Thermal and Optical Characterization of Linear Hydrogen Bonded Supramolecular Liquid Crystal Mixture

T Vasanthi, V Balasubramanian, P Subhasri, R Jayaprakasam, V N Vijayakumar

Abstract**:** ***Supramolecular HBLC (hydrogen bonded liquid crystal) mixture is prepared through non-mesogenic compound of 4-Aminobenzoic acid (ABA) and mesogenic compound of 4-(Dodecyloxy)benzoic acid (12OBA). The presence of functional group and forming of intermolecular H-bond between the HBLC mixture is verified by FT-IR spectroscopy. Mesophase transition temperature, order of transitions and enthalpy values are the LC parameters which have been evidenced through optical and thermal studies. Nuclear Magnetic Resonance (^{1}H NMR) spectroscopic studies are added evident to the existence of intermolecular complementary and cyclic type of H-bonding in the present mixture. A noteworthy observation highly ordered Smectic C mesogenic phase along with the new Smectic X mesogenic phase is noticed as finger-print texture. Nematic (N) to Smectic (Sm X) mesogenic phase is identified as 1st order transition. Another interesting observation of the present work is the identification of wider phase width of mesogenic phases and decreased enthalpy values in the present mixture which is compared to the individual compounds.***

Keywords: HBLC, Smectic X, ^{1}H NMR, FT-IR, Smectic C.

I. INTRODUCTION

The enhanced properties and its potential applications in different field liquid crystals (LCs) play an important role in our day-to-day life. HBLC moieties are derived from the combination of mesogenic compound or non-mesogenic compounds [1]. Alkoxybenzoic acid (i.e. carboxylic acid group) is exhibiting LC behavior [2, 3]. Intermolecular interaction between the molecules enhances the LC phase behavior. Electron donor and acceptor interaction raise the orientational forces between the LC molecules which is responsible for the molecular order in the LC phases [4]. LC molecule is self-assembled by the non-covalent interaction between acceptor and donor moieties [5].

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Existing polymorphism (alkoxy benzoic acids) supports covelent bonding with dicarboxylic acid [6, 7]. Thus the intermolecular interaction between mesogenic and non-mesogenic compound induces liquid crystal behavior [8]. microscopic slide. It is covered with the glass slip and placed As a result, the hydrogen bonding between different molecules provides various types of HBLCs [9, 10]. H-bond through complementary nature drawn more attention among the researchers [11-13]. Hydrogen bonding between different carboxylic acid mixture exhibit mesogenic properties had already been reported [14-16].

LC is used in the various possible applications [17] such as electro-optic device, optical shutters and modulators, etc. Kato reported [18] that modulator and optical shutter applications are the novel categories of hydrogen bonded LC materials (HBLCs). The properties such as birefringence, chemical stability, color and its molecular structure plays pivotal role for various potential applications.

With our previous experience single, double and multiple h-bonded LCs have been reported [19-21]. In this present work we successfully synthesized and characterized the HBLC mixture from 4-Aminobenzoic acid (ABA) and 4-(Dodecyloxy)benzoic acid (12OBA). Also, extended mesogenic range in smectic X phase is reported in the present communication

II. EXPERIMENTAL TECHNIQUES

4-(Dodecyloxy)benzoic acid (12OBA), 4-Aminobenzoic acid (ABA) and DMF were purchased from Sigma Aldrich, Germany. Physicochemical properties of the compounds are given in table 1. Due to the unidirectional rubbing on the glass slide, homogenous alignment of the LC molecules was achieved. For optical studies, LC sample is taken in a under POM. LC sample was kept in hot and cold stage MHCS400 (MicrOptik) which was controlled by programmed software MTDC600 with temperature accuracy of 0.1^{o}C. For textural observation hot and cold stage was kept below crossed polarizer Olympus microscope attached along with CCD camera (ToupTek). LC images were recorded with the help of CCD.17. UH310 USB camera (Sony) by the scan rate of 1^{o}C/min. Shimadzu DSC60 with TA60 software was used for thermal characterization of present HBLC mixture. BRUKER ALPHA FT-IR instrument was used to record FTIR spectrum. ^{1}H NMR (400 MHz, Bruker) spectrum was used to analyze molecular environment of the present ABA+12OBA HBLC mixture.

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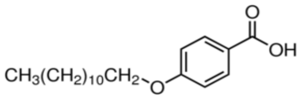
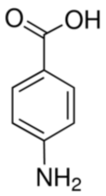
compound	chemical structure	molecular weight (g/mol)
4-(Dodecyloxy) benzoic Acid		306.446
4-Aminobenzoic acid		137.14

Table 1: Molecular structure for ABA and 12OBA compounds.

