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Transitions between the B_2 phase and more usual smectic phases in binary systems of banana-shaped with calamitic mesogens

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Three phase diagrams of binary systems are presented where one of the mixing components is a bent-core mesogen and the other is a calamitic mesogen. In two of these systems transitions between the 'banana phase' B_2 and more usual smectic phases in the sequences B_2–SmA, B_2–SmC, B_2–SmC–SmA, B_2–SmC–SmA–N could be observed. The mesophases have been identified by their textures, by X-ray investigations and by electro-optical measurements.

1. Introduction

In only a few years banana-shaped mesogens have been developed to a new fascinating sub-field of liquid crystal research. These new mesogens are of particular interest since not only do new smectic-like mesophases without in-plane order occur, but also some of these mesophases exhibit unusual and interesting physical properties, e.g. chirality and ferroelectricity, although the individual molecules are achiral. At present at least five new mesophases are known that are formed by bent-core molecules [1]. They are designated with the code letters B_1, B_2, B_5, B_6, B_7 according to a preliminary recommendation proposed at a workshop on banana-shaped liquid crystals held in 1997 in Berlin. The most frequently investigated B phase is the B_2 phase which was discovered by Niori *et al.* [2]. In this smectic phase the banana-shaped molecules are packed in the bent direction for steric reasons thereby defining a polar axis parallel to the layer planes. In addition, the molecules are tilted with respect to the layer normal so that the local symmetry of the smectic layers is C_2 [3]. Each layer exhibits two symmetry-breaking elements—the intralayer polar order and the tilt of the molecules. This gives rise to a chirality of the smectic layers as a whole [3]. Furthermore, it follows from electro-optical measurements that the B_2 phase has an antiferroelectric ground state which can be switched into ferroelectric states [3–5].

In first preliminary studies on binary systems it was found that in the phase diagrams the regions of the B_2 phase (and of other B phases) were clearly separated from those of more usual smectic phases (SmA, SmC), indicating a pronounced incompatibility of these different types of mesophase. But recently we were able to detect transitions between the B_2 phase and typical mesophases of calamitic compounds in pure bent-core mesogens; for example the phase sequences B_2–SmA [6–8], B_2–SmA–SmC [7, 8] B_2–SmC–SmA–N [7–9] and B_2–N [9]. The experimental findings indicate that an essential precondition for such transitions is a change of the molecular conformation as a function of the temperature. In the case of bent-core mesogens with perfluorinated terminal chains it seems that temperature-dependent segregation between the perfluorinated chains and the hydrocarbon segments plays a dominant role [6].

The occurence of B_2 phases together with SmA and SmC phases in pure banana-shaped compounds stimulated us to study binary systems between bent-core and calamitic mesogens in more detail. In this paper we present the isobaric phase diagrams of three binary systems. In two of these, it will be shown that by selection of suitable mixing components the polymorphism variants B_2–SmA, B_2–SmC–SmA, B_2–SmC–SmA–N can also be realized.

2. Experimental

To study the phase diagrams of the binary systems, contact preparations as well as mixtures of known concentrations were investigated. The phase transition temperatures were determined by polarizing optical microscopy (Leitz-Orthoplan), and in some cases also by differential scanning calorimetry (DSC Pyris 1, Perkin Elmer). For some selected mixtures X-ray diffraction (XRD)

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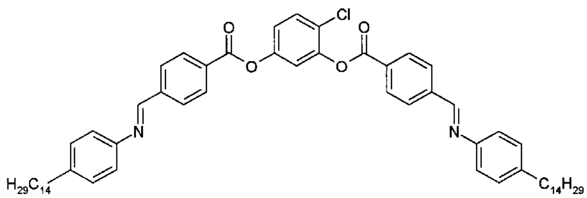
measurements have been made. Investigations on non-oriented samples were carried out using a Guinier goniometer or a Guinier film camera. X-ray investigations on oriented samples were carried out using a 2D area detector (HI star, Siemens AG). Electro-optical measurements were made using the usual experimental set-up described in earlier papers [10].

3. Materials

As bent-core mesogen we used the following compound **A** which exhibits a B_2 phase in a relatively wide temperature range (°C):

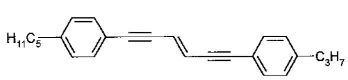
A



Cr 76 B_2 130 I [11]

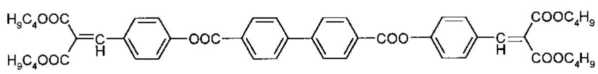
The calamitic mixing components were:

B



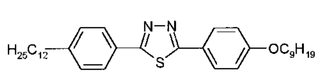
Cr 64 N 150 I [12]

C



Cr 105 N 172 I [13]

D



Cr 78 SmC 172 I [14]

4. Experimental results

4.1. *The binary system* ***A/B***

The calamitic mixing component for the banana-shaped mesogen **A** is the compound **B** which exhibits a nematic phase in a wide concentration range. As seen from the phase diagram in figure 1, there is no complete transition between the B_2 phase and the nematic phase since the heterogeneous regions are broadened. As a result, only a coexistence of these phases could be observed but no complete transition.

