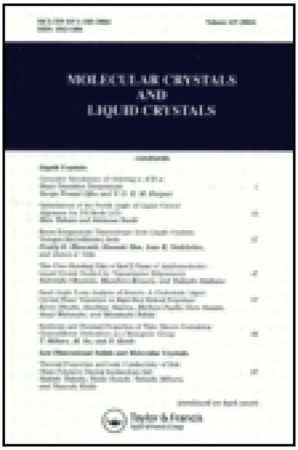


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Cholesteric and Nematic Lyotropic Mesophases from Di-Sodium N-Lauroyl-Aspartate

Maria Regina Alcantara [a] , Maria Veronica Marques Correia De Melo [b] , Vera Regina Paoli [a] & JosÉ Atilio Vanin [a]

[a] Institute de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brasil

[b] Departamento de Quimica, Universidade Federal do Rio Grande do Norte, Natal, 59000, Rio Grande do Norte, Brasil

Version of record first published: 20 Apr 2011.

To cite this article: Maria Regina Alcantara , Maria Veronica Marques Correia De Melo , Vera Regina Paoli & JosÉ Atilio Vanin (1983): New Cholesteric and Nematic Lyotropic Mesophases from Di-Sodium N-Lauroyl-Aspartate, Molecular Crystals and Liquid Crystals, 90:3-4, 335-347

To link to this article: http://dx.doi.org/10.1080/00268948308072459

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 335–347
0026-8941/83/9004-0335$18.50/0

New Cholesteric and Nematic Lyotropic Mesophases from Di-Sodium N-Lauroyl-Aspartate:

NMR and Textural Investigation

MARIA REGINA ALCANTARA, MARIA VERONICA MARQUES CORREIA DE MELO,† VERA REGINA PAOLI and JOSÉ ATILIO VANIN

Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brasil

†Departamento de Química, Universidade Federal do Rio Grande do Norte, Natal, 59000, Rio Grande do Norte, Brasil

(*Received June 21, 1982; in final form August 3, 1982*)

Lyotropic liquid crystals are prepared from racemic and optically active *di*-sodium *N*-lauroyl aspartate (SNLA). The optically active levo enantiomer is a suitable amphiphile for obtaining cholesteric lyotropic mesophases. In the present work, different types of mesophases, including cholesteric and nematic, were prepared and their type I or II magnetic behavior characterized by deuterium and ^{23}Na NMR. The polarizing microscope textures were investigated, particularly with regards to magnetic field effects upon the samples. The usual chevron pattern was obtained for particular sample orientations and several characteristic effects were observed for the type I cholesteric lyomesophase in the first few minutes following removal of the sample from the magnetic field. Although the head group of *di*-sodium *N*-lauroyl aspartate possesses two negative charges, compositions are not too different from those reported for other amphiphile lyotropic systems.

1. INTRODUCTION

Thermotropic cholesteric mesophases or chiral nematics have been of interest since the first work on liquid crystals, i.e., the classic paper of Reinitzer[1] on cholesterol derivatives. Although Reinitzer did not recognize their exact nature, by the early 1920's the helicoidal arrangement of mesomorphic molecules had been proposed[2] and the concept of cholesteric liquid crystals as a particular nematic phase with optical activity had already been established.

In comparison lyotropic cholesteric mesophases are a relatively new subject. Robinson[3,4] initiated the field of non-aqueous cholesteric lyotropic phases, utilizing polypeptides solubilized in several organic solvents. The first aqueous lyotropic cholesteric mesophase, reported by Diehl and Tracey,[5] was obtained by adding optically active sodium 2-decyl-sulfate to a sodium *n*-decyl-sulfate phase. In this system, the chiral detergent, present as a guest in the anisotropic micelles, induced the twist and a detectable pitch. Using this same approach, Saupe and co-workers[6,7] induced cholestericity by dissolving optically substances such as cholesterol, brucine sulfate, or tartaric acid in lyomesophases based on sodium decyl-sulfate or decyl-ammonium chloride.

The first intrinsic cholesteric lyomesophase was prepared in 1980 by Acimis and Reeves.[8] This mesophase was based on a chiral cationic amphiphile, the decylester of α-alanine hydrochloride, obtained by esterification of the optically active amino-acid. Subsequently, Reeves and co-workers[9] also succeeded in preparing mesophases from the anionic amphiphile potassium lauroyl-*l*-alaninate. The cholesteric mesophases prepared by these authors[8,9] undergo spontaneous orientation in a magnetic field (B_0) with either positive or negative diamagnetic susceptibilities.

