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APPLICATION OF IMAGE ANALYSIS USING TEXTURES OF Py14BA:*n*FA FOR MESOGEN PARAMETERS

Ch. Kamalakar[1], C.J. Sreelatha[1], K. Mallika[2], A.V.N. Ashok Kumar[3] and S. Sreehari Sastry[2,✉]

[1]Department of Physics, Faculty of Physical Sciences, Kakatiya University, Warangal-506009, India
[2]Department of Physics, Faculty of Physical Sciences, Acharya Nagarjuna University, Nagarjunanagar-522510, India
[3]Department. of Physics, Faculty of Physical Sciences, Jawaharlal Nehru Technological University Kakinada, Kakinada-533003, India
✉Corresponding author: sreeharisastry@yahoo.com

ABSTRACT

Thermal and optical properties of two supra molecule mesognes: Py14BA:*n*FAs (*n*=14 and 16) (4-Pyridyl)-benzylidene-4'- n-tetradecyl aniline(PyB14A)**:**aliphatic carboxylic acids (*n*FA where *n* = 14 and 16) are investigated. This study is carried out with a polarizing optical microscope and image analysis method.It isbased on the temperature dependence of intensities of the mesogen textures. Intermolecular hydrogen bond formation between the two nonmesogens gives rise to mesogen complexes Py14BA:*n*FAs (*n*=14 and 16). The properties of these mesogen complexes are computed from the images (textures) through MATLAB software. Transition temperatures, heat enthalpy, thermal stability factor, Birefringence dispersion, Phase retardation, Transient transmission and order parameter studies are carried out. The results manifest that hydrogen-bonded mesogens exhibit good thermo-optical properties.

Keywords: Hydrogen bonded mesogens, Textures, Image Analysis, Transition Temperatures, Optical Parameters

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INTRODUCTION

Supra molecular liquid crystals with induction of new phases and different thermal stabilities started a new research area of enhanced performance of the material towards device applications, especially in displays.[1-3] Supra molecular liquid crystals show profound influence on the thermal and optical properties of the individual liquid crystal. Many authors reported the different hydrogen-bonded liquid crystal complexes (HBLCs) of types obtained from the complexation of mesogenic - nonmesogenic and mesogenic – mesogenic compounds) towards device applications.[4,5] In this paper, the third alternative HBLC complex obtained from the complexation of nonmesogenic - nonmesogenic compounds is considered and the investigation is carried out for their utility in device applications. The considered nonmesogenic compounds are (4-pyridyl)-benzylidene-4'- n-tetradecyl aniline (PyB14A) and aliphatic carboxylic acids (*n*FA), where *n*=14 and 16. Intermolecular hydrogen-bonded liquid crystal (HBLC) complexes Py14BA:*n*FAs (*n*=14 and 16) is taken place.[6] In this case proton acceptor and donor are the N-atom in pyridyl derivative and fatty acids respectively.

Generally, all the applications of liquid crystal materials depend on their thermal and optical behavior.[7,8] Several experimental and theoretical techniques are available to study the thermal and optical behavior of compounds.[9,10] Here, an image analysis technique with the use of polarizing optical microscope (POM) textures is employed to compute the optical properties of HBLCs (Py14BA:*n*FA (*n*=14 and 16)). In cooling and heating cycles the phases of the material undergo changes which will be taken in the textures with the help of POM attached with a high-resolution color camera.[11] The variations are in the intensities of colors. Temperature dependence of these intensities can be investigated for the thermal optical characteristics of the hydrogen-bonded mesogens : Py14BA:*n*FAs (*n*=14 and 16).

