

Origin and Stabilization of Novel Single Phase Variant, Smectic-F Among $nO.m$ Compounds

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Smectic and comprehensive investigations on the phase transition studies of p - n -alkoxybenzylidene- p - n -alkyl anilines ($nO.m$'s) reveal the occurrence of direct smectic-F transition from isotropic liquid in higher homologues. We report the influence of terminal alkyl- and/or alkoxy-chain lengths on the manifestation and stabilization of this unique phase variant.

Key words: Smectic-F; Isotropic to Smectic-F; $nO.m$'s; Phase variant; Alkyl- and Alkoxy-chain Lengths.

Investigations on isotropic to liquid crystalline phase transitions, especially involving smectic phases, allow theoretical predictions [1] for the growth of 2D and 3D crystals from the isotropic liquid phase. The growth of a smectic-F phase from an isotropic liquid involves the formation of 2D structural order. In fact, very few compounds are reported that exhibit directly this transition [2–4]. The smectic-F phase with monoclinic symmetry and long-range tilt order, possessing a hexagonal molecular packing within the smectic layers (normal to the long axis of the molecules), has a quasi two-dimensional solid structure (i.e. poor correlation between layers). Materials exhibiting a 2D smectic ordering possessing a long-range bond orientational order with short-range tilted order [5] are important both in fundamental and applicational research, since piezoelectric response is reported [6] for the chiral version of the smectic-F phase. The isotropic to smectic-F phase transition involves the growth of an ordered tilted smectic phase.

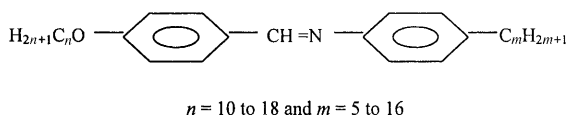


Fig. 1. Molecular structure of higher homologues of $nO.m$ compounds.

The higher homologues of p - n -alkoxybenzylidene- p - n -alkyl anilines (commonly known as $nO.m$ compounds) (Fig. 1) stand as potential candidates for the realization of a smectic-F phase along with other high temperature smectic phases. Our systematic and comprehensive studies on higher homologues of $nO.m$ compounds exhibiting this unique phase variant [7–12] enable us to construct a typical plot (Fig. 2) on the basis of phase transition data (Table 1) for a selective $nO.m$ series, viz. 10 $O.m$, 11 $O.m$, 12 $O.m$, 15 $O.m$ and 18 $O.m$ (where m represents the alkyl carbon length varied from 5 to 14). A glance at such a master graph infers the trend in the manifestation of smectic-F phase from isotropic liquid; from which one can easily predict the number of compounds that exhibit direct isotropic to smectic-F transition as a function of varied alkoxy carbon number. This figure also provides quantitative information on the number of compounds exhibiting direct smectic-F as it increases with increase of the alkoxy carbon number (n). Further, this figure envisages the selective combination of a particular alkyl chain number (m) with a given

Table 1. Alkoxy and alkyl carbon end chains required for an I-F transition to occur in higher $nO.m$'s

Alkoxy carbons (n)	Alkyl carbons (m)	Number compounds	n/m Ratio
10	14	1	0.71
11	≥ 12	3	0.91
12	≥ 12	3	1.00
15	≥ 7	7	2.14
18	≥ 5	9	3.6

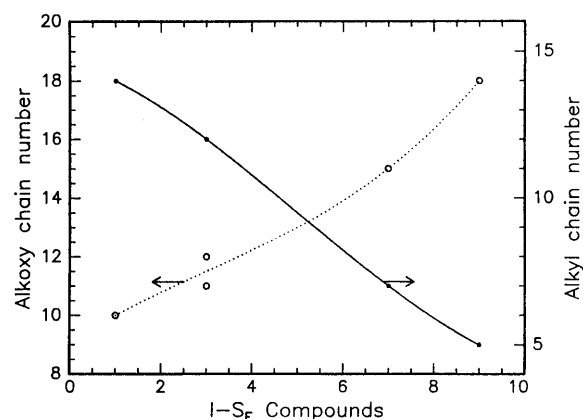


Fig. 2. Origin of a direct smectic-F phase in higher homologues of $nO.m$ compounds.

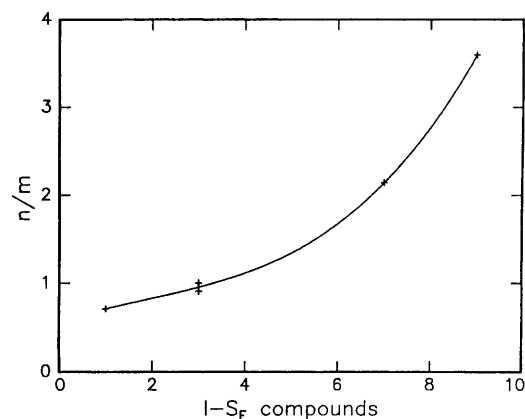


Fig. 3. Manifestation of smectic-F phase as a function of n/m .

alkoxy carbon number for the occurrence of this significant transition.

From the master plot it is predicted that the alkyl carbon number (m) required for alkoxy carbon numbers viz., 13, 14 and 16 are ≥ 9 , ≥ 8 and ≥ 6 , respectively, for a direct smectic-F occurrence from an isotropic melt on

cooling. The validity of this prediction is confirmed successfully by the isolation and phase studies of higher homologous series, viz. 13 O.*m* [4, 10, 13], 14 O.*m* [4, 10, 13] and 16 O.*m* [13]. For instance, a total of five compounds across the 13 O.9 series shows the occurrence of this transition, starting from 13 O.9 to 13 O.16.

Moreover, it is found that the ratio between terminal alkoxy and alkyl carbons (n/m ratio) plays a significant role on the origin and stabilization of this rarely occurring transition in higher homologues of n O.*m* compounds (Fig. 3). In fact, Fig. 3 envisages the n/m ratio required to exhibit a direct isotropic to smectic-F transition, above which no such transition occurs with an exception in the case of the 10 O.*m* series where one compound, 10 O.14 showed the direct smectic-F transition. It is concluded from our extensive investigations that the total number of n O.*m* compounds exhibiting the isotropic to smectic-F transition (by varying n and m from 1 to 18 and 1 to 16, respectively) is 42.

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