Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Comparative analysis of basic physical properties of a ferroelectric liquid crystal and a polymer dispersed ferroelectric liquid crystal

E. P. Pozhidaev; D. Ganzke; V. Ya. Zyryanov; S. L. Smorgon; W. Haase

To cite this Article Pozhidaev, E. P. , Ganzke, D. , Zyryanov, V. Ya. , Smorgon, S. L. and Haase, W.(2002) 'Comparative analysis of basic physical properties of a ferroelectric liquid crystal and a polymer dispersed ferroelectric liquid crystal', Liquid Crystals, 29: 10, 1305 — 1310

To link to this Article: DOI: 10.1080/713935618

URL: http://dx.doi.org/10.1080/713935618

LIQUID CRYSTALS, 2002, VOL. 29, NO. 10, 1305–1310

Taylor & Francis
Taylor & Francis Group

Comparative analysis of basic physical properties of a ferroelectric liquid crystal and a polymer dispersed ferroelectric liquid crystal

E. P. POZHIDAEV†‡, D. GANZKE†, V. YA. ZYRYANOV§, S. L. SMORGON§
and W. HAASE†*

†Institute of Physical Chemistry, Darmstadt University of Technology,
D-64287 Darmstadt, Germany
‡P. N. Lebedev Physical Institute, Leninsky pr. 53, Moscow 117924, Russia
§L. V. Kirensky Institute of Physics, Krasnoyarsk 660036, Russia

(*Received 8 February 2002; accepted 26 May 2002*)

A polymer film of polyvinylbutyral with dispersed droplets of a ferroelectric liquid crystalline mixture (FLC309c) has been prepared and characterized. The collective processes have been studied by dielectric relaxation spectroscopy in the frequency range 10 Hz to 13 MHz. In comparison with the FLC309c mixture, the polymer dispersed ferroelectric liquid crystal (PDFLC309c) based on FLC309c exhibits a Goldstone-like mode relaxation with a much higher relaxation frequency, but a smaller dielectric strength than the Goldstone mode observed for the FLC309c mixture. The spontaneous polarization of PDFLC309c decreases by nearly one order of magnitude in comparison with FLC309c, while the tilt angle decreases by 20%. Considering these results, we believe that a non-switching region exists near the polymer boundaries and that significant deformations of the helical structure occur due to stronger anchoring.

1. Introduction

Polymer dispersed ferroelectric liquid crystals (PDFLCs) combine the advantages of polymer dispersed liquid crystals (mechanical flexibility, thermal and time stability etc.) [1, 2] with the fast electro-optic response of ferroelectric liquid crystals (FLCs). The samples present planar-aligned polymer films with FLC droplets dispersed therein. The FLC director in all droplets is aligned in the same direction and parallel to the surface of the polymer web. Under an applied bipolar electric field, the director turns by an angle of 2θ (θ is the molecular tilt angle) within the film web.

When placed between crossed polarizers, the PDFLC film can act as a phase plate [3], similar to the planar-aligned FLC layer in a surface stabilised FLC cell [4]. A maximal contrast can be reached for a switching angle of 45° and a phase shift of $\pi/2$. Due to a matching and dismatching of the refractive index, the light scattering effect can be utilized [1, 2, 5] as a light modulator. The FLC309c mixture used is optimized to exhibit a matching of the ordinary refractive index with that of the surrounding polymer ($n_D = 1.485$). Light scattering PDFLC modulators can be designed both with a polarizer [1, 2, 5, 6] and polarizer-free [7]. The different textures of the droplets and the importance of a uniform alignment for the light transmission characteristics have been demonstrated in [8]. A PDFLC is also a model system for FLCs in confined geometries [9].

The aim of this paper is to study the influence of the encapsulation of FLC droplets on the liquid crystalline parameters.

