Solidification-induced and shear-induced band texture in thermotropic liquid crystalline polymer films

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Lamellar, columnar and cubic mesophases in binary systems of a new double-swallow-tailed compound

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Two phase diagrams of a six-ring double-swallow-tailed compound are presented where the mixing components involve electron-acceptor compounds. In the mixed phase region, nematic, smectic A and C, cubic and columnar phases are induced. In this way transitions between lamellar, cubic and columnar phases can be realized by variation of the concentration. The mesophases occurring in these systems have been characterized by X-ray investigations.

1. Introduction

In binary systems of double-swallow-tailed compounds with calamitic compounds, smectic A phases can be induced mainly because of steric interactions. It was shown that the short rod-like molecules are incorporated into the 'gaps' between the aromatic parts of the double-swallow-tailed compounds so that an orthogonal packing of the molecules within the smectic layers is favoured [1,2]. Therefore this kind of induced smectic A phase is called a 'filled smectic A phase'.

The same effect can be observed for corresponding binary systems of biforked or phasmidic compounds if the admixed calamitic compounds have pronounced electron acceptor properties [3]. In this case the stronger lateral cohesion caused by the additional electron donor–acceptor interaction stabilizes the smectic A mixed phase.

In this paper we show that in binary systems of a new six-ring double-swallow-tailed compound and calamitic electron acceptor compounds, a variety of quite different mesophases can occur.

2. Materials

The following double-swallow-tailed compound (DS)

has been used; this exhibits an oblique columnar phase D_{ob} over a relatively wide temperature range [4].

$$Cr \xleftrightarrow{111^{\circ}C} D_{ob} \xleftrightarrow{206^{\circ}C} I$$
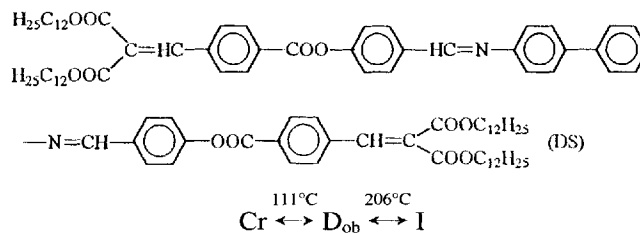
$L = 75\cdot4\,\text{Å}$ (L: molecular length of the most extended conformation)

The electron acceptor compounds used as mixing components were: trinitrofluorenone: (TNF)

$$Cr \xleftrightarrow{175^{\circ}C} I$$

$L = 14\cdot0\,\text{Å}$
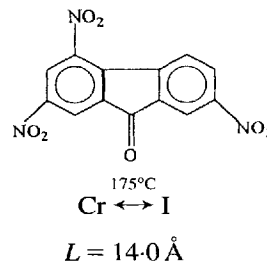
and 4-n-butyloxyphenyl 4-nitrocinnamate (BN) [5]

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$$O_2N-\langle\bigcirc\rangle-CH{=}CH-COO-\langle\bigcirc\rangle-OC_4H_9$$

$$Cr \xrightarrow{\quad 128°C \quad} I$$
$$N \xleftarrow{\quad 124°C \quad}$$

$$L = 22{\cdot}4 \text{ Å}$$

TNF has no mesomorphic properties whereas BN exhibits a monotropic nematic phase.

3. Experimental

To study the phase diagrams of the binary systems, the phase transitions of mixtures of known concentration were determined by polarizing optical microscopy. For some selected mixtures, the transition temperatures were measured by differential scanning calorimetry (DSC 7, Perkin–Elmer). X-ray investigations have been performed using the Guinier method.

4. Experimental results

4.1. *The binary systems TNF/DS*

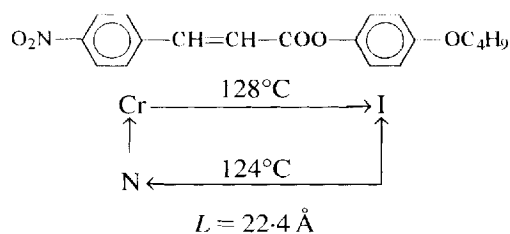Figure 1 presents the phase diagram of the double-swallow-tailed compound DS with the non-mesogenic trinitrofluorenone (TNF). Similarly to the binary systems described in [3], at high concentrations of the acceptor compound, a smectic A phase is induced. The induced smectic A phase disappears in a three-phase transition at 225°C into the isotropic liquid and the nematic phase. This intermediate nematic phase exists only in a small temperature–concentration region, but it shows a maximum in the transition curve nematic → isotropic at 228°C ($x_{DS} = 0{\cdot}35$).

