperature, the molecules are tilted with a fixed tilt angle and are
 282 azimuthally distributed randomly on a cone so that $\langle \cos\varphi \rangle = 0$. When the electric field E is
 283 applied, E is coupled to the polarization. The resulting free energy equals $U = -pE\cos\varphi$,
 284 where p is the local dipole moment. But the model though partly successful has failed to
 285 explain the correct shape of the curves for apparent tilt angle versus E for temperatures closer
 286 to the SmA* to SmC* transition. In 2013 Shen *et al.* introduced a modification to this model
 287 and is now called the generalized Langevin-Debye [27]. This considers the orientational
 288 distribution with a complete azimuthal degree of freedom. In addition, the tilt angle can
 289 change with applied E only within a range of values. The free energy has a quadratic term
 290 scaled by a phenomenological parameter α . This is especially introduced to explain the
 291 sigmoidal response of Ω_o vs. E . The free energy is expressed as $U = -p_0E\sin\Omega\cos\varphi -$
 292 $\alpha p_0E^2\sin\Omega\cos^2\varphi$ where $p = p_0\sin\Omega$ is the dipole moment of the tilt correlated domain.

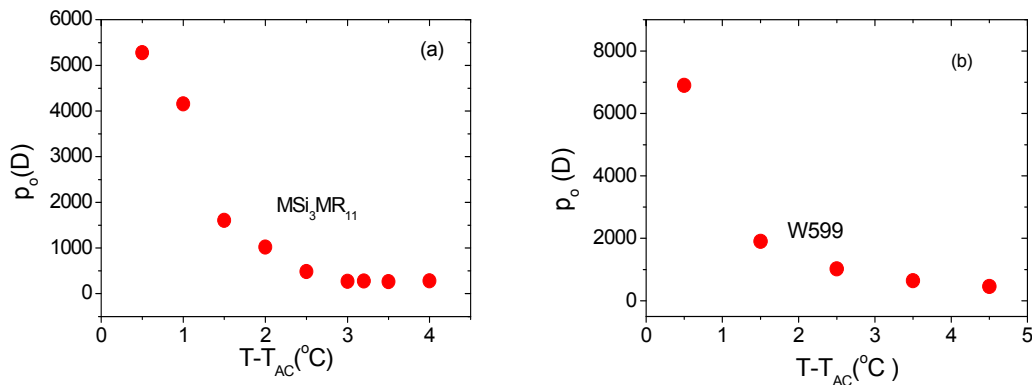
293 The apparent electro-optical tilt angle is given by:

$$\tan 2\Omega_o = \frac{\langle \sin 2\Omega \cos \varphi \rangle}{\langle \cos^2 \Omega - \sin^2 \Omega \cos^2 \varphi \rangle} \quad (4)$$

294 An average $\langle X \rangle$ is written as $\langle X \rangle = \int_{\Omega_{min}}^{\Omega_{max}} \int_0^{2\pi} X(\Omega, \varphi) f(\Omega, \varphi) \sin\Omega d\Omega d\varphi$, where the mean
 295 field orientation distribution is given by [25]

$$296 \quad f(\Omega, \varphi) = \exp[-U/k_B T] / \int_{\Omega_{min}}^{\Omega_{max}} \int_0^{2\pi} \exp[-U/k_B T] \sin\Omega d\Omega d\varphi.$$

297 This formalism is used here to fit the tilt angle obtained from the infrared measurements of
 298 $\text{MSi}_3\text{MR}_{11}$ and W599. The angle in the lower limit Ω_{min} is extracted from the experimental
 299 birefringence measurements made in the absence of the electric field applied to the cell. The
 300 birefringence data are taken from the literature [26, 27]. It can be observed from Figs. 5(a)
 301 and 5(b) that this model fits well the experimental data. The maximum tilt angle saturated at
 302 high fields (Ω_{max}) is 28.4° for $\text{MSi}_3\text{MR}_{11}$ and 28.6° for W599. The fitting parameter p_o , called
 303 the local dipole moment (see Fig. 10), increases on cooling from the SmA^* phase close to the
 304 SmA^* to SmC^* transition. As the temperature approaches the transition temperature, p_o
 305 diverges as the azimuthal angle condenses to values first restricted within a limited range and
 306 then it finally condenses to a single value. For W599, values of p_o are similar in magnitude to
 307 those obtained in reference [27] at temperatures well above the SmA^* to SmC^* transition
 308 temperature. But p_o increases to higher values of the order of 10^3 at temperatures closer to
 309 SmA^* to SmC^* transition temperature. Such large values of the local dipole moment were
 310 previously reported by Selinger *et al.* for TSiKN65 and DSiKN65 [30].



