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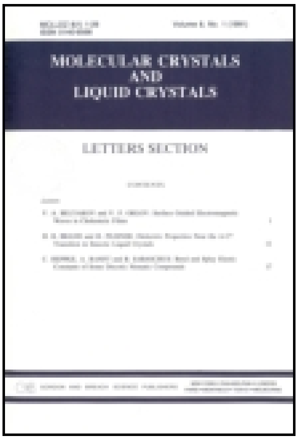

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Study of Mixed Mesomorphism in Binary Systems of Azo-Ester Mesogens With Structurally Dissimilar Nonmesogenic As Well As Mesogenic Ester Homologues

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Study of Mixed Mesomorphism in Binary Systems of Azo-Ester Mesogens With Structurally Dissimilar Nonmesogenic As Well As Mesogenic Ester Homologues

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*We have studied mixed mesomorphism in four binary systems comprising two azo-ester mesogens, viz. 4-(4′-*n*-alkoxybenzoyloxy)3-methylphenyl azo-2″ and 4″-dimethylbenzenes (where* n*-alkoxy is* n*-butoxy or* n*-hexyloxy), and two ester nonmesogenic and mesogenic components, viz. 4-nitrophenyl-4′-*n*-alkoxybenzoates (where* n*-alkoxy is* n*-butoxy or* n*-hexyloxy). All the four binary systems are mesogenic in nature, showing nematic phase with threaded/marble texture. The phase diagrams of the binary systems are plotted and eutectic transition temperatures and maximum mesophase ranges of the nematic mesophase in all the systems are determined.*

Keywords Azo-ester mesogens; binary systems; mixed mesomorphism; nematic; non-mesomorphic and mesomorphic ester homologues; phase diagrams

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 [1–14] have suggested the formation of mixed mesomorphism by mixing compounds where none, one, or both of them are mesogens. Most of the binary mixtures do not undergo any change in their mesomorphic textures, though a few have been reported giving rise to different textures [15]. Emergence of the mesophase, increase or decrease of the mixed mesomorphic ranges and thermal stabilities, and the study of the factors that influence the modification have received more attention [15–19]. Our group has reported mixtures were a higher-order smectic phase emerges from mixtures of nematogens and a lower-order nematic phase emerges from mixture of a smectogen [8] and a nonmesogen; binary systems of structurally similar and dissimilar mesogens and nonmesogens [9, 20] have also been reported. Keeping this in view, we report here four binary systems consisting of azo-ester mesogens with nonmesogenic and mesogenic carboxy esters to examine the properties of mixed mesophases.

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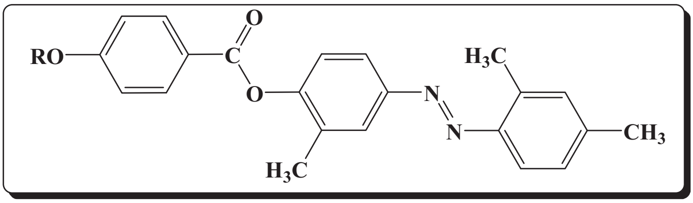
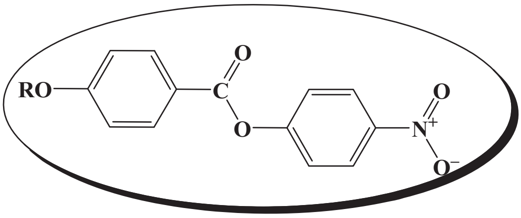
The binary mixtures are composed of azo mesogens, namely, 4-(4′-*n*-butoxybenzoyloxy)3-methylphenyl azo-2″,4″-dimethylbenzene and 4-(4′-*n*-hexyloxybenzoyloxy)3-methylphenyl azo-2″,4″-dimethylbenzene, and nonmesogenic as well as mesogenic esters, namely, 4-nitrophenyl-4′-*n*-butoxybenzoate and 4-nitrophenyl-4′-*n*-hexyloxybenzoate, respectively.



Where,
R = C_4H_9, [BBMPAD]
A1 = 4-(4′-*n*-butoxybenzoyloxy)3-methylphenyl azo-2″,4″-dimethylbenzene [Cr 90 N 155 I]
R = C_6H_{13}, [HBMPAD]
A2 = 4-(4′-*n*-hexyloxybenzoyloxy)3-methylphenyl azo-2″,4″-dimethylbenzene [Cr 95 N 145 I]



Where,
B1 = R = C_4H_9, 4-nitrophenyl-4′-*n*-butoxybenzoate [Cr 55 I] [NPBB]
B2 = R = C_6H_{13}, 4-nitrophenyl-4′-*n*-hexyloxybenzoate [Cr (52) N 68 I] [NPHB]
The binary systems studied are (1) BBMPAD + NPBB, (2) HBMPAD + NPBB, (3) BBMPAD + NPHB, and (4) HBMPAD + NPHB.

