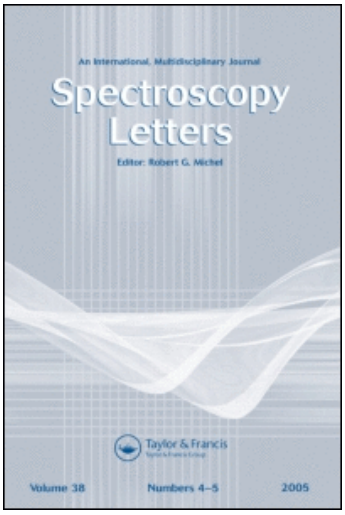


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Dynamical Properties of Ferroelectric Chiral Liquid Crystals by Electro-Optical and Dielectric Spectroscopy

J. Hemine[a]; A. Daoudi[b]; M. Zazoui[a]; C. Legrand[c]; N. Isaert[d]; A. El kaaouachi[e]; H. T. Nguyen[f]
[a] Laboratoire de Physique de la Matière Condensée, Université Hassan II, FST Mohammedia, Mohammedia, Morocco [b] Laboratoire de Thermophysique de la Matière, Université du Littoral-Côte d'Opale, Dunkerque, France [c] Laboratoire d'Etude des Matériaux et des Composants pour l'Electronique, Université du Littoral-Côte d'Opale, Calais, France [d] Laboratoire de Dynamique et Structures des Matériaux Moléculaires, URA no. 801, Université de Lille 1, Villeneuve d'Ascq, France [e] Laboratoire de Physique de la Matière Condensée, Faculté des Sciences Ibnou Zohr, Agadir, Morocco [f] Centre de Recherche Paul Pascal, Université de Bordeaux 1, Pessac, France

Online publication date: 22 June 2010

To cite this Article Hemine, J. , Daoudi, A. , Zazoui, M. , Legrand, C. , Isaert, N. , kaaouachi, A. El and Nguyen, H. T.(2008) 'Dynamical Properties of Ferroelectric Chiral Liquid Crystals by Electro-Optical and Dielectric Spectroscopy', Spectroscopy Letters, 41: 6, 285 — 291
To link to this Article: DOI: 10.1080/00387010802286684
URL: http://dx.doi.org/10.1080/00387010802286684

Spectroscopy Letters, 41:285–291, 2008

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010802286684

Taylor & Francis
Taylor & Francis Group

Dynamical Properties of Ferroelectric Chiral Liquid Crystals by Electro-Optical and Dielectric Spectroscopy

J. Hemine[1], A. Daoudi[2], M. Zazoui[1], C. Legrand[3], N. Isaert[4], A. El kaaouachi[5], and H. T. Nguyen[6]

[1]Laboratoire de Physique de la Matière Condensée, Université Hassan II, FST Mohammedia, Mohammedia, Morocco
[2]Laboratoire de Thermophysique de la Matière, Université du Littoral-Côte d'Opale, Dunkerque, France
[3]Laboratoire d'Etude des Matériaux et des Composants pour l'Electronique, Université du Littoral-Côte d'Opale, Calais, France
[4]Laboratoire de Dynamique et Structures des Matériaux Moléculaires, URA no. 801, Université de Lille 1, Villeneuve d'Ascq, France
[5]Laboratoire de Physique de la Matière Condensée, Faculté des Sciences Ibnou Zohr, Agadir, Morocco
[6]Centre de Recherche Paul Pascal, Université de Bordeaux 1, Pessac, France

Received 2 July 2007;
accepted 12 November 2007.

Address correspondence to J. Hemine, Laboratoire de Physique de la Matière Condensée, Université Hassan II, FST Mohammedia, BP 146, Mohammedia, Morocco. E-mail: hemine1@yahoo.fr

ABSTRACT Structural, electro-optical, and dielectric investigations of a ferroelectric liquid crystal (FLC) exhibiting the chiral smectic C phase (SmC*) are reported. This study has been performed on the pure FLC showing the SmC*–SmA–N* phase sequence and having high spontaneous polarization and a large relaxation frequency. We have determined the Goldstone rotational viscosity and the twist elastic constant in the SmC* phase from the experimental data of helical pitch, tilt angle, polarization, dielectric strength, and relaxation frequency of the Goldstone-mode relaxation. An Arrhenius-type behavior of the Goldstone rotational viscosity was obtained, and the corresponding activation energies were evaluated.

