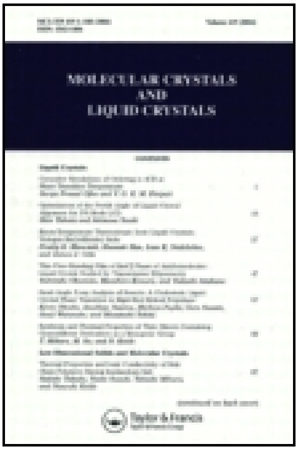

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# The Reentrant Nematic Phase in Mixtures of Polar Smectic A

B. Ważyńska [a]

[a] Warsaw University of Technology, 02524, Warsaw, Poland

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# The Reentrant Nematic Phase in Mixtures of Polar Smectic $A_1$

B. WAŻYŃSKA
*Warsaw University of Technology, 02524 Warsaw, Poland*

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The phase diagrams are studied of binary mixtures of compounds belonging to the following series: 4-cyanobiphenyl-4-yl-4*n*-alkylbiphenyl-4 carboxilates (*n*CBB) and isothiocyanotophenyl 4-(*trans*-4-*n* alkylcyclohexyl) benzoates (*n*TPCHB). It is shown that the dimerization of the *n*CBB compounds decreases with the increasing polarity of the *n*TPCHB matrix. The kind and concentration of the *n*TPCHB matrix has an essential effect on the temperature range in which the reentrant nematic phase exists.

## 1. INTRODUCTION

The nematic reentrant phase is observed in a wide temperature range in mixtures of compounds with a polar terminal group one of which at least has a smectic A phase partly dimolecular. The change of the monomer to dimer ratio in the smectic layer as a function of temperature results in that the ordering in the layer disappears at lower temperatures and the nematic phase reappears.[1–4] In References 5 and 6 it has been shown that the reentrant nematic phase may be observed also in binary systems composed of polar $A_1$ smectics.

The nematic reentrant phase was observed[5,6] in binary systems composed of compounds belonging to the following series: 4-cyanobiphenyl-4-yl-4′-*n*-alkylbiphenyl 4 carboxilates (*n*CBB)† and 4-(trans-4*n*-decylocyclohexyl) benzoates (10XPCHB). In the quoted works it has been shown that the generation of the reentrant nematic phase in mixture of this type is due to the dimerization of the compound with a strongly polar terminal group CN (compounds *n*CBB) in the matrix of the compound of lower polarity (10XPCHB). In the present work the effect is studied of the increase of polarity of component *n*XPCHB on the phase diagrams.

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†In References 5 and 6 this series was referred to as CBnAB.

TABLE I

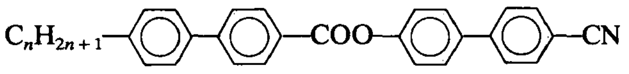
| Compound | Smectic layer spacing $d$ [nm] | Length of molecule 1 [nm] |
|---|---|---|
| 5CBB | 2.75 | 2.97 |
| 6CBB | 2.85 | 3.06 |
| 7CBB | 3.08 | 3.21 |
| 8CBB | 4.05 | 3.29 |
| 5TPCHB | 2.65 | 2.7 |
| 7TPCHB | 2.95 | 2.96 |
| 8TPCHB | 3.1 | 3.1 |
| 9TPCHB | 3.25 | 3.2 |
| 10TPCHB | 3.4 | 3.3 |

## 2. EXPERIMENTAL

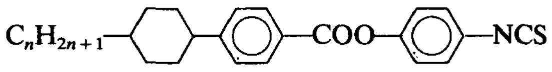
### 2.1. Materials and methods

Binary mixtures tested are composed of compounds belonging to the following series:

4-cyanobiphenyl-4-yl 4′-*n*-alkylbiphenyl-4 carboxilates (*n*CBB) of formula

I 

isothiocyanotophenyl 4-(trans-4-*n*-alkylcyclohexylbenzoates) (*n*TPCHB) of formula

II 

Both series of compounds were synthesized in Professor Dabrowski's laboratory according to the methods described in References 7 and 8. The smectic layer spacings were measured by Professor Przedmojski's in Guinier camera by using the free standing method described in Reference 9. The smectic layer spacings and lengths of the molecules found in References 8, 10 and 11 are summarized in Table I.