In the present work, we report a new lyotropic system based on the dianionic amphiphile *di*-sodium *N*-lauroyl aspartate (SNLA). The racemic amphiphile provides type I cylindrical micelles (CM) and type II disk-like micelles (DM). Cholesteric mesophases are obtained with the optically active enantiomer *l*-SNLA. The classification of mesophases as type I CM or type II DM follows from the work of Fujiwara and Reeves[10] and the micellar structure determinations of Amaral and co-workers.[11,12,13]

In the present report, the lyomesophases are characterized by NMR[14] and on the basis of their polarizing microscope textures.

2. EXPERIMENTAL

The amphiphile was synthesized by acylation of the α-amino group of aspartic acid with lauroyl chloride, according to the procedure of Jungermann *et al.*[15] Both the racemic product and the levo enantiomer were recrystallized from absolute ethanol. The specific rotatory power of the amphiphile was determined by usual polarimetric techniques;[16]

TABLE I

Mesophases composition (% molar fraction)

	NLAS	electrolyte	H_2O^a (pH = 11)	D_2O	Decanol	type[b]	$\Delta\nu$ HDO (Hz)
1	*dl*: 3.28	Na_2SO_4: 2.55	91.12	1.67	1.38	I (CM)	754
2	*dl*: 3.33	$(NH_4)_2SO_4$: 3.38	89.79	1.64	1.86	II (DM)	294
3	*dl*: 3.53	NH_4Cl: 4.05	88.96	1.63	1.83	II (DM)	260
4	*dl*: 3.66	NaCl: 3.56	89.90	1.60	1.24	I (CM)	829
5	*l*: 4.09	NH_4Cl: 5.91	68.05	20.42	1.53	II chol	291
6	*l*: 4.23	Na_2SO_4: 2.99	70.38	21.11	1.29	I chol	871

[a] The water was adjusted to pH = 11 with NaOH.
[b] CM = cylindrical micelles
DM = disk-like micelles
chol = cholesteric.

the value found for the levo enantiomer was $[\alpha]_D^{25°} = -2.36°$. The same parameter for the starting *l*-aspartic acid is $[\alpha]_D^{25°} = -4.36°$.[17]

The mesophases were prepared by standard procedures,[8,10] typical compositions being given in Table I.

Four electrolytes were tested in the preparation of the mesophases. Only type I systems were obtained with Na_2SO_4 or NaCl, whereas both type I and type II lyomesophases were obtained with $(NH_4)_2SO_4$ or NH_4Cl. Lyotropic phases were identified by deuterium NMR using a Varian-XL-100-12-FT spectrometer with the Gyrocode Option at a frequency of 15.3 MHz. The same accessory was used for ^{23}Na NMR operating at 26.5 MHz. In all cases, a sufficient number of transients (typically <50) were accumulated so as to obtain a good signal to noise ratio.

For each sample three deuterium NMR spectra were registered: at the original position of the sample tube in the magnetic field, after 90° rotation of the tube, and finally on the spinning sample. This is the usual procedure for phase type identification.[14]

^{23}Na spectra were readily obtained by averaging 20 to 40 transients and exhibit the expected triplet pattern for a spin 3/2 nuclide in an anisotropic medium.[18-20]

For the cholesteric type I systems, several spectra were recorded in order to verify the temporal effects of the magnetic field (Figure 1).

Photomicrographs were obtained with a Zeiss Universal model Polarizing Microscope with attached camera. The samples were contained in high quality flat capillary cells, 500 μm in thickness. Oriented samples were photographed using crossed polarizers immediately after removal from a magnetic field of 1.4T oriented in direction normal to or

