

Application of Image Analysis Technique to Supramolecule PyB14A: *n*FA Liquid Crystals through Hydrogen Bond

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ABSTRACT: In this paper, optical properties of supramolecule through hydrogen bond of liquid crystal viz., (4-pyridyl)-benzylidene-4'-*n*-tetradecyl aniline (PyB14A): long-chain aliphatic fatty acid (FAs) *n*FAs possessing different alkyl chain lengths (where $n = 12, 14, 16$) have been investigated by applying Image analysis technique in conjunction with Polarizing Optical Microscope (POM). Textures of liquid crystal complexes are captured using POM and the changes in textural features as a function of temperature is useful to compute thermo optical properties of the samples. These textures are analyzed using MATLAB software. Phase transitions are studied from the second order statistical parameters: Entropy, Energy, Homogeneity, Contrast and thermo optical parameters are optical transmission, Absorption coefficient and birefringence are computed for PyB14A: *n*FAs, where $n = 14$ and 16. Experimentally, this is a simple technique to observe the behavior of the optical parameters of different liquid crystals as a function of temperature.

KEYWORDS: Liquid crystals, Supramolecule, Hydrogen bond, Textures, Image analysis Thermo optical properties,.

I. INTRODUCTION

Supramolecules formed through the hydrogen bonding interactions of complementary molecules are studied extensively [1-5]. The main interaction in the synthesis of such of hydrogen bonded liquid crystals is due to their thermal stability, molecular shapes and structures, high directionality and dynamics for chemical and biological processes in nature [6-9]. In recent years, liquid crystal complexes have become more important as novel materials for display applications like flat panel displays, electro optic displays, optical switches, photovoltaic cells, Fluorescent films etc [10-16]. The phase transitions and optical behavior of the complexes are considerable properties for those applications. Liquid crystal complexes formed by the hydrogen bonds between mesogenic and non mesogenic compounds exhibit the interesting properties. Complexes of unlike molecules (mesogenic and non mesogenic) producing liquid crystals frequently involve donor molecules derived from carboxylic acids and acceptor molecules derived from pyridine, benzoates, aniline, etc [17,18]. This paper deals with non mesogenic materials: long-chain aliphatic fatty acid (FAs) *n*FAs possessing different alkyl chain lengths (where $n = 12, 14$ and 16) and (4-pyridyl)-benzylidene-4'-*n*-tetradecyl aniline (PyB14A). The thermo optical properties are investigated using image analysis technique in conjunction with POM on MATLAB platform. There are several techniques to study the temperature dependence optical properties of liquid crystals [19-22], but they involve the technical difficulties in measuring required parameters. In image analysis technique textures of liquid crystal complexes are captured from the solid phase of the sample to the isotropic phase using POM and the changes in textural features as a function of temperature is useful to compute the thermo optical properties of samples. Image analysis technique has been developed to aid the interpretation of microscopic images and to extract as much information as possible from image objects by means of applying some computational algorithms on image data or intensity values. MATLAB R, a software product by Math

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Works, Inc., (Natick, MA) [23,24] is used for the analysis of liquid crystal textures. A systematic investigation of thermo optical parameters of the systems such as optical transmission, Absorption coefficient, and birefringence are carried out for PyB14A: *n*FAs, where *n* = 14 and 16.

II. EXPERIMENTAL

Supramolecular liquid crystal viz., (4-pyridyl)-benzylidene-4'-*n*-tetradecyl aniline (PyB14A): long-chain aliphatic fatty acid (FAs) *n*FAs (where *n* = 12- Lauric acid, 14-myristic acid and 16 -palmitic acid) possessing different alkyl chain lengths were synthesized [25] as reported in literature. The molecular structures of the compounds are given below.



