

# STRUCTURAL AND THERMOMECHANICAL INVESTIGATION OF LYOTROPIC LIQUID CRYSTAL PHASES DOPED WITH MONODISPERSE MICROPARTICLES

A. PONTON<sup>1\*</sup>, C. MEYER<sup>2</sup>, G. FOYART<sup>1,2</sup>, L. AYMARD<sup>3</sup>, K. DJELLAB<sup>4</sup>

<sup>1</sup>Laboratoire Matière et Systèmes Complexes (MSC), UMR 7057 CNRS & Université Paris Diderot-Paris 7, Batiment Condrcet, CC 7056, 75205 Paris Cedex 13, France

<sup>2</sup>Laboratoire de Physique des Systèmes Complexes, Université de Picardie Jules Verne, EA 4663, 33 Rue St-Leu, 80039 Amiens, France

<sup>3</sup>Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie Jules Verne, UMR 7314, 33 Rue St-Leu, 80039 Amiens, France

<sup>4</sup>Plateforme de Microscopie électronique de l'Université de Picardie Jules Verne, 33 Rue St-Leu, 80039 Amiens, France

\*Corresponding author: [alain.ponton@univ-paris-diderot.fr](mailto:alain.ponton@univ-paris-diderot.fr)

Fax: x33.1.57276211

Received: 17.10.2013, Final version: 16.11.2013

## ABSTRACT:

We present a study of the structural and thermomechanical properties of lyotropic phase in the quasi ternary system made of Cetylpyridinium chloride (CPCl)/hexanol/salt water (0.9 % by mass) with and without cobalt microparticles. Phase transition temperatures of the structural sequence isotropic L<sub>i</sub>/nematic calamitic N<sub>c</sub>/hexagonal H have been determined by differential scanning microcalorimetry. Temperature induced developable domains in hexagonal phase H and disclinations in calamitic nematic phase N<sub>c</sub> were observed in crossed polar optical microscopy in confined geometry. A rheological study of calamitic nematic phase N<sub>c</sub> highlighted structuring effect of cobalt microparticles from a concentration of 2 % to be demonstrated by an increase in viscosity and viscoelastic moduli. This could be explained by a stabilization of disclinations.

## KEY WORDS:

cement, limestone, rheology, stabilising agent, coarsely dispersed systems, diutan gum, starch ether

## 1 INTRODUCTION

Since their discovery at the end of 19<sup>th</sup> century and their first application as display devices [1] liquid crystals are gaining considerably in importance because of development into highly successful research fields for example in nanoscience [2]. Indeed the combination of fluidity and long range order from orientation or position correlation of building blocks (often rods or discs) gives them both fluid and solid properties very suitable in materials science on nanostructured materials. Conversely to thermotropic liquid crystals built up with individual molecules and no solvent, lyotropic liquid crystals required a solvent and can self-assemble in solution to form simple individual structures (monomolecular film, spherical or cylindrical micelles) or long-range periodic stacks (lamellar phases, hexagonal phases, sponge phases, ...) [3]. In the absence of electrostatic interactions between the layers of amphiphilic molecules, such swollen lamellae are generally stabi-

lized by steric repulsions: the confinement of flexible membranes decreases their entropy by reducing thermal fluctuations, resulting in repulsive interactions between membranes [4]. Another very attractive feature of liquid crystals is the possibility to elaborate composite systems by incorporating particles such as silica microbeads, carbon nanotubes, semiconductor or metal nanorods [5, 6].

In order to elaborate stimuable hybrid materials, several studies have been devoted to the investigation of liquid crystalline phases containing magnetic particles. By swelling a lyotropic lamellar phase in a solution of nanoparticles of iron oxide magnetic, Fabre et al. [7] obtained a ferrosmectic phase with combined properties of the swollen lamellar phases and ferrofluids. The comparison with other lyotropic lamellar phases doped with particles of non-magnetic iron oxides was studied [8]. Ramos et al. [9] examined the compatibility of lyotropic lamellar phases containing magnetic particles of maghemite coated by a shell of adsorbed sodi-

This is an extract of the complete reprint-pdf, available at the Applied Rheology website  
<http://www.appliedrheology.org>

