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# The Induced Antiferroelectric Phase - Structural Correlations

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## 1. Introduction

Chiral synclinic ( $\text{SmC}^*$ ) as well as anticlinic ( $\text{SmC}^*_A$ ) phases are promising in the display application. The displays using these phases are characterized by shorter response time and larger viewing angle in comparison to nematic displays. In displays based on surface stabilized ferroelectric liquid crystals (SSFLC) the permanent polarisation of layers as well as pretransitional effect appear. In displays based on surface stabilized antiferroelectric liquid crystals (SSAFLC) the permanent polarisation of layers does not appear but the pretransitional effect still exists thus leading to small contrast; the advantage is that the gray scale is big. In displays based on surface stabilized orthoconic antiferroelectric liquid crystals (SSOAFLC) the advantages of antiferroelectric phase remain and disadvantages vanishes because the lack of pretransitional effect leads to the excellent contrast ratio. Thus antiferroelectric phase is even better than ferroelectric phase for display application. Unfortunately the number of compounds with antiferroelectric phase is limited [Fukuda et al. 1994, Matsumoto et al. 1999, Drzewiński et al. 2002]. Only mixtures have application meaning in display technology, because they enable to adjust the properties in a broader range. The induction of antiferroelectric phase is a way to increase the potential number of compounds useful for mixtures preparation, because the compounds not having this phase may be used for this purpose. In mixtures of compounds different non-additive behaviors can be found such as destabilization, enhancement or induction. For example when two compounds having antiferroelectric phase are mixed together the thermal stability of this phase can be increased because additional intermolecular interaction appears between molecules, see Fig. 1a. When one of compounds has similar structure to compounds forming  $\text{SmC}^*_A$  phase but does not form this phase by itself (compound C in Fig. 1b) it can still give the enhancement of this phase in a mixture. This compound has so called virtual antiferroelectric phase. The compound with virtual antiferroelectric phase can be mixed with the compound of similar structure to compound B but not forming antiferroelectric phase then induction of antiferroelectric phase appears, Fig. 1c.

The induction and enhancement of antiferroelectric phase was observed for the first time in 2000 by Dąbrowski and Gauza [Gauza et al. 2000, Dąbrowski 2000, Gauza et al. 2002].

The first system in which the induction was observed was the bicomponent mixture of compounds 1 and 2 [Dąbrowski 2000].

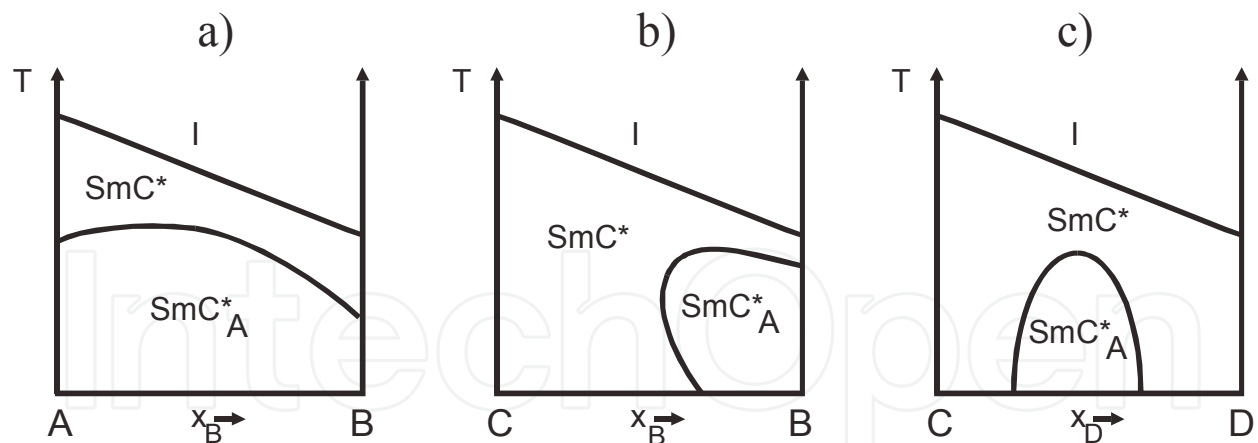
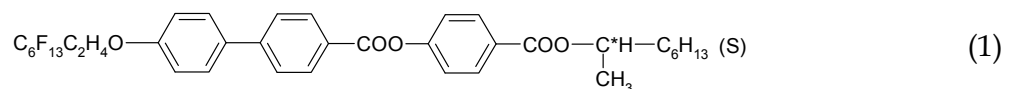
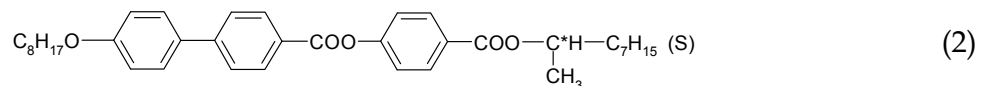


Fig. 1. Schematic phase diagrams with enhanced (a, b) and induced (c) antiferroelectric phase



Cr<sub>1</sub> 80.07 Cr<sub>2</sub> 98.9 SmC\* 141.4 SmC\* $\alpha$  149.0 SmA 184.0 I [Drzewiński et al. 1999, Mandal et al. 2006]



Cr 79.0 (SmI\* 65.8) SmC\* 118.6 SmC\* $\alpha$  119.6 SmA 144.1 I [Gauza et al. 2000, Kobayashi et al. 1999]

Their phase diagram is presented in Fig. 2. Compounds 1 and 2 do not form antiferroelectric phase, but this phase appears in their mixture for the middle concentrations. The highest thermal stability corresponds to composition 1:1.

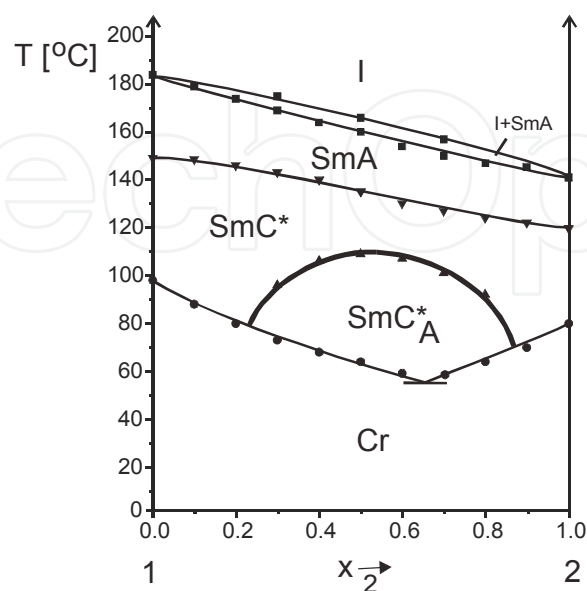


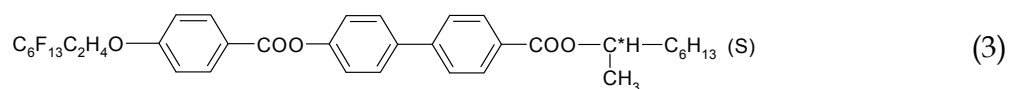
Fig. 2. Phase diagram of the system 1-2 [Dąbrowski 2000].

Next many new systems were found in which the induction of antiferroelectric phase was observed [Tykarska et al. 2006, Skrzypek and Tykarska 2006, Tykarska and Skrzypek 2006, Czupryński et al. 2007]. The compounds giving the induction of  $\text{SmC}^*_\text{A}$  phase have to differ in polarity. Usually one of compounds is of lower polarity (terminating with an alkyl terminal chain) and another one with fluoroalkyl terminal chain or with terminal chain terminated with cyano group. The comparison of the ability of fluoro- and cyanoterminated compounds for the induction of  $\text{SmC}^*_\text{A}$  phase is given. The influence of the rigid core and nonchiral chain length is tested. The analysis is made based on phase diagrams constructed with the use of polarized optical microscopy of the mixtures of polar compounds with compounds of few homologous series with alkylated terminal chain. The special attention is put to antiferroelectric phase this is why the subphases of ferroelectric phase as well as smectic  $\text{I}^*$  phase are not marked on phase diagrams.

