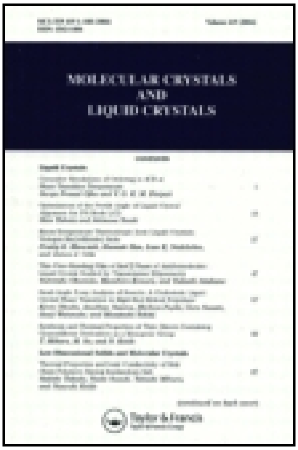
This article was downloaded by: [University of Haifa Library]
On: 16 August 2012, At: 12:42
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bicomponent Systems with Induced or Enhanced Antirerroelectric SmC_A^* Phase

S. Gauza [a] , K. Czupryński [a] , R. Dabrowski [a] , K. Kenig [a] , W. Kuczyński [b] & F. Goc [b]

[a] Military University of Technology, 00-908, Warsaw, Poland

[b] Institute of Molecular Physics, Polish Academy of Science, 60-179, Poznań, Poland

Version of record first published: 24 Sep 2006

To cite this article: S. Gauza, K. Czupryński, R. Dabrowski, K. Kenig, W. Kuczyński & F. Goc (2000): Bicomponent Systems with Induced or Enhanced Antirerroelectric SmC_A^* Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 351:1, 287-296

To link to this article: http://dx.doi.org/10.1080/10587250008023278

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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.

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

Mol. Cryst. and Liq. Cryst., 2000, Vol. 351, pp. 287-296
Reprints available directly from the publisher
Photocopying permitted by license only

© 2000 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

Bicomponent Systems with Induced or Enhanced Antirerroelectric SmC$_A$* Phase

S. GAUZA[a], K. CZUPRYŃSKI[a], R. DĄBROWSKI[a], K. KENIG[a],
W. KUCZYŃSKI [b] and F. GOC[b]

[a]*Military University of Technology, 00–908 Warsaw, Poland and* [b]*Institute of Molecular Physics, Polish Academy of Science 60–179 Poznań, Poland*

A new method of the formulation of liquid crystalline antiferroelectric (C$_A$*) materials from smectic C* and smectic A components is demonstrated. The phase diagrams of the induced C$_A$* systems and the temperature dependence of their smectic layer spacings and switching behavior are shown.

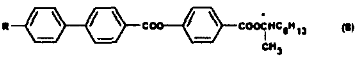
Keywords: Induced antiferroelectric phase; phase diagrams; X-ray scattering; switching properties

INTRODUCTION

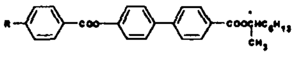
The discovery of the threshold antiferroelectricity [1] and then V-shaped switching [2] by Fukuda's team has aroused great interest among scientists involved in technology of active and passive matrices and has opened new prospects for development of smectic C$_A$* compounds and mixtures.

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

The nature of intermolecular forces responsible for alternating tilt order in the SmC_A^* phase is not fully understood yet, but it is believed that both large transverse permanent electric dipole moments at the terminal chains of molecules and steric effects are responsible for the antiferroelectric order in smectic layers [3]. Similarly, polar and steric forces are also very important for the induction of new phases in mixtures which occurs in multicomponent systems of the same polarity as well as different polarity [4]. Considering these conditions we were looking actively for the compounds which were able to induce the antiferroelectric phase from the components not having this phase. We believed that in the systems with induced SmC_A^* phase the induction strength may be easily changed as it was observed for the induction of SmA_d phase [5,6]. According to this prediction the SmC_A^* phase strongly ordered or strongly disordered may be created even in the same systems only by a change of the components concentration. It would give a new possibility of better understanding of the origin of the SmC_A^* phase. In this paper we present the first systems in which SmC_A^* is actually induced. We have found such ability for chiral esters of formulae I or II having partially fluorinated terminal chain R such as $C_6F_{13}CH_2CH_2O$. The structure I with this terminal group (compound 1)



I



II

and the structure II with the same one (compound 2) have the following phase transition temperatures [7]:

Compound 1	Cr_1 80.7 Cr 98.9 SmC* 150.4 SmA 184.4 Iso
Compound 2	Cr 94.3 SmC* 155.0 SmA 184.0 Iso

Both of the compounds have SmC* phase in a broad temperature range and it is strongly tilted (angle θ is about 40 degree). As the partner for compounds 1 and 2 the following compounds of structure I and II have been investigated.

