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

A novel liquid crystal showing antiferroelectric smectic C* and twist grain boundary phases

Yoshio Aoki

Online publication date: 06 August 2010

To cite this Article Aoki, Yoshio(1999) 'A novel liquid crystal showing antiferroelectric smectic C* and twist grain boundary phases', Liquid Crystals, 26: 1, 97 — 100
To link to this Article: DOI: 10.1080/026782999205597
URL: http://dx.doi.org/10.1080/026782999205597

LIQUID CRYSTALS, 1999, VOL. 26, NO. 1, 97–100

A novel liquid crystal showing antiferroelectric smectic C* and twist grain boundary phases

YOSHIO AOKI and HIROYUKI NOHIRA

Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-ohkubo, Urawa, Saitama 338, Japan

(*Received 13 June 1998; accepted 18 August 1998*)

A novel antiferroelectric liquid crystal, 4-[5-(4-octyloxyphenyl)-2-pyrimidinyl]phenyl 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoate (TFMB) showing twist grain boundary phases was found and investigated. In optically active TFMB, a diffuse liquid–liquid transition was observed above the clearing point. TFMB exhibited a stable antiferroelectric smectic C* phase. The relationship between antiferroelectricity and the molecular structure is discussed.

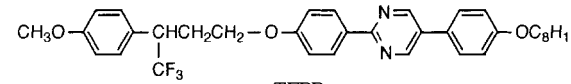
1. Introduction

Antiferroelectric liquid crystals (AFLCs), applicable to flat panel display devices, are attractive materials. Moreover, AFLCs are of scientific interest because of their physical properties, such as antiferroelectricity [1]. Therefore, a number of AFLCs have been synthesized, and relationships between structure and properties have been investigated. Since the discovery of MHPOBC [2, 3], similar AFLCs have been synthesized mainly for use in display devices.

In addition, the twist grain boundary (TGB) phase was discovered by Goodby and coworkers in 'highly' chiral liquid crystals [4, 5]. The TGBA phase has helical ordering that is a result of the frustration between molecular chirality and smectic layer ordering. Goodby and coworkers reported similarities between the related melting processes of blue phase III, the TGBA phase, and the cubic D phase to isotropic liquid, and discussed the presence of a diffuse liquid–liquid transition above the clearing point [6, 7].

Recently a liquid crystal showing antiferroelectric smectic C* (SmC_A^*) and TGB phases was reported by Nguyen and coworkers [8]. The novel AFLC showed BP (blue phase), N*, TGB, ferroelectric, ferrielectric and antiferroelectric phases, which were identified by miscibility and X-ray diffraction studies. It is interesting that this AFLC has a phenyl ring substituted with two fluorine atoms.

Several years ago, we synthesized another AFLC, 2-{4-[3-(4-methoxyphenyl)-4,4,4-trifluoro]butyloxy}-phenyl-5-(4-octyloxyphenyl)pyrimidine (TFPP) which has a very different structure from that of MHPOBC, making it apparent that a carbonyl moiety is not indispensable for obtaining AFLC phases (see figure 1) [9, 10]. Some AFLCs similar to TFPP were synthesized in order to clarify the relationship between structure and antiferroelectricity. Here we report that 4-[5-(4-octyloxyphenyl)-2-pyrimidinyl]phenyl 4,4,4-trifluoro-3-(4-methoxyphenyl)-butanoate (TFMB) shows not only antiferroelectric phases but also a TGBA phase (see figure 2). In this paper, we report the mesomorphic properties of TFMB and discuss the relationship between antiferroelectricity and molecular structure.



TFPP

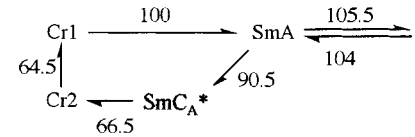
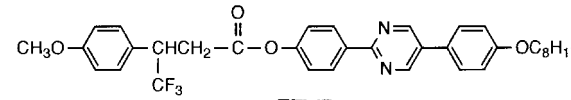


Figure 1. The structural formula and phase transition of TFPP. Cr indicates crystal solid; SmC_A^* indicates chiral smectic C_A phase; SmA indicates smectic A phase; I indicates isotropic liquid.

