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Graphical Abstract



Transfer of chirality from the enclosed ferroelectric liquid crystals to the strands of an organic gel structure.

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ARTICLE TYPE

Influence of polarization-tilt coupling on the ferroelectric properties of smectic gels

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We have studied composites of a ferroelectric liquid crystal mixture with a simple organic gelating agent, employing structural, thermal, electrical and mechanical probes, investigating the influence of the coupling between the polarization and tilt angle on the ferroelectric properties of smectic gels. The calorimetric data, presenting clear signatures of the gelation occurring in the smectic A (Sm A) phase or the isotropic phase, depending on the concentration of the gelator, help in constructing a rich diagram in the temperature-gelator 10 concentration phase space. The atomic force microscopy imaging brings out the interesting feature of the transfer of chirality from the ferroelectric liquid crystal (FLC) to the gel strands, as exemplified by the creation of nanorope structures which have attracted much attention in recent times. The influence of gelation on the magnitude of the tilt angle appears to be dependent on the probe employed: There is no change in the values obtained by Xray diffraction, which looks at the projection of the entire molecular length on to the layer normal. In contrast, the value from the electro-optic method, wherein the molecular-core is responsible for the results, diminishes with 15 gelator concentration. The latter feature is copied by the magnitude of the polarization also. Dielectric spectroscopy shows that gelation weakly influences the soft mode in the SmA phase. However, the Goldstone mode behaviour is strongly dependent on the gelator concentration, with the appearance of two modes in the smectic C* (SmC*) phase of higher gel concentrations. With information obtained upon application of DC bias, the origin of the two relaxations is discussed. These data are analyzed in terms of the predictions of the Landau model proposed for the ordinary (non-gel) SmA-SmC* transition showing that the gel network enhances the linear ²⁰ polarization-tilt coupling over the biquadratic one. Upon gelation the system becomes mechanically strong with a large increase in the elastic moduli.

Introduction

- Physical gels are soft materials formed by weak interactions ²⁵ between fibrous aggregation of low molecular weight gelators and the surrounding liquid medium. Since non-covalent interactions such as a van der Waals forces or hydrogen bonds are involved in the gelation process, these systems are generally thermally reversible. If the liquid is replaced by a liquid crystal ³⁰ (LC), it brings in the dimension of anisotropy. Although, as far as
- ³⁰ (EC), it brings in the dimension of anisotropy. Annough, as far as confinement of LC in a network is concerned, these systems resemble a polymer dispersed LC material, the thermal reversibility of the LC gel is an advantage. The mesophase involved in the investigations on LC organogels has mostly been ³⁵ the nematic,¹⁻⁴ but a few substances with chiral smectic C
- (SmC*) phase have also been studied. Kato et al^{5a} reported the gelating transformation occurring within the smectic region yielding phase sequences of a sol-state^{5b} smectic to a gel-state smectic. In a rather unique study on a free-standing film of a
- ⁴⁰ mixture of a FLC gel, Li et al ⁶ found that the size of individual phase-separated LC microdomains decreases with higher content of gelling agent in the sample, whereas the width of the gel striations remains the same. These authors also noted that the network creates a memory of the frozen-in texture and influences
- ⁴⁵ the electro-optic switching behaviour of the ferroelectric phase considerably. Employing a chiral gelator, Zhao and Guan⁷ realized pitch compensation in the chiral nematic phase of a FLC

composite. Consequently, molecular alignment of excellent quality could be obtained even by quenching the sample to the ⁵⁰ required mesophase. However, there did not appear to be any influence of the gel network on the FLC properties. Deindorfer et al⁸ studied the influence of photoisomerization of azobenzene containing gelator molecules on the gelation of a SmC* material and find that the gelling ability can be reversibly switched on and ⁵⁵ off by *trans-cis* isomerization. More recently, Meziane et al.⁹ used dielectric spectroscopy to investigate the dynamic behaviour of FLC in gel matrices formed from semicarbazide or bisacylurea derivatives finding that gelation influences the spontaneous polarization as well the Goldstone mode, with the ⁶⁰ latter essentially vanishing. They also argued that the dielectric property can be used as a tool to detect gelation.

Here we report results of dielectric, rheological, electrical switching measurements, and AFM studies on a chiral mixture with a large spontaneous polarization, and its composites with a ⁶⁵ simple organogelator. The results indicate that large changes seen in the relaxation parameters of the collective dielectric relaxations, as well as the spontaneous polarization are not caused by a mere extent of gelation, a measure of which is the storage elastic modulus, but the confinement due to the fibrous network.

70 Results and Discussion

Differential scanning calorimetry



Fig 1: (a) Differential scanning calorimeter (DSC) scans for FLC0 (solid line) and FLC1 (dotted line). The enthalpy variation for FLC0 and its change across the Sm A-Sm C* transition for different concentrations are shown as insets (i) and (ii). (b) DSC 5 scans for FLC3 (open symbols), FLC5 (grey line) and FLC10 (dark line), exhibiting isotropic (sol)-isotropic gel(isogel)-Sm A-Sm C* sequence, with the smectics being in the gel state for the latter two composites The inset shows that the strength of the transition between the sol and gel forms of the isotropic phase 10 increases for FLC10, and that there exists a thermal anomaly above the isotropic sol state (marked B), associated with the creation of long-range hydrogen bonding. (c) Permittivity at a frequency of 305 Hz for FLC10 presenting striking changes at the

