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BINARY MIXTURES OF POLAR SMECTICS A_1 WITH A NEMATIC GAP AND NEMATIC REENTRANT PHASE

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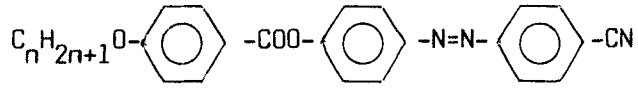
Abstract Phase diagrams (T=f(x)) are determined for binary mixtures composed of p-alkoxybenzoyloxy-p'-cyanoazobenzenes (nOBCAB) and isothiocyanatophenyl 4-(trans-4n-alkylcyclohexyl) benzoates (nTPCHB). It is shown that in these mixtures the smectic phase of OBCAB is destabilized and a nematic gap, as well as the reentrant nematic phase appear. The generalized conclusion is drawn that such behaviour is typical for mixtures in which one of the components belongs to a homologous series whose members with shorter aliphatic chains reveal the smectic A_1 phase and those with longer chains the A_d one, and the other component is a smectic A_1 of lower polarity.

INTRODUCTION

In several works it has been shown |1,2,3| that in systems consisting of compounds belonging to such classes as: 4-cyanobiphenyl-4-alkylbiphenylates (nCBB) and 4-(trans-4n-alkylcyclohexyl)benzoates (nXPCHB) lowering of the stability of the smectic A_1 phase takes place leading to the appearance of the nematic gap, even if the A_1 smectic layer spacings of the mixture components are identical. Besides in such systems the presence of the nematic reentrant phase has been ascertained below the smectic phase which is untypical for polar smectic A_1 systems |4|. It has been shown |2| that this anomalous behaviour is due to the dimerization of compounds with the CN terminal group (nCBB) in mixtures with compounds 10XPCHB with terminal groups: X=F, NSC or $COCH_3$ of lower polarity.

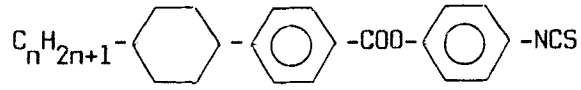
The aim of the present work is to check whether the behaviour observed for the nCBB homologous series is typical of homologous

series in which the members with shorter terminal chains yield the A_1 phase and those with longer chains the A_d one. For this purpose the p-alkoxybenzyoloxy-p'-cyanoazobenzene homologous series (nOBCAB) of the formula:



described in |5| was used. The compounds of this series are smectics A_1 if $n \leqslant 8$ and A_d if $n \geqslant 9$ |5|.

The second component of the binary mixtures was compound belonging to the isothiocyanatophenyl 4(trans-4n-alkylcycloheksyl) benzoates (nTPCHB) homologous series of the formula:



The compounds of nTPCHB series are smectics A_1 |3|.

EXPERIMENTAL

The following series of binary mixtures were studied:

(I) nOBCAB - 10TPCHB with n = 6 to 9

(II) 8OBCAB-nTPCHB with n = 5 to 10.

The phase diagrams were determined by the thermal microscopic method described in |1|.

RESULTS

In the 9OBCAB-10TPCHB (Fig.1a) system the smectic A_d phase of 9OBCAB mixes in the whole concentration range with the S_{A1} phase of 10TPCHB. The compounds of the nOBCAB series with n = 8 yield the smectic A_1 phase which in mixture with 10TPCHB (Fig.1b) undergoes destabilization and at $x_{10TPCHB}$= 0.25 mole fraction a nematic gap is observed. As the content of 10TPCHB increases the smectic phase reappears in an extended temperature range, and the nematic reentrant phase is observed at lower temperatures. The character of the $N-S_A$ and S_A-N_{re} phase transition lines indicates that on

the right-hand side of the nematic gap the smectic phase is a mixture of the virtual smectic A_d phase of 8OBCAB and smectic A_1 phase of 1OTPCHB. As the length of the aliphatic chain of nOBCAB decreases the width of the nematic gap increases but the shape of the $N-S_A$ and especially S_A-N_{re} transition lines remain unchanged (Fig.1c,d). In all the mixtures studied near nematic gap wide diphase regions (nematic and smectic) are observed.

The effect of aliphatic chain length in nTPCHB is illustrated in Fig.1b, 2a-d. As this length decreases the destabilization of the smectic phase on the side of 8OBCAB and its extension on the side of nTPCHB excess also decrease.

For the 8OBCAB-8TPCHB system (Fig.2b) the nematic gap was not observed, however, in these mixtures a very deep minimum occurs which points also to the lack of miscibility of the smectic phases of both components.

This minimum decreases with decrease of the aliphatic chain in nTPCHB (n = 7 or 5, Fig.2c or d).

