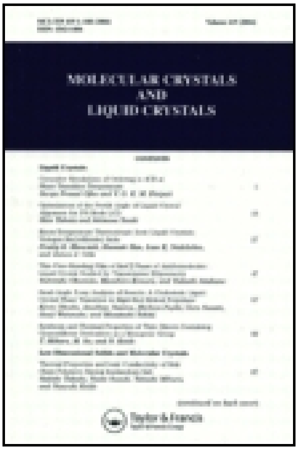

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INVESTIGATIONS OF MIXTURES OF POLAR AND NON-POLAR COMPOUNDS WITH THE A_1 SMECTIC PHASE

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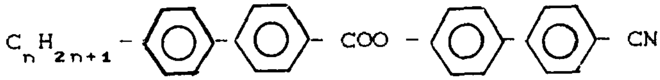
Abstract Binary mixtures composed of 8OBCAB with polar nTPCHB and nonpolar nMPCHB as well with nonpolar A-n compounds have been investigated. It is shown that dimerization of 8OBCAB compound takes place only in polar matrix. Study of the effect of dilution of the polar matrix nTPCHB with a nonpolar component nMPCHB is shown that generation of smectic A_d is due to the application a matrix with a long aliphatic chain and not to the lowering of its polarity.

INTRODUCTION

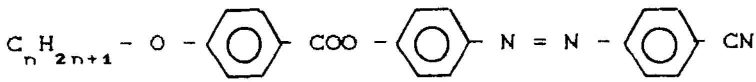
Studies conducted recently on mixtures of polar compounds with the A_1 smectic phase have shown that in some systems two opposed behaviours appear on the equilibrium plots. On one side of thediagram we observe a destabilization of the smectic phase leading to the appearance of the nematic gap, while on the other side of the diagram an enhancement of the smectic phase occurs with the appearance of the reentrant nematic phase [1-4].

In ref. [3,4] it has been shown that such behaviour is typical formixtures whose one component has a strongly polar terminal group CN and belongs to the homologous series in which the compounds with shorter aliphatic chains yield the A_1 smectic phase, and those with the longer chains yield the A_d smectic phase. 4-cyanobiphenyl-4-yl-4-n-al-kylbiphenyl 4-carboxylate of the formula



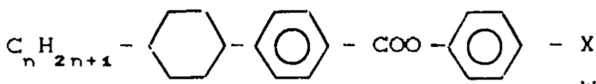
(nCBB),

as well as p-alkoxybenzoyloxy-p'-cyanoazobenzene of the formula



(nOBCAB)

are examples of such compounds. The second component of these mixtures is a component of smaller polarity reveiling only the A_1 smectic phase. The compounds used here belong to the 4(trans-4n-alkylcyclohexyl)benzoate homologous series nXPCHB of the formula



where X=F, $COCH_3$, NCS.

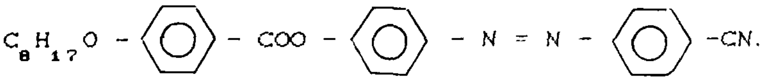
This non-typical behaviour is due to that the compound with the strongly polar terminal group CN revealing the A smectic phase in mixtures yields the A_d smectic phase [2,3]. When mixing the compound 8OBCAB with nTPCHB compounds we observe that the A_d smectic phase and the N_{re} one are generated only then when the component nTPCHB has an aliphatic chain with n $\geq$ 9.

Since the growth of length of the aliphatic chain produces a lowering of polarity of the system, it was initially expected that the decrease of polarity of the matrix enhances the process of generation of the S_{Ad} and N_{re} phases in the mixtures.

In the present work the effect of the decreasing polarity of the system due to the increase of the length of the aliphatic chain of the polar matrix or to dilution of the latter with a non-polar component on the appearance of the enhanced smectic phase will be studied, and besides systems with polar and non-polar matrices with chains of various lengths will be compared and the behaviour of compound 8OBCAB in both types of matrices will be explained.

