DOI 10.5012/bkcs.2011.32.8.3057

Cyclic Co-oligomeric Ferroelectric Liquid Crystals with Fast Switching Properties, Wide SmC* Temperature Range and de Vries-type SmA*-SmC* Transition[†]

Seung Beom Park, Tai-Yon Cho, Kyung-Hwan Yoon, Ji Young Chang,[‡] Rudolf Zentel,[§] and Do Y. Yoon[*]

Department of Chemistry, Seoul National University, Seoul, 151-747, Korea. [*]E-mail: dyyoon@snu.ac.kr
[‡]School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea
[§]Institute of Organic Chemistry, University of Mainz, D-55099 Mainz, Germany

Received May 6, 2011, Accepted June 18, 2011

We have synthesized and characterized the first cyclic co-oligomeric ferroelectric liquid crystals (FLCs) based on cyclic siloxanes and found that the co-oligomer containing two different mesogenic units exhibits SmC* mesophase over a wide temperature range from 65 °C to 135 °C, much wider than those of the monomer counterparts and the cyclic homo-oligomers. The cyclic co-oligomeric liquid crystal readily filled the display cell and exhibited fast switching times in the range of 4 ms to 6 ms over the entire SmC* phase. Moreover, the practical absence of layer shrinkage, attributed to de Vries-type transition, shows an additional significant advanage for cyclic co-oligomeric FLCs in LCD applications.

Key Words : Ferroelectric liquid crystal, Cyclic co-oligomeric liquid crystal, Switching time, LCD, de Vries-type transition

Introduction

The thin-film transistor liquid crystal display (TFT-LCD) has become very important as the most dominant flat panel display technology with its ubiquitous applications in variety of devices. Since the initial work of Lechner *et al.* (RCA Corporation, USA) in 1971, the TFT-LCD technology employing nematic liquid crystals has seen continuous, impressive improvements in the image quality, the response time, and the device fabrication efficiency, as a result of enormous research efforts over the last 40 years.[1-3] Currently, TFT-LCD products occupy approximately 70~80% of the overall display market, with a total annual revenue of nearly one hundred billion dollars. However, the response time of current LCD devices is quite inferior to the other competing technologies such as plasma display panel (PDP) or organic light-emitting diode (OLED). This shortcoming becomes more serious in the recently emerging advanced display devices, such as 3D displays or field sequential color (FSC) displays, for which the required response times are shorter than 1 ms. Such a fast switching time becomes really challenging for the current LCDs due to the intrinsically slow switching dynamics of nematic liquid crystals.

In this regard, ferroelectric liquid crystals (FLCs), which are known to have intrinsically fast switching properties with the response time as short as 50 μs, offer an excellent opportunity to overcome the limits of LCD technology.[4-6] Such a fast switching time of FLCs arises from a large spontaneous electric polarization, as first discovered in 1975 by Meyer,[7] and five years later Clark and Lagerwall devised a novel method to take advantage of their unique properties for display applications.[8] Although a variety of FLC-based display devices have since been demonstrated, serious problems still remain to be solved in order to realize the inherent potential of the FLC materials.[4-6] Specifically, low molecular-weight monomeric ferroelectric liquid crystals (MFLCs) exhibit the problems of alignment instability and a narrow temperature range of suitable FLC phase. Although these problems can be minimized with polymeric ferroelectric liquid crystals (PFLCs), they limit the switching time and present serious difficulties in the fabrication process due to very high viscosities of polymeric materials.[4-6,9-12] Another problem associated with the use of FLCs are the "Chevron instabilities",[13] which result as a consequence of the smectic layer shrinkage at the smectic A – smectic C* transition. A possible solution for this problem can be liquid crystalline materials with a de Vries-type phase transition, in which the transition happens with a negligible layer shrinkage.[14-16] In recent years, several such liquid crystalline materials have been reported, some of which contain a siloxane backbone.[17-20]

Therefore, oligomeric ferroelectric liquid crystals (OFLCs) became of interest in order to overcome the problems of both MFLCs and PFLCs. Previous works demonstrated a variety of structural variations on this theme. In particular, oligomeric siloxanes possessing pendant mesogenic groups attracted lots of interest,[21-33] since the siloxane moieties readily give rise to a nano-phase-separated structure as is well known for liquid crystalline polysiloxanes.[11,12] As a result, the temperature range of the smectic phase becomes enlarged, whereas the switching times stay relatively short, due to their oligomeric nature.[12] Despite such progress, further improvements of OFLCs are critically needed in the following two aspects: (i) further broadening the temperature range of the chiral smectic C phase and (ii)

[†] This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.

preventing the Chevron defects by enabling de Vries-type transitions. In this regard, a chemically bonded "mixing" of different mesogens on the oligomeric backbone seems to be an attractive method for broadening the chiral smectic C* phase, in contrast to the physical mixing method. In addition, introduction of such a chemical disorder might disrupt an abrupt change in the layer spacing at the smectic A – smectic C* transition and thus promotes a de Vries-type transition,

In this paper, we describe the first preparation and characterization of cyclic co-oligomeric ferroelectric liquid crystals, based on cyclic tetramer siloxanes with pendant chiral mesogenic groups, as an attempt to broaden the temperature range of the chiral smectic C* phase and to promote the desired de Vries-type transitions. Understanding the characteristics of co-oligomeric FLCs, as compared with homo-oligomers, is expected to provide helpful insights in developing new FLC materials critically desired for the advanced LCD technology.

