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Filled smectic A phases in binary liquid-crystalline systems of terminal-nonpolar compounds

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Filled smectic A phases in binary liquid-crystalline systems of terminal-nonpolar compounds

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We present five phase diagrams of binary systems in which one component is a bi-swallow tailed compound and the second component is a compound with pronounced nematogenic properties. The common feature of these binary systems is the induction of smectic A phases which have been investigated using X-ray. The smectic A induction seems largely to be the result of specific steric interactions between the components.

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1. Introduction

The induction of smectic A (S_A) phases in binary mixtures of liquid-crystalline substances can occur for differing molecular reasons. In binary systems consisting of terminal-polar and terminal-nonpolar compounds, dipole interactions are normally invoked [1, 2]. In certain binary systems the induction of smectic A phases is obviously due to electron donor-acceptor interactions [2–7]. In binary systems of two terminal-nonpolar compounds steric factors probably play an important role [8–12]. An excellent example of the strong influence of steric factors on the induction of S_A phases is the recently published binary system consisting of a bi-swallow tailed compound [13] and a nematogenic two-ring substance [14]. The pronounced S_A induction in this system can be interpreted by the filling of the gaps between the bulky swallow tailed ends by the small molecules of the second component. Therefore, the term 'filled S_A phase' was used for this new type of induced phase.

In this paper, we present the phase diagrams of five binary liquid-crystalline systems in which one of the components is a bi-swallow tailed compound. For the second component we used nematogenic compounds with carefully selected molecular structures. It was our aim to examine the effect of the molecular structure of these compounds on the occurrence of filled smectic A phases.

2. Materials

For the bi-swallow tailed compound, we used three members of the homologous series, the 4,4′-bis[di-*n*-alkyl 4-carbonyloxybenzylidenemalonate]-biphenyls. The propyl homologue (BS3) exhibits nematic behaviour only, the pentyl (BS5) and heptyl (BS7) homologues have an additional metastable S_C phase [14];

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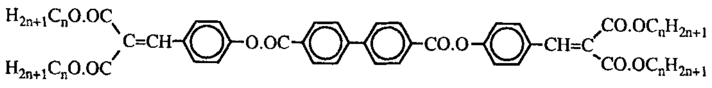
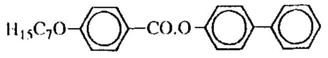


	n	C		S_C		N		I	L/nm
BS3	3	●	142	–		●	201	●	
BS5	5	●	95	●	(60)	●	151	●	4·24
BS7	7	●	81	●	(76)	●	122·5	●	4·72

Brackets denote monotropic transitions. *L* represents the molecular length of the most elongated conformation. The mixing components added to the bi-swallow tailed compounds possess only nematic phases;

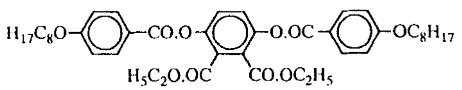
A



L = 2·68 nm

C 128 N 132 I [15, 16]

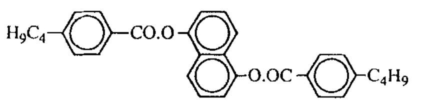
B



L = 3·84 nm

C 96·5 N 109·5 I [17]

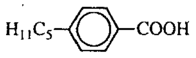
C



L = 2·88 nm

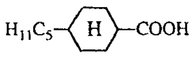
C 109·5 N 195 I [18]

D



C 88 N 126·5 I [19]

E

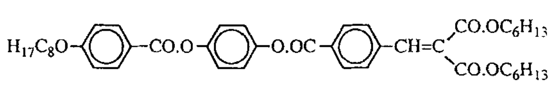


C 54 N 105 I [20]

dimer length = 2·8 nm.

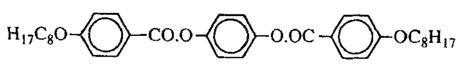
For the mixing components of compound B we used;

F



C 53 S_A 86 N 102 I [21]

G



C 123·5 S_C 129 N 195 I [22]

3. Phase diagrams

The phase diagrams of the binary systems were constructed using a polarizing microscope by means of the contact method [23] and the determination of transition temperatures of selected mixtures of known concentrations.

