This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Comparison of the pitch induced from lamellar and nematic regions in some lyotropic liquid crystal systems

M. Acimis; A. Agar; A. Gok

Online publication date: 06 August 2010

To cite this Article Acimis, M. , Agar, A. and Gok, A.(1998) 'Comparison of the pitch induced from lamellar and nematic regions in some lyotropic liquid crystal systems', Liquid Crystals, 24: 3, 369 — 373

To link to this Article: DOI: 10.1080/026782998207172

URL: http://dx.doi.org/10.1080/026782998207172

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1998, VOL. 24, NO. 3, 369–373

Comparison of the pitch induced from lamellar and nematic regions in some lyotropic liquid crystal systems

by M. ACIMIŞ*
Abant Izzet Baysal University, Department of Chemistry, 14280 Bolu, Turkey

A. AGAR
Ondokuz Mayıs University, Department of Chemistry, 55139 Samsun, Turkey

and A. GOK
Süleyman Demirel University, Department of Chemistry, 32260 Isparta, Turkey

(*Received 9 April 1997; in final form 4 July 1997; accepted 5 August 1997*)

Lamellar phases (L_α) composed of decylammonium chloride (DACl), NH_4Cl and H_2O were doped with cholesteryl-2-ethoxyethoxyethyl carbonate (CEEC) and with L-mandelic acid (L-MA) or its racemic mixture (DL-MA). L_α phases of the novel intrinsic optically active L-serine hydrochloride decylester (L-SDE) and its racemic mixture (DL-SDE) were also prepared. From the chiral L_α phases, cholesteric phases (Ch_D) were induced with increased temperature and it was found that the pitch length shortened as the temperature was raised. This phenomenon is new for micellar cholesterics. The non-chiral L_α phases gave pseudo-isotropic and nematic regions with increased temperature. On the basis of these results and those in the literature, a new interpretation of the distorted micelle shape and the formation of the fingerprint texture is presented. The pitches induced from L_α regions were always larger than those obtained from nematic regions. From these results it is inferred that the interactions between the micelles in the cholesteric state at room temperature are of 'ideal' type. In addition, the temperature dependence of the pitch in micellar cholesterics is discussed.

1. Introduction

The formation of the helicoidal structure in micellar cholesterics has been explained by two mechanisms. The first mechanism assumed pairwise interactions between the chiral molecules contained in adjacent micelles. The second, however, presumed a distorted micelle shape caused by the inclusion of the chiral dopant into the nematic phase. It was proposed in each case that the interactions between the micelles would lead to the macroscopic twist [1]. Much work has been done to verify these models and the present experimental results either partly support the distortion model [2–5] or neither of them [6].

In order to detect the actual shape of the chiral micelles in cholesteric phases, some X-ray diffraction studies have been undertaken. The results, however, do not permit differentiation between undistorted micelles in nematic phases (N_D, N_C and N_B) and the chiral micelles in the cholesteric phases (Ch_D, Ch_C and Ch_B) [7–9]. The letters N and Ch stand for nematic and cholesteric and the subscripts indicate the shape of the micelles, being disk-like (D), cylindrical (C) or biaxial (B).

So far the preceeding information shows that the shape of the micelles in cholesteric phases and consequently, chiral induction are still not well understood. Usually micellar cholesterics are obtained either by doping nematic phases with chiral dopants or by using pure enantiomeric amphiphiles. The micellar cholesterics are recognized by the fingerprint texture, and the pitch measurements are usually made on this texture. Recently we have shown for the first time that micellar cholesterics could also be induced from doped lamellar phases with increased temperature [10]. Generally the micelles in lamellar phases were found to be infinite bilayers separated by thin water layers. However, in a recent investigation it was revealed that the bilayers may exhibit some fragmentation [11]. These phases do not give any fingerprint texture, i.e. the lamellar phases cannot be twisted by chiral molecules at room temperature [10].

Since the chiral information in the fingerprint texture is conveyed vertically between the different planes built

---

*Author for correspondence.

0267–8292/98 $12·00

up of finite micelles dispersed in water and also horizontally between micelles contained in a plane, the repeating spacing and the intermicellar distance must be critical in the formation of this texture.