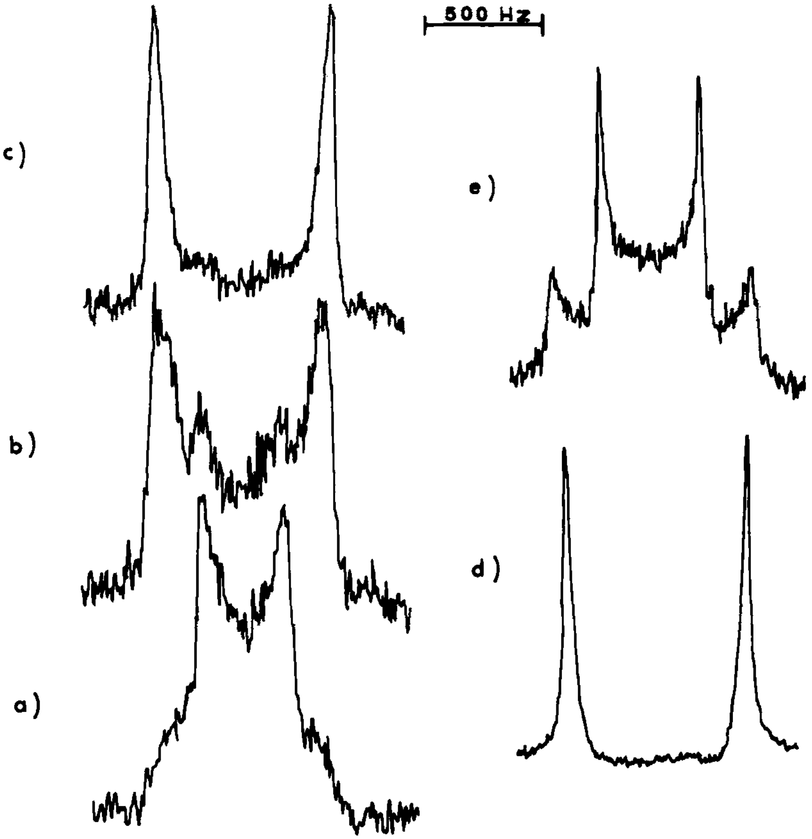


FIGURE 1 Untwisting of a cholesteric type I lyomesophase, followed by ^2H NMR of HDO. (a) Spectrum taken immediately after insertion of the sample into the magnet. Non-spinning sample. (b) After 6 min. Non-spinning sample. (c) After 15 min. Non-spinning sample. (d) After 60 min. Non-spinning sample. (e) Spinning sample.

parallel to the flat glass surfaces of the cell (hereafter referred to as "perpendicular orientation" and "parallel orientation", respectively).

3. RESULTS AND DISCUSSION

3.1 NMR spectra

The observed ^{23}Na NMR splittings are in the range of those reported for other lyotropic micellar phases.[18–20] Thus, for a type I mesophase (sample 4, Table I) a typical splitting between the flanking lines of the central peak of the triplet is $\Delta\nu = 13.23 \pm 0.08$ kHz (Figure 2a). The corresponding splitting is $\Delta\nu = 5.01 \pm 0.08$ kHz (Figure 2b) for a typical type II mesophase (sample 3, Table I).

The ^2H quadrupole splittings of type I and type II lyomesophases, listed in Table I, correspond to values determined on non-spinning samples maintained at the original orientation relative to the magnetic field.

3.2 Microscope texture

3.2.1 Lyomesophases prepared with d,l-SNLA The racemic amphiphile provides either type I CM or type II DM[8,10] "nematic" mesophases.

Parallely oriented type I mesophases exhibit a bright illuminated field, with intense birefringence colors that change upon rotation of the microscope stage. Highly ordered samples show a very homogeneous color distribution.

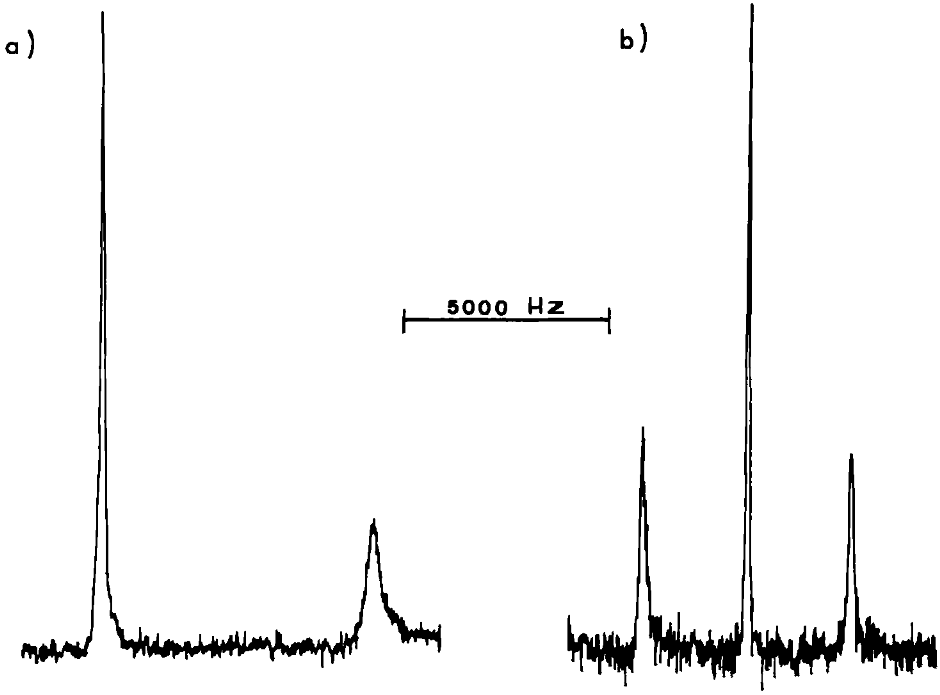


FIGURE 2 ^{23}Na NMR spectra of "nematic" lyomesophases prepared from *d,l*-SNLA. (a) Type I, sample 4 in Table I. Only half of the triplet is shown. (b) Type II, sample 3 in Table I.

The pattern observed for the perpendicularly oriented type I lyomesophase (Figure 3) consists of a rough periodic organization which is the same as that reported by Charvolin[21] for a type I sodium decylsulfate lyomesophase and attributed by him to a hydrodynamic effect.

