



Treball Final de Grau

Preparation and characterisation of graphene-based lyotropic liquid crystals.

Preparació i caracterització de cristalls líquids liotrópics basats en grafè.

Beatriz Calvo Ruiz

Juny 2015

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Nuestra recompensa se encuentra en el esfuerzo y no en el resultado. Un esfuerzo total es una victoria completa.

Mahatma Gandhi

A mis padres, que son la fuerza que me impulsa a seguir adelante día tras día.

A mi familia, y en especial, a mi tía Loli, a quién nunca dejaré de admirar.

A mis amigos, que consiguen sacarme una sonrisa siempre que lo necesito.

Agrair a en Pau Guillamat, a en Marc Mora, a en Jordi Ignés i a en Francesc Sagués el seu ajut i els seus consells durant tots aquests mesos de treball al laboratori.

REPORT

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1. SUMMARY

Since graphene was discovered, interest on this material has been on the rise for the last few years. This is due to its extraordinary properties and its wide variety of applications. On the other hand, another result of interest for research purposes is the possibility to form lyotropic liquid crystals with dispersed micro or nanoscale objects by self-assembling processes.

Combining the above items and taking into account their current relevance, the preparation of graphene oxide lyotropic liquid crystals by dispersing graphene oxide flakes in water is presented as an option with potentially high relevance.

In this project, we have prepared graphene oxide liquid crystals by following different protocols reported by some research groups. Characterisation by polarizing optical microscopy has allowed us to observe the formation of textures reminiscent to those observed in standard liquid crystals, both at interfacial regions or around inclusions. Moreover, we were able to detect that graphene oxide dispersions undergo phase separation with time, resulting in a birefringent phase and an isotropic phase. Finally, we have explored how the sample is affected by external factors, such as temperature or a strong magnetic field.

Keywords: graphene oxide, liquid crystal, nematic, lyotropic, self-assembly, polarizing optical microscopy.

2. RESUM

Des del seu descobriment, el grafè ha estat un dels materials més en auge dels últims anys. Això és degut a les excel·lents propietats que presenta, juntament amb l'ampli ventall d'aplicacions que permet plantejar. Per altra banda, un altre fet d'interès per a la recerca ha estat la possibilitat de què cossos d'escala micromètrica o nanomètrica puguin formar cristalls líquids liotròpics a través de processos d'autoensamblatge.

Considerant conjuntament aquests ítems i la seva importància actual, la preparació de cristalls líquids liotròpics a partir de la dispersió de nano-escates d'òxid de grafè en aigua es presenta com una opció de gran interès.

En aquest projecte s'han preparat cristalls líquids d'òxid de grafè fent servir protocols publicats per diversos grups de recerca. La caracterització per microscòpia òptica de polarització ha permès observar la formació de certes textures semblants a les descrites en la literatura de cristalls líquids en la proximitat de zones interfacials i al voltant d'inclusions presents a les mostres. A més, s'ha pogut detectar que les dispersions d'òxid de grafè experimenten separació de fases amb el temps, esdevenint una fase birefringent i l'altra isòtropa. Finalment, s'ha investigat quin efecte exerceixen sobre el sistema factors externs com ara la temperatura o un camp magnètic intens.

Paraules clau: òxid de grafè, cristall líquid, nemàtic, liotròpic, auto-assemblatge, microscòpia òptica de polarització.

3. INTRODUCTION

In 1888, the botanist Friedrich Reinitzer found something surprising. He discovered a substance that seemed to show two melting points. At that moment, he was not aware of the great importance his accidental discovery would have in the future.

More than a century later, the scientific world has studied a lot of substances with the same behaviour Reinitzer found.

What are the above substances? The answer is “LIQUID CRYSTALS”.

3.1. LIQUID CRYSTALS (LCs)

The concept ‘liquid crystal’ seems to be a contradiction in terms. How can a crystal be liquid? Or, conversely, how can a liquid be crystal?

Well, the key to understand it requires keeping the words ‘liquid’ and ‘crystal’ strongly tied. In fact, the term ‘liquid crystal’ means a state of aggregation that is intermediate between the crystalline solid state and the amorphous liquid.¹ In other words, what it really refers to is a degree of order intermediate between the molecular disorder of a liquid and the regular structure of a crystal.² Figure 1 shows graphically this circumstance so as to facilitate its comprehension.

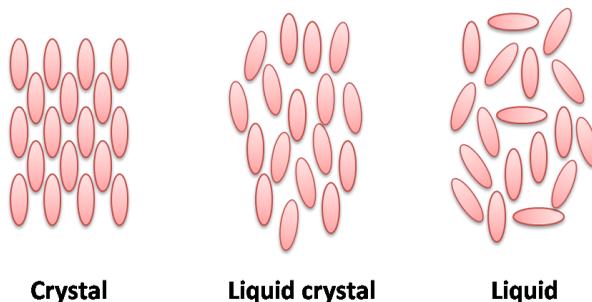


Figure 1. Comparison between molecular order of a crystal, liquid crystal and liquid states.

In LCs, talking about 'order' or 'degree of order' requires commenting the long-range orientational order they have, which is the most important property of these materials. Long-range orientational order implies that the molecules which integrate the LC have the tendency to point along a common axis, called the director. At the centre of the previous image, the reader can appreciate how molecules are oriented in a particular direction (i.e. along the longest side of the page), although they do not have as much order as the perfect crystalline solid. This feature is the origin of anisotropy of LCs, which is another very interesting characteristic that will be explained in detail in section 3.3.

Finally, it is important to become familiar with some of the terms frequently used in the LCs area, like 'mesogen' and 'mesophase'. On the one hand, mesogens are molecules that are capable to organize in LC phases. In general, they are particles with a rod-like (also called calamitic) or a disc-like (also called discotic) shape. On the other hand, mesophase is used as a synonym of 'LC phase'.

The next subsections are focused on giving a general vision about the vast world of LCs. For that reason, the next two subsections describe the two types LCs are traditionally classified in: thermotropic LCs (those that take place in a determined temperature range) and lyotropic LCs (those that take place in certain concentration ranges). Afterwards, we will talk about the mesophases of these substances and their characteristics. Finally, this project presents a brief overview of defects in LCs, giving details such as their nomenclature, their textures under polarizing microscopy, or their formation.

3.1.1. Thermotropic liquid crystals

Since more than a century, thermotropic LCs have been thoroughly studied, in contrast with lyotropic LCs, which started being investigated more recently.

The prefix thermo- is the result of the combination of the Greek forms *thermos* ("hot", "warm") and *therme* ("heat"), and it is used to refer to 'hot', 'heat' and/or 'temperature' in scientific and technical words.³

So, in the case of LCs, the term 'thermotropic' indicates that the transitions between different mesophases are influenced by temperature changes. Materials showing thermotropic LC phases are usually organic substances, although only about 1% of all organic molecules

melt from the solid crystal phase to form a thermotropic LC phase before eventually transforming into an isotropic liquid at still higher temperature.^{2,4}

An example of an organic substance that presents LC behaviour is 4-cyano-4'-pentylbiphenyl, more frequently known as 5CB, which is its common name.

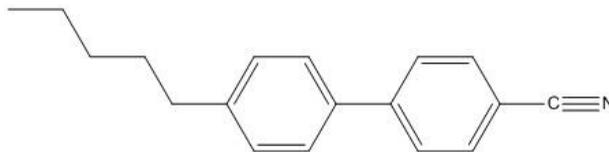


Figure 2. Structure of 5CB.