2. Experimental

The synthesis of TFMB has been previously reported [11]. The liquid crystalline phases were observed with a polarizing microscope (Nikon OPTIPHOT2-POL) equipped with a heating stage (METTLER FP-82HT) and a thermal control unit (METTLER FP-90). The phase transition temperatures were determined by



TFMB

Figure 2. The structural formula of TFMB.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

DSC (MAC SCIENCE DSC3100). The electro-optical properties were examined using a polarizing microscope equipped with a photomultiplier (HAMAMATU R2228) and an oscilloscope (Hewlett Packard 54520A). The dielectric constants were measured using a LCR Hi Tester (HIOKI 3520), in which the applied voltage was 0.1 V and the frequency was 1 kHz. The cell gap was *c.* 1.4 μm, and was determined by capacitance measurements. X-ray diffraction measurement was made using a Rigaku RU-200 (20 kV, 40 mA).

3. Results and discussion

Since TFMB did not show any liquid crystalline phases on heating, all physical properties and phase transition temperatures were measured on cooling. The phase transition temperatures are summarized in table 1. Differential scanning calorimetry (DSC) thermograms of TFMB are shown in figure 3.

In optically active TFMB, a diffuse liquid–liquid transition was observed above the clearing point. Such phenomena have been discussed in detail by Goodby and coworkers [6, 7]. This diffuse peak in the thermogram may be explained as a formation of cybotactic clusters, which have TGB-like local ordering, producing a phase which is optically isotropic. Therefore, the phase transition from isotropic to TGBA may correspond to a formation of lattice-like ordering, namely that of screw dislocations. However, a diffuse peak was not observed in racemic TFMB, which showed a nematic phase over a narrow range of temperature. Therefore, the degree of chirality of TFMB is high, and the chiral–chiral interaction probably influences the phase transition. The temperature from the isotropic phase to nematic phase of the racemate is nearly equal to that of the diffuse liquid–liquid transition. However, the relationship between the liquid phase and nematic phase is not clear. The sum or the enthalpies of the liquid–TGBA and the liquid–liquid transitions of optically active TFMB was nearly equal to that of isotropic liquid–N and N–SmA phase transitions of the racemate ($\Delta H = \sim 3$ J g^{-1}). The liquid phase of optically active TFMB has a certain ordering, while the TGBA phase has local SmA-like ordering and macro helical structure. Therefore, the cybotactic clusters of TFMB may have only local SmA-like ordering. In optically active TFMB, the observed phase sequence was TGBA–FI (ferrielectric phase)–SmC^*_A, while the phase sequence of N–SmA–SmC–SmC_A was seen in the racemate. The racemate thus shows mesogenic behaviour different from that of the enantiomers, and the TGBA phase was replaced by SmA. The macro helical structure of TGBA phase was probably cancelled out in the racemate. In the TGBA phase, a characteristic filament texture was observed under the polarizing microscope (figure 4).

The enantiomers showed FI phase and SmC^*_A phase, and a typical electro-optical behaviour was observed.

Table 1. Phase transition temperatures of TFMB on cooling. DSC cooling rate = 5°C min^{-1}. Cr = crystal solid. SmC_A = smectic C_A phase. SmC = smectic C phase. SmA = smectic A phase. N = nematic phase. I = isotropic liquid. FI = ferrielectric phase. TGBA = twist grain boundary A phase.

Optical form	Phase transition temperature (T/°C)
(±)	Cr2 47.5 Cr1 56.1 SmC_A 83.2 SmC 89.5 SmA 115.8 N 117.1 I
(*S*)-(+)	Cr 60.2 SmC^*_A 88.1 FI 90.8 TGBA 107.5 I
(*R*)-(−)	Cr 60.5 SmC^*_A 88.4 FI 90.8 TGBA 107.7 I

