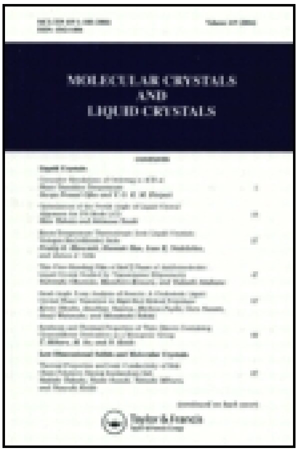

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Effect of the Polymer Network Morphology Created Under Electric Field in the Short Pitch FLC on the Dielectric Responses

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Polymer-stabilized ferroelectric liquid crystals (PSFLCs) are made by photo polymerizing of 7% reactive mesogenic monomer in a highly twisted ferroelectric liquid crystal (FLC). This study reveals that both the dielectric intensity and the relaxation frequencies of the collective relaxations mechanisms namely soft and the Goldstone modes are strongly affected not only by the presence of the polymer network but also by the polymerization conditions. It is shown that, for sample polymerized with the presence of electric field, the dielectric strengths decrease and the relaxation frequencies are shifted to high frequencies compared to the sample polymerized without the presence of the electric field. This behavior was found strongly dependent of the structure of the polymer fibers. A simple phenomenological model is proposed to explain the behavior of the soft mode dielectric intensity.

Keywords Dielectric relaxation; modeling; morphology; PSFLC

1. Introduction

The effects of the confined geometry of the ferroelectric liquid crystal (FLC) in various configurations on the collective modes, namely soft and the Goldstone modes have already been studied by many groups [1–7]. The molecular relaxations of the FLC molecules in a restricted geometry differ from those of the bulk state. The majority of studies reveal that the dynamics of collective modes of a FLC are strongly influenced by confinement effects. Generally, the confined geometry of the FLC in different configurations leads to the reduction of the Goldstone dielectric intensity [1–7].

Detailed dielectric spectroscopic study over a wide temperature and frequency ranges in the PSFLC systems confirmed the presence of the soft and Goldstone collective relaxation modes in this type of composites [8–10]. It was reported [8–10] that the dielectric strength of the Goldstone mode decreases with increasing polymer concentration, however, the relaxation frequency was found to be high for the PSFLC composite film compared to that of the corresponding pure FLC. These results were

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Address correspondence to M. Petit, Université du Littorale Côte d'Opale, UDSMM, Dunkerque, France. E-mail: mpetit8@hotmail.com interpreted by the increase of the elastic coupling interaction between the polymer and the liquid crystal due to the excess surface energy at the polymer–LC interface [8–10]. However, the behavior of the soft mode dielectric strength is not completely explained yet. Kundu *et al.* [11] have showed for polymer stabilized ferroelectric liquid crystal (PSFLC) systems that the soft mode dielectric strength remains unchanged when the FLC cells are stabilized by a polymer network formed from a nonmesogenic reactive monomer. In our previous study [8], although the range of the SmA phase is very narrow, the effect of the polymer network on the soft mode was clearly observed. By increasing the polymer concentration the dielectric strength is reduced and the relaxation frequency is increased [8].

On the other hand, the polymerization in the SmC* phase under and without electric field causes significant differences. Kaur *et al.* [9] are showed that the value of the Goldstone mode relaxation frequency (f_G) for sample polymerized in the SmC* phase under electric field was found lower than those polymerized without electric field. The combination of liquid crystals with polymers resulted in many interesting new morphologies, which have been investigated for application in electro-optic systems.

The morphology of the polymer fibrils was found strongly depends on the polymerization conditions; the polymer network formed under electric field differs from that formed without the presence of an electric field [12]. These authors showed that the polymer network formed under E suppress the cone of rotation of FLC and thus facilitate the switching [12]. The response time of the PSFLCs is found fast compared with that of the bulk state [12]. Archer *et al.* [13] have showed that the defect of the FLC twisted grain boundary were found printed on the polymer network structure.

