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Determination of Thermo Optical Parameters Using Image Analysis Technique in *n*BA: 7HB Hydrogen Bonded Liquid Crystals

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ABSTRACT: In this paper, thermo optical properties of homologous series of hydrogen bonded liquid crystals: *p-n* alkyl benzoic acid (*n*BA): heptyl *p* - hydroxybenzoate (7HB) (where *n*=5 to 10) have been investigated by means of applying Image analysis technique in conjunction with Polarizing Optical Microscope. Textures of liquid crystal complexes are captured. The changes in textural features as a function of temperature are useful to compute the thermo optical properties. These microscopic textures are analysed using MATLAB software. The investigated thermo optical parameters are optical transmission, Absorption coefficient, Phase retardation, birefringence and order parameter. Experimentally, this is a simple technique to observe the behaviour of the optical parameters of different liquid crystals as a function of temperature.

KEYWORDS:**:**Liquid crystals, Hydrogen bond, Thermo optical parameter, Textures, Image analysis

I. INTRODUCTION

Liquid crystal complexes 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 behaviour 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 [17-20]. This paper deals with homologous series of mesogenic materials: *p-n* alkyl benzoic acid (*n*BA): heptyl *p* - hydroxybenzoate (7HB) (where *n*=5 to 10). The thermo optical properties (including phase transition behaviour) 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 [21-24], 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 Works, Inc., (Natick, MA) [25,26] is used for the analysis of liquid crystal textures. A systematic investigation on thermo optical parameters of the systems such as optical transmission, Absorption coefficient, Phase retardation, birefringence and order parameter are carried out.

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II. EXPERIMENTAL

Materials:

The used chemical ingredients *p-n* alkyl benzoic acid (*n*BA) where *n*=5 to 10, heptyl *p* - hydroxybenzoate (7HB) are the products of Frinton laboratory, New Jersey, USA. The purity of the studied compounds is 99%. The phase transition temperatures of pure *p-n* alkyl benzoic acid and its complexes are *p-n* alkyl benzoic acid (*n*BA): heptyl *p* - hydroxybenzoate (7HB) (where *n*=5 to 10) can be found in [27]. The phase transition temperatures measured by us is in good agreement with the standard techniques.

Method:

A small quantity of sample is placed on a commercially available glass slide usually which will be kept in the hot stage of the Polarizing Optical Microscope (Meopta DRU 3 Model) to observe the textures of the samples. The accuracy of the temperature measurements is ± 0.1^0C. The thickness of the liquid crystal slide is measured using travelling microscope technique and the thickness is equal to 100 μ m.

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 colour 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.

III. DETERMINATION OF PARAMETERS

The behaviour of light with respect to temperature and material is defined in terms of thermo optical properties and are measured using optical parameters like optical transmission, Absorption coefficient, Phase retardation, Phase stability, and birefringence, order parameter. These optical properties provide important information regarding the molecular ordering, molecular dynamics and type of molecular interactions in the sample. In liquid crystal complexes the hydrogen bond interactions profoundly influence the thermal properties of liquid crystalline phases, viz., melting points, enthalpies, and thermal stability. Therefore, it is necessary to investigate the thermo optical properties of liquid crystal complexes. Thermo optical properties of liquid crystals are defined in terms of image intensity values as follows.

Optical transmittances of the mesogens are measured by computing average transmitted intensity of the image texture recorded from the crossed polarizer's condition and given as [28]

$$\text{Optical Transmittance}\ \frac{1}{N}\sum_{i=1}^{m}\sum_{j=1}^{n} I(i,j) \qquad (1)$$

where I (i,j) is the image intensity value observed at the location (i, j) from the crossed polarization component of the texture image. In between crossed polarizers, the value of optical transmittance is zero in isotropic liquid phase of sample**.**

Incident, transmitted intensity values and thickness of the liquid crystal layer d connected with the absorption coefficient (AC) as [21,29]

$$\text{Absorption Coefficient}\ \ a = \frac{1}{d} * \log\left(\frac{I_0}{I}\right) \qquad (2)$$

where $\boldsymbol{a}$ denotes the coefficient of absorption (AC), I is image intensity value observed between crossed polarizers when there is a sample, I_0 is the image intensity value observed between the parallel polarizers when there is no sample which is equal to approximately incident intensity. Because when there is no sample, the total light intensity is transmitted from the parallel polarizers Using Equation 2, temperature dependence optical absorption coefficient (AC) for the mesogens have been computed.