Experimental Section

General. Reactions requiring an inert gas atmosphere were conducted under argon, and the glassware was oven-dried (140 °C). THF and toluene were distilled over sodium prior to use. Methylene chloride was distilled over calcium hydride. Commercially available chemicals were used as received without further purification unless otherwise stated. ^{1}H NMR spectra were recorded on a Bruker DPX-300 MHz spectrometer. Chemical shifts are given in ppm, referenced to residual proton resonances of the solvents. Thin-layer chromatography was performed on aluminum plates precoated with Merck 5735 silica gel 60 F_{254}. Column chromatography was performed with Merck silica gel 60 (230 ± 400 mesh). FT-IR transmission spectra were obtained with JASCO FT-IR spectrometer (660 Plus equipment) using 4 cm^{-1} spectral resolution and averaged over 512 scans.

Synthesis

4-(1-(*R*)-Methylheptyloxy)-3-nitrobenzoic acid 4'-(undec-10-enyloxy)-biphenyl-4-yl ester (mesogen 1): 4-(Undec-10-enyloxy)-4'-hydroxybiphenyl (**3**) (1.15 g, 3.4 mmol), 3-nitro-4-(1-(*R*)-methylheptyloxy)benzoic acid (**1**) (1.0 g, 3.4 mmol) and 4-*N,N'*-dimethylaminopyridine (DMAP, 25 mg, catalytic amount) were dissolved in 80 mL of dry CH_2Cl_2/THF (1:1). After cooling the solution to 0 °C, a solution of *N,N'*-dicyclohexylcarbodiimide (DCC, 0.89 g, 4.3 mmol) in 10 mL of dry CH_2Cl_2 was added and reaction mixture was stirred for 3 hr at 0 °C and overnight at room temperature. The urea was filtered off and the solvent was evaporated. The residue was dissolved in ether and filtered again to remove urea. The solvent was evaporated and the remaining crude product was purified by column chromatography on silica gel (yield 61 %, yellowish white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H, ArH), 8.30 (d, 1H, ArH), 7.57 (d, 2H, ArH), 7.47 (d, 2H, ArH), 7.21 (d, 2H, ArH), 7.15 (d, 1H, ArH), 6.96 (d, 2H, ArH), 5.79 (m, 1H, $CH_2=C\underline{H}$), 4.97 (d, 1H, $C\underline{H}_2$=CH-trans), 4.91 (d, 1H, $C\underline{H}_2$=CH-cis), 4.63 (q, 1H, C*-H), 3.98 (t, 2H, CH_2-O), 2.01 (m, 2H, $CH_2=CH-C\underline{H}_2$), 1.29-1.81 (m, 27H, $C\underline{H}_2$, O-C*H-$C\underline{H}_3$), 0.87 (t, 3H, $CH_2-C\underline{H}_3$); IR (NaCl, cm^{-1}) : 3050, 2954, 2850, 1738, 1624, 1538, 1500, 1284, 1246, 1218.

4-(10-Undecenyloxy)biphenyl-4-yl 2(*S*)-chloro-3-(*S*)-methylpentanoate (5) (mesogen 2): 4-(Undec-10-enyloxy)-4'-hydroxybiphenyl (**3**) (4.0 g, 11.8 mmol), (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**2**) (1.78 g, 11.8 mmol) and 4-*N,N'*-dimethylaminopyridine (DMAP, 50 mg, catalytic amount) were dissolved in 100 mL of dry CH_2Cl_2/THF (1:1). After cooling the solution to 0 °C, a solution of *N,N'*-dicyclohexylcarbodiimide (DCC, 3.1 g, 15 mmol) in 25 mL of dry CH_2Cl_2 was added and reaction mixture was stirred for 3 hr at 0 °C and overnight at room temperature. The urea was filtered off and the solvent was evaporated. The residue was dissolved in ether and filtered again to remove urea. The solvent was evaporated and the remaining crude product was purified by column chromatography on silica gel (yield 68 %, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, 2H, ArH), 7.48 (d, 2H, ArH), 7.16 (d, 2H, ArH), 6.96 (d, 2H, ArH), 5.81 (m, 1H, $CH_2=C\underline{H}$), 4.99 (d, 1H, $C\underline{H}_2$=CH-trans), 4.93 (d, 1H, $C\underline{H}_2$=CH-cis), 4.39 (d, 1H, Cl-C*H), 3.99 (t, 2H, O-CH_2), 2.23 (m, 1H, C*$\underline{H}$-CH_3), 2.04 (q, 2H, $CH_2=CH-C\underline{H}_2$), 1.80 (m, 2H, O-CH_2-$C\underline{H}_2$-CH_2), 1.25-1.55 (m, 14H, CH_2 and C*-$C\underline{H}_2$-CH_3), 1.15 (d, 3H, C*-$C\underline{H}_3$), 0.99 (t, 3H, C*-CH_2-$C\underline{H}_3$); IR (NaCl, cm^{-1}) : 3078, 2968, 2922, 2874, 2862, 1760, 1606, 1498, 1476, 1286, 1268, 1250, 1250, 1214, 1172, 1156, 830.