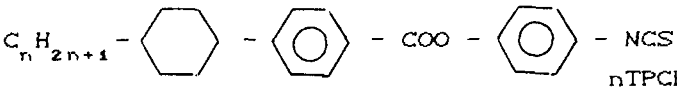
MATERIALS AND METHODS

In the experiment we used 4-octyloxybenzoyloxy-4'-cyanoazobenzene (8OBCAB) of the formula



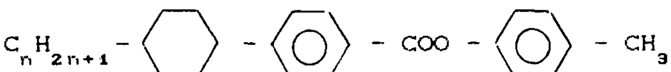
This compound was mixed with:

(1) polar compounds belonging to the 4-isothiocyanatophenyl 4-(trans-4-alkylcyclohexyl)benzoate homologous series of the formula



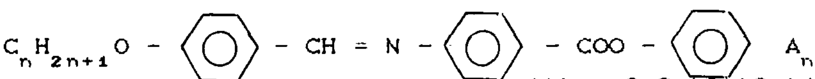
nTPCHB, n=12,10 or 5

(2) non-polar compounds from the methylphenyl 4(trans-4-alkylcyclohexyl) benzoate series of the formula



nMPCHB with n=12,10 or 5

(3) non-polar compounds of structure similar to that of 8OBCAB from the phenyl 4(4-alkoxybenzylidene-amino)benzoate homologous series of the formula



A_n with n=8,9,10,12,14 or 16.

The enumerated compounds have the smectic A phase coexisting with the nematic. Except the compound 5MPCHB that only shows the nematic phase.

Besides, two series of ternary systems were tested. They were treated, however as binary systems. One component was 8OBCAB and the second one was the mixture of polar and non-polar components. In the first series the matrix was a mixture of compounds 12TPCHB + 12MPCHB in various proportions. In the second series the matrix was a mixture of 10TPCHB + 5MPCHB.

The phase diagrams were obtained by the thermomicroscopic

method described in ref. [1]. The observation of the phase transitions were conducted by means of a polarization microscope with a heated stage manufactured by VEB Analytic Dresden.
For selected systems X-ray measurements were made of the smectic layer spacings in the Guinier camera by the free standing film method described in ref. [5].

RESULTS AND DISCUSSION

Comparison of the mixtures of compound 8OBCASB with polar and non-polar matrices.

The equilibrium phase diagrams of mixtures of 8OBCAB with polar (nTPCHB) and non-polar (nMPCHB) components with aliphatic chains of the same length are presented in Fig. 1. The 8OBCAB-10TPCHB system was already described in ref.[5]. If we compare that system with the syst ems 8OBC-AB-12TPCHB we can see that the character of their behaviour is similar. However, if we use a polar compound with a longer aliphatic chain (n=12) as a matrice we can see that the A smectic phase vanishes quickly on the side of excess of the 8OBCAB component, while on the side of excess of component nTPCHB this phase is significantly enhanced. The use a polar compound with a shorter aliphatic chain (5TPCHB) as a matrice results in that the above described anomalies do not occur. The smectic phases A_1 of both components mix completely. In the diagram we can see only small deviations of the $S_A \rightarrow N$ phase transition line from theoretical one for ideal solutions.
X-ray measurements of smectic layer spacing were carried out for the above systems. The results for the 8OBCAB-10TPCHB system have already been described in ref. [3]. The data for the 8OBCAB-12TPCHB systems are summarized in table 1. The experimentally measured smectic layer spacings for the tested systems have been compared with those

