

# The Liquid Crystal Behavior of New Non-ionic Azobenzene-Amphiphiles

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## Abstract

The new non-ionic amphiphiles **2**, **3** and **4** presented interesting thermotropic liquid crystal (LC) behavior as determinate by Differential Scanning Calorimetry (DSC) and Optical Polarizing Microscopy (OPM). Compound **2** exhibited a non-cooperative phase transition presenting a nematic mesophase. Compound **3** and **4** showed a smectic polymorphic behavior. In addition compound **4** presented a lamellar mesophase at high temperature (240°) similar to those observed in common ionic amphiphiles.

**Keywords:** amphiphiles, smectic, nematic, thermotropism

## Introduction

Molecular self-assembly process of biological building blocks enables the formation of complex architectures and machinery; our interest in studying amphiphilic systems is due to their potential development as supramolecular systems capable of interacting with lipid membranes. [1] Ionic azobencenes amphiphiles have been previously reported in order to investigate the physicochemical properties of biomimetic membranes. [2-4] The charged headgroup on these surfactants have such large effective cross-sectional areas that the conformation change taken by the tails as a result of the illumination has little effect on the packing of the amphiphile in the absorbed interfacial layer. [5] In order to obtain systems with potential use as membrane modulators, we have synthesized new non-ionic amphiphilic systems based on azobenzene. [6] Initially, it is necessary to evaluate the capability of the system to form liquid crystal (LC) mesophases. Fundamentally, LC materials are classified as being either thermotropic or lyotropic depending on whether their self-organization occurs only on heating of the pure compounds (thermotropic liquid crystals) or is induced by isotropic solvents (lyotropic liquid crystalline phases). Amphiphilic systems due to nature are able to present both behavior. [7]

The mesophases of thermotropic LCs are thermodynamically stable but only partially ordered phases are presented. Each mesophase is described by its degree of order. If the mesophase has orientational order only, it is called nematic (N), if it has both orientational and positional order it is called smectic (Sm). Most of the known thermotropic LCs are calamitic or rod-like [8-10]. Calamitic LCs are those mesomorphic compounds that possess an elongated shape, responsible for the form anisotropy of the molecular structure, as the result of the molecular length (l) being significantly greater than the molecular breadth(b) (Fig. 1)

A calamitic mesogen molecule consists of a core, terminal chains and lateral substituents. The core provides rigidity which is required for anisotropy, whereas the terminal chains provide flexibility to stabilize the molecular alignment within the mesophase. These calamitic molecules form both nematic and smectic mesophases depending upon the type of the substituents and their combinations [10, 11].

The studied Amphiphiles (Fig. 2 and 3) are classified as calamitic due to its general chemical structure that can be grouped in four structural components: a long

hydrophobic tail composed of 12 carbons, a rigid core segment based on azobenzene group, an hydroxyl group as a polar non-ionic head and a triethyleneglicol group as spacer between the rigid segment and the head (Fig 2)

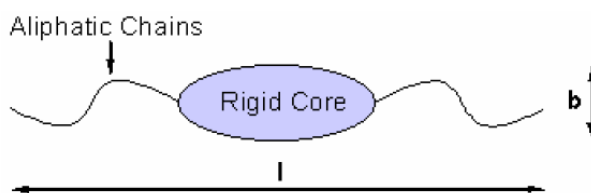


Fig. 1 Cartoon representation of calamitic LCs, where length( $l$ )  $\gg$  breadth( $b$ )

Taking into account the amphiphilic nature of the synthesized compounds, they can present amphitropic behavior, which is that they could be thermotropic, due to the organic structure and potentially lyotropic in water to the polar head.

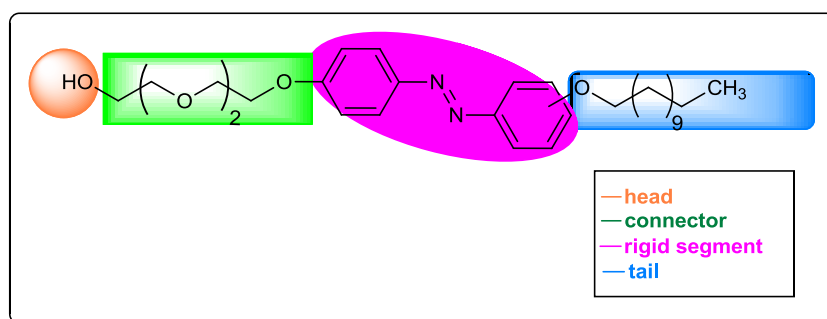


Fig 2. General Structure of the Amphiphiles presented

Herein, it is presented the thermal and morphological characterization of new non-ionic amphiphilic azobenzene compounds in solid state, evaluated by Differential Scanning Calorimetry (DSC) and Optical Polarizing Microscopy (OPM).