- ¹⁵ Figure 1 depicts the differential scanning calorimetry (DSC) scans obtained at a cooling rate of 2 K/min for the host mixture FLC0 and four composites, FLC1, FLC3, FLC5 and FLC10. FLC0 as well as FLC1, behave very similar with a strong peak representing the isotropic (Iso) to SmA transition and a step-like ²⁰ change for the SmA-SmC* transition. On the other hand, the
- higher concentration composites, especially FLC5 and FLC10,



Fig 2: Strain amplitude dependence of the storage (G') and loss (G") elastic moduli in the SmA phase for FLC0 and a representative composite, FLC3. Below a certain critical value, 25 both G' and G" are weakly dependent on strain, but exhibit a strong decrease above it. The fact that the solid-like behaviour (G' > G") is seen for FLC0 even though the SmA is in its sol form should be due to the network of defects. Gelation does enhance not only the absolute values, but also the ratio between 30 G' and G".

exhibit a richer thermal behaviour. As the sample is cooled, first a weak step-like feature is seen followed by a broad peak prior to another strong one. In comparison with FLC0 and FLC1, the strong peak is identified as the clearing point associated with the 35 appearance of the SmA mesophase. Taking into consideration the rheological data to be presented in the next section, we identify the broad peak above the clearing point to correspond to the gelation of the sample, and label the phases on the high and low temperature sides of it, as isotropic (Iso) and isotropic gel 40 (Isogel), respectively. The weak signature at the highest temperature is perhaps the point at which hydrogen bonding occurs (may be on a local scale) in the medium. The Xray profile in the wide angle region (See Fig SI-1 in Supporting Information), is in conformity with an earlier report^{10a} arguing the 45 existence of hydrogen bonding in similar systems. It may be recalled that calorimetric signatures of such hydrogen bonding transformations have been reported for carboxylic acid LC materials.10b It is interesting to note that marked changes corresponding to the Iso-Isogel-SmA gel -SmC* gel transitions 50 are seen in the temperature-dependent permittivity data collected at a fixed frequency of 305 Hz for FLC10(see Figure 1c).

different transformations seen in (b).



Fig 3: Temperature dependence of the storage (G', filled symbols) and loss (G", open symbols) elastic moduli for the host mixture and two composites displaying changes in the mechanical properties at the different thermodynamic transitions, s as indicated by the vertical lines.

Rheological measurements

To establish the gel nature of the phases, rheological characterization was carried out in terms of the storage (G') and loss (G") elastic moduli. Since these substances are expected to ¹⁰ exhibit non-linear behaviour of the moduli with strain, we first characterized the strain-dependence of the moduli for the host mixture FLC0, as well as the composites FLC3 and FLC5. The data obtained at an angular frequency of 1 rad/s in the SmA phase of FLC0 and the Sm A gel for a representative composite, FLC3 ¹⁵ are shown in Figure 2; the profiles are similar for FLC5. For all

- the materials studied a solid-like behaviour (G' > G'') at low strain values and a crossover to liquid-like behaviour (G' < G'') at high strain values are seen with a well defined linear viscoelastic (LVR) regime. While this behaviour is expected for the gels, the 20 fact that SmA in its sol state (for FLC0) also exhibits this
- ²⁵ there that only 1 m his sor state (for 1 Eco) also exhibits this behaviour must be due to the presence of a defect network that gets formed in this one- dimensional solid. In fact, the existence of a defect network has been argued to be responsible for the observation of a similar elastic behaviour in a chiral nematic ²⁵ doped with silica nanoparticles.¹¹ We will not discuss here the nonlinear behaviour seen above the critical strain, although the

The thermal dependence of the G' and G" for FLC0, FLC3 and FLC5, measured in the cooling mode (1°C/min rate) at a fixed ³⁰ angular frequency 1 rad/second and a strain value of 10⁻⁴ (and

gel concentration has an important influence on such a feature.

thus in the LVR region) are shown in Figure 3. For FLC0, G' and G" are low and comparable to each other in the Iso phase indicating the expected liquid-like behaviour (It is possible that G'' > G', in this region, but the resolution of the set up used does 35 not permit the feature to be established). Upon transformation to the SmA phase both the moduli increase abruptly. The transition to the SmC* is marked by a clear slope change in the thermal variation of the parameters. On the other hand, the composites, FLC3 and FLC5 show a richer behaviour. Cooling the sample, 40 the liquid-like behaviour (G'~G") deep in the isotropic changes to the solid-like behaviour (G^{2}) precisely at the temperature at which a broad, but clear peak is seen in the DSC scans. Polarizing optical microscope (POM) observations exhibiting a dark field of view (albeit the presence of strands of low birefringence 45 representing gel network) between crossed polarisers show that the phase is still isotropic over this temperature range confirming the assignment of isotropic gel (See Fig SI-2 in Supporting Information). At a slightly lower temperature, the transition from the Iso gel to Sm A gel is marked by a change in the slope of G' 50 and G" data. It may be noted that no abrupt changes are seen across the transition from Sm A gel to Sm C* gel. Concluding this section we would like to point out that the elastic moduli are orders of magnitude higher for the composites in comparison to the values in FLC0, suggesting that the gel network makes a 55 significant contribution to the mechanical strength over and above that from the intrinsic defect network of the smectic phases. In fact, the G' and G" values obtained for the gels studied here are quite similar to those for the composites of a non-chiral smectic LC with aerosil particles¹², exhibiting soft glassy 60 rheological behaviour. With the combined information from calorimetry, observations under an optical polarizing microscope, and rheological behaviour, we propose a temperatureconcentration phase diagram, as shown in Figure SI-3 (see Supporting Information)