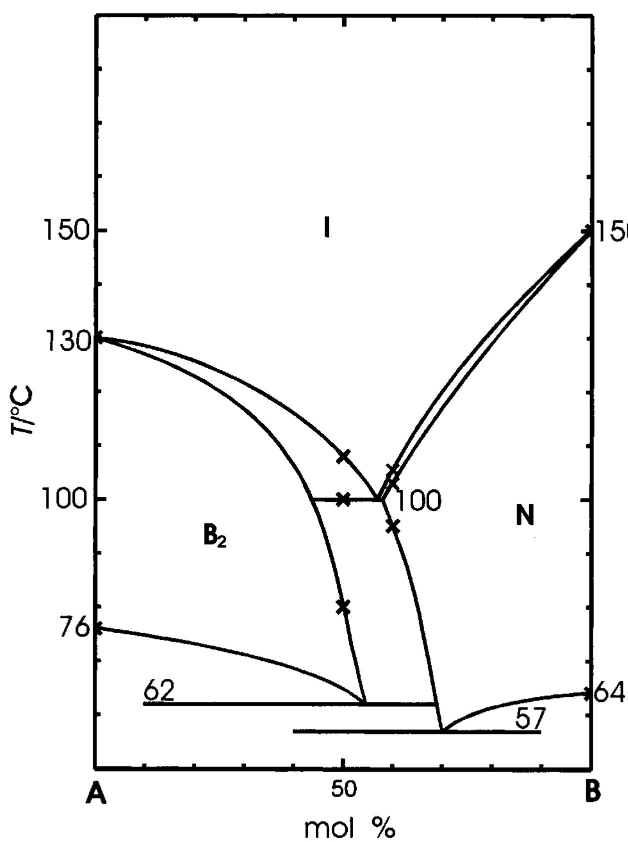


Figure 1. The isobaric composition–temperature phase diagram for the binary system with components **A** and **B**.

4.2. *The binary system* ***A/C***

Figure 2 presents the phase diagram involving the bent-core mesogen **A** and the double-swallow-tailed compound **C** which exhibits a nematic phase in a wide temperature range. Surprisingly we do not observe any contact between the B_2 and nematic regions because an intermediate SmA region arises between these two phases. In this way not a B_2–N transition, but a B_2–SmA transition appears in a relatively wide concentration interval (20–62 mol % **C**). At the phase transition the smooth fan-shaped texture of the SmA phase, figure 3 (*a*), transforms into a grainy fan-shaped texture characteristic of a B_2 phase, figure 3 (*b*). The SmA phase can also exhibit a homeotropic texture and the B_2 phase then forms a schlieren-like texture. The B_2 phase could be identified by XRD and by electro-optical measurements. The X-ray pattern of the B_2 phase shows a strong reflection together with its higher orders on the meridian. The maximum of the diffuse outer scattering lies out of the equator, but the tilt angle derived from the pattern is rather low ($\alpha \approx 10°$). In figure 4, the layer spacing d is shown as a function of temperature. It is seen that in the SmA phase the d-value slightly increases with

