Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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Version of record first published: 24 Sep 2006.

To cite this article: Yoichi Takanishi , Yukio Ouchi , Hideo Takezoe , Atsuo Fukuda , Akihiro Mochizuki & Masakatsu Nakatsuka (1991): Spontaneous Formation of Quasi-Book-shelf Layer Structure in New Ferroelectric Liquid Crystals Derived from a Naphthalene Ring, Molecular Crystals and Liquid Crystals, 199:1, 111-118

To link to this article: http://dx.doi.org/10.1080/00268949108030922

Mol. Cryst. Liq. Cryst., 1991, Vol. 199, pp. 111–118
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Printed in the United States of America

Spontaneous Formation of Quasi-Bookshelf Layer Structure in New Ferroelectric Liquid Crystals Derived from a Naphthalene Ring

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(Received July 27, 1990)

We have studied ferroelectric liquid crystal mixtures of naphthalene and phenyl pyrimidine derivatives, and found that the layer structure can be controlled by changing mixture ratios. By decreasing temperature, a bookshelf layer structure with the optical tilt angle of 5° is realized spontaneously in a mixture containing 40 wt% naphthalene derivative.

Keywords: ferroelectric LC, x-ray, quasi-bookshelf, layer structure control

1. INTRODUCTION

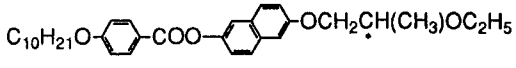
To realize an excellent electro-optic display using SSFLC device,[1,2] it is ideal to have a layer structure of bookshelf type, where the layer is perpendicular to the glass substrate plates. But in the chiral smectic C phase (SmC*), the samples homogeneously aligned by a conventional method usually have the chevron layer structure,[3–6] and the effective spontaneous polarization decreases and the switching speed becomes slow. To realize the bookshelf layer structure, several forced alignment methods have been proposed; SiO oblique evaporation,[7] high-pretilt-induced

polyimide rubbing,[8] AC field application,[9] etc. In marked contrast to these forced methods, we reported in a previous paper[10] that a ferroelectric liquid crystal mixture containing naphthalene derivatives forms a quasi-bookshelf layer structure spontaneously and exhibits a good electro-optic properties when prepared the cell by a conventional rubbing method.[11] We concluded that this layer formation is due to the intrinsic temperature dependence of the interlayer spacing.[10]

Trying to understand the real cause of the characteristic temperature dependence and to obtain an ideal mixture of which smectic layer spacing is temperature independent, we have made the similar measurements using a pure compound with the naphthalene ring, MTLC-8010, and Merck mixture, ZLI-4139. The temperature change of the layer spacing appears to depend critically on the mixing ratio; a mixture with the ratio of (MTLC-8010)/(ZLI-4139) = 4/6 was found to have a layer spacing almost independent of temperature. Some preliminary results will be reported in the following.

2. EXPERIMENTAL

Samples used were mixtures of a pure compound, MTLC-8010,



and ZLI-4139, a mixture containing phenyl pyrimidine derivatives, with the mixing ratios of MTLC-8010 to ZLI-4139, 3 to 7 (MT30) and 4 to 6 (MT40). The phase sequences are as follows.

MTLC-8010	**Cryst**	**49.0°C**	**SmC***	**59.0°C**	**SmA**	**64.0°C**	**N***	**73.0°C**	**Iso**
ZLI-4139	**(Cryst)**		**SmC***	**63.0°C**			**N***	**80.0°C**	**Iso**
MT30	**(Cryst)**		**SmC***	**50.0°C**	**SmA**	**66.0°C**	**N***	**79.0°C**	**Iso**
MT40	**(Cryst)**		**SmC***	**39.5°C**	**SmA**	**64.5°C**	**N***	**75.8°C**	**Iso**

To measure the layer tilt angle of the samples, we prepared the homogeneously aligned sample cells by rubbing glass plates after coating with poly(vinylalcohol). The glass plates were 150 μm in thickness, and the cell gap was about 4 μm. X-ray scattering measurements were performed using the Rigaku RU-200 (Cu Kα) and its temperature control unit (±0.1°C or better in accuracy). The scattering geometry was the same as in the previous paper.[6] For the measurement of the interlayer spacing, homeotropically aligned cells were prepared. The cell gap was 25 μm. The surfactant used for homeotropic alignment was AY43-021 (Toray Dow Corning Silicone). Interlayer spacing d was measured by a conventional 2θ-θ scan. Texture observation was performed under a polarizing microscope, Nikon OPTIPHOTO-POL. For the measurement of the apparent optical tilt angle, the transmitted light was detected by a photomultiplier tube to determine the extinction direction by rotating the stage of the polarizing microscope under the crossed polarizers.

