

Liquid Crystalline Properties of Dimers Having *o*-, *m*- and *p*- Positional Molecular Structures

Joo-Hoon Park,[‡] Ok-Byung Choi, Hwan Myung Lee,[‡] Jin-Young Lee,[‡] Sung-Jo Kim,[‡] Eun-Hee Cha,[‡] Dong-Hyun Kim,[‡] B. Ramaraj,[†] Bong-Keun So, Kyung-Hwan Kim, Soo-Min Lee, and Kuk Ro Yoon^{*}

Department of Chemistry, Hannam University, Daejeon 306-791, Korea. *E-mail: kryoon@hannam.ac.kr

[‡]Central Institute of Plastics Engineering and Technology, Ahmedabad-382445, India

[†]College of Natural Science, Hoseo University, Chungnam 336-795, Korea

Received January 10, 2012, Accepted February 15, 2012

With the objective to design and synthesis of Schiff's base symmetrical liquid crystal dimers and to study the effect of molecular structure variation (*o*-*ortho*, *m*-*meta*, *p*-*para*) and change in alkoxy terminal chain length on mesomorphic properties of liquid crystals, We have synthesized Schiff base dimers from dialdehyde derivative containing 2-hydroxy-1,3-dioxypopylene as short spacer with aniline derivatives having different lengths of terminal alkoxy chains ($n = 5, 7, 9$). The chemical structure of the final products was characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy and fourier transform infrared (FT-IR) spectroscopy. The mesomorphic properties and optical textures of the resultant dimers were characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The existence of smectic A phase transition was confirmed by the observation of bâtonnets and fan shaped textures in optical microscopy when compound were heated from crystalline phase. All of the dimers of this series, with the exception of **2S₅**, -*ortho*, -*meta*, -*para*, were thermotropic liquid crystal. The compound **2S₉**, -*meta* was monotropic, while the rest were enantiotropic. It was found that the change in terminal alkoxy chain length has pronounced effect on the mesomorphic properties. The temperature range of smectic A phase window widens with increasing alkoxy chain length.

Key Words : Dimesogenic compounds, Bent-shaped liquid crystals, Differential scanning calorimetry, Optical microscopy

Introduction

Since the discovery of liquid crystal dimers¹ and subsequent interest in these materials² many dimeric systems have been reported. Liquid crystal dimers are of interest because they act as models for main group liquid crystalline polymers that allow the study of flexibility and properties of different mesogenic groups. Thus dimeric liquid crystals retain the crucial structural components of many thermotropic main group polymers. Furthermore, as a distinct class of compounds with unusual properties and potential application, dimeric liquid crystals is of interest in their own right. In typical dimers where two individual mesogenic entities are attached to each other by flexible polymethylene spacer units, the mesomorphic behavior of these compounds is basically dependent on its molecular architecture in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. Dimers containing identical mesogenic units are referred as symmetric dimers, while the non-symmetric dimers consist of two differing mesogenic groups. The structure of the mesophases can be modified through change in spacer length and terminal chain length. A liquid crystal dimer is composed of molecules containing two mesogenic groups linked *via* a flexible spacer, normally alkyl and alkoxy chains. The initial interest in liquid crystal dimers arose,

therefore, from their potential use as model compounds with which to understand the more complex polymeric systems. It quickly became apparent, however, that the dimers themselves were of significant interest in their own right as they exhibited quite different behaviour to conventional low molar mass liquid crystals. More recently and in order to investigate how the liquid crystal properties evolve from dimers to polymers, a range of higher monodisperse oligomers have been characterized.³⁻⁵

Recently we have reported the synthesis and mesomorphic properties of 1,3-bis[4-,3-,2-((4-dodecyloxybenzylidene)-amino)phenoxy]propan-2-ol³ and 1,3-bis(4-((4-alkyloxy phenylimino)methyl)phenoxy)propan-2-ol.⁶ These dimesogenic compounds have aromatic Schiff base type mesogenic units bracketing a central 2-hydroxy-1,3-dioxypopylene (-OCH₂CH(OH)CH₂O-) spacer. Also we studied the preparation and thermotropic properties of 1,3-bis[4-((4-alkyloxy phenylimino)methyl)phenoxy]propane⁷ and 1,2-bis(4-(4-(4-alkoxy benzoyloxy)benzylidene)amino)phenoxy)ethane.⁷ These compounds are composed of aromatic Schiff base and aromatic ester Schiff base type mesogenic units bracketing a central 1,3-dioxypopylene(-OCH₂CH₂CH₂O-) and 1,2-dioxyethylene (-OCH₂CH₂O-) spacer. The thermal transition behaviour of the dimesogenic compounds was strongly dependent on the nature of the *ortho*-, *meta*- and *para*-positional molecular structures and the length of the terminal

alkoxy chain.