The following series of binary mixtures were tested:

I. 7CBB-*n*TPCHB where $n$ = 5, 7, 8, 9, 10†

II. 5CBB-*n*TPCHB where $n$ = 5, 7, 8, 9, 10

III. *n*CBB-10TPCHB where $n$ = 5, 6, 7, 8.

The phase diagrams of all the tested binary mixtures were obtained by determining the phase transition points by the thermomicroscopic method (heated stage

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†The binary mixture 7CBB-1OTPCHB is described in six.

and VEB Analytic, Dresden, polarization microscope). The mixtures were prepared and the thermomicroscopic tests carried out as in References 5 and 6.

### 2.2. The phase diagrams

In Figures 1 and 2 the phase diagrams are presented for series I and II, respectively. In all the tested *n*CBB-*n*TPCHB systems no deviations were observed as regards the stability of the nematic phase from the behavior of ideal solutions as was the case in References 5 and 6. The N → I phase transition points were found to be in agreement with those calculated from the CSL equation. Conversely, there is no such agreement as regards the $S_A \rightarrow$ N transition points. For instance, in the 7CBB–10TPCHB system, described in the previous work,[6] destabilization of the smectic phase is observed on the side of the 7CBB component, while the range of the smectic phase on the side of component 7TPCHB is enhanced. The smectic phase regions are separated by a nematic gap. In the concentration range of 0.3–0.7 mole fractions of 10TPCHB the reentrant nematic phase is observed.

As the length of the aliphatic chain in *n*TPCHB decreases, the destabilization of the smectic phase on the side of component 7CBB becomes smaller and the extension of the smectic phase range on the side of *n*TPCHB decreases. For the 7CBB–9TPCHB system a distinct change of shape of the $S_A \rightarrow$ N and $S_A \rightarrow N_{re}$ phase boundaries as compared with the 7CBB–10TPCHB system is observed (Figure 1b).

The boundary of the $S_A \rightarrow$ N transition in the 7CBB–9TPCHB system is concave as distinguished from that for the system with $n = 10$, and the boundary of the $S_A \rightarrow N_{re}$ transition is even more convex than that for the system with $n = 10$. This results in a significant narrowing of the smectic phase temperature range in the 7CBB–9TPCHB system.

In the case of the 7CBB–8TPCHB system (Figure 1c) the range of the smectic phase decreases further on the side of TPCHB. In this system the presence of the nematic reentrant phase has been detected below the smectic phase even after the samples were supercooled to 25°C. The nematic gap occurs in a wide range of concentrations: from 0.3 to 0.7 8TPCHB mole fraction, and it is shifted with respect to that in the 7CBB–10TPCHB and 7CBB–9TPCHB systems in the direction of greater proportions of *n*TPCHB owing to the lower destabilization of the 7CBB smectic phase in the 7CBB–8TPCHB system.

A further decrease of the length of the terminal aliphatic chain in *n*TPCHB to $n = 7$ (Figure 1d) or $n = 5$ (Figure 1e) results in that the nematic gap does not appear. In these systems the character of the $S_A \rightarrow$ N phase transition boundary, which reveals a district minimum, constitutes an indication immiscibility of the smectic phases of the mixture components. As the length of the aliphatic chains decreases from $n = 7$ to $n = 5$ the minimum becomes less pronounced and is shifted in the direction of greater *n*TPCHB concentrations.

The effect of the length of the *n*TPCHB aliphatic chain in series II (the 5CBB–*n*TPCHB systems) shown in Figure 2 is identical as in the case of series I. In series II no enhancement of the smectic phase is observed even in the case of longest $n = 10$ aliphatic chains in *n*TPCHB (Figure 2a). The reentrant nematic phase