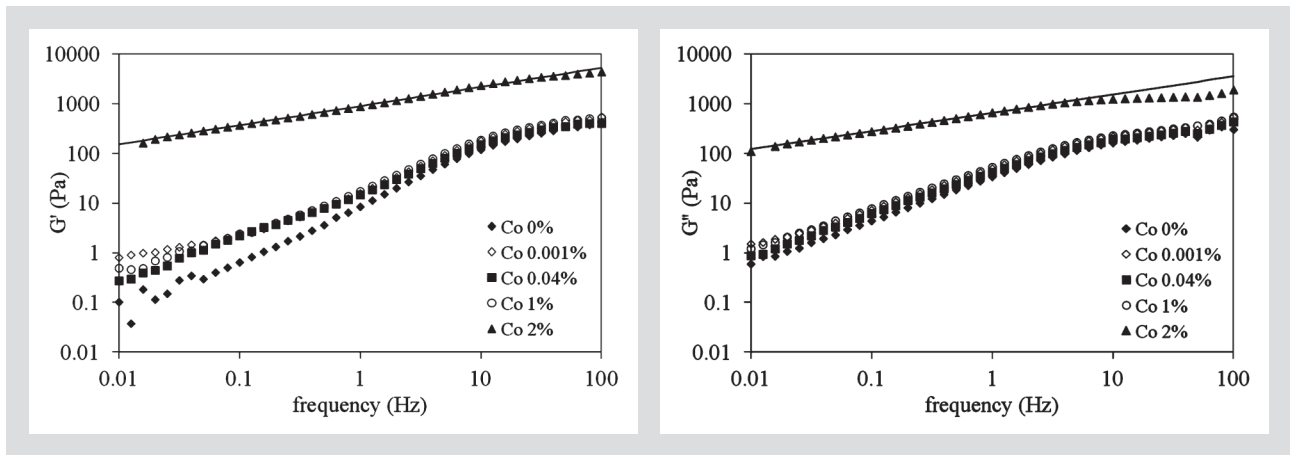


Figure 11: Frequency dependence of (a) elastic modulus  $G'$  and (b) loss modulus  $G''$  for nematic calamitic phase  $N_c$  with cobalt microparticles at different concentrations. Solid lines correspond to a fitting up to 10 Hz by a power law.

$$\eta \propto \dot{\gamma}^{-n} \quad (2)$$

with a value of exponent  $n$  about 0.65 for the three studied concentrations of cobalt microparticles (1, 2.21, and 4.8%). Shear thinning power-law behavior had been highlighted [19] in the smectic phase A of liquid crystals with an exponent  $n \sim 0.4$  independent of the chemical nature of the lamellar phases but associated with identical macroscopic defects textures: oil striations which oriented in the direction of the flow as the shear rate increases. A theoretical model based on the theory of high temperature creep and involving the movement of dislocations screws, had allowed to reproduce the observed experimental behavior. In the same way, it could be suggested that the exponent  $n \sim 0.65$  may be related to the presence of specific macroscopic defects in the nematic calamitic phase doped with cobalt microparticles as observed in optical microscopy (Figure 5b). Moreover the increase of viscosity at very low shear rate  $\eta_0$ , the decrease of critical shear rate and the shear thinning index (Figure 10) could be also explained by a structuring effect of such specific macroscopic defects also expected at concentration of cobalt microparticles less than 1%.

### 3.3.2 Oscillatory shear measurements

For all studied samples, the linear viscoelastic domain was observed up to 1% of strain and was found not to depend on the studied range concentration of cobalt microparticles. The frequency dependence of the elastic modulus  $G'$  and the viscous modulus  $G''$  was then determined at a fixed strain value of 0.5%. All the samples with a concentration of microparticles up to 1% showed a viscoelastic behavior. For a concentration of cobalt microparticles of 2%, the observed behavior was a viscoelastic solid with elastic modulus  $G'$  always higher than the viscous modulus  $G''$  in the studied frequency range. By considering frequency up to 10 Hz (Figure 11) both moduli show a power law frequency dependence with the same exponent (0.38) characteristic of a soft gel-like behavior. This effect of structuration from 2% of cobalt microparticles is in a good agreement with the increase of viscosity observed on flow curves (Figure 10).

Zapotocky et al. [20] reported solid like response of shear stress when colloidal silica particles are dispersed in cholesteric liquid crystals whose origin is a stabilization of oily streak network under tension. By direct optical visualization with crossed polarizers, the authors clearly demonstrated that the colloidal particles were located preferentially at the nodes of the defect network and stabilized it by decreasing dramatically the coarsening rate of defects observed without particles. Similar elasticity enhancement was observed in lyotropic lamellar phase  $L_\alpha$  upon addition of spherical particles several microns in diameter and also explained by a network of oily streak defects which persists partially under shear treatment [21]. Based on these studies, it could be conjectured that addition of cobalt microparticles in the nematic calamitic phase  $N_c$  studied here stabilized disclinations observed by optical microscopy between crossed polarizers (Figure 5) and is responsible to elastic behavior. This explanation is also supported by the increase of viscosity when the concentration of microparticles is increased (Figure 10). Indeed stabilization of defects by colloidal particles and solid like behavior are maintained under shear unlike to other systems where no defects structures are present [20].

