Dilatometric Studies Across the Isotropic to Smectic-F Transition

M. Srinivasulu, D. M. Potukuchi, and V. G. K. M. Pisipati

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences,
Nagarjuna University, Nagarjunanagar-522510, India

Thermal Microscopy (TM), Differential Scanning Calorimetry (DSC) and dilatometric studies were carried out to characterise the liquid crystalline phases and mesomorphic transitions exhibited by three higher homologues of N-(p-n-dodecyloxy benzylidene)p-n-alkyl anilines, viz., N-(p-n-dode-cyloxy benzylidene)p-n-dodecyl aniline, (12O.12), N-(p-n-dodecyloxy benzylidene)p-n-tetradecyl aniline, (12O.14) and (N-(p-n-dodecyloxy benzylidene)p-n-hexadecyl aniline, (12O.16). The three compounds exhibit enantiotropic smectic-F and smectic-G liquid crystalline phases between the isotropic liquid and the solid crystal. The change in density across the phase transformations and the thermal expansion coefficient confirm the first order nature of the isotropic to smectic-F (I-SmF) and smectic-F to smectic-G (SmF-SmG) transitions. The dilatometric studies infer strong pre-transitional fluctuations in a relatively large thermal range. The pre-transitional effects are estimated by α_{eff} in the vicinity of the mesomorphic fluctuation-dominated non-linear region (FDNLR) of the I-SmF transition. The strength of non linear growth of density fluctuations is discussed in the wake of reports at the I-N, I-SmA and I-SmC transitions.

Introduction

The smectic-F phase with monoclinic symmetry and long range tilt order, possessing 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). It is a 2D system exhibiting long-range bond orientational order and short-range positional order. Materials exhibiting the SmF phase with tilted order [1, 2] are important both in fundamental and applicational research, since piezoelectric response is reported [3] for the chiral version of the SmF phase.

The Isotropic to SmF transition involves the growth of an ordered tilted smectic phase. In the SmG phase the molecules form a pseudo-hexagonal close packing (in the plane) at right angles to the tilt direction. The layers are well correlated, giving a three dimensional structure. Hence the SmF-SmG transition involves the growth of strong positional correlations between the layers and forms a 3D close packing of molecules, involving first order SmF-SmG transition.

Experimental

The N-(p-n-dodecyloxy benzylidene)p-n-alkyl anilines (12O.m series, m = 12, 14 and 16) were synthesised by the condensation reaction between p-n-dodecyloxy benzaldehyde (0.01 mmol) and p-n-alkyl (dodecyl, tetradecyl and hexadecyl) anilines (0.01 mmol) as described in [4]. The liquid crystalline phases were texturally characterised by using a Hertel-Reuss super pan-II polarising microscope equipped with a self constructed hot stage, accurate to $\pm 0.1\,°C$. The density investigations were carried out by a U-shaped bicapillary pyknometer as reported in [5]. The error in density investigations was $\pm 10^{-4}\ \text{g/cm}^3$. The cooling rate during the density measurements was $0.5\,°C$ per hour. The differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC-7. The general molecular formula of the 12O.m compounds is

$$\text{H}_{25}\,\text{C}_{12}\,\text{O-\textcircled{O}-CH=N-\textcircled{O}-}\text{C}_m\,\text{H}_{2m+1}$$
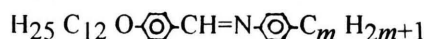
Results and Discussion

The observed transition temperatures (in °C) obtained by thermal microscopy (TM), differential scanning calorimetry (DSC) and dilatometric methods, the density variations ($\Delta\varrho/\varrho \times 100$) and the volume expansion coefficient maxima (α_{V}) associated with the phase

Table 1. Transition temperatures (in °C) from thermal microscopy, differential scanning calorimetry and dilatometry. Density jumps ($\Delta\varrho/\varrho \times 100$) and maximal volume expansion coefficients (α_v) along with the enthalpy values (ΔH in kJ/mol).