A. Preparation of ABA+12OBA mixture

Initially, the dimeric nature of 12OBA is transformed into monomer by using the solvent THF. For synthesizing the HBLC mixture, one mole of ABA and 12OBA is measured and dissolved in the dimethyl formamide (DMF). After, the solution is continuously stirred for 10 hours with 750rpm by using the magnetic stirrer. ABA+12OBA HBLC mixture is obtained as a white crystalline powder.

Fig. 1 shows the synthetic route of the HBLC mixture (ABA+12OBA).

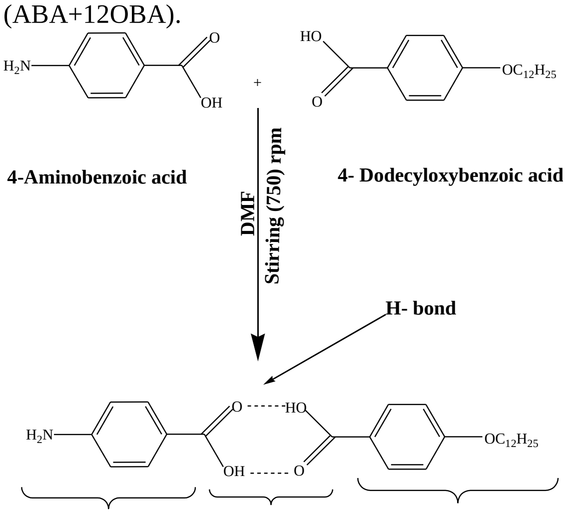


Fig. 1 Molecular Structure of ABA+12OBA HBLC mixtures.

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopic (FTIR) Studies

IR is a powerful tool to recognize the chemical bond (i.e., functional group) by KBr pellet method. Nakamoto discussed [22] that the carbonyl stretching ν(C=O) at 1685cm^{-1}and at 1695cm^{-1} in carboxylic acids. In ABA+12OBA HBLC mixture ν(C=O) is found at 1678cm^{-1}, hydroxyl stretching ν(O-H) at 2921cm^{-1} (h-bond), alkyl group of stretching ν(C-H) at 2850cm^{-1}, ν(C-O) at 1255cm^{-1}, C-H out-plane bending vibration at 844cm^{-1}, O-H out of plane bending vibration at 944cm^{-1}, broad peak of free OH at 3774 cm^{-1} and methylene group stretching vibrational ν(C-C) at 1470cm^{-1} are denoted in Fig. 2.

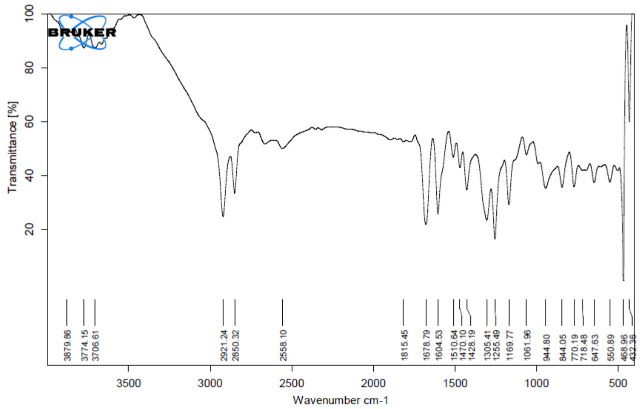


Fig. 2 FT-IR spectrum of ABA+12OBA mixture.

B. [1]H- NMR Spectrum Studies

$CDCl_3$ solvent is used in [1]H NMR studies. The [1]H NMR spectrum of ABA+12OBA HBLC mixture is given in the Fig. 3. Also, the subsequent peaks are identified and mentioned below,

(i) A triplet at δ 0.91ppm (3 protons) indicates the existence of $-CH_3$ group in the ABA+12OBA HBLC mixture.

(ii) A multiplet at δ 1.286ppm indicates the presence of methylene ($-CH_2$) protons of 12OBA in the ABA+12OBA HBLC mixture.

(iii) A multiplet in the range of (δ 1.446 – 1.518ppm) is assigned to methylene protons next to end methyl group.

(iv) A multiplet in the range of (δ 1.792 - 1.862ppm) shows the existence of $-CH_2$ and its neighboring $–OCH_2$- group in 12OBA [23].

(v) A triplet at δ 4.043ppm shows of $–OCH_2$- protons of 12OBA.

(vi) A multiplet in the range of δ 6.673 - 8.081ppm is assigned to the aromatic protons of ABA+12OBA HBLC mixture.

(vii) A singlet at δ 7.284ppm is assigned [24] to the solvent ($CDCl_3$).

Spectral studies like FT-IR and [1]H NMR confirm the H-bond formation and the molecular environment of ABA+12OBA HBLC mixture in the solid phase.