Thermotropic LCs show anisotropic phases with long-range orientational order, but no long-range translational order (i.e. the positions of molecules are not repeated in space in a regular arrangement). Mainly, these molecules are rod-like shaped, but there are disc-like shaped too. However, each type produces different LC phases: calamitic molecules can produce nematic, cholesteric and smectic phases, whereas discotic molecules can produce nematic and columnar phases. Furthermore, some of these phases are also found in lyotropic LCs. For this reason, section 3.1.3. will do a general analysis about them.

3.1.2. Lyotropic liquid crystals

Lyotropic LCs are mesophases that arise in solutions where the dispersed species has tendency for self-assembly. In fact, the prefix lyo- comes from the Greek for 'solvent', which indicates that concentration is the main controlling variable in the phase behaviour of lyotropic LCs.⁵

The solvent used in formation of lyotropic LCs can be aqueous or non-aqueous, although lyotropic LCs formed in water are by far the most widely studied ones.

Depending on the nature of the molecules mixed with the solvent, three types of lyotropic LCs can be found:

- Lyotropic LCs based in amphiphiles, which are the most common ones.

- Lyotropic chromonic LCs (LCLC). They are formed by molecules with ionic groups at the periphery that associate into stacks through non-covalent self-assembly while in water.⁶
- Lyotropic LCs based in nanoplatelets, as graphene-based LCs.

To a better understanding of the lyotropic LCs behaviour, the next paragraphs will briefly explain the fundamentals of lyotropic LCs based on amphiphiles, since they were discovered first and are the most widely studied.

3.1.2.1. Lyotropics based on amphiphiles

An important feature that makes them different from thermotropics is the self-assembly of the amphiphilic molecules as supramolecular structures, which are their basic units.

The term amphiphilic comes from the Greek 'amphis', which means 'both' or 'double', and 'philia', which means 'love' or 'friendship'.⁷ So, an amphiphile is a molecule that shows "double love" or double affinity, from an electrostatic point of view. How can be this possible? Because these molecules possess two different parts: a polar, hydrophilic head one and a non-polar, hydrophobic tail (Figure 3).

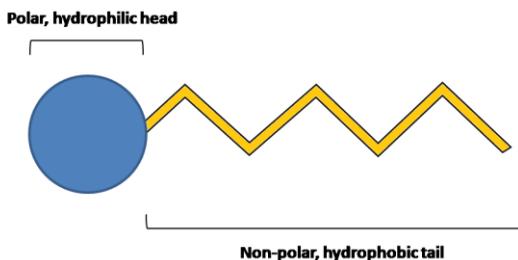


Figure 3. Representation of an amphiphilic molecule.

This special conformation of amphiphiles makes possible that, under suitable conditions of temperature and relative concentrations, mixtures of amphiphilic molecules generate self-assembled super-structures of several shape anisotropies and sizes, which are fundamental in the development of this type of lyotropic LCs.

The most common aggregate structures (usually termed “normal structures”)² are called micelles, and they can be divided in two types: spherical micelles and rod-like or cylindrical micelles. The formation of each type depends on the difference in cross-sectional areas of the head group and the chain of the molecules, because they adopt the conformation that provides the most efficient packing. This relation is analysed or established by a *surfactant packing parameter*, a very important concept in the study of amphiphiles and their molecular structures, which is not going to be described here, but is widely explained in literature.²

One more mode of aggregation is a layer structure (commonly called amphiphilic bilayer), which forms a planar interface. That is, for example, the conformation of cell membranes.

Apart from that, when the medium is hydrophobic, inverse structures appear.

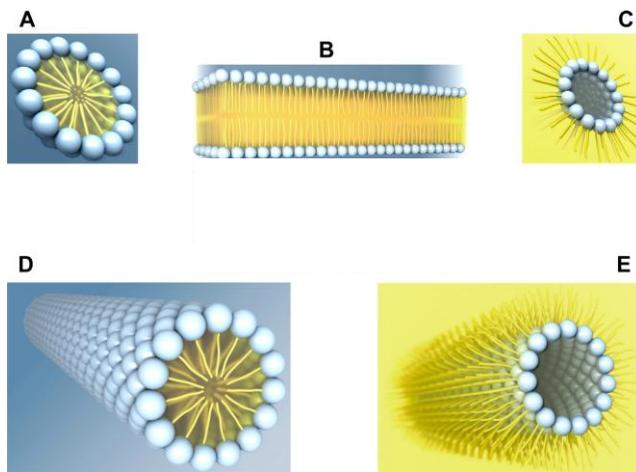


Figure 4. Amphiphilic molecular aggregates. A: micelle. B: bilayer. C: inverted micelle. D: cylindrical micelle. E: inverted cylindrical micelle.

(Extracted image of David B. N. Lee et al. *Am. J. Physiol. Renal Physiol.* **2008**, 295, F1601-F1612)

3.1.3. Liquid crystal phases

Depending on the shape and the spatial disposition of molecules constituting the LC, it can present different mesophases.

The next scheme is summarizing some of the possibilities:

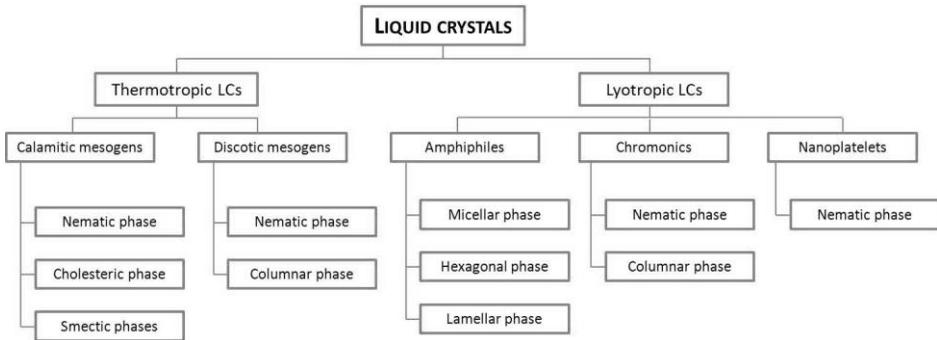


Figure 5. Scheme about the most common LCs phases for each type of LC, considering factors such as shape and/or nature of the molecules.

We will summarize here the main features of each of these mesophases, paying special attention at nematic phase, which is the main objective of the experimental part of this project, and which is present in both type of LCs.

- Nematic phase. The main feature of this phase is the absence of long-range translational order, just as in a normal isotropic liquid, but the presence of a high degree of long-range orientational order of the molecules, which tend spontaneously to be parallel to some common axis, represented by a unit vector, called the director.⁸ (For more information, see subsection 3.1.4.)
- Cholesteric phase. It has the same behaviour as nematic phase with a special additional feature: it is composed of chiral molecules, which give to the structure a spontaneous twist about an axis normal to the preferred molecular directions.
- Columnar phase. It is typical of discotic molecules, which are stacked forming columns. Depending on the positioning of these packs, a number of variants exist.
- Smectic phase. It is a mesophase that has layered organization with well-defined interlayer spacing.⁸ A variety of molecular arrangements are possible within each layer.

