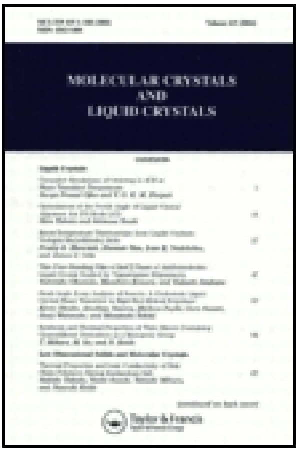

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The Stability of the Smectic C Phase in Mixtures: An Influence of a Dopant on the Phase Sequence and the Tilt Angle

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THE STABILITY OF THE SMECTIC C PHASE IN MIXTURES AN INFLUENCE OF A DOPANT ON THE PHASE SEQUENCE AND THE TILT ANGLE

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(*Received March 13, 1991*)

Abstract The paper describes methods for obtaining mixtures with a broad range of the smectic C phase and with the smectic A phase above the smectic C phase. It was demonstrated that doping is a very useful method for modification of the smectic C mixtures and for adjusting the tilt angle. It was also shown that smectic C mixture may be composed of compounds having no smectic C phase and that the concentration of these compounds can be large.

Keywords:* *smectic C, ferroelectric mixtures, tilt angle of molecules in smectic C phase

INTRODUCTION

For ferroelectric liquid crystal display materials are needed which show strictly defined set of physical and physicochemical properties. These properties are as follows:

- a high chemical, photochemical and electrochemical stability,
- a wide temperature range of the chiral smectic C phase,
- either long helical pitch $p > 8$ μm (when Clark-Lagerwall effect is used) or short (for Beresnev effect) $p \ll 8$ μm,
- the tilt angle of molecules in the smectic C layers nearby 22.5° (to achieve maximum of the optical contrast),
- a moderate value of spontaneous polarization (the values in the range 8 to 20 nC/cm^2 guarantee good response times and allow to avoid stable polarization of the liquid crystal layer),
- a low rotational viscosity of the smectic C phase,
- a negative dielectric anisotropy (usually more preferable),
- a phase sequence $S_C^* \rightarrow S_A^* \rightarrow N^* \rightarrow I$ to facilitate good alignment by interaction with the cell surfaces.

No individual compound is able to fulfill all such requirements. The mixing of different compounds is the method for formulating the convenient liquid crystal substances.

In this paper we like to concentrate mainly on the following questions:

- how to obtain the mixture with a broad range of the smectic C phase,
- how to induce the smectic A phase above the smectic C phase and how to adjust the tilt angle.

MIXTURES WITH BROAD RANGE OF THE SMECTIC C PHASE

The problem can be solved in two steps:

in the first step a mixture with a broad range of the smectic C phase is prepared from non-chiral compounds (a basic mixture),

in the second step different chiral and non-chiral compounds are added to the base mixture to adjust its properties (doping process).

Since compounds with the smectic C phase often reveal a tendency to destabilize the smectic C phase when mixed together it is not easy to obtain the mixture with a large temperature range of smectic C phase starting from accidentally chosen smectic C compounds[1]. The reason for this phenomenon is not known yet satisfactorily. The example of such a behavior is illustrated on the diagram of the bicomponent mixture (Figure 1)[2] comprising very similar compounds, referring to their chemical structure, namely 4-hexyloxyphenyl 4-octyloxybenzoate and 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate. We observe that the smectic C phase of both compounds is strongly depressed in the middle range of concentration, and the gap between C phases exists. The smectic C phases are separated by smectic A phase.

A wide nematic gap separating the smectic C phases was also found. This phenomenon was found for 1,2-bis(butylbenzenenonyloxyazobenzene-4)ethane and 1,2-bis(butylazoxybenzene-4)ethane (see Figure 1 in Ref.3). The reason for the existence of the gap is not understood yet. Probably one of the reasons is a difference in an internal structure of the smectic C layers of components. The components of these two systems were carefully studied by X-ray. For the first pair of compounds for which the smectic C phases transform into the smectic A phase the differences in the X-ray pattern were not seen but a large difference in the tilt angle of molecules in the smectic C layers was observed[3]. For the second system in which the wide nematic gap separates the smectic C phases the X-ray pattern indicates that one of the components has two-dimensional ordering and is characterized by a high value of the tilt angle, which varies with temperature but slightly. Four strong diffraction maxima in the form of spots along the direction perpendicular to the magnetic field and four very weak reflexes in the form of hyperbola were observed. The second component shows only one pair of diffused weak reflexes which become stronger near the smectic A phase. For this compound smectic layer spacing changes with the temperature and the tilt angle changes from 30° to 0°. Taking into account the results mentioned above one should state that for obtaining a mixture with a broad range of smectic C phase we must choose components which get mixed in an additive way.

