Synthesis and Characterization of Smectic Polymorphism in Higher Homologues of N-(*p*-*n*-Alkoxybenzylidene)-*p*-*n*-(Alkylanilines)

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Higher homologues of N–(*p*-*n*-alkoxybenzylidene)–*p*–*n*-alkylanilines (*n*O.*m*) compounds with $n = 15$ and 18 and $m = 4$ to 10, 12, 14, and 16 have been synthesized and the smectic polymesomorphism is studied. The transition temperatures were obtained both from thermal polarizing microscopy and differential scanning calorimetry. The compounds exhibit a smectic-F phase from the isotropic melt, their amount increasing with the number of the alkoxy chain. This implies that with the alkoxy chain number the manifestation of smectic-F occurs with shorter alkyl chain. The phase variants were confirmed with miscibility studies.

Key words: *n*O.*m* Compounds; Smectic Polymorphism; Smectic-F; Miscibility Studies; Phase Diagrams.

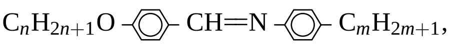
1. Introduction

The research on liquid crystals involves the design, synthesis and characterization of phase variants involving different techniques. The N–(*p*-*n*-alkoxybenzylidene)–*p*–*n*-alkylanilines, (*n*O.*m*), attracted much attention as they exhibit rich but subtle polymorphism [1 – 3]. The lower homologues exhibit [4, 5] the nematic and orthogonal smectic phase, while the higher ones exhibit [6] the interesting tilted smectic phases including smectic-F with the quenching of the nematic phase. However, the compounds with intermediate of chain lengths show [7, 8] both the nematic and smectic phases. The higher homologues with $n \geq 10$ are found [2] to be rich in the manifestation of a direct tilted smectic-F phase from the isotropic melt. As a part of the systematic studies involving the synthesis and characterization of higher homologues of *n*O.*m* compounds, the authors present in this communication the synthesis and phase characterization of two higher homologues of the *n*O.*m* series, *viz*. N–(*p*-*n*-pentadecyloxybenzylidene)–*p*–*n*-alkylanilines, (15O.*m*) and N–(*p*-*n*-octadecyloxybenzylidene)–*p*-*n*-alkylanilines, (18O.*m*) series.

2. Experimental

The compounds were prepared [6, 9] by condensation of the respective alkoxy benzaldehyde (0.1 mole) and alkyl aniline (0.1 mole) in refluxing absolute ethanol in the presence of a few drops of glacial acetic acid. After refluxing the reactants for four hours, the solvent was removed by distillation under reduced pressure. The crude sample was subjected to repeated recrystallisation from cold absolute ethanol, till the transition temperatures were found to be reproducible.

The homologous series N–(*p*-*n*-alkoxybenzylidene)–*p*–alkylanilines are Schiff's bases with the general molecular formula



where *n* and *m* represents the number of carbon atoms in the alkoxy and alkyl end chains, respectively. All the compounds in the present work were synthesized for the first time.

The anilines used for the synthesis of the above compounds are commercially available, but the alkoxyaldehydes were prepared at the Centre for Liquid Crystal Research and Education (CLCRE), Nagarjuna University, Nagarjunanagar 522 510, India by the synthetic route described below.

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Table 1. Transition temperatures (°C) from thermal microscopy (TM) and differential scanning calorimetry (DSC) (enthalpy values given in J/gm) of 15O.*m* compounds.