Therefore, there are many different smectic phases, although the most important ones are the Smectic A phase, where the molecules are upright in each layer; and the Smectic C phase, where the molecules are tilted inside the layer.^{1,9}

- Hexagonal phases. In this situation, amphiphilic molecules are packed as long cylinder-like aggregates, with large shape anisotropy, and these cylinders are packed forming a hexagonal lattice. Once again, the normal and the inverse phase exist (labelled H_1 and H_2 , respectively), depending on the concentration.¹⁰
- Lamellar phases. In this case, amphiphilic molecules are organized in different bilayers, which tend to stack forming a structure with large shape anisotropy.¹⁰

3.1.4. Nematic phase

Nematic phase is the simplest LC phase.² It appears in thermotropic LCs and in lyotropic LCs and it can be formed by almost all different types of molecules: calamitic and discotic mesogens, platelets...

When a nematic phase is observed between crossed polarizers, it presents what is known as schlieren textures, which shows dark brushes. These brushes are regions where the director is either parallel or perpendicular to the plane of polarization of the incident light, and the points where two or four brushes meet correspond to line singularities of the director.¹

Precisely these singularities, called disclinations, are very important in the study of LCs because through their study is possible to understand the structural organisation and the topology of LCs. For this reason, the next subsection analyses the typical disclinations of nematic texture.

3.1.4.1. Disclinations in the nematic phase

Disclinations are characterized by its charge (the number of turns the director makes around the singular point). The absolute value of this charge is equal to one fourth of the number of brushes around the defect. The text commented previously that in nematic phase typically points where two or four brushes coincide are observed. Therefore, typically $\pm\frac{1}{2}$ and ± 1 disclinations exist in this type of phase.

The rotation of the sample is very useful in order to distinguish the disclinations of different sign. When the LC sample is rotated, the black brushes move continuously showing that the orientation of the director changes. If the brushes rotate in the same direction as the sample, the point has a negative sign; and if the brushes turn in the contrary direction, the sign is positive.

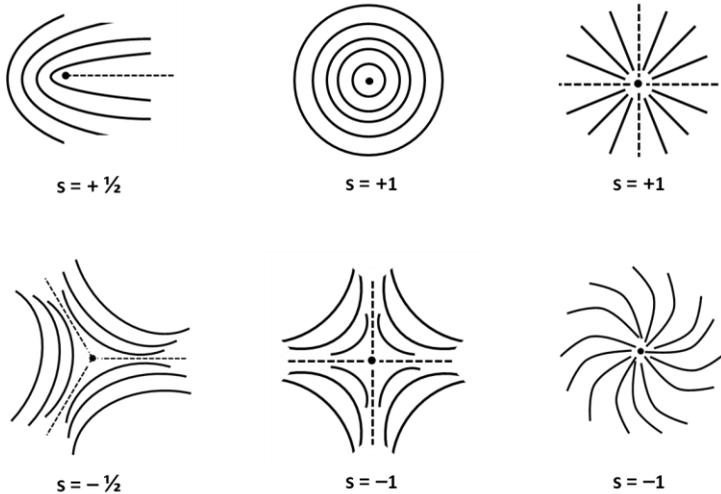


Figure 6. Representation of disclinations in the nematic phase.

3.2. GRAPHENE-BASED LIQUID CRYSTALS

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice¹¹, where each carbon atom forms each vertex. It exhibits a large number of outstanding optical and electronic features in comparison with other materials.¹²

Regarding as the relation of graphene and LCs, graphene can be considered as a disk-like nano-object with very high aspect ratio, so upon dispersion in sufficiently high concentrations it might exhibit liquid crystalline behaviour.¹²

In this work, we will focus on the liquid crystalline behaviour of a derivative of graphene: graphene oxide (GO).

GO is the oxygenated form of a monolayer graphene platelet. It has hydrophilic surface functional groups, such as epoxide, hydroxyl and carboxyl groups that decorate the basal plane and the edge of GO (see Figure 7). It is mass-producible from natural graphite by chemical oxidation and subsequent exfoliation.¹³

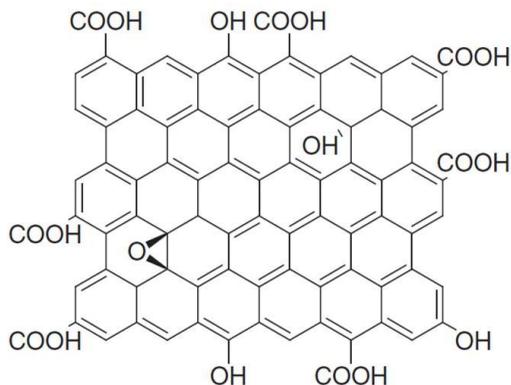


Figure 7. Chemical structure of GO.
(Extracted image of Bisoyi, H. K. et al, ref. 12)

Recently, some research groups have reported the liquid crystallinity of GO dispersions in water¹³⁻¹⁷ and other solvents¹⁸. In fact, GO dispersions belong to the class of lyotropic LCs, so their behaviour deeply depends of the dispersion concentration.

The liquid crystallinity of GO seems to be useful so as to produce self-aligned assemblies of graphitic materials in the form of fibers and films with high mechanical properties.¹⁴ Moreover, it is also proposed that the self-assembled GO nanostructure can be applied in areas such as energy-storage devices, for example.¹⁵ Finally, it is also reported that “the aqueous surrounding of GO LCs also provides the foundation for its biological applications, especially for the fabrication of highly ordered, self-assembled chiral biomolecules/graphene conjugates”.¹⁴ This last option exposes the possible biocompatibility of GO LCs. It supposes a great advantage in comparison with thermotropic LCs or lyotropic LCs based in surfactants, which are not biocompatibles.

Taking into account the chemical structure of GO showed above, we can see that, in a certain way, GO can be considered as an amphiphilic entity because it includes different hydrophilic and hydrophobic parts. Therefore, at a very-low concentration of GO with a high

content of water, the GO dispersion can become isotropic; while upon increase in the concentration, it is plausible that the GO sheets form a self-assembled structure (Figure 8).¹⁵

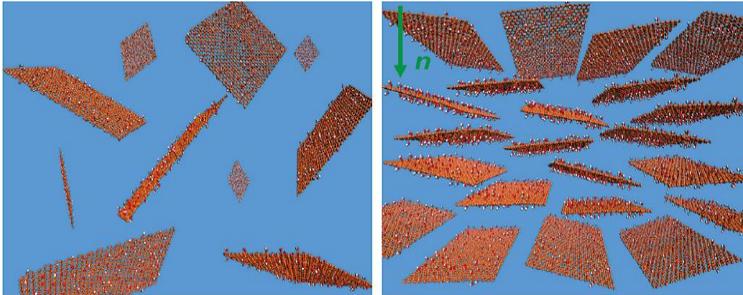


Figure 8. Schematic representation of isotropic (left) and nematic (right) phases of GO dispersions in water. GO sheets show a chaotic distribution in dilute dispersions (I phase) whereas ordered alignments in more concentrated dispersions (N phase).
(Extracted image of Xu, Z. et al, ref. 14)

Observing GO dispersions between crossed polarizers, Schlieren textures were reported with disclinations of various signs and strengths (Figure 9), although GO LCs exhibited a high density of $\pm\frac{1}{2}$ disclinations, which is a typical feature of nematic LCs, as was explained in subsection 3.1.4. On this point, different values of concentration at which nematic phases appear are reported, but the lowest filler content ever report is above 0.1 wt%.¹⁵ Below these critical concentrations, the phase is isotropic without birefringence (i.e. optical property that lies in orientation-dependent differences in refractive index). Finally, the possibility that the nematic phase of GO sheets could evolve into a lamellar phase upon increasing GO concentration is also proposed.¹⁴