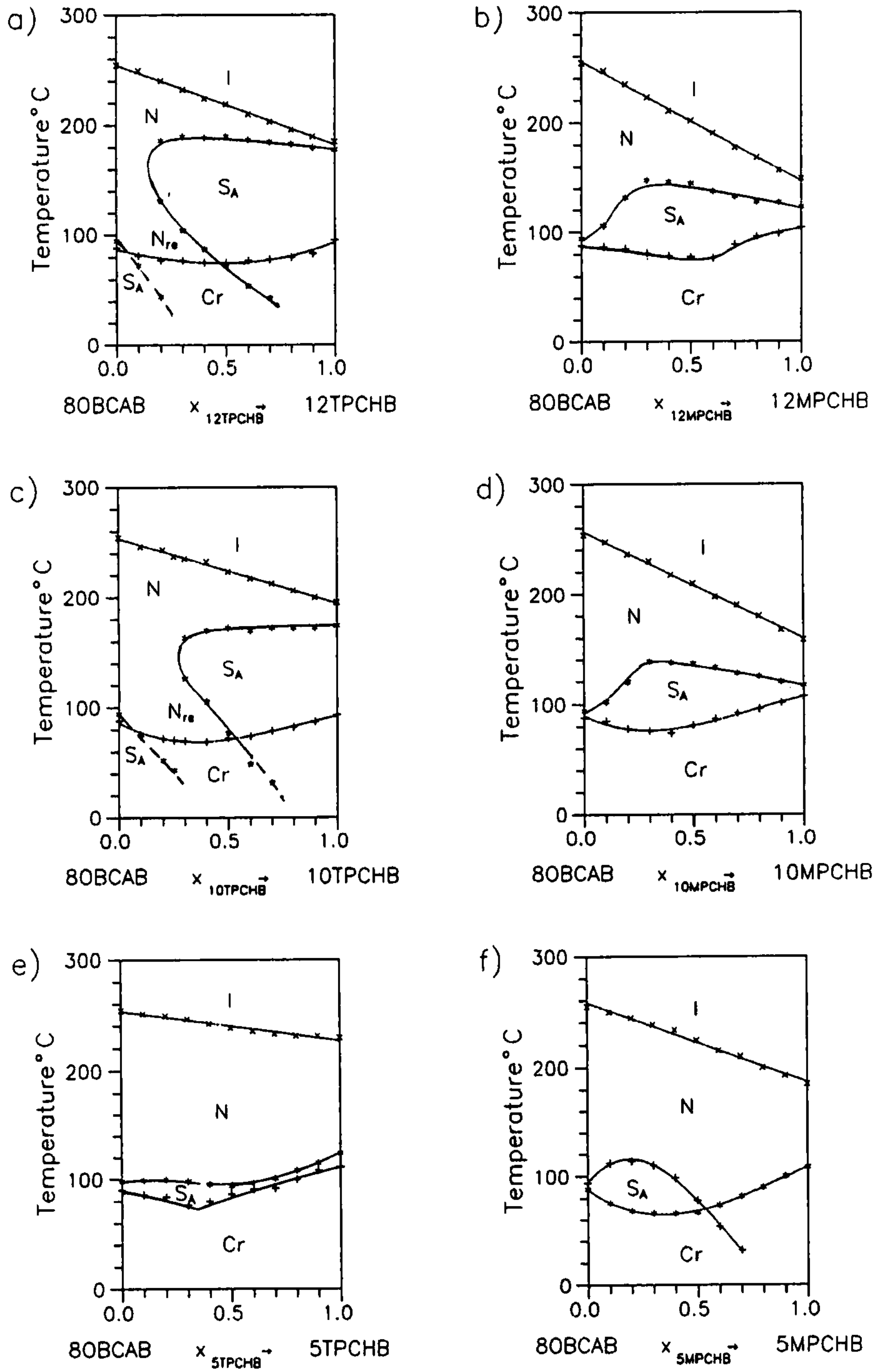


Fig. 1. Phase diagrams of 8OBCAB-nTPCHB and 8OBCAB-nMPCHB.

Table 1. Smectic layer spacing for 8OBCAB-12TPCHB

mole fraction of 12TPCHB $x_{12TPCHB}$	temperature of measurement °C	measured smectic layer spacing d/nm	calculated smectic layer spacing case I d/nm	calculated smectic layer spacing case II d/nm
0	90	3,045		
	95	3,060		
0.2	140	3,795	3,1668	3,360
	160	3,847		
0,5	100	3,657	3,342	3,482
	120	3,661		
	140	3,698		
0,8	100	3,723	3,597	3,653
	120	3,755		
	140	3,744		
1,0	100	3,634		
	120	3,669		
	140	3,739		

Table 2. Smectic layer spacing for 8OBCAB-5TPCHB

mole fraction of 5TPCHB x_{5TPCHB}	temperature of measurement °C	measurd smectic layer spacing d/nm	calculated smectic layer spacing case I d/nm	calculated smectic layer spacing case II d/nm
0	95	3,05		
0,55	90	2,89	2,87	3,045
1	120	2,70		

Table 3. Smectic layer spacing for 8OBCAB-10MPCHB system

mole fraction of 10MPCHB $x_{10MPCHB}$	temperature of measurement °C	measured smectic layer spacing d/nm	calculated smectic layer spacing case I d/nm	calculated smectic layer spacing case II d/nm
0,0	90	3,045		
	95	3,060		
0,2	90	3,012		
	100	3,029	3,026	3,230
	110	3,058		
0,5	80	2,960		
	100	2,980	2,980	3,130
	120	3,031		
0.8	100	2,948	2,953	3,009
	110	2,969		
	120	2,969		
1,0	110	2,929		

calculated under the assumption of additive mixing of smectic layers. The calculations were made using this formula

$$d_m = X_{8OBCAB} d_{8OBCAB} + X_{8OBCAB} d_{nTPCHB}$$

where: X is the molar fraction of the given compound, d is the smectic layer spacing. The smectic layer spacings were calculated for two cases:

case I - the A_1 smectic phases of both compounds combined,

case II - the A_1 smectic phase of the component nTPCHB combines with the virtual A_d smectic phase of compound 8OBCAB (dimeric structure).

