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Study on binary system comprising a non-mesogen and a mesogen

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Mixed liquid crystal formation has been studied in a new binary system comprising *para*-nitroazobenzene derivatives, in which one component was a mesogen and the other was a non-mesogen. The mixtures were found to exhibit a monotropic nematic phase which was converted to an enantiotropic phase in specific ranges of temperature and concentration. The latent liquid crystal–isotropic transition temperature (LTP) of the non-mesogen was obtained by using the extrapolation method of the transition temperature–composition curve and the equal-*G* analysis method. The LTPs of the non-mesogen obtained by the above two methods showed good agreement with each other. The low-temperature transition of the mixtures detected by DSC was attributed to a change of the crystallite size.

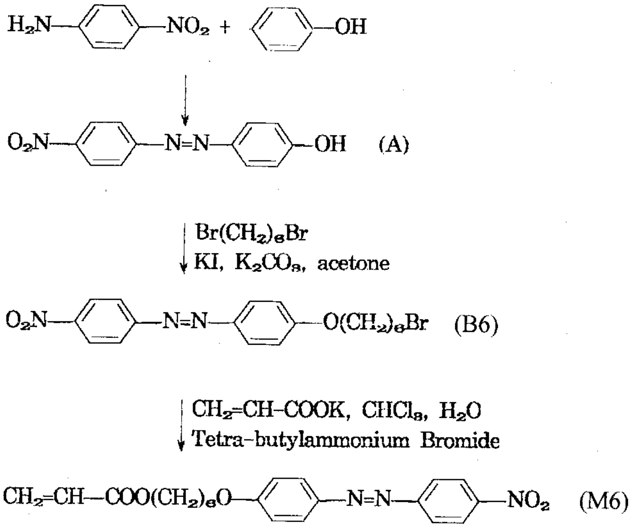
1. Introduction

A number of binary systems have been reported in the literature. A binary system could consist of either two mesogenic compounds [1], a mesogen and a non-mesogen [2] or two non-mesogens [3]. Most phase diagrams of binary systems of nematic liquid crystals showed simple eutectic points, some showed an induction of a smectic phase [4], some showed new phenomena [5, 6]. Mixed liquid crystal formation has been extensively studied by Dave and Vasanth [7], Yu and Labes [3], and Gupta and Vora [1]. Binary and ternary mixtures of mesogens have provided better formulations and applications in various fields, especially in LC display. This has given impetus for the studies of binary and ternary systems comprising mesogens or non-mesogens. In the present study, we report the phase transitional properties of mixtures of azobenzene derivatives in which one was a mesogen and the other a non-mesogen. The unique low-temperature transitional property of this system has also been studied, with results showing that it was change of crystallite size caused enthalpic and morphological changes.

2. Experimental

2.1. *Preparation of compounds and mixtures*

The compounds studied in this work are referred to as B6 and M6; their structures are given in the scheme. The raw material, 4-hydroxy-4′-nitroazobenzene (A), was prepared by the coupling of a diazotized aniline with phenol, as described elsewhere [8].



Scheme. Synthesis route for B6 and M6.

2.1.1. *1-Bromo-6-(4-nitroazo benzene-4′-oxy)hexane (B6)*

Compound A was mixed with a 10-fold excess of 1,6-dibromohexane using potassium carbonate as a base and potassium iodide as a catalyst, in dry acetone according to the typical procedure [8]. The reaction mixture was heated under reflux for 24 h, after which the inorganic residues were filtered off, the acetone evaporated, and the remaining mixture poured into cold hexane. The resultant precipitate was filtered off and recrystallized from hot ethanol to ensure the complete removal of any dimeric side products which might have been formed during the reaction. IR(KBr): $\nu = 1524$, 1342 cm^{-1} (NO_2 stretch). The ^1H NMR spectrum of B6 is given in figure 1 (*a*).