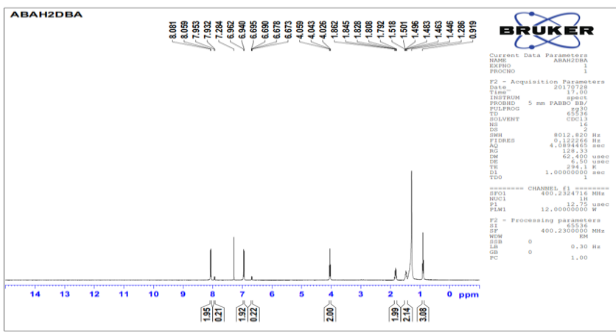


Fig. 3 [1]H NMR Studies of ABA+12OBA mixture.

C Optical studies: Mesophases Variance of

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ABA+12OBA HBLC mixture

Generally, LC is made up of small organic molecules with specific geometric shapes. LC appears an isotropic fluid phase, which is having short range positional molecular order and orientational disorder of molecules. The optically uniaxial phase is nematic whereas tilted smectic phase is optically biaxial. Nematic phase of the calamitic LC possess symmetry of T(3) x D∞h. Smectic LCs have molecular structure layer and clear interlayer spacing.

Compound	Mesophase Variance	Method	Cycle	Unit	Crystal-Melt	Nematic	Smectic X	Smectic C	Smectic F	Crystal
ABA+12OBA (1:1)	NC	POM	Heating	°C	94.6	131.7	121.3	*	*	
	NXCF		Cooling	°C		131.5	127.3	79.2	64.5	49.6
	NC	DSC	Heating	°C (J/g)	93.2 (178.01)	130.6 (9.73)	120.5 (5.09)	*	*	
	NXCF		Cooling	°C (J/g)		133.2 (2.39)	126.5 (4.14)	78.6 (6.52)	64.9 (26.53)	48.9 (59.37)

Table 2: Mesophase transition temperature/enthalpy values (J/g) of ABA+ 12OBA hydrogen bonded LC mixture.

The present HBLC mixture (ABA+ 12OBA) is taken in mole ratio of 1:1. HBLC mixture is highly stable at room temperature ~30°C and the same are melting at ~95 °C. G.W gray et al reported [25] the dissimilar traditional textures. Chemical stability and thermal stability of the ABA+12OBA mixture is confirmed through continual thermal scanning via POM and DSC. The present HBLC mixture shows nematic and smectic phases. Mesophase transition temperatures are presented in Table 2. As well as its corresponding mesophases textures are shown in Fig. 4.

On heating, ABA+12OBA mixture exhibit two phases such as nematic and smectic C. On cooling this mixture shows four phases like, nematic with droplet four brush texture (Fig. 4a, 4b) at 133.5°C and 131.5° C. Followed by nematic four brush threaded texture a finger-print texture of SmX at 127.3°C (Fig. 4c), broken focal conic mesophase texture of SmC at 79.2° C (Fig. 4d) and checkered board mesophase texture of SmF at 64.5° C (Fig. 4e). Mesophases sequence of ABA+12OBA is given by,

Iso ⇌ Nematic ⇌ Smectic X ⇌ Smectic C ← Smectic F ← Crystal.

In general, nematic phase have long range orientational where as positional order is observed as short range (i.e. rod-like molecules). However, presence of defect in the nematic LC, the director n(r) may not distinct. Due to disclination [26] in nematic phase line defects are observed in ABA+12OBA HBLC mixture.

Fig. 4a and 4b clearly show two and four brushes defect which is due to the disclination indicated to the breakup of the molecular symmetry.

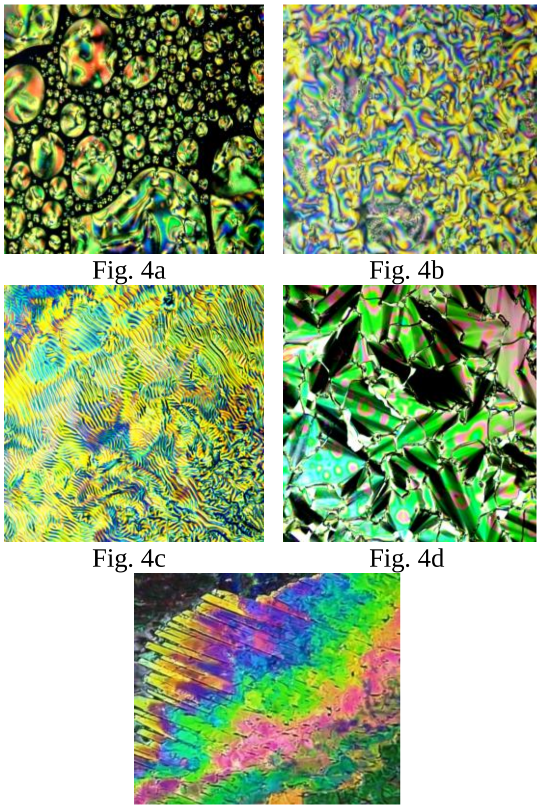

Fig. 4a Fig. 4b Fig. 4c Fig. 4d Fig. 4e

Fig. 4 Mesogenic phases in ABA+12OBA HBLC mixture.