2. Experimental

2.1 Synthesis

All the chemicals used were of Loba chemie, and Merck grade. 4-(4′-*n*-alkoxybenzoyloxy)3-methylphenyl azo-2″,4″-dimethylbenzenes and 4-nitrophenyl-4′-*n*-alkoxybenzoates were synthesized by reported methods. 4-*n*-alkoxy benzoic acids and 4-*n*-alkoxy benzoyl chlorides were synthesized by the known method [21] and 3-methyl-4-hydroxyphenylazo-2′,4′-dimethyl benzene was also prepared by known method [22]. The above compounds A1 & A2 were synthesized by adding drop wise a cold solution of 3-methyl-4-hydroxyphenylazo-2′-4′-dimethyl benzene in dry pyridine to a cold solution of 4-*n*-butoxy benzoyl chloride and 4-n-hexyloxy benzoyl chloride, respectively. The mixture was allowed

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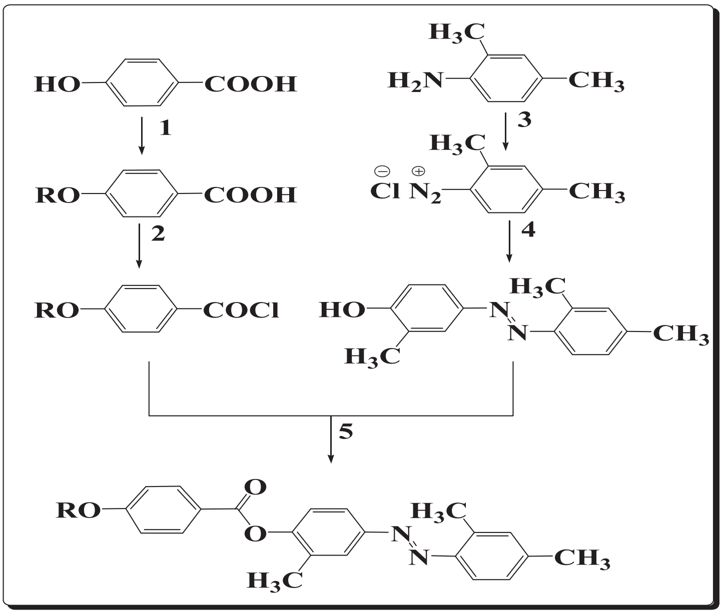
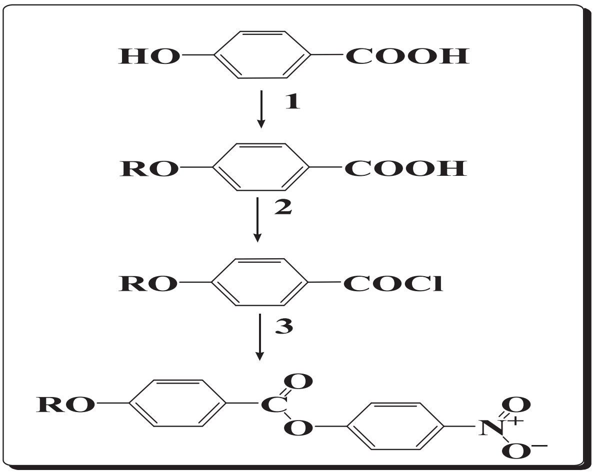
to stand overnight at RT. It was acidified with 1:1 cold HCl and the separated solid was filtered and recrystallized from ethanol until constant transition temperatures were obtained. TLC shows single spot product. The synthetic route is shown in Scheme 1 and Scheme 2.



Scheme 1. Synthetic route 1.

IR spectra: were recorded on a Shimadzu IR-408. Component HBMPAD: 2954–2857 (C—H St, Alkyl CH_3, SP^3 hybridization), 1734 (—C=O— St. of ester), 1601 (—N=N— St.), 1577–1503 (—C=C— St. of aromatic ring), 1477 (—C—H bending of —CH_2—), 1247 (aromatic ether St.), 1061(—C—O— St. of ester), 893 (strong —C—H— bending for 1:2:4 tri substituted benzene ring), 725 (weak —C—H— bending for polymethylene-$(CH_2)_n$-) cm^{-1}.



Scheme 2. Synthetic route 2.