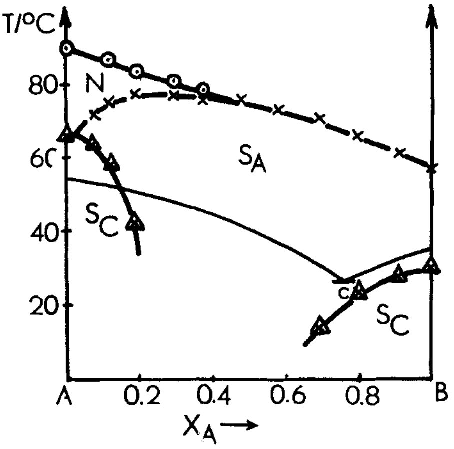
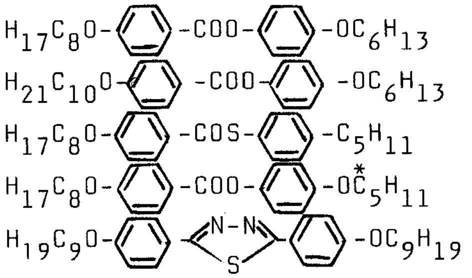


FIGURE 1. Phase diagram of the binary mixture composed of 4-hexylphenyl 4-octyloxybenzoate (A) and 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate (B)[2].

We have found that the smectic C compounds can be divided into two groups. The compounds, which belong to the first group, mix nearly additively with 4-hexyloxyphenyl 4-octyloxybenzoate and non-additively with 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate whereas the compounds, which belong to the second group mix additively with 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate and non-additively with 4-hexyloxyphenol 4-octyloxybenzoate[3].

It is also possible to find compounds which are able to mix with compounds from both these groups, but usually a minimum of stability of the C phases for one pair is observed, see for example the mixture of compounds: 4-(2-methylbutyloxy)phenyl 4-octyloxybenzoate and 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate.

By miscibility studies we are able to select compounds which mix without destabilization of the smectic C phase and therefore allow to prepare a multicomponent mixture with a broad range of smectic C phase. The example of such a mixture is the four component mixture 1:



17.3 wt.%
13.9 wt.%
20.4 wt.%
43.9 wt.%
4.5 wt.%

having the phase transition in °C: Cr 0 S_C^*50.7S_A66.7N^*77 I.

The next question which is to be answered is as follows. Are the compounds with smectic C phase the only suitable compounds to be used for preparing a mixture with a broad range of the smectic C phase? Can other compounds be used for this purpose? The answer can be concluded from phase diagrams of bicomponent mixtures comprising 4-hexyloxyphenyl 4-octyloxybenzoate and 1-/‾5-(4-hexylphenyl)pyrimidyl-2_7-2-(4-hexyloxyphenyl) or 4′,4″-bis(1-methylheptyloxycarbonyl)-p-terphenyl, Figure 2.

One component of the first mentioned mixture has the smectic A and B phases and it can be introduced even in amounts of 60 wt.% without the significant destabilization of the smectic C phase. In the second mixture, one component is isotropic (C), and this component enhances the stability of the smectic C phase in the region of concentration up to 25 wt.%. Therefore mesogen not having smectic

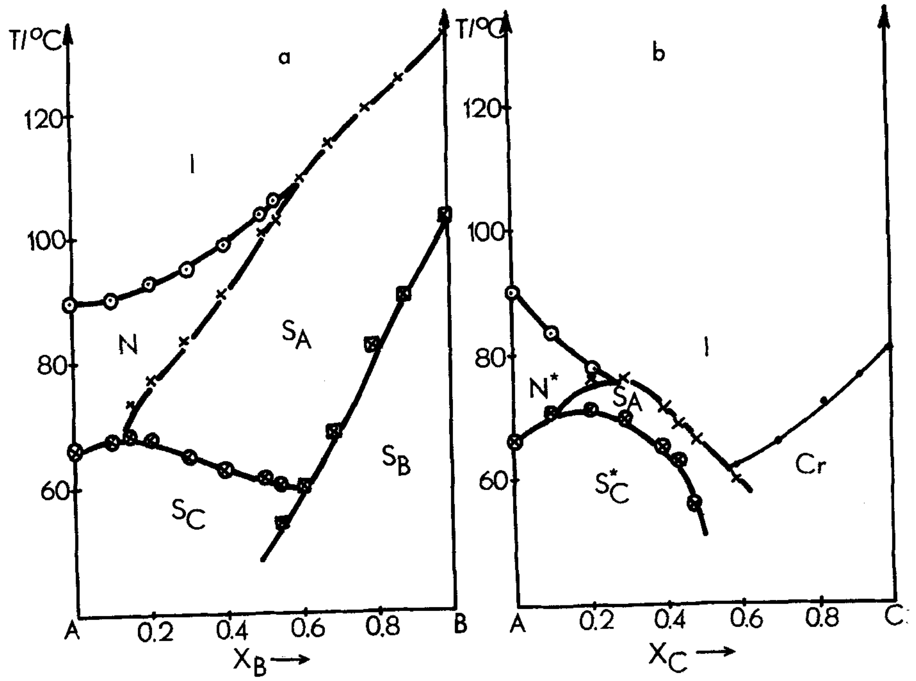
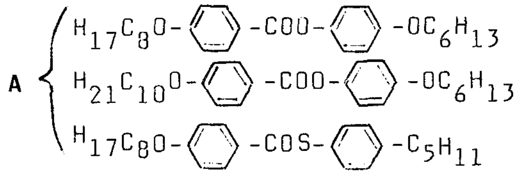


FIGURE 2. Phase diagram of binary mixture composed of 4-hexyloxyphenyl 4-octyloxybenzoate (A) and 1-(5-hexylphenyl) pyrimidyl-2)-2-(4-hexyloxyphenyl)ethane (B) - a.(Ref.4) or 4´,4´´-bis(1-methylheptyloxycarbonyl)-p-terphenyl (C) - b (repeated after Ref.5)

C phase and non-mesogenic compounds can be useful and can be taken into account as the main mixture components (not only as chiral dopants in small amounts).