Compound	Transition	Thermal Micros-copy	Differential Scanning Calorimetry (DSC)		Dilato-metry	$(\Delta\varrho/\varrho)$ $\times 100$	ΔH	α_{max} $(\times 10^{-4})°C^{-1}$
			Heating	Cooling				
12O.12	I-F	88	90.3	87.7	88	0.94	17.31 (h)*	116.1
	F-G	86.5	88.8	–	86.5	0.16	17.80 (c)*	91.7
	G-K	68	68.6	–	–	–	55.13 (h)	–
12O.14	I-F	87.4	89.9	87.4	87.4	0.83	19.68 (h)*	136.3
	F-G	86.4	88.9	86.4	86.4	0.22	19.18 (c)*	119.6
	G-K	73	74	45.6	–	–	69.84 (h) 47.64 (c)	–
12O.16	I-F	88.1	88.1	85.3	88.1	0.79	20.37 (h)*	113.7
	F-G	86.9	87	–	86.9	0.3	21.71 (c)*	88.3
	G-K	78.1	78.1	45	–	–	75.49 (h) 50.02 (c)	–

ΔH (in kJ/mol.) with asterisk involves both the IF and FG transition with unresolved peaks.

transitions, along with the enthalpy changes (ΔH in kJ/mol.) involved in the mesomorphic transitions are presented in Table 1. There is a slight disagreement between transition temperatures from TM and DSC, probably due to the different rates of cooling. However, the considerable differences in the crystallisation and melting temperatures are due to supercooling.

The lower homologues of 12O.*m* compounds ($m < 10$) exhibit the phase sequence SmA-SmB-SmF-SmG [6], while the higher homologues ($m > 12$) exhibit the phase sequence SmF-SmG between the isotropic liquid and the crystalline phase. That is, the higher homologues are found to exhibit a quasi two dimensional bond orientationally ordered tilted smectic-F phase directly from the isotropic liquid without the occurrence of orthogonal smectic (A, B) phases (exhibited by the lower homologues). The sample taken without the coverslip on a glass slide exhibited [7] a six sectored polygon under crossed polarisers as a characteristic of the growth of a bond orientational (BO) ordered SmF phase mediated [6] through weak forces. The present case of the direct growth of a SmF phase from the isotropic liquid (with increase of the flexible chain length in 12O.*m* series) along with observations in 10O.*m* series of *n*O.*m* compounds are in agreement with the mean field excluded volume theories [8] developed for the micellar systems. It is generally observed that the increase in flexible end-chain length of a molecule favours the occurrence of higher ordered phases. It is also noticed [9] that the ratio of the flex-

ible end chain length to the rigid core length (tuned by increase of the alkyl flexible chain length) in the 10O.*m* series (at $m = 14$) may be the reason for the observation of a bond orientational smectic F phase directly from the isotropic liquid.

The estimated molar volume per methylene group ($-CH_2$) in the isotropic liquid at $(T_{IF} + 5)°C$ for the 12O.*m* series is found to be 15.32 to $14.47 \cdot 10^{-6}$ cm^3 mol^{-1}, in agreement with other liquid crystalline *n*O.*m* compounds [9]. Also the rate of the decrease of the density with temperature in the isotropic phase agrees with other liquid crystalline compounds [10]. The density $\varrho(T)$, and the volume expansion coefficient $\alpha(T)$ for 12O.12, 12O.14, and 12O.16 are illustrated in Figs. 1, 2, and 3, respectively.

The Isotropic to smectic-F phase transition is indicated by a sudden jump in density at 88.0°C for 12O.12, at 87.4°C for 12O.14, and at 85.5°C for 12O.16. The density change $\Delta\varrho/\varrho$ at the transition is evaluated from the vertical distance between the extrapolated density values from the Isotropic and smectic-F regions. The discontinuity in density and thermal expansion coefficient maxima at the Isotropic to SmF transition suggest that this transition is of first order.