DISCUSSION

The presented phase diagrams of the nOBCAB-nTPCHB systems are analogous to those obtained for the nCBB-nXPCHB ones in [1,2,3]. The cause of the behaviours observed in both systems is the dimerization of the compound with the strongly polar CN group in the matrix of the compound of lower polarity. The dimerization is confirmed by X-ray investigations of the 7CBB-1OXPCHB [2] and 8OBCAB-1OTPCHB [6] systems. In these systems we probably have to do with mixtures of two types of smectics A_1. The recent studies [7,8] show that smectics A_1 with the strongly polar CN group have regions with locally oriented arrangement of dipoles separated by "walls" like in the structure of smectic $\tilde{A}$ only that the latter shows a random distribution of the "walls" in its structure. In distinction, smectics A_1 with terminal NCS group (compound 7TPCHB in [8]) are so-called "classic" smectics A_1 and show a random (up-and-down) orientation of the

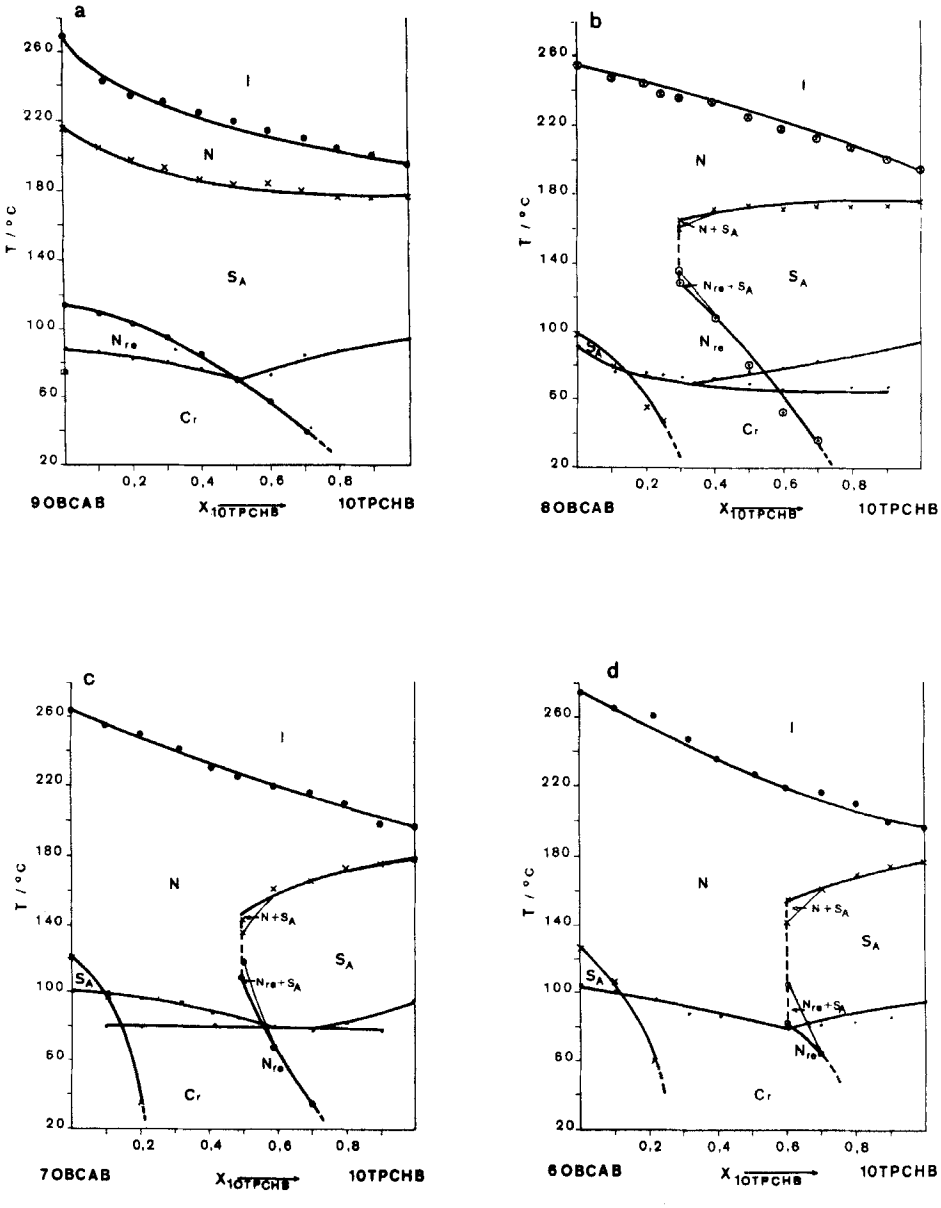


FIGURE 1 Phase diagrams for the binary mixtures of the series I

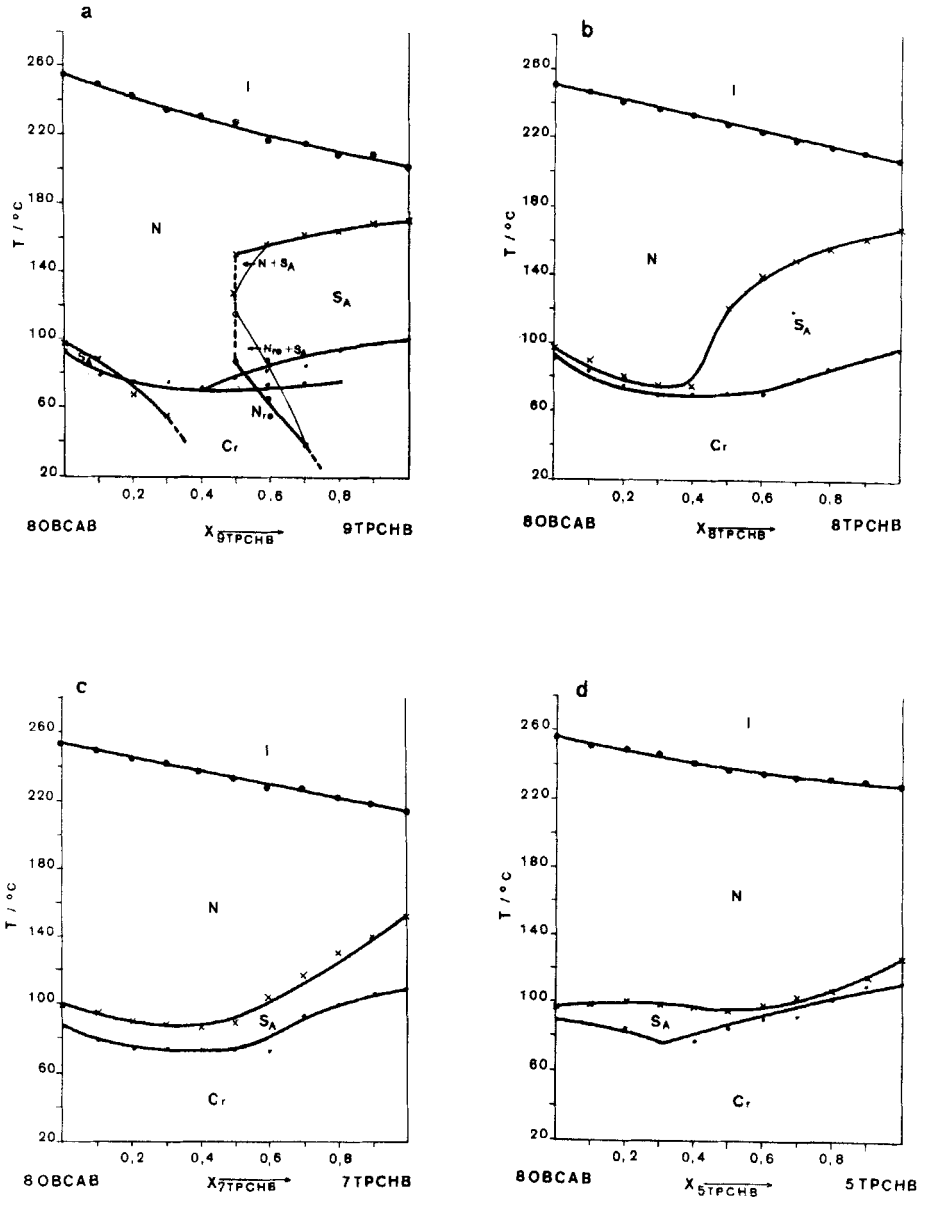


FIGURE 2 Phase diagrams for the binary mixtures of the series II

dipoles. The above presented phase diagrams show that smectics of both these types do not mix. The addition to a smectic A_1 with the strongly polar group CN of a classic smectic A_1 disturbes the structure of the former and leads to the occurrence of the nematic gap. However, a further increase of concentration of the classic smectic in the mixture allows rearrangement of the molecular structure of the compound with terminal group CN and the formation of dimers. This result in a significant expansion of the smectic phase on the side of the 10TPCHB excess (Fig.1b). The S_A-N phase transition