In a recent study we have demonstrated that the twisted morphology of the polymer network formed in the short pitch FLC allow us to give more description of the increase of the critical unwinding field [14]. This twist morphology is also used to explain the behavior of the electroclinic effect versus polymer concentration [15,16]. The introduction of a polymer network has a great technological relevance for flexible displays applications [17], light shutter bases in PSLC [18–23]. Knowledge of the polymer network distribution through the LC layer is therefore necessary to understand qualitatively, and to model quantitatively, the influence of the presence of the electric field during the photopolymerization on the polymer networks morphology and on the dielectric properties of liquid crystal devices. In this paper we describe how the creation of the polymer network in the ferroelectric phase with electric field affects the dielectric responses. The polymerization in the SmC* phase under and without electric field causes significant differences on the dielectric properties. This behavior was found to strongly depend on the polymer network structure.

2. Experiments

The ferroelectric liquid crystal compound used in this work is the ROLIC 8823 (Rolic research Ltd) which exhibits, on heating, the following phase sequence between the crystalline (*Cr*) and the isotropic liquid (*I*) phases: *Cr*-−27°C-*SmC**-63.5°C-*SmA*-65°C-*I*, where *SmC** and *SmA** are the chiral smectic-C and smectic-A phases, respectively. In the *SmC** phase, at room temperature, the helical pitch is about 0.3 μm and the spontaneous polarization $P_s \approx 100\,nC/cm^2$. The polymer network is prepared using a reactive diacylate mesogen as a photocurable monomer

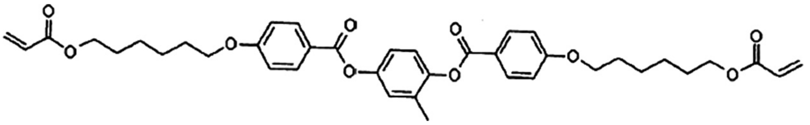

Figure 1. The molecular structure of the monomer.

which exhibits the nematic (*N*) phase between *Cr* and *I* phases (*Cr* -88°C-*N*-118°C-*I*). The molecular structure of this monomer is shown in Figure 1.

The photopolymerization was initiated with Irgacures 369 which was added to the monomer with a concentration of 0.5 weight %. The reactive monomer, together with photoinitiator, was dissolved into the ferroelectric liquid crystal in its isotropic phase to make a homogeneous mixture. The monomer concentration in the solution was fixed at 7 weigth %. A 5 μm thick EHC-cell (EHC Inc, Japan) with polyimide aligning layers was filled with a mixture in its isotropic phase. In order to obtain a good alignment in the SmC* phase, an electric field of 5 ($V\,\mu m^{-1}$ 1, 10 Hz) was applied to cells, and they were slowly cooled at a 0.1 ($°C\,min^{-1}$) cooling rate down to room temperature. Two sample cells were then exposed to ultraviolet light (wavelength $\lambda = 365$ nm) at 25°C with an intensity of 18 (mw/cm^2) for 30 minutes. One of each is polymerized without the presence of electric field, however, the other cell is polymerized with the presence of AC electric field at 5 $V\,\mu m^{-1}$ and for $f = 1$ Hz. During these studies, the cell was placed on a hot stage (Linkam TMS 93) for temperature control. The textures observations of the cells were carried out by means of a polarized optical microscope (POM) (LEICA DMRXP). Dielectric measurements were performed in the frequency range of 10 Hz to 13 MHz (HP 4192A). In order to obtain the characteristic dielectric strengths and relaxation frequencies of the ferroelectric relaxation modes, the dielectric spectra were fitted simultaneously by the Cole-Cole function:

$$\varepsilon^* = \varepsilon_\infty + (\Delta\varepsilon_G)/(1 + jf/f_G)_G^{1-\alpha} + (\Delta\varepsilon_s)/(1 + jf/f_s)_s^{1-\alpha} + (\sigma/j2\pi f\varepsilon_0), \qquad (1)$$

where f is the frequency, ε_∞ is the high frequency limit of the dielectric permittivity, $\Delta\varepsilon_G$ and $\Delta\varepsilon_s$ represent the dielectric strengths corresponding to Goldstone and soft modes, respectively; f_G and f_s represent the relaxation frequencies of the two modes, α_G and α_s are the distribution parameters, and σ is the electric conductivity. The temperature dependencies of different dielectric processes are reported and discussed below. To get the image of the topography of polymer networks a Veeco Multimode Atomic Force Microscopy (AFM) equipped with a Nanoscope IIIa controller was used. All AFM scans were taken in tapping mode with commercially available tips made of Phosphorus doped Silicon.

