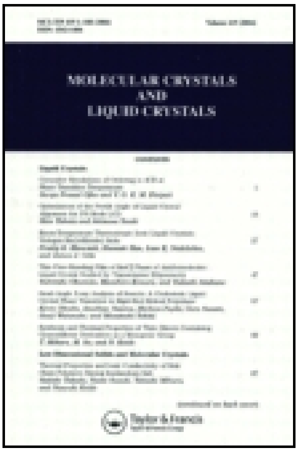

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Induction of Smectic A_d, Phase in Mixtures of Polar Esters

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INDUCTION OF SMECTIC A_d PHASE IN MIXTURES OF POLAR ESTERS

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Abstract Bicomponent mixtures of esters (4-cyanobiphenylyl-4′ 4′-alkylbiphenylcarboxylate-4 (nCBB) or 4-cyanobiphenylyl-4′ 4-alkylbenzoate (nBCB) with 4-cyanophenyl 4-alkylbenzoate (n.CN)) were studied by the thermomicroscopic method and their phase diagrams were established. The strong enhancement of a smectic A_d phase in mixtures with the smectic members of n.CN ($n>9$) and the induction of a smectic A_d phase in a shape of an island surrounded by a nematic phase in mixtures with the nematic members of nCB ($n\leq 9$) were observed. The influence of the aliphatic chain length on the observed phenomenon was discussed. The temperatures of transitions from the virtual A_d to the nematic phase for pure nCBB and nBCB were estimated.

INTRODUCTION

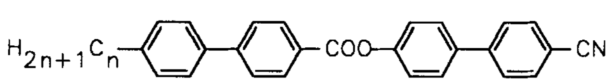
Liquid crystals have variety of phases. The additional feature of them is that it is possible to obtain other phases in the mixture than the pure components have. It is the well known behavior of the induction of liquid crystalline phases.[1] Two compounds can have only smectic phase and in their mixture the nematic phase can appear.[2,3] The less ordered smectics can appear in the mixture of more ordered smectics, for example smectic A in the mixture of compounds with smectic E phase.[4-6] Mixing nematic compounds it is possible to obtain the smectic phases. The known behavior is the induction of smectic A_1, B and E phases. Recently we have found the bicomponent mixtures in which the induction of A_d phase is possible.[7] This is the continuation of previous work.

We have tested few esters of similar structure, differing the number of benzene rings in the rigid core. They belong to the homologous series which members with longer alkyls have smectic A_d phase and with shorter alkyls have nematic or nematic and smectic A_1 phase. Many examples of such homologous series were given by Nguyen.[8] The compounds have tendencies to create nematic reentrant phase. Mixing compounds with long core and short core which do not have smectic A_d phase causes that this phase appears in the mixture. The innovation is that the induced smectic A_d phase appears in a shape of an elliptical island surrounded by a nematic phase.

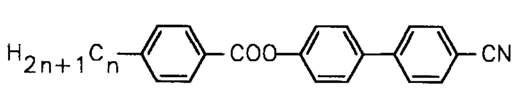
The aim of this work is to discuss our last results referring to the influence of the length of an alkyl chain and to estimate the temperatures of the virtual A_d to the nematic phase transition for pure compounds.

EXPERIMENTAL

The compounds of the following formula were investigated:

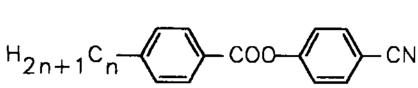


(nCBB)[9]



(nBCB)[10]

with n=7, 6, 5



(n.CN)[11]

with n=10, 9, 8, 7, 6, 5, 4, 3, 2.

More information are given in our previous paper.[7]

The phase transition temperatures of pure compounds and their mixtures were measured by the thermomicroscopic method using the polarizing microscope (BIOLAR) and hot stage unit - Linkam TMS 91. In the region of the phase transition the heating ratio was 1°C/min.