Cyclic Homo-Oligomer 1: To a solution of 4-(1-(*R*)-methylheptyloxy)-3-nitrobenzoic acid 4'-(undec-10-enyloxy)-biphenyl-4-yl ester (mesogen **1**) (100 mg, 0.163 mmol) and 2,4,6,8-tetramethylcyclotetrasiloxane (**6**) (8.9 mg, 0.037 mmol) in 2 mL of dry toluene was added 50 μL of platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4 % Pt). The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 5 hr. The solvent was removed and the crude product purified by column chromatography on silica gel. The excess of monomers was separated first using a petroleum ether/ethyl acetate mixture (vol. ratio 5:1). The tetramer was finally eluted with chloroform. The product was then precipitated in 50 mL n-hexane. Centrifugation and drying for 12 hr at room temperature *in vacuo* yielded the pure homo-tetramer (yield 65 %, yellowish white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 4H, ArH), 8.29 (d, 4H, ArH), 7.56 (d, 8H, ArH), 7.46 (d, 8H, ArH), 7.21 (d, 8H, ArH), 7.14 (d, 4H, ArH), 6.94 (d, 8H, ArH), 4.62 (q, 4H, C*-H), 3.96 (t, 8H, CH_2-O), 1.78 (m, 8H, O- CH_2-$C\underline{H}_2$), 1.1-1.7 (m, 116H, $C\underline{H}_2$ and O-C*H-$C\underline{H}_3$), 0.87 (t, 12H, CH_2-$C\underline{H}_3$), 0.50 (t, 8H, Si-CH_2), 0.05 (s, 12H, Si-CH_3).

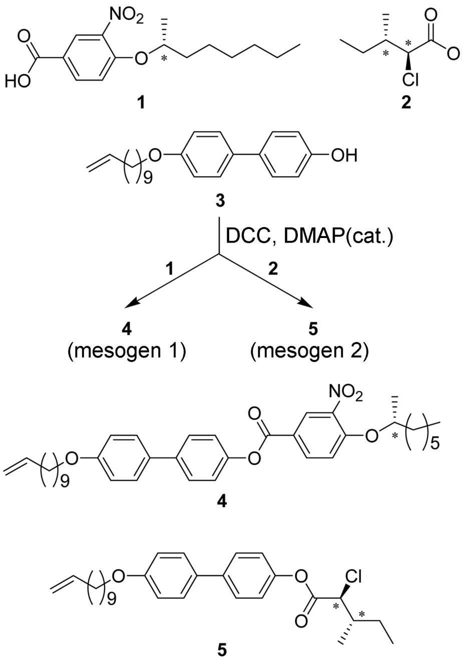
Cyclic Homo-Oligomer 2: To a solution of 4-(10-undecenyloxy)biphenyl-4-yl 2(*S*)-chloro-3-(*S*)-methyl-pentanoate (**5**) (mesogen **2**) (101.3 mg, 0.215 mmol) and 2,4,6,8-tetramethylcyclotetrasiloxane (**6**) (11.8 mg, 0.049 mmol) in 3 mL of dry toluene was added 50 μL of platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4 % Pt). The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 5 hr. The solvent was removed and the crude product purified by column chromatography on silica gel. The excess of monomers was separated first using a petroleum ether/ethyl acetate mixture (vol. ratio 5 : 1). The tetramer was finally eluted with chloroform. The product was then precipitated in 100 mL *n*-hexane. Centrifugation and drying for 12 hr at room temperature *in vacuo* yielded the pure homo-tetramer (yield 77 %, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, 8H, ArH), 7.44 (d, 8H, ArH), 7.13 (d, 8H, ArH), 6.93 (d, 8H, ArH), 4.37 (d, 4H, Cl-C*H), 3.95 (t, 8H, O-CH_2), 2.21 (m, 4H, C*Cl-C*H), 1.77 (m, 8H, O-CH_2-$C\underline{H}_2$), 1.2-1.7 (m, 72H, CH_2 and C*-CH_2), 1.12 (d, 12H, C*-CH_3), 0.97 (t, 12H, C*-CH_2-$C\underline{H}_3$), 0.50 (m, 8H, Si-CH_2), 0.04 (s, 12H, Si-CH_3).