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

	Compounds	Phase transition temperatures [°C]
No	R in structures I	
3	$C_8H_{17}O$	Cr 84SmC$_A^*$118.6SmC$_\gamma$119.9SmC$_\beta$120.6SmC$_\alpha$122.4SmA148I
4	$CF_3CH_2O(CH_2)_3O$	Cr 107.4SmC$_A^*$ 127.0SmA151.2I
5	$CF_3CF_2CF_2COO(CH_2)_3O$	Cr 83.5SmC$_A^*$121.0SmC* 123.6SmA128.8I
6	$C_2H_5OCH_2CH_2O$	Cr 102 SmI$_A^*$ (90.5) SmA148.1 I
7	$C_4H_9OCH_2CH_2CH_2O$	Cr 73.3 SmA 125.0 I
8	$CH_3COOCH_2CH_2CH_2O$	Cr 60 SmI$_A^*$ (56) SmA 131.0 I
	R in structure II	
9	$C_4H_9OCH_2CH_2CH_2O$	Cr 90.5 SmA (86.6) I

INDUCED SMECTIC ANTIFERROELECTRIC PHASE (SmC$_A^*$)

Phase diagrams of bicomponent systems with induced SmC$_A^*$ phase

The phase diagrams were obtained by the single concentration method (separated samples were weighted for each concentration). The total weight of the single sample was 0.02 g. To obtain the better mixing of components they were solved in chloroform and the solvent was evaporated by heating. Temperatures of phase transitions were determined using a hot stage LINKAM THMS 600 unit and BIOLAR PZO polarizing microscope. The temperature change rate was 1 deg/min in the phase transition region. Monotropic transitions were measured using a second external heater for quick heating and then the sample was placed on THM 600 unit at the fixed temperature. The phase diagrams of the following pairs of bicomponent mixtures containing compound 1: 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9 and containing compound 2: 2-3, 2-5, 2-6, 2-7, 2-9 were worked out, see examples in Figure 1a, b (for the systems with the enhanced SmC_A^* phase) and Figure 2a, b, c, d (for the systems with the induced SmC_A^* phase).

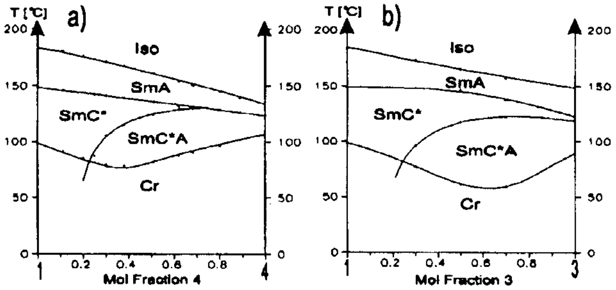


FIGURE 1 Phase diagrams of bicomponent mixtures: 1-4, 1-3 with enhanced SmC^*_A phase and the same for 2-3 and 2-5.

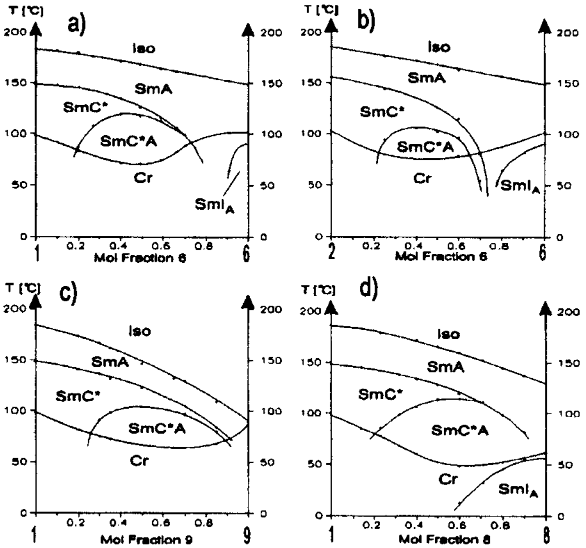


FIGURE 2 Phase diagrams of bicomponent mixtures: 1-6, 2-6, 1-9, 1-8 with induced SmC^*_A phase.

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

The presence of 1 or 2 is necessary for induction SmC_A^*, the compounds 3÷8 (mixed themselves) didn't induce or enhance the phase stability. In the investigated bicomponent systems the induced SmC_A^* phase was observed in the concentration range of 0.2÷0.9 mole ratio of the non fluorinated compound and temperature 120°C was the maximum value for thermal stability of the induced SmC_A^* phase. The data for all investigated systems with induced SmC_A^* are listed below.