RESULTS AND DISCUSSION

The phase diagrams of 7CBB-n.CN system are shown in Figure 1. There is a smectic A_d area in the central part of it, in spite of both compounds does not have this phase. Compound 7CBB has nematic and smectic A_1 phase and compound n.CN has nematic phase. The smectic A_d phase induces in their mixture. The A_d area decreases and displaces in the direction of higher concentration of 7CBB when the alkyl of n.CN shortens. The 7CBB compound belong to the homologous series which members with longer alkyls have A_d phase. It is possible that 7CBB has tendencies to create this phase, i.e. has virtual A_d properties, but their alkyls are too short to stabilize this phase (see Madhusudana's calculations[12]). The induced A_d phase exists in a very large temperature range and it was not possible to overcool samples to such low temperatures and to find if there is a reentrant nematic phase below an A_d phase, as it was found for the system nCBB-nOCB.[7]
The shorter members of the same homologous series nCBB, n=6 and 5 also give the induction of the smectic A_d phase in the mixture with n.CN, see Figure 1b. Because their virtual A_d properties are weaker the induced A_d phase areas are smaller and placed closer to the 9.CN. In this case it was possible to measure the temperatures of phase transitions from the reentrant nematic phase to the smectic A_d phase, 5CBB-9.CN).

Use of another compound (7BCB), which belong to the similar kind of homologous series with virtual A_d properties, let also observed the induction of smectic A_d phase, see phase diagram of the system 7BCB-n.CN in Figure 2a.

The induced A_d area is well seen in a shape of an elliptical island surrounded by a nematic phase. The A_d phase also partially exists below melting curves but compound 7BCB has lower melting temperature and enthalpy so it was possible to overcool the samples and to measure the N_{re}-A_d phase transitions very precisely. In case of this system the A_d area decreases and displaces forward the higher concentration of 7BCB when the alkyl of n.CN shortens, similarly as in previous example.

The shorter member of nBCB, n=6, also gives the induction of A_d phase in the mixture with n.CN, see Figure 2b. The A_d area is smaller than in case of 7BCB compound and it is placed closer to n.CN compound. Because the 6BCB has shorter