Cyclic Co-Oligomer: To a solution of 4-(1-(*R*)-methylheptyloxy)-3-nitrobenzoic acid 4'-(undec-10-enyloxy)-biphenyl-4-yl ester (Mesogen **1**) (100 mg, 0.163 mmol) and 2,4,6,8-tetramethylcyclotetrasiloxane (11.5 mg, 0.048 mmol) in 2 mL of dry toluene was added 50 μL of platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4 % Pt). The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 2 hr; then 4-(10-undecenyloxy) biphenyl-4-yl 2(*S*)-chloro-3-(*S*)-methylpentanoate (Mesogen **2**) (22.5 mg, 0.048 mmol) was added and the mixture was stirred for another 2 hr. The solvent was removed and the crude product purified by column chromatography on silica gel. The excess of monomers was separated first using a petroleum ether/ethyl acetate mixture (vol. ratio 5 : 1). The oligomer was finally eluted with chloroform. The product was precipitated in 50 mL *n*-hexane. Centrifugation and drying for 12 hr at room temperature *in vacuo* yielded the pure co-tetramer (yield 27 %, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 3.4H, ArH), 8.31 (d, 3.4H, ArH), 7.58 (d, 8H, ArH), 7.49 (d, 8H, ArH), 7.23 (d, 6.8H, ArH), 7.15 (d, 4.6H, ArH), 4.64 (m, 3.4H, O-C*H), 4.39 (d, 0.6H, Cl-CH*), 3.98 (t, 8H, O-CH_2), 2.25 (m, 0.6H, C*Cl-C*H), 1.79 (m, 8H, O-CH_2-$C\underline{H}_2$), 1.25-1.75 (m, 109.4H, CH_2, O-C*-CH_3), 1.15 (d, 1.8H, C*-C*H_3), 0.98 (t, 1.8H, C*-CH_2-$C\underline{H}_3$), 0.89 (t, 10.2H, CH_2-$C\underline{H}_3$), 0.53 (m, 8H, Si-CH_2), 0.06 (s, 12H, Si-CH_3).

Fabrication of LC Test Cells. Indium-tin-oxide (ITO) electrode layers were vacuum deposited on cleaned glass substrates and subsequently etched to obtain the square pattern (20 mm × 20 mm). A solution of polyimide (PI), SE-7492 from Nissan Chemical, was printed on the ITO-coated substrates and then hard baked at 220 °C for 2 hr. The PI layers on two separate substrates were rubbed along anti-parallel direction with velvet cloth. The two substrates were then assembled, keeping the two rubbing axis anti-parallel, into a LC cell by applying a sealant and polymer-bead spacers. The empty cells were then filled with neat liquid crystals by capillary forces on a hot stage.

Results and Discussions

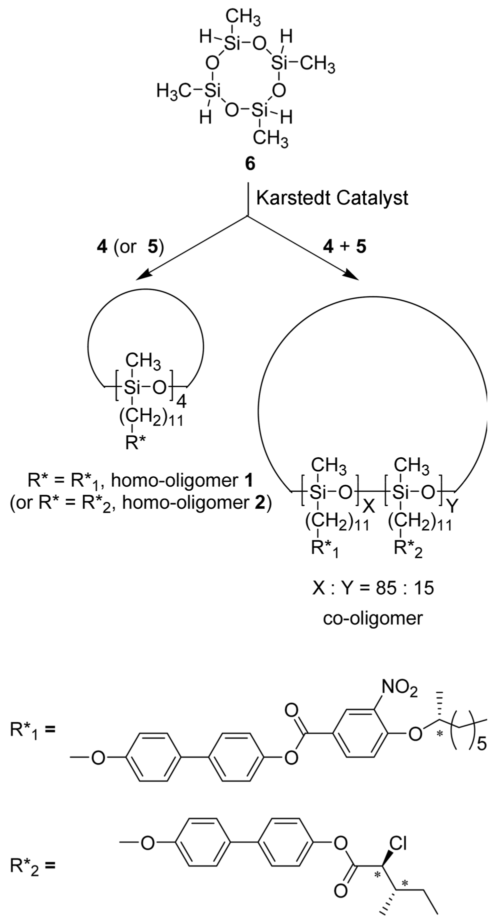
Two monomeric mesogen compounds which have 2 or 3 aromatic rings were first prepared according to known methods.[11,34-37] Coupling reaction of 4-(undec-10-enyloxy)-4'-hydroxybiphenyl (**3**) and 3-nitro-4-(1-(*R*)-methylheptyloxy) benzoic acid (**1**) was carried out under basic condition to give compound **4** (mesogen **1**). In the same way, 4-(undec-10-enyloxy)-4'-hydroxybiphenyl (**3**) and (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**2**) give compound **5** (mesogen **2**). Synthesis scheme is shown in Scheme 1.



