

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 877 (2008) 50-55

www.elsevier.com/locate/molstruc

# Synthesis and mesomorphic properties of chiral liquid crystal dimers containing lactate units

S. Senthil <sup>a,\*</sup>, D. Srividhya <sup>c</sup>, S. Manjunathan <sup>c</sup>, S. Thirumaran <sup>d</sup>, S.-L. Wu <sup>b</sup>

<sup>a</sup> Department of Chemistry, Anna University, Chennai 600 025, India

<sup>b</sup> Department of Chemical Engineering, Tatung University, 40 Chungshan N. Road, 3rd Section, Taipei 104, Taiwan, ROC

<sup>c</sup> Department of Chemistry, Sona College of Technology, Salem, Tamil Nadu, India

<sup>d</sup> Department of Chemistry, Annamalai University, Tamil Nadu, India

Received 1 April 2007; received in revised form 3 July 2007; accepted 11 July 2007 Available online 24 July 2007

# Abstract

A series of symmetrical chiral ferroelectric liquid crystal dimers viz., alkyl bis{(R)-2-[4-(4'-decyloxyphenyl)benzoyloxyphenoxy] propionates}, ABDBP-*n* (n = 6-10), containing lactate units were synthesized and characterized. The length of the methylene spacer was increased from 6 to 10 in between the two chiral carbons located at the inner side of dimer. All the synthesized dimers exhibited polymorphism by showing N<sup>\*</sup>, SmA<sup>\*</sup>, SmC<sup>\*</sup> and SmX<sup>\*</sup> (unidentified) mesophase sequence. The mesophases and their corresponding transition temperatures were identified by polarized microscopy and differential scanning calorimetric measurements. Electro-optic switching studies of these dimers in SmC<sup>\*</sup> phase has exhibited ferroelectric bistable switching characteristics with the maximum spontaneous polarization of about 60.74 nC cm<sup>-2</sup>. The tilt angles of the SmC<sup>\*</sup> phase was also measured to confirm the tilted phase characteristics.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ferroelectric liquid crystals; Mesomorphism; Electro optical properties; Liquid crystal dimmers; Chiral lactates

#### 1. Introduction

Liquid crystalline dimers claim their significant contribution towards the understanding of the mesomorphic behaviour of liquid crystalline polymers as well as low molecular weight liquid crystals [1–3]. The length and the type of spacer between two mesogenic units in twins provide more information about the appearance of polymorphism in liquid crystals [4,5]. Generally, in the case of liquid crystal dimers, groups attached to chiral center produce large variations on both mesomorphic and physical properties [7]. The effect of length and parity of the flexible spacer in form chirality of the chiral phase has also been reported in twins with the chiral centers located either at the free end of the molecule [6] or at the inner side of the molecule. Liquid crystals derived from lactic acid shows, interesting ferroelectric, antiferroelectric orders and V-shaped electro-optic switching properties [8-13]. In lactic acid derivatives, the chiral carbon placed near to the rigid core produces anticlinic phases, and further addition of the same type of chiral carbon produce only SmC\* phase with pronounced mesophase stability. This behaviour of chiral lactates tempts us to investigate the mesomorphic properties of liquid crystal dimers having chiral lactate units placed in between rigid rod units. Separation of chiral centers by methylene chain will help in understanding the behaviour of lactate units in producing polymorphic mesophases. This investigation deals with the synthesis of liquid crystal dimers containing chiral centers at the inner side of the molecule separated by methylene spacers. The effect of

<sup>\*</sup> Corresponding author. Tel.: +91 44 22203155; fax: +91 44 22200660. *E-mail address:* shendils@gmail.com (S. Senthil).

<sup>0022-2860/\$ -</sup> see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2007.07.022

the length of the spacer attached to the chiral center on the mesomorphic and physical properties of such dimers have been studied. The formula of the target molecule is depicted as mentioned below.

