

# Phase Transition Behavior and Electro-Rheological Effect of Liquid Crystalline Cyclic-Siloxanes with Fluorine Atoms

Kosuke Kaneko, Yusuke Miwa, Naotake Nakamura

Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, Shiga 525-8577, Japan

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**ABSTRACT:** The phase transition behavior of liquid crystalline cyclic-siloxanes containing fluorine atoms in the terminal mesogenic groups is reported. The series has different spacer length and the number of fluorine atoms that are included in the terminal mesogenic group. The thermal property of the compounds was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The influence of the spacer length between cyclic-siloxane core and the terminal mesogenic groups on the mesomorphic properties was discussed. Moreover, we measured rheological property

of these compounds in the presence of electric field. We described their electro-rheological effect (ER effect) in consideration of the influence of molecular structure. The cyclic compounds exhibited considerably large ER effect of which the response time to an electric field was fast. They were expected to be used as novel ER fluids in engineering field. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2474–2481, 2007

**Key words:** cyclic-siloxane; hydrosilylation; fluorine atom; electro-rheological effect

## INTRODUCTION

The main field of an industrial application of liquid crystals is in that of displays. To expand the application to commercial field, it will be expected for use as electro-rheological (ER) fluids. ER fluids are materials whose rheological properties can be controlled by an external electric field. The viscosity of liquid crystals increases when an electric field is applied. On the other hand, if an electric field is removed, the viscosity returns to inherent value. This phenomenon is called ER effect. Liquid crystalline polymers have large viscosity increment and relatively long response time to an applied field, while low molecular weight liquid crystals have fast response time. The long response time obstructs applications of the liquid crystalline polymers into any fields.<sup>1</sup> In view of this, we focused on the liquid crystalline oligomers.

It is preferable to be able to synthesize the liquid crystalline oligomer with narrow molecular weight distributions. Hydrosilylation can be considered as a general method for the synthesis between Si—H bond and alkene part. Then, we prepared cyclic-siloxanes by the typical hydrosilylation reaction with Pt catalyst. By this reaction, the desired liquid crys-

talline oligomers, in particular cyclic siloxane compounds, were easily synthesized.

The first report concerning cyclic liquid crystalline side chain siloxanes was published in 1981.<sup>2</sup> Several reports about liquid crystalline cyclic-siloxanes having cholesteryl groups have appeared since then, with special attention on their optical properties and potential applications as optical data storage.<sup>3,4</sup> In some studies, the comparison of the thermal properties between cyclic compounds and linear ones were carried out.<sup>5–7</sup> Based on the results, some of the properties of the cyclic ones were markedly different from those of their linear ones,<sup>6</sup> while some exhibited similar thermal properties to the linear ones.<sup>7,8</sup> In addition, side chain polysiloxanes especially exhibit advantageous properties caused by the high flexibility of the siloxane backbone. This leads to reduced viscosities and low glass transition temperatures.<sup>9–12</sup>

In this work, a series of liquid crystalline cyclic siloxanes containing three different number of fluorine atoms were prepared with the expectation that outstanding properties will be obtained. Mesogenic side groups containing fluorine atoms were selected to gain high polarity. Fluorine atoms have large electro-negativity and the size of the atom is small. These compounds are expected in the field of electro-chemistry, rheology and so on, but there have been no reports concerning the cyclic products having fluorine atoms. We now describe influence of molecular structure of the mesogenic side groups

Correspondence to: K. Kaneko (rc003987@se.ritsumei.ac.jp).

and the spacer length on the thermal properties of liquid crystalline cyclic-siloxanes. Then, ER effect of these compounds was investigated.