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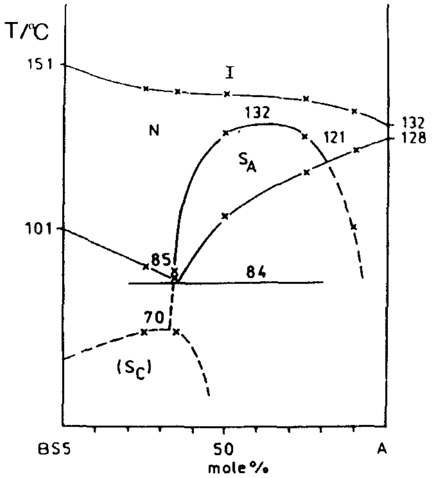

Figure 1. The concentration-temperature phase diagram for the binary mixture of BS5 and A. Dotted lines indicate transitions in the supercooled state.

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3.1. *System BS5/A* (*figure 1*)

The topology of the phase diagram is reasonably similar to that described in [14] (see figure 1). Although both components form only stable nematic phases an extended region of an induced S_A phase is observed. The metastable S_C phase of the bi-swallow tailed compound BS5 generates a metastable S_C mixed phase region with a maximum in the transition curve S_CN. For the mixture 60 mole-per cent A, the layer spacing, d, of the S_A phase was measured by X-ray diffraction using small angle equipment. The d-value was found to be 3·63 nm which is clearly higher than the average molecular length,

$$\bar{L} = x_{\mathrm{BS5}}\bar{L}_{\mathrm{BS5}} + x_{\mathrm{A}}L_{\mathrm{A}} = 3{\cdot}33\,\mathrm{nm}$$

where x is the molar fraction; and L the molecular length; the ratio d/L is 1·09.

3.2. *System BS7/B* (*figure 2*)

Figure 2 is similar to figure 1; the main characteristic is the appearance of an induced S_A phase in a wide concentration range (19–72 mole % B). The metastable S_C phase of BS7 exists in the mixed phase region up to 37 mole-per cent BS7. The special features of the diagram are the minimum in the clearing temperature curve and the maximum in the melting curve. Contrary to the system BS5/A, the layer spacing d is smaller than the average molecular length; for an equimolar mixture we found $d = 4{\cdot}04\,\mathrm{nm}$, $\bar{L} = 4{\cdot}38\,\mathrm{nm}$, and the ratio $d/\bar{L} = 0{\cdot}92$.

3.3. *System BS3/C* (*figure 3*)

It is clear from figure 3 that in the system BS3/C a S_A phase is also induced, although this can only be observed by supercooling the nematic phase. The monotropic behaviour of the smectic A phase is the result of the far higher melting points exhibited by these mixtures, but the thermal stability of the smectic A phase is actually higher than that of the BS7/B system (figure 2).

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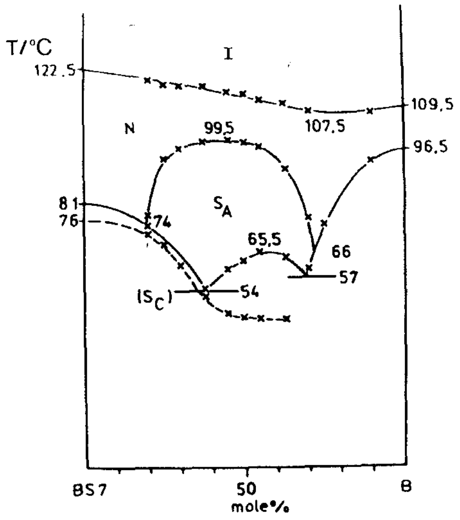

Figure 2. The concentration-temperature phase diagram for the binary mixtures BS7 and B. The dotted line indicates transitions in the supercooled state.

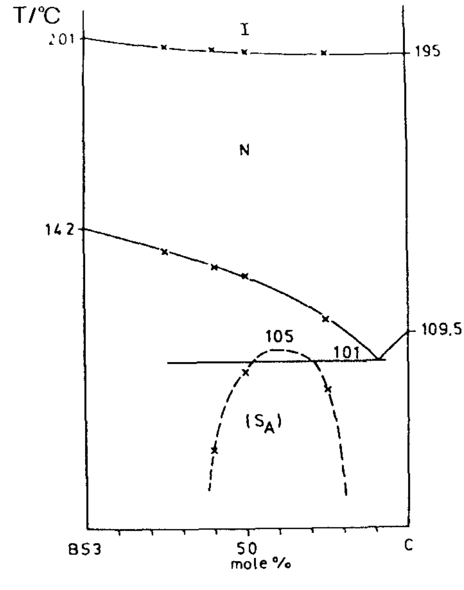

Figure 3. The concentration-temperature phase diagram of the binary mixture BS3 and C. The dotted line indicates transitions in the supercooled state.