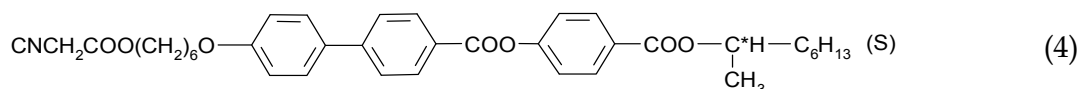
## 2. Systems with different polarity

### 2.1 The structure of compounds giving the induction or enhancement

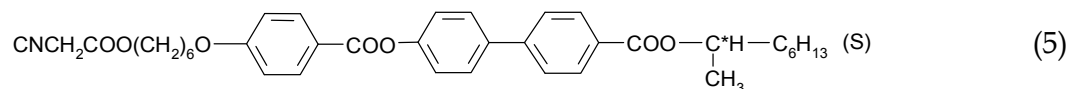
The structure of compounds used for testing the ability of more polar compounds for the induction of  $\text{SmC}^*_\text{A}$  phase are given by formulas 1, 3-5:



$\text{Cr}_1$  94.3  $\text{Cr}_2$  97.9  $\text{SmC}^*$  155.6  $\text{SmA}$  184.6 I [Drzewiński et al. 1999]

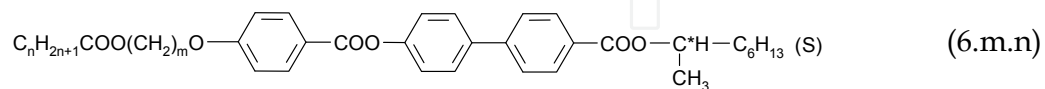


$\text{Cr}$  62.2  $\text{SmC}^*$  90.5  $\text{SmA}$  97.6 I [Dziaduszek et al. 2006]



$\text{Cr}$  69.6 ( $\text{SmC}^*$  61.6)  $\text{SmA}$  80.2 I [Dziaduszek et al. 2006]

Compounds of smaller polarity used as a second component of mixtures have alkyl terminal chain. The used compounds belong to the homologous series 6.m.n and 7.m.n [Drzewiński et al. 1999, Gąsowska et al. 2004]:



$$m=3$$

$n=1$   $\text{Cr}$  72.3  $\text{SmA}$  104.3 I

$n=2$   $\text{Cr}$  80.6  $\text{SmA}$  106.7 I

$n=3$   $\text{Cr}$  109.9 ( $\text{SmA}$  107.1) I

$n=4$   $\text{Cr}$  111.9 ( $\text{SmA}$  104.8) I

$n=5$   $\text{Cr}$  71.3  $\text{SmC}^*$  75.2  $\text{SmA}$  101.1 I

$n=6$   $\text{Cr}$  71.4  $\text{SmC}^*$  75.1  $\text{SmA}$  97.1 I

n=7 Cr 67.2 SmC\* 78.2 SmA 95.7 I

m=6

n=1 Cr 70.6 (SmC\* 69.8) SmA 98.8 I

n=2 Cr 54.6 (SmC\*<sub>A</sub> 43.0) SmC\* 74.4 SmA 96.1 I

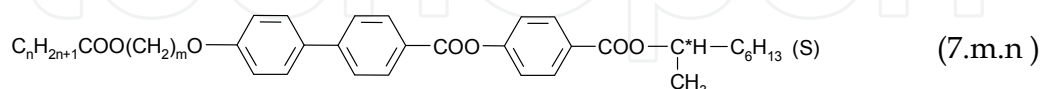
n=3 Cr 76.0 (SmC\*<sub>A</sub> 58.0 SmC\* 75.1) SmA 89.0 I

n=4 Cr 76.2 (SmC\*<sub>A</sub> 68.0 SmC\* 74.9) SmA 87.2 I

n=5 Cr 64.9 (SmC\*<sub>A</sub> 57.0) SmC\* 73.0 SmA 84.6 I

n=6 Cr 54.9 SmC\*<sub>A</sub> 64.4 SmC\* 72.6 SmA 83.1 I

n=7 Cr 50.5 SmC\*<sub>A</sub> 60.3 SmC\* 71.7 SmA 82 I



m=3

n=1 Cr 62.6 (SmI\* 52.7) SmA 129.7 I

n=2 Cr 77.3 (SmI\* 49.2) SmC\*<sub>A</sub> 88.2 SmA 123.6 I

n=3 Cr 66.6 (SmI\* 43.0) SmC\*<sub>A</sub> 92.4 SmA 117.3 I

n=4 Cr 62.2 (SmI\* 31.9) SmC\*<sub>A</sub> 92.8 SmA 111.7 I

n=5 Cr 73.6 (SmI\* 26.3) SmC\*<sub>A</sub> 92.5 SmA 109.1 I

n=6 Cr 69.2 (SmI\* 22.0) SmC\*<sub>A</sub> 91.0 SmC\* 92.2 SmA 106.6 I

n=7 Cr 49.5 (SmI\* 25.0) SmC\*<sub>A</sub> 89.9 SmC\* 91.9 SmA 105.4 I

m=6

n=1 Cr 66.7 (SmC\*<sub>A</sub> 48.0) SmC\* 104.9 SmA 117.3 I

n=2 Cr 58.1 SmC\*<sub>A</sub> 95.2 SmC\* 103.5 SmA 112.2 I

n=3 Cr 61.0 SmC\*<sub>A</sub> 87.5 SmC\* 98.1 SmA 104.5 I

n=4 Cr 64.8 SmC\*<sub>A</sub> 93.3 SmC\* 96.2 SmA 101.7 I

n=5 Cr 68.4 SmC\*<sub>A</sub> 87.6 SmC\* 93.9 SmA 99.5 I

n=6 Cr 68.5 SmC\*<sub>A</sub> 89.8 SmC\* 91.7 SmA 97.5 I

n=7 Cr 70.4 SmC\*<sub>A</sub> 85.9 SmC\* 89.9 SmA 96.9 I

Phase diagrams for all compounds 6.m.n and 7.m.n have been constructed, but here only chosen phase diagrams are presented.

## 2.2 Systems with fluoroterminated compounds

Mixtures of compound 1 with compounds 6.m.n and 7.m.n show different behaviour depending on the existence or not of SmC\*<sub>A</sub> phase in alkylated compounds. In case of compounds 6.3.n, none of them have SmC\*<sub>A</sub> phase thus the induction of this phase appears in all mixtures with compound 1, Fig. 3 [Tykarska et al. 2006, Tykarska and Skrzypek 2006]. In case of compounds 6.6.n and 7.3.n the shortest compounds does not form SmC\*<sub>A</sub> phase thus the induction of SmC\*<sub>A</sub> phase is observed for their mixtures with compound 1 but for longer homologues forming SmC\*<sub>A</sub> phase by themselves the enhancement of this phase appears in the mixtures, Figs. 4 [Tykarska and Skrzypek 2006] and 5. In case of compounds 7.6.n all members form SmC\*<sub>A</sub> phase thus the enhancement of this phase in the mixtures with compound 1 in all cases is observed, Fig. 6.

The maximum temperature of existence of antiferroelectric phase in pure compounds with alkylated terminal chain are presented in Fig. 7a. Taking into account ability of pure

compounds for formation of  $\text{SmC}^*_\text{A}$  phase it can be found that compounds with biphenylate core ( $\text{PhPhCOOPh}$ , 7.m.n) have bigger tendency for creation of anticlinic ordering in comparison to compounds with benzoate core ( $\text{PhCOOPhPh}$ , 6.m.n). There is no big difference in thermal stability of  $\text{SmC}^*_\text{A}$  phase between compounds with biphenylate structure and different polymethylene length  $m=3$  and 6 (7.3.n and 7.6.n series), but for compounds with benzoate core (6.m.n) only longer polymethylene spacer ( $m=6$ ) let the  $\text{SmC}^*_\text{A}$  phase to be formed and shorter one ( $m=3$ ) does not.

