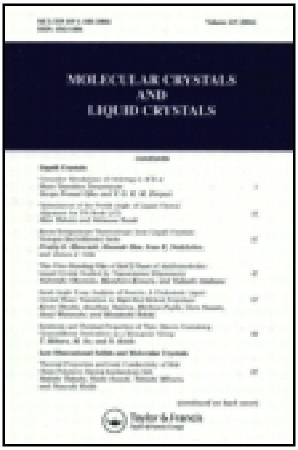


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrohydrodynamic Instabilities in Doped M5 Nematic Liquid Crystals

C. Vena [a] , C. Versace [a] , G. Strangi [a] , S. D'Elia [a] & R. Bartolino [a]

[a] Licryl INFM-CNR Regional Laboratory and Centro d'Eccellenza CEMIF.CA. Dipartimento di Fisica, Università della Calabria, Rende, CS

Version of record first published: 22 Sep 2010

To cite this article: C. Vena, C. Versace, G. Strangi, S. D'Elia & R. Bartolino (2007): Electrohydrodynamic Instabilities in Doped M5 Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 465:1, 217-225

To link to this article: http://dx.doi.org/10.1080/15421400701205990

Mol. Cryst. Liq. Cryst., Vol. 465, pp. 217–225, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701205990

Electrohydrodynamic Instabilities in Doped M5 Nematic Liquid Crystals

C. Vena
C. Versace
G. Strangi
S. D'Elia
R. Bartolino
Licryl INFM-CNR Regional Laboratory and Centro d'Eccellenza
CEMIF.CA. Dipartimento di Fisica, Università della Calabria, Rende, CS

We report the study of the electrodynamic behavior of the nematic mixture M5 doped at several percentages by its reaction precursors 4-(n-Octyloxy)phenol and 4-Heptylbenzoic acid [1]. The influence of the doping impurities on the M5 clearing temperature has been studied by micro differential scanning calorimetry and their conductivities have been determined by impedance analysis as well as their dielectric constants. Finally we studied by polarizing microscopy the influence of the dopants on the voltage threshold for the onset of the orientational instabilities and we determined the cut-off frequency of the low frequency conductive regime.

Keywords: anisotropic media; electrodynamics; instabilities; liquid crystals

1. INTRODUCTION

Electrohydrodinamic convection (EHC) in nematic liquid crystals is a well known standard system for dissipative pattern formation (for a general review, see [2]). It provides a rich scenario of dissipative structures which can be readily controlled by experimental parameters as electric field strength and frequency. Moreover, the hydrodynamic and electric equations involved are well known and the observation of the textures is straightforward by means of optical microscopy. These characteristics have allowed to liquid crystals to become an important paradigm to study generic aspects of pattern forming

---

Address correspondence to C. Vena, Licryl INFM-CNR Regional Laboratory and Centro d'Eccellenza CEMIF.CA., Dipartimento di Fisica, Universita della Calabria, 87036 Rende, CS. E-mail: cvena@fis.unical.it

mechanisms. To extend this already rich scenario is the transition between the two turbulent states called dynamic scattering modes, that occur in these materials for particular values of the control parameters, (DSM's) [3]. This transition is not a very common phenomenon in nature and Stokes polarimetry allows its further characterization by means of the determination of the polarization degree of the light transmitted by the sample [4]. These studies often require a huge observation time during which very long experimental series are recorded, therefore it is desirable to have a very stable mesogenic compound, to prevent sample degradation.

So far the majority of the EC studies have been carried out on the Methoxy benzylidene butylaniline (MBBA) nematogen compound, which not only possesses a value of both the dielectric anisotropy ($\Delta\varepsilon < 0$) and conductivity anisotropy ($\Delta\sigma > 0$) necessary for EHC but also it is a self-doping materials in the sense that MBBA produces itself the ions that are indispensability for EHC via photochemical and electrochemical degradation. On the other hand MBBA rather degrades when it is irradiated with light and when it is used in EHC experiments. As a consequence of the increase of the ionic impurities concentration a drifts in the physical proprieties of the system can be observed, this compromises the reproducibility of the experiments. Recently the M5 mixtures doped by its reaction precursors has been proposed as MBBA replacement in these studies [1]. In fact in ref. [1] it is emphasized that M5, is an excellent material for experiments on EC because its chemical stability.

