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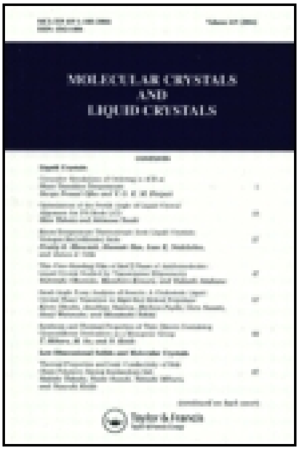

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Emergence of Mixed Nematic Mesophase in Binary System of a Non-Mesogen and a Smectogen

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An interesting binary system consisting of a non-mesogen and a smectogen viz. *p*-chlorophenyl-*p*'-methoxycinnamate (A) and *p*-chlorophenyl-*p*'-*n*-octyloxycinnamate (B), respectively, which belong to the same homologous series[1] viz. *p*-chlorophenyl-*p*'-*n*-alkoxycinnamates is now reported in which mixed monotropic nematic and mixed enantiotropic nematic mesophases emerge over a wide range of temperature and concentration. It is observed that the mixed smectic mesophase gets depressed as the concentration of the non-mesogen increases, yielding simultaneously enantiotropic mixed nematic phase; the mixed phase diagram exhibits nematic as well as smectic phases. As the concentration of the non-mesogen increases further, the mixed smectic phase enters into monotropic state while the mixed nematic phase continues to be enantiotropic. However, with more than about 60 mole% (A), the mixed nematic enantiotropic mesophase becomes monotropic nematic which ends by about 92 mole% of the non-mesogen (A). The characteristic modifications in the mixed mesomorphism are correlated with the structural characteristics of the components of the molecular forces displayed by them.

Keywords: non-mesogen, smectogen, mesophase texture, enantiotropic nematic, polymesomorphism, nematic mesophase

INTRODUCTION

Physical properties of individual mesogens may or may not undergo modifications in their mixtures. Sometimes, the modifications become characteristic thereby making the study of mixtures important. Earlier studies[2–11] have suggested the formation of mixed mesomorphism by mixing compounds where none, one or both compounds are mesogens. Emergence of mesophase,[12,13–15] increase or decrease of the mixed mesomorphic ranges and thermal stabilities and the study of the factors

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which influence the modifications have received more attention. We have reported a mixture where a high order smectic phase emerges by mixing two nematogens.[2] Dave et al.[16] studied binary systems comprising of a smectogen and a non-mesogen. Mixed smectic liquid crystals were obtained over a range of concentration and temperature.

In the present study, we report a binary system of a non-mesogen and a smectogen belonging to the same homologous series[1] and it exhibits an emergence of nematic mesophase, both in monotropic, as well as, enantiotropic conditions.

EXPERIMENTAL

Synthesis: *p*-*n*-alkoxybenzaldehydes[17] [R = $-OCH_3$, $-O(CH_2)_7CH_3$], trans *p*-*n*-alkoxycinnamates,[18] trans *p*-*n*-alkoxycinnamoyl chlorides,[19] *p*-chlorophenyl-*p*'-methoxycinnamate[1] (A) and *p*-chlorophenyl-*p*'-*n*-octyloxycinnamate (B) have been synthesized by reported methods.

Study: The mesomorphic characteristics were studied by the optical method as well as under the polarizing microscope using Kofler heating stage. The transitions are recorded in Table I.

TABLE I

Binary system: *p*-chlorophenyl-*p*'-methoxycinnamate (A); *p*-chlorophenyl-*p*'-*n*-octyloxycinnamate (B)

Mole % of A	Transition Temperature °C		
	Smectic	Nematic	Isotropic
00.00	81.0	-	122.0
12.89	77.5	-	117.0
24.99	69.0	106.0	112.0
36.35	79.0	88.5	106.0
47.04	(73.5)	87.0	103.5
57.12	-	93.5	101.0
66.64	-	(104.0)	118.0
75.64	-	(102.0)	124.0
84.20	-	(104.0)	129.0
92.28	-	(105.5)	132.0
100	-	-	136.5

Values in parenthesis indicate monotropy

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RESULTS AND DISCUSSIONS

The binary system consists of two components *p*-chlorophenyl-*p*′-methoxycinnamate (A) and *p*-chlorophenyl-*p*′-*n*-octyloxycinnamate (B) of the same homologous series viz. *p*-chlorophenyl-*p*′-*n*-alkoxycinnamates[1]: Component A is a C-1 member and is a non-mesogen (K 136.5 I) and component B is a C_8 member, a smectogen (K 81 S 122 I). The components have the identical molecular geometry except in the number of $—CH_2$ units in the alkoxy chain lengths at the left hand of the molecules.

