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Synthesis and characterization of smectic polymesomorphism in higher homologues of *n*O.*m* compounds

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Some of the higher homologues of the N-(*p*-*n*-alkoxybenzylidene)*p*-*n*-alkylanilines, *n*O.*m*, compounds with $n \geqslant 8$ and $m \geqslant 5$ have been synthesized and the smectic polymesomorphism studied. The transition temperatures were obtained from both thermal microscopy and differential scanning calorimetry. These compounds in the *n*O.*m* series exhibit the usual phase sequences, viz. $S_AS_CS_BS_G$, and $S_AS_BS_G$ apart from $S_AS_CS_FS_G$ by 9O.8 (and some higher *n*O.*m*, like 9O.6). These phases were confirmed by miscibility studies with standard materials. The smectic F phase in 9O.8 compound is also confirmed by an X-ray diffraction study.

1. Introduction

The N-(*p*-*n*-alkoxybenzylidene)*p*-*n*-alkylanilines (*n*O.*m*), which exhibit not only rich and subtle liquid crystal polymorphism [1–5] at ambient temperatures, but are also useful as model systems in phase transition phenomena, have attracted considerable attention over the past few years and have been extensively studied by different experimental techniques [6–11]. Further, recent interest has focused on the identification of the various smectic phases to widen the range of smectic polymorphism [1–5]. The common phase variants observed in *n*O.*m* compounds are derived from the variant $NS_AS_CS_BS_FS_G$ which is observed in the material 5O.6 [2]. However the smectic F phase is observed in only a few compounds of this series. The identification of the smectic F phase is challenging because of the uncommon phase sequences observed along with the smectic F phase with a small thermal range. A few uncommon characteristic phase sequences, i.e. the $S_AS_FS_G$ variant in 9O.4 [12], $NS_AS_CS_BS_FS_G$ in 5O.6 [2] and $S_AS_BS_F$ in 8O.10 [4] have been reported. It is apparent that in 9O.4 the S_F phase is observed on cooling the less ordered S_A phase while it appeared below the ordered S_B phase in 5O.6 and 8O.10. The other materials (7O.6 [13], 5O.5 [14], 10O.6 [15]) exhibit the S_F phase below the smectic C phase with the variants drawn from the common variant $NS_AS_CS_FS_G$. Generally, the S_F phase is observed below the S_C phase in different homologous series [5, 16, 17]. In continuation of our studies on the *n*O.*m* compounds, we report here the synthesis and the characterization of the phase sequences in seven compounds of the *n*O.*m* series.

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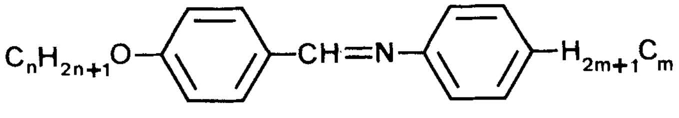
2. Experimental

The compounds were prepared following the standard procedure described earlier [6] and were recrystallized repeatedly in absolute ethanol until the transition temperatures were reproducible. Thermal microscopy (TM) was carried out using a Hertel and Reuss superpan II polarizing microscope with an attached heating block. Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer DSC-2. The sharpness of the melting transition indicates the purity of the compounds. X-ray diffraction on aligned samples of 9O.8 was carried out using nickel filtered Cu Kα radiation on a Philips GX-20 rotating anode generator.

The general structural formula of the compounds studied is:



N-(*p*-*n*-octyloxybenzylidene)*p*-*n*-pentylaniline (8O.5); N-(*p*-*n*-octyloxybenzylidene)*p*-*n*-hexylaniline (8O.6); N-(*p*-*n*-octyloxybenzylidene)*p*-*n*-heptylaniline (8O.7); N-(*p*-*n*-octyloxybenzylidene)*p*-*n*-nonylaniline (8O.9); N-(*p*-*n*-nonyloxybenzylidene)*p*-*n*-octylaniline (9O.8); N-(*p*-*n*-nonyloxybenzylidene)*p*-*n*-nonylanile (9O.9); N-(*p*-*n*-nonyloxybenzylidene)*p*-*n*-decylaniline (9O.10).

3. Results and discussion

Our preliminary textural studies with TM showed that the nematic phase is absent and all compounds exhibit only enantiotropic smectic phases. The observed transition temperatures from TM and DSC and the enthalpy values are given in the table. The DSC thermogram of 9O.8 (Heating) is shown in figure 1.

