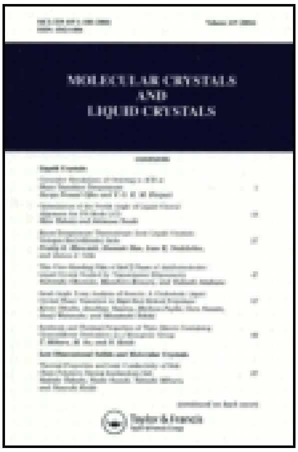

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Miscibility Study of Two Kinds of the Smectic A

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MISCIBILITY STUDY OF TWO KINDS OF THE SMECTIC A_1

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Abstract Phase diagrams (T=f(x)) are determined for binary mixtures composed of two homologous series nOBCAB–nTPCHB. It is shown the immiscibility of the smectic A_1 of both components. The smectic A_1 phase of nTPCHB compounds with longer aliphatic chain is miscible with smectic A_d of 9OBCAB component and involves the dimerization of compounds nOBCAB with short aliphatic chain. The results confirm that investigated homologous series form different kinds of the smectic A_1 phase.

INTRODUCTION

The large number of the smectic A phase [1, 2] is a characteristic feature of liquid crystaline compounds with terminal polar groups.

The last investigations of Gramsbergen as well as de Jeu [1, 3] and the authors in cooperation with Dąbrowski, Czupryński and Przedmojski [4] have shown that two kinds of smectic A_1 can exist.

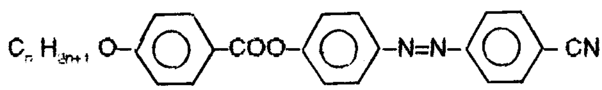
The first type of smectic A_1 called "classical smectic A_1" according to [3] or "enhanced monolayer smectic A_1" according to [4] shows a random (up–and–down) orientation of the dipoles in the smectic layers. Furthermore the spacing of smectic layers is slowly expanding with the increase of the aliphatic chain length in the homologous series of compounds forming this type of smectic. It causes that the structure of this type of smectic A_1 becomes more like to the structure A_d with the increase of the aliphatic chain length. The homologous series of compounds with the terminal polar groups –NCS, –F –Cl, –J, $-COC_mH_{2m+1}$ create this type of the smectic A_1

The second type of smectic A_1 is shown by the homologous series of compounds with a terminal –CN group. The smectic A_1 layer spacing of this phase is equal to the molecular length but the smectic A_1 layers have regions with locally oriented arragement of dipoles resambling smectic A_2. The bilayer regions are randomly distributed. This kind of smectic A_1 is rapidly transformed into the smectic A_d with the increase of the aliphatic chain length of the respective molecules.

The aim of the present work is to investigate the binary mixtures of compounds belonging to the homologous series which create both type of smectic A_1 and to study the influence of the aliphatic chain length of both homologous series on the smectic phases stability in the mixtures.

MATERIALS AND METHODS

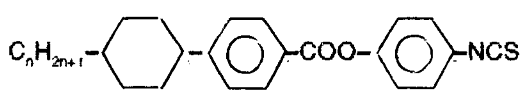
For the tests, the compounds have been used from the p–alkoxybenzoyloxy–p'–cyanoazobenzene homologous series (nOBCAB) of the formula:



The compounds of those series are smectic A_1 if $n \leq 8$ and A_d if $n \geq 9$ [10].

Therefore, there are a homologous series in which the smectic A_1 is rapidly transforming into smectic A_d with increase of the aliphatic chain length from 8 to 9 carbon atoms. The compounds with n=6, 7, 8 (smectic A_1) and n=9 (smectic A_d) were examinated.

As second component of the binary mixtures isothiocyanatophenyl 4(trans–4n–alkylcyclohexyl) benzoates (nTPCHB) of the formula:



were used.

The compounds of the nTPCHB series show "enhanced monolayer smectic A_1" (A_{1e}) phases according to [4].

All these compounds were synthesised in Profesor Dąbrowski laboratory from Military Technical Academy according to the methods described in [10, 11].

The following series of binary mixtures have been studied by thermomicroscopic methods:

Series 1. 6OBCAB–nTPCHB for n=5, 7, 8, 9, 10, 12

Series 2. 7OBCAB–nTPCHB for n=5, 7, 8, 9, 10, 12

Series 3 8OBCAB–nTPCHB for n=5, 7, 8, 9, 10, 12

The phase diagrams of mixtures 8OBCAB–nTPCHB which were described in [8] are also included in this work.

