A novel class of materials for ferroelectric liquid crystals containing siloxy chain end groups

Kazuyuki Sunohara[a]; Kohki Takatoh[a]; Masanori Sakamoto[a]

[a] Display Laboratory, Toshiba Research and Development Center, Kawasaki, Japan

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by KAZUYUKI SUNOHARA*, KOHKI TAKATOH
and MASANORI SAKAMOTO

Display Laboratory, Toshiba Research and Development Center,
Komukai, Saiwai-ku, Kawasaki, 210 Japan

Novel liquid crystals containing a siloxy chain as an end tail group instead of an alkyl chain were synthesized. The substitution effects were studied for ferroelectric liquid crystal materials. It was found that the temperature range for the chiral smectic C phase was reduced and shifted to lower temperature in comparison with the analogous alkyl chain derivatives. The crystallinity of the siloxy chain derivatives decreased and cholesteric phases were not observed. The influence of siloxy chains on ferroelectric liquid crystal properties, especially spontaneous polarizations and tilt angles, also greatly depended upon the mesogenic group structure. The X-ray diffraction results showed that the end tail group occupied a larger thickness in the chiral smectic C layer for the siloxy chain derivative than that for the alkyl chain derivative.
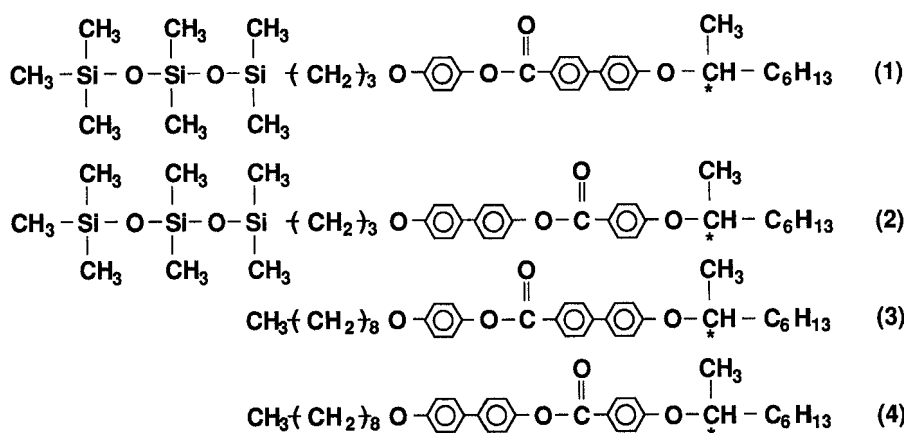
1. Introduction

The structure of the ferroelectric liquid crystal molecule consists of several parts, for example, mesogenic groups, end tail groups and chiral groups. The end tail group fills the space between the mesogenic groups in the liquid crystal phase and can act as a spacer; it regulates the intermolecular spacing and thus controls the molecular forces which cause the liquid-crystalline state [1]. From the hydrodynamic point of view, the end tail group plays a significant role; it determines the length of the molecules and therefore, the radius of gyration which is important for the viscosity.

For most ferroelectric liquid crystal molecules, the end tail groups are alkyl chains. The replacement of alkyl chains with more flexible ones might result in decreasing rotational viscosity as the gyration radius would decrease. Materials with polysiloxane structures, known as silicone oil, show lower viscosity and lower freezing temperatures than their alkyl counterparts, with equal chain length. This is ascribed to the chain flexibility for polysiloxane. In fact, liquid-crystalline polymers, having a siloxane backbone structure, show low transition temperatures and low viscosity. Finkelmann and Rehage [2] synthesized liquid-crystalline polysiloxanes with glass transitions at low temperature from vinyl substituted mesogenic molecules and poly(hydrogenmethylsiloxane). Pranoto and Hassae [3] showed by comparison of a liquid-crystalline polysiloxane and a polyacrylate analogue, the viscosity of the polysiloxane was about 20 times smaller than that of the polyacrylate. The model compounds of liquid-crystalline polymers having siloxy chains instead of alkyl chains show low transition temperatures and low order parameters [4, 5]. In consequence, we could expect to change the character of a ferroelectric liquid crystal material by

* Author for correspondence.

