Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Barbara Ważyńska (1992): Effect of Polarity on the Properties of Smectic A_1 Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 212:1, 327-334

To link to this article: http://dx.doi.org/10.1080/10587259208037274

Mol. Cryst. Liq. Cryst. 1992, Vol. 212, pp. 327–334
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Printed in the United States of America

EFFECT OF POLARITY ON THE PROPERTIES OF SMECTIC A_1 MIXTURES

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(Received March 12, 1991)

Abstract Phase diagrams have been determined of systems composed of the compound 8OBCAB and a binary mixture of a polar (nTPCHB) and non-polar (nMPCHB) compounds. It has been shown that extension of the smectic phase range and the appearance of the nematic reentrant phase connected with the dimerization of the 8OBCAB component require an adequate length of the aliphatic chain of the matrix.

Keywords: smectic A_1 mixtures, nematic reentrant phase, dimerization of smectic, mixture of polar and nonpolar compounds, pc

INTRODUCTION

Recently a number of works [1-5] were devoted to mixtures of polar smectics A_1 for which the phase diagrams revealed on one side a destabilization of the smectic A_1 phase leading to the appearance of a nematic gap, and on the other side a strong extension of the smectic phase range accompanied by the appearance of the nematic reentrant phase. It was shown [4-5] that such a behaviour is observed when one of the mixture components has a strongly polar -CN terminal group and belongs to a homologous series whose members with short aliphatic chains present a smectic A_1 phase and those with long chains an A_d one. 4′-cyanobiphenyl-4′-n-alkylbiphenyl-4-carboxylates (nCBB) and p-alkoxybenzoyloxy-p*-cyanoazobenzenes (nOBCAB) [7] belong to such homologous series. It has been proved [2,4] that the cause of such a behaviour, so untypical for mixtures of A_1 smectics, is the dimerization of the component with the strongly polar -CN terminal group in the matrix of the other compound.

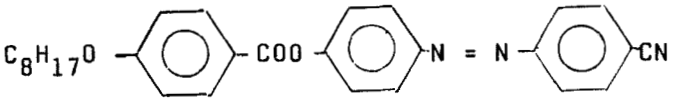
In the earlier works [1,5] compounds from the 4-(trans-4-n-alkylcyclohexyl) benzoate series (nXPCHB) with terminal

groups X= F, $-COCH_3$ or -NCS were used as the matrix. It was shown that the decrease of the length of the aliphatic chain of the nXPCHB component renders dimerization impossible. This decrease of the chain length produces an increase of polarity of nXPCHB leading to the conclusion that the decrease of polarity of the matrix is the cause of dimerization.

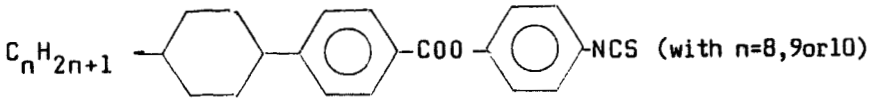
In the present work it was decided to follow the effect of reducing the polarity of the matrix by diluting it with a non-polar compound with a varying length of the aliphatic chain or by extending the length of the aliphatic chain of the polar compound.

EXPERIMENTAL

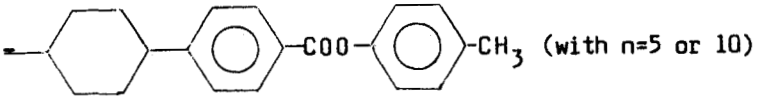
Phase diagrams were studied of systems in which the compound 8OBCAB of the formula



was one of the components.
The matrix was a mixture of polar and non-polar compounds of the formulae



denoted as nTPCHB

and 

denoted as nMPCHB.

The studied compounds yield smectic A_1 phase with the exception of 5MPCHB which yields nematic phase only.

The following series of mixtures were studied:

I 8OBCAB + (9TPCHB+8TPCHB)

II 8OBCAB + (10TPCHB+5MPCHB)

III 8OBCAB + (1OTPCHB+1OMPCHB).
The results of studies of these ternary systems are presented on graphs analogously as for binary systems. It was assumed that compound 8OBCAB constitutes one component and the mixture of compounds, in different proportions, given in parentheses is the second one.

The phase transitions were studied by the thermomicroscopic method described in [1].

RESULTS

The results of studies for the particular series have been summarized in Figs. 1 to 3. In each case a full phase diagram is given for one system of the given series, while for the remaining ones only the $N \rightarrow S_A$ and $S_A \rightarrow N_{re}$ phase transition lines are shown.

