

International School of Liquid Crystals  
15<sup>th</sup> Workshop

## Liquid Crystal Phases and Nano-Structures

*A Workshop to celebrate ten years of the  
International Liquid Crystal School  
and Claudio Zannoni 60<sup>th</sup> birthday*

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# Posters

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# Absence of any thermal signature of the $N_u$ - $N_b$ phase transition in high-resolution calorimetry of a liquid crystalline organo-siloxane tetrapode with a $N_b$ phase

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## Abstract

We report on a detailed high-resolution adiabatic scanning calorimetry (ASC) investigation of the liquid crystalline organo-siloxane tetrapode DW-16 reported to exhibit an isotropic to nematic (I-  $N_u$ ) transition around 320 K and a uniaxial to biaxial nematic ( $N_u$ - $N_b$ ) transition around 310 K [1]. In the range between 295 K and 325 K sequential ASC heating and cooling runs were performed with different scanning rates between  $0.15 \text{ Kh}^{-1}$  and  $3.4 \text{ Kh}^{-1}$ . The enthalpy and specific heat capacity ( $C_p$ ) results for the I- $N_u$  transition were fully reproducible for different scanning rates and upon heating and cooling. The transition temperature was constant at  $T_{INu} = 318.06 \pm 0.01 \text{ K}$ . The transition is very weakly 1<sup>st</sup> order with a latent heat  $L = 0.20 \pm 0.02 \text{ J/g}$  and substantial pre-transitional  $C_p$  increases were observed. Around the expected  $N_u$ - $N_b$  transition at 310 K and in the whole range between 303 K and  $T_{INu}$  no thermal signature could be detected in our ASC scans or in DSC scans performed at much faster scanning rates [2].

Our observations indicate that the transition from the  $N_b$  to the  $N_u$  phase must involve an extremely small transition heat (smaller than  $0.001 \text{ J/g}$ ). In several of the runs for temperatures below 303 K strongly 1<sup>st</sup> order transitions (rate dependent) were observed by ASC, though not by DSC measurements. These transitions are ascribed to the melting or solidification of the compound.

It seems impossible so far to detect the  $N_b$  phase in measurements that do not involve any external field [2, 3]. These findings seem to support the recent theoretical predictions that the  $N_u$ - $N_b$  transition is rather field-stabilised than spontaneous [4]. Further systematic experimental investigations are definitely needed in order to arrive at a solid conclusion.

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## REORIENTATION EFFECT ON THE CURRENT-VOLTAGE CHARACTERISTICS OF A NEMATIC CELL

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### Abstract

Possible mechanisms explaining the character of the relation  $I=I(V)$  for nematic cell subjected to a large electric field are discussed, taking into account the reorientation effect of the nematic director induced by the external electric field. An interpretation of the experimental data is rather simple, if the sample can be considered free of ions. In fact, in this case, the liquid crystal behaves as an isotropic medium, whose conductivity and dielectric constant are the ones perpendicular to the nematic director. When we work with a large electric field, the liquid crystal behaves as a uniaxial crystal, whose optical axis coincides with the director. In this work, we present a theoretical approach that connects the current in the external circuit with the nematic deformation, in the simple case where the time variations of the difference of potential applied to the sample is slow with respect to the diffusion time for the nematic orientation. In addition, it is shown that the time variation of the equivalent capacitance of the cell is equivalent to a pure resistance, and is responsible for a current peak when the applied voltage overcomes the threshold voltage for the transition of Fréedericksz.

# Self-Assembled Chiral Superstructures Composed of Rigid Achiral Molecules and Molecular Scale Chiral Induction by Dopants

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We explore the phase behavior of a rigid achiral bent-core model system. Nematic and smectic phases form at higher densities, whereas micelles and columns composed of chiral clusters of these molecules self-assemble at lower densities. No nucleation mechanism requiring transient chirality is possible in the formation of these chiral superstructures due to the rigid achiral nature of the substituents. We show the chiral micelles are minima of the potential energy surface using energy minimization and parallel tempering simulations. Chiral dopants were found to induce the system to adopt a consistent chiral twist direction, the first molecular scale computer simulation of this effect.