substitution of the siloxy chains for alkyl chains as end tail groups. The chain flexibility would especially influence the thermal stability of the liquid-crystalline state and the viscosity. Reduction of viscosity is of great interest, from the application point of view, because it dominates the switching time of the ferroelectric liquid crystal display. To clarify these points, we synthesized compounds with siloxy end tail groups, (1) and (2), designated as TSiPPOB and TSiPBOP, respectively, and measured their ferroelectric liquid-crystalline properties. For comparison, we have also synthesized the analogues with alkyl end tail groups (3) and (4), designated as IB-9 and IIB-9, respectively. IB-9 and IIB-9 are typical ferroelectric liquid crystal materials, having high spontaneous polarizations and wide temperature ranges for the chiral smectic C phase [6]. Those materials, which showed good alignment for surface stabilized ferroelectric liquid crystal spontaneous polarization and switching time measurements were carried out. For TSiPBOP and IIB-9, the liquid-crystalline structure was analysed by X-ray diffraction measurement at room temperature.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\{CH_2\}_3\ O-\bigcirc\!\!\!\!\bigcirc-O-\overset{\overset{O}{\|}}{C}-\bigcirc\!\!\!\!\bigcirc\bigcirc\!\!\!\!\bigcirc-O-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-C_6H_{13}\quad(1)$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\{CH_2\}_3\ O-\bigcirc\!\!\!\!\bigcirc\bigcirc\!\!\!\!\bigcirc-O-\overset{\overset{O}{\|}}{C}-\bigcirc\!\!\!\!\bigcirc-O-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-C_6H_{13}\quad(2)$$

$$CH_3\{CH_2\}_8\ O-\bigcirc\!\!\!\!\bigcirc-O-\overset{\overset{O}{\|}}{C}-\bigcirc\!\!\!\!\bigcirc\bigcirc\!\!\!\!\bigcirc-O-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-C_6H_{13}\quad(3)$$

$$CH_3\{CH_2\}_8\ O-\bigcirc\!\!\!\!\bigcirc\bigcirc\!\!\!\!\bigcirc-O-\overset{\overset{O}{\|}}{C}-\bigcirc\!\!\!\!\bigcirc-O-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-C_6H_{13}\quad(4)$$

2. Results and discussion

2.1. *Synthesis of TSiPPOB, TSiPBOP, IB-9 and IIB-9*

Synthetic routes for the materials are summarized in figure 1. Detailed conditions are described in the Experimental. Characterization of the intermediate and final products were carried out with ^{1}H NMR.

2.2. *Mesophase behaviour*

The transition temperatures for these materials are listed in table 1.

For TSiPPOB a smectic A phase was observed and a chiral smectic C phase was observed only on cooling. On the other hand, the cholesteric phase was observed only for the alkyl chain analogues. The introduction of siloxy groups eliminated the cholesteric phase and generated the smectic A phase. This transition temperature result differs from the rule that was shown by Coates [7]. He showed that a compound, whose alkyl chain is attached to a biphenyl moiety, as in IB-9, has a smectic C–nematic transition. This would be a characteristic of siloxy liquid-crystalline compounds. However, in this case, because of the smectic phase stabilization effect observed in TSiPPOB, the increase in the lateral interaction or the decrease in the longitudinal interaction between liquid crystal molecules was suggested through the substitution of
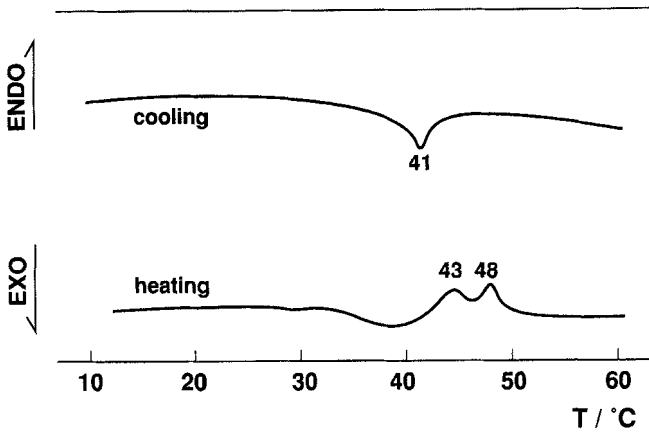
$$HO \text{-} \langle\text{O}\rangle_l \text{-} OH \xrightarrow[\text{CH}_3\text{(CH}_2\text{)}_8\text{Br}]{\text{CH}_2=\text{CH-CH}_2\text{-Br}} \text{CH}_2=\text{CH-CH}_2\text{-O-}\langle\text{O}\rangle_l\text{-OH} \quad (5)$$

