Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

![ESRF logo]	**Experiment title:** **Liquid crystal nanoparticle dispersions**	**Experiment number**: **HD-538**
Beamline: **ID 02**	**Date of experiment**: from: **23 Sep 2011** to: **25 Sep 2011**	**Date of report**: **1 Sept 2012**
Shifts: **6**	**Local contact(s)**: **Manuel Fernandez-Martinez** (email: manuel.fernandez@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Main Proposer:

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Co-Proposer:

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Report:

Liquid crystals (LCs) are essential for modern display applications. During the last years, the development of nanotechnology has initiated international efforts to study the influence of nanoparticles (NPs) dispersed in liquid crystals. It is known that doping LCs with NPs can enhance or disturb the electro-optic performance of LCs, significantly. Adding a few per cent of NPs can even reverse the electro-optic contrast of a display. However, basic studies on the microscopic effect of NPs on the LC structure are pre-mature. This project is focussed on studying the effects of ferroelectric $BaTiO_3$ particles on the phase transitions, structure and degree of order of

1) the nematic and smectic phase of thermotropic liquid crystals and

2) mesophases formed by aggregation of dye molecules in aqueous solution (chromonics).

In the 6 shifts of beamtime that were allocated to us at beamline ID02, we achieved the following results:

1) Influence of ferroelectric nanoparticles on nematic (N) and smectic A (SmA) phases of thermotropic liquid crystals

As an LC model system, we used a binary mixture of 4'-octyl-biphenyl-4-carbonitrile (8CB) and 4'-octyloxy-biphenyl-4-carbonitrile (8OCB), which shows the phase sequence crystalline (Cr) – smectic A (SmA) – nematic (N) – isotropic (I) in a convenient temperature range. To study the influence of ferroelectric nanoparticles, we utilized a new technique, where grinding $BaTiO_3$ yields both ferroelectric (tetragonal) and non-polar (cubic) nanoparticles of similar size, which can be separated in a subsequent "harvesting" process by means of a strong inhomogeneous electric field [G. Cook, J. L. Barnes, S. A. Basunm D. R. Evans, R. F. Ziolo, A. Ponce, V. Y. Reshetnyak, A. Glushchenko, and P. P. Banerjee, J. Appl. Phys. **108**, 064309 (2010)].
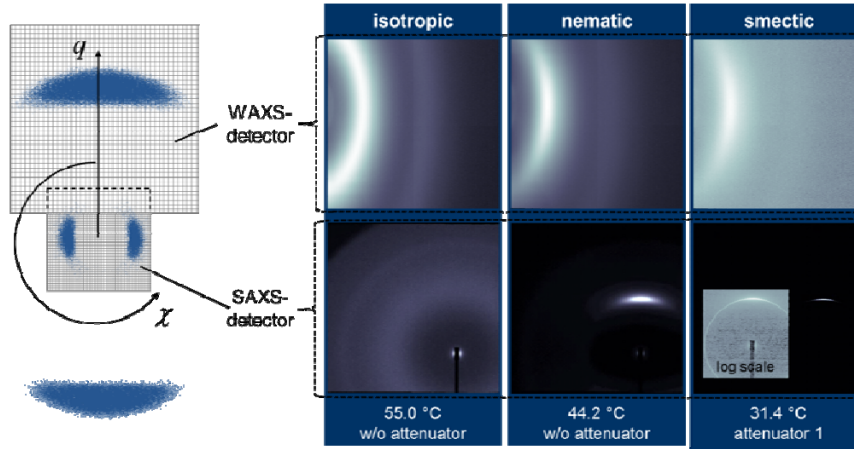
Fig. 1. Recording of the diffraction patterns (scheme). To the right: Recorded diffraction patterns of a LC in the isotropic, nematic and smectic phase, respectively.