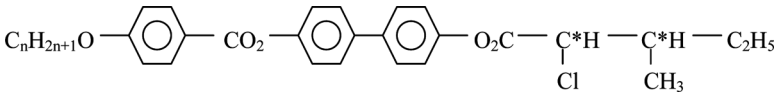
KEYWORDS dielectric relaxation spectroscopy, electro-optical study, ferroelectric liquid crystals, Goldstone mode, rotational viscosity, twist elastic constant

INTRODUCTION

Ferroelectric liquid crystal (FLC) materials exhibiting the chiral smectic C (SmC*) phase have attracted increasing interest in recent years. Taking into account the reduced symmetry in the SmC*, Meyer has shown that the FLC SmC*[1] possesses a ferroelectric polarization. The development of spontaneous helical structure due to the chirality of the molecules causes the director to precess around the tilt cone, and the macroscopic polarization of the sample vanishes to zero. Nevertheless, the helical structure can be unwound by the surface effects if the samples are sufficiently thin. This leads to the surface stabilized ferroelectric liquid crystal (SSFLC) geometry, reported for the first time by Clark and Lagerwall.[2]

The periodic structure can also be deformed by applying an external electric field to the samples parallel to the smectic layers. R. Blinc has shown, in this case, that the dielectric relaxation response is linked to four dielectric relaxations.[3] Two of these modes are connected to fluctuations of the polarization and are called *polarization mode*.[4] The other two modes[3, 5] are connected with the director reorientational motions and have relaxation frequencies lower than those observed for the polarization modes. The first

TABLE 1 Chemical Structure, Phase Sequences, and Transition Temperatures (°C) for the Homologous Biphenyl Benzoate Series



n	Cr		Sm		SmC*		SmA		N*		BP		I
7	•	100	•	(52)	•	134	–		•	166	•	166.1	•
8	•	88	–		•	138	–		•	165.5	•	166.5	•
9	•	89	–		•	142	–		•	162	•	162.1	•
10	•	88	–		•	143	•	144	•	159	•	160	•
11	•	88	–		•	146	•	149	•	157	•	157.1	•
12	•	81	–		•	145.5	•	150	•	154	•	154.5	•

Cr, crystalline phase; Sm, smectic phases A, C*; N*, cholesteric phase; BP, blue phase; I, isotropic phase; ( ), monotropic transition.

of these modes is called the Goldstone mode, which corresponds with the fluctuations in the phase of the tilt angle. This dielectric process appears in the SmC* phase with low relaxation frequency and high amplitude. The second contribution corresponds with the fluctuations in the magnitude of the tilt angle and is called the soft mode.[3, 6] The dielectric strength and relaxation frequency of the Goldstone mode are provided by the Landau model.[7] These dielectric characteristics are related to different parameters, namely helical pitch, tilt angle, and spontaneous polarization.

In previous investigations,[8–10] we have studied C8, C10, and C11 compounds of the homologous biphenyl alkyloxy benzoates series gathered in Table 1. We extend our work here to the pure chiral C12 compound, which displays the SmC*–SmA–N* phase sequence. The dynamic properties of the ferroelectric SmC* phase have been performed by electro-optical and dielectric spectroscopy. We have also measured the helical pitch in the SmC* and N* phases. The electro-optical properties of the SmC* phase have been studied, including measurements of tilt angle and spontaneous polarization. We focused our dielectric investigations on the Goldstone mode contribution. From the dielectric analysis spectra, we report the dielectric response in the SmC* phase via dielectric amplitudes and relaxation frequencies. Using results of the Landau model and experimental data, the Goldstone-mode rotational viscosity and the twist elastic constant were determined. An Arrhenius-type behavior of the rotational viscosity is observed, and the activation energy of the mechanism was evaluated.

MATERIALS AND METHODS

Ferroelectric properties have been studied for C11 (n = 11) and C12 (n = 12) compounds of the homologous biphenyl alkyloxy benzoates series (Table 1). The synthesis procedures for these homologous series (C7 to C12) have been already published.[9] The phase identifications and the transition temperatures have been determined on heating at atmospheric pressure both by thermal microscopy (Mettler FP 5, Greifensee, Switzerland) and differential scanning calorimetry (Perkin-Elmer DSC 7, Waltham, MA, USA).