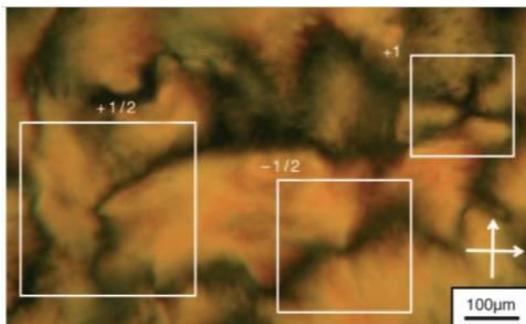


Figure 9. Schlieren texture observed between crossed polarizers of a 0.3 wt% dispersion of GO.
(Extracted image of Kim, J. Et al, ref. 13)

3.3. ANISOTROPY

In the above sections we have repeatedly invoked the term 'anisotropy'. A definition is in order.

The Encyclopaedia Britannica defines this term as "in physics, the quality of exhibiting properties with different values when measured along axes in different directions".¹⁹

In LCs field, anisotropy plays an important role, as the reader has probably guessed. In fact, due to the orientational order of the molecules, LC phases are anisotropic. It can be verified, for example, by the response of these substances to electrical or magnetic field. In both cases, they induce the generation of a dipole moment and its orientation in the direction of the field.

However, the most important anisotropic property for this work is optical anisotropy.

3.3.1. Optical anisotropy ^{2,20}

To say that a material possesses optical anisotropy means that its refractive index, n , has a different value parallel to the director (n_{\parallel}) than perpendicular to it (n_{\perp}); i.e. light propagates with different speeds along these directions. This difference ($\Delta n = n_{\parallel} - n_{\perp}$) leads to the definition of optical anisotropy, also called optical birefringence.

In other words, optical birefringence is formally defined as the double refraction of light in a transparent, molecularly ordered material, which is manifested by the existence of orientation-dependent differences in refractive index.

All previous concepts mean that, when an incident ray enters the birefringent substance, it is separated into ordinary and extraordinary rays, whose polarizations are oriented perpendicular to each other. Ordinary ray travels with the same velocity in every direction through the material, while extraordinary ray travels with a velocity that is dependent upon the propagation direction within the substance.

But, how is this phenomena manifested in LCs?

When a LC sample is observed between crossed polarizers, it shows dark and bright zones (see Figure 10). Dark areas are those in which the director orientation is perpendicular or parallel to the axes of the polarizers; and bright areas are those in which the director makes an angle with the polarizer axes different than 0° or 90° . On account to that, the appearance of these dark and bright zones changes if the sample is turned.

In order to understand better this optical phenomenon and to know how it is studied, the next section revises a little some concepts about polarization and polarizing optical microscopy (POM).

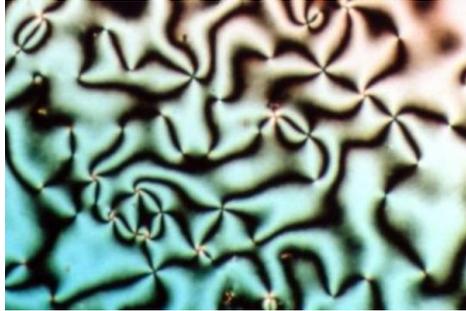


Figure 10. Schlieren texture of liquid crystal nematic phase.
(Minutemen, 13/5/2015 via Wikimedia Commons, Creative Commons Attribution)

3.4. LIGHT AND POLARIZATION

3.4.1. Polarized light

Light is electromagnetic radiation, formed by an electric field and a magnetic field.

Sunlight and almost every other form of natural and artificial illumination produces light waves whose electric field vectors vibrate in all planes that are perpendicular with respect to the direction of propagation. This is referred to as non-polarized light. However, if the electric field vectors are restricted to a single plane by filtration of the beam with specialized materials, known as polarizers, then the light is referred to as linearly polarized.²¹ The next scheme shows this process and also shows graphically the concept of crossed polarizers, which is fundamental for polarized light microscopy.

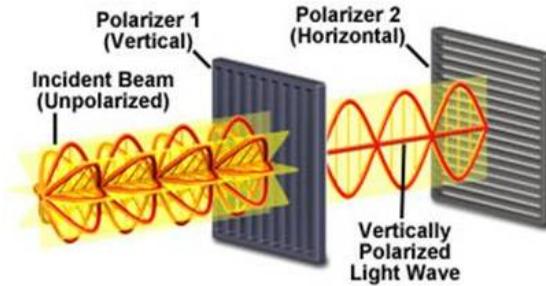


Figure 11. Red sinusoidal waves represent electric field vectors of incident beam. When they arrive at polarizer 1, only the waves having vertical electric field vectors (the same direction of polarizer 1) get to pass. The result is linearly polarized light, which is blocked by polarizer 2 because direction of polarized light and polarizer 2 isn't the same. Polarizer 1 and 2 are crossed polarizers.
(Extracted image of Nikon MicroscopyU, ref. 20)

3.4.2. Polarized light microscopy²²

Polarized light microscopy (or polarized optical microscopy, POM) is a contrast-enhancing technique that improves the quality of the image obtained with birefringent materials when compared to other techniques. In fact, one of its most important features is its capability to distinguish isotropic and anisotropic substances.

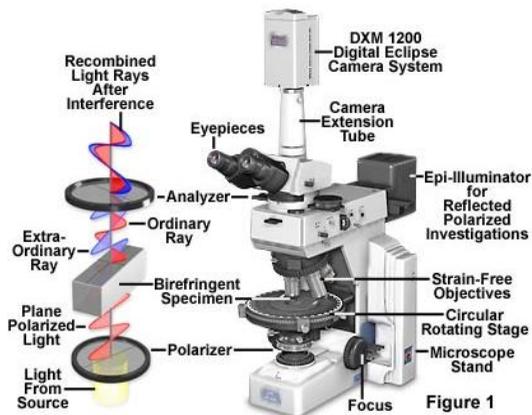


Figure 12. General scheme of a polarized light microscope configuration.
(Extracted image of Nikon MicroscopyU, ref. 22)

Figure 12 shows the configuration and the main parts of a polarized light microscope.

The essential components of a polarized light microscope are the polarizers. There are two polarizing filters in a polarizing microscope, termed the polarizer and the analyser. The polarizer is positioned under the sample stage and the analyser is placed above the objectives. When both filters are rotated at 90 degrees to each other, they are said to be crossed.

Other important components of polarized light microscope are a specialized stage (a 360-degree circular rotating sample stage) and the compensator and/or retardation plates, which are placed between the crossed polarizers and cause colour changes in the sample so as to improve contrast. These colour changes can be interpreted with the help of a polarization colour chart (see Figure 13).

