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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Online publication date: 12 May 2010

To cite this Article Sridevi, B. , Chalapathi, P. V. , Srinivasulu, M. , Pisipati, V. G. K. M. and Potukuchi Corresponding author, D. M.(2004) 'Influence of hydrogen bonding on phase abundance in ferroelectric liquid crystals', *Liquid Crystals*, 31: 3, 303 – 310

To link to this Article: DOI: 10.1080/02678290410001648705

URL: <http://dx.doi.org/10.1080/02678290410001648705>

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Influence of hydrogen bonding on phase abundance in ferroelectric liquid crystals

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(Received 24 July 2003; accepted 26 October 2003)

The synthesis and characterization of five hydrogen-bonded ferroelectric liquid crystal complexes (HBFLCs) prepared from mesogenic *p-n*-alkoxy benzoic acids and non-mesogenic propionic/butyric acids with different chiral centres are reported. Complementary intermolecular hydrogen bonding is confirmed through IR study. HBFLCs are found to exhibit chiral nematic (N*), smectic C* (SmC*) and smectic G* (monotropic) phases in their cooling profiles during polarizing thermal microscopy and differential scanning calorimetry. Phase coexistence regions are observed above the IN* transition. The chiral nematic to smectic C* transition is found to be of first order. The temperature variation of spontaneous polarization exhibited by these HBFLC complexes in their SmC* phase is presented. The effect of non-covalent interaction imparted by the soft hydrogen bonding in these LC complexes on enhanced or induced thermal stability of tilted LC phases is discussed.

1. Introduction

Liquid crystal materials possess anisotropic properties and have been recognized as new dynamic functional molecular materials. In recent times, hydrogen-bonded liquid crystal complexes (HBFLCs) have been reported [1–13], and are synthesized from key functional materials selected on the basis of their molecular recognition and self-assembly capability. Owing to the demand for a wide variety of electro-optic materials with properties suitable for the display applications [14–17], research activity has grown in this area of materials involving supramolecular aspects of chemistry.

Although the first reports of H-bonding in LCs date back to the 1960s [3, 4], much research took place in the last two decades of the twentieth century [5–13, 18–22]. It was noticed that their lower bonding and activation energies showed a profound influence on their thermal properties, viz. melting points, enthalpies of vapourization and mesomorphic phase behaviour. The occurrence of hydrogen bonding in LCs, often

referred to as the fifth fundamental type of interaction, is considered to be the basis for the origin of new stable mesophases with a wide thermal stability. It has been well established [10] that the formation of hydrogen bonding in liquid crystalline materials can be tuned, through the proper selection of complementary interacting components, to fix the configuration (with respect to the direction of the LC rigid core) of the H-bonds formed.

Subsequently, many other HBFLCs have been reported with different types of moieties [5–13, 18–22]. The body of the literature on such intermolecular LC H-bonded complexes shows that the proton donor and/or acceptor molecules are not always mesogenic [18] by themselves. The thermal properties exhibited by H-bonded LC complexes, viz. new phase induction [10, 18–22] and occurrence of ferroelectricity, can be tuned by the proper selection of constituent moieties with varied conjugational environment and chiral centre [2, 6, 7].

Many reports in the current literature involve the formation of LCs through the H-bonding of aromatic carboxylic acids, as well as from mixtures of unlike molecules capable of interacting through H-bonding [2, 7, 10, 13–21]. The uniqueness of HBFLCs lies in the

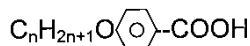
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fact that the central rigid core is not built by covalent bonds alone. Succinctly, in HBFLCs, the rigid core part of the molecule (leading to LC phases) is supported by non-covalent bond interactions (i.e. H-bonding as it extends along the length of rigid core). Hence, a distinctly tunable LC phase abundance, and molecular dynamics different from those of normal covalently bonded LCs, are expected to be exhibited by these LC complexes [2].

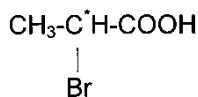
In this paper we present the results of synthesis and characterization of HBFLC complexes formed from the selection of a mesogenic ligand (*n-p*-alkoxybenzoic acids, *nO*.BAs) and a non-mesogenic moiety (an aliphatic carboxylic acid bearing a chiral centre). In this way, a comparative study on the occurrence of LC phases and the effect of H-bonding on possible FLC phases is presented.