15O.*m*	Method	S_1	S_2	S_3	K
		S_A / S_F	S_B / S_F	S_F / S_G	
15O.2	TM@	73.70	72.60		69.60
	DSC (H)	—	—		78.68
	ΔH	—	—		162.03
	DSC (H)	73.99	—		67.29
	ΔH	21.56	—		132.01
15O.3	TM	86.00	78.0		52.0
	DSC (H)	86.08	79.62		70.75
	ΔH	11.99	6.45		55.73
	DSC (C)	84.4	77.58		50.46
	ΔH	11.48	6.32		49.83
15O.4	TM	80.40	72.40	66.40	44.90
	DSC (H)	82.90	76.30	74.55	67.70
	ΔH	14.16	7.39	0.05	70.05
	DSC (H)	81.03	74.34	72.82*	44.97
	ΔH	14.21	7.96	—	69.12
15O.5	TM	86.40	84.00	70.50	44.00
	DSC (H)	89.56	85.08	84.14*	64.79
	ΔH	21.47	13.15	—	87.23
	DSC (C)	87.23	82.96	—	—
	ΔH	21.33	12.62	—	—
15O.6	TM	84.80	82.70	80.60	43.00
	DSC (H)	87.47	85.43	—	63.17
	ΔH	18.09	13.27	—	72.69
	DSC (H)	85.21	83.23	82.69*	—
	ΔH	17.86	12.99	—	—
15O.7	TM	87.20		86.00	39.00
	DSC (H)	90.83		—	59.90
	ΔH	38.64			42.41
	DSC (H)	88.32			—
	ΔH	37.89			—
15O.8	TM	87.50			38.00
	DSC (H)	90.19			68.65
	ΔH	35.57			102.15
	DSC (C)	87.93			—
	ΔH	35.34			—
15O.9	TM	88.60			35.00
	DSC (H)	91.68			64.86
	ΔH	27.66			74.86
	DSC (C)	89.74			—
	ΔH	28.36			
15O.10	TM	89.00			42.50
	DSC (H)	86.50			70.61
	ΔH	37.37			111.70
	DSC (C)	89.59			—
	ΔH	36.39			—
15O.12	TM	87.50			46.50
	DSC (H)	90.87			74.74
	ΔH	23.17			76.89
	DSC (C)	88.98			—
	ΔH	24.29			—
15O.14	TM	88.60		86.8	
	DSC (H)	91.05			79.85
	ΔH	30.00			69.70
	DSC (C)	88.35			58.55
	ΔH	30.30			78.50
15O.16	TM	88.40		88.00	67.1
	DSC (H)	90.61		—	75.60
	ΔH	39.65		—	136.53
	DSC (C)	87.18		84.50	66.50
	ΔH	38.03		—	119.77

* DSC transitions are not well resolved. @TM values are from cooling.

2.1. Synthesis of p-n-penta/octadecyloxybenzaldehyde

To a cyclohexanone solution containing p-hydroxybenzaldehyde (1.83 gm / 15 mmol) and n-pentadecyl bromide (5.82 ml / 20 mmol), 5.15 gm / *n*-octadecyl bromide (6.82 ml / 20 mmol), 5.15 gm of (37.5 mmol) of anhydrous potassium carbonate was added slowly with constant stirring. The reaction mixture was then heated under reflux for 3 hrs until the evolution of CO_2 ceased. After cooling to room temperature, the reaction mixture was filtered off to remove excess of K_2CO_3 and KBr formed during the reaction. The precipitate was washed repeatedly with excess of ether. On evaporating the excess ether and cyclohexanone under reduced pressure, a colourless oil product (82 % yield) was obtained. The oil product was further purified by passing through a silica gel column using a mixture of benzene and acetone in the volume ratio 1:4.

The thermal microscopy was carried out using a Hertel and Reuss super pan II Polarizing Microscope in conjunction with a PC monitored INSTEC mK temperature controller to an accuracy of ±0.01 K. A Perkin Elmer DSC 7 system was used to record the transition temperatures and enthalpies involved at the transitions.

3. Results and Discussion

3.1. Characterization of the Liquid Crystalline Phases in N-(p-n-pentadecyloxybenzylidene)-p'-n-alkylanilines (15O.m)

The 15O.*m* compounds exhibit five different types of phase variants, namely AB, ABF, ABG, F, and FG. The lower alkyl chain members 15O.2 and 15O.3 exhibit an AB phase variant, while 15O.4, 15O.5 and 15O.6 show ABF, ABG and ABG phase variants, respectively. The compounds with *m* = 8, 9, 10, and 12, which belong to the middle members of the series, exhibit a single-phase variant, namely F. These compounds are the classic examples for the manifestation of a direct smectic-F production from the isotropic melt. These exist in addition to 10O.14 [6] and the