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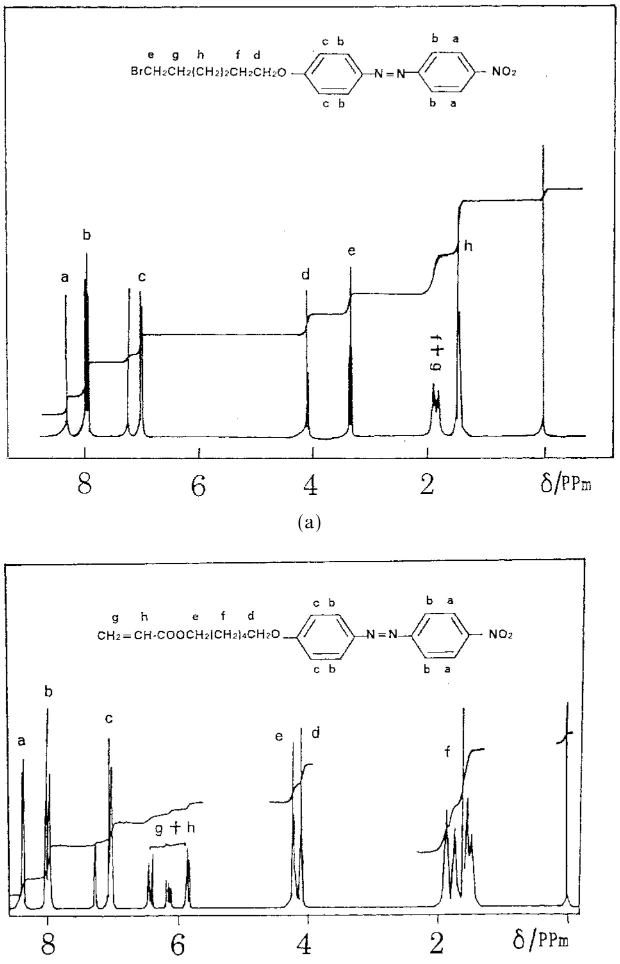
2.1.2. *1-[4-(4-nitrophenylazo)phenoxy]hexyl acrylate (M6)*

Compound M6 was synthesized through a phase-transfer catalysed reaction over 96 h between B6 in chloroform and potassium acrylate in water using tetrabutylammonium bromide as the phase transfer catalyst. Compound M6 was extracted from the mixture with chloroform, the chloroform was removed by distillation and the M6 precipitated by addition of methanol. IR(KBr): $\nu = 1735\,\mathrm{cm}^{-1}$ (C=O stretch). The ^{1}H NMR spectrum of M6 is given in figure 1 (*b*).

2.2. *Characterization*

The proposed molecular structures for the compounds were confirmed by ^{1}H NMR spectroscopy with a Varian Unity 400 MHz spectrometer, and by IR spectroscopy with a 5DX FTIR spectrometer. The optical texture observation was performed with a Zeiss-Jena polarizing optical microscope equipped with a hot stage. Thermal properties of the mixtures were investigated with a Perkin-Elmer DSC-2C differential scanning calorimeter. The WAXD studies were performed on a Philips PW1700 automatic powder diffractometer.



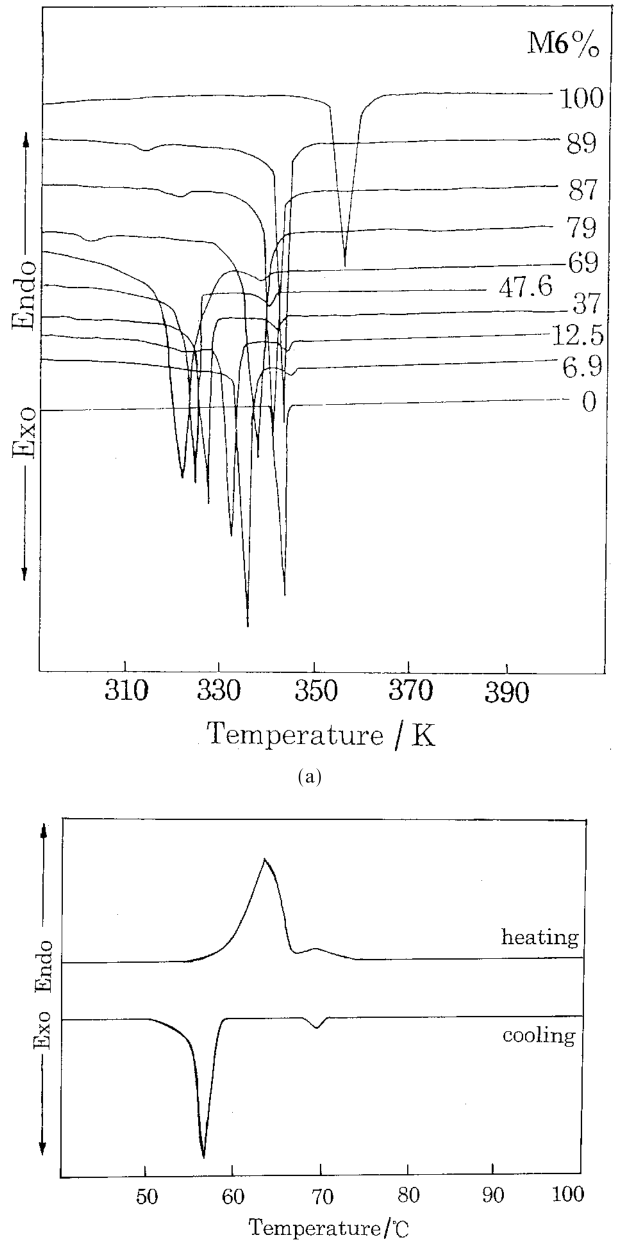
(a)