THE CONTROL OF THE RANGE OF THE SMECTIC A PHASE ABOVE THE SMECTIC C PHASE

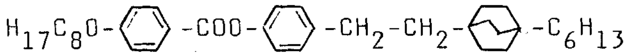
The problem how to control the range of the smectic A phase above the smectic C phase will be discussed using as an example mixture 2 comprising alkoxybenzoates and one bicyclooctane derivative:



23.55 wt.%

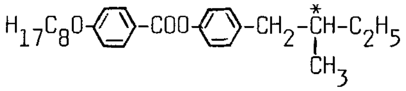
18.80 wt.%

25.41 wt.%

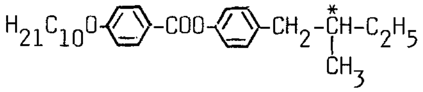
B  32.44 wt.%

This mixture has a large value of the tilt angle, about thirty degrees in room temperature[6]. We suppose that it would be easier to lower the tilt angle than to increase it by doping.

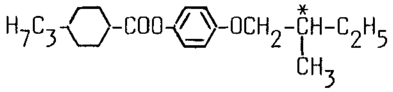
A large group of dopants was selected and added to the mixture 2, and their ability to induce the smectic A phase above smectic C phase was tested. These are chiral and non-chiral mesogenes and also isotropic compounds:



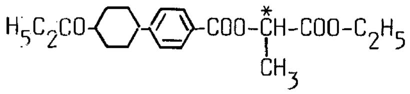
1 Cr 47.5 (N*42) I



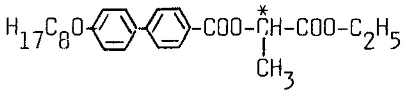
2 Cr 42.5 S_A 44 N 47 I



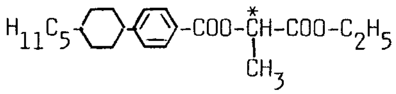
3 Cr 38 (S_A22.5) I



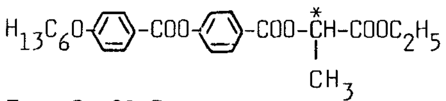
4 Cr 69 I



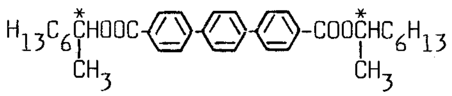
5 Cr 45 (S_A 42.5) I



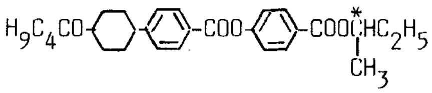
6 Cr (-2) I



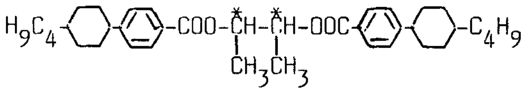
7 Cr 20 I



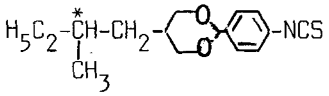
8 Cr 82 I



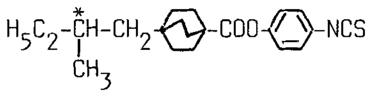
9 Cr 103 S_B 129.8 N* 134 I



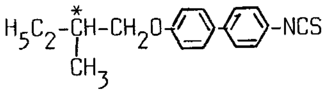
10 Cr 42 I



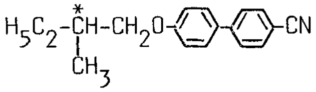
11 Cr 55 (47 S_A) I



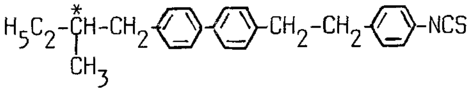
12 Cr 42.5 (S_A 42) I



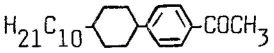
13 Cr 116 I



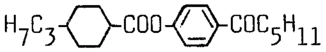
14 Cr 53 (9 N*) I



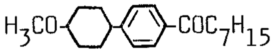
15 Cr 72.5 S_A 99 I



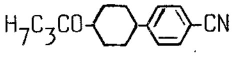
16 Cr 77 I



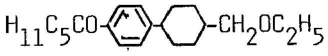
17 Cr 64 S_A 89 I



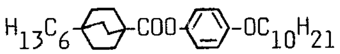
18 Cr 65 I



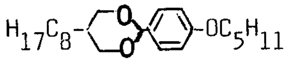
19 Cr 51 I



20 Cr 37.5 I

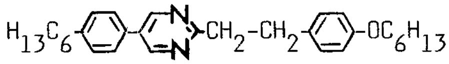


21 Cr 55 ($35S_B$)S_A77.8 N 89.5 I

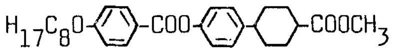


22 Cr 42.2 S_B 52.7 S_A 62.7 I

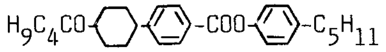
23 Cr 56.5 S_A 57 N 65.5 I



24 Cr 95.5$S_{B_{hex}}$ 103.2 S_A 131.5 I



25 Cr 92.5 N 183 I



26 Cr 89 S_B121.5 S_A160.5N172.2I

The mentioned compounds were introduced to the base mixture 2 in increasing amounts, the phase transition temperatures of mixture 2 with a dopant were measured and the existing phases were identified by the thermomicroscopic method. Different types of behavior were observed after introducing the dopants.

a) The dopant 8 increases the smectic C - chiral nematic phase transition temperature up to the concentration of about 25% and then the $S_C^* \rightarrow N^*$ phase transition temperature is slowly decreasing, Figure 3. It is very useful that the $N^* \rightarrow I$ phase transition temperature is decreasing. We have found such a behavior only for this dopant, but we suppose

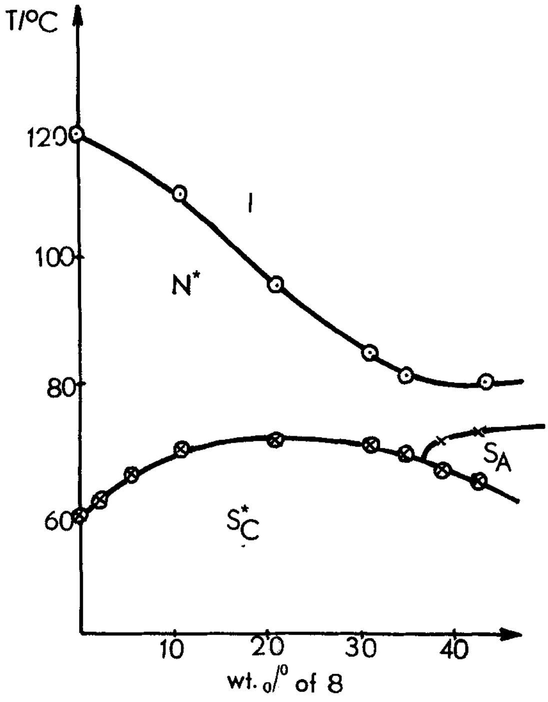


FIGURE 3. Phase transition temperatures of mixture 2 versus concentration of dopant 8.

that it will be characteristic for other compounds with a similar structure.

b) Dopants 1, 3, 4, 6, 10, 11, 23 decrease smectic C - nematic phase transition temperature (Figure 4a, b) in the following way 23 $<1 < 11 < 10 < 4 < 3 < 6$. The decrease of the stability of smectic C phase depends on the kind of a dopant, but it is interesting to remark that in the case of the investigated compounds, which do not have the smectic C phase, the depression of the smectic C phase of the base mixture 2 caused by them is smaller than in the case of some mentioned earlier pairs of compounds with smectic C properties (see Figure 1).

c) For small concentration of the dopants 21 and 2 the smectic C - nematic phase transition temperature is nearly independent of the concentration (Figure 5) and for higher concentration of the dopants smectic A phase is induced with a low or moderate intensity. The stability of the smectic C phase does not change (compound 21, Figure 5a) or decreases slowly (compound 2, Figure 5b). Compounds with such properties may be useful for preparing mixtures with a short range of the smectic A phase above the smectic C phase e.g. with S_C^* -S_A^* -N^*→I phase transition sequence.

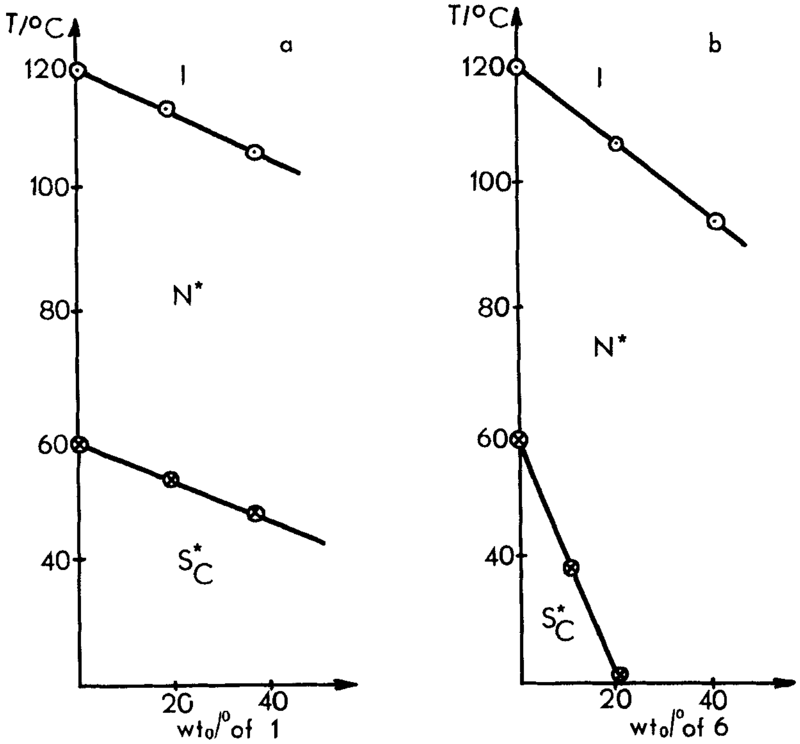


FIGURE 4. Phase transition temperatures of mixture 2 versus concentration of dopant 1 (a) or 6 (b).