It is observed that the density jump at the I-SmF transition decreases with increasing number of methylene units of the flexible alkyl-end chain. A similar trend was reported [10] for the Isotropic to SmC transition in the TBnA series (14 to 16). The trend of
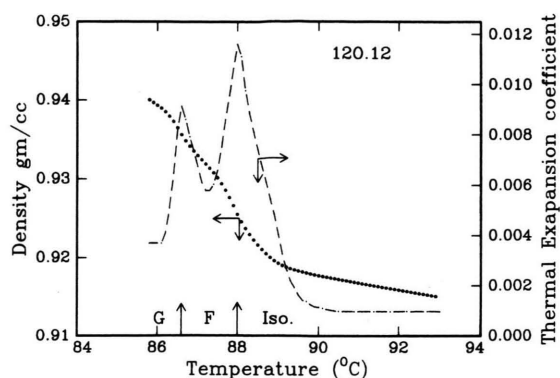
Fig. 1. Variation of density (ϱ) and thermal expansion coefficient (α) with temperature for the compound 12O.12.
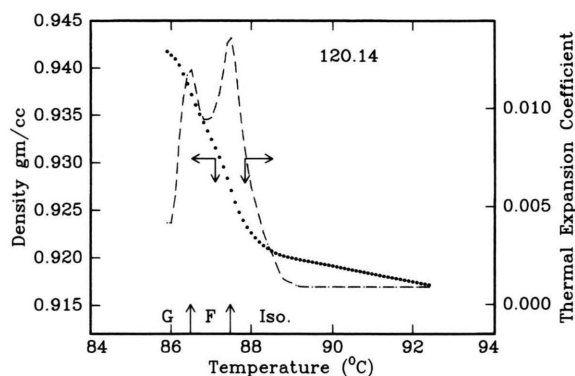

Fig. 2. Variation of density (ϱ) and thermal expansion coefficient (α) with temperature for the compound 12O.14.
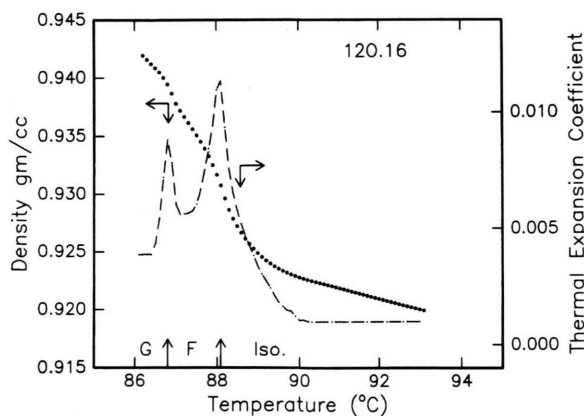

Fig. 3. Variation of density (ϱ) and thermal expansion coefficient (α) with temperature for the compound 12O.16.

decreasing density jump with increasing length of the flexible end chain and the resumption of a tilted phase from Isotropic liquid signifies a decreasing thermal potential barrier across the Isotropic to tilted mesomorphic interface. These results agree with those across the I-SmC transition [10]. However, the behaviour at the I-SmF interface in the 12O.*m* series differs from that at the I-SmC interface, because additional in-plane hexagonal positional correlations must be considered (in addition to the long-range tilt orientation in the former case). Hence, as a result of the relatively higher symmetry breaking at the I-SmF interface, the higher potential barrier is supposed to result in a higher density jump ($\Delta\varrho/\varrho$) with increase of the length of the flexible end chain. However, a decreasing trend of $\Delta\varrho/\varrho$ with increasing *m* is found in the 12O.*m* series (Table 1). The results underline the dominant role of liquid crystalline characteristic tilt-mediated orientational potential barrier, which is obviously more prone to the temperature (rather than the potential barrier relevant to the positional correlations).

The density change (Table 1) across the I-SmF transition in these compounds is bigger than that across the I-N interface [11], but comparable to that across the I-SmA transition in other liquid crystalline compounds [12].

Pretransitional Effects
at the Isotropic-Smectic-F Phase Transition

It is observed (Figs. 1–3) that the density varies linearly with temperature in the Isotropic phase except in the vicinity of the I-SmF transition, where fluctuations and nonlinearity start to grow. These fluctuations diverge at the transition (Fig. 4) and persist on the low temperature side of the I-SmF phase transition. A comparative study of pretransitional fluctuations was carried out by fitting the observed density data to the relation

$$|\varrho_{\text{I-LC}} - \varrho_{\text{T}}| \propto |T_{\text{I-LC}} - T|^{(1-\alpha_{\text{eff}})},$$