Experimental observations gave us results which differ substantially with those presented in ref. [1]. In particular to obtain a system suitable for EHC we had to shift forward highest concentrations of dopants (up to 14wt% vs 3.8wt% reported in ref. [1]), we motivate these differences by the fact that we used for our systems industrial products (SYNTHON Chemicals GmbH & Co KG) which are in principle much more pure, indeed their minimum essay is 99 wt% (measured by HPLC).

Therefore we prepared M5 in our laboratory by mixing its components following the recipe given in ref. [1]. Then we doped at several percentages the M5 by its reaction precursors 4-(n-Octyloxy)phenol and 4-Heptylbenzoic acid to obtain the low frequency electrohydrodynamic instabilities.

In the following we report the experimental study of EHC systems based on M5. Firstly, the electric and optical properties of doped and pure M5 have been investigated, then we studied the influence of the dopants on the EHC scenario, in particular we determined the threshold voltage for the onset of the instabilities to measure the cut-off frequency of the low frequency electrohydrodinamic regime.

2. RESULTS

Four compounds mixed in different ratios (see [1]) make up the mixture M5: 4-hexyloxyphenyl-4′-methoxybenzoate 22,0 wt%; 4-octyloxyphenyl-4′-pentyloxybenzoate 30,3 wt%; 4-heptyloxyphenyl-4′-hexyloxybenzoate 13,3 wt%; 4-butyloxyphenyl-4′-hexylbenzoate 34,4 wt%.

Every compounds is solid at room temperature, therefore we heated them up to the isotropic liquid phase before mix and filter the mixtures. Then different percentages of 4-(n-Octyloxy)phenol and 4-Heptylbenzoic acid are been added to the mixture in order to obtain system suitable EHC. We noted at room temperature the saturation concentrations of both 4-Heptylbenzoic acid (acid) 4-(n-Octyloxy)-phenol (salt) in M5 to determine the maximum dopant percentages for our systems, these at room temperature were 6 wt% and 20 wt% for the acid and the salt respectively.

2.1. Thermal Behavior

The clearing point temperature T_C of both doped and undoped M5 has been determined by differential scanning calorimetry (Thermal Analysis DSC 2020). In Figure 1 we report T_C as function of the dopant concentrations.

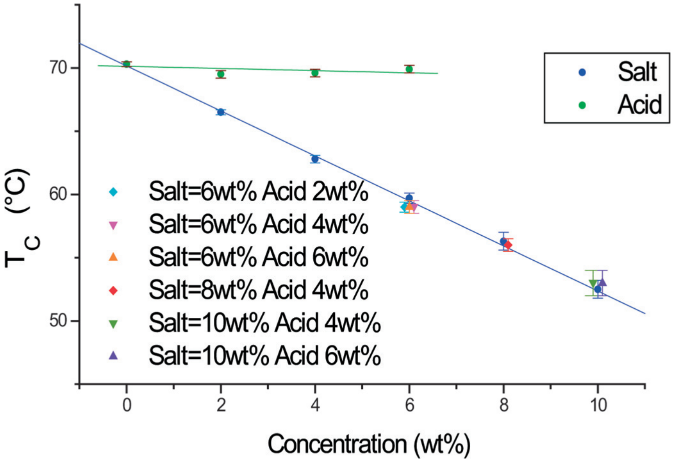


FIGURE 1 Clearing point temperatures T_C as function of the concentration. We can see that T_C is almost independent from the acid concentration (green line), on the contrary T_C linearly decreases when the salt concentration increases (blue line). This behavior has been observed either if we dope separately by the acid and the salt or if we use salt and acid together to dope M5. (See COLOR PLATE XIV)

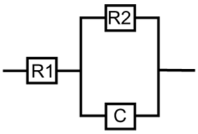
The mixture M5 shows a nematic-isotropic transition at $T_C = 70{,}3 \pm 0{,}2°\mathrm{C}$ and we expected that the inclusion of ionic impurities would decrease T_C; in fact we found that T_C decreases almost linearly for increasing salt percentages but T_C is almost independent from the acid concentration. In particular the 10wt% of salt doping fell T_C of approximately 17°C and a concentration up to 6wt% does not affect the clearing point of pure M5. In the case of the salt we have fitted the data in Figure 1 by $Y = A + B * X$ and the values of the fitting parameters are $A = 70,\ 2 \pm 0{,}1$, $B = -1,\ 780 \pm 0{,}03$. Moreover T_C show a linear behavior until this salt percentage.