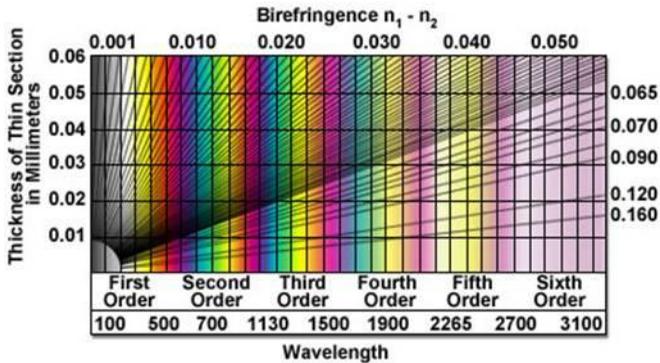


Figure 13. Michel-Levy Birefringence Interference Colour Chart.
(Extracted image of Nikon MicroscopyU, ref. 22)

4. OBJECTIVES

The main aim of this project is the preparation and characterisation of graphene-based lyotropic liquid crystals, as the title indicates.

However, the achievement of this objective supposes the accomplishment of a sequence of minor (but also important) items. Some of them are:

- As regard to theory:
 - Acquisition of general knowledge about LCs, which includes things like to know what types of LCs exist, what are their main features or how are they characterised.
 - To know what is graphene and, especially, what is GO and to understand why it should be able to form LCs.
 - To learn about the general fundamentals of POM.
- As regard to experimental work:
 - Preparation of nanoplatelets of GO from commercial graphite flakes, following different protocols reported in literature.
 - Characterisation of GO samples and evaluation of their lyotropic liquid crystalline behaviour. It includes the use of POM in order to identify LC phases and their typical disclinations. Moreover, it also considers the possibility of recognising other interesting features, as their type of anchoring or their behaviour under magnetic field or under temperature changes.

5. EXPERIMENTAL SECTION

This section describes how the synthesis of graphene oxide was carried out, describing in detail the materials and the protocols used and indicating the most important observations that were did during the process.

5.1. MATERIALS

Graphite flakes were obtained from Alfa Aesar. Potassium persulfate ($K_2S_2O_8$) was purchased from Merck. Phosphorus pentoxide (P_2O_5) and hydrogen peroxide (H_2O_2) 33% w/v were acquired from Panreac. Concentrated H_2SO_4 (96%) was bought from Acros Organics. Potassium permanganate ($KMnO_4$) was obtained from Probus. Concentrated H_3PO_4 (85%) was purchased from Sigma-Aldrich.

5.2. SYNTHESIS OF GRAPHENE OXIDE (GO)

5.2.1. Method 1: a double-step oxidation

In this method, GO was prepared following Ref. 23 with some modifications.

In the preoxidation step, 2.5 g of graphite flakes, 2.1 g of $K_2S_2O_8$ and 3.1 g of P_2O_5 were added into a 250 mL round-bottom flask. Next, 150 mL of H_2SO_4 were slowly added. The mixture was kept at 80 °C for 5 h in an oil bath at 400 rpm stirring. After that, the mixture was deeply black. After cooling to room temperature (it was led to cool overnight), the mixture was transferred to a 2 L beaker and then it was diluted with 1 L of Milli-Q water (high exothermicity process), vacuum-filtered using a 0.22 μm pore polycarbonate membrane (Whatman, 47mm diameter) and washed with 1 L of Milli-Q water. The resultant solid (aspect: bright, black) was dried in air for 2 days. In order to facilitate the drying of solid, during these two days it was occasionally stirred with a spatula.

In second oxidation step, the preoxidized graphene was added into 100 mL of concentrated H_2SO_4 , previously chilled to 0 °C in an ice bath. Maintaining the round-bottom flask inside the ice bath in order to keep it below 10 °C, 7.5 g $KMnO_4$ were added slowly under continuous

stirring at 600 rpm. Then, the mixture was heated to 35 °C and stirred for 2 h at 400 rpm. During this time, its colour changed from black to very dark green. The mixture was transferred to a 2 L beaker and was diluted with 1 L of Milli-Q water (high exothermicity process), changing its colour to dark brown. After that, 5 mL of 33% H₂O₂ were added dropwise under continuous stirring, and there was a colour change to light orange. The mixture was left undisturbed for 2 days and most of the nearly clear supernatant was decanted. The precipitate was repeatedly washed with Milli-Q water and centrifuged successively with 1 M HCl solution to remove residual metal oxides and then washed with Milli-Q water until the decantate became approximately neutral (pH~5-6).

This method was tested twice, but in the second case, small modifications were introduced, some of them according to Ref. 14. These changes were:

- Use of deionized water, instead of Milli-Q water.
- After the first dilution (preoxidation step), the mixture was left undisturbed and cooling to room temperature for 4 h, before filtration.
- The second dilution (second oxidation step), was divided in two parts. First, the mixture was diluted with 0.25 L of deionized water and was kept under stirring for 2 h. Then, 0.75 L of water was added and this final mixture was stirred for 5 minutes.

5.2.2. Method 2: an improved oxidation

In this method, GO was prepared by process of Refs. 17 and 24 with some modifications.

A 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (144:16 mL) was introduced into a 250 mL round-bottom flask. Then, 1.2 g of graphite flakes and 7.2 g of KMnO₄ were introduced in the flask under continuous stirring at 400 rpm. When only the graphite was added, the mixture was deeply black, and it turned to dark green after potassium permanganate addition. The reaction was heated to 50 °C in an oil bath for 10 h. Later, the mixture was cooled to room temperature (it was led to cool overnight) and poured slowly onto ~ 100 mL of ice and 60 mL of deionized water under stirring. The colour of the mixture changed to purple. 3.3 mL of H₂O₂ 33% were added dropwise under continuous stirring. At this point, the mixture turned to bright yellow. The mixture was left undisturbed for 2 days. The precipitate was repeatedly washed with Milli-Q water and centrifuged successively with 1 M HCl solution and then washed with Milli-Q water until the decantate became approximately neutral (pH~5-6).

5.3. PREPARATION OF GO AQUEOUS DISPERSIONS

The precipitate remaining inside the centrifugation tube was mixed with Milli-Q water by gentle stirring with Vortex, obtaining a yellowish-brown dispersion.

In some cases, sonication was needed in order to get good dispersibility of GO. This fact will be analysed in section of “Results and discussion”.

On the other hand, to determine the concentration of the final dispersion was more challenging, because the quantity of GO that was mixed with water was not known due to a gel was formed (see “Results and discussion”). In order to estimate it, 1 mL of dispersion was warmed on a clean glass slide, whose weight is known, until total evaporation of water. When only a brown thin film remained, the glass slide was cooled to room temperature and was weighted again. By the difference of weight and the total volume of dispersion warmed previously, an approximated value of concentration was found.

5.4. PREPARATION OF LIQUID CRYSTALS CELLS

Optical analysis of birefringence of LC samples typically requires the preparation of a thin film of the fluid under controlled confined conditions. So, correct preparation of liquid crystal cells is an indispensable step in order to study the behaviour of GO samples. To do that, two (or three) processes were required: first, good glass cleaning; second, functionalization of glass surfaces (if necessary); and third, cell construction.

5.4.1. Glass cleaning

In order to obtain clean glass to prepare LC cells, microscope glass slides were first cleaned with a soapy solution, rinsed with copious amounts of deionised water and dried with nitrogen. Then, they were introduced in fresh piranha solution²⁵ (H_2O_2 (33% w/v, from Panreac) / H_2SO_4 (lab grade), 1:3) for 30 min. Because the mixture is a strong oxidising agent, it removes organic matter, such as possible residual from previous washing step, and it also hydroxylates the surface, making it highly hydrophilic. The piranha solution may be mixed before application or directly applied to the material, introducing first the sulphuric acid, followed by the peroxide.²⁶ In this case, the first option was applied. (NOTE: Mixing of sulphuric acid and oxygen peroxide is an exothermic process. Moreover, it is a dangerous reaction, due to both strongly acidic and strong oxidizing capability, so working with extreme caution is essential).

