Phase Sequences of Mixtures Formed by Bell-shaped and Calamitic Compounds

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Abstract

We have studied the miscibility of a non-mesomorphic bent-core molecule of new chemical architecture (bell-shape) with a polymorphic rod-like liquid crystal. Mesomorphic properties of their binary mixtures have been tested by polarizing microscopy and some structural parameters were determined using X-ray diffraction. It has been found that the mesophases exhibited by the calamitic component are preserved in certain concentration range only.

Key words: Bent-core compounds, liquid crystals, X-ray diffraction, molecular parameters

1. Introduction

Compounds with bent-core (banana-shaped) molecular architecture [1] represent a new class of non-conventional thermotropic liquid crystals exhibiting occasionally mesomorphic properties different from those of classical mesogens formed by calamitic (rod-like) or disk-like molecules [2, 3]. They have intensively been studied in the last decade [4-6] since ferroelectric switching had first been observed in an achiral Schiffs base banana compound exhibiting rich polymorphism [7]. Investigations have aimed at designing compounds with higher chemical stability (e.g. of ester type [2, 8]), lower mesomorphic temperature range and exotic phases.

Mixing compounds with different molecular structure has been proven a useful tool for adjusting phase ranges and physical properties of liquid crystals. Miscibility studies among bent-core compounds are, nevertheless, not yet as common as among calamitic liquid crystals. Though earlier trials have indicated only limited miscibility of banana

compounds, mixing bent-core molecules with calamitic ones have resulted recently in successful extension of the mesophases toward lower temperatures [9].

In search for novel mesomorphic architectures a new bell-shaped compound 5-(9-decenyloxy-carbonyl)-1,3-phenylene bis(4-nonyloxy biphenyl) carboxylate (**I**) has been synthesized. Its chemical structure is shown in Figure 1; details of the synthesis will be given elsewhere [10].
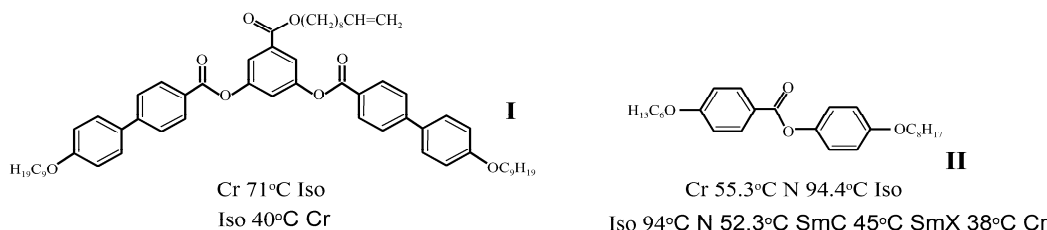

Figure 1. General formula of the studied materials: **I** bell-shaped compound, **II** rod-like molecule.

Although the compound has no mesophases, it exhibits low melting and freezing points. These properties have prompted us to test this compound as a component of binary mixtures. In the present paper we report on miscibility studies of compound **I** with a calamitic liquid crystal 4-(n-octyloxy)phenyl-4-(n-hexyloxy)-benzoate [8] (**II**), which exhibits an enantiotropic nematic (N) as well as two monotropic smectic (SmC and SmX) phases. The chemical structure and the phase sequence of compound **II** is also depicted in Figure 1.

2. Experimental

Investigations were carried out by complementary experimental techniques: polarizing optical microscopy and X-ray diffraction. For the optical studies a polarizing microscope Amplival Pol-U was used. The temperature of the samples was controlled with a Boetius hot-stage. Miscibility was first roughly checked by contact preparations; then binary mixtures of selected composition were investigated in more detail. Phase sequences and phase transitions temperatures were determined via the temperature variation of characteristic textures observed and recorded by a CCD camera attached to the microscope. Occasionally planar oriented sandwich cells with ITO electrodes were also used to check the electro-optical responses.

In order to obtain information on the structure and thus help the identification of mesophases X-ray diffraction was also performed on the mixtures. For these studies non-oriented samples were measured in transmission geometry using a conventional powder diffractometer, Seifert V-14, equipped with an automatic high temperature kit Paar HTK-10. Transmission measurements were carried out at CuK_α radiation of $0.154\,nm$.