RESULTS

The results of thermomicroscopic testing are summarized in the equilibrium phase diagrams T=f(x). The comparision of all phase diagrams include 8OBCAB–nTPCHB series is shown in Figure 1.

The phase diagrams of 6OBCAB–nTPCHB (Fig. 1a), 7OBCAB–nTPCHB (Fig. 1b) and 8OBCAB–nTPCHB (Fig. 1c) have the same character. The pure components create only the smectic A_1 phase. As we can see from the phase diagrams (Fig. 1 – a1,b1, b2, c1, c2, c3) the smectic A_1 phases of both component are partially immiscible. In the mixtures with the short aliphatic chain of the nTPCHB component a minimum on the phase transition lines S_A – N is observed.

The increase of the aliphatic chain lenght of the nTPCHB component causes:

1) the increase of the destabilization of the smectic A_1 phase on the side of the excess of the nOBCAB component which conducts to the disappearance of this phase and to the appearance of the nematic gap
2) the increase of the smectic A_1 phase range on the side of the nTPCHB component excess with simultanously appearence of the nematic reentrant phase.

These changes are due to the rearengement of the molecular structure of the smectic A_1 phase of the nOBCAB component and the formation of the smectic A_d phase. This one was confirmed by the X-ray studies [9, 12]. In mixtures 8OBCAB–5TPCHB the process of formation of the smectic A_d of the 8OBCAB compounds does not take place [12]. The phase diagrams for series 6OBCAB–nTPCHB and 7OBCAB–nTPCHB indicate that the essential influence of the aliphatic chain length of the nTPCHB compounds on the creating process of the smectic A_d is a common feature of all compounds from nOBCAB homologous series.

The binary mixtures of the 9OBCAB–nTPCHB series (figure 1d) show different character with respect to the series presented above. It is caused by the fact that the 9OBCAB component yields smectic A_d and nematic reentrant phases above the temperature region of the smectic A_1 phase. For these purpose the 9OBCAB component is a good example for testing miscibility of both smectic A phases of these compounds with the smectic A_1 phase of the component belonging to the nTPCHB homologous series.

In the phase diagrams of 9OBCAB–5TPCHB and 9OBCAB–7TPCHB mixtures a minimum on the S_{A1}–N phase transition line is observed. The character of this transition