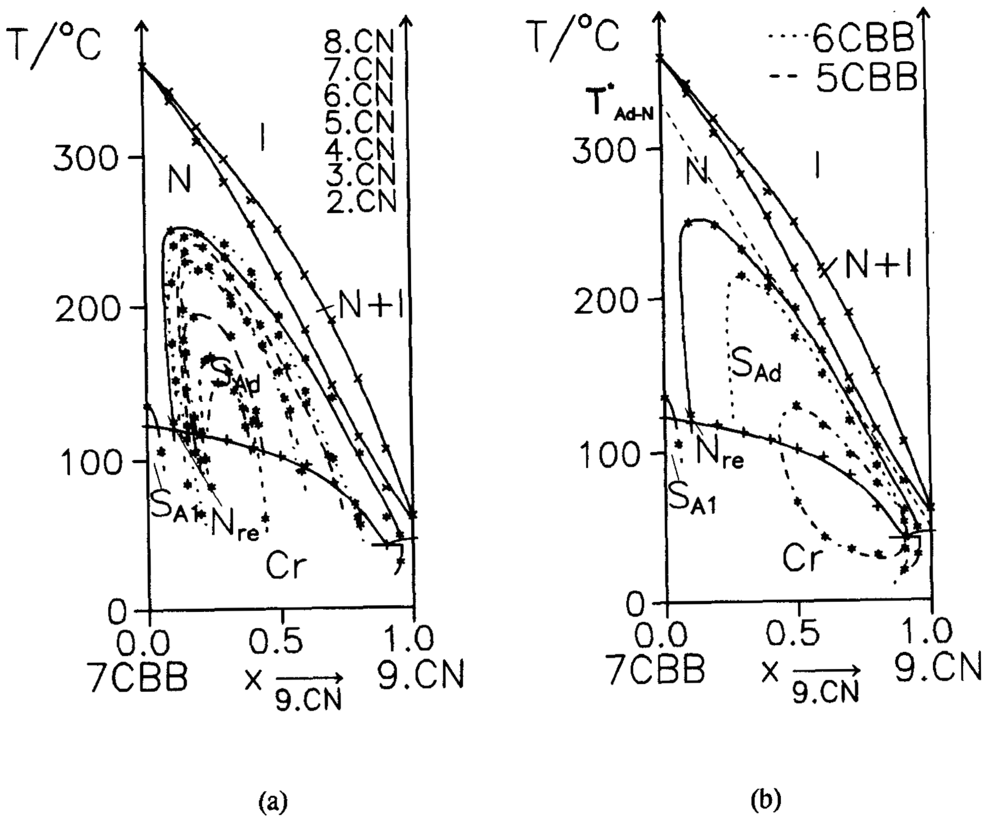


FIGURE 1 Phase diagrams of mixtures 7CBB-n.CN, n=9-2 (a) and nCBB-9.CN, n=7-5 (b).

alkyl its tendencies to create smectic phase are weaker and the induced A_d phase is observed only for members of n.CN with long alkyls (n=9 and 8).

The reason for the appearance of a smectic A_d phase and a nematic reentrant phase is a change of the ratio of associated and nonassociated forms of molecules (monomer-dimer-triplet) as a result of a change of the temperature and the competition between long and short range order.

The induction of an A_d phase is connected with the virtual A_d features of compounds. The nematic phase existing above smectic A_1 phase contains a great number of cybotactic structures which have an A_d character, they increase when environment of

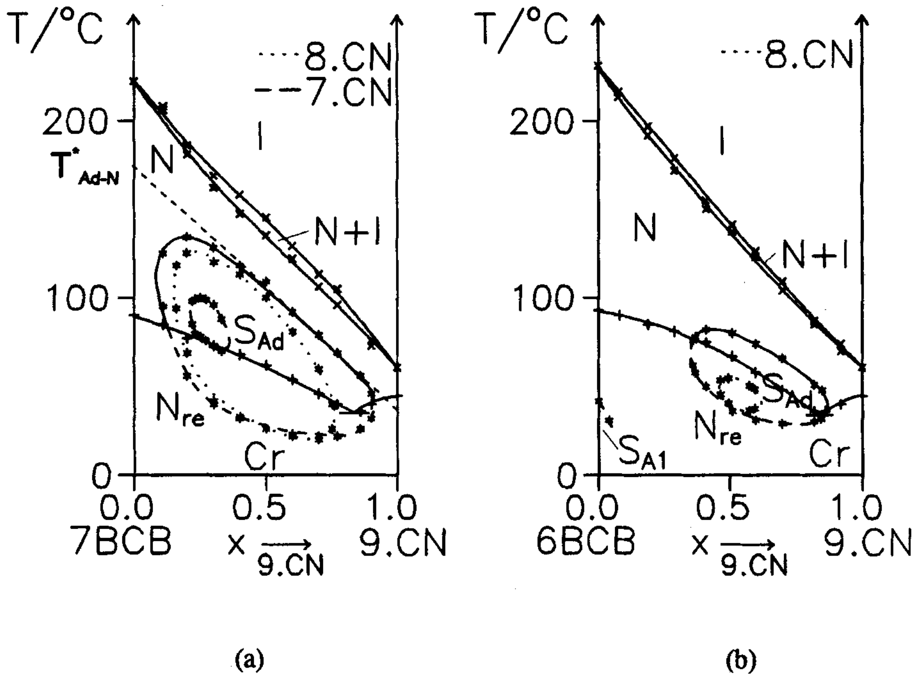


FIGURE 2 Phase diagrams of mixtures 7BCB-n.CN, n=9-7 (a) and 6BCB-n.CN, n=9-8 (b).