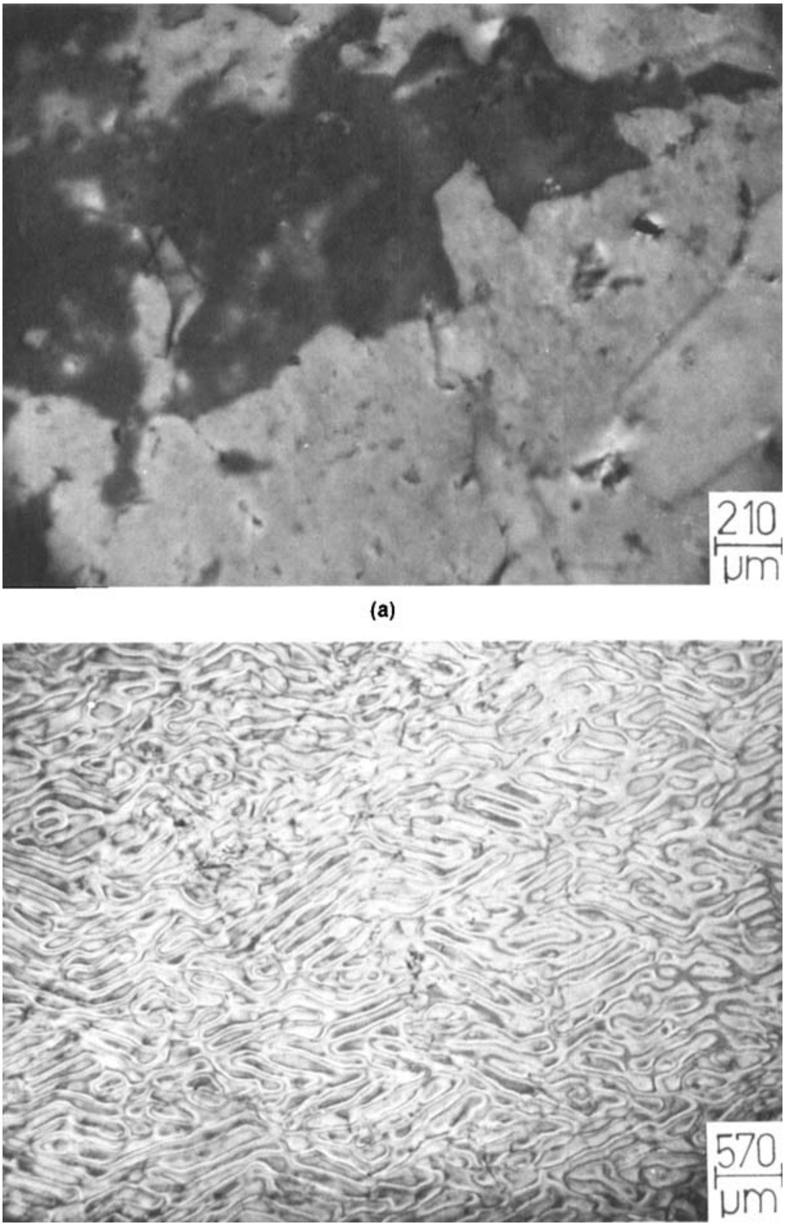
In the perpendicular orientation, type II mesophase, present large regions of uniform color generally green and magenta, with occasional nematic thread-like disclination.[22] In the parallel orientation, type II lyomesophase exhibit a homeotropic or pseudo-isotropic texture, as would be expected if the director of disk-like micelles were oriented normal to the flat glass surface of the cell.

All of these results, for our "nematic" phases are in accord with detailed microscope observations of lyomesophases.[21,23-27]

3.2.2 Mesophases prepared from l-SNLA In the parallel orientation, the type II cholesteric mesophases exhibit the expected chevron texture[6,7] shown in Figure 4a, a pattern compatible with a helicoidal axis co-linear with the magnetic field. Typical values for the pitches are in the range of 60 to 80 μm, depending on the phase composition and temperature. For the same type II sample in the perpendicular orientation, the focal conic texture shown in Figure 4b is obtained.

In the perpendicular orientation, type I cholesteric mesophases exhibit (Figure 5) a complex helicoidal pattern with λ^+ and τ^+ disclinations.[28,29] We have also encountered this "spaghetti-like" texture in an induced type I cholesteric mesophase[30] and have interpreted[30] it as being the result of two competitive orientation times, i.e., for alignment of the helicoidal axis along B_0 and for untwisting of the helix as a result of their alignment of the phase directors along B_0. This is in accord with the fact that this texture is evident only in the first few hours after application of the magnetic field effect, a pseudo-isotropic pattern being observed when the sample is left for several days in the magnetic field.