The helical pitch was measured by the Grandjean–Cano method[11, 12] using the defect lines. In the N* phase, a prismatic planar anchoring of the samples was obtained. In this configuration, the molecules are parallel and the helical axis is perpendicular to the glass surface. To measure the helical pitch in the SmC* phase, *pseudo-homeotropic* samples were prepared, which led to an orientation of both the molecular long axis and the helical axis perpendicular to the glass plates. The orientations of the Grandjean–Cano lines and optical properties of the sample were observed by means of a polarized optical microscope in the transmitted mode. During this optical study, the FLC cells were then placed in a heating stage for temperature control. Using this technique, we obtained an excellent orientation formed with regular Grandjean–Cano steps in the N* and SmC* phases allowing helical pitch measurements.

The tilt angle θ and the spontaneous polarization P_S, were measured as a function of temperature for samples in SSFLC geometry.[2] Sample cells with a thick-

ness of about 3 μm were used. A high-amplitude and low-frequency electric field ($E = 5\,\mathrm{V\,\mu m^{-1}}$; $F = 0.2$ Hz) was applied to the samples. The tilt angle was measured from the value of the microscopic stage rotation between extinction states ($+\theta/-\theta$) obtained by reversing the applied electric field ($+E/-E$). To measure P_S, the well-known reverse current technique with **a** triangular wave electric field was used.[13] The applied voltage to saturate the polarization is around 18 V for a frequency of about 1 kHz.

The dielectric measurements were carried out on a planar orientation of the sample in the frequency range of 5 Hz to 1 MHz using a previously described experimental procedure.[14] The electric field was applied perpendicular to the SmC* helical axis and parallel to the smectic layers. The planar orientation of the sample was achieved by means of polyvinyl alcohol (PVA) coating and rubbing. To obtain a good alignment, the cell was slowly filled by capillary action from the isotropic phase into the SmC* phase, under an applied electric field. The cell thickness of 30 μm was chosen to be much higher than the pitch value to obtain a planar-wound geometry in the SmC* phase. The sample orientation and transition temperatures were checked using a polarizing microscope equipped with a heating stage. These measurements were made without adding a DC bias to the measurement electric field.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the pitch in the N* and SmC* phases for C12. In the N* phase, this pitch is very short ($p \sim 0.25\,\mu$m) near the N*–BP transition. It then regularly increases and diverges at the N*–SmA transition temperature. In the SmC* phase, we have obtained two temperature ranges where the helical pitch is very small and constant: $p \sim 1.75\,\mu$m in the temperature range $35.6 \leq T_C - T \leq 53.7$°C and $p \sim 1.4\,\mu$m for 15.6°C $\leq T_C - T \leq 30.6$°C, where T_C is the SmC*–SmA transition temperature. When approaching the SmA phase, the pitch increases up to 2.2 μm. Close to T_C, the Grandjean–Cano defects may become invisible because the rotatory power vanishes roughly as the tilt angle. The "flat drop" method[15] has been used and gives the limit value of the pitch (1.5 μm) at T_C.

In Fig. 2, we present the temperature dependence of the tilt angle and the spontaneous polarization for C12 material. At low temperatures, a tilt angle of 35° was observed. When the temperature is increased, the tilt angle continuously decreased up to T_C, where it is almost equal to 8°. This non-zero value of θ at T_C is due to the coupling between the applied electric field and the electroclinic effect. The temperature dependence of the spontaneous polarization is also shown, indicating that our compounds display high values of P_S. At a reduced temperature, $T_C - T =$ 50°C, values of $P_S = 160$, 150, and 140 $\mathrm{nC\,cm^{-2}}$ for C10,[9] C11,[10] and C12 were found, respectively. For these materials, an increase of the polarization was observed as the alkyloxy chain length is shortened. Hence, this may be quite understood by the fact that for the C12 compound, the longer alkyloxy chain hinders rotational motion of the molecules[16] as the electric field is reversed. We can also notice