Birefringence Δn of the liquid crystals was measured as a function of temperature by placing the sample of thickness d between crossed polarizers condition given in below equation [21,30-32]

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$$I = I_0 \sin^2 \frac{\pi d \Delta n}{\lambda} \quad (3)$$

Where I is image intensity value observed from the crossed polarizers, I_0 is the image intensity value observed from the parallel polarizers when there is no sample, λ is wavelength of color components (R, G, B).Optical birefringence of mesogens are calculated using Equation (3).

Phase retardation (δ) of the liquid crystal was given by the birefringence Δn, wavelength of light λ and thickness of the sample d: [32-34]

$$\delta = \frac{2\pi d \Delta n}{\lambda} \quad (4)$$

Order parameter of the liquid crystals is determined from the Kuczynski equation by using the direct measurement of birefringence values. The birefringence values are computed from equation (3) [35-37].

$$S = \frac{\Delta n}{(\Delta n_0)} \quad (5)$$

where S is order parameter of the system given by Kuczynski.

The well known equation for the determination of temperature dependent birefringence is:

$$\Delta n = (\Delta n)_0 \left(1 - \frac{T}{T_c}\right)^{\beta} \quad (6)$$

where $(\Delta n)_0$ is the birefringence value liquid crystal at temperature T = 0K, β is material constant, T_c clearing temperature of the sample. The values of $(\Delta n)_0$, β are obtained from the linear regression method using equation (6) in the following way.
Applied "log"to the equation (6):

$$\log(\Delta n) = \log(\Delta n)_0 + \beta \log\left(1 - \frac{T}{T_c}\right) \quad (7)$$

While applying linear regression method to eq (4), the values of $(\Delta n)_0$ and β are calculated. The order parameter value S is calculated using eq (2) with the obtained values of $(\Delta n)_0$ and (Δn). This procedure is similar to the extrapolation of $(\Delta n)_0$ for the absolute temperature while proceeding with the assumption that the order parameter (S) is 1 at absolute temperature. The temperature dependent order parameter values of the samples are obtained from three color image planes red (600nm), green (530nm), blue (470nm).

IV. RESULTS AND DISCUSSION

Homologous series of liquid crystal complexes *n*BA:7HB are exhibited the typical textures of Crystal G phase and only 7BA:7HB exhibits Crystal 2 phase before the Crystal G phase but thermal stability of this phase is small. This can be observed from the all thermo optical properties of the complexes. In the homologous series of *n*BA: 7HB, the formation of hydrogen bond is attributed to the quenching of nematic phase in *n*BA and inducement of Crystal G phase for the series of compounds.

As a function of temperature textures of the compounds are recorded from the solid phase of the sample to the isotropic liquid phase through POM with hot stage and camera attachment. For small values of temperature, there is no change in the textures. As the temperature is increased, changes in textural features occurred reveals the phase transition. While passing a phase from initial phase (solid phase) to other liquid crystal phase or liquid crystal phase to isotropic phase, orientation of the molecules with respect to the temperature affects the transmitted intensity values of the textures in terms of textural feature changes. It gives the information for understanding the thermo optic