311

312 **Fig. 10** (color online). The local dipole moment p_o obtained from the fitting of the
 313 experimental data to the model as a function of the reduced temperature in the SmA^* phase.

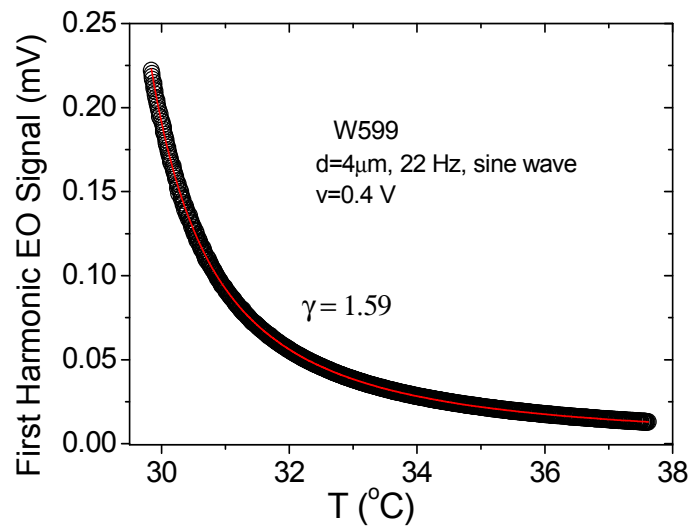
314 Another model called the generalized 3D X-Y model [31] has recently been introduced. This
 315 gave an explanation for the first order SmA^* to SmC^* transition and of the sigmoidal
 316 response observed for $\text{MSi}_3\text{MR}_{11}$ and W599. Using Monte Carlo simulations they
 317 demonstrated that polarization as a function of the electric field follows the sigmoidal
 318 response for a liquid crystal compound W530 and this feature is attributed to the steric
 319 interactions inbuilt in a hollow cone of de Vries smectic A^* phase.

320 The model suggested by Zappitelli *et al.* [32] considers both bulk and surface electroclinic
 321 effects in SmA^* phase and analyses the tilt dependent layer spacing and the effect of applied

322 electric field on the layer-spacing for de Vries smectics exhibiting first order SmA* to SmC*
 323 transition. These have low orientational order parameter in agreement with our experimental
 324 findings. The order parameter with and without electric field for both smectic phases shown
 325 in Fig. 9 is lower than for the conventional smectics. Such low values of order parameter
 326 were previously observed by Collings *et al.* [33] for TSiKN65 and DSiKN65 with dyes
 327 dissolved in them. They attributed these low order parameters to the segregation of siloxane
 328 segments within each layer. Hayashi *et al.* [34] using Raman spectroscopy found low order
 329 parameter for TSiKN65 both with and without field. They attributed this to a large tilt ($\sim 30^\circ$)
 330 of the mesogen (treated as a rigid core) from the long molecular axis-

331

332 3.3 Electro-optic response in SmA* phase



333

334 **Fig. 11** (color online) Electro-optical response of W599 as a function of temperature in the
 335 SmA* phase.

336 The electroclinic (EO) response arising from the tilt of the mesogen induced by a weak field
 337 (sinusoidal signal of amplitude 0.4 V at frequency of 22 Hz applied across a homogeneously
 338 aligned cell of thickness 4 μm) has been measured. The planar-aligned liquid crystal cell is
 339 mounted in a hot stage. The latter is fixed to the rotating stage of a polarizing microscope
 340 with crossed polarizer and analyser. In the absence of the electric field, the transmitted
 341 intensity I , is given by [35],

342
$$I = I_0 \sin^2(2\alpha) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \quad (5)$$

343 I_0 is the incident intensity, α is the angle between the optical axis of the cell and the
 344 polariser, α is fixed at 22.5° in order to get a maximum change in the intensity of the
 345 transmitted light due to a change in α with field. Δn is the birefringence, d is the thickness of
 346 the sample cell and λ is the wavelength of the incident light. When a weak electric field is
 347 applied across the cell, a change in the intensity of the transmitted light with angle induced
 348 by the field, $d\alpha = \theta_{ind}$, results to differentiating eqn (5) with respect to α ,

349
$$\delta I = 4I_0 \sin 4\alpha d\alpha \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \quad (6)$$

