Physica B 406 (2011) 4139–4144

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Thermally controlled optical shutter in an inter-molecular hydrogen bonded liquid crystal

V.N. Vijayakumar, M.L.N. Madhu Mohan*

Liquid Crystal Research Laboratory (LCRL), Bannari Amman Institute of Technology, Sathyamangalam 638401, India

ARTICLE INFO

Article history:
Received 8 September 2010
Received in revised form
3 August 2011
Accepted 4 August 2011
Available online 11 August 2011

Keywords:
Liquid crystals
Chemical synthesis
Phase transitions
Optical properties

ABSTRACT

Novel homologs series of supra-molecular liquid crystals have been isolated. Hydrogen bond is formed between mandelic acid (MD) and various homologs of p-*n*-alkyloxy benzoic acids (nOBA) and has been confirmed by FTIR studies. Optical polarizing microscopic observations show that all these materials exhibit rich liquid crystallinity with various mesophases. Phase transition temperatures and enthalpy values are experimentally evaluated by DSC studies and the phase diagram of homologous series has been constructed. An interesting feature is the observation of thermally controlled reversible optical shuttering action in one of the homolog, wherein with the increment of temperature the homeotropic texture changes to homogenous texture of smectic F. Thus, this optical shuttering phenomenon is reversible. Optical tilt angle data of two homologs have been fitted to power law equation and it is found that the mean field theory prediction is valid. The light intensity profile in homeotropic region of smectic F in one complex has been experimentally analyzed and a steep sudden decrement of the intensity of light manifesting the distortion of the molecular alignment is experimentally found.

1. Introduction

Liquid crystals science is gaining importance in the last few decades. Among the various types of liquid crystals thermotropic liquid crystals form an exclusive class. Many research groups [1–4] around the globe are involved in these materials, which are being used in display device applications. For the formation of liquid crystalline materials through hydrogen bonding interactions, complementarity of the interacting components coupled with the directionality of hydrogen bonds is the main factor [5–8] contributing to the exhibition of liquid crystallinity. The first ever hydrogen bonded liquid crystalline material has resulted from the dimerization of aromatic p-*n* alkyloxy carboxylic acids (nOBA) [9,10]. There are reports in the literature [11,12] that to obtain a mesogenic hydrogen bonded liquid crystal it is enough if one of the compounds exhibits mesogenic properties. It is a great surprise to note that a mesogenic hydrogen bonded liquid crystal (HBLC) can be formed through two non-mesogenic compounds [13,14] by hydrogen bonding. Room temperature liquid crystals are derived [15,16] from the interaction of stilbazole derivatives with several mono/dicarboxylic acids. Kato and his group [17–21] did extensive work on synthesis and characterization of various types of HBLC. In the recent past, many groups [16–19] worked on HBLC due to their ease of synthesis, abundant availability of various acceptor and donor functional groups and versatility for commercial applications. For a liquid crystalline material to be exploited for commercial applications, it should possess a large magnitude of tilt angle, large thermal range of smectic C phase and optimum response time. Another interesting application of these materials is in the area of light modulation. Thermotropic liquid crystalline materials are reported [22] in the literature to exhibit optical shuttering action and light modulating applications.

Design, synthesis and characterization of supra-molecular materials that can be used for applicational purposes is a challenging task. These hydrogen bonded materials can be used for applications only if they possess a phase that can be tuned by an external stimulus like an electric or thermal field. The design of the molecular structure helps in a proper molecular alignment of the phase, which plays a pivotal role in ascertaining the extent of utility of the mesogen. With our previous experience [23–30] in synthesis and characterizing of various types of liquid crystals and with the above aims, novel series of hydrogen bonded mesogens are synthesized. Light modulation and optical shuttering action can be realized with proper design of the mesogens. In the present work thermally controlled optical shuttering action has been examined in one of the mesogens, which can be exploited for commercial applications.

2. Materials and methods

The p-*n*-alkyloxy benzoic acids (*n*OBA) and mandelic acid are supplied by Sigma Aldrich, Germany, and all the solvents used

---

* Corresponding author. Tel.: +91 9442437480; fax: +91 4295 223 775.
E-mail address: mln.madhu@gmail.com (M.L.N. Madhu Mohan).