## Experimental Procedure

### Materials:

All compounds were obtained as previously reported. Compound 1 and 2 were purified by further recrystallization on MilliQ water. Compound 3 and 4 were first purified by neutral alumina column chromatography followed to recrystallization water/ethanol mixture (80:20). All compounds were placed under vacuum at 35°C for 24 h. Previously to the calorimetric experiments it was determined the melting point of all the compounds by polarized light microscopy.

### Methods:

Phase transition temperatures and thermodynamic parameters were determined by using a DSC Q20 V23.4 Build 64 scanning calorimeter (Universal V4.4A, TA Instruments, Binghamton, NY) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating and cooling rates were 5°C min<sup>-1</sup> with a nitrogen flow rate of 50 mL/min. Phase transition temperatures were collected during the second heating and the second cooling scans. Phase identification was performed by polarized light microscopy using an Olympus BX50 (Japan) polarizing optical microscope (OPM) equipped with a Linkam THMSE-600 (Linkam, England) hot stage and a TMS 92 control unit.

## Results and Discussion

Taking account small changes in molecular architecture can markedly affect the mesomorphic behavior of LC compounds [11], it was interesting to evaluate the effect of the spacer between the core and the polar head and the position of the hydrophobic tail. For this purpose the azobenzene derivatives substituted on position 4:4' and 4:3' were prepared with the polar hydroxyl head directed attached to the rigid segment (compounds 1 and 2, Fig. 2) or with a trietilenglycol spacer in between (compounds 3 and 4, Fig. 2). Due to their amphiphilic nature all compounds were very difficult to recrystallize. They presented high solubility in organic solvents like chloroform, methanol, dichloromethane, acetone and ethanol. Recrystallization from water or water/ethanol mixtures led to gummy and waxy solids, treatment of the solids under vacuum at 35°C during 24 h. led to the stable solids used for DSC and OPM.

**Thermal Behavior and Morphological Observation.** The phase transition temperatures as well as phase transition enthalpy changes were determined using DSC and the result of the second heating and cooling scans. Morphological changes were performed by OPM using a temperature controlled hot stage. A summary is presented in Table 1.