The maximum temperature of existence of antiferroelectric phase in the mixtures of compounds 6.m.n and 7.m.n with compound 1 are presented in Fig. 7b. Increasing the number of carbon atoms in a nonchiral terminal alkyl chain ( $n$ ) causes that the maximum temperature of induced antiferroelectric phase existence in the mixture decreases. There is an exception, because for compounds with hexamethylene spacer  $m=6$  and one carbon atom in alkyl group  $n=1$  (6.6.1 and 7.6.1) the maximum temperatures are lower than for corresponding homologues  $n=2$  (6.6.2 and 7.6.2), Fig. 7b. Although the maximum temperature of induced  $\text{SmC}^*_\text{A}$  phase decreases, the temperature-concentration area of existence of this phase in phase diagrams increases, thus one can say that the tendency for creation of  $\text{SmC}^*_\text{A}$  phase increases with the increase of alkyl chain length. Also shorter compounds in pure state do not form  $\text{SmC}^*_\text{A}$  phase.

The comparison of the influence of polymethylene spacer length on the ability for induction of  $\text{SmC}^*_\text{A}$  phase in mixtures shows that more convenient for this purpose is trimethylene spacer ( $m=3$ ), because the maximum temperature of this phase existence is higher than for corresponding hexamethylene compounds ( $m=6$ ), Fig. 7b. It is opposite to the situation in pure compounds, for which compounds with hexamethylene spacer ( $m=6$ ) form anticlinic arrangement easier, also the number of compounds with  $\text{SmC}^*_\text{A}$  phase is bigger than in series with trimethylene spacer ( $m=3$ ).

The comparison of the influence of the core structure on the ability for induction of  $\text{SmC}^*_\text{A}$  phase shows that biphenylate core is more convenient than benzoate core for the stability of antiferroelectric ordering because in the former case the maximum temperature as well as temperature-concentration area of existence of  $\text{SmC}^*_\text{A}$  phase in mixtures with compound 1 observed on phase diagrams are higher. This may be conclude also from the fact that bigger number of compounds with biphenylate core form  $\text{SmC}^*_\text{A}$  phase in pure state.

Mixing the compounds of the series 6.m.n and 7.m.n with compound 3, which has benzoate core instead of biphenylate as it is for compound 1, it can be noticed that the rules observed for alkylated compounds, namely that biphenylate core favours antiferroelectric ordering more than benzoate core and for the same core the trimethylene spacer gives bigger induction of  $\text{SmC}^*_\text{A}$  phase, is true also in these mixtures. For example, in mixtures of compound 3 with compounds 6.3.1, 6.6.1 and 7.3.1 ( $n=1$  in each case) maximum temperature of induced  $\text{SmC}^*_\text{A}$  phase is higher in mixture with biphenylate compound 7.3.1 (Fig. 8c) than with benzoate compound 6.3.1 (Fig. 8a). In both compounds there is trimethylene spacer, but the smallest induction is observed for benzoate compound with hexamethylene spacer 6.6.1, Fig. 8b.

It can be noticed that the ability for induction of  $\text{SmC}^*_\text{A}$  phase of compound 3 is smaller than for compound 1. The rule observed for alkylated compounds (that biphenylate core favours antiferroelectric ordering more than benzoate core) is valid also for fluorinated compounds. It is well visible after comparing the phase diagrams presented in Fig. 8a with Fig. 3a, and Fig. 8b with Fig. 4a, as well as Fig. 8c with Fig. 5a; the temperature-concentration area of existence of  $\text{SmC}^*_\text{A}$  phase is smaller for mixtures with compound 3.

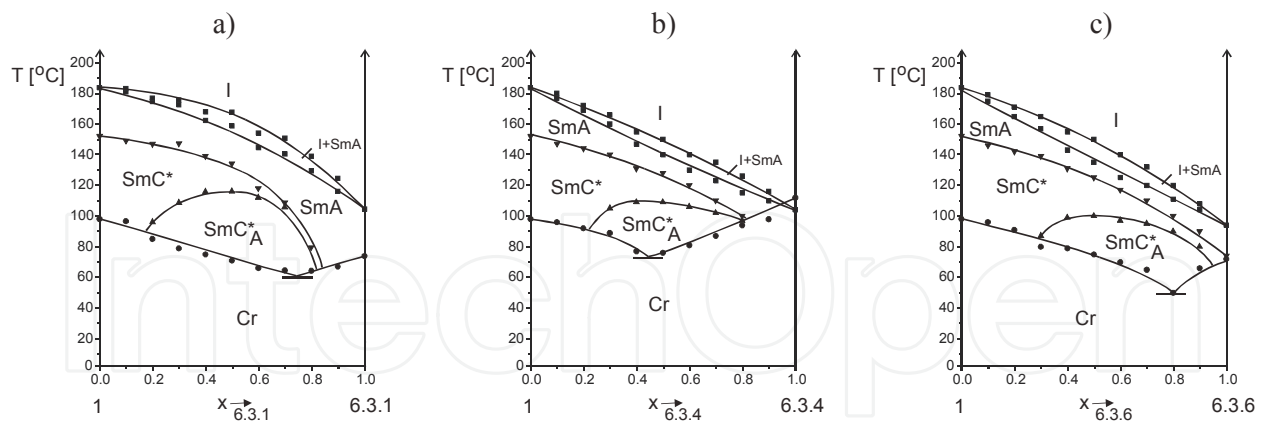


Fig. 3. Phase diagrams of bicomponent mixtures of compound 1 with compounds 6.3.1 (a), 6.3.4 (b) and 6.3.6 (c); [Tykarska et al. 2006, Tykarska and Skrzypek 2006]

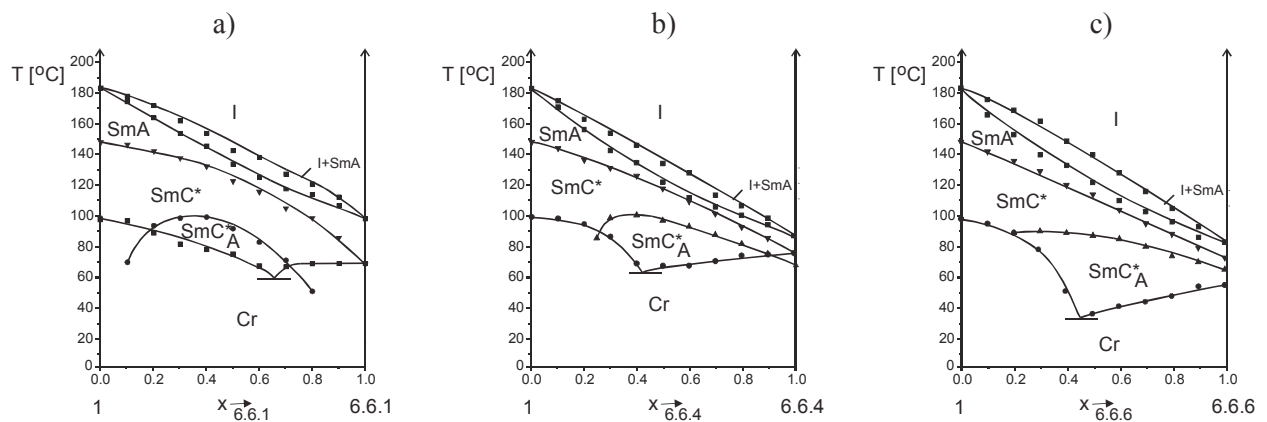


Fig. 4. Phase diagrams of bicomponent mixtures of compound 1 with compounds 6.6.1 (a), 6.6.4 (b) and 6.6.6 (c); [Tykarska and Skrzypek 2006]

