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New Intrinsic Cholesteric Lyomesophases from Potassium *l-N*-Lauroylserinate. I. Type I Systems: Textural and Magnetic Characterization

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Type I intrinsic cholesteric lyotropic mesophases were prepared from potassium *l-N*-lauroyl-serinate. This chiral amphiphile was synthesized by the acylation of *l*-serine amino-group with lauroyl chloride. Lyomesophases were obtained from mixtures of amphiphile, electrolyte (KCl), *n*-decanol and water whose pH was controlled by KOH addition. The resolved form or an unbalanced mixture of the amphiphile were used for cholesteric mesophase preparation. The cholesteric properties were investigated by deuteron NMR and characterized by optical microscopy under polarized light. The magnetic behavior was similar to that reported for induced and intrinsic cholesteric systems. For these type I mesophases, textural investigations on oriented samples were essential for the identification of the cholesteric properties since these mesophases were untwisted by the applied magnetic field.

With parallel orientation we observed a chevron pattern whose lines were disposed perpendicularly to the magnetic field. The perpendicular orientation yielded a texture of helicoidal pairs disclinations. After several days under the action of a magnetic field both observed textures underwent changes, indicating an untwisting of the helical arrangement. These observations make evident that type I intrinsic cholesteric lyomesophases can exhibit two orientational times, one for the alignment of the helicoidal axis in a direction perpendicular to that of the applied magnetic field and a different one for the helix untwisting process.

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1. INTRODUCTION

Cholesteric lyotropic liquid crystals have been intensively investigated in recent years.[1-4] Several lyomesophases have been described; some of them are based on micellar systems[1-4] while others concern non-micellar solutions.[5,6] The former are the subject of the present work.

Cholesteric properties of micellar lyomesophases (essentially amphiphile/water systems) can be induced by the addition of small amounts of a chiral solute (induced cholesteric phase)[1,2,7,8] or obtained directly by using a chiral amphiphile for phase preparation (intrinsic cholesteric phase).[3,4,9]

The observed textures for both cholesteric mesophases under the polarizing microscope are quite similar and deuteron NMR spectra of HDO showed a similar quadrupole splitting angular dependence.[4,7,9]

The helical axis of the cholesteric arrangement can be oriented by a magnetic field perpendicularly (type I) or parallelly (type II) to it, depending on the sign of micellar diamagnetic anisotropy.[10,11] For type I phases, at sufficiently high magnetic field, the helicoidal array is untwisted.

In the present work, we report new type I intrinsic cholesteric lyomesophases based on potassium *l*-*N*-lauroyl-serinate (*l*-KNLS). Deuteron NMR and optical microscopy under polarizing light were used to characterize cholesteric properties of the prepared mesophases.

2. EXPERIMENTAL

l-KNLS was synthesized by acylation of the serine α amino group, according to a procedure described by Jungermann *et al.*[12] The prod-

TABLE I

Mesophase compositions (% molar fraction)

	l-KNLS	*d*, *l*-KNLS[a]	KCl	*n*-DeOH[b]	H_2O	D_2O	KOH
A	2.57	—	1.42	0.49	89.83	3.36	2.33
B	2.63	—	1.45	0.46	89.78	3.36	2.32
C	2.67	—	1.58	0.49	89.58	3.36	2.32
D	2.72	—	1.42	0.47	75.91	17.09	2.39
E	0.63	2.03	0.82	0.92	—	93.44	2.16

[a] *d*, *l*-KNLS = racemic mixture of potassium *N*-lauroyl-serinate.
[b] *n*-DeOH = *n*-decanol.

uct was recrystallized from absolute ethanol and the observed melting point was in the range 92–94°C. The specific rotatory power, using usual polarimetric techniques[13] was $[\alpha]_D^{25} = |10.40°|$.