# 2.3. Preparation of materials

The starting chiral material, (R)-2-(4-hydroxyphenoxy)propionic acid, was purchased from Aldrich Chemical



# 2. Experimental

## 2.1. General synthetic procedure

The hydroxyl group of (R)-2-(4-hydroxyphenoxy)propionic acid, was protected by the benzyl group and was esterified with various aliphatic diols in presence of N,N-dicyclohexylcarbodiimide(DCC) and 4-(dimethylamino) pyridine (DMAP). The benzyl group was deprotected by using 10% palladium on carbon and cyclohexene. The resulting bisphenol was esterified with 4-(4'-alkoxyphenyl)benzoic acid using DCC and DMAP to get the target dimers. All the intermediates and final products were purified by column chromatography passing over silica gel and using dichloromethane as eluent. The detailed synthetic scheme is furnished in Scheme 1.

# 2.2. Characterization of materials

The chemical structures of the intermediates and the target materials were analyzed by nuclear magnetic resonance spectroscopy using Jeol EX-400 FTNMR spectrometer. Purity was checked by thin layer chromatography and further confirmed by elemental analysis using a Perkin-Elmer 2400 elemental analyzer. Transition temperatures and phase transition enthalpies were determined by differential scanning calorimetry using Perkin-Elmer DSC7 calorimeter at the heating rate of 5 °C min<sup>-1</sup>. Mesophases were identified by microscopic texture of the materials sandwiched between two glass plates by polarizing optical microscopy using a Nikon Microphot-FXA in conjunction with Instec HS1 hot stage.

The physical properties of ferroelectric SmC\* phase for the materials were measured in antiparallel aligned cells purchased from E.H.C Co. Japan. The spontaneous polarization (Ps) was measured by the triangular wave method [14]. The measurement of optical transmittance versus applied electric field was conducted using He–Ne laser (5 mW, 632.8 nm) as a probe beam [15,16] passing through the cell between crossed polarizers, whose axes were parallel and perpendicular to the smectic layer normal, was detected by a photodiode. The signals were detected by using HP54502A digital oscilloscope. The voltage applied to the cell was produced by an arbitrary wave form generator (AG1200) and was amplified by a homemade power preamplifier. Company with purity greater than 99%. 4-(4-decyloxyphenyl)benzoic acid were prepared by reported method elsewhere [17]. Thin layer chromatography was performed with TLC sheets coated with silica; spots were detected by UV irradiation. Silica gel (MN Kieselgel 60, 70–230 mesh) was used for column chromatography. The organic reagents and solvents dichloromethane, cyclohexene, ethanol and ethyl acetate were purified before use. The schematic synthetic procedures are depicted in the scheme and the representative synthetic procedures for HBDBP-n (n = 6) are described as follows. The value of 'n' indicates the number of methylene carbons placed between the two mesogens.

### 2.3.1. (R)-2-(4-Benzyloxyphenyloxy)propionic acid

(R)-2-(4-Hydroxyphenoxy)propionic acid (3.64 g, 0.02 mole) and potassium iodide (0.5 g) were dissolved in the solution of KOH (0.85 g, 0.021 mol), water (25 ml) and ethanol (150 ml). The mixture was heated to reflux. Benzyl chloride (2 g, 0.02 mol) was added drop wise in ethanol (50 ml). After complete addition, the reaction mixture was further refluxed for 15 h. The mixture was then cooled and acidified with dilute HCl. The white crystals formed were filtered and recrystallized using ethyl alcohol (Yield 80%).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>,  $\delta$  ppm): 1.63 (d, 3H, -\*CHCH<sub>3</sub>), 4.7 (q, 1H, -\*CH), 5.00 (s, 2H, -CH<sub>2</sub>-), 6.8-7.4 (m, 4H, ArH).

# 2.3.2. Hexyl bis[(R)-2-(4-benzyloxyphenyloxy)propionate]

(*R*)-2-(4-Benzyloxyphenyloxy)propionic acid (1.5 g, 0.006 mol) 1,6-hexanediol (0.56 g, 0.006 mol) and DMAP (0.12 g, 0.001 mol) were added to dry dichloromethane (25 ml). DCC (1.32 g, 0.0065 mol) was then added and the resulting mixture was stirred at room temperature for 3 h. Precipitated urea was removed by filtration. The solution was washed with 5% acetic acid ( $3 \times 50$  ml) and saturated NaCl ( $3 \times 50$  ml) followed by water. Organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was stripped out under reduced pressure. The product was purified by column chromatography using dichloromethane as eluent and recrystallized using ethanol yielding a white solid. Yield = 1.7 g.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>,  $\delta$  ppm): 1.5(d, 3H, -\*CHCH<sub>3</sub>), 1.45–1.46 (m, 8H, -CH<sub>2</sub>–), 4.62 (q, 1H, -\*CH), 5.02 (s, 2H, -OCH<sub>2</sub>), 6.8–7.42 (m, 4H, ArH).