An indium–tin oxide-coated homogeneous cell of dimensions $5 \times 5 \text{ mm}^2$ with $6.8 \mu\text{m}$ spacing (tolerance $\pm 0.2 \mu\text{m}$), was obtained from Instec, USA [26]. The LC complexes were injected into liquid crystal cells by capillary action on heating the sample to the isotropic state. The different phase transitions were observed in heating and cooling cycles using Meopta Polarising Optical Microscope. The textural characterization of phases exhibited by the present PyB14A:*n*FA's were carried out with the help of a optical microscope in conjunction with an heating stage as described by Gray [27]. Canon EOS Digital REBEL XS/ EOS1000D is a digital single lens reflex camera with a 10.10 mega pixel image sensor is used to record the texture images of the sample through the crossed polarizer's of the POM. The image is having 3888X2592 pixel size depicting 24 bit tonal levels in a true color production within the range of 0 to 255 gray levels in each three primary spectral frequency of red, green and blue separately. Thermo optical parameters of the complexes of three primary wavelengths are computed as a function of temperature using MATLAB software. Thermo optical properties of hydrogen bonded liquid crystals are defined in terms of image intensity values in [28-32].

III. RESULTS AND DISCUSSION

The present analysis deals with the thermo optical properties of hydrogen bonded liquid crystals PyB14A:*n*FAs where *n* = 14, and 16. Textures of given compounds are recorded using polarizing microscope in arthroscopic mode attached to the high resolution camera. The textures of liquid crystals are captured as a function of temperature, from the isotropic liquid state of the sample to the crystalline state. On cooling the isotropic liquid of supramolecules, PyB14A:*n*FAs exhibits monotropic nature in the case of (*n*=14) and found to bear glossy focal conic fan textures which is noticed as Smectic B crystal phase while *n*=16 exhibits enantiotropic nature with glossy focal conic fan texture Smectic B crystal phase and marble threaded texture of Smectic F phase. The SmF phase exhibited by PyB14A:16FA remains till ambient ($\sim 30^\circ\text{C}$) temperatures in the cooling cycle. The data of transition temperatures and the LC phases identified by the present POM textural changes in cooling cycles are presented in Table 1.

Table 1: Phases and Phase transition temperatures of PyB14A:*n*FA (where *n* = 12, 14, and 16)

Compound	Phases	Phase transition temperatures ($^\circ\text{C}$)	
		POM and Image analysis	DSC [25]
<i>n</i> = 12	I – Sm B - Kr	61.9 - 52.0 - 49.0	62.6 - 49.96 – 43.0
<i>n</i> = 14	I – Sm B - Kr	68.0 - 63.5 - 54.0	67.4- 64.60 - 55.0
<i>n</i> = 16	I – Sm B – Sm F - Kr	71.5-61.8-59.5	70.1-62.0-59.0

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(Kr:Crystal; sm B – Smectic B; sm F – Smectic F; I:Isotropic).

Statistical properties of hydrogen bonded liquid crystals given in Equations [28-30], are drawn against the temperature and are shown in Fig. 1.