In our ongoing efforts to investigate the correlation between molecular structures and mesomorphic properties liquid crystal properties,³⁻¹⁰ here we report the synthesis and the liquid crystal properties of symmetric Schiff base dimesogenic compounds (**2S₅**-*ortho*-, *meta*-, *para*-; **2S₇**-*ortho*-, *meta*-, *para*-, **2S₉**-*ortho*-, *meta*-, *para*-), which have terminal alkoxy chains (-OC_nH_{2n+1}; *n* = 5, 7, 9) and 2-hydroxy-1,3-dioxypopylene (-OCH₂CH(OH)CH₂O-) as a central flexible spacer. The acronym used to refer to these dimesogenic compounds is “**2S_n**”-*ortho*-, *meta*-, *para* (*n* = 5, 7, 9), where “**2**” represents the number of mesogenic units, “**S**” stands for Schiff base mesogenic group and “**n**” refers the number of carbon atoms in the terminal alkoxy chain. The molecular structures of the intermediates and final dimesogenic compounds were confirmed by ¹H NMR and FT-IR spectrophotometer. Thermal behavior and thermotropic properties were examined by differential scanning calorimetry (DSC) method. Optical textures were observed on the hot-stage of a polarizing optical microscopy (POM).

Experimental

Materials. Epichlorohydrin, hydroxybenzaldehyde (*o*-, *m*-, *p*-), alkylbromide (*n* = 5, 7, 9), 4-nitrophenol, potassium hydroxide (KOH), hydrazine monohydrate, palladium on activated carbon (Pd/C, 10%), *p*-toluenesulfonic acid (PTSA), anhydrous ethanol (EtOH) were purchased from Aldrich Chemical Co. and used as received. All other solvents and reagents were purchased commercially and used without further purification.

Synthesis of Schiff Base Dimesogens (2S_n). The synthetic routes used in the preparation of final *ortho*- (Series I), *meta*- (Series II) and *para*- (Series III) Schiff base (**2S_n**, *n* = 5, 7, 9) dimesogens were illustrated in Scheme 2. The synthetic route used in the preparation of Schiff dimesogens (**2S_n**) involved four steps: 1) reaction of 4-nitrophenol with alkylbromide (*n* = 5, 7, 9) in presence of potassium hydroxide to obtain 4-nitroalkoxybenzene (**NBn**); 2) then the reduction of nitro group with hydrazine monohydrate in the presence of palladium on activated carbon to obtain 4-aminoalkoxybenzene (**ABn**); 3) the 1,3-bis(2-,3-,4-formylphenoxy)propane-2-ol (**FP-2, 3, 4**) was obtained by reacting hydroxybenzaldehyde (*ortho*-, *meta*-, *para*-) with epichlorohydrin; 4) the final products 1,3-bis(2-,3-,4-((4-alkoxyphenyl-imino)methyl)phenoxy)propan-2-ols were prepared by condensing 1,3-bis(2-,3-,4-formylphenoxy)propane-2-ols (**FP-2, 3, 4**)¹¹ with 4-aminoalkoxybenzene (**ABn**). The synthetic details for final diimine compounds are as follows: FPP-2-, 3-, 4(1 eq.) was dissolved in anhydrous ethanol. 4-Pentyl-oxyaniline (2 eq.) and 4-heptyloxyaniline and a catalytic quantity of *p*-toluenesulfonic acid were poured into the solution, and then the reaction mixture was stirred for 24 hours at the room temperature. The precipitate formed was collected by filtration and purified by the recrystallization of CHCl₃/EtOH (1:1, v/v) solvents. Final products thus obtained were found to be pure enough by TLC. The syntheses of

final products were confirmed by FT-IR and ¹H NMR.

Synthesis of 4-Nitroalkoxybenzene (NBn, n = 5, 7, 9).

4-Pentylloxynitrobenzene (NB-5): 5.02 g (52%), yellow liquid, IR (KBr, cm⁻¹): 3120 (aromatic C-H); 2943, 2878 (aliphatic C-H); 1508, 1349 (-NO₂). ¹H-NMR (CDCl₃, ppm): 0.93 (t, 3H, -CH₃), 1.21-1.40 (m, 4H, -(CH₂)₂-), 1.79 (m, 2H, -CH₂CH₂O-), 3.96 (t, 2H, -CH₂CH₂O-), 6.93, 7.98 (dd, 4H, Ar-H).

4-Heptyloxynitrobenzene (NB-7): 5.97 g (54%), yellow liquid, IR (KBr, cm⁻¹): 3100 (aromatic C-H); 2935, 2872 (aliphatic C-H); 1510, 1345 (-NO₂). ¹H-NMR (CDCl₃, ppm): 0.91 (t, 3H, -CH₃), 1.20-1.49 (m, 8H, -(CH₂)₄-), 1.81 (m, 2H, -CH₂CH₂O-), 3.99 (t, 2H, -CH₂CH₂O-), 6.96, 8.10 (dd, 4H, Ar-H).