$$\xrightarrow{} \text{CH}_3\text{(CH}_2\text{)}_8\text{O-}\langle\text{O}\rangle_l\text{-OH} \quad (6)$$

$$HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{-OH} \xrightarrow{\underset{*}{\text{Ts-O-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-C}_6\text{H}_{13}}} HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{O-}\underset{*}{\overset{\text{CH}_3}{\overset{|}{\text{CH}}}}\text{-C}_6\text{H}_{13} \xrightarrow{\text{SOC}\ell_2} C\ell\text{-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{O-}\underset{*}{\overset{\text{CH}_3}{\overset{|}{\text{CH}}}}\text{-C}_6\text{H}_{13} \quad (7)$$

$$(5) + (7) \xrightarrow{} \text{CH}_2=\text{CH-CH}_2\text{-O-}\langle\text{O}\rangle_l\text{O-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{O-}\underset{*}{\overset{\text{CH}_3}{\overset{|}{\text{CH}}}}\text{-C}_6\text{H}_{13} \quad (8)$$

$$\xrightarrow{\underset{\text{CH}_3 \quad \text{CH}_3}{\overset{\text{CH}_3 \quad \text{CH}_3}{\text{CH}_3\text{-Si-(O-Si)}_2\text{H, Pt}}}} \text{CH}_3\text{-Si-(O-Si)}_2\text{(CH}_2\text{)}_3\text{O-}\langle\text{O}\rangle_l\text{O-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{O-}\underset{*}{\overset{\text{CH}_3}{\overset{|}{\text{CH}}}}\text{-C}_6\text{H}_{13}$$

$$(6) + (7) \xrightarrow{} \text{CH}_3\text{(CH}_2\text{)}_8\text{O-}\langle\text{O}\rangle_l\text{O-}\overset{O}{\overset{\|}{C}}\text{-}\langle\text{O}\rangle_m\text{O-}\underset{*}{\overset{\text{CH}_3}{\overset{|}{\text{CH}}}}\text{-C}_6\text{H}_{13}$$

Figure 1. The synthetic routes to the ferroelectric liquid crystal compounds. For TSiPPOB and IB-9, $l = 1$, $m = 2$. For TSiPBOP and IIB-9, $l = 2$, $m = 1$.

Table 1. Transition temperatures of the compounds.

	Transition temperature/°C
TSiPPOB	$C \xrightarrow{47} S_A \underset{71}{\overset{79}{\rightleftarrows}} I$; $\underset{15}{\nwarrow} S_C^* \overset{31}{\nwarrow}$
IB-9	$C \underset{48}{\overset{81}{\rightleftarrows}} S_C^* \underset{98}{\overset{107}{\rightleftarrows}} Ch \underset{111}{\overset{119}{\rightleftarrows}} I$
TSiPBOP	$C \underset{—}{\overset{43}{\rightleftarrows}} S_C^* \underset{41}{\overset{48}{\rightleftarrows}} I$
IIB-9	$C \underset{63}{\overset{84}{\rightleftarrows}} S_C^* \underset{94}{\overset{104}{\rightleftarrows}} Ch \underset{112}{\overset{121}{\rightleftarrows}} I$

the siloxy chain for the alkyl chain. The temperature range for the chiral smectic C phase was reduced and shifted to lower temperature. For TSiPBOP, only the chiral smectic C phase was observed and the temperature range was also shifted to lower temperature. This seems to be ascribed to the flexibility of siloxane, such that liquid-crystalline polymers containing a siloxane backbone structure show low transition temperature [2]. Thus for TSiPPOB and TSiPBOP, the bulky and flexible siloxy end tail group might act so as to reduce the shape anisotropy of the molecules.

DSC thermograms of TSiPBOP and IIB-9 are shown in figures 2 and 3, respectively.