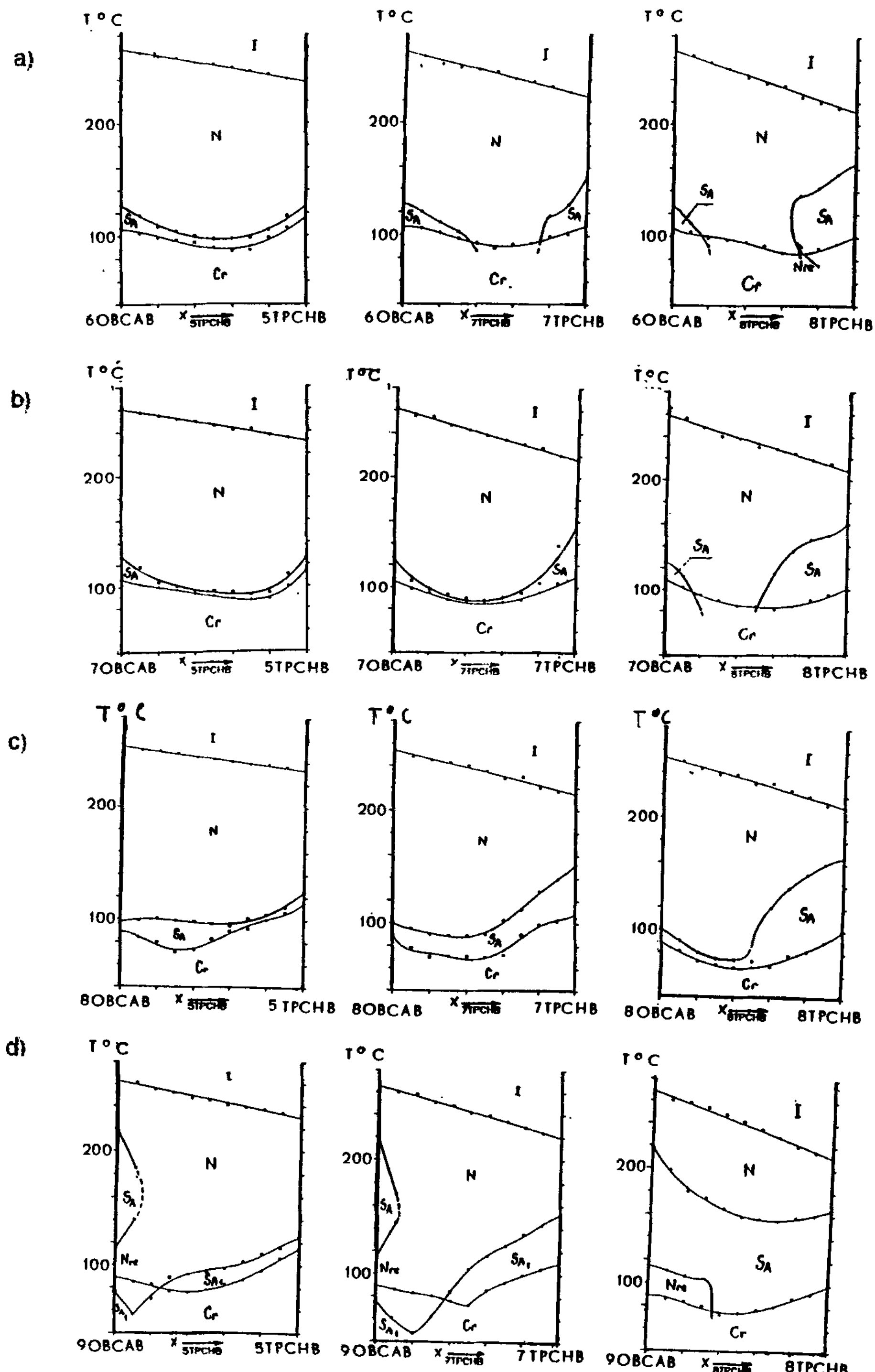


Fig. 1. Phase diagrams of the nOBCAB–nTPCHB systems.