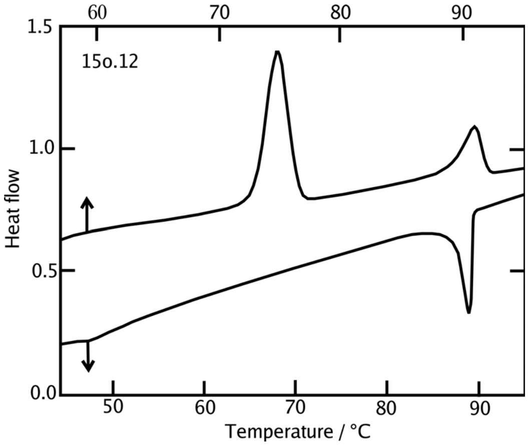

Fig. 1. DSC heating and cooling thermograms of compound 15O.12.

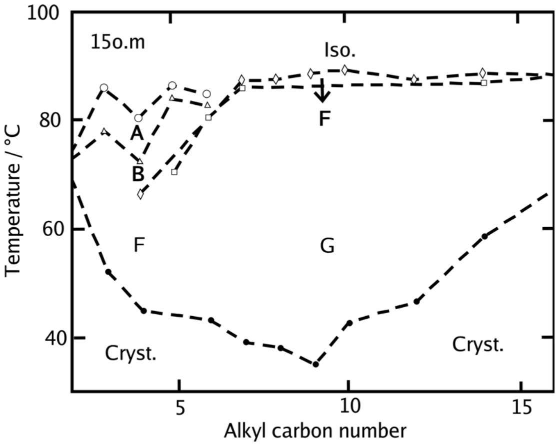

Fig. 2. Phase diagram of 15O.*m* compounds.

higher members of 11O.*m* [2] and 12.O*m* [10] series. The rest of the compounds in this series with the alkyl chain lengths m = 7, 14, and 16 show a double variant, namely FG. The textural observation of these compounds shows that, when $n > 7$, a direct smectic-F phase results from the isotropic melt. From the body of the data available on *n*O.*m* compounds which exhibit a direct smectic-F phase from the isotropic melt follows that the alkoxy chain length plays a dominant role and overshadows the alkyl change length influence in exhibiting a direct smectic-F.

On cooling the samples with m = 2, 3, 4, 5, and 6 from isotropic liquid, a mesomorphic phase S_1 appears in the form of batonnets at 73.70, 86.0, 80.4, 86.4, and 84.8 °C for 15O.2, 15O.3, 15O.4, 15O.5, and 15O.6, respectively. On further cooling, these batonnets settle to form a focal conic fan texture, a characteristic natural texture of the smectic-A phase. This phase also exhibits a homeotropic texture, indicating that it is an orthogonal phase. These observations confirm the phase as smectic-A.

On further cooling, the smectic-A phase transforms into another smectic phase S_2 at 72.60, 78.0, 72.40, 84.0, and 82.70 °C, in the case of 15O.2, 15O.3, 15O.4, 15O.5, and 15O.6, respectively. This transition is indicated by the transient transition bars across the focal conic fans of smectic-A phase. These transient transition bars disappeared after the completion of the transition, leading to a smooth focal conic fan texture. The smooth focal conic fan texture (different from that observed in smectic-A) and the appearance of transient transition bars across the phase boundary (on the fans) characterize the phase as smectic-B. The transient transition bars across the $S_A - S_B$ phase transition and the smooth focal conic fan texture of the S_2 phase are similar to the textures observed for the smectic-B phase in 9O.5 [11], 5O.9 [11], and 11O.4 [2]. The cooling of the S_2 phase in 15O.4 transforms into another smectic phase, S_3 at 66.4 °C. The transition is indicated by the appearance of a broken fan texture. Unlike the case of 15O.4, cooling of the smectic-B phase of 15O.5 and 15O.6 transforms to another smectic, S_3 phase by the formation of mosaics from the smectic-B smooth fan texture. The difference in the textural observations of the above compounds, 15O.4 on one hand and 15O.5 and 15O.6 on the other hand, confirm that the smectic S_3 modification is different in 15O.4 from the other two compounds. In the former case it can be characterized as smectic-F, and in the later two compounds it is a smectic-G phase. These textural observations concur with the results obtained in the other *n*O.*m* compounds, which exhibit [6, 10] the same phase variants. The results indicate that these compounds show trimorphic phase sequences ABF, ABG, and ABG, respectively.