3. Results and Discussion

3.1. *Atomic Force Microscopy Observations*

Figures 2 and 3 show examples of AFM images and height profiles in the *z* direction of the Figure 9 of the polymer networks. These figures reveal that the separation distance between two polymer fibers (in the *Y* direction of the Fig. 9) varies

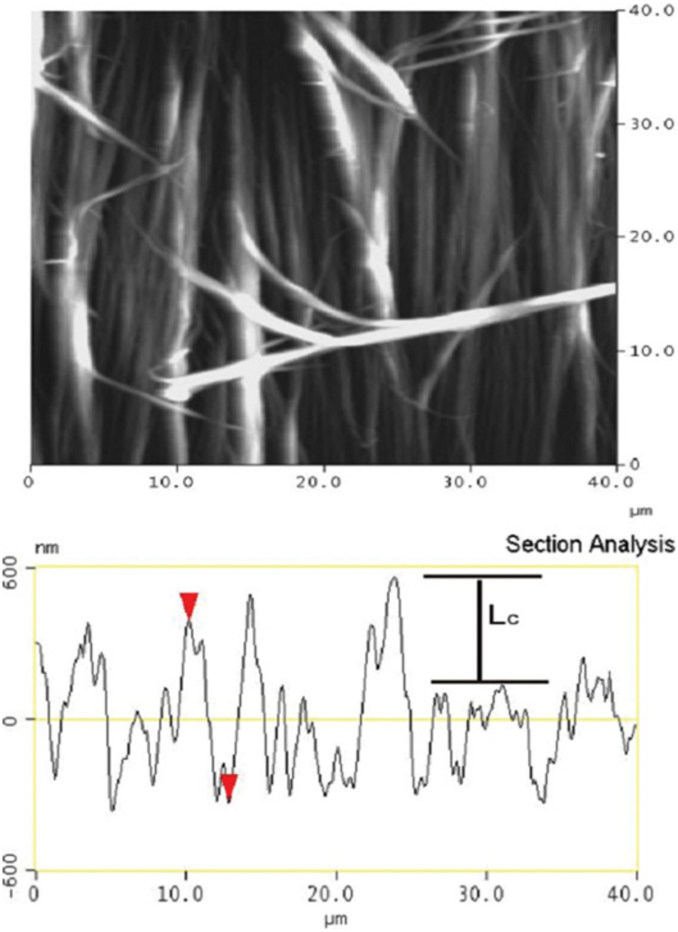

Figure 2. Tapping mode AFM images of polymer network structure of 40 × 40 µm^2 (upper) and the height profile of the network structure (lower) of the 7% polymer concentration (polymerization without electric field). (Figure appears in color online.)

from 1 µm to 3 µm for the cell polymerized without electric field and from 300 nm to 500 nm for a sample polymerized under electric field. The diameter of the fibrils was found varied between 500 nm and 1 µm for a sample polymerized without electric field. However, it is found between 200 nm and 700 nm for a sample polymerized under electric field.

Figures 2 and 3 (lower) represent the height profiles (on the z direction in the Fig. 9) of the polymer networks. The height profiles show two successive groups of fibers. The mean distance between them (L_c) was evaluated for each sample and are about 480 nm and 250 nm for samples when no field was applied during the polymerization and those polymerized under electric field respectively.

In conclusion, it must be noted from these observations that the polymerization under electric field is a principal factor affecting the polymer network structure. In the next section we confirm how the changes of the polymer network structure affect the dielectric response of the PSFLC films.