2. Experimental

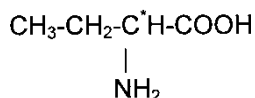
H-bonded complexes were synthesized using members of a series of *p-n*-alkoxybenzoic acids (for $n=9-12$) which are inherently mesogenic [3, 13, 23] and whose general molecular formula is given by:



and the non-mesogenic chiral centre-bearing aliphatic carboxylic acid, 2-bromopropionic acid:



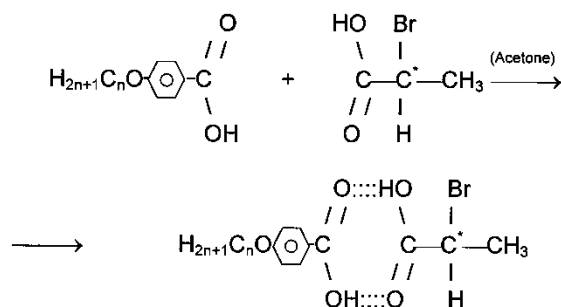
Another HBFLC complex was prepared using mesogenic *p-n*-dodecyloxybenzoic acid, and a non-mesogenic aliphatic carboxylic acid possessing a qualitatively different chiral centre, 2-aminobutyric acid:



The H-bonded FLCs were synthesized by heating under reflux equimolar quantities of the respective *p-n*-alkoxybenzoic acid and *S*(-)-2-bromopropionic acid in acetone solution with the help of a magnetic stirrer for about 3 h, until a clear solution was formed (see scheme 1). The white powdered complex was obtained on removing the acetone by distillation.

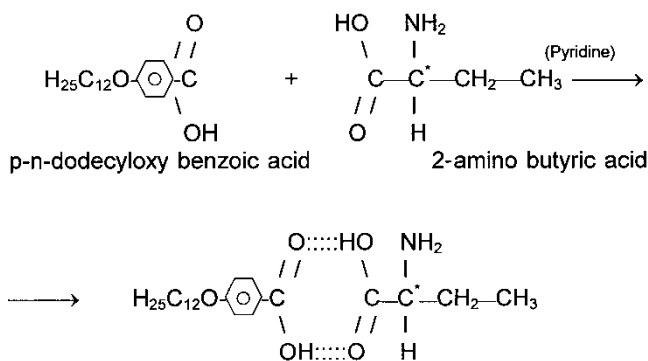
The HBFLC complexes formed from the corresponding mesogenic benzoic acids ($n=9-12$) are labeled as 9bpa, 10bpa, 11bpa and 12bpa.

The other HBFLC complex was prepared by heating



Scheme 1.

under reflux a stirred pyridine solution of equimolar quantities of *p-n*-dodecyloxybenzoic acid and 2-aminobutyric acid for 3 h, and then distilling out the pyridine (see scheme 2).



Scheme 2.

The HBFLC complex synthesized using mesogenic *p*-dodecyloxybenzoic acid and the non-mesogenic moiety with amino-substitution at the chiral centre is labelled 12aba.

The identification of the LC phases exhibited by the HBFLC complexes, and the determination of the relevant transition temperatures, were carried out using an Olympus polarizing microscope in conjunction with a PC-monitored Instec mK1 heating stage. A Perkin-Elmer DSC-7 calorimeter was used to determine phase transition temperatures and associated enthalpy changes; heating and cooling scanning rates followed were 5°min^{-1} . A Perkin-Elmer FTIR BX series infrared spectrometer was used to confirm the formation of a hydrogen-bonded complex between the constituent mesogenic and non-mesogenic moieties. An APT-III instrument was used to measure spontaneous polarization P_s in the SmC^* phase exhibited by the complexes, with Device Tech. (USA) cells of $4.5 \mu\text{m}$ spacing. A triangular wave of $100 \text{V}_{\text{p-p}}$ and 15Hz was used during the P_s measurements, in the auto-balance mode of operation.

3. Results and discussion

The use of the two synthetic routes for preparing complexes, through the hydrogen bonding of mesogenic *p-n*-alkoxybenzoic acids with a non-mesogenic moiety possessing a chiral centre, has increased the length of the rigid core part of the mesogen. The designed LC molecules also conspicuously possess an asymmetric carbon on the flexible end chain. The H-bonded complexes thus obtained are white crystalline solids, stable at room temperature. Moreover, they exhibit a high degree of thermal stability when subjected to repeated thermal scans during thermal microscopy and DSC studies.