2. Preparation of PDLFC films

The PDFLC films under investigation have been produced by the 'temperature induced phase separation' (TIPS) [10] method from a mixture of 40 wt % of ferroelectric liquid crystal mixture FLC309c (with a tilt angle $\theta = 19.2^\circ$ and a helical pitch $p_0 = 0.4\,\mu m$ at 25°C) and 60 wt % of polyvinylbutyral. The uniaxial alignment of the samples was achieved by shear deformation during the cooling process. The average droplet size in the film web was $6 \times 10\,\mu m^2$; the average film thickness was about 10 μm. Figure 1 shows two typical textures of the droplets [8]. The focal-conic domains, figures 1 (*a*) and 1 (*c*), are a typical type of defect which diminishes strongly the possible contrast ratio. A wave-like structure, figures 1 (*b*) and 1 (*d*), however allows a good dark state. It is clearly seen that several deformations of the liquid

---

*Author for correspondence;
e-mail: haase@chemie.tu-darmstadt.de

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290210000017960

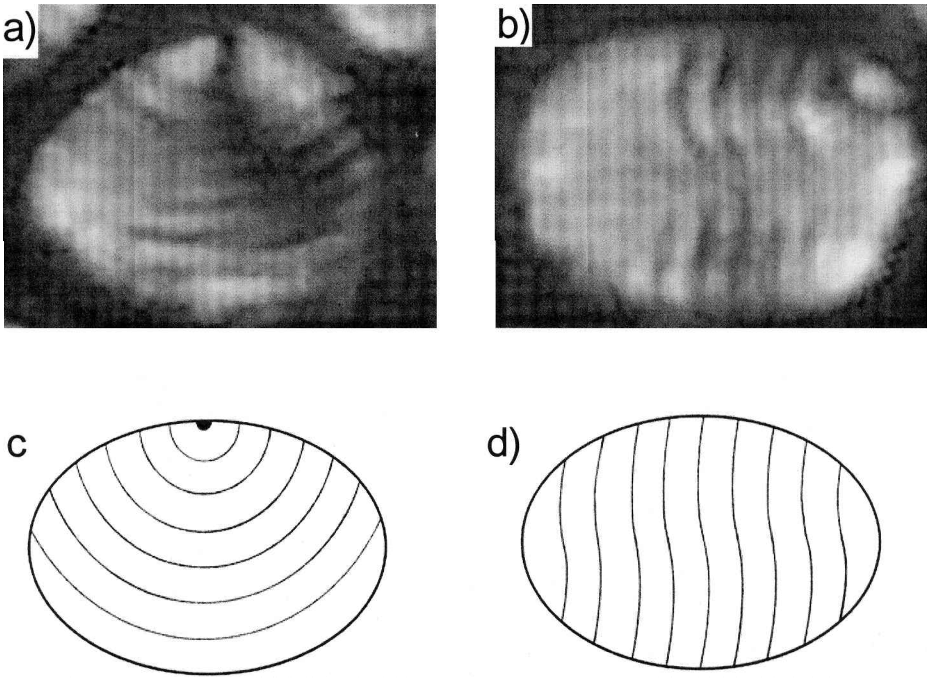

Figure 1. Micrographs of FLC droplets with disclinations of (*a*) the concentric type (single focal-conic domain) and (*b*) the wave-like type, (*c*) and (*d*) are the corresponding configurations of the smectic layers inside the droplets.

crystalline orientation take place. This makes it almost impossible to calculate the wave vector. The resolution of the image is close to the maximal resolution of the optical microscope ($d_{\min} \approx \lambda/2$).

3. Experimental

The dielectric studies have been performed using ITO coated cells (FLC309c and PDFLC309c). To be sure that relaxation processes from the polymer did not influence the dielectric spectra of PDFLC309c, a Gold-cell filled with polyvinylbutyral was used for the dielectric measurements in a parallel experiment. The α-relaxation of the polymer lies at lower frequencies or higher temperatures and appears only above 60°C in our spectral range. This is in full agreement with the results obtained by other groups [10]. The dielectric measurements were made using an impedance analyser (HP4192A) in the frequency range 10 Hz to 13 MHz. The temperature was stabilized with a temperature controller (Eurotherm 818) with an accuracy better than 0.05 K. The temperature was measured directly on the sample using a Ni-Cr-Ni thermoelement and a HP34401A multimeter. The dielectric strength $\Delta\varepsilon$, the relaxation frequency $f_r = (2\pi\tau)^{-1}$ and the distribution parameter α were determined by fitting the semi-empirical Cole–Cole function (1).

$$\varepsilon^* = \frac{\Delta\varepsilon}{1 + (i\omega\tau)^{1-\alpha}} + \varepsilon_\infty \qquad (1)$$

There was no need to subtract a conductivity part due to the high relaxation frequencies and low conductivity. The oscillation voltage was specially chosen in order to receive an optimal signal to noise ratio without greatly disturbing the probe. The electric and electro-optical investigations were made using a HP33120A function generator combined with an amplifier F20A from FLC Electronics and a HP54815R oscilloscope. The spontaneous polarization was measured through the reversal current at 500 Hz. Tilt angle and switching time were measured with a HeNe-laser, a photomultiplier and a Newport M-495 rotational stage at 500 Hz.

