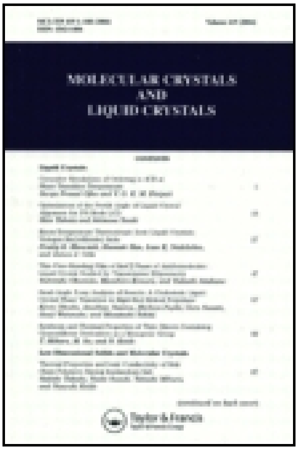


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Molecular Structure and Physical Properties of Chiral Liquid Crystalline Compounds

Monika Marzec [a] , Adriana Mikułko [a] , Stanisław Wróbel [a] , Agnieszka Szymańska [a] & Roman Dąbrowski [b]

[a] Institute of Physics, Jagiellonian University, Kraków, Poland

[b] Military University of Technology, Warsaw, Poland

Version of record first published: 22 Sep 2010

To cite this article: Monika Marzec, Adriana Mikułko, Stanisław Wróbel, Agnieszka Szymańska & Roman Dąbrowski (2008): Molecular Structure and Physical Properties of Chiral Liquid Crystalline Compounds, Molecular Crystals and Liquid Crystals, 480:1, 140-148

To link to this article: http://dx.doi.org/10.1080/15421400701826035

Mol. Cryst. Liq. Cryst., Vol. 480, pp. 140–148, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701826035

Molecular Structure and Physical Properties of Chiral Liquid Crystalline Compounds

Monika Marzec[1], Adriana Mikułko[1], Stanisław Wróbel[1], Agnieszka Szymańska[1], Roman Dąbrowski[2]
[1]Institute of Physics, Jagiellonian University, Kraków, Poland
[2]Military University of Technology, Warsaw, Poland

Influence of molecular structure on physical properties of chiral compounds is presented. It is shown that fluorinating of the achiral chain have great influence on physical properties of liquid crystalline phases. As an example, two compounds: (S)-(+)-4-(1-Metyloheptyloxy-carbonylbiphenyl) 4′-(6-perfluoropentanoyloxyhex-1-oxy) benzoate and (S)-(+)-4-(1-Metyloheptyloxycarbonylbiphenyl) 4′-(6-pentanoyloxyhex-1-oxy) benzoate have been selected. Phase transition temperatures and stability of these compounds have been studied by DSC calorimetry, texture observation, electrooptic measurements and dielectric spectroscopy. Based on these studies it was found that the SmC^**–*SmA^* *transition is a continuous one for both compounds studied.*

Keywords: dielectric processes; ferroelectric and antiferroelectric liquid crystal; phase transition; spontaneous polarization

INTRODUCTION

Since the discovery of liquid crystalline state lots of liquid crystalline substances – liotropic and thermotropic – have been synthesized and investigated [1]. Ferroelectric liquid crystals (FLC) as well as antiferroelectric liquid crystals (AFLC) are widely being studied now. Starting from 1974 when FLC with bistable switching were found [2] and later on in 1989 when AFLC with tristable switching were obtained [3], a lot of theoretical [4–6] and experimental [7–10]

Three of us (S.W., A.M. and M.M.) would like to thank the State Committee for Scientific Research (KBN) for financial support in scope of the grant No. 1 P03B 056 28.

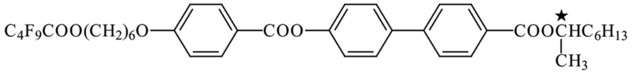
Address correspondence to Monika Marzec, M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, Krakow 30-059, Poland. E-mail: ufmarzec@if.uj.edu.pl

papers discussing phase transitions between para- and ferroelectric phases as well as para- antiferroelectric and ferro- antiferroelectric ones have been published. Physical properties of ferroelectric and antiferroelectric phases and their temperature range are very interesting because of their possible application in liquid crystal displays (LCD).

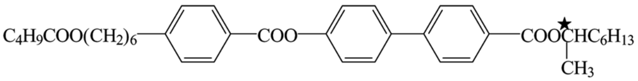
By changing molecular structure of liquid crystalline substances one can modify their physical properties. In this article we show how small modification of molecular structure influences the properties of liquid crystalline compounds. As an example, two compounds (4H6B and 4F6B) built of three benzene rings and two side chains have been chosen. The difference between them is in partially fluorinating of the left-hand side achiral chain. Interesting is that this modification causes change from ferroelectric to antiferroelectric behavior. Temperature dependence of layer thickness and tilt angle for both compounds have been published earlier [11,12]. In this article we present measurements performed by DSC calorimetry, polarizing microscope and dielectric spectroscopy methods and discuss similarities and differences between these two compounds. The order of the para- ferroelectric phase transition for both substances studied is also debated.