The room temperature IR spectra (KBr) of the synthesized HBFLC complexes exhibit an absorption line at $\sim 1680\text{ cm}^{-1}$. The relevant IR spectrum of the HBFLC complex formed by the mesogenic dodecyloxybenzoic acid and 2-aminobutyric acid (12aba) is presented in figure 1. The 12aba complex exhibits a strong absorption line at 1685 cm^{-1} . It may be recalled [23, 24] that *p-n*-benzoic acids exhibit a double-peaked absorption at 1700 cm^{-1} corresponding to carbonyl ($>C=O$) stretching; this double-peaked absorption is interpreted as due to dimer formation. Hence, our observation of shifts around 1680 cm^{-1} (15 cm^{-1} in 12aba, 24 cm^{-1} in 12bpa, 8 cm^{-1} in 11bpa, 21 cm^{-1} in 10bpa and 7 cm^{-1} in 9bpa), and the simultaneous disappearance of the double peak at this absorption, confirm the participation of the alkoxybenzoic acid

carbonyl group with the non-mesogenic moiety (bearing a chiral centre) in the formation of the HBFLC complex.

The phases and corresponding transition temperatures of the HBFLCs, along with that of *p-n*-undecyloxybenzoic acid 11O.BA, determined from the microscopy textural observations [26] are given in table I. In order to study the influence of hydrogen bonding on the LCs, the corresponding phase diagrams with details of the LC phase variants for *p-n*-alkoxybenzoic acids and their HBFLC complexes are given in figures 2 and 3, respectively. It is observed that the I-N-SmC variant exhibited by the 11O.BA used in this work is found to agree with the reported trend of phase variants of the *n*O.BA series of LC compounds [3, 13, 23]. In the context of these reported results, the observed nematic to isotropic transition temperature (135.16°C) in 11O.BA follows the expected odd-even effect (due to the alternating contributions of dipole moments with methylene group increment in the alkoxy end chain) [27–29]. However, this effect is found to be more pronounced at I→N (clearing) and Sm→Cr (melting) transitions than at the N→SmC transition.

All the HBFLC complexes are found to exhibit I-N*-SmC*-SmG*-Cr variants during cooling, and Cr-SmC*-N*-I on heating; this indicates the monotropic occurrence of the smectic G phase. The corresponding microscopic textures (fingerprint pattern as observed for cholesterics in chiral nematic N*, marble (coloured)