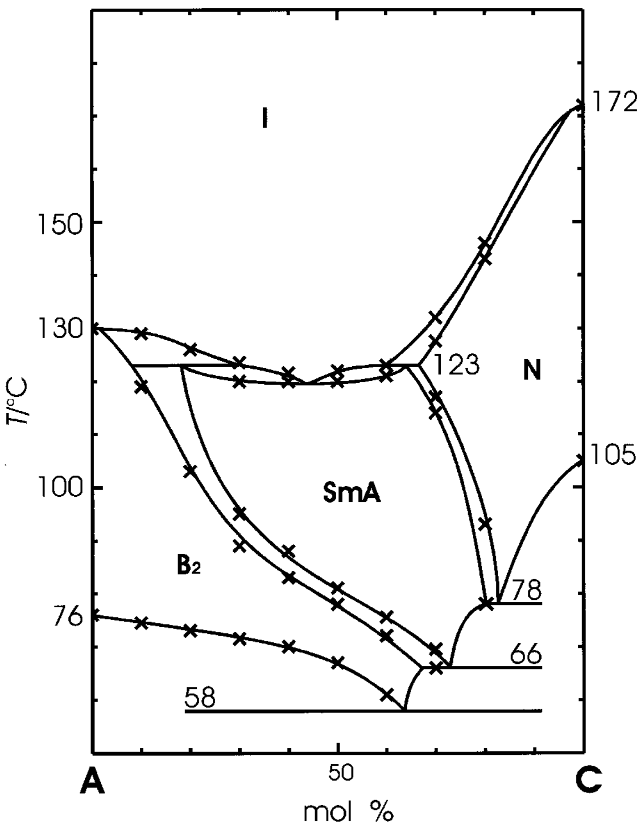
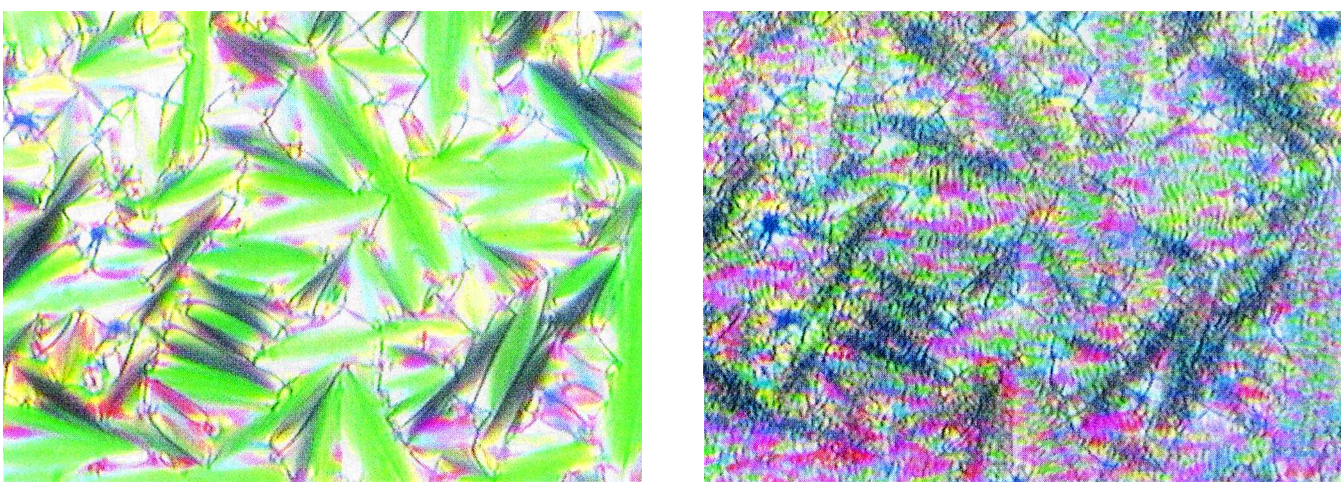


Figure 2. The isobaric composition–temperature phase diagram for the binary system with components **A** and **C**.

decreasing temperature, whereas in the B_2 phase a small decrease is observed. For comparision, the *d*-value of the B_2 phase of the banana-shaped compound **A** ($d = 46$ Å) is somewhat smaller than that for the B_2 phase of the mixture. In contrast, the tilt angle ($\alpha = 39°$) is clearly higher than that in the mixture. Furthermore, on applying a sufficiently high electric field, the sample could be switched and the texture of the switched states was independent of the polarity of the field. This finding points to a racemic ground state of the B_2 phase. The current response—two current peaks per half period of a triangular voltage—gives evidence for the antiferroelectric nature of this phase (figure 5). From the current response a spontaneous polarization $\mathbf{P}_S = 160$ nC cm^{-2} was determined which is about half the value obtained using the pure compound **A** ($\mathbf{P}_S = 330$ nC cm^{-2}).

4.3. *The binary system A/D*

Compound **D** forms a SmC phase in a wide temperature range. In the binary system **A**/**D** an intermediate SmA and a nematic phase appear in the mixed phase region as shown in the phase diagram of figure 6. In different concentration ranges, different phase sequences can be observed. At high concentrations of compound **A** (78–80 mol %) a transition B_2–SmC occurs. Between 68 and 78 mol % **A**, a phase sequence B_2–SmC–SmA is found with increasing temperature. Samples with a concentration between about 45 and 63 mol % **A** display the phase sequence B_2–SmC–SmA–N. This interesting polymorphism variant, which was first observed for two pure bent-core compounds [7–9], can be detected according to the characteristic textures of the mesophases. Figure 7(*a*) shows the marbled texture of the nematic phase for a mixture of 54 mol % **A**. On cooling, the marbled texture is transformed into the fan-shaped texture of the SmA phase, figure 7(*b*). The SmC phase appears as a broken fan-shaped texture, figure 7(*c*),



(*a*) (*b*)

Figure 3. Textures of the mesophases formed by the binary mixture with 40 mol % **C**: (*a*) fan-shaped texture of the SmA phase (95°C); (*b*) grainy fan-shaped texture of the B_2 phase (75°C).

