A single parameter determines mesophase transitions in Swollen Liquid Crystals

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ABSTRACT

We report how the control of a single parameter, the co-surfactant, determines the phase transitions of oil-in-water swollen liquid crystals (SLCs) prepared with cetyltrimethylammonium bromide (CTAB), from cubic to hexagonal, lamellar, and finally sponge-like structures. SLCs are complex mixtures (surfactant + co-surfactant + water + salt + oil) usually prepared to form hexagonal mesophases, with cell parameters tunable between 3 and 30 nm. These hexagonal mesophases were successfully used as nanoreactors to prepare a broad range of nanostructured materials. Because the potential of these mesophases as adaptive nanoreactors has not been extended to other liquid crystal geometries than the hexagonal, we studied in a first step the structure evolution of SLCs made with CTAB, cyclohexane, pentanol-1, water and different stabilising salts. We used small-angle X-ray scattering (SAXS), polarised light microscopy and Freeze-Fracture TEM to provide a partial phase diagram and list the different mesophases obtained as a function of composition. We report that the adjustment of a single parameter, the co-surfactant (pentanol-1), determines the phase transition between cubic, hexagonal, lamellar, and sponge-like structures, all other parameters such as the nature and concentration of salt, or amount of oil being constant.
1. Introduction

Hexagonal oil-in-water (O/W) swollen liquid crystals (SLCs) have been reported to be adaptive dynamic nanoreactors, where either the oil, or the aqueous phases, are used as a reaction medium [1]. These systems contributed to the extension of ‘integrative chemistry’ or ‘integrative syntheses’, an interdisciplinary approach initially theorised by Mann [2], and Sanchez [3], where tools from chemistry, physical chemistry of complex fluids and biology are combined to compose multi-scale architectures bearing targeted functionalities.[4,5] Beyond their intrinsic properties, SLCs are also relevant to the group of specific reacting matrices, such as foams, [6] emulsions,[7] lyotropic mesophases,[8] bio-polymers,[9] three-dimensional colloidal opal-like textures, [10] or even millifluidic platforms,[11] which are now broadly used in integrative syntheses.

SLCs used as nanoreactors led to unique nanostructured materials, such as Pt or Pd nanorods,[1] nanowires or even nanoballs,[12–14] zirconia needles[15] and polymeric nanowires.[1] For example, preparation of large thin film electrodes made by spin-coating of polypyrrole (PPy) nanoparticles was achieved when PPy was synthesised within the aqueous phase of an SLC, which could not be achieved with synthesis in bulk solvent.[16] This was the result of the spontaneous self-assembly of tile-like nanoparticles shaped by the confinement within the SLC, whereas reaction in bulk leads to spherical nanoparticles that could not self-assemble upon spin-coating.

Until now, from our knowledge, only hexagonal SLCs were clearly identified as nanoreactors and their domain of stability studied in a complex, multi-component phase diagram that combines water, oil, surfactant, salt and co-surfactant.[17] Exploring new geometries in SLCs would increase the range of potential nanoreactors already in use, but their actual use would require their domain of stability to be well characterised. Besides, the stability of non-hexagonal mesophases cannot result from a fine balance between components in a narrow domain of the phase diagram, which would make their use as nanoreactor impossible in practice. We describe thereafter the domain of existence of several mesophases in SLC, which were fully identified by combining several analytical techniques. We demonstrate also that the domain of stability of these mesophases is large enough to allow them to be further used as nanoreactors, with the transition between these different geometries being easily triggered by the variation of a single component, the co-surfactant.

Stabilisation of the hexagonal SLC was demonstrated to be the result of a fine balance between several components, where a co-surfactant (1-pentanol) is used as a wedge between surfactants molecules, to adjust the spontaneous curvature of the surfactant-covered oil–water interface. For a given amount of surfactant, the diameter of the oil-containing cylinders of the hexagonal SLC geometrically depends on the amount of oil (e.g., cyclohexane) that swells the cylinders, and addition of a salt (NaCl, NaF, Na$_2$SO$_4$) is required to balance the repulsive interaction between ionic surfactant heads, resulting from the cylinder-given curvature. Since the amount of salt to be added depends on the specific cylinder curvature, which is a result of the amount of oil, it was demonstrated experimentally that a specific relationship exists between the amount of salt and the oil over water ratio:[18]

$$n \cdot [\text{salt}] (\text{mol}\text{L}^{-1}) = 0.156 \times (V_{\text{cyclohexane}} / V_{\text{water}}) - 0.104$$

(1)

(n: salt valence)