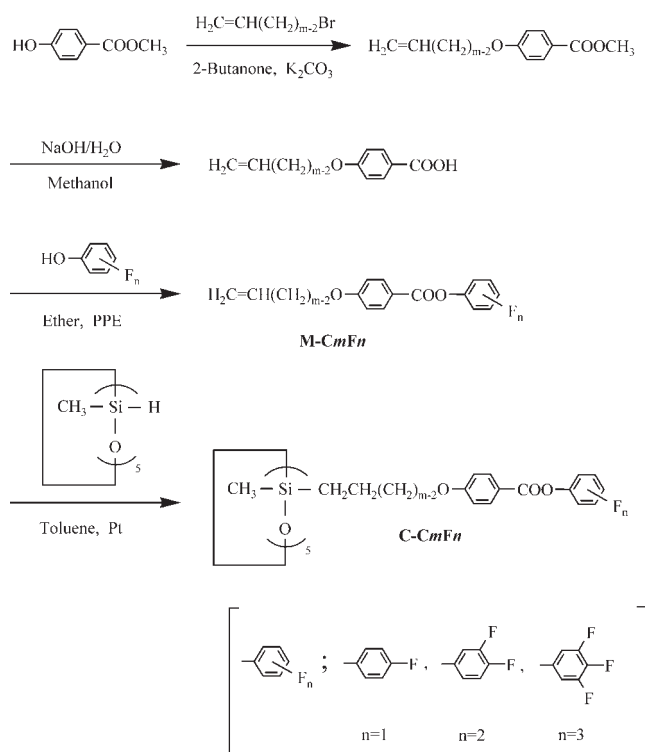
## EXPERIMENTAL

### Materials

Methyl 4-hydroxybenzoate and allyl bromide were purchased from Nacalai Tesque. The reagents used here, 4-fluorophenol, 3,4-difluorophenol, 3,4,5-trifluorophenol 4-bromo-1-butene, 5-bromo-1-pentene and 6-bromo-1-hexene, were purchased from Tokyo Kasei Kogyo. 1,3,5,7,9-Pentamethylcyclopentasiloxane was obtained from Shin-Etsu. The catalyst, polyphosphoric ester (PPE) was prepared according to literature.<sup>13</sup> Ether and toluene used in this research were dried by sodium wire, and other solvents were used without further purification. The synthetic route of cyclic-siloxane compounds prepared in this research is shown in Figure 1. They are denoted by C-CmFn, where *m* is a number of carbon atoms in the spacer and *n* is that of fluorine atoms at the mesogenic group. In addition, M-CmFn indicates its corresponding side chain parts.

### Characterization

<sup>1</sup>H-NMR measurements were made with a JEOL ALPHA-400 FT NMR (400 MHz) spectrometer using



**Figure 1** Synthetic route of cyclic-siloxane compounds, where *m* is a number of carbon atoms in the spacer and *n* is that of fluorine atoms at the mesogenic group.

$\text{CDCl}_3$  and DMSO as a solvent. In the final reactions of the cyclic-siloxane compounds, FTIR spectrometer (Perkin Elmer, Waltham, MA) was used to check the completeness of the reactions while monitoring the disappearance of the Si-H signal at  $2160\text{ cm}^{-1}$ . Gel permeation chromatography (GPC) measurements were carried out using Tosoh HLC-8020 instrument (Tokyo, Japan) with tetrahydrofuran as eluent to check the purity of the samples. Standard polystyrenes were used for calibration.

Thermal properties were measured with Diamond DSC (Perkin Elmer) with heating and cooling rates of  $5^\circ\text{C}/\text{min}$ . The textures of the liquid crystalline phases were observed with a Nikon ECLIPSE E600 optical polarizing microscope (Tokyo, Japan) equipped with a Mettler Toledo FP-82 hot stage and a Mettler Toledo FP-90 central processor (Columbus, OH).

### Synthesis

#### Methyl 4-allyloxybenzoate

Methyl 4-hydroxybenzoate (10.7 g; 0.07 mol),  $\text{K}_2\text{CO}_3$  (11.1 g; 0.08 mol) and allyl bromide (16.9 g; 0.14 mol) were dissolved in 100 mL of 2-butanone, and the mixture was refluxed for 18 h. Then, the solution was washed with water and an objective compound was extracted with ethyl acetate. After the solvent was distilled off, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 by volume) as eluent. As a result, 12.8 g of methyl 4-allyloxybenzoate was obtained as a transparent colorless liquid. Yield 95%. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.98 (dt, 2H,  $J = 9.4, 2.4$  Hz), 6.92 (dt, 2H,  $J = 9.4, 2.4$  Hz), 6.09–5.99 (m, 1H), 5.42 (dd, 1H,  $J = 17.1, 1.5$  Hz), 5.31 (dd, 1H,  $J = 10.5, 1.2$  Hz), 4.58 (td, 2H,  $J = 3.2, 1.6$  Hz), 3.88 (s, 3H).

#### 4-Allyloxybenzoic acid

The obtained methyl 4-allyloxybenzoate (11.5 g; 0.06 mol) was dissolved in 100 mL of methanol. This solution was poured into a solution containing NaOH (4.8 g; 0.12 mol) in 70 mL of water and methanol (2:5), and the mixture was refluxed for 1.5 h. After the solvent was distilled off, the residue was dissolved in water, and hydrochloric acid was added until the solution became acidic, whereupon a white precipitate formed. The resulting white precipitate was filtered and washed with water. The residue was then washed with hexane and dried to obtain 10.1 g of 4-allyloxybenzoic acid as a white solid. Yield 95%. <sup>1</sup>H-NMR ( $\text{DMSO-d}_6$ )  $\delta$ : 12.66 (s, 1H), 7.89 (t, 2H,  $J = 4.1$  Hz), 7.04 (d, 2H,  $J = 8.5$  Hz), 6.10–6.01 (m, 1H), 5.42 (dd, 1H,  $J = 17.3, 1.7$  Hz), 5.29 (dd, 1H,  $J = 10.6, 1.3$  Hz), 4.65 (d, 2H,  $J = 5.1$  Hz).