In the case of other compounds with m = 7 to 10, 12, and 16, the microscopic texture separates out from the isotropic liquid (on cooling) with spherical droplets exhibiting hexagonal crosses of optical discontinuity centers in them. The observed texture is similar to those observed in 10O.14 [6], 12O.12 [10], 12O.14 [10], 12O.16 [10], 11O.12 [2], 11O.14 [2], 13O.14, 14O.14, 15O.14, and 16O.14 [12], which show a direct smectic-F phase on cooling the isotropic melt. These observations suggest that the $S_1$is phase in these compounds is smectic-F.

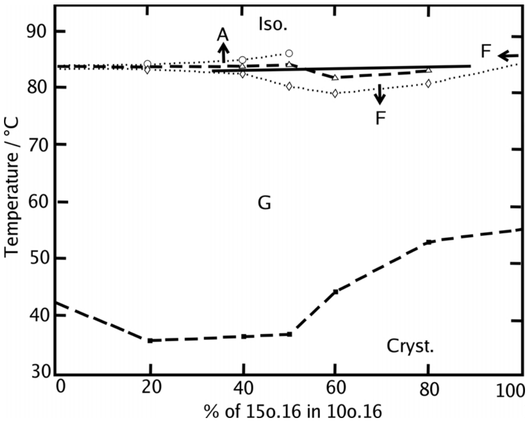

Fig. 3. Miscibility diagram of 15O.16 + 10O.16.

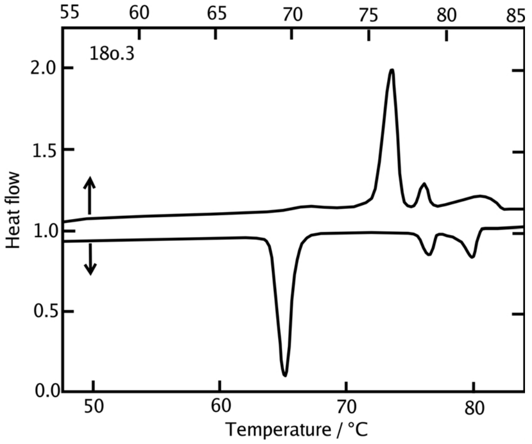

Fig. 4. DSC heating and cooling thermograms of compound 18O.3.

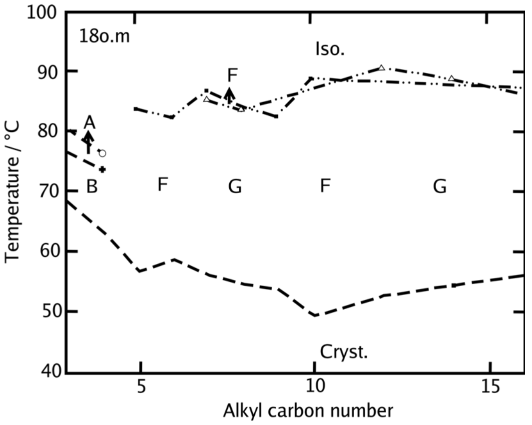

Fig. 5. Phase diagram of compounds 18O.*m*.

On further cooling, the smectic-F in the case of m = 7, 16, transforms into another smectic phase (S_2) with broken or stripped fan texture at 86.0 °C and 88.0 °C in the case of 15O.7 and 15O.16, respectively, characterizing the phase possibly as smectic-G. Further, these S_1 and S_2 phases are characterized and confirmed by miscibility studies. The compound 15O.16 is mixed with a known compound 10O.16 [6], which exhibits an AFG variant (15O.16 is taken as a representative member for miscibility studies). These studies confirm the S_1, S_2 phases as smectic-F and smectic-G, respectively, as they are continuously miscible to the F and G phase of 10O.16.

The transition temperatures from thermal microscopy, and those with the enthalpy values from DSC, along with the observed phase variants, are given in Table 1.