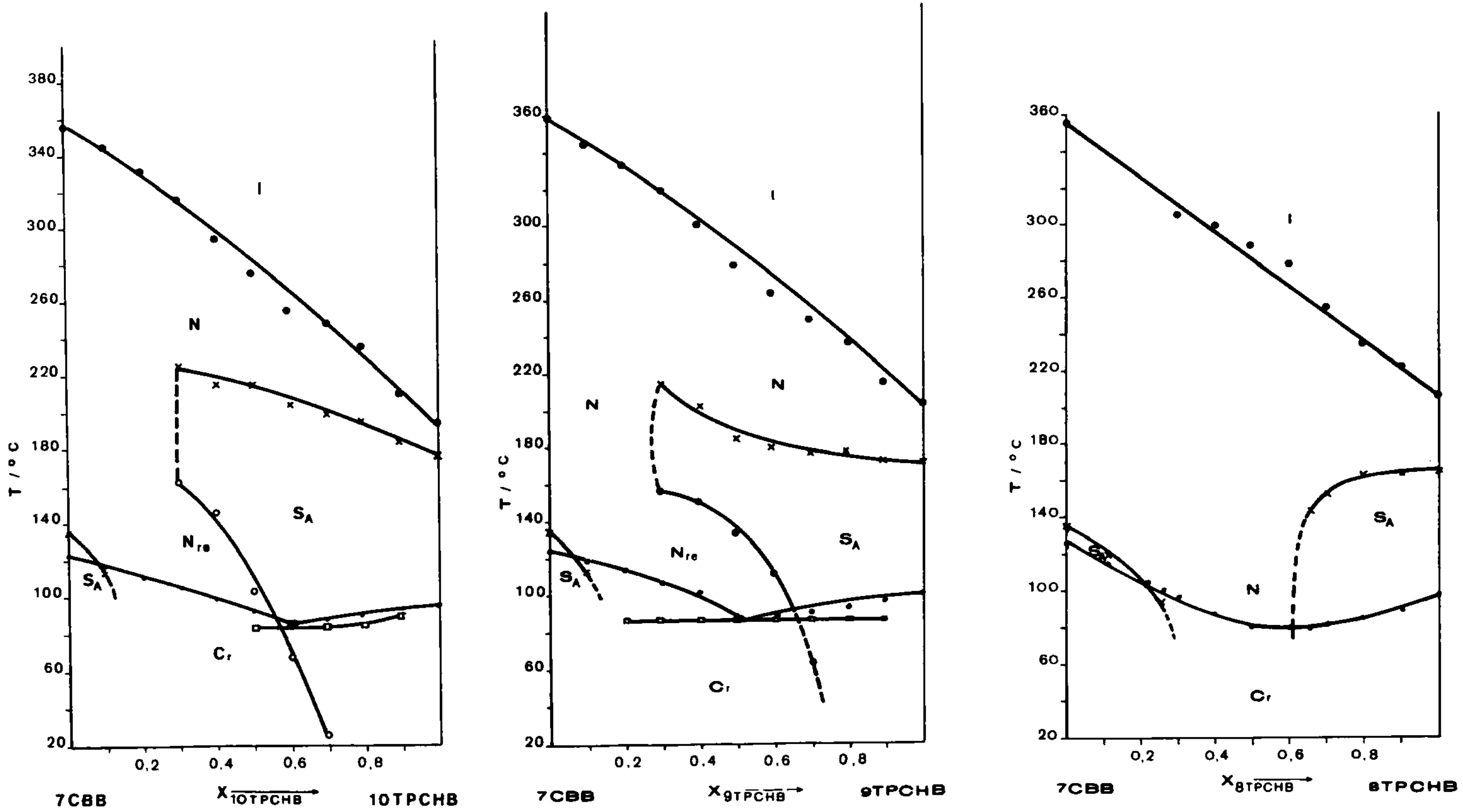

FIGURE 1 Phase diagrams of binary mixtures for the series I 7CBB–*n*TPCHB. a) $n = 10$, b) $n = 9$, c) $n = 8$, d) $n = 7$, e) $n = 5$.