The results of studies of series I are given in Fig. 1. In this series a mixture of polar 8TPCHB and 9TPCHB compounds in different proportions constitutes the matrix. The data given in the figure show that the range of the extended smectic and reentrant nematic phase decreases with increase in the matrix of component with the shorter aliphatic chain (8TPCHB). When the content of 8TPCHB in the matrix reaches 80%, the nematic reentrant phase does not appear. In the phase diagram of this mixture only a minimum appears on the $N \rightarrow S_A$ phase transition line.
These data confirm the earlier observed effect of the length of the aliphatic chain in nTPCHB on the dimerization of the 8OBCAB component. The results of investigations of series I determine this effect with greater accuracy for n = 8 to 9.

In series II the behaviour is presented of compound 8OBCAB in a matrix composed of a polar component with a long chain n = 10 (1OTPCHB) and of a non-polar component with a short chain n = 5 (5MPCHB). Beginning with a 10% content of component 5MPCHB in the matrix we observe a significant decrease of the extended smectic range and of the

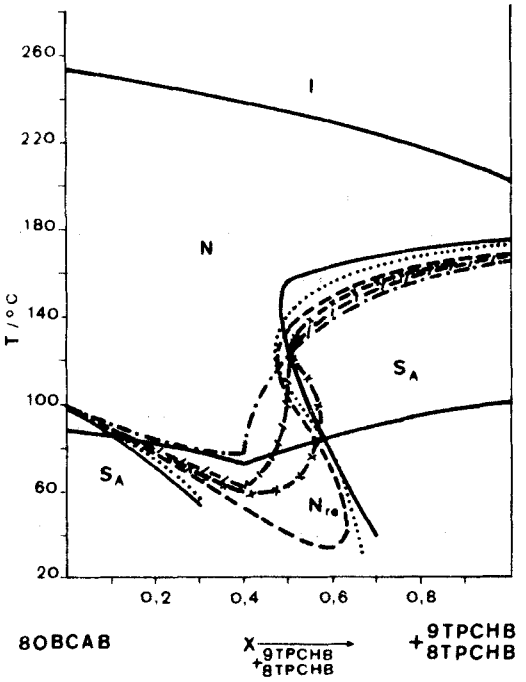


Figure 1. Phase diagram of the 8OBCAB-(100%9TPCHB+0%8TPCHB) system. The phase transition lines N→S_A and S_A→N_{re} for other systems of the first series
.... 8OBCAB-(80%9TPCHB + 20% 8TPCHB)
---- 8OBCAB-(50%9TPCHB + 50% 8TPCHB)
-x-x 8OBCAB-(30%9TPCHB + 70% 8TPCHB)
-/-/ 8OBCAB-(20%9TPCHB + 80% 8TPCHB)
-.-. 8OBCAB-(0%9TPCHB + 100% 8TPCHB)

reentrant nematic phase. The latter decreases further at a 20% content of 5MPCHB. The use of a matrix with a 50% content of 10TPCHB and a 50% content of 5MPCHB results in that the extended smectic range does not appear at all. This proves that dimerization of 8OBCAB does not take place in such a matrix.

A different behaviour is observed for series III, where the compound 8OBCAB is placed in a matrix consisting of a mixture of polar and non-polar components with aliphatic chains of the same lengths n=10 (10TPCHB+10MPCHB). A 10% content of the non-polar component in the matrix does not

cause any changes with respect to the 8OBCAB-1OTPCHB system, i.e. one not containing any non-polar mixture. When the proportion of compounds 1OTPCHB and 1OMPCHB in the matrix is 1:1 we still observe the extension of the smectic phase up to the content of x_{8OBCAB}= 0.7 mole fraction as was the case for the 8OBCAB-1OTPCHB system.

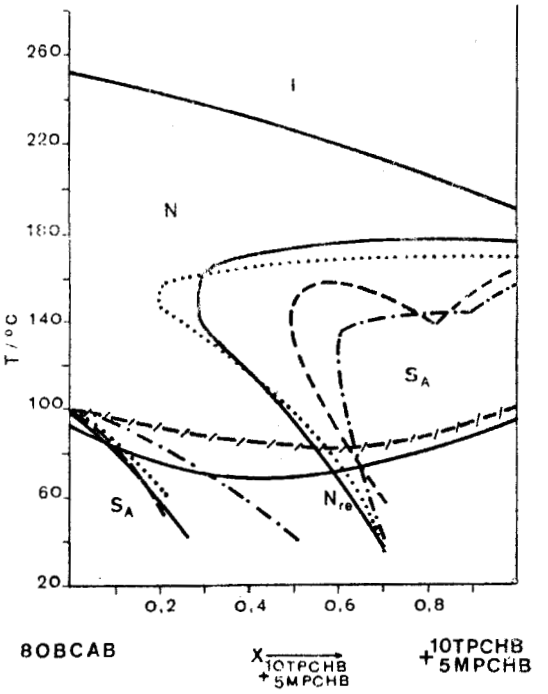


Figure 2. Phase diagram of the 8OBCAB-(100% 1OTPCHB + 0% 5MPCHB) system. The phase transition lines N→S_A and S_A→N_{re} for the other systems of the second series.
.... 8OBCAB - (95% 1OTPCHB + 5% 5MPCHB)
---- 8OBCAB - (90% 1OTPCHB + 10% 5MPCHB)
-.-. 8OBCAB - (80% 1OTPCHB + 20% 5MPCHB)
-/-/ 8OBCAB - (50% 1OTPCHB + 50% 5MPCHB)