d) The smectic C - nematic phase transition temperature is decreasing in all the concentration region of the dopant and smectic A phase is created in moderate efficiency only for higher concentration of the dopant. The compounds 20 and 22 have such properties, Figure 6.

e) For a small concentration of the dopants the enhancement of the smectic C phase is observed. Maximum of its stability is observed between 5 and 10 wt.%. For larger concentrations of the dopant the smectic A phase is induced strongly and, simultaneously, the smectic C phase begins to destabilize more quickly. It is observed that when the A phase induces strongly the smectic C phase destabilizes quickly (Figure 7a,b,c). The compounds 9, 13, 15, 18, 26 have such properties behave.

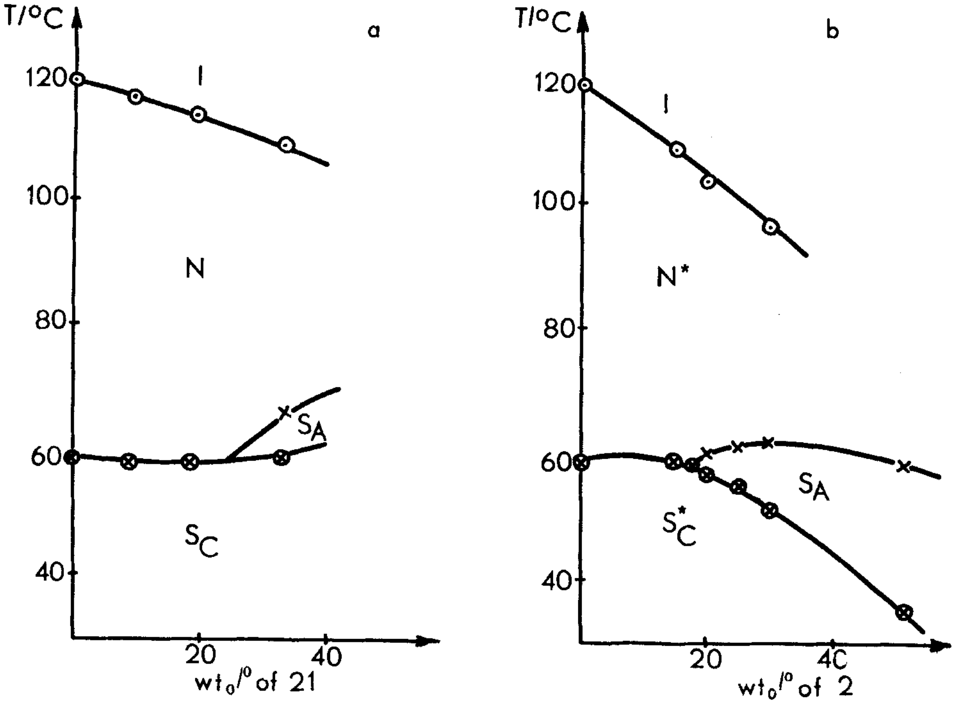


FIGURE 5. Phase transition temperatures of mixture 2 versus concentration of the dopant 21.

f) The smectic C phase is destabilized in all the region of the concentration and the smectic A phase is induced above the concentration of 5-10 wt.%, Figure 8a,b,c,d. In such a way behave the compounds 12, 14, 16, 17 and 19. For compounds with CN terminal group (14,19) smectic C phase is depressed most drastically and the smectic A phase induces in the highest degree, Figure 8c, d.

From the above discussed phase diagram study the following conclusion can be drawn out:

- It is possible to transform a mixture with a smectic C - nematic ($S_C\to N$ or $S_C^*\to N^*$) sequence to a mixture with the smectic C - smectic A - nematic phase sequence ($S_C\to S_A\to N$ or $S_C^*\to S_A\to N^*$).

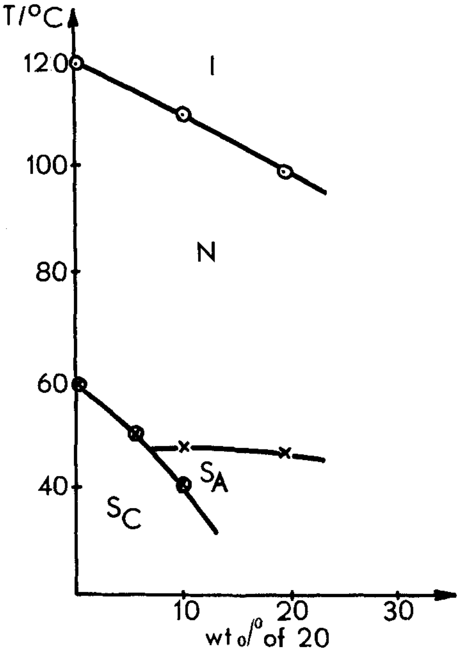


FIGURE 6. Phase transition temperatures of mixture 2 versus concentration of the dopant 20.