The compounds 8O.5 and 8O.9 (8O.8 and 8O.10 have already been reported [4, 18]) exhibit three smectic phases while 8O.6, 8O.7, 9O.8, 9O.9 and 9O.10 show four smectic phases. All of the materials on cooling from the isotropic phase exhibit a mesomorphic phase (S_1) which appeared with a focal conic fan texture. This phase also exhibited a homeotropic or pseudo-isotropic texture, thus indicating the phase to be orthogonal. The transition temperatures are given in the table. In 8O.5, 8O.9 and 8O.10, on further cooling, transient transition bars appear across the fans which immediately transformed into a smooth focal conic fan texture (S_3). The S_1 and S_3 phases of these compounds may be smectic A and smectic B, respectively. Further, these phases were confirmed by the miscibility method using 8O.4 which exhibits the $S_AS_BS_G$ phase sequence variant as the standard material. In the materials 8O.6, 8O.7, 9O.8, 9O.9 and 9O.10 the clear fans of the S_1 phase on cooling became broken and then a sanded or grained appearance appeared while the homeotropic texture gave rise to the schlieren texture (S_2 phase) at the temperatures given in the table. These two phases, S_1 and S_2, may, therefore, be smectic A and smectic C phases respectively. The small thermal ranges of the S_2 phase in 8O.6 and 8O.7, which, after repeated TM runs, are confirmed to be 0·8°C and 0·2°C respectively, showed no enthalpy peak in DSC analysis at this transition. Even though no enthalpy peak appeared in the other compounds at this transition, the phase was easily detected from the textural observations.

Transition temperatures from thermal microscopy, differential scanning calorimetry and enthalpy values.

Compound	I	S_1	S_2	S_3	S_4	S_5	C
8O.5	T†/°C	85·5		70·6		52·5	42·0†
	T‡/°C	85·2		70·6		51·9	41·5‡
	ΔH/kJ mol^{-1}	5·43		3·42		—	29·34
8O.6	T†/°C	86·0	75·6	74·8		64·8	44·5
	T‡/°C	85·8	—	72·9		64·9	44·4
	ΔH/kJ mol^{-1}	6·70		4·07		55	40·64
8O.7	T†/°C	86·8	74·4	74·2		58·0	
	T‡/°C	86·6	—	74·2		56·4	29·1
	ΔH/kJ mol^{-1}	6·53	—	3·59		—	29·37
8O.9	T†/°C	87·2		76·5		47·0	
	T‡/°C	86·6		75·7		46·0	
	ΔH/kJ mol^{-1}	7·73		3·72		—	
9O.8	T†/°C	87·0	80·5		77·5	75·0	
	T‡/°C	84·8	78·4		75·3	—	50·0
	ΔH/kJ mol^{-1}	7·64	—		3·91	—	47·63
9O.9	T†/°C	87·0	80·7	78·4		72·5	47·5
	T‡/°C	86·9	—	78·1		—	47·0
	ΔH/kJ mol^{-1}	8·42	—	4·36		—	42·29
9O.10	T†/°C	83·9	78·5	76·0		73·0	56·2
	T‡/°C	83·5	—	75·3		—	56·1
	ΔH/kJ mol^{-1}	8·58	—	4·16		—	58·02

† Values from TM.
‡ Values from DSC.