The phase transition N $\rightarrow$ SmA is of second or weakly first order. The phase transition temperature can be extracted from the peak shape of the SAXS signal [A. Primak, M. Fisch, S. Kumar, Phys. Rev. E. 66, 051707 (2002)] by analyzing the smectic structure factor

$$S(q) \propto \frac{1}{\xi_{\parallel}(q - q_{center})^2} \qquad (1)$$

In a fitting routine, the SAXS signal was deconvolved with a Gaussian of variable width. Subsequently, the temperature dependence of the smectic correlation length $\xi_{\parallel}$ was extracted (Fig. 2).
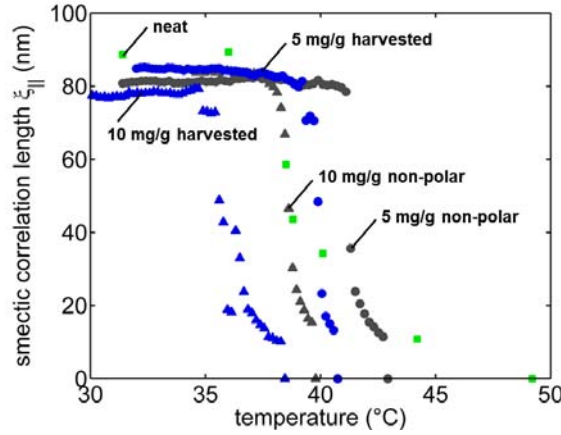

Fig. 2. Smectic correlation length vs. temperature.

Doping with BaTiO$_3$ nanoparticles leads to small increases in $d_{//}$ in the SmA$_d$ phase as compared to the pure LC (Fig. 3). Non-polar nanoparticles increase $d_{//}$ by 0.5% and 1.2% in 5 mg/g and 10 mg/g concentrations, respectively. Harvested nanoparticles lead to a slightly larger increase in $d_{//}$ of 1.5% and 3.3% for 5 mg/g and 10 mg/g concentrations, respectively.

The well-known method of Davidson, et al., [P. Davidson, D. Petermann, and A. M. Levelut, J. Phys. II 5, 113 (1995).] was used to estimate the orientational order parameter S from azimuthal scans (χ-scans) of the diffuse peaks in the WAXS region of the diffraction patterns of calamitic LCs. The position of this peak is a measure of the average intermolecular separation in the direction perpendicular to the molecular long axis ($d_\perp$) [W. L. McMillan, Phys. Rev. A 4, 1238 - 1246 (1971).]. Analysis of χ-scans through this peak yields information on S because the peak-width depends on the degree of orientational order of molecules in the scattering volume. Doping decreases the isotropic $\rightarrow$ nematic phase transition temperature (Fig. 4).
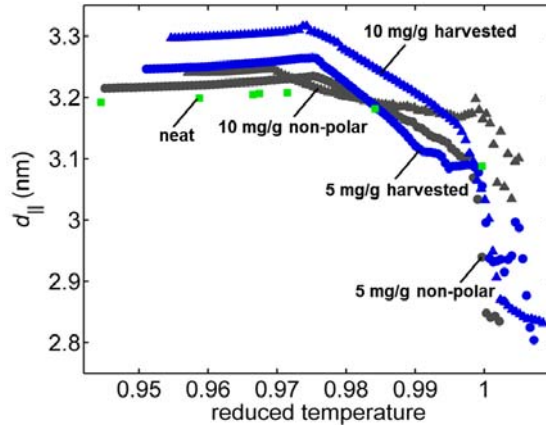
Fig. 3. Temperature dependence of the smectic layer spacing $d_{||}$.