0921-4526/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2011.08.014

were of HPLC grade. Inter-molecular hydrogen bonded mesogens are synthesized by the addition of one mole of p-*n*-alkyloxy benzoic acids (*n*OBA) with 1 mole of mandelic acid to N,N-dimethyl formamide (DMF). Further, they are subjected to constant stirring for 12 h at ambient temperature (30 °C) till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF are then recrystallized with dimethyl sulfoxide (DMSO) and the yield varied from 75% to 90%. Yield of higher homologs complexes are observed to be more (90%) compared to their lower counterparts (75%). The molecular structure of the present homologous series of p-*n*-alkyloxy benzoic acids with mandelic acid is depicted in Fig. 1, where *n* represents the alkyloxy carbon number. The temperature control of the liquid crystal cell is equipped by Instec HCS402-STC 200 temperature controller (Instec, USA) to a temperature resolution of ±0.1 °C. This unit is interfaced to a Pentium computer by IEEE-STC 200 to control and monitor the temperature. Optical textural observations are made with a Nikon polarizing microscope equipped with Nikon digital CCD camera system with 5 mega pixels and 2560 × 1920 pixel resolutions. The liquid crystalline textures are processed, analyzed and stored with the aid of ACT-2U imaging software system. The liquid crystal sample is filled by capillary action in its isotropic state into a commercially available (Instec, USA) polyamide buffed cell with 4 μm spacer. Silver wires are drawn as leads from the cell. The optical extinction method is used for calculating optical tilt angle. The light intensity profile has been experimentally analyzed by controlling the temperature and the intensity of the light from the liquid crystal sample is measured by a photodiode (TSL 252) connected to a 6½ digit digital multimeter (Keithley 2100). The transition temperatures and corresponding enthalpy values are experimentally obtained by differential scanning calorimetry (DSC; Shimadzu DSC-60).

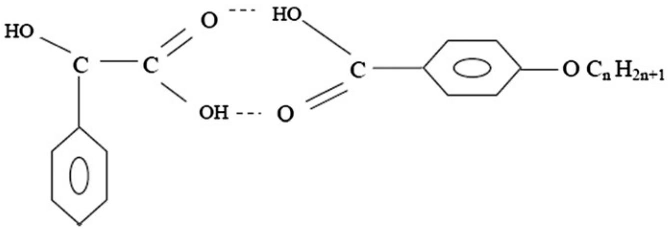

Fig. 1. Molecular structure of MD+*n*OBA inter-hydrogen bonded complex.

3. Results and discussion

All the mesogens isolated under the present investigation are white crystalline solids and are stable at room temperature. They are insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, and benzene and dichloro methane. However, they show a high degree of solubility in coordinating solvents like dimethyl sulfoxide (DMSO) and pyridine. All these mesogens melt at specific temperatures below 115 °C (Table 1). They show high thermal and chemical stabilities when subjected to repeated thermal scans performed during polarizing optical microscope (POM) and DSC studies.

3.1. Phase identification

The observed phase variants, transition temperatures and corresponding enthalpy values obtained by DSC in cooling and heating cycles for various homologous complexes are presented in Table 1.

3.2. Infrared spectroscopy (FTIR)

Infrared spectra of free p-*n*-alkyloxy benzoic acid, mandelic acid and their inter-molecular H-bonded complexes are recorded in the solid state (KBr) at room temperature. As a representative case, Fig. 2 illustrates the FTIR spectra of the hydrogen bonded

Table 1
Comparison of transition temperatures obtained by various techniques.