More complex effects are found for the cholesteric type I mesophases in the parallel orientation, as illustrated by the sequence in Figure 6. Immediately after the sample is removed from the magnet, a bright field with interference colors is seen (Figure 6a). After four minutes out of the field, a texture of approximately parallel lines develops (Figure 6b), becoming more clearly defined after 10 minutes (Figure 6c). The sequence of photomicrographs in Figure 6 can be interpreted as follows. The initial pattern (Figure 6a) is due to untwisting of the helices under the influence of B_0. Upon removal of B_0, the cholesteric helix twists again in a process that might involve contributions from wall effects (Figure 6b and 6c). The final pattern resembles a "roughly-oriented" chevron, the observed striations being remarkably similar to



(a)

(b)

FIGURE 3 Textures of type I "nematic" mesophases (crossed polarizers). (a) Parallel orientation. (b) Rough periodic organization (hydrodynamic effect) observed in the perpendicular orientation.

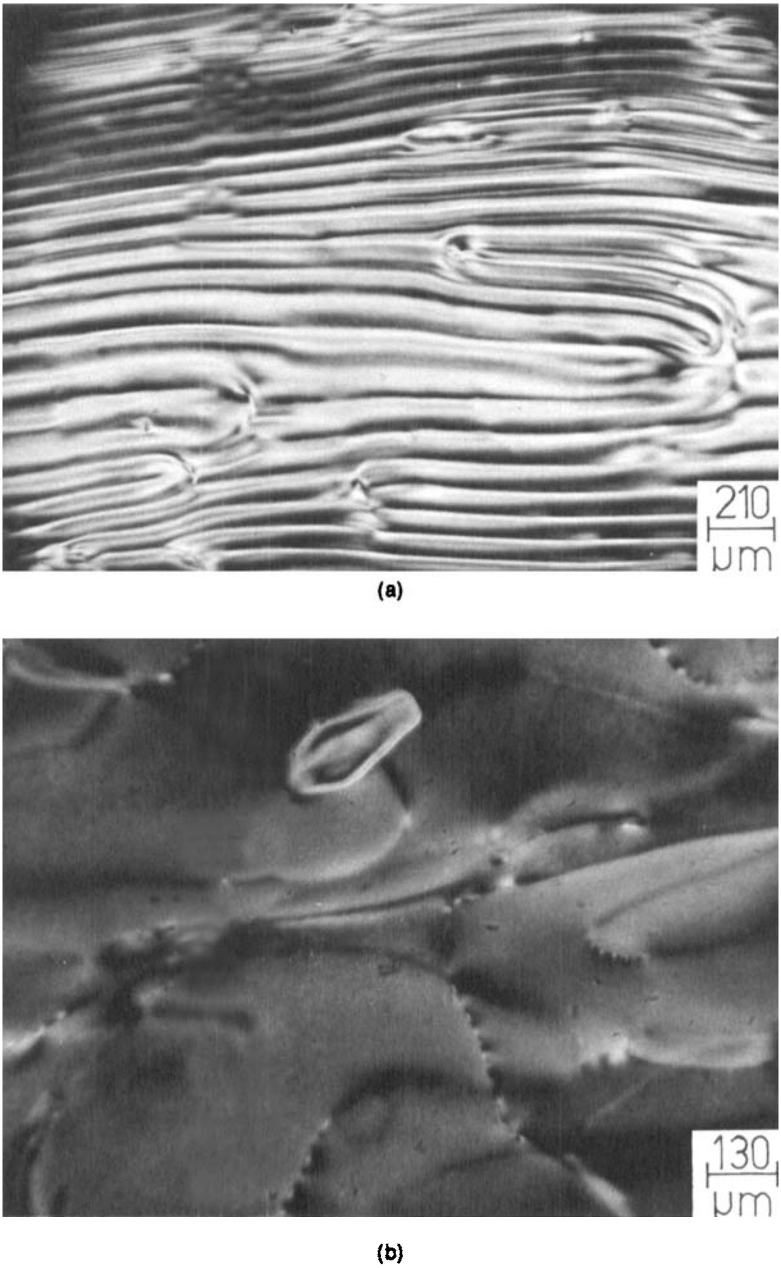


FIGURE 4 Textures of the lyotropic cholesteric type II phase (crossed polarizers). (a) Parallel orientation. (b) Perpendicular orientation.