4-Nonyloxynitrobenzene (NB-9)⁴: 8.87 g (85%), yellow liquid, IR (KBr, cm⁻¹): 3088 (aromatic C-H), 2930, 2865 (aliphatic C-H), 1514, 1341, (-NO₂). ¹H NMR (CDCl₃, ppm): 0.88 (t, 3H, -CH₃), 1.20-1.55 (m, 12H, -(CH₂)₆), 1.82 (m, 2H, -CH₂CH₂O-), 4.01 (t, 2H, -CH₂CH₂O-), 6.96, and 8.13 (dd, 4H, Ar-H).

Synthesis of 4-Aminoalkoxybenzene (ABn, n = 5, 7, 9).

4-Pentyloxyaminobenzene (AB-5): 3.50 g (78%), brown liquid, IR (KBr, cm⁻¹): 3308, 3209 (-NH₂, stretching), 1628 (-NH₂, bending). ¹H-NMR (CDCl₃, ppm): 0.95 (t, 3H, -CH₃), 1.36-1.48 (m, 4H, -(CH₂)₂), 1.82 (m, 2H, -CH₂CH₂O-), 3.93 (t, 2H, -CH₂CH₂O-), 3.35 (broad, -NH₂), 6.67, 6.87 (dd, 4H, Ar-H).

4-Heptyloxyaminobenzene (AB-7): 4.04 g (78%), brown liquid, IR (KBr, cm⁻¹): 3405, 3315 (-NH₂, stretching), 1635 (-NH₂, bending). ¹H-NMR (CDCl₃, ppm): 0.92 (t, 3H, -CH₃), 1.25-1.50 (m, 8H, -(CH₂)₄-), 1.79 (m, 2H, -CH₂CH₂O-), 3.95 (t, 2H, -CH₂CH₂O-), 3.30 (broad, -NH₂), 6.65, 6.77 (dd, 4H, Ar-H).

4-Nonyloxyaminobenzene (AB-9)⁴: 3.59 g (80%), brown liquid, IR (KBr, cm⁻¹): 3090 (aromatic C-H), 2932, 2863 (aliphatic C-H), 3412, 3321 (-NH₂ stretching), 1655 (-NH₂ bending). ¹H NMR (CDCl₃, ppm): 0.90 (t, 3H, -CH₃), 1.15-1.46 (m, 12H, -(CH₂)₆), 1.75 (m, 2H, -CH₂CH₂O-), 3.96 (t, 2H, -CH₂CH₂O-), 3.20 (broad, -NH₂), 6.65, and 6.80 (dd, 4H, Ar-H).

Synthesis of 1,3-Bis(2-,3-,4-formylphenoxy)propane-2-ol (FP-2, 3, 4).

1,3-Bis(2-formylphenoxy)propan-2-ol(FPP-2): 9.15 g (61%), brown solid, IR (KBr, cm⁻¹): 3505 (-OH), 1680 (C=O). ¹H-NMR (CDCl₃, ppm): 2.50 (br, -OH), 4.25 (d, 4H, -CH₂-), 4.63 (m, 1H, -CH-), 7.08-7.94 (dd, 8H, Ar-H), 10.35 (s, 2H, -CHO).

1,3-Bis(3-formylphenoxy)propan-2-ol (FPP-3): 11.3 g (75%), white solid, IR (KBr, cm⁻¹): 3495 (-OH), 1685 (C=O). ¹H-NMR (CDCl₃, ppm): 2.62 (br, -OH), 4.16 (d, 4H, -CH₂-), 4.65 (m, 1H, -CH-), 7.21-7.55 (dd, 8H, Ar-H), 9.99 (s, 2H, -CHO).

1,3-Bis(4-formylphenoxy)propan-2-ol (FPP-4): 12.2 g (81%), yellow solid, IR (KBr, cm⁻¹): 3493 (-OH), 1688 (C=O). ¹H-NMR (CDCl₃, ppm): 2.52 (br, -OH), 4.22 (d, 4H, -CH₂-), 4.65 (m, 1H, -CH-), 7.08-7.92 (dd, 8H, Ar-H), 9.92 (s, 2H, -CHO).

Synthesis of 1,3-Bis(2-,3-,4-((4-alkyloxyphenylimino)methyl)phenoxy)propan-2-ols.

1,3-Bis(2-((4-pentyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₅-ortho): 1.85 g (74%), yellow powder, IR (KBr, cm⁻¹): 3420 (stretch., -OH), 1618 (stretch., -CH=N-). ¹H-NMR (CDCl₃, ppm): 0.90 (t, 6H, -CH₃), 1.22-1.53 (m, 8H, (-CH₂)₂), 1.79 (m, 4H, -CH₂CH₂O-), 3.97 (t, 4H, -CH₂CH₂O-), 4.31 (d, 4H, -OCH₂CH(OH)CH₂O-), 4.45 (m, 1H, -OCH₂CH(OH)CH₂O-), 5.10 (broad, 1H, -OCH₂CH(OH)CH₂O-) 6.90 (d, 4H, Ar-H), 7.00 (d, 2H, Ar-H), 7.08 (m, 2H, Ar-H), 7.20 (d, 4H, Ar-H), 7.39 (m, 2H, Ar-H), 7.93 (d, 2H, Ar-H), 8.76 (s, 2H, -CH=N-).