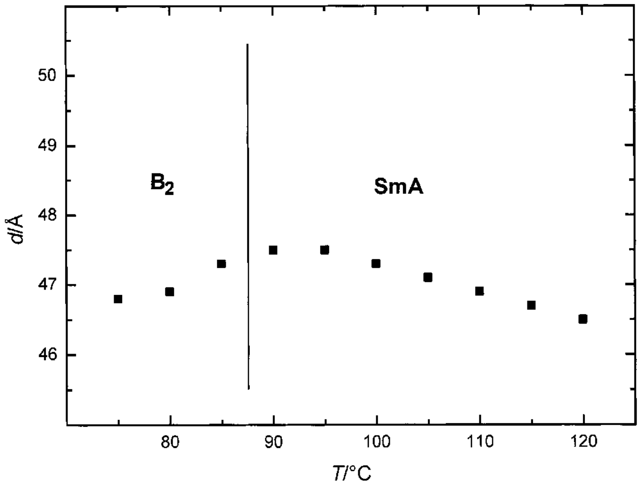


Figure 4. Layer spacing d in the SmA and B_2 phase of the mixture with 40 mol % **C**.

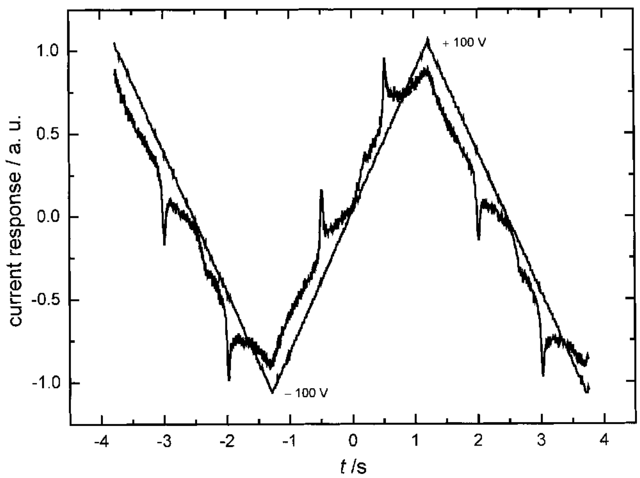


Figure 5. Switching current response in the B_2 phase of the mixture with 40 mol % **C** (200 V_{PP}; 0.2 Hz; cell thickness 10 μm; temperature 70°C).

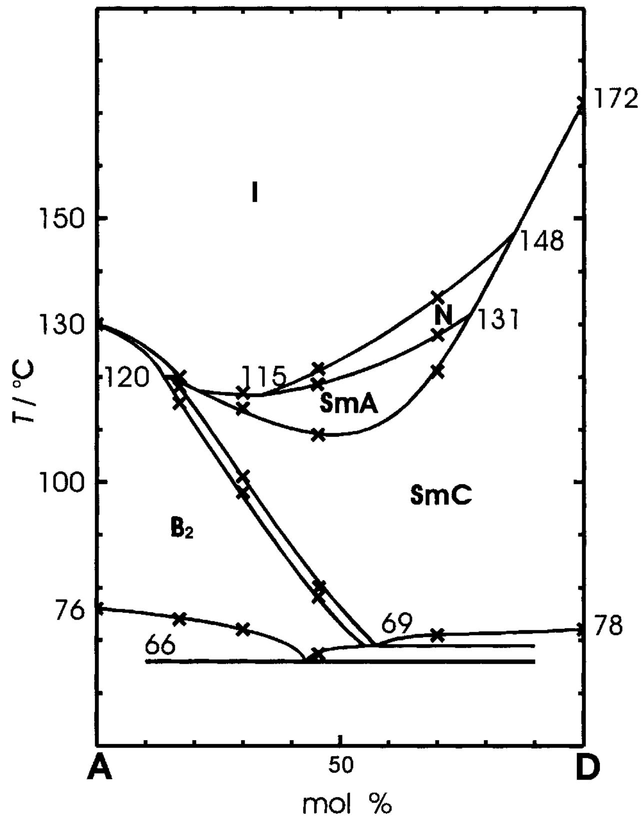


Figure 6. The isobaric composition–temperature phase diagram for the binary system with components **A** and **D**.