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^{1}H NMR: for HBMPAD ($CDCl_3$, 300 MHz, δ, ppm, standard TMS)

$\delta = 0.93$ (t, 3H, aliphatic $-CH_3$), 1.35–1.82 (m, 10H, 5($-CH_2$-)), 1.85 (Qunt. 2H, $-COCH_2$), 4.04(t, 3H, $-OCH_2$), 2.32, 2.37, 2.68 (s, 3H, Ar$-CH_3$), 6.95–7.06 (m, 4H, ArH), 7.13–8.17 (m, 6H, ArH).

For azo-ester mesogens:
$R = C_nH_{2n+1}$ [$n = 4$ or 6];
(1) alcohol, KOH, *n*-RBr, (2) $SOCl_2$, (3) HCl, $NaNO_2$, H_2O/0–5°C, (4) 2-methyl phenol, aq. NaOH, at 0–10°C, pH 8–12, (5) dry pyridine, 1:1 cold HCl.

For nonmesogenic and mesogenic compounds:
$R = C_nH_{2n+1}$ [$n = 4$ or 6]; (1) alcohol, KOH, RBr, (2) $SOCl_2$, (3) 4-nitrophenol, dry pyridine, 1:1 cold HCl.

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 to four 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 1: BBMPAD (A1) + NPBB (B1)

In this system (Table 1, Fig. 1), the ester component B1 is nonmesomorphic in nature (K 55 I), whereas the azo-ester mesogen A1 is mesomorphic in nature (K 90 N 155 I) exhibiting nematic phase with Schlieren texture. The mesogenic characteristic commences in the form of enantiotropic nematic with the addition of as low as 7.74 mole% of A1 component to B1 and it continues to be exhibited till the last binary mixture studied. System shows

Table 1. BBMPAD (A1) + NPBB (B1)

Mole% of A1	Transition temperature (Nematic, °C)	Transition temperature (Isotropic, °C)
0.00	—	55
7.74	49	58
15.89	51	70
24.49	55	85
33.54	52	88
43.07	46	94
53.19	45	115
63.85	52	128
75.20	62	134
87.21	80	143
100.00	90	155

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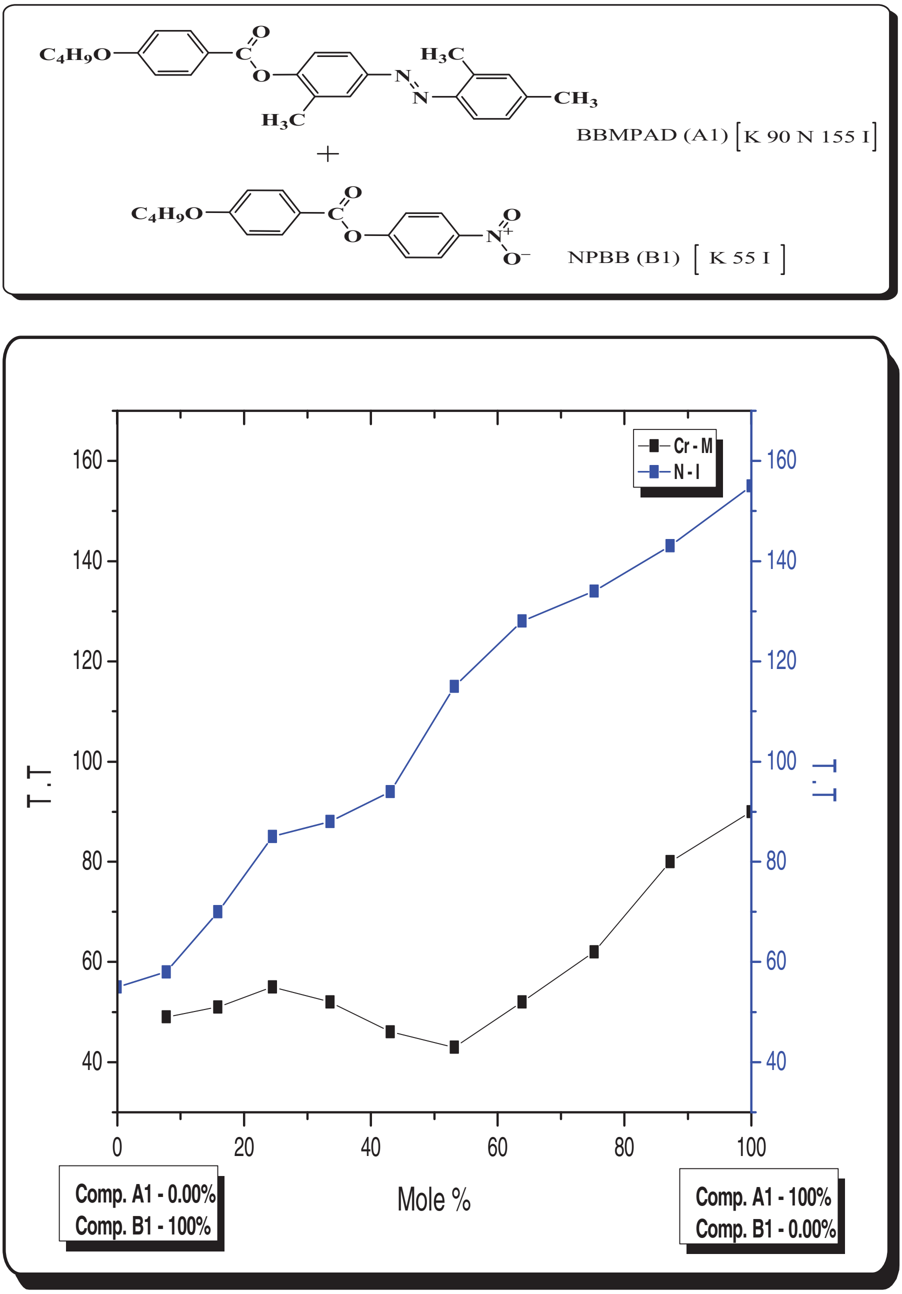