Consequently, from Equation (1), for a given volume of water, the two parameters – salt and oil – are related, and cannot vary independently. Before the present study, the role of the co-surfactant regarding the stability of different mesophases was not studied. Its amount was only adjusted experimentally during the preparation of the hexagonal SLC, with a slow addition under stirring until a stable, rigid and transparent mesophase is obtained, as a proof of the formation of the hexagonal mesophase. We describe how this co-surfactant is actually the triggering parameter for the transition between the different SLCs. With the help of small-angle X-ray scattering (SAXS), Freeze-Fracture TEM and polarised optical microscopy, we identified various mesophases, and drew the stability limits for each in a partial phase diagram. We studied whether different concentrations in cyclohexane/salt, or the nature of the salt, bearing either a divalent (ammonium persulfate already used as a catalyst in the synthesis of nanolamellae of polypyrrole [16]), or monovalent (sodium fluoride previously used in our studies on the stability of hexagonal SLCs [1]) anion, could influence the formation of, for example, hexagonal mesophases in relation with the amount of co-surfactant to be added. This report demonstrates that they have no influence, and that the phase transitions are only driven by the co-surfactant.

2. Materials and methods

2.1. Materials

Pyrrole, cetyltrimethylammonium bromide (CTAB), cyclohexane, 1-pentanol, ammonium persulfate
((NH₄)₂S₂O₈) (AP), sodium fluoride (NaF) and hydrochloric acid (HCl) were purchased from Aldrich and used as received without purification.

2.2. Synthesis

All samples were prepared with pre-defined amounts of 1-pentanol. Typically, the salt was dissolved in water previously acidified with hydrochloric acid at a pH close to 0, at three different concentrations: 0.05 M, 0.1 M and 0.15 M for AP, and 0.1 M, 0.2 M and 0.3 M for NaF. Two millilitres of this aqueous solution were mixed in warm water with 1 g of CTAB and then placed in an ultrasound bath till a transparent homogeneous solution was obtained. Pre-determined amounts of 1-pentanol were added at this stage. With the concentration in salt pre-defined as stated earlier, and the volume of water left constant at 2 mL, the volume of cyclohexane to be added was calculated according to Equation (1).

The mixture was homogenised with a vortex mixer and stored for 1 week before analysis. In the following, samples are labelled AP/M/R or NaF/M/R, when prepared with AP or NaF, respectively, with M being the salt concentration and R the 1-pentanol over surfactant molar ratio. We prepared three series of AP/M/R samples with different amounts of 1-pentanol, and three concentrations in AP (0.05 M, 0.1 M, 0.15 M) – calculated in respect of the volume of water. The volume of cyclohexane was calculated from the initial concentration in salt, and volume of water (2 mL), according to Equation (1), with \( n = 2 \). With the amount in CTAB constant (1 g), R (1-pentanol over CTAB molar ratio) was varied between 0.3 and 2.2. All preparations and studies were carried out at room temperature.

2.3. Characterisation

The samples were characterised by small-angle X-ray scattering (SAXS) on a Nanostar (Bruker Co.), equipped with a Siemens Copper anode (40kV, 35mA). The apparatus is equipped with two crossed Goebel mirrors in order to select the CuKα wavelength (0.154 nm) and produces a parallel beam, the final collimation being adjusted with a three-pinhole setup (with a 300 µm diameter for pinhole-2 setting the beam size). SAXS patterns were acquired using a 22 × 22 cm 2D gas detector HiStar from Bruker Co., positioned at a distance D of the sample. Silver behenate was used as a calibration standard, yielding D = 1.06 m. The scattering wave vector range used was 0.1–2.0 nm⁻¹.

The mesophases were also observed under cross-polarised light with a Leica DM2500P optical microscope equipped with a CCD FireWire Leica DFC420 camera.

We confirmed the structure of the mesophases with direct observation by Freeze-Fracture Transmission Electron Microscopy (FF-TEM) operated with a TEM Hitachi H600 apparatus using a Tungsten filament at an accelerating voltage of 75 kV. One small drop of a solution was placed, either on a gold support, or between two copper supports, before being immersed quickly into liquid propane, cooled down by liquid nitrogen. The samples were then transferred into the chamber of the freeze-fracture apparatus (Leica BAF 060) and either cut with a blade (Gold support), or fractured by pulling apart the two Copper supports. A 4 nm layer of platinum–carbon and a 30 nm carbon layer were sputtered. The replicas were cleaned and deposited onto a copper grid (400 mesh), before being observed.