The well-known method of Davidson, et al., [P. Davidson, D. Petermann, and A. M. Levelut, J. Phys. II 5, 113 (1995).] was used to estimate the orientational order parameter S from azimuthal scans (χ-scans) of the diffuse peaks in the WAXS region of the diffraction patterns of calamitic LCs. The position of this peak is a measure of the average intermolecular separation in the direction perpendicular to the molecular long axis ($d_\perp$) [W. L. McMillan, Phys. Rev. A 4, 1238 - 1246 (1971).]. Analysis of χ-scans through this peak yields information on S because the peak-width depends on the degree of orientational order of molecules in the scattering volume. Doping decreases the isotropic $\rightarrow$ nematic phase transition temperature (Fig. 4).
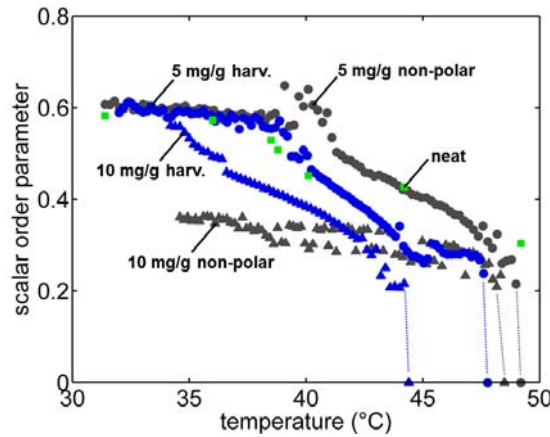

Fig. 4. Scalar order parameter S vs. temperature.

In addition to basic studies on the structure of nematic and smectic host, we used the beamtime at ESRF to test an experimental procedure that is intended to enable us perfoming X-ray studies while applying an electric field to the sample. This is very delicate problem because realigning a liquid crystal requires very high electric field strength, which is usually achieved at moderate voltage by confining the liquid crystal between electrodes with a spacing of only a few microns. For our studies, we tested a liquid crystal with negative dielectric anisotropy and used two cover slides coated with ITO as electrodes. The preliminary results show clearly that the substrates used in our setup are sufficiently transparent to allow X-ray studies while applying a sufficiently high electric field: As expected, the WAXS signal decreased, while the SAXS signal increased with increasing voltage, indicating the realignment of the LC director (Fig. 5a,b). However, this preliminary study yielded also an unexpected result, which was not observed in the smectic system: Additional first-, second-, and third-order reflections were observed in small angle X-ray scattering curves of a NP-doped nematic LC (EN 18) at $q_1 = 1.367$ nm^{-1}, $q_2 = 2.735$ nm^{-1}, and $q_3 = 4.101$ nm^{-1} (Fig. 5c). These signals can be attributed to Bragg diffraction from micro-crystallites with a correlation length of ≈ 377 nm. The d-spacing inside these micro-crystallites is 4.56 nm, which approximately corresponds to the double of the molecular length l. Obviously, the observed micro-crystallites consist of ≈ 80 molecular bilayers of LC molecules.

(a,b) **(c)**
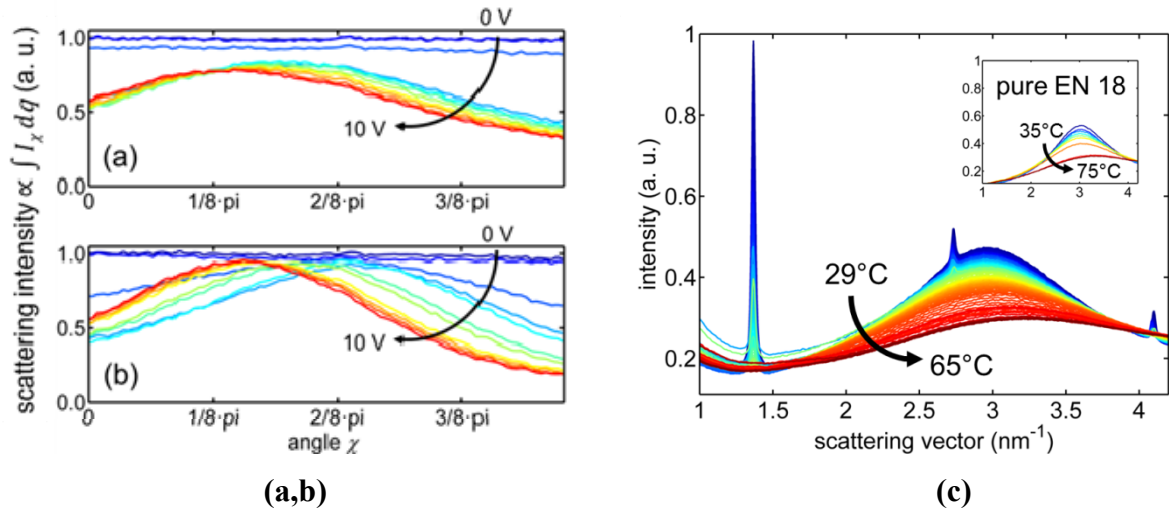
Fig. 5. Scattering intensity observed for EN 18: (a,b) χ-scans for different voltages. (c) Development of the intensity vs. magnitude of scattering vector with temperature for EN 18 doped with ferroelectric NPs and undoped (inset), respectively. The samples were slowly heated (start and end-temperature indicated).