Figure 1. BBMPAD (A1) + NPBB (B1).

threaded/marble texture of nematic phase. The N-I curve shows deviation from linearity. The maximum mesophase range of 76°C is obtained at 63.85 mole% of A1. Eutectic point is obtained at 53.19 mole% of A1 with eutectic temperature 45°C and mesophase range of 70°C at this point.

Table 2. HBMPAD (A2) + NPBB (B1)

Mole% of A2	Transition temperature (Nematic, °C)	Transition temperature (Isotropic, °C)
0.00	—	55
7.30	52	65
15.05	51	76
23.31	55	81
32.09	50	88
41.37	47	91
51.54	38	96
62.30	55	131
73.96	63	132
86.47	84	141
100.00	95	145

3.2 Binary System 2: HBMPAD (A2) + NPBB (B1)

In this system (Table 2, Fig. 2), the ester component B1 is nonmesomorphic in nature (K 55 I), whereas the azo mesogen A2 is mesomorphic in nature (K 95 N 145 I) exhibiting nematic phase with Schlieren texture. The mesogenic characteristic commences in enantiotropic nematic form with the addition of as low as 7.30 mole% of A2 component and it continues to be exhibited till the last binary mixture studied. The eutectic point is sharp and obtained at 38°C with 51.54 mole% of A2; the N-I curve shows deviation from linearity and highest mesophase range of 76°C is obtained at 62.30 mole% of A2.

3.3 Binary System 3: BBMPAD (A1) + NPHB (B2)

In this system (Table 3, Fig. 3), the ester component B2 is monotropic mesomorphic in nature (K (52) N 68 I), whereas the azo-ester mesogen A1 is enantiotropic mesomorphic in nature

Table 3. BBMPAD (A1) + NPHB (B2)

Mole% of A1	Transition temperature (Nematic, °C)	Transition temperature (Isotropic, °C)
0.00	(52)	68
8.38	52	58
17.10	53	68
26.10	52	74
35.49	50	78
45.18	47	103
55.29	54	111
65.79	63	116
76.74	76	122
88.11	82	125
100.00	90	155

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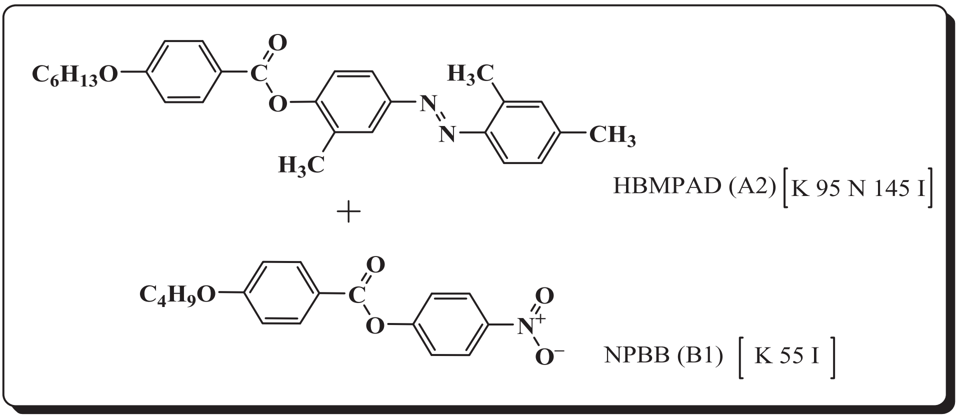