65 Electrical properties

Theoretical background

Before discussing results of the dielectric relaxation spectroscopy (DRS), as well as the polarization and tilt angle measurements, we provide a brief background to the phenomena involved, from 70 a Landau theory point of view. The starting point of such a theory is that for the SmC* phase the tilt and polarization are identified as the primary and secondary order parameters respectively. Considering this important feature, a generalized mean field (GMF) model¹³ to account for various physical parameters of the 75 SmC* phase and the different aspects of the SmC*-SmA transition, has been proposed. According to this model the free energy of the system, with T_c as the SmA-SmC* transition temperature, is written as

$$F = F_o + \frac{a}{2}\theta^2 + \frac{b}{4}\theta^4 + \frac{c}{6}\theta^6 - \Lambda q\theta^2 + \frac{K_3}{2}q^2\theta^2$$
$$-\mu q P \theta + \frac{P^2}{2\chi} - CP \theta - \frac{\Omega}{2}P^2\theta^2 - PE \qquad (1)$$

⁸⁰ Here *a*, *b* and *c* are the usual Landau coefficients, with $a = \alpha$ (T-T_c), being an explicit temperature dependent term, and the 6th order term with the coefficient *c* included for explaining the

possibility of a tricritical point. Apart from the elastic terms (terms 5-7 in eq. 1) with q (= 2π /pitch) as the wavevector of the helix, two important terms in this equation are terms 9 and 10 which describe respectively the bilinear and biquadratic coupling between the palarization **R** and the tilt angle 0 of the medium.

- s between the polarization P and the tilt angle θ of the medium. In the SmC* phase, the dynamics of such a system exhibits two collective modes associated with the fluctuations of the polar and azimuthal angles of the generalized tilt. In the absence of a strong DC bias, the former mode (amplitude mode) occurring at high
- ¹⁰ frequencies is normally seen only close to the transition to the SmA phase, due to the higher energy involved. Owing to its low energy cost, the latter mode, referred to as the Goldstone mode (GM), occurs at low frequencies (< kHz) with a large dielectric strength. Since the helix is formed by the precession of the ¹⁵ azimuth of the tilt in adjoining layers, the relaxation parameters
- of this mode are strongly connected with the pitch of the helix. In the SmA phase the two modes become degenerate resulting in a mode labelled as the soft mode (SM). The GMF model has the following predictions for the relaxation frequency f_S , f_G and 20 strength $\Delta \varepsilon_S$, $\Delta \varepsilon_G$ of SM and GM.

For the SM in the SmA phase,

$$f_{S} = \frac{1}{2\pi\eta_{S}} \left(\alpha \left(T - T_{C} \right) + Kq_{0}^{2} \right)$$
(2)
$$\Delta \varepsilon_{S} = \frac{\varepsilon_{0} \left(\varepsilon C \right)^{2}}{Kq_{0}^{2} + \alpha \left(T - T_{C} \right)}$$
(3)

and for the GM in the SmC* phase,

$$f_G = \frac{K q^2}{2\pi\eta_G}$$
(4)
$$\Delta \varepsilon_G = \frac{1}{K} \left(\frac{P}{q\theta}\right)^2$$
(5)

25

Here $K = K_3 - \epsilon \mu^2$, $q_o = q$ at the transition, η_S , η_G are the viscosities associated with the two modes, ϵ and ϵ_0 are the high temperature and free space permittivity, respectively. The model ³⁰ introduces an all important term $\beta \propto C/\Omega$ to represent the relative contribution of the bilinear to biquadratic terms; higher the value of β , the system is closer to the classical case of entirely bilinear coupling. This GMF model is also used to make predictions for the dependence of polarization on the magnitude of the tilt angle. ³⁵ Specifically, Giesselmann and Zugenmaier, ¹⁴ employed the

following simple expression,

$$P = \frac{C\theta}{1/\chi - \Omega\theta^2} \tag{6}$$

Of course, here too P would be strictly linear in θ , when the biquadratic contribution becomes negligible.



⁴⁰ Fig 4: Frequency dependence of the imaginary (ε") part of the permittivity in the (a) SmC* and (b) SmA phases FLC0 and the composites (the number against each profile indicates the gelator concentration). In the SmC* phase there is a drastic reduction in the strength of the Goldstone mode as the HSA concentration is
⁴⁵ increased. For FLC5 and FLC10, an additional peak could be resolved (gray lines in the insets). The solid line in the main diagrams (a) and (b) in all the cases represents a fit of the data to the Cole-Cole expression. The single relaxation seen in the SmA phase (panel b) is attributed to the soft mode.

50 Dielectric relaxation spectroscopy (DRS)

Representative DRS profiles of the frequency (f) dependence of real (ε ') and imaginary (ε '') parts of the permittivity in the SmA and SmC* phases for FLC0 and the composites are shown in Figures 4(a) and (b) [As seen from the rheology data presented ⁵⁵ above, for X \ge 1%, the SmA and SmC* phases are actually the gel version of the structure. However, for the analysis of the dielectric data we do not discriminate between the sol and gel versions]. While FLC0, FLC1 and FLC3 exhibit a single relaxation in both the phases, the other two composites show a ⁶⁰ single relaxation only in the SmA phase. In the SmC* phase the profiles for these materials could be resolved into two relaxations. To extract the relaxation frequency, the ε '' vs. frequency profiles data were fit to the Cole-Cole expression,

$$\varepsilon^{*}(\mathbf{f}) = \varepsilon_{\infty} + \sum_{k=1}^{n} \frac{\Delta \varepsilon}{1 + (i\mathbf{f}/\mathbf{f}_{R})^{\nu}}$$
(7)