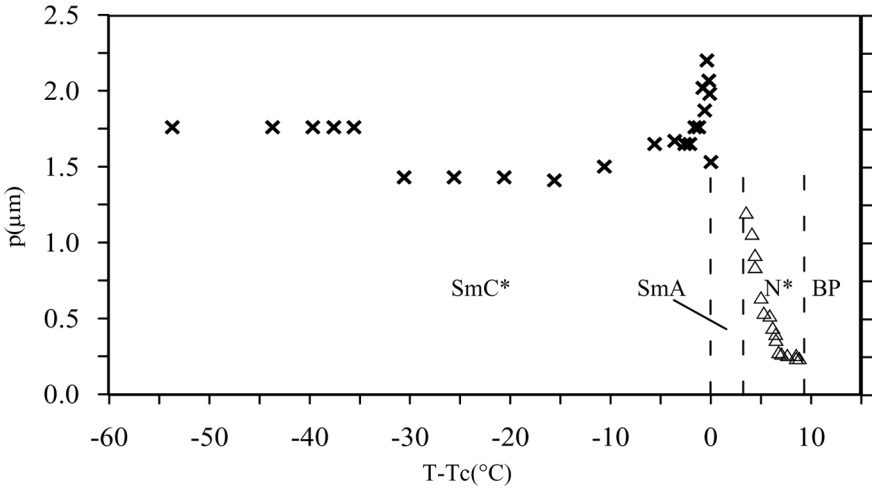


FIGURE 1 **Pitch temperature dependence in the SmC* and N* phases for C12.**

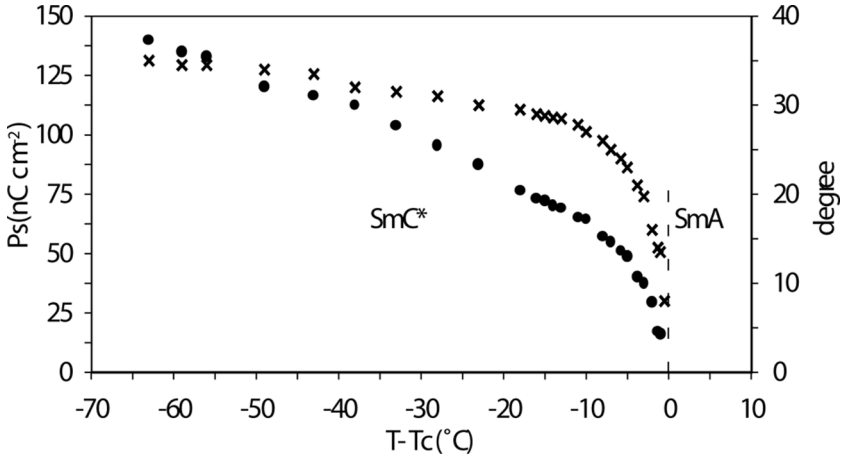


FIGURE 2 **Tilt angle (•) and spontaneous polarization (x) temperature dependencies for C12.**

that the presence of a halogen substituent (Cl) in the vicinity of the ester group −COO− and the biphenyl core favors high values of the spontaneous polarization for our compounds.

The dielectric relaxation spectroscopy in the SmC* phase shows a single relaxation domain. This mechanism process disappears when the helical structure is unwound by applying a DC bias voltage. Consequently, it is attributed to the Goldstone-mode relaxation. The dielectric amplitude $\Delta\varepsilon_G$ and critical relaxation frequency f_G variations versus temperatures for C12 are given in Fig. 3. At lower temperatures and far from T_C, $\Delta\varepsilon_G$ and f_G are rather temperature-independent as the helical pitch and have relatively high values ($\Delta\varepsilon_G = 140$ and $f_G = 1\,\text{kHz}$) compared with those observed on other compounds.[17] The high experimental value of f_G measured in this work can be explained by the low helical pitch value[10, 18] (see Eq. 2) for our compounds. With increasing temperature, $\Delta\varepsilon_G$ slowly increases and reaches a maximum value of 190, which occurs slightly below T_C. At $T = T_C$, , the dielectric strength decreases to reach $\Delta\varepsilon_G = 120$. The critical frequency increases and grows up to a high value of $f_G = 3\,\text{kHz}$. Such behaviors of $\Delta\varepsilon_G$ and f_G are due to the soft-mode (electroclinic effect) contribution, which becomes predominant close to T_C.