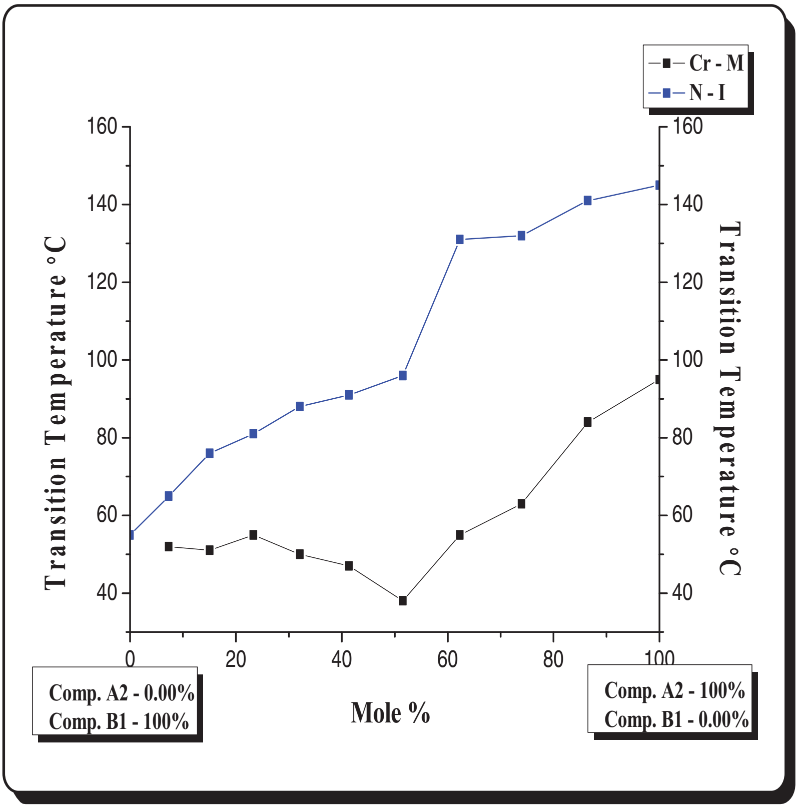

Figure 2. HBMPAD (A2) + NPBB (B1).

(K 90 N 155 I) showing nematic mesophase. The mesogenic characteristic commences in enantiotropic nematic form with the addition of as low as 8.38 mole% of A1 component and it continues to be exhibited till the last binary mixture studied. Binary system shows threaded/marble texture of nematic phase. The N-I curve shows deviation from linearity and highest mesophase range of 57°C is obtained at 55.29 mole% of A1 component. Eutectic point is obtained at 45.18 mole% of A1 component with eutectic temperature 47°C.

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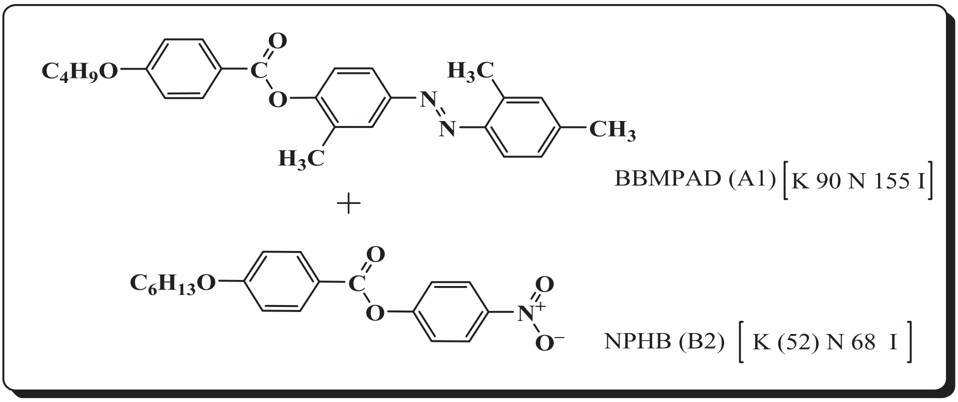

