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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

SMECTIC-F/G TO ISOTROPIC LIQUID PHASE TRANSITION IN NO.M HOMOLOGUES

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Version of record first published: 24 Sep 2006

To cite this article: M. Jitendra Nadh, C. G. Rama Rao, M. Srinivasulu & V. G. K. M. Pisipati (2001): SMECTIC-F/G TO ISOTROPIC LIQUID PHASE TRANSITION IN NO.M HOMOLOGUES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 47-59

To link to this article: <http://dx.doi.org/10.1080/10587250108023947>

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Smectic-F/G to Isotropic Liquid Phase Transition in nO.m Homologues

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The search for the hexatic phases such as smectic-F and G in N-(p-n-alkoxybenzylidene)-p-n-alkyl anilines, nO.m s series has revealed that a number of higher homologues of this series exhibit a direct isotropic liquid to hexatic smectic-F and G phases in addition to the lone compound hitherto known in nO.m series viz., 10O.14. The compounds of the 12O.m series (with m = 12, 14 and 16), 11O.12 and nO.14 series (with n = 10 to 16) exhibit a direct smectic-F, while the compound 18O.14 exhibits a direct smectic-G transition from isotropic liquid.

Keywords: nO.m; hexatic smectic-F and G phases; Misibility studies; Phase diagrams

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INTRODUCTION

The smectic-F and smectic-G phases are hexatic in nature and the liquid crystals exhibiting such phases are of considerable interest because of their structural properties and associated uncommon phase sequence variants^[1]. Some of the interesting phase sequences reported in the nO.m compounds are AFG (9O.4)^[1,2] NACBFG (5O.6)^[1,3] ABG (8O.10)^[4,5] FG (10O.14, 12O.12, 12O.14 and 12O.16)^[6,7] and TBnA series show ACIFG (TB10A)^[8] CIFG (TB12A, 14A, 16A)^[9,10] phase sequences. The special feature of this transition Isotropic-smectic-F/G is that the characteristic long range bond orientational order along with the coexisting short range/long range positional order in the case of smectic-F/G phase vanish simultaneously. It may be recalled generally, mesophases of the type B, I, F and G undergo^[3] transition to other smectic phase or with lower order nematic phase possessing orientational order alone.

The formation of smectic-F phase of direct cooling of an isotropic phase is reported^[6,7,11] first for esters of the type p-n-alkynoloxo-p-n-octyloxybiphenyl (with n = 9, 11 and 13 and in 10O.14 in nO.m series). The systematic studies^[6,7] on higher homologues of nO.m compounds show that these stand as potential candidates for the realisation of smectic-F and G phases along with other high temperature smectic phases, in addition to the occurrence of direct smectic-F and G phases from isotropic. The compounds of 11O.m series with m = 4, 5 exhibit AB, m = 6, 7, 8 and 10 show AFG and m = 12 and 14 account for FG phase variants. However, the higher homologues of nO.14 series with n = 10 to 16 exhibit FG while the compound 18O.14 shows a direct smectic-G phase quenching the smectic-F phase. This is the first compound to exhibit a single liquid crystalline smectic phase in nO.m series. All the compounds reported here are synthesised for the first

time.

The continuation of the earlier work on the systematic study of the synthesis, characterisation and phase transition studies in nO.m series of compounds, we present in this paper our experimental results of Thermal Microscopy (TM), Differential Scanning Calorimetry (DSC) and miscibility studies of these 11O.m and nO.14 compounds. These new benzylidene aniline compounds are synthesised following standard procedure^[1,3]. The molecular formula of these compounds is shown below.



where $n = 11$ and $m = 4$ to $8, 10, 12$ and 14 (11O.m compounds)

and

$n = 7$ to $9, 11, 13$ to 16 and 18 ; $m=14$ (nO.14 compounds)

N-(p-n-undecyloxybenzylidene)-p-n-alkylanilines, (11O.m)

The compounds 11O.4, 11O.5 and 11O.12, 11O.14 exhibit two, while compounds 11O.6, 11O.7, 11O.8 and 11O.10 show three enantiotropic liquid crystalline phases between solid crystal and the isotropic liquid. The characterisation of phases and the corresponding transition temperatures (K) from T.M., DSC along with enthalpy values are presented in table-1.