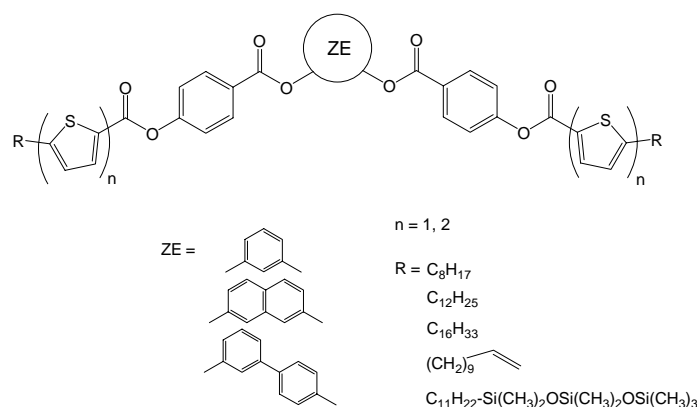
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# Bent – core molecules with thiophene units

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Oligothiophenes are a present topic in materials science research especially due to the use as conductors and semiconductors in organic field-effect transistors, organic light-emitting diodes and solar cells. Herein a novel class of bent-core molecules with a thiophene unit has been synthesized and investigated. The general structure of the compounds is shown in the figure below.



As central unit a benzene ring, a naphthalene core or a biphenyl unit is used. From the chosen substitution pattern the typical bending angle of about 120° results. At the end of the two rod-like wings either 2,5-disubstituted thiophene rings or 5,5'-disubstituted 2,2'-bithiophene units were integrated. Terminal side chains of different lengths are attached. In addition a bent-core molecule containing siloxan units was synthesized.

The self-organization of these molecules was investigated by polarization microscopy, DSC, X-ray scattering and electrooptical methods. The banana-shaped molecules exhibit different mesophases. Besides non switchable columnar phases, antiferroelectric and ferroelectric smectic phases were achieved.

## Acknowledgments

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## Novel complex mesophases by bolaamphiphilic terphenyl derivatives

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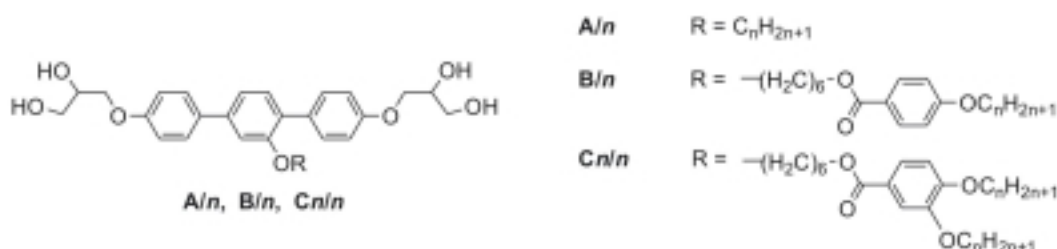
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Novel bolaamphiphiles, consisting of a rod-like terphenyl unit, polar glycerol groups at each end and a linear alkoxy chain in a lateral position, have been synthesized.

These polyphilic triblock molecules were investigated by variation the length of the alkyl chain. In addition compounds with bulky benzoate substituents attached to the end of the alkyl chain also have been synthesized [1].



The mesophase behaviour of the synthesized compounds was investigated by means of polarization microscopy, DSC and X-ray scattering. By enlarging the lateral substituent, these bolaamphiphilic terphenyl derivatives show a similar mesophase sequence like analogue biphenyl derivatives [2]. A transition from a distorted layer structure ( $\text{SmA}^+$ ) via a series of columnar cylinder structures ( $\text{Col}_r/c2mm$ ,  $\text{Col}_{sq}/p4mm$ ,  $\text{Col}_r/p2gg$ ,  $\text{Col}_{hex}/p6mm$ ) to a lamellar phase ( $\text{Lam}_{sm}$ ) takes place.