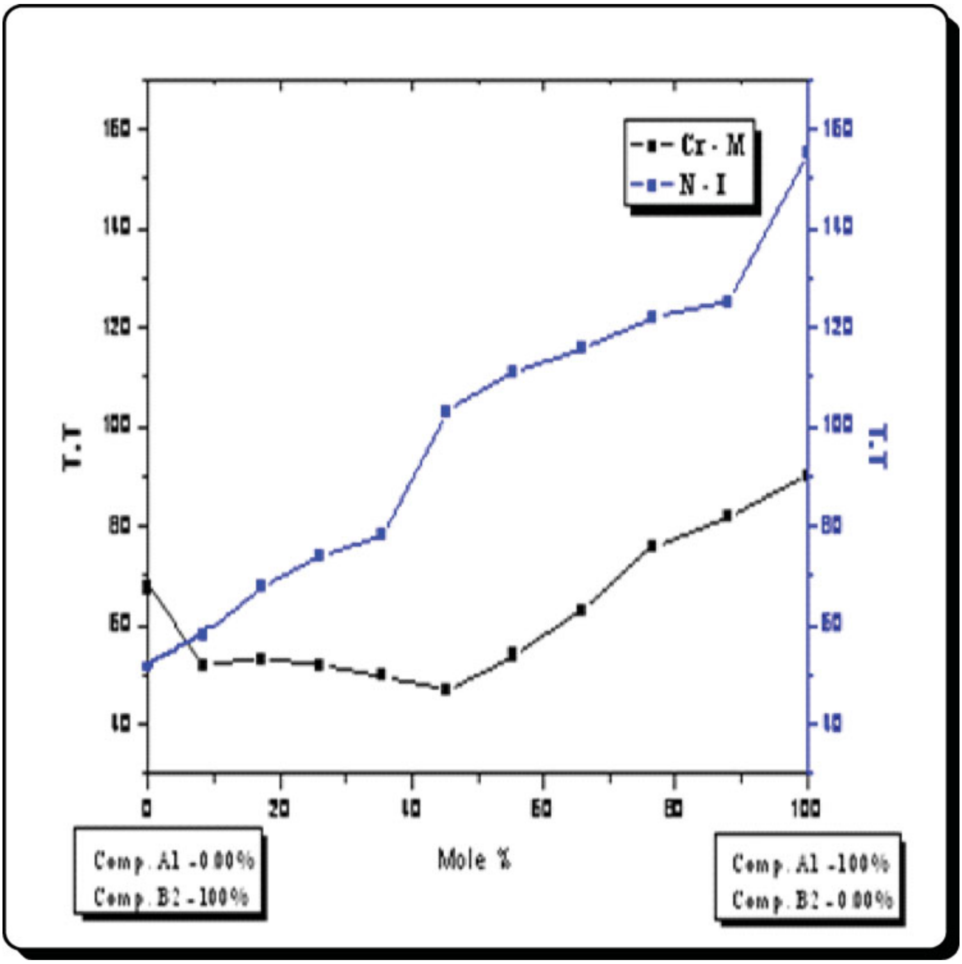

Figure 3. BBMPAD (A1) + NPHB (B2).

Table 4. HBMPAD (A2) + NPHB (B2)

Mole% of A2	Transition temperature (Nematic, °C)	Transition temperature (Isotropic, °C)
0.00	(52)	68
7.75	52	63
15.92	52	73
24.50	54	85
33.55	52	88
43.10	46	94
53.17	43	109
63.87	53	114
75.18	65	121
87.21	84	128
100.00	95	145

3.4 Binary System 4: HBMPAD (A2) + NPHB (B2)

In this system (Table 4, Fig. 4), the ester component B2 is monotropic nematogen (K (52) N 68 I), whereas the azo mesogen A2 is enantiotropic nematogen (K 95 N 145 I). The mesogenic characteristic commences in enantiotropic nematic form with the addition of as low as 7.75 mole% of A2 component and it continues to be exhibited till the last binary mixture studied. Binary system shows threaded/marble texture of nematic phase. Here the eutectic point is sharp at 53.17 mole% of A2; N-I curve shows deviation from linearity and maximum mesophase range of 66°C is obtained at eutectic point.

Study of these binary systems indicates that as the molecular geometry of the two components in the binary mixture differs, N-I deviate from linearity. This nonlinear tendency could be due to different structural moieties forming the terminal groups and central linkages. Nonlinear behavior of binary phase diagrams, where one of the components has a strong polar end group, has been reported by other workers earlier also [23–25]. In these binary systems, deviation from linearity can be attributed to the high tendency of the nitro group of favoring 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 crystallize. In all the binary systems, nematic mesophase emerges with the addition of about 10 mole% of azo-ester mesogens (A1 or A2) in ester components (B1 or B2). All the binary systems show sharp eutectic point.

So study of liquid crystalline behavior of above-prepared binary mixtures shows that mixture of two mesogenic components gives better mesomorphic range than individual components as well as depress solid to mesomorphic transition temperature in mixture.

3.5 Polarizing Optical Microscopic Images of Synthesized Compounds and Prepared Binary Systems

The mesophases exhibited by systems 1–4 were examined by polarizing optical microscopy (POM). Thin films of the samples were obtained by sandwiching them between a glass slide and cover slip. All the prepared binary systems 1–4 were found to exhibit mesomorphism.