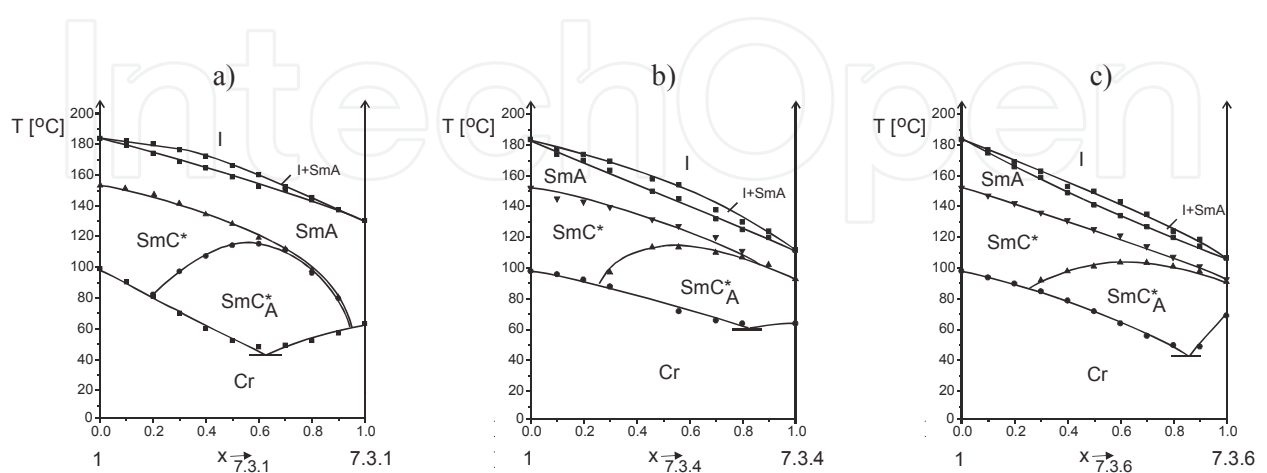


Fig. 5. Phase diagrams of bicomponent mixtures of compound 1 with compounds 7.3.1 [Czupryński 2007] (a), 7.3.4 (b) and 7.3.6 (c)

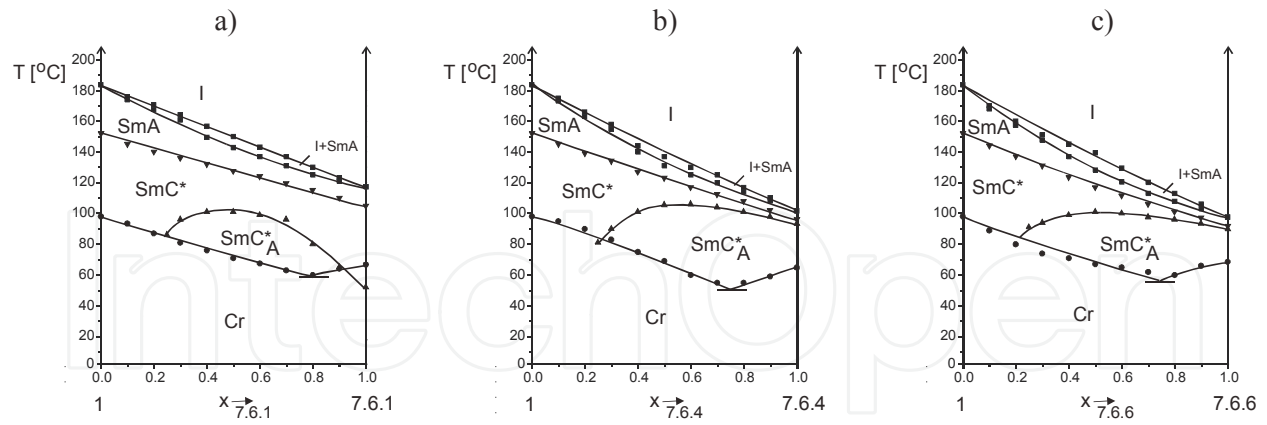


Fig. 6. Phase diagrams of bicomponent mixtures of compound 1 with compounds 7.6.1 (a), 7.6.4 (b) and 7.6.6 (c)

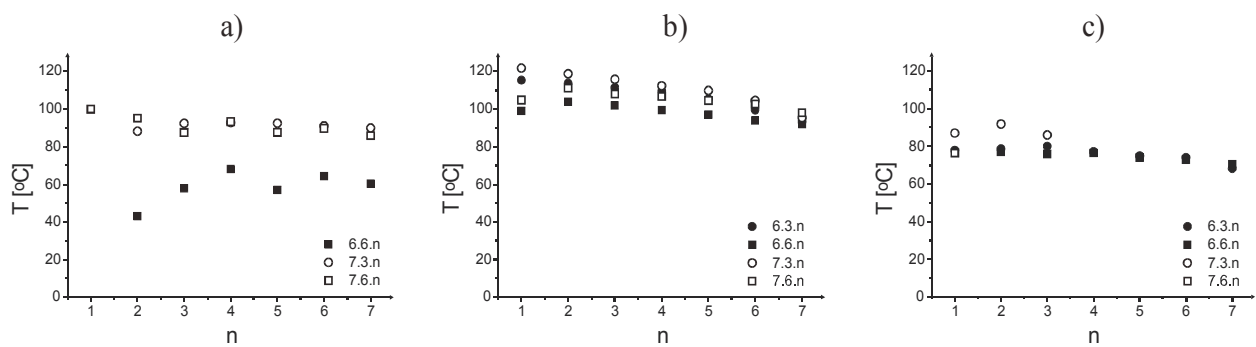


Fig. 7. Comparison of maximum temperature of existence of  $SmC^*_A$  phase in pure compounds of series 6.m.n and 7.m.n (a), and in their mixtures with compound 1 (b) and compound 4 (c)

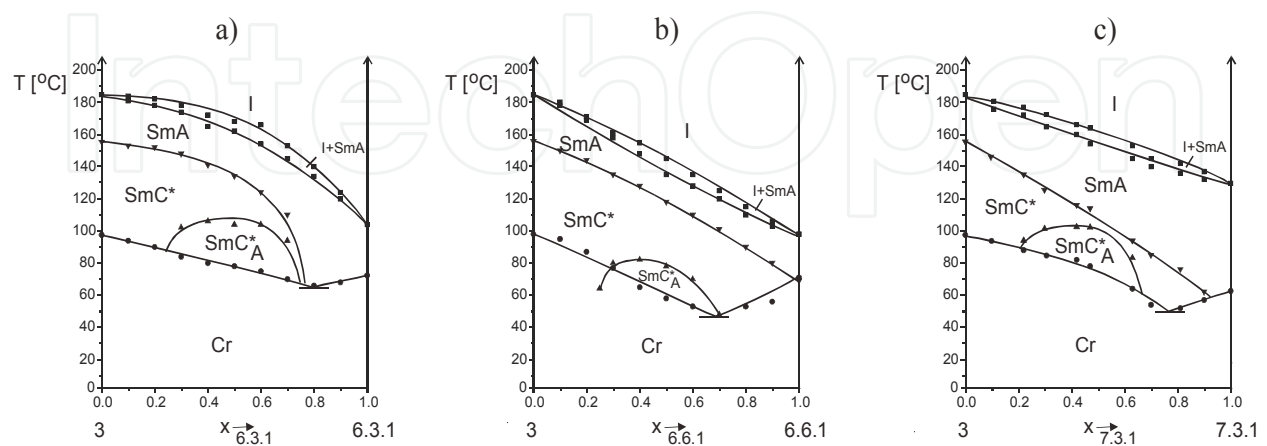


Fig. 8. Phase diagrams of bicomponent mixtures of compound 3 with compounds 6.3.1 (a) [Czupryński 2007], 6.6.1 (b) and 7.3.1 (c)



### 2.3 Systems with cyanoterminated compounds

Mixing the compounds of the series 6.m.n and 7.m.n with compound 4, which has the same biphenylate core as compound 1 but different nonchiral chain, namely terminated with cyano group, the induction of  $\text{SmC}^*_\text{A}$  phase is also observed. The rules for structure correlations with the induction of  $\text{SmC}^*_\text{A}$  phase of alkylated compounds in these systems are the same as were observed for fluorinated compounds. For example, the compound 4 mixed with members of homologous series of benzoate compounds with hexamethylene spacer 6.3.n gives the induction for all members and the temperature-concentration area of existence of this phase increases with the increase of alkyl chain length, Fig. 9. Maximum temperature of existence of  $\text{SmC}^*_\text{A}$  phase in mixtures is presented in Fig. 7c. The compositions corresponding to maximum temperature of existence of  $\text{SmC}^*_\text{A}$  phase are shifted in the direction of the excess of cyanoterminated compound in phase diagrams for most of the systems.

