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New Intrinsic Cholesteric Lyomesophases From Potassium *l-N*-Lauroylserinate. II. Type II Systems: Unusual Textural and Deuteron NMR Behavior

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New type II intrinsic cholesteric lyomesophases based on potassium *l-N*-lauroyl-serinate and on unbalanced *d, l* mixtures were prepared. Cholesteric properties were characterized by deuteron NMR and polarizing microscopy. For spinning samples, the HDO ^{2}H NMR line-shape was different from that reported previously for other cholesteric lyotropic systems. In the present work this line-shape was associated with a partial untwisting of the helicoidal arrangement, creating a privileged distribution of orientations of micelle directors. The textures seen under the polarizing microscope for magnetically oriented samples were unusual, indicating a large cholesteric pitch. When in parallel orientation a pseudo-isotropic pattern was observed. Samples in perpendicular orientation give a more complex texture, exhibiting two kinds of disclinations: thread-like and straight lines. This pattern can be explained by the formation of helical pairs, which are a consequence of the curvature of the cholesteric layers. The present work points out that special care should be taken with the techniques used for characterization of long pitch cholesteric systems. The length of the helical pitch with respect to the sample cell thickness in the polarizing microscope or to the length of the NMR spectrometer detection coil are decisive in understanding the observed textures and NMR spectra.

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1. INTRODUCTION

In Part I of this series[1] we have reported on the existence of micellar type I cholesteric lyomesophases based on potassium *l*-*N*-lauroylserinate (*l*-KNLS). The investigation of type II cholesteric lyotropic mesophases is a natural extension of those studies.

A cholesteric lyomesophase is classified as type II when the axis of its helicoidal super-structure aligns parallel to an applied magnetic field, B_0. In this condition, the micellar director (i.e., the micelle simmetry axis) is oriented perpendicularly to the field B_0. Contrary to the type I case, the deuterium NMR technique is an efficient and sufficient tool to characterize the magnetic behavior and the cholesteric properties of type II systems.[2-5]

The textures seen under the polarizing microscope can be used as an additional identification method.

Usually, the optical patterns observed are:

a) Chevron texture, after orientation by a field B_0 applied in the plane of the sample cell.[2-5]

b) Focal conic texture,[6-8] when in planar orientation, which is achieved by a magnetic field applied perpendicular to the surface of the sample cell.[4,5]

Although these optical patterns are normally used for cholesteric type characterization, they are not the only ones possible as it will be shown in the present report.

2. EXPERIMENTAL

The preparation of the *l*-KNLS amphiphile was mentioned in Part I of this series. Additionally, in the present study, we have synthesized the racemic form of the amphiphile. Its observed melting point range was 101°-103°C.

The usual homogenization procedure[9] was adopted for the preparation of the mesophases. Typical compositions appear in Table I. Cholesteric phases were prepared from *l*-KNLS or from the racemic form of the amphiphile which was unbalanced by addition of *l*-KNLS.

Deuterium NMR spectra and photomicrographs under polarized light of magnetically oriented samples were obtained as described in Part I. Again we will refer to "perpendicular orientation" or "parallel orientation" as that resulting from a magnetic field applied, respectively, perpendicular or parallel to the sample cell surface.

TABLE I

Compositions of type II cholesteric lyomesophases
(% molar fraction)

	l-KNLS	*d*, *l*-KNLS[a]	KCl	*n*-DeOH[b]	H_2O	D_2O	KOH
A[c]	—	2.53	1.58	0.92	75.57	16.99	2.41
B	2.46	—	2.77	0.52	83.09	9.03	2.13
C	2.48	—	3.00	0.51	82.59	8.99	2.43
D	1.50	1.15	1.97	0.64	75.42	16.02	2.40
E	2.50	—	0.80	0.96	—	94.03	1.71
F	1.10	1.57	1.99	0.65	75.36	16.92	2.41
G	0.29	2.39	0.88	0.95	—	93.43	2.06

[a] *d*, *l*-KNLS = racemic mixture of potassium *N*-lauroyl-serinate.
[b] *n*-DeOH = *n*-decanol.
[c] Type II nematic lyomesophase prepared for comparative purposes.