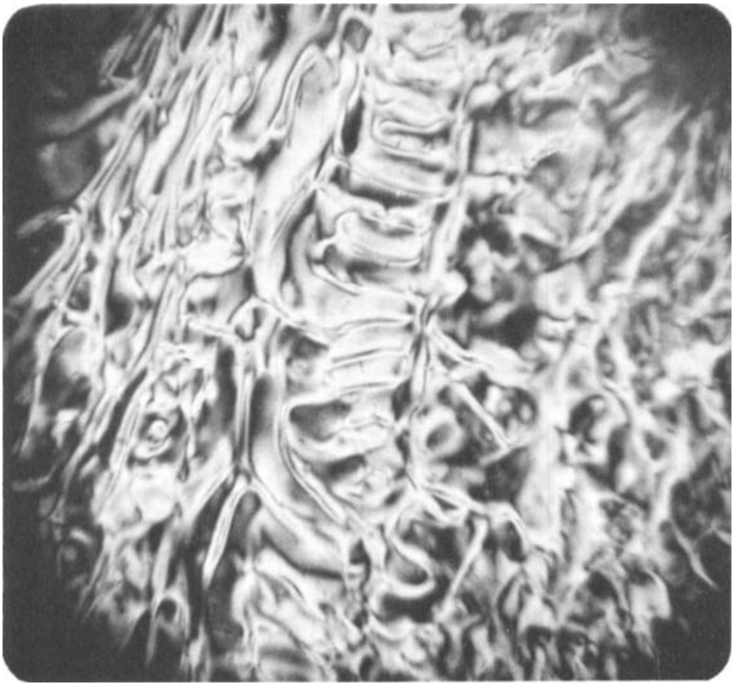


FIGURE 5 Helicoidal pairs observed in cholesteric type I SNLA samples, perpendicularly oriented. The diameter of the microscope field of view is 1,890 μm (crossed polarizers).

those reported for dioxane solutions of poly-γ-benzyl-*L*-glutamate.[31]

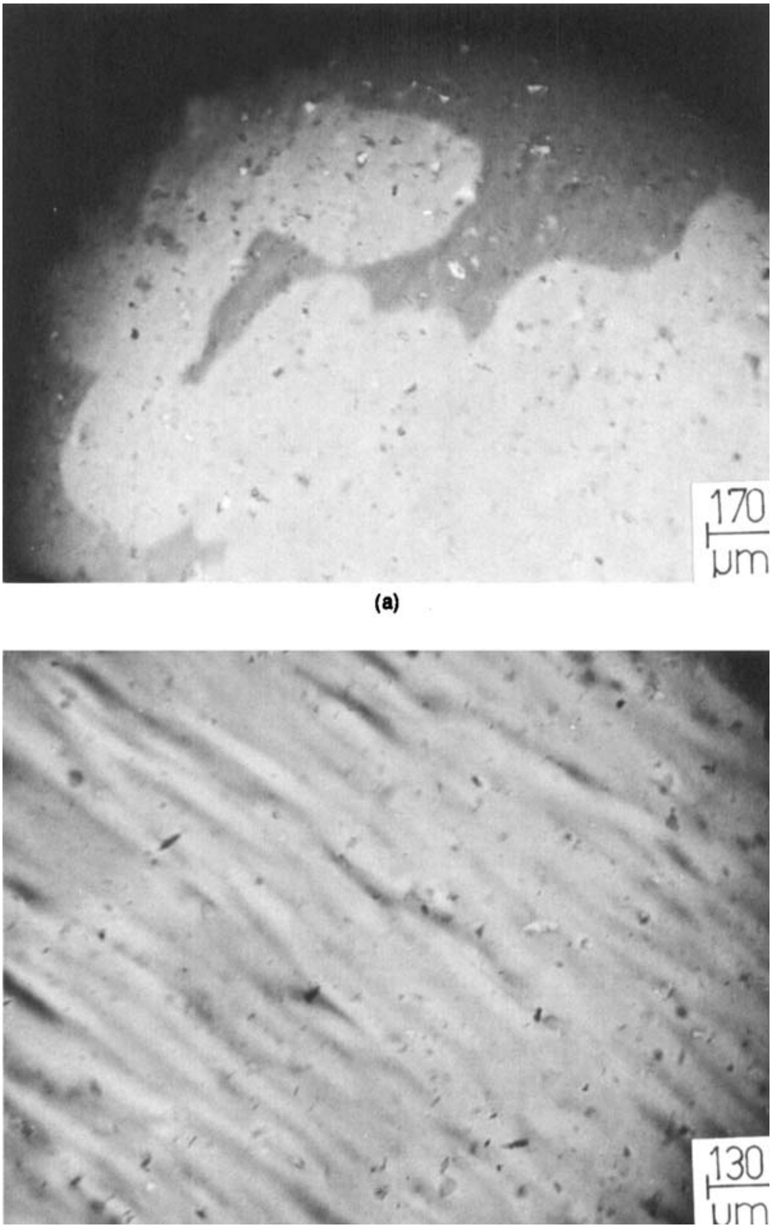
The curious pattern in Figure 7 was observed for a type II cholesteric mesophase in the parallel orientation.

This particular mesophase was prepared from a mixture of *d,l* and *l*-amphiphile, the composition in mole% being *d,l*-SNLA = 1.30; *l*-SNLA = 2.96; water (at pH = 11) = 88.10; NH_4Cl = 6.00 and decanol = 1.64.