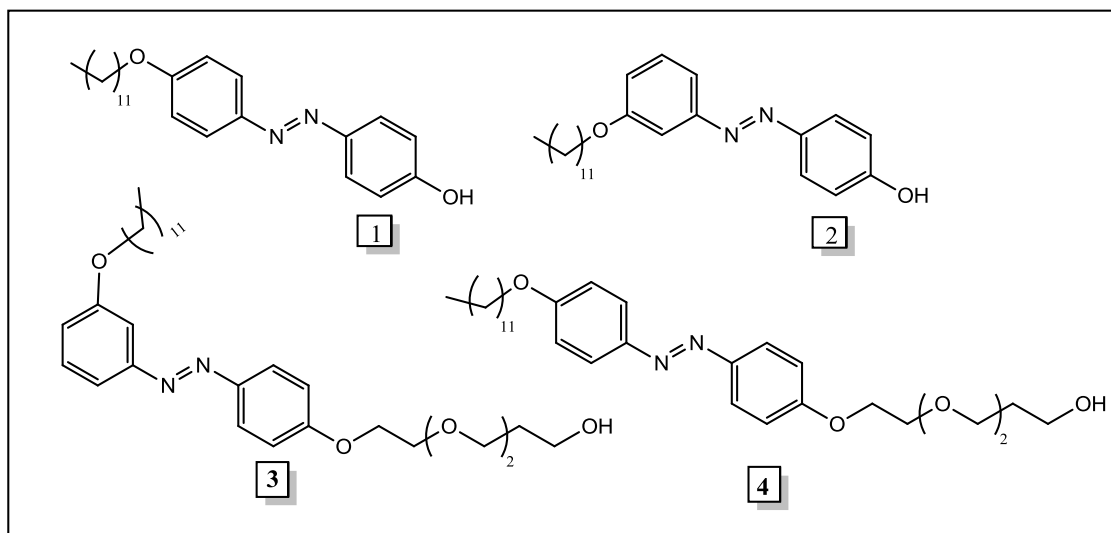


Fig 3. Structures of the Amphiphiles evaluated

Compound	Transition temperature (T/°C) and associated transition enthalpies values ( $\Delta H \text{ J g}^{-1}$ )
1	2nd Heating Cr 102.87 (116.3) I 2nd Cooling I 96.72 SmA 95.25 (83.49) Cr
2	2nd Heating Cr1 66.27 (43.65)N-I 2nd Cooling I-N 48.31 (37.83) Cr2
3	2nd Heating Cr 58.98 (111.7) I 2nd Cooling I 40.10 (96.56) SmA-SmC 30.27 (2.75) Cr
4	2nd Heating Cr-SmC 91.67 (88.10) SmA 107.28 (33.77) PI-Ln 2nd Cooling Ln-PI 100.02 (27.51) SmA 89,00 SmC 87.24 (94.29) Cr

Table 1: Phase transition temperatures and enthalpies obtained from DSC scans of 1, 2, 3, 4 Abbreviations; CoA= Coagel; Cr = Crystal; SmA = Smectic A; N = Nematic; I = Isotropic phase; PI= Pseudoisotropic phase; Ln = Lamellar neat.

**Compound 1**, possess the hydroxyl head directed attached to the rigid core and is 4:4' substituted, DSC thermogram of **3** showed one peak on heating process and two close peaks on cooling. On heating the phase transition occurred at 102, 87°C. The enthalpy of the transition ( $116, 3 \text{ J g}^{-1}$ ) can be associated to a transition from crystal (Cr) to isotropic (I); that was confirmed by OPM observation.

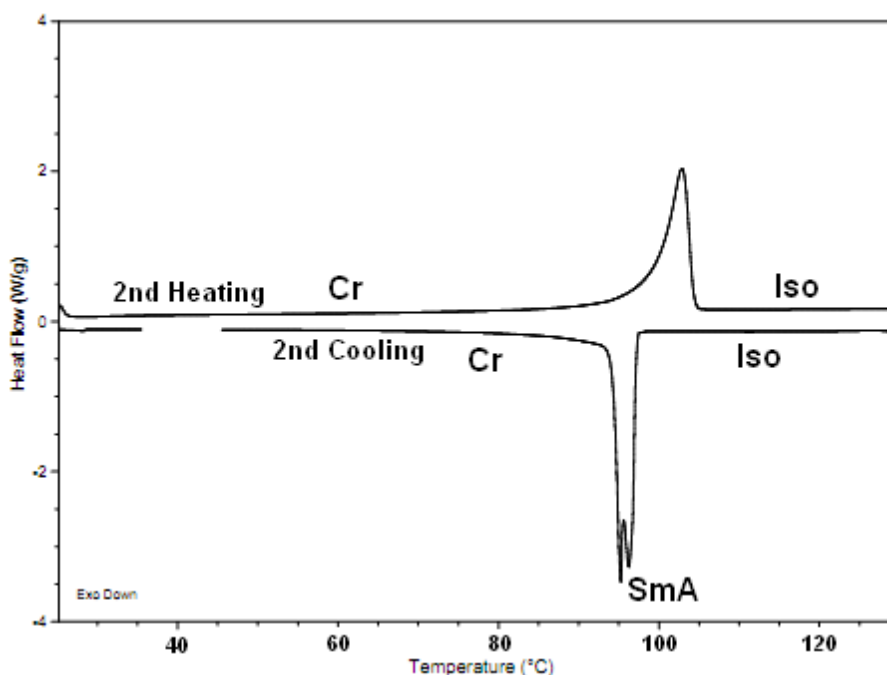


Fig. 4: DSC Heating and cooling traces of compound 1 ( $5^{\circ}\text{C min}^{-1}$ )

On cooling cycle it was possible to observe two peaks one at 96, 72°C and 95, 25°C ( $83, 49 \text{ J g}^{-1}$ ) By OPM, it was detectable the existence of a I-SmA transition (93°C)

close to the crystallization temperature (90°C). The texture of fan is characteristic of SmA mesophases.