## 4-Fluorophenyl 4-(2-propenyloxy) benzoate (M-C3F1)

4-Allyloxybenzoic acid (4.43 g; 0.025 mol), 4-fluorophenol (3.43 g; 0.025 mol), and an excess amount of PPE (17 g) were dissolved in 150 mL of ether under argon atmosphere, and the mixture was refluxed for 24 h. Then, 200 mL of water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. After the solvent was distilled off, the residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent. As a result, 5.45 g of 4-fluorophenyl 4-(2-propenyloxy) benzoate was obtained as a white solid. Yield 73%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.14 (dt, 2H, *J* = 9.4, 2.4 Hz), 7.19–7.07 (m, 4H), 7.00 (dt, 2H, *J* = 9.6, 2.2 Hz), 6.12–6.02 (m, 1H), 5.45 (dd, 1H, *J* = 17.6, 1.5 Hz), 5.34 (dd, 1H, *J* = 10.2, 1.5 Hz), 4.63 (d, 2H, *J* = 5.4 Hz).

## 4-Fluorophenyl 4-(3-butenyloxy) benzoate (M-C4F1)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.13 (dt, 2H, *J* = 9.3, 2.3 Hz), 7.19–7.08 (m, 4H), 6.98 (dt, 2H, *J* = 9.3, 2.3 Hz), 5.97–5.87 (m, 1H), 5.20 (dd, 2H, *J* = 17.1, 1.5 Hz), 5.15 (dd, 2H, *J* = 10.2, 1.5 Hz), 4.11 (t, 2H, *J* = 6.8 Hz).

## 4-Fluorophenyl 4-(4-pentenyl) benzoate (M-C5F1)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.13 (dt, 2H, *J* = 9.4, 2.4 Hz), 7.19–7.07 (m, 4H), 6.97 (dt, 2H, *J* = 9.6, 2.2 Hz), 5.91–5.81 (m, 1H), 5.06 (tt, 2H, *J* = 16.8, 3.5 Hz), 4.06 (t, 2H, *J* = 6.3 Hz), 2.27 (q, 2H, *J* = 7.2 Hz), 1.97–1.90 (m, 2H).

## 4-Fluorophenyl 4-(5-hexenyloxy) benzoate (M-C6F1)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.13 (dt, 2H, *J* = 9.4, 2.3 Hz), 7.16 (tt, 2H, *J* = 6.8, 2.7 Hz), 7.10 (dq, 2H, *J* = 14.1, 3.3 Hz), 6.97 (dt, 2H, *J* = 9.4, 2.4 Hz), 5.89–5.79 (m, 1H), 5.03 (m, 2H, *J* = 22.9, 13.7, 1.5 Hz), 4.05 (q, 2H, *J* = 5.9 Hz), 2.15 (q, 2H, *J* = 7.2 Hz), 1.88–1.81 (m, 2H), 1.60 (td, 2H, *J* = 11.6, 5.7 Hz).

## 3,4-Difluorophenyl 4-(2-propenyloxy) benzoate (M-C3F2)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.12 (dt, 2H, *J* = 9.6, 2.2 Hz), 7.21 (q, 1H, *J* = 9.3 Hz), 7.12–7.07 (m, 1H), 7.02–6.93 (m, 3H), 6.07 (dq, 1H, *J* = 22.4, 5.4 Hz), 5.45 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.35 (dd, 1H, *J* = 10.5, 1.2 Hz), 4.64 (d, 2H, *J* = 5.4 Hz).

## 3,4-Difluorophenyl 4-(3-butenyloxy) benzoate (M-C4F2)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.13–8.10 (m, 2H), 7.20 (q, 1H, *J* = 9.1 Hz), 7.12–7.07 (m, 1H), 7.00–6.93 (m, 3H), 5.97–5.86 (m, 1H), 5.21–5.15 (m, 2H), 4.11 (t, 2H, *J* = 6.6 Hz), 2.59 (q, 2H, *J* = 6.5 Hz).

## 3,4-Difluorophenyl 4-(4-pentenyl) benzoate (M-C5F2)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.11 (dt, 2H, *J* = 9.3, 2.4 Hz), 7.20 (q, 1H, *J* = 9.3 Hz), 7.10 (dq, 1H, *J* = 10.7, 3.3 Hz), 6.99–6.93 (m, 3H), 5.91–5.81 (m, 1H), 5.11–5.01 (m, 2H), 4.06 (t, 2H, *J* = 6.3 Hz), 2.27 (dt, 2H, *J* = 11.9, 5.1 Hz), 1.97–1.90 (m, 2H).

## 3,4-Difluorophenyl 4-(5-hexenyloxy) benzoate (M-C6F2)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.11 (dt, 2H, *J* = 9.4, 2.4 Hz), 7.20 (q, 1H, *J* = 9.3 Hz), 7.09 (ddd, 1H, *J* = 10.7, 6.8, 2.4 Hz), 6.97–6.95 (m, 3H), 5.89–5.79 (m, 1H), 5.08–4.98 (m, 2H), 4.06 (t, 2H, *J* = 6.6 Hz), 2.15 (q, 2H, *J* = 7.2 Hz), 1.85 (dt, 2H, *J* = 15.1, 6.6 Hz), 1.64–1.56 (m, 2H).