3.2. *Dielectric Studies*

3.2.A. *Goldstone Mode of the SmC**. In Figures 4 and 5 the parameters $\Delta\varepsilon_G$ and f_G obtained from the curve-fit procedure are displayed. For all studied samples, the behavior of $\Delta\varepsilon_G$ versus temperature shows the same general features (Figs. 4 and 6). As seen in Figure 4, $\Delta\varepsilon_G$ increases slightly to reach a maximum at T_{max} (3°C below T_c). Above T_{max}, $\Delta\varepsilon_G$ abruptly decreases. Usually the maximum observed in $\Delta\varepsilon_G$ is related to that exhibited by the helical pitch (Fig. 6), and indicates that the helical structure of the FLC is preserved in two PSFLC systems. This behavior agrees with the results which are reported in [14], especially that illustrate the helical structure of the ferroelectric phase still exists despite the presence of the polymer network. At room temperature ($T = 25°C$), $\Delta\varepsilon_G$ decreases from 110 at pure FLC to 30 at sample polymerized without electric field. One can see that at room temperature, the value

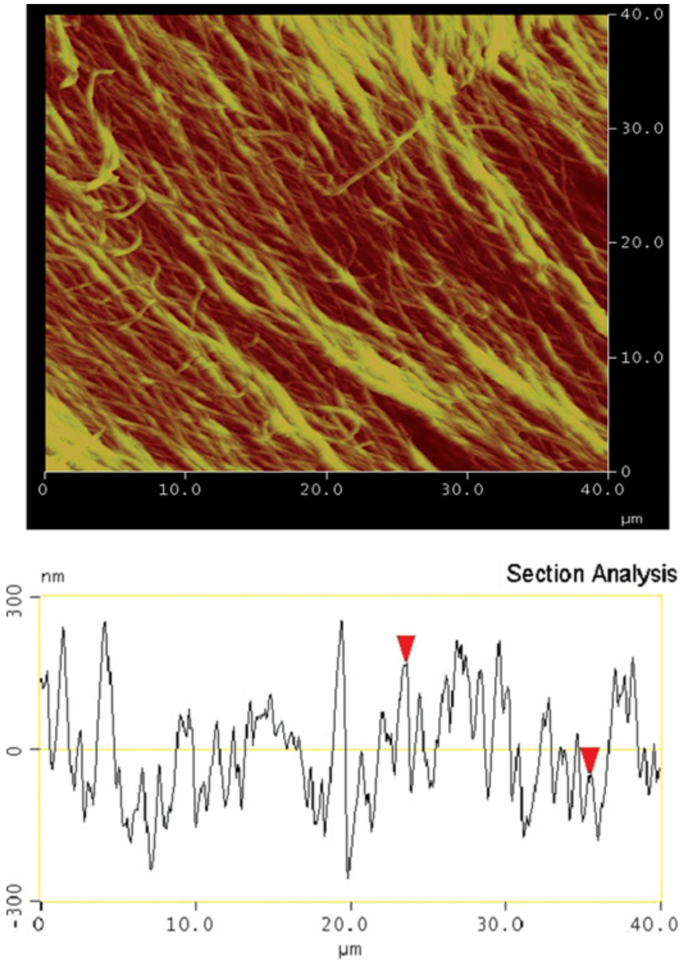

Figure 3. Tapping mode AFM images of polymer network structure of $40 \times 40\,\mu m^2$ (upper) and the height profile of the network structure (lower) of the 7% polymer concentration (polymerization under AC electric field). (Figure appears in color online.)

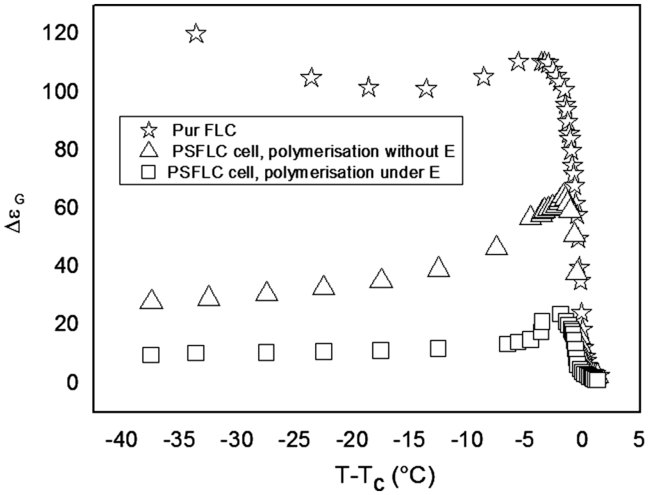

Figure 4. Temperature dependence of the Goldstone mode dielectric intensity.

of the $\Delta\varepsilon_G$ for the sample polymerized with electric field is 3 times lower compared to the sample when no field was applied during the polymerization (Fig. 4).