Scheme 1. Scheme of the synthesis of chiral liquid crystals.

# 2.3.3. Hexyl bis[(R)-2-(4-hydroxyphenyloxy)propionate]

Bis[hexyl (R)-2-(4-benzyloxyphenyloxy)propionate] (1.56 g, 0.005 mol) was dissolved in a 1:1 mixture (25) of ethyl acetate:ethanol (95%). Cyclohexene (1 ml) was then added to the mixture and refluxed under slight nitrogen pressure. The course of the reaction was followed by TLC examination. After the completion of reaction, the solvents were removed under vacuum. The resulting product was purified by column chromatography over silica gel using dichloromethane and ethyl acetate mixture (V:V = 5:1) with an yield of 0.9 g (85%) of pure white solid. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>, δ ppm): 1.55 (d, 3H, -\*CHCH<sub>3</sub>), 1.44–1.46 (m, 4H, -CH<sub>2</sub>), 4.14 (q, 1H, -\*CH), 4.71 (t, 2H, -OCH<sub>2</sub>), 6.9-7.6 (m, 4H, ArH), 9.68 (s, 1H, -OH).

2.3.4. Hexyl bis{(R)-2-[4-((4'-decyloxyphenyl)benzoyloxy) phenoxy[propionate] (ABDBP-6)

Hexyl bis[(R)-2-(4-hydroxyphenyloxy)propionate] (0.25 g, 0.001 mol), 4-(4'-decyloxyphenyl)benzoic acid (0.35 g, 0.0011 mol) and DMAP (1.2 g) were added in dry dichloromethane (25 ml). DCC (0.31 g, 0.0015 mol) was then added and the resulting mixture was stirred at room temperature for one day. Precipitated materials were removed by filtration. The solvent was stripped out under reduced pressure. The product was purified by column chromatography using dichloromethane as eluent and recrystallized using ethanol giving a white solid. Yield = 0.55 g. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ ppm): 1.63 (d, 3H, -\*CHCH<sub>3</sub>), 0.8-2.17 (m, -CH<sub>2</sub>), 4.16 (q, 1H, -\*CH), 4.74 (t, 2H, -OCH<sub>2</sub>), 6.90-8.21 (m, ArH).

# 3. Results and discussion

#### 3.1. Mesomorphic properties

The mesophases and their corresponding phase transition temperatures observed were summarized in Table 1. It shows N\*, SmA\*, SmC\* and unidentified SmX\* phases on cooling (Fig. 1). SmA\* was obtained by the formation of focal-conic fan. SmC\* phase was characterized by the existence of broken focal conic textures. SmX\* phase was appeared as paramorphotic short grainy phase which is shown in Fig. 3. Liquid crystalline property of these phase confirmed by observing a very low enthalpy transition in DSC and by observing viscous fluidity while applying slight mechanical stress on glass plates. The polarized microscopic investigation of the compounds showed that the shorter methylene spacer chain compounds (ABDBP-6 and ABDBP-7) exhibit N\*, SmA\*, SmC\*, SmX\* mesophase sequence and compounds ABDBP-8 and ABDBP-9 exhibit SmA\*, SmC\*, SmX\* mesophase sequence, where as ABDBP-10 show SmA\* and SmX\* mesophases. A phase diagram as a function of transition temperatures was drawn (Fig. 2) which reveals that, the stability of the  $SmC^*$  phase was drastically reduced when 'n' increases as expected. In addition, increase of spacer between two core units produced suppression of multiple mesophases and enhance the stability of SmA\* mesophase. ABDBP-10 exhibited considerably wide SmA\* mesophase at about 103 °C.