3. RESULTS AND DISCUSSION

3.1. Deuteron NMR results for type II cholesteric mesophases

The deuterium NMR spectra of the lyomesophase HDO show the typical angular dependence expected for a type II phase.[10] Figure 1.a shows the doublet associated with the quadrupole splitting of an oriented sample, which had been placed for a few minutes in a

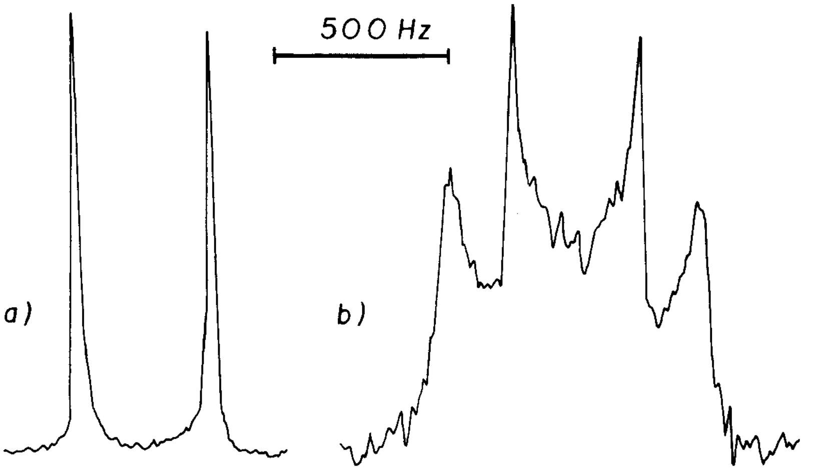

FIGURE 1 HDO deuteron NMR spectra of a type II intrinsic cholesteric lyomesophase. (a) At the original sample tube position in the magnetic field. (b) After 90 ° rotation of the sample tube.

magnetic field. It is known that cholesteric type II lyomesophases orient in a magnetic field maintaining their helical axis parallel to it.[1] Less time is required for the ordering of a type II cholesteric lyomesophase than for a cholesteric type I lyomesophase; characteristic values for the HDO quadrupole splitting are in the 400 Hz range. Immediately after a sample rotation of 90° around the NMR sample tube axis a bidimensional spectrum is seen (Figure 1.b).

The spectrum of Figure 1.a is compatible with an orientation of micelle directors in all directions of a plane perpendicular to B_0. In this case, the 90° rotation of the sample tube brings the micelle directors distributed in a plane which contains B_0, giving the bidimensional spectrum of Figure 1.b.

After completely oriented, the same sample was spun about an axis perpendicular to B_0, at the usual rates for NMR experiments. The spectrum then obtained is shown in Figure 2. A well characterized "powder-diagram" would be expected[2,11] for this sample, as the directions of the micelle directors would be randomized by the spinning process (or in other words, the helicoidal axes would be distributed in a plane). However in the line-shape of Figure 2, the outer edges of each doublet component are sharp while their inner edges tail off gradually towards the center of the spectrum. This same spectral shape was found by Luz, Poupko and Samulski[12] for thermotropic cholesteric mesophases based on cholesteryl alkanoates.

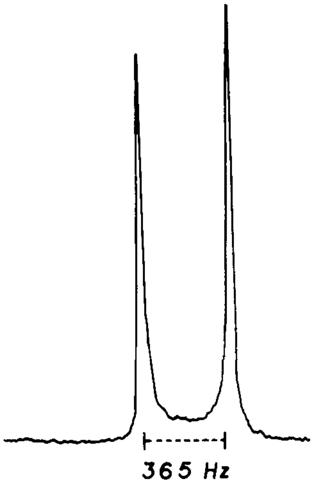

FIGURE 2 HDO deuteron NMR spectra of spinning type II intrinsic cholesteric sample.

In the present case, when the sample is spun, the helicoidal array is partially destroyed; a privileged distribution of orientations of micellar directors is created within a solid angle disposed about a line perpendicular to B_0 and parallel to the spinning axis. Nevertheless, due to the twisting power of the lyomesophase, the helical arrangement is not fully untwisted. The resulting complex distribution of directors leads to a spectral shape similar to that of Figure 2.

For a nematic lyomesophase (sample A in Table I) a well defined doublet was obtained.[4,10]

3.2. Microscope textures

The textures seen under the polarizing microscope for cholesteric type II lyomesophases of *l*-KNLS are very different from those reported previously for other systems.[4,5,13]

For samples in parallel orientation a pseudo-isotropic texture with some birefringent spots is observed. This unexpected pattern, instead of the classical "chevron" texture, shows the trend towards mesophase untwisting by the magnetic field where the micellar directors are perpendicular to the cell walls. The birefringent spots are a consequence of disclinations, i.e., orientation defects due to the cholesteric properties of the phase and maybe to additional wall effects.