Carbon	Phase variance	Technique	Crystal to melt	N	C	F	G	Crystal
5	F	DSC (H)	108.8 (115.68)			#		
		DSC (C)				107.6 (37.54)		84.6 (48.65)
		POM (C)				108.1		84.9
6	NF	DSC (H)	95.9 (79.0)	#		102.0 (79.0)		
		DSC (C)		109.4 (1.03)		93.6 (36.85)		79.1 (34.11)
		POM (C)		109.8		93.9		79.4
7	NF	DSC (H)	93.5 (58.25)	#		104.8 (merged)		
		DSC (C)		108.7 (4.48)		87.5 (6.70)		72.4 (28.02)
		POM (C)		109.2		89.9		72.7
8	NFG	DSC (H)	75.1 (26.97)	#		106.9 (37.85)	100.7 (18.30)	
		DSC (C)		109.2 (1.25)		94.5 (63.3)	90.3 (Merged)	50.3 (20.34)
		POM (C)		109.6		94.9	90.7	50.6
9	NFG	DSC (H)	94.1 (58.55)			106.8 (3.78)	#	
		DSC (C)		105.1 (3.00)		103.0 (8.57)	89.3 (17.98)	81.8 (44.46)
		POM (C)		105.5		103.4	89.8	82.1
10	NCF	DSC (H)	86.30 (37.22)	#	#	95.8 (19.83)		
		DSC (C)		108.8 (3.52)	100.0 (4.30)	90.6 (58.78)		72.9 (36.52)
		POM (C)		109.2	100.3	90.9		73.2
11	NCFG	DSC (H)	97.4 (58.23)	110.8 (merged)	#	#	#	
		DSC (C)		113.9 (1.10)	101.9 (12.70)	87.0 (14.58)	72.4 (8.03)	62.1 (27.10)
		POM (C)		114.2	102.3	87.5	72.9	62.5
12	NC	DSC (H)	95.3 (83.74)	111.9 (merged)	#			
		DSC (C)		108.7 (4.34)	86.9 (21.94)			70.7 (49.22)
		POM (C)		109.1	87.3			71.1

#, monotropic transition; H, heating run; C, cooling run.

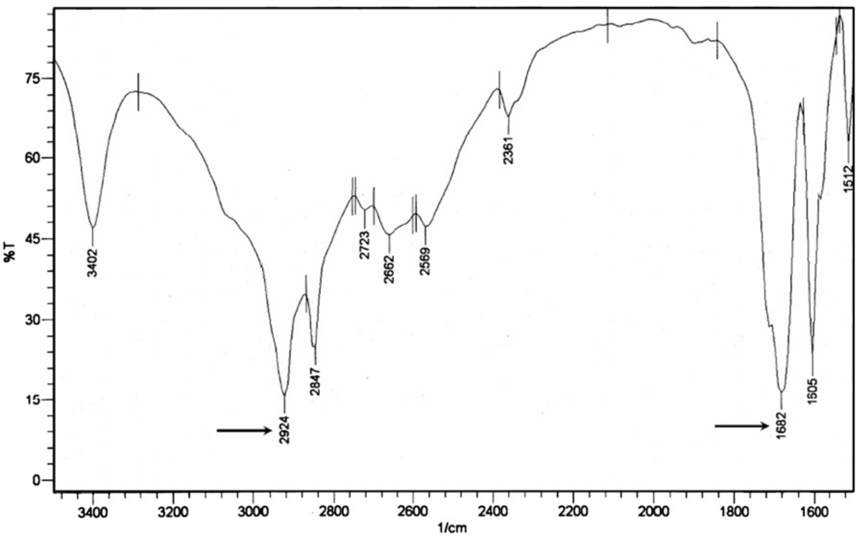

Fig. 2. FTIR spectra of MD+9OBA inter-hydrogen bonded complex.

complex of MD+9OBA in solid state at room temperature (31 °C). The solid state spectra of free alkyloxy benzoic acid are reported [31] to have two sharp bands at 1685 cm^{-1}and at 1695 cm^{-1} due to the frequency ν(C=O mode). The doubling feature of this stretching mode confirms the dimeric nature of alkyloxy benzoic acid at room temperature [31]. Further, in the present MD+9OBA hydrogen bonded complex a band appearing at 2924 cm^{-1}is assigned to ν(O–H mode) of the carboxylic acid group.

The doubling nature of ν(C=O mode) may be attributed to the dimeric nature of the acid group at room temperature [31]. The corresponding spectrum of solution state (chloroform) shows a strong intense band, suggesting the existence of monomeric form of benzoic acid. A noteworthy feature in the spectra of MD+9OBA complex is the appearance of a broad band at 1682 cm^{-1} and non-appearance of the doubling nature of ν(C=O mode) of benzoic acid moiety. This clearly suggests that the dimeric nature of the benzoic acid dissociates and prefers to exist in a monomeric form upon complexation.