- A temperature range of the existing smectic A phase above the smectic C phase can easily be controlled as we wish. In some cases a small amount of dopants is able to transform smectic C mixture to a broad range smectic A mixture. It is supposed that such smectic A mixtures can be interesting for electroclinic effect.
- The preferable results for improving the properties of the basic mixture are obtained, when two dopants are introduced to it. The first dopant is used for inducing the smectic A phase and the other one for enhancing the smectic C phase and simultaneously for introducing the chiral properties. This procedure can be demonstrated by

by the following examples:

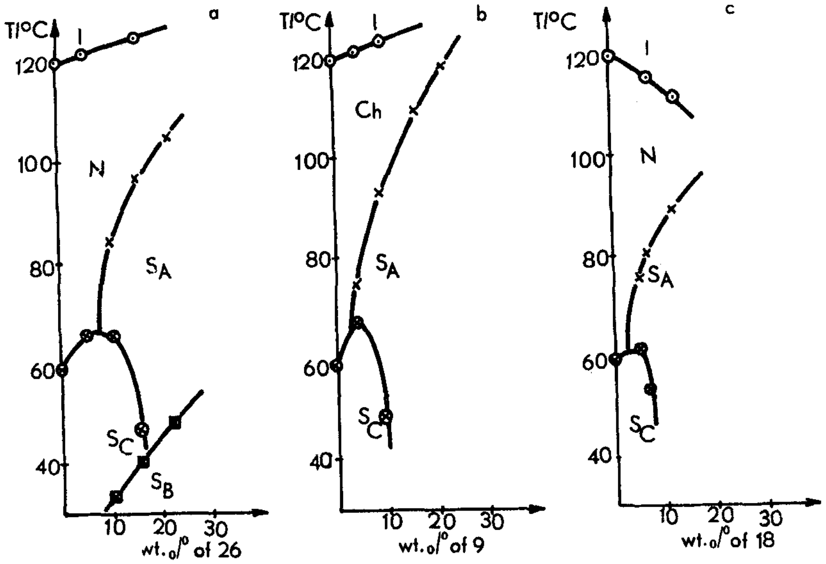


FIGURE 7. Phase transition temperatures of mixtures 2 versus concentration of dopant 26 (a) or 9 (b) or 18 (c).

a) We have introduced 22.8 wt.%, 28 wt.% of compound 2 to the base mixture and to the two obtained mixtures we have added the chiral compound 8 in increasing amounts. The obtained phase diagrams are shown on , Figure 9a, b. These two mixtures differ in the range of smectic A phase. The range of the smectic A phase may be shortened by introducing smaller amounts of compound 2.

b) For another dopant having stronger ability to induce the smectic A phase a smaller concentration of it is necessary for creating the smectic A phase, see Figure 10a, b.