The mesophases were prepared by standard procedures[3,4] and typical compositions are shown in Table I. As can be seen in this table, intrinsic cholesteric mesophases were prepared from *l*-KNLS or from an unbalanced mixture (*l* + *d*, *l*-KNLS). Both showed the same magnetic and optical behavior.

Deuteron NMR spectra were obtained with a Varian XL-100-12-FT spectrometer operating with Gyrocode Option at the frequency of 15.3 MHz.

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 1.4 T oriented normal or 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. Deuteron NMR Results

Deuteron NMR spectra of HDO in stationary samples of type I lyotropic mesophase showed the same general behavior of another intrinsic cholesteric system based on di-sodium *l*-*N*-lauroyl-aspartate, which we have previously reported.[4]

Immediately after the insertion of the sample into the magnet a "powder spectrum" was observed (Figure 1.a). Few minutes later, the intensity of the wings of the spectrum were seen to increase (Figure 1.b and 1.c) and after 30 minutes a doublet with a quadrupole splitting usually in the range of 500 to 600 Hz becomes well defined (Figure 2.a). When this oriented sample is rotated by 90° around the sample tube axis, the observed splitting decreases to half of its initial value (Figure 2.b).

Any attempt to spin the sample yielded a bi-dimensional spectrum[11] (Figure 2.c), usually showing intense field modulation if the spinning rate is not properly adjusted.

These experiments show that the magnetic behavior and the quadrupole splitting angular dependence exhibited by type I choles-

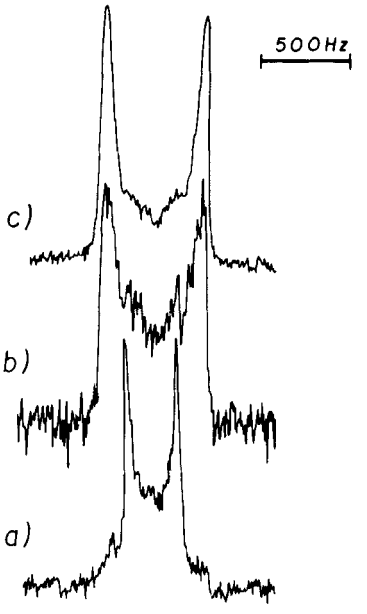

FIGURE 1 Deuteron NMR spectra of a cholesteric type I non-spinning sample (sample D in Table I). (a) Immediately after insertion into the magnet. (b) After 8 min. (c) After 12 min.

teric lyotropic mesophase are not enough to characterize its cholesteric properties. In fact, it is known that any type I nematic lyomesophase will show such magnetic comportment.[11]

For type I nematic systems the line shape evolution is a consequence of the alignment process of mesophase director by a magnetic field (which is not instantaneous), while for type I cholesteric systems involves the helical array untwisting and a reorientation of the micellar directors parallel to the magnetic field, B_0.

Therefore, the textures of oriented samples seen under the polarizing microscope are decisive for a complete and unequivocal characterization of the cholesteric lyomesophase.

3.2. Microscope Textures

Photomicrographs of *l*-KNLS type I cholesteric lyomesophase in parallel and perpendicular orientations are shown in Figure 3.

The texture associated to the parallel orientation is a repetitive pattern (Figure 3.a) that has the same origin as the chevron texture[14]; it can be explained as result of an helicoidal arrangement partially