On cooling the samples 11O.4, 11O.5 and 11O.12 and 11O.14 from the isotropic liquid the mesomorphic phase S₁ appears in the form of batonnets at 356.7 K for 11O.4, 361.2 K for 11O.5, 359.6 K for 11O.12 and at 361.6 for 11O.14 respectively. While in the case of 11O.12 and 11O.14, two distinguished textures leading to the natural mosaic texture is observed (plate -1). This clearly implies phase exhibited by compounds with $m = 4, 5$ and $m = 12, 14$ are different. The batonnets coalesce into a focal conic fan texture. This phase also exhibits the homeotropic texture indicating it as an orthogonal phase or pseudo -

TABLE I Transition Temperatures(K) from thermal microscopy, differential scanning calorimetry and enthalpy values (KJ/mole) for 11O.m compounds.

11O.m	Method	S_1 (S_A/S_F)	S_2 (S_B/S_F)	S_3 (S_G)	K
11O.4	T.M.	356.65	345.2		323.2
	D.S.C.(H)	357.5	345.7		325.0
	ΔH	4.85	2.85		18.87
	(C)	356.4	344.6		---
11O.5	ΔH	4.66	2.79		---
	T.M.	361.2	350.7		323.2
	D.S.C. (H)	360.5	350.2		
	ΔH	6.8	3.65		
11O.6	(C)	360.7	350.1		
	ΔH	6.61	3.58		
	T.M.	359.8	352.0	349.2	318.2
	D.S.C. (H)	360.0	351.3	---	317.9
11O.7	ΔH	7.53	4.51		27.98
	(C)	359.7	352.4	350.0	
	ΔH	6.85	----		
	T.M.	363.2	357.2	354.9	321.2
11O.8	D.S.C. (H)	364.1	357.2		319.5
	ΔH	9.77	6.2		34.74
	(C)	363.6	356.9		
	ΔH	9.26	5.71		
11O.10	T.M.	362.2	358.9	357.2	325.2
	D.S.C. (H)	363.0	358.0		326.8
	ΔH	8.04	5.15		44.08
	(C)	362.3	357.4		
11O.12	ΔH	8.12	5.07		
	T.M.	361.7	358.6	356.2	323.3
	D.S.C. (H)	364.1	361.2		
	ΔH	6.01	9.45		
11O.14	(C)	361.5	358.8		
	ΔH	6.02	10.10		
	T.M.	359.6		359.0	322.2
	D.S.C. (H)	362.9		362.2	329.8
11O.14	ΔH	18.56		---	
	(C)	360.3		359.8	321.7
	ΔH	17.25		---	52.52
	T.M.	361.6		360.8	346.2
11O.14	D.S.C. (H)	362.4		361.6	345.7
	ΔH	17.1		---	71.23
	(C)	358.0			
	ΔH	18.26			

isotropic texture in 11O.4 and 11O.5 compounds. The transition is indicated by the transient transition bars across the focal conic fans of phase, which disappeared after the completion of the transition leading to a smooth focal conic fan texture. The smooth focal conic fan texture and the appearance of transient bars across the phase boundary characterise the S₂ phase as smectic-B (S_B) phase. The transition bars across S_A-S_B and smooth focal conic fan textures of S₂ phase are similar to the textures obtained^[12] for S_B phase in 9O.5 and 5O.9 compounds.



PLATE 1 Natural optical texture of Smectic-F phase
See Color Plate I at the back of this issue.

In the case of 11O.12 and 11O.14 compounds the microscopic texture (as it separates out from the isotropic liquid with spherical droplets exhibits hexagonal cross of optical discontinuity centered in them. the observed textures are similar to those reported^[6,7,11] for esters of p-n-alkoxy p-n-octyloxybiphenyl, and in 10O.14, 12O.12, 12O.14 and 12O.16 of nO.m series

which exhibited direct smectic-F phase on cooling the isotropic liquid. These textural observations suggest that (S_1) phase in these compounds is smectic-F. On further cooling, the S_1 phase transforms in to the S_2 phase, with broken or striped fan texture (at 359.5 K for 11O.12 and 360.8 K for 11O.14), characterising the phase possible as smectic-G. The S_1 and S_2 phases of these two compounds are further characterised by miscibility studies^[12]. The compound 11O.14 is mixed with 10O.14 which also exhibits smectic F and G phases. These studies are carried out for the conformation of