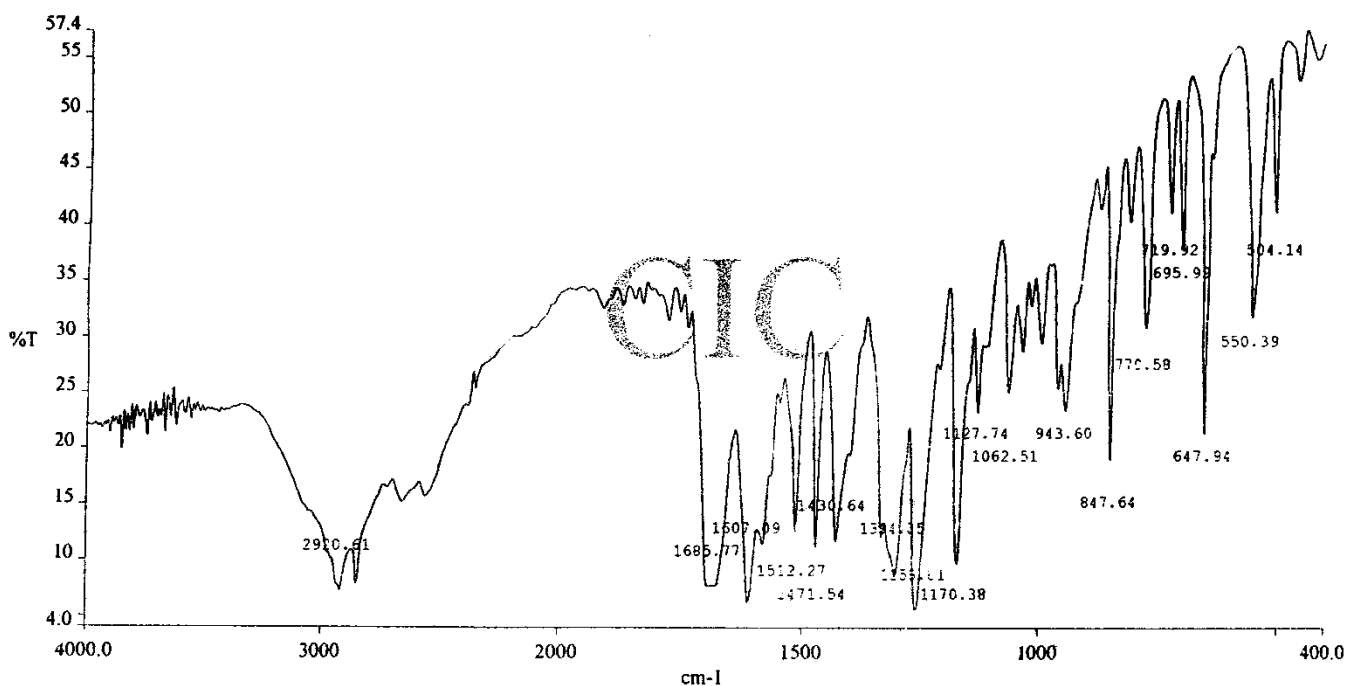


Figure 1. Infrared spectrum (KBr) for the HBFLC complex 12aba.

Table I. Liquid crystal phase transition temperatures and enthalpies exhibited by HBFLCs by TM and DSC studies (arrows indicate the direction of scanning, ie. heating or cooling).

Compound		Phase sequence, transition temperatures (in °C) and enthalpy (in J gm ⁻¹)
11O.BA	TM	Cr→105.2→SmC→135.5→N→142.3→I.
	DSC	I→135.1→N→124.5→SmC→83.5→Cr. Cr→105.24→SmC→131.51→N→142.36→I. (117.05) (6.79) (8.11) I→135.16→N→124.48→SmC→83.4→Cr. (8.32) (5.72) (31.36)
9bpa	TM	Cr→99.2→SmC*→118→N*→143.6→I.
	DSC	I→139.5→N*→114→SmC*→89.2SmG*→65.2→Cr. Cr→99.25→SmC*→117.99→N*→143.64→I. (103.06) (4.84) (6.11) I→139.46→N*→113.98→SmC*→89.17→SmG*→65.17→Cr. (6.13) (4.53) (30.56) (61.05)
10bpa	TM	Cr→101.0→SmC*→128→N*→138.5→I.
	DSC	I→135.3→N*→115.5→SmC*→91→SmG*→74.6→Cr. Cr→101.15→SmC*→128.02→N*→138.56→I. (198.03) (9.74) (13.21) I→135.25→N*→115.45→SmC*→91.07→SmG*→74.76→Cr. (17.83) (8.94) (77.96) (55.41)
11bpa	TM	Cr→101.1→SmC*→128→N*→138.5→I.
	DSC	I→134.1→N*→124→SmC*→84.7→SmG*→72→Cr. Cr→101.15→SmC*→128.02→N*→138.55→I. (198.86) (9.74) (13.4) I→134.08→N*→123.92→SmC*→84.76→SmG*→72.02→Cr. (13.67) (9.8) (53.46) (35.27)
12bpa	TM	Cr→95.1→SmC*→126.6→N*→136.6→I.
	DSC	I→128.6→N*→120.4→SmC*→78.3→SmG*→60.8→Cr. Cr→95.17→SmC*→126.5→N*→134.66→I. (79.95) (2.64) (3.86) I→128.58→N*→120.35→SmC*→78.2→SmG*→60.79→Cr. (5.15) (2.43) (24.66) (13.17)
12aba	TM	Cr→100.2→SmC*→130.8→N*→135.9→I.
	DSC	I→130.9→N*→126.3→SmC*→86.5→SmG*→74.5→Cr. Cr→100.23→SmC*→130.8→N*→135.8→I. (90.67) (3.06) (1.8) I→130.85→N*→126.25→SmC*→86.65→SmG*→74.56→Cr. (2.91) (3.57) (27.02) (56.26)

threaded for smectic C* and mosaic (concentric splintered) in Sm G*, along with the observed coexistence region at the N*-I interface with different thermal spans for the different complexes) are presented in figures 4 (a-f).