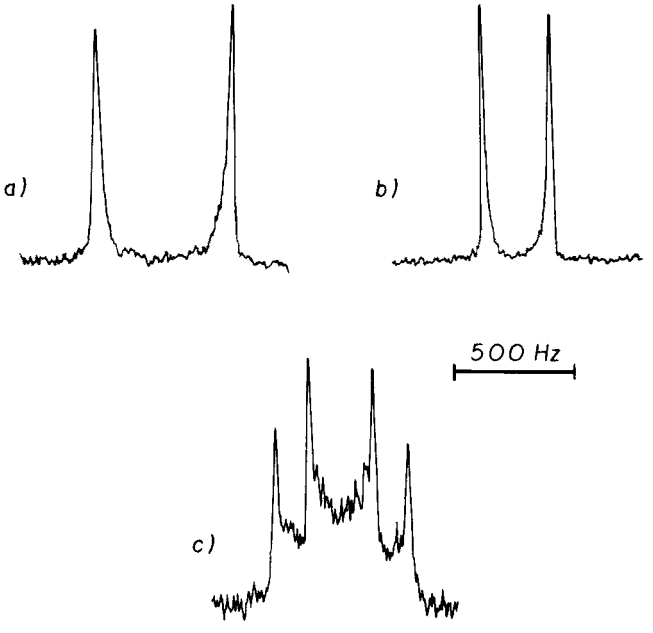

FIGURE 2 Deuteron NMR spectra of a cholesteric type I lyomesophase, after 30 min. under magnetic field action (Sample D in Table I). (a) At the original position of the sample tube in the magnetic field. (b) After 90° rotation of the sample tube. (c) Spinning sample.

untwisted, but still maintaining the preferential orientation of the helical axis perpendicular to the magnetic field.

The texture of Figure 3.a has already been reported by us in a previous work[7] for oriented samples of induced cholesteric type I lyomesophases based on potassium laurate (KL)/cholesterol system.[7-9] It should be noted that this repetitive pattern is different from that reported for nematic type I lyomesophases in perpendicular orientation[2,16] which was ascribed by Charvolin[16] to an hydrodynamic back-flow effect.

After several days of parallel magnetic field action the repetitive pattern of Figure 3.a changes to a mosaic texture[15] or marble type. This change is associated to the complete untwisting of the helicoidal super-structure.

Figure 3.b shows the "spaghetti-like" texture associated to the sample in perpendicular orientation. This pattern has also been previously reported by us for other cholesteric systems, one based on di-sodium *l-N*-lauroyl-aspartate (intrinsic)[4] and another on potassium