whereas the B_2 phase forms a paramorphotic grainy fan-shaped texture, figure 7 (*d*). The four mesophases can also be distinguished by their electro-optical behaviour. In the nematic phase, electrohydrodynamic instabilities with one- or two-dimensional domain patterns are observed. The SmA phase shows no electro-optical response. Furthermore, the SmC phase exhibits a Fréedericksz transition accompanied by electrohydrodynamic processes. In the low temperature phase, a switching takes place above a threshold voltage of 2.5–3 V which is clearly lower than that for the B_2 phase of compound **A** (10 V). The textures of the switched state differ for opposite signs of the applied electric field, pointing to a ferroelectric or antiferroelectric behaviour. But the current response (two current peaks per half period of a triangular voltage) proves the existence of an antiferroelectric ground state which is switched into ferroelectric states. As seen in figure 8, the spontaneous polarization reaches values of about 230 nC cm^{-2}. Figure 9 presents the XRD patterns of oriented samples for all the smectic phases which occur in the mixture with 54 mol % **A**. In the SmA phase the small angle reflections are located at the meridian and the diffuse outer scattering maximum is on the equator. The pattern of the SmC phase is quite similar, the only difference being a small shift of the diffuse wide angle maxima out of the equator, indicating a small tilt between 5° and 10°. For comparison, the SmC phase of the pure compound **D** has a tilt angle α of about 30° which was estimated from the layer spacing ($d = 30.5$ Å) and the molecular length L according to $\cos \alpha = d/L$.

In the B_2 phase, figure 9 (*c*), the diffuse outer scattering maxima are off the equator and the tilt angle α now increases up to about 15°. The tilt angles have been obtained by a scan along the outer diffuse crescent-like scattering. Figure 10 shows the layer spacing d as a function of the temperature. In the SmA phase the d-value slightly increases with decreasing temperature,