Compound 4 in mixtures with compounds 6.6.n does not give the induction of  $\text{SmC}^*_\text{A}$  phase in the case of compound 6.6.1 (Fig. 10a) because the tendency of cyanoterminated compounds for induction is smaller than in the case of fluoroterminated compounds. For compounds with longer alkyl chains 6.6.n the enhancement of  $\text{SmC}^*_\text{A}$  phase is observed (Fig. 10b and c), the same as for fluoroterminated compounds, but the maximum temperature of existence of the induced  $\text{SmC}^*_\text{A}$  phase in this case is smaller.

Compound 4 in mixtures with compounds 7.3.n gives the induction of  $\text{SmC}^*_\text{A}$  phase in the case of compound 7.3.1 (Fig. 11a), but for compounds with longer alkyl chains the enhancement of  $\text{SmC}^*_\text{A}$  phase is observed, Fig. 11b and c. It is interesting that the highest temperature of  $\text{SmC}^*_\text{A}$  phase existence is for pure compounds in case of mixtures with alkylated compounds having more than 3 carbon atoms in alkyl group. This is why these mixtures are not presented in Fig. 7c. In case of mixtures of compound 4 with compounds 7.6.n, homolog 7.6.1 is the only one which gives the induction. In case of longer homologs the enhancement of  $\text{SmC}^*_\text{A}$  phase is observed, but the temperature range of existence of this phase in mixtures is smaller than for pure alkylated compounds this is why they are not marked in Fig. 7c.

Compound 5 being the analog of compound 4, but having benzoate rigid core, has much smaller ability for induction of  $\text{SmC}^*_\text{A}$  phase because the number of compounds which give the induction in mixtures with compound 5 is smaller than in case of compound 4.

In mixtures of compound 5 with members of series 6.3.n it has been found that the induction appears for longer homologues ( $n=6$  and  $7$ ), but for shorter homologues ( $n=1-5$ ) the induction does not appear, Figs. 12a ( $n=2$ ) and 12b ( $n=6$ ).

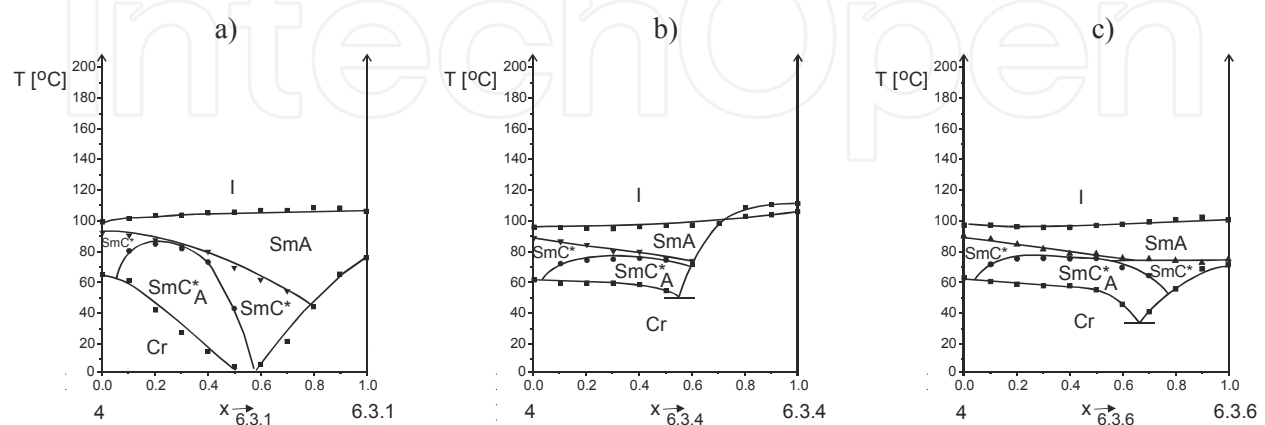


Fig. 9. Phase diagrams of bicomponent mixtures of compound 4 with compounds 6.3.1 (a), 6.3.4 (b) and 6.3.6 (c); [Skrzypek and Tykarska 2006, Czupryński 2007]

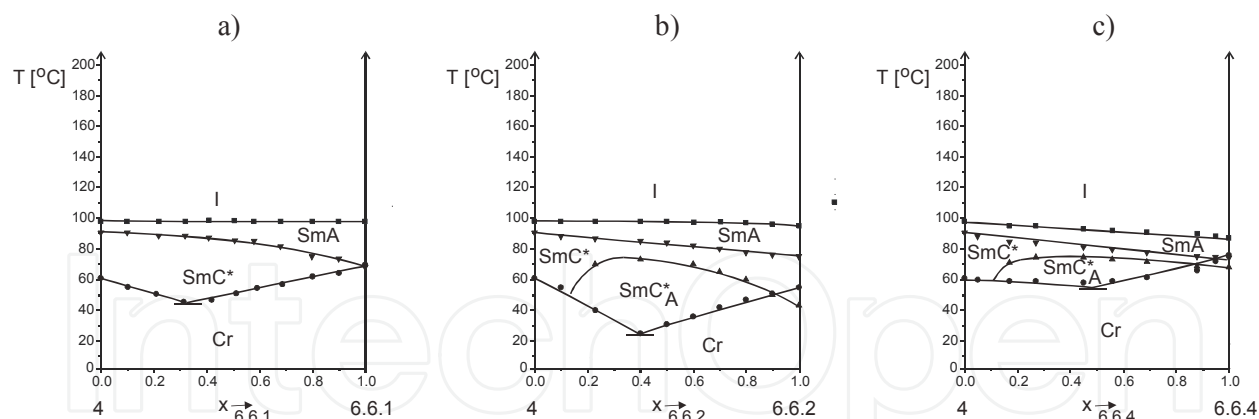


Fig. 10. Phase diagrams of bicomponent mixtures of compound 4 with compounds 6.6.1 (a), 6.6.2 (b) and 6.6.4 (c)

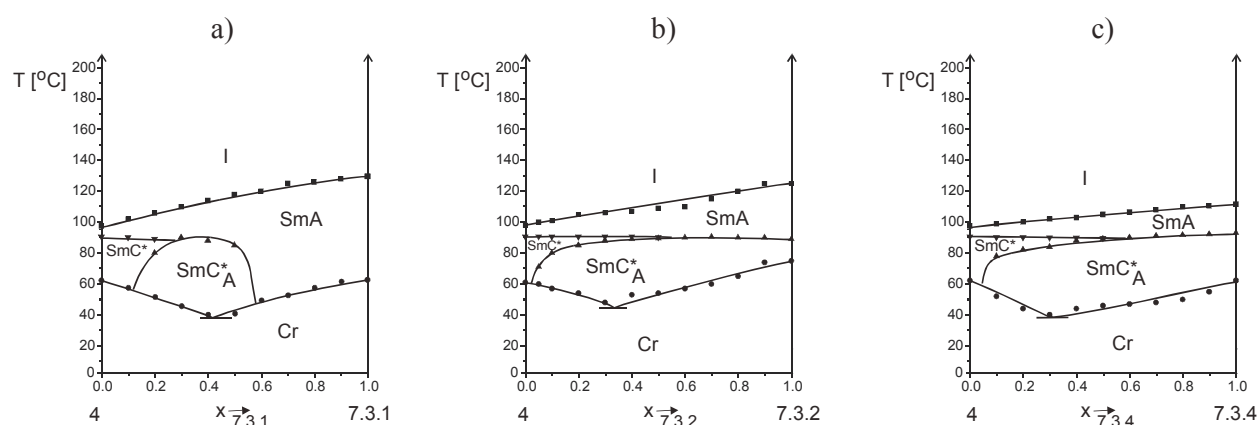


Fig. 11. Phase diagrams of bicomponent mixtures of compound 4 with compounds 7.3.1 (a), 7.3.2 (b) and 7.3.4 (c)

The comparison of induction ability of compounds 4 and 5 lead to the conclusion that compounds with biphenylate core more favourise antiferroelectric ordering than with benzoate core, similarly as it was observed for fluorinated compounds and alkylated compounds.