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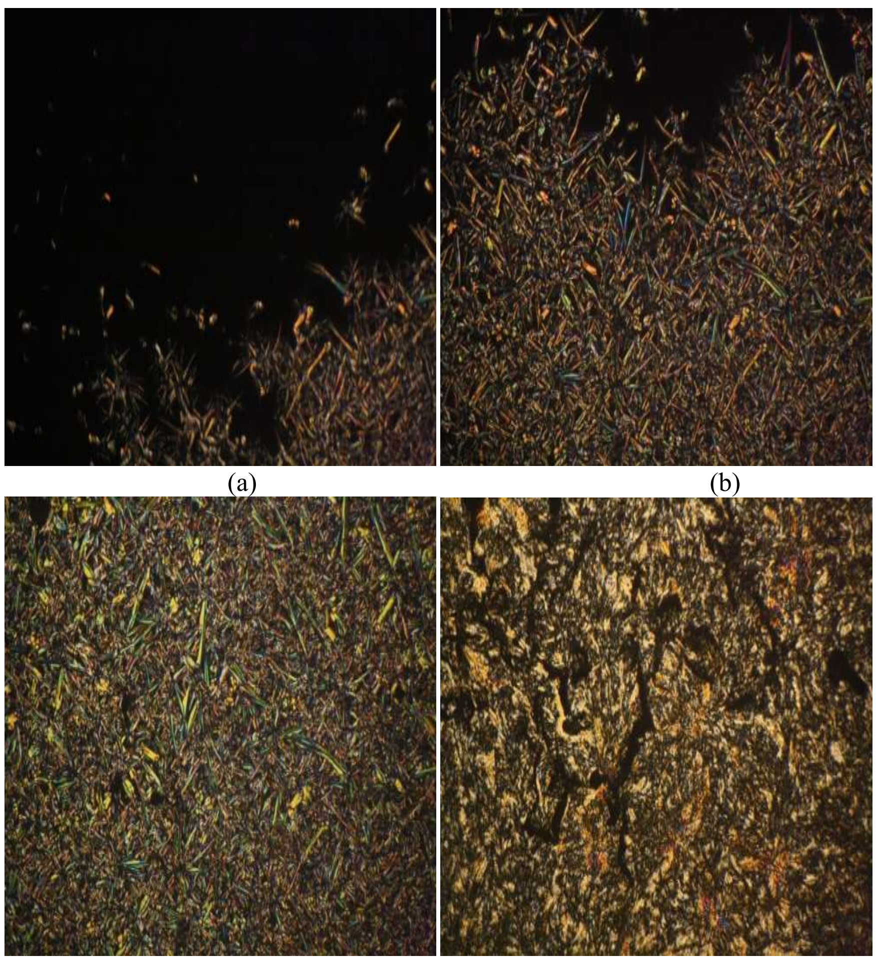
Microscopic textures are analyzed using MATLAB.[12-15] Here, thermal and optical properties are computed for given HBLCs .Such thermal properties: transition temperatures, heat enthalpy, thermal stability factor and optical properties: Birefringence dispersion, phase retardation, transient transmission and order parameter. The said optical properties are computed from the birefringence of samples.

EXPERIMENTAL

Mesogens Py14BA:*n*FA (*n*=14 and16),preparation and their synthetic route were reported.[6] Display Tech Inc., USA company Sample cell with 8.7μm thickness is used for textural observation and analysis. Temperature dependence of textures of the compounds is obtained through a hot stage kept in POM (of SD-Tech Co., India) attached with high-resolution colour Canon EOS 1000D camera. Recorded textures or images have a resolution of 3888X2592 pixels with true color production of 24-bit tonal levels in the 0 to 255 gray levels. The cell preparation and corresponding mathematical equations related to the analysis can be found in the literature.[12-15]