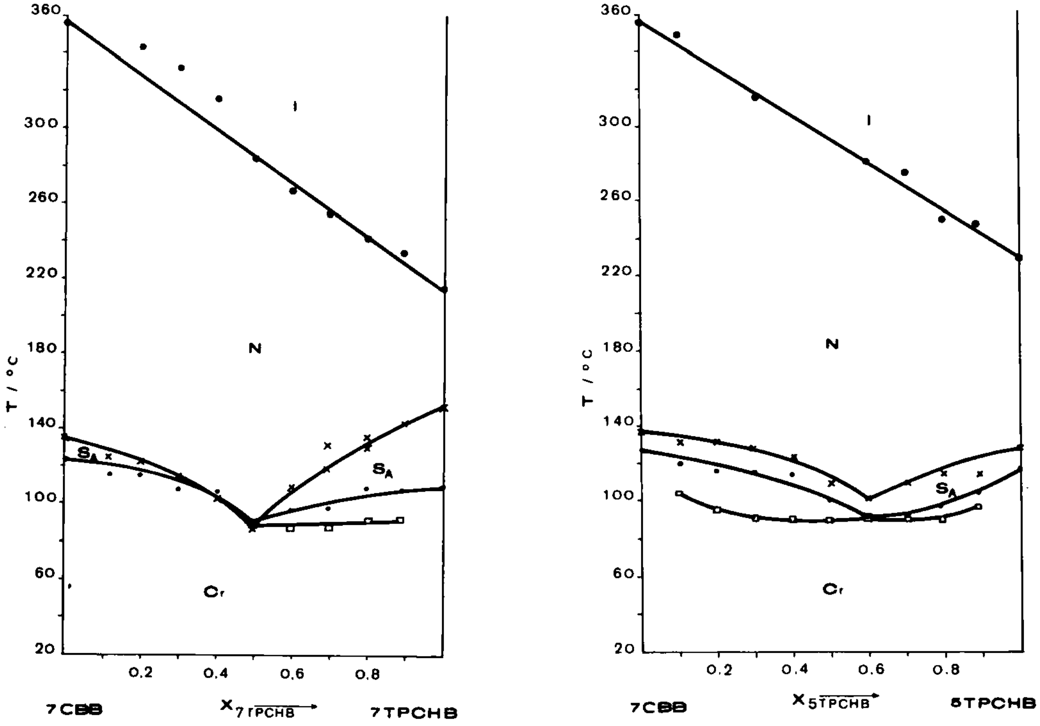

FIGURE 1 (continued)