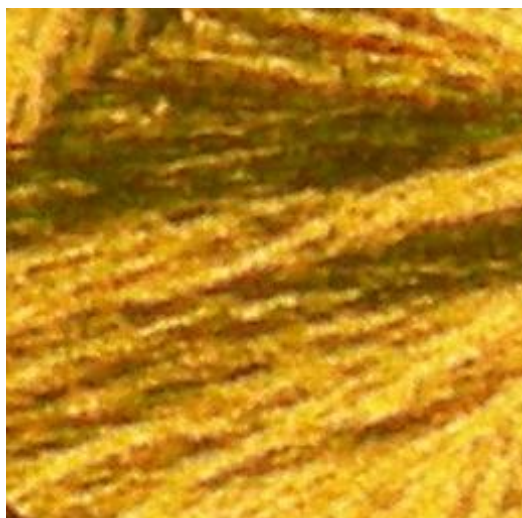


Fig. 5: Smectic A mesophase of compound **1** observed on cooling from the isotropic liquid at 96°C. Fan texture. Crossed polarizers, magnification ca.200x

**Compound 2**, has the same functional groups as **1** but it is 4:3' substituted. DSC experiments showed only one broad peak on heating (66, 27°C; 43,65 J g<sup>-1</sup>) and another on cooling cycle (48,31°C; 37,87J g<sup>-1</sup>). Presence of broad peaks in DSC could correspond to non-cooperative transitions, associated with the presence of microdomains probably to the bad packaging of the molecules due to the substitution 4:3'.

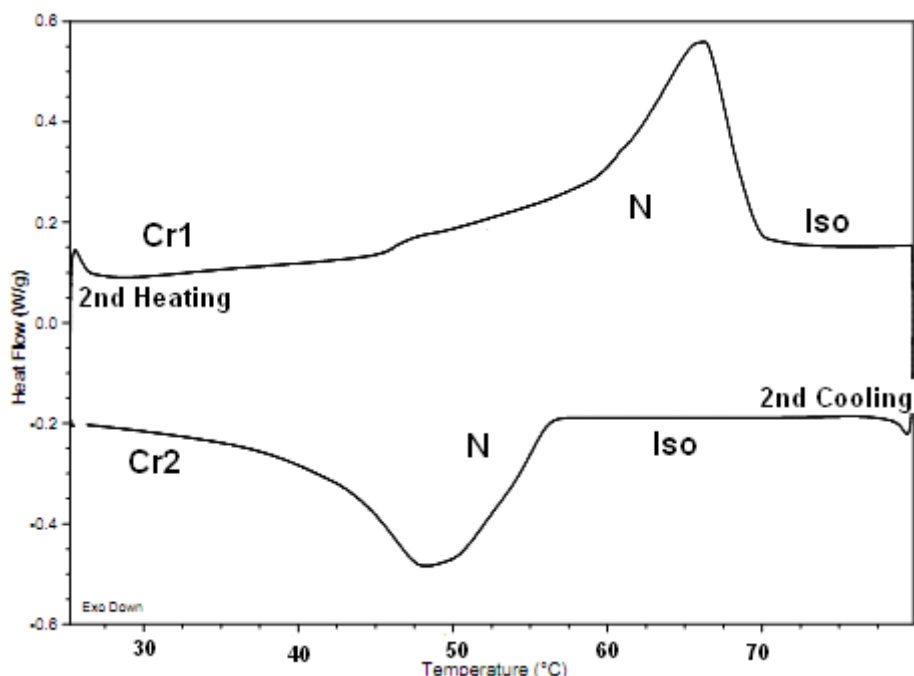


Fig. 6: DSC Heating and cooling traces of compound **2** (5°C min<sup>-1</sup>)

Compound **2** was difficult to manipulate due to its “varnish type” nature, under microscopic observation can be associated to a waxy crystal structure (Fig. 7a), which became fluid at 40°C observing a phase transition from Cr1 to Nematic (N) with a

characteristic marbled non geometrical texture (Fig. 7b) stable until 65°C where the N-I transition occurred.