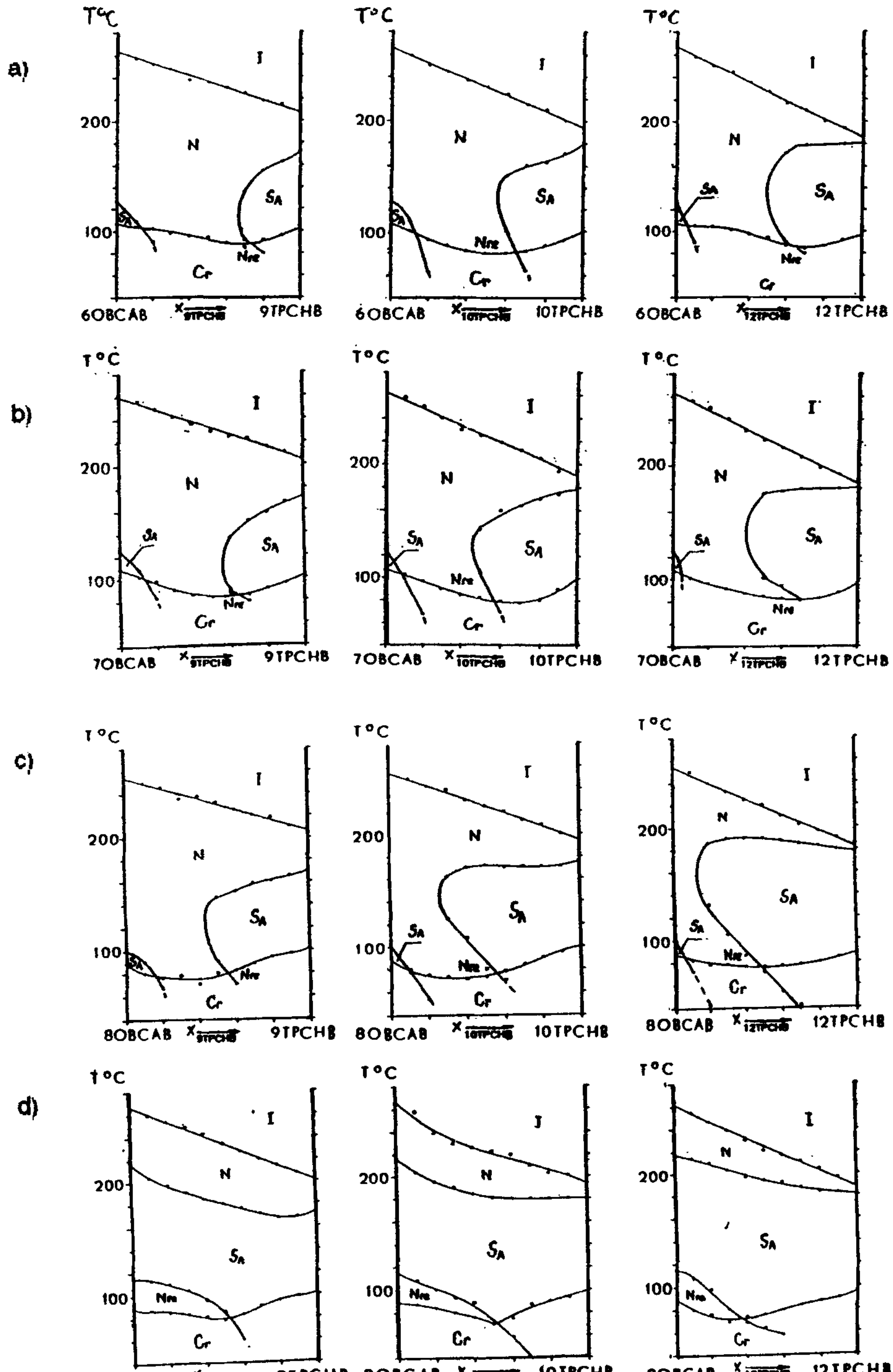


Fig. 1.(continued) Phase diagrams of the nOBCAB–NTPCHB systems

line remind of a system with the eutectic point. It suggests that smectic A_1 phases of both component belonging to the different homologous series are immiscible. In spite of the fact that the smectic layer spacing of both compounds is equal to the length of their molecules length (d=l) [12].

Increase of the aliphatic chain length of the nTPCHB component into n$\geq$8 causes that the smectic A_1 phase of these compounds mix with the smectic A_d phase of the 9OBCAB components. The completly miscibility of two phases: the smectic A_1 phase of the nTPCHB compounds with the longer aliphatic chain and the smectic A_d phase of the 9OBCAB compounds confirms that the smectic A_1 of the nTPCHB homologous series is more like the smectic A_d one.

The influence of the aliphatic chain length of the nOBCAB compound is also observed. The decrease of the aliphatic chain length of the nOBCAB component causes:

1) the increase of the destabilization of the smectic A_1 phase on the side of the excess of the nOBCAB component. It provides to the appearence of the nematic gap in the 6OBCAB–nTPCHB system with the shorter aliphatic chain of the nTPCHB component in compared with 7OBCAB–nTPCHB and 8OBCAB–nTPCHB system. In the former system the length of the aliphatic chain in the nTPCHB (n=7) is require to the appearence of the nematic gap while in the other two n=8 and n=9 respectively.
2) the decrease of the observed extension of the smectic A phase range on the other side of the phase diagrams (the side of the nOBCAB component excess).

It indicates that decreasing of the aliphatic chain of the nOBCAB component lovering its tendency to dimerize in the nTPCHB mixtures. However, the nOBCAB compounds with shorter aliphatic chain require the shorter aliphatic chain of the nTPCHB matrix in order to the rearangement its structure.

CONCLUSIONS

1. The smectics A_1 of both homologous series show a lack of miscibility. This is a confirmation of the supposition that the smectic phases of both homologous series create the different types of the smectic A_1
2. The smectic A_1 of the nTPCHB compounds with the longer aliphatic chain n≥8 show the completly miscibility with the smectic A_d of the 9OBCAB compounds. It confirms that the structure of the smectic A_1 phase of the nTPCHB series (enhanced monolayer smectic A_1) with increasing of the length of the alkyl chain is changing to

be more like a smectic A_d phase

3. The compounds of the nOBCAB series which create only smectic A_1 phase (n=6, 7 and 8) for pure component in the mixture with the nTPCHB compounds yield the smectic A_d phase. The rearrangement of the molecular structure of the smectic A_1 occures by the suitable length of the aliphatic chain of the nTPCHB compounds, it means when the structure of the smectic A_1 phase of the nTPCHB compound is more like smectic A_d phase.
4. All investigated compounds of the nOBCAB homologous series which create the smectic A_1 (n=6, 7, 8) have the tendency to create the smectic A_d in the mixtures with the nTPCHB component. However, this tendency decreases with the decreasing of the aliphatic chain length of the nOBCAB component, but the smectic A_d phase of the nOBCAB component with the shorter aliphatic chain length is formed in the mixtures with the shorter aliphatic chain length of the nTPCHB matrix.

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