3. RESULTS AND DISCUSSION

Figures 1 (a) and (b) show temperature dependence of the layer tilt angle, δ, of MT30 and MT40; here $\delta + 90°$ is an angle between the layer normal and the glass plate normal. In MT30, δ_A in the smectic A phase is about 2°; hence the layer structure changes to the chevron type from the bookshelf type, and δ_C increases monotonically until the saturated value of $\delta_C \approx 13°$ is attained at 30°C. In the heating process, the layer structure change follows the cooling process reversibly.

The layer structure change of MT40 differs from that of MT30. In the SmA phase, three peaks are observed. With decreasing temperature, the layer tilt angle gradually decreases, and the layer structure becomes a bookshelf in the SmC* phase. Immediately after reversing the process from cooling to heating, single peak

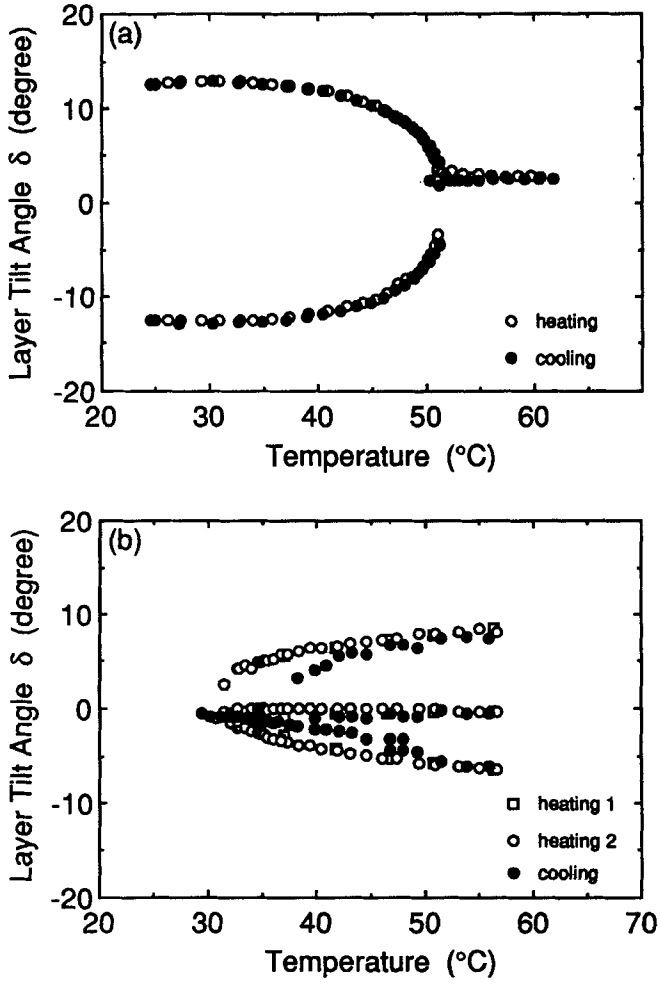


FIGURE 1 Temperature dependence of the layer tilt angle of mixture in the SmA and SmC* phases; (a) MT30, (b) MT40.

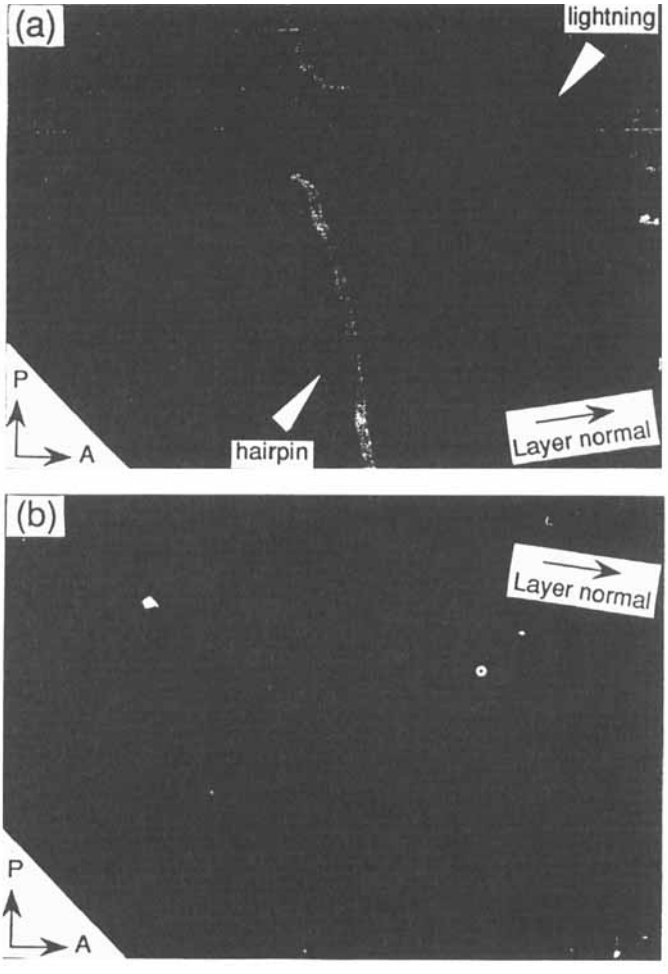


FIGURE 2 Optical micrographs of homogeneously aligned mixture at 28°C; (a) MT30, ×100, (b) MT40, ×100.