EXPERIMENTAL

Molecular structure and full name of the substances (4F6B and 4H6B) studied by complementary methods are presented in Figure 1. The results of textures observation, DSC, dielectric and electrooptic measurements allowed us to compare the phase sequence and the character of the ferroelectric-paraelectric transition. Texture observation has been done on polarizing microscope Jenapol Carl Zeiss. Calorimetric measurements have been performed on Pyris 1 DSC



(S)-(+)-4-(1-Metyloheptyloxy-carbonylbiphenyl) 4’-(6-perfluoropentanoyloxyhex-1-oxy) benzoate (4F6B)



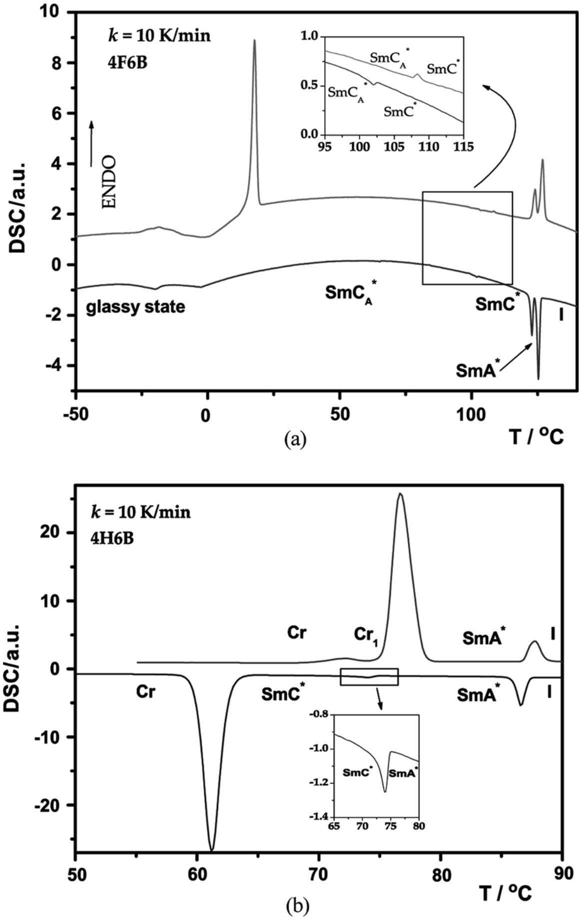
(S)-(+)-4-(1-Metyloheptyloxycarbonylbiphenyl) 4’-(6-pentanoyloxyhex-1-oxy) benzoate (4H6B)

FIGURE 1 Molecular structure and full name of the substances studied.

calorimeter during heating and cooling of the samples at different rates. Aluminum pans filled by ca. 5 mg of substance studied have been used. The reversal current method [13,14] has been used to check the temperature behavior of the spontaneous polarization. The triangular wave of $U_{p\text{–}p} = 200\,\mathrm{V}$ and $v = 50\,\mathrm{Hz}$ was applied. The temperature dependences of the dielectric parameters such as dielectric increment and critical frequency of these two compounds have been measured by using frequency domain dielectric spectroscopy method [15,16]. Dielectric measurements have been carried out on Agilent impedance analyzer. Using gold-coated cells (thickness ca. 23 μm) one could measure complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ in the frequency range from 40 Hz to 20 MHz.

RESULTS AND DISCUSSION

DSC measurements were performed for different heating and cooling rates: 1, 3, 5, 10, 15, 20, 25, 30 K/min. The results did not show any qualitative changes in the thermograms. It means that the rate does not influence the phase diagram of the compounds studied apart from crystallization temperature which strongly depends on the rate. As an example, DSC curves for heating and cooling of the 4F6B and 4H6B samples at rate equal to 10 K/min are presented in Figures 2(a) and 2(b), respectively. The peak of crystallization is appearing during cooling of the 4H6B sample whereas for 4F6B during further heating – the fluorinated compound displays glassy state transition during cooling. Even the transition between ferroelectric and antiferroelectric phases is connected with small enthalpy changes the petite anomaly is visible during both heating and cooling of 4F6B. Comparison of the DSC results allows one to conclude that liquid crystalline state is broader for fluorinated compound than for hydrogenated one. Additionally, liquid crystalline antiferroelelctric phase is a room temperature one for 4F6B. Type of the liquid crystalline phase was identified by texture observation under polarizing optical microscope. The electric field was also applied to identify smectic phases. Figure 3 presents textures under electric field taken for both substances studied. It is seen that mono-domains can be obtained for each of smectic phase: para- (Figs. 3(a), 3(d)), ferro- (Figs. 3(b), 3(e)) and antiferroelectric (Fig. 3(c)) one. Based on DSC and texture observation results one can conclude that fluorinating of the chain causes appearance of the enantiotropic both antifferroelectric $\mathrm{SmC}_\mathrm{A}^*$ and ferroelectric SmC^* phases in the phase sequence of 4F6B while 4H6B compound is a ferroelectric one with monotropic



