

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

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Vol. 7, Issue 9, September 2018

Phase Transition Temperatures Through Statistical Parameters By Image Analysis On Py14BA:*n*FA Mesogens

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ABSTRACT: Using statistical image analysis, phase transition temperatures of linear hydrogen-bonded liquid crystals Py14BA:*n*FAs due to non liquid crystal (4-Pyridyl)-benzylidene-4'-*n*-tetradecyl aniline (Py14BA) and another non liquid crystal aliphatic fatty acids (*n*FAs) where *n*= 12,14, and 16 are investigated. Textures of liquid crystals are captured as a function of temperature using polarizing optical microscope attached with hot stage and camera. In this image analysis, statistical parameters namely, mean, standard deviation, skewness and kurtosis of the liquid crystal textures are computed using MATLAB software. The statistical parameters show abrupt changes and fluctuations as a function of temperature which relates the phase transition of the sample. Statistical image analysis results are compared with the literature values which are in good agreement.

KEYWORDS: Py14BA:*n*FA liquid crystals; Hydrogen bond; Transition Temperature; Image analysis; Statistical Parameters

I. INTRODUCTION

The most spectacular and remarkable events in nature are the transformations between the various states of matter. Liquid crystal is a fourth state of matter, which is a transformation between the solid and conventional liquid. Phase transitions exhibited by these liquid crystal samples (Mesogens) are an important aspect of their properties and directly related to their structure in terms of molecular ordering [1]. These mesogens exhibits a multitude of transitions having new phases and studies of these phases have wide range applications on scientific fields. Each of the liquid crystal phases can form its own characteristic textures as a function of temperature which can be viewed under an polarizing optical microscope (POM). Identification of transition temperatures of these phases are important quantities that characterize the liquid crystal samples and is a necessary thing to study the physical properties of the material. The difference in transition temperatures between the melting and clearing point gives the range of stability of the liquid crystalline phase [2,3].

POM, Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), etc. are available for the measurement of transition quantities. Most widely used techniques in identification of phase transition temperatures are DSC and DTA, provides extremely rich data on the temperatures, heats of transitions and heat capacity of various phases. Although, DSC and DTA reveals the presence of phase transitions in a material by detecting enthalpy and entropy changes associated with each phase transition, a precise phase identification cannot be made. The phase transitions involved in small enthalpy and entropy changes are not identified by this DSC and DTA. Accordingly, DSC or DTA is used in conjunction with POM to determine the phase transitions temperatures of the samples and POM is a standard tool in the identification of liquid crystals phases [1,4]. In the present work, statistical parameters such as mean, variance, skewness and kurtosis computed from the textures of Py14BA:*n*FA where *n* = 12,14 and 16 liquid

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crystal samples which are viewed and recorded with the help of POM are used to identify the phase transition temperatures using image analysis technique.

II. EXPERIMENTAL

Non liquid crystal (4-Pyridyl)-benzylidene-4'-*n*-tetradecyl aniline (Py14BA) and non liquid crystal aliphatic fatty acids (*n*FAs) formed liquid crystals through hydrogen bond liquid crystals of Py14BA:*n*FAs where *n*= 12,14, and 16 are synthesized [5] and used. The experiment involved polarizing optical microscope (Meopta company) in the arthroscopic mode attached with hot stage and high resolution colour camera for viewing and recording the textures as a function of temperature [6]. The colour images or textures of given mesogens are recorded using camera with resolution 2816x1880 pixels, which represents the 24bit true color pixel tone. Intensity values of the images are ranges from 0 to 255 in Red, Green and Blue colours. The translated gray scale image is used for analysis and the defined statistical parameters are computed using Matlab software.

III. THEORY

Statistical image analysis involves the computation of statistical parameters which extracts the information about the textural features of the image based on the gray level intensities of the image pixels. An image or texture $I(i, j)$ is of size *m*-by-*n* is a two dimensional function and it is composed of *m* pixels in the vertical direction and *n* pixels in the horizontal direction, *i, j* are horizontal and vertical co- ordinates of the image. The total number of pixels in the image is $m \cdot n = N$, $0 \leq i \leq m, 0 \leq j \leq n$. The defined statistical parameters are [7,8]

(i) Mean:

The mean (μ) is defined as the average level of intensity values of the image or texture $I(i, j)$.

$$\mu = \frac{1}{N} \sum_{i=1}^m \sum_{j=1}^n I(i, j) \quad (1)$$

(ii) Standard Deviation:

Standard Deviation of the image is defined as the square root of the variance. Variance measures the variability about the mean value of a image. If the value closer to mean, standard deviation is less.

$$\text{Standard Deviation of an image: } \sqrt{\frac{\sum_{i=1}^m \sum_{j=1}^n (I(i, j) - \mu)^2}{N - 1}} \quad (2)$$

(iii) Skewness: It defines the symmetry around the mean intensity value.

$$\text{Skewness} = \frac{\left(\sum_{i=1}^m \sum_{j=1}^n I(i, j) - \mu \right)^3}{(N - 1) * S^3} \quad (3)$$

where *S* is standard deviation of the image.