2.2. Electrical Behavior

We performed all the experiments on standard sandwich cells with etched electrodes of area $1\,\mathrm{cm}^2$ and with thickness $25\,\mu\mathrm{m}$, the cell surfaces were covered by rubbed polyimide to induce a planar homogeneous anchoring of the nematic liquid crystal films. The impedance analysis has been carried out by an EG&G model 348 impedance analyzer. We have prepared the mixtures listed in the following table in which each mixture is labelled with a different color.

The empty sample cells were firstly characterized by impedance analysis both to determine the cell thickness and to find out spurious capacities. Then impedance measurements were performed on the filled sample cells at two different temperature in the nematic phase temperature range. We report the data plot in Figure 2 and we show both Bode plot and Nyquist plot at 35°C and 50°C. We note that the Nyquist plots show a semicircle at high frequency region and a straight line at low frequency region. This low frequency constant phase behavior is characteristic of low frequency diffusive processes. Increasing the concentration of dopants the impedance decreases, both real and imaginary parts, and the observed semicircles shrink. Also the diffusion tails shift at lower values of $Re(Z)$ and the frequency F_0 at which the diffusion tail appears in the Nyquist plot increases. The frequencies F_0 at which the diffusive tails start are reported in the 2nd and 3rd columns of Table 2.

Impedance data have been fitted to an equivalent circuit model:



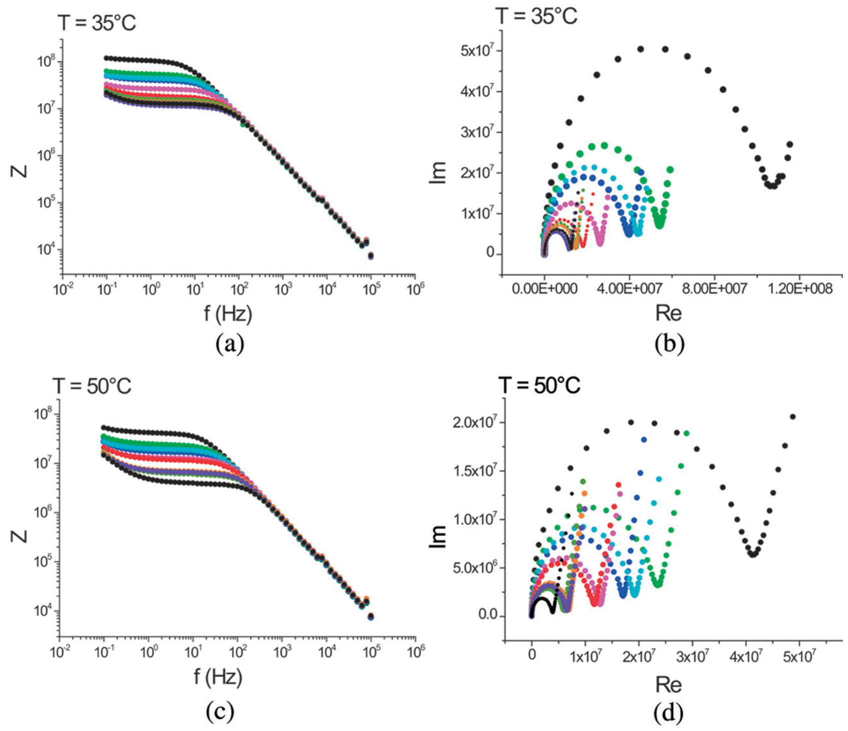


FIGURE 2 Impedance plots at two different temperatures (35°C and 50°C). The Bode (a and c) and the Nyquist (b and d) plots are reported for the different mixtures. Color association is given by Table 1. (See COLOR PLATE XV)

in order to extract the capacity C and the resistance **R2** of the samples. **R1** represents the series resistance due to the connecting cables and the ITO electrodes and it isn't of physical interest to examine it. Note that we didn't include in the equivalent circuit any constant phase

TABLE 1 Association Between Color and Dopant Concentration (See COLOR PLATE XVI)

no doped M5		⬛
Salt=8wt%		🟩
Salt=10wt%		🟦
Salt=6wt%	Acid=2wt%	🟦
Salt=6wt%	Acid=4wt%	🟪
Salt=8wt%	Acid=4wt%	🟥
Salt=6wt%	Acid=6wt%	🟧
Salt=10wt%	Acid=4wt%	🟫
Salt=10wt%	Acid=6wt%	🟪
Salt=12wt%	Acid=5wt%	⬛