After the action of piranha solution, the cleaned and activated glass was rinsed with copious amounts of Milli-Q water and dried with nitrogen.

5.4.2. Functionalization of glass surfaces

In most cases, glass surfaces are functionalised with polyvinyl alcohol (PVA) for improved sample affinity and more reproducible results.

5.4.2.1. Polyvinyl alcohol (PVA) coating

PVA is a water-soluble synthetic polymer, whose structure is shown in Figure 14.

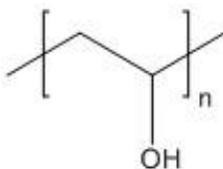


Figure 14. Chemical structure of PVA.

PVA coating²⁷ was performed onto glass slides cleaned using piranha solution as explained above. Then, an aqueous PVA solution 3% (88% hydrolysed, M. W.: 88.000 g/mol, from Sigma-Aldrich) is filtered through a 0.2 μm Nylon filter and spin-coated at 3000 rpm for 30 s. After that, the PVA-coated slides were heated at 150 $^{\circ}\text{C}$ for 1 h in order to evaporate residual traces of water. Finally, they were cooled to room temperature and kept in a desiccator.

5.4.2. Cell construction

The samples were introduced in LC cells prepared by assembling two parallel plates of glass (PVA-coated or not, depending on the case) with double side tape (80 μm , ScotchTM from 3M) between them, acting as spacers. The LC cells were filled due to capillarity. Then, the parallel plates were glued using photopolymerizable glue (Norland optical adhesive 81 from Norland Products, INC), which sealed to prevent evaporation and to confer robustness to the system.

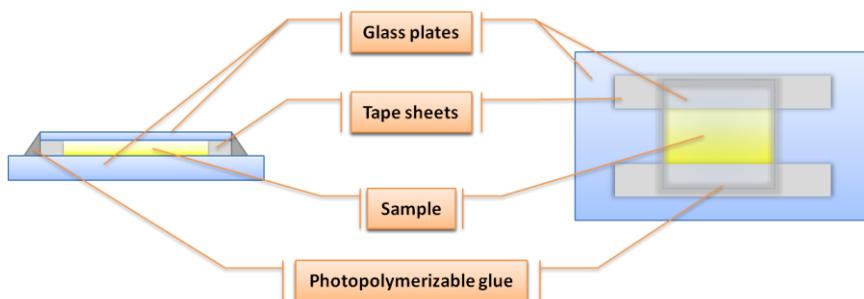


Figure 15. Representation of LC cells. Left: lateral view. Right: top view

5.5. CHARACTERISATION

The characterisation of LC samples was made by POM, performing the observations with a Nikon Eclipse 50iPol upright microscope with 20x and 40x objectives. Black and white images were acquired with an AVT Marlin 131B CMOS digital video camera. Colour images were acquired with a Logitech C920 camera. Further processing was carried out with the software ImageJ.

6. RESULTS AND DISCUSSION

6.1. EVALUATION OF THE SAMPLES LIQUID CRYSTALLINE BEHAVIOUR

Although the protocols we used resulted in birefringent samples, they were more heterogeneous than those reported in the literature.¹³⁻¹⁷ On the one hand, if the dispersion with which the sample was prepared had not been sonicated, we observed birefringent crystals in an isotropic medium (Figure 16).

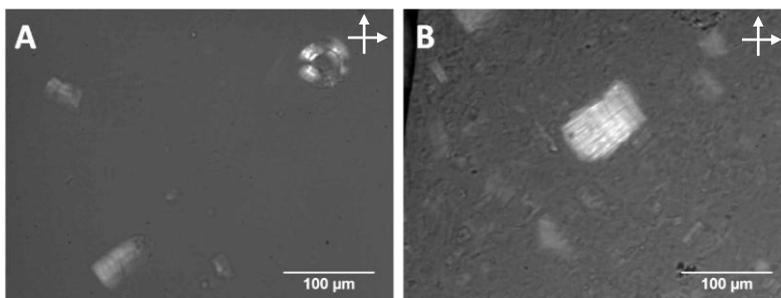


Figure 16. POM images of birefringent structures found on the GO samples. A: GO synthesized by method 1. B: GO synthesized by method 2.

On the other hand, in those cases in which the dispersion was sonicated, we could appreciate the presence of birefringent zones (Figure 17). This happened in samples of GO synthesized by both protocols and either the glass was no coated or PVA-coated. The birefringence showed in Figure 17 was manifested when the circular rotating sample stage of the microscope was rotated. Then, the colour variations that we observed were in agreement with the ones reflected in Figure 13, taking into account the correct wavelength (~ 580 nm) and the correct value of thickness for our case. Images labelled with a C were particularly interesting because we could detect a +1 defect, as the one drawn in Figure 6. Herein, the total birefringence of the first and the third quadrants of the defect was stronger than the birefringence of the second and the fourth quadrants. It means that the average orientation of the director on the first and the third quadrants and the average orientation of the director on the

second and fourth quadrants were perpendicular between each other. Due to that, on the first and the third quadrants the birefringence of the birefringent plate was added to the LC birefringence; whereas on the other two quadrants, these two birefringences were subtracted.

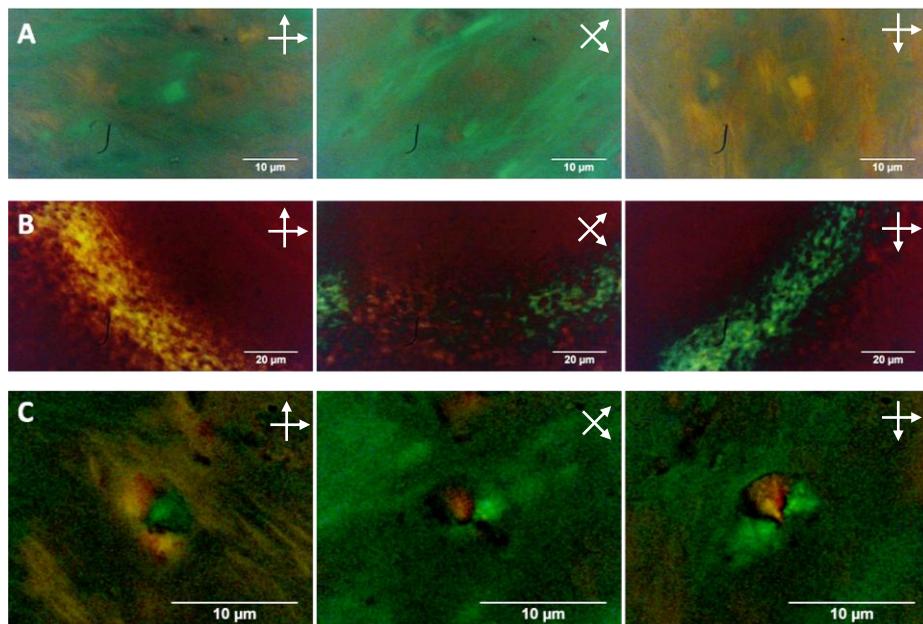


Figure 17. POM images of 80 μm layers of 0.8% w/v GO suspensions that display birefringence. Images were obtained with a 530 nm birefringent plate (Nikon, Japan) inserted in the optical path for improved contrast. A: GO method 1, glass cleaned with Piranha. B: GO method 2, glass cleaned with Piranha. C: GO method 1, PVA-coated glass.