lines are in this part of the plot similar to those observed for the 90BCAB-10TPCHB system (Fig.1a) in which the smectic A_d phase of 90BCAB mixes with the smectic A_1 phase of 10TPCHB. The good miscibility of the smectic A_d phases of compounds nOBCAB with the smectic A_1 ones of compounds 10TPCHB may be due to the fact that the dimers of the former and monomers of the latter (classic smectic A_1) may easily form correlated triplets which, according to the Indekeu-Berker theory [9], stabilize the smectic phase by forming an extended network, the molecular polymer, in the plane of the layer. At lower temperature the polymer lattice cannot be formed which leads to the reappearance of the nematic phase.

The rearrangement of the molecular structure of the smectic A_1 with the CN terminal group and the formation of dimers is more difficult for compounds with shorter aliphatic chains (Fig.1c,d). Furthermore, it is more difficult in mixtures with nTPCHB compounds with shorter terminal chains due to the increased polarity of the system (Fig.2).

It seems that the behaviour observed in the nOBCAB-nTPCHB systems consisting in the destabilization of the smectic A_1 phase on the one hand and the extension of its range and formation of the nematic reentrant phase due to rearrangement to the A_d structure, on the other hand, is general. It is observed for systems composed of two smectics A_1, one of which has the strongly polar CN group and belongs to the homologous series in which the members with longer

aliphatic chains yield the smectic A_d phase and those with shorter chains the A_1 one, and the second one has a terminal group of lower polarity and has an aliphatic chain of adequate length.

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