Mixture	concentration range of SmC_A^* [X_{mol}]	max. $t_{CA^*-C^*}$ transition [°C]
1-9	0.25 - 0.87	107
1-8	0.20 - 0.93	114
1-6	0.20 - 0.80	120
2-6	0.15 - 0.70	107
1/2-9	0.25 - 0.65	104
1/2-6	0.28 - 0.76	120

Temperature and concentration dependence of smectic layer spacings in systems with induced SmC_A^* phase

The smectic layer spacing was measured by diffractometer DRON-UH2 and by Guinier camera. Semifree liquid crystal film was used. The change of the smectic layer spacing (d) for the bicomponent system 2-6 upon temperature and concentration is given in Figure 3, as an example.

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

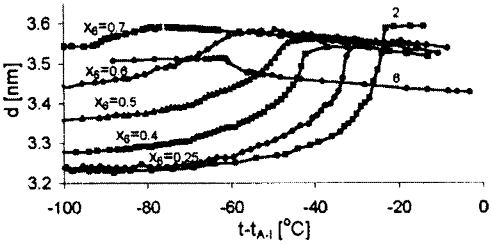


FIGURE 3 Temperature dependence of the smectic layer spacing for system 2-6, $t_{A\text{-}I}$ - clearing point.

The components 2 and 6 had different d for the smectic A layers but in their mixtures d_A was changed only a little upon the concentration, Figure 3. The observed value d_A for mixtures was nearer the value d_A of compound 2 than the average value d_A, but the temperature dependence of d_A was similar to the one observed for component 6 (d_A was increasing with the decreasing values of temperature). In the temperature range of tilted phases the increase of the concentration 6 resulted in the fact that the layers were less tilted and the temperature range for the plateau temperature dependence d was shortened.

The switching behavior

The switching phenomena were investigated using the apparatus described in [8]. The cells 5 μm thick were provided with semitransparent electrodes made of ITO coated with an orienting layer of polyimide and rubbed in one direction. A typical dependence of the intensity of the light passing through the sample on the voltage applied to the electrodes is shown in Figure 4.

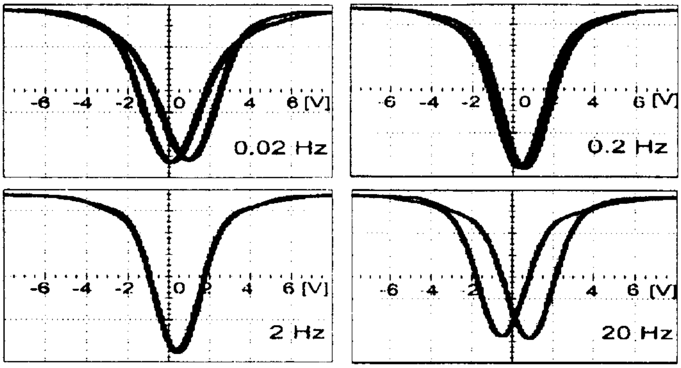


FIGURE 4 V-shaped switching in the mixture 1-6 for 0,75 mole ratio of compound 1 for various frequencies at temperature 100°C.

Thresholdless deformation of the $\vec{c}$ -director is demonstrated as the V-shaped changes in the light intensity. Ionic polarization effects of electrodes probably cause a slight shifting of the curves, visible at the lowest frequencies in Figure 4. On the other hand, similar hysteresis at high frequencies is probably related to the delay of the response of the $\vec{c}$ -director in the electric field due to the viscosity effects.

The V-shaped deformation appears in the binary mixtures 1-6 in a broad temperature range in the neighborhood of the line in the phase diagram, which separates antiferroelectric SmC$_A$* ferroelectric SmC* phases (see the diagram in Figure 2a and Figure 5a).

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

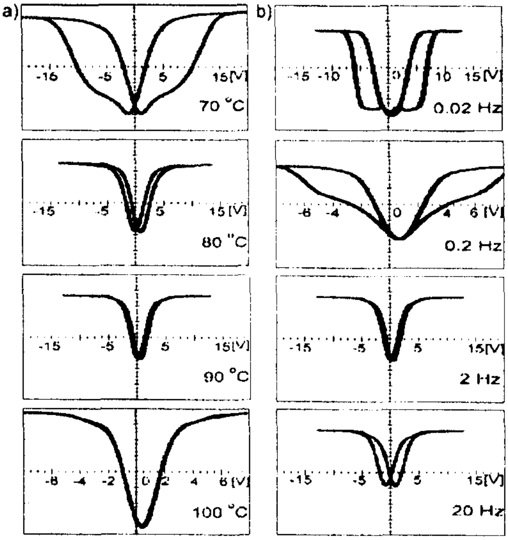


FIGURE 5 Switching effect observed in the mixture 1-6 for 0,75 mole ratio of compound 1 for various temperatures, measured at frequency 2Hz (a) and for various frequencies at temperature 90^{0}C (b).