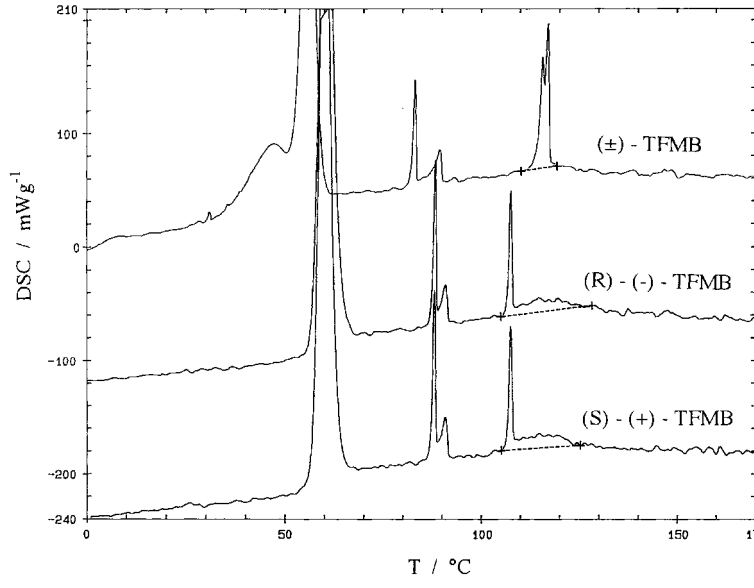


Figure 3. DSC thermograms of TFMB. Cooling rate = 5°C min^{-1}.

Figure 4. A typical filament texture of TGBA phase of TFMB. $T = 102°C$.

The temperature dependence of the dielectric constant is shown in figure 5. Any changes of ε value were not observed at the liquid–liquid transition, while the value of ε rapidly increased in FI phase. The discontinuous change of ε at the transition point showed that the transition from FI to SmC_A^* was likely of the first order. The phase transition temperatures in the cell were slightly lower than that in the DSC pan; this is probably due to a surface effect in the cell. The temperature dependence of ε, tilt angle (θ) and threshold voltage (V_{th}) as shown in figure 6. The discontinuous change of the V_{th} value at the transition from FI to SmC_A^* was observed, while the magnitude of θ gradually increased with a decrease in temperature. The V_{th} value of TFMB was relatively large ($V_{th} > 50$ V μm^{-1} at 80°C), which meant that the SmC_A^* phase of TFMB has a tight structure.

On the other hand, in order to explain the structure of the SmC_A^* phase, the Px-model has been proposed by Fukuda and co-workers [12], and they have reported orientations of AFLC molecules using spectroscopic

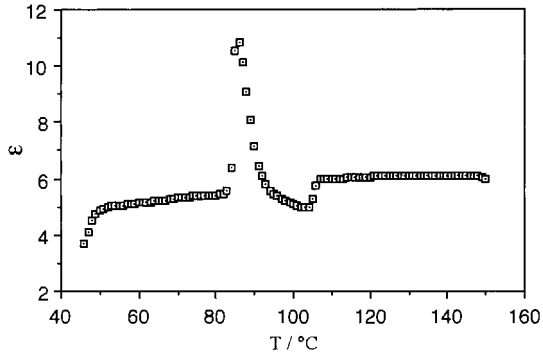


Figure 5. Temperature dependence of the dielectric constant of TFMB. $E = 0.1$ V, $f = 1$ kHz, cell gap = 1.4 μm, cooling rate = 3°C min^{-1}.

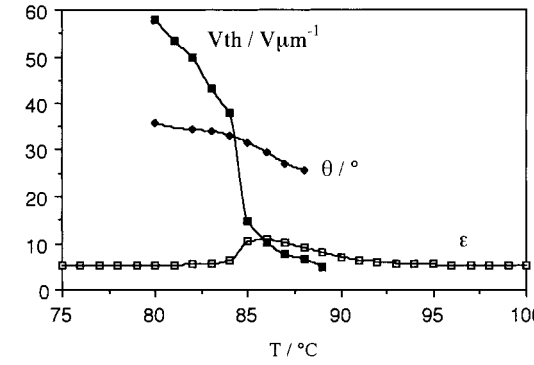


Figure 6. Temperature dependence of V_{th}, tilt angle and dielectric constant of TFMB.

methods [13]. Some physical properties of TFPP and TFMB are summarized in table 2. The $\mathbf{P}_s$ value of TFPP is about twice as large as that of TFMB, while the V_{th} of TFPP is smaller than that of TFMB. It seems that the $\mathbf{P}_s$ value does not relate to the threshold voltage of AFLC, and that the carbonyl moiety of TFMB scarcely contributes to the magnitude of $\mathbf{P}_s$. Therefore, the dipole of the carbonyl moiety probably stabilizes the SmC_A^* phase, and raises the threshold voltage of TFMB.