where $\varrho_{\text{I-LC}}$ is the observed density at the clearing temperature, $T_{\text{I-LC}}$ is the clearing temperature, ϱ_{T} and T are the observed density and corresponding temperature relevant to the fluctuation dominated nonlinear region and α_{eff} describes the power law dependence of fluctuations on the high temperature side of the transition.
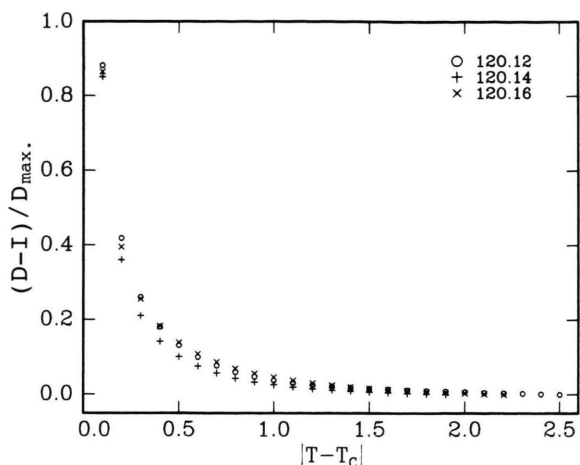
Fig. 4. Divergence of density fluctuations $(D-1)/D_{max}$ near the transition point as a function of $|T-T_C|$.

Table 2. Pretransitional effects at the Isotropic to smectic-F transition for $T_i > T_{IF}$.

Compound	α_{eff}	χ^2	$(\Delta T)_{FDNLR}$	p
12O.12	3.78×10^{-1}	1.85×10^{-3}	$2.5\,^{\circ}C$	>0.995
12O.14	3.98×10^{-1}	1.22×10^{-3}	$1.9\,^{\circ}C$	>0.995
12O.16	3.91×10^{-1}	6.76×10^{-4}	$2.2\,^{\circ}C$	>0.995

The quality of the fit is demonstrated through the χ^2-test (obtained p-values are >0.995). The estimated α_{eff} values and their thermal stability are given in the Table 2. The observed values infer the growth of SmF like regions in the isotropic liquid with a comparatively small thermal range of density fluctuations. It is observed that the density fluctuations across the I-SmF transitions in the 12O.m series exhibit the largest thermal span ranging from 1.9 to 2.5 °C at a cooling rate of 0.5 °C/hr. However, the α_{eff} values computed from the dilatometric data of the fluctuation dominated non-linear region (FDNLR), for $T > T_{IF}$ are found to range around 0.39 ± 0.002. The lower α_{eff} values observed (Table 2) in these compounds compared to the density fluctuations of nematic [12], smectic-A [11] and smectic-C [10] phases in the Isotropic liquid underlines the higher strength of density fluctuations at the IF interface. This is due to the growth of the relatively higher ordered (bond orientational order) SmF phase. The mean extensions of S_F like seeds are found to originate well before (2.5 °C) the I-SmF transition.

Acknowledgements

[1] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).
[2] D. R. Nelson and A. I. Halperin, Phys. Rev. B. **19**, 2457 (1979).
[3] B. Bonev, V. G. K. M. Pisipati, and A. G. Petrov, Liq. Cryst. **6**, 133 (1991).
[4] N. V. S. Rao and V. G. K. M. Pisipati, Phase Trans. **3**, 317 (1983).
[5] N. V. S. Rao and V. G. K. M. Pisipati, J. Phys. Chem. **87**, 899 (1983).
[6] D. M. Potukuchi, G. Padmaja Rani, M. Srinivasulu, and V. G. K. M. Pisipati, Molecular Crystals and Liquid Crystals (Communicated).
[7] G. W. Gray and J. W. Goodby, Smectic Liquid Crystals – Textures and Structures, Leonard Hill, Heydon & Son Inc. 1982, p. 127.
[8] P. Van der School, J. Chem. Phys. **104**, 1130 (1996).
[9] N. V. S. Rao, G. P. Rani, D. M. Potukuchi, and V. G. K. M. Pisipati, Z. Naturforsch. **49a**, 559 (1994).
[10] S. Lakshminarayana, C. R. Prabhu, D. M. Potukuchi, N. V. S. Rao, and V. G. K. M. Pisipati, Liq. Cryst. **20**, 177 (1996).
[11] N. V. S. Rao, D. M. Potukuchi, P. V. Sankara Rao, and V. G. K. M. Pisipati, Liq. Cryst. **12**, 127 (1992).
[12] N. V. S. Rao, D. M. Potukuchi, and V. G. K. M. Pisipati, Mol. Cryst. Liq. Cryst. **196**, 71 (1991).