Fig 5: Thermal variation of the (a) relaxation frequency (solid symbols) and (b) its strength corresponding to the Goldstone mode (f_G , $\Delta \varepsilon_G$) in the SmC* phase and soft mode (f_s , $\Delta \varepsilon_s$) in the SmA phase for FLC0 and the composites. With increasing HSA concentration, f_G ($\Delta \varepsilon_G$) increases (decreases) whereas f_s is hardly affected. The open symbols in panel (a) indicate the relaxation frequency for the additional mode that appears for FLC5 and FLC10. The inset in this panel depicts the concentration dependence of the three modes with the open symbol representing the data for the additional relaxation at T_c -T=5K. The inset in panel (b) shows that $\Delta \varepsilon_G$ and $\Delta \varepsilon_s$ are comparable for FLC10.

- Further, $\Delta \varepsilon^a$, the strength of the additional mode behaves like the soft mode in the SmC* phase, normally obtained with a DC bias.
- ¹⁵ where $\varepsilon^*(f)$ is the complex permittivity at a frequency f. The first term on the right hand side is the high frequency permittivity which includes the dielectric strengths of all the high frequency modes other than the ones under consideration. f_R is the relaxation frequency and $\Delta\varepsilon$, the dielectric strength, *y* - a measure ²⁰ of the distribution of the relaxation times for the considered mode. A single Cole-Cole expression (n=1 in eq. (7)) was used in both phases of FLC0, FLC1 and FLC3 as well as the SmA gel of FLC5 and FLC10 samples; in the SmC* phase of the last two
- mentioned samples, n=2. In all the cases, to account for the ionic ²⁵ contribution from the sample the term, $i\sigma_0/f^N$ was added to the right hand side of eq. (1), with σ_0 being the DC conductivity and N, a fitting parameter. y = 1 for FLC0, FLC1 and FLC3, but progressively decreases with increasing concentration of the gelator, with the value being further lower in the SmC* phase
- $_{30}$ (especially so for the higher frequency mode) than the in the corresponding SmA phase. The experimental value of *y* deviating



Fig 6: AFM image of the fibre strands exhibiting a twisted stripe pattern with a periodicity of ~ 100 nm for FLC10

³⁵ from the ideal Debye value of 1 signifies distribution of relaxation times, a feature expected for gelated samples owing to slightly different environments for the LC molecule in the vicinity of a gel fibre and away from it. From the theoretical background described in the previous section, it is clear that the ⁴⁰ mode in the SmA phase is the soft mode, and the low frequency one in the SmC* phase, the Goldstone mode. A little later in this section we shall discuss about the high frequency relaxation observed in the SmC* of some composites. It may be mentioned that down to 2 mHz no dielectric mode was observed which can ⁴⁵ be associated with the formation of ferroelectric domains.

The temperature dependence of the relaxation frequency and the dielectric strength of the cooperative mode in the SmA phase extracted from the fits of the data to eq. (7) are shown in Figure 5. As expected, all samples show a strong decrease of f_s as the 50 sample approaches the SmC* from the SmA phase. Concomitantly, the strength of the mode $\Delta \varepsilon_{s}$ exhibits a large increase, clearly establishing the associated mode to be the soft mode. For a quantitative description of the temperature dependence of the relaxation parameter of the soft mode, we 55 employ eqs. 2 and 3. As seen from these equations the wave vector of the helix q plays an important role in determining the relaxation parameters. Observation of a thin film of the sample under the POM shows dechiralization lines for FLC0 and FLC3 materials enabling estimation of the helical pitch (We used 60 samples with an open surface, so as to determine the free pitch length wherein the influence of the surface is absent). This was not the case for FLC10 perhaps owing the dense gel network. For this reason the quantitative comparison of the different parameters has been done only between FLC0 and FLC3. The 65 pitch values determined from the dechiralization lines are comparable for FLC0 and FLC3 (FLC0: 0.88 \pm 0.03 μm and FLC3: 0.97 \pm 0.03 µm). From the AFM image (Figure 6) a stripe pattern on the strands with an average diameter of 150 nm, and periodicity of ~ 100 nm is seen, whereas the fibre density is 70 estimated as $20/\mu m^2$. Although such a pattern suggests that the LC phase is transferring its chiral nature to the strand, the length scale that determines the periodicity is not clear, since the SmC* pitch values are much higher. A point to be highlighted is the ease with which chirality transfer takes place in this case creating 75 nanorope structures. (A subtle feature seen in Figure 6 is that the twisting is clear for strands along the diagonal from left bottom to right top, than for those along the other diagonal. We are in the process of understanding this difference.) Bringing in tunability *Table 1: Exponent* γ *obtained for the host FLC mixture* (x=0) *and the composites* (x=1, 3, 5 *and* 10) *by fitting thermal* s *dependence of the dielectric strength in the Sm A phase to Eq. 8.*

x	γ
0	1.09±0.01
1	1.09±0.01
3	1.08±0.01
5	1.01±0.04
10	1.02±0.02

Table 2: The values of elastic term Kq_0^2 , Landau coefficient α , the bilinear coupling coefficient C, biquadratic coefficient Ω , and C/Ω for the host FLC mixture and the composite FLC3 are listed below.