3.3. *MD+nOBA homologous series*

The mesogens of the mandelic acid and alkyloxy benzoic acid homologous series are found to exhibit characteristic textures [32], viz., nematic (Schlieren threaded), smectic C (marble threaded), smectic F (checkered board texture) and smectic G (multi-colored mosaic texture). The general phase sequence of the mandelic acid and alkyloxy benzoic acids in the cooling run can be shown as

Isotropic→Sm F→Crystal (MD+5OBA)

Isotropic→N→Sm F→Crystal (MD+6OBA, MD+7OBA)

Isotropic→N→Sm F→Sm G→Crystal (MD+8OBA, MD+9OBA)

Isotropic→N→Sm C→Sm F→Crystal (MD+10OBA)

Isotropic→N→Sm C→Sm F→Sm G→Crystal (MD+11OBA)

Isotropic→N→Sm C→Crystal (MD+12OBA)

3.4. *DSC studies*

DSC thermograms are obtained in heating and cooling cycles. The sample is heated at a scan rate of 10 °C/min and held at its isotropic temperature for 1 min so as to attain thermal stability. The cooling run is performed with the same scan rate of 10 °C/min. The respective equilibrium transition temperatures and corresponding enthalpy values of the mesogens of the homologous series are listed separately in Table 1. POM studies also confirm these DSC results along with the results of monotropic transition.

As a representative case, the phase transition temperatures and enthalpy values of nonyloxy benzoic acid and mandelic acid mesogen (MD+9OBA) are discussed. Fig. 3 illustrates the thermogram of MD+9OBA hydrogen bonded complex recorded at a scan rate of 10 °C/min for the heating and cooling runs. The cooling run of DSC thermogram shows four distinct transitions, namely isotropic to nematic, nematic to smectic F, smectic F to smectic G and smectic G to crystal with transition temperatures 105.1, 103.0, 89.3 and 81.8 °C and corresponding enthalpy values 3.00 J/g, 8.57 J/g, 17.98 J/g and 44.46 J/g, respectively, while in the heating cycle two distant transitions, namely crystal to melt and melt to smectic F are obtained at 94.1 °C and 106.8 °C with corresponding enthalpy values of 58.55 J/g and 3.78 J/g, respectively. Nematic and smectic G are observed to be monotropic transitions in the heating run.

All these transition temperatures of the present homologous series concur with those of optical polarizing microscopic studies.

3.5. *Phase diagram of MD+nOBA homologous series*

The phase diagram of pure p-*n*-alkyloxy benzoic acid is reported [23] to compose of three phases, namely nematic, smectic C and smectic G. The phase diagram of mandelic acid with p-*n*-alkyloxy benzoic acid complexes is depicted in Fig. 4. A careful observation of Fig. 4 reveals the following points:

a) The phase diagram is composed of four phases namely nematic, smectic C, smectic F and smectic G.
b) Nematic phase is present in all homologs while the higher ordered smectic F phase is observed in all homologs except MDA+12OBA.
c) It is interesting to note that MD+11OBA exhibits all the four phases (NCFG), while MD+5OBA has only one phase (F).
d) Smectic F phase of MD+11OBA exhibits both homogenous and homeotropic alignments.
e) In general, MD+5OBA has the smallest mesogenic thermal range while MD+8OBA has the largest mesogenic thermal range.
The lower homologs (MD+*n*OBA, $n=5$–7) exhibit mono/bi phase variance with the phase being either nematic or smectic F or both.

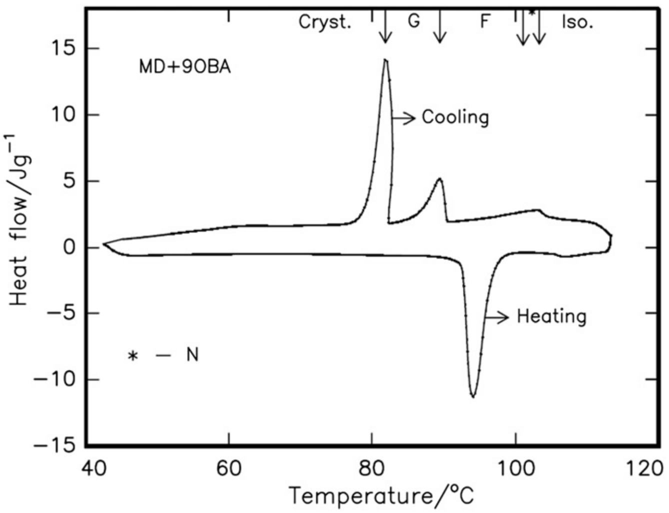

Fig. 3. DSC thermogram of MD+9OBA inter-hydrogen bonded complex.