The temperature dependence of the Goldstone mode relaxation frequency (f_G) is displayed in Figure 5. This Figure shows that f_G slightly increases with temperature, reaches a maximum, then rapidly decreases to a minimum value at a temperature corresponding to T_{max}. It can be seen from the Figure 5 that at room temperature, the f_G values are about 1.5 kHz, 4 kHz and 7 kHz for pure FLC, cell polymerized without and that polymerized with electric field, respectively. Significant differences were reported by Kaur *et al.* [9] in another PSFLC systems. These authors were reported that the relaxation frequency f_G for the case when an bias field is applied

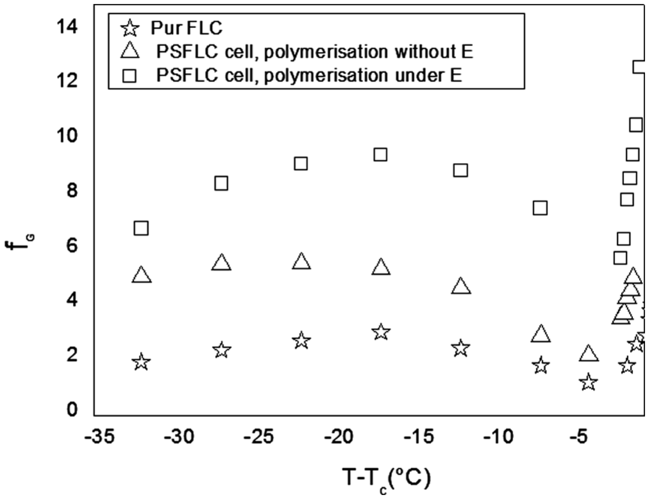

Figure 5. Temperature dependence of the Goldstone mode relaxation frequency.

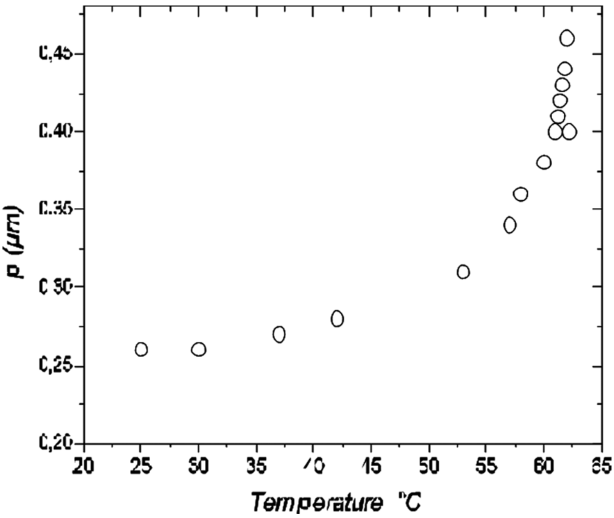

Figure 6. Temperature dependence of the helical pitch of the pure FLC measured by mean of Grandjean-Cano method [23].

during the polymerization is very lower than in the case for sample when no bias was applied during the polymerization.

For the dielectric strength and the relaxation frequency of the Goldstone mode one obtains [24]:

$$\Delta\varepsilon_G = (\mathrm{P_s}/\theta)^2/(2\varepsilon_0 \mathrm{K}_\varphi \mathrm{q}_0^2) \tag{2}$$