(a)

(b)

FIGURE 2 DSC curves obtained during heating and cooling of 4F6B (a) and 4H6B (b).

SmC^* phase. Phase sequences obtained based on DSC and texture observation results are as follows:

4F6B
Heating: glassy state −39.1°C Cr 15.2°C $\mathrm{SmC}_\mathrm{A}^*$ 106.3°C SmC^* 121.8°C SmA^* 124.6°C I
Cooling: I 126.1°C SmA^* 123.4°C SmC^* 105.2°C $\mathrm{SmC}_\mathrm{A}^*$ −2.3°C glassy state
4H6B
Heating: Cr 69.7°C Cr_1 75.5°C SmA^* 86.9°C I
Cooling: I 87.6°C SmA^* 74.9°C SmC^* 64.8°C Cr

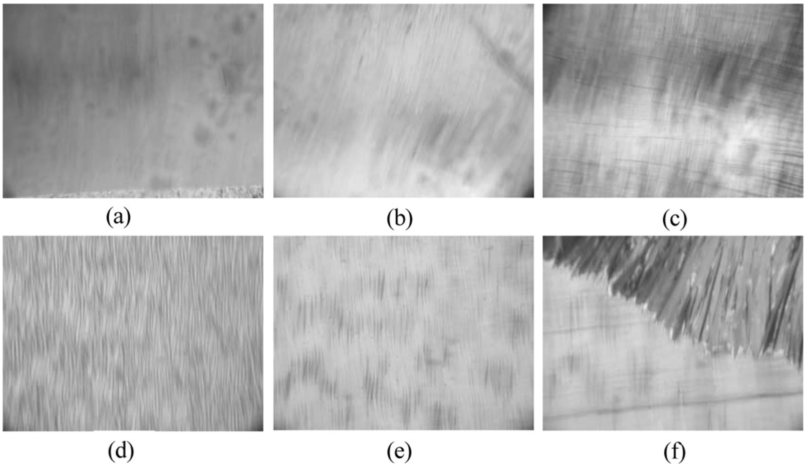
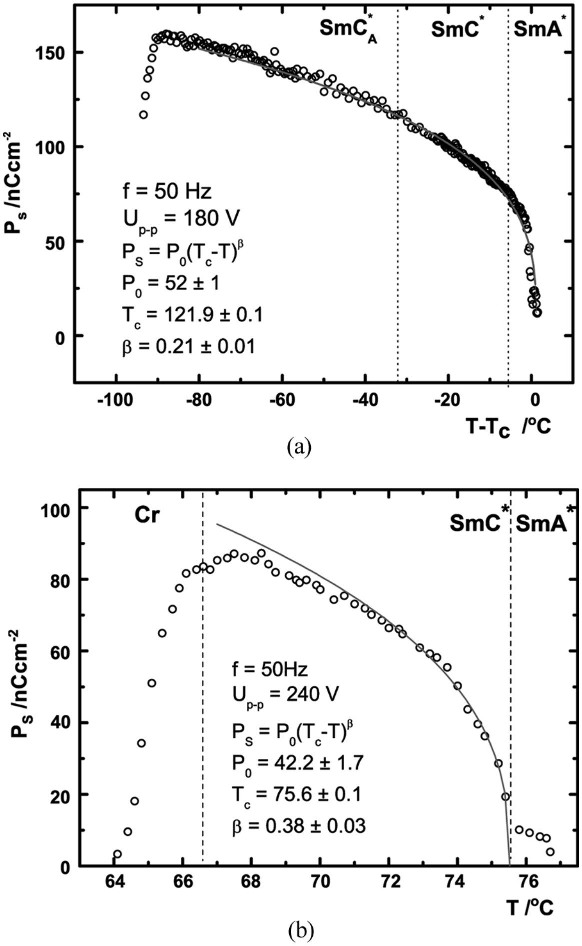


FIGURE 3 Texture under electric field taken for 4F6B (a–c) and 4H6B (d–f); SmA* phase (a, d), SmC* phase (b, e), SmC$^*_{\mathrm{A}}$ phase (d) and transition SmC*–Cr (f); $U_{p\text{–}p} = 200\,\mathrm{V}$, $v = 5\,\mathrm{Hz}$.