From structural, electro-optical, and dielectric data, some characteristic parameters for the Goldstone-mode relaxation can be determined using the predictions of the generalized Landau models[7] around the SmC*–SmA transition. The Goldstone-mode dielectric strength and relaxation frequency in the SmC* phase are given by:

$$\varepsilon_0 \Delta\varepsilon_G = \frac{1}{2K_{33}q^2}\left(\frac{P_S}{\theta}\right)^2 \qquad (1)$$

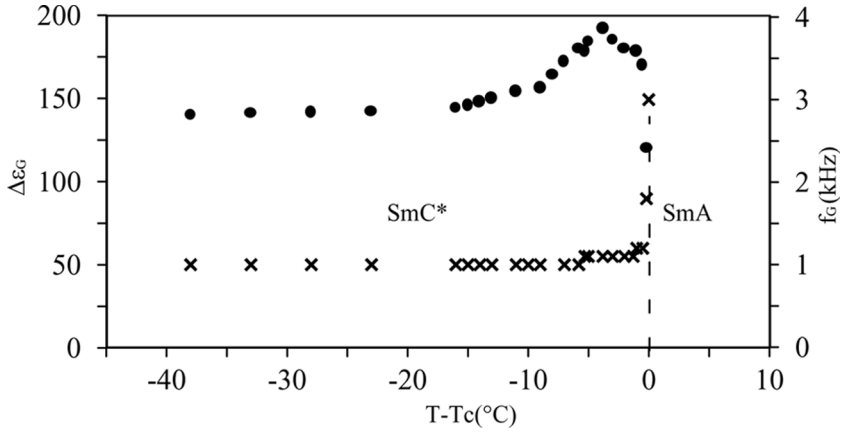


FIGURE 3 **Dielectric strength (•) and relaxation frequency (x) temperature dependencies of the Goldstone mode in the SmC* phase for C12.**

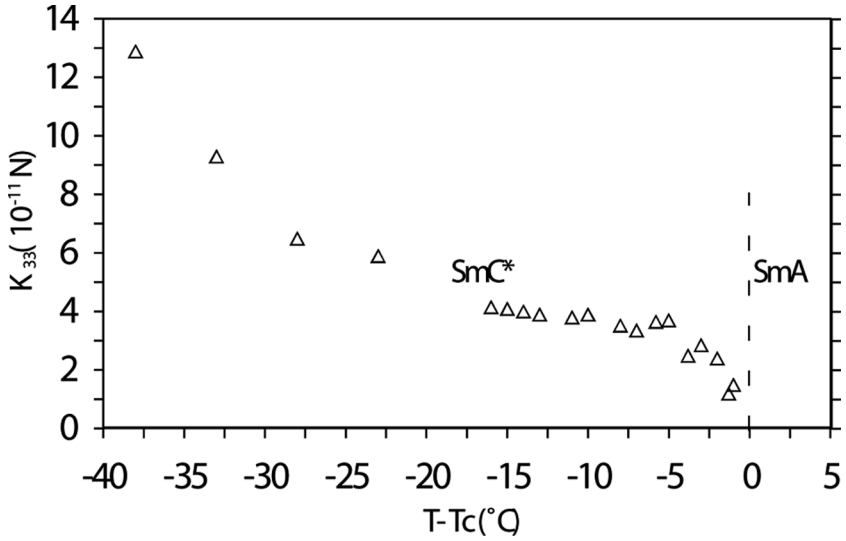


FIGURE 4 **Temperature dependence of the twist elastic constant in the SmC* phase for C12.**

$$f_G = \frac{K_{33} q^2}{2\pi\gamma_G} \tag{2}$$

where P_S is the spontaneous polarization, θ is the tilt angle, $q = 2\pi/\mathrm{p}$ is the wave vector of the modulated SmC* phase, K_{33} and γ_G are, respectively, the twist elastic and the Goldstone rotational viscosity, and ε_0 is the permittivity of free space. From Eq. (1), we can deduce the twist elastic constant:

$$K_{33} = \frac{1}{8\pi^2\varepsilon_0}\left|\frac{p^2}{\Delta\varepsilon_G}\right|\left|\frac{P_S}{\theta}\right|^2. \tag{3}$$