The thermograms of the compound 15O.12 for heating and cooling cycles are depicted in Figure 1. The phase diagram of the 15O.*m* series is shown in Figure 2. The miscibility diagram of 15O.16 with 10O.16 is shown in Figure 3.

As the thermal ranges of smectic-F and smectic-G are narrow, in some of the compounds, these transitions could not be detected from DSC.

3.2. *Characterization of Liquid Crystalline Phases in N–(p-n-octadecyloxybenzylidene)– p′-n-alkylanilines (18O.m)*

The 18O.*m* compounds show four different types of phase variants, namely AB, F, FG and G. The compounds with alkyl chain length 3 and 4, *viz.*, 18O.3, 18O.4, exhibit an AB phase variant, while the compounds 18O.5, 18O.6 and the middle members *viz.*, 18O.9, 18O.10 show a single-phase variant smectic-F phase. These compounds are an addition to those which manifest a direct smectic-F phase from the isotropic melt. The compounds with alkyl chain lengths 7, 8, and 16 show a double variant, with smectic-F and smectic-G phases. Smectic-G phase appears directly from isotropic phase on cooling in the case of compounds with m = 12 and 14.

On cooling the samples 18O.3 and 18O.4 from the isotropic liquid the mesomorphic phase S_1 appears in the form of batonnets at 80.51 and 76.4 °C, respectively. On further cooling, these batonnets coalesce to form a focal conic fan texture, a natural texture of the smectic-A phase. This phase also exhibits a homeotropic texture, indicating it as an orthogonal phase as in the case of the compounds of the 15O.*m* series, which exhibit a smec-

Table 2. Transition temperatures (°C) from thermal microscopy (TM) and Differential scanning calorimetry (DSC) (enthalpy values given in J/gm) of 18O.*m* compounds.

18O.*m*	Method	S_1 S_A / S_F / S_G	S_2 S_B / S_G	K	18O.*m*	Method	S_1 S_A / S_F / S_G	S_2 S_B / S_G	K
18O.3	TM	80.51	76.54	68.20	18O.9	TM	82.39		53.47
	DSC (H)	82.12	78.51	76.49		DSC (H)	83.57		65.68
	ΔH	20.46	10.53	112.59		ΔH	31.73		84.35
	DSC (C)	79.91	76.49	65.22		DSC (C)	81.13		45.14
	ΔH	22.69	12.63	121.2		ΔH	24.48		81.13
18O.4	TM	76.40	73.60	63.10	18O.10	TM	88.78		49.06
	DSC (H)	79.19	76.51	73.72		DSC (H)	90.25		72.44
	ΔH	11.57	8.6	110.90		ΔH	27.14		79.54
	DSC (H)	76.72	74.21	61.38		DSC (C)	88.10		—
	ΔH	12.74	10.47	127.04		ΔH	30.76		—
18O.5	TM	83.70		56.64	18O.12	TM	90.60		52.50
	DSC (H)	85.49		70.20		DSC (H)	92.79		78.17
	ΔH	25.13		107.50		ΔH	41.75		104.68
	DSC (H)	83.24		56.07		DSC (C)	91.19		—
	ΔH	39.73		106.12		ΔH	41.70		—
18O.6	TM	82.30		85.50	18O.14	TM$^{\#}$	88.80		—
	DSC (H)	85.25		69.42		DSC (H)	91.55		81.75
	ΔH	27.24		79.54		ΔH	23.56		71.68
	DSC (H)	83.10		52.50		DSC (C)	88.85		—
	ΔH	30.76		68.58		ΔH	28.80		—
18O.7	TM	86.80	85.20	55.98	18O.16	TM	87.27	86.30	56.87
	DSC (H)	87.11	85.79	65.33		DSC (H)	90.51	—	88.10
	ΔH	29.87	—	61.11		ΔH	—	—	171.04
	DSC (H)	85.24	83.71	51.51		DSC (C)	85.65	—	52.11
	ΔH	27.23	—	62.82		ΔH	42.73	—	79.42
18O.8	TM	84.20	83.50	54.40					
	DSC (H)	85.60	—	66.50					
	ΔH	36.86	—	46.27					
	DSC (H)	84.28	—	114.85					
	ΔH	37.16	—	66.75					

* DSC transitions are not well resolved. # No crystal transition is observed [12].

tic-A phase. These observations indicate the phase as smectic-A.