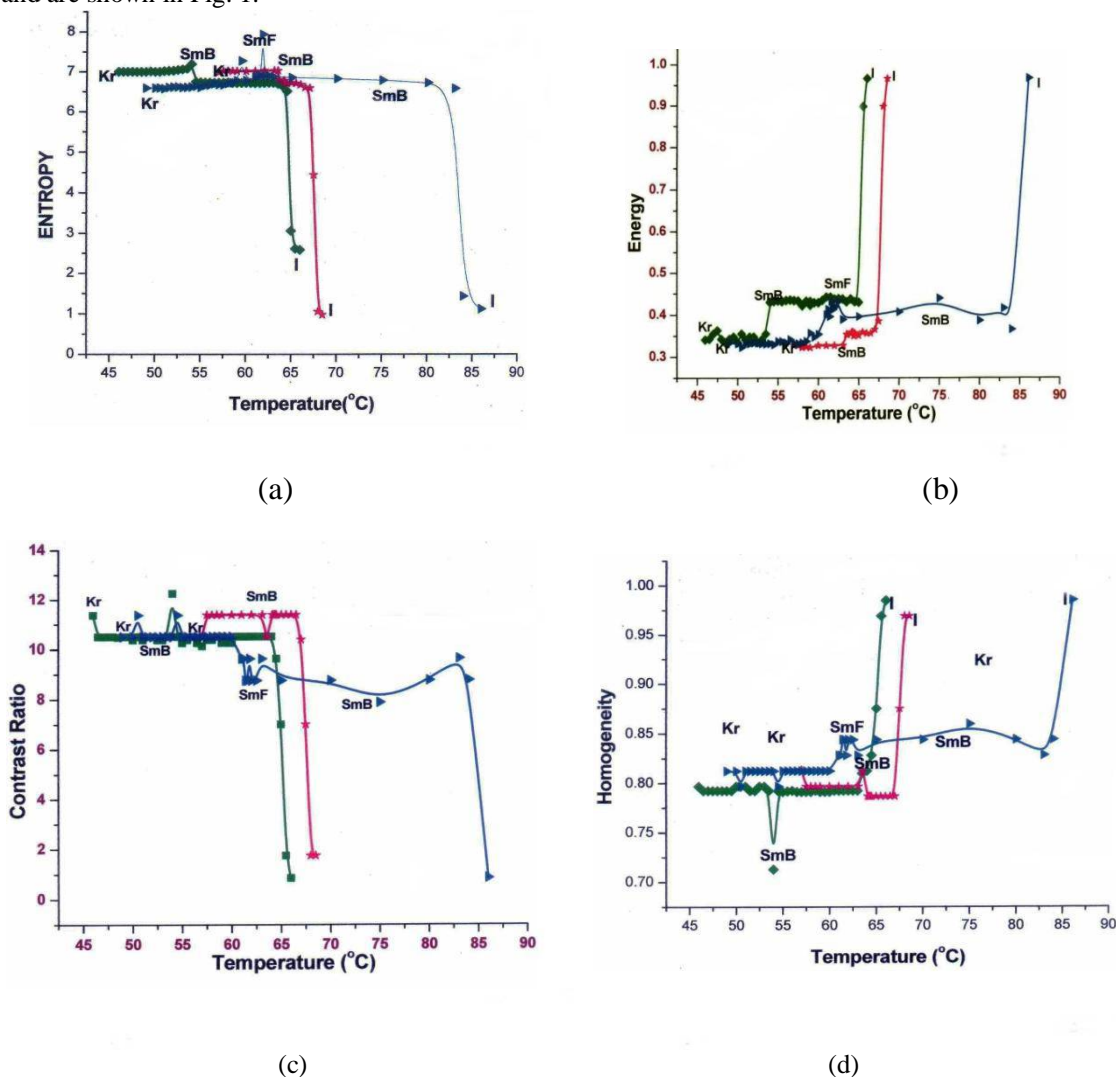





Fig . 1. Statistical parameters of PyB14A:nFA (where n = 12,14, and 16) (a) Entropy; (b) Energy; (c) Contrast; (d) Homogeneity as a function of temperature where the phase transitions are indicated. (Kr:Crystal; sm B – Smectic B; sm F – Smectic F; I:Isotropic).
(for n = 12 , 14  and 16 .)

Entropy is a measure of randomness of grey levels in the texture which arises due to small changes in heat capacity of the material. From Fig. 1(a) entropy values are high at SmB phase in PyB14A:nFA (n=12,14) and also SmF phase in PyB14A:nFA (n=16) compared to crystal phase. This kind of transitional entropy between the liquid crystalline state to SmB/SmF state and then to isotropic state are related to the degree of internal order present in the system. Shorter phase change time is related with a less entropy generation rate, indicates less energy destruction during the process, from Fig.1 and from Table.1 it is also noticed that energy destruction in PyB14A:nFA with PyB14A:12FA <

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PyB14A:14FA < PyB14A:16FA with variation of temperature as the phase change occurred. Relatively small entropy change shows that the liquid crystalline states are associated with more subtle structural changes.