In summary, the results on thermotropic liquid crystals yield the following conclusions:

- Adding $BaTiO_3$ nanoparticles reduces the smectic A – nematic transition temperature. This effect is larger for ferroelectric particles than for non-polar particles (Fig. 2).

- Adding $BaTiO_3$ nanoparticles leads to an increase of the smectic layer spacing, which can be attributed to enhanced dimer formation. Again, this effect is larger for ferroelectric particles than for non-polar particles (Fig. 3).

- Adding $BaTiO_3$ nanoparticles reduces the smectic nematic – isotropic transition temperature. This effect is also larger for ferroelectric particles than for non-polar particles. However, the higher concentration (10 mg/g) of non-polar particles caused a dramatic reduction of the orientational order parameter in the nematic phase, which was not observed for ferroelectric NPs (Fig. 4).

- Preliminary studies on electric field effects confirm that we have succeeded in preparing samples which enable X-ray diffration studies under the influence of large electric field strengths (Fig. 5a).

- Doping EN 18 with ferroelectric NPs may induce the formation of molecular microcrystallites (Fig. 5b). This phenomenon was not observed for nonpolar NPs and undoped samples, and never in the smectic LC that was studied.

These fundamental studies on the influence of ferroelectric NPs in LCs are - to the best of our knowledge – the first systematic studies on the difference between ferroelectric and non-polar NPs dispersed in LCs, which utilize synchroton radiation, thereby yielding detailed informations on the mesophase structure. Our interesting first results leave several open questions, which need investigation in forthcoming studies:

- To which extent are the structure changes observed in the smectic LC universal? Do they appear also in other liquid crystal hosts?

- Which structural changes cause the dramatic changes in the electro-optic performance that were reported for other LCs, which are important for applications? Here, the successful test of our sample preparation is an important milestone.

- Does the formation of molecular microcrystals play an important role in amplifying the effect of small amounts of nanoparticles on the mesophase structure?

We plan to continue the studies at ESRF in order to further invesitgate these important questions.

2) Structure of Nematic and Columnar Chromonic Mesophases of Disodium Cromoglycate

by [a] *Dena M. Agra-Kooijman*, [b] *Alexander Lorentz,* [a] *Gautam Singh,* [b] *Heinz Kitzerow,* and [a] *Satyendra Kumar* [[b] *University of Paderborn, Paderborn Germany;* [a] *Kent State University, Kent, OH USA 44242*]