X-ray diffraction studies on nematic phases (N_D) have shown that the repeat spacing and the intermicellar distance are of the order 42 and 70 Å, respectively [12, 13]. The repeat spacing found for nematic phases is approximately twice as large as that for lamellar phases [14]. This is understandable because the nematic phases are obtained with a larger quantity of water. The spacing data for the nematics (N_D) can also be assumed to be similar for the other micellar cholesterics [7–9]. Therefore, we consider that the chiral induction from lamellar phases with increased temperature is important because it is to be expected that the cholesteric phases obtained will exhibit different spacings and intermicellar distances, as well as different micelle sizes from the usual cholesterics already known to exist at room temperature.

With this in mind, we have investigated the lamellar phase composed of DACl, NH_4Cl, CEEC and water in detail. We also extended our studies to lamellar phases of the DACl system doped with L- or DL-MA, and to intrinsic optically active and racemic lamellar phases obtained from L- and DL-SDE. Furthermore we have investigated the corresponding nematic and cholesteric phases of these systems at room temperature to compare the pitches obtained from lamellar and nematic regions. As will be shown, the measured values of the pitches allow us to interpret the chiral induction as well as the temperature dependence of the pitch in a new way.

2. Experimental

DACl, L-SDE and DL-SDE were synthesized according to procedures given in [15]. CEEC, L-MA and DL-MA were purchased from Eastman-Kodak Company (USA) and Fluka (Germany). L-MA and DL-MA were of sufficient purity for direct use. CEEC, however, was purified

Table. The compositions (mol %), textures, phase transition temperatures and variations of the pitch for the phases of the systems studied.

Decylammonium chloride/CEEC system

	Component/mol %					Transitions/°C		
Sample	DACl	NH_4Cl	CEEC	H_2O	Texture at ~20°C	pseudo-iso	cholesteric	Variation in pitch (μm)
A	6·88	2·20	0·06	90·86	Oily streak, L_α	40	42–60	90–35
B	6·54	2·46	0·09	90·89	Oily streak, L_α	33	35–50	75–30
C	6·61	2·39	0·15	90·85	Oily streak, L_α	29	30–45	65–25
D	5·00	1·50	0·03	93·47	Fingerprint, Ch_D	—	—	15

Decylammonium chloride/L-MA system

	Component/mol %					Transitions/°C		
Sample	DACl	NH_4Cl	DL-MA	L-MA	H_2O	Texture at ~20°C	pseudo-iso	cholesteric	Variation in pitch (μm)
E	7·65	2·80	0·96	—	88·96	Oily streak, L_α	35	—	—
F	7·66	2·78	—	0·99	88·56	Oily streak, L_α	36	38–58	70–35
G	7·38	2·64	—	0·93	89·04	Oily streak, L_α	33	36–55	55–28
H	6·25	2·26	1·20	—	90·29	Schlieren, N_D	—	—	—
I	6·01	2·19	—	1·19	90·60	Fingerprint, Ch_D	—	—	10

L-Serine hydrochloride decylester system

	Component/mol %					Transitions/°C		
Sample	DL-SDE	L-SDE	NaCI	H_2O	Texture at ~20°C	pseudo-iso	cholesteric	Variation in pitch (μm)
K	7·02	—	2·95	90·01	Oily streak, L_α	38	—	—
L	6·39	—	2·66	90·94	Schlieren, N_D	—	—	—
M	5·34	1·06	2·64	90·96	Fingerprint, Ch_D	—	—	9
N	—	6·80	2·90	90·30	Oily streak, L_α	37	40–60	102–60
O	—	6·53	2·71	90·76	Oily streak, L_α	28	30–45	87–48
P	—	5·73	2·27	92·00	Fingerprint, Ch_D	—	—	32

according to the procedure in [16]. Pitch lengths were measured by polarizing light microscopic and laser diffraction methods [2]. For microscopic measurements, micro-slides of 0·2 and 0·3 mm thickness (Camlab UK) were used. The micro-slides were carefully sealed by flame at both ends, and the variation in temperature was achieved using a Unkam apparatus. Laser diffraction measurements were carried out on NMR samples of 5 mm diameter which were aligned in a magnetic field of 0·3 T prior to the measurements. Temperature measurements were made by placing the NMR samples in a brass holder adapted to allow a flow of thermostated water and a path for laser light. The results are summarized in the table.