1,3-Bis(3-((4-pentyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₅-meta): 2.03 g (81%), white powder, IR (KBr, cm⁻¹): 3476 (stretch., -OH), 1612 (stretch., -CH=N-). ¹H-NMR (CDCl₃, ppm): 0.93 (t, 6H, -CH₃), 1.20-1.40 (m, 8H, (-CH₂)₂), 1.78 (m, 4H, -CH₂CH₂O-), 2.52 (s, 1H, -OCH₂CH(OH)CH₂O-), 3.88 (t, 4H, -CH₂CH₂O-), 4.23 (d, 4H, -OCH₂CH(OH)CH₂O-), 4.39 (m, 1H, -OCH₂CH(OH)CH₂O-), 6.87 (d, 4H, Ar-H), 7.02 (m, 2H, Ar-H), 7.17 (d, 4H, Ar-H), 7.39 (m, 4H, Ar-H), 7.48 (s, 2H, Ar-H), 8.40 (s, 2H, -CH=N-).

1,3-Bis(4-((4-pentyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₅-para): 2.35 g (94%), yellow powder, IR (KBr, cm⁻¹): 3472 (stretch., -OH), 1604 (stretch., -CH=N-). ¹H-NMR (DMSO-*d*₆, ppm): 0.87 (t, 6H, -CH₃), 1.19-1.47 (m, 8H, (-CH₂)₂), 1.70 (m, 4H, -CH₂CH₂O-), 3.96 (t, 4H, -CH₂CH₂O-), 4.09-4.25 (m, 5H, -OCH₂CH(OH)CH₂O-), 4.50 (s, 1H, -OCH₂CH(OH)CH₂O-), 6.94 (d, 4H, Ar-H), 7.09 (d, 4H, Ar-H), 7.22 (d, 4H, Ar-H), 7.85 (d, 4H, Ar-H), 8.53 (s, 2H, -CH=N-).

1,3-Bis(2-((4-heptyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₇-ortho): 1.80 g (72%), white crystal, IR (KBr, cm⁻¹): 3421 (stretch, -OH), 1610 (stretch, -CH=N-). ¹H-NMR (CDCl₃, ppm): 0.91 (t, 6H, -CH₃), 1.20-1.56 (m, 16H, (-CH₂)₄), 1.82 (m, 4H, -CH₂CH₂O-), 3.95 (t, 4H, -CH₂CH₂O-), 4.33 (d, 4H, -OCH₂CH(OH)CH₂O-), 4.50 (m, 1H, -OCH₂CH(OH)CH₂O-), 6.93 (d, 4H, Ar-H), 7.00-7.03 (d, 6H, Ar-H), 7.33-7.45 (m, 4H, Ar-H), 8.02 (d, 2H, Ar-H), 8.83 (s, 2H, -CH=N-).

1,3-Bis(3-((4-heptyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₇-meta): 1.80 g (75%), white powder, IR (KBr, cm⁻¹): 3480 (stretch, -OH), 1625 (stretch, -CH=N-). ¹H-NMR (CDCl₃, ppm): 0.92 (t, 6H, -CH₃), 1.20-1.47 (m, 16H, (-CH₂)₄), 1.82 (m, 4H, -CH₂CH₂O-), 2.58 (s, 1H, -OCH₂CH(OH)CH₂O-), 3.92 (t, 4H, -CH₂CH₂O-), 4.26 (d, 4H, -OCH₂CH(OH)CH₂O), 4.43 (m, 1H, -OCH₂CH(OH)CH₂O-), 6.89 (d, 4H, Ar-H), 7.04 (m, 2H, Ar-H), 7.20 (d, 4H, Ar-H), 7.36 (m, 4H, Ar-H), 7.51 (s, 2H, Ar-H), 8.43 (s, 2H, -CH=N-).

1,3-Bis(4-((4-heptyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₇-para): 2.13 g (85%); yellow powder, IR (KBr, cm⁻¹): 3468 (stretch, -OH), 1602 (stretch, -CH=N-); ¹H-NMR (DMSO-*d*₆, ppm): 0.95 (t, 6H, -CH₃), 1.25-1.51 (m, 16H, (-CH₂)₄), 1.76 (m, 4H, -CH₂CH₂O-), 4.01 (t, 4H, -CH₂CH₂O-), 4.12-4.30 (m, 5H, -OCH₂CH(OH)CH₂O-), 4.52 (s, 1H, -OCH₂CH(OH)CH₂O-), 7.13 (d, 4H, Ar-H),

7.17 (d, 4H, Ar-H), 7.26 (d, 4H, Ar-H), 7.92 (d, 4H, Ar-H) 8.59 (s, 2H, -CH=N-).

