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Liquid crystalline behaviour of mixtures of structurally dissimilar mesogens in binary systems

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Abstract. We have studied four binary systems comprising four ester components, viz. 4-nitrophenyl-4′-*n*-alkoxybenzoates (where *n*-alkoxy is *n*-butoxy, C_4, *n*-hexyloxy, C_6, *n*-octyloxy, C_8 and *n*-decyloxy, C_{10}) and one azo component, 4-*n*-decyloxy phenylazo-4′-isoamyloxy benzene. A variety of mesomorphic properties are observed in these mixtures. The properties of these systems are discussed on the basis of phase diagrams.

Keywords. Binary mixture; non-mesomorphic; smectic A; nematic.

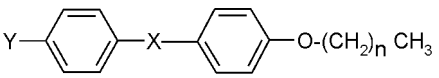
1. Introduction

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[1–10] have suggested the formation of mixed mesomorphism by mixing compounds where none, one or both of them are mesogens. Emergence of the mesophase[11], increase or decrease of the mixed mesomorphic ranges and thermal stabilities and study of the factors which influence the modifications have received greater attention. We have reported a mixture where a high order smectic phase emerges by mixing two nematogens[11] and a lower order nematic phase emerges from mixture of a smectogen[12] and a non-mesogen.

We have also reported binary systems of structurally similar and dissimilar mesogens and non-mesogens[13]. Continuing our research in this field, we report here four binary systems consisting of structurally dissimilar mesogens and a nematogen with a branched terminal group and the study of their effect on mixed mesomorphism, arising due to the differences in structural characteristics of these components.

The binary mixtures are composed of mesomorphic azo derivative (A), 4-*n*-decyloxy-phenylazo-4′-isoamyloxybenzene and esters (B_1–B_4), 4-nitrophenyl-4′-*n*-alkoxy-benzoates.

The components have the following general structural formula



*For correspondence

where

A is 4-*n*-decyloxyphenylazo-4′-isoamyloxybenzene: DPIB, *n* = 9

$$X = -N{=}N-; \quad Y = -O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3,$$