Energy is a measure of uniformity in the texture. Maximum energy of the texture or image occurs when the grey level distribution of given image is either constant or a periodic uniform. Fig. 1(b) shows energy levels are high at SmB phase in PyB14A:nFA ($n=12,14,16$) and SmF phase in PyB14A:nFA($n=16$), when compared to crystal phase. Further comparing with Sm B, energy value is more at Sm F phase due to decrease in polarizability and also lower thermal stability exists because of very weak intermolecular inductive interactions. In comparison of three compounds energy level is higher in PyB14A:nFA with PyB14A:12FA > PyB14A:16FA > PyB14A:14FA with variation of temperature. The energy levels vary at phase transition due to intermolecular inductive interactions. Low thermal stability arises between the phases due to decrease in polarizability.

Contrast is major determinant of perceived picture quality. Contrast is created by the difference in intensity, i.e., the amount of reflected light from two adjacent surfaces. The degree of difference of an LCD monitor's ability to produce bright whites and the dark blacks decides the quality of display. If a picture has high Contrast, it is judged to be sharper and crisper than a picture with lower CR. From Fig.1(c) it is noticed that contrast levels are high at phase transitions Sm B and Sm F phase transitions due to dipole-dipole interactions between the molecules of the sample PyB14A:nFA. Individually higher contrast levels are observed in PyB14A:nFA sample in order :12FA > PyB14A:14FA > PyB14A:16FA with variation of temperature which is due to long aliphatic chains and amphiphilic interactions in the system.

Homogeneity means property of the material is uniform at every point without irregularities when the material is subjected to external field. It is observed that from Fig.1(d) homogeneity levels are high in isotropic state for all the three series, due to stronger dipole-dipole interactions between the molecules and its reaction with incident light. Individually higher homogeneity levels are observed in PyB14A:nFA sample in order PyB14A:12FA > PyB14A:14FA > PyB14A:16FA with variation of temperature which is due orientation of molecules and stronger dipole-dipole interactions. Polymorphism arises between the transformations of crystal to isotropic fluid due to weak intermolecular forces that imparts the equilibrium, results in well defined phase changes in all the three samples with variation of temperature. Energy and homogeneity are similar measures; the only difference is that energy considers the elements of the Grey level co-occurrence matrix (GLCM) and homogeneity considers the probability of GLCM values.

Thermo optical properties [30-32] of hydrogen bonded liquid crystals PyB14A:nFAs where $n= 14$ and 16 have been discussed at three wavelengths 600nm, 530nm, 470nm.

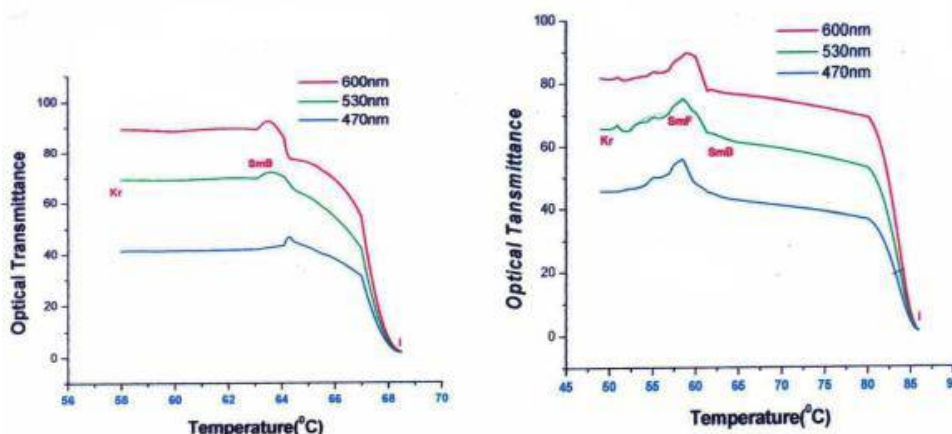


Fig. 2. Temperature dependence of Optical transmittance of PyB14A:nFA (a) where $n = 14$; (b) where $n = 16$ (Kr:Crystal; sm B –Smectic B; sm F– Smectic F; I:Isotropic).