1,3-Bis(2-((4-nonyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₉-ortho)⁴: 2.00 g (80%), white crystal, IR (KBr, cm⁻¹): 3418 (stretching, -OH), 1614 (stretching, -CH=N-). ¹H NMR (CDCl₃, ppm): 0.93 (t, 6H, CH₃), 1.19-1.60 (m, 24H, (CH₂)₆), 1.85 (m, 4H, CH₂CH₂O), 3.93 (t, 4H, CH₂CH₂O), 4.36 (d, 4H, OCH₂CH(OH)CH₂O), 4.53 (m, 1H, OCH₂CH(OH)CH₂O), 6.92 (d, 4H, Ar-H), 6.98-7.00 (d, 6H, Ar-H), 7.30-7.46 (m, 4H, Ar-H), 8.06 (d, 2H, Ar-H), and 8.90 (s, 2H, -CH=N-).

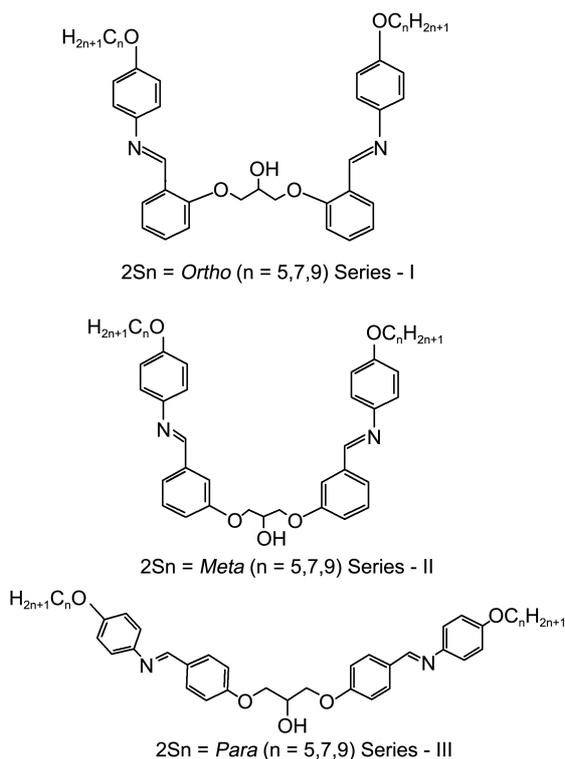
1,3-Bis(3-((4-nonyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₉-meta)⁴: 2.13 g (85%), white crystal, IR (KBr, cm⁻¹): 3474 (stretching, OH), 1614 (stretching, -CH=N-). ¹H NMR (CDCl₃, ppm): 0.95 (t, 6H, CH₃), 1.29-1.57 (m, 24H, (CH₂)₆), 1.80 (m, 4H, -CH₂CH₂O), 2.63 (s, 1H, OCH₂CH(OH)CH₂O), 3.98 (t, 4H, CH₂CH₂O), 4.28 (d, 4H, OCH₂CH(OH)CH₂O), 4.46 (m, 1H, OCH₂CH(OH)CH₂O), 6.92 (d, 4H, Ar-H), 7.07 (m, 2H, Ar-H), 7.23 (d, 4H, Ar-H), 7.40 (m, 4H, Ar-H), 7.56 (s, 2H, Ar-H), and 8.45 (s, 2H, -CH=N-).

1,3-Bis(4-((4-nonyloxyphenylimino)methyl)phenoxy)propan-2-ol(2S₉-para)⁴: 2.45 g (98%), white crystal, IR (KBr, cm⁻¹): 3474 (-OH), 1604 (-CH=N-). ¹H NMR (DMSO-*d*₆, ppm): 0.99 (t, 6H, -CH₃), 1.20-1.59 (m, 24H, (CH₂)₆), 1.81 (m, 4H, CH₂CH₂O), 4.11 (t, 4H, CH₂CH₂O), 4.09-4.32 (m, 5H, OCH₂CH(OH)CH₂O), 4.55 (s, 1H, OCH₂CH(OH)CH₂O), 7.16 (d, 4H, Ar-H), 7.20 (d, 4H, Ar-H), 7.28 (d, 4H, Ar-H), 8.01 (d, 4H, Ar-H), and 8.61 (s, 2H, -CH=N-).