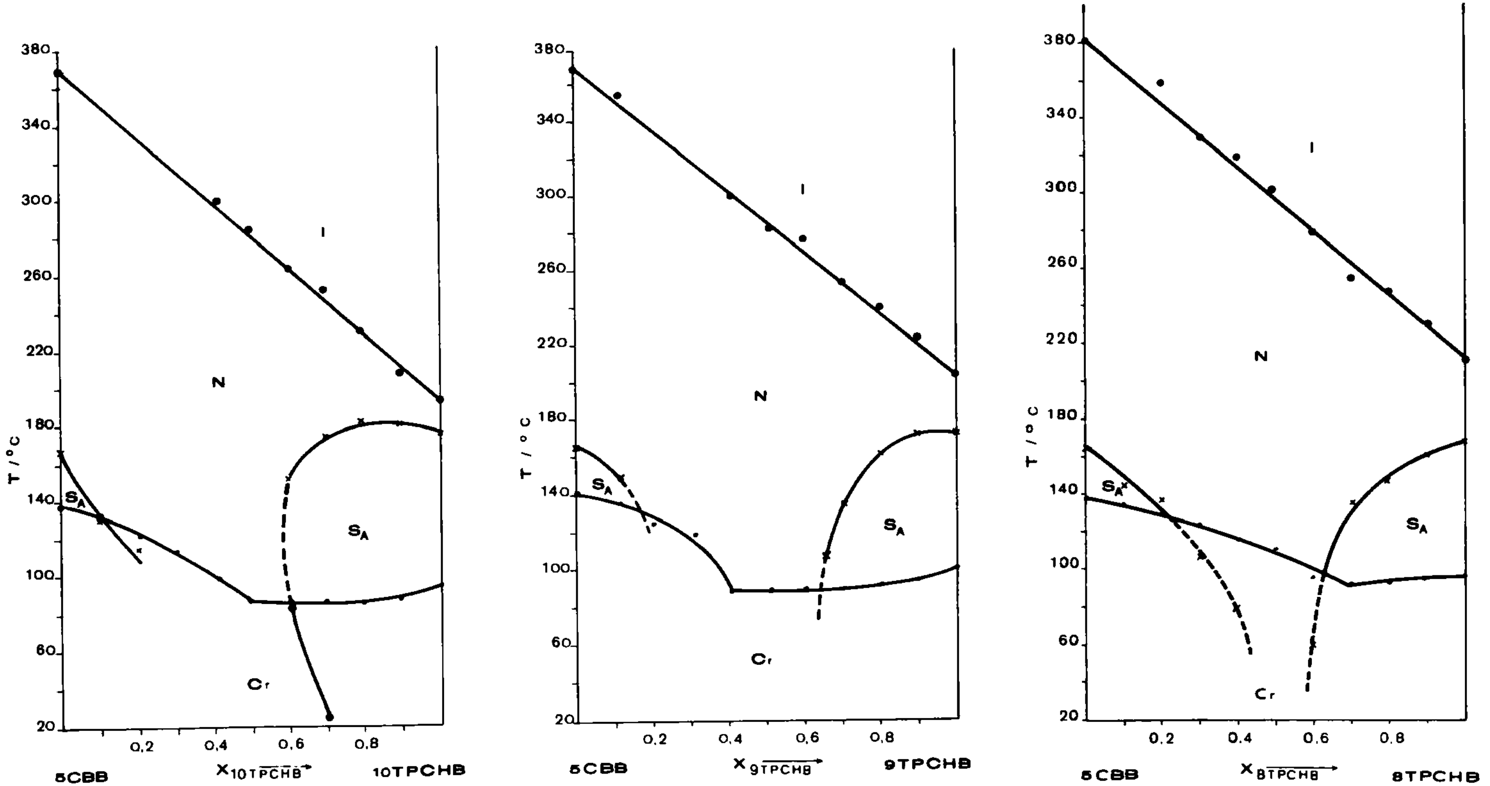

FIGURE 2 Phase diagrams of binary mixtures for the series II 5 CBB–*n*TPCHB. a) $n = 10$, b) $n = 9$ c) $n = 8$ d) $n = 7$ e) $n = 5$.

