This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 11:07 Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered

office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl20

Experimental Proof of an Anomalous Behavior in the Nematic Phase of the Liquid Crystal E7

F. A. De Sousa $^{\rm a}$, R. N. Michels $^{\rm a}$, P. M. M. Cardoso $^{\rm a}$ & M. M. A. De Jesus $^{\rm a}$

^a Universidade Tecnológica Federal do Paraná-Câmpus Apucarana, Rua Marcílio Dias, 635 CEP, 86812-460, Apucarana, PR, Brasil Published online: 14 Jun 2013.

To cite this article: F. A. De Sousa, R. N. Michels, P. M. M. Cardoso & M. M. A. De Jesus (2013) Experimental Proof of an Anomalous Behavior in the Nematic Phase of the Liquid Crystal E7, Molecular Crystals and Liquid Crystals, 576:1, 106-117, DOI: 10.1080/15421406.2013.789711

To link to this article: http://dx.doi.org/10.1080/15421406.2013.789711

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 576: pp. 106–117, 2013 Copyright © Taylor & Francis Group, LLC ISSN: 1542-1406 print/1563-5287 online

DOI: 10.1080/15421406.2013.789711

Taylor & Francis
Taylor & Francis Group

Experimental Proof of an Anomalous Behavior in the Nematic Phase of the Liquid Crystal E7

F. A. DE SOUSA, R. N. MICHELS, P. M. M. CARDOSO, AND M. M. A. DE JESUS*

Universidade Tecnológica Federal do Paraná–Câmpus Apucarana, Rua Marcílio Dias, 635 CEP 86812-460-Apucarana, PR, Brasil

Experimental proof about a no reported anomalous behavior in the nematic phase of the Liquid Crystal E7 (Merck) are demonstrated by means of optical, electrical and density measurements. Optical measurements were made by use of polarized light transmittance, electrical measurements were obtained using impedance spectroscopy and density measurements were made using a precision density meter. Evidence of a temperature range in which is contained a not related anomalous behavior in the nematic phase of the Liquid Crystal E7 is observed in optical measurements performed on a PDLC sample at different temperatures, and proven by electrical permittivity and volumetric density measurements. The temperature range of anomalous observation occurs between 23°C and 43°C and present a peak at about 32°C, coincidentally close to 35°C, the N-I temperature of the liquid crystal 5CB, major constituent of the mixture that composing the eutectic liquid crystal E7 [1]. With regard to the application of this liquid crystal, it is clear the need to consider the existence of a temperature range in which the electro optical responses of E7 features a behavior, unknown until then.

Keywords Experimental measurements; anomalous behavior

1. Introduction

The LC E7 (Merck) is a thermotropic liquid crystal frequently used in the manufacture of information display and in academic research. This LC is made of a eutectic mixture of four different kind of thermotropic LC whose chemical structures and concentrations [1] are shown in Fig. 1.

The frequent use of the LC E7 by industry and in academic research occur because it material have a great temperature range in the nematic phase and a high N-I temperature, about 60° C [1,2]. In this way, the actual literature describe just two liquid crystalline mesophase for this material: Smetic ($T_{Sm-N} = -30^{\circ}$ C [3]) and Nematic ($T_{N-I} = 58,4^{\circ}$ C [2]). Therefore, the present work has an important finding: the confirmation of an unknown anomalous behavior in the nematic phase of the Liquid Crystal E7 that may be considered, with strong consequences in application and basic research of this LC.