For TSiPBOP, on cooling, the crystallization exothermic peak was not observed, even below −10°C. On heating, a broad exothermic peak, at around 30°C, and a small endothermic peak at 43°C for a solid phase and liquid-crystalline phase transition, were detected. This implies that supercooling occurred. After cooling to room temperature, the slow transition between the chiral smectic C phase and the solid was observed under the microscope. Figure 4 shows the photomicrograph of TSiPBOP at room

Figure 2.   DSC thermogram of TSiPBOP. Scanning rate: $1°C\,min^{-1}$.
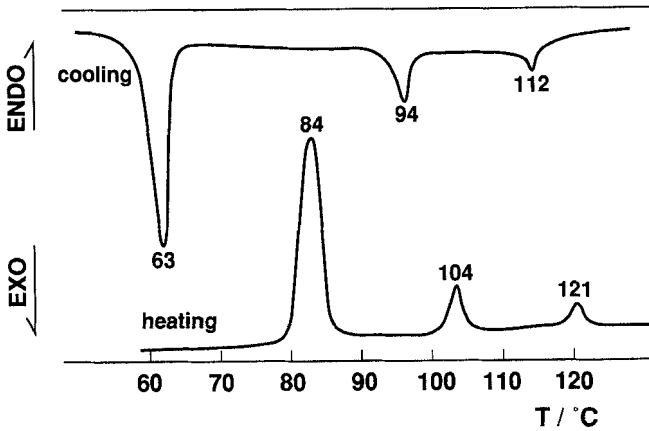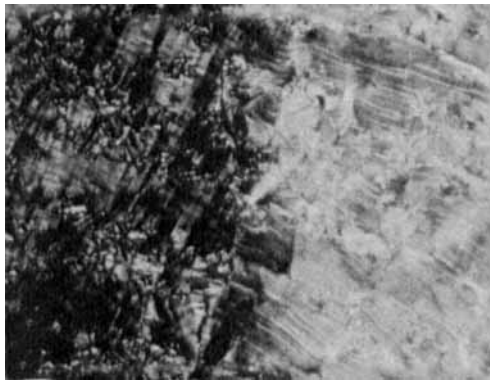

Figure 3.   DSC thermogram of IIB-9. Scanning rate: $1°C\,min^{-1}$.

Smectic C* phase | Solid phase

Figure 4.   Photomicrograph of TSiPBOP at 20°C on cooling. Slow solidification occurred (magnification: × 20).

temperature. A slow solidification with a time scale of several hours was observed as the interface between the chiral smectic C and solid phases proceeded into the chiral smectic C region under the microscope. Supercooling and extensive cold crystallization were also observed for the twin model compounds of the liquid-crystalline polymers containing a siloxane chain composed of twin mesogenic groups connected by a siloxane chain [5]. Conversely for IIB-9, the crystallization peak was clearly observed on cooling. Therefore, it is suggested that the introduction of a siloxy group reduced the crystallinity, just as for polymers and compounds containing siloxane chains.

2.3. *Ferroelectric liquid crystal properties*

In figures 5 and 6, the spontaneous polarizations (P_s) for the surface stabilized ferroelectric liquid crystal configuration with $2\,\mu m$ thickness for TSiPPOB and IB-9,
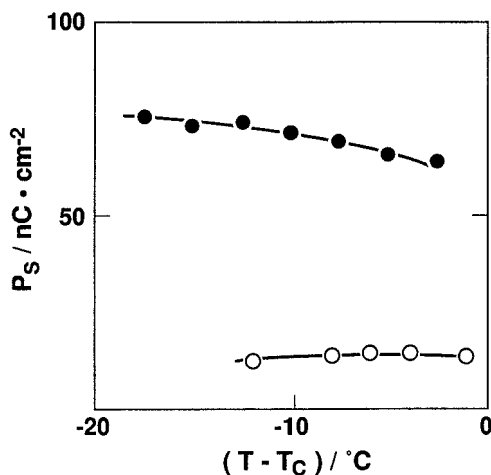
Figure 5.   Temperature dependence of the spontaneous polarizations for TSiPPOB (○) and IB-9 (●). T_c denotes the temperature at which the higher temperature phase freezes to the chiral smectic C phase.
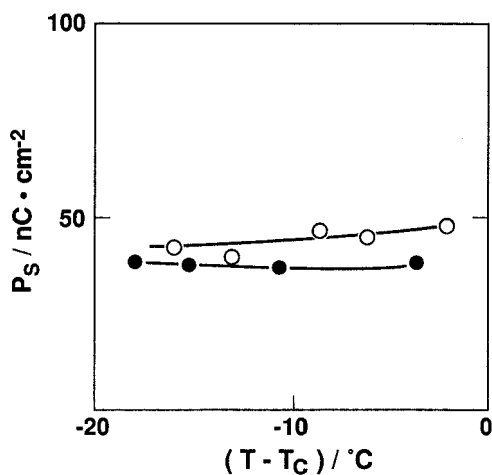
Figure 6.   Temperature dependence of the spontaneous polarizations for TSiPBOP (○) and IIB-9 (●). T_c denotes the temperature at which the higher temperature phase freezes to the chiral smectic C phase.