## 3,4,5-Trifluorophenyl 4-(2-propenyloxy) benzoate (M-C3F3)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.10 (dt, 2H, *J* = 9.4, 2.2 Hz), 7.00 (dt, 2H, *J* = 9.4, 2.2 Hz), 6.92 (dq, 2H, *J* = 16.7, 4.6 Hz), 6.09–6.05 (m, 1H), 5.45 (dd, 1H, *J* = 17.6, 1.5 Hz), 5.35 (dd, 1H, *J* = 10.5, 1.2 Hz), 4.64 (d, 2H, *J* = 5.4 Hz).

## 3,4,5-Trifluorophenyl 4-(3-butenyloxy) benzoate (M-C4F3)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.10 (dt, 2H, *J* = 9.5, 2.4 Hz), 7.00–6.96 (m, 2H), 6.95–6.88 (m, 2H), 5.97–5.86 (m, 1H), 5.23–5.13 (m, 2H), 4.11 (t, 2H, *J* = 6.7 Hz), 2.59 (tdd, 2H, *J* = 8.7, 4.4, 2.2 Hz).

## 3,4,5-Trifluorophenyl 4-(4-pentenyl) benzoate (M-C5F3)

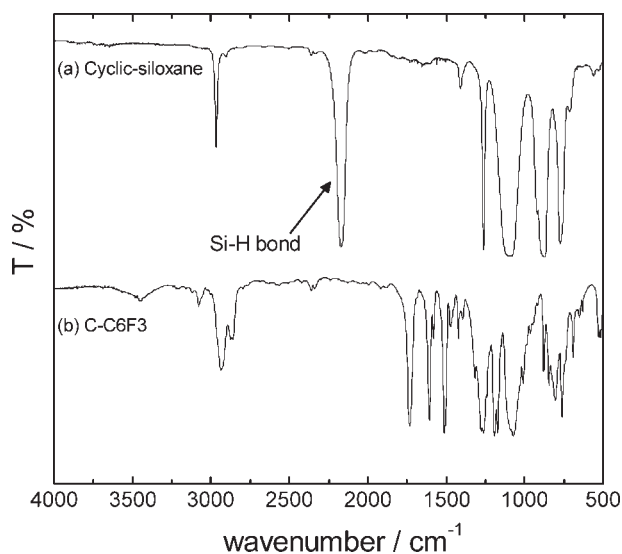
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.09 (dt, 2H, *J* = 9.4, 2.4 Hz), 6.99–6.88 (m, 4H), 5.91–5.81 (m, 1H), 5.09–5.04 (m, 2H), 4.07 (t, 2H, *J* = 6.3 Hz), 2.27 (q, 2H, *J* = 7.2 Hz), 1.97–1.90 (m, 2H).

## 3,4,5-Trifluorophenyl 4-(5-hexenyloxy) benzoate (M-C6F3)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 8.09 (dt, 2H, *J* = 9.3, 2.3 Hz), 6.99–6.88 (m, 4H), 5.89–5.79 (m, 1H), 5.03 (ddt, 2H, *J* = 21.9, 12.1, 4.4 Hz), 4.06 (t, 2H, *J* = 6.6 Hz), 2.15 (q, 2H, *J* = 7.2 Hz), 1.88–1.81 (m, 2H), 1.60 (dt, 2H, *J* = 16.1, 7.1 Hz).

Cyclic-siloxane compound (C-C<sub>m</sub>F<sub>n</sub>)

Cyclic-siloxane compound (C-C3F1) was prepared by a typical hydrosilylation of allyl-bearing substituted compound [4-fluorophenyl 4-(2-propenyloxy) benzoate (M-C3F1)] with 1,3,5,7,9-pentamethylcyclopentasiloxane having Si-H groups under plati-

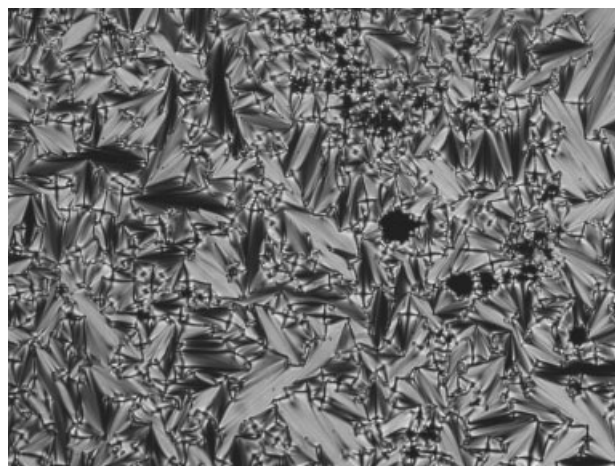


**Figure 2** IR spectra of (a) 1,3,5,7,9-pentamethylcyclopentasiloxane and (b) one of the cyclic-siloxane compounds (C-C6F3).

num catalyst. 1,3,5,7,9-Pentamethylcyclopentasilox openyloxy) benzoate (10.9 g; 0.037 mol) were dissolved in 100 mL of dried toluene. Hydrogen hexachloroplatinate(IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) dissolved in a few milliliters of 2-propanol was poured into the solution, and the mixture was refluxed for 24 h. The reaction mixture was poured into an excess of methanol to precipitate the sample. The sample obtained was reprecipitated from its acetone solution into an excess of methanol, and dried in vacuum. Purity of the compound was identified by GPC with checking disappearance of the peak due to nonreacted mesogens. If the purification was not enough, the sample was reprecipitated again by the same manner as mentioned above. Concerning the synthesis of other cyclic-siloxane compounds, each side chain part (M-C $m$ F $n$ ) was used instead of 4-fluorophenyl 4-(2-propenyloxy) benzoate (M-C3F1), respectively.