Initially, the texture upon removal from the magnetic field consists of stripes separated from each other by narrow homeotropic transition regions (Figure 7a). Upon standing, these regions become birefringent and the edges of the stripes become less sharp (Figure 7b). These effects are similar to those reported for long pitch cholesterics placed between glass plates whose spacing is smaller than a given critical thickness.[32]

4 Conclusions

l-SNLA is a suitable amphiphile for preparing cholesteric lyomesophases. The nature of the added electrolytes plays an important role in



(a)

(b)

FIGURE 6 Textural behavior of the type I cholesteric mesophase after parallel orientation (crossed polarizers): (a) immediately after removal of the sample cell from the magnet; (b) after four minutes out of the magnet; (c) *ibid.*, after ten minutes.

(c)

determining the preferred micellar form (probably disks or cylinders), as is usually the case in amphiphilic lyotropic systems.[18,20]

The optical behavior of these lyomesophases under polarizing light is analogous to that of thermotropic cholesteric mesophases. In this regard, the magnitudes of the measured pitches (several μm) are similar to those observed for induced thermotropic cholesteric mesophases.[33,34]

Type I *l*-SNLA cholesteric phases are untwisted under the influence of an external magnetic field action, a behavior typical of thermotropic[35] and lyotropic systems[9] in which the helicoidal axis tends to orient perpendicular to the magnetic field.

The reconstruction of the helicoidal array after removal of the magnetic field implies that intermicellar forces not only play an essential role in maintaining the lyotropic cholesteric edifice, but are also stronger than those responsible for the wall effects. An assymetric distribution of the micellar surface charge density, of the type we have previously proposed for induced cholesteric lyomesophases,[30] would lead to this kind of interaction.

Despite the presence of two anionic head groups, the overall compositions (molar fraction basis) of nematic and cholesteric SNLA mesophases are in the range of those typical for lyomesophases.

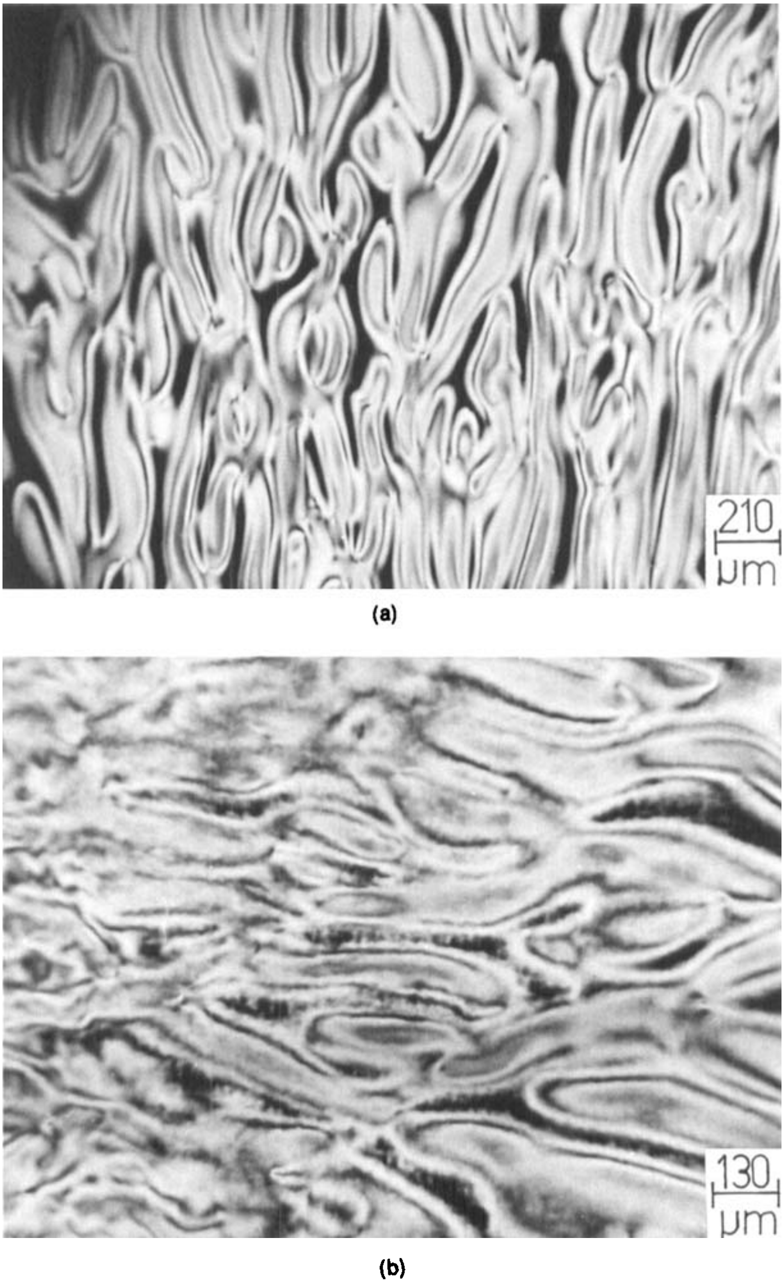


FIGURE 7 Textures of cholesteric type II lyomesophase prepared from a mixture of *d,l* and *l*-SNLA. (a) Immediately after removal of the sample cell from the magnet. (b) Observed loss of ordering after twenty minutes at rest on the microscope stage.