^{*}Address correspondence to M. M. A. De Jesus. Phone: +55 (43) 34256460 Fax.: +55 (43) 34256460. E-mail: manoelmessias@utfpr.edu.br

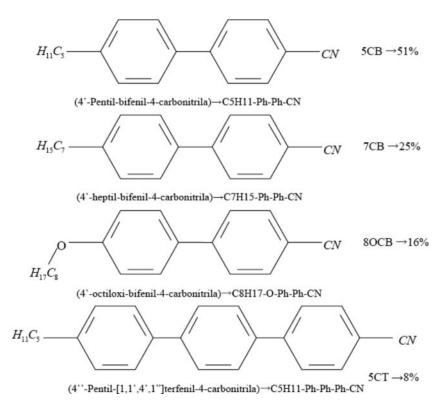


Figure 1. Chemical structure and concentrations of the liquid crystals that compound the LC E7 [1].

2. Experimental Procedure

The polarized light transmittance technique has been used in liquid crystal systems characterization for decades to determination of some specifics characteristics of these materials and its behavior in different physical conditions [3–9]. In this work, the samples were placed between two glass substrate covered by a thin conductive and transparent SnO₂ film and their temperatures were controlled by a thermo system represented in Fig. 2.

Fig. 3 shows the set up used in the optical transmittance measurement, basically with a He-Ne laser (633 nm) and a photo-diode. The data acquisitions were obtained by use of a digital oscilloscope (Tektronix TDS 5032B).

The electrical measurements were obtained using impedance spectroscopy. There are some works using impedance spectroscopy related at literature, including some results in liquid crystalline and biological systems [11–16]. Although the Debye's pioneer work in 1929 has been established the dielectric relaxation theory, the impedance spectroscopy was been used since the century XIX [10].

The technique is relatively simple and consist in analyze the behavior of a material placed between two conductive electrodes, applying a known electric signal and measure the electric response of these material.

Normally the hold sample cell is constituted by a parallel plates capacitor and the impedance measurements results can be converted, by means of mathematical calculation in a microscope characteristic of the physical medium as the electric permissivity, for

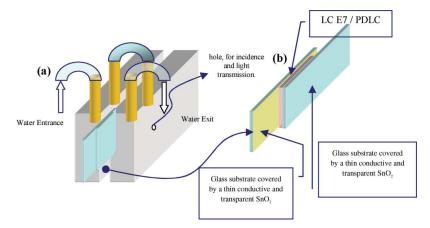


Figure 2. a) Representation of the thermal control used to the sample temperature stabilization; b) Representation of the hold sample.

example. In this way, the technique can be called dielectric spectroscopy, with experimental and theorycal study greatly related at literature [17–21].

The impedance measurements in all range of frequency was made with a commercial impedance analyzer, Solartron SI1260, that works in a frequency range from 10 μ Hz to 32 MHz. Fig. 4 show the electric model used in the permissivity and impedance determination. In another hand, the experimental apparatus used in the electrical measurements can be presented in Fig. 5.

The admittance can be written in the form:

$$Y = \frac{1}{R_0(\omega)} + i\omega \ C(\omega). \tag{1}$$

And the complex permissivity can be obtained considering that [22]:

$$Y = \left(\varepsilon''(\omega) + i\varepsilon'(\omega)\right)\omega C_0. \tag{2}$$

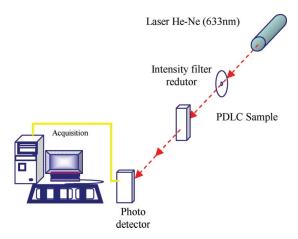


Figure 3. Experimental setup for optical transmittance measurements in PDLC samples.

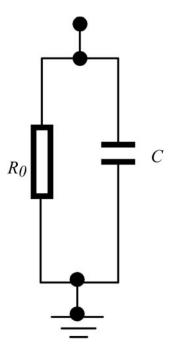


Figure 4. Electrical equivalent circuit used.