splits into three peaks and the layer structure changes to the chevron. With the increase of temperature, the layer tilt angle increases gradually but the central peak does not disappear; the layer tilt angle depends on its thermal hysteresis and is not a unique function of temperature.

These behaviors are also confirmed with microscope observation. Figures 2 (a) and (b) show the optical micrographs of MT30 and MT40 in the SmC* phase, respectively; typical zig-zag defects are observed in (a), but not in (b).

These layer structure changes arise from the temperature dependence of the interlayer spacing as already pointed out in the previous paper.[10] Figures 3 (a) and (b) show the temperature dependence of the layer spacing, d, in MT30 and MT40, respectively. It decreases monotonically with decreasing temperature in MT30. The layer spacing of MT40, on the other hand, increases slightly and almost constant.

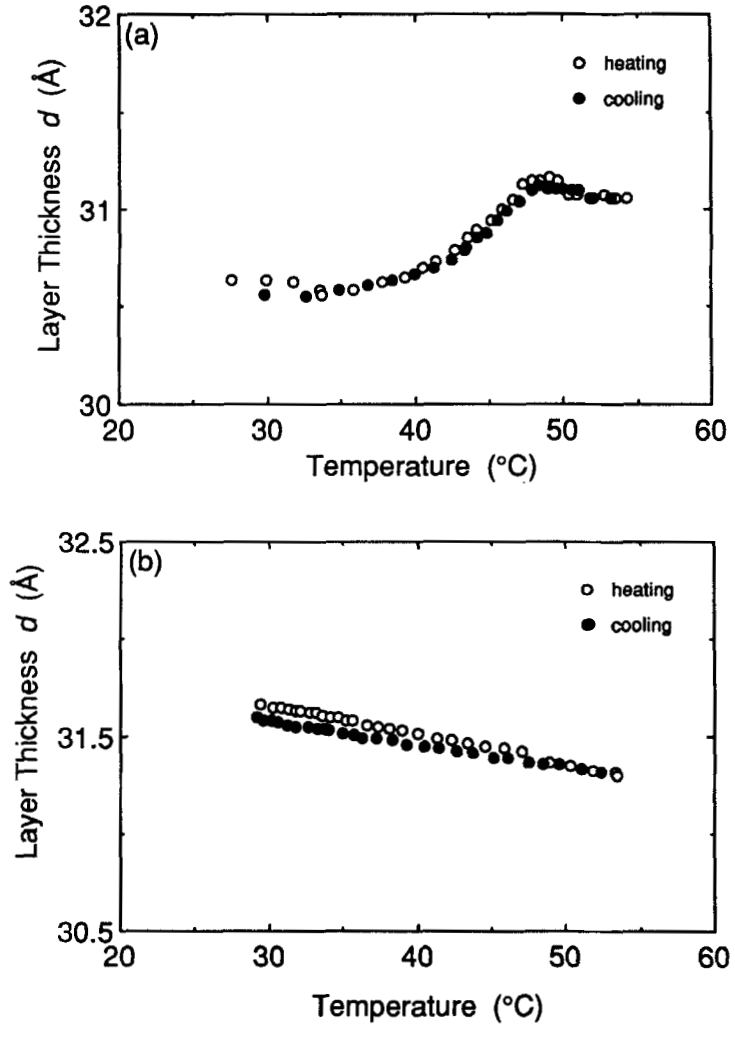


FIGURE 3 Temperature dependence of the interlayer spacing, d in the SmA and SmC* phases; (a) MT30, (b) MT40.