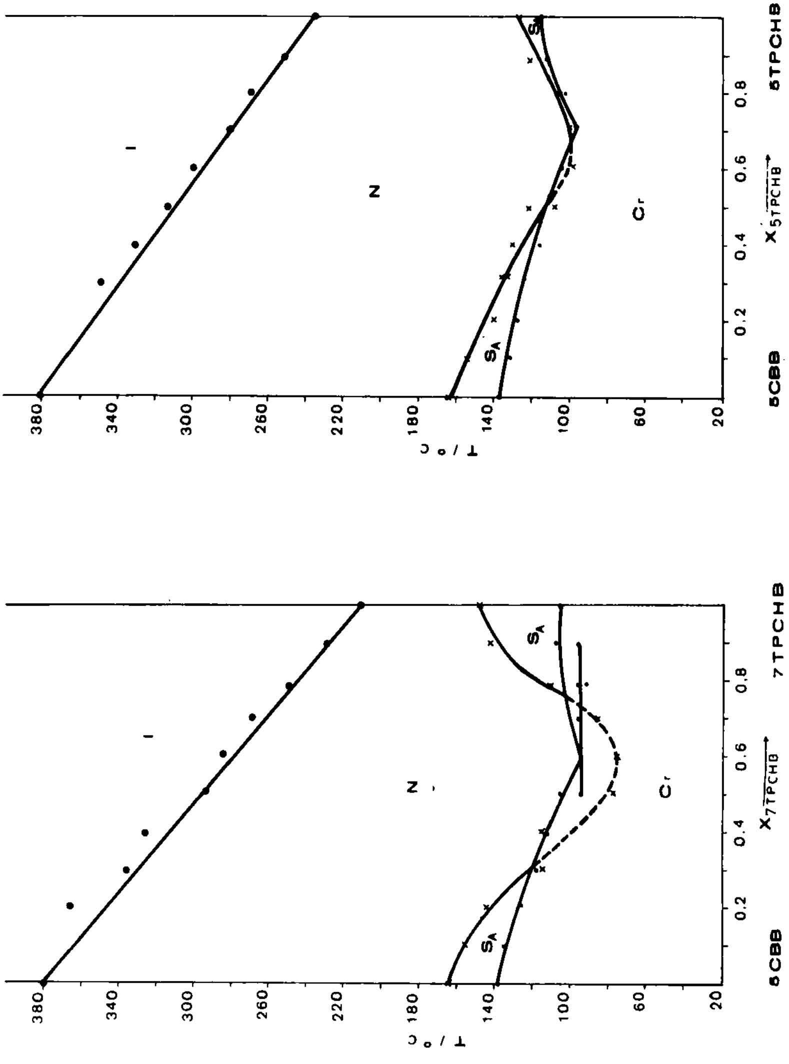

FIGURE 2 (continued)

occurs only in the 10TPCHB concentration range of 0.6–0.7 mole fraction as a monotropic phase. As the length of the chain decreases, the destabilization of the smectic phase of 5CBB becomes smaller and the region of the smectic phase on the side of *n*TPCHB is reduced. The nematic reentrant phase is observed in the 5CBB–9TPCHB system only for the mixture containing a 0.3 mole fraction of 9TPCHB (Figure 2b). In the system with the *n*TPCHB compound with a shorter aliphatic chain, $n = 8$, the reentrant nematic phase did not appear (Fig. 2c) and the nematic gap was distinctly narrower. In the case of systems in which the chain in *n*TPCHB is still shorter i.e. $n = 7$ or $n = 5$, the nematic gap is not observed at all. The observed phase boundary minimum becomes, like in series I, less and less pronounced and shifted towards higher concentrations of *n*TPCHB.

In Figure 3 the phase diagrams are shown of *n*CBB–10TPCHB systems with $n = 5, 6, 7, 8$. As it is seen, the decrease of the length of the aliphatic chain in *n*CBB results in the diminished destabilization of the smectic phase A on the side of the component *n*CBB and in the decreased extension of the smectic phase on the side of the component 10TPCHB. A similar effect of the length of the aliphatic chain was observed in References 5 and 6.

It deserves attention that the temperature boundary of the reentrant nematic phase appearing in systems including compounds *n*CBB that reveal the $A_1$ smectic phase where $n = 5, 6, 7$ remains unchanged for all three systems. The length of the chain influences only the range of concentrations in which the reentrant nematic phase occurs (Figure 3a).

Similar relationships are observed for the 5CBB–9TPCHB (Figure 1b) and 7CBB–9TPCHB (Figure 2b) systems. If the lengths of the aliphatic chain in *n*TPCHB is the same, the $N_{re} \rightarrow S$ phase transition points are identical for both systems in the concentration range in which the transition takes place.

It has been found that in the 8CBB–10TPCHB system (Figure 3b) the smectic $A_d$ phase of compound 8CBB reveals complete miscibility with the smectic A phase of compound 10TPCHB. A similar behavior was observed in References 5 and 6 for mixtures of 8CBB with 10FPCHB, 10TPCHB or 10APCHB.

## 3. DISCUSSION

The lack of miscibility of the $A_1$ smectic phases of the mixture components of similar molecule lengths is due to the dimerization of the *n*CBB compounds in the 10TPCHB matrix of lower polarity. It has been shown in References 5 and 6 that destabilization of the smectic $A_1$ phase of compounds *n*CBB ($n \leq 7$) is caused by non-commeasurability of the molecular dimension in the layer of the mixture composed of dimers (*n*CBB), and single molecules of 10TPCHB. At a certain concentration the ratio of dimers and single molecules is such that the smectic lattice is strongly disturbed and the nematic gap is created. Also the extension of the smectic $A_1$ region of the side of excess of the 10TPCHB component may be explained by formation of dimers $(n\mathrm{CBB})_2$. Hence the $S_{A_1} \rightarrow N$ transition temperature of the mixture changes as for a compound with a virtual transition $S_{A_d} \rightarrow N$ (component *n*CBB) and enantiotropic transition $S_{A_l} \rightarrow N$ (component 10TPCHB). The $S_{A_d}$