However, here neither the reentrant nematic phase nor the nematic gap appear. A similar shape of the N→S_A phase transition line is observed in the 8OBCAB-1OMPCHB system, i.e.

when compound 8OBCAB is mixed with a fully non-polar matrix with a n=10 length of the aliphatic chain.

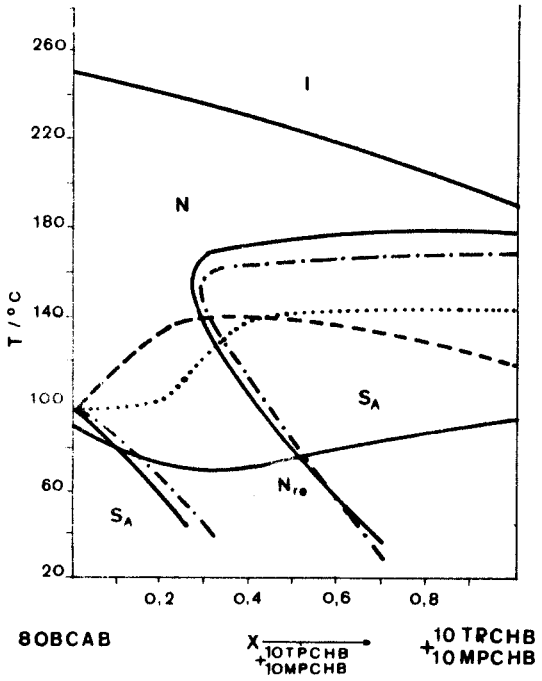


Figure 3. Phase diagram of the 8OBCAB-(100%10TPCHB+0%10MPCHB) system. The phase transition lines N→S_A and S_A→N_{re} for the other systems of the third series.
-.-. 8OBCAB - (90% 10TPCHB - 10% 10MPCHB)
.... 8OBCAB - (50% 10TPCHB - 50% 10MPCHB)
---- 8OBCAB - (0% 10TPCHB -100% 10MPCHB)

DISCUSSION

In the described phase diagrams two behaviours occur. One

consists in the extension of the range of the smectic phase, and the other in the appearace of the reentrant nematic phase and of the nematic gap. Both these behaviours occured in the 80BCAB-10TPCHB system and were explained by the dimerization of 80BCAB in the 10TPCHB matrix [4]. In the present work these behaviours should be considered separately in view of the fact that they are influenced in a different manner by non-polar compounds. The results of the present work show that the extension of the smectic phase occurs when a compound with an adequate length of the aliphatic chain $n \geq 8$ is used as the matrix. The dilution of the polar matrix with a non-polar compound containing an aliphatic chain of length n=10 (10MPCHB) does not produce a lowering of the $N \rightarrow S_A$ phase transition points as distinguished from dilution with a non-polar compound with a aliphatic chain of smaller length n=5. This allows us to conclude that the extension of the smectic phase range resulting from dimerization of 80BCAB requires an adequate length of the aliphatic chain in the matrix and not the reduction of its polarity.

The appearance of the nematic gap and of the reentrant nematic phase is a different question. Such a behaviour occurs if 80BCAB mixes with the polar matrix or if the content of the non-polar component is small.

The nematic reentrant phase or the nematic gap appear according to the theory of Indekeu and Berker [10] in polar compound systems due to dipolar frustration. In the case of mixtures of polar and non-polar components the effect of dipolar frustration does not take place. The short-range attractive interactions of the flexible aliphatic chains is a factor which stabilizes the smectic phase. Peltz et al. have recently described [8,9] the appearance of the reentrant nematic phase also in systems composed by non-polar components giving the unfavourable packing of the rigid and flexible parts of molecules as the cause. In the systems described above the adequate length of the aliphatic chain makes possible the arrangement of molecules in the

smectic layer and does not lead to its disturbing.

The present author is very oblied to professor Roman Dąbrowski of the Military Technical Academy for supplying the compounds for the study and for the valuable discussions.
The work received financial support from the Ministry of National Education.

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