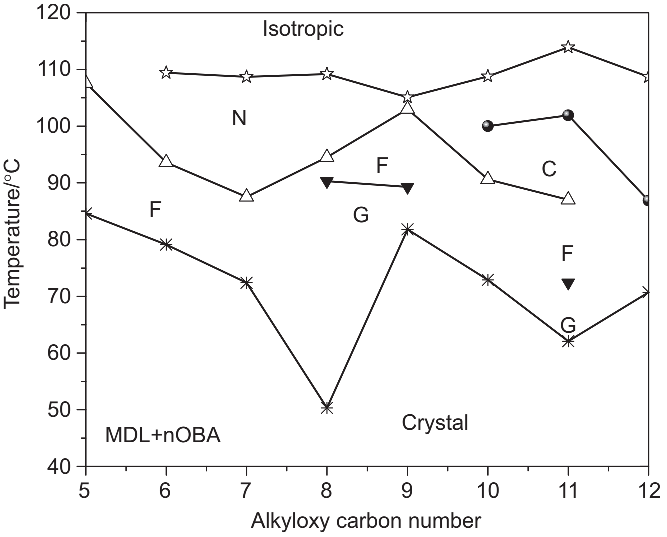

Fig. 4. Phase diagram of MD+*n*OBA homologous series.

f) In contrast, the higher homologs (MD+*n*OBA, n=7–11) exhibit three/four phase variance with the phases being nematic, smectic C, smectic F and smectic G.

g) New phases are induced at regular increment of alkyloxy carbon number. As an example, in MD+6OBA nematic phase is induced and in MD+8OBA smectic G phase is induced while in MD+10OBA smectic C phase is induced

3.6. *Optical tilt angle studies*

For the hydrogen bonded MD+10OBA and MD+11OBA complexes, optical tilt angles have been experimentally measured by the optical extinction method [33] in corresponding smectic C phase. From Fig. 5 it is observed that the tilt angle increases with decreasing temperature and attains a saturation value, which is in accordance with the mean field theory [34]. The saturated values of the tilt angle in MD+10OBA and MD+11OBA are observed to be around 20°. These large magnitudes of the tilt angle are attributed [16] to the direction of the soft covalent hydrogen bond interaction, which spreads along molecular long axis with finite inclination.

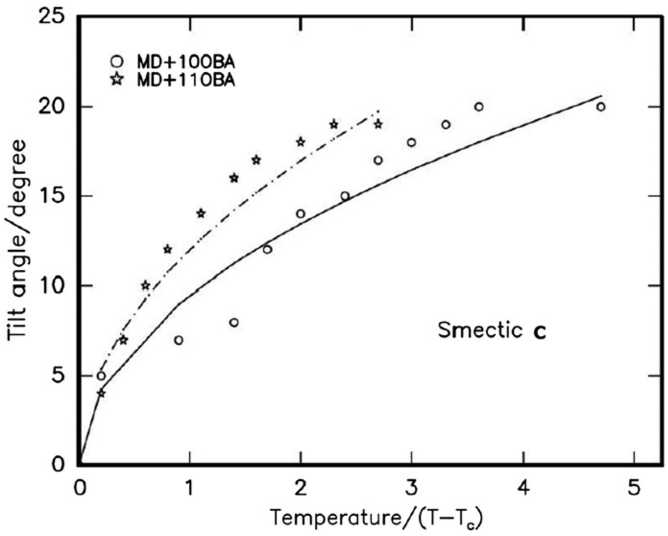

Fig. 5. Temperature variation of tilt angle in smectic C phase of MD+10OBA and MD+11OBA. Dotted and solid lines denote the fit.

Tilt angle is a primary order parameter [33,35] in tilted phases, viz., smectic C. The temperature variation is estimated by fitting the observed data of $\theta(T)$ to the relation

$$\theta(T)=A(T-T_C)^{\beta} \tag{1}$$

The critical exponent β value estimated by fitting the data of $\theta(T)$ to the above Eq. (1) is found to be 0.50 in both the complexes and agrees with the mean field [34] prediction. The value of the constant A is found to be 9.5 and 12 for MD+10OBA and MD+11OBA, respectively. The dotted and solid lines in Fig. 5 depict the fitted data. Further, the agreement of β with mean field value shows the long-range interaction of transverse dipole moment for the stabilization of tilted smectic C phase.