Scheme 1. Synthesis of chiral mesogens **4** and **5**.

The cyclic homo-oligomeric ferroelectric liquid crystals and cyclic co-oligomeric ferroelectric liquid crystals were prepared through hydrosilylation between the 2,4,6,8-tetramethylcyclotetrasiloxane (**6**) and 4-(1-(*R*)-methyl-heptyloxy)-3-nitrobenzoic acid 4'-(undec-10-enyloxy)-biphenyl-4-yl ester (**4**) (mesogen **1**) or 4-(10-undecenyloxy) biphenyl-4-yl 2(*S*)-chloro-3-(*S*)-methylpentanoate (**5**) (mesogen **2**) in the presence of platinum-divinyltetra-methyldisiloxane complex in xylene (2.1-2.4 wt-% Pt) (Karstedt) as catalyst (Scheme 2).[38,39] The products were purified by repeated filtration over silica gels to remove catalyst, excess monomers and side products, and then dried *in vacuo*. The structure and purity of the synthesized cyclic oligomer products was confirmed by the disappearance of the Si-H stretching vibration peak in the IR spectrum (2160 cm^{-1}) and the absence of the olefinic C-H signals, as well as the results of ^{1}H-NMR spectrum including a correct ratio of the protons.

The phase behavior of the synthesized compounds was investigated by three widely used methods: hot-stage polarizing optical microscopy, differential scanning calorimetry (DSC), and x-ray scattering measuremnts. Figure 1 summarizes the results of phase transition characteristics of our samples, noted on the DSC thermogram. Both monomeric mesogens **1** and **2** form smectic phases (mesogen **1**: Cr 58 SmC* 81 SmA* 87 iso and mesogen **2**:



Scheme 2. Synthesis of cyclic homo-oligomers and cyclic co-oligomer

Cr 52 SmA* 57 iso) but only mesogen **1** exhibits a chiral smectic C (SmC*) phase (see Figure 1). Again, only cyclic homo-oligomer **1** (shown by (d)) shows a SmC* phase. Comparison of the phase transition temperatures of the monomeric mesogens and the corresponding cyclic homo-oligomers shows the conventional behavior of liquid crystalline polysiloxanes and oligosiloxanes,[12] i.e., the stabilization of the liquid crystalline phases through an increase of the clearing temperature (cyclic homo-oligomer **1**: Cr 85 SmX 110 SmC* 141 SmA* 152 iso and cyclic homo-oligomer **2**: Cr 80 SmX 90 SmA* 120 iso). However, the cyclic homo-oligomer **1** (shown by (d)) does not show a significant broadening of the temperature range in the desired SmC* phase due to the increased melting point and the occurrence of a higher ordered smectic phase (denoted here as smectic X). The existence of the latter could be confirmed by calorimetric detection of a very small endothermic transition to the SmC* phase, suggesting a strong similarity between the two phases.[12]

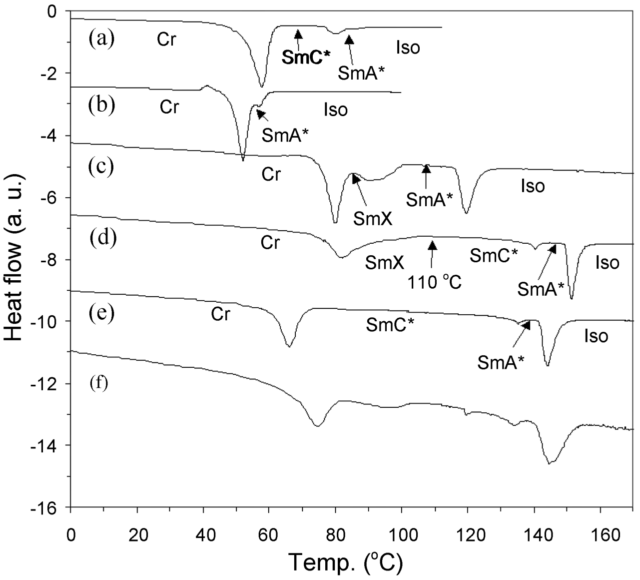


Figure 1. Comparison of the phase transition characteristics of the synthesized compounds, as determined by DSC (heating scan, 10 K min^{-1}), polarizing microscopy and XRD: (a) mesogen 1, (b) mesogen 2, (c) cyclic homo-oligomer 2, (d) cyclic homo-oligomer 1, (e) cyclic co-oligomer of mesogen 1 (85 %) and mesogen 2 (15 %), (f) mixture of cyclic homo-oligomer 1 (85%) and cyclic homo-oligomer 2 (15%) (Cr = crystalline, SmC* = chiral smectic C, SmA* = chiral smectic A, SmX = chiral smectic I or chiral smectic F, Iso = isotropic).