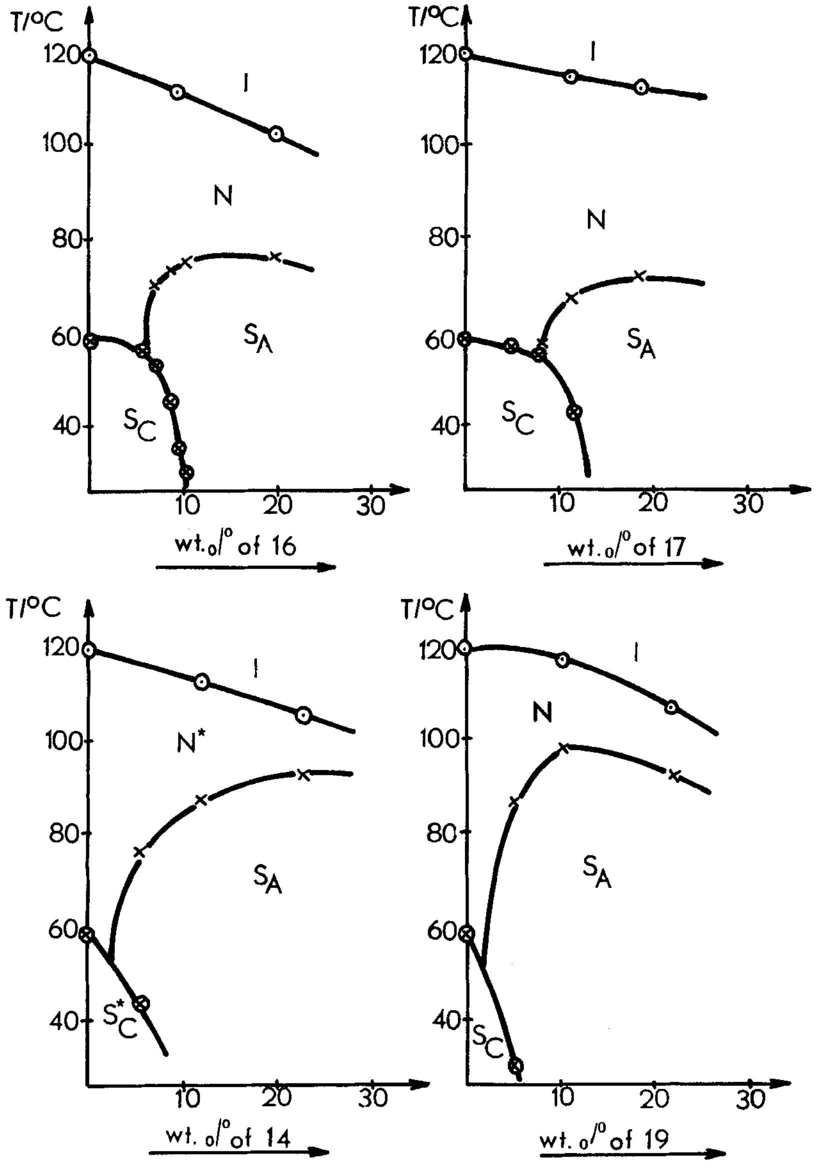


FIGURE 8. Phase transition temperatures of mixture 2 versus concentration of dopant 16 (a) or 17 (b) or 14 (c) or 19 (d).

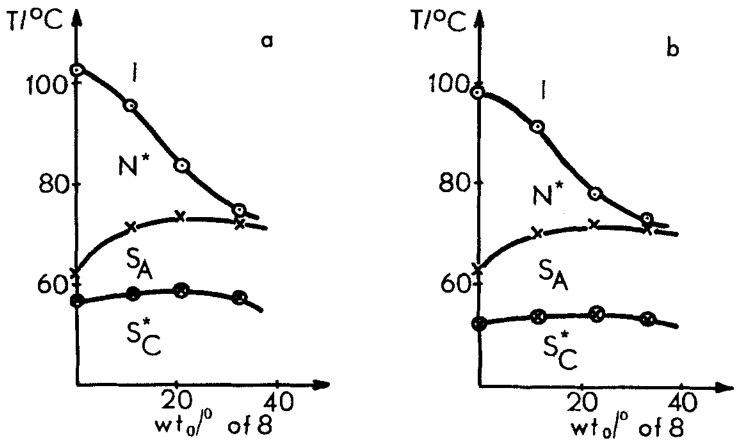


FIGURE 9. Phase transition temperatures of the mixture 2 including 22.8 wt.% (a) or 28 wt.% (b) of the dopant 2 versus concentration of the second dopant 8.

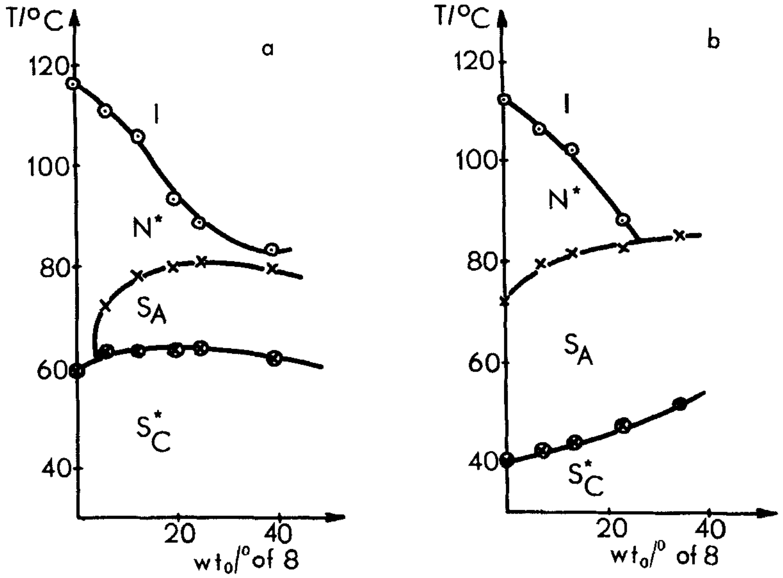


FIGURE 10. Phase transition temperatures of the mixture 2 containing 4 wt.% (a) or 8.6 wt.% (b) of the second dopant 16 versus concentration of the dopant 8.

ADJUSTING THE TILT ANGLE OF THE SMECTIC C LAYERS

The dopants 5, 2, 16, 21 having different ability to destabilize the smectic C phase (21 > 2 > 5 > 16) and the dopant 8 enhancing its thermal stability were chosen. The tilt angle of basic mixture changes with the concentration of dopants in the following way, Figure 11.