4. Thermally controlled optical shuttering action

Optical shutters are usually realized by the application of external electrical stimulus [26,36] to the liquid crystalline sample. The orientation of the molecules with respect to the increasing thermal field gives rise to gradual optical extinction, which is referred to as optical shuttering action.

In the present compound (MD+11OBA) the optical shuttering action is observed with variation of thermal field. In the sense that when the liquid crystal sample is cooled from isotropic to smectic F, in the smectic F phase the optical light intensity is observed to fall gradually in small steps with the decrease of temperature.

It is interesting to note a homeotropic like alignment in smectic F phase of MD+11OBA complex which has been established by various techniques like DSC thermogram, textural observations, optical tilt angle and light intensity studies. Thus, this mesogen can be used in optical shutter applications. The following sections describe in detail about the results obtained.

4.1. *DSC thermogram of MD+11OBA*

The DSC thermogram of MD+11OBA is illustrated in Fig. 6. From the cooling run of the DSC thermogram all the phase transitions exhibited by the compound, viz., isotropic to nematic, nematic to smectic C, smectic C to smectic F (homogeneous), smectic F (homogenous) to smectic F (homeotropic), smectic F (homogenous) to smectic G and smectic G to crystal with transition

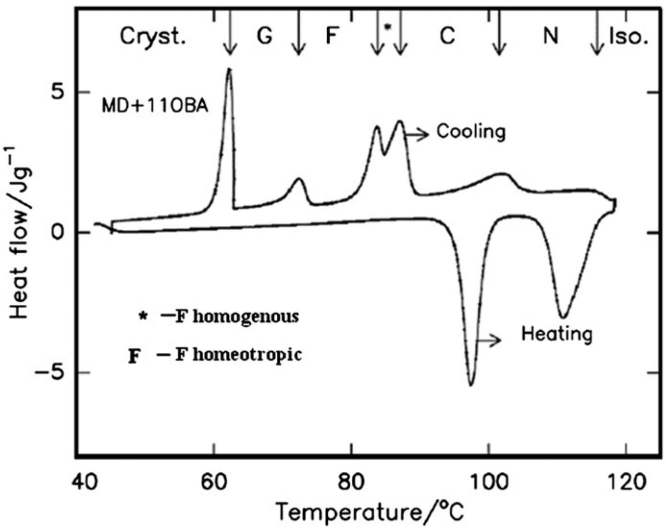

Fig. 6. DSC thermogram of MD+11OBA inter-hydrogen bonded complex.

temperatures 113.9, 101.9, 87, 85.1, 72.4 and 62.1 °C with corresponding enthalpy values 3.11 J/g, 12.70 J/g, 14.58 J/g, merged, 8.03 J/g and 27.10 J/g, respectively, are clearly identified as peaks at various temperatures. An interesting observation is that the transition from homeotropic to homogenous alignment smectic F is clearly identified as a prominent peak in the DSC thermogram.

4.2. *Optical polarizing microscopic textural observation*

As discussed above the compound MD+11OBA exhibits rich phase polymorphism with phases like nematic, smectic C, smectic F and smectic G. Checkered board texture is a token of evidence for the smectic F phase.

When this sample is cooled from isotropic, various phase transitions are observed. The Schlieren threaded texture of nematic is transformed to marble threaded texture of smectic C. On further cooling the marble threaded texture changes to a dark region, which is designated as the homeotropic region of smectic F (Plate 1). With further decrement of temperature this homeotropic region of smectic F paves way for homogenous region of smectic F with a texture of checkered board (Plate 2).

This serves as a strong textural evidence to suggest the presence of homeotropic and homogenous textures in smectic F.