Mixing is the classical way to lower the crystallization temperature in liquid crystals. In the case of oligomers, it can be achieved in an additional chemical way by attaching both mesogens in one oligomer (co-oligomer). According to Figure 1 this concept has a significant advantage compared to the classical physical mixing. That is, the cyclic co-oligomer (shown by (e)), in which the pendant mesogens consist of mesogen **1** (85%) and mesogen **2** (15%), shows a pronouncedly wide SmC* temperature range of 70 K (wider than the mixture), yielding a low viscosity material with a switchable SmC* phase at relatively low temperatures. Moreover, the higher ordered smectic phase is suppressed due to disruption of structural regularity by co-oligomerization. Finally, it is important to consider the relative sharpness of the transitions in Figure 1. The broad transition peaks for the mixture of the homo-oligomers (shown by (f)) are a result of demixed, co-existing bi-phases around the phase transition. This is not found for the co-oligomer, as the different mesogens are covalently linked to one cyclic oligosiloxane backbone.

The next observation is concerned with the layer spacing. The change in the smectic layer thickness was determined by temperature-dependent small angle x-ray scattering (SAXS) measurements on powder samples carried out at a synchrotron beam line in Pohang Accelerator Lab (PAL). The corresponding layer spacings obtained for homo-oligomer **1** and co-oligomer are shown in Figure 2. On heating through the SmC* phases the variation of layer spacing of the co-oligomer is very small in the SmC* phases (see Figure 2 bottom). The layer spacing differs by less than 5 % (1.7 Å). The small change of the layer spacing at the SmA*-SmC* transition is contrasted by a large optical tilt angle, which saturates at about 32 ° for the co-oligomer (at 80 °C). The expected SmC* layer spacing can be estimated

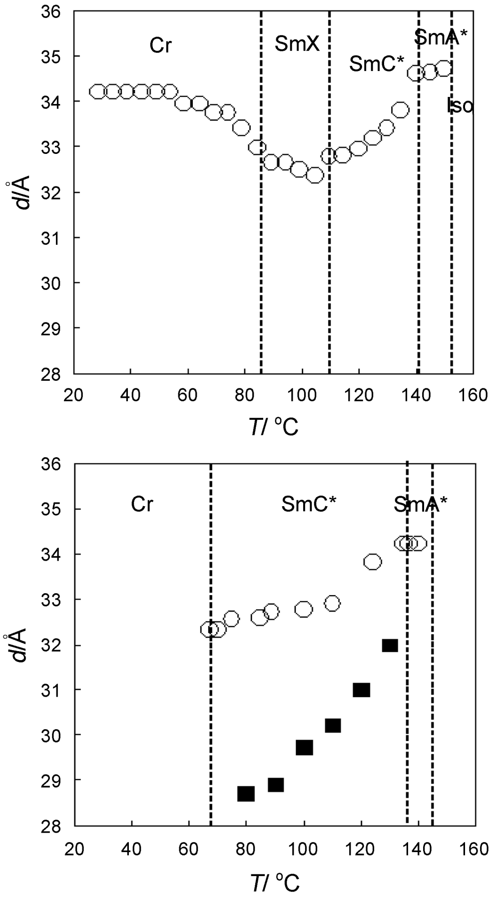


Figure 2. Temperature-dependant layer spacing *d* in the cyclic homo-oligomer **1** (top) and cyclic co-oligomer (bottom). The actual *d*-values of the cyclic co-oligomer observed by small angle X-ray scattering (open circles) are compared with the hypothetical values (filled squares) which are expected from the measured optical tilt angle $\theta_{\rm opt}$ in the SmC* state according to equation (1).

from the measured optical tilt angle, $\theta_{\rm opt}$, assuming that the mesogenic molecules simply behave as rigid rods. The smectic layer spacing $d_{\rm C}$ of the SmC* phase should then vary as:

$$d_{\rm C} = d_{\rm A} \cos \theta_{\rm opt} \tag{1}$$

where $d_{\rm A}$ denotes the smectic layer thickness of the SmA* phase. From the optical tilt data a layer shrinkage of 5.4 Å would be expected for the co-oligomer on cooling the SmA* phase into the tilted SmC* phase. Compared with this estimate, the layer shrinkage (in SmC* phase) actually observed by the X-ray measurement is very small, indicating that the co-oligomer exhibits, most likely, a de Vries-type transition.