3.4. *Systems BS7/D* (*figure 4*) *and BS7/E* (*figure 5*)

Figures 4 and 5 show that the common features of the phase diagrams for the BS7/D and BS7E mixtures is the occurrence of an induced smectic A phase and the minimum in the N–I transition curve which is in the same concentration range as the maximum of the smectic A phase region. In contrast to the BS7/D system (figure 4), the phase diagram of the non-aromatic compound E (figure 5) shows that the induced smectic A phase exists at lower temperatures and is metastable with

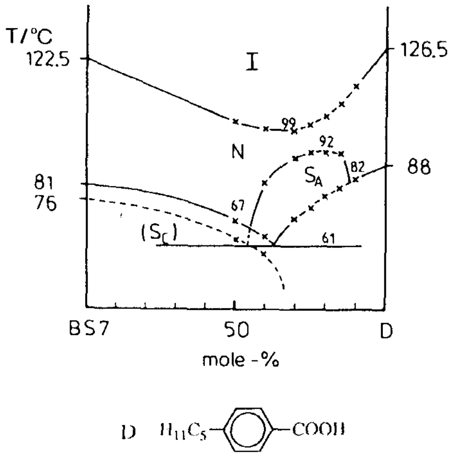

Figure 4. The concentration-temperature phase diagram of the binary mixture BS7 and D. The dotted line indicates the transitions, in the supercooled state.

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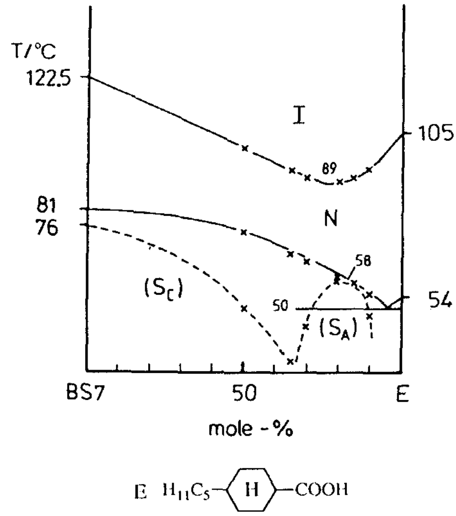

Figure 5. The concentration-temperature phase diagram of the binary mixtures BS7 and E. The dotted line indicates transitions in the supercooled state.

respect to the solid state. Furthermore, the smectic A phase region is less extended than in the corresponding phase diagram of the BS7/D system.

4. Discussion

The bi-swallow tailed compounds, characterized by two terminal branches at each end of the molecule, exhibit nematic phases and the long-chain homologues in addition exhibit metastable S_C phases. If such molecules are arranged such that the director is perpendicular to the plane of the smectic layer then this would result in unfavourable packing whereas a tilted alignment (S_C structure) allows a far higher packing density of the molecules. If the free space between the bulky ends of the molecules is filled by shorter molecules, then the perpendicular alignment in layers (S_A

structure) is more stable than either the nematic or S_C phases. In such an arrangement, the lateral attraction between the aromatic cores should be enhanced. It is reasonable to suppose that according to this simple packing model, the layer spacing of the S_A phase may be greater than the average molecular length, *L*, as verified experimentally for the BS5/A system (see also [14]). In this binary system, the molecular length of compound A is approximately equal to the distance between the terminal branches of the bi-swallow tailed molecule (2·4 nm to 2·7 nm). Thus a favourable dense packing results giving rise to the stabilization of the S_A phase over a certain concentration-temperature range.

