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INDUCTION OF SMECTIC A_d PHASE IN BINARY MIXTURES COMPOSED OF COMPOUNDS WITH NEMATIC OR SMECTIC PHASES

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Abstract Two series of binary mixtures nBCB-nTPCHB and nCPB-nTPCHB were investigated by the thermomicroscopic method. A strong enhancement of the smectic phase region with simultaneous appearance of the reentrant nematic phase on the phase diagrams is observed. The appearance of the reentrant nematic phase confirm that the smectic A_d phase is formed in these binary mixtures. It was shown that the length of the aliphatic chain of both component plays an important role on the induction of the smectic A_d and nematic reentrant phase.

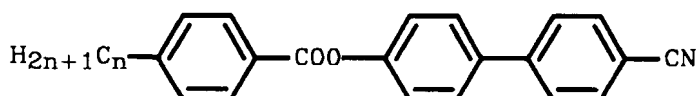
INTRODUCTION

The smectic A_d phase was identified for the first time in 1974 by Gray¹. This phase concentrate large interest especially after the discovery by Cladis of the reentrant phase phenomenon². Nevertheless, despite numerous studies, the model of the smectic A_d phase as well as the reentrant phase phenomenon have not been as yet fully explained. It has been found, however, that the nematic reentrant phase exist below the range of existence of the smectic A_d ($N-S_A-N_r$)³. Therefore the observed occurrence of the reentrant nematic phase in polar A_1 smectic systems was not typical⁴. In the course of a range of studies it was found that those non-typical behaviours are due to the induction of the A_d smectic phase. So far this induction was observed in A_1 polar smectic systems in which one of the components belong to a homologous series with a strongly polar CN terminal group, and the members of this series with a long alkyl chain yield the A_d smectic phase. In works⁴⁻⁹ series nCBB and nOBCAB fulfilling this condition were studied. As second component of the mixtures in which induction of the A_d smectic phase occurs compounds belonging to the 4X-phenyl 4- (trans-4n-alkylcyclohexyl) benzoates series were used (were $X=NCS, F, Br, I, ClOCH_3$). At present these compounds are classified in the enhanced A_1 smectic phase, A_{1e} ¹⁰.

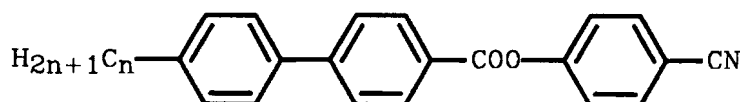
The aim of the present work was to study the possibility of smectic A_d phase induction also for systems in which the component with the terminal CN group does not yield at all the smectic phase but only the nematic one.

MATERIALS AND METHODS

For the study two homologous series were selected basing on Nguyen data¹¹ so that the members with short aliphatic chains $n \geq 7$ yielded solely the nematic phase, and those with long chains $n \geq 8$ the smectic A_d one. These were esters: 4-cyanobiphenyl-4'-alkylbenzoate of the formula

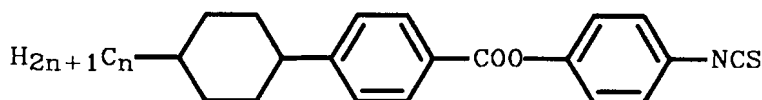


denoted as BCB with $n=5,6,7$
and 4-cyanophenyl-4'-alkylbiphenylcarboxylate of the formula



denoted as nCBB with $n=5$ and 7 .

These compounds were combined with a component belonging to the isothiocyanatophenyl 4-(trans-4-n-alkylcyclohexyl)benzoate homologous series of the formula



denoted as nTPCHB with $n=5,6,7,8,9,10$, and 12 .

The following series of the binary mixtures have been studied:

I 7BCB - nTPCHB for $n=5,6,7,8,9,10$ and 12

II nBCB - 12TPCHB for $n=5,6,7$

III 7CPB - nTPCHB for $n=5,6,7,8,9,10$ and 12

IV nCPB - 12TPCHB for $n=5$ and 7

The phase diagrams were obtained by the thermomicroscopic method.