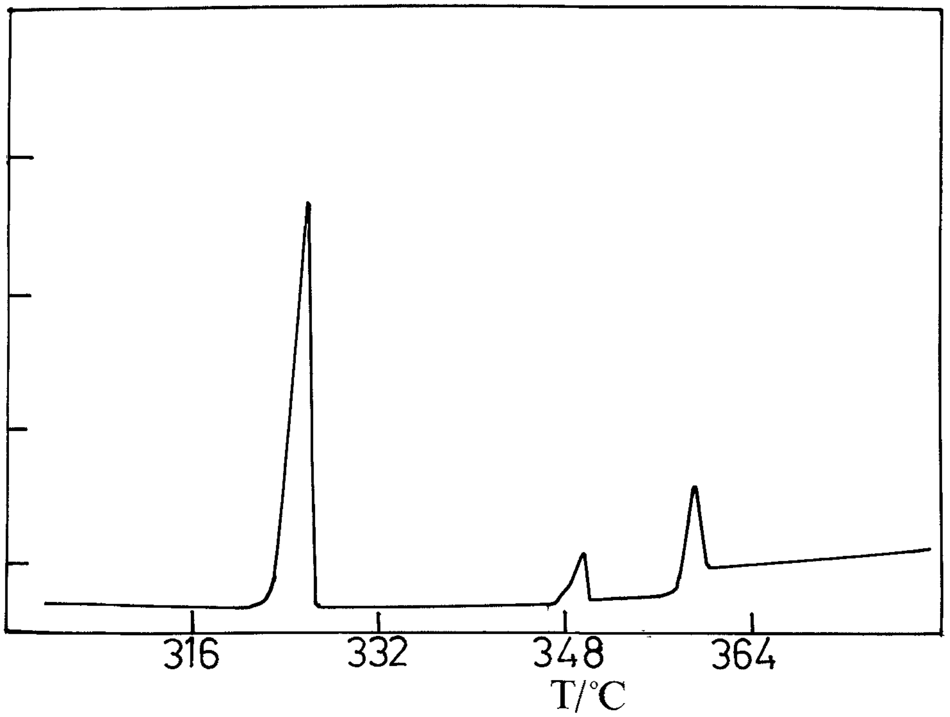


Figure 1. DSC thermogram of 9O.8; heating rate 2·5 K min^{-1}.

On further cooling the S_2 (smectic C) phase in samples 8O.6, 8O.7, 9O.9 and 9O.10 the broken focal conic fan texture depicting the S_C phase transformed to a smooth focal conic fan texture after exhibiting typical transient transition bars at this transition. The range of the presence of transient transition bars at the transition varied from compound to compound (0·3°C to 0·8°C) before exhibiting the smooth focal conic fan texture characterizing this phase as a smectic B.

In the sample 9O.8, below the smectic C phase, a S_4 phase formed at 77·5°C with two characteristic textures, viz. the broken focal conic fan texture similar to the smectic F in 9O.4 [12] and 7O.6 [13] and the schlieren-mosaic texture similar to the S_F phase in TBPA [17]. On further cooling, a S_5 phase formed at 75°C with slight changes in the S_4 phase texture. The broken texture of the preceding phase changed to large dark patches and these patches have a more chunky appearance. The texture is similar to that observed for the smectic G phase in 9O.4. Therefore, these two phases in this compound