The transition temperatures and associated heats of transition (figure 5), as observed during DSC heating and cooling runs, are given in table I. The phase coexistence region at LC clearing temperatures is observed to persist over a considerable temperature span during microscopy. The phase coexistence region is also perceptible through a careful examination of the DSC scans (figure 5), which develop shoulders on the higher temperature side of the clearing transition peak. Corresponding DSC curves for 12aba indicate a

maximum phase coexistence region of 1.5°C. However, the relevant microscopic textures, figures 4 (a) and 4 (b) are indicative of a smeared I-N* transition (as observed through DSC shoulders) and a finite phase coexistence region.

Our observation of a first order N*-SmC* transition accompanied by a considerable ΔH value is found to agree with reports for other FLCs [30, 31]. It is found that a large ΔH accompanies the melting (Cr-SmG*) transitions during the heating runs; however, during cooling, this large enthalpy seems to resolve into those for SmC*-SmG* (monotropic) and SmG*-Cr transitions. The observed comparable ΔH value at these transitions might be due to the growth of an almost 3D structure in the SmG* phase.

The present observation of SmG* phases in HBFLC

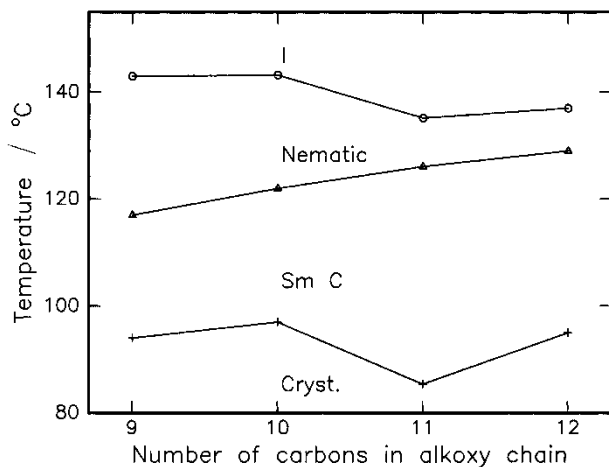


Figure 2. Phase diagram of n O.BA compounds (for $n=9-12$).

complexes agrees with previous reports of H-bonding and the formation of SmG phases in other non-FLCs [13–22]. It was also noted that the total thermal span of tilted LC phases (thermal span of SmC* and SmG* phases taken together) in any of the HBFLC complexes is found to be greater than that reported in the corresponding mesogenic moiety [3, 13, 23].

The H-bonding in these complexes is known to extend the length of the rigid core of the LC molecule through non-covalent interactions. These interactions contribute to an increment in the dipole moments (which are directed off the longitudinal component). The increased tilted smectic phase thermal stability in HBFLCs thus agrees with the predictions of molecular theories [32]. This observation further supports the argument that the direction of these non-covalent interactions (H-bonding) is somewhat away from the molecular long axis, inducing or enhancing tilted LC

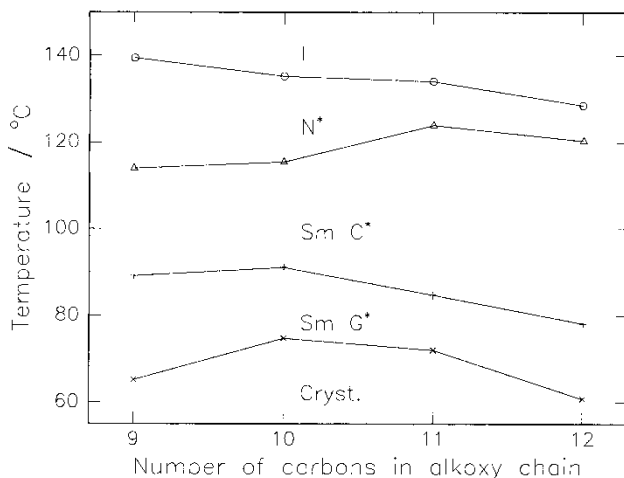


Figure 3. Phase diagram of HBFLC complexes 9bpa, 10bpa, 11bpa and 12bpa.

phase stability. An overview of figures 2, 3 and 5 is indicative of the influence of H-bonding in the following way:

- to decrease LC clearing temperatures in the direction of ambient temperatures;
- to materialize the display-relevant phases (N* and SmC*) at lower temperatures;
- to increase the overall thermal span of tilted phases;
- to induce the SmG phase.