We can estimate the elastic constant K_{33} of the SmC* phase from the measured values of p, P_S, θ, and $\Delta\varepsilon_G$. The temperature dependences of K_{33} for C12 are plotted in Fig. 4. At low temperatures ($T_C - T = 40^{\circ}\mathrm{C}$), $K_{33} \approx 13 \times 10^{-11}$ N for C12. The value of K_{33} found here is the same order of magnitude as that obtained by Gouda et al.[19] for other compounds. The determined value of K_{33} for C12 is however 2 times greater than that obtained for C11 ($K_{33} \approx 7 \times 10^{-11}$ N[20]). This interesting result can be understood using Eq. (3). From our electro-optical study performed on C11,[20] we have measured a similar ratio of $P_S/\theta \approx 213\,\mathrm{nC/cm^2}$ rad, found here for C12. The ratio of the twist elastic constants (see eq. 3) of C12 and C11 can then be

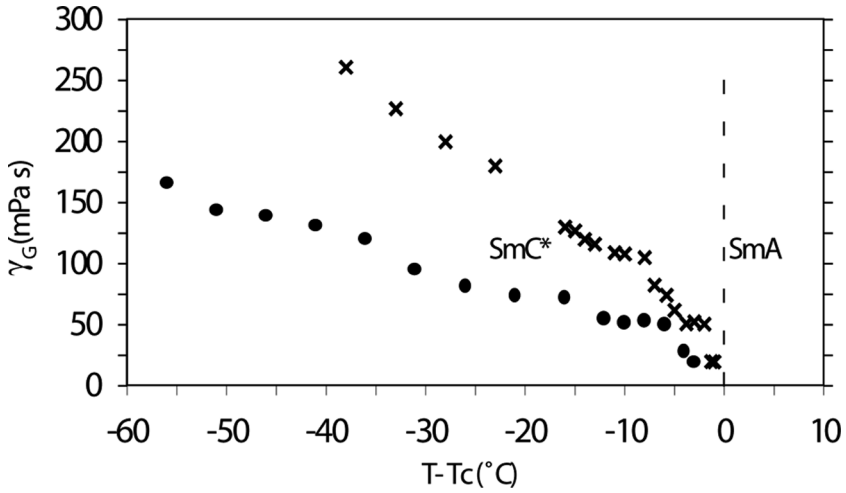


FIGURE 5 **Experimentally determined temperature dependence of the Goldstone rotational viscosity γ_G in the SmC* phase for C11 (•) and C12 (x).**

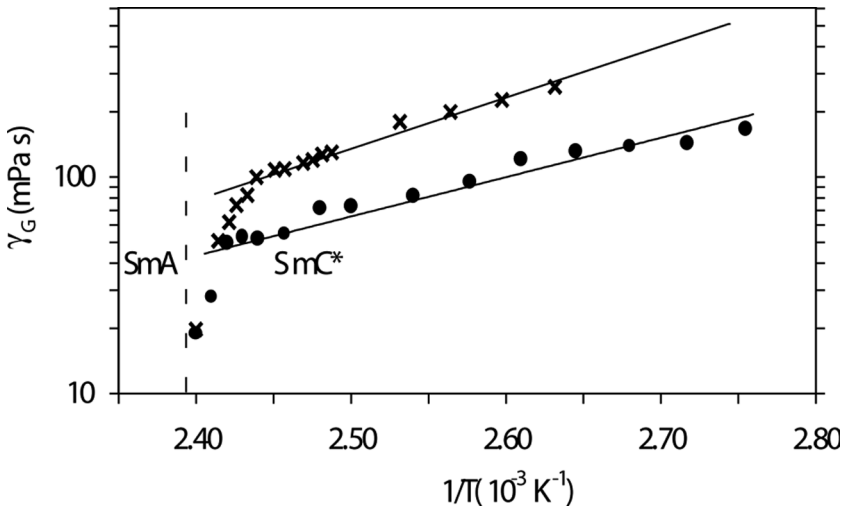


FIGURE 6 **Arrhenius plot of the experimentally determined Goldstone-mode rotational viscosity for C11 (•) and C12 (x).**

expressed as:

$$\frac{K_{33(C12)}}{K_{33(C11)}} \cong \left(\frac{p^2}{\Delta\varepsilon_G}\right)_{C12} \times \left(\frac{\Delta\varepsilon_G}{p^2}\right)_{C11}. \quad (4)$$