4. Results

Dielectric and electro-optic measurements were made on the neat FLC309c mixture and the PDFLC309c film. This enabled us to compare the FLC with the PDFLC and to study the effects of the confinement.

4.1. *FLC309c*

The mixture FLC309c consists of the compounds shown in figure 2 and exhibits the following phase sequence: Cr −3°C SmC* 39.5°C SmA* 70°C I.

In the SmC* phase, the neat FLC309c mixture shows a pronounced Goldstone mode with a dielectric strength $\Delta\varepsilon = 60.0$ and a relaxation frequency $f_r = 1.5$ kHz at 30°C, figure 3. The relaxation frequency f_r is nearly constant in the SmC* temperature range and increases sharply at the transition to the SmA* phase, due to appearance of the soft mode. For temperatures above 43°C in the SmA* phase an Arrhenius type relaxation process is observed. This can indicate a molecular process related to rotation around the molecular short axes. Deep in the SmC* phase the dielectric strength $\Delta\varepsilon$ is

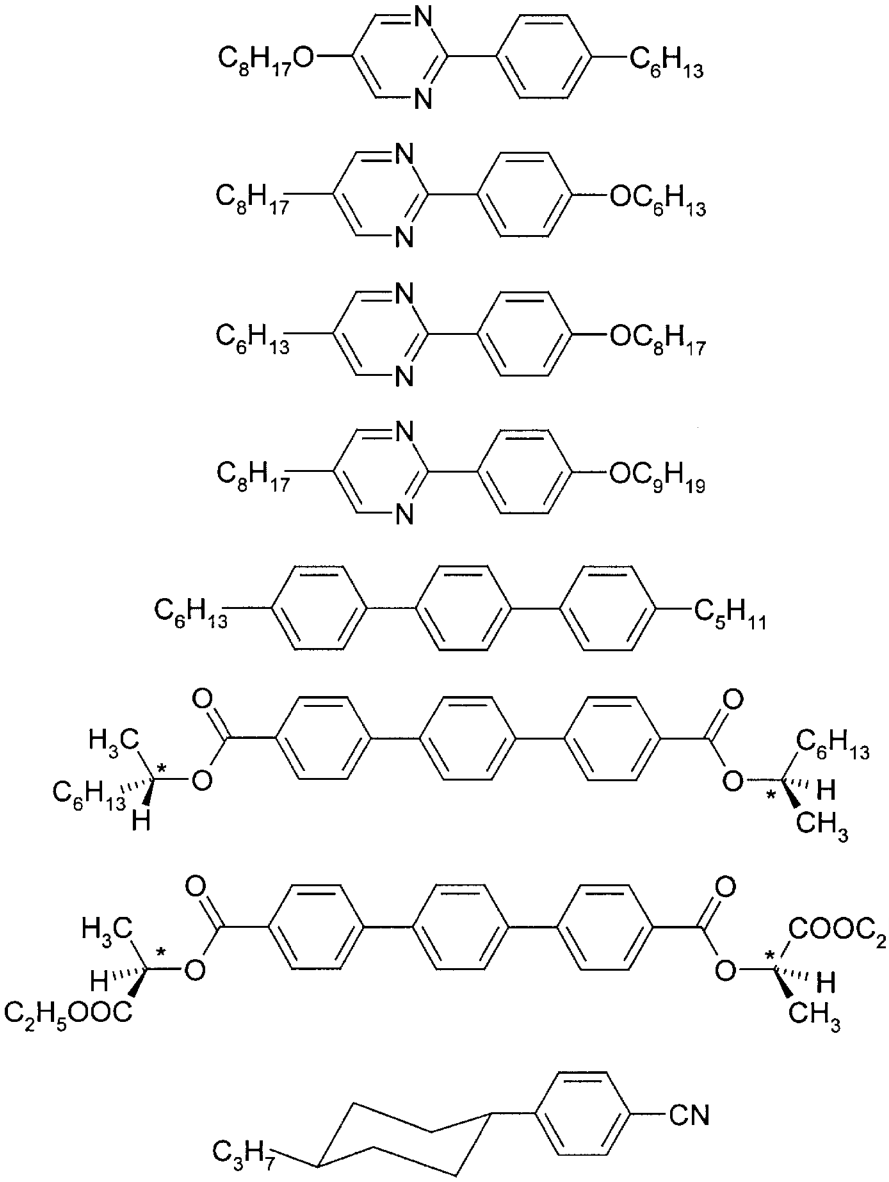

Figure 2. The compounds used for making FLC 309c.