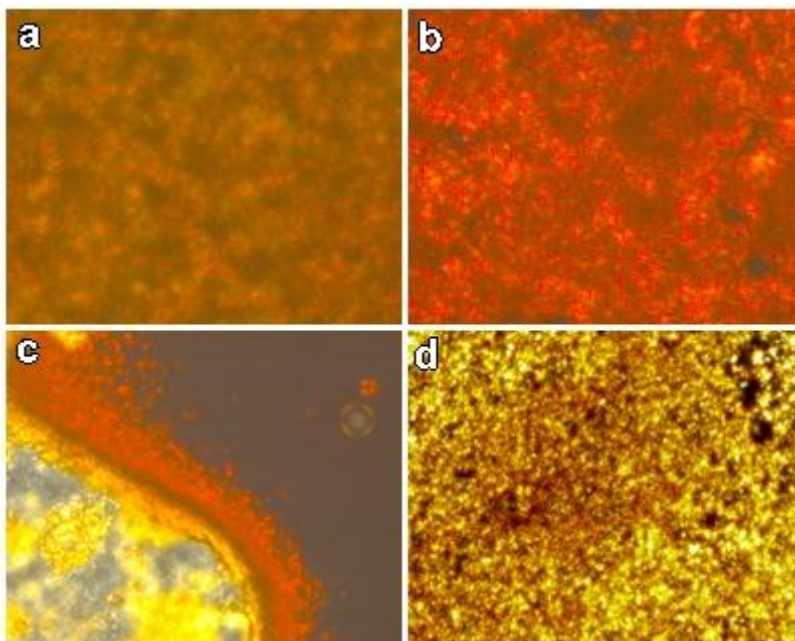


Fig. 7: Optical photomicrograph of **2** obtained with a polarizing microscope (a) Initial crystalline structure (Cr1) at 25°C. (b) Nematic phase on heating at 67°C. Marbled non geometrical texture. (c) On cooling from the nematic phase (right) to the crystalline structure (left) 45°C. (d) Final crystalline structure at 30°C. (a)(b)(d): Cross polarizer magnification  $\times 150$ . (c) Cross polarizer magnification  $\times 40$

On cooling, the I-N transition was observed at 50°C, the presence of only positive spherulytic and uniaxial figures confirmed the nematic mesophase (Fig. 7c). At 45°C a transition N-Cr2 was observed. The granular bright crystal structure was determined as a laminar one, characteristic of crystalline surfactant systems [12-15] and it was stable at room temperature (Fig. 7c and 7d).

**Compound 3** is 4:3' substituted and has a triethyleneglycol linker among the polar head and the rigid segment of the amphiphile. The corresponding DSC thermogram of **3** showed one peak (58, 95 °C; 111,7 J g<sup>-1</sup>) on heating and two peaks on cooling (40, 10°C; 96,56 J g<sup>-1</sup> and 30, 27 °C; 2,75 J g<sup>-1</sup>).

Compound **3** showed a waxy crystal structure (Fig. 9a) usually associated to a laminar structure in amphiphile systems [12-15]; the transition Cr-I was observed at 59 °C (Fig. 9b). On cooling I-SmA transition occurs at 40°C and another smectic phase was detected. The SmA fan texture (Fig 9c) and SmC broken fan texture (Fig. 9d) observed was confirmatory of a SmA-SmC structure transition. [16] The low enthalpy detected for the transition SmC-Cr (30, 27°C; 2,75 J g<sup>-1</sup>), also support the presence of SmC mesophase.