The combination of Equations 1 and 2, results:

$$\varepsilon^* = \varepsilon'(\omega) + i\varepsilon''(\omega) = \frac{C(\omega)}{C_0} + i\frac{1}{\omega C_0 R_0(\omega)}.$$
 (3)

In this way, the real and imaginary parts of the complex permissivity, ε^* , can be determined:

$$\varepsilon'(\omega) = \frac{C(\omega)}{C_0} \tag{4a}$$

and

$$\varepsilon''(\omega) = \frac{1}{\omega C_{\scriptscriptstyle 0} R_{\scriptscriptstyle 0}(\omega)}.$$
 (4b)

The values of $C(\omega)$ and $R_0(\omega)$ are obtained directly from the impedance analyzer and the real and imaginary parts of the complex permissivity are determined indirectly knowing the area and the space between two electrodes of the hold sample.

Finally, density measurements were obtained by means of a commercial density meter, Anton Paar DMA 5000. It is a very good accurate density meter. Measurements were made in a temperature range from 10° C to 80° C with step of 0.5° C ($\pm 0.01^{\circ}$ C). The accuracy in the density measurements is 5 mg/cm³.

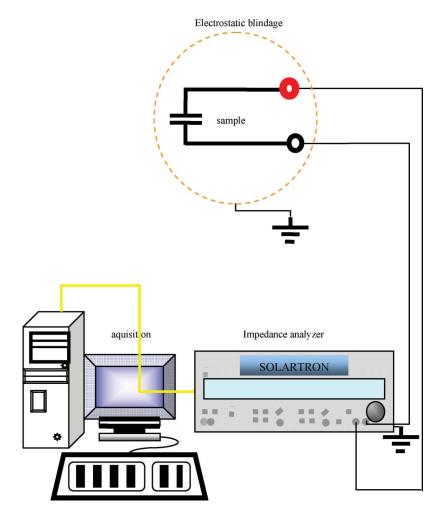


Figure 5. Representation of the experimental apparatus used in the electrical measurements.

3. Results

3.1. Optical Transmittance Measurements

The first observation can be noted in the transmittance measurements of a PDLC sample made of LC E7 (Merck) and polymer NOA 65 (Norland optical adhesive) in a 50% / 50% in weight proportion. Fig. 6 shows the thermo-electro-optical behavior of a PDLC sample. The measurements were did in a range from 17,8°C to 70°C ($\pm 0,05$ °C) with voltage ranging from 0 V to 85 V applied in a sample with 25 μ m thickness and area of 4 cm².

Fig. 7 shows the points where was obtained the critical voltage (V_c) and de saturation voltage (V_{sat}) (consequently the saturation intensity and the critical intensity).

The analysis of Fig. 6 shows three distinct behavior of the electro-optical response of the LC E7 (PDLC) confined in a polymeric matrix, before the critical temperature T_{N-I} . This behavior can be observed in Fig. 8.

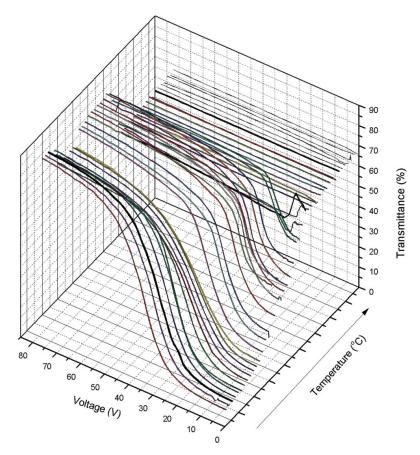


Figure 6. Behavior thermo-electro-optical of a LC E7 confined in a polymeric matrix (PDLC).

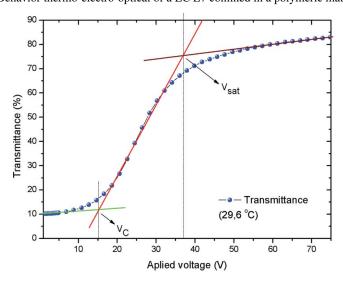


Figure 7. Indication of the critical voltage V_c and saturation voltage V_{sat} obtained in the transmittance graphic.