A further observation from Table I, regarding the phase variants exhibited by the HBFLC complexes (with a view to studying the effect of qualitatively different chiral centres) involves the data of complexes 12bpa and 12aba, which differ by $-\text{Br}$ and $-\text{NH}_2$ substitutions at the chiral centre. In view of the I–N–SmC phase variant exhibited by 12O.BA, the data from the HBFLC complexes 12bpa and 12aba show the following relative influence of bromide over amino substitution at the chiral centre:

- depression of LC clearing temperature (T_{IN} is 137°C in 12OBA, T_{IN^*} is 128.6°C in 12bpa and 130.85°C in 12aba);
- depression of SmC* phase occurrence temperatures (T_{NC^*} is 129°C in 12OBA, $T_{\text{N}^*\text{C}^*}$ is 120.35°C in 12bpa and 126.25°C in 12aba);
- increased thermal stability of overall tilted LC phases (34°C for SmC in 12O.BA, 59.56°C for SmC*+SmG* in 12bpa, and 52.05°C for SmC*+SmG* in 12aba);
- promotion of SmG phase (12.2°C in 12aba and 17.4°C in 12bpa as chiral SmG* phase).

To characterize the ferroelectric nature of the SmC* phase in the HBFLC complexes, the temperature variation of spontaneous polarization $P_s(T)$ was studied, and is presented in figure 6 for three representative complexes. The maximum P_s value is found to increase with decreasing temperature in the SmC* phase. The phase value in these HBFLC complexes is found to be somewhat greater than those reported in other non H-bonded compounds which interact covalently [14, 15]. Thus, these soft-bonded interactions (non-covalent) seem to tune the physical properties of the LC phases. However, these HBFLC complexes are found to exhibit relatively lower P_s value in comparison with those reported in AFLC compounds [18]. It is noted that the polarization current peaks of these complexes are too small to be measured. It may be concluded that involvement of H-bonding in the FLCs could effectively reduce the thermal abundance of FLC phases towards ambient temperatures and thus tune the P_s value.