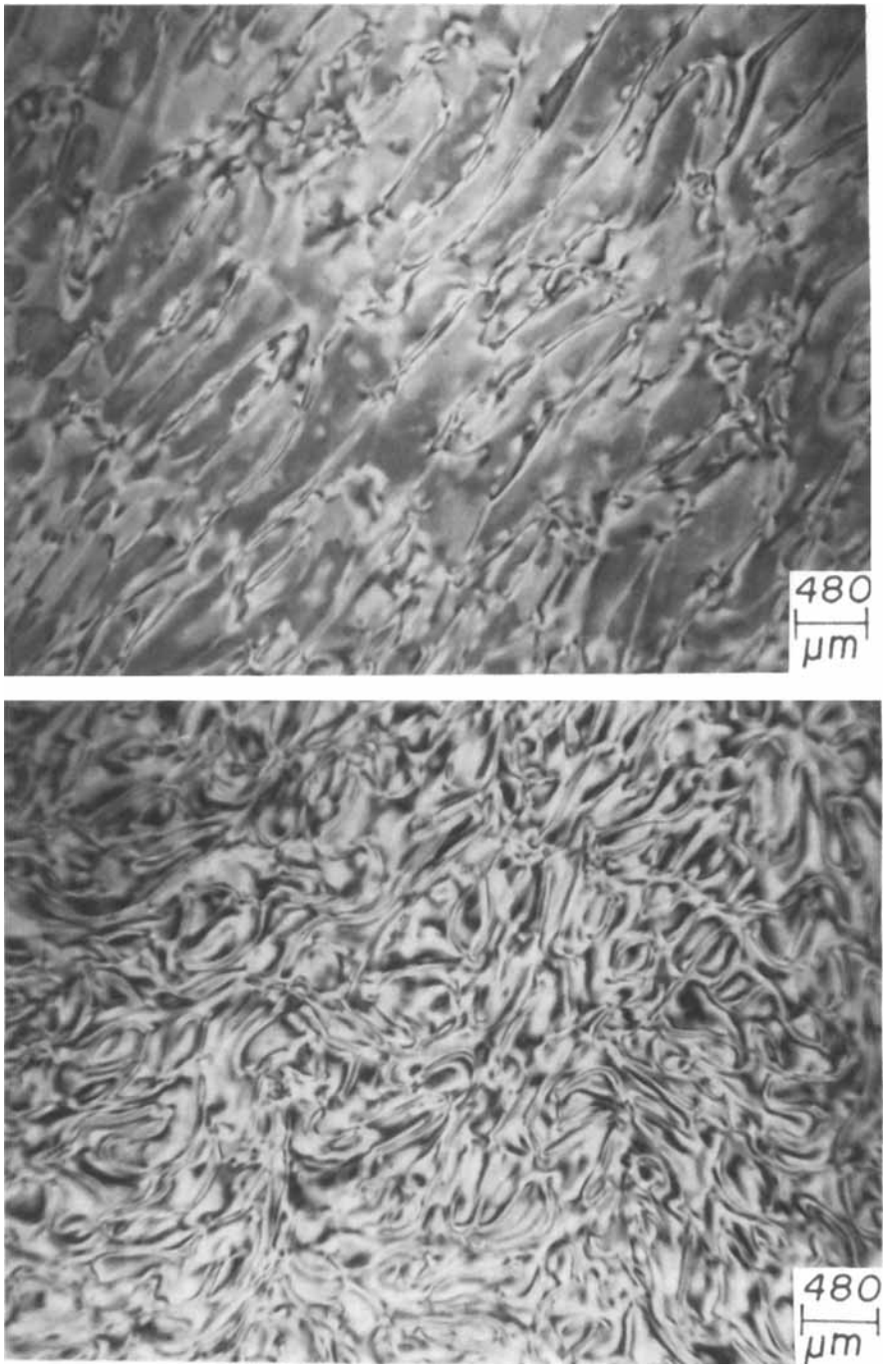

FIGURE 3 Textures of magnetically oriented type I intrinsic cholesteric lyomesophases (crossed polarizers). (a) Parallel orientation. (b) Perpendicular orientation. See Color Plate III, Vol. 111.

laurate/cholesterol (induced).[7] This texture corresponds to helicoidal pairs resulting from τ^+ and λ^+ disclinations.[17,18] After several days under the magnetic field action an homeotropic texture was observed.

Comparison of the present results with those from the laurate/cholesterol system[7] makes evident that induced and intrinsic cholesteric lyomesophases have the same orientational behavior in magnetic fields. Therefore two orientational times can be proposed for intrinsic systems, as it has already been done for induced mesophase: one for the alignment of the helicoidal axis perpendicular to B_0 and another one for the helical untwisting process.

The chemical nature of the amphiphile and wall effects certainly are additional factors to be considered in order to understand which process predominates for a sample under the action of a magnetic field.

4. CONCLUSIONS

l-KNLS is a suitable amphiphile for the preparation of a type I intrinsic cholesteric lyomesophase. Although the *l*-KNLS amphiphile has a complex polar head involving an ionic carboxilate and a polar OH group, this is not a drawback to the mesophase preparation. The obtained phases are chemically stable, not undergoing hydrolysis for a long term at room temperature. Since it was observed that KNLS rarely gives biphasic mixtures, it appears to be an attractive system for investigations in cholesteric lyotropic liquid crystals.

The observed deuteron NMR spectra and microscopic textures are quite similar to those reported previously for induced cholesteric mesophases (potassium laurate/cholesterol).[7] It was again possible to experimentally observe the existence of two orientational times in this new intrinsic cholesteric system.

It should be noted that the sample orientation process in a microscope cell is strongly influenced by wall effects. Therefore, the observed times for helical axis orientation and for cholesteric array untwisting detected by microscopic methods or by NMR should be different.

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