Surprisingly in the medium concentration region ($x_{DS} = 0{\cdot}26{-}0{\cdot}65$), a second lamellar phase is induced which could be identified as a smectic C phase. This smectic C phase generally appears as a schlieren texture. On heating, the smectic C phase also disappears *via* a three-phase equilibrium at 187°C. In this case the smectic C phase forms a smectic A phase and a cubic phase.

It should be noted that the transition of the smectic C phase into the cubic phase is extended over a wide temperature interval (10–15°C).

The hexagonal columnar phase (D_h) appears in a narrow concentration region between the D_{ob} phase of the double-swallow-tailed compound and the cubic and smectic C phase, respectively. A last special feature of this phase diagram is the occurrence of a mixing gap in the isotropic liquid at a high concentration of TNF (between 201 and 271°C, see figure 1). This miscibility gap in the isotropic state could be clearly detected in a contact preparation as a borderline between two liquid phases

which disappears at 271°C. Also, in a sample with a specified concentration (94 mol% TNF), within the liquid phase, droplets of another liquid phase are visible in the same temperature range. It should be noted that a similar behaviour was found for binary systems of phasmidic compounds with TNF [3].

For mixtures of selected concentration, X-ray investigations were performed to characterize and to identify the mesophases which occur in this binary system.

For a mixture with $x_{DS} = 0{\cdot}3$, the following phase sequence is observed (see figure 1):

$$Cr \xleftrightarrow{120°C} S_C \xleftrightarrow{163°C} S_A \xleftarrow{220-225°C} I$$
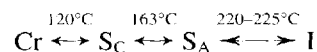
In table 1 the layer spacings d in the smectic A and smectic C are presented. It follows from this table that in the smectic A phase the layer spacing d is nearly independent of temperature. The measured value (59·3 Å) is clearly higher than the average molecular length L which can be calculated by the additivity rule $L = x_{TNF}L_{TNF} + x_{DS}L_{DS}$ where x_{TNF}, x_{DS}: molar fractions of compounds TNF and DS, respectively, and L_{TNF}, L_{DS}: molecular lengths of
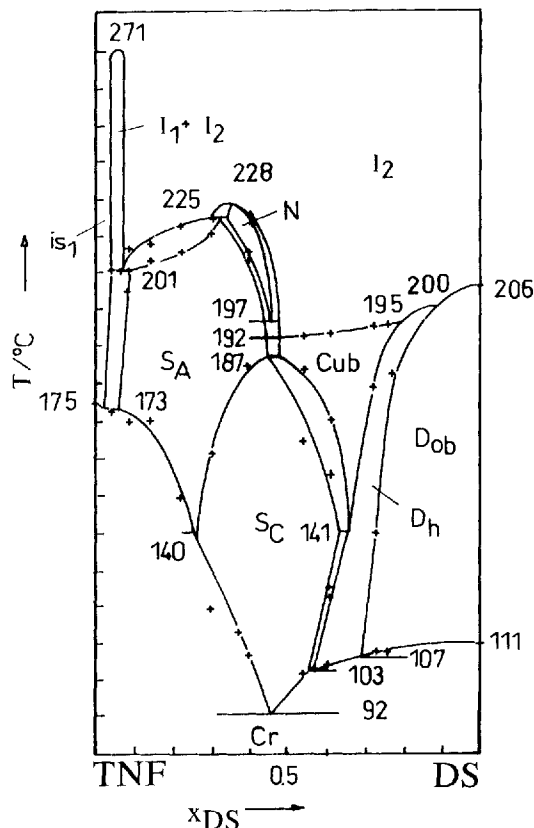

Figure 1. The composition–temperature phase diagram for the binary system with components TNF and DS. If the transition intervals are very small (~ 1°C), the heterogeneous regions are not shown.