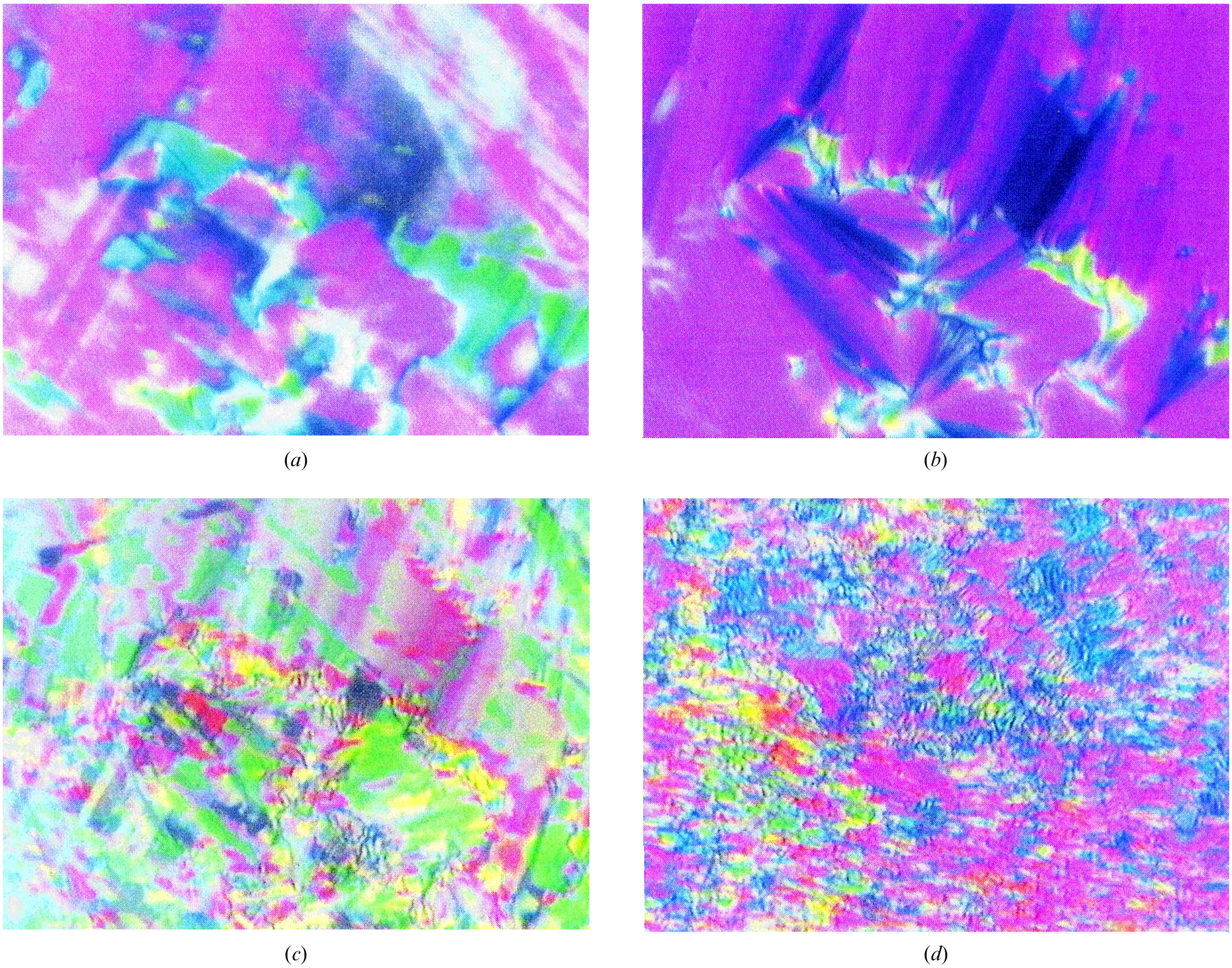


Figure 7. Textures of the mesophases formed by the binary mixture with 46 mol % **D**: (*a*) nematic phase (119°C); (*b*) SmA phase (115°C); (*c*) SmC phase (85°C); (*d*) B_2 phase (74°C).

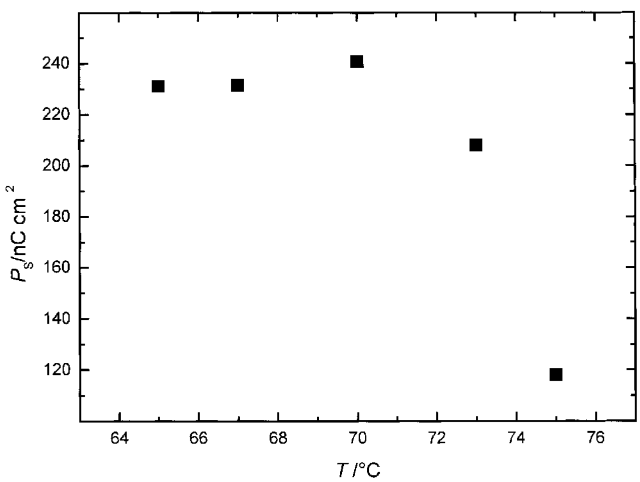


Figure 8. The spontaneous polarization $\mathbf{P}_S$ of the B_2 phase as a function of the temperature (mixture with 46 mol % **D**).

whereas in the SmC phase a weak decrease is observed which is due to the tilting of the molecules with respect to the layer normal. At the transition into the B_2 phase a discontinuous decrease of the layer spacing occurs which is obviously the result of an enlarged tilt of the molecules. In this binary system the layer spacing of the B_2 phase is clearly smaller than that of the pure compound **A**, but also smaller than that of the mixture **A**/**C**. It can be assumed that the differences in the molecular lengths of compounds **C** and **D** are mainly responsible for the differences of the *d*-values in the binary mixtures, provided that we consider the same concentration.

5. Discussion

In recent times we have investigated many binary systems where one component is a bent-core mesogen