3. Results and discussion

The aim of the studies presented here was to understand the miscibility of bell-shaped molecules with rod-like ones and explore the mesomorphic properties of their binary mixtures. The studies were carried out on the pure compounds and on five mixtures (**Mix1**, ,

Mix5) with different concentrations (8.5 %, 20 %, 41 %, 50 % and 67 % by weight, respectively) of the bell-shaped compound **I**. Results of the polarizing microscopy observations are summarized in the phase diagram in Figure 2 which shows how the phase sequence of the mixtures varies with the concentration of the ingredients. As the pure calamitic compound **II** has monotropic mesophases, the data presented in Figure 2 were measured during cooling slowly from the isotropic phase.
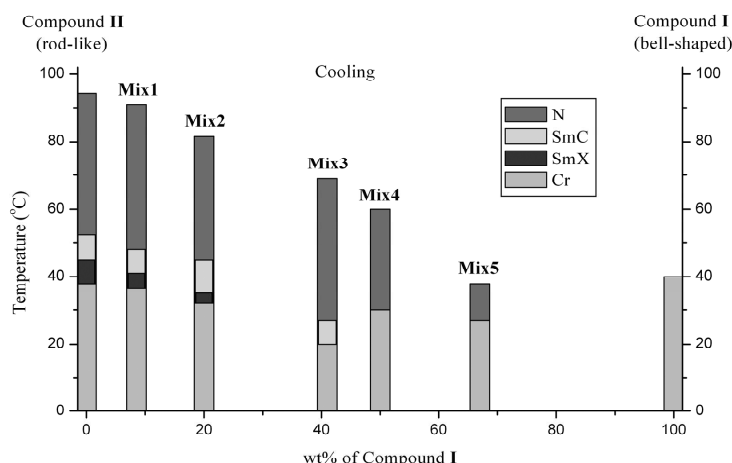

Figure 2. Phase diagram for binary mixtures of rod-like and bell-shaped molecules.

It is seen that the clearing point decreases with increasing concentration of the bell-shaped component which might be attributed to the low melting point of compound **I**. This is accompanied with a reduction of the width of the nematic temperature range which is not surprising as compound **I** is non-mesogenic. A similar tendency can also be observed in the N-SmC and SmC-SmX phase transition temperatures. The SmX phase disappears for concentrations of bell-shaped molecules higher than $20\,wt\%$, while above $40\,wt\%$ even the SmC phase does not exist. It has to be noted that both smectic phases are monotropic in the mixtures just as in the pure compound **II**.

X-ray diffraction studies were carried out both on the calamitic compound and on the prepared binary mixtures which exhibited mesophases. Characteristic diffraction profiles of various phases are presented in Figures 3a for compound **II** and in 3b for **Mix1**. Analyzing the dependence of the diffraction intensities on the scattering angle 2θ the layer spacing d could be calculated from the position of the small angle diffraction peak using Braggs law: $n = 2d\sin\theta$. Analogously, the average intermolecular distance D between neighbouring molecules (in a direction perpendicular to the long axes) could also be obtained from the position of the large angle diffraction peak [11, 12]. These results are summarized in Table 1. The parameters d and D were calculated with an error of $\delta_d \approx \pm 0.1\,A$ and $\delta_D \approx \pm 0.2\,A$, respectively.
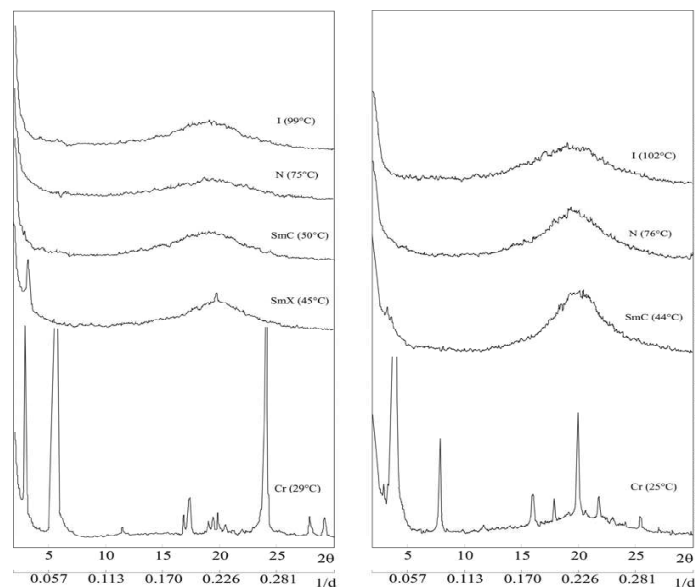
Figure 3. X-ray diffraction profiles for:
(a) rod like molecule **II**,   (b) mixture **Mix1**.

The layer structure in the SmC phase of compound **II** is characterized by one reflection at a small angle $2\theta = 3.1^o$. In mixtures **Mix1** and **Mix2**, similarly, one reflection peak could be found at small angles at the same position as for the rod-like molecule, indicating the presence of the SmC phase.