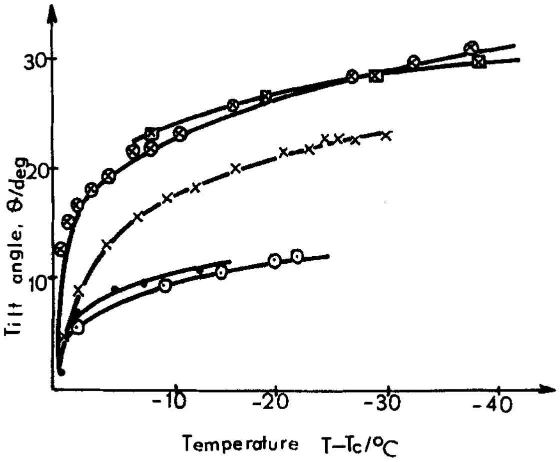


FIGURE 11. Tilt angle Θ of the molecules in the smectic C layer versus the distance from the smectic C - nematic or smectic C - smectic A phase transition temperature for mixture 2 - ⊠ and mixture 2 doped with 20 wt.% of compound 8 - ⊗ or 20 wt.% of 5 - ✗ or 20 wt.% of 2 - • or 8.6 wt.% of 16 - ⊙

The basic mixture 2 doped with 20 wt.% of compound 8, nearly does not change the tilt angle. It was found from the phase diagram study that this compound enhances only the smectic C phase stability. The compounds 2, 5 and 16 lower the value of the tilt angle; the compound 5 lowers weaker than the compound 2 and the compound 16.

The compound 5 does not induce the smectic A phase, the compound 2 induces the smectic A phase in a moderate way and the compound 16 induces drastically the smectic A phase and in the same way destabilizes the smectic C phase.

The tilt angle depends on the concentrations of the compound 21, Figure 12.

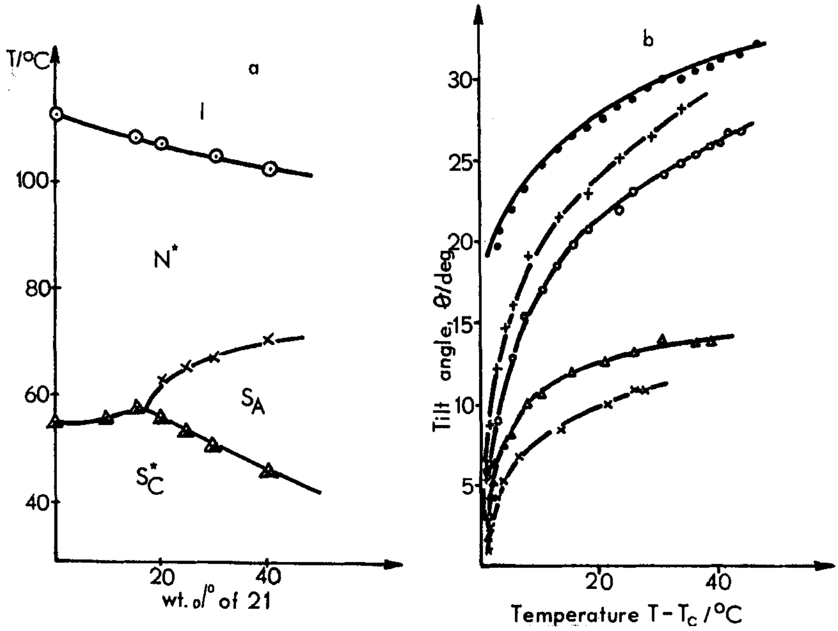


FIGURE 12. a) Phase transition temperatures of mixture 2 containing 8 wt.% of compound 5 versus the concentration of compound 21.

b) Tilt angle θ of molecules in the smectic C layer of mixture 2 with dopant 5 • and mixture 2 with dopant 5 containing additionally 9.8 - +, 20 - o, 30.1 - Δ and 40.2 - x wt.% of compound 21.

The tilt angle value is correlated directly with the existing range of the smectic A phase above the smectic C phase. We see it distinctly when we compare the phase diagram (Figure 12a) with the changes of the tilt angle value, (Figure 12b). The tilt angle decreases when the concentration of the dopant is increasing, but the changes are not directly proportional to the concentration and when the A phase induction is involved and the smectic C phase is depressed then lowering of the tilt angle drops more quickly. Such a behavior was found in other investigated by us systems. Similar observation was made by Kondo[7].

For every pair of dopants introduced to basic mixture 2 it is possible to find such a concentration of them, which gives the optimal value of the tilt angle and the optimal value of the spontaneous polarization. For example, when basic mixture 2 and chiral dopants 8 or 5 and the dopant 2 or 16 or 21 inducing the smectic A phase are used the preferable compositions are shown in Table I.

TABLE I. The preferable compositions of the mixtures

Resulting mixtures	Base mixture	Weight % of dopants				
		8	5	2	16	21
I	84-88	4-6		8-10		
II	89-93	4-6			3-5	
III	58-72		8-12			20-30

The spontaneous polarization of the mixture 2 containing 4 wt.% of compound 16 depends on the concentration of dopand 8 in the way shown in Table II [8].

TABLE II. The spontaneous polarization P at 20°C of mixture 2 with dopant 16.

wt.% of dopant	P (nC/cm^2)
6	17
12	43.7
20	75
25	103

The concentrations of dopant 8 below 6 wt.% are sufficient for obtaining mixtures for practical applications.

CONCLUSIONS

Doping is a very useful method for the creation of the mixtures with S_C-S_A-N sequence from mixtures with S_C-N sequence. The compounds not having smectic C phase are useful for this purpose and can be introduced in large amounts without destroying smectic C phase.

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