From this expression, the 2 times greater value of K_{33} measured for C12 can be essentially explained by the structural parameter of the SmC* phase; namely, the helical pitch p. Indeed, for C12, $p \approx 1.75\,\mu m$ is higher than $p \approx 1.3\,\mu m$ found for C11 compound.[20]

From eqs. (1) and (2), we can also derive the following expression:

$$\gamma_G = \frac{1}{4\pi\varepsilon_0}\left(\frac{1}{\Delta\varepsilon_G f_G}\right)\left(\frac{P_S}{\theta}\right)^2. \quad (5)$$

From this equation and from the experimental values of P_S, θ, $\Delta\varepsilon_G$, and f_G, one can evaluate γ_G in the SmC* phase. The temperature dependencies of this parameter thus obtained for C12 and C11 are reported in Fig. 5. Far from the SmC*–SmA phase transition, we can compare the experimental values of γ_G for C11 and C12 materials. We obtained, at $T_C - T = 40°C$, $\gamma_G = 260$ and 131 mPa s, respectively, for C12 and C11; therefore, γ_G for C12 is 2 times larger than the value found for C11: $\gamma_{G(C12)} = 2 \times \gamma_{G(C11)}$. This result of γ_G can be explained by the values of the dielectric strength and relaxation frequency, which are closely related to the helical pitch ($p = 2\pi/q$) of the SmC* phase (see eqs. 1 and 2).

Finally, our attention will be focused on the evaluation of the rotational viscosity activation energy with the Arrhenius equation:

$$\gamma_G = \gamma_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (6)$$

where E_a is the activation energy of the molecular rotation on the cone when the applied electric field is reversed (+E/−E) and k_B is Boltzmann's constant. The inverse temperature $1/T$ dependence of $ln\gamma_G \sim E_a/(k_B T)$ of the obtained rotational viscosity for C11 and C12 is plotted in Fig. 6. Far from the SmC*–SmA phase transition, we observe a linear behavior with versus reverse temperature. The slopes of the Arrhenius plots give the activation energy values in the SmC* phase; we thus obtained $E_a = 0.32$ and 0.42 eV for C11 and C12, respectively. Such values were found to be in quantitative agreement with those obtained by other authors using the same methods.[21, 22]

CONCLUSIONS

Structural, electro-optical, and dielectric investigations of FLC exhibiting N*–SmA–SmC* phase sequence have been studied as a function of temperature. From dielectric relaxation spectroscopy, we have studied the Goldstone-mode relaxation, which appears with a high relaxation frequency. From structural (helical pitch), electro-optical (tilt angle and spontaneous polarization), and dielectric studies (dielectric strength and relaxation frequency), we show how the Goldstone-mode rotational viscosity and twist elastic constant in the SmC* phase can be determined from a combination of theoretical model

and experimental data. The activation energies were also determined by applying the Arrhenius behavior of the Goldstone-mode rotational viscosity.