# 3.2. Switching behaviour

The switching current behaviour of all the compounds was measured in a 5 µm homogeneous cell, under a triangle wave voltage with field frequency and amplitude 5  $V_{P-P}$ . It was observed that, compounds ABDBP-n (n = 6-9) show a single switching current response attributed to the formation of ferroelectric mesophase as represented by an example of ABDBP-8 in Fig. 2. Unidentified SmX\* mesophase formed in the samples were also investigated for its switching behaviour. But it fails to show the switching response indicated that, these phases are not tilted by nature.





Fig. 1. Plot of transition temperature as a function of spacer length on cooling.



Fig. 2. Switching behaviour of ABDBP-6 in SmC\* phase in  $5\,\mu m$  homogeneously aligned cell at the frequency 1 Hz.

# 3.3. Spontaneous polarization and tilt angle measurements

The magnitudes of the spontaneous polarizations (Ps) for ABDBP-n (n = 6-9) in the SmC<sup>\*</sup> phase are plotted in

Table 1

Mesophases, transition temperatures (°C) and enthalpies of transition (J/g, in square brackets) observed in the chiral liquid crystals

Compound name	Transition temperature (°C) <sup>a</sup>											
	M.P <sup>c</sup>	Cr		$\mathrm{SmX}^*$		$\mathrm{SmC}^*$		$SmA^*$		$N^*$		Iso
ABDBP-6	61.12 [2.314]	•	24.8 [2.23]	•	58.59 [1.95]	•	78.45 <sup>b</sup>	•	143.48 [6.86]	•	145.56 [3.99]	•
ABDBP-7	62.46 [3.189]	•	23.56 [3.08]	•	60.09 [1.25]	•	82.23 <sup>b</sup>	•	145.3 [1.68]	•	147.23 [9.75]	•
ABDBP-8	53.75 [11.52]	•	22.89 [3.78]	•	48.45 [0.93]	•	55.56 <sup>b</sup>	•	-	_	137.49 [3.09]	•
ABDBP-9	59.97 [8.40]	•	18.25 [2.36]	•	42.05 [0.76]	•	53.5 <sup>b</sup>	•	_	_	134.47 [7.91]	•
ABDBP-10	54.69 [8.36]	-	1.525 [2.90]	•	-	_	33.37 [2.07]	•	_	_	135.42 [8.81]	•

DSC thermograms obtained on cooling at 5 °C min<sup>-1</sup>.

<sup>a</sup> Values taken from DSC thermograms at cooling rate of 5 °C min<sup>-1</sup>. The values in brackets are correspond to enthalpy of the transition.

<sup>b</sup> Enthalpies were too small to calculate by the instrument.

<sup>c</sup> Melting points were measured on first heating cycle.



Fig. 3. Optical polarizing microscopic picture of ABDBP-7 at (a) 60  $^{\circ}C$  (SmC\*) and (b) 55  $^{\circ}C$  (SmX\*).



Fig. 4. Spontaneous polarization as a function of temperature of ABDBP-6–9 in SmC<sup>\*</sup> phase in 5  $\mu$ m cell.

Fig. 4. The Ps values steeply increases at the interface of transition from  $\text{SmA}^*-\text{SmC}^*$  phase and it gradually decreases before  $\text{SmC}^*-\text{SmX}^*$  transition. Highest Ps value was observed for ABDBP-6 (60.74 nC cm<sup>-2</sup>) and the lowest value was observed for ABDBP-9 (4.43 nC cm<sup>-2</sup>). It is interesting to observe that the Ps value of the twins were decreasing drastically while increasing the spacer length



Fig. 5. A plot of tilt angle measurement against the temperature of ABDBP-6 and ABDBP-7 in SmC<sup>\*</sup> phase in 5  $\mu$ m cell.

