ESRF	**Experiment title:** Nematic to centered rectangular to hexagonal transitions in neutral DNA lamellar phase : a supported film experiment.	**Experiment number**: 32-02-655
Beamline: BM32	**Date of experiment**: from: **10-Oct-2007** to: **17-Oct-2007**	**Date of report**: 02/2010
Shifts: 18	**Local contact(s):** Jean Sébastien MICHA	*Received at ESRF:*

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Report:

Objective & expected results

On capillary samples (non oriented) we observed a phase transition from a "nematic" DNA (diluted systems) to a centered rectangular columnar DNA lattice (concentrated systems) organization between the neutral lipid bilayers of a lamellar phase. Unfortunately, the limited resolution, as well as the low intensity of our set up did not enable us to definitely index all the Bragg reflections. **The aim of this new experiment was to study precisely this unexpected phase transition,** using oriented samples (supported or suspended films) with a special chamber for humidity control.

Results and the conclusions of the study

We studied the structure of our neutral system varying the lipid-to-DNA weight ratio and the water concentration. The various samples were prepared and controlled at Centre de Recherche Paul-Pascal. We used the supported film geometry in order to obtain well oriented samples as established during the SI-1304 and SI-2260 runs. Our new chamber with humidity control was brought from CRPP. It easily fits to the BM32 goniometer with a specific holder. We worked with the selected energy of 12 keV, corresponding to a wavelength of λ=1.0332Å. The scattered X-rays were recorded on a 2D CCD array detector (Princeton 1242*1242 pixels). In order to check the film orientation, we used the reflectivity geometry.

First step: we checked the new chamber for humidity control stability.

Second step: the first film experiment allowed us to adjust the geometry, to choose the slit width, the beam size and the sample-to-detector distance in order to optimize the resolution and the accessible wave vector domain. The first few films (two different films) were realized with DNA-free samples (ϕ_{lipid} = 0.6 and ϕ_{water} = 0.4) in order not to spoil too many DNA samples. We observed a difficulty to reach 100% relative humidity in the sample with the new device. In order to get fully hydrated lamellar phases, we added a water tank inside the device to saturate the environment. We were then able to precisely control the variation of the smectic periodicity by finely adjusting the temperature of the film and the temperature of the water tank located under the supported film.

Third step: Supported films were made with a sample containing DNA (ϕ_{lipid} = 0.6, ϕ_{water} = 0.29, ϕ_{DNA} = 0.11). Fig. 1a displays the scattering data taken while the film is being hydrated in the humidity chamber. This snapshot indicates that the supported film is fairly well oriented with the stacking axis of the lamellae normal to the glass slide (homeotropic orientation) since the diffracted intensity appears as regularly-spaced Bragg spots localized along the vertical axis. The azimuthally-averaged scattered intensity is displayed as a function of the modulus q of the scattering wave vector in Fig. 1b, with up to 6 diffraction orders in the ratio 1:2:3:4:5:6 as expected for a one-dimensional, periodic structure. The inset in the same Fig. 1b corresponds to the radially-averaged intensity at the position of the first-order Bragg peak: The narrow width of the line (FWHM 5.4 deg) confirms that the orientation of the film is indeed quite good, as qualitatively suggested in Fig. 1a. As a function of time the locations in reciprocal space of all the peaks (or significant shoulders) have been followed in azimuthally-averaged spectra, *i.e.* irrespective of their on-axis or off-axis position. The confinement is increased by dehydrating the complex in a controlled way, which leads to a decrease of the water channel thickness separating the periodically-stacked bilayers. Three distinct domains may be identified from the data. A structural phase transition is evidenced, where the "classical" 2D nematic phase of DNA rods embedded within the one-dimensionally ordered lipid lamellar phase observed at high hydration (domain I -Fig.1) is replaced by a 2D hexagonal structure of DNA molecules intercalated between the lipid bilayers (domain III - Fig. 2b).