We realised these birefringent regions always appeared at interfacial zones, such as tape edges in contact with the GO dispersion or around air bubbles. In some cases, we identified these zones as dried GO because we distinguished a change in the homogeneity of the sample, so we do not consider them as appearances of LC textures. But, in other cases in which the sample looked homogeneous, we concluded they had a typical LC behaviour. Consulting more bibliography about GO LCs so as to understand if this behaviour was normal or not, on the one hand, we found that some research groups had obtained GO dispersions of suitable concentration through processes of partial evaporation of water, until acquiring a concentration in which the nematic texture appeared^{16,28}. That could be the reason why interfacial areas showed birefringence. On the other hand, Guo *et al.* reported that the liquid crystallinity of those

areas could reveal the surface anchoring state of GO. They commented that “GO layers anchor homeotropically (face-on) at the liquid-glass and liquid-air interfaces” and they indicated that “an evidence of this behaviour is seen at the surfaces of air bubbles trapped between two glass slides confining GO suspensions”.²⁸

6.2. COMPARISON BETWEEN TWO OXIDATION METHODS

The first method was tried because literature defines it as “widely effective and has been used to obtain dispersible (highly soluble single-layered) GO by many research groups”.¹⁴ Moreover, its main advantage is the synthesis of exfoliated graphene using a chemical method instead of sonication.

The second method was selected because it had been used by many other research groups, and because it is defined as an improved method with better properties than the rest.

Notable differences between these two protocols have not been found in this project, because the samples of each method showed the same liquid crystalline behaviour, as the previous subsection explained. However, some spots and foreign bodies were observed in POM images of GO samples synthesized by the second method; while in the other samples, it did not occur.

So, we consider that the double-step oxidation is better than the improved method. For that reason, all the results described later are referred to samples of GO synthesized through the first oxidation method (unless otherwise noted).

6.3. PHASE SEPARATION WITH TIME

We left a GO dispersion undisturbed inside a centrifugation tube, which was sealed to avoid water evaporation, for 3 weeks. We noted a phase separation: the upper phase was yellowish-brown and the bottom phase was dark brown (Figure 18a). Moreover, we observed macroscopic birefringence by naked eye placing the dispersions between crossed polarizers (Figure 18b). Herein, we differentiate three zones in the centrifugation tube: a birefringent upper zone, a non-birefringent bottom zone and an intermediate zone with a little birefringence. After three weeks, no further changes were observed. These results were totally unexpected. In a lyotropic LC, when increasing concentration, the transition I-N occurs. Therefore, we thought the lower phase should not have been isotropic given that it was probably the most concentrated due to sedimentation. In fact, our reasoning was confirmed by the data reported in literature, in

which the upper phase was isotropic without birefringence and the bottom phase showed colourful birefringence.^{13,14}

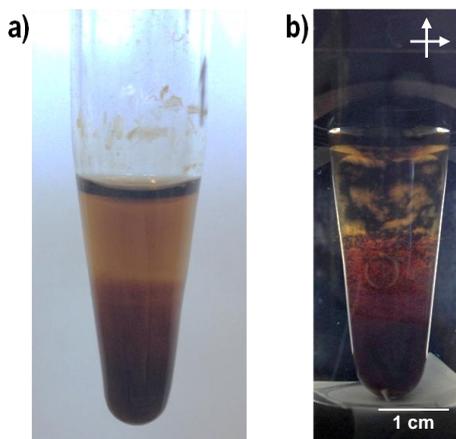


Figure 18. a) Dispersion of GO showing phase separation four weeks after preparation. b) Dispersion of GO located between crossed polarizers.

We prepared three LC cells, one for each phase in centrifugation tube and we observed them by POM. These samples did not show any LC texture, but the number of birefringent structures like the one commented in section 6.1. increased going from the upper to the lower phase (Figure 19).

The differences between medium and upper phases are not appreciable in the above image. However, we could observe that the upper phase did not show any birefringence, apart from the area captured on the image, in which little birefringent filaments appeared; whereas in the intermediate phase, these filaments were more abundant and they were distributed through the entire sample.

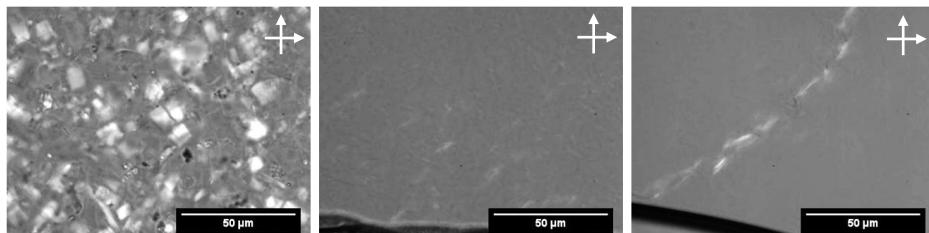


Figure 19. From left to right, POM images of the bottom, medium and upper phases previously described.

6.4. PRESENCE OF INCLUSIONS IN THE SAMPLE

In a similar way to the behaviour observed at air-water interfaces and in contact areas between tape and the sample, structures reminiscent of LC textures appeared around inclusions such as dust or precipitates, for example (Figure 20a).

This fact suggested that GO samples could need certain contour conditions in order to form a mesophase. For that reason, we decided to prepare a sample with $\sim 50 \mu\text{m}$ (range: 10-100 μm) diameter glass spheres dispersed so as to observe whether birefringent zones also appeared around these inclusions.

Effectively, the resultant POM images showed birefringence around the spheres, although it was not as remarkable as we expected (Figure 20b).

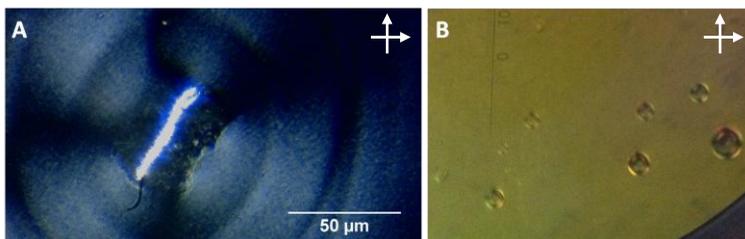


Figure 20. Birefringence around a contaminant particle (A) and glass spheres (B).

6.5. OTHER OBSERVATIONS

6.5.1. Gelation of GO

During the sequential cycles of centrifugation and washing of GO, we realised that solid GO underwent volume expansion, which suggested the formation of a gel. Bibliography confirms this fact affirming that GO dispersions tend to undergo gelation as the dispersion pH increases during the washes.²⁹

Moreover, we also observed that increasing the concentration of the dispersion, increased its difficulty to flow (Figure 21).

In order to solve this problem, which rendered centrifugation quite difficult, we tested a two-step, acid-acetone washing procedure²⁹ to avoid gelation. In our case, the obtained results allowed us to confirm that this process was efficient to reduce the moisture content of GO solid, but it did not avoid completely the gelation.



