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The Smectic F Phase in nO.m Compounds

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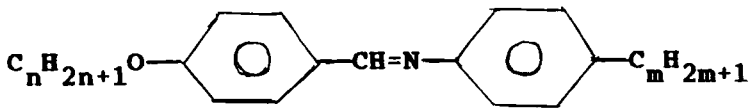
A search for smectic F phases in N-(*p*-n-alkoxybenzylidene)*p*-n-alkylanilines (n and m = 4 to 10) has revealed that the new compounds 90.6, 90.8, 100.6, 100.8, 100.10 exhibit the phase sequence variant ACFG, in addition to the established cases of compounds 50.5(NACFG), 50.6(NACBFG), 70.6(ACFG), 80.10(AB(F)) and 90.4(AFG).

Keywords: smectic F, nO.m compounds, Schiff's bases

The homologous series of N-(*p*-n-alkoxybenzylidene)*p*-n-alkylanilines(nO.m's) are Schiff's bases with the following general structure



where n and m take values between 1 to 12, and exhibit a large number of liquid crystalline phases, and many of these compounds exhibit complex smectic polymorphism.[1–6] The mesomorphic properties in the N-(*p*-n-alkoxybenzylidene)*p*-n-alkylanilines(nO.m's) were first examined by Smith, Gardlund, and Curtis[1,4] in a systematic way and their observations have stood the scrutiny of many other research workers. Smith and Gardlund[1] expressed doubt as to whether an unknown phase in N-(*p*-n-pentyloxybenzylidene)*p*-n-pentylaniline, 50.5 below ~48°C was S_F; later this phase was confirmed as S_F.[7] Further, they[1] observed five smectic phases in 50.6; this was the largest variant in the nO.m compounds of which only the smectic A, smectic B and possibly smectic C phases were identified. Later studies[2] reported that 50.6 exhibited the smectic F phase. The first observation of the smectic F phase in N-(*p*-n-nonyloxybenzylidene)*p*-n-butylaniline, 90.4 reported by Goodby and Gray[8] in 1979, confirmed the existence of smectic F phases in the nO.m compounds as expressed earlier by Smith *et al.*[1,4] Billard[9] reported the phase sequence nematic, smectic A, smectic C, smectic F and smectic G, in N-(*p*-n-heptyloxybenzylidene)*p*-n-heptylaniline, 70.7, apparently confirming that the nO.m's were the source of a further smectic F phase. However, Doucet and Levelut[10]

reported that 70.7 exhibits the phase sequence variant NACBG rather than NACFG as reported earlier.[9] As a consequence, individual nO.m compounds have become a subject of some discussion regarding the identification of their various smectic phases.

The nO.m compounds are also interesting because of the uncommon phase sequences that they exhibit. For example, 90.4 was the first material[8] which exhibited the direct smectic A to smectic F transition with the new phase sequence variant AFG.[2] Also Goodby *et al.*[2] reported the smectic F phase in N-(*p*-n-pentyloxybenzylidene)*p*-n-hexylaniline, 50.6, existing in the phase sequence variant NACBFG, which is the largest variant in nO.m compounds. The smectic F is continuously miscible across the diagram of state for the binary systems, terephthalylidene-bis-*N*-(*p*-n-pentylaniline) +50.6, and 90.4 + 50.6. The smectic F phase in 50.6 exhibits the arced or chequered board focal conic fan texture and the fine mosaic texture.[11] This compound is of great interest as it provides a model system in which a 2-D smectic F is positioned on the temperature scale between two 3-D smectic phases (B and G). Recent results on 50.6[12] show that the tilt angle in the smectic F is independent of temperature.

Later, the smectic F phase was reported in 70.6[13] and 80.10.[14] Thus, five compounds in nO.m. homologous series have been found to exhibit the smectic F phase. The transition temperatures (°C) and the phases of these compounds are presented below.