The spacing of the virtual smectic layer A_d of 8OBCAB is unknown, we assumed that it has an analogous structure to the A_d layer of 9OBCAB. The smectic layer spacing of the latter compound is known and it is equal to 3.57 nm. According to the A_d smectic layer model of Longa and de Jeu [6] the smectic layer spacing of compound 8OBCAB is smaller by the length of two methylene groups and amounts to 3.33 nm.

The smectic layer spacings measured for the 8OBCAB-12TPCHB system are close to those calculated in accordance with the case II, and much higher than those calculated according to the case I. Similar data have been obtained in [3] for the 8OBCAB-10TPCHB system. This indicates that in these systems the smectic phase of 8OBCAB undergoes restructuring. This compound in mixtures with a component with a long aliphatic chain yields the A_d smectic phase.

The study of smectic layer spacing for the 8OBCAB-5TPCHB system (table 2) has shown that the measured various are almost identical with those calculated according to the case I. This indicates that in case of a polar matrix with a short chain the A_1 smectic phase of component 8OBCAB does not undergo rearrangement. This conclusion is confir med by the result of thermomicroscopic tests of this system. The studies of mixtures of 8OBCAB with the non-polar matrix nMPCHB have been carried out for a compound with the same length of the aliphatic chain as for the polar matrix, i.e. n=12,10 or 5. The equilibrium diagrams for these systems are presented in Figs. 1d,1e and 1f. In these diagrams we can see that in case of a non-polar matrix an extension of the range of the smectic phase also occurs.

This extension occurs irrespectively of the length of the aliphatic chain. Even in the case of 5MPCHB, i.e. compound with the shortest chain which as the pure component does not yield the smectic phase, an extension takes place in the concentration range X=0.1 to 0.3 molar fraction of component 5MPCHB. Besides, in distinction from the system with the polar matrice neither destabilization of the A_1 smectic phase occurs nor the nematic reentrant phase is formed.

The X-ray studies of the smectic layes spacing were carried out, in view of the similarity of behaviours, only for one system, i.e. 8OBCAB -10MPCHB. The results are summarized in Table 3. Like the former series the experimental values have been compared with the theoretical ones found according to the both cases. The measured values are close to those calculated from the case I ,i.e. under the assumption that the A_1 smectic phases of both components combine. These data indicate that the A_d phase is not generated in the system. The increase of stability of the smectic phase is connected in this case with the generation of the so-called enhanced smectic phase.

There were also studied systems in which compound 8OBCAB was mixed with non-polar component A_n of a different chemical structure of the core, however, similar to that of 8OBCAB. The equilibrium diagrams of the 8OBCAB-A_n systems are shown in Fig. 2. In this series of studies,