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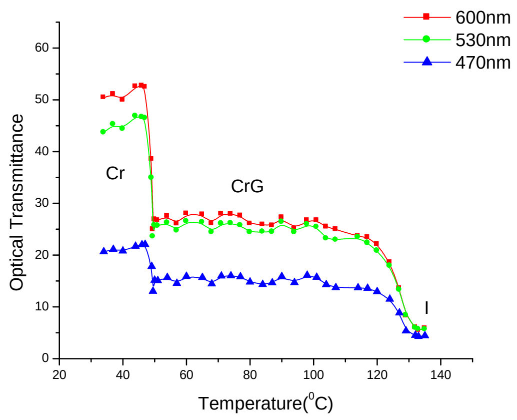
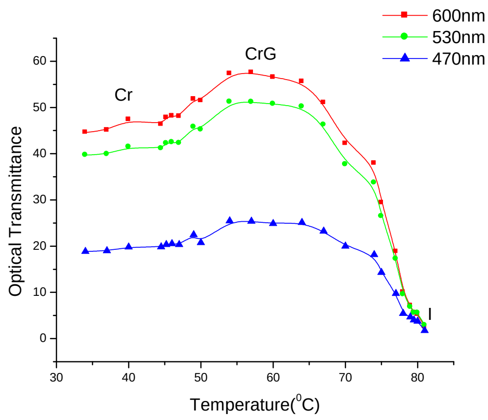
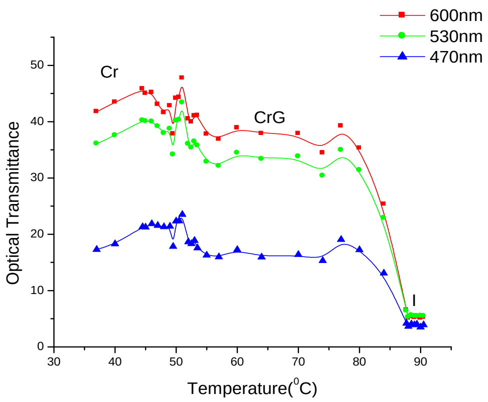
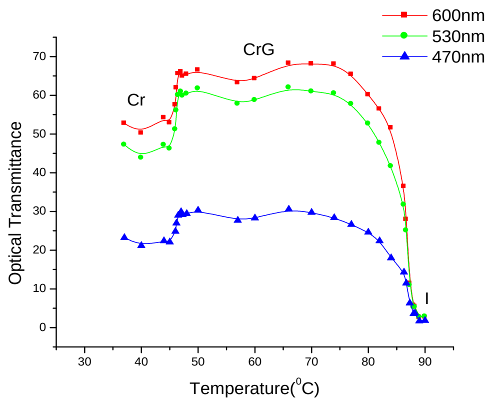
characteristics of liquid crystals. Computed properties using Equations (1)- (7) are plotted against the temperature and are shown in Figures 1 - 5.



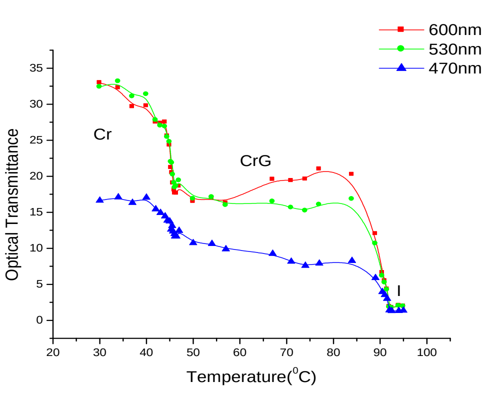


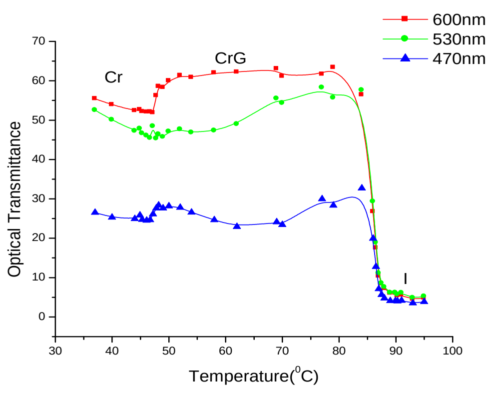
(a) **(b)**





(c) **(d)**





(e) **(f)**

Figure 1: Optical transmittance of *n*BA : 7HB (a) 5BA:7HB; (b) 6BA:7HB; (c)7BA:7HB; (d) 8BA:7HB; (e) 9BA:9HB; (f) 10BA:7HB.