RESULTS AND DISCUSSION

The results for the series I and II are presented in fig.1, and those for series III and IV in fig.2. As it is seen the smectic A_d phase is induced in the systems nBCB-nTPCHB which points to the presence of the reentrant nematic phase in these systems. However, the length of the aliphatic chain in both components has been found to have a significant effect. The effect of the length of the aliphatic chain of the component nTPCHB (series I and III) is revealed by that the reentrant nematic phase occurs when the aliphatic chain of compound nTPCHB is longer and so for the series 7BCB-nTPCHB (fig.1) beginning with 7BCB-6TPCHB, i.e for $n \geq 6$, and for the series 7CPB-nTPCHB (fig.2) beginning with 7CPB-8TPCHB, i.e $n \geq 8$. As the length of the aliphatic chain of component nTPCHB increases we observe the increase of the range of appearance of the induced A_d smectic phase, i.e both the concentration and temperature ranges.

The effect of the length of the aliphatic chain of compounds nBCB or nCPB may be observed for the series II and IV in Figs. 1g, 1h, 1i and Fig.2g and 2h. It has been shown that the induction of the A_d smectic phase takes place in all the studied systems nBCB-12TPCHB and nCPB-12TPCHB, however, the range of occurrence of the induced A_d smectic phase decreases with decreasing length of the aliphatic chain of components nBCB and nCPB.

Similar relations concerning the effect of the length of the aliphatic chain on the smectic phase induction were obtained for the nOBCAB-nTPCHB series⁹, and for nCBB-nTPCHB⁶. In work¹² it has been shown in distinction that induction of nBCB with a strongly polar terminal group CN is possible.

It follows from the presented studies that the ability of induction of the smectic A_d phase depends on the chemical structure of molecules with the terminal group CN. The compounds of the series nCPB reveal a much lower ability to yield the smectic A_d phase as compared with the compounds from the nBCB series. This follows from the range of existence of the smectic A_d phase as well as from the calculated for the systems 7BCB-12TPCHB (fig.1g) and 7CPB-12TPCHB (fig.2g) temperatures of the virtual phase transition SA_d-N which for 7BCB and 7PCB is 170°C and 145°C , respectively.

The induction of the smectic A_d phase in the tested systems is due to the properties of the compounds with the polar terminal group CN (nBCB and nCPB). The compounds from these series with long aliphatic chains, $n \geq 8$, may yield the smectic A_d phase. The compounds with short chains do not yield the smectic A_d phase for steric reasons. The formation of (nBCB)₂ or (nCPB)₂ dimers by compounds with low values of n ($n \leq 7$) would lead to the generation of voids. Such tendencies are in agreement with the calculations made by Madhusadana¹³. It is only the presence of component nTPCHB with a suitably long chain that stabilizes the laminar structure of the dimers (nBCB₂) or (nCPB₂), since the long chain of the nTPCHB allows for better filling of the voids created after the production of the dimers. Also in models of smectic A_d described by Longa and de Jeu¹⁴ and Netz and Berker¹⁵ the length of the aliphatic chain play an imported role.