Generally, plank-like molecules with ionic groups at their periphery form columnar assemblies via face-to-face stacking when dissolved in water. The assemblies thus formed undergo macroscopic orientational and positional ordering to form the nematic (N) and columnar (M) liquid crystalline phases, respectively. These systems are referred to as chromonic liquid crystals. Aqueous solutions of disodium chromoglyacate (DSCG) constitute one of the chromonic systems that has drawn much attention from scientific community. Evidence of chimney-like organization of columnar stacks of DSCG was reported some time ago [J. Lydon, *New Models for the Mesophases of Disodium Cromoglycate*, Mol. Cryst. Liq. Cryst. **64**, 19 (1980)]. But, a different type of molecular assembly was recently reported on the basis of a neutron scattering study [L. Wu, J. Lal, K. Simon, E. Burton and Y.-Y Luk, *Nonamphiphilic Assembly in Water: Polymorphic Nature, Thread Structure and Thermodynamic Incomplatibility*, J. Am. Chem. Soc. **131**, 7430 (2009)]. This study professed a 'threadlike' assembly of molecules, resembling a linear-polymer in place of columnar stacking, consisting of two or more layers of molecules connected through salt bridges. The threads then supposed to assemble to form the N and M phases.

In order to have deeper insight into the nature of DSCG molecular assemblies and mesophase formation and to determine which of the two models (if either) describes their structure, we investigated aqueous solutions at 18, 20 and 25 wt % concentrations of DSCG at ESRF during the beamtime allocated to our team led by Prof. Kitzerow. These concentrations were chosen to access the different parts of the phase diagram and mesophases at different temperatures.
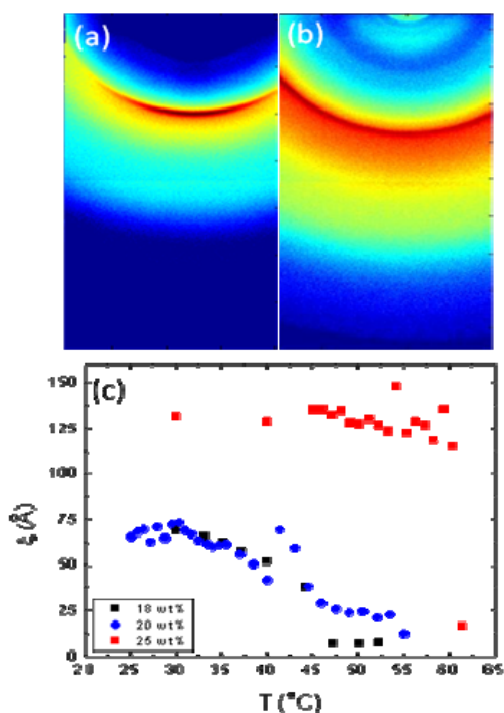

Fig. 6. WAXS patterns at (a) 33ºC (N) and at (b) 53ºC (M). Temperature dependence of the aggregate height at various concentrations.
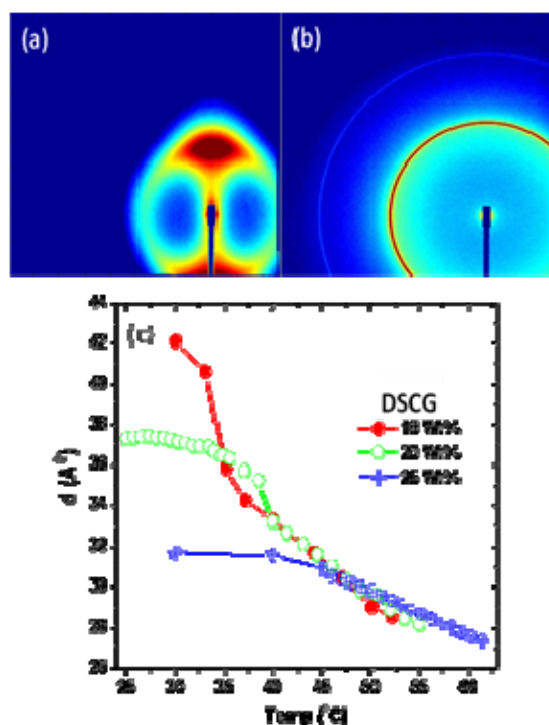

Fig. 7. SAXS patterns at (a) 33ºC (N) and at (b) 53ºC (M). (c) T dependence of d-spacing at various concentrations.