REFERENCES

1. Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. Ferroelectric liquid crystals. *J. Phys. Lett*. **1975**, *36*, L69.
2. Clark, N. A.; Lagerwall, S. T. Submicrosecond bistable electro-optic switching in liquid crystals. *Appl. Phys. Lett*. **1980**, *36*, 899.
3. Blinc, R.; Zeks, B. Dynamics of helicoidal ferroelectric smectic-$\tilde{C}$ liquid crystals. *Phys. Rev. A* **1978**, *18*, 2.
4. Benguigui, L. Dielectric relaxations in a liquid crystal with helicoidal dipole ordering. *J. Phys*. **1982**, *43*, 915.
5. Levstik, A.; Carlsson, T.; Filipic, C.; Levstik, I.; Zeks, B. Goldstone mode and soft mode at the smectic–*A*-smectic-*C** phase transition studied by dielectric relaxation. *Phys. Rev. A* **1987**, *35*, 3527.
6. Martinot-Lagarde, Ph.; Durand, G. Dielectric relaxation in a ferroelectric liquid crystal. *J. Phys. France* **1981**, *42*, 269.
7. Carlsson, T.; Zeks, B.; Levstik, A.; Filipic, C.; Levstik, I.; Blinc, R. Theoretical model of the frequency and temperature dependence of the complex dielectric constant of ferroelectric liquid crystals near the smectic-*C**-smectic-*A* phase transition. *Phys. Rev. A*. **1990**, *42*, 877.
8. Legrand, C.; Isaert, N.; Hmine, J.; Buisine, J. M.; Parneix, J. P.; Nguyen, H. T. Destrade, C. Electroclinic effect in the N* phase near a N*–SA–SC* multicritical point. *Ferroelectrics* **1991**, *121*, 21.
9. Legrand, C.; Isaert, N.; Hmine, J.; Buisine, J. M.; Parneix, J. P.; Nguyen, H. T.; Destrade, C. Biphenyl alkyloxy benzoates ferroelectric liquid crystals: structural, thermodynamic and dielectric studies of the octyl and the decyl homologous; electroclinic effect in the N* phase near a N*–SA–SC* multicritical point. *J. Phys. II France* **1992**, *2*, 1545.
10. Hmine, J.; Legrand, C.; Isaert, N.; Nguyen, H. T. Dielectric spectroscopy investigation for determining the rotational viscosity and the twist elastic constant for the ferroelectric chiral smectic C liquid crystals. *J. Phys. Condens. Matter* **2003**, *15*, 4677.
11. Grandjean, F. C. R. *Acad. Sci. Paris* **1922**, *172*, 71.
12. Cano, R. Interprétation des discontinuités de Grandjean. *Bull. Soc. Fr. Min. Cryst.* **1968**, *91*, 20.
13. Martinot Lagarde, Ph.; Duke, R.; Durand, G.; Temperature dependence of tilt, pitch and polarization in ferroelectric liquid crystals. *Mol. Cryst. Liq. Cryst.* **1981**, *75*, 249.
14. Legrand, C.; Parneix, J. P. Study of the SA–SC* phase transition by a dielectric method. *J. Phys. France* **1990**, *51*, 787.
15. Brunet, M.; Isaert, N. Periodic structures in smectic C* pitch and unwinding lines. *Ferroelectrics* **1988**, *84*, 25.
16. Nguyen, H. T.; Babeau, A.; Léon, C.; Marcerou, J. P.; Destrade, C.; Soldera, A.; Guillon, D.; Skoulios, A. Diarylethane α-chloroester ferroelectric liquid crystals. *Liq. Cryst.* **1991**, *9*, 253.
17. Filipic, C.; Carlsson, T.; Levestik, A.; Zeks, B.; Blinc, R.; Gouda, F.; Lagerwall, S. T.; Skarp, K. Dielectric properties near the smectic-C*-smectic-A phase transition of some ferroelectric liquid-crystalline systems with a very large spontaneous polarization. *Phys. Rev. A* **1988**, *38*, 5833.
18. Hemine, J.; Legrand, C.; Daoudi, A.; Isaert, N.; Nguyen, T. H. Influence of the proximity of a N*–SmA–SmC* multicritical point on the electroclinic effect in the cholesteric phase. *Liq. Cryst.* **2007**, *34*, 241.
19. Gouda, F.; Skarp, K.; Lagerwall, S. T. Results from new evaluation models in the dielectric spectroscopy of chiral smectic liquid crystals. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 99.
20. Hemine, J.; Legrand, C.; Daoudi, A.; Isaert, N.; El kaaouachi, A.; Nguyen, T. H. Electro-optical and dielectric characterizations of the goldstone mode relaxation in the ferroelectric chiral smectic C liquid crstals. *J. Phys. Condens. Matter* **2007**, *19*, 296203.
21. Levstik, A.; Kuntnjak, Z.; Filipic, C.; Levstik, I.; Bregar, Z.; Zeks, B.; Carlsson, T. Dielectric method for determining the rotational viscosity in thick samples of ferroelectric chiral smectic-C* liquid crystals. *Phys. Rev. A* **1990**, *42*, 2204.
22. Buivydas, M.; Lagerwall, S. T.; Dierking, I.; Gouda, F.; Mochizuki, A. The dielectric characterization of a material without layer shrinkage. *Ferroelectrics* **1998**, *212*, 67.