(b)

Figure 1. ^{1}H NMR spectra of B6 (*a*) and M6 (*b*) in $CDCl_3$.

3. Results and discussion

Figure 2 (*a*) shows DSC traces of the mixtures in the course of cooling. Clearly, there are two exothermic peaks, which correspond to the isotropic–liquid crystal and the liquid crystal–crystal transition for the mixtures with a molar content of M6 lower than 70%; and to the



(a)

(b)

Figure 2. (*a*) DSC curves of the mixtures in the course of cooling. (*b*) DSC curves of the mixture (M6/B6 = 3/2).

isotropic–crystal and the low-temperature transition for mixtures with a molar content of M6 larger than 70%. The mixture with a 60% molar content of M6 showed enantiotropic liquid crystalline behaviour and its DSC curves are shown in figure 2 (*b*).

Pure M6 showed no liquid crystalline behaviour and its DSC curve on cooling is given in figure 2 (*a*).

Polarized optical micrographs of the mixtures in their LC states are shown in figure 3. It can be seen that B6 showed a droplet texture in its LC state, although its mesomorphic transition could not be detected by DSC due to the narrow mesophase range. The mixed liquid crystals showed different kinds of texture, such as schileren and fine thread-like textures, which are typical of the nematic phase.

From the results of DSC and polarized optical microscopy it can be concluded that the mixtures showed mesomorphism over a wide range of temperatures and concentrations, even though they contained a non-mesogen. Compared with other usual binary LC mixtures, mixtures of M6 and B6 exhibited a very interesting phenomenon in that they showed a low-temperature transition which took place before the melting of the crystals and after the crystallization of the mixtures—within a certain range of concentrations. The transition temperature and transitional enthalpies of the low-temperature transition during heating are listed in table 1.

As can be seen from table 1 and figure 2, both the transition temperature and transition enthalpy changed with composition, the transition enthalpies being significantly less than those of the melting and the crystallization peaks. In order to investigate the basis of the low-temperature transition of this system, POM and WAXD were used. Figure 4 shows the optical textures of a mixture (M6/B6 = 12·5/87·5) before and after the low-temperature transition; clearly, the size of the domain changed during the transition. WAXD studies