and TSiPBOP and IIB-9 are plotted as a function of temperature, respectively. All the data were taken on cooling. T_c denotes the transition temperature where the higher temperature phase freezes to the chiral smectic C phase as shown in table 1. For IB-9, a large P_s of $70 \, nC \, cm^{-2}$ was observed. TSiPPOB showed a P_s four times smaller than IB-9. On the other hand, TSiPBOP and IIB-9 showed a similar P_s, about $45 \, nC \, cm^{-2}$ which is intermediate between IB-9 and TSiPPOB. The distance between the dipole (C=O group in this case) and chiral centre is shorter in IIB-9 than in IB-9. The P_s is, however, twice as large for IB-9 than IIB-9 though there are many cases where P_s is determined by the distance between the dipole and chiral centre [8].

In figures 7 and 8, the tilt angles for TSiPPOB and IB-9, and TSiPBOP and IIB-9 are plotted as a function of temperature, respectively. The results, obtained for tilt
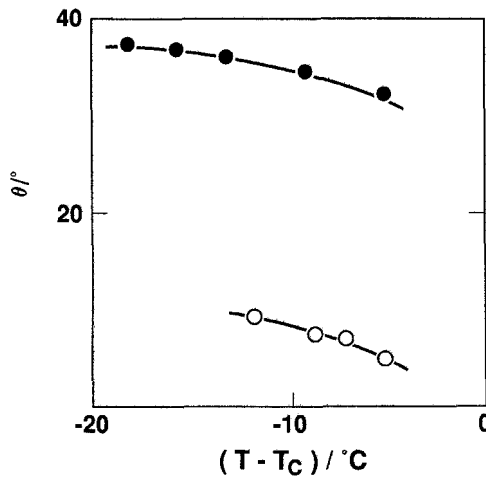
Figure 7.   Temperature dependence of the tilt angles for TSiPPOB (○) and IB-9 (●). T_c denotes the temperature at which the higher temperature phase freezes to the chiral smectic C phase.
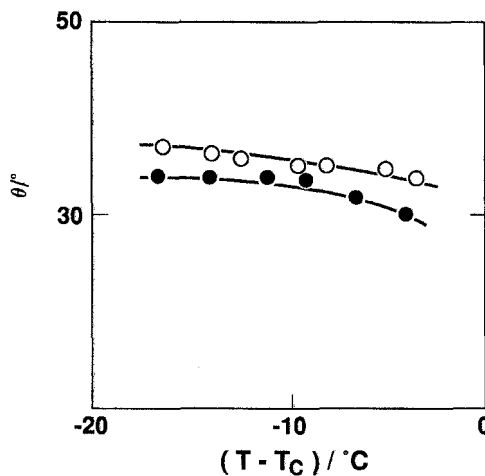
Figure 8.   Temperature dependence of the tilt angles for TSiPBOP (○) and IIB-9 (●). T_c denotes the temperature at which the higher temperature phase freezes to the chiral smectic C phase.

angles, showed tendencies similar to the P_s values. For IB-9, a large tilt angle of 35° was observed. The tilt angle for TSiPPOB was 5°. On the other hand, TSiPBOP and IIB-9 showed a similar tilt angle, which was about 35°.

For TSiPPOB, both P_s and tilt angle were markedly smaller than those of IB-9. The parallel dependence of P_s and tilt angle was pointed out by Patel and Goodby [9]. Thus, the result, where both P_s and tilt angle of TSiPPOB were reduced, is reasonable.