Based on X-ray diffraction pattern the structure of the  $\text{SmA}^+$  phase was characterized and represents a distorted organization of rhombic cylinders.

Also a new rectangular columnar phase with a  $p2mm$  symmetry was observed.

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# **Aerosil dispersed cyanobiphenyls: results from dielectric spectroscopy on 9CB and 10CB**

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## **Abstract**

The dielectric study of aerosil dispersed liquid crystals has shown that both surface and disorder effects stem from the presence of these network-forming nanoparticles [1]. The interaction with the surface results in a retarded molecular relaxation, showing as an additional low frequency process. The disorder effect can be seen in different ways. Some approaches will be discussed and applied to cyanobiphenyls. In this work, results will be presented for 9CB and 10CB.

The ratio of the dielectric strengths of both relaxation processes in the nematic phase will be used as a measure for the order in a sample. This approach can be used for the cyanobiphenyls, for which the dipole moment is mainly along the long molecular axis. Comparison of the ratio for bulk samples and aerosil dispersions shows that the aerosil dispersion are disordered, even in the presence of an strong external aligning field.

The effect of disorder can also be seen in the liquid crystalline phases. Comparison of the relaxation times shows an acceleration of the short axis relaxation in aerosil dispersed liquid crystals. This is attributed to the disturbance of the nematic order by the aerosil network. The sample appears somewhat more isotropic-like and the relaxation process evolves in the direction of the smaller relaxation times of the isotropic phase [1,2]. These effects are seen for both 9CB and 10CB.

Finally, a smaller acceleration has been found in the isotropic phase of cyanobiphenyls, which we have attributed to the disturbance of the dipole-dipole interaction of these association liquid crystals [3]. We verified this for 9CB.

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# Statistical temperature molecular dynamics simulations of self-organising fluids

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Recently developed Statistical Temperature Molecular dynamics (STMD) uses the relation between statistical temperature and density of states [1-3]; effectively combining multicanonical molecular dynamics with Wang-Landau sampling by dynamic update of the statistical temperature estimate, generating a random walk in potential energy space.

Here we show STMD can be applied to self assembling liquids. We provide results for the isotropic-nematic phase transition of model liquid crystal system where the new soft-core spherocylinder potential [4] is used. We validate the results by comparing them with traditional canonical (*NVT*) simulations. Further on we show that the technique can be used to find mesophases in more complex molecular system by applying it to model diblock copolymer system at the vicinity of isotropic-nematic phase transition.

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# Order and dynamics inside H-PDLC nanodroplets: an ESR spin probe study

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## Abstract

We have performed a detailed study of the order and dynamics of the commercially viable BL038 liquid crystal (LC) inside nanosized (50–300 nm) droplets of an actual reflection-mode Holographic-PDLC (H-PDLC) device where the nanodroplets are located in layers alternated to polymer layers forming a diffraction grating. We have determined the macroscopic configuration of the LC local nematic domain director and we have derived a model of the nanodroplet organization inside the layers. To do this we have taken advantage of the high sensitivity of the electron spin resonance (ESR) spin probe technique, not previously used to study these materials. The spectroscopic analysis was conducted at a series of temperatures ranging from the nematic to the isotropic phase of the LC. In conjunction with SEM images of the H-PDLC cross-section, which provide additional information on the nanodroplet size and shape distribution, the observed director configuration has been modeled as a bidimensional (cylindrical) distribution of elongated nanodroplets (prolate ellipsoid) whose long axis is, on the average, parallel to the layers and whose internal director configuration is a quasi-monodomain (“stretched” bipolar) aligned along the nanodroplet long axis. Interestingly, at room temperature the molecules tend to keep an average orientation parallel to the nanodroplet layers even when these are perpendicular to the magnetic field, suggesting that the molecular organization is dictated mainly by the confinement. This result might explain, at least in part, (i) the need for switching voltages significantly higher and (ii) the observed faster turn-off times in H-PDLCs compared to standard PDLC devices.