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(iv) **Kurtosis:** Kurtosis is a measure of peaked ness i.e. whether the intensity values are peaked or flat around the mean intensity value.

$$Kurtosis = \frac{\left(\sum_{i=1}^m \sum_{j=1}^n I(i, j) - \mu \right)^4}{(N - 1) * S^4} \quad (4)$$

All the defined parameters are extremely sensitive to changes in the textural features of liquid crystals as a function temperature. Matlab software is used to compute the defined statistical parameters of the image. Image analysis using Matlab supports images generated by a wide range of devices, including digital camaras. The standard data and image formats include JPEG, JPEG-2000, TIFF, PNG etc. Matlab provides tools for image analysis tasks such as statistical analysis, features extraction and property measurement.

IV. RESULTS AND DISCUSSION

All the defined parameters are extremely sensitive to changes in the textural features of liquid crystals as a function temperature. Matlab software is used to compute the defined statistical parameters of the image. Image analysis using Matlab supports images generated by a wide range of devices, including digital camaras. The standard data and image formats include JPEG, JPEG-2000, TIFF, PNG etc. Matlab provides tools for image analysis tasks such as statistical analysis, features extraction and property measurement.

The present image analysis deals with the transition temperatures of hydrogen bonded liquid crystals Py14BA:nFAs where $n= 12,14,$ and 16. Textures of these compounds are recorded using polarizing optical 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 hydrogen bonded liquid crystals (HBLC) complexes, Py14BA:nFAs exhibits monotropic nature in the case of ($n=12,14$) and found to bear glossy focal conic fan textures shown in Fig 1 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 shown in Fig 2. The SmF phase exhibited by Py14BA: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 heating and cooling cycles are presented in Table 1 .

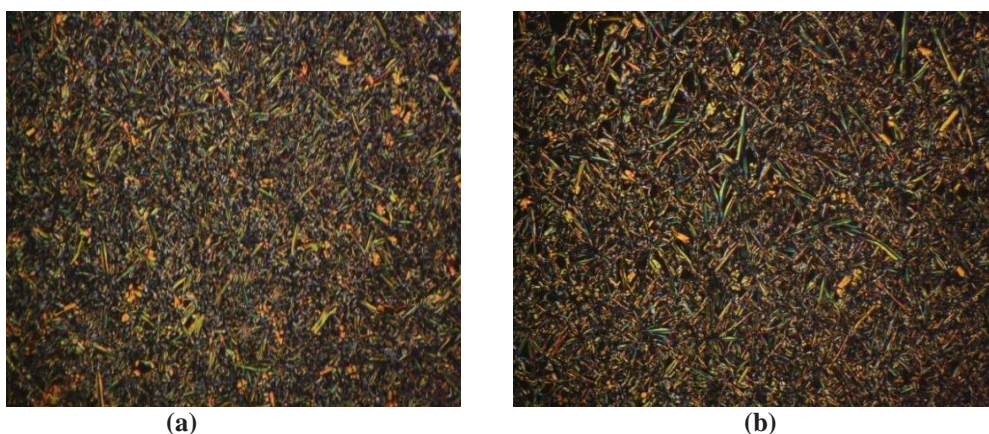


Fig. 1. Optical textures of (4-Pyridyl)-benzylidene-4'-n-Tetradecyl aniline (Py14BA): long-chain aliphatic carboxylic acid (FAs) nFAs (a) Smectic B phase in $n = 12$. (b)Smectic B phase.

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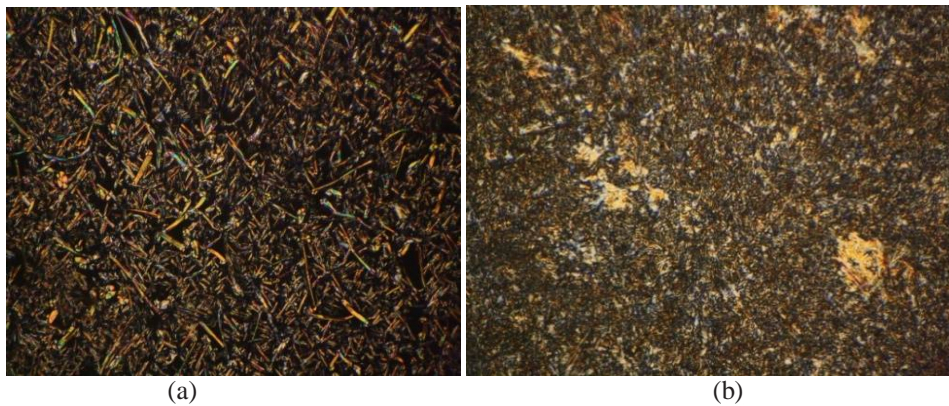