The molecular lengths of compound C (2·88 nm) and particularly of compound B (3·84 nm) are too large for an optimal filling of the gaps between the bulky ends of the bi-swallow tailed compounds. In addition it is known from the literature [24] that compounds with lateral aliphatic chains, for example, compound B as well as naphthalene derivatives, for example, compound C preferably exhibit nematic phases. This fact is reasonable because the bulky central part of these molecules causes a perpendicular arrangement in the smectic layers to be unfavourable for packing reasons. The induction of S_A phases in mixtures with bi-swallow tailed compounds should be due largely to a more favourable packing. The free space between the terminal branches of the bi-swallow tailed molecules is probably too small to be filled completely by the whole molecules of the second component (compound B or C), however, the filling should be possible by just their bulky central part. In the sense of this packing model, it is reasonable to suggest that the smectic layer spacing, d, is approximately equal to the average molecular length, $\bar{L}$, of the smectic A mixed phase as is often observed in binary systems of terminal-nonpolar compounds [25].

The phase diagrams shown in figures 6 and 7 demonstrate that the smectic A induction is due largely to the special molecular structure of the bi-swallow tailed compound. In these phase diagrams, the bi-swallow tailed component of the system BS5/B is replaced by the one-swallow tailed compound F [21] and by a compound without terminal branches, G [22]. Both compounds F and G possess approximately

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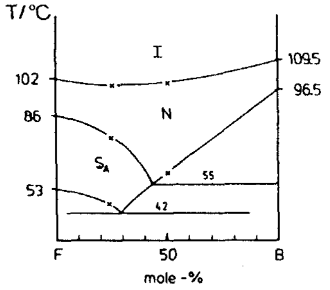
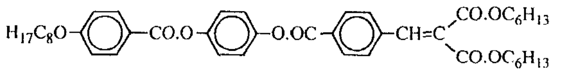


F


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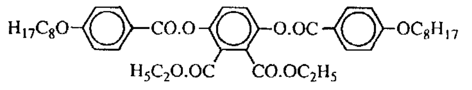
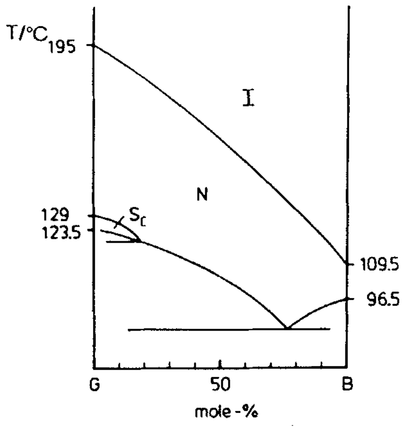


Figure 6. The concentration-temperature phase diagram for the binary mixture, F and B.



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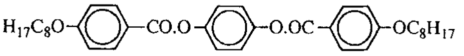

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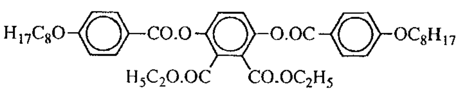

Figure 7. The concentration-temperature phase diagram for the binary mixture G and B.

the same molecular length as compound B. It is seen from the phase diagrams that in these cases there is no enhancement of the smectic A phase (figure 6) or no smectic induction (figure 7). These findings give rise to the assumption that for the binary systems BS5/B and BS3/C steric interactions are mainly responsible for the induction of the smectic A phase so that in these cases the term 'filled smectic A phase' may also be justifiable.

The influence of the lateral attraction may be studied using the binary systems BS7/D and BS7/E the phase diagrams of which are shown in figures 4 and 5, respectively. In these binary systems the same bi-swallow tailed compound is combined with a nematogenic aromatic compound, D, as well as with the corresponding non-aromatic compound E. The molecules of these compounds form dimers linked by hydrogen bonds, the length of which (approximately 2·8 nm) is compatible with the gaps between the bulky ends of the bi-swallow tailed molecules. In the case of the non-aromatic compound an induction of the smectic A phase is observed which is less pronounced than in the corresponding system of the aromatic compound. Obviously the greater lateral attraction of the aromatic cores which is due to the higher polarizability of compound F ($24{\cdot}5\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$) compared with compound G ($22{\cdot}7\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$) is an additional stabilizing effect on the formation of a filled smectic A phase.

We conclude from our results that the essential criterion for the occurrence of filled smectic A phases is the special shape of the bi-swallow tailed molecules characterized by two bulky terminal ends. In this way a smectic A phase can be stabilized by the incorporation of small rod-like molecules into the gaps between the bulky ends. The filling of the gaps seems to be possible also by the bulky central parts of the molecules of the filling component. Although the steric interaction seems to be the predominant factor in stabilizing the filled smectic A phases, the lateral attraction yields an additional stabilizing effect.

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