RESULTS AND DISCUSSION

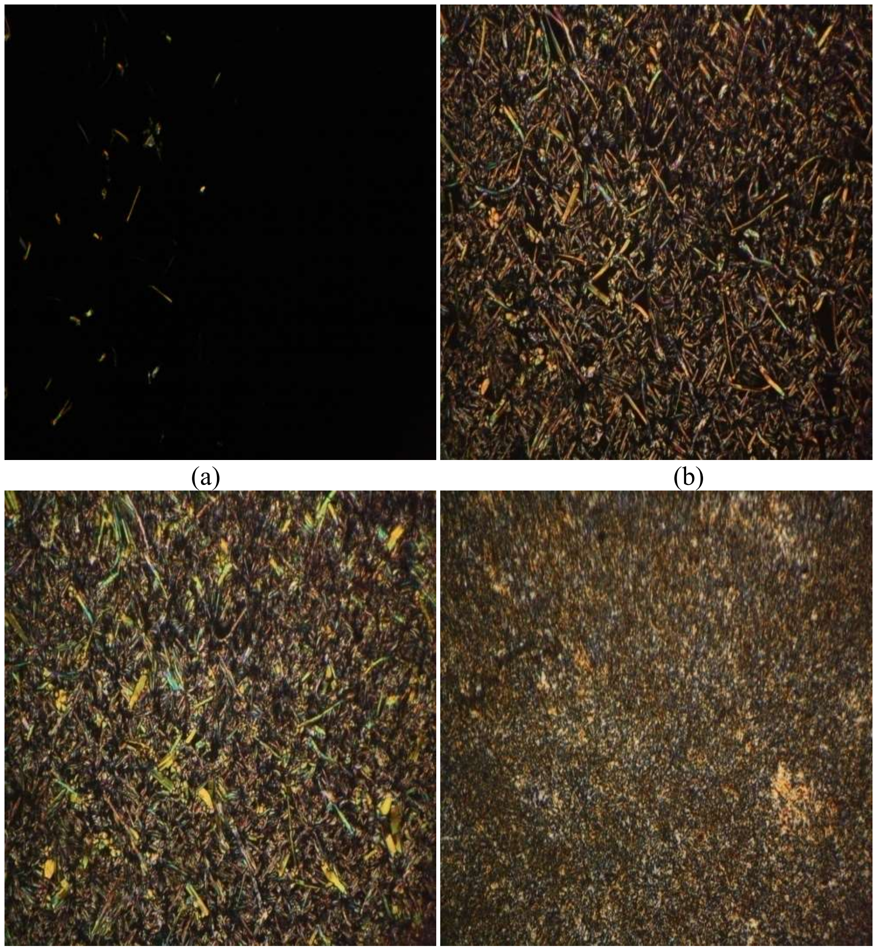
Supra molecular liquid crystals: Py14BA:*n*FA synthesized from nonmesogenic compounds Py14BA and *n*FA (*n*=14 and 16) exhibit enantiotropic nature having smectic phases. The involvement of hydrogen bond interactions in the molecular bodies causes the induction of mesogenic phases in the synthesized HBLCs. Mesogenic phases of HBLCs in terms of optical textures are shown in Figs.-1 and 2.



(a) (b) (c) (d)

Fig.-1: Optical Microscopic Textures of HBLC Py14BA:*n*FAs,Where *n*=14 (a,b) I - Smectic B Phase, (c) Smectic B Phase ; (d) Crystal Phase.

The presence of hydrogen bonds in the liquid crystal complexes has the ability to influence the thermal and optical behavior of the samples. Thermal behaviors of the samples were measured from the properties like phase transition temperatures, heat enthalpy, and thermal stability factor. Phase transition temperatures obtained from the POM and Thermal analysis (DSC) techniques are given in Table-1.



(a) (b) (c) (d)

Fig.- 2: Optical Microscopic Textures of HBLC Py14BA:*n*FAs,Where *n*=16 (a) I – SmB Phase, (b) SmB Phase ; (c) SmF Phase; (d) Cr Phase.
SmB - Smectic B; SmF - Smectic F; Cr – Crystal.

Table-1: Phases, Phase Transition Temperatures and Heat Enthalpy Changes of HBLCs:Py14BA:*n*FAs (on cooling)

Compound Py14BA:*n*FAs	Phases	Phase transformation temperatures (°C) DSC	Phase transformation temperatures (°C) POM and Image analysis	Enthalpy change (j/g))
n=14	I – SmB - Cr	67.4- 64.6	67.50 – 63.60	27.1- 24.78
n=16	I – SmB – SmF - Cr	70.1-62.0-59.0	71.50 - 61.8 - 59.5	1.6 – 31.49 – 1.05

(Cr:Crystal;smF – SmecticF;smB – Smectic B; I:Isotropic)

The mesophase range for the sample Py14BA:*n*FA (*n*=16) is more compared to the sample Py14BA:*n*FA (*n*=14). The Phase transformation temperatures obtained from POM and DSC[7] are in good agreement. The enthalpy changes of the samples measured from the DSC are also given in Table-1.
The thermal stability factor is another useful property to study the optical behavior of the liquid crystal complexes.[2,3] This factor governs the utility of the mesogens in optical device applications. For long-time operating devices, it is necessary to maintain high phase stability in materials which are shown in Table-2.