$$f_G = (\mathrm{K}_\varphi \mathrm{q}_0^2)/(2\pi\gamma_\varphi), \tag{3}$$

where γ_φ is the rotational viscosity, K_φ is the effective elastic constant. θ and $\mathrm{P_s}$ are the tilt angle and spontaneous polarization, respectively. $\mathrm{q}_0 = 2\pi/\mathrm{p}_0$ with p_0 is the helical pitch of the FLC. If we think that the Eqs. (2) and (3) are applicable for the PSFLC composite, q_0 is considered here constant. For all samples, and at low temperature the $(\mathrm{P_s}/\theta)$ was found about $210\,\mathrm{nC\,cm^{-2}}$, so a ratio $(\mathrm{P_s}/\theta)$ is not polymer concentrations dependent. The decrease of the dielectric strength cannot be explained by the decrease of the spontaneous polarization to the tilt angle ratio. Then, according to Eq. (2) and Eq. (3) the dielectric strength in the case of pure FLC is about 10 times high compared to sample polymerized under *E* and about 4 times high than the sample polymerized without electric field.

The decrease of the dielectric strength and the increase of the f_G are due to the increase of the effective elastic constant K_φ. From the Eq. (2), the values of K_φ are found about $0.5 \cdot 10^{-11}\,\mathrm{N}$, $2 \cdot 10^{-11}\,\mathrm{N}$ and $5.6 \cdot 10^{-11}\,\mathrm{N}$ for pure FLC, mixtures polymerized without and those polymerized under electric field, respectively. In conclusion, a lower dielectric strength (or larger relaxation frequency) could appear for a result of an increase of the elastic constant.

3.2.B. *Soft Mode of the Sma* Phase.* In Figures 7 and 8 the temperature dependences of the dielectric strength, $\Delta\varepsilon$, and the relaxation frequencies, f_s, are

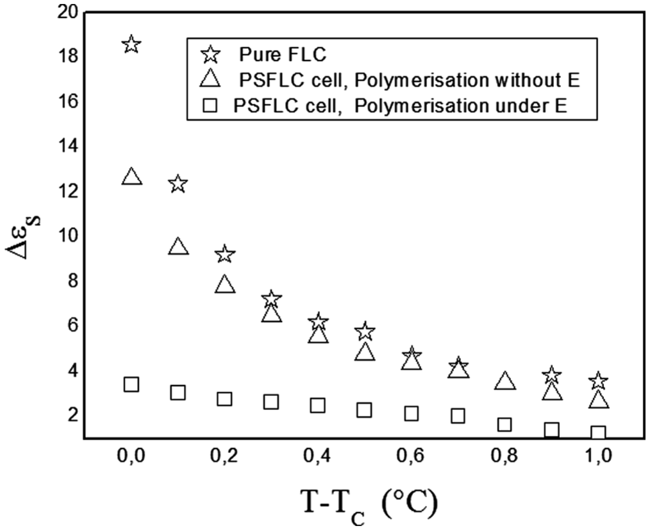

Figure 7. Temperature dependence of the dielectric intensity.

shown for the soft mode detected in the SmA phase, respectively. One can see that for $(T-T_c)=0.1°C$, an increase in the polymer concentration leads to the strong reduction of the soft mode dielectric strength. At the same temperature, $\Delta\varepsilon_s$ for a mixture polymerized without electric field is three times higher than those polymerized under electric field.

The reduction of the $\Delta\varepsilon$ has already observed in another confining systems based in the dispersed silica particles near the SmA*-SmC* phase transition [5,6], FLC confined in aerogel pores [4]. However, Kundu *et al.* [11] show that for other PSFLC

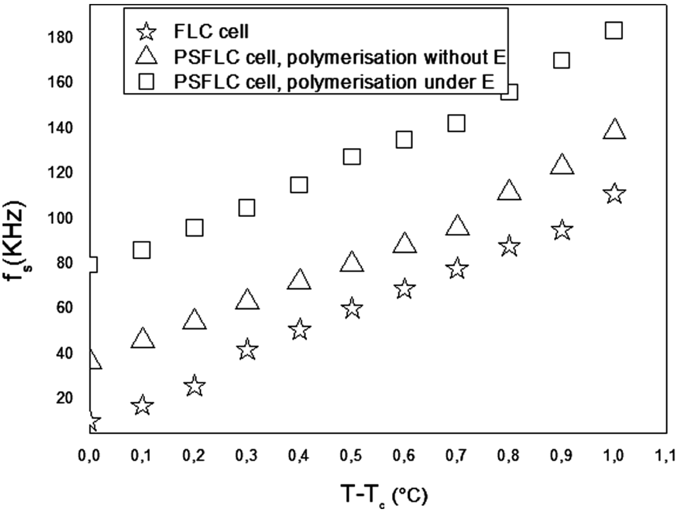

Figure 8. Temperature dependence of the relaxation frequency of the soft mode in the smectic A* phase.