3. Results and discussion

We observed first the influence of 1-pentanol on the structure of the SLC by visual inspection of samples after 1-week rest. All samples remain homogeneous and both turbidity and viscosity evolve with increasing R. With the AP/0.1/R series, prepared with 0.4 < R < 1.8 (Figure 1) (the yellowish colour is due to AP), no macroscopic phase separation was observed over the whole R range and the SLCs remained homogeneous and perfectly stable over months. At low R (R = 0.4), the mesophase is very viscous, almost solid-like, and turbid. Increasing R to 0.8 leads to a still very viscous, but fully transparent mesophase, which flows slowly. Increasing slightly R (R = 1.1) reduces catastrophically the viscosity, and the SLC turns into a very fluid, transparent liquid at R = 1.8.

The combination of SAXS and optical microscopy allowed us to identify the structure of the different mesophases present as we increase R in the AP/0.1/R series. The diffraction patterns reveal that the liquid crystal structure of the SLC changes with R, from 3D cubic to 2D hexagonal to 1D lamellar, until a disordered 3D (sponge-like) structure is obtained. All SAXS patterns (Figure 2, see also individual SAXS patterns in Figure S1 in ESI) display well-defined, and most often sharp, diffraction peaks, characteristic of long-range ordered (oil-rich or water-rich) domains with repeating distances (deduced from the first-order peak location in reciprocal space) in the 10–30 nm range. These large values confirm that the studied mesophases definitely belong to swollen liquid crystals. Phase coexistence, for instance, between 3D cubic and 2D hexagonal structures, is inferred from the coexistence of distinct sets of diffraction peaks. Since phase separation is not observed at macroscopic scales, high viscosities (for low R values) or almost equal mass densities (at large R) may prevent the locally phase-separated domains to reach macroscopic sizes.
This analysis of the structure of SLCs by SAXS was completed by the direct observation of these mesophases under polarised light microscopy (Figure 3 for AP/0.1/R; see also Figure S2 for AP/0.15/R). Samples with $R < 0.5$ are optically isotropic (no birefringent image observed), which is compatible with either a cubic or a sponge-like (disordered) structure. However, the comparison with SAXS results and the existence of several diffraction lines with characteristic ratios (Figures 2 and S3) discards the option of a sponge-like structure and confirms the cubic symmetry with a diffraction peak position ratio equal to $\sqrt{8/3}$ with $R$ in range 0.3–0.7. For $R = 0.6$, parallel fringes are observed by microscopy, as small islands (Figure 3(a)) and across the whole sample.
at $R = 0.8$ (Figure 3(b)). These parallel fringes are characteristic of a hexagonal symmetry and their extension reveals that the sample at $R = 0.6$ is an intermediate phase between cubic and hexagonal, whereas the sample at $R = 0.8$ is fully organised as a hexagonal phase. Malta crosses typical of a lamellar structure are observed for $R = 1.15$ (Figure 3(c)) and $R = 1.6$ (Figure 3(d)). Finally, the sample at $R = 1.8$ is optically isotropic again (no birefringence observed), but the existence of a single, and rather broad peak (instead of several narrow diffraction lines) observed by SAXS favours the occurrence of a sponge-like symmetry instead of a cubic structure.

The first level of analysis of the structural evolution of SLCs as a function of $R$ allowed us to point the successive transitions as follows: cubic – hexagonal – lamellar – sponge-like. This analysis was refined by plotting the SAXS patterns in the Porod representation ($I \times Q^4 = f(Q)$), to emphasise scattering contributions at higher $Q$ than those easily observed in the raw SAXS patterns (Figure S3 for individual SAXS patterns and Table S1 in ESI). An asymptotically flat signal in this representation, here observed for $Q$ larger than typically $1 \text{ nm}^{-1}$, is indeed characteristic of the presence of locally planar interfaces. Contributions evidenced in the Porod representation actually result from well-defined shapes (eg, spherical, cylindrical or platelet-like shapes) of the regularly stacked hydrophobic (cyclohexane + tail of the CTAB and 1-pentanol molecules) domains. With this second level of analysis, we could confirm the liquid crystal structure of SLCs as a function of $R$, and draw the frontiers between each phase.

We plotted the variation of the characteristic correlation distances as a function of $R$ (Figure 4). These correlation distances $d_i$ were identified from Figure S3 in ESI, and defined as $d_i = 2\pi/q_i$, where $q_i$ is the location in the reciprocal space of the $i$th peak or hump. The different correlation distances are numbered from $d_1$ to $d_7$, to ease reading.