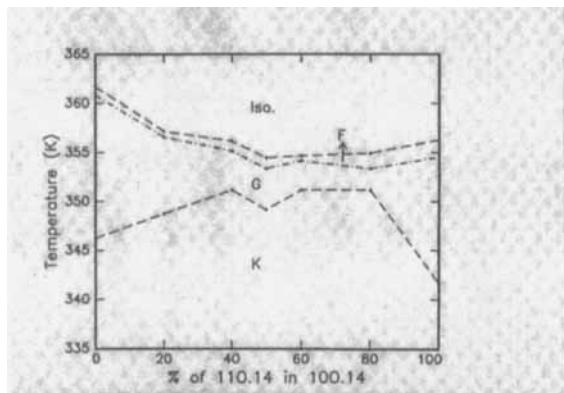


FIGURE 1 The miscibility phase diagram of 11O.14 and 10O.14

observations from thermal microscopy. The miscibility diagram of 11O.14 and 10O.14 is shown in figure-1. These two phases are co-miscible with the phases of 11O.14 and 10O.14. Hence, the above mentioned compounds are found to be exhibit FG phase variant.

The preliminary thermal microscopic studies of the compounds 11O.6, 11O.7, 11O.8 and 11O.10 show three enantiotropic mesomorphic phases. A liquid crystalline phase S_1 appears in the form of batonnets (at 359.8 K for 11O.6, 363.2 K for 11O.7, 362.2 K for 11O.8 and 361.7 K for 11O.10) on cooling the isotropic liquid, and these batonnets coalesce into a focal conic fan texture as observed^[13] in 9O.m compounds. This phase

also exhibits the homeotropic texture indicating its orthogonal structure or pseudo - isotropic texture. These observations indicate that the phase may be S_A phase. Further, cooling, produces the second phase S_2 which exhibits both broken focal conic fan and schlieren mosaic textures formed from the focal conic fans and homeotropic textures of S_1 phase (at 352.0 K for 11O.6, 357.2 K for 11O.7, 358.9 K for 11O.8 and 358.6 K for 11O.10 respectively). These textures are similar to those observed for the smectic-F (S_F) phase in the compounds 9O.4^[14] 9O.6 and 9O.8^[13]. Therefore, S_2 phase may be S_F . Subsequent cooling leads to S_3 , phase

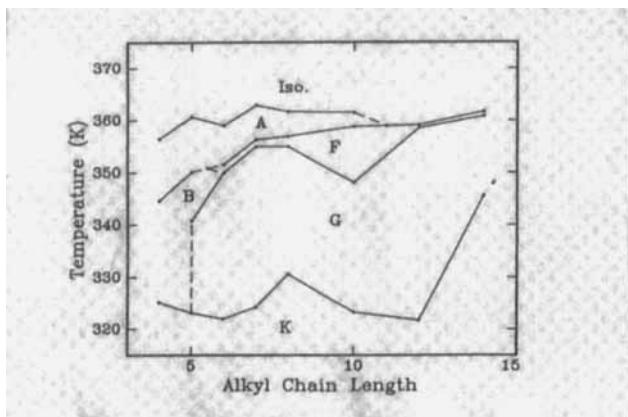


FIGURE 2 Phase Diagram of 11O.m compounds

which forms with slight changes in the colour of texture. The breakages in the S_2 texture change to the form of large dark streaks, patches and these patches had a more chunky appearance and the texture is similar to that observed^[14] for the S_G phase of 9O.4. The smectic phases S_1 , S_2 and S_3 are identified as smectic-A , smectic-F and smectic-G. The phase diagram of 11O.m compounds is illustrated in figure - 2.

N-(p-n-alkyloxybenzylidene)-p-n-tetradecylanilines, (nO.14)

The preliminary thermal microscopic studies indicate that the compounds with $n = 7, 8$ and 9 exhibit three enantiotropic liquid crystalline phases while other compounds with $n = 11, 13, 14, 15$ and 16 exhibit two enantiotropic liquid crystalline phases. The compound with $n = 18$ (18O.14) shows one mesomorphic smectic phase. The characterisation of the phases, the corresponding transition temperatures (K) from T.M., DSC and enthalpy values are given in table - 2. The DSC thermograms for the compound 13O.14 are presented in figure - 3.