In a general sense, a binary system where one component is a liquid crystal and another is not a liquid crystal,[20] a series of mixed liquid crystals of the original variety of the liquid crystal component is expected to be formed over a range of temperature and concentration. Such binary systems are capable of throwing light on the extent to which a non-liquid crystalline component is causing hindrance to the exhibition of mixed mesophase on account of the difficulty in the packing of the molecules and weakening of the terminal and or lateral attractions of the molecules. Simultaneously, in many cases, it can also throw light on the nature of the disturbing forces and probability of the non-liquid crystalline substance showing a mesophase on maintaining certain conditions of cooling or structural changes.

Somewhat more interesting systems of this kind can be those which cause change on the mesophase texture in the mixed conditions.[6–8] In the present system, mixtures of a smectogen (smectic A) (C_8 homologue) with a non-mesogen (C_1 homologue) of the same series[1] yield nematic mesophase in monotropic as well as enantiotropic conditions while the smectic A phase of the smectogen B remains intact over a small concentration of about 15 mole% of the non-mesogen A.

Starting from the non-liquid crystalline side of the phase diagram (Figure 1), the mixtures melt to isotropic phase at proper transitions; the curve AF represents this change. While no mesophase is observed on heating, supercooling of the mixtures results at suitable transitions into monotropic nematic phase. The monotropic-nematic mesophase continues up to 33 mole% addition of the smectogen B. The mixed monotropic nematic mesophase is induced with only 8 mole% addition of the smectogen B. The curve HF limits the boundary of the monotropic nematic phase. The K-I transition curve AF shows regular depression in the transitions up to 33 mole% addition of B. With 43 mole% addition of B an enantiotropic nematic emerges in the mixture and it continues to show up to about 75 mole% addition of B; this includes a part of the mixed smectic and nematic mesophases region also. The I-N curve enters the enantiotropic nematic region at F and continues as the curve FG.

The K-I curve AF crosses the N-I curve HG at F with a sort of apparent non-continuity after which it seemingly merges with the K-N curve. From the figure it can be observed that the enantiotropic nematic phase is exhibited up to 59.5 mole% of B at E; beyond which on further addition of the smectogen both smectic A as well as nematic phases get exhibited along the curve ED, which is in continuation with FE. At D the eutectic temperature is obtained. The K-S curve on the left of the eutectic segment CG′D meets the eutectic concentration at D. This phenom-

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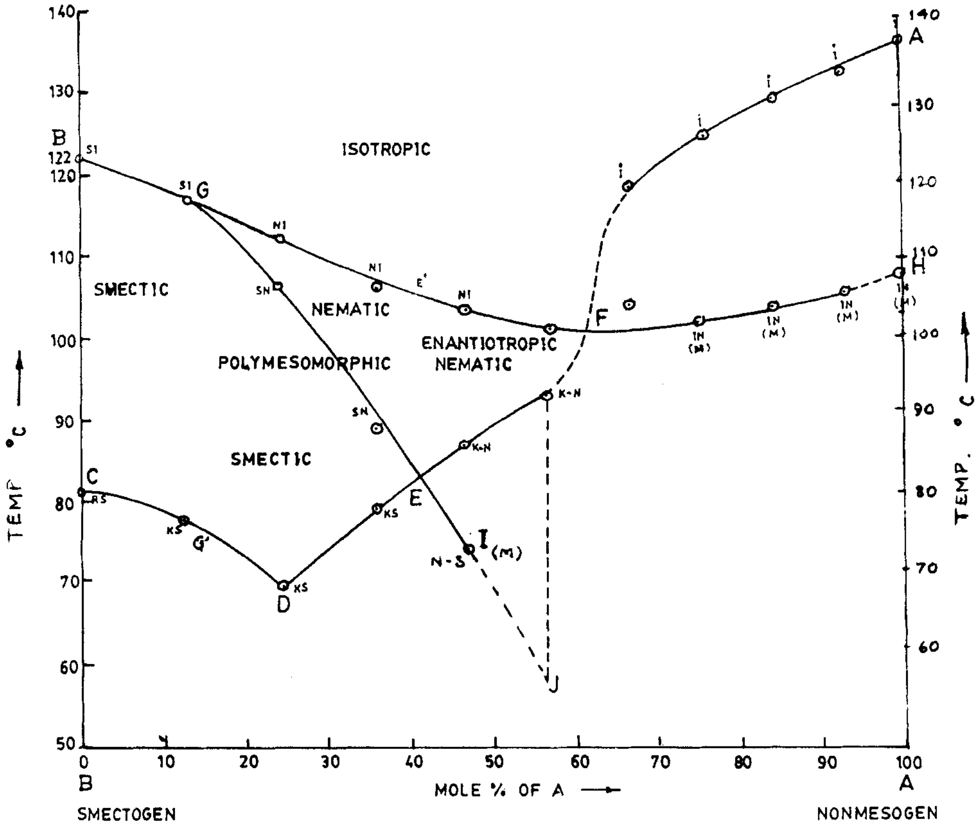