4.3. *Intensity profile of the optical texture*

The sample MD+11OBA is filled in a commercially available buffed cell (Instec) and silver leads are drawn for contact. The intensity profile in homeotropic region of smectic F has been experimentally analyzed by varying the thermal field and the intensity of the light from the liquid crystal sample is measured by a photo-diode (TSL 252). As temperature is decremented in small steps, the variation of the intensity of the texture is noted at each step and plotted as shown in Fig. 7. During the transition from homogenous region to homeotropic region of biaxial smectic F there is a steep sudden decrement of the intensity of light, manifesting the distortion of the molecular alignment. In the homeotropic region of smectic F, which is referred to as the optical shutter, the optical profile is completely vanished. As temperature is further decreased, the homogenous region of smectic F reappears. Thus the intensity of light again starts to increase as shown in Fig. 7. Thus the phase variance in the cooling run can be given as

Sm F (homogenous)→Sm F (homeotropic)→Sm F (homogenous)

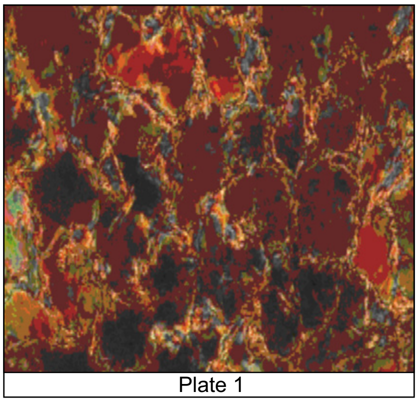

Plate 1. Homeotropic texture of smectic F phase of MD+11OBA. (All the textures are digitally recorded with a magnification of 10 × .)

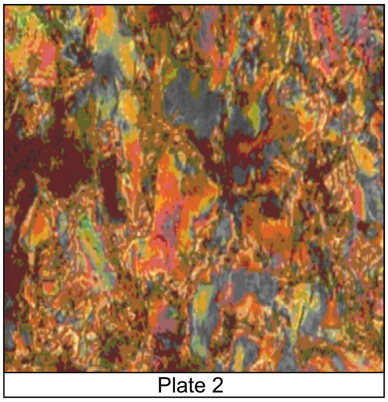

Plate 2. Homogenous texture of smectic F phase of MD+11OBA. (All the textures are digitally recorded with a magnification of 10 × .)

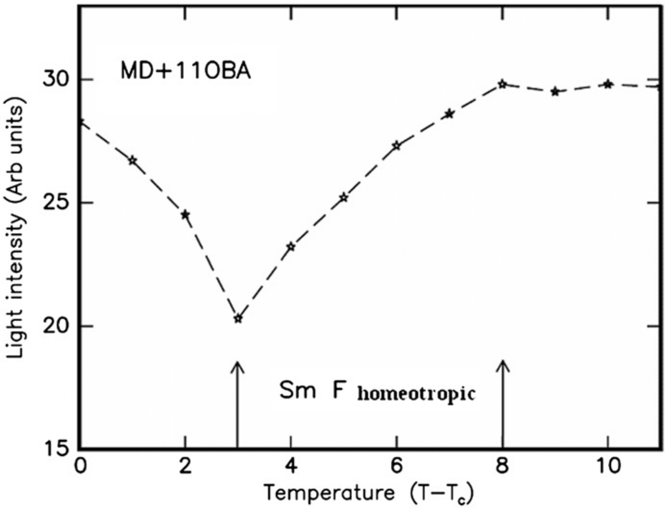

Fig. 7. Temperature variation of intensity in the smectic F phase of MD+11OBA.

It has been recently reported [36] that in the biaxial phase the Schlieren texture will not be completely extinct since the field does not affect the distribution of second director normal to the main director. The present result is in concurrence with the above published observation. Thus the liquid crystal behaves as an optical shutter (Plate 1). Hence this HBLC may be used as a light modulator.

5. Conclusions

The central idea of designing hydrogen bonded liquid crystals is towards the development of new complementary components that can be utilized for commercial applications. Homologous series of eight complexes have been investigated. All the samples are found to be mesogenic. As expected increasing the chain length favored occurrence of smectic C phase in higher homologs, quenching the thermal span of smectic F. Extended chain length of the present series influenced the steep fall of isotropic temperatures compared to the pure benzoic acids. One of the synthesized complexes, MD+11OBA, exhibits thermally controlled reversible optical shuttering action.

Acknowledgments

The authors acknowledge the financial support rendered by Department of Science and Technology (DST), New Delhi, and infrastructural support provided by Bannari Amman Institute of Technology.