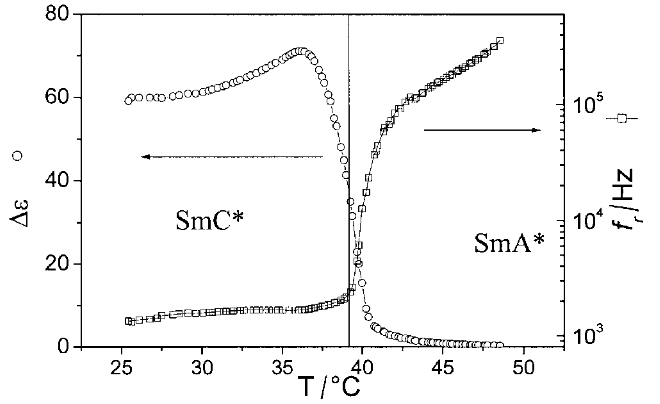

Figure 3. Dielectric strength $\Delta\varepsilon$ and relaxation frequency f_r versus temperature for FLC309c, oscillation voltage 0.1 V, bias 0, layer thickness 1.8 μm.

only weakly temperature dependent. Close to T_c a maximum in $\Delta\varepsilon$ is observed followed by a strong decrease. The soft mode has its maximal value at T_c and decreases hyperbolically with $(T - T_c)$.

The temperature dependences of the spontaneous polarization $\mathbf{P}_s$ and the electro-optic response time τ are shown in figure 4. The line represents a square root fit of $\mathbf{P}_s$ on $(T_c - T)$. The switching times are quite fast (20 μs at 25°C and 12 MV m^{-1}) and decrease with increasing temperature.

The dependence of the tilt angle on the temperature is illustrated in figure 5. As seen, a strong influence of the applied voltage is found especially near the phase transition. The apparent calculated Landau-parameters [11, 12] $\alpha = 31.5\,\mathrm{kJ\,m^{-3}\,K^{-1}}$, $b = 778\,\mathrm{kJ\,m^{-3}}$ indicate a second order phase transition. The piezoelectric constant

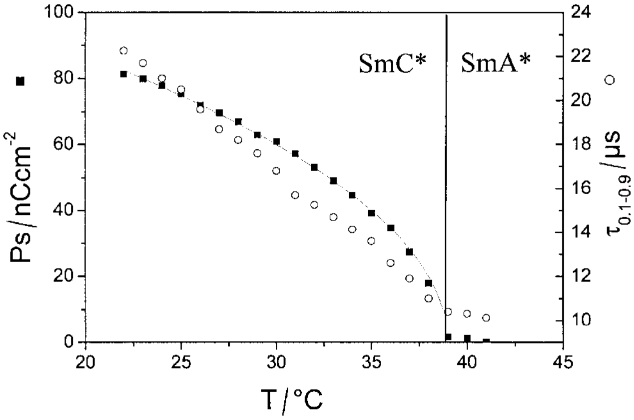

Figure 4. Spontaneous polarization (■) $\mathbf{P}_s$ and electro-optic response time (○) $\tau_{0.1-0.9}$ as a function of temperature for FLC 309c, layer thickness 1.8 μm, voltage ± 21 V, f = 500 Hz.

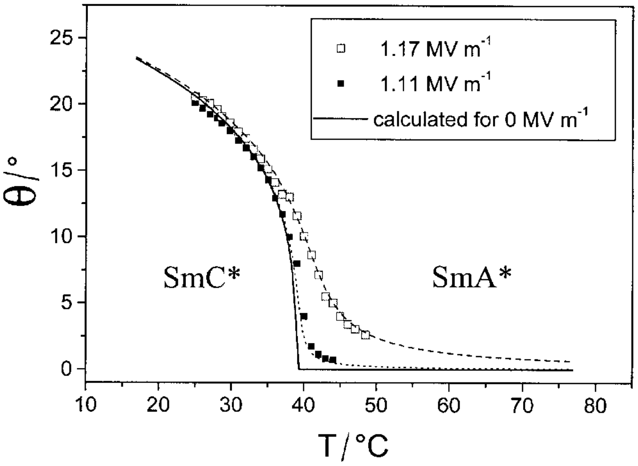

Figure 5. Tilt angle θ versus temperature for FLC 309c, layer thickness 1.8 μm applied voltage ± 2 V (■), ± 21 V (□) and calculated for 0 V (—), f = 500 Hz.