3. Results and discussion

In the lamellar region (L_α) the liquid crystalline DACl/NH_4Cl/H_2O system has been doped with optically active CEEC or L-MA, and also with DL-MA. L_α phases were also prepared from the novel intrinsic optically active detergent (L-SDE) and its racemic mixture (DL-SDE) with NaCl and H_2O. The compositions of these phases (given in the table) exhibited oily streak textures at 20°C. The chiral L_α phases of DACl/NH_4Cl/H_2O/CEEC (samples A, B, and C), DACl/NH_4Cl/H_2O/L-MA (samples F and G) and L-SDE/NaCl/H_2O (samples N and O) had one common feature, and showed the following phase sequence with increased temperature:

$$L_\alpha \rightarrow \text{pseudo-isotropic} \rightarrow \text{cholesteric} \rightarrow \text{isotropic}.$$

The non-chiral L_α phases (samples E and K) of DACl/NH_4Cl/H_2O/DL-MA and DL-SDE/NaCl/H_2O, respectively, also exhibited a unique behaviour with increased temperature.

$$L_\alpha \rightarrow \text{pseudo-isotropic} \rightarrow \text{nematic} \rightarrow \text{isotropic}.$$

The approximate phase transition temperatures can be deduced from the table for each system. A peculiar feature in the phase sequence of the non-chiral L_α phases was that the pseudo-isotropic phase remained until the nematic range was reached. In this range a faint schlieren texture appeared, which remained for approximately three degrees before it became isotropic. Another common behaviour of the chiral L_α phases was observed in the induced cholesteric regions, i.e. the pitch length shortened with increased temperature. The shortening in the pitch length of the three systems was approximately 60% for DACl/CEEC, 50% for DACl/L-MA and 40% for the L-SDE system. The results of the pitch (P) versus temperature (T) measurements are represented in figure 1. It was found that the relation between P and T obeyed the equation $P^{-1} = \beta\, T$, where β is the helical twisting power of the chiral dopant or chiral amphiphile forming the phase.

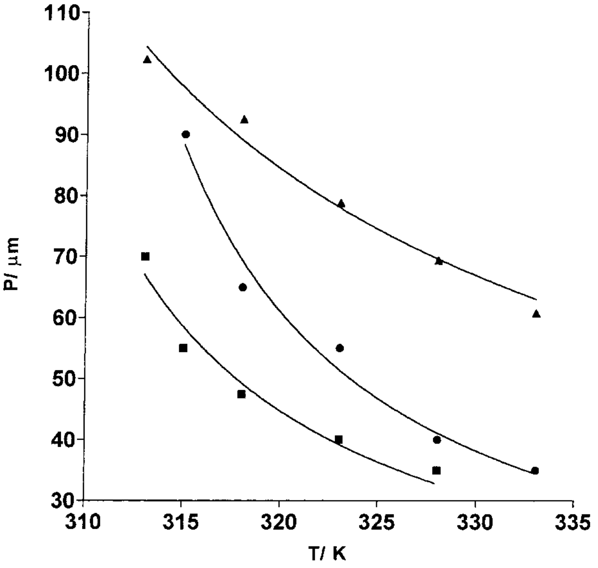

Figure 1. Temperature dependence of the pitch (P) induced from L_α regions. The systems from top to bottom are L-SDE (sample N), DACl/CEEC (sample A) and DACl/L-MA (sample F).

The shortening of the pitch length with increased temperature is a new phenomenon for micellar cholesterics, because systems investigated in the literature so far show that the pitches lengthen [3, 4, 6] or are not modified [8, 9] with increased temperature.