## 4 CONCLUSION

Phase transition temperatures of the structural sequence (isotropic  $L_1$ /nematic calamitic  $N_c$ /hexagonal H) in the quasi ternary system made of Cetylpyridinium chloride (CPCI)/hexanol/salt water (0.9% w/w) were determined by differential scanning microcalorimetry. Temperature induced developable domains in hexagonal phase and disclinations in calamitic nematic phase were observed in optical polarized microscopy. In the studied range of cobalt microparticles concentration, the textures of macroscopic defects were globally unchanged. Conversely, the increase in the viscosity at very low shear rate deduced from steady state shear flow measurements and viscoelastic moduli suggested a structuring effect of cobalt microparticles from a concentration of 2% by a stabilization of disclinations.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website <http://www.appliedrheology.org>

## ACKNOWLEDGEMENTS

We thank Julien Mascot for his help in the use of the electron microscopy platform of the University of Picardie Jules Verne.

## REFERENCES

- [1] Ivanov PA, Chelnokov VE: Recent developments in SIC single-crystal electronics, *Semicond. Sci. Technol.* 7 (1992) 863–880.
- [2] Bisoyi HK, Kumar S: Liquid-crystal nanoscience: An emerging avenue of soft self-assembly, *Chem. Soc. Rev.* 40 (2011) 306–319.
- [3] Collins PJ: *Liquid Crystals: Nature's Delicate State of Matter*; Princeton University Press, Princeton (1990).
- [4] Helfrich W: Steric interaction of fluid membranes in multilayer systems, *Z. Naturforsch.* 28 (1973) 693–703.
- [5] Hegmann T, Qi H, Marx VM: Nanoparticles in liquid crystals: Synthesis, self-assembly, defect formation and potential applications, *J. Inorg. Organomet. Polym. Mater.* 17 (2007) 483–508.
- [6] Lagerwall JPF, Scalia G: A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio- and microtechnology, *Curr. Appl. Phys.* 12 (2012) 1387–1412.
- [7] Fabre P, Quillet C, Veyssié M, Nallet F, Roux D, Cabuil V, Massart R: Anisotropy of the diffusion coefficients of submicronic particles embedded in lamellar phases, *Europhys. Lett.* 20 (1992) 229–235.
- [8] Quillet C, Fabre P, Cabuil V: Doping of lyotropic smectics with nonmagnetic particles: comparison with ferro-smectics, *J. Phys. Chem.* 97 (1993) 287–289.
- [9] Ramos L, Fabre P, Dubois E: Compatibility between solid particles and a lamellar phase: a crucial role of the membrane interactions, *J. Phys. Chem.* 100 (1996) 4533–4537.
- [10] Ramos L, Fabre P, Fruchter L: Magnetic field instabilities of a doped lyotropic hexagonal phase, *Eur. Phys. J. B* 8 (1999) 67–72.
- [11] de Silva JP, Poulos AS, Pansu B, Davidson P, Kasmi B, Petermann D, Asnacios S, Meneau F, Impéror M: Rheological behaviour of polyoxometalate-doped lyotropic lamellar phases, *Eur. Phys. J. E* 34 (2011) 1–9.
- [12] Fievet F, Lagier JP, Blin B, Beaudoin B, Figlarz M: Homogeneous and heterogeneous nucleations in the polyol process of micron and micron and submicron size metal particles, *Solid State Ionics* 32–33 (1989) 198–205.
- [13] Ducamp-Sanguesa C, Herrera-Urbina R, Figlarz M: Synthesis and characterization of fine and monodisperse silver particles of uniform shape, *J. Solid State Chem.* 100 (1992) 272–280.
- [14] Fievet F, Fievet-Vincent F, Lagier JP, Dumont B, Figlarz M: Controlled nucleation and growth of micrometre-size copper particles prepared by the polyol process, *J. Mater. Chem.* 3 (1993) 627–632.
- [15] Berret JF, Roux D, Porte G, Lindner P: Shear-induced isotropic-to-nematic phase transition in equilibrium polymers, *Europhys. Lett.* 25 (1994) 521–526.
- [16] Frank FC: I. Liquid crystals: On the theory of liquid crystals, *Discuss. Faraday Soc.* 25 (1958) 19–28.
- [17] Kleman M: Developable domains in hexagonal liquid crystals, *J. Phys. France* 41 (1980) 737–745.
- [18] de Gennes PG, Prost J: *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1993).
- [19] Meyer C, Asnacios S, Kleman M: Universal properties of lamellar systems under weak shear, *Eur. Phys. J. E* 6 (2001) 245–253.
- [20] Zapotocky M, Ramos L, Poulin P, Lubensky TC, Weitz DA: Particle-Stabilized Defect Gel in Cholesteric Liquid Crystals, *Science* 283 (1999) 209–212.
- [21] Basappa G, Suneel, Kumaran V, Nott PR, Ramaswamy S, Naik VM, Rout D: Structure and rheology of the defect-gel states of pure and particle-dispersed lyotropic lamellar phases, *Eur. Phys. J. B* 12 (1999) 269–276.



This is an extract of the complete reprint-pdf, available at the Applied Rheology website  
<http://www.appliedrheology.org>