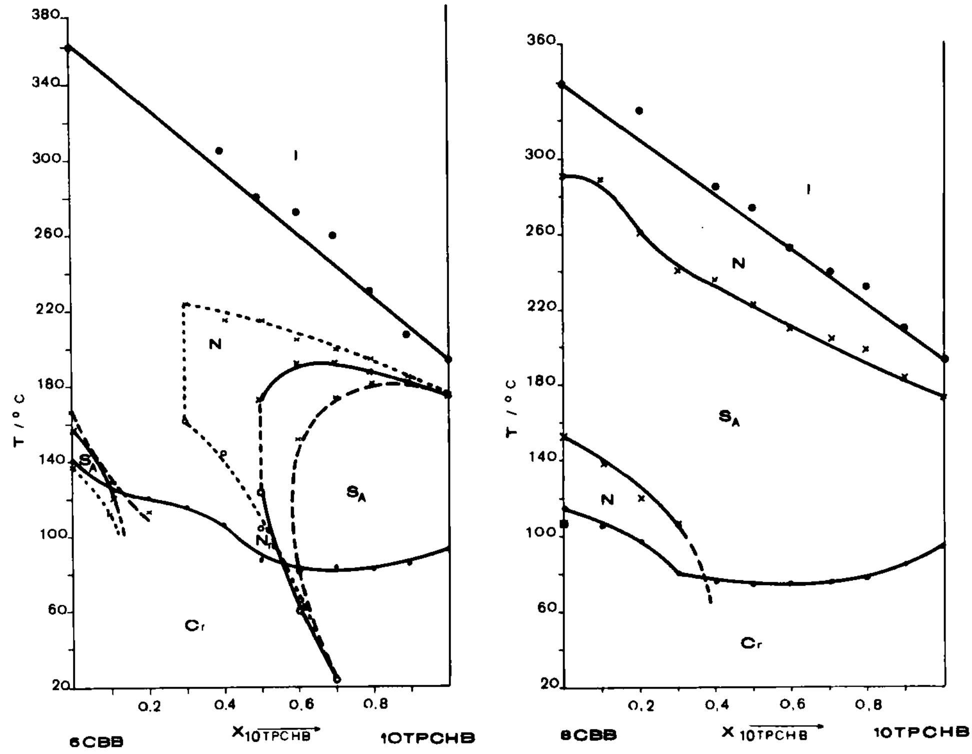

FIGURE 3 Phase diagrams of binary mixtures for the series III *n*CBB-10TPCHB. a) *n* = 6. The dashed line represent the $S_A$-N transition temperature for the 7CBB-10TPCHB system, the dotted line for the 5CBB-10TPCHB; b) *n* = 8.

phase of the *n*CBB compounds (*n* = 8) mixes with the $S_{A_1}$ phase of the 10TPCHB compound (Figure 3b).

In the tested *n*CBB-*n*TPCHB systems the destabilization of the *n*CBB smectic phase decreases and the extension of the smectic phase range on the side of component *n*TPCHB diminished with decreasing length of the aliphatic chain in compound *n*TPCHB. As the length of the aliphatic chain of the matrix decreases, the polarity of the system increases. In turn, the growth of polarity results in a decreased tendency of the *n*CBB compounds to dimerize.

An interesting relationship has been observed in the studied systems that relates to the temperature range of existence of the nematic reentrant phase. It has been found that in binary *n*CBB-*n*TPCHB systems the S → $N_{re}$ phase transition points depend on the kind of the *n*TPCHB component. In the case of equal length of the aliphatic chains in the *n*TPCHB matrix the boundary of the S → $N_{re}$ phase transition lies in the same temperature range irrespectively of the length of the terminal chain in the *n*CBB compound. Similar relationships are also observed for the *n*CBB-10TPCHB systems described in Reference 5.

The reentrant nematic phase is always related to the occurrence of comeasurability in the smectic phase, i.e. it occurs if monomers and dimers appear alongside. In the *n*CBB–*n*XPCHB binary systems the monomers of *n*XPCHB appear in the smectic phase in equilibrium with the monomers and dimers of *n*CBB. It follows from the studies presented here that the kind and concentration of the *n*TPCHB monomers has an essential effect on the temperature range of the nematic reentrant phase.

## Acknowledgements

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