One of our aims was to explain which factors do affect the pitch length within a micellar cholesteric system. For instance, do the spacings between micelles have any effect on the pitches induced from lamellar and nematic regions? Therefore, we have prepared nematic phases (N_D) from DACl/DL-MA and DL-SDE systems (samples H and L) which exhibited a schlieren texture and which turned into a pseudo-isotropic phase of positive optical anisotropy (Δn). The cholesteric phases of the same systems (samples I and P) at 20°C gave pitches of 10 and 32 µm, respectively, which are shorter than the pitches induced from the L_α regions. The cholesteric phase DACl/CEEC system (sample D) also exhibited a shorter pitch length (15 µm) than the pitches induced from an L_α region. A drastic shortening of the pitch was measured when part of the DL-SDE was substituted by L-SDE (sample M). The pitch length of this phase was 9 µm, whereas the pitch length of the cholesteric phase of L-SDE was 32 µm. This phenomenon may be explained by the low viscosity of the DL-SDE nematic phase. Then as DL-SDE was replaced gradually by L-SDE, the cholesteric phase became more viscous, and this gave a longer pitch for the L-SDE phase. A similar phenomenon has been reported as an L-isomer was added to its racemic mixture [4]. From these results we can infer that the short distances 'expected', for the induced Ch$_{\mathrm{D}}$ phases from L$_{\alpha}$ regions do not produce shorter pitches than the nematic regions.

The nematic phases (N$_{\mathrm{D}}$) which we have investigated align with their optical axis perpendicular to the magnetic field direction. Consequently the induced cholesteric phases (Ch$_{\mathrm{D}}$) from L$_{\alpha}$ and N$_{\mathrm{D}}$ regions align with their helix axis parallel to the magnetic field direction and the micelles retain their local axis perpendicular to the helix axis [1, 17].

At the transition from pseudo-isotropic to cholesteric state, Δn changed from positive to negative. The change in Δn can only be understood if the micelles become 'distorted or twisted'. Nevertheless, as far as we are aware there is no clear picture on the distorted or twisted micelle shape in the literature. In the cholesteric phases formed by intrinsic chiral amphiphiles, the molecules are placed back to back at opposite interfaces, whereby each interface experiences a torque through the chiral molecules in opposite directions. Therefore the micelles assume a twisted shape. This means that the micelles of untwisted shape possess a $D_{\infty\mathrm{h}}$ symmetry and in the twisted shape a D_{∞} symmetry which is chiral [18]. Accordingly we can construct the fingerprint texture by considering a resultant vector of each micelle which is rotated by a definite angle (ϕ) compared with adjacent micelles along the magnetic field direction (B$_{\mathrm{Z}}$), figure 2. It can be inferred from the illustration that if the micelles are stacked in the XY-planes, which would be parallel to each other, but perpendicular to the Z-axis, they would rotate by the angle ϕ with respect to each other to complete a 2π-cycle. The sign curve in figure 2 constitutes one pitch length and exhibits two complete minima and two maxima which correspond to the four alternating dark and light stripes in the fingerprint texture perpendicular to the helix axis [2, 7].