However the influence of the siloxy chain on P_s and tilt angle was observed only in the case of TSiPPOB. Therefore, this result could be explained by the difference in the molecular dipole moment between TSiPPOB and TSiPBOP. The transverse dipole moment, which is either attached laterally to the mesogenic groups or attached to their end, such as carbonyl and ether groups, is important for thermal stability of the smectic C phase [10, 11]. Dimethylsiloxy groups are bulky and flexible in comparison with alkyl groups. Thus more vigorous thermal agitation to the siloxy group than to the alkyl group may cause a fluctuation in the dipole in the mesogen core. In the case of TSiPPOB and TSiPBOP, the distances between the siloxy group and carbonyl group in the molecules are different. As the distance is shorter in TSiPPOB than in TSiPBOP, it could be expected that the siloxy group would fluctuate the dipole moment on the carbonyl group and reduce the P_s in TSiPPOB.

On the other hand, for the alkyl analogues, the P_s was larger in IB-9 than in IIB-9 where the distance between the chiral centre and the carbonyl group was shorter than in IB-9. In this case, the biphenyl structural rigidity might work such as to fix the carbonyl group direction more effectively than the phenyl structure in IIB-9.

2.4. *X-ray diffraction*

Figure 9 shows the X-ray diffraction pattern of TSiPBOP. The measurement results are summarized in table 2 together with those for IIB-9. For TSiPPOB the X-ray measurements were not successful, because the chiral smectic C phase of TSiPPOB is monotropic and the temperature range is too narrow to measure. In figure 9 there is a large peak at 3·3° and a broad peak in the wide angle region around 20°. The large peak shows the layer spacing and the broad peak shows the lateral distance between molecules in the chiral smectic C layer. The diffraction pattern for IIB-9 was just the
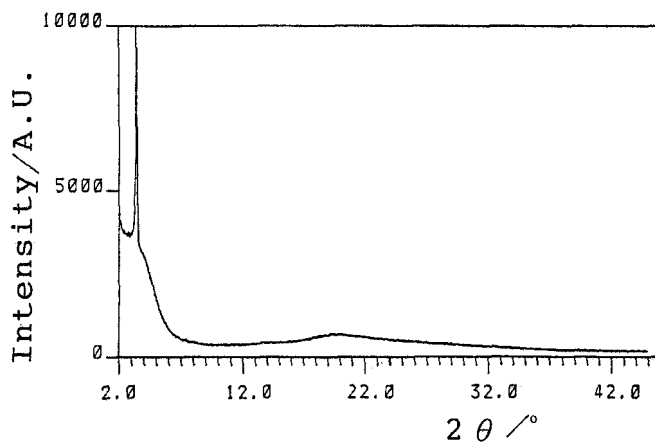

Figure 9. X-ray diffraction pattern for the chiral smectic C phase of TSiPBOP. Cu–K$_\alpha$ radiation.
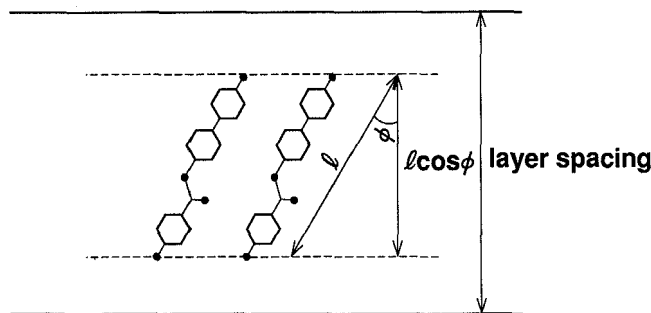
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Table 2.   The layer spacing of the chiral smectic C phase.

	Layer spacing/Å†	$\phi/°$‡	l/Å§	$l\cos\phi$/Å
TSiPBOP	26·0	38	16·0	12·6
IIB-9	26·0	34	16·0	13·3

† From small angle diffraction pattern.
‡ Tilt angle.
§ Length of mesogenic group.