Material	FLC0	FLC3
$Kq_0^2 (10^4 N/m^2)$	0.91	1.75
$\alpha (10^5 \text{ N m}^{-2} \text{ K}^{-1})$	1.02	2.21
$C(10^7 NC^{-1})$	8.43	12.36
$\Omega (10^9 \mathrm{Nm^2 C^{-2}})$	33.97	5.03
$C/\Omega (10^{-3}C/m^2)$	2.48	24.5

10

of the length scale to such structures is important and of much significance especially from the viewpoint of biological systems in creating functionalities such as antibody recognition.¹⁵

According to eq. (4), the reciprocal of the dielectric strength ¹⁵ should be linear in the reduced temperature (T-T_c). However, to account for a more general situation, we replaced the term α (T-T_c), with a power law term, α (T-T_c)^{γ}, where γ , being the critical exponent of the susceptibility, has a value of 1 for in the mean field limit. Thus, the fit done to

$$\frac{1}{\Delta\varepsilon_s} = \frac{Kq_0^2}{\varepsilon_0(\varepsilon C)^2} + \frac{\alpha (T - T_C)^{\gamma}}{\varepsilon_0(\varepsilon C)^2}$$
(8)

20

- describes the data well. The exponent obtained for each case is listed in Table 1. The exponent value appears to have two regimes, decreasing for higher concentrations. By symmetry considerations, the SmA-SmC* transition, being described by a ²⁵ two-component tilt order parameter, is expected to belong to the XY universality class, which predicts $\gamma = 1.317$ (See e.g., Ref. 16). However, with very few exceptions¹⁷ the SmA-SmC* transition
- has been found¹⁸ to be of the mean field (MF) type with $\gamma = 1$. For the presently studied system, it is noted that for the host ³⁰ mixture, as well as the lower concentration composites, γ lies between the two theoretical limits mentioned above, but attains the MF value for higher concentrations. It is thus possible that the influence of the order parameter fluctuations diminishes when the gelator concentration is high, or in other words when the system
- ³⁵ becomes mechanically stronger. Perhaps the increased strand density and the consequent influence from the virtual surfaces may also be responsible for this behaviour. The intercept of the linear fit done to eq. (8) yields the ratio of the twist to the piezo energy, $Kq_{a}^{2}/\varepsilon_{a}\varepsilon^{2}C^{2}$. Using this ratio and the value of the
- ⁴⁰ bilinear coupling coefficient C, determined in the manner to be described in a later section, we have calculated the elastic term Kq_o^2 for the host mixture and the FLC3 composite. These values are listed in Table 2. Inset to Figure 5(a) shows the concentration

dependence of the relaxation frequency of the soft mode at a 45 Fig 7: Temperature dependence of the soft mode viscosity for



FLC0 and FLC3 materials showing that upon gelation there is a large increase in the value and further that the singular behaviour near the transition is also enhanced.

- ⁵⁰ reduced temperature of T_c+5 K. The gelation hardly affects the relaxation frequency, but substantially (~ 20%) lowers the strength of the mode. However, from Table 2 it is seen that Kq_o² and α get doubled for the FLC3 composite. Hence the nonvariation of f_s should be resulting from an increase in rotational ⁵⁵ viscosity associated with the soft mode that matches the contribution from Kq_o² and α terms. A feature that may be commented upon is that as mentioned already the helical pitch does not change much between FLC0 and FLC3. Therefore the doubling of Kq_o² must mean that the elastic constant K enhances
- ⁶⁰ by a factor 2 for the FLC3 composite. It may be recalled that a similar increase in the Frank elastic constant was seen for a nematic in a gel environment.⁴ It is possible that the gain in the elastic constant is a standard feature achieved in liquid crystals upon gelation.

⁶⁵ To find out the influence of gelation on the soft mode viscosity, we used the product of Eqs. 2 and 3 to yield,

The temperature dependence of η_S determined using the above

$$\eta_s = \frac{\varepsilon_0 (\varepsilon C)^2}{2\pi \varepsilon_s f_s} \tag{9}$$

equation is shown for FLC0 and FLC3 in Figure 7. The value of η_S goes up by a factor of 3 when the material is gelated, ⁷⁰ suggesting that the existence of gel network influences the cooperative rotational motion of the molecules. The diverging nature of the thermal dependence of η_S , especially for FLC3, prompted us to analyse the data in terms of critical behaviour of the parameter. For this we consider the thermal variation of η_S to ⁷⁵ be made of singular and non-singular contributions. For the latter we take a constant and a term linear in temperature. Thus the equation for η_S can be written as,

Figure 7 shows data fit to Eq. 10 very well with the exponent z

$$\eta_s = A + B(T - T_c)^{-z} + D(T - T_c)$$
(10)

being 0.88 ± 0.07 and 1.90 ± 0.02 for FLC0 and FLC3 ⁸⁰ respectively. Whether the presence of the gel fibers and the



Fig 8: DC bias field dependence of the relaxation frequency, f_G for FLC0 and f_1 and f_2 for FLC10 at T_c -T=5K.

consequent virtual surfaces are responsible for a higher z value is 5 not clear to us. As discussed in the theoretical section, the cooperative dynamics is dominated by the Goldstone mode, which is associated with the presence of the helix. As we have already shown the elastic term has a significant role to play in gelated systems. Thus it can be expected that gelation influences 10 the Goldstone mode relaxation parameters substantially and