Table-2: Thermal Stability Factor Obtained from Present Technique and DSC

Compound Py14BA:*n*FAs	ΔT [DSC]	T_{mid} [DSC]	S[DSC]
n=14	3.9 [2.8]	99.3 [99.7]	387.27 [279.16]
n=16	12.0 [11.1]	65.5 [64.55]	786.0 [716.50]

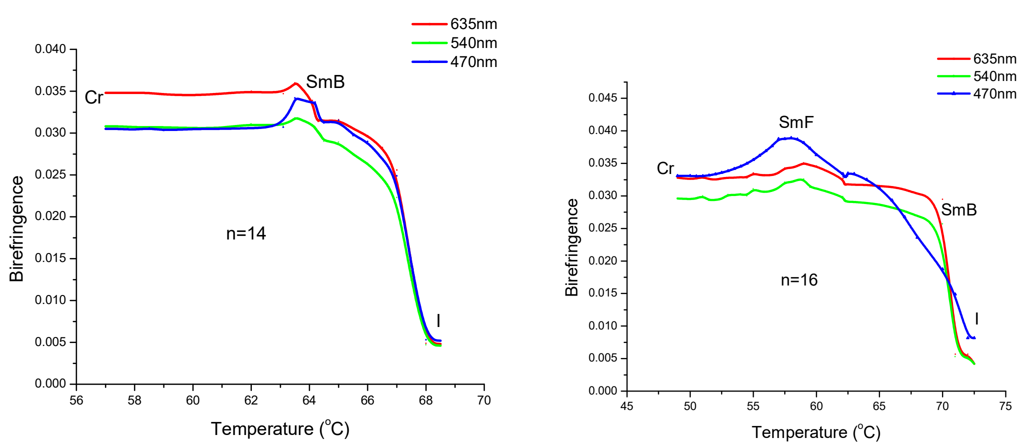
(ΔT: Temperature Difference, T_{mid}:Middle Phase of Temperature, S: Thermal Stability Factor).

From Tables-1 and 2, it is observed that thermal behaviors mesophase range, heat enthalpy and thermal stability factor are high for the complex Py14BA:*n*FAs (*n*=16) compared to the Py14BA:*n*FAs (*n*=14).With the increase of chain length from 14 to 16, the hydrogen bond strength of the orientational disorder fluctuations seems to be turned.[5,8,16]

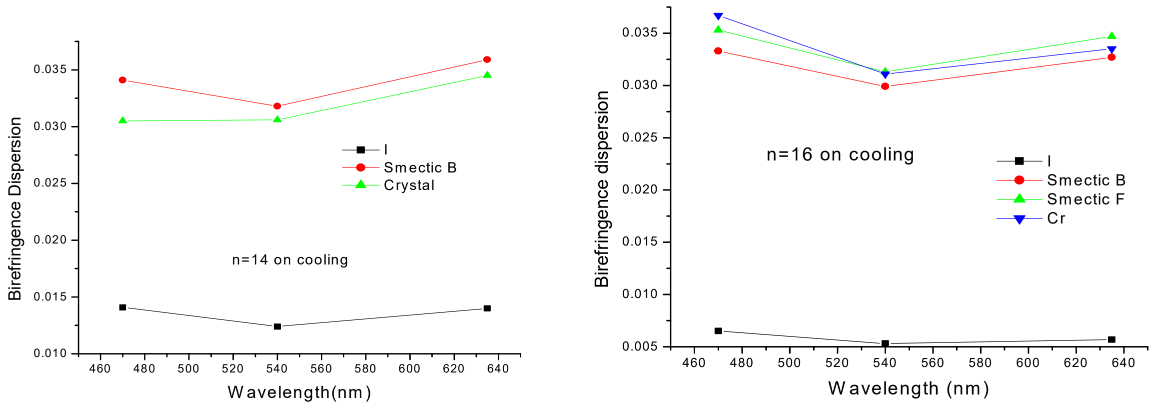
The formation of liquid crystal complexes through intermolecular interactions has a significant effect on the temperature dependence of optical properties.[17,18] Phase change occurs with the variation of temperature which is due to disturbance in molecules directions. Polarization is zero in the isotropic phase of the mesogen or molecule directors are random. Hence the texture appears dark. Realignment of molecular directions shows phase transitions in the cooling cycle.

