Experimental report

06/10/2019

Proposal: **9-11-1882** **Council:** 4/2018

Title: Gelled Lamellar Liquid Crystals-
the interplay between liquid crystalline order and gel morphology

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-1858

Main proposer: **Sonja DIETERICH**

Experimental team:
Sonja DIETERICH
Frank GIESSELMANN
Thomas SOTTMANN
Kristina SCHNEIDER
Johanna BRUCKNER
Julian FISCHER

Local contacts: Sylvain PREVOST

Samples: D20, H2O, decanol (h22), decanol (d22), sodium dodecyl sulphate (h25), sodium dodecyl sulphate (d25), 12-hydroxyoctadecanoic acid (h36), 12-hydroxyoctadecanoic acid (d36)

Instrument	Requested days	Allocated days	From	To
D11	3	2	08/10/2018	10/10/2018

Abstract:

Gelled lyotropic liquid crystalline phases are soft materials in which the anisotropy of a lyotropic liquid crystal (LLC) is combined with the mechanical stability of a gel. The two coexisting structures can take over different functions, e.g. in transdermal drug delivery applications a gel would guarantee a convenient application while a lyotropic LC is needed for an effective solubilisation of water-insoluble drugs. Additionally, the combination of LLC and gel may result in synergistic material properties such as stimuli responsive behavior to variations in temperature. Goal of our study is to figure out how the gel network influences structure and order of the lyotropic liquid crystalline phase and vice versa. For this the gelled LLC has to be compared with its "parent systems", the non-gelled liquid crystal and the binary gel. SANS measurements will be an important complementing method to our X-ray measurements since due to contrast variations we will be able to observe the individual contributions of the sub-structures gel and liquid crystal to the scattering profile.

Gelled Lamellar Liquid Crystals- the interplay between liquid crystalline order and gel morphology

9-11-1882

Sonja Dieterich, Ralf Schweins, Sylvain Prévost, Thomas Sottmann, Frank Giesselmann

Abstract: Gelled lyotropic liquid crystalline phases are soft materials in which the anisotropy of a lyotropic liquid crystal is combined with the mechanical stability of a gel. The aim of this study is to determine whether the two coexisting structures (L_α phase and physical organogel) form independently of each other (orthogonal self-assembly) or, if not, in which ways the two structures influence each other. Using the model system D_2O – *n*-decanol – SDS and the low molecular weight organogelator 12-hydroxy-octadecanoic acid (12-HOA), we developed a procedure for the simultaneous formation of the L_α phase and the gel network. Adjusting the contrast allowed us to only observe the scattering contribution of the gel network. We found a pronounced shoulder at $q \approx 0.02$ Å^{-1}, which appears only in case of the gelled L_α phase and not in the gelator-free L_α phase nor in the binary gel. This shoulder vanishes at temperatures above the gel-sol transition temperature $T_{\text{gel-sol}}$. Hence, the lamellar layer structure and the gel fiber network influence each other mutually so that a new supramolecular structure is formed which only occurs if the L_α phase and the physical organogel coexist (cooperative effect).

Motivation: The gelation of lyotropic liquid crystals, which combines the unique properties of a physical gel and an anisotropic fluid, leads to a new class of soft anisotropic materials.Goal of our study was to figure out how the gel network influences the structure and ordering of the lyotropic lamellar phase and vice versa. Therefore, the properties of the gelled L_α phase was compared with its "parent systems", the gelator-free L_α phase and the binary gel (gelled *n*-dodecane). If the two coexisting self-assembled structures form independent of each other, the system is called an orthogonal self-assembled system. If one of the structures influences the other the term soft templating should rather be used.

Investigated System and Experimental Setup: As lyotropic liquid crystalline system, a ternary mixture containing sodium dodecylsulfate (SDS) as surfactant, *n*-decanol (DOH) as cosurfactant and D_2O as solvent is used. As gelator we used the low molecular weight organogelator 12-hydroxyoctadecanoic acid (12-HOA). To systematically investigate the general structure of the gelled lyotropic lamellar phase we performed SANS measurements starting from the composition 67 wt% D_2O, 9 wt% DOH and 24 wt% SDS. Subsequently, we varied the bilayer volume fraction, the co-surfactant to surfactant ratio, the gel network density (used gelator amount) as well as the temperature (below and above the gel-sol transition temperature $T_{\text{gel-sol}}$). For comparison, the structure of the binary organogel *n*-dodecane/12-HOA and the non-gelled L_α phases were studied as well. In order to separate scattering contributions from the fiber network and the lamellar domains we adjusted the contrast by using deuterated surfactant, deuterated co-surfactant and D_2O so that only the scattering of the gel network was monitored. SANS measurements were performed on D11 using a neutron wavelength of $\lambda = 5.3$ Å and sample to detector distances of $d = 2$ m, 8 m and 39 m, which results in a q-range of $0.0014 < q/\text{Å}^{-1} < 0.38$. The experiments were carried out in Hellma cells of 1 mm neutron path length, which were placed in a home-built cell holder for accurate temperature control.

Results: A comparison of the scattering curves of the gelled L_α phase and the gelator-free one exhibits that the lamellar layer distance remains the same in both samples, since the respective lamellar layer peaks of first and second order appear at the same q-value. However, in case of the gelled L_α phase a pronounced shoulder at $q \approx 0.02$ Å^{-1}, which occurs not in the gelator-free L_α phase nor in the binary gel (see Figure 1a). At temperatures above the gel-sol transition temperature $T_{\text{gel-sol}}$ this shoulder vanishes, as can be seen in Figure 1b. Hence, in the gelled L_α phase a new structure has been formed, which only exists if the L_α phase coexists with the gel network. With increasing amount of gelator 12-HOA an additional small peak appears at $q \approx 0.042$ Å^{-1} (see Figure 2a). As expected, by adjusting the gel contrast, only the scattering of the gel fibers contributes to the SANS curve (Figure 2b). However, comparing the scattering of the gel fibers in the gelled lamellar phase and the binary gel a broad peak can be observed in the former system at $q = 0.14$ Å^{-1} indicating of a stronger ordering of the layered gel fibers.