transition temperatures (°C): Cr 84 N 100 I,

B_1 is 4-nitrophenyl-4′-*n*-butyloxybenzoates: NPBB, *n* = 3

$$X = -COO-; \quad Y = -NO_2,$$

transition temperature (°C): Cr 55 I,

B_2 is 4-nitrophenyl-4′-*n*-hexyloxybenzoates: NPHB, *n* = 5

$$X = -COO-; \; Y = -NO_2,$$

transition temperatures (°C); Cr (52) N 68 I,

B_3 is 4-nitrophenyl-4′-*n*-octyloxybenzoates: NPOB, *n* = 7

$$X = -COO-; \; Y = -NO_2,$$

transition temperatures (°C): Cr 49 SmA 62 N 66 I,

B_4 is 4-nitrophenyl-4′-*n*-decyloxybenzoates: NPDB, *n* = 9

$$X = -COO-; \; Y = -NO_2,$$

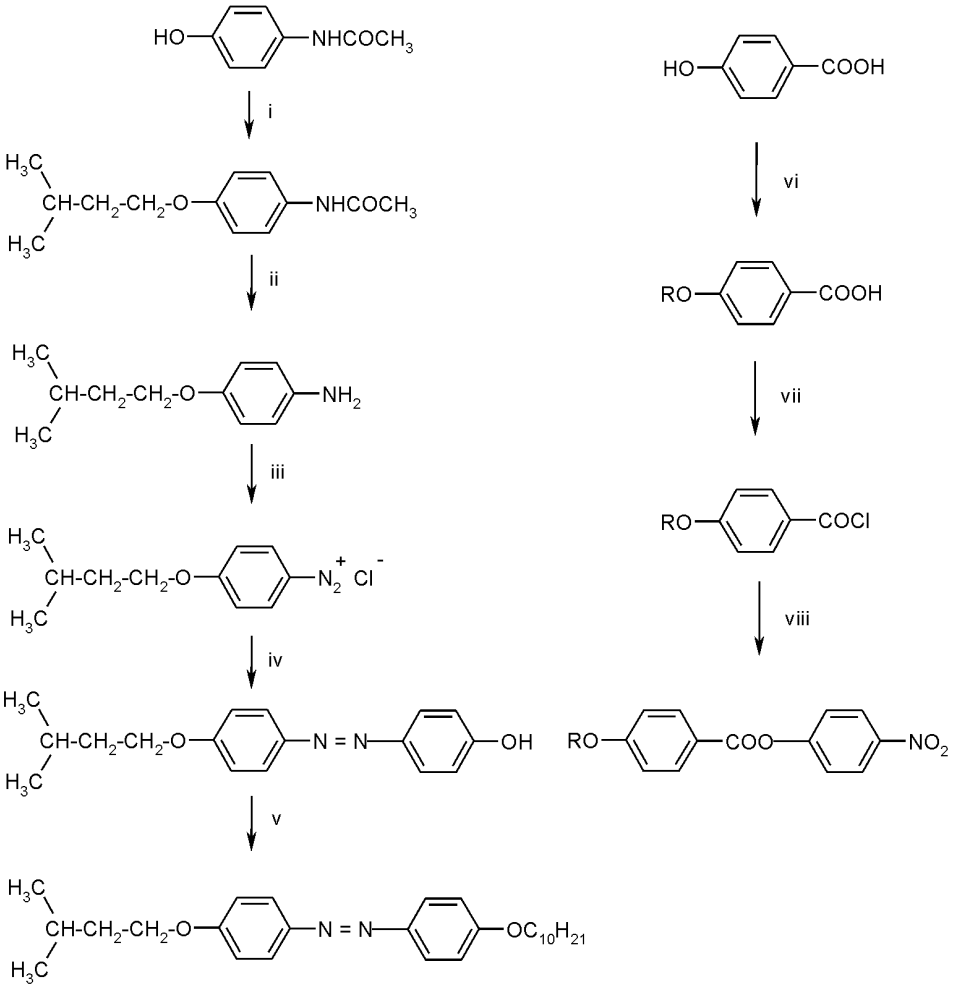
transition temperatures (°C): Cr 60 SmA 78 I.

The binary systems studied are (I) DPIB + NPBB, (II) DPIB + NPHB, (III) DPIB + NPOB, and (IV) DPIB + NPDB.

2. Experimental

2.1 *Synthesis*

All the chemicals used were of Fluka, BDH or Aldrich grade. Isoamyloxy aniline [14,15], 4-hydroxyphenylazo-4′-isoamyloxybenzene [16] and 4-nitrophenyl-4′-*n*-alkoxybenzoates [13] were synthesised by reported methods. 4-*n*-decyloxyphenylazo–4′-isoamyloxybenzene was prepared by alkylating the 4-hydroxyphenylazo-4′-isoamyloxybenzene with *n*-decyl bromide [17]. The synthetic route is shown in scheme 1. The final compounds were recrystallized from ethanol and their elemental analysis were carried out in Coleman USA CHN analyzer and conform to theoretical values. IR spectra were recorded on a Shimadzu IR-408. Component A: 2925, 2853, 2599, 1496, 1241, 1146. 924, 845, 553 cm^{-1}.



(i) K_2CO_3, isoamylbromide, acetone
(ii) H_2O, HCl
(iii) HCl, $NaNO_2$, 0–5°C
(iv) Phenol, aq. NaOH, 0–10°C
(v) K_2CO_3, acetone, *n*-$C_{10}H_{21}Br$
(vi) KOH, RBr, ethanol/HCl
(vii) $SOCl_2$
(viii) *p*-Nitrophenol, pyridine/HCl

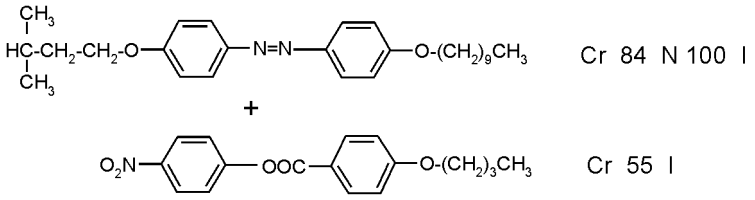
Scheme 1.

2.2 *Preparation and study of binary mixtures*

The components were weighed in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogeneous mixture, after which they were cooled. This procedure was repeated three times. The solid obtained was finally ground and used for determining transition temperatures, by using a Leitz laborlux 12 POL polarizing microscope fitted with a Kofler heating stage.