$C = 1.85$ mC m^{-3} explains the voltage dependence of the tilt angle even deep in the SmC* or SmA* phase. The third Landau coefficient $c = 204$ MJ m^{-3} is determined through minimizing the free energy F, equation (2) [13].

$$F = F_0 + \frac{1}{2}\alpha(T - T_c)\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 + \frac{1}{2\varepsilon_0\chi}\mathbf{P}^2 - \frac{C\mathbf{P}\theta}{\varepsilon_0\chi} - \mathbf{PE}\cdot \qquad (2)$$

The saturation voltage is 2 V (1.11 MV m^{-1}), which is confirmed by electro-optic and dielectric measurements. When a 5.0 V bias field suppresses the Goldstone mode, the maximum of the soft mode occurs at 41.6°C. This represents an electrically induced shift of T_c by 2.1 K to higher temperatures. Several groups [14–16] have calculated the expected shift of the soft mode maximum with electric field using a Landau approach with only the first two coefficients:

$$\Delta T = 3\left(\frac{bC^2}{16\alpha^3}\right)^{1/3}\mathbf{E}^{2/3} \qquad (3)$$

According to this formula, we should observe $\Delta T = 1.035$ K instead of 2.1 K. This disagreement can be understood in terms of the large Landau coefficient c of this material, see equation (2).

4.2. *PDFLC309c*

The Goldstone mode of the PDFLC309c film has a relaxation frequency f_r of 15 kHz, which is one order of magnitude larger than that of the neat FLC309c mixture. At the same time, the dielectric strength $\Delta\varepsilon$ decreases by a factor of ten, see figure 6. The relaxation is also broader in comparison with that for pure FLC309c—distribution parameters: $\alpha = 0.24$ (PDFLC), $\alpha = 0.11$ (FLC309c). This broadening is a result of the different relaxation time of the droplets. Both f_r and $\Delta\varepsilon$ show a similar, but more pronounced, temperature dependence. Similar dielectric results were presented for examples of DOBAMBC confined in a porous material [17]. Also in the PDFLC film, an Arrhenius type relaxation process is observed for temperatures above 46°C. The phase transition temperature SmC*/SmA* of the PDFLC is 4.1 K higher than that for the FLC309c mixture. Normally a decrease in the phase transition temperature is observed when incorporating a FLC into a polymer [18]. This unexpected shift may be due to strong interaction with the surrounding polymer.

Electro-optic and electrical measurements also show a decrease in both the spontaneous polarization $\mathbf{P}_s$ (14 nC cm^{-2} at 25°C, which cannot be explained alone by a volume effect—74 × 0.4 nC cm^{-2} = 29.6 nC cm^{-2}) and the tilt angle (15.4° in comparison with 19.2° at 25°C),

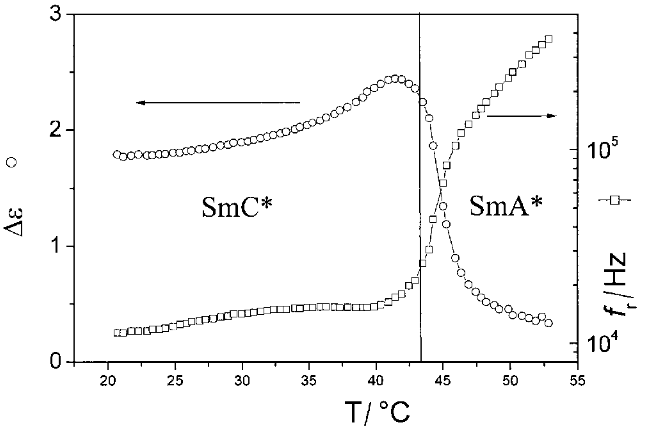

Figure 6. Dielectric strength $\Delta\varepsilon$ and relaxation frequency f_r as a function of temperature for PDFLC309c, oscillation voltage 1.0 V, bias 0, layer thickness 10 μm.

see figure 7. This effect can be explained by a non-switching of the regions near the polymer boundaries due to strong anchoring. The saturation field increases significantly from 1.11 to 6.0 MV m^{-1}. A strong decrease of $\mathbf{P}_s$, the pyroelectric coefficient or the piezoelectric coefficient has also been found elsewhere [1, 19].