The same sample in perpendicular orientation (Figure 3) shows a bright field, usually yellow, magenta and green, with two kinds of disclinations: straight lines and schlieren texture. This last pattern was previously observed by Nehring and Saupe[14] in thermotropic nematic phases which are slightly twisted due to optically active impurities. Their mesophases correspond to induced cholesteric systems with a long pitch. The pattern of Figure 3 is characteristic of cholesteric type II lyomesophases of *l*-KNLS, since it could be reproduced for all samples prepared with this amphiphile in different type II cholesteric compositions.

For a complementary verification, nematic lyotropic mesophases (as sample A of Table I) were prepared from the racemic form of the amphiphile. These samples, when oriented in the same conditions as the cholesteric phase (same sample cell, temperature, B_0) yielded a bright field without disclinations, showing a highly uniform alignment. This proves unequivocally that the texture shown in Figure 3, although unusual, corresponds to a cholesteric pattern.

Straight line patterns in cholesteric thermotropic liquid crystals have been known since 1921, from the work of Grandjean.[15] His observations on long pitch cholesteric samples in a wedge-shaped cell, previ-

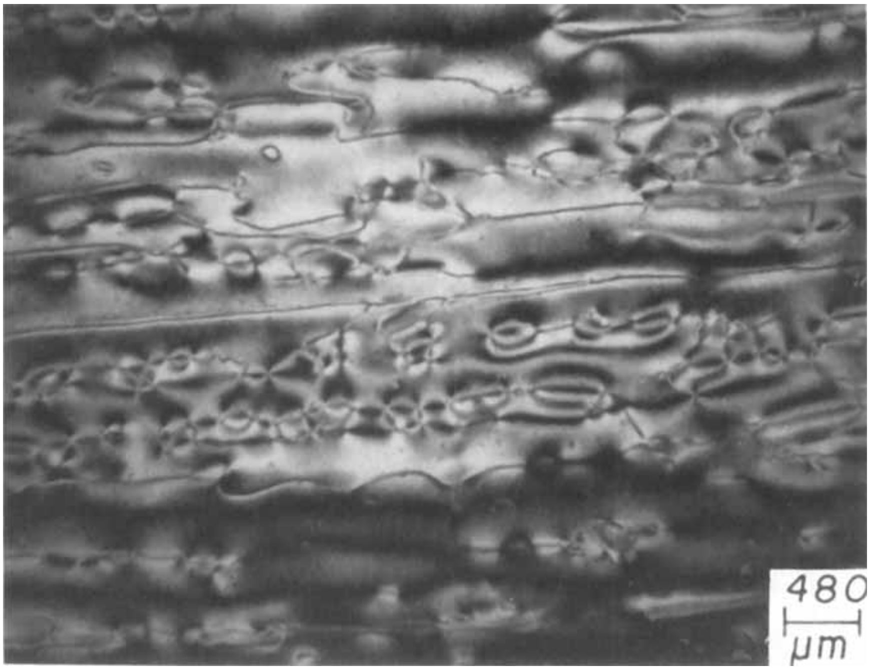

FIGURE 3 Texture observed for a perpendicularly oriented type II intrinsic cholesteric lyomesophase (crossed polarizers). See Color Plate VI, Vol. 111.

ously treated for parallel alignment, showed a texture of parallel lines whose spacement was related to the change of wedge thickness.[16-18] More recently, Bouligand[19-24] has pointed out that these lines appear perpendicularly to the helical axis, due to a curvature effect of the cholesteric layer.

On the other hand, the thread-like or schlieren textures are shown in the literature as due to curvature defects in smectic or cholesteric planes (λ and τ disclinations)[19-27] or to curvature in the preferential order of the directors in the nematic mesophase (χ disclinations).[14,22,26,28,29] In any case, a localized disorganization of directors is established.

The line pattern in the texture shown in Figure 3 can be attributed to the formation of helical pairs, due to the micelle interactions with the cell walls, which orient the helical axis parallel to the cell surfaces. Figure 4 shows an idealized picture of the origin of the line texture, due to formation of $\lambda^+\lambda^-$ pairs.[19,22,25,26] Additionally, the curvature