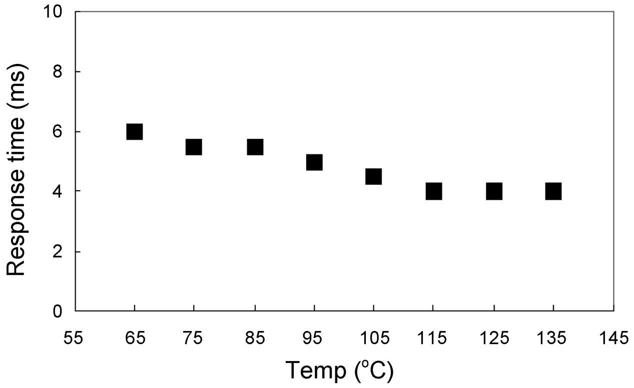


Figure 3. Response times $\tau_{10\text{-}90}$ versus temperature for the cyclic co-oligomeric ferroelectric liquid crystal (Vpp = 5 V/μm, 5 Hz square wave, 2 μm thick ITO coated cell with rubbed polyimide coatings).

Due to their highly ordered structure, ferroelectric liquid crystals tend to be very susceptible to defect formation. Particularly, the issue of smectic layer shrinkage has received a significant interest due to its relevance to the performance of electro-optic devices based on ferroelectric SmC* liquid crystals. In these devices the competition between surface-anchoring and layer shrinkage induces the formation of so-called 'Chevrons', that are folding instabilities of the smectic layer structure where the domains of opposite fold direction are mediated by 'zigzag' walls.[13] Such zigzag defects tend to deteriorate the electro-optic properties of the display devices. In this regard, our cyclic co-oligomer, which has very small layer shrinkage characteristics, could have a definite advantage over conventional FLCs in the display applications.

Measurements of the ferroelectric properties give typical results of spontaneous polarization (P_s), with the P_s values of the cyclic homooligomer **1** up to 250 nC/cm^2 as expected from similar compounds.[12] Investigations of the switching behavior were performed on a 2 μm-thick LC test cell, prepared as described in the Experimental section. Good planar alignment was obtained for the cyclic co-oligomer liquid crystal which readily filled the cell by capillary forces on a hot stage. In the SmC* phase temperature range of the cyclic co-oligomer, the response times were measured as a function of temperature according to the conventional method of determining the switching time ($\tau_{10\text{-}90}$) for changing the transmitted light intensity from 10 % to 90 % between the cross polarizers. As plotted in Figure 3, the response time varies from 6 ms to 4 ms from 65 °C to 125 °C, which demonstrates sufficiently fast switching characteristics and alignment stability over a wide temperature range. The response times measured for the cyclic co-oligomeric FLC are definitely much faster than normal nematic liquid crystals, but are quite slower than the monomeric FLCs. This may arise from the rather high molar mass of oligomers. Although the response times of the cyclic homo-oligomer FLC were not measured for comparison, due to the difficulty in preparing defect-free FLC cells, its switching speed is expected to be quite similar considering the molar mass effect.

Conclusion

In summary, we have developed a novel cyclic co-oligomeric ferroelectric liquid crystal, and found that a cyclic co-oligomer comprised of two different mesogenic units exhibits SmC* mesophase over a wide temperature range from 65 ºC to 135 ºC, much wider than those of the monomer counterparts and the homo-oligomers. This cyclic co-oligomer liquid crystal readily filled the display cell and exhibited fast switching times in the range of 4 ms to 6 ms. Moreover, we observed de Vries-type SmA*-SmC* phase transition for this cyclic co-oligomer FLC, exhibitng very small shrinkage of the layer spacing in the SmC* state. LCD applications usually require a combination of desired properties for the liquid crystal materials and practical, stable alignment schemes. In this regard, our results are expected to be helpful to developing new FLC materials critically desired for the advanced LCD technology.

Acknowledgments. The financial support from the Chemistry and Molecular Engineering Program of Brain Korea 21 Project and the Korea-Germany Internaional Research Training Group, jointly sponsored by National Research Foundation of Korea and German Research Foundation (GRK 1404), is gratefully acknowledged. The authors also thank Samsung Electronics Co. for providing the LC test cells and the equipments for response time measurements and Pohang Accelartor Lab. (PAL) for allowing the synchrotron X-ray scattering measurements.