- indeed found to be true (Figure 5) for the host mixture and the four composites. For the low concentration gel, FLC3, the frequency of the mode (Figure 5a) f_G increases by a factor of ~ 2 whereas the strength of the mode $\Delta \varepsilon_G$ (Figure 5b) decreases by a
- ¹⁵ similar factor. For a much higher concentrations, say, FLC10, the strength diminishes drastically⁸ with a concomitant appearance of a second relaxation. This additional mode has an order of magnitude higher relaxation frequency than GM, i.e., ~ 25 to 40 kHz (see Figure 5a), but a low strength (see Figure 5b). Further
- 20 the strength having a negative temperature coefficient as well as becoming maximum at the transition are features reminiscent of the soft mode in the SmC* phase. Normally, owing to the dominating feature of GM and further that tilt order parameter fluctuations are not favoured in the SmC*, the soft mode is not 25 observed except in the immediate vicinity of the transition to the
- ²⁵ observed except in the immediate vicinity of the transition to the SmA phase. Thus, a commonly used method to examine SM in the SmC* phase is to apply a DC bias in the plane of the layers which would unwind the helix, creating a situation conducive for the observation of SM. To find out the behaviour in the presence
- $_{30}$ of the bias field, we performed DRS measurements at a fixed temperature of $T_c\text{-}T\text{=}5\text{K}$ in the SmC* for FLC0 and FLC10 materials. Figure 8 shows the bias field (V_{DC}) dependence of f_G for FLC0, and f_1 and f_2 , the two relaxations for FLC10. It is seen that for the host mixture the frequency of f_G is weakly dependent
- $_{35}$ on V_{DC} up to a certain value and then exhibits a step-like increase to saturate at higher voltages. In contrast both f_1 and f_2 are essentially independent of V_{DC} in the case of FLC10. More importantly, f_1 is comparable to f_G (of FLC0) at low V_{DC} and f_2 is about the same as f_G at high V_{DC} . The step-like increase for FLC0
- ⁴⁰ can be associated with the unwinding of the helix, and consequently the high-field value of this mode can be taken to be the relaxation frequency of the soft mode.



⁴⁵ Fig 9: Thermal variation of the tilt angle in the SmC* phase determined from (a) Xray diffraction and (b) electro-optic methods for the host mixture and two composites. The values from Xray are nearly identical for the different materials, unlike the electro-optics ones.

Hence, f_1 and f_2 of the gelated system are nothing but the GM and SM of FLC0. The fact that both of them coexist even in the absence of DC bias, and that their frequency (and also their dielectric strength) are hardly dependent on the bias value, ⁵⁵ suggests that there must be two different regions coexisting in the sample independently giving rise to the two modes. The regions which are in the vicinity of the gel fibres would have the helix unwound by the surface forces of the fibres, and thus do not exhibit GM, but rather show SM relaxation. The material that is ⁶⁰ away from the fibres, would have the helix unaltered (at least in the absence of bias), and thus presents GM. The applied bias (even up to $4V/\mu m$) is not able to alter this scenario very much.

Tilt angle and polarization measurements

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As discussed in the theoretical section, the ratio of the bilinear to 65 the biquadratic term plays an important role from the viewpoint of the Landau model. To determine these parameters, which were also required for the calculation of other terms in the Landau model, we carried out polarization and tilt angle measurements for the host mixture and two composites, viz., FLC3 and FLC10 70 using the electrooptic method described in the Experimental section. The tilt angle was also determined by the Xray technique. Figure 9 (a) shows the thermal variation of the tilt angle determined from the expression $\theta_{xray} = \cos^{-1}(d_c/d_A)$, where d_c and d_A are the layer spacings in the SmC* and SmA phases



Fig 10: Schematic diagram to illustrate (a) that the HSA fibres run through the smectic layers creating intralayer segregation of the fibres and LC molecules, and (b) the origins of the tilt angle as measured by the Xray (θ_{xray}) and electro-optic (θ_{opl}) s techniques. Notable is the feature that for the non-gel system (left

- panel) θ_{opt} is greater than θ_{xray} , a feature that gets reversed upon gelation. We attribute the lowering of θ_{opt} to anchoring caused by the gel fibres.
- respectively obtained from Xray diffraction measurements, for ¹⁰ FLC0, FLC3 and FLC10. It is observed that over the entire temperature range studied the values for the three materials are essentially the same. This is all the more surprising in view of the behaviour of the tilt angle obtained by the electro-optic method, to be discussed below. It is possible that since the value measured
- ¹⁵ in the SmC* phase is from the projection of the entire molecule on to the layer normal direction, gelation does not influence θ_{xray} values. It is interesting to see that d_A , the layer spacing in the SmA phase also remains unchanged for the gel materials. Here we would like to draw some parallels with Xray data obtained on
- ²⁰ smectic phases contained in a polymer network¹⁹. When the polymer creating the network does not contain an anisometric entity, a substantially large increase was seen in the layer spacing. But when the anisometric units were present, the change in the spacing was quite small. This behaviour was explained¹⁷ on the
- ²⁵ basis of different nature of segregation, viz., interlayer, and intralayer variety, of the polymer and LC molecules in the two cases, respectively. Thus it is unexpected that in the present case where the network is formed by a gelator which does not contain any anisometric units, the layer spacing measured is hardly
- ³⁰ different for the gelated composites. Borrowing the analogy with the scenario described for the polymer network, we hence propose that the HSA fibres, despite not containing anisometric units, run through the smectic layers creating an intralayer segregation of the fibres and the LC molecules, schematically ³⁵ shown in Figure 10(a).