Figure 21. Fluidity of GO dispersions with different concentration. Left: ~0.2% w/v. Right: ~1.6% w/v

6.5.2. Effect of temperature changes and magnetic field on GO samples

We also investigated the effect of temperature changes on GO samples. We used a control temperature in order to subject the GO samples from 25 °C to 40 °C and evaluating possible temperature-induced phase changes. Nevertheless, no variations were observed.

On the same way, we prepared a GO sample in a LC cell that was suitable to perform observations under a magnetic field (0.5 T). We left the sample under these conditions for a night in order to observe if a magnetic-field-induced alignment of GO LCs happened or not. However, we did not notice significant changes either.

7. CONCLUSIONS

Once this project has been finished, the main conclusions extracted of it are detailed below:

- The chemical structure of GO platelets makes them capable to form lyotropic LCs, as some papers reported.
- An increase in GO dispersions concentration involves a rise in the number of birefringent structures observed when the sample was not sonicated. Moreover, increasing the dispersion concentration, the system evolves to a state which ceases to flow.
- Interfacial areas (air-water and tape-water) often show birefringence, with an appearance similar to LC textures.
- LC textures also appear around inclusions. This suggests the option of GO LCs require certain contour conditions to be formed.
- Apparently, GO samples are not aligned by a modest magnetic field and do not undergo temperature-induce phase changes.
- Due to the presence of hydrophilic surface functional groups, GO dispersions are prone to undergo gelation.

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9. ACRONYMS

GO: graphene oxide

I-N: isotropic to nematic phase transition

LC: liquid crystal

LCLC: lyotropic chromonic liquid crystal

POM: polarized optical microscopy

PVA: polyvinyl alcohol

APPENDICES

APPENDIX 1: EXPANSION OF FIGURE 17-A

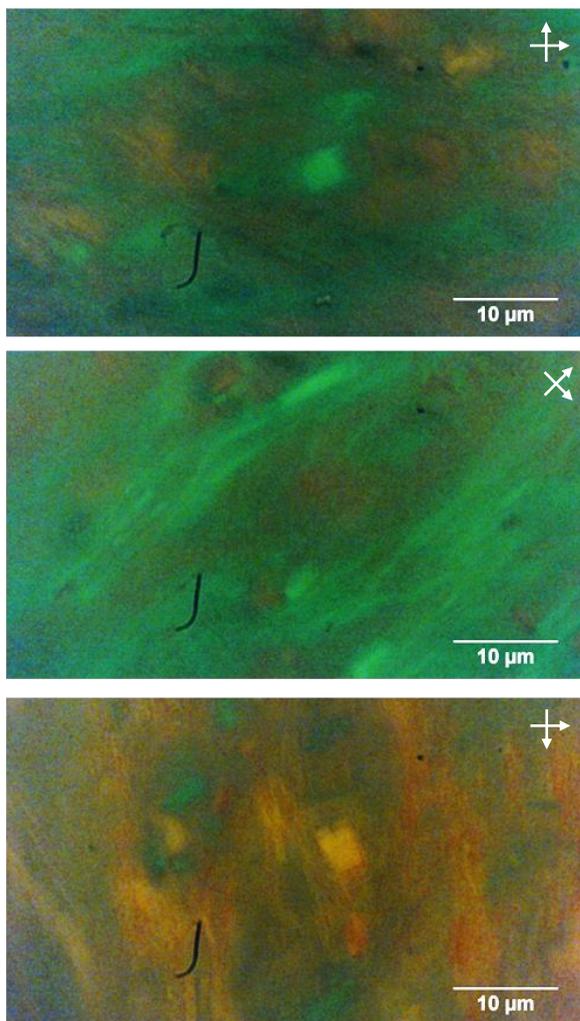


Figure 17-A (expansion). POM images of a GO sample (GO prepared by method 1; glass cleaned with Piranha).

APPENDIX 2: EXPANSION OF FIGURE 17-B

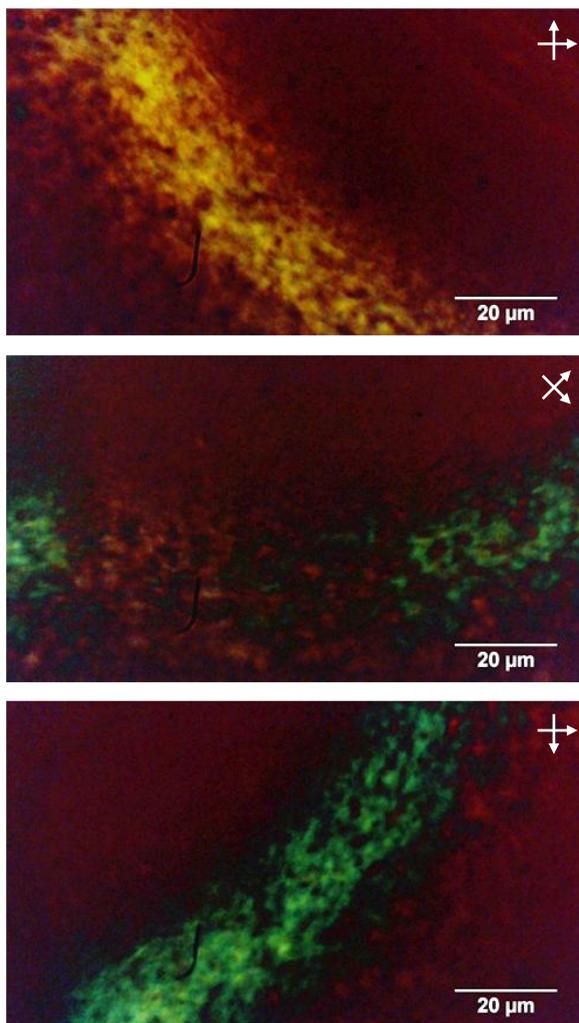


Figure 17-B (expansion). POM images of a GO sample (GO prepared by method 2; glass cleaned with Piranha).

APPENDIX 3: EXPANSION OF FIGURE 17-C

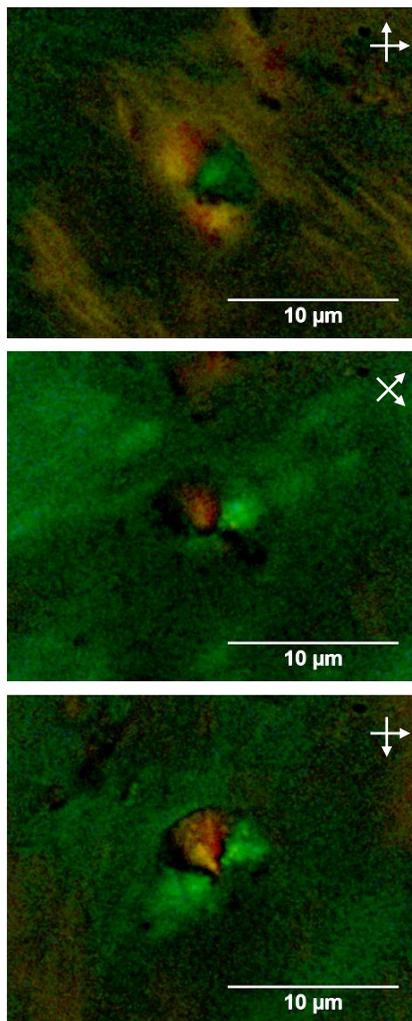


Figure 17-C (expansion). POM images of a GO sample (GO prepared by method 1; PVA-coated glass).