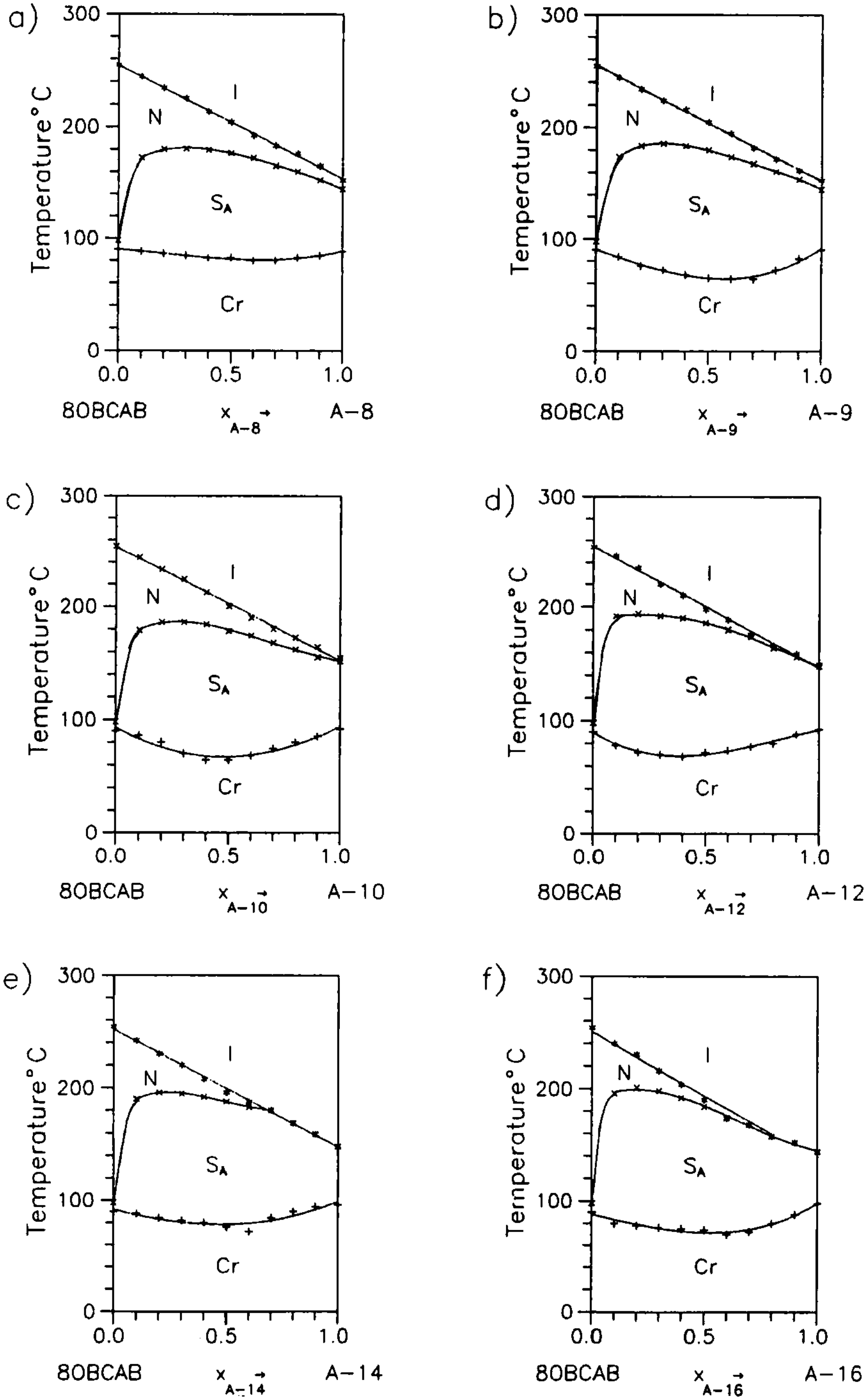


Fig. 2. Phase diagrams of 8OBCAB-A$_n$ systems.

like in case of 8OBCAB-nMPCHB systems, a significant increase of stability of the A smectic phase took place. This increase was observed already at concentrations X=0.1 molar fraction of component A_n. The character of changes of the smectic layer stability was similar in all six systems. The length of the aliphatic chain of the non-polar component did not seem to have any effect. The reentrant nematic phase was not observed in any of the systems.

X-ray studies of the smectic layer spacings were carried out only for the 8OBCAB-A_{10} system. The results show (table 4) that A_1 smectic phases of both components combine. These data indicate that in case of a fully non-polar matrice no dimerization of component 8OBCAB occurs.

Table 4. Smectic layer spacing for 8OBCAB-A_{10}

mole fraction of A_{10}	temperature of measurement	measured smectic layer spacing	calculated smectic layer spacing	
			case I	case II
x_A	°C	d/nm	d/nm	d/nm
0	95	3,05		
0,3	100	3,169	3,092	3,33
1	100	3,189		

Study of the effect of dilution of the polar matrix with a non-polar component.