The calculated layer tilt angle, δ', in MT30 by applying the simple rule,[2]

$$\delta' = \cos^{-1}(d_C/d_A) \tag{1}$$

is almost coincident with δ in Figure 1(a). Here d_A and d_C are the interlayer spacings in the SmA and SmC phases, respectively. As d_C is longer than d_A in MT40, we have to replace d_A by the maximum value of d_C and d_C by $d_A(T)$ or $d_C(T)$ in Equation (1) when discussing the relation between δ and d. We recognize that the chevron layer structure in the SmA phase of MT40 is a result of the heating process from the room temperature. Probably, in the cooling process from the N* phase,

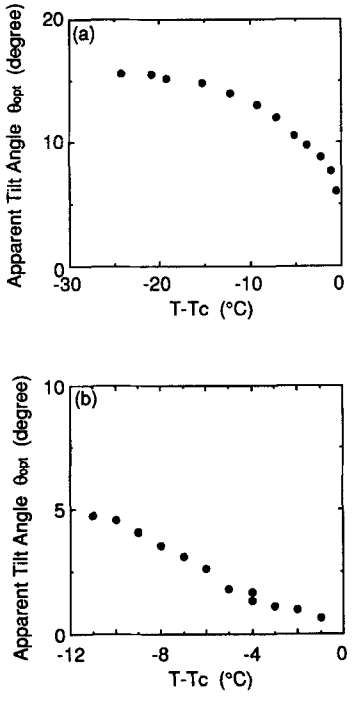
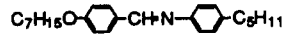


FIGURE 4 Temperature dependence of the apparent tilt angle, θ_{opt}; (a) MT30, (b) MT40.

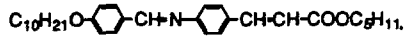
a bookshelf layer structure will be kept in a wide range of temperature of the SmA and SmC* phases.

Figures 4 (a) and (b) show temperature dependence of the apparent tilt angle, θ_{opt}, of MT30 and MT40, respectively. In MT30, θ_{opt} increases monotonically from zero at the SmA-SmC* phase transition with decreasing temperature. In MT40, although θ_{opt} in the temperature ranging from the SmA-SmC* phase transition to $T_C - T = 5°C$ is considerably small due to the coexistence of the SmA and SmC* phases, θ_{opt} increases almost monotonically from zero at the SmA-SmC* phase transition. Consequently, MT40 sample almost attains an ideal SSFLC state in which the layer structure is of bookshelf type, though the optical tilt angle is small. Even MT30 sample has a chevron layer structure of which the layer tilt angle is smaller than ordinary FLC mixtures but the apparent tilt angle θ_{opt} is as large as 16°. Therefore the material with a mixing ratio between MT30 and MT40 may have a relatively large optical tilt angle and a bookshelf layer structure due to temperature independence of the interlayer spacing in a wide range of temperature. We are in the process of detailed investigation.

The temperature dependence of interlayer spacing similar to MT40 was reported by de Jeu and de Poorter[12] in



and by de Vries[13] in



In their report, interlayer spacing did not change significantly over the wide temperature range of the SmC* and SmA phases and de Vries designated this transition as A3-C3 transition.†

Additionally, from DSC data, de Vries reported that the A3-C3 transition is of the first order, and Mochizuki *et al.*[14] also reported that the enthalpy change, ΔH, between the SmA and SmC* phases of mixtures containing 30 ~ 50 wt% naphthalene derivative is larger than that between the N* and isotropic phases. Hence, this transition also must be of the first order. The only difference between them is the tilt angle. de Vries *et al.* reported that the tilt angle of molecules is not zero in the SmA phase, approximately 15°, and explained that in the SmA phase, tilted layers are stacked in a random fashion, and in the SmC* phase in an ordered manner. But in MT40, θ_{opt} increases monotonically from zero at the SmA-SmC* phase transition with decreasing temperature. Therefore molecular arrangement of MT40 seems to be substantially different from de Vries' model.

In the ordinary smectic C liquid crystals, θ_{opt} increases and interlayer spacing d decreases due to molecular tilt from the layer normal with decreasing temperature in the SmC* phase. But in the case of MT40, both θ_{opt} and d increase monotonically. From this result, we suggest as follows: by tilting molecules, interdigitation between the neighboring molecules will be loosened or the repulsive force will be exerted, so that d increases even if molecules tilt from the layer normal in the SmC* phase. In fact, this mixture is prepared by blending a pure compound, MTLC-8010 with a commercial mixture, ZLI-4139; hence the molecular arrangement in a layer will be much more complex than that of a mixture composed of two pure compounds. By considering that most of the mixtures so far blended are quite normal in their behavior, this behavior may be attributable to the effect of the mixing of a naphthalene derivative liquid crystal which has an asymmetric core. We are taking a much interest in analyzing the molecular shape and in measuring the temperature dependence of the density and the second order X-ray diffraction peak due to the interlayer spacing.

4. CONCLUSION

We have investigated ferroelectric liquid crystal mixtures of naphthalene and phenyl pyrimidine derivatives, and confirmed that layer structure can be controlled by changing mixing ratio. In this performance, we realized the layer structure to approach to the ideal structure of SSFLC states, namely, a bookshelf layer structure.

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† de Vries designated the smectic C phase with a large and essentially temperature independent tilt angle as C1 and that with a much smaller tilt angle that is strongly dependent on temperature and goes to zero at A-C transition as C2.

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