between two mesogens, which indicates that the polarization of the molecule could largely depend on the distance between the two chiral centers. The tilt angles were measured in a 5 µm homogeneously aligned cells placed between crossed polarizers. A positive pulse exceeding the threshold voltage (+2 to +3 V) applied across the cell. The stage was rotated to some angle to attain darkest state of the cell attained and the angle was noted. Then the pulse was switched to negative and again rotated an angle to attain the darkest position. The difference between these two angles was taken as title angle. The experiment was repeated at different temperature at the SmC\* phase. The temperature dependence of the tilt angles for ABDBP-6 and ABDBP-7 in the SmC\* phase was shown in Fig. 5. It shows that the highest tilt angle of the compounds was about  $34^{\circ}$  and  $24.5^{\circ}$  as observed in ABDBP-6 and ABDBP-7, respectively. The magnitudes of the tilt angle for compounds ABDBP-8 and ABDBP-9 in SmC\* phase were not measured due to the SmC\* phase was formed monotropically with short temperature range and has crystallized in the homogeneously aligned cells.

# 4. Conclusion

A series of liquid crystalline twins having lactate groups as chiral part in the inner side of the molecule have been synthesized for the investigation of their mesophases and the physical properties. ABDBP-n (n = 6-9) displayed ferroelectric SmC<sup>\*</sup> phase and ABDBP-10 exhibited only SmA<sup>\*</sup> and SmX<sup>\*</sup> phases up to room temperature. The highest Ps value was observed to be 60.5 nC cm<sup>-2</sup> and the highest tilt angle reached 34° for ABDBP-6 in SmC<sup>\*</sup> phase.

# Acknowledgement

The authors are grateful for the financial support from the Department of Science and Technology (SR/FTP/CS-31), New Delhi, India.

### References

- [1] A.C. Griffin, T.R. Britt, J. Am. Chem. Soc. 103 (1981) 4957.
- [2] G.R. Luckhurst, Macromol. Symp. 96 (1995) 1.
- [3] C.T. Imrie, P.A. Henderson, Curr. Opin. Coll. Inter. Sci. 7 (2002) 298.
- [4] A. Ferrarini, G.R. Luckurst, P.L. Nordio, S.J. Roskilly, Liq. Cryst. 21 (1996) 373.
- [5] P.A. Henderson, O. Niemeyer, C.T. Imrie, Liq. Cryst. 28 (2001) 463.
- [6] A.E. Blatch, I.D. Fletcher, G.R. Luckurst, J. Mater. Chem. 7 (1997) 9.
- [7] I. Nishiyama, J. Yamamoto, J.W. Goodby, H. Yokoyama, Liq. Cryst. 29 (2002) 1409.

- [8] M. Kaspar, M. Glogarova, V. Hamplova, H. Sverenyak, S.A. Pakhomov, Ferroelectrics 148 (1993) 103.
- [9] M. Kaspar, H. Sverenyak, V. Hamplova, M. Glogarova, S.A. Pakhomov, P. Vanek, B. Trunda, Liq. Cryst. 19 (1995) 775.
- [10] M. Kaspar, V. Hamplova, S.A. Pakhomov, I. Stibor, H. Sverenyak, M.A. Bubnov, M. Glogarova, P. Vanek, Liq. Cryst. 22 (1997) 557.
- [11] V. Hamplova, M. Kaspar, S.A. Pakhomov, M.A. Bubnov, M.P. Glogarova, Mol. Cryst. Liq. Cryst. 322 (1999) 181.
- [12] M.A. Bubnov, V. Hamplova, M. Kaspar, P. Vanek, D. Pociecha, M.P. Glogarova, Mol. Cryst. Liq. Cryst. 366 (2001) 547.
- [13] M. Kaspar, V. Hamplova, V. Novotna, M.P. Glogarova, D. Pociecha, P. Vanek, Liq. Cryst. 28 (2001) 1203.
- [14] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, Jpn. J. Appl. Phys. 22 (1983) L661.
- [15] A.D.L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takazoe, A. Fukuda, Jpn. J. Appl. Phys. 27 (1988) L729.
- [16] J. Lee, A.D.L. Chandani, K. Itoh, Y. Ouchi, H. Takezoe, A. Fukuda, Jpn. J. Appl. Phys. 29 (1990) 1122.
- [17] A. Kazuki, Y. Xiaotun, Y. Shinichi, T. Kato, S. Takeuchi, Liq. Cryst. 27 (2000) 839.