There have been studied systems in which the matrix consisted of a mixture of polar and non-polar compounds with long aliphatic chain (12TPCHB + 12MPCHB) and a polar compound with a long chain and a non-polar compound with a short chain (10TPCHB + 5TPCHB). The results of thermomicroscopic tests of both series are shown in Figs. 3 and 4. It follows from these data that the length of the aliphatic chain of the non-polar component affects the destabilization of the A_d smectic phase. Addition of a non-polar component with a long aliphatic chain, 12MPCHB (Fig. 3) results in that the destabilization of A_1 phase of 8OBCAB

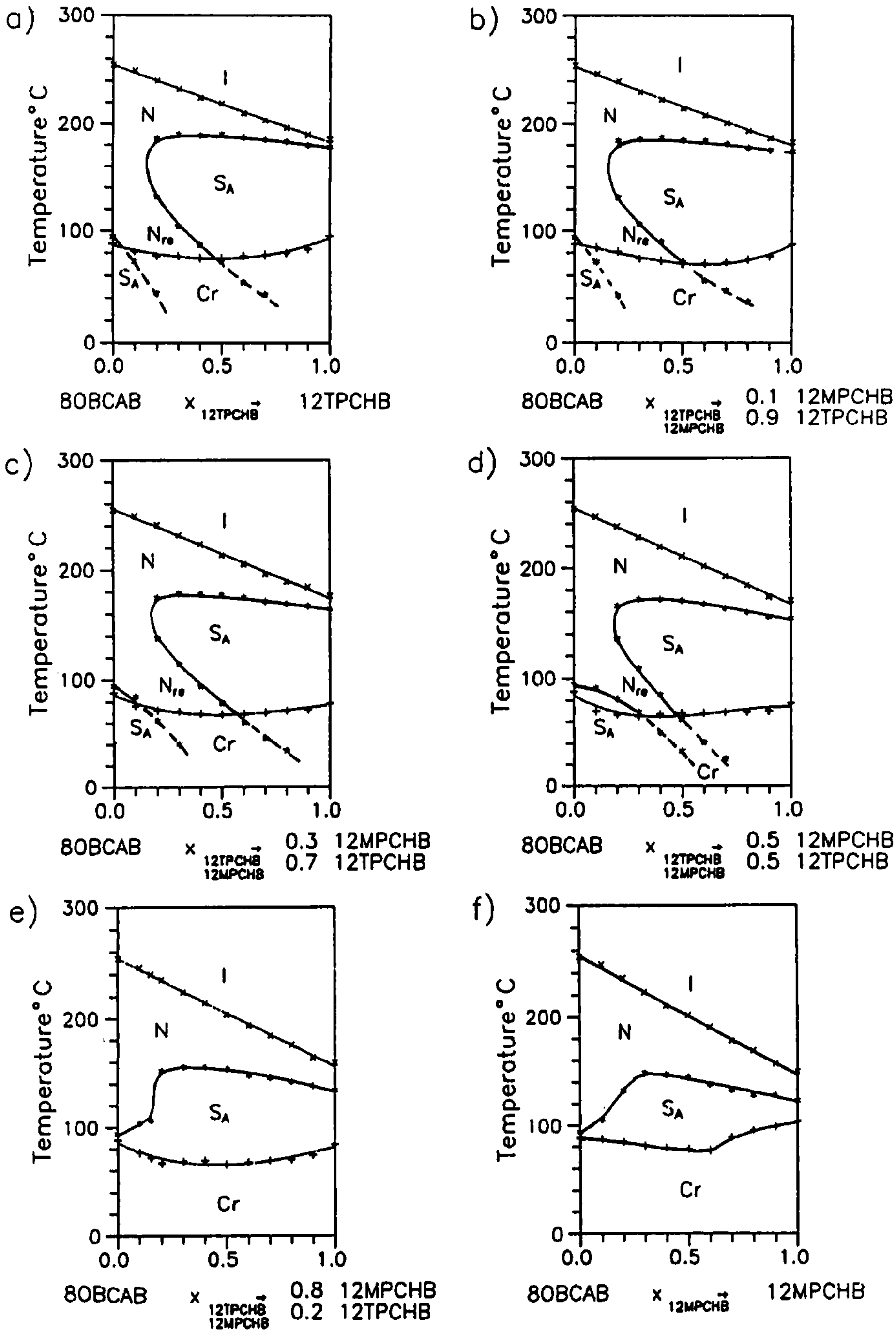


Fig. 3. Phase diagrams of 8OBCAB+(12TPCHB+12MPCHB).