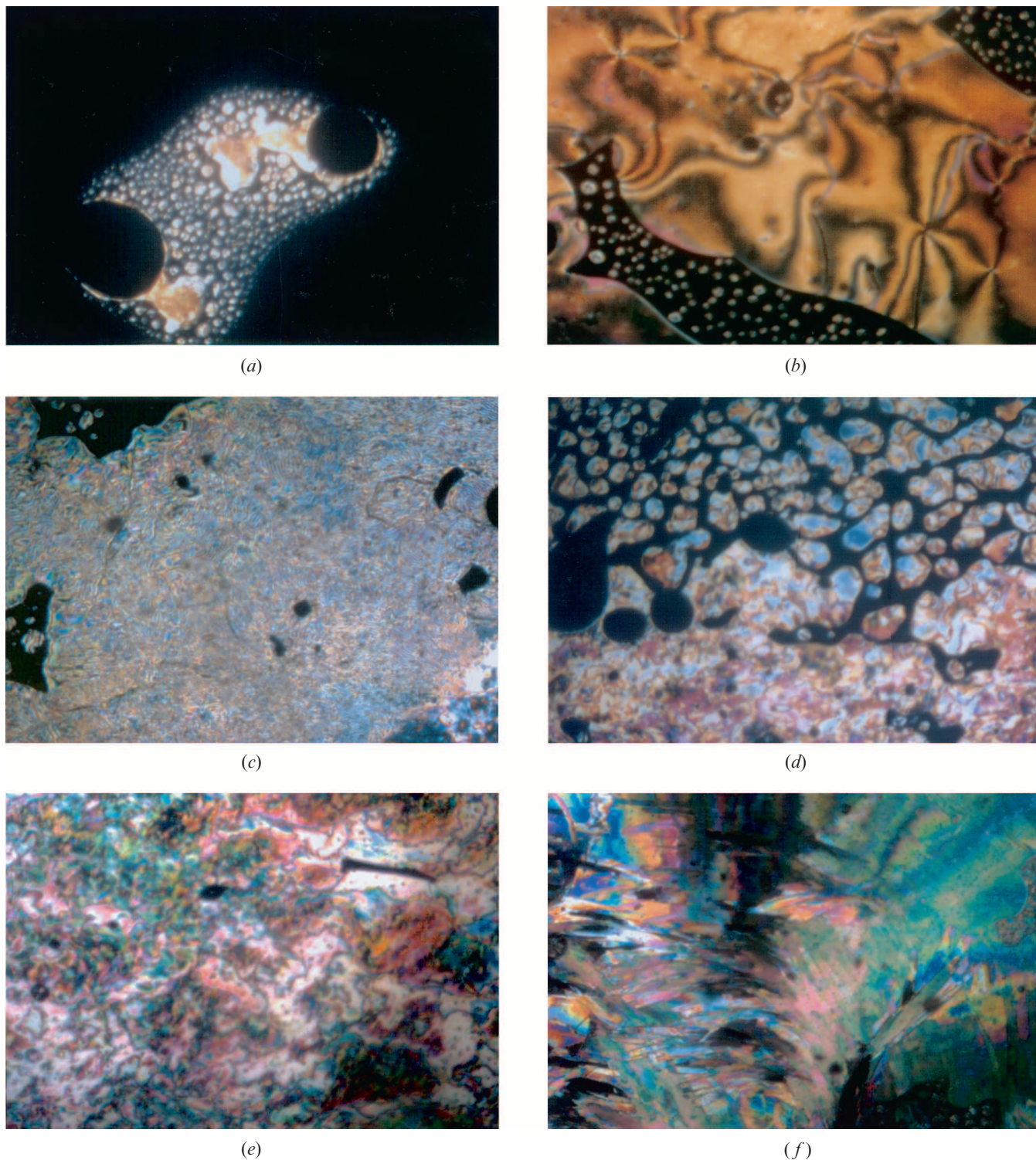


Figure 4. (a) Phase coexistence region (with resemblance to nematic droplets) in 12aba at 131.4°C before the I-N* transition. (b) Phase coexistence region (with nematic-like schleiren brushes) exhibited by 11bpa at 134.35°C before the I-N* transition. (c) Fingerprint (cholesteric-like) texture in the N* phase exhibited by 11bpa at 127°C. (d) Marble threaded texture exhibited by 12bpa in the SmC* phase at 112.2°C. (e) Marble (coloured) threaded texture exhibited by 10bpa in its SmC* phase at 114°C. (f) Mosaic texture of the SmG* phase exhibited by 11bpa at 80°C.

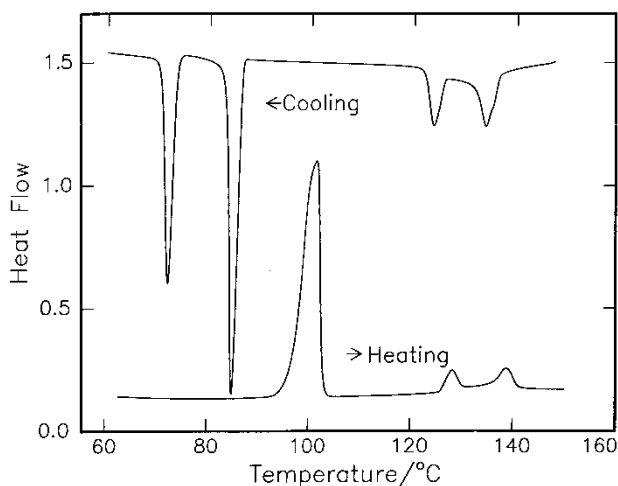


Figure 5. DSC Thermogram of HBFLC complex 10bpa.

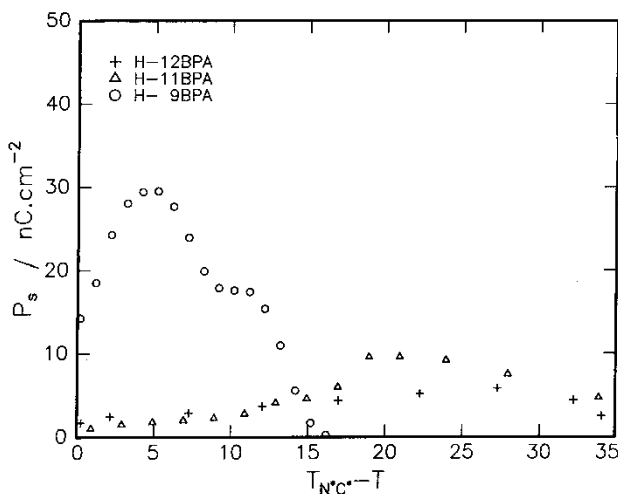


Figure 6. Temperature variation of spontaneous polarization P_s for the HBFLC complexes 9bpa, 11bpa and 12bpa in their SmC^* phase.

The authors are grateful for the IR spectra from the Central Instrumentation Centre, Kakatiya University, Warangal.

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