The WAXS data show that the position of the reflection at 3.38 Å, corresponding to the π-π stacking of the aromatic part of the DSCG molecules, is essentially temperature independent. Correlation length in the direction of the aggregate's long axis (i.e., height of the columns), estimated from the peak width reveals how it changes with temperature and concentration, Fig.6. The ratio of the aggregate height to the π-π stacking of molecules (3.38 Å) gives us the number of molecules per stack at a given concentration and temperature. In the nematic phase (N), there are 18-20 molecules per stack while in the columnar phase (M) there are more than 40 molecules per stack.

The other pair of reflections at small angles is in the direction perpendicular to the direction of molecular stacks (Fig. 7a and 7b) and measures the lateral distance between the columnar stack. From the width of the SAXS peaks, we estimate between 2-4 columns being positionally correlated in the N phase. This number in the M phase is much higher and limited by the average cluster size.

The results clearly show that the inter-column separation is compatible with simple hexagonal packing and does not support chimney-like organization. On the other hand, a threadlike assembly of DSCG molecules would have a very short correlation length in the lateral direction and long correlation length in the direction of the fibers. We see no evidence of this behavior. Clearly, simple columnar aggregation and orientational and hexagonal ordering appears to be taking place in the N and M phases, respectively.

This work about chromonics was presented at the March APS 2012 meeting and at the ILCC 2012 [see below], and a manuscript is in preparation for submission to PRE.

References

The results of this study were presented at the International Liquid Crystal Conference 2012 and at the March APS 2012 meeting:

- A. Lorenz, N. Zimmermann, S. Kumar, D. R. Evans, G. Cook, M. Fernández Martínez und H.-S. Kitzerow: „Doping an eutectic mixture of 8CB and 8OCB with harvested ferroelectric nanoparticles", Poster PIII-087 (Abstract 5551-0161), 24th International Liquid Crystal Conference, Mainz, Germany, 19.08.-24.08.2012.

- Satyendra Kumar: "Molecular Aggregation in Disodium Cromoglycate", Oral presentation at March American Physical Society Meeting, Boston (MA), March 2012.

- Satyendra Kumar: "Structure of nematic and columnar chromonic mesophases of disodium cromoglycate: New perspectives", Oral presentation, 24th International Liquid Crystal Conference, Mainz, Germany, 19.08.-24.08.2012.

In addition, the results have been published in the following peer-reviewed scientific journals:

- Lorenz, N. Zimmermann, S. Kumar, D. R. Evans, G. Cook, and H.-S. Kitzerow: "Doping the nematic liquid crystal 5CB with milled $BaTiO_3$ nanoparticles", Phys. Rev. E **86**, 051704 (2012). DOI: 10.1103/PhysRevE.86.051704

- Lorenz, N. Zimmermann, S. Kumar, D. R. Evans, G. Cook, M. Fernández Martínez und H.-S. Kitzerow: "Doping a Mixture of Two Smectogenic Liquid Crystals with Barium Titanate Nanoparticles", J. Phys. Chem. B **117 (3)**, 937–941 (2013). DOI: 10.1021/jp310624c

- Lorenz, N. Zimmermann, S. Kumar, D. R. Evans, G. Cook, M. Fernández Martínez und H.-S. Kitzerow: "X-ray scattering of a nematic liquid crystal nano-dispersion with negative dielectric anisotropy", Invited Article, Applied Optics **52 (22)**, E1-E5 (2013); DOI: 10.1364/AO.52.0000E1

- D. M. Agra-Kooijman, G. Singh, A. Lorenz, P. J. Collings, H.-S. Kitzerow, and S. Kumar: „Columnar Molecular Aggregation in the Aqueous Solutions of Disodium Cromoglycate", Phys. Rev. E **89**, 062504 (2014); DOI: 10.1103/PhysRevE.89.062504