References

[1] R.B. Meyer, L. Liebert, L. Strezelecki, P. Keller, J. Phys. Lett 30 (1975) 69.
[2] H. Kelker, R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980.
[3] L. Yu, Liq. Cryst. 14 (1993) 1303.
[4] C.M. Paleos, D. Tsiourvas, Liq. Cryst. 28 (2001) 1127.
[5] C.M. Paleos, D. Tsiourvas, Angew. Chem. Int. Ed. Engl. 34 (1995) 1696.
[6] T. Kato, Supramol. Sci. 3 (1996) 53.
[7] C.T. Imrie, Trends Polym. Sci. 3 (1995) 22.
[8] A. Treybig, C. Dorscheid, W. Weissflog, H. Kresse, Mol. Cryst. Liq. Cryst. 260 (1995) 369.
[9] G.W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, London, 1962.
[10] H. Kelker, R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980.
[11] Z. Sideratou, C.M. Paleos, A. Skoulios, Mol. Cryst. Liq. Cryst. 285 (1995) 19.
[12] Z. Sideratou, D. Tsiourvas, C.M. Paleos, A. Skoulios, Liq. Cryst. 22 (1997) 51.
[13] F. Hentrich, S. Diele, C. Tschierske, Liq. Cryst. 17 (1994) 827.
[14] Y. Kobayashi, Y. Matsunage, Bull. Chem. Soc. Jpn. 60 (1987) 3515.
[15] Y.Q. Tian, X.H. Xu, Y.Y. Zhao, X.Y. Tang, T.J. Li, X.M. Huang, Mol. Cryst. Liq. Cryst. 309 (1998) 19.
[16] B. Gundogan, K.B. Binnemans, Liq. Cryst. 27 (2000) 851.
[17] T. Kato, J.M.J. Frechet, Macromol. Symp. 98 (1995) 311.
[18] T. Kato, H. Adachi, A. Fujishima, J.M.J. Frechet, Chem. Lett. (1992) 265.
[19] T. Kato, J.M.J. Frechet, J. Am. Chem. Soc. 111 (1989) 8533.
[20] T. Kato, H. Kihara, T. Uryu, S. Ujiie, K. Iimura, J.M.J. Frechet, U. Kumar, Ferroelectrics 148 (1993) 161.
[21] T. Kato, T. Uryu, F. Kaneuchi, C. Jin, J.M.J. Frechet, Liq. Cryst. 14 (1993) 1311.
[22] T. Kato, Handbook of Liquid Crystals, Wiley–VCH, Weinheim, 1998.
[23] V.N. Vijayakumar, K. Murugadass, M.L.N.Madhu Mohan, Mol. Cryst. Liq. Cryst. 515 (2009) 39.
[24] X. Han, S. Zhang, R.A. Shanks, D. Pavel, React. Funct. Polym. 68 (2008) 1097.
[25] L.G. Chen, R. Shanks, Liq. Cryst. 34 (2007) 1349.
[26] V.N. Vijayakumar, M.L.N.Madhu Mohan, Solid State Commun. 149 (2009) 2090.
[27] V.N. Vijayakumar, M.L.N.Madhu Mohan, Solid State Sci. 12 (4) (2010) 482.
[28] X. Han, X. Wei, X. Wang, R.A. Shanks, Adv. Mater. Res. (2011) 152 and 284.
[29] V.N. Vijayakumar, M.L.N.Madhu Mohan, Braz. J. Phys 39 (2009) 601.
[30] V.N. Vijayakumar, M.L.N.Madhu Mohan, Physica B (2010) 4418.
[31] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Co-ordination Compound, Interscience, New York, 1978.
[32] G.W. Gray, J.W.G. Goodby, Smetic Liquid Crystals—Textures and Structures, Leonard Hill, London, 1984.
[33] C. Noot, S.P. Perkins, H.J. Coles, Ferroelectrics 244 (2000) 331.
[34] H.E. Stanley, Introduction to Phase Transition and Critical Phenomena, Clarendon, Press, 1971.
[35] P.G. de Gennes, The Physics of Liquid Crystals, Oxford Press, London, 1974.
[36] K.V. Le, M. Mathews, M. Chambers, J. Harden, Q. Li, H. Takezoe, A. Jakli, Phys. Rev. E 79 (2009) 030701.