Acknowledgments

We are indebted to the financial support from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Financiadora de Estudos e Projetos (FINEP). We are also indebted to Dr. Frank H. Quina for his help with the manuscript.

References

1. F. Reinitzer, *Monatsh. Chem.*, **9**, 421 (1888).
2. G. Friedel, *Ann. Physique*, **18**, 273 (1922).
3. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
4. C. Robinson and J. C. Ward, *Nature Lond.*, **180**, 1183 (1957).
5. P. Diehl and A. S. Tracey, *FEBS Lett.*, **59**, 131 (1975).
6. L. J. Yu and A. Saupe, *J. Am. Chem. Soc.*, **102**, 4879 (1980).
7. K. Radley and A. Saupe, *Molec. Phys.*, **35**, 1405 (1978).
8. M. Acimis and L. W. Reeves, *Can. J. Chem.*, **58**, 1533 (1980).
9. B. J. Forrest, L. W. Reeves, M. R. Vist, C. Rodger and M. E. M. Helene, *J. Am. Chem. Soc.*, **103**, 690 (1981).
10. F. Y. Fujiwara and L. W. Reeves, *J. Phys. Chem.*, **84**, 653 (1980).
11. L. Q. Amaral and M. R. Tavares, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 203 (1980).
12. L. Q. Amaral, C. A. Pimentel, M. R. Tavares and J. A. Vanin, *J. Chem. Phys.*, **71**, 2940 (1979).
13. A. M. Figueiredo Neto and L. Q. Amaral, *Mol. Cryst. Liq. Cryst.*, **74**, 109 (1981).
14. B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981).
15. E. Jungermann, J. F. Gerecht and I. J. Krems, *J. Am. Chem. Soc.*, **78**, 172 (1956).
16. G. W. Ewing, "Instrumental Methods of Chemical Analysis," Mc. Graw-Hill Book Company, 1969.
17. CRC, Handbook of Chemistry and Physics, 60th Ed. R. C. Weast and M. J. Astle, Ed. Chemical Rubber Pub. Co., Florida (1979).
18. K. Radley, L. W. Reeves and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
19. N. O. Persson, G. Lindblom, B. Lindman and G. Arvidson, *Chem. Phys. Lipids*, **12**, 261 (1974).
20. D. M. Chen, K. Radley and L. W. Reeves, *J. Am. Chem. Soc.*, **96**, 5251 (1974).
21. J. Charvolin and Y. Hendrikx, *J. Physique Lett.*, **41**, L-597 (1980).
22. A. Saupe, in "Liquid Crystals & Plastic Crystals," vol. 1, pag. 18, G. W. Gray and P. A. Winsor, Eds., John Wiley and Sons, N.Y., 1974.
23. Y. Hendrikx and J. Charvolin, *J. Physique*, **42**, 1427 (1981).
24. J. Charvolin, E. Samulski and A. M. Levelut, *J. Physique Lett.*, **40**, L-587 (1979).
25. F. B. Rosevear, *J. Soc. Cosmet. Chem.*, **19**, 581 (1968).
26. A. Saupe, *J. Colloid Interface Sci.*, **58**, 549 (1977).
27. N. Boden, P. H. Jackson, K. McMullen and M. C. Holmes, *Chem. Phys. Lett.*, **65**, 476 (1979).
28. M. Kléman and J. Friedel, *J. Physique*, **30**, C4, 43 (1969).
29. M. Kléman, in "Liquid Crystals & Plastic Crystals," vol. 1 pag. 76, G. W. Gray and P. A. Winsor, Eds., John Wiley and Sons, N.Y., 1974.
30. M. R. Alcantara, M. V. M. C. Melo, V. R. Paoli and J. A. Vanin, submitted.
31. A. Elliott and E. J. Ambrose, *Disc. Faraday Soc.*, **9**, 246 (1950).
32. A. E. Stieb, *J. Physique*, **41**, 961 (1980).
33. Orsay Liquid Crystal Group, *Phys. Lett.*, **28A**, 687 (1969).
34. Orsay Liquid Crystal Group, *J. Physique*, **30**, C4, 38 (1969).
35. R. B. Meyer, *Appl. Phys. Letters*, **14**, 208 (1969).