On further cooling, as in the case of 15O.3 and 15O.4, the smectic-A phase transforms into another smectic phase S_2 at 76.54 and 73.6 °C, respectively. The transition is evidenced by the appearance of the transient transition bars across the focal conic fans of the smectic-A phase. These transient transition bars slowly disappear after the completion of the transition, leading to a smooth focal conic fan texture. This texture is different from that observed in smectic-A, and the appearance of transient transition bars across the phase boundary (on the fans) characterizes the S_2 phase as smectic-B. The transient transition bars across the smectic-A and smectic-B phase boundary and the smooth focal conic texture of the S_2 phase are similar to those observed in case of 15O.3, 15O.4, 9O.5 [11], 5O.9 [11], and 11O.4 [2].

In the case of *n* = 5 to 10 and 16, on cooling the samples from the isotropic phase, phase S_1 separates with the appearance of spherical droplets exhibiting hexagonal crosses of optical discontinuity centers in them, as in the 15O.*m* series. The observed textures are similar to those observed in 10O.14 [6], 12O.12 [10], 12O.14 [10], 12O.16 [10], 11O.12 [2], 11O.14 [2], 13O.14 [12], 14O.14 [12], 15O.14 [12], and 16O.14 [12], which show a di-

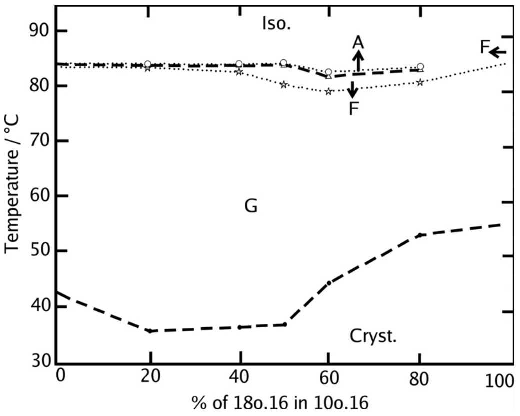

Fig. 6. Miscibility diagram of 18O.16 + 10O.16.

rect smectic phase on cooling the isotropic melt. These observations suggest that this phase (S_1) is smectic-F.

On further cooling, the smectic-F transforms into another smectic phase (S_2) with broken or striped fan texture at 80.7, 77.5, and 85.3 °C in the case of 18O.7, 18O.8 and 18O.16, respectively, characterizing the phase possibly as smectic-G. Further, the S_2 phase is confirmed by miscibility studies. The compound 18O.16 is mixed with 10O.16, which exhibits an AFG variant (18O.16 is taken as a representative compound in miscibility studies). These studies confirm S_1 and S_2, phases as smectic-F and smectic-G since they are continuously miscible with the F and G phases of 10O.16.

In the case of 18O.12, thermal microscopy as well as DSC studies indicated a single enantiotropic smectic phase on cooling the isotropic liquid. The mesophase appeared with broken focal conic and mosaic textures in the homeotropic and homogeneous regions, respectively. This textural results indicate the LC phase as a tilted smectic-G phase, similar to that observed in 18O.14 [12].

The transition temperatures and enthalpies from DSC, as well as the transition temperatures from thermal microscopy are given in Table 2.

The thermogram of the compound 18O.3 for heating and cooling cycles is depicted in Figure 4. The phase diagram of the 18O.*m* series is given in Figure 5. The miscibility diagram of 18O.16 with 10O.16 is shown in Figure 6.

The salient features observed in this study are:

- The lower members, i.e., $n \leq 6$ exhibit orthogonal phase *viz.*, smectic-A and smectic-B phases.
- With $n \geq 7$, the orthogonal phases are quenched with the onset of either smectic-F or smectic-G phase.
- A unique single phase variant (F) or (G) among the higher members of *n*O.*m* compounds is observed for $n \geq 10$. The number of compounds exhibiting this phase variant increases with increase of the alkoxy chain length.
- All the phases reported in these two series are enantiotropic in nature.

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