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Fig. 2(a) shows the variation in the values of optical transmittance at the transitions SmB-> Kr and Fig. 2(b) shows the variation in the values of optical transmittance at the transitions SmB->SmF->Kr. This is due to the fact that in different phases there are changes in the textural features as a function of temperature. The temperature decrease of the sample is inversely proportional to the optical transmittance under crossed polarizers. The darker area means high concentration of optical energy, while bright areas indicate a low energy concentration. The optical transmittance values are slightly higher with $n=16$ in comparison to $n=14$. Hence $n=16$ is preferable to $n=14$.

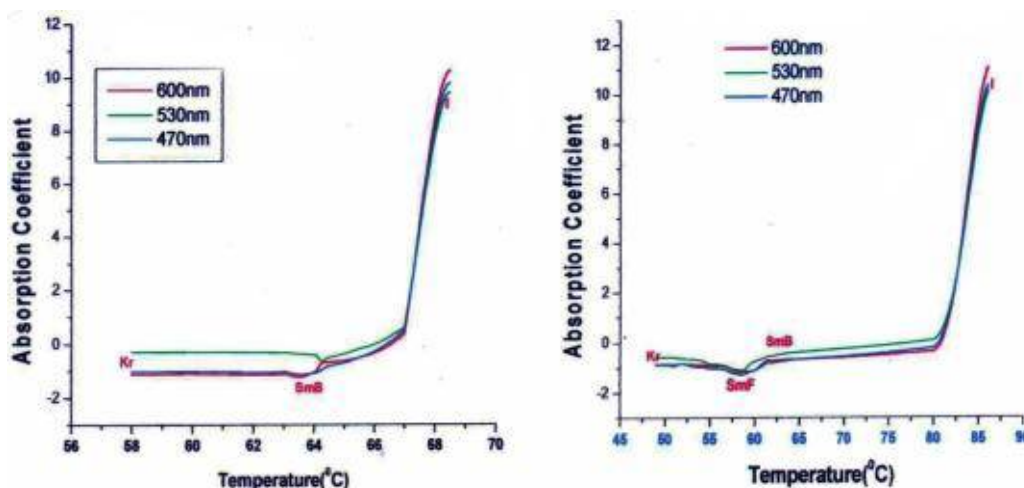


Fig. 3 Temperature dependence of Absorption coefficient of PyB14A:nFA (a) where $n = 14$; (b) where $n = 16$ (Kr:Crystal; sm B – Smectic B; sm F – Smectic F; I:Isotropic).

Temperature- dependent optical absorption coefficient (AC) for PyB14A:nFA ($n = 14$ or 16) have been computed, as shown Fig. 3(a) and 3(b). Absorption is dominant factor contributing to the total attenuation. Absorption effect occurs when photons excite electrons to a higher energy level through energy transfer in the liquid crystal sample. The energy of the photon gradually decreases with increase of photon wavelength i.e., energy decreases from red to green to blue, which means smaller number of photons will be capable of exciting electrons to higher energy levels, absorption gradually decreases with wavelength. Absorption loss increases with further increase in optical wavelength due to increased energy transfer from photons to chemical bonds [33]

From Fig. 3(a) and 3(b) it is seen that the value of AC is a maximum in the isotropic state for both $n=14$ and 16 . In this phase the molecular orientation is random and there is no transmission of light. On cooling of the sample $n=14$, there is a sudden decrease in AC in the biphasic region of the I-SmB phase temperature interval and in $n=16$ there is a sudden decrease in AC in biphasic region of I-SmB phase and maintains stability for long interval of time and there is again a sudden decrease of AC from SmB-SmF and slowly AC increases till crystalline state. This is due to the fact that the transmission of light takes place in the SmB phase alignment of the molecules. Sharp textural transformations of SmB-SmF and SmF-Kr give abrupt changes in the values of AC. The optical transmittance of the sample is inversely proportional to AC. The absorption coefficient values are slightly lower with $n=16$ in comparison to $n=14$. Hence $n=16$ is preferable to $n=14$.