Between 70^{0}C and 80^{0}C we observed a change in the switching characteristics from tristable to thresholdless one. On the other hand, it appears from Figure 5b that a similar increase of the switching character is observed at 90°C, when the frequency increases from 0,2 Hz up to 2 Hz. The analysis of switching curves shown in Figures 4 and 5 proved that so called "thresholdless switching" is not only a property of a phase, expressed by its presence in certain materials in a given temperature range. Its presence is also strongly dependent on some experimental conditions. The effect of surface interactions is already well documented (see, e.g., [9,10]). Our experiments proved that the frequency of the

Downloaded by [University of Haifa Library] at 12:42 16 August 2012

applied electric field is also of great importance. The results enabled us to draw the conclusion, that the thresholdless switching occurs when (i) the antiferroelectric structure is not stable in small electric fields and (ii) the bistable switching takes place at low frequencies.

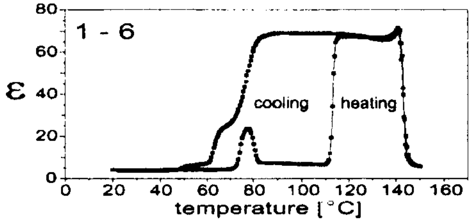


FIGURE 6 Temperature hysteresis of the dielectric permittivity of the measured at frequency 440Hz in the mixture 1-6 for 0.75 mole ratio of compound 1.

It is assumed that the thresholdless switching phenomenon is related to the competition of ferroelectric and antiferroelectric interactions existing between adjacent smectic layers [10,11] and with disturbances resulting from this competition. Some indications of such behaviour were evident in our experiments. Figure 6 shows the temperature dependence of the dielectric susceptibility of the 1-6 mixture with 0.75 molar fraction of 1. The dielectric constant is rather low in the antiferroelectric phase, typically 5÷7. In the ferroelectric state, however, the permittivity reaches values about 70. The curves presented in Figure 6 are an excellent illustration of the transitions between ferroelectric and antiferroelectric states. An outstanding property of the permittivity is the huge hysteresis of the phase transition smectic C_A* - smectic C* (about 50°C). This hysteresis results from the mentioned above interactions.

Acknowledgments
This work was supported by the Polish Committee for Scientific Research under grant No 3T09A07315 and No 2PO3B09715.

References

[1] A.D.L .Chandanii, T. Hagiwara, Y. Susuki, Y. Ouchi, H. Takezoe, A. Fukuda, *Jpn. J. Appl. Phys.*, **28,** L1261 (1989).
[2] A. Fukuda, *Proc. of Asia Display'95,* 61 (1995).
[3] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikara, H. Takezoe, *J. Mat. Chem.*, **4,** 997 (1994).
[4] R. Dąbrowski, K. Czupryński, Modern Topics in Liquid Crystals, „Induced Smectic and Nematic Phases and Reentrant Phenomena", p. 125 ed. A.Buka, World Scientific 1993.
[5] M. Brodzik, R. Dąbrowski, *Liq.Cryst.*, **18,** 61 (1995).
[6] M. Brodzik, R. Dąbrowski, *Liq.Cryst.*, **20,** 99 (1996).
[7] W. Drzewiński, K. Czupryński, R. Dąbrowski, M. Neubert, *Mol. Cryst. Liq. Cryst.*, in press (1999).
[8] F. Goc, W. Kuczyński, R. Dąbrowski, B. Stryła, H. Gierszal, *Proc. SPIE* in press (1999).
[9] S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, *Jpn. J. Appl. Phys.* **36,** 3586 (1997).
[10] E. Górecka, D. Pociecha, M. Glogarova, J. Mieczkowski, *Phys. Rev. Lett.*, **81,** 2946 (1998).
[11] T. Matsumoto, A. Fukuda, *Liq. Cryst. Today,* **8** (4), 6 (1998).

Downloaded by [University of Haifa Library] at 12:42 16 August 2012