350 On dividing equation (6) by equation (5) and on substituting $\alpha = 22.5^\circ$ and on having

351
$$\theta_{ind} = d\alpha$$

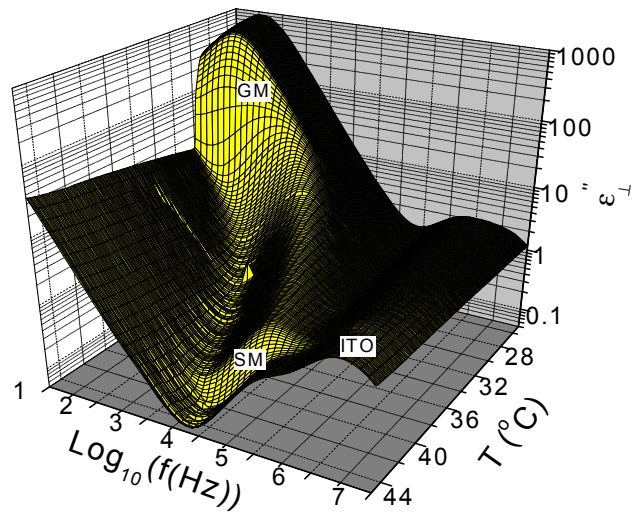
352

353 We obtain
$$\theta_{ind} = \frac{\delta I}{4I} \quad (7)$$

354 θ_{ind} is proportional to the first harmonic EO signal. I is the dc component of the signal. The
 355 electro-optic response given by $\delta I/4I$ is proportional to θ_{ind} . The latter is linearly related to
 356 the field in the low-field approximation. The curve so obtained can be fitted to the power law
 357 equation as below

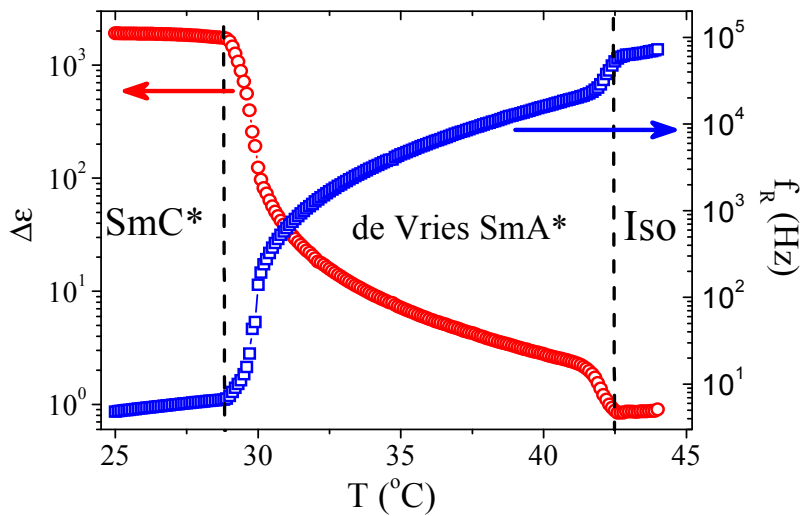
358
$$E O \text{ response} = \frac{B}{(T - T_c)^\gamma} \quad (8)$$

359 B is the scaling factor, T_c is temperature of the SmA*-SmC* transition and γ is the power law
 360 exponent that expresses the magnitude of EO response with temperature for temperatures
 361 closer to the SmA*- SmC* transition. Fig. 11 represents the temperature dependent electro-
 362 optical response of W599. The magnitude of γ is found to be 1.59, which lies in between 1.4
 363 to 2, appropriate for the de Vries smectics that exhibit short-range correlations in a smectic
 364 layer as well across the smectic layers and display a weak first order SmA* to SmC*
 365 transition. The short-range correlation in de Vries smectics extends from 2 to 3 dimensions as
 366 opposed to a conventional two dimensional ($\gamma = 1.32$) fluid as smectic [36].



367

368 **Fig. 12** (color online) Three dimensional (3D) dielectric loss spectra as a function of
 369 frequency and temperature for a homogenously aligned $7\ \mu\text{m}$ cell of W599. Here, GM, SM
 370 denote Goldstone mode, soft mode and the peak arising from a finite resistance of indium
 371 tin oxide (ITO) coating in series with the cell capacitance; this is marked as ITO.



372

373

374 **Fig.13** (color online) Plots of the relaxation frequency (f_R) and the dielectric relaxation
 375 strength ($\Delta\epsilon$) with temperature for W599 in a homogeneous planar-aligned $7\ \mu\text{m}$ thick cell.