90.4	I	80.9	S_A	68.2	S_F	66	S_G	50	K					
50.6	I	72.8	N	60.3	S_A	51.8	S_C	50	S_B	42.4	S_F	38.5	S_G	36 K
70.6	I	80	S_A	68.5	S_C	66	S_F	55	S_G	37.5	K			
50.5	I	77.8	N	54.4	S_A	53.1	S_C	49	S_F	47	S_G	28	K	
80.10	I	86.6	S_A	77.0	S_B	42.5	S_F	37.5	K	mp=61.8				

The smectic F phase has therefore been observed on cooling the smectic A phase, the smectic B phase and (commonly in other systems) the smectic C phase, and isotropic-smectic F transitions are known to occur for some esters.[15]

The search for the S_F phase in compounds in nO.m homologous series with n and m = 4 to 10 has now revealed that 90.6, 90.8, 100.6, 100.8 and 100.10 also exhibit smectic F phases. The experimental results from thermal microscopy, DSC and miscibility studies involving these compounds are presented below.

THERMAL MICROSCOPY AND MISCIBILITY STUDIES

Initial studies by thermal microscopy show that the compounds 90.6, 90.8, 100.6, 100.8 and 100.10 possess four enantiotropic liquid crystalline phases and the transition temperatures are presented in Table I.

Differential scanning calorimetry (DSC) studies also show that all the materials

TABLE I

	ISO				
nO.m	S_1	S_2	S_3	S_4	K
90.6	85.5	76.0	75.2	72.0	47[a]
	85.3	76.4	74.7	—	45[b]
	9127	—	4200	—	43468[c]
90.8	87.0	80.5	77.5	75.0	49
	84.8	78.4	75.3	—	50.0
	7636	—	3906	—	47629
100.6	87.5	78.5	78.0	74.0	mp < 20
	86.2	—	76.9	74.3	—
	8591	—	4946	—	—
100.8	89.8	84.8	82.2	81.8	43.0
	89.1	—	82.3	—	42.3
	8385	—	5251	—	42635
100.10	89.0	86.1	85.0	84.8	55.0
	88.8	—	84.1	—	53.0
	9289	—	5770	—	49640

[a] Values from TM (°C).
[b] Values from DSC (°C) in Joules/mole.
[c] ΔH values in Joule/mole.

PLATE 1 See Color Plate I.

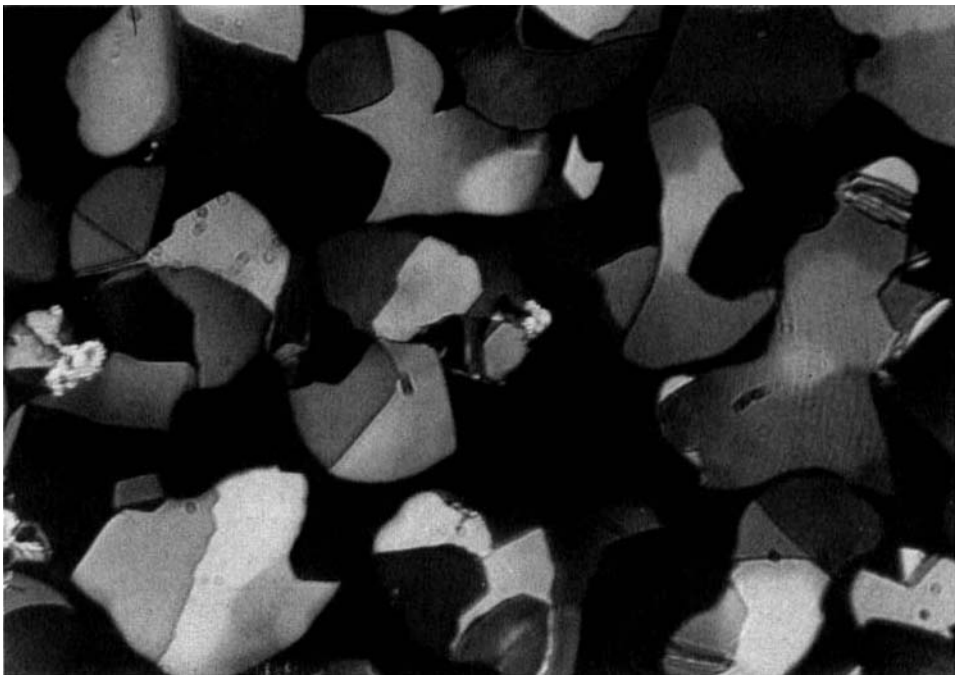


PLATE 2 See Color Plate II.

exhibit four liquid crystalline phases. The transition temperatures (°C) and enthalpy values from DSC data are presented in Table I.