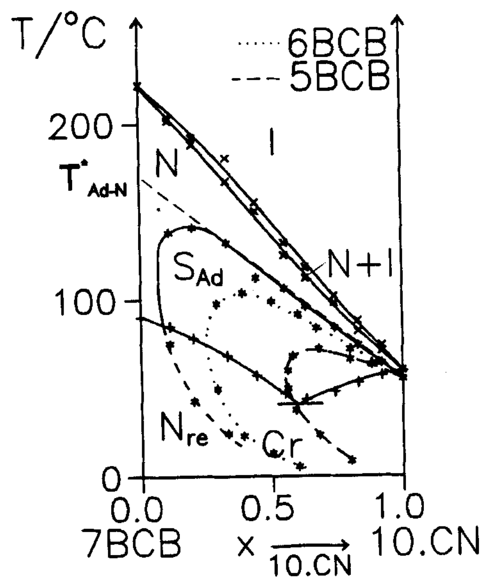


FIGURE 3 Phase diagrams of mixtures nBCB-10.CN, n=7-5.

molecules is more convenient for layering. So we conclude that this phase posses the virtual A_d phase. We estimated the phase transition temperature between virtual smectic A_d and N phases ($T^*_{Ad\text{-}N}$) for pure compounds nCBB and nBCB on the base of mixtures of these compounds with first member of homologous series, n.CN n=10, with A_d phase, see Figure 3. On their phase diagrams the boundary of an A_d-N transition is nearly linear and can be easily extrapolated to x_{nCBB} or x_{nBCB} = 1. The virtual phase transition temperatures are the following: $T^*_{Ad\text{-}N}$(7CBB)=330°C, $T^*_{Ad\text{-}N}$(7BCB)=170°C, $T^*_{Ad\text{-}N}$(6BCB)=150°C and $T^*_{Ad\text{-}N}$(5BCB)=110°C . The same values can be obtain when we extrapolate the linear part of the A_d-N transition boundary on the diagrams of mixtures of these compounds with compound 9.CN.

The compounds nCBB, nBCB and n.CN have very similar structure, so intermolecular attraction forces are very similar, therefore the change of them upon the change of the concentration ought to be small.

Both the structure of molecules and the length of the alkyl chain have a great influence of the ability to induce smectic A_d phase. In case of the nCBB and nBCB series the virtual properties weakens when the alkyls shortens so the island decreases and displaces forward the higher concentration of n.CN compound. In case of n.CN series the area of induced A_d phase decreases when the alkyl length shortens. The area displaces forward the higher concentrations of nCBB and nBCB what points that the small concentration of n.CN is enough to remove uncomfortable condition which disturb an existence of an A_d phase in pure 7CBB. Even the molecules with very short alkyl (n=2) can stabilize the A_d phase. Short molecules place between long molecules and do not let them freely permit forming smectic layers.

Usually when the alkyl of compound nBCB shortens its virtual properties weaken this is why for members of n.CN with shorter alkyls the smectic A_d phase is not injected at all (for example 7BCB-6.CN and 6BCB-7.CN).

CONCLUSION

The results show that the strong induction of A_d phase in mixtures of polar nematic compounds is possible. The area of induced A_d phase appears in a shape of an island surrounded by a nematic phase. The length of both compounds influence on the induction ability. When the alkyl length of biring esters n.CN shortens the area of induced A_d phase decreases and displaces forward the higher concentration of compounds of nCBB and nBCB series. When the alkyl length of compounds with virtual A_d properties nCBB and nBCB shortens the area of induced A_d phase decreases and displaces forward the higher concentration of biring esters n.CN.

Such behavior results from the virtual A_d properties of tested three and four ring compounds. The estimated phase transition temperatures from the virtual A_d to the nematic phase for these compounds seems to reflect the structure of their nematic phase which is not typical but contains great number of cybotactic groups.

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