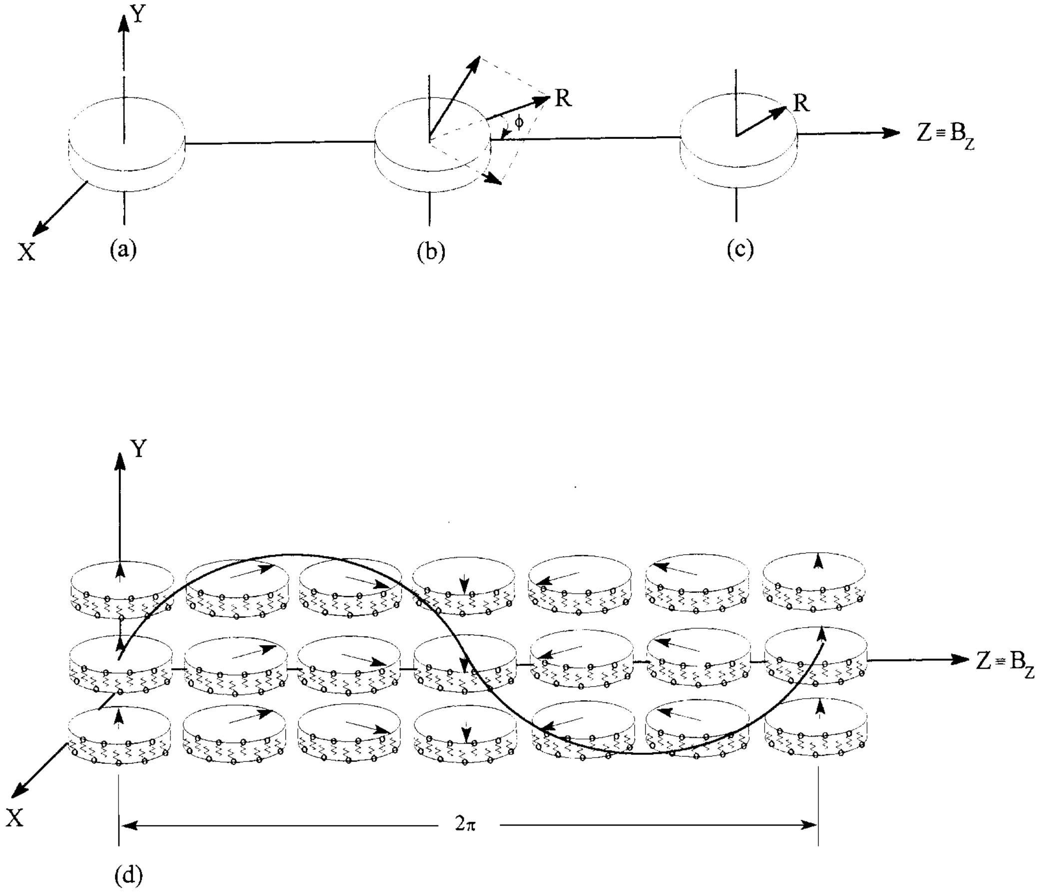

Figure 2. (*a*) Undistorted micelle shape (N$_{\mathrm{D}}$ phase) with $D_{\infty\mathrm{h}}$ symmetry. (*b*) Screw-like shape of the twisted micelle with D_{∞} symmetry, resulting through torques caused by the chiral amphiphiles at opposite interfaces. As a result, a rotating vector **R** (resultant vector) with respect to a direction is obtained. (*c*) For simplicity the resultant vector **R** is drawn on the surface of the micelle. (*d*) A slice of micelles (two micellar separations) in the YZ-plane, with the resultant vectors rotating with respect to each other to complete a 2π cycle, is illustrated. This illustration indicates the formation of the fingerprint texture and can be extended in the XZ-plane.

Now the change in the twist angle ϕ can be calculated, for example for the DACl/CEEC system (sample A) where the pitch length varied between 90 and 35 μm with increased temperature. If we assume a micelle diameter of 90 Å [19], the number of micelles in a complete cycle will vary from 10^4 to $3{\cdot}9 \times 10^3$ and ϕ will change from 0·036° to 0·09°. As presented here, the values of ϕ are very small and this might be the reason why X-ray studies did not differentiate between the shapes of the micelles in nematic and cholesteric phases [7–9].

In the light of these results, we present an explanation for the shortening of the pitch induced from L_α regions with increased temperature. Since the fingerprint texture comes about shortly after the pseudo-isotropic phase, we can infer that the interactions between the micelles are too strong in the pseudo-isotropic phase and therefore the micelles are not twisted. Another possible explanation could be based on the large micelle sizes in the pseudo-isotropic phase which do not give Ch_D phases. Since the Ch_D regions come about a few degrees (*c.* 2°) after the pseudo-isotropic phase, it is unlikely that the micelle size became smaller through this temperature increase. Thus, X-ray diffraction studies indicate that micelle dimensions in N_D regions are not very responsive to temperature change [12]. At the beginning of the cholesteric phase, the twist angle is small, but increases with increased temperature because the interactions between the micelles weaken; therefore they become easily twisted by the chiral molecules, and this gives rise to shorter pitch lengths. This explanation is in accordance with the measured short pitches from the cholesterics at room temperature: for example, the shortest pitch length induced from the lamellar phase DACl/L-MA (sample G) was 28 μm, but that of the same system at room temperature (sample I) was just 10 μm. This means that the twist angle ϕ of the cholesteric phase is 2·8 times larger than that induced from the L_α phase. This simple calculation allows us to assume that the interactions between the micelles in cholesteric phases with the shortest pitch lengths at room temperature approach an 'ideal state'. This is not the case in the cholesteric phases induced from L_α regions; therefore the increase in temperature is used to overcome the interactions between the micelles. When the pitch of cholesterics is lengthened with increased temperature, this can be explained on the basis of the increased molar volume. The increase in molar volume of the micelle decreases the twist angle ϕ [(figure 2 (*b*)] as was assumed for thermotropic cholesterics [20]. As a result, the pitch length is then increased. On this aspect, however, we will report in greater detail elsewhere.