Table 1. Molecular parameters of the investigated mixtures for all observed phases.

Mixture	T (^oC)	2θ (^{o})	d (nm)	D (nm)
II (0 % of **I**)	99 (Iso)	1.91		0.464
	76 (N)	1.94		0.457
	50 (SmC)	0.31	2.845	
		1.98		0.448
	43 (SmX)	0.33	2.674	
		1.97		0.450
Mix1 (8.5 % of **I**)	102 (Iso)	1.89		0.469
	76 (N)	1.91		0.464
	44 (SmC)	0.31	2.845	
		2.01		0.441
Mix2 (20 % of **I**)	106 (Iso)	1.87		0.474
	76 (N)	1.89		0.469
	53 (SmC)	0.32	2.845	
		2.02		0.439
Mix3 (41% of **I**)	79 (Iso)	1.96		0.452
	59 (N)	1.94		0.457
Mix4 (50% of **I**)	68 (Iso)	1.92		4.62
	35 (N)	2.02		0.439
Mix5 (67 % of **I**)	53 (Iso)	1.96		0.452
	35 (N)	2.01		0.441

This result is in agreement with the phase diagram in Figure 2, obtained from texture observations and is also confirmed by measuring the temperature dependence of the integrated transmitted intensity at crossed polarizers in oriented cells of fixed thickness (Figure 4).
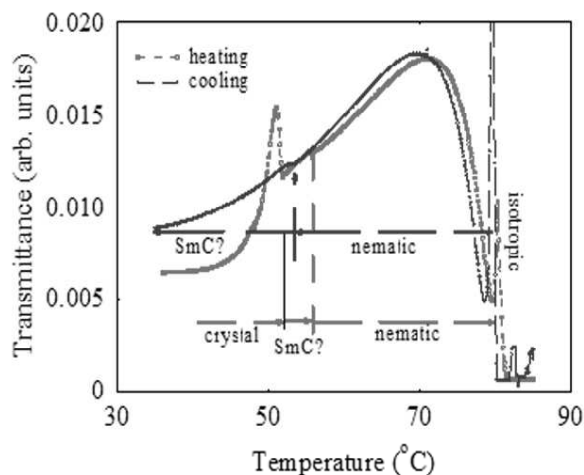

Figure 4. Temperature dependence of the integrated transmitted intensity for **Mix2**.

Here the small jump on the curve seen at $55.5\,^oC$ on heating and at $53\,^oC$ in cooling indicates the N-SmC transition. In case of the other mixtures (**Mix3** - **Mix5**) the SmC phase could not be detected and crystallization occurred directly from the N phase. The X-ray data indicate coexistence of two crystalline modifications in all investigate mixtures.

In the case of the rod-like compound **II** in the SmX phase an additional reflection was found at $2\theta \sim 19.7\,^o$ which is superimposed on the broad diffusion peak (which appears in the range of $2\theta = 12\,^o - 26\,^o$). This suggests the appearance of positional order within the smectic layer. Since the layer spacing in the SmX phase is smaller than in the SmC one can conclude that the SmX is also a tilted phase. Analogous reflection peak superposed on the broad diffusion peak did not show up in any of the investigated mixtures down to room temperatures, only some crystalline modifications could be identified. Thus the X-ray measurements could not justify the appearance of the SmX phase in **Mix1** or **Mix2**, in contrast to polarizing microscopy observations.

3. Conclusions

The present studies aimed to explore the miscibility of a non-mesomorphic bell-shaped bent-core molecule with a polymorphic rod-like liquid crystal via studying mesomorphic properties of their binary mixtures by polarizing microscopy and X-ray diffraction. Both methods confirmed that the enantiotropic nematic phase was preserved in all mixtures (i.e. up to $67\,wt\%$ of the bell-shaped compound) with gradual decreasing of the clearing point and of the width of the nematic range, while upon cooling a monotropic smectic C phase occurred only in **Mix1** and **Mix2**. By polarizing microscopy at slow cooling SmC was seen in addition in **Mix3**, and the monotropic SmX could be observed in **Mix1** and

Mix2. This difference between the two methods might be attributed to the fact that the phases in question are monotropic and their ability for supercooling (i.e. the temperature for crystallization) may depend on the experimental conditions (sample geometry, cooling rate, etc.). The X-ray diffraction studies of non-oriented samples have shown that all the time the SmC phase is present in the mixtures the layer spacing (d) remains unaltered when increasing the $wt\%$ of the bell-shaped compound.

Acknowledgments

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