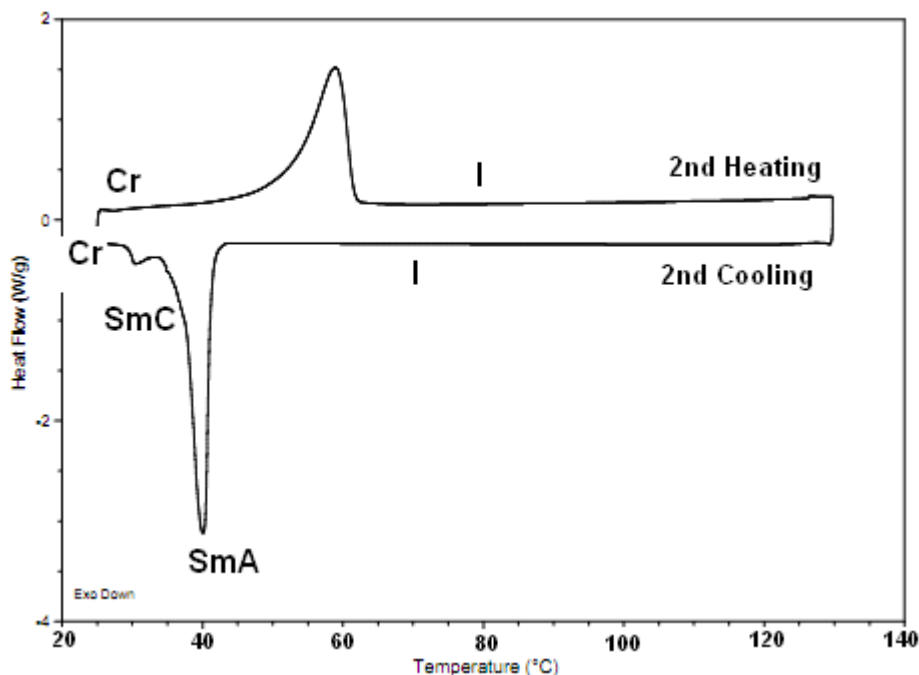


Fig. 8: DSC Heating and cooling traces of compound **3** ( $5^{\circ}\text{C min}^{-1}$ )

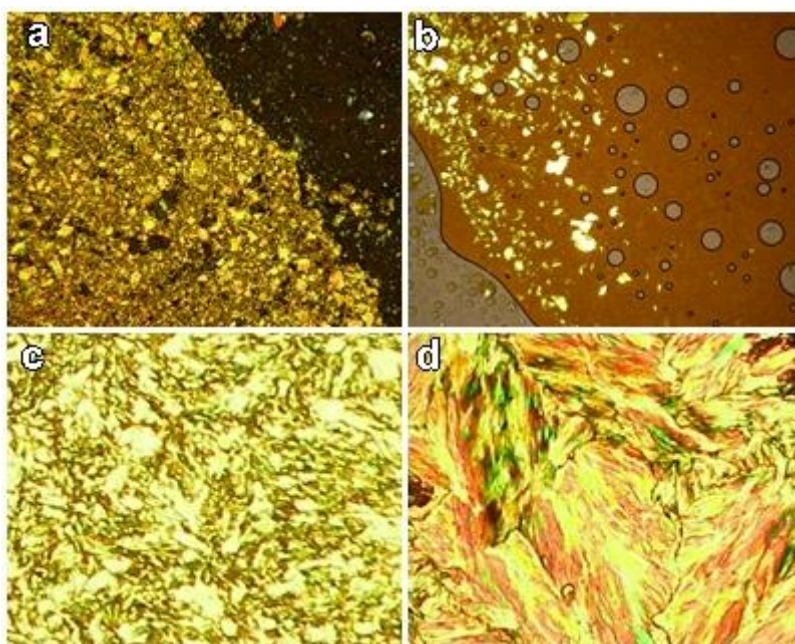


Fig. 9. Optical photomicrograph of **3** obtained with a polarizing microscope (a) Crystalline structure at  $25^{\circ}\text{C}$ . (b) On heating to isotropic liquid at  $59^{\circ}\text{C}$ . (c) Smectic A phase on cooling from the isotropic liquid at  $37^{\circ}\text{C}$ . (d) Smectic C phase at  $32^{\circ}\text{C}$ . (a)(b) Cross polarizer magnification $\times 40$ . (c) Cross polarizer magnification $\times 150$ . (d) Cross polarizer magnification $\times 200$ .

**Compound 4** is 4:4' substituted possess the flexible linker between the core and the polar head. DSC experiment of **4** revealed two transition on heating at  $91, 67^{\circ}\text{C}$  ( $88, 10 \text{ J g}^{-1}$ ) and  $107, 28^{\circ}\text{C}$  ( $33,77 \text{ J g}^{-1}$ ). On cooling three phase transition occurs at  $100, 02^{\circ}\text{C}$  ( $27, 51 \text{ J g}^{-1}$ ),  $89, 00^{\circ}\text{C}$  and  $87, 24^{\circ}\text{C}$  ( $94, 29 \text{ J g}^{-1}$ ).