The temperature dependence of the electro-optic tilt angle is presented in Figure 9(b), which, unlike the Xray data, exhibits significant diminution upon gelation: the value drops by $\sim 15\%$ for the FLC10 mixture in comparison to that for FLC0. To



⁴⁰ Fig 11: Polarization as a function of temperature in the SmA and SmC* phases for the host mixture and two composites exhibiting that gelation diminishes the value.

explain the discrepancy in the tilt angle behaviour between Xray 45 and optical probes, we proceed as follows. It is well known that whereas the entire molecule (rather its length) is considered for determining the tilt angle in the Xray measurements, it is the molecular core which contributes significantly to the birefringence of the system, and thus the electro-optic tilt. Hence, 50 upon gelation the reduced tilt of the molecular core has to be compensated by the chain portions of the molecule to keep the layer spacing unaltered with respect to that for the ungelated material. A possible scenario is depicted in Figure 10(b). The presence of the gel fibres creates the effect of virtual surfaces, 55 and the chains of the LC molecule may want to have substantial interactions with such surfaces leading a significant leaning of the chain portion of the LC molecule towards the fibre. The hindrance provided by such an anchoring may limit the maximum tilt angle achievable by the molecular core. The overall effect will 60 lead to a reduced electrooptic tilt, but retain the layer spacing unaltered

Gelation also has a large impact on the spontaneous polarization, reducing it by ~ 30% for the FLC10 mixture (see Figure 11). Further, whereas the data away from the transition ⁶⁵ seems to be having a similar temperature dependence, the growth near the transition appears to be dependent on the HSA concentration, and is lowered by ~ 36% for the FLC10 composite. Both these features in conjunction with the fact that the tilt angle reduces by ~ 15% only suggests that the ⁷⁰ polarization-tilt coupling must be getting affected upon gelation. In order to estimate quantitatively such as a coupling we employ eq. (6) given by the Landau model developed for the SmA-SmC* transition of non-gel materials, and described above. We make a slight change to eq. (6) to add a term ²⁰ to include the applied ⁷⁵ electric field,

$$P = \frac{C\theta + E}{1/\chi - \Omega\theta^2} \tag{11}.$$

Figure 12 shows that eq. (11) describes the data well for the host mixture as well as the two composites. The two P- θ coupling coefficients determined from such a fitting are tabulated in Table 2. The linear coupling coefficient C increases by a factor of 1.5



Fig 12: Dependence of polarization on the electro-optic tilt angle. While the host mixture shows a noticeable nonlinear variation, the composites have essentially a linear behaviour suggesting that the importance of the biquadratic polarization-tilt coupling is reduced upon gelation.

for FLC3. On the other hand, the biquadratic coefficient reduces by a larger factor of 6 for the composite. According to the Landau ¹⁰ model, the ratio C/Ω is a characteristic term describing the overall Ps- θ coupling, and this term increases by an order of magnitude for FLC3, thereby showing that the linear coupling term dominates for the composite. Recalling the behaviour of the Goldstone mode parameters discussed in the DRS section, it ¹⁵ should not be surprising that the strength of the mode decreases substantially as the P/ θ ratio decreases (by 26%) and the elastic term increases.

Conclusions

- We have investigated composites of a ferroelectric liquid crystal ²⁰ mixture with a simple organic gelating agent, employing Xray, calorimetric, dielectric, rheological, electro-optic switching and AFM probes. The calorimetric data exhibit clear signatures of the gelation and show that it occurs in the smectic A phase at low concentrations, but in the isotropic phase for higher ²⁵ concentrations of the gelator. AFM studies bring out the fact that
- the FLC material effectively transfers its chirality to the gel strands made out of the non-chiral gelator, creating nanorope structures of much significance in biology. However, what is surprising is that the length scale of the twisted structure of the
- ³⁰ strands does not appear to be correlated to the helical pitch of the confined FLC material. A study wherein a large change in helical twisting power can be made, e.g., by changing the twist sense of the host material, could serve as a better tool to understand the chirality transfer. While the tilt angle determined from Xray
- ³⁵ measurements is impervious to the amount of the gelator, the electro-optic tilt angle gets affected substantially. To explain this discrepancy we have made an argument based on the anchoring of the terminal chains to the gel strands and the different origins of what gets probed as tilt angle in the two methods. Dielectric as spectroscopy shows that gelation weakly influences the soft mode.
- $_{\rm 40}$ spectroscopy shows that gelation weakly influences the soft mode

over the biquadratic one, moving the systems closer to a classical picture. Rheological measurements display the rigidity of the static material upon gelation with large increase in the elastic moduli. It may be anticipated that tuning the chirality of the host has a significant influence on the network structure and other properties of such FLC gels, an aspect that we are currently working on.
 De-optic tilt nonlinear behaviour rization-tilt The molecular structures of the two LC components, MCP7OB and 7OPDOB for short, used to prepare the host mixture, and that of the organogelator HSA are shown in Figure 13; the figure also gives the phase sequence and transition temperatures for the LC components. MCP7OB shows a first order smectic A (Sm A) to 65 Sm C* phase transition²¹ with the chiral smectic C phase exhibiting a large spontaneous polarization (P) of 300 nC/cm² whereas 70PDOB is an achiral compound showing a second

order Sm A to Sm C phase transition. The concentration of the mixture was chosen to be 14% (by weight) of 7OPDOB in 70 MCP7OB keeping in mind the following points: (i) the SmA-Sm C^* transition is second order for this mixture²², (ii) the Sm C^* phase is thermally stable almost down to ambient temperatures, and (iii) the magnitude of P is only slightly lower than for pure MCP70B. This host mixture, referred to in the article as FLC0, 75 obtained by heating the two LC compounds to 100 °C and mechanical stirring to ensure homogeneous mixing, exhibits a Sm A to Sm C* transition at 45.6 °C with Sm C* phase stable down to ~ 30 °C. The FLC gels were realized by adding the required quantity of HSA to FLC0, heating the mixture to 100 °C while ⁸⁰ constantly stirring for an hour, followed by cooling to ambient temperature. Gels having HSA concentration of 1, 3, 5 and 10 (by weight) were prepared for the present study. These materials are referred to as FLCx, where x indicates the concentration by wt% of HSA in the mixture.