Table 1. The d values (Å) in the smectic A and smectic C phases of a mixture with $x_{DS} = 0.3$ (system TNF/DS). The angle β is the tilt angle.

Phase	$T/°C$	$d/Å$	$\beta/°$
S_C	130	51·9	29
	150	55·1	22
S_A	170	59·3	
	190	59·3	

Table 2. Bragg angles and d values for a mixture with $x_{DS} = 0.73$ (system TNF/DS) at 120°C (h k: Miller indices).

(hk)	$\theta/°$	$d/Å$
(10)	0·89	49·7
(01)	1·08	41·0
(11)	1·54	28·7
(20)	1·78	24·9

Table 3. Bragg angles and d values for a mixture with $x_{DS} = 0.73$ (system TNF/DS) at 146°C.

(hk)	$\theta/°$	$d/Å$
(10)	0·89	49·7
(11)	1·54	28·7
(20)	1·78	24·9

compounds TNF and DS, respectively. For the mixture under discussion a d/L ratio of 1·8 can be determined which is typical for 'filled' smectic A phases, whereby obviously two TNF molecules fit into the gaps between the DS molecules [2].

In the smectic C phase, because of the tilt of the molecules, the d values decrease in comparison to those for the smectic A phase. Using the relation

$$\cos \beta = d(S_C)/d(S_A) \qquad (6)$$

the tilt angle β in the smectic C phase could be estimated to be between 29° and 22°. In the case of a mixture with $x_{DS} = 0.73$, by microscopic observation, the transition between the columnar phases D_{ob} and D_h is indicated by a clear change in the optical texture. The D_{ob} phase exhibits a mosaic texture, whereas the D_h phase appears as a focal conic-like texture, but this transition could not be detected by calorimetric measurements. The classification of the columnar phase was possible by X-ray investigations. Tables 2 and 3 show the X-ray reflections and the corresponding d values obtained by the Guinier film method for a mixture with $x_{DS} = 0.73$ having the phase transition sequence

$$
\begin{array}{ccccccc}
& 107°C & & 140°C & & 183°C & & 195°C \\
Cr & \longleftrightarrow & D_{ob} & \longleftrightarrow & D_h & \longleftrightarrow & cubic & \longleftrightarrow & I
\end{array}
$$
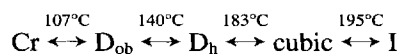
The reflections of the low temperature columnar phase (see table 2) point to an oblique columnar phase. The parameters of the 2D unit cell are found to be $a = 50.9$ Å, $b = 42.0$ Å, and $\gamma = 102.6°$.

The reflections of the high temperature columnar phase (see table 3) can be described by a hexagonal unit cell, the lattice parameter of which is 57·4 Å. It is seen from the tables 2 and 3 that three small angle reflections of the D_h and D_{ob} phases are identical. Therefore it can be assumed that only minor structural and energetic changes accompany the D_{ob}–D_h transitions, as is also indicated by the lack of a calorimetric effect. However, considering the space requirements per molecule in the D_{ob} and D_h phases, respectively ($A_{obl} = 2091$ Å^2; $A_{hex} = 2853$ Å^2) calculated on the basis of the X-ray data a clear change can be seen.

Unfortunately, the cubic phase could not be identified by X-ray measurements, but the transition of the cubic mesophase into the isotropic liquid could be clearly detected microscopically, as indicated by a pronounced decrease in viscosity.

4.2. The binary systems BN/DS

Figure 2 presents the phase diagram of the double-swallow-tailed compound DS with the mesogenic electron acceptor compound BN. It is seen that there are some common features, but also some differences in comparison to the phase diagram in figure 1. The common feature is the occurrence of induced smectic A, smectic C and cubic phases. The monotropic nematic phase of compound BN is stabilized in the mixed phase region, giving rise to a pronounced maximum in the clearing curve at 226°C at about the same concentration as that found for the maximum in the transition curve smectic A–nematic. Furthermore, in the system BN/DS, a hexagonal columnar phase does not occur and a mixing gap in the isotropic liquid state was not observed.