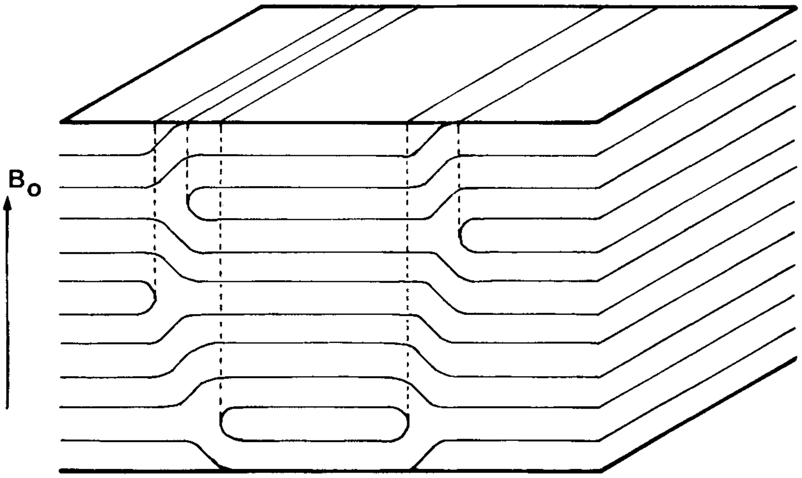

FIGURE 4 Idealized representation of $\lambda^+\lambda^-$ helical pairs in a cholesteric lyomesophase and the associated straight line texture. Modified from Bouligand.[19]

of the cholesteric layers involved in these disclinations produces in each plane a local non-uniformity in the directors distribution, giving rise to the χ disclinations and the associated schlieren texture.

Finally, it should be noted in Figure 4 that $\lambda^-\lambda^+$ pairs are indicated simultaneously with $\lambda^+\lambda^-$ pairs. This is a necessary condition to maintain the same micelle concentration within the entire sample.

3.3. Temperature effects on type II KNLS cholesteric lyomesophases

^{2}H NMR spectra and optical patterns were observed for type II cholesteric mesophases at several temperatures. Figure 5 shows the line shape variation with temperature for spinning samples. The spectra corresponding to 21°C and 24°C exhibit the same line-shape as those of Figure 2, typical for this kind of cholesteric mesophase. The spectrum at 39°C, at first glance, looks like that of a normal nematic lyomesophase. However under the polarizing microscope the textures resemble those of Figure 3 for all temperatures.

It has been known since the first studies with thermotropic phases that the cholesteric pitch is dependent on temperature.[30] The spectrum at 39°C can be assigned to a mesophase with a pitch length longer than that of the same sample at 21°C or 24°C. If the cholesteric pitch distance was approaching the detector coil length at the NMR probe, we should expect that this technique would give spectra (like those

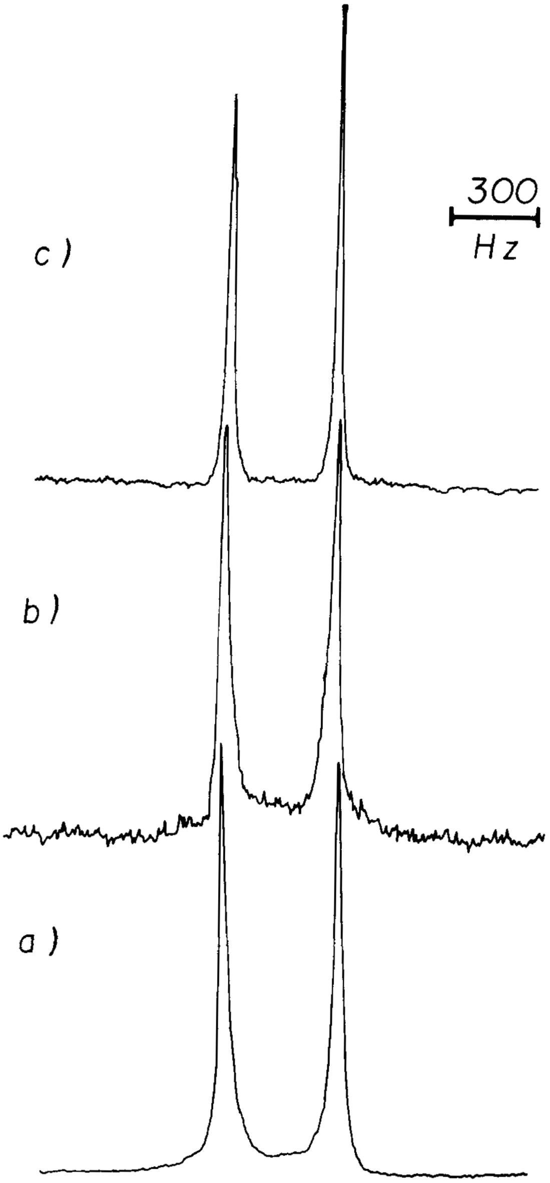

FIGURE 5 Type II intrinsic cholesteric lyomesophase deuteron NMR spectra at several temperatures. Spinning samples. (a) 21 °C, (b) 24 °C, (c) 39 °C.

observed at Figure 5b and c) corresponding to a nematic instead of a cholesteric arrangement. In this case, the textures at the polarizing microscope have fundamental importance for the characterization of cholesteric samples. On the other hand, if the cholesteric pitch is larger than the thickness of the cell used for the microscope observations, the customary "chevron" texture can not be seen; in this case, new characteristic cholesteric textures are expected.