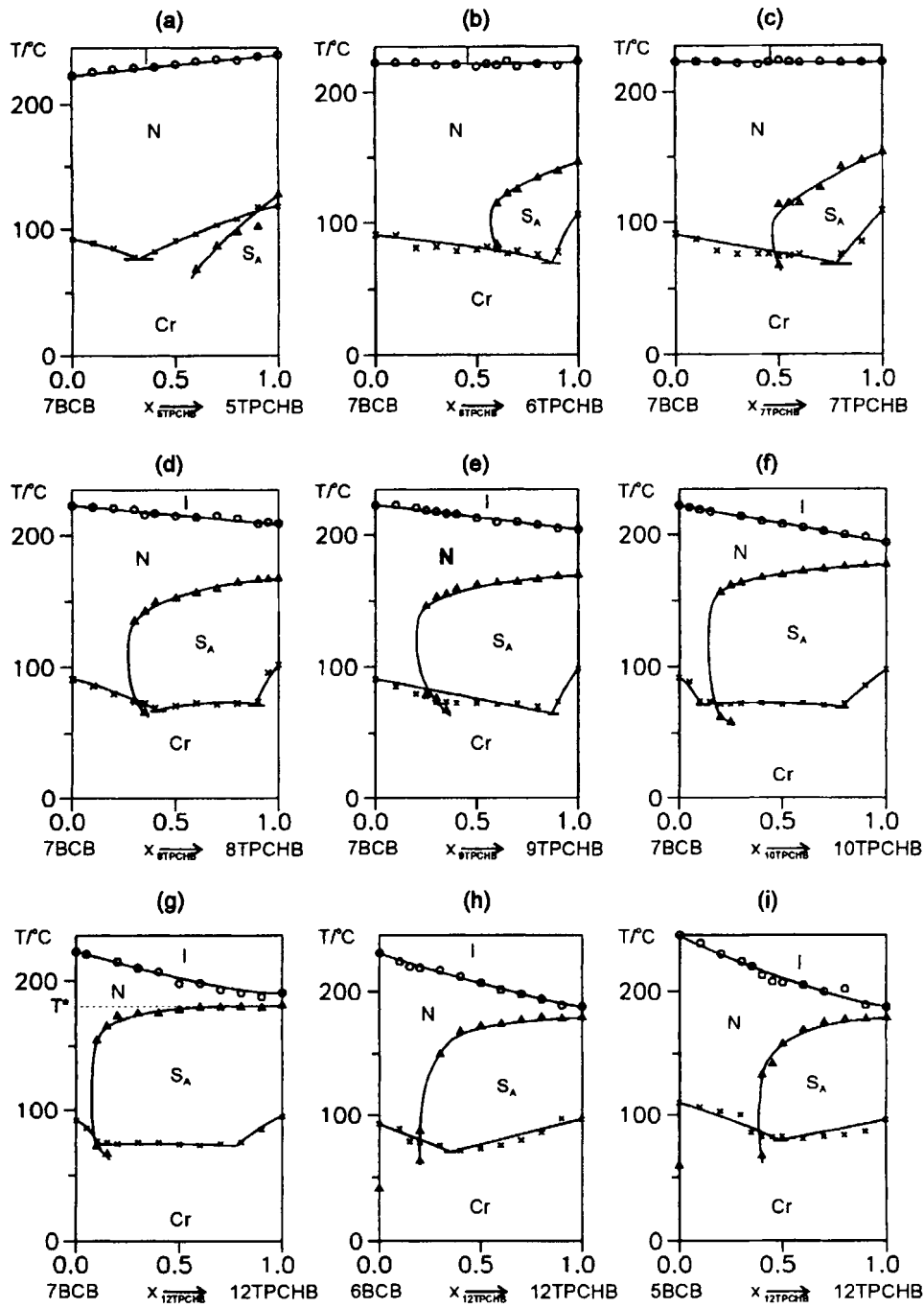


FIGURE 1 Phase diagrams of the nBCB-nTPCHB

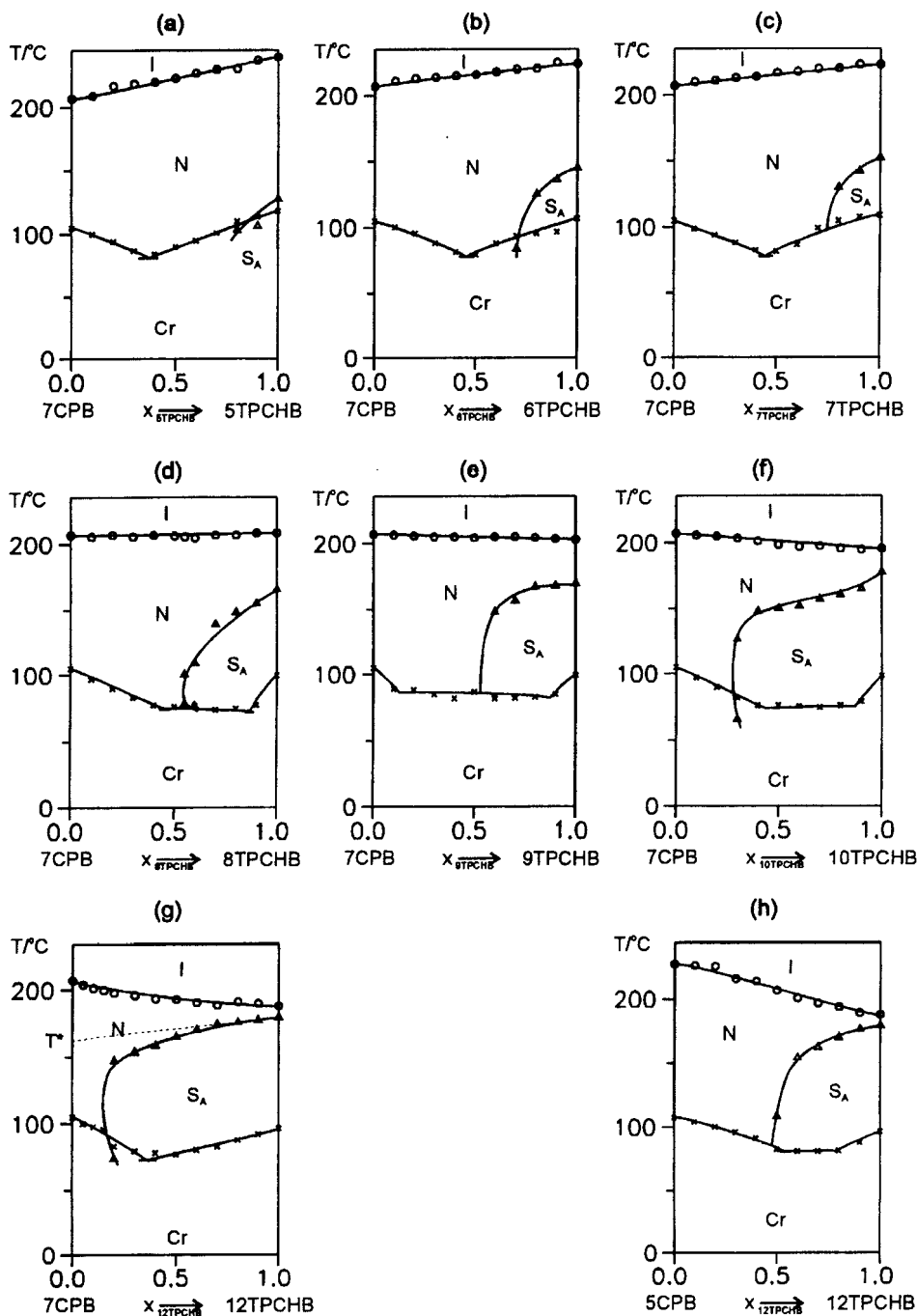


FIGURE 2 Phase diagrams of the $n\text{CPB}-n\text{TPCHB}$

CONCLUSIONS

It has been found that the phenomenon of induction of the smectic A_d phase occurs for compounds with a strongly polar terminal group CN of the homologous series which can produce the smectic A_d phase for members with long aliphatic chains, irrespective of that whether they yield a smectic A_l phase or a nematic one for members with a short aliphatic chain. Such compounds contain the so-called virtual smectic A_d phase. This phase appears in suitable condition, viz. after addition of a component that does not yield the smectic A_d phase but has a longer aliphatic chain.

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