5. Discussion

For an undistorted helix two terms must be added to the free energy, a Lifshitz term for a helical distortion $-\Lambda q\theta^2$ and an effective energy $0.5K_\varphi q^2\theta$ with an effective elastic constant K_φ [20]. With this free energy the temperature dependence of the Goldstone mode and the soft mode relaxation can be calculated. For the dielectric strength and relaxation frequency of the Goldstone mode one obtains [20]:

$$\Delta\varepsilon_G = \frac{1}{2\varepsilon_0 K_\varphi q^2}\left(\frac{\mathbf{P}_s}{\theta_s}\right)^2 \tag{4}$$

$$\nu_G = \frac{K_\varphi q^2}{2\pi\gamma_\varphi} \tag{5}$$

where γ_φ is the rotational viscosity, q is the wave vector and K_φ is the effective elastic constant. For a bulk sample with an undistorted helix of pitch p we can define an elastic energy:

$$W_{el} = \frac{1}{2}K_\varphi q^2 = \frac{1}{2}K_\varphi\left(\frac{2\pi}{p}\right)^2. \tag{6}$$

With $\mathbf{P}_s = 76$ nC cm^{-2}, $\theta_s = 19.2°$ and $\Delta\varepsilon_G = 60$ at 25°, the elastic energy W_{el} of FLC309c in the SmC* phase is 1.61 kJ m^{-3}. This is larger in comparison with the results reported in [21] as determined by current reversal measurements on the same substance, but using a 20 μm cell instead of a 1.8 μm cell. It is well known [14–16] that the dielectric strength of the Goldstone mode decreases (the relaxation frequency increases) with decreasing cell thickness. This is explained by a surface-induced deformation of the helical structure (equation (4) is not valid for this case). A lower dielectric strength (or larger relaxation frequency) leads to an increase in the elastic energy according to equation (3) and [20]. However, even in a completely unwound state of the sample, a Goldstone-like mode can be present, which is related to a polarization profile in the smectic layers due to surface anchoring [14, 16]. These contributions to the dielectric susceptibility are detectable in this cell where the much stronger Goldstone mode is basically suppressed. In thick cells ($d \gg$ helix pitch) they are oversimplified due to a strong non-linearity with the electric field. Thus, in thick cells the bulk properties dominate those of the boundary.

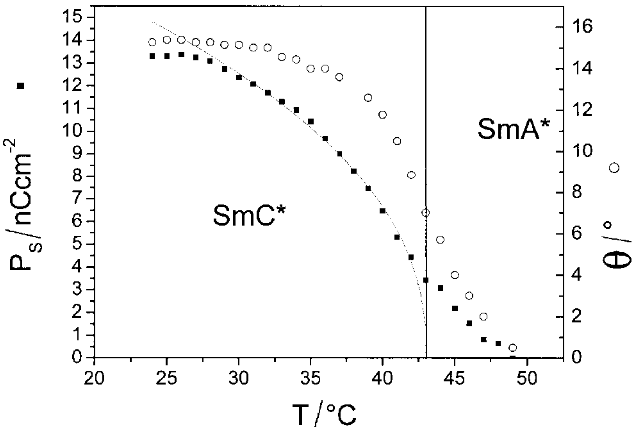

Figure 7. Spontaneous polarization $\mathbf{P}_s$ and tilt angle θ as a function of temperature for PDFLC 309c, layer thickness 10 μm, voltage ± 120 V, $f = 500$ Hz.

The increase in the relaxation frequency and the decrease in the dielectric strength cannot be explained by the decrease in the spontaneous polarization only. It is also not clear, whether the elastic energy of PDFLC309c increases due to additional defects or if a stronger anchoring causes stronger helix deformations.

The response time of PDFLC309c is nearly half that of FLC309c at the same electric field. A reason for this could be a systematic effect due to stronger anchoring. The frequency dependence of the response time is quite pronounced. A similar behaviour is also found in deformed helix FLCs and can be explained by an orientation diffusion model [22].