Figure 10.   Schematic arrangement of molecules in the chiral smectic C phase. l, mesogenic group length; ϕ, tilt angle.

same as that for TSiPBOP. In table 2, $l\cos\phi$ shows the calculated values for mesogenic group thickness in the chiral smectic C phase layer estimated from the observed tilt angle and bond length tables [12]. Figure 10 shows an idealized molecular arrangement in the chiral smectic C phase. The values in table 2 indicate that the end group occupies a larger space in the chiral smectic C layer for TSiPBOP than for IIB-9. Therefore, it is suggested that there exists a difference between the configurations for the siloxy chain and those for the alkyl chain. In other words, this difference in the configuration of the end chains might lead to the difference in the interlayer molecular interactions along the long axes. The diffraction peaks in the wide angle region were too broad to analyse for detailed discussion.

2.5. *Switching time*

For surface stabilized ferroelectric liquid crystals, the switching time τ is expressed as [13, 14]

$$\tau = \eta_r / P_s E, \qquad (1)$$

where η_r and E denote the rotational viscosity and the electric field, respectively. As the spontaneous polarizations for TSiPBOP and IIB-9 were almost the same, it could be expected that the difference in the switching time between TSiPBOP and IIB-9 was due to the difference in η_r. The rotational viscosity depends upon temperature. Therefore, a comparison at the same temperature would be necessary to clarify the contribution of the siloxy end tail group to the rotational viscosity of the ferroelectric liquid crystals, but unfortunately there is no overlap in the temperature range of the chiral smectic C phase between TSiPBOP and IIB-9.
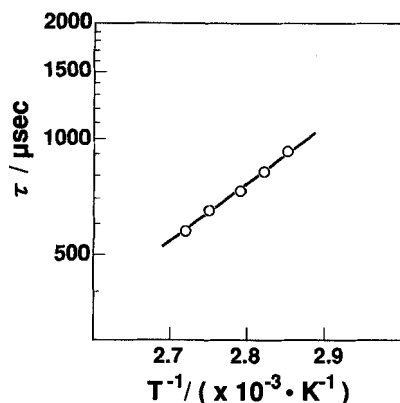
Figure 11. Dependence of switching time on temperature for IIB-9.

Table 3. The switching times for the surface stabilized ferroelectric liquid crystal.

	$d/\mu m$†	$\tau/\mu sec$‡
TSiPBOP	2·1	1280
IIB-9	2·2	3960

† Cell gap.
‡ At 35°C. For IIB-9, τ was the extrapolated value from the $1/T$ plot in figure 11.

Figure 11 shows the dependence of the switching time versus temperature for IIB-9. From figure 11, the switching time at the lower temperature could be estimated. The experimental switching time for TSiPBOP and the extrapolated one for IIB-9 are listed in table 3, for comparison, for a cell gap of about 2 μm at 35°C. The switching time was three times smaller for TSiPBOP than for IIB-9. This would result from the contribution of the siloxy end group to the rotational viscosity. The replacement of the alkyl end tail group with the more flexible siloxy group would reduce the rotational viscosity.

3. Conclusions

We can make the following conclusions for the siloxy end tail group in comparison with their alkyl end tail analogues.

The temperature range for the chiral smectic C phase was shifted to lower temperature by the introduction of a siloxy chain as the end tail group though the temperature range of the phase was decreased. For TSiPBOP the crystallinity was reduced and only the chiral smectic C phase was observed. For TSiPPOB a smectic A phase was observed instead of a cholesteric phase and the chiral smectic C phase was monotropic. The spontaneous polarization and tilt angle was lower for TSiPPOB, while for TSiPBOP, they were almost the same as for its alkyl analogue. The switching time at the low temperature for TSiPBOP was shorter than the extrapolated value for IIB-9. The rotational viscosity was reduced by the introduction of the siloxy chain as the end tail group.

The low temperature range of the chiral smectic C phase and the low rotational viscosity for the siloxy end group analogues would be useful for a device, which could be operated especially at low temperature.