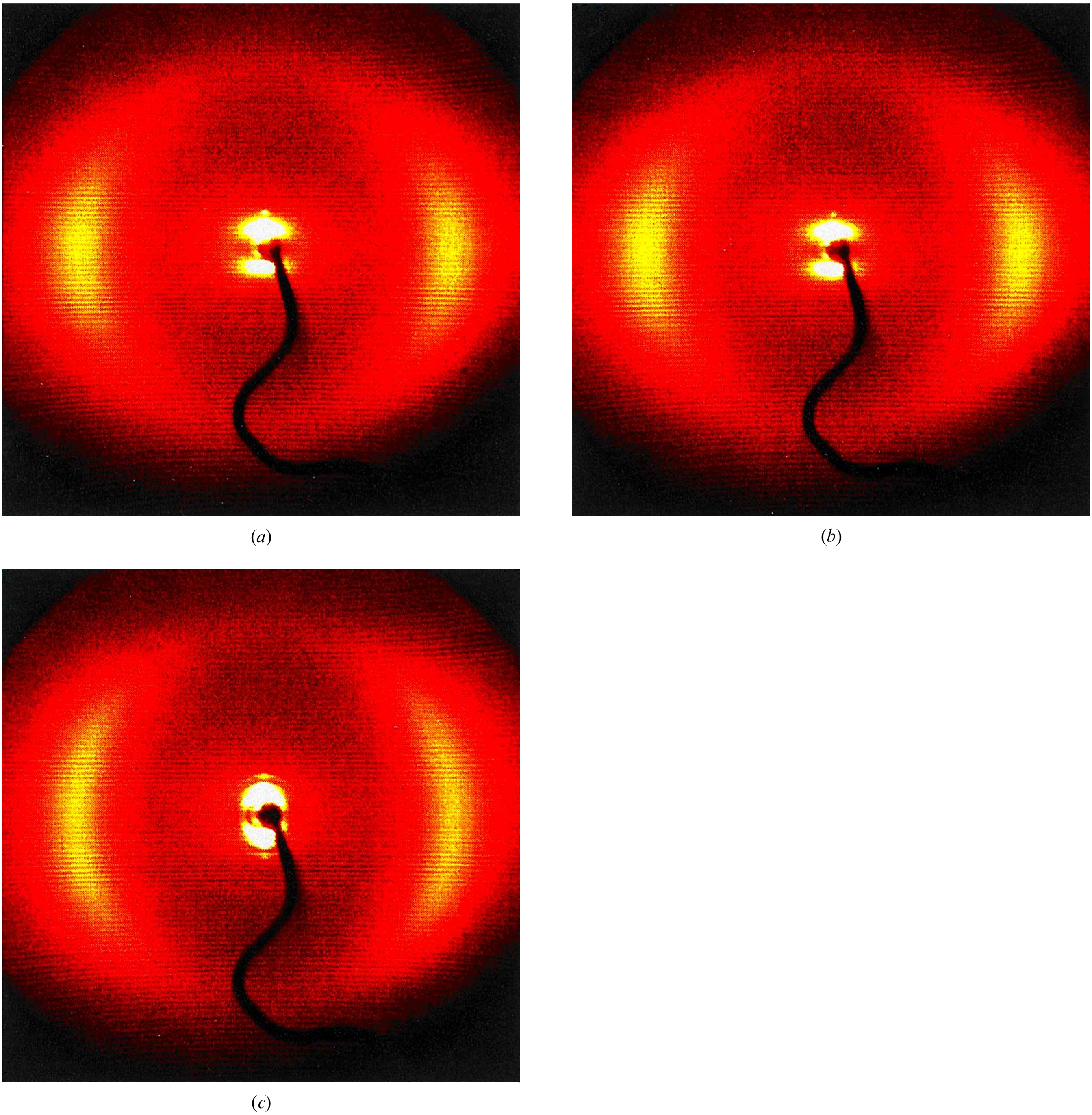


Figure 9. X-ray patterns of oriented samples in the SmA, SmC and B_2 phase of the mixture with 46 mol % **D**; (*a*) SmA phase (115°C); (*b*) SmC phase (100°C); (*c*) B_2 phase (70°C).

and the other is a calamitic compound. In the majority of the phase diagrams the region of the 'banana phases' and those of the nematic or smectic phases are separated by isotropic phase regions or by broad heterogeneous regions which are nearly parallel to the temperature axes. In the latter case there is a coexistence between the B_2 phase and the nematic or more usual smectic phases, but no complete transitions between them (see figure 1).

In the other two binary systems presented here, the heterogeneous regions between the B_2 phase and the

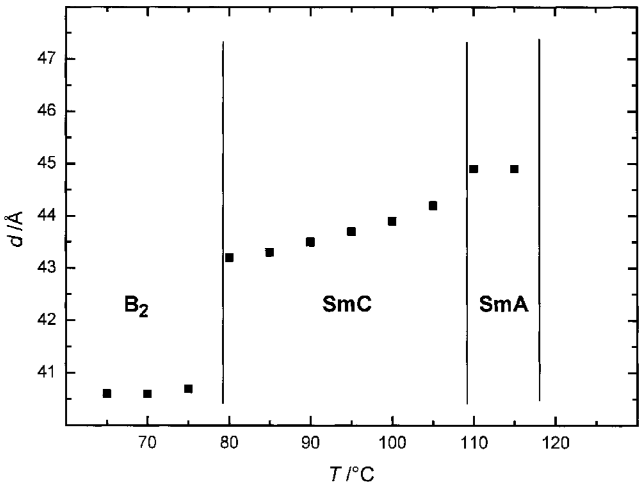


Figure 10. Temperature dependence of the layer spacing d for the smectic phases of the mixture with 46 mol % **D**.

SmA or SmC phase are sufficiently small so that complete transitions between these phases could be observed. We can assume that the preconditions for such unusual phase sequences in binary systems are similar to those which have been proved for pure compounds and reported in [6–9]. An essential precondition is that even in the smectic A or smectic C phase the molecules adopt a bent shape, the bending angle between the wings of the bent-core molecules being of the order of magnitude 140°. Furthermore, the bending angle should decrease with decreasing temperature which presumes a relatively wide temperature range of the mesophases. At higher temperatures the bent molecules can freely rotate around the molecular long axes so that SmA or SmC phases (or nematic phases) can be formed. At sufficiently low temperatures the free rotation is increasingly hindered giving rise to a polar packing which is characteristic for the B_2 phase.