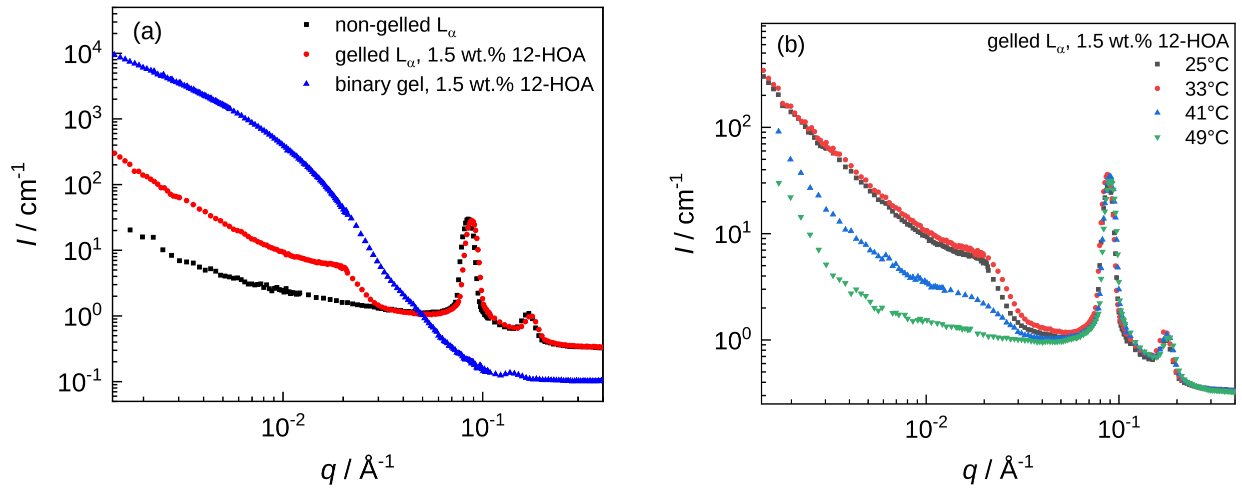

Figure 1: (a) SANS curves of the gelled (1.5 wt% 12-HOA, red) and gelator free L_α phase (black) of the system D_2O – *n*-decanol – SDS, as well as the binary gel *n*-dodecane/12-HOA (blue). (b) Temperature dependent SANS measurements of the gelled L_α phase of the system D_2O – *n*-decanol/12-HOA – SDS.

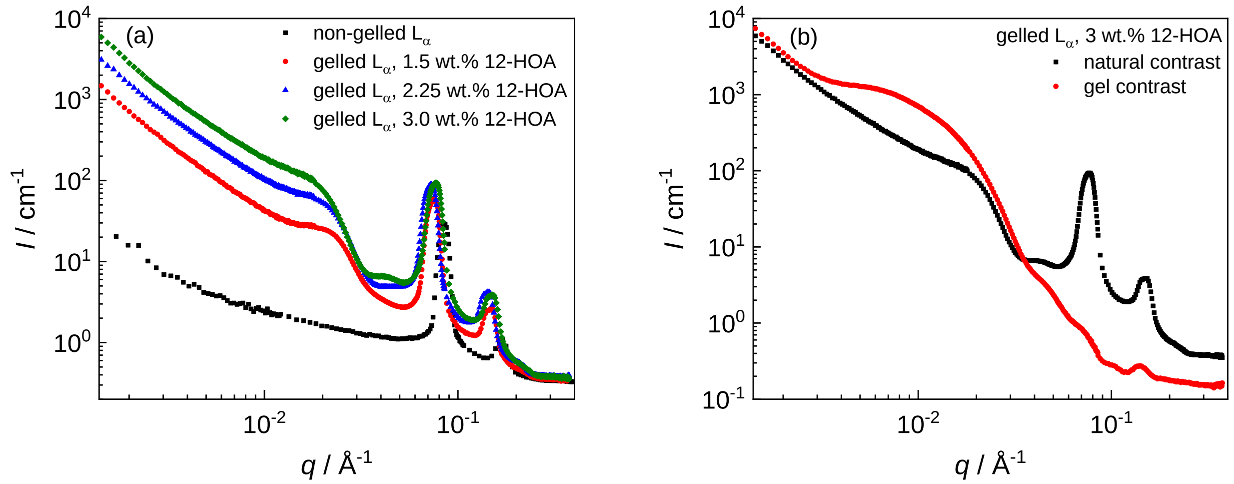

Figure 2: (a) SANS curves of the gelled L_α phase of the system D_2O – *n*-decanol/12-HOA – SDS with varying amount of gelator 12-HOA. (b) SANS measurements of the gelled L_α phase at two different contrasts. In the natural contrast (protonated surfactant, co-surfactant and gelator in D_2O, black) the scattering of both, surfactant bilayers and gel fibers contributes to the SANS curve. In the gel contrast (adjusted d25-SDS/SDS, d21-DOH/DOH, D_2O and protonated gelator, red) only the scattering contribution of the gel fiber network is present.

We currently analyze the recorded data quantitatively. The data will be the core of an upcoming manuscript. Submission is envisaged beginning of 2020.