### Rheological measurements

The rheological properties were measured by a rotational rheometer (Rheosol-G2000, UBM, Kyoto, Japan) equipped with an electric field controller (Matsusada Precision Devices high-voltage supply, Shiga, Japan). All measurements were performed using parallel plates with a diameter of 15 mm and a gap of 0.1 mm. The sample was placed between the parallel plates in an isotropic phase, and was held at the temperature in an isotropic phase for about 10 min. Then, the sample was cooled to the desired temperature, and the gap was adjusted. The electric field of 2 kV/mm was applied between upper and lower plates under shearing at a constant



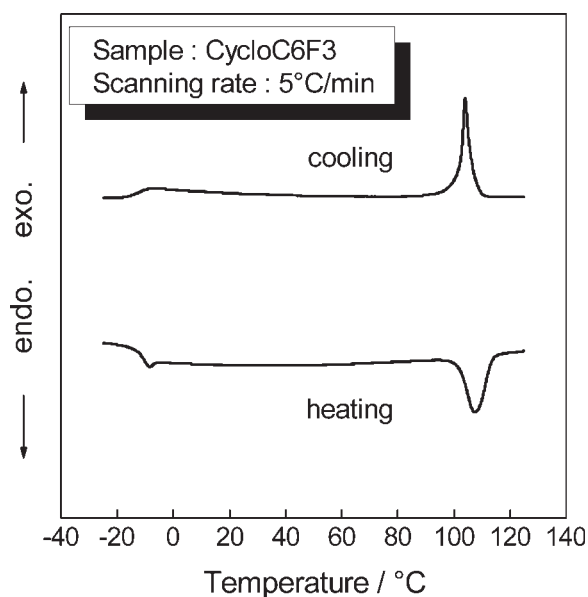
**Figure 3** Focal conic fan texture of C-C6F3 taken at 85 °C, which is characterized as smectic A phase.

shear rate. Generated shear stress was defined as the difference between the measured shear stress in the presence and absence of application of the electric field. Shear rates reported in this article have been defined as the shear rate at the edge of the plate, because the fixtures did not provide a uniform shear strain.