systems the soft mode dielectric strength remains unchanged when the polymer concentration increases. In our case and for all studied samples, the soft mode relaxations frequencies f_s exhibit a linear behavior with temperature and obey to the Curie-Weiss law (Fig. 8). It can be seen that, at $T-T_c=0.1°C$, an increase of the polymer concentration from 0 to 7% leads to an increase of f_s from 10 KHz to 40 KHz, respectively. It can be seen from this figure that, at $T-T_c=0.1°C$ the cell polymerized under electric field presents a high f_s value about 80 KHz. In order to examine how the polymer network structure influences the soft-mode dielectric strength of the PSFLC, we used the model previously developed [8] to explain the effect of the polymer network density on the soft mode intensity. We point out hereafter only on the principal results of this model. The total free-energy density was expressed as

$$f_t = f_0 + (1/2)\,\alpha(T-T_c)\theta^2 - CP\theta + (P^2/\varepsilon_0\chi C) - PE + (1/2)\,K_2(\partial\theta/\partial z)^2 + (1/2)\,W_p\theta^2, \tag{4}$$

where the f_0 term represents contribution of the undistorted SmA phase to the total free-energy density, α is the mean field coefficient, C is related to the piezoelectric couplingbetween the field-induced polarization P_{ind} and the induce electroclinic tilt θ_{ind}, ε_0 is the vacuum permittivity, and χ is the dielectric susceptibility. K_2 is the twist elastic constantand W_p is the coupling coefficient describing the interaction between the polymer network and the liquid crystal molecular director. By minimizing f_t, the equilibrium of the system is obtained [8] for the average values.

The equilibrium values of P and θ are found by minimizing the free energy f_t with respect to P and θ respectively [15]. Averaging the $\theta(z)$ [15] and $P(z)$ values over the $0 \le z \le L_c$ domain (Fig. 9) gives the expression of the mean induced tilt and polarization

$$<\theta^{PSFLC}> = (\varepsilon_0\chi CE)/\alpha(T-T_c')[1 - tanh(L_c/2a)/(L_c/2a)] \tag{5}$$

$$<P^{PSFLC}> = (\varepsilon_0\chi E) + (\varepsilon_0\chi^2C^2E)/\alpha(T-T_c')\;[1 - tanh(L_c/2a)/(L_c/2a)], \tag{6}$$

where

$$a = K_2(\alpha(T-T_c'))^{-1}. \tag{7}$$

$T'_c = T_c - W_p/\alpha$ is the SmC*-SmA* transition temperature of the PSFLC system; L_c is the mean distance between two successive polymer fibers in the z direction (Figure 9)

The average induced polarization can also be written as

$$<P^{PSFLC}> = (\varepsilon_0\chi E) + (\varepsilon_0 E\Delta\varepsilon^{PSFLC}) \tag{8}$$

The identification between Eqs. (6) and (8) gives the expression of the dielectric strength of the soft mode, $\Delta\varepsilon^{PSFLC}$, as a function of L_c

$$\Delta\varepsilon^{PSFLC} \approx (\varepsilon_0\chi^2C^2E)/\alpha(T-T_c')\;[1-H], \tag{9}$$