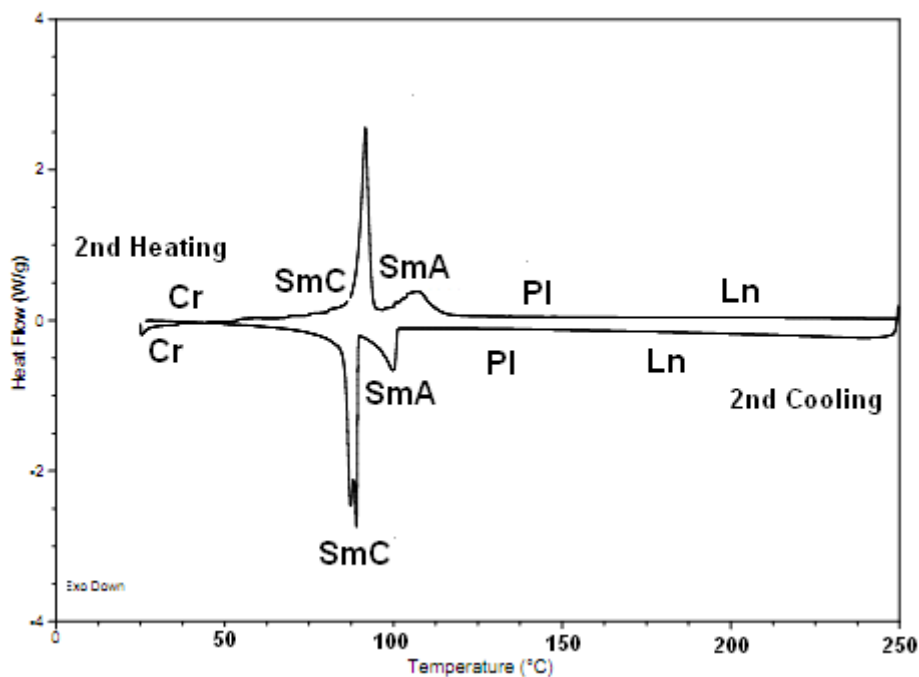


Fig. 10. DSC Heating and cooling traces of compound **4** ( $5^{\circ}\text{C min}^{-1}$ )

Amphiphile **4** presented a polymorphic behavior as observed by OPM. At room temperature it presented a waxy crystal structure [12-15] characteristic of smectic or laminar mesophases of ionic amphiphiles (Fig. 11a). On heating it was possible to detect the transition from Cr to different smectic mesophases, due to the textures observed it was possible to assign SmC-SmA transition at  $88^{\circ}\text{C}$  (Fig. 10b, 10c, 10d). In this case the SmC texture observed is a biaxial schieleren one (Fig. 11d) [16] Observations of positive and negative spherules figures confirmed the smectic mesophases (Fig. 11c).



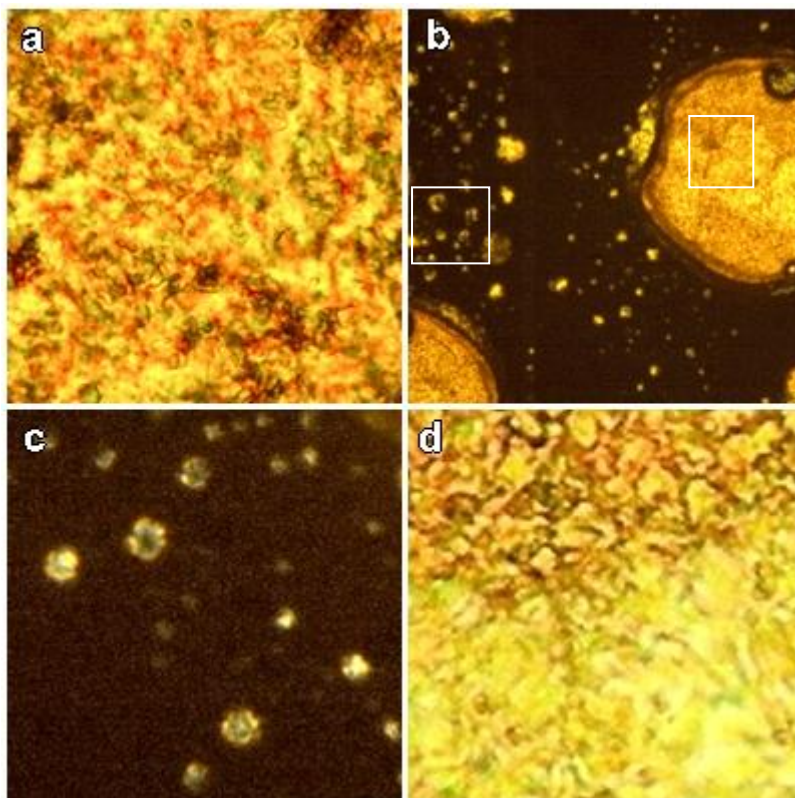


Fig. 11 Optical photomicrograph of **4** obtained with a polarizing microscope (a) Crystalline structure at 25°C. (b) Transition of SmC to SmA phase on heating at 89°C. (c) Expansion of (b) showing the positive spherules. (d) Expansion of (b) showing the transition of the SmC (up) to the SmA (down) phase. (a)(d) Cross polarizer magnification×200 (b) Cross polarizer magnification×40 (c) Cross polarizer magnification×100.