Spontaneous polarization was measured on the planar aligned sample. The EHC cell of 5 μm thickness was used. The amplitude of the aligning electric field was about $U_{p\text{–}p} = 200\,\mathrm{V}$ per 5 μm. Spontaneous polarization measurements were done versus temperature for different frequencies of driving triangular wave (5, 10, 20, 50 Hz). Temperature dependences of spontaneous polarization at 50 Hz for 4F6B and 4H6B are presented in Figure 4. As one can see ferroelectric – paraelectric transition in both cases seems to be a continuous one, even though the critical parameter calculated for this transition differs from that of the second order type (0.5) and are equal to 0.21 and 0.38 for 4F6B and 4H6B, respectively. Additionally, the induced polarization is observed in the paraelectric SmA* phase for 4H6B what suggests that this phase may be tilted de Vries type SmA* phase. To verify this conclusion the dielectric measurements were performed.

Frequency domain dielectric spectroscopy (FDDS) method has been used to study relaxation processes existing in liquid crystalline phases. The gold coated cells having capillary gap of 23 μm and 32 μm were used. Measurements of $\varepsilon^*(\omega)$ have been done during cooling of the samples. Figure 5 presents temperature dependences of the critical frequencies and dielectric increment of Goldstone mode (GM) and soft mode (SM) in the vicinity of the SmC*–SmA* transition. Their temperature behavior qualitatively agrees with that predicted

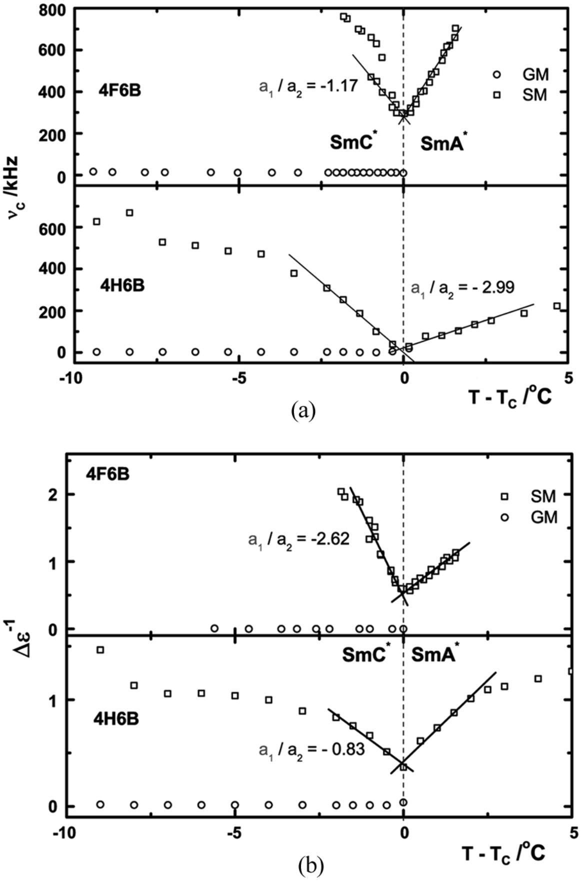


(a)

(b)

FIGURE 4 Temperature dependence of spontaneous polarization for 4F6B (a) and 4H6B (b). Solid line is fitting curve obtain by fitting formula placed in the figure.

by the mean – field model [4]: a characteristic "V" – shape behavior for the soft mode and temperature independent Goldstone mode are observed. The slope ratios of SM are equal to -1.17 and -2.99 (for critical frequency) and -2.62 and -0.83 (for inverse of the dielectric increment) for 4F6B and 4H6B, respectively. Based on the dielectric results as well as spontaneous polarization measurements presented above one can conclude that the SmC*–SmA* transition is not clear of the second order for both substances studied.



(a)

(b)

FIGURE 5 Temperature dependence of the critical frequencies (a) and inverse of dielectric increment (b) of SM and GM in the vicinity of the ferro- paraelectric phase transition for both substances studied.