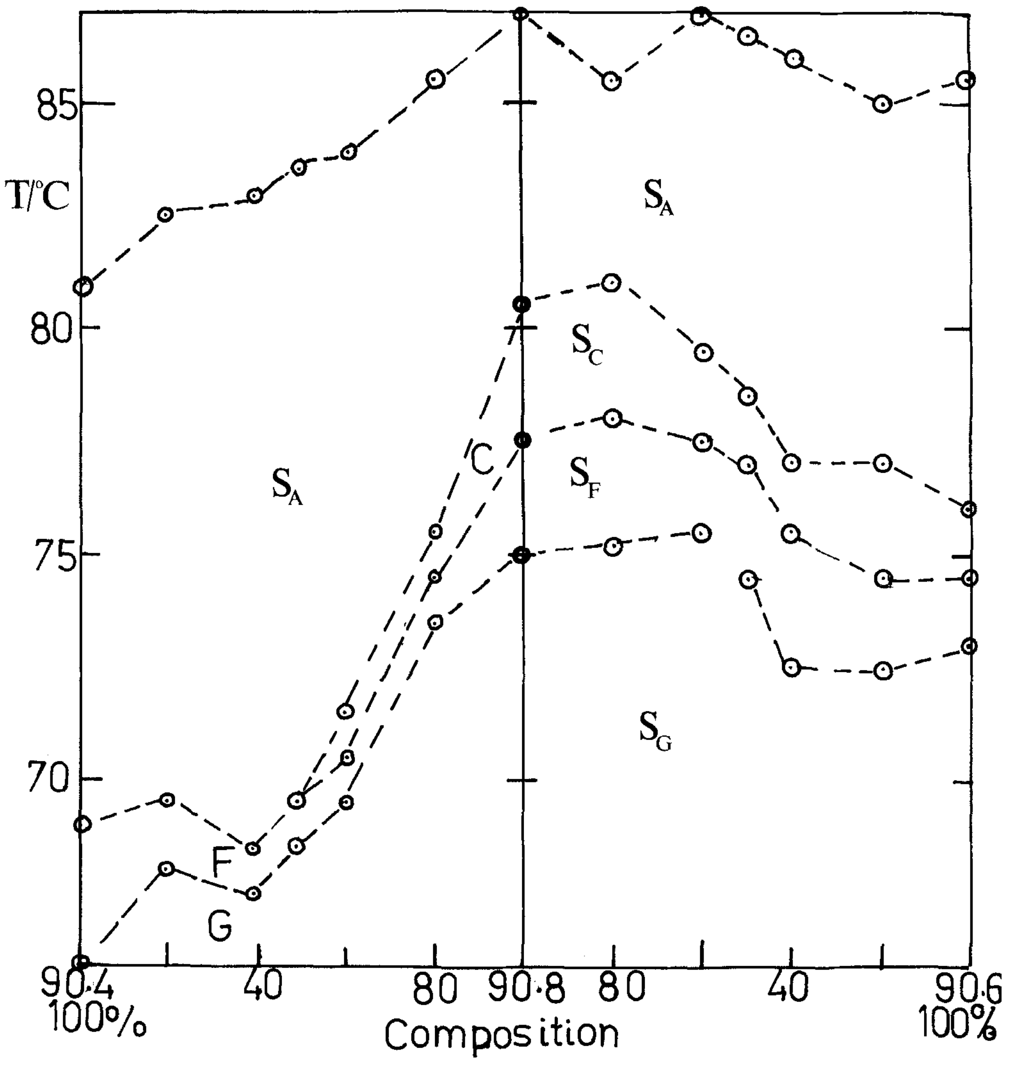


Figure 2. Miscibility diagram for 9O.6+9O.8 and 9O.4+9O.8.

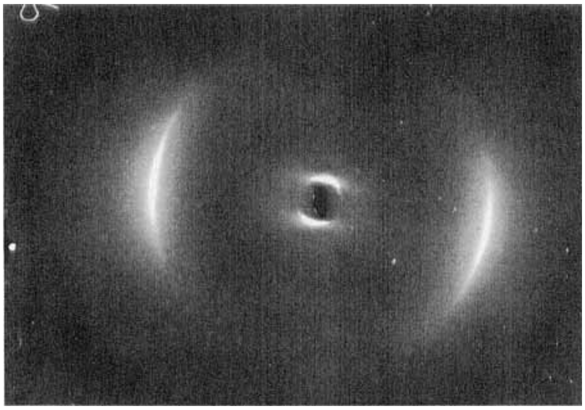


Figure 3. The X-ray diffraction pattern from an aligned sample of 9O.8.

may be smectic F and smectic G. This smectic–smectic transition could not be detected in the DSC scan for this compound even though this second order transition appeared as a small DSC peak for other compounds of this series. Using the miscibility method of like smectic phases, the S_1, S_2 and S_5 phases in this compound are confirmed as smectic A, smectic C and smectic G phases, respectively, using 9O.6 and 9O.4 as standard compounds which exhibit $S_AS_CS_FS_G$ and $S_AS_FS_G$ phase sequence variants, respectively. Further, the interesting S_4 phase is confirmed as a smectic F phase by miscibility studies, the miscibility diagrams of 9O.6 + 9O.8 and 9O.4 + 9O.8 are shown in figure 2. The smectic F phase is continuously miscible across the diagram of state for both the binary systems. Hence the phase miscibility studies confirm the S_4 phase as smectic F. The X-ray diffraction pattern (see figure 3) recorded from the aligned 9O.8 sample shows sharp wide angle reflections while, from the small angle region, a tilt angle of about 17° (which is the angle made by the director with the layer normal) calculated from layer spacing data in the S_4 phase further confirms this phase to be a smectic F. The temperature variation of the tilt angle in the S_4 phase could not be determined because of the limitations of the temperature control. Thus the material 9O.8 exhibits four enantiotropic smectic phases, viz. $S_AS_CS_FS_G$.

On further cooling, the smectic B phase in the other compounds changes to the smectic G phase as shown by a broken focal conic fan texture; this is confirmed by miscibility studies. The transition is observed as a small enthalpy peak in DSC measurements.

These experimental results show the following phase sequence variants for the compounds studied:

8O.5	$S_AS_BS_G$
8O.6	$S_AS_CS_BS_G$
8O.7	$S_AS_CS_BS_G$
8O.9	$S_AS_BS_G$
9O.8	$S_AS_CS_FS_G$
9O.9	$S_AS_CS_BS_G$
9O.10	$S_AS_CS_BS_G$

The following salient features are observed:

(1) In these higher homologues, as expected, the nematic phase is absent.
(2) The presence of the smectic F phase in 9O.8 and our studies on other compounds in this series [15] confirm that the higher homologues of *n*O.*m* compounds are materials with a potential to exhibit the hexatic smectic F phase.
(3) One new observation is that the total range of the mesomorphic state decreases as the alkoxy chain number is increased even though there is no reduction in the number of mesomorphic states.
(4) It is interesting to note that the different phase sequence variants of the compounds are derived from the common variant $NS_AS_CS_BS_FS_G$ exhibited by 5O.6.

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