(Cr:Crystal;Cr2: Crystal2; Cr G: Crystal G; I:Isotropic).

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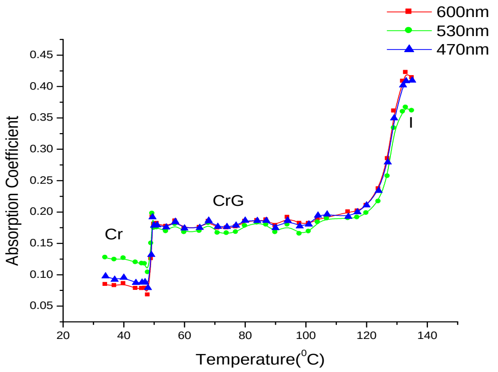
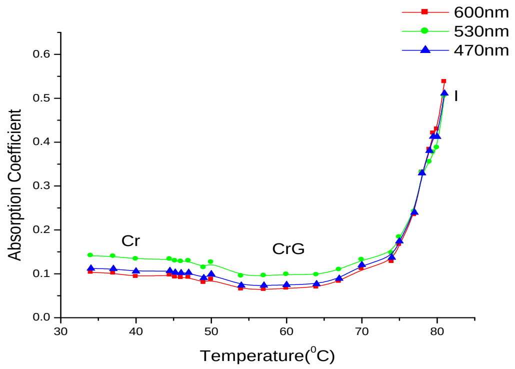
Figure 1 shows the variation in the values of optical transmittance at the transitions Cr – Cr G and Cr G - I. This is due to the fact that, at different phases there are changes in the textural features as function of temperature. The value of optical transmittance slowly decreases with increasing temperature near to Cr G - isotropic phase transition and as soon as the sample goes to the isotropic phase the value of optical transmittance is zero and the texture would appear dark in color in between crossed polarisers [21,38,39]. And also Figure 1, reveals that, optical transmittance of Crystal - liquid crystal phase is very high for the liquid crystal complexes with even number of carbon atoms compared to the odd number of complexes. This result is associated with different alkyl chain lengths.



(a)



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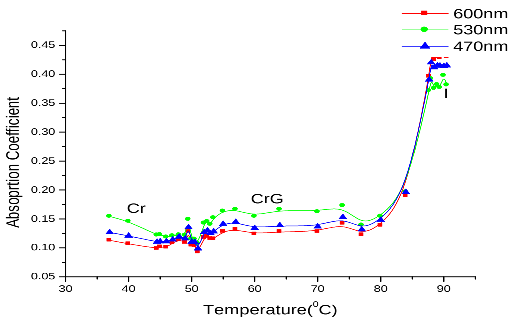

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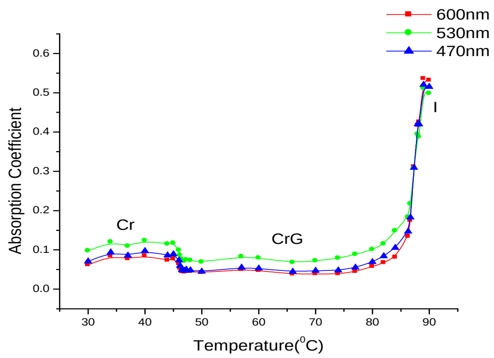

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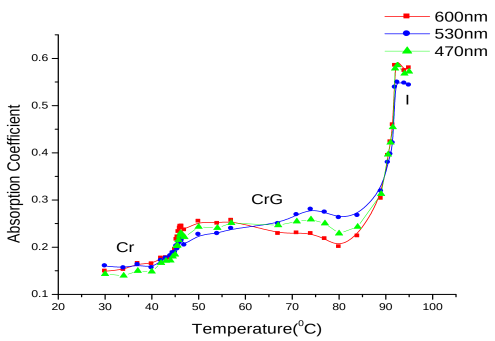