FIGURE 1

enon of exhibiting smectic A and nematic phases ends at C′ beyond which up to 100 mole% of B only smectic mesophase is seen.

Within the mixed mesophases region G′DEE′G, the S-N transition curve GE is in continuation with the S-I curve BG. Similarly, the S-I curve is also in smooth continuation with the N-I curve FG.

The S-N curve GE can be extended to the point I, the monotropic N-S transition point which is experimentally determined, and the curve can further be extrapolated up to J, a composition which does not permit monotropic smectic phase to emerge. In other words, J is a point which is not experimentally determinable but theoretically achievable. This may be because it happens to be a temperature which is about 17° lower than the eutectic temperature, the phase below the eutectic is expected to be the mixed solid one.

The molecular geometry of both the components of the system is almost similar, hence the law of mixtures should have been ideally followed. However, the K-I transition curve AF and the S-I and N-I transition curve BGE′ deviates from the linear nature of the ideal transition curves; the extent of deviation would speak for the differentiating manner in which the molecular forces arising from the terminal groups and central bridges of the moieties play their role. The non-linear

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behavior of the binary phase diagrams where one of the components has a strong polar end group have been reported by various workers.[13,16,21–24] On account of the deviation from ideal behavior, due to the molecular forces, the maximum mixed mesomorphic range turns out to be of about 43°C; this is incidentally over the eutectic composition and inclusive of the mixed nematic phase—the additional phase, as far as this binary system is concerned.

The N-I transition curve GE′F shows a concave nature in its curvature. The OCH_3 component A, though a non-mesogen has been assigned LTT 110° on the basis of intrapolation of the N-I curve of the homologous series *p*-chlorophenyl-*p*′-*n*-alkoxycinnamates.[1] The curve GE′F shows a depression of about 11°C more than the ideal one; this would mean that the molecular forces responsible for offering resistance to thermal agitations are rather weak and that the terminal attractions have also grown weak enough to yield isotropic phase earlier than expected. It seems that the —OC_8H_{17} component B endorse the molecules with sufficient polarizability besides enhanced length with the —OC_8H_{17} group. It can be concluded thus that with the sufficient polarity due to the OCH_3 and Cl terminal groups of the component A, the polarizability of the molecules of component B adds to the combination of the molecular forces in a manner as to induce a nematic orientation in a mixed form. Around 5–7 mole% of the smectogen B seems to be enough to induce monotropic nematic phase and somewhat more than 40 mole% makes the emergence of enantiotropic nematic mesophase quite possible and gets enhanced up to 59.5 mole% of B. The smectic mesophase here is absent. This is really a very interesting phenomena.

The curve EI when further extrapolated up to J, the concentration at which the last single enantiotropic nematic mesophase is observed experimentally. It does not seem to be probable to get more smectic transition in the monotropic condition beyond about 50 mole% of A. The extrapolation of the curve beyond this value indicates a monotropic transition below the eutectic temperature, which is rather absurd.

The monotropic I-N transition curve when extrapolated up to the point H, a value of 108°C is obtained which can be the LTT value of the non-mesogen A. This value is within the experimental error of about +2°C when compared with the LTT value obtained similarly, for the non-mesogen A from the study of its homologous series.[1] These two values can be viewed as in fine agreement, thereby lending credibility to the concept of extrapolation method for determining the latent transition temperatures.[11] It can further be concluded that the binary system is quite conspicuous by its rich content in terms of varied orientations of the mesomorphic state. It shows a predominant effect of the non-mesogen A in subduing the smectic character of the pure smectogen B, and of the nematic character both in monotropic as well as enantiotropic states.

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