On cooling 90.6 from the isotropic liquid, a mesomorphic phase S_1 appeared in the form of bâtonnets at 85.5°C. These coalesced on further cooling (0.1 to 0.3°C) to give a phase exhibiting the focal conic fan texture. The phase also exhibits the homeotropic or pseudo-isotropic texture, thus indicating it as an orthogonal phase as in the case of 80.10.[14] On further cooling, at 76.0°C the clear fans of the preceding phase S_1 transform into broken fans with a sandy or grained appearance. The homeotropic texture gave rise to the typical, birefringent schlieren texture (S_2 phase). Similar textures were also observed for the compounds 90.8, 100.6, 100.8 and 100.10. The S_1 and S_2 phases of these compounds may therefore be smectic A and smectic C phases respectively. The range of S_2 phase is small in the compounds 90.6, 100.6 and 100.10. Repeated runs confirm the range of the S_2 phase to be 0.8°C in 90.6, 0.5°C in 100.6 and 1.1°C in 100.10. After the S_2 phase, the S_3 phase forms with two textures in all these compounds, i.e., the broken focal-conic fan texture (Plate 1 for the compound 90.6) and the schlieren mosaic texture (Plate 2 for the compound 100.6). The broken focal conic fan texture is similar to that of the smectic F phase in 90.4[8] and 70.6.[13] The schlieren-mosaic texture is similar to that of the smectic F phase in TBAA(5).[16] Therefore, the S_3 phase may be smectic F for all the compounds. On further cooling the S_4 phase forms with slight changes. The breakages in the S_3 phase texture changed to the form of large dark patches, and these breakages or patches have a more chunky appearance and are similar to those of the S_G phase in 90.4. Therefore S_4 may be S_G. Using the concept

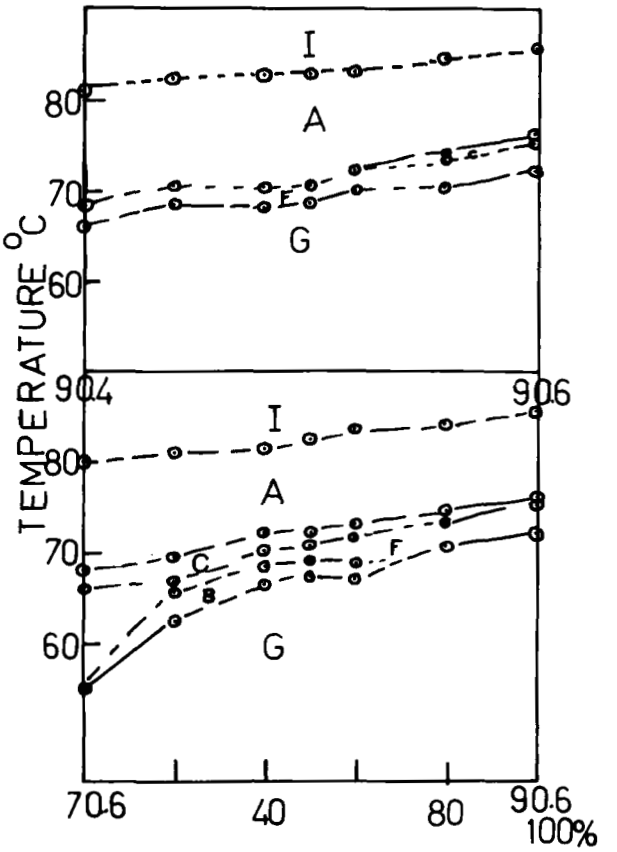


FIGURE 1 Miscibility diagram for 70.6 + 90.6 and 90.4 + 90.6.