TABLE 2 Summary of the Impedance Analysis Results Giving the Frequency F_0 in which the Diffusive Tails Start, the Perpendicular Dielectric Constant $(\varepsilon_\perp)$ and the Perpendicular Resistivity $(\rho_\perp)$ of the Mixtures at Two Different Temperatures. Color Association is given by Table 1

		F_0(Hz)		$\varepsilon_\perp$		$\rho_\perp(\times 10^8)$	
		T = 35°C	T = 50°C	T = 35°C	T = 50°C	T = 35°C	T = 50°C
no doped M5		0,5	1,3	4,54 ± 0,08	4,4 ± 0,1	5,7 ± 0,1	2,28 ± 0,06
Salt = 8 wt%		0,8	2	4,9 ± 0,1	4,7 ± 0,1	2,81 ± 0,06	1,23 ± 0,04
Salt = 10 wt%		1,0	2,5	4,7 ± 0,1	4,5 ± 0,2	2,05 ± 0,06	0,89 ± 0,04
Salt = 6 wt%	Acid = 2 wt%	0,8	2,0	4,5 ± 0,1	4,4 ± 0,1	2,28 ± 0,06	1,01 ± 0,04
Salt = 6 wt%	Acid = 4 wt%	1,6	3,2	4,3 ± 0,1	4,2 ± 0,2	1,35 ± 0,04	0,67 ± 0,03
Salt = 8 wt%	Acid = 4 wt%	2,5	4,0	4,3 ± 0,1	4,1 ± 0,2	0,76 ± 0,03	0,36 ± 0,02
Salt = 6 wt%	Acid = 6 wt%	2,8	6,0	4,5 ± 0,1	4,4 ± 0,2	0,94 ± 0,03	0,61 ± 0,03
Salt = 10 wt%	Acid = 4 wt%	2,8	6,3	4,5 ± 0,2	4,3 ± 0,2	0,79 ± 0,03	0,32 ± 0,2
Salt = 10 wt%	Acid = 6 wt%	3,2	6,3	4,6 ± 0,2	4,4 ± 0,2	0,60 ± 0,02	0,35 ± 0,02
Salt = 12 wt%	Acid = 5 wt%	3,2	11,2	4,6 ± 0,2	4,4 ± 0,3	0,66 ± 0,03	0,21 ± 0,01

element and we restricted our attention only to the high frequency region, because the diffusion dependent part of the Nyquist plots are clearly not of Warburg type. From C and **R2** we extracted the perpendicular dielectric constant $(\varepsilon_\perp)$ and the perpendicular resistivity $(\rho_\perp)$ of the mixtures respectively, which are also reported in Table 2.

2.3. Orientational Instabilities

In this section we report the study of the orientational instabilities which take place in M5 mixtures. The observation were performed by polarized optical microscopy on same cells we have thermally and electrically characterized. To determine the threshold for the orientational instabilities we applied at the sample cells a low frequency ac voltage and we slowly increased the applied voltage, starting from an applied voltage of 0 V and holding fixed the frequency. Obviously in planar geometry we can't observe any Freedericks transition but different type of orientational instabilities can be observed. We recorded the voltage at which we observed the first changes in the sample orientations. We performed the determination of the threshold voltage at two different temperatures (Figure 3).

The curves in Figure 3 show the classic behavior: vanishing frequency dependence at low frequencies followed by a sharp increase in the conduction regime and then an abrupt increase in the curve at the so-called cut-off frequency F_C above which one observes the dielectric regime. Increasing the dopants concentration also the cut-off frequency increases and we measure higher values of F_C if the dopant concentration and the temperature increase. Although the result are appreciable it is not enough to reach a certain condition

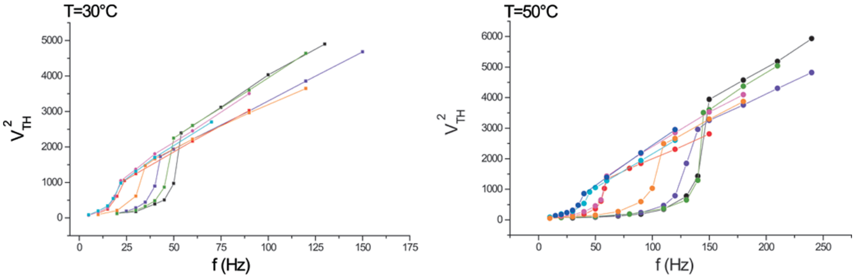


FIGURE 3 The square of the critical voltage for the onset of the electron-convection vs frequency for different mixtures at two different temperatures. (See COLOR PLATE XVII)