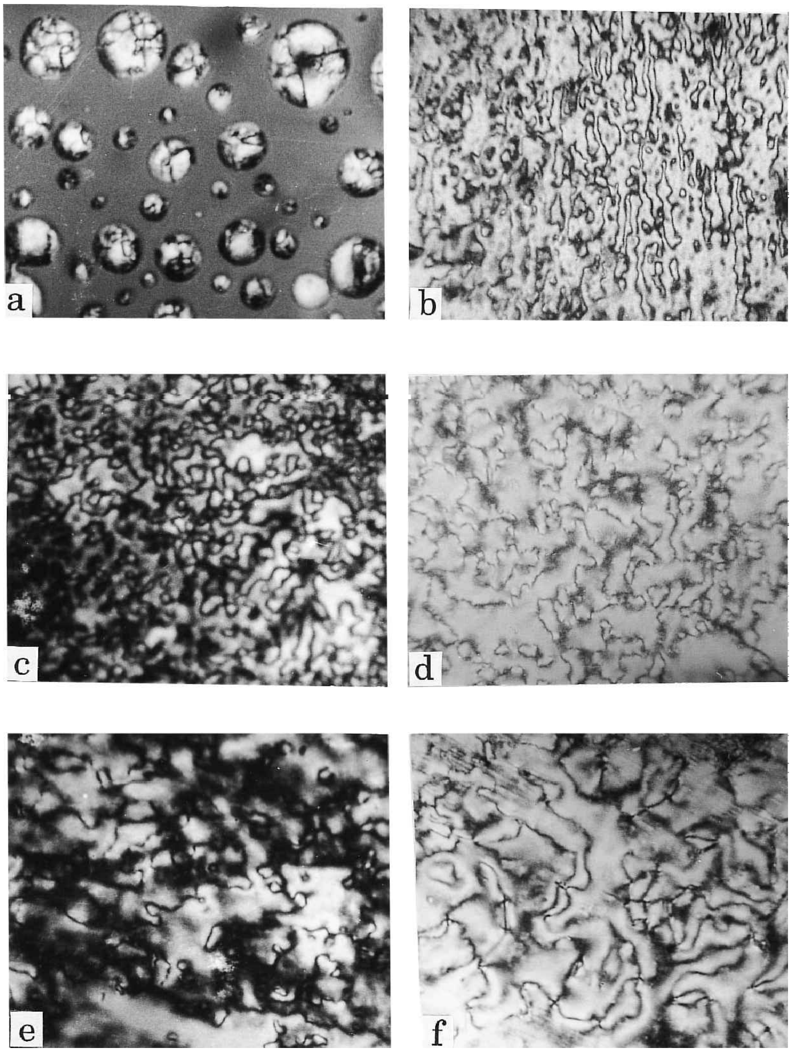


Figure 3. Polarized optical micrographs of the mixtures and B6 in their LC states (×600). (*a*) B6, (*b*) 6·9%M6, (*c*) 12·5%M6, (*d*) 37%M6, (*e*) 47·6%M6, (*f*) 60%M6.

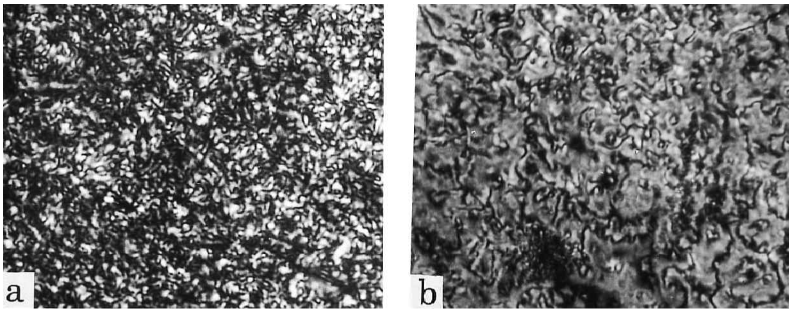


Figure 4. Polarized optical micrographs of the mixtures (×600). (*a*) 12·5%M6 298 K, (*b*) 12·5%M6↓333 K.

Table 1. Transition temperatures and the enthalpies of the low-temperature peaks of the mixture on heating.

M6 content/mol %	ΔH/J g^{-1}	T/K
6·9	1·39	327·6
12·5	3·59	331
69	6·61	331·2
79	1·82	332
90	—	333

on the mixture, before and after the low-temperature transition, showed that neither the position nor the relative intensities of the diffraction peaks changed, suggesting that no structural change of the crystals took place. In studying the crystallite size change, the Scherrer equation was used:

$$L_{hkl} = 5{\cdot}73K\lambda/\beta\cos\theta \text{ (nm)}.$$

Here L_{hkl} is the mean dimension of the crystallites perpendicular to $h\,k\,l$ planes, K is the shape factor ($K = 0{\cdot}9$), λ is the X-ray wavelength, β is the width of the peaks at their half-height, 2θ is the Bragg angle, $\beta^2 = B^2 - \beta^2$, β is the pure broadening profile (deg.), B is the measured half-width of the experimental profile (deg.), and b_0 is the instrumental broadening factor (deg.).