X-ray investigations give evidence that the induced smectic A phase is a 'filled' smectic. According to table 4, for a mixture with $x_{DS} = 0.37$, the d value is 58·8 Å at 145°C, corresponding to a d/L ratio of 1·4. At the transition into the smectic C phase, the d value decreases; the tilt angle at 120°C and 130°C is 14·6° and 7·5°, respectively. Table 5 shows the small angle reflections in the columnar phase of a mixture with $x_{DS} = 0.85$ (170°C). These reflections can be described by a 2D oblique lattice with the cell parameters $a = 44.8$ Å, $b = 39.7$ Å and $\gamma = 116.4°$.

5. Discussion

Because of the special molecular structures of the mixing components, anisotropic steric interactions and electron donor–acceptor (EDA) interactions play a domi-
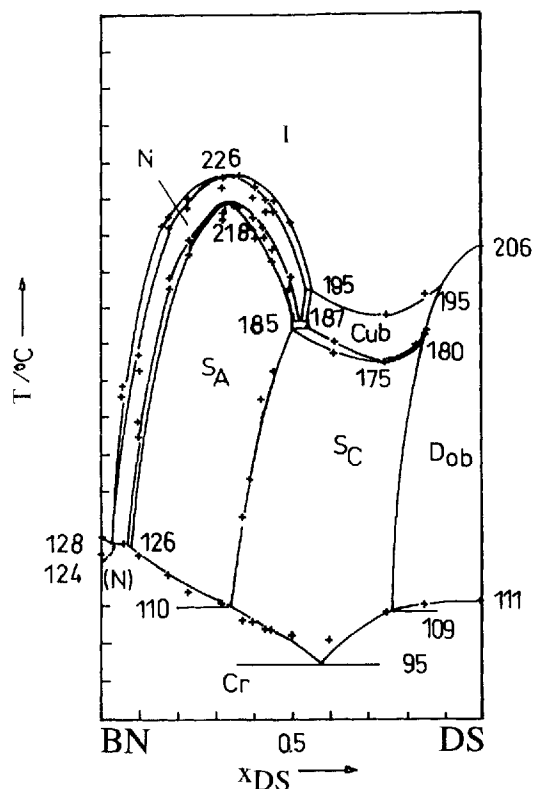
Figure 2.   The composition–temperature phase diagram for the binary system with components BN and DS. If the transitions intervals are very small (~ 1°C), the heterogeneous regions are not shown.

Table 4.   The layer spacings d in the smectic A and smectic C phases of a mixture with $x_{DS} = 0.37$ (system BN/DS).

Phase	$T/°C$	$d/Å$
S_C	120	56·9
	130	58·3
S_A	145	58·8

Table 5.   The Bragg angles and the d values of the columnar phase of a mixture with $x_{DS} = 0.85$ (system BN/DS) at 170°C (hk: Miller indices).

(hk)	$\theta/°$	$d/Å$
(10)	1·10	40·1
(01)	1·24	35·6
(11)	1·99	22·1
(20)	2·20	20·1

nant role in the binary systems under discussion. It is known from binary systems of calamitic liquid crystals that EDA interactions generally give rise to a stabilization of the smectic A phase [7, 8]. In binary systems of

disc-shaped electron donors with non-mesogenic electron acceptors such as trinitrofluorenone (TNF), the formation of columns of disc-shaped molecules is favoured, so that columnar mesophases (D_h) and columnar nematic phases can be induced [9–11]. In the binary systems presented here, one of the components is an electron acceptor (TNF, BN). The second component—the double-swallow-tailed compound DS, which only exhibits a columnar mesophase—acts as a weak electron donor. Unlike the systems described in [9–11], in the binary systems TNF/DS and BN/DS (see figures 1 and 2), nematic, lamellar and cubic mesophases are stabilized in the mixed phase region, as also found in analogous binary systems without significant EDA interaction. This result indicates that steric interactions are mainly responsible for the phase induction.

Of course, EDA interaction, which causes additional lateral cohesion, must also be taken into consideration. This seems to be the reason why columnar mesophases can also be induced as seen in the system TNF/DS.

In this way transitions between lamellar, cubic and columnar phases can be realized not only by change of temperature, but also by change of the concentration, because the intermolecular interactions (here preferably steric, and EDA interaction) are continuously varied by change in concentration.

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