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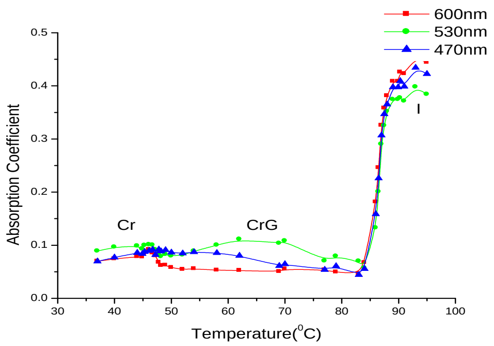

(f)

Figure 2: Absorption coefficient of *n*BA: 7HB (a) 5BA:7HB; (b) 6BA:7HB; (c) 7BA:7HB; (d)8BA:7HB; (e) 9BA:9HB; (f) 10BA:7HB.

(Cr:Crystal;Cr2: Crystal2; Cr G: Crystal G; I:Isotropic).

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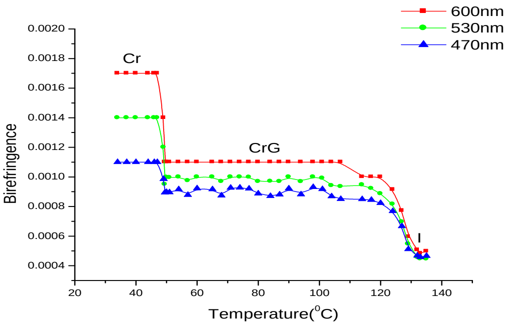
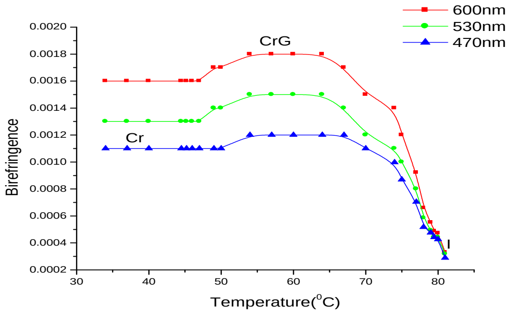
In Figure 2, the value of AC is maximum in isotropic state is noticed. In this phase the molecular orientation is random and there is no transmission of light and the value of AC is less in liquid crystal phase. On heating of the sample, there is a sudden increase of absorption coefficient values that takes place in the biphasic region of Cr G – I temperature interval. The steep change in the values of AC infers the sharp transformations in textures. Optical transmittance of the sample is inversely proportional to the Absorption coefficient (AC) [21,38,39].



(a)



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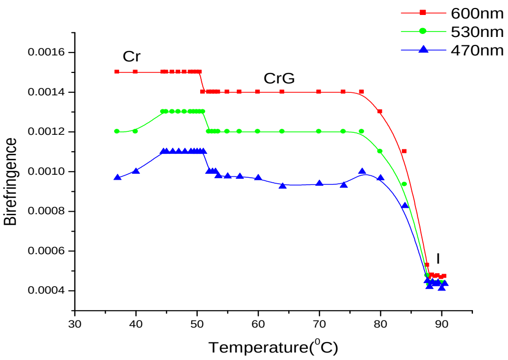

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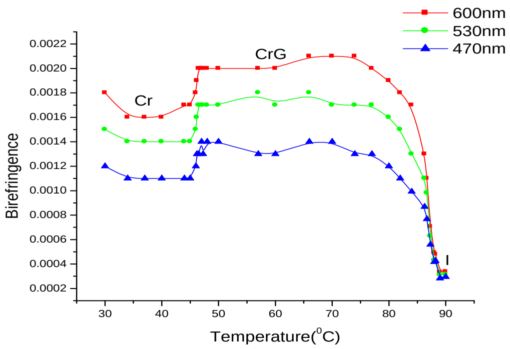