From isotropic phase to mesophase or mesophase to solid phase, the orientation of the molecules and transmitted intensity values also change (Figs.-1,2). Temperature dependence of textural intensity analysis allows the information of thermo optical properties under investigation of Py14BA:*n*FAs. Optical properties: Birefringence dispersion, Phase retardation, Transient transmission and Order parameter are computed using equationsreported in the literature.[12-15] These properties are plotted with temperature variations which are shown in Figs.-3 to 5.

Temperature dependence of birefringence for red, green and blue colors are shown in Figs.-3(a) and 3(b). Intensity variations in textures of the mesophases resulted in computing birefringence values. A common behavior is seen in all phases. Changes in the birefringence values can be attributed to considerable destruction and ordering in the molecular alignment in the corresponding phases. In the cooling cycle, birefringence increased sharply in the Isotropic – smectic biphase region and small changes in Smectic B - Cr phases. Little changes in the curves apart from phase transitions may be explained because of small changes in the refractive index values either with respect to temperature or wavelength. These are clearly noticed in Figs.-1 and 2. From Figures-(3c) and (3d) the birefringence and birefringence dispersion, Py14BA:*n*FAs where *n*=16 shows a high birefringence value compared to *n*=14. Further, birefringence values for the three wavelengths are small and linear. In other words, there is no significant change in birefringence values for the three wavelengths at any particular temperature.

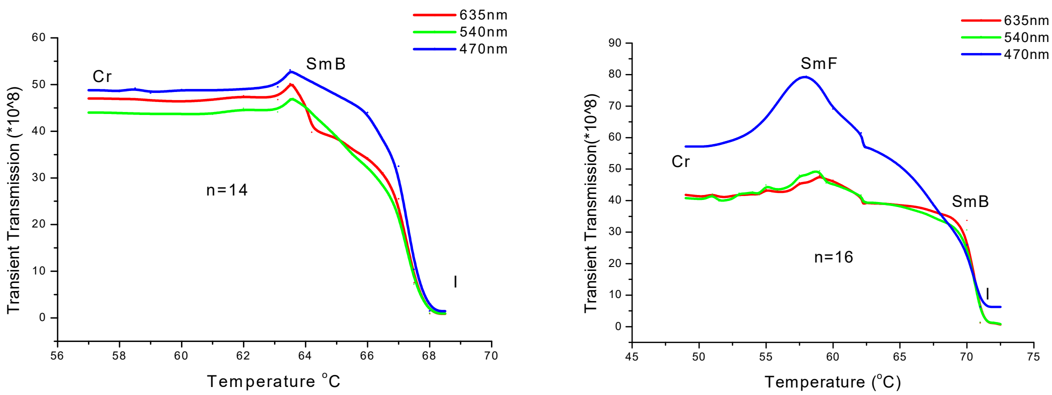


(a) (b)



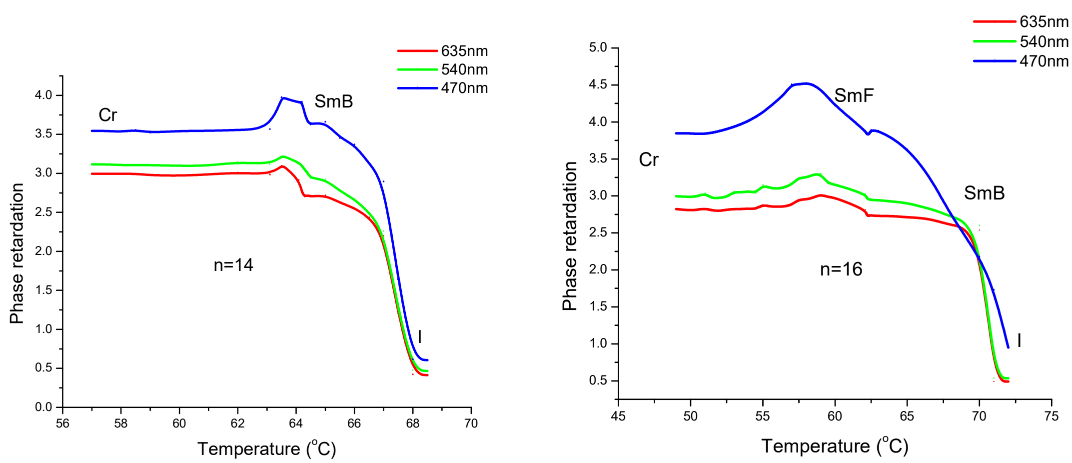
(c) (d)