In the binary systems studied here the situation is more complicated in comparison with that for single compounds. XRD yields the layer spacing and the tilt angle, but no detailed information about the packing of the different molecules within the mixed phase. It is not clear whether or how the admixed calamitic molecules possibly change the conformation of the bent molecules. It was found in our binary systems that the tilt angle of the B_2 phase strongly depends on the concentration (whereas it is nearly independent of the temperature in the pure compounds). This means that it decreases with increasing concentration of the rod-like compound. In this way the tilt angle reaches a sufficiently small value ($\alpha \approx 14°$) like that found in pure compounds with a B_2–SmA sequence. In binary systems of smectic phases with tilted rod-like molecules it is well-known that at mid-concentration the tilt angle can decrease [15]. An additional support for this finding is that in nearly all cases the induced smectic phases in binary systems possesses an orthogonal alignment of the molecules although the mixing components form tilted phases. A similar situation is found in our mixtures of bent-shaped and calamitic molecules where both kinds of molecule adopt a tilt, but the tilt angle decreases at mid-concentrations. With respect to the phase sequence N–SmA–B_2 we can assume that the polar packing caused by the bent molecular structure is destroyed by the admixed calamitic molecules. Therefore rotation around the molecular long axes is possible at high temperatures. In this way the occurrence of N, SmA and SmC phases can be understood. At lower temperatures, the rotation is more and more hindered and the polar packing arises which characterizes the B_2 phase. The appearance of the B_2 phase over a wide concentration range in the binary system **A**/**C** (figure 2) is a very surprising result. In binary systems with double-swallow-tailed compounds, like compound **C**, so-called 'filled phases' are observed, where the double-swallow-tailed compound forms the host matrix [16]. The appearance of the wide region of induced SmA phase points to such a behaviour in the system under investigation, too. But, with respect to this, the explanation of the polarization within the layer of the B_2 phase, which is a cooperative property, needs further investigations.

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References

[1] PELZL, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mat.*, **11,** 707.
[2] NIORI, T., SEKINE, F., WATANABE, J., FURUKAWA, T., and TAKEZOE, H., 1996, *Liq. Cryst.*, **6,** 1231.
[3] LINK, D. R., NATALE, G., SHAO, R., MACLENNAN, J. E., CLARK, N. A., KÖRBLOVA, E., and WALBA, D. M., 1997, *Science*, **278,** 1924.
[4] DIELE, S., GRANDE, S., KRUTH, H., LISCHKA, CH., PELZL, G., WEISSFLOG, W., and WIRTH, I., 1998, *Ferroelectrics*, **212,** 169.
[5] MACDONALD, R., KENTISCHER, F., WARNICK, P., and HEPPKE, G., 1998, *Phys. Rev. Lett.*, **81,** 4408.
[6] WEISSFLOG, W., KOVALENKO, L., WIRTH, I, DIELE, S., PELZL, G., SCHMALFUSS, H., and KRESSE, H., 2000, *Liq. Cryst.*, **27,** 677.
[7] KOVALENKO, L., WEISSFLOG, W., GRANDE, S., DIELE, S., PELZL, G., and WIRTH, I., 2000, *Liq. Cryst.*, **27,** 683.
[8] WIRTH, I., DIELE, S., EREMIN, A., PELZL, G., GRANDE, S., KOVALENKO, L., PANCENKO, N., and WEISSFLOG, W., 2001, *J. mater. Chem.*, **11,** 1642.
[9] WEISSFLOG, W., NADASI, H., DUNEMANN, U., PELZL, G., DIELE, S., EREMIN, A., and KRESSE, H., 2001, *J. mater. Chem.*, **11,** 2748.

[10] Pelzl, G., Diele, S., Grande, S., Jakli, A., Lischka, Ch., Kresse, H., Schmalfuss, H., Wirth, I., and Weissflog, W., 1999, *Liq. Cryst.*, **26,** 401.
[11] Weissflog, W., Lischka, Ch., Diele, S., Pelzl, G., and Wirth, I., 1999, *Mol. Cryst. liq. Cryst.*, **328,** 101.
[12] Provided by the Chisso Corporation.
[13] Weissflog, W., Wiegeleben, A., Diele, S., and Demus, D., 1984, *Cryst. Res. Technol.*, **19,** 583.
[14] Diele, S., Pelzl, G., Humke, A., Wünsch, S., Schäfer, W., Zaschke, H., and Demus, D., 1989, *Mol. Cryst. liq. Cryst.*, **173,** 113.
[15] Diele, S., and Sackmann, H., 1989, *Ber. Bunsenges. Phys. Chem.*, **13,** 467.
[16] Diele, S., Pelzl, G., Weissflog, W., and Demus, D., 1988, *Liq. Cryst.*, **3,** 1047.