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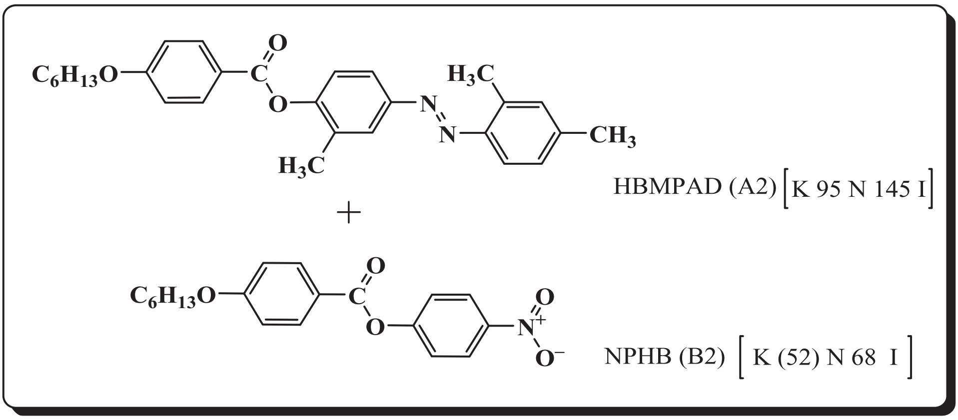


HBMPAD (A2) [K 95 N 145 I]

NPHB (B2) [K (52) N 68 I]

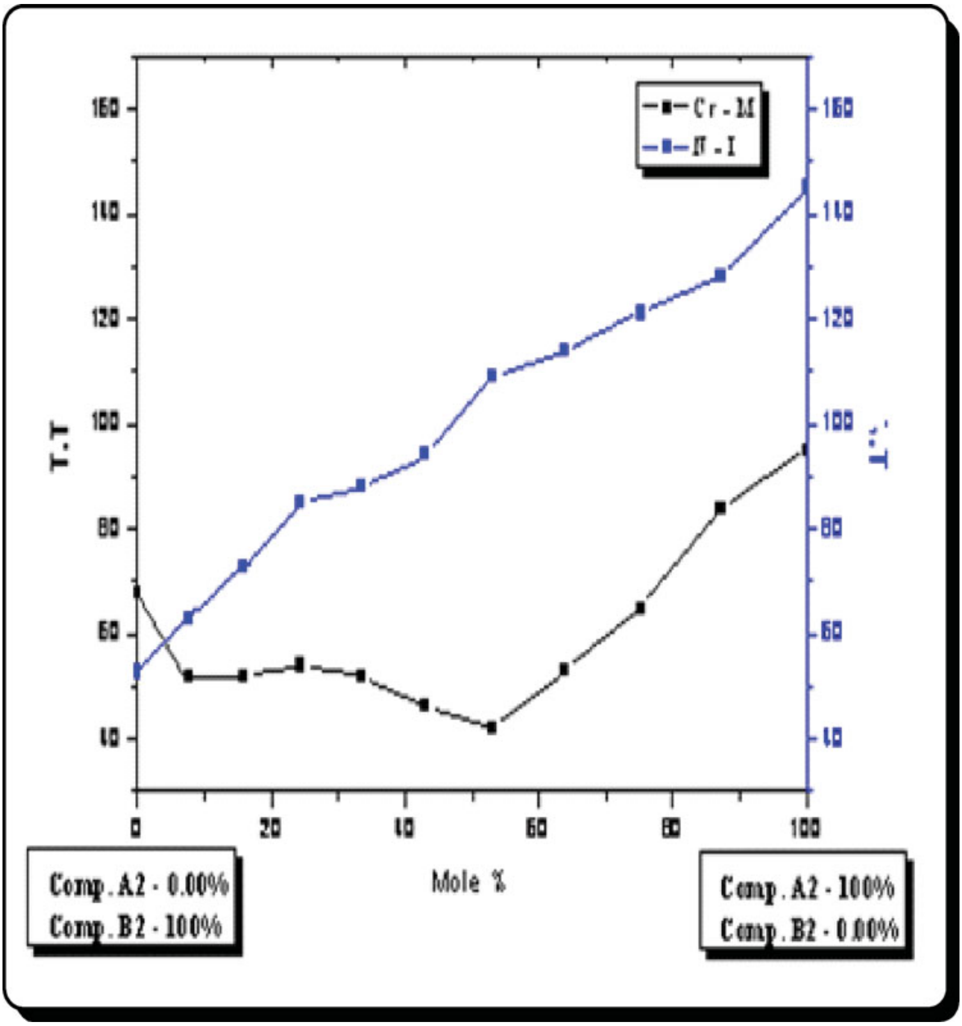
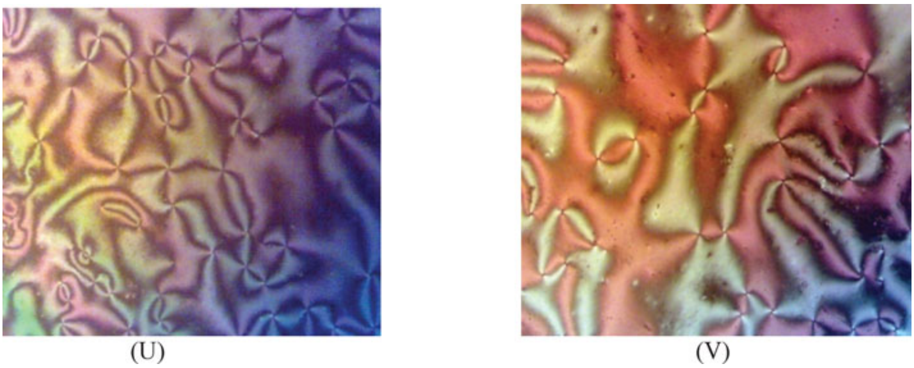