As it was pointed out above the small non-zero spontaneous polarization was observed in the paraelectric phase of 4H6B. This is connected with the electroclinic effect and is induced by non-zero tilt angle in this phase [17], what indicates that this phase could be de Vries type. Moreover, temperature dependence of critical frequency of SM for this compound is not typical “V”-shape what is also characteristic for de Vries transition [18]. Therefore, these properties substantiate that paraelectric SmA* phase of 4H6B may be de Vries type whereas paraelectric phase of 4F6B is rather ordinary orthogonal SmA* phase.

After comparison the results obtained by complementary methods it is seen that partial fluorination of the achiral left hand side chain of molecule drastically changes ferroelectric properties. The ferroelectric liquid crystal exhibiting monotropic ferroelectric SmC* phase transforms to antiferroelectric liquid crystal with enantiotropic room temperature antiferroelectric and ferroelectric phases.

CONCLUSIONS

- The difference in molecular structures of two liquid crystals studied is in fluorinating of the left-hand side achiral chain – in the phase sequence of 4F6B it causes appearance of two enantiotropic phases: antiferroelectric SmC$_A$* and ferroelectric SmC*.
- Based on spontaneous polarization results, the transition between para- and ferroelectric phases was classified as a continuous one for both substances.
- The electroclinic effect observed in the SmA* phase of 4H6B suggests that this phase is the de Vries type. The dielectric results confirm this conclusion.

REFERENCES

[1] Demus, D. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 25–91.

[2] Meyer, R. B. Presentation at 5th International Liquid Crystal Conference, Stockholm, Sweeden, 1974; Meyer, R. B., Liebert, L., Strzelecki, L., & Keller, P. (1975). *J. Phys. Lett.*, *36*, L69–L71.

[3] Chandani, A., Górecka, E., Ouchi, Y., Takezoe, H., & Fukuda, A. (1989). *Jpn. J. Apel. Phys.*, *30*, L1265–L1268.

[4] Blinc, R. & Žekš, B. (1978). *Phys. Rev. A*, *18*, 740.

[5] Žekš, B. & Čepič, M. (2003). In: *Relaxation Phenomena*, Haase, W. & Wróbel, S. (Eds.), Springer-Verlag: Berlin, Heidelberg, Section 5.1 Modeling of ferroelectric and antiferroelectric liquid crystals, 257.

[6] Lorman, V. L., Bulbith, A. A., & Toledano, P. (1994). *Phys. Rev. E*, *49*, 1367–1374.

[7] Marzec, M., Mikułko, A., Wróbel, S., Haase, W., & Dąbrowski, R. (2005). *Mol. Cryst. Liq. Cryst.*, *437*, 169–180.

[8] Merino, S., de Daran, F., de la Fuente, M. R., Perez Jubindo, M. A., & Sierra, T. (1997). *Liquid Crystals*, *23*, 275–283.

[9] Sigarev, A. A., Vij, J. K., Panarin, Y., & Goodby, J. (2000). *Phys Rev. E*, *62*, 2269–2278.

[10] Lagerwall, J. P. F. & Giesselmann, F. (2006). *Chem. Phys. Chem.*, *7*, 20–45.

[11] Dąbrowski, R., Gąsowska, J., Otón, J., Piecek, W., Przedmojski, J., & Tykarska, M. (2004). *Displays*, *25*, 9–19.

[12] Piecek, W., Raszewski, Z., Perkowski, P., Kędzierski, J., Rutkowska, J., Zieliński, J., Nowinowski-Kruszelnicki, E., Dabrowski, R., Tykarska, M., & Przedmojski, J. (2005). *Mol. Cyst. Liq. Cyst.*, *436*, 146–165.

[13] Takezoe, H. (1999). International 7th Conference on Ferroelectric Liquid Crystals, Tutorials, Germany, Darmstadt.

[14] Ahuja, J. K. & Raina, K. K. (2000). *Jpn. J. Appl. Phys.*, *39*, 4076–4081.

[15] Wróbel, S. (1999). International 7th Conference on Ferroelectric Liquid Crystals, Tutorials, Germany, Darmstadt.

[16] Wróbel, S. (2003). In: *Relaxation Phenomena*, Haase, W. & Wróbel, S. (Eds.), Springer-Verlag: Berlin, Heidelberg, Section 1.1 Frequency domain dielectric spectroscopy, 13–34.

[17] Garoff, S. & Meyer, R. B. (1977). *Phys. Rev. Lett.*, *38*, 848.

[18] Panarin, Y. (2005). Oral presentation (O-25) at 10th Conference on Ferroelectric Liquid Crystals, 12–17th September, Stare Jabłonki, Poland.