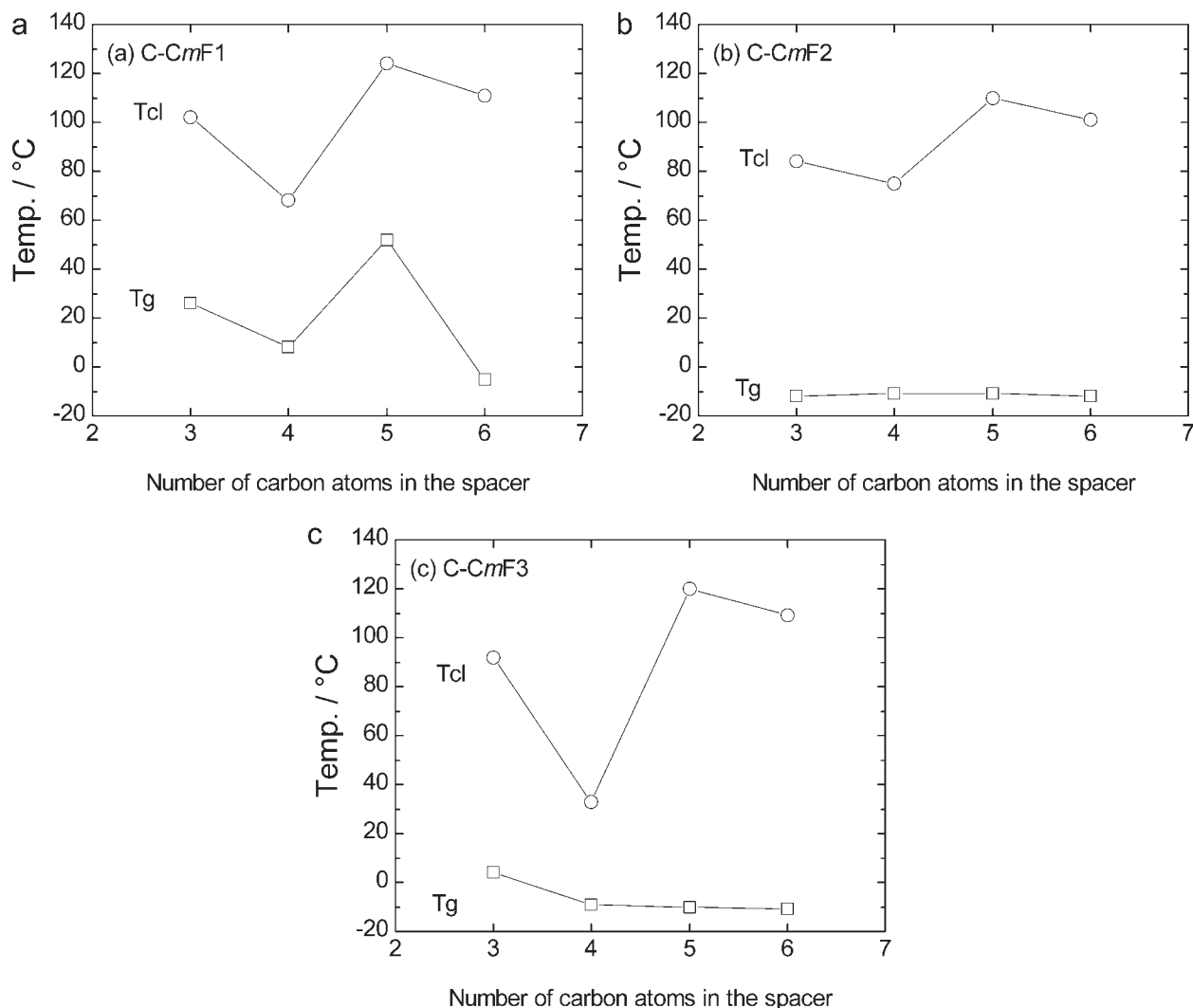
## RESULTS AND DISCUSSION

### Structural characterization of cyclic-siloxane compounds

Figure 2 shows the IR spectra of (a) 1,3,5,7,9-pentamethylcyclopentasiloxane and (b) one of the cyclic-siloxane compounds (C-C6F3), respectively. As can be seen from the figure, 1,3,5,7,9-pentamethylcyclopenta-



**Figure 4** DSC diagram of C-C6F3 (Scanning rate: 5°C/min).



**Figure 5** Phase transition behavior of the cyclic-siloxane compounds summarized based on the classification of the number of fluorine atom in the mesogenic group: (a)  $n = 1$ , (b)  $n = 2$ , (c)  $n = 3$ .

siloxane exhibited a sharp absorption at  $2160\text{ cm}^{-1}$  due to the Si—H bond. However, for C-C6F3, the peak disappeared in the spectrum. Similar results were observed for all the other cyclic-siloxane compounds, indicating that the mesogenic groups were completely grafted into the cyclic-siloxane core. In addition, the molecular structure of the target compounds was further confirmed with  $^1\text{H-NMR}$  spectroscopy by checking that the absorption peak owing to a proton of Si—H bond disappeared. All cyclic-siloxane compounds showed similar  $^1\text{H-NMR}$  traces to the corresponding mesogenic group with the loss of the vinylic protons  $\delta = 5.80$  and  $\delta = 5.00$ , and the appearance of the  $\text{CH}_3\text{Si}$  proton at  $0.59\text{ ppm}$ .

### Phase transition behavior

Here, we describe the phase transition behavior of C-C6F3 through an example. From the POM observation, C-C6F3 exhibited bâtonnet texture at around

$103^\circ\text{C}$  on cooling from the isotropic melt. Then, the texture changed gradually with decreasing temperature, consequently a focal conic fan texture was formed. The texture taken at  $85^\circ\text{C}$  is shown in Figure 3. The texture did not change while temperature decreased to  $-30^\circ\text{C}$ . Figure 4 shows DSC diagram of C-C6F3. In DSC diagram, a clear exothermic peak was detected at  $108^\circ\text{C}$  that was in good agreement with the temperature at which the texture appeared on POM. This behavior in the texture was characterized as an appearance of smectic A phase.<sup>14</sup> Baseline shift was observed at  $-11^\circ\text{C}$ , which corresponded to its glass transition temperature. Similar result was observed for all the other compounds. Phase transition behavior of all the compounds obtained is summarized based on the classification of the number of fluorine atom in the mesogenic group in Figure 5(a–c), respectively.

For the series of C-CmF1, the clearing points obviously showed an odd-even effect with increasing the

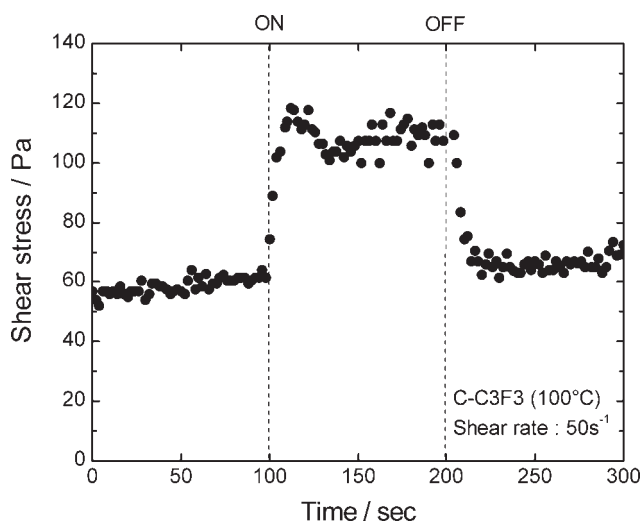
length of the spacer in which the number of the carbon atoms was varied from 3 to 6. The glass transition temperature of all the compounds was almost the same except for C-C5F1, indicating that it was completely independent of the length of the spacer. In general, the glass transition temperature of side chain liquid crystalline polymers is strongly influenced by the flexibility of polymer backbone and molecular weight. It is assumed that cyclic-siloxane core also generated similar effect on glass transition temperature like polymer backbone.