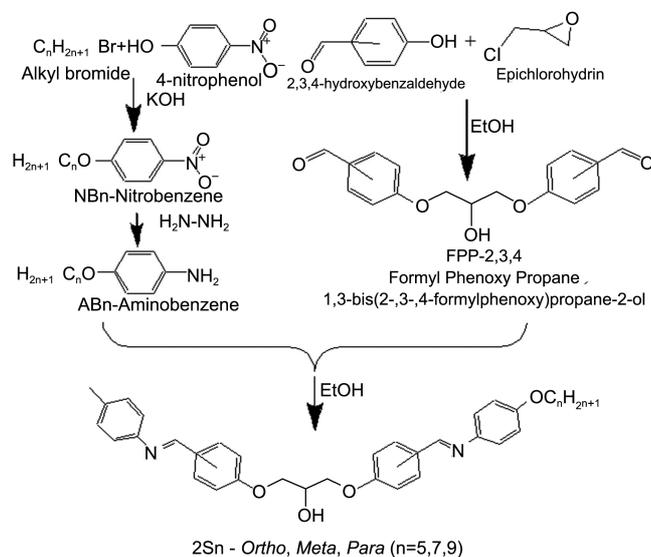
Characterization. The structures of all intermediates and final dimesogenic compounds were verified using ¹H NMR (Varian Unity 300 (300 MHz) NMR spectrometer and FT-IR (Perkin-Elmer 1000 FT-IR spectrophotometer) spectroscopy. The high purity of final products was demonstrated using thin layer chromatography. Thermal transition temperatures of the dimesogenic compounds were studied on a TA instrument 910S DSC apparatus under dry nitrogen atmosphere. Heating and cooling rates were maintained at 10 °C/in in the compounds. Indium was employed for calibration. The position of peak maxima was taken as thermal transition temperatures. The textures of the mesophases were examined on a Nikon Labophot-2 polarizing microscope fitted with a RTC-1 temperature controller (Instec Inc., Broomfield, Co.) and a Mettler FP-82HT hot stage.

Result and Discussion

Synthesis and Characterization. The synthetic process for the final dimesogenic compounds are shown in the Scheme 2. The new -CH=N- bent shaped dimesogenic compounds, 1,3-bis(2-,3-,4-((4-alkyloxyphenylimino)methyl)phenoxy)propan-2-ols (2S_n-*ortho*-, *meta*-, *para*-, *n* = 5, 7, 9), were prepared starting from *ortho*-, *meta*- and *para*-dialdehyde derivative (FPP-2, -3, -4). The dimesogenic compounds, 2S_n-*ortho*-, *meta*-, *para*- (*n* = 5, 7, 9), were then synthesized by the condensation reaction between diamines and dialdehyde (Scheme 2). The structures of final dimeso-



Scheme 1. The structures and designation of the Series I, II and III compounds.



Scheme 2. The synthetic pathways for Series I, II and III compounds.

genic compounds were confirmed by the $^1\text{H-NMR}$ and FT-IR spectroscopy. The IR spectral frequencies of the prepared $2S_n$ -*ortho*-, -*meta*-, -*para* dimesogenic compounds were obtained using KBr pellets as described in experimental section. All of the final products exhibited relatively strong IR absorption band at about $1602\text{--}1625\text{ cm}^{-1}$ for the -CH=N- stretching vibration and $3420\text{--}3480\text{ cm}^{-1}$ for the -OH stretching vibration. In the proton NMR, the spectral data displayed similar patterns: $2S_n$ -*ortho*-, -*meta*-, -*para* ($n = 5, 7, 9$) showed -CH=N- peaks at $8.43\text{--}8.83\text{ ppm}$, the central

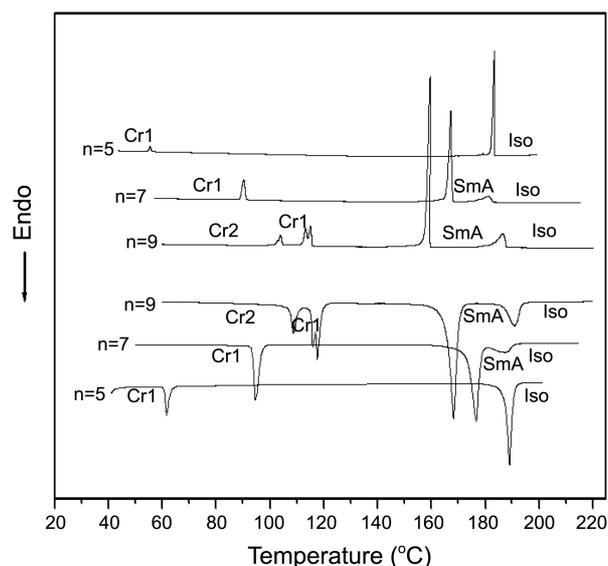


Figure 1. Differential scanning calorimetry curves for dimers ($2S_n$ -*para*) in the heating and cooling scans ($10\text{ }^\circ\text{C/min}$).

-CH- peaks at $4.39\text{--}4.50\text{ ppm}$ and -OH peaks were located at $4.50\text{--}5.10\text{ ppm}$, respectively.