3. Results and discussion

3.1 *Binary system I:* DPIB (A) + NPBB (B_1)



In this system (table 1, figure 1) the ester component B_1 is non-mesomorphic in nature, whereas the azo component A is nematogen showing only the nematic (N) phase. The smectic A (SmA) mesophase, showing focal-conic fan-shaped texture; commences in enantiotropic form, with the addition of as low as 13 mole% of B_1 and exists till about 25 mole% of B_1. As the concentration of B_1 increases to about 36.5 mole% in the binary mixture, only smectic A phase is shown with complete elimination of the nematic phase. This can be attributed to the fact that the terminal attractions are no longer sufficient to cause nematic orientations as layered orientations become predominant. The SmA phase is enantiotropic till about 75.8 mole% of B_1 after which it becomes monotropic at about 84 mole% of B_1. It is observed that nematic phase reemerges at about 75 mole% of B_1 as an enantiotropic phase and is exhibited till about 84 mole% of B_1; however, the last mixture with 92 mole % shows only nematic phase, with threaded texture. The eutectic point is observed at 75 mole% of B_1 at 50°C and maximum mesophase range of 45°C is observed at 58.65 mole% of B_1. Within the mixed mesophase region the SmA-I curve is continuous with the N-I and SmA-N curves and deviates from linearity.

Table 1. Binary system I. DPIB + NPBB.
Values in parentheses indicate monotropic transitions.

	Transition temp. (°C)		
Mol% B_1	SmA	N	I
0	–	84	100
13·01	82	90	102
25·17	80	100	104
36·58	71	–	103
47·29	62	–	103
58·65	55	–	100
66·87	55	–	95
75·84	50	84	88
84·33	(45)	51	76
92·37	–	56	66
100	–	–	55

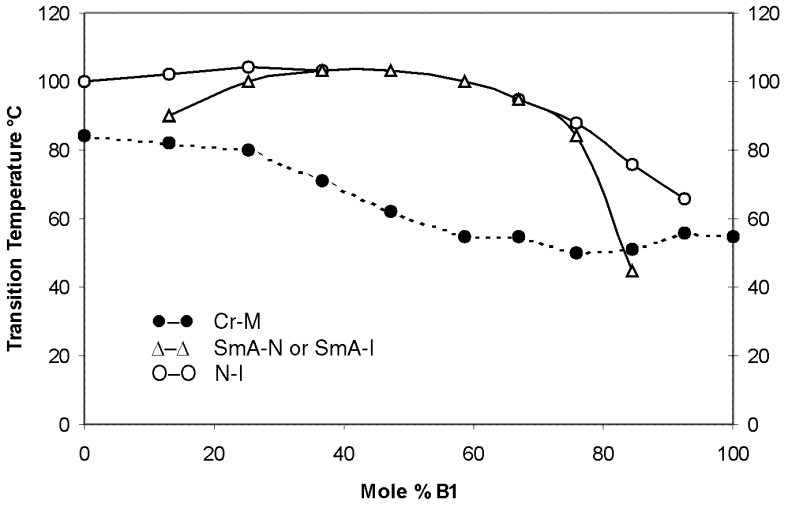
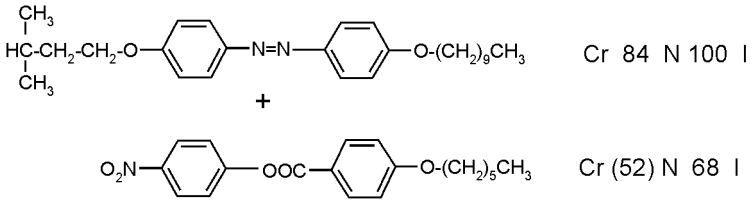


Figure 1. Binary system I (DPIB + NPBB).

3.2 *Binary system II:* DPIB (A) + NPHB (B_2)



Phase diagram of this system (table 2, figure 2) shows that with the addition of about 12 mole% of monotropic nematogen B_2 to nematogen A, smectic A phase emerges along with nematic phase in the mixture and this trend continues up to about 23 mole% of B_2, after which only smectic A phase prevails till about 83 mole% of B_2. The SmA phase becomes monotropic in nature and nematic phase emerges again at about 91.8 mole% of B_2. Eutectic point is obtained at 56°C at about 56 mole% of B_2 showing a maximum mesophase range of about 53°C. In this system also SmA-I curve is continuous with SmA-N and N-I curves and they deviate from linearity.