Fig.-3: Birefringence of Py14BA:*n*FAs (a) *n*=14; (b) *n*=16; Birefringence Dispersion ofPy14BA:*n*FAs (c) *n*=14; (d) *n*=16



(a) (b)

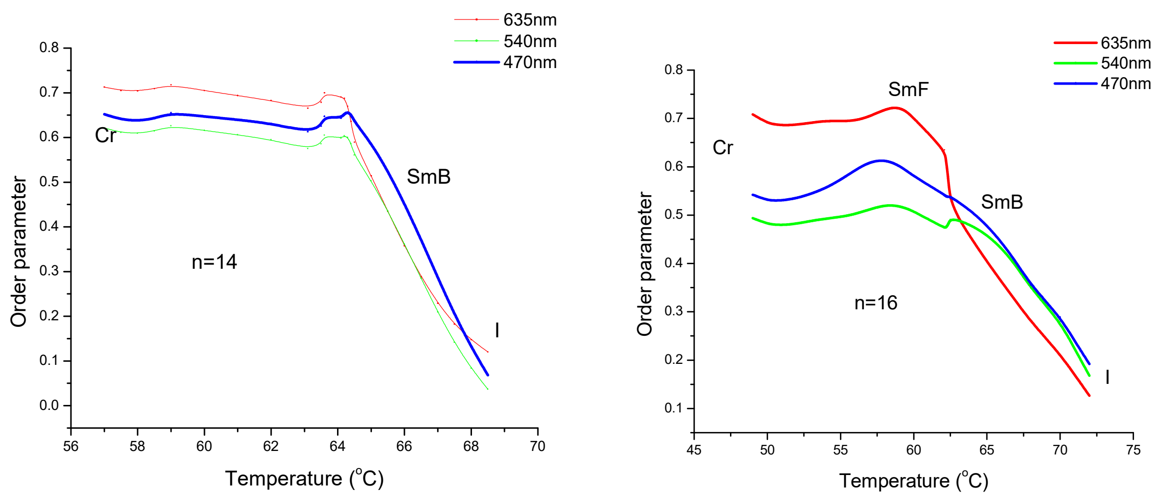
Fig.-4: Transient Transmission of Py14BA:*n*FAs (a) *n*=14; (b) *n*=16.
(Cr:Crystal;smA – Smectic A; smB – Smectic B; I:Isotropic)



(a) (b)

Fig.- 5: Phase Retardation of Py14BA:*n*FAs (a) *n*=14; (b) *n*=16.
(Cr:Crystal;smA – Smectic A; smB – Smectic B; I:Isotropic).

Figures- 4 and 5 show that the values of transient transmission and phase retardation of HBLCs are small in the isotropic phase due to crossed polarizer's condition. When the temperature is decreased from its isotropic state, the re-alignment of molecules in corresponding phases causes the birefringence feature to reappear, allowing the sample to be transmitted.[19] Complexes Transient Transmission and Phase Retardation characteristics differ depending on their wavelengths and Phase transitions. Among all phases of the complexes, the overall values of the Transient Transmission and phase retardation are significantly high for Py14BA:nFAs where *n*=16 compared to *n*=14. Larger the Δn values, the larger the transient transmission and phase retardation values since they were computed from the birefringence values.
Not only optical properties of transient transmission, phase retardation but also order parameter (S) of the HBLCs are also computed from the birefringence measurements. Kuczynski equation is used to compute HBLCs Py14BA:*n*FAs where *n*=14 and 16 order parameters from birefringence values. These measurements are done from isotropic to crystal phase and the corresponding temperature-dependent order parameter is shown in Fig.-6. Due to gray level intensity values of the image analysis, the order parameter between the isotropic to smectic phase is 0.1 and the smectic to crystal phase is around 0.7.



(a) (b)

Fig.-6:Order Parameter of Py14BA:*n*FAs (a) *n*=14; (b) *n*=16.
(Cr:Crystal;smA – Smectic A; smB – Smectic B; I:Isotropic)

CONCLUSION

Thermo optical properties of two supra molecular mesogens: Py14BA:*n*FAs (*n*=14 and 16) are investigated successfully through image analysis. Comparing the properties of the two studied mesogens, it is observed that mesogen's phase stability increased along with tilted phases of smectics are more due to the increase of end chain length. Py14BA:*n*FAs where *n* =16 shows high values of Birefringence, transient transmission and phase retardation for all wavelengths compared to *n*=14. This implies that Py14BA:*n*FAs where *n* =16 is more suitable for the device applications.