Fig. 4c shows the fully grown Sm X phase with stabilized finger-print texture. This mesophase is originated from four brush threaded nematic texture as shown in Fig. 4b. The finger-print region of Sm X mesophases canal span width increases whereas decreasing the mesophase temperature. Also, Sm C and Sm F phases are induced. The dipole moment perpendicular to the lengthy molecular axis is helped to the form smectic phases. Due to breaking of symmetry in Sm C, Sm X, molecular layers are tilted. Sm F (Fig. 4d) phase is having short range hexagonal molecular order with no long range association between the molecular layers.

D Thermal studies (DSC)

DSC thermogram peaks are acquired from the heating (endothermic) and cooling (exothermic) cycles for the present HBLC mixture. Mesophase transition temperature and their enthalpy value are presented in Table 2. Fig. 5 shows the DSC thermogram of ABA+12OBA. ABA+12OBA HBLC mixture, heating cycle (Fig. 6) shows three peaks, such as crystal to melt at 93.2°C (peak a), smectic X phase at 120.5°C (peak b) and nematic phase at 130.6°C (peak c).

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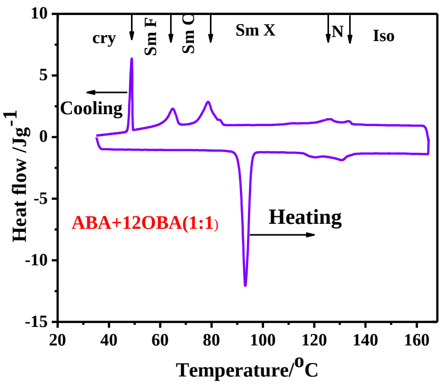

Fig. 5 DSC thermogram for ABA+12OBA HBLC mixture.

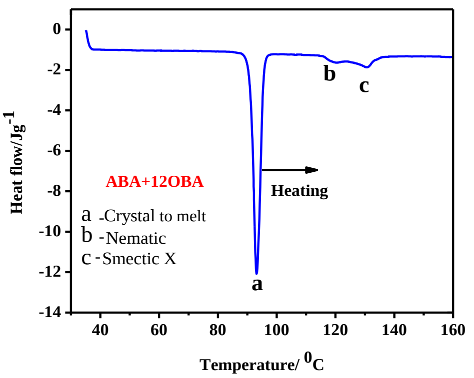

Fig. 6 DSC thermogram for ABA+12OBA HBLC mixture during heating cycle.

During cooling cycle, ABA+12OBA mixture (Fig. 7) exhibit five peaks such as, nematic phase at 133.2°C, smectic X phase at 126.5°C, smectic C phase at 78.6°C, smectic F phase at 64.9°C and crystal at 48.9°C. The span width of nematic is identified as 6.7, smectic X is 47.9, smectic C is 13.7 and smectic F is 16. Thermal stability of nematic, Sm X, Sm C and Sm F is calculated as 869, 4912, 982 and 1820 respectively. The increased stability of individual phase is noticed while the span width increasing.

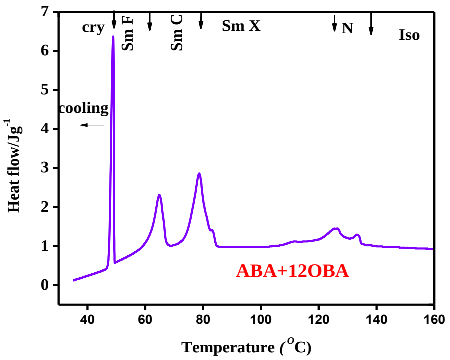

Fig. 7 DSC thermogram for ABA+12OBA HBLC mixture during cooling cycle.

Thermal span width and stability of Sm X shows high value as compared to the other phases. Smectic phases (Sm X, Sm C and Sm F) are noted as 1st order transition by their higher enthalpy values (Table 2). It is clear that the induced Sm X is tilted phase with higher enthalpy values.

IV. CONCLUSION

Hydrogen bonded ABA+12OBA mixture has been successfully synthesized and characterized. It is observed that the H-bond formation by intermolecular interaction influence the thermal span of mesogenic range in the present ABA+12OBA HBLC mixture. The induced Sm X is analyzed through POM and DSC studies. Extended mesogenic width and its thermal stability factor have been described. In addition to that the, nematic mesophase defect are also explained in the present work.

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