It can be seen that very wide smectic A range was observed for all the compounds synthesized in this study. Comparing cyclic-siloxane compounds with corresponding monomers, it can be expected that the liquid crystallinity would be stable because one side of each monomer was fixed by cyclic-siloxane core. Thus, it is predicted that the connection between the cyclic-siloxane core and mesogenic groups led to stabilization of thermal properties. This behavior was also confirmed by Sołtysiak et al.<sup>15</sup>

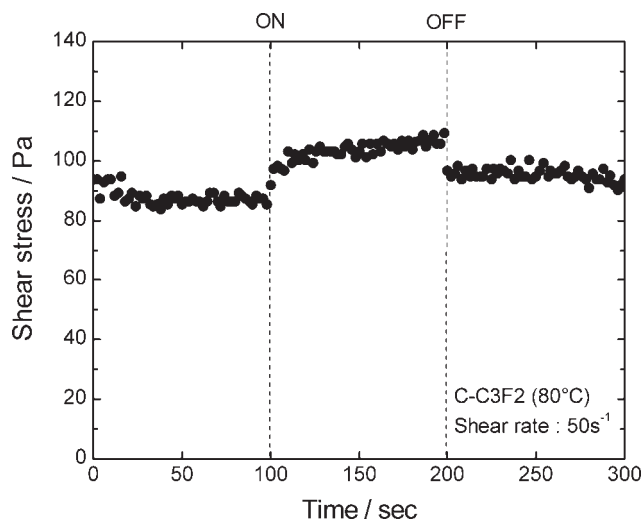
### Rheological properties

#### ER effect of C-3Fn

Figure 6 shows the result of ER effect measurement for C-C3F3 obtained in a condition of which shear rate was  $50 \text{ s}^{-1}$ . The measurement was performed at the vicinity of its clearing point. The reason for this is that there was no change in its shear stress because its viscosity was very low in the isotropic phase and very high in smectic phase. Inoue et al.<sup>16</sup> had found that large ER effect could be obtained just above the clearing point for side chain liquid crystalline polymers. An electric field was applied for 100 s under steady flow. As shown in this figure, the shear stress increased immediately after applying the electric field,



**Figure 6** ER effect of C-C3F3 as a function of time at  $100^\circ\text{C}$ . An electric field of  $2 \text{ kV/mm}$  was applied for 100 s.

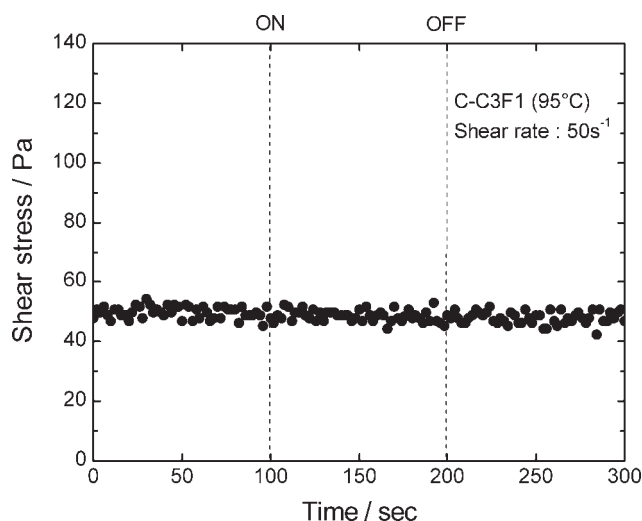


**Figure 7** ER effect of C-C3F2 as a function of time at  $80^\circ\text{C}$ . An electric field of  $2 \text{ kV/mm}$  was applied for 100 s.

and the removal of the electric field caused a satisfactory reduction in shear stress. Shear stresses under an electric field of C-C3F2 at  $80^\circ\text{C}$  and C-C3F1 at  $95^\circ\text{C}$  are shown in Figures 7 and 8, respectively. It was apparently seen that few or no ER effect was obtained in these cases. It is considered that this is due to their lower dielectric anisotropy constant in the mesogenic groups. Comparing the ER effect of the cyclic-siloxane compounds studied here with that of liquid crystalline polymers, the response time of shear stress to applied electric field for compounds with lower molecular weight was fast. From the viewpoint of utility for mechanical field, this fast response is desirable.