Differential Scanning Calorimetry. The mesomorphic properties of dimesogenic compounds were determined by means of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) with a hot stage. In this series, the length of the terminal alkoxy chain and *ortho*-, *meta*- and *para*- positional mesogenic units were varied and its effect on the thermal and mesomorphic properties of the compounds was investigated. Figure 1 shows representative DSC heating and cooling traces of dimesogen Series “ S_n ”-*para* ($n = 5, 7, 9$) compounds and its thermal transition temperatures and mesomorphic phases are summarized in Table 1. The transition temperatures for melting and those for smectic phase to isotropic liquid state (Table 1) were obtained from the second heating and cooling cycles of the DSC analyses. All of the dimers of this series, with the exception of $2S_5$ -*ortho*-, -*meta*-, -*para*, were thermotropic liquid crystal. The compound $2S_9$ -*meta* was monotropic, while the rest were enantiotropic. In the heating scan of $2S_5$ -*para*, it shows a crystal to crystal phase transition at $61.5\text{ }^\circ\text{C}$ and a crystal to isotropic liquid phase transition at $189.1\text{ }^\circ\text{C}$. In the cooling scan of $2S_5$ -*para*, it shows a crystal to crystal phase transition at $55.2\text{ }^\circ\text{C}$ and an isotropic liquid phase to crystal phase transition at $182.2\text{ }^\circ\text{C}$. The $2S_5$ -*para* is non-liquid crystalline material. In the heating curve of $2S_7$ -*para*, it shows a crystal to crystal phase transition at $94.5\text{ }^\circ\text{C}$, a crystal to smectic A phase transition at $176.6\text{ }^\circ\text{C}$ and a smectic A to isotropic liquid phase transition at $187.4\text{ }^\circ\text{C}$. In the cooling curve of $2S_7$ -*para*, it shows an isotropic liquid phase to smectic A phase transition at $180.4\text{ }^\circ\text{C}$, a smectic A to crystal phase transition at $166.8\text{ }^\circ\text{C}$ and a crystal to crystal phase transition at $90.3\text{ }^\circ\text{C}$. The thermal and thermotropic properties of $2S_9$ -*para* on the liquid crystal behaviour of this Series III were similar to that seen in $2S_7$ -*para*. In the heating and cooling scans, $2S_7$ -*para*, $2S_7$ -*meta*, $2S_7$ -*ortho*,

Table 1. Phase transition temperature of Series I (*Ortho*), Series II (*Meta*) and series III (*Para*)

Series	n	Phase and transition temperature (°C)	
		Heating	Cooling
Series I <i>Ortho</i>	5	Cr 87.9 I	No Peaks
	7	Cr 89.8 SmA 100.8 I	No Peaks
	9	Cr 117.0 SmA 131.9 I	I 110.3 SmA 102.6 Cr
Series II <i>Meta</i>	5	Cr 63.4 Cr 83.5 I	No Peaks
	7	Cr 85.8 SmA 104.0 I	No Peaks
	9	Cr 132.0 I	I 114.8 SmA 104.8 Cr
Series III <i>Para</i>	5	Cr 61.5 Cr 189.1 I	I 182.2 Cr 55.2 Cr
	7	Cr 94.5 Cr 176.6 SmA 187.4 I	I 180.4 SmA 166.8 Cr 90.3 Cr
	9	Cr 108.7 Cr 117.6 Cr 168.2 SmA 190.8 I	I 185.9 SmA 157.8 Cr 114.7 Cr 103.7 Cr

Cr = crystalline state, SmA = smectic A phase, I = isotropic state. All data were obtained from 2nd heating and cooling scans at 10 °C/min.

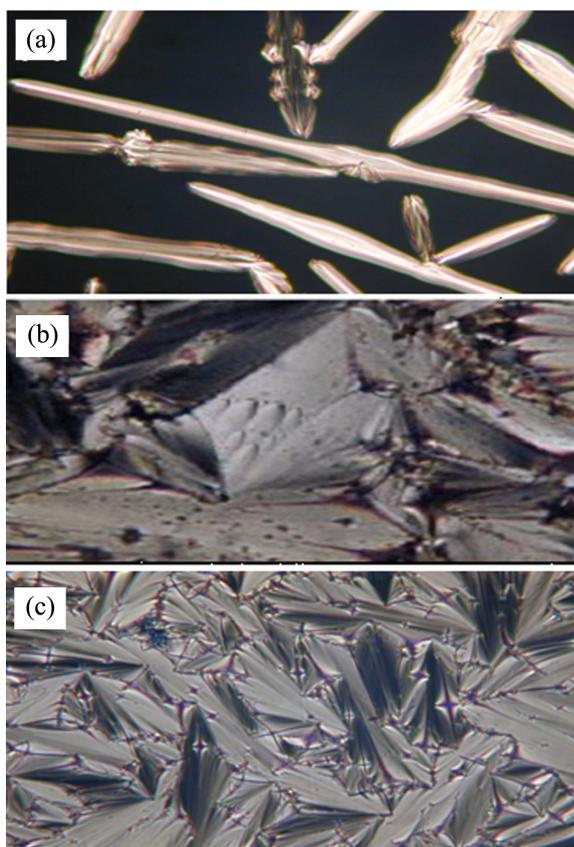


Figure 2. Optical polarizing micrographs obtained on cooling from the isotropic liquid of the samples (2 °C/min, magn \times 100): (a) SmA, batonnets of $2S_9$ -*para* (190.2 °C); (b) SmA texture of $2S_9$ -*para* (171 °C); (c) SmA, fan shaped texture of $2S_7$ -*para* (180 °C).

$2S_9$ -*para* and $2S_9$ -*ortho* were shown as an enantiotropic liquid crystalline. While $2S_9$ -*meta* was monotropic.