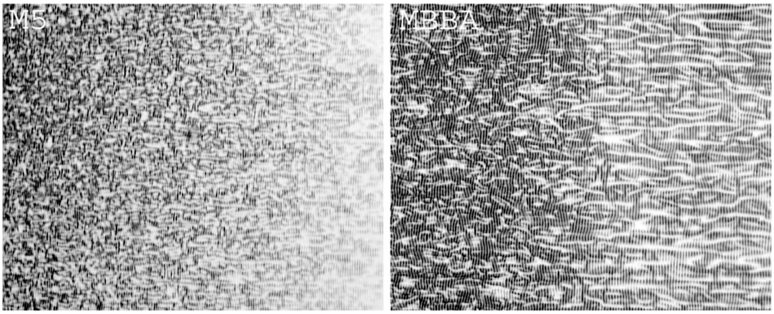


FIGURE 4 Pattern gradients in M5 and MBBA respectively.

of experimental stability. In fact, as we show in Figure 4, when we apply a electric field after sometime it appears a ions concentration gradient. This gradient produces different patterns in different cell areas. In Figure 4 we can observe this phenomena both for M5 and MBBA liquid crystals, in particular if we use very pure MBBA that still doesn't posses more charge. We suppose that when in MBBA the charge reaches a greater concentration, degrading the material, the ion diffusion balances and crosses the ions migration and so we have an uniform ions distribution.

3. CONCLUSIONS

We have tested M5 with different concentrations of salt and acid dopants by various analysis. We obtained that the clearing point temperature T_C decreases when the salt concentration increases.

On the contrary T_C is almost independent from the acid concentration, meanwhile increasing the acid concentration we observed an increasing of both the perpendicular resistivity and the cutoff frequency. The perpendicular dielectric constant doesn't change significantly in any case.

The mixtures with $\mathrm{SALT} = 8\mathrm{wt\%} \div 12\,\mathrm{wt\%}$ and $\mathrm{ACID} = 2\mathrm{wt\%} \div 6\mathrm{wt\%}$ are good candidates to replace MBBA for electroconvenction experiments but we must be able to reach greater ions concentration and it's not possible by our dopants. In particular the impurities present in M5 preparations (in presence of the acid and salt dopants) could play a fundamental role for this purpose but more studies are required. The author are indebted with dr. Marco Castriota and prof. Enzo Cazzanelli for helpful discussion on electrical impedance analysis.

REFERENCES

[1] Shi, J., Wang, C., Surendranath, V., Kang, K., & Gleeson, J. T. (2002). *Liquid Crystals*, *29*(6), 877.

[2] de Gennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, 2nd ed., Oxford University Press, Oxford, New York, Tokyo.

[3] (a) Kai, S. & Zimmerman, W. (1990). *Rev. Lett.*, *64*, 1111.
  (b) Kai, S. & Zimmerman, W. (1989). *Prog. Theor. Phys. Suppl.*, *99*, 458
  (c) Kai, S., Hayashi, K., & Hidaka, Y. (1996). *J. Phys. Chem.*, *100*(19), 007.
  (d) Kai, S., Andoh, M., & Yamaguchi, S. (1992). *Phys. Rev. A*, *46*, R7375.
  (e) Kai, S. & Zimmermann, W. (1992). *Phys. Rev. A*, *46*, 4954.
  (f) Scaramuzza, N., Versace, C., & Carbone, V. (1995). *Mol. Cryst. Liq. Cryst.*, *266*, 85.
  (g) Carbone, V., Scaramuzza, N., & Versace, C. (1997). *Physica D*, *16*, 314.

[4] (a) Strangi, G., Versace, C., Scaramuzza, N., Lucchetta, D. E., Carbone, V., & Bartolino, R. (1999). *Phys. Rev. E*, *59*(5), 5523.
  (b) Vena, C., Versace, C., Strangi, G., Bruno, V., Scaramuzza, N., & Bartolino, R (2005). *Mol. Cryst. Liq. Cryst.*, *441*, 1.