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# Study of de Vries properties in Antiferroelectric Smectic Liquid Crystals

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Here we present the results of experimental study on different antiferroelectric liquid crystal (AFLC) materials using a number of techniques such as optical birefringence, electro-optics and measurements of optical thickness of free standing films. Despite differences in the molecular structures all studied AFLC materials also possess de Vries type of SmA in a temperature range higher than SmC\*.

Figure 1 presents the temperature dependence of the normalized optical film thickness for (○) having conventional SmA (Felix-18) and number of de Vries materials which are also antiferroelectric LCs. This technique shows a good correlation with X-ray measurements of smectic layer thickness [1] In SmA phase conventional SmA-SmC material shows smectic layer expansion on cooling while de Vries AFLC materials show a bump in SmA phase due to increasing molecular tilt.

Figure 2 shows the temperature dependence of the birefringence without (○) and with (●) applied voltage and the de Vries cone (tilt) angle (□) for D2R1-14. The cone angle was calculated from the comparison of two birefringence values measured with ( $\Delta n_0$ ) and without ( $\Delta n_{eff}$ ) electric field.

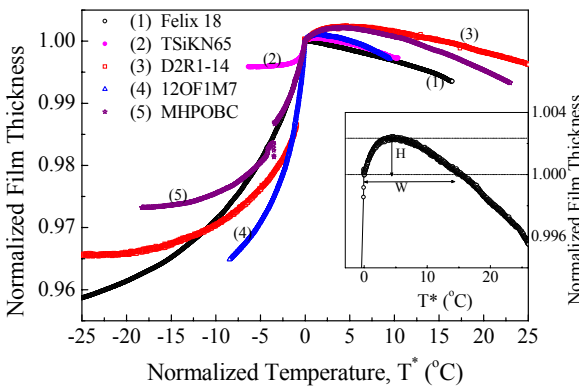


Figure 1

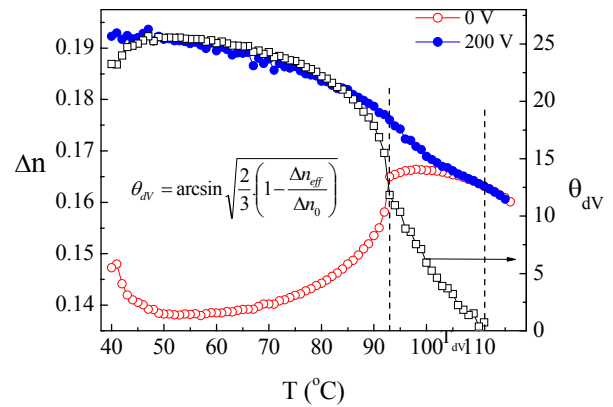


Figure 2

Usually the AFLC and de Vries materials were studied independently of each other. Nevertheless all the studied materials show both classes of sub-phases: the de Vries and antiferro- and ferri-electric. This coincidence leads to the conclusion that these two different classes of liquid crystals are related to each other. Moreover, they may probably have the same physical origin, namely the existence of weak synclinic (or reduced anticlinic) correlations between the neighbouring molecular tilt directions.

The results of our experimental study provide a challenge for new theoretical approaches to describe both classes of smectics is needed.