#### 2.4 Comparison of systems with fluoroterminated and cyanoterminated compounds

When compounds: one with fluoroterminated group (1) and the other with cyanoterminated group (4), are mixed together they do not give the induction of  $\text{SmC}^*_A$  phase [Tykarska et al. 2011]. The ability for induction of  $\text{SmC}^*_A$  phase of both compounds (1 and 4) in ratio 2:1, 1:1 and 1:2 has been checked. Such bicomponent mixtures were doped with 6.3.2 compound. The results are presented in collective phase diagram presented in Fig. 13a, in which the curves separated  $\text{SmC}^*_A$  phase from other phases for all tested systems have been marked [Tykarska et al. 2011]. The dependence is not linear with the concentration of compound 4, Fig. 13b. Compound with fluoroalkyl group 1 has stronger ability for induction of  $\text{SmC}^*_A$  phase and it forces the arrangement of molecules in mixtures. In the phase diagram (Fig. 13a) the boundary of the temperature-concentration region of existence of  $\text{SmC}^*_A$  phase in phase diagram for all mixtures containing compound 1 are close to each other but further from the curve corresponding to the mixture with cyanoterminated compound 4.

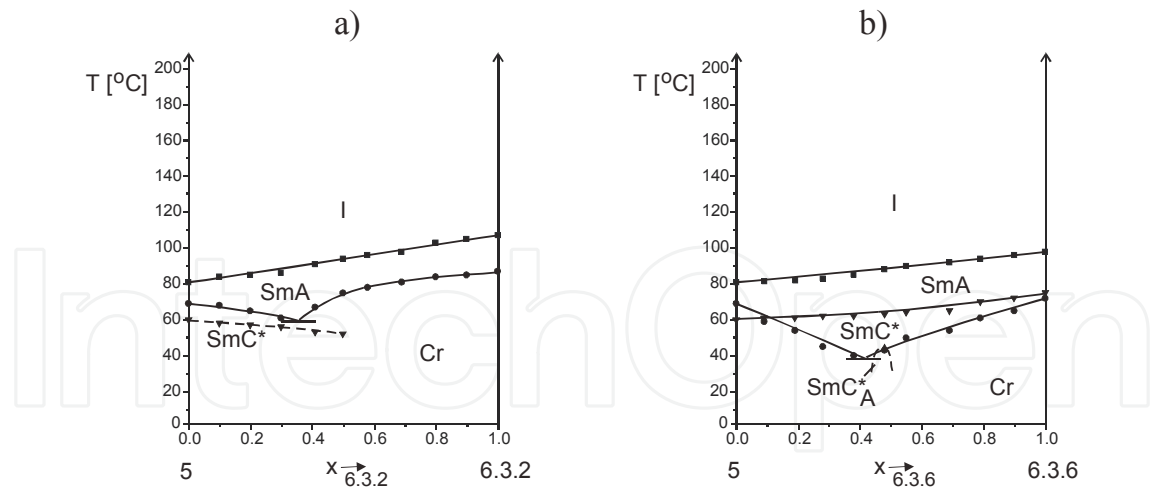


Fig. 12. Phase diagrams of bicomponent mixtures of compound 5 with compounds 6.3.2 (a) and 6.3.6 (b)

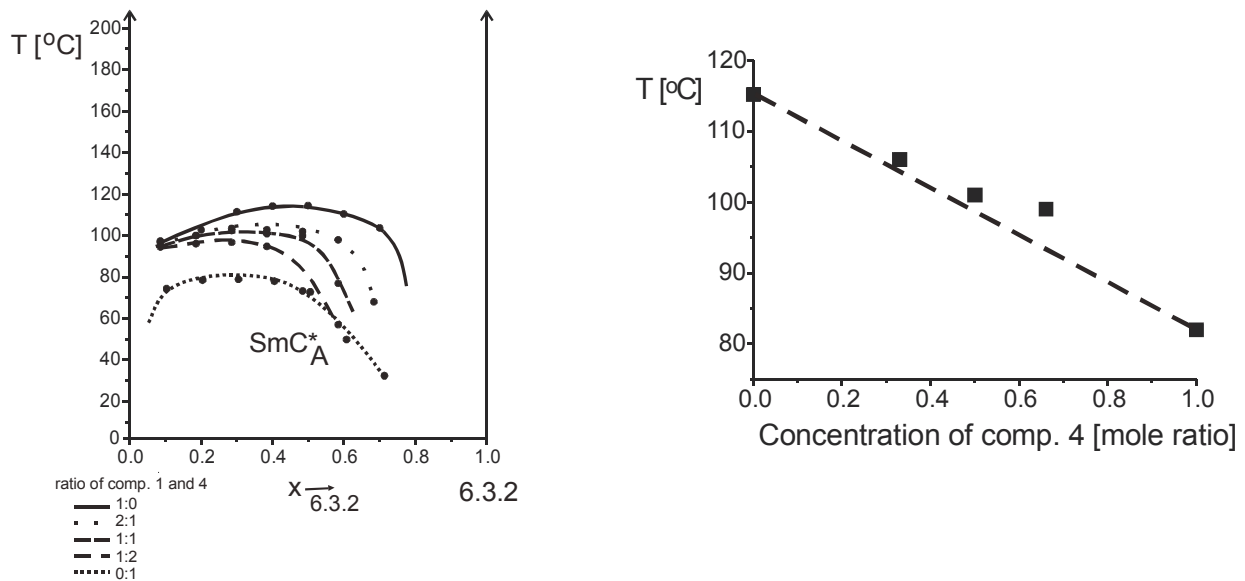


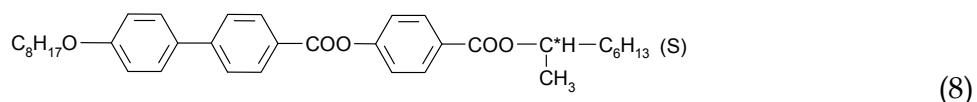
Fig. 13. The collective phase diagram showing curves corresponding to phase transition temperature from SmC\*\_A phase in mixtures of different concentration of compounds 1 and 4 (1:0, 2:1, 1:1, 1:2 and 0:1) with compound 6.3.2 (a), maximum temperature of SmC\*\_A existence versus concentration of compound 4 (b) [Tykarska et al. 2011]

The results of dielectric measurements, described in Ref. [Skrzypek et al. 2009], prove that the induced phase is really antiferroelectric phase. Properties of SmC\*\_A phase obtained by the induction are the same as properties of SmC\*\_A phase in pure compounds and their mixtures [Czupryński et al. 2007, Tykarska et al. 2008, Dąbrowski et al. 2004].

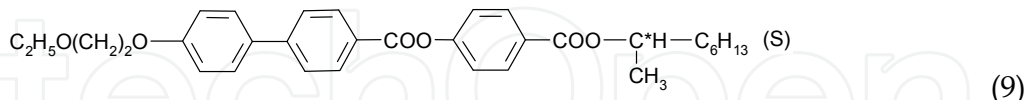
### 3. Systems with similar polarity

#### 3.1 The structure of compounds

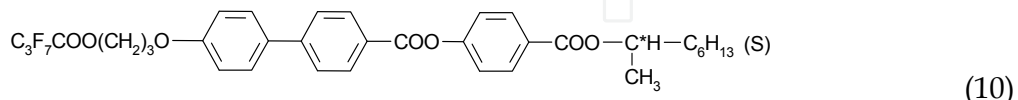
The compounds of the structure given by formulas 8-13 were used for showing the dependence of miscibility in systems of similar polarity with and without SmC\*\_A phase.