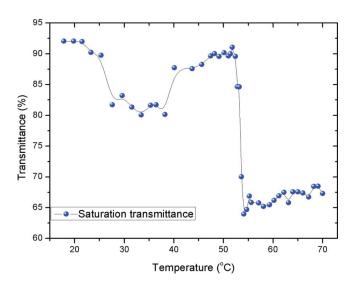


Figure 8. Saturation Intensity (I_{sat}) in a PDLC sample in different temperatures.

Fig. 8 shows the saturation transmitted light intensity. That is very clear the existence of a discontinuity not related in the literature, in a range from 20°C to 40°C, with a pick near to 35°C (the T_{N-I} of the 5CB). In another hand, Fig. 9 shows the dependence of the critical voltage V_c of the PDLC on the temperature.

One more time a discontinuity is detected. In this way, Figures 8 and 9, suggest strongly the existence of a not related anomalous comportment in the nematic phase of the LC E7.

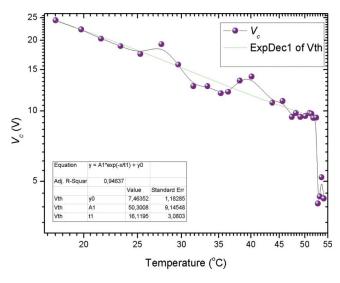


Figure 9. Critical voltage (Vc) in a PDLC sample in different temperatures.

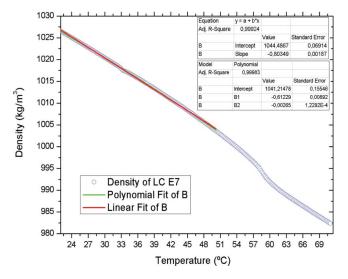


Figure 10. Density of the LC E7 in different temperatures.

Of course that one can think that this comportment is a confinement effect, because the critical temperature T_{N-I} of the LC E7 have a decrease, verified in the transmittance analysis. But its modification in the critical temperature is related in the literature [23–26], and its increase and decrease according to the confinement condition combination (Polymer and liquid crystal). Its dependence can be analyzed in another paper.

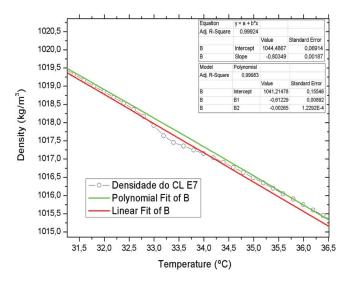


Figure 11. Density of the LC E7 in different temperatures (confirmation of a discontinuity in the density values near of the 5CB T_{N-I}).

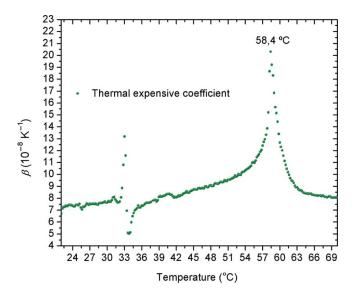


Figure 12. The E7 thermal expansive coefficient.

3.2. Density Measurements

The proof of the existence of a not related anomalous comportment in the nematic phase of the LC E7 can be enhanced with density measurements, shown in Figs. 10 and 11.

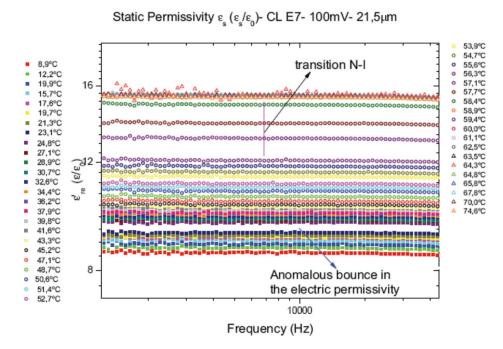


Figure 13. Real part of the complex permissivity of the LC E7 in different temperatures.