4. Conclusions

In the light of the pitch values obtained from L_α regions with increased temperature, a new interpretation of the 'twisted micelle shape' is presented. The shortening or lengthening of the pitch with increased temperature is interpreted as a weakening of intermicellar interactions and an increase in the molar volume of the micelles, respectively.

M. A. wishes to thank Volkswagen-Foundation for the gift of equipment used in the project I/67579 in 1992. This work was also supported by Abant Izzet Baysal University Research Funds under project 95.03.03.03. M. A. is also grateful to Dr N. Çelebi for helping with the drawings.

References

[1] Radley, K., and Saupe, A., 1978, *Mol. Phys.*, **35,** 1405.
[2] Covello, P. S., Forrest, B. J., Marcondes Helene, M. E., Reeves, L. W., and Vist, M., 1983, *Phys. Chem.*, **87,** 176.
[3] Lasic, D. D., Marcondes Helene, M. E., and Reeves, L. W., 1983, *Can. J. Chem.*, **61,** 1921.
[4] Radley, K., and Tracey, A. S., 1985, *Can. J. Chem.*, **63,** 95.
[5] Tracey, A. S., and Radley, K., 1985, *Mol. Cryst. liq. Cryst.*, **122,** 77.
[6] Radley, K., 1992, *Liq. Cryst.*, **11,** 753.
[7] Figueiredo Neto, A. M., Liebert, L., and Levelut, A. M., 1984, *J. Physique*, **45,** 1505.
[8] Figueiredo Neto, A. M., and Marcondes Helene, M. E., 1987, *J. phys. Chem.*, **91,** 1466.
[9] Marcondes Helene, M. E., and Figueiredo Neto, A. M., 1988, *Mol. Cryst. liq. Cryst.*, **162B,** 127.
[10] Acimiş, M., Dorr, E., and Kuball, H.-G., 1994, *Liq. Cryst.*, **17,** 299.
[11] Holmes, M. C., Charvolin, J., and Reynolds, D. J., 1988, *Liq. Cryst.*, **3,** 1147.
[12] Galerne, Y., Figueiredo Neto, A. M., and Liebert, L., 1987, *J. chem. Phys.*, **87,** 1851.
[13] Oliveira, E. A., Liebert, L., and Figueiredo Neto, A. M., 1989, *Liq. Cryst.*, **5,** 1669.
[14] Gutman, H., Luz, Z., Wachtel, E. J., Poupko, R., and Charvolin, J., 1990, *Liq. Cryst.*, **7,** 335.
[15] Acimiş, M., 1987, *Liq. Cryst.*, **2,** 549; Acimiş, M., 1989, *Liq. Cryst.*, **4,** 697.
[16] Onusseit, H., 1983, PhD thesis, Paderborn University, Germany, p. 8.
[17] Acimiş, M., and Reeves, L. W., 1980, *Can. J. Chem.*, **58,** 1533.
[18] Toledano, P., Figueiredo Neto, A. M., Lorman, V., Mettout, B., and Dmitriev, V., 1995, *Phys. Rev. E*, **52,** 5040.
[19] Spada, G. P., Gotarelli, G., Samori, B., Bustamante, C. J., and Wells, K. S., 1988, *Liq. Cryst.*, **3,** 101.
[20] Gibson, H. W., 1979, *Liquid Crystals, the Fourth State of Matter*, edited by F. D. Saeva (Marcel Dekker Inc.), Chap. 3.