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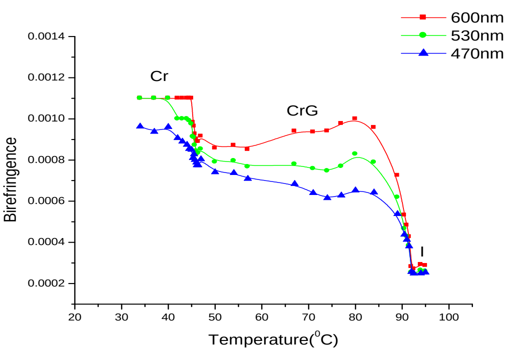

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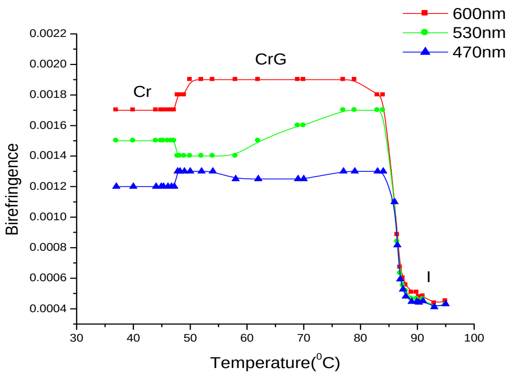

(f)

Figure 3: Birefringence of *n*BA: 7HB (a) 5BA:7HB; (b) 6BA:7HB; (c) 7BA:7HB; (d) 8BA:7HB; (e) 9BA:9HB; (f) 10BA:7HB.

(Cr:Crystal;Cr2: Crystal2; Cr G: Crystal G; I:Isotropic).

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Figure 3 clearly indicates that the birefringence values plotted against the isotropic temperature remains constant and is nearly equal to zero .The absence of birefringence property in isotropic liquid state is the reason for the zero value of birefringence. The disappearance of birefringence property in isotropic state of the samples is attributed to the destruction of molecular alignment that led to the decrease of birefringence value to zero [21,38-40]. The small variations in the optical parameter curves other than transitions are due to change in the refractive index of the samples which leads to changes in textural features as a function of temperature. The phase transitions from Cr – Cr G – I are very well established in all plots of thermo optical properties which is also further confirmed from the order parameter graph.