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REFERENCES

1. Shinya Takarabe, Junji Morishita, Hidetake Yabuuchi, Hiroshi Akamine, Noriyuki Hashimoto, Yasuhiko Nakamura, Yoshio Matsuo, Akiko Hattori, *Radio Physics Technology,***7**, 73(2014) https://doi.org/10.1007/s12194-013-0233-2

2. J.A. Castellano, 1992, Handbook of Display Technology, Academic Press., San Diego, pp.181-187.
3. A. K. Srivastava,V.G. Chigrinov, H.S. Kwok, *Journal of the Society for Information Display,* **23,** 253(2015), https://doi.org/10.1002/jsid.370
4. B.T.P. Madhav, D. Sreenivas Rao, K. Supraja, A. Tejaswini, A. Phanikumar, A. Nagarjunareddy, R. Sai Prakash, A.N. Meena Kumari, *Rasayan Journal of Chemistry,* **10**, 866(2017), http://dx.doi.org/10.7324/RJC.2017.1031679
5. T. Kajitani, S. Kohmoto, M. Yamamoto, K. Kishikawa, *Journal of Materials Chemistry*, **14**, 3449(2004), https://doi.org/10.1039/B408672D
6. M. Muniprasad, M. Srinivasulu, P.V. Chalapathi, D.M. Potukuchi, *Molecular Crystals Liquid Crystals*, **557**, 102(2012), https://doi.org/10.1080/15421406.2011.636662
7. Martin Stalder, Martin Schadt, Nematic Liquid Crystal Electrooptical Element and Device, *U.S. Patent, A1 0147033*, 2003.
8. S.M. Kelly, 2000, Hand Book of Advanced Electronic and Photonic Materials and Devices, Academic Press, U.S.A, pp.185-206.
9. P.J. Collings, M. Hird, 1998, Introduction to Liquid Crystals: Chemistry and Physics, Taylor and Francis Ltd., UK, pp.185-278.
10. D. Demus, J. Goodby, G.W. Gray, H.W. Spiess, V. Vill, 1999, Physical Properties of Liquid Crystals, Wiley- VCH., Singapore, pp.1-301.
11. W. Gray, 1962, Molecular Structure and the Properties of Liquid Crystals, Academic press, New York,pp.25-300.
12. J. Eccher , A.R. Sampaio, R.C. Viscovin, G. Conte, E. Westphal, H. Gallardo, I.H. Bechtold, *Journal of Molecular Liquids*, **153,** 162(2010), https://doi.org/10.1016/j.molliq.2010.02.010
13. S. Sreehari Sastry, S.T. Ha, B. Gowri Sankara Rao, K. Mallika, T. Vindhya Kumari, *Liquid Crystals,* **39**,1414(2012), https://doi.org/10.1080/02678292.2012.719041
14. T. Kalyani, K. Mallika, A.V.N. Ashok Kumar, S. Sreehari Sastry, *Liquid Crystals,* **48**, 1(2021),https://doi.org/10.1080/02678292.2020.1760382
15. S. Sreehari Sastry, Sandeep Kumar, T. Vindhya Kumari, K. Mallika, B. Gowri Sankara Rao, S.T. Ha, *Liquid Crystals,* **39**,1527(2012), https://doi.org/10.1080/02678292.2012.725870
16. S. Padmaja, M. Ramakrishna Nanchara Rao, P. V. Datta Prasad, and V.G.K.M. Pisipati, Z. Naturforsch, **60a**, 296(2005)
17. M. Tejaswi, M.C. Rao, P.V. Datta Prasad, G. Giridhar, V.G.K.M. Pisipati and R.K.N.R. Manepalli, *Rasayan Journal of Chemistry,* **9**, 697(2016).
18. Sk. Suriya Shihab, Shaik. Babu & S. Sreehari Sastry, *Rasayan Journal of Chemistry,* **9**, 641(2016).
19. S. Singh, 2002, Liquid Crystals Fundamentals, World Scientific., Singapore, pp.1-299.

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