of miscibility of like smectic phases,[17] the S_1, S_2, S_3 and S_4 phases in these compounds have been confirmed as smectic A, smectic C, smectic F and smectic G respectively using standard compounds. The miscibility diagrams of 70.6 + 90.6, 90.4 + 90.6, 70.6 + 100.6, and 90.4 + 100.6 are shown in Figures 1 and 2 respectively. The smectic A, smectic C, smectic F and smectic G phases are continuously miscible in the binary systems 70.6 + 90.6, and 70.6 + 100.6. The smectic F phase, together with the A and G phases, are continuously miscible in the binary systems 90.4 + 90.6 and 90.4 + 100.6. In the binary systems 90.4 + 90.8, 90.6 + 90.8 and 90.6 + 100.6 all the four phases are found to be continuously miscible. In the major regions of three of the binary systems (70.6 + 90.6, 70.6 + 100.6 and 90.4 + 100.6), an injected smectic phase is observed between the F and G phases. The injected smectic phase exhibits a texture with smooth focal conic fans and has the features of a smectic B phase. Particularly for the composition 40% 90.4 and 60% 100.6, the smectic F phase is almost completely absent (the S_F phase may exist over a range of only 0.2 to 0.3°C), and the transition appeared just like a smectic A to smectic B transition exhibiting transition bars. It is not only interesting, but also unusual to observe the induced smectic B phase in binary systems.

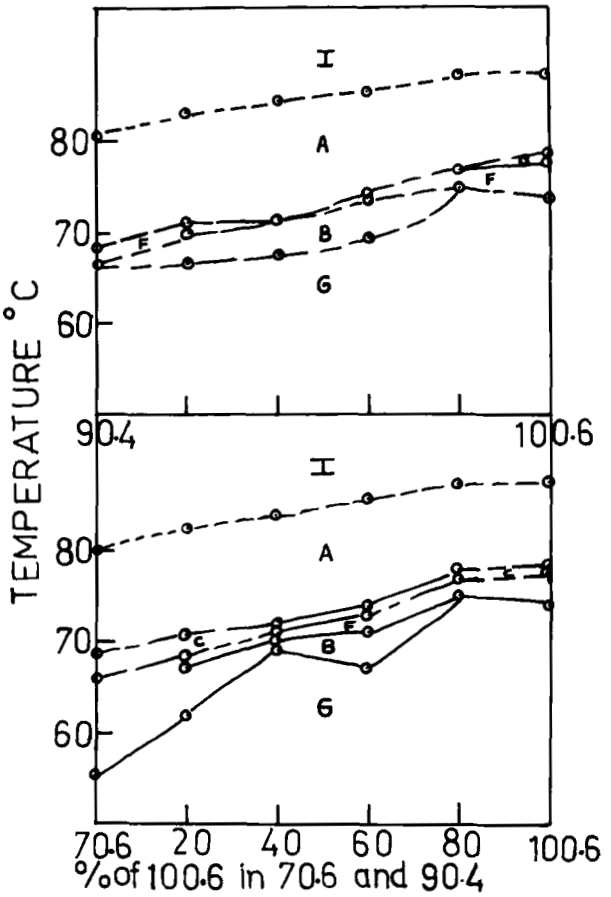


FIGURE 2 Miscibility diagram for 70.6 + 100.6 and 90.4 + 100.6.

Further, it is to be mentioned that no such induced phase is observed in the binary systems 90.4 + 90.6 and 100.6 + 90.6.

This type of injected smectic phase is also observed for 80% of 90.4 in 50.5.[7] The injection of smectic B phase characteristics in mixtures of F materials has also been reported earlier.[2]

Thus the compounds 90.6, 90.8, 100.6, 100.8 and 100.10 exhibit enantiotropic smectic A, smectic C, smectic F and smectic G phases. In addition to 70.6, these are therefore the other compounds which exhibit the phase sequence variant ACFG in nO.m compounds.

This search for smectic F phase in nO.m compounds shows that the nO.m's, like the TBAA series,[13] are a good source of this type of phase as well as of new phase sequence variants.

EXPERIMENTAL

The compounds used in this work were prepared by a standard procedure from appropriate alkoxybenzaldehydes and alkylanilines described elsewhere.[7] Thermal

microscopy was carried out using a Hertel and Reuss superpan II polarizing microscope. DSC measurements were carried out using a Perkin Elmer DSC 2.

Acknowledgment

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