Fig. 2. Optical textures of (4-Pyridyl)-benzylidene-4'-n-Tetradecyl aniline (Py14BA): long-chain aliphatic carboxylic acid (FAs) nFAs (where $n = 16$) liquid crystal. (a) Smectic B phase, (b) Smectic F phase of Py14BA:nFA where $n=16$

From, equations (1) to (4), statistical parameters of the liquid crystal textures are computed using MATLAB software. Once the parameters are computed, the plots are drawn for parameters as a function of temperatures of the samples from the isotropic state to the solid state and the plots are shown in Fig 3. On cooling, hydrogen bonded liquid crystals Py14BA:nFAs undergoes a phase transition from the crystalline state to the isotropic state via an intermediate smectic phase at different temperatures.

Table 1: Phases and Phase transition temperatures of Py14BA:nFA (where $n = 12, 14, \text{ and } 16$)

Compound	Phases	Phase transition temperatures ($^{\circ}\text{C}$)	
		POM and Image analysis	DSC [5]
$n = 12$	I – Sm B - K	61.9 - 52.0 - 49.0	62.6 - 49.96 – 43.0
$n = 14$	I – Sm B - K	68.0 - 63.5 - 54.0	67.4- 64.60 - 55.0
$n = 16$	I – Sm B – Sm F - K	71.5-61.8-59.5	70.1-62.0-59.0

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

From Fig 3, it is observed that phase transitions of the liquid crystal samples are characterized by abrupt changes, discontinues and strong fluctuations in the statistical parameters curves. The abrupt changes in the statistical parameters indicate the consequent changes in the textural features of the samples due to the phase transition of material with respect to temperature [6,9,10]. In case of DSC and DTA, there are peaks corresponds to transition temperatures of the sample which gives the heat flow. In the present analysis, distinctive and abrupt changes observed in the parameter curve at temperature corresponding to the transition temperature of samples make the proposed methodology a very sensitive method for identification of phase transitions of liquid crystals. These two methods use the POM to recognize the kind of textures exhibited by the liquid crystal samples.

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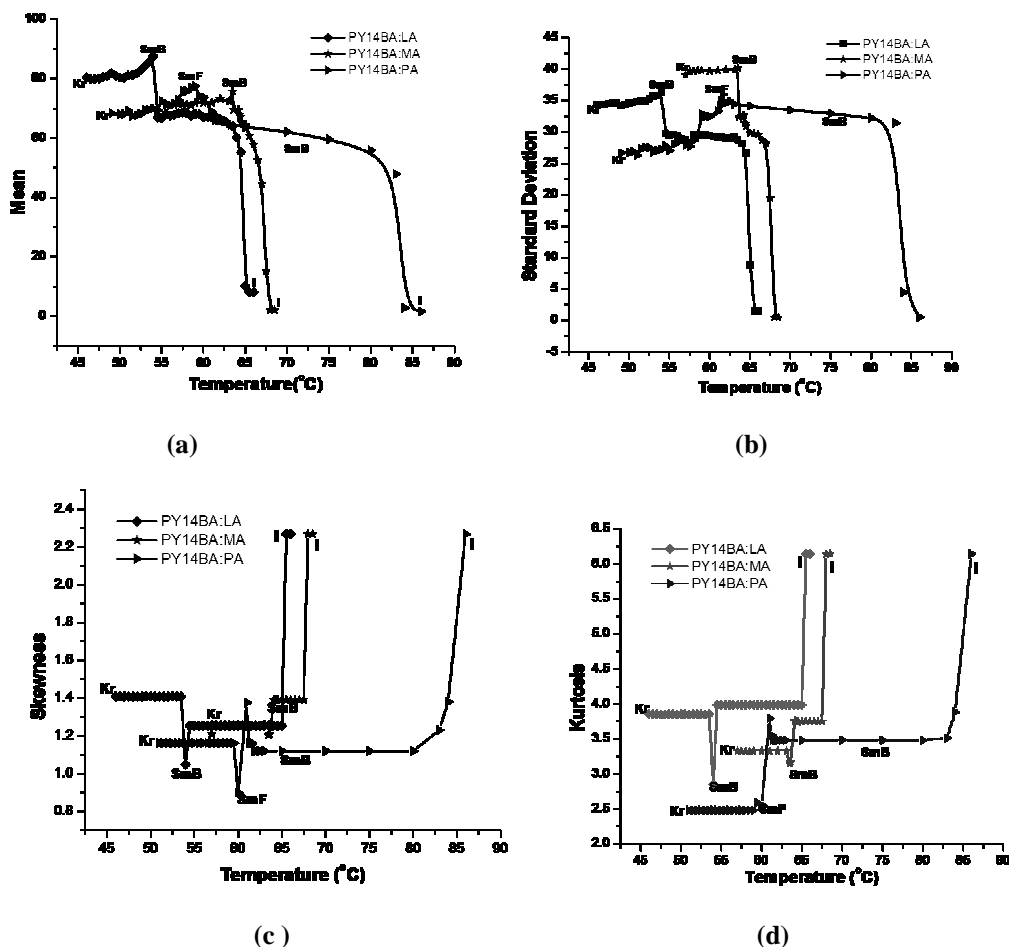