Optical Properties. As summarized in the Table 1, all the present compounds form only smectic A phase, and representative optical textures are shown in Figure 2. This Figure 2 show batonnets and fan shaped texture characteristic of the smectic A mesophase.^{12,13} The smectic phase window is increased from 10.8 °C ($2S_7$ -*para*) to 22.6 °C ($2S_9$ -*para*) of Series III and 11.0 °C ($2S_7$ -*ortho*) to 14.9 °C ($2S_9$ -*ortho*) of

Series I. Since the molecules are bent shaped dimesogenic compounds with two terminal alkoxy chains, increasing the terminal alkoxy chain length is anticipated to increase significantly the length-to-breadth ratio in resulting liquid crystal phases, and particularly smectic phases, being stabilized at higher temperatures for higher homologues. We also note that the temperature range of the smectic mesophase increased with the terminal alkoxy chain length. The compound of $2S_9$ -*para* shows the largest temperature interval extending to 22.6 °C. These results demonstrate that the tendency toward smectic mesomorphism and the thermal stability of tilted smectic phase increased with increasing terminal alkoxy chain length. This may be the result of the terminal alkoxy chains lying at an angle to the long molecular axis inducing the molecular tilt between neighboring molecules. The effects of the terminal alkoxy chain length on the transition temperatures and phases behavior observed in this series are in accordance with those observed for conventional low molar mass mesogens⁷.

Conclusions

We have synthesized a new series of schiff base liquid crystalline compounds from dialdehyde derivative containing 2-hydroxy-1,3-dioxypopylene as short spacer with aniline derivatives having different lengths of terminal alkoxy chains ($n = 5, 7, 9$). The chemical structures of the final products were investigated by FT-IR and ¹H NMR spectroscopy. The mesomorphic properties and optical textures of the resultant dimers were characterized by DSC and OM. The existence of smectic A phase transition was confirmed by the observation of batonnets and fan shaped textures in optical microscopy when compound were heated from crystalline phase. All of the dimers of this series, with the exception of $2S_5$ -*ortho*-, *meta*-, *para*-, were thermotropic liquid crystal. The compound $2S_9$ -*meta* was monotropic, while the rest were enantiotropic. It was found that the change in terminal alkoxy chain length has pronounced effect on the mesomorphic properties. The temperature range of smectic A phase window widens with increasing alkoxy chain length.

Acknowledgments. This research was supported by the Academic Research fund of Hoseo University in 2011 (20110032).

References

1. Vorlander, D. Z. *Phys. Chem.* **1927**, 126, 449.
 2. Griffin, A. C.; Britt, T. R. *J. Am Chem. Soc.* **1981**, 103, 4957.
 3. So, B.-K.; Lee, S.-M.; Choi, O.-B.; Lee, H. M.; Lee, J.-Y.; Kim, S.-J.; Cha, E.-H.; Kim, R. H.; Park, J.-H. *Bull. Korean Chem. Soc.* **2009**, 30(7), 1634.
 4. Yoon, K. R.; So, B.-K.; Kim, K.-H.; Lee, S.-M.; Uma, R. S. A.; Choi, O.-B.; Lee, H. M.; Lee, J.-Y.; Kim, S.-J.; Cha, E.-H.; Lee, E. H.; Park, J.-H. *J. Ind. Eng. Chem.* **2012**, 18, 6.
 5. So, B.-K.; Jang, M.-C.; Park, J.-H.; Lee, K.-S.; Song, H.-H.; Lee, S.-M. *Opt. Mater.* **2002**, 21, 685.
 6. So, B.-K.; Kim, W.-J.; Lee, S.-M.; Jang, M.-C.; Song, H.-H.; Park, J.-H. *Dyes and Pigments* **2007**, 75, 619.
 7. Kim, T. H.; Lee, C. S.; Ramaraj, B.; Jeon, H. J.; Song, H.-H.; Lee, S. M.; Yoon, K. R. *Mol. Cryst. Liq. Cryst.* **2008**, 492, 102.
 8. Lee, C. S.; Kim, T. H.; Ramaraj, B.; Ryu, S. G.; Song, H. H.; Lee, S. M.; Yoon, K. R. *Mol. Cryst. Liq. Cryst.* **2008**, 492, 117.
 9. So, B.-K.; Kim, Y.-S.; Choi, M.-M.; Kim, J.-E.; Park, J.-H.; Lee, K.-S.; Lee, S.-M. *Liq. Cryst.* **2004**, 31, 169.
 10. So, B.-K.; Kim, H.-J.; Song, H. H.; Park, J.-H.; Lee, S.-M. *Dyes. Pigments* **2006**, 70, 38.
 11. Zhao, B.; Wu, W. J.; Tao, J. C.; Yuan, H. Z.; Mao, X. A. *Polyhedron* **1996**, 15, 1197.
 12. Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystal-Textures and Structures*; Leonard Hill: Philadelphia, 1984.
 13. Dierking, I. T. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, 2003.
-