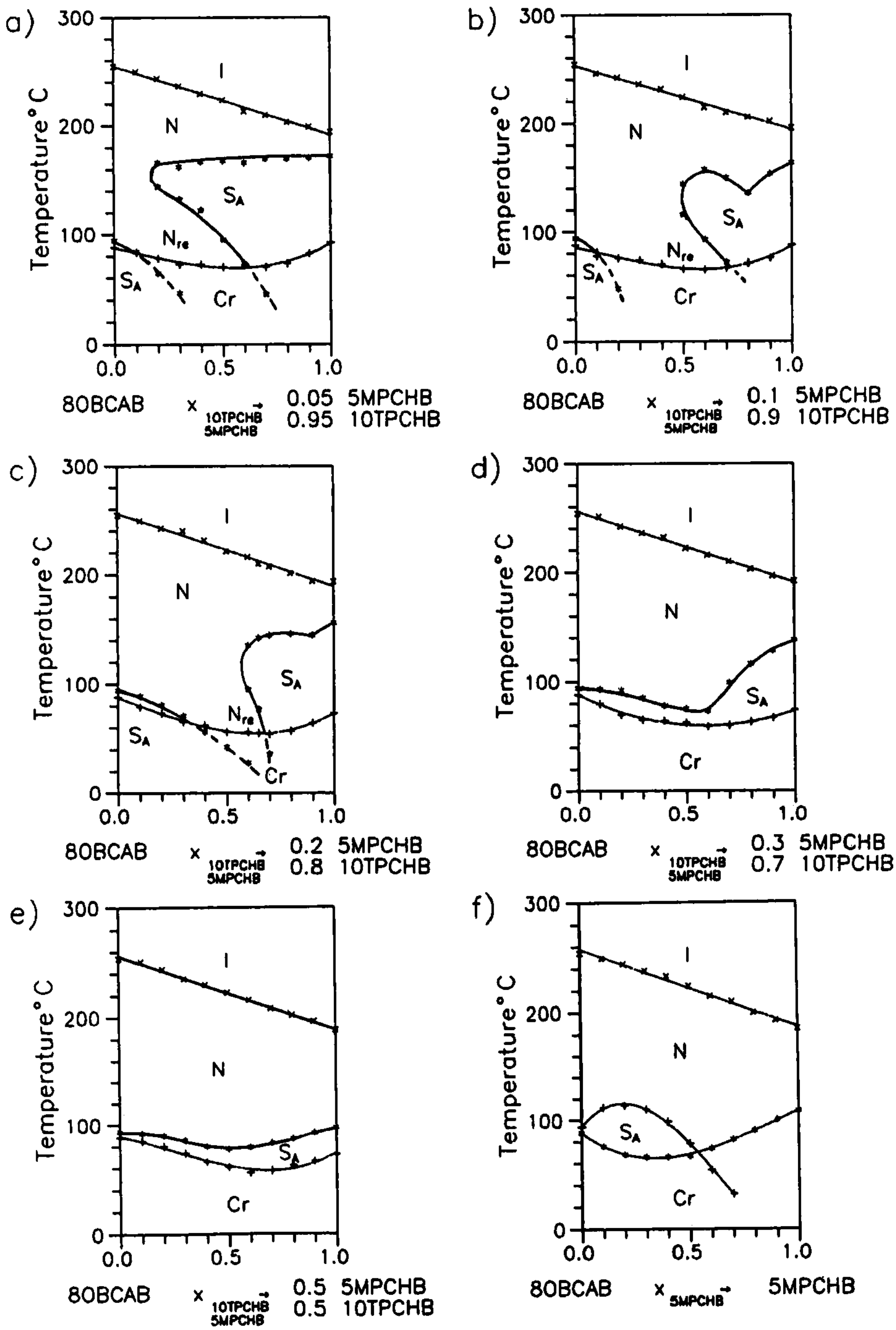


Fig. 4. Phase diagrams of 8OBCAB+(10TPCHB+5MPCHB).

does not proceed rapidly before and the A_d smectic phase, as well as the reentrant nematic phase exist up to the content of X = 0.5 molar fraction of component 12MPCHB in the mixture. Similar mixtures comprising the component with yhe short chain, 5MPCHB (Fig. 4), its amound of X = 0.3 molar fraction causes, in turn, that the nematic reentrant phase does not occur what indicates that the A_d smectic phase is not generated.

CONCLUSIONS

The studies indicate that:

(1) Generation of the A_d phase is due to the use of a matrice with a long aliphatic chain and not to the lovering of its polarity.

(2) Extension of the length of the aliphatic chain of the polar matrix nTPCHB from n=10 to n=12 enhances the generation of the A_d smectic structure of component 8OBCAB.

(3) Use of a non-polar matrix stabilizes the A_1 smectic phase irrespectivly of the length of the aliphatic chain and results in the generation of the enhanced A_1 smectic region.

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