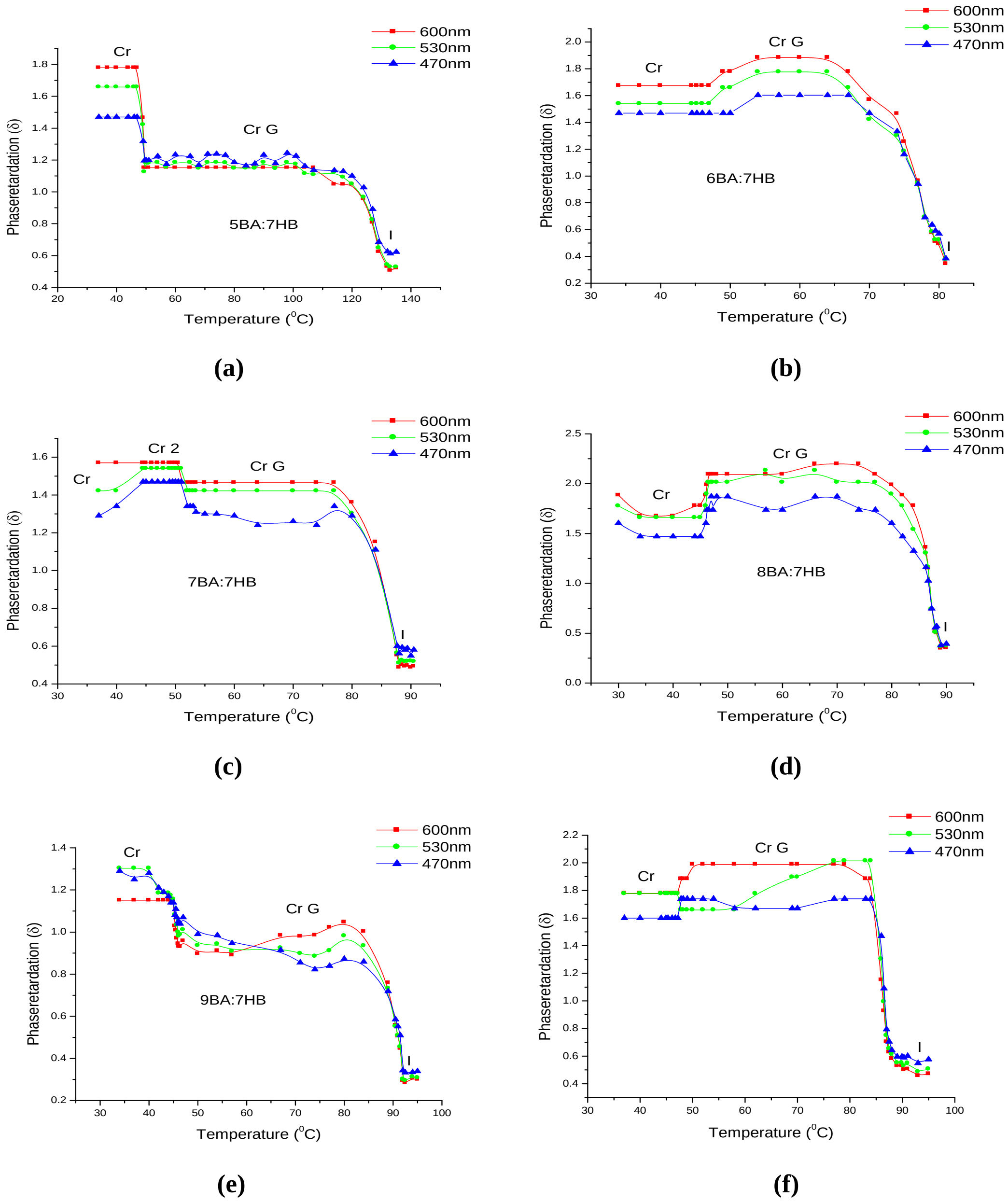

Figure 4: Phase retardation of *n*BA : 7HB (a) 5BA:7HB; (b) 6BA:7HB; (c)7BA:7HB; (d) 8BA:7HB; (e) 9BA:9HB; (f) 10BA:7HB.

(Cr:Crystal;Cr2: Crystal2; Cr G: Crystal G; I:Isotropic).

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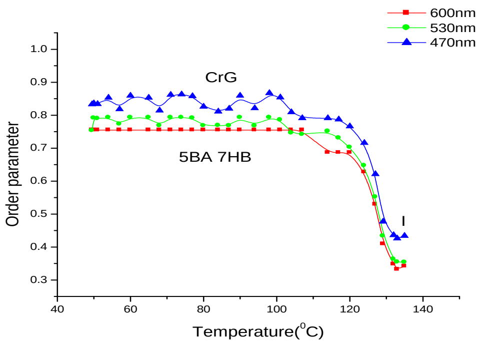
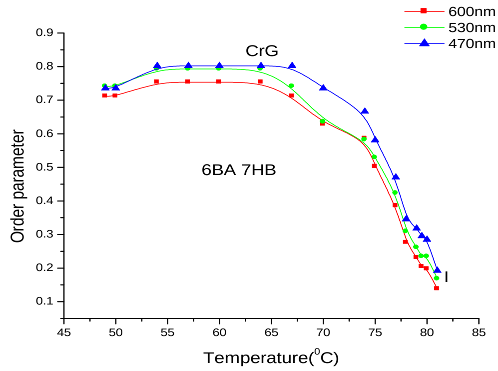
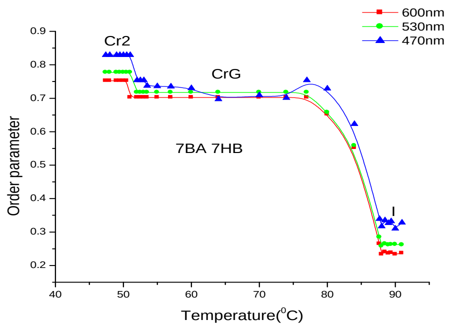
Figure 4 shows the temperature dependent phase retardation of *n*BA:7HB liquid crystal complexes at the wavelengths 600nm, 530nm and 470nm. As a function of temperature, phase change occurs due to disturbance in directions of the molecules. Changes in phase retardation values are function of single variable Δn. In solid phase liquid crystal molecule directors remain undisturbed and no phase change occurs. While passing the phase, orientation of molecular directions results small changes in the phase retardation values. In this regime the value of phase retardation is inversely proportional to temperature. This can be clearly observed for two samples from Figure 4 at three wavelengths.