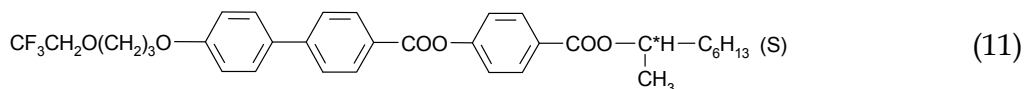
Cr 82.7 (SmI\* 65.3) SmC\*<sub>A</sub> 118.2 SmC\*<sub>γ</sub> 119.1 SmC\*<sub>β</sub> 120.0 SmC\*<sub>α</sub> 121.9 SmA 147.6 I [Chandani et al. 1989, Mandal et al. 2006]



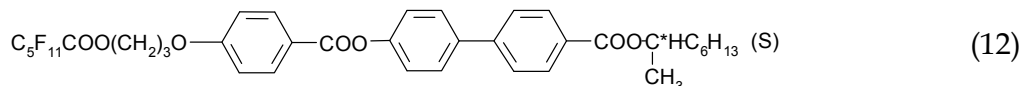
Cr 102.8 (SmI\* 90.2) SmA 148.5 I [Drzewiński et al. 1999]



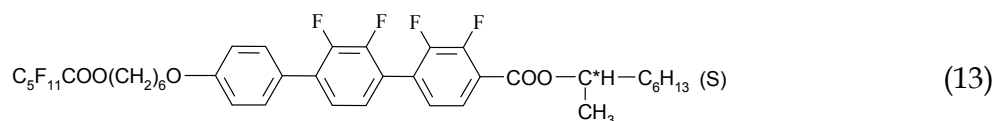
Cr 82.1 (SmI\* 54.0) SmC\*<sub>A</sub> 122.0 SmC\* 124.5 SmA 129.9 I [Drzewiński et al. 1999]



Cr 107.8 SmC\*<sub>A</sub> 124.4 SmA 134.1 I [Drzewiński et al. 1999]



Cr 61.2 SmC\*<sub>A</sub> 118.5 SmC\* 128.3 SmA 137.8 I [Gąsowska 2004]



Cr 49.0 (SmC\* 47.4) SmA 58.6 I [Kula 2008]

### 3.2 Both compounds are alkyloterminated

Usually when compounds of the same polarity are mixed together no one expect the non-additive behaviour. Characteristic examples of mixtures of compounds with alkyl chain are presented in Fig. 14. When both compounds do not form SmC\*<sub>A</sub> phase by themselves, this phase does not induces in their mixture (system 2-6.3.7), Fig. 14a. When both compounds form SmC\*<sub>A</sub> phase thus it mixes additively (system 8-7.3.2), Fig. 14b. In mixtures, in which one compound forms SmC\*<sub>A</sub> phase, but the other does not, this phase destabilizes less (system 8-9) or more (system 7.3.2-9) with the increase of the concentration of the compound without this phase, Fig. 15a and b.

### 3.3 Both compounds are fluoroterminated

Similar situation is observed when both compounds are of the same polarity but they are terminated with fluoroalkyl group. When both compounds do not form SmC\*<sub>A</sub> phase by themselves, this phase does not induces in their mixture (system 1-3), Fig. 16a. When both compounds form SmC\*<sub>A</sub> phase thus it mixes additively (system 10-11), Fig. 16b. In mixtures,

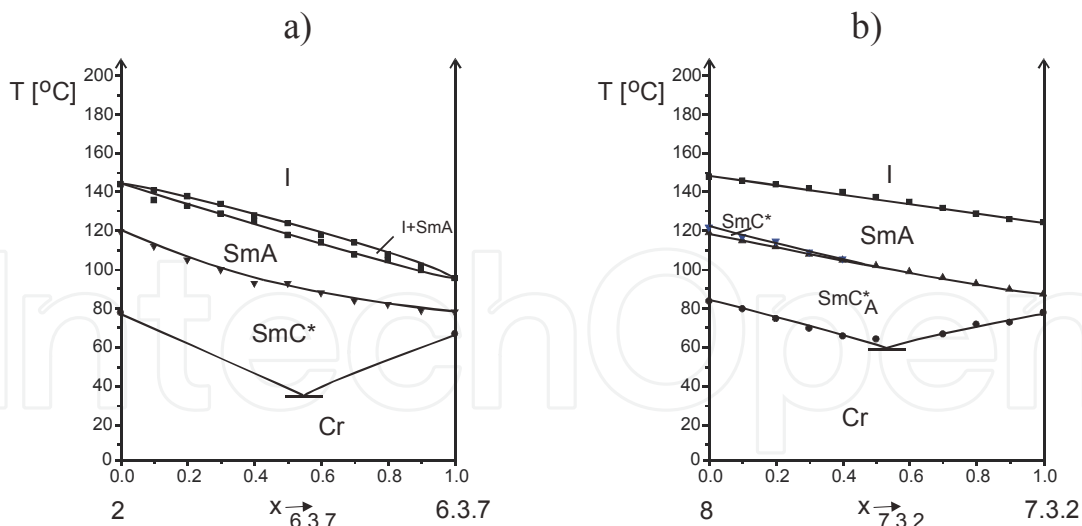


Fig. 14. Phase diagrams of bicomponent mixtures of compounds with alkyl group with additive miscibility of  $\text{SmC}^*$  phase - system 2-6.3.7 (a), and with additive miscibility of  $\text{SmC}^*_A$  phase - system 8-7.3.2 (b)

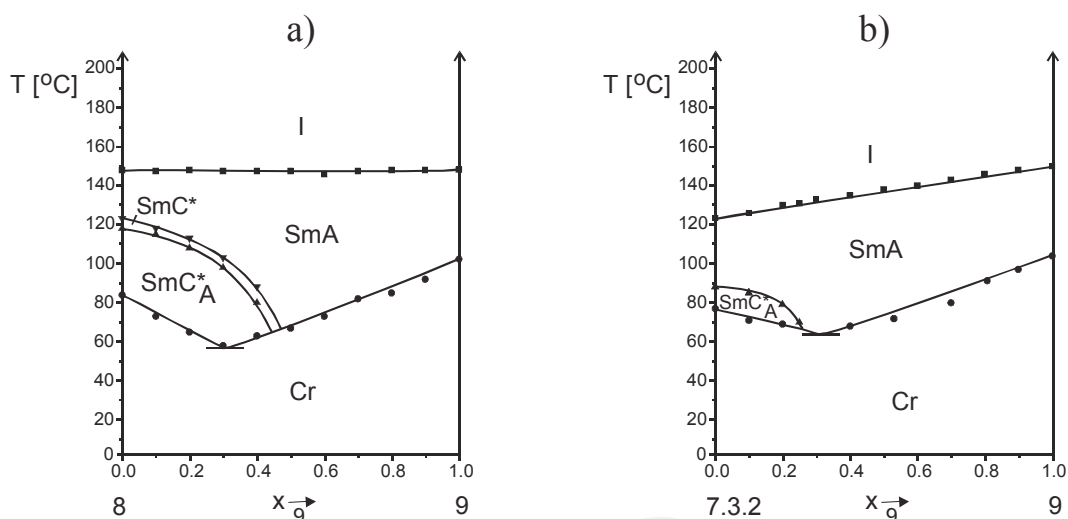


Fig. 15. Phase diagrams of bicomponent mixtures of compounds with alkyl group with destabilization of  $\text{SmC}^*_A$  phase - weaker in system 8-9 (a), and stronger in system 7.3.2-9 (b)

in which only one compound forms  $\text{SmC}^*_A$  phase, this phase usually destabilizes, but few systems were found in which the small enhancement of  $\text{SmC}^*_A$  phase was observed instead of destabilization, Fig. 17. The biggest enhancement was observed in case of compound 11 (Fig. 17a), having only one perfluorinated carbon atom in alkyl chain, thus the system is similar to the typical systems observed for compounds with different polarity. Increasing the number of perfluorinated carbon atoms to three (compound 10) or to five (compound 12) causes that the enhancement becomes smaller, Figs. 17b and c.