3.3 *Binary system III:* DPIB (A) + NPOB (B_3)

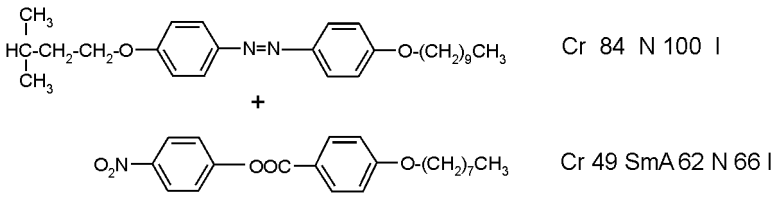


Table 2. Binary system II. DPIB + NPHB.
Values in parentheses indicate monotropic transitions.

	Transition temp. (°C)		
Mol% B_2	SmA	N	I
0	–	84	100
12·07	82	91	101
23·60	80	98	103
34·63	75	–	106
45·17	70	–	110
56·57	56	–	109
64·96	57	–	107
74·25	58	–	103
83·18	59		92
91·81	(57)	63	75
100	–	(52)	68

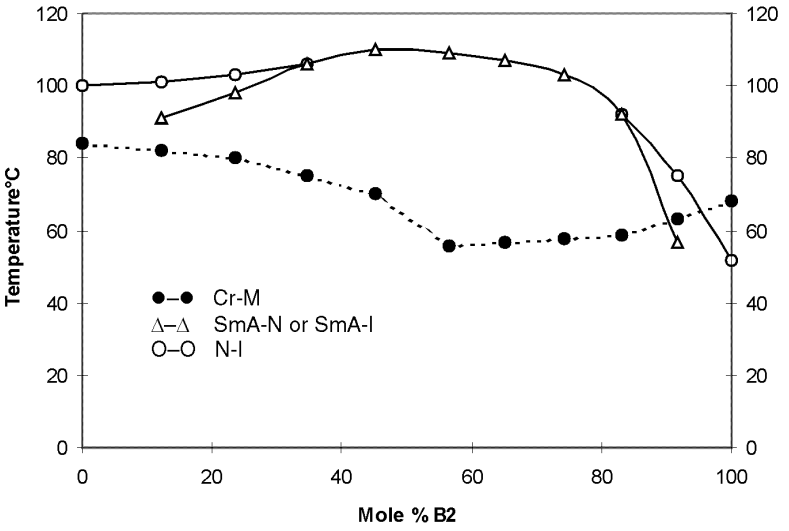


Figure 2. Binary system II (DPIB + NPHB).

This system (table 3, figure 3) consists of component A, a nematogen and B_3, which is a polymesomorph, showing SmA and nematic phases. It is observed that on addition of as low as 11.26 mole% of B_3 there is an emergence of SmA phase along with nematic phase; both the phases are present till about 22.2 mole% of B_3, after which only smectic A phase prevails till about 91 mole% of B_3. As the concentration of component B_3 increases in the mixture, it causes Cr-M transition to depress successively to a minimum of 44°C at about 72.2 mole% of B_3 which is the eutectic point of the system; the maximum mesophase range of 62°C is obtained at this molar concentration of B_3. In this system also the N-I and SmA-I curves are in continuous with each other, deviating from linearity.

Table 3. Binary system III. DPIB + NPOB.

	Transition temp. (°C)		
Mol% B_2	SmA	N	I
0	–	84	100
11·26	82	95	100
22·22	79	97	101
32·87	73	–	105
43·24	68	–	111
54·63	55	–	113
63·15	49	–	111
72·72	44	–	106
82·05	46	–	99
91·14	45	–	85
100	49	62	66

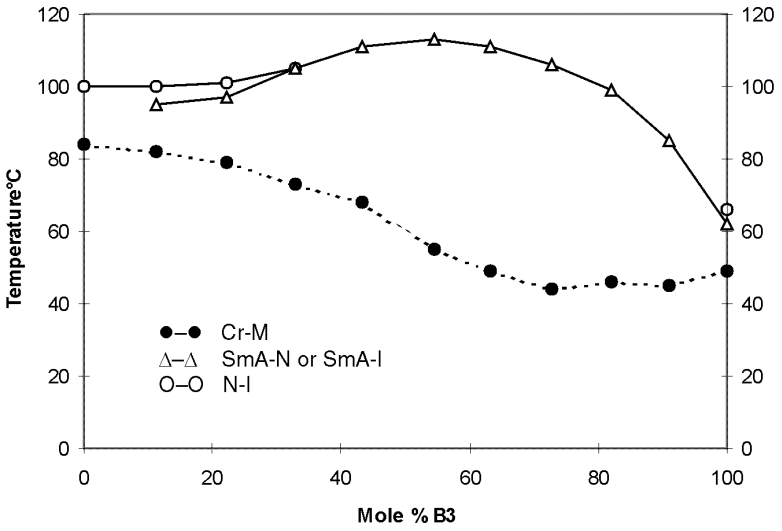
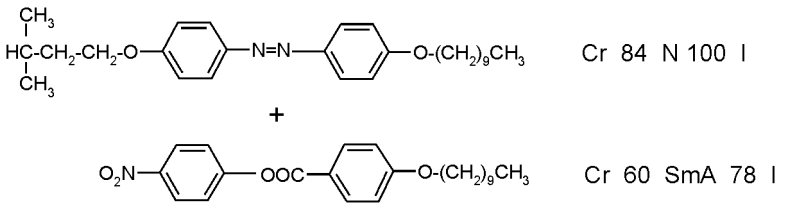