#### Enhanced shear stress for C-CmF3

Figure 9 shows the increase in ratio of the shear stress as a function of the number of carbon atoms

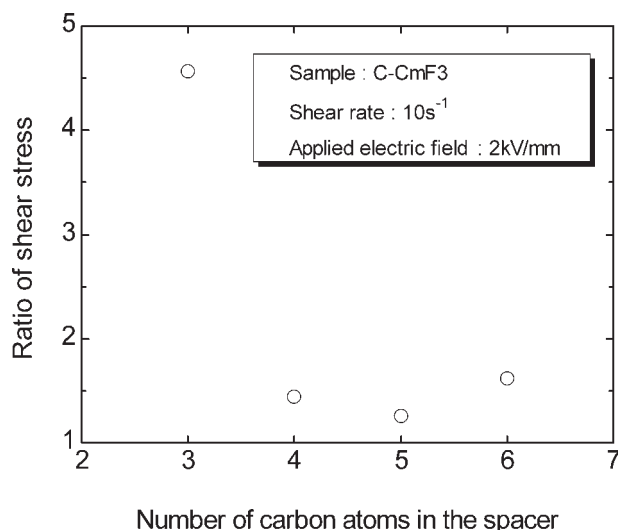


**Figure 8** ER effect of C-C3F1 as a function of time at  $95^\circ\text{C}$ . An electric field of  $2 \text{ kV/mm}$  was applied for 100 s.

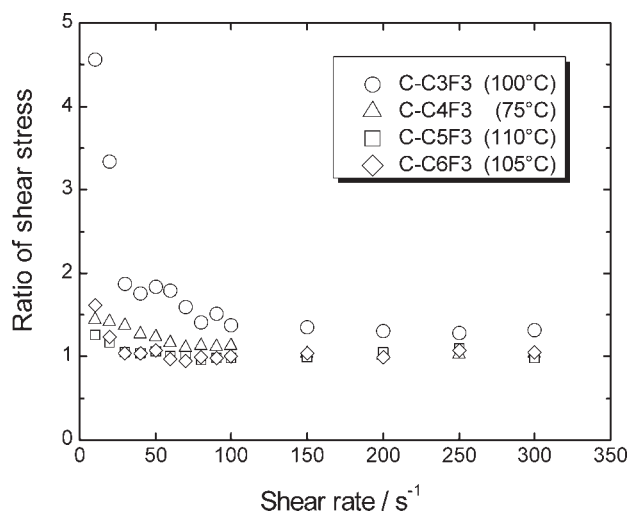
in the spacer for C-CmF3. The measurement was performed with  $10 \text{ s}^{-1}$  of shear rate and  $2 \text{ kV/mm}$  of electric field was applied to the samples for 100 s. The cyclic compound with shortest spacer exhibited the largest ER effect. In the case of C-C3F3, 4.5 times the ER effect was observed in maximum. On the other hand, for C-C4F3, C-C5F3, and C-C6F3, there was no marked increase in shear stress by the ER effect. The ratio of generated shear stress for the compounds having longer spacer remained around 1.5 times. We could conclude that shorter spacer played a very significant role in the appearance of ER effect. The ER effect concerning these compounds was influenced apparently by the distance between cyclic-siloxane core and terminal mesogenic groups. In the case of the compounds with shorter spacer, strong interaction between cyclic-siloxane core and terminal mesogenic groups would be generated when an electric field is applied. As a result, dense domains including the core and arranged mesogenic groups might be formed.

#### Shear rate dependence of ER effect for C-CmF3

The shear rate dependence on the increase ratio of shear stress for C-CmF3 is shown in Figure 10. On the basis of the result presented, it is clear that the compounds with shorter spacer showed larger ER effect for all shear rates. With increasing shear rate until  $100 \text{ s}^{-1}$ , increase in shear stress by ER effect drastically decreased, then took a constant value in high shear rate range. Even if the orientation of mesogenic groups and the formation of domains by the application of electric field occur under steady flow, the increase in shear stress would be undetect-



**Figure 9** Increase in ratio of the shear stress as a function of the number of carbon atoms in the spacer for C-CmF3.



**Figure 10** Shear rate dependence on the increase ratio of shear stress for C-CmF3.

able because of very big strain that may destroy it. In addition, a partial slip between the sample and plates might relate to a reduction in the generated shear stress.

## CONCLUSIONS

Liquid crystalline cyclic-siloxanes were synthesized while varying the length of the spacers and the number of fluorine atoms in the mesogenic groups. They all showed very wide smectic A range. This could be explained by the fact that the mobility of each mesogenic group was controlled by the connection with cyclic-siloxane core. As a result, this led to its stable liquid crystal phase in wide temperature range. It was found that the spacer length strongly affected its transition behavior, resulting to a notable odd-even effect on the clearing temperatures.

Concerning rheological property, the compounds with high dielectric anisotropy in the mesogenic groups showed large ER effect. In addition, short spacer was also useful for the appearance of the effect. The response time to an electric field was very desirable, and the shear stress increased instantly by the application of an electric field. This suggests that liquid crystalline cyclic compounds would be useful as one of electro rheological fluids similar to liquid crystalline polymers which had been studied up to the present.

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