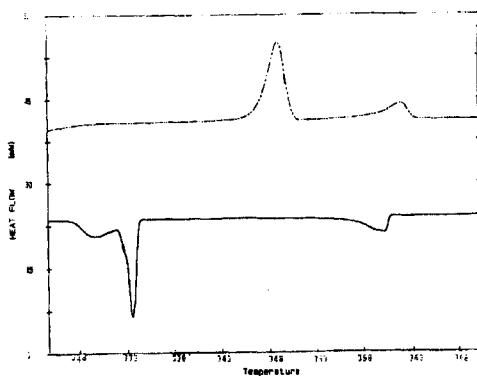


FIGURE 3 The DSC Thermogram of 13O.14 compound

The compounds 7O.14, 8O.14 and 9O.14 on cooling from the isotropic liquid exhibit an optical texture in the form of the battonets (S_1) (at 350.7 K for 7O.14, 355.7 K for 8O.14 and 356.3 K for 9O.14 respectively) and these battonets coalesce into a focal conic fan texture. This phase also exhibits the homeotropic texture indicating it as an orthogonal phase or pseudo - isotropic texture in all the three compounds. These observations indicate that the phase

TABLE II Transition Temperatures (K) from Thermal Microscopy, Differential Scanning Calorimetry and Enthalpy values (KJ/mol.) for nO.14 compounds

nO.14	Method	S_1 $S_A/S_F/S_Q$	S_2 S_B/S_Q	S_3 S_B/S_Q	K
7O.14	T.M. D.S.C. (H) ΔH (C) ΔH	350.7 352.2 6.70 350.9 6.66	340.8 342.3 3.29 341.0 3.31	339.3	335.9 337.4 13.25
8O.14	T.M. D.S.C. (H) ΔH (C) ΔH	355.7 358.3 7.89 355.8 7.87	349.4 351.5 3.74 349.4 3.94	347.6	346.2 348.5 62.05
9O.14	T.M. D.S.C. (H) ΔH (C) ΔH	356.3 354.5 5.07	353.0 349.4 3.4	344.6	336.6 337.6 45.1
11O.14	T.M. D.S.C. (H) ΔH (C) ΔH	361.6 362.4 17.10 358.0 18.26	360.8 361.6		346.2 345.7 71.23
13O.14	T.M. D.S.C. (H) ΔH (C) ΔH	360.9 362.1 18.0 360.9 16.4	360.0		347.3 349.1 68.9 333.7 32.7
14O.14	T.M. D.S.C. (H) ΔH (C) ΔH	361.5 363.8 21.5 361.5 19.0	360.4		347.6 350.3 59.8 330.1 44.3
15O.14	T.M. D.S.C. (H) ΔH (C) ΔH	361.6 364.2 30.0 361.5 30.3	359.8		350.1 353.0 69.7 331.7 78.5
16O.14	T.M. D.S.C. (H) ΔH (C) ΔH	360.9 364.5 26.6 360.9 30.3	359.7		348.1 352.8 68.9
18O.14	T.M. D.S.C. (H) ΔH (C) ΔH	361.8 364.7 23.56 361.8 28.80			351.5 354.9 71.68

is confirmed as smectic-A phase. On further cooling, the S_A phase transforms into another smectic phase S_2 (at 340.8 K for 7O.14, 349.4 K for 8O.14 and 353.0 K for 9O.14). The transition is indicated by the transient transition bars acrosss the focal conic fans of S_A phase, which disappeared after the completion of the transition leading to a smooth focal conic fan texture. The smooth focal conic fan textures and the appeareance of transient bars across the phase boundary characterise the S_2 phase as smectic-B (S_B) phase. The transition bars across S_A - S_B and smooth focal conic fan textures of S_2 phase are similar to the texture of those observed in the case of 11O.m and in 9O.5 and 5O.9^[12] compounds. Hence the S_2 phase of these compounds is confirmed as smectic B phase. On further cooling, the above mentioned compounds exhibit a striped - broken focal conic fan texture (at 339.3 K, 347.6 K and 344.6 K for 7O.14, 8O.14 and 9O.14 respectively) characterising the phase as smectic - G (S_G). Hence, the phase variant observed in 7O.14, 8O.14 and 9O.14 is ABG.

Preliminary studies by thermal microscopy shows that the materials 11O.14, 13O.14, 14O.14, 15O.14 and 16O.14 exhibits only two enantiotropic smectic phases. A smectic phase S_1 with two distinct types of optical textures, viz., the focal conic texture (with the appearance of spherulites and lancets) and the droplet texture leading to the normal mosaic pattern of the smectic-F phase is observed at 361.6K, 360.9K, 361.5 K, 361.6 K and 360.9 K for 11O.14, 13O.14, 14O.14, 15O.14 and 16O.14 compounds on cooling the isotropic liquid respectively. The microscopic texture of this phase appearing, (as it separates out from the isotropic liquid), with spherical droplets exhibits hexagonal cross of optical discontinuity centered in them. The observed textures are similar to those reported^[6,7,11] for esters of p-n-alkanoxy-p-n-octyloxybiphenyl which exhibited the formation of the smectic-F phase directly on cooling the isotropic liquid. These textural observations suggest that this phase S_1 in these compounds to be smectic-F. On further cooling, the S_1 phase transforms into the S_2 phase, with broken or stripped fan texture (at 360.8K, 360.0K, 360.4K, 359.8K

which is similar to that observed in the case of 10O.14^[6] and in 12O.12, 12O.14 and 12O.16^[7]. Hence, the above mentioned compounds exhibit FG variant. The variant is further confirmed with the miscibility studies.