At 106 °C, the system passed to a pseudoisotropic mesophase with the appearance of uniaxial figures (Fig. 12a). At 240 °C, another smectic or lamellar neat phase occurred with an oily-streak lines texture. The high temperature mesophase is stable till 280°C where the compound irreversibly decomposes. If cooling was initiated at 250 °C, the lamellar neat oily-streak mesophase coexisted in the pseudoisotropic phase until 103°C where positive bright spherules growing from the isotropic phase appeared. At 89°C a structure transition from SmA to SmC was detected. Textures were similar to those observed on heating cycle at the same temperature range.

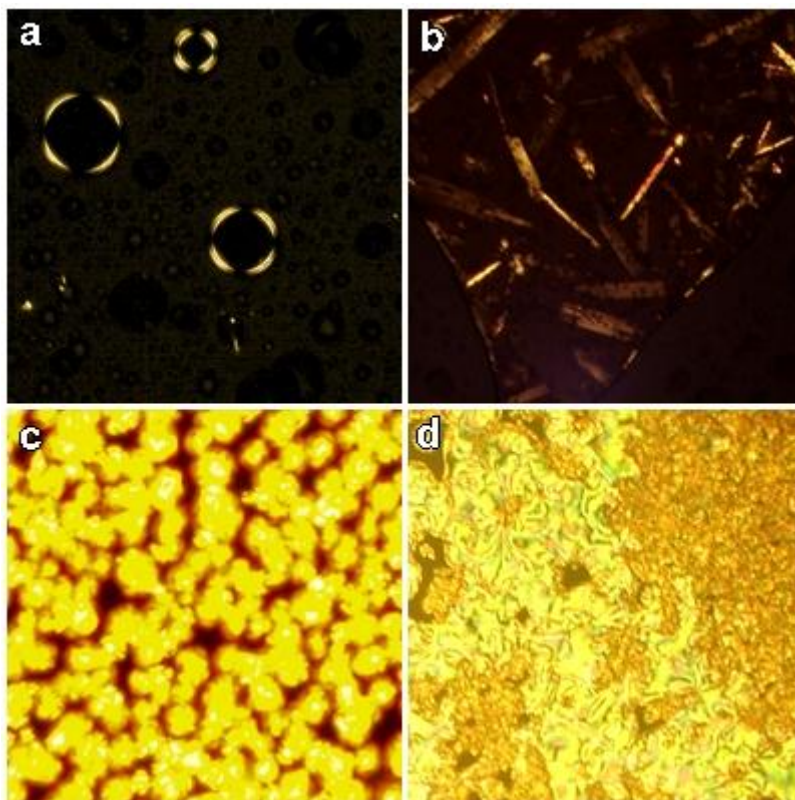


Fig. 12 Optical photomicrograph of **4** obtained with a polarizing microscope (a) Uniaxial figures on heating to pseudoisotropic liquid at 110°C (b) Lamellar neat mesophase with oily-streak lines texture 240°C. (c) Positive bright spherules growing from the isotropic liquid on cooling at 103°C (d) Transition from Smectic A (left) to Smectic C (right) on cooling 89°C. (a)(c) Cross polarizer magnification×100. (b) Cross polarizer magnification×40 (d) Cross polarizer magnification×150.

## Conclusion

The new non-ionic amphiphiles **2**, **3** and **4** presented interesting thermotropic liquid crystal (LC) behavior as determined by Differential Scanning Calorimetry (DSC) and Optical Polarizing Microscopy (OPM). The smectic polymorphism observed in compound **3** and **4** are similar of those observed for ionic amphiphiles. In general a smectic, when placed between glass slides, does not assume the simple form. The layers, preserving their thickness, become distorted and can slide over one another in order to adjust to the surface conditions. The optical properties (focal conic texture) of the smectic state arise from these distortions of the layers [17]. In addition compound **4** presented a lamellar mesophase at high temperature (240°) similar to those observed in common ionic amphiphiles. X-ray Crystallography evaluation is under process in order to confirm OPM observation.

Our findings reveal the capability of the designed amphiphiles to act as potential membrane modulators.

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