6. Conclusion

The encapsulation of a ferroelectric liquid crystal in a polymer matrix decreases the spontaneous polarization $\mathbf{P}_s$ by more than the expected effect from the decreased volume (only 40% of the PDFLC consists of the ferroelectric liquid crystal which contributes to the spontaneous polarization), while the apparent tilt angle decreases by 20%. This effect is explained in terms of a non-switching of the region near the polymer boundaries due to strong anchoring. The saturation field increases significantly. The dielectric strength decreases by more than one order of magnitude, while a ten-fold increase in the relaxation frequency is observed.

The dielectric results can be understood in terms of the decrease in the spontaneous polarization and a stronger influence of the polymer boundaries. Thus, the encapsulation of the FLC causes significant additional deformations of the helical structure.

The phase transition temperature SmC*/SmA* for the PDFLC309c film is 4 K higher than that of the FLC309c mixture. This unexpected shift may be due to a larger elastic energy of PDFLC309c and the piezoelectric and/or flexoelectric contribution to the free energy.

References

[1] Kitzerow, H. S., 1994, *Liq. Cryst.*, **16,** 1.

[2] Kitzerow, H. S., Molsen, H., and Heppke, G., 1992, *Appl. Phys. Lett.*, **60,** 3093.

[3] Born, M., and Wolf, E., 1980, *Principles of Optics*, 2nd Edn (Frankfurt: Pergamon Press).

[4] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36,** 899.

[5] Zyryanov, V. Ya., Smorgon, S. L., and Shabanov, V. F., 1993, *JETP Lett.*, **57,** 15.

[6] Zyryanov, V. Ya., Smorgon, S. L., and Shabanov, V. F., 1993, *Ferroelectrics*, **143,** 271.

[7] Zyryanov, V. Ya., Smorgon, S. L., Shabanov, V. F., and Pozhidaev, E. P., 1996, *Proc. SPIE*, **2731,** 188.

[8] Zyryanov, V. Ya., Pozhidaev, E. P., Smorgon, S. L., Barannik, V. A., Presnjakov, V. V., Andreev, A. L., Kompanets, I. N., Shevtchenko, S. A., Ganzke, D., and Haase, W., 2000, *Ferroelectrics*, **243,** 179.

[9] Crawford, G. P., and Zumer, S., 1992, *Liquid Crystals in Complex Geometries* (London: Taylor & Francis).

[10] Mikhailov, G. P., 1955, *Usp. Khim.*, **24,** 875.

[11] Saxena, K., Blinov, L. M., Beresnev, L. A., and Haase, W., 1997, *Ferroelectrics*, **200,** 21.

[12] Blinov, L. M., Ganzke, D., Palto, S., Pozhidaev, E. P., Weyrauch, T., and Haase, W., 1999, *Mol. Mater.*, **11,** 241.

[13] Gießelmann, F., and Zugenmaier, P., 1995, *Phys. Rev. E.*, **52,** 1762.

[14] Glogarova, M., and Paval, J., 1989, *Liq. Cryst.*, **6,** 3, 325.

[15] Blinov, L. M., Beresnev, L. A., and Haase, W., 1996, *Ferroelectrics*, **181,** 187.

[16] Schacht, J., Gießelmann, F., Zugenmaier, P., and Kuczynski, W., 1998, *Ferroelectrics*, **209,** 483.

[17] Rozanski, S., Stannarius, R., Kremer, F., and Diehl, S., 2001, *Liq. Cryst.*, **28,** 1071.

[18] Gasser, M., Gembus, A., Ganzke, D., and Dierking, I., 2000, *Mol. Mater.*, **12,** 347.

[19] Bartolino, R., Scaramuzza, N., Barna, E. S., Ionescu, A. Th., Beresnev, L. A., and Blinov, L., 1998, *J. appl. Phys.*, **84,** 2835.

[20] Carlsson, T., Zeks, B., Filipic, C., and Levstik, A., 1990, *Phys. Rev. A*, **42,** 877.

[21] Andreev, A. L., Pozhidaev, E. P., Kompanets, I. N., Fedosenkova, T. B., Zyryanov, V. Ya., Smorgon, S. L., Weyrauch, T., and Haase, W., 2000, *Ferroelectrics*, **243,** 189.

[22] Pozhidaev, E. P., Pikin, S. A., Ganzke, D., Shevtchenko, S., and Haase, W., 2000, *Ferroelectrics*, **246,** 235.