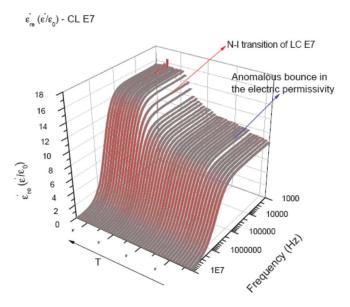


Figure 14. Real part of the complex permissivity of the LC E7 in different temperatures.

The E7 thermal expansive coefficient was obtained by means of Eq. 5,

$$\beta = -\frac{1}{\rho} \frac{d\rho}{dT} \tag{6}$$

and shown in Fig. 12.

Analysis of Fig. 12 shows clearly the existence of two discontinuity in the thermal expansive coefficient of the LC E7, evidencing the phase transition temperature (58,4°C) and another discontinuity, that can be associated to an anomalous comportment in the nematic phase of the LC E7. The first peak is not related at actual literature and occurs in 32,5°C, coincidently, very near of the N-I temperature of the LC 5CB, the LC with more concentration in the E7 mixture.

3.3. Electrical Measurements

Finally, impedance measurements close the proof of the existence of an anomalous comportment in the nematic phase of the LC E7, with another microscope analyses (the electric permissivity). This measurement is shown in Figs. 13 and 14.

It is possible to verify the existence of a brusque discontinuity in the comportment of real component of de electric permissivity in a temperature very far than the TN-I of the LC E7.

4. Concluding Remarks

The critical temperature transition of the CL E7 was verified by means of three different characterization technique and a not related anomalous comportment in the nematic phase of this LC was founded with base in the analyses of the electrical, optical and density measurements. The results shows the existence of this anomalous comportment in a range localized between 25° C and 40° C.

In the application view point, this information is very relevant, because a not waited behavior of a information display made of LC E7 can occur in a unwanted situation and its can compromise an operational system, that can be very dangerous in same situations, for example in aviation control information displays and others similar situations.

It is possible to verify the existence of a brusque discontinuity in the comportment of real component of de electric permissivity in a temperature very far than the TN-I of the LC E7, confirmed by optical and density measurements.

This results suggest that new measurements of DSC and X-ray diffractometry can be used in the future investigation with objective to verify if there is an no related modification in the molecular organization of nematic phase of the LC E7 in the temperature range related.

Acknowledgments

The authors are grateful to Brazilian agencies CAPES and CNPq and the Parana government agency Araucaria Foundation and State Secretary Science and Technology (SETI) for financial support.

References

- [1] Yakuphanoglu, F. et al. (2008). Dielectric anisotropy, and diffraction efficiency properties of a doped nematic liquid crystal. *Dyes and Pigments*, 76, 721.
- [2] Merck E7 data sheet, (2003).
- [3] Kawanishit, Y., Tamaki, T., & lchimura, K. (1991). Reversible photoinduced phase transition and image recording in polymer-dispersed liquid crystals. *J. Phys. D: Appl. Phys.*, 24, 782.
- [4] Koval'chuk, A. V., Kurik, M. V., Lavrentovich, O. D., & Sergan, V. V. (1990). Electrooptical effects in the polymer dispersed nematic liquid crystal: Response time. *Mol. Cryst. Liq. Cryst.*, 193, 217–221.
- [5] Fuh, A. Y. G., Huang, K. L., Lin, C. H., Lin, I-I C., & Jiang, I. M. (1990). Studies of the dependence of the electro-optical characteristics of polymer dispersed liquid crystal films on curing temperature. *Chinese Journal of Physics*, 28–6, 551.
- [6] Carter, S. A. et al. (1997). Morphology and electro-optic properties of polymer-dispersed liquidcrystal films. J. Appl. Phys., 81, 5992.
- [7] Amundson, K. (1996). Electro-optical properties of a polymer-dispersed liquid-crystal film: Temperature dependence and phase behavior, *Phys. Rev. E*, 53–3, 2412.
- [8] Karapinar, R. (1998). Electro-optic response of a polymer dispersed liquid crystal film. Tr. J. of Physics, 22, 227.
- [9] Boussoualem, M., & Roussel, F. (2004). Thermophysical, dielectric, and electro-optic properties of nematic liquid crystal droplets confined to a thermoplastic polymer matrix. *Phys. Rev. E*, 69, 031702.
- [10] Fricke, H. (1931). The electric conductivity and capacity of disperse systems. *Physics*, 1, 106–115.
- [11] Bordi, F., Cametti, C., & Colby, R. H. (2004). Dielectric spectroscopy and conductivity of polyelectrolyte solutions. J. Phys.: Condens. Matter., 16, R1423–R1463.
- [12] Bengoechea, M. R., Basu, S., & Aliev, F. M. (2004). Dielectric relaxation in liquid crystal confined to cylindrical pores: Effect of different layer thicknesses and boundary conditions. *Mol. Cryst. Liq. Cryst.*, 421, 187.
- [13] Sinhá, G. P., & Aliev, F. M. (1998). Dielectric spectroscopy of liquid crystals in smectic, nematic, and isotropic phases confined in random porous media. *Phys. Rev. E*, 58, 2001.
- [14] Köysal, O., Okutan, M., Durmus, M., Yakuphanoglu, F., San, S. E., & Ahsen, V. (2006). Diffraction efficiency and dielectric relaxation properties of nickel phthalocyanine doped nematic liquid crystal. *Synthetic Metals*, 156, 58–64.