Distances $d_1$ to $d_6$ evolve continuously within their definition range, but with a continuous increase of the correlation distances $d_1$ to $d_4$, and a decrease for $d_5$ and $d_6$. The change in trend occurs at $R = 1.0$. The distance labelled $d_7$ remains constant and close to 7 nm over the whole $R$ range. This distance is assigned to an internal dimension independent of the mesophase structure, corresponding to the size (radius, or thickness) of the hydrophobic (spherical/cylindrical, or platelet-like) domains, made of the two layers of CTAB alkyl chains, and cyclohexane/1-pentanol contained within. The sphere radius is indeed found close to 7.8 nm with the quantitative analysis of AP/0.1/0.4. This corresponds to a sphere volume fraction about 43%, considering the centre-to-centre distance 18.6 nm.
The phase identification was further confirmed by direct observation by FF-TEM, and Figure 5 shows three representative structures of the whole series. For $R = 0.45$ (Figure 5(a)), a network of small nearly spherical objects arranged in a close packed array is observed, which matches with the hypothesis of a cubic organisation of discrete objects, instead of a bi-continuous phase. For $R = 0.81$ (Figure 5(b)), multi-facetted columnar structures are representative of a hexagonal structure. Finally, the sample prepared with $R = 1.7$ (Figure 5(c)) exhibits two different structures, with parallel lines (see arrow), and a worm-like structure, which correspond to the cross section and surface of lamellar domains, respectively.

We finally summarised in Figure 6 all the results to display a complete picture of the structural evolution of SLCs upon variation of $R$. Analysis of this evolution was conducted by plotting the evolution of the larger over second and third distance ratios (see Figure 4), which are the best fingerprint of a specific geometry. These results are displayed along with the information resulting from the other techniques. A face-centred...
cubic (fcc) A1 structure (peaks at: 1 (111), √(4/3) (200), √(8/3) (220), and √(11/3) (311)) is clearly observed at R = 0.3 – the √(4/3) line being merged with the first peak, since d₁/d₂ = √(8/3), and d₁/d₃ = √(11/3), but this structure is confirmed by FF-TEM. The H1 hexagonal structure, in coexistence with another one, or as a single-phase structure, is observed between R = 0.8 and 1.0, with the first four diffraction lines (namely 1, √3, 2 and √7), being observed. As it can be observed from the SAXS patterns (Figure S13), the SAXS pattern of AP/0.1/R0.8 – 0.9 corresponds to two-phase samples, including the hexagonal phase, whereas the AP/0.1/R1.0 sample displays only the hexagonal phase. A single sharp line for R = 1.15, and a single broadened line for R greater than 1.8, together with the coexistence of the broad and sharp lines in the R = 1.33–1.7 range, are interpreted in terms of a La lamellar structure transforming into a L3 sponge-like mesophase with the increase in 1-pentanol content. Between the well-defined mesophases identified by squares in Figure 6, there are intermediate domains that can combine domains of mesophases, or a structurally ill-ordered region.

The same analysis made with SLCs prepared with either other concentrations in AP, or NaF in place of AP did not reveal any significant change in the phase transitions. A similar evolution was observed (Figure S4.a), whatever the salt – and oil – concentration, according to Equation (1) and the frontiers in phase transition remain the same: A1 → H1 → La → L3. A parallel study with NaF used in place of AP confirms that the structural evolution as a function of the addition of pentanol is also similar to that observed with AP (Figure S4.b).

4. Conclusion

CTAB/salted water/Cyclohexane/1-pentanol quaternary systems form unique swollen liquid crystals with different structures. These structures are the actual missing link between continuous binary crystals and swelled discrete objects like micro- and nano-emulsions. The SLC hexagonal mesophases have already demonstrated their large potential as nanoreactors with unique nanomaterials of various natures being synthesised within, but expanding the domain of use of these nanoreactors from hexagonal to non-hexagonal SLCs is a challenge that requires first a full knowledge and good control of the other mesophases. We were able to demonstrate in the present report that the controlled variation of one single parameter, the co-surfactant, determines the geometry of these mesophases, from cubic to hexagonal, then lamellar, and finally sponge-like. Moreover, similar analyses with different concentrations in salt/oil or nature of salt confirm that the co-surfactant is the unique controlling parameter. These results are an important milestone in the understanding and control of these swollen mesophases, which will give access to future knowledge-based design of nanostructured materials and colloids. Indeed, 3D sponge-like structures can be favourably used as nanoreactors for the preparation of 3D porous materials, as we demonstrated before. [19] They are actually stable in a broader range of composition, and the present study gives the insight required to achieve the fabrication of ‘advanced materials by design’. [20]

Disclosure statement

No potential conflict of interest was reported by the authors.

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