The thermal microscopic as well as DSC studies indicated a single enantiotropic smectic phase on cooling the isotropic liquid in the case of 18O.14. The liquid crystalline phase appeared with both broken focal conic as well as mosaic textures in homeotropic and homogeneous regions respectively. This optical textural results indicate that liquid crystalline phase may be either an orthogonal or a tilted phase. However, the studies on nO.m compounds especially of 10O.m and 11O.m series confirm the quenching of orthogonal phases at higher alkyl chain length. Hence, these observations may be considered to indicate that this phase may be either F or G phase. The identification of the phase in 18O.14 is not only confirmed as smectic-G with the miscibility studies carried out with 5O.1 (figure - 4) which exhibits a phase sequence variant of NG but also the characteristic textural changes observed regarding the formation of smectic - G phase either from a high temperature orthogonal (smectic-A or smectic-B) or tilted (smectic-C or smectic-F) phases.

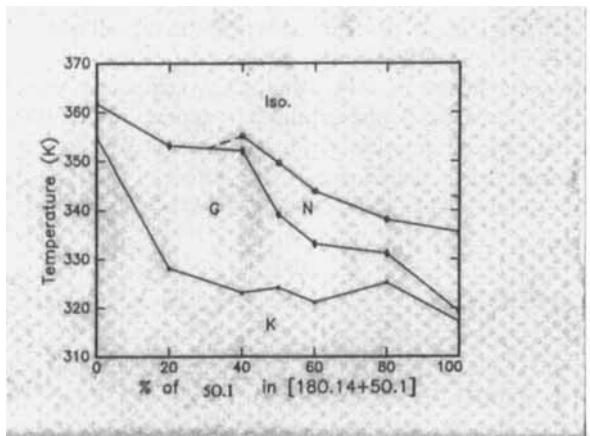


FIGURE 4 The miscibility phase diagram of 18O.14 and 5O.1

On cooling the isotropic liquid, the phase nucleates via a dendric growth pattern and subsequently forms a mosaic platelets as observed^[14] in (\pm)-4-(2'-chlorobutynoyloxy)-4'-n-pentyloxybiphenyl. However, on cooling the smectic-F phase of other nO.14 compounds, the mosaic platelets are

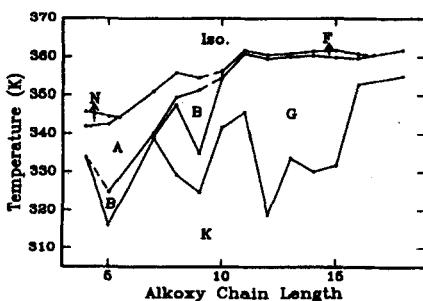


FIGURE 5 Phase diagram of nO.14 compounds

quite large and they are highly coloured as observed in TBnA series^[8-10]. The phase diagram of nO.14 compounds is illustrated in figure - 5.

This systematic studies of 11O.m and nO.14 compounds envisage the quenching of orthogonal phases and the appearance of tilted bond orientational ordered smectics (with the increase of alkyl or alkoxy chains) in the higher homologues. The effect is found to be more prominent with the alkoxy chain rather than alkyl chain length.

CONCLUSIONS

Our present experimental results in higher homologues of nO.m compounds confirm the direct occurrence of smectic-F and smectic-G phases (on cooling the isotropic liquid) as well as the occurrence of these phases along with orthogonal smectic-A and smectic-B phases. The

phase variants of the compounds studied are given below.

N-(p-n-undecyloxybenzylidene)-p-n-alkylanilines, (11O.m)

$m = 4, 5$	-----	AB
$m = 6, 7, 8, 10$	-----	AFG
$m = 12, 14$	-----	FG

N-(p-n-alkyloxybenzylidene)-p-n-tetradecylanilines, (nO.14)

$n = 7$ to 9	-----	ABG
$n = 11, 13$ to 16	-----	FG
$n = 18$	-----	G

Acknowledgements:

Financial assistance is provided by CSIR, DST, AICTE, and DAE, New Delhi, India.

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