Figure 4. HBMPAD (A2) + NPHB (B2).

On cooling from the isotropic liquid to mesomorphic and then mesomorphic to crystals exhibited nematic mesophase.

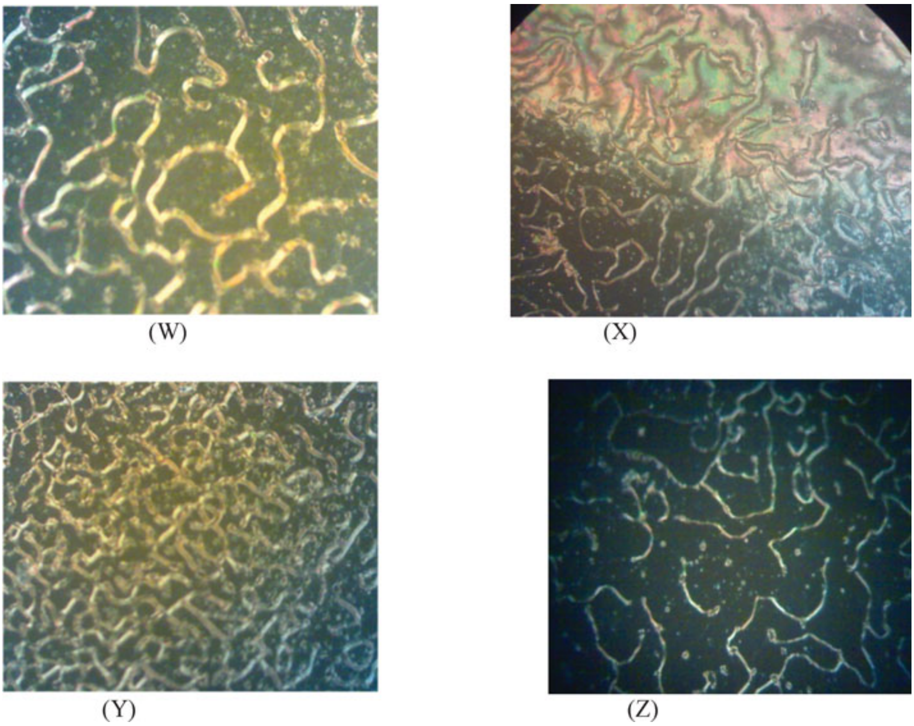
Polarizing optical microscopic images of liquid crystalline state of azo mesogens are as under:



(U) (V)

Polarizing optical microscopic images of Schlieren texture of nematic (U) at 114°C and (V) at 121°C of compound A1 and A2 exhibited while cooling.

Polarizing optical microscopic images of liquid crystalline state of prepared binary systems are as under:



(W) (X)

(Y) (Z)

Polarizing optical microscopic images of threaded texture of nematic (W) at 101°C, (X) at 102°C, (Y) at 78°C, and (Z) at 97°C of prepared binary systems 1–4 exhibited while cooling.

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4. Conclusion

Four binary systems are reported with structurally dissimilar azo-ester mesogens and nonmesogenic as well as mesogenic ester components. In all binary systems, nematic mesophase emerges in enantiotropic nematic form with the addition of less than 10 mole% of azo-ester mesogenic components. In all the four binary systems, N-I curve deviates from linearity. Some of the mixtures super cool below 35°C, which can be potential mixtures for optical display applications.

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