Figure 3. Binary system III (DPIB + NPOB).

3.4 *Binary system IV:* DPIB (A) + NPDB (B_4)



This system (table 4, figure 4) consists of components B_4, a smectogen, showing SmA phase and component A showing only nematic phase. Addition of about 10.5 mole% of

Table 4. Binary system IV. DPIB + NPDB.

	Transition temp. (°C)		
Mol% B_4	SmA	N	I
0	–	84	100
10·55	83	98	102
20·98	80	–	102
31·28	74	–	108
41·46	68	–	110
52·82	50	–	110
61·44	49	–	109
71·25	49	–	106
80·95	48	–	101
90·53	46	–	94
100	60	–	78

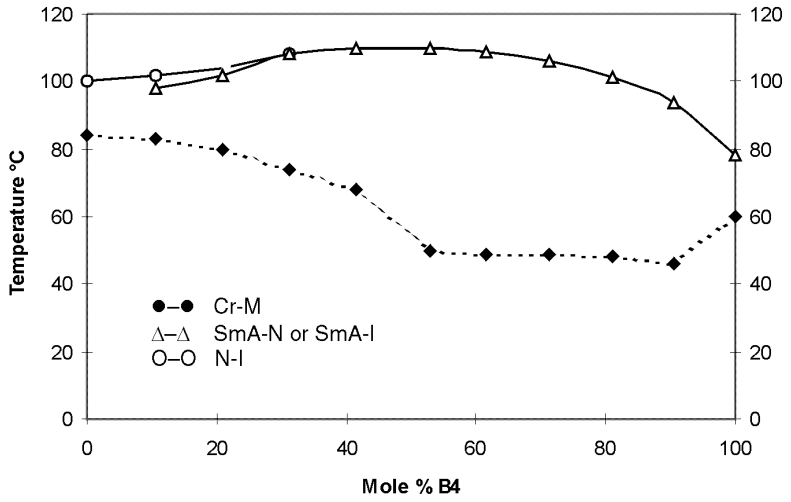


Figure 4. Binary system IV (DPIB + NPDB).

smectogen B_4 to component A causes the more ordered smectic A phase to appear along with nematic phase; however, the binary mixture with 20.98 mole% of B_4 onwards shows only SmA phase till about 90.53 mole% of B_4, with the complete elimination of nematic phase. The eutectic point is obtained at 61.4 mole% of B_4 at 49°C showing maximum mesophase range of 60°C. Here too, the SmA-I curve is continuous with the N-I curve, deviating from linearity.

4. Conclusion

Study of these binary systems indicates that as the molecular geometry of the two components in the binary mixture differs, N-I, SmA-N and SmA-I curves deviate from

linearnity. This nonlinear tendency could be due to different moieties forming the terminal groups and central bridges. Nonlinear behaviour of binary phase diagrams where one of the components has a strong polar end group have been reported by other workers earlier also [18–20]. In these binary systems, deviation from linearity can be attributed to the high tendency of the nitro group of favouring the formation of oriented fluids. Most of the textures show super cooling below 35°C i.e. they remain in the liquid crystalline phase below 35°C and then they crystallise.

It has been also observed that with successive increase of two methylene units, (–CH_2–) from component B_1 to B_4 the binary systems show more smectogenic than nematogenic characteristics; this can be attributed to the fact that as the number of flexible –CH_2– units are added to the component B, the lateral attractions become more predominant than terminal attractions, thereby causing more layered orientations to persist for smectic properties to be exhibited.

Acknowledgement

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