The layer spacing of TFMB was measured by X-ray scattering. The relationship between temperature and layer spacing of TFMB is shown in figure 7. In the TGBA phase, the layer spacing of about 35 Å slightly increased with a decrease in temperature. A discontinuous change of the layer spacing at the transition from TGBA to FI phase was observed. The layer spacing rapidly decreased

Table 2. Physical properties of TFPP and TFMB. V_{th} = threshold voltage of AFLCs, θ = tilt angle

Compound	$\mathbf{P}_S$/nC cm^{-2}	V_{th}/V μm^{-1} [a]	θ/° [b]
TFPP	132	42	33
TFMB	54	50	34

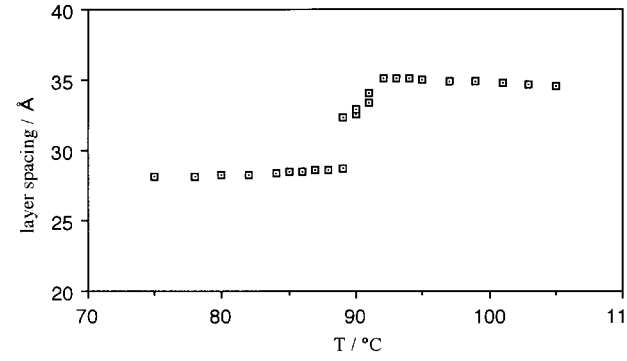


Figure 7. The relationship between temperature and the layer spacing of TFMB.

in the FI phase, because liquid crystalline molecules tilted in the smectic layer. The distinct change (about 3.6 Å) of the layer spacing at the transition from FI to SmC_A^* phase was observed, and the layer spacing slightly decreased in the SmC_A^* phase. These jumps of the layer spacing clearly show that the transitions of TGBA–FI–SmC_A^* phase are of the first order.

The authors are indebted to Prof. A. Fukuda and Dr Y. Takanishi for the X-ray scattering experiment and the many useful suggestions on antiferroelectric liquid crystals. They also wish to thank Dr I. Nishiyama for help and advice with twist grain boundary phases. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 06555276) from the Ministry of Education, Science and Culture.

References

[1] Fukuda, A., Takanishi, Y., Isozaki, T., Ishikawa, K., and Takezoe, H., 1994, *J. mater. Chem.*, **4**, 997.
[2] Chandani, A. D. L., Ouchi, Y., Takezoe, H., Fukuda, A., Terashima, K., Furukawa, K., and Kishi, A., 1989, *Jpn. J. appl. Phys.*, **28**, L1261.
[3] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., and Fukuda, A., 1989, *Jpn. J. appl. Phys.*, **28**, L1265.
[4] Goodby, J. W., Waugh, M. A., Stein, S. M., Chin, E., Pindak, R., and Patel, J. S., 1989, *J. Am. chem. Soc.*, **111**, 8119.
[5] Goodby, J. W., 1991, *J. mater. Chem.*, **1**, 307.
[6] Booth, C. J., Dummur, D. A., Goodby, J. W., Kang, J. S., and Toyne, K. J., 1994, *J. mater. Chem.*, **4**, 747.
[7] Goodby, J. W., Dummur, D. A., and Collings, P. J., 1995, *Liq. Cryst.*, **19**, 703.
[8] Navailles, L., Ngyuyen, H. T., Barois, P., Isaert, N., and Delord, P., 1996, *Liq. Cryst.*, **20**, 653.
[9] Aoki, Y., and Nohira, H., 1995, *Liq. Cryst.*, **19**, 15.
[10] Aoki, Y., and Nohira, H., 1996, *Ferroelectrics*, **178**, 213.
[11] Aoki, Y., and Nohira, H., 1995, *Liq. Cryst.*, **18**, 197.
[12] Miyachi, K., Matsushima, J., Takanishi, Y., Ishikawa, K., Takezoe, H., and Fukuda, A., 1995, *Phys. Rev. E*, **52**, R2153.
[13] Kim, K. H., Ishikawa, K., Takezoe, H., and Fukuda, A., 1995, *Phys. Rev. E*, **51**, R2166.