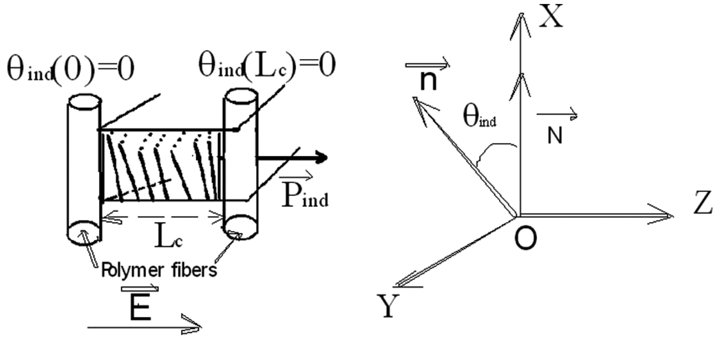

Figure 9. Tilt angle induced by electric field in the SmA* phase; distortion due to the anchorage at the polymer boundaries (on the left). L_c is the average distance between two successive polymer fibers parallel to the direction of the electric field. Cell normal and layer normal are parallel to the Z and X axis, respectively.

where $H = tanh\ (L_c/2a)/(L_c/2a)$, which we called the elastic parameter, depends on the network density via L_c. For a given reduced temperature, $(T-T'_c)$, the Eq. (9) can be expressed as:

$$\Delta\varepsilon^{PSFLC} \approx \Delta\varepsilon^{FLC}\ [1 - H]. \tag{10}$$

$\Delta\varepsilon^{FLC}$ denotes the soft mode dielectric strength of the pure FLC. Equation (10) shows that, in the SmA* phase, the main parameter that governs the soft mode dielectric strength in the PSFLC films is L_c. This means that the stored elastic energy arising from the distortion of the director upon application of electric field is as much larger than the L_c becomes smaller, which causes a decreases of the soft mode dielectric strength (Eq. (10)).

According to this equation, the $\Delta\varepsilon$ is reduced by the increase of the polymer network density, or by decreasing the distance L_c. To explain quantitatively the behavior of the reduction of the soft mode dielectric strength we can use the expression given by Eq. (10). Using the values of $\alpha \approx 8.8 \cdot 10^{+3}\,\mathrm{N\,m^{-2}\,K^{-1}}$, $a = 0.12\,\mu\mathrm{m}$ [15], and the values of $\Delta\varepsilon_s$ presented in Figure 8 at $T - T_c = 0.1°C$, with a reasonable value of the twist elastic constant, typically, $K_2 \approx 10^{-11}\,\mathrm{N}$, the Eq. (10) was graphically resolved to evaluate L_c. We obtain a mean inter-fiber distance $L_c \approx 500\,\mathrm{nm}$ and 200 nm, for samples polymerized without and those polymerized with electric field, respectively. These calculated values are in accordance with those measured by AFM experiments (section 3.1).

In conclusion, the main parameter which governs the dielectric strength and the relaxation frequency in our PSFLC systems is the distance L_c which separates between two layers of the polymer network in the Z direction, parallel to the direction of the electric field. The changes observed on the dielectric response are confirmed by AFM pictures. The polymerization under electric field is another factor affecting the structure of the polymer network formed in liquid crystals. It can be seen that, the polymer fibrils, which are formed without electric field, differs than those formed with electric field (Figs. 2 and 3). The decreases of the average distance leads to a reduction of the soft mode dielectric strength (Eq. (10)). We can remember that although the cells were polymerized under electric field, our proposed model stayed valid and explains well the modifications presented by the polymer network on the dielectric properties.

4. Conclusion

It has been demonstrated that the collective relaxation mechanisms, namely the soft and Goldstone modes, of the polymer stabilized ferroelectric liquid crystal cells can be controlled by the morphology of the polymer network formed in a liquid crystal environment. The application of the electric field during the photopolymerization has a profound effect on the structure of the polymer network. The most important results of this paper is that the morphology of the polymer network which is created under electric field confirms the presence of the two relaxations modes.

The AFM images reveal that the polymer network structure formed with AC electric field differs from those formed without AC field. The size of fibrils and the distance between two fibers were found to be the main parameters which govern the dielectric response. The experimental results are discussed and applied to a simple phenomenological model, extended from the Landau model, which includes the bulk free energy arising from the anisotropic interaction between the polymer network and the liquid crystal director, and the elastic free energy resulting from the anchoring (supposed rigid) of the liquid crystal molecules at the polymer boundaries. The characteristic length scale of the polymer network, which defines the average distance between two successive layers of the polymer fibers in the direction of the electric field, was also calculated and found to be in full agreement with that measured by means of AFM experiments.

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