References

1. Lechner, B. J.; Marlowe, F. J.; Nester, E. O.; Tults, J. *Proc. IEEE* **1971**, *59*, 1566
2. Kawamoto, H. *Proc. IEEE* **2002**, *90*, 460
3. Funada, F.; Hijikigawa, M. *Sharp Technical Journal* **1997**, *69*, 5
4. Goodby, J. W. *Ferroelectric Liquid Crystals*; Gordon and Breach Science Publishers: 1991
5. Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: 1998
6. Lagerwall, S. T. *Ferroelectric and Antiferroelectric Liquid Crystals*; John Wiley & Sons: 1999
7. Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett.* **1975**, *36*, L69
8. Clark, N.; Largerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899
9. Kanbe, J.; Inoue, H.; Mizutome, A.; Hanyuu, Y.; Katagiri, K.; Yoshihara, S. *Ferroelectrics* **1991**, *114*, 3
10. Koden, M.; Katsuse, H.; Tagawa, A.; Tamai, K.; Itoh, N.; Miyoshi, S.; Wada, T. *Jpn. J. Appl. Phys*. **1992**, *31*, 3632
11. Poth, H.; Zentel, R. *Liq. Cryst*. **1994**, *16*, 749
12. Poth, H.; Wischerhoff, E.; Zentel, R.; Schönfeld, A.; Henn, G.; Kremer, F. *Liq. Cryst*. **1995**, *18*, 811
13. Rieker, T. P.; Clark, N. A.; Smith, G. S.; Parmar, D. S.; Sirota, E. B.; Safinya, C. R. *Phys. Rev. Lett*. **1987**, *59*, 2658
14. Takanishi, Y.; Ouchi, Y.; Takezoe, H.; Fukuda, A.; Mochizuki, A.; Nakatsuka, M. *Jpn. J. Appl. Phys*. **1990**, *29*, L894
15. Giesselmann, F.; Zugenmaier, P.; Dierking, I.; Lagerwall, S. T.; Stebler, B.; Kaspar, M.; Hamplova, V.; Glogarova, M. *Phys. Rev. E* **1999**, *60*, 598
16. Radcliffe, M. D.; Brostrom, M. L.; Epstein, K. A.; Rappaport, A. G.; Thomas, B. N.; Shao, R. F.; Clark, N. A. *Liq. Cryst*. **1999**, *26*, 789
17. Spector, M. S.; Heiney, P. A.; Naciri, J.; Weslowski, B. T. Holt, D. B.; Shashidhar, R. *Phys. Rev. E* **2000**, *61*, 1579
18. Giesselmann, F. ; Lagerwall, J. P. F.; Radcliffe, M. D. *Phys. Rev. E* **2002**, *66*, 051704
19. Rössle, M.; Zentel, R.; Lagerwall, J. P. F.; Giesselmann, F. *Liq. Cryst*. **2004**, 883
20. Lagerwall, J. P. F.; Giesselmann, F. *Chem. Phys. Chem*. **2006**, *7*, 20
21. Redmond, M.; Coles, H. J.; Wischerhoff, E.; Zentel, R. *Ferroelectrics* **1993**, *148*, 323
22. Newton, J.; Coles, H. J.; Owen, H.; Hodge, P. *Ferroelectrics* **1993**, *148*, 379
23. Sunohara, K.; Takatoh, K.; Sakamoto, M. *Liq. Cryst*. **1993**, *13*, 283
24. Coles, H. J.; Newton, J.; Owen, H.; Hodge, P. *Liq. Cryst.* **1993**, *15*, 739
25. Wischerhoff, E.; Zentel, R.; Redmond, M.; Mondain-Monval, O.; Coles, H. J. *Macromol. Chem. Phys*. **1994**, *195*, 1593
26. Owen, H.; Newton, J.; Hodge, P.; Coles, H. J. *Mol. Cryst. Liq. Cryst.* **1995**, *265*, 563
27. Kloess, P.; McComb, J.; Coles, H. J.; Zentel, R. *Ferroelectrics* **1996**, *180*, 233
28. Grüneberg, K.; Naciri, J.; Wolff, D.; Shashidhar, R. *Proceedings of SPIE* **1996**, *2651*, 186
29. Corsellis, E. A.; Guillon, D.; Kloess, P.; Coles, H. J. *Liq. Cryst*. **1997**, *23*, 235
30. Robinson, W. K.; Carboni, C.; Kloess, P.; Perkins, S. P.; Coles, H. J. *Liq. Cryst*. **1998**, *25*, 301
31. Medeiros, D. R.; Hale, M. A.; Hung, R. J. P.; Leitko, J. K.; Willson, C. G. *J. Mater. Chem*. **1999**, *9*, 1453
32. Mann, T. E.; Lacey, D. *Liq. Cryst.* **2000**, *27*, 299
33. Lacey, D.; Mann, T. E. *Liq. Cryst.* **2003**, *30*, 1159
34. Mitsunobu, O. *Synthesis* **1981**, *1*, 1
35. Koppenhöfer, B.; Schurig, V. *Org. Synth*. **1988**, *66*, 151
36. Percec, V.; Heck, J. *J. Polym. Sci. Part A: Polym. Chem*. **1991**, *29*, 591
37. Neises, B.; Steglich, W. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 522
38. Hehl, G. H.; Goodby, J. W. *Chem. Commun.* **1999**, 13
39. Gray, G. W.; Lacey, D.; Nestor, G.; White, M. S. *Macromol. Chem., Rapid Commun*. **1986**, *7*, 71