- [15] Janik, M. et al. (2006). Pretransitional behavior in the isotropic phase of a nematic liquid crystal with the transverse permanent dipole moment. J. Chem. Phys., 124, 144907.
- [16] Asami, K. (2002). Characterization of heterogeneous systems by dielectric spectroscopy. *Prog. Polym. Sci.*, 27, 1617–1659.
- [17] Bordi, F., Cametti, C., & Colby, R. H. (2004). Dielectric spectroscopy and conductivity of polyelectrolyte solutions. J. Phys.: Condens. Matter., 16, R1423–R1463.
- [18] Bose, T. K., Campbel, B., Yagihara, S., & Thoen, J. (1987). Dielectric-relaxation of alkil-cyianobiphenyl liquid crystals using time-domain spectroscopy. *Phys. Rev. A*, 36, 5767.
- [19] Feldman, Y. et al. (2003). Time domain dielectric spectroscopy of biological systems. *IEEE Transactions on Dielectrics and Electrical Insulation*, 10, 5, 728–753.
- [20] Leyderman, A., & Qu, Shi-Xian (2000). Multifractal phase transitions in the non-Debye relaxation processes. Phys. Rev. E, 62, 3293.
- [21] Alim, M. A., Bissell, S. R., & Mobasher, A. A. (2008). Analysis of the AC electrical data in the Davidson–Cole dielectric representation. *Physica B*, 403, 3040–3053.
- [22] Barsoukov, E., & Macdonald, J. R. (2005). Impedance Spectroscopy Theory, Experiment, and Applications, second edition, John Wiley & Sons, Inc.: New Jersey.
- [23] Srivastava, A., Sa, D., & Singh, S. (2007). Pressure variation of reentrant transition temperature in liquid crystals. Eur. Phys. J., E 22, 111.
- [24] Kozak, M. M., Kowalsky, W., & Caspary, R. (2005). Low-loss glue splicing method to join silica and fluoride fibres. ELECTRONICS LETTERS, 41–16.
- [25] Gnatyuk, I. I., Puchkovskaya, G. A., Goltsov, Yu. G., Matkovskaya, L. A., & Drozd, M. (2000). Influence of confinement on the phase transition and spectral characteristics of nematic liquid crystals. *Journal of Thermal Analysis and Calorimetry*, 62, 365.
- [26] Crawford, G. P., & Zumer, S. (1997). Liquid Crystals in Complex Geometries, Taylor & Francis: London.