The presented results show that the compounds which are terminated with fluoroalkyl group and do not form  $\text{SmC}^*_A$  phase (e.g. compound 1) have big tendency to form anticlinic order when they are placed in the suitable matrix. The most appropriate for this purpose is the neighbourhood of compounds of smaller polarity, favourably terminated with alkyl chain, because then the additional molecular interaction appears. A system was found,

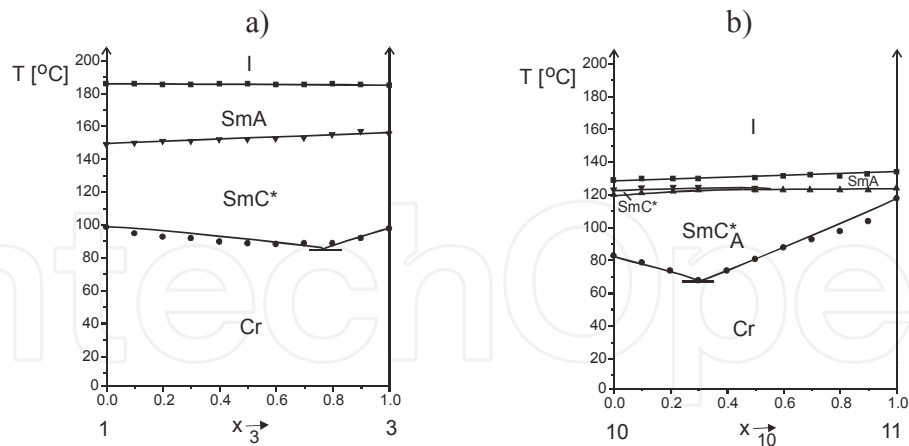


Fig. 16. Phase diagrams of bicomponent mixtures of compounds with fluoroalkyl group with additive miscibility of  $SmC^*$  phase - system 1-3 (a), and with additive miscibility of  $SmC^*_A$  phase - system 10-11 (b)

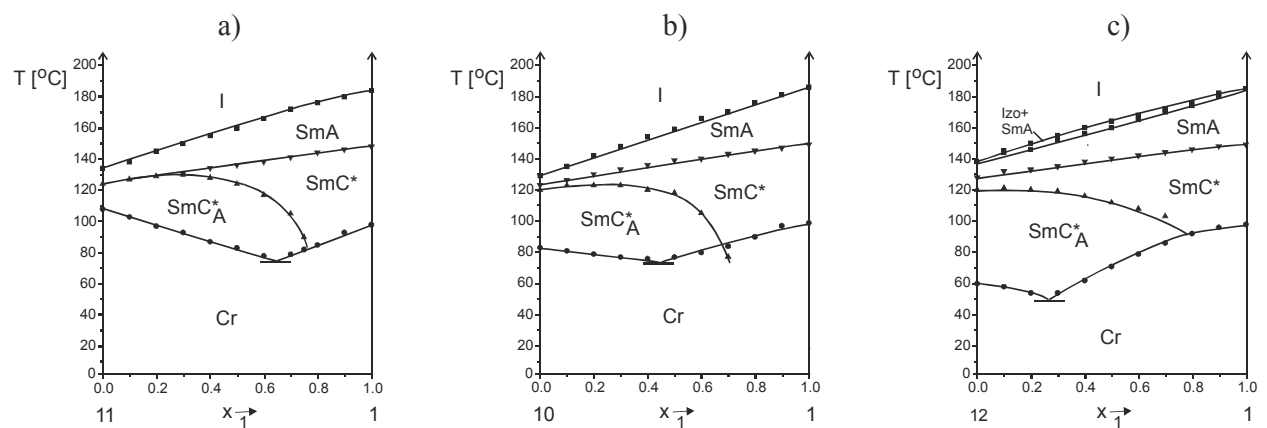


Fig. 17. Phase diagrams of bicomponent mixtures of compound 1 with compounds 11 (a), 10 (b) and 12 (c) giving the small enhancement of  $SmC^*_A$  phase

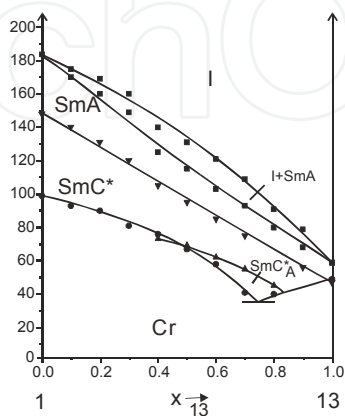


Fig. 18. Phase diagrams of bicomponent mixtures of compounds 1-13 with fluoroalkyl group giving the induction of  $SmC^*_A$  phase

composed only of compounds with fluoroalkyl group, giving the induction of  $\text{SmC}^*_A$  phase. Compound 1 was doped with compound 13, having terphenyl rigid core laterally substituted by four fluorine atoms, Fig. 18. This example is an exception from the rule that induction of  $\text{SmC}^*_A$  phase can appear in mixtures of compounds differing in the polarity. The steric factors play also a crucial role in this behaviour, because the induction of  $\text{SmC}^*_A$  phase was not found in mixtures of both nonchiral compounds. For the last system, it cannot be also excluded that the appearance of  $\text{SmC}^*_A$  phase could be a result of interactions between nonfluorinated and fluorinated rigid core.

#### 4. Conclusion

There are many systems in which the induced antiferroelectric phase can be observed. Compounds with polar group (1, 3-5) have virtual  $\text{SmC}^*_A$  phase. They have similar structure to compounds forming  $\text{SmC}^*_A$  phase by themselves; e.g. the structure of compound 1 and 4 is similar to the structure of the first antiferroelectric compound MHPOBC; they have the same rigid core and chiral terminal chain. The placement of molecules of compounds with virtual  $\text{SmC}^*_A$  phase, which have a tendency to form the antiferroelectric phase but cannot fulfil all conditions, in a suitable matrix of less polar compounds causes the appearance of an antiferroelectric phase.

The ability of more polar compounds with virtual  $\text{SmC}^*_A$  phase for induction of this phase decreases in the following order: compounds 1, 3, 4 and 5. Compounds with cyano group in terminal chain have smaller ability than compounds with fluoroalkyl group. Compounds with biphenylate core have bigger ability than compounds with benzoate core. The same is observed in group of less polar compounds with alkyl group in the terminal chain, i.e. the biphenylate core is more preferable, as well as the increase of the terminal chain causes the increase of tendency to induce  $\text{SmC}^*_A$  phase.

In systems of similar polarity nonadditive behaviour can be observed when fluorinated part of the non-branched chain is short.

The appearance of liquid crystalline phases is possible due to intermolecular interactions. Interactions between permanent dipoles play a crucial role but interactions between induced dipoles cannot be neglectable. The steric interactions are also important.

The possibility of obtaining antiferroelectric phase from compounds forming  $\text{SmC}^*$  phase or only  $\text{SmA}$  phase broadens the range of compounds useful for preparation of antiferroelectric mixtures for display application.

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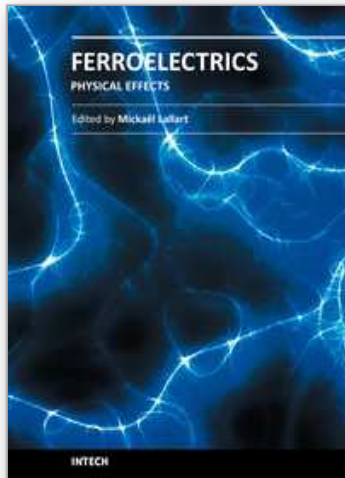
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## **Ferroelectrics - Physical Effects**

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Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the underlying mechanisms of ferroelectric materials, including general ferroelectric effect, piezoelectricity, optical properties, and multiferroic and magnetoelectric devices. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric systems, allowing a deep understanding of the physical aspect of ferroelectricity.

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