Following the Scherrer equation, three pairs of L_{hkl} were calculated and are listed in table 2. It can be seen that the crystallite size along the three different directions changed during the low-temperature transition, causing the morphological change and resulting in a small enthalpic change. These results from WAXD, DSC and POM suggested that the unique low-temperature transition of this mixture was due to the change in crystallite size.

Ignoring the low-temperature transition, and considering only T_m, T_{cryst}, and T_{NI}, the phase diagram of the binary system is given in figure 5. This diagram can be divided into four regions, A, B, C, and D according to phase behaviour.

The mixtures in regions A and C, where T_{NI} was lower than T_m, but higher than T_{cryst}, showed monotropic liquid crystalline behaviour. In region B, both T_m and T_{cryst} were lower than T_{NI} and the mixtures showed enantiotropic LC behaviour. No liquid crystalline behaviour could be observed for mixtures in region D where T_{NI} was lower than T_{cryst} and T_m.

Using extrapolation on the T_{NI}–composition curve, which showed linearity, the latent nematic–isotropic transition temperature of M6 was obtained, as 337 K. The latent liquid crystal–isotropic transition temperature

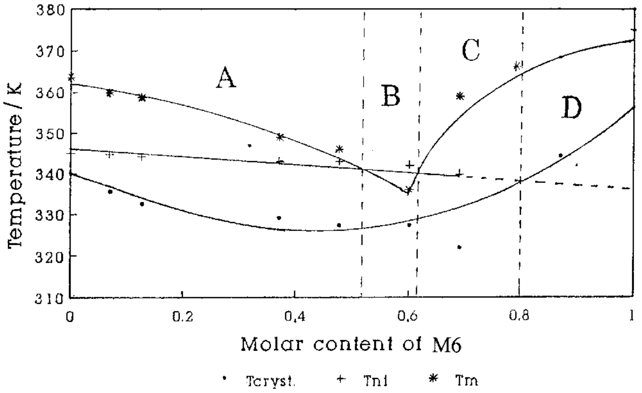


Figure 5. The phase diagram of the mixtures.

Table 2. Three pairs of different crystallite size of the mixture (M6/B6 = 12·5/87·5, mol %). B_1, β_1 and L_{hkl1} are the measured and calculated values from WAXD of the mixture at 298 K; B_2, β_2 and L_{hkl2} are at 333 K, respectively.

2θ/°	$\cos\theta$	B_1/°	B_2/°	β_1/°	β_2/°	L_{hkl1}/nm	L_{hkl2}/nm
17·69	0·9881	0·3846	0·5769	0·3541	0·5571	22·73	14·45
25·16	0·9757	0·5769	0·4231	0·5571	0·3956	14·62	20·60
27·22	0·9719	0·3077	0·3846	0·2687	0·3542	30·45	23·10

of M6 was also calculated by using a method derived by Araya [9] from Van Hecke's equal-G analysis; this gave 336·5 K, showing good agreement with the extrapolation method.

4. Conclusions

Mixtures of compounds M6 and B6 have been studied by DSC and WAXD. The phase diagram of this binary system was obtained and the latent liquid crystal–isotropic transitional temperature of the non-mesogen estimated by two methods. The unique low-temperature transition of this system is attributed to the change of crystallite size which results in a small enthalpic change as well as a morphological change in some mixtures.

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References

[1] Gupta, R., and Vora, R. A., 1984. *Mol. Cryst. liq. Cryst.*, **106,** 147.

[2] Vora, R. A., and Rajput, S. J., 1991, *Mol. Cryst. liq. Cryst.*, **209,** 265.

[3] Yu, L. J., and Labes, M. M., 1979, *Mol. Cryst. liq. Cryst.*, **54,** 1.

[4] Park, J. W., Bak, C. S., and Labes, M. M., 1975, *J. Am. chem. Soc.*, **97,** 4398.

[5] Cladis, P. E., 1975, *Phys. Rev. Lett.*, **35,** 48.

[6] Longa, L., and De Jeu, W. H., 1982, *Phys., Rev. Lett. A*, **26,** 1632.

[7] Dave, J. S., and Vasanth, K. L., 1969, *Indian J. chem. Soc.*, **7,** 498.

[8] Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G., and Tatchell, A. R., 1987, *Vogel's Textbook of Practical Organic Chemistry*, 4th Edn (New York: Longman).

[9] Araya, K., 1991, *Mol. Cryst. liq. Cryst.*, **201,** 23.