(a)



(b)



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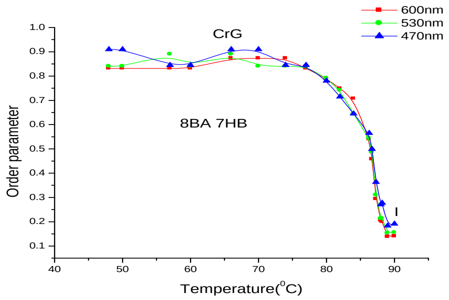

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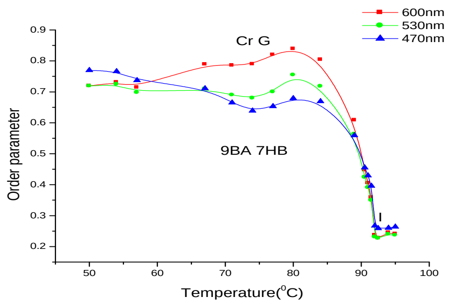

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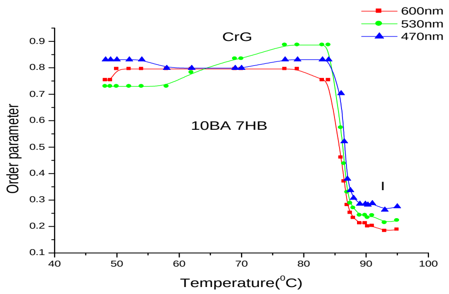

(f)

Figure 5: Order parameter of *n*BA : 7HB (a) 5BA:7HB; (b) 6BA:7HB; (c)7BA:7HB; (d) 8BA:7HB; (e) 9BA:9HB; (f) 10BA:7HB.
(Cr:Crystal;Cr2: Crystal2; Cr G: Crystal G; I:Isotropic).

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The temperature dependent birefringence values of the samples obtained from Equation (3) are used to compute the temperature dependent order parameter of the *n*BA:7HB complexes. These measurements are made in the phase transition regions of Cr – Cr G - I phase of the sample and the measured order parameter values are plotted against the temperature. The order parameter (S) shown in Figure 5 is maximum in Cr – Cr G transition state and it goes on decreasing as the temperature is incremented towards the isotropic phase of the sample which has the lowest order parameter of the order of 0.15. The values of order parameter during the transition from the Cr – Cr G - I phases are in the range of 0.85 to 0.15. Here the parameters are computed purely based on gray level intensity vales of the image textures [41,42], where as in the other case the parameters are obtained based on the light transmitted intensity, molecular polarizabilities, refractive indices and densities of the sample etc [31,37,41] . Order parameter values plotted against temperature in Figure 5 also evince the different transitions in *n*BA:7HB mesogens.

V. CONCLUSION

Thermo optical properties of homologous series of hydrogen bonded liquid crystals: *p-n* alkyl benzoic acid (*n*BA): heptyl*p* - hydroxybenzoate (7HB) (where *n*=5 to 10) are investigated using Image analysis technique on MATLAB plat form. As a function of temperature, the sample undergoes different phase transitions showing different textures. Textural features of the samples in relation to temperature provided the information approximately suitable to determine the optical properties of the samples. The computed thermo optical parameters all plotted against temperature well established the different transitions and their corresponding transition temperatures in *n*BA:7HB mesogens under investigation.

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