376

377 **3.4 Dielectric spectroscopy**:-The dielectric loss peak of W599 in a planar-aligned cell in
 378 SmA* is (see Fig. 12) identified as due to the soft mode (SM). This arises from the softening
 379 of fluctuations in the tilt. The response in the SmC* is due mainly to the Goldstone mode
 380 (GM), the azimuthal reorientation on the cone is seen in the low frequency region (see Fig.
 381 12). The dielectric relaxation frequency and dielectric strength are obtained by fitting the
 382 complex permittivity plots to the Havriliak-Negami equation using the WINFIT software
 383 purchased from Novocontrol GmbH. Since only a single mode is dominant in each phase,
 384 Havriliak-Negami equation is used for a single mode of relaxation [37]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha}]^{\beta}} - \frac{i\sigma_{dc}}{\varepsilon_0\omega} \quad (9)$$

385 Here ε_{∞} is the high frequency permittivity depending on the atomic and electronic
 386 polarizability, $\omega=2\pi f$ is the angular frequency, ε_0 is the permittivity of free space, $\Delta\varepsilon$ refers to
 387 the dielectric relaxation strength and α ($0 \ll \alpha \leq 1$) and β ($0 \ll \beta \leq 1$) are the symmetric and
 388 asymmetric broadening parameters of the complex dielectric function. The contribution of dc
 389 conductivity to ε'' is due to the term $\sigma_{dc}/\varepsilon_0\omega$. The relaxation frequency, f_R , of the relaxation
 390 process is related to its relaxation time τ as [38]:

391

$$f_R = \frac{1}{2\pi\tau} \left[\sin\left(\frac{\alpha\pi}{2 + 2\beta}\right) \right]^{1/\alpha} \left[\sin\left(\frac{\alpha\beta\pi}{2 + 2\beta}\right) \right]^{-1/\alpha} \quad (10)$$

392 Fig. 13 shows a strong variation in the dielectric parameters, $\Delta\varepsilon$ and f_R in the SmA* phase.
 393 The relaxation strength increases continuously in the SmA* phase and reaches a maximum as
 394 the temperature tends to approach the SmA*-SmC* transition. The dielectric relaxation
 395 strength is large and is of the order of 10^3 . Such large values were previously reported by
 396 some authors [39, 40]. Also, the decrement in the relaxation frequency is incessant over a
 397 broad temperature range in the SmA* phase. This result is in stark contrast to the trend
 398 exhibited by conventional SmA* phase where sudden jumps in values of the relaxation
 399 frequency and the dielectric strength are observed close to the transition temperature [41].
 400 The soft mode fluctuations are also very strong and consequently the dielectric absorption in
 401 SmA* is significantly large - another definite signature of de Vries smectics. Some of the
 402 observed features here are similar to those observed by Kocot *et al.* [42] for a siloxane
 403 polymer. This may have been the first polymeric chiral smectic studied in the literature to
 404 have de Vries characteristics.

405 **4 Conclusion**

406 In conclusion, the two materials reported here show de Vries characteristics, these also
407 exhibit a significantly large electroclinic effect, and low orientational order parameters in
408 their SmA* and SmC* phases. The low value of the orientational order parameter (below
409 0.62) as compared to conventional smectics (~0.8) indicates the absence of long-range
410 correlations. The change in the dichroic ratio, the order parameter with the electric field,
411 point towards the de Vries characteristics. The dependence of the tilt angle on the electric
412 field can be explained by the generalized Langevin-Debye model. The results support the de
413 Vries diffuse-cone model where the tilt angle is confined to lie within a range of values in
414 between Ω_{\min} and Ω_{\max} . The apparent tilt angle varying with temperature/field in between
415 these two limiting values. The change in the tilt angle with the field follows a similar trend to
416 what has already been observed through electro-optical experiments. The strong soft mode
417 fluctuations in the SmA* are observed through a large dielectric relaxation strength signal,
418 which continually increases with decreasing temperature, one of the typical de Vries
419 characteristics. The relaxation frequency softens and eventually goes towards that of the
420 Goldstone mode in SmC* phase. The two different techniques of IR and dielectric
421 spectroscopy yield new results on the order parameter, the dichroic ratio, the relaxation
422 strength and frequency (of the dielectric process/es). The dependencies of these parameters
423 on field and temperature and their interpretations in terms of models advances the
424 understanding of de Vries smectics.

425

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