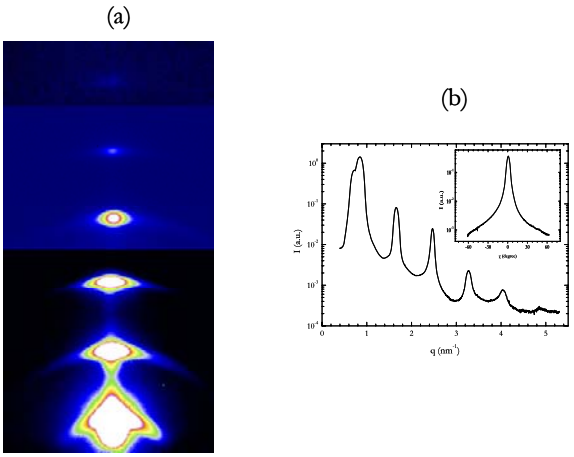

Figure 1 : a) 2D images of the oriented lamellar phase. b) azimuthally-averaged scattered intensity as a function of the wave vector q.

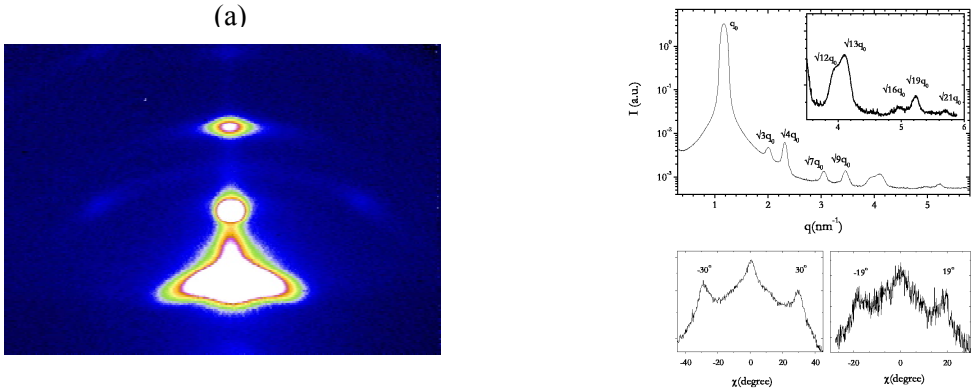

Figure 2: (a) 2D image representative of the complex spectra observed in the later part of domain II. The film remains oriented with respect to the beam line axes and exhibits well defined off-axis diffraction peaks. (b) Azimuthally-averaged spectrum, characteristic of the later stage of domain III, with up to the √21 Bragg reflection visible. Radially-averaged spectra, at the two positions $\sqrt{3}q_0$ and $\sqrt{7}q_0$, exhibit characteristic off-axis peaks at +/-30 deg and +/-19 deg, respectively

We describe a new structural organization in a highly-dehydrated DNA-lipid complex, where DNA rods form a 2D hexagonal structure that intercalates in-between the lipid bilayers of a lamellar structure. Though other two-dimensionally ordered DNA-lipid hydrated complexes have previously been found, where either the lamellar lipid structure was associated to a centered-rectangular DNA assembly, or both lipids and DNA displayed hexagonal order, such a 2D hexagonal (DNA) / lamellar (lipids) is here observed for the first time. At contrast with other studies where the DNA-lipid complexes are prepared in excess water we control the amount of water present in the system, and dehydrate the complex significantly below its swelling limit. This amounts to varying the confinement of the DNA molecules by the lipid bilayers, acting as soft “walls”. The replacement of the usual DNA-lipid nematic (and, therefore, somehow “dilute”) complex by one with the 2D hexagonal symmetry, though still displaying the lamellar structure for the lipid component may thus be seen as a confinement-induced structural transition. It is important to note that the confining lipid “walls” are soft. Our system appears to be original and well suited to the study of confinement effects in DNA-lipid, and possibly other, hydrated complexes.