in the SmA phase. In contrast, the Goldstone mode behaviour is strongly dependent on the gelator concentration. Interestingly

higher concentration gels show two modes in the SmC* phase. Taking the help of bias-dependent data, we argue that the

45 contributions to the two modes arise from different regions of the

sample, viz., the so called bulk, and regions lying in the vicinity

of the gel strands. The magnitude of spontaneous polarization is

seen to be significantly lowered upon gelation. We have analysed these data in terms of the Landau model proposed for the 50 ordinary (non-gel) SmA-SmC* transition and show that the presence of gel network influences the polarization-tilt coupling in such a way as to increase the dominance of the linear coupling

Methods

Differential scanning calorimetry (DSC)

DSC measurements were carried out using Perkin Elmer Diamond DSC in the cooling mode with the temperature ramping 90 done at a rate of 2 K/min. The thermal signatures of the scans were used to obtain the phase transition temperatures and the associated enthalpy changes.

Polarizing optical microscopy (POM)

A Leica Polarizing microscope (Leica DM4500 P) in conjunction ⁹⁵ with a hot-stage (Instec or Mettler FP82 HT) was used to identify the phases in the sol as well as the gel forms, and also to determine the pitch of the helix in the SmC* phase.

X-Ray diffraction (XRD)



Iso - 58.8 °C - Sm A - 45.4 - Sm C*

Fig 13: The molecular structures of the LC compounds and the organogelator used in this study along with the phase sequence s and transition temperatures for the LC materials.

XRD experiments were performed in the transmission geometry by having the samples in a glass capillary (Capillary Tube Supplies Ltd, UK) to determine the layer spacing in the Sm A and

- ¹⁰ Sm C* phases which in turn was used to calculate the tilt angle of molecules in the Sm C* phase by assuming that the molecules tilt in a rigid-rod fashion. The XRD apparatus (X'Pert PRO MP, PANalytical) employing CuK α ($\lambda = 0.15418$ nm) radiation consists of a focusing elliptical mirror for beam preparation
- ¹⁵ optics providing a well focused line beam, a fast high resolution multichannel solid state detector (PIXCEL), and operated at 45 kV and 30 mA rating. Collimation with 20 mrad Soller slits on the input as well as the diffracted beam sides provides a very good vertical resolution.

20 Dielectric relaxation spectroscopy (DRS)

DRS measurements were carried out using an impedance analyser (HP 4194A) over a frequency range of 10^2 Hz to 10^7 Hz. DC bias-dependent measurements were carried out using a LCR meter (Agilent 4284A). For this purpose, samples were inserted

- ²⁵ in test cells (nominal thickness of 10 μ m defined by PET spacers, and measured using an interferometer technique) fabricated using a pair of electrically conducting transparent substrates, viz., indium tin oxide (ITO) coated glass plates having very low sheet resistivity (<10 Ω / unit area, Thin Film Devices Inc.,
- ³⁰ USA) coated with a polyimide solution and rubbed unidirectionally to aid planar alignment. The sample temperature was varied using Mettler FP82 HT hot stage.

Spontaneous polarization measurements

Spontaneous polarization (P) in the Sm C* phase was measured

- ³⁵ using the well-known triangular wave field method.²³ Application of the field to the samples in the ferroelectric state yielded a single current peak per half cycle of the applied field. The area under the peak is a direct measure of spontaneous polarization. The electric field required to completely unwind the helical pitch
- ⁴⁰ was determined by measuring electric displacement as a function of applied field well within the Sm C* phase. The saturating field

obtained from such a data was used for the temperaturedependent measurements.

Optical tilt angle (θ) measurements

- ⁴⁵ The optical tilt angle was determined by recording the intensity of the laser beam transmitted through the sample placed between crossed polarisers. The method involves application of a low frequency square wave field across the sample thickness and monitoring the magnitude of rotation of the optic axis for the two ⁵⁰ signs of the field. For this purpose the sample was mounted on a
 - rotation stage controlled by a micro position controller (Holmarc, India) interfaced to a computer.

Rheological measurements

Dynamic rheological measurements were carried out using a ⁵⁵ controlled stress rheometer (ARG2, TA instruments), details of which are described in an earlier publication.²⁴ A parallel plate geometry of 8 mm diameter with a gap of 0.8 mm was employed for the experiments. The temperature-dependent measurements were performed with the help of a Peltier temperature controller ⁶⁰ having a precision of 0.01 °C.

Atomic Force Microscopy (AFM)

Samples were prepared by smearing the FLC gel in its isotropic phase on a previously cleaned n- type silicon substrate. The gel network morphology was imaged at room temperature using an ⁶⁵ Atomic Force Microscope (Agilent 5500 AFM) in the noncontact mode employing a rectangular shaped silicon probe (NSC-15 from MikroMasch, Bulgaria) with a resonance frequency of 325 kHz, a force constant of 46 N/m and a nominal tip radius < 20 nm. All the images were acquired under ambient ⁷⁰ conditions with a scanning speed of 1 line /s and analyzed using Picoview software from Agilent.

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Notes

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