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# Aligned Single Wall Carbon Nanotubes in Thermotropic Polymer Liquid Crystals: Preparation and Characterization

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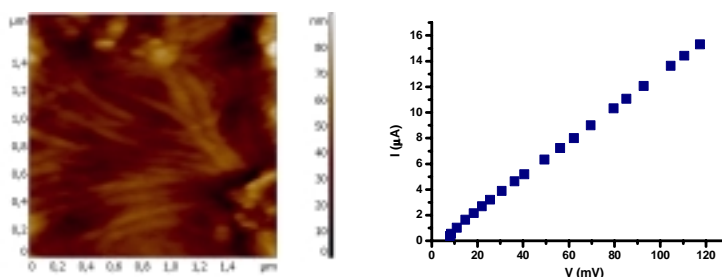
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Polymer Liquid Crystals (LCPs) are materials that, under suitable conditions of temperature, pressure and concentration exist as a Liquid Crystal (LC) mesophase[1]: it means a state of aggregation intermediate between the crystalline solid and the amorphous liquid. Although LCs combine the properties of a solid and an isotropic liquid, they exhibit very specific electrooptical phenomena, which have no corresponding analogues in solids or in isotropic liquids. Transition to those intermediate states may be brought about by thermal processes (*thermotropic* mesomorphism) or by the influence of solvents (*lyotropic* mesomorphism).[1]

In this work we investigated the possibility to use thermotropic liquid crystal polymer PET/HBA (poly 4-hydroxybenzoic acid-coethylene terephthalate) for preparation of Single Wall Carbon Nanotubes (SWNTs) based nanocomposites. These materials have been characterized both in morphology and in physical chemical properties. As shown in a typical AFM image (fig.1) the use of proper experimental conditions allowed us to achieve a good alignment of nanotubes bundles. The resulting composites are characterized by interesting charge transport properties and a characteristic ohmic behaviour has been highlighted in I-V measurements.



These well ordered systems represent an important new class of materials, promising for application in the field of non linear optics , of plastic electronics and for fabrication of MEMS devices.

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## DIRECTOR PROFILE OF A NEMATIC LBETWEEN TWO CONCENTRIC CILINDERS IN WEAK AND STRONG ANCHORING SITUATIONS

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Systems that involve liquid crystal alignment between two concentric cylinders have been investigated in connection with the flexoelectric instability [1], with the stability analysis of the orientational profile [2], and the Fréedericksz transition occurring in the absence of external electric field [3]. The starting point of these analysis was the original problem proposed by Meyer, solved in a special case by Parodi, and then discussed in the book by de Gennes [4]. Subsequently, the same problem was reexamined by Williams [5] by considering that the elastic constants of splay and bend are different, in the strong anchoring approximation. The determination of the equilibrium director profile can be formulated in terms of boundary value problems [6]. On the other hand, the situation in which the easy axes characterizing the preferred surface alignment change direction continuously with time is relevant to investigate systems whose surfaces are covered with photopolymeric films [7]. We face here a generalization of the model, characterized by a nematic confined between two cylinders, like in Refs. [3, 5]. This system is formed by considering that on each cylindrical surface the treatment has ensured a spatial distribution of the easy directions. The present approach also incorporates time dependence in the distribution of easy axes on the surfaces, in the situation of weak anchoring, which is a more difficult mathematical problem, but can represent a more realistic physical situation. Our analysis is quite general in the framework of the usual approximation of one-elastic constant; it takes into account an external field, directed along the radius of the cylinders, in the limit of small distortions. To face the dynamical reorientation problem in a complete manner it is necessary to take into account that the motion of the fluid is coupled with the fluid flow, i.e., to consider backflow effects, that in the present problem, is a consequence of the confinement. Therefore, the resulting flow patterns are quite complicated and even keeping the small distortion approximation as we are doing in the present analysis, the set of equations to be solved are hardly treatable in analytical manner, reason for the which, we restrict the present analysis to the very simplified case in which backflow effects are not taken into account. Anyway, the formalism presented here in terms of Green function and Bessel function of modified argument constitutes the appropriate mathematical framework to explore orientational field effects in nematic samples in confined geometries.

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