Fig . 3. Statistical parameters of Py14BA:*n*FA (where *n* =12,14, and 16) (a) Mean; b) standard deviation; (c) Skewness; (d) Kurtosis, as a function of temperature where the phase transitions are indicated. (*K*:Crystal; *sm B* – Smectic B; *sm F* – Smectic F; *I*:Isotropic).

For all compounds under study of the hydrogen bonded liquid crystals, statistical parameters show the abrupt changes at the texture transitions which relates the phase transitions temperatures of the liquid crystals and was shown in Fig 3(a-d). Mean intensity levels of the present sample is varying linearly with the rise of temperature except at SmB and SmF phase transitions . As the temperature increases, intensity exhibits oscillations due to change in phase retardation at phase transition and hence increased lateral forces favours smectic phase B and F. From Fig 3(a) it is observed that in comparison of three compounds mean intensity levels are fine in the order of Py14BA:*n*FA with $n=16 > 14 > 12$ with variation of temperature as there exists high thermal stability between the phases due to increase in polarizability. The higher the standard deviation, the wider the distribution of the molecules in the matter and greater the random error and the poorer the precision of the method while smaller the standard deviation, the narrower and sharper the distribution of molecules in the matter, the smaller the random error, and the better the precision of the method. From Table.1 and Fig 3(b) present sample Py14BA:*n*FA with standard deviation levels with $n=16 > 14 > 12$ with variation of temperature indicates that there is wider distribution of molecules between crystal to Smectic phases and then to isotropic phase which is due long aliphatic chains and amphiphilic interactions in the system. Skewness is a measure for the degree of symmetry in the variable distribution. Skewness characterizes the symmetry of the height variation about its mean line

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in graphical representation. Skewness arise due to the impact of sample size. . From Fig 3(c), it is observed that tails of the distribution and height of the graphical line for Py14BA:*n*FA samples are in the order of $n=12>14>16$ with variation of temperature. It may be due to the impact of sample size, long aliphatic chain distribution and amphiphilic interactions in the system. Kurtosis constitutes a dimensionless measure of tail strength of a distribution, it depends on the structure size, which actually depends on mean particle size in the sample. Kurtosis characterizes the uniformity of height variations in graphical representation. From Fig 3(d), it is observed that tails of the distribution and height of the graphical line for Py14BA:*n*FA samples are in the order of $n=12>14>16$ with variation of temperature. It may be due to the impact of sample size, long aliphatic chain distribution and amphiphilic interactions in the system. Skewness and kurtosis are the two dimension less parameters which are inter-related to each other. The behaviors of statistical parameter curves of hydrogen bonded liquid crystals are different for different compounds. In the observed sequence, there are pronounced variations in the respective phase transition temperatures and the clearing point of samples decreases with increasing chain length. The observed transition temperatures of are in agreement with those reported in the literature [5]. Similar observation is reported [11]. The transition temperatures of Py14BA:*n*FA proposed method and other technique (DSC) are shown in the table 1 which are in good agreement

V. CONCLUSION

Statistical parameters defined from the analysis of the textures as function of temperature is successful in identifying the liquid crystal phase transitions between the isotropic liquid phase to smectic phase and solid phase. Image analysis in conjunction with POM is a reliable and sensitive technique to identify phase transition temperatures of hydrogen bond liquid crystals.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. K. Mallika for help in this work. One of the author (SSS) would like to acknowledge the UGC, New Delhi for providing BSR Faculty Fellow research grant No.F.18-1/2011 (BSR), dated January 4, 2017

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