3.4. Unbalanced mesophases

In a previous work we described the preparation of a mesophase based on an unbalanced enantiomer mixture of di-sodium *N*-lauroyl-aspartate.[4] The mesophase pitch length for that particular system was greater than that of cholesteric lyomesophases based exclusively on the levo-form. The reported texture was associated with a cholesteric phase with a critical pitch length with respect to the sample cell thickness.[4,31]

In the present work, we have also prepared unbalanced mesophases from the racemic mixture of KNLS with additional *l*-KNLS enantiomer, as it is seen for samples *D*, *F* and *G* in Table I. The magnetic behavior detected by ^{2}H NMR and the characteristic optical textures were the same as those obtained for mesophases prepared exclusively with the *l*-form of the amphiphile.

For these unbalanced mixtures we should expect a helical pitch longer than that found on phases based exclusively on the *l*-enantiomer. This would be a natural consequence of the lower number of effective twisting chiral centers in cholesteric micelles, therefore decreasing the twisting of the mesophase.

The non-variation of the observed textures when comparing unbalanced and *l*-enantiomer systems is a clear evidence that, in both cases, the cholesteric pitches are above the critical relative dimensions quoted by Stieb.[31] In these circumstances, the observed texture does not contain any direct information about relations between the pitch length and the d/l enantiomer ratio in the cholesteric mesophase.

4. CONCLUSIONS

l-KNLS is a suitable amphiphile for the preparation of cholesteric lyomesophases. Both type I (as reported in Part I) and type II mesophases can be prepared by varying the phase composition. Mesophases prepared from the racemic mixture of the amphiphile unbalanced by the addition of the *l*-enantiomer showed the same general magnetic and optical behavior of phases prepared exclusively from *l*-KNLS.

The observed ^{2}H NMR spectra for type II spinning cholesteric samples showed a line-shape dependence on the non-homogeneous distribution of the micelle directors.

Additionally, a new cholesteric texture was observed. For these type II lyomesophases, the problem of the pitch length and its detection method (NMR and microscopy) can be discussed. The relative dimensions of the pitch (P) and the sample cell thickness (C) used in the polarizing microscope work or the length (L) of the NMR spectrometer detection coil, are decisive to understand the observed textures and NMR spectra.

The following cases summarize the different situations found in the experimental studies on type II cholesteric mesophases:

(i) $P < C$ and $P < L$. This is the most common condition, and in fact, represents the typical behavior already reported in the literature for other systems.[2-4] The observed optical patterns are the usual chevron (parallel orientation) and the focal conic texture (perpendicular orientation). Spinning samples yield a powder diagram for the HDO ^{2}H NMR spectrum.

(ii) $P \geq C$ and $P < L$. This situation corresponds to a long pitch cholesteric mesophase. A homeotropic pattern is observed for samples in parallel orientation instead of the chevron texture. For perpendicular orientation these phases bring the new pattern here reported (Figure 3) in place of the expected focal conic texture. The observed ^{2}H NMR spectrum of spinning samples is a doublet similar to that of Figure 2, arising from an inhomogeneous distribution of micelle directors around the helical axis.

(iii) $P > C$ and $P > L$. The textures seen at the polarizing microscope are analogous to that seen in case (ii), and they really characterize the cholesteric properties of the mesophase. The observed ^{2}H NMR spectrum of spinning samples is a sharp doublet (Figure 5c), which could lead to a fallacious identification of the sample as a nematic one.

In the case of cholesteric lyomesophases, the characterization of helical pitches of the same or greater magnitude than that of the optical cells or detector coil sizes involved in the techniques used for the mesophase studies deserves special attention. Recent literature[2] on lyotropic cholesteric phases has pointed out the existence of a nematic

$\rightleftharpoons$ cholesteric equilibrium, associated with temperature variation. Remembering that in the thermotropic case this equilibrium cannot exist[30,32,33] we think previous studies on cholesteric lyomesophases should be revised, since a variation of pitch length might be involved.

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