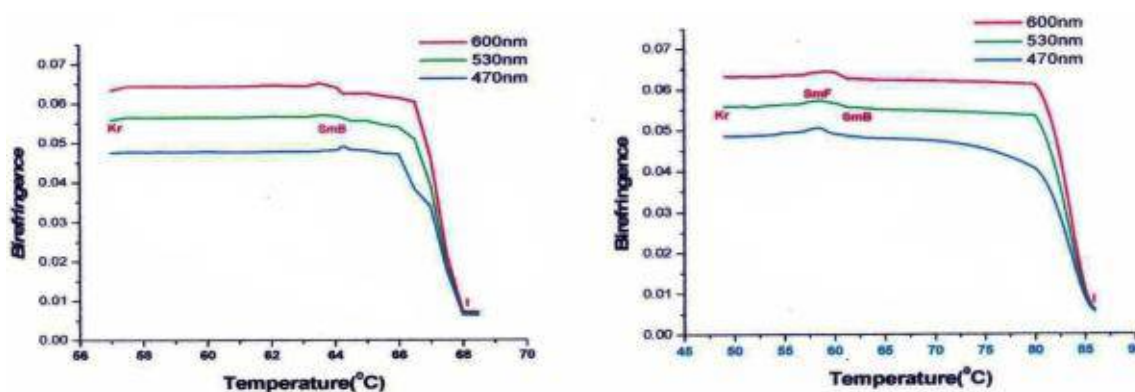


Fig. 4. Temperature dependence of Birefringence of PyB14A:nFA (a) $n = 14$; (b) $n = 16$

Variation of birefringence with temperature is shown in Figs. (4(a) and 4(b)). For the samples in the isotropic state the absence of molecular alignment in their respective phases causes the disappearance of birefringence, giving it a value of zero, this is due to the molecular order in the sample gets extinguished. On cooling the sample from its isotropic phase, the value of birefringence increases abruptly in the biphasic region of the I–SmB temperature interval in sample with $n=14$ and there are small fluctuation in its value in the SmF→Kr phases on further cooling with $n=16$. The birefringence values of the samples may be used to predict the temperature-dependent order parameter of the systems. The degree of order of smectic liquid crystals decreases gradually as the temperature rises due to the thermal agitation of liquid crystal molecules [34]. With the increase of temperature further, molecular order decreases and the birefringent nature becomes less significant and after the isotropic temperature birefringence vanishes and the sample behaves like any ordinary organic liquid [35]. Birefringence values are slightly higher in $n=16$ in comparison to $n=14$ especially during the phases. So, for better display devices $n=16$ is preferable when compared to $n=14$.

IV. CONCLUSION

Supramolecule due to hydrogen bonding interaction between pyridyl derivatives and Fatty Acids lead to the variation of statistical properties in liquid crystal phases which was demonstrated by image analysis technique in conjunction with polarizing optical microscope. From, the investigated properties, Increasing the length of flexible end chain in PyB14A:nFA series promotes the enhancement of liquid crystal phase stability and the tilted smectic phase abundance and hence influences the thermo optical parameters and display device standard optical parameters. In comparison of the both complexes, the compound with $n = 16$ is more suitable for display devices in the case of optical transmittance, absorption coefficient, birefringence, . So $n=14$ compound is preferable to $n=16$ compound in case of Contrast ratio.

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