4. Experimental

The transition temperatures were determined using an Olympus polarizing microscope in conjunction with a Mettler FP 82 heating stage and a FP 80 control unit for microscopic observations. A Daini Seikohsha differential scanning calorimeter, model SSC-560S, was used for thermal analysis. ^{1}H NMR spectra were measured with a JEOL JNM-FX-90 NMR spectrometer using $CDCl_3$ or $(CD_3)_2CO$ with tetramethylsilane as the internal standard. The spontaneous polarizations were measured by the triangular wave method [15] using cells constructed with two glass plates with a 1 cm^2 electrode area, whose surfaces were coated by polyimide and rubbed in a direction to obtain homogeneous alignment. The cell spacing was 2 μm, which was obtained using fibre spacers. The tilt angles were measured by the method reported previously by Patel, Leslie and Goodby [16, 17], with the cell used for spontaneous polarization measurements. X-ray diffraction was carried out on a Rigaku Digital Survey Meter TGS-501.

4.1. *Preparation of 4-allyloxyphenol* [18] *(5)*

To a solution of 34·2 g (0·311 mol) of hydroquinone and 42·9 g (0·311 mol) of dried potassium carbonate in 50 ml of dried acetone, was added 25 g (0·207 mol) of allyl bromide. The mixture was stirred for 8 h at 60°C. After adding 250 ml of water, the solution was extracted with toluene. After evaporating the solvent, 25 g of crude product was obtained. Recrystallization in ethanol, afforded 10 g (0·067 mol) of 4-allyloxyphenol. δ_H (CDCl$_3$): 5·2–5·5 (2 H, m), 5·9–6·4 (2 H, m), 6·6–7·2 (1 H, m), 7·6 ppm (3 H, d).

4.2. *Preparation of* (R)-4'-(1-methylheptyloxy)-4-biphenylcarboxylic acid

To a solution of 50·1 g (0·234 mol) of 4'-hydroxy-4-biphenylcarboxylic acid [19] and 13·1 g (0·234 mol) of potassium hydroxide in 800 ml of methanol and 100 ml of water, was added 54·9 g (0·234 mol) of (*S*)-1-methylheptyl 4-toluenesulphonate, which was prepared from (*S*)-1-methylheptanol and 4-toluenesulphonyl chloride in pyridine [20], and refluxed for 6 h. The mixture was poured into ice water, afterwards neutralized with hydrochloric acid and the precipitate was filtered off. After recrystallization from ethanol, 10·5 g (0·0322 mol) of (*R*)-4'-(1-methylheptyloxy)-4-biphenylcarboxylic acid was obtained. δ_H ((CD$_3$)$_2$CO): 0·8–2·2 (16 H, m), 4·3–4·7 (1 H, m), 6·8–7·7 ppm (4 H, m).

4.3. *Preparation of* (R)-4-allyloxyphenyl
4'-(1-methylheptyloxy)-4-biphenylcarboxylate *(8)*

To a solution of 2·5 g (7·67 mmol) of (*R*)-4'-(1-methylheptyloxy)-4-biphenyl-carboxylic acid chloride, prepared from (*R*)-4'-(1-methylheptyloxy)-4-biphenylcarboxylic and thionyl chloride, and 0·78 g (7·67 mmol) of triethylamine in 25 ml of dried tetrahydrofuran, 4-allyloxyphenol was added and stirred for 3 h at room temperature. Then, it was poured into ice water. The precipitate was filtered off and purified by column chromatography. 1·5 g (3·28 mmol) of (*R*)-4-allyloxyphenyl 4'-(1-methylheptyloxy)-4-biphenylcarboxylate was obtained. δ_H ((CD$_3$)$_2$CO): 0·8–2·0 (16 H, m), 4·4–4·7 (3 H, m), 5·1–5·6 (2 H, m), 5·8–6·3 (1 H, m), 6·9–8·3 ppm (6 H, m).

4.4. *Preparation of* (R)-4'-(3-heptylmethyltrisiloxypropyloxy)-4-biphenyl
4-(1-methylheptyloxy)benzoate *(TSiPPOB)*

1·5 g (3·28 mmol) of 4-allyloxyphenyl 4'-(1-methylheptyloxy)-4-biphenylcarboxyl-ate and 0·49 g (3·28 mmol) of heptamethyltrisiloxane were dissolved in 50 ml of

tetrahydrofuran. After addition of 0·025 g of Pt catalyser (Toshiba Silicone: Pt-Cat.-2), the solution was stirred for 6 h at 45°C. After the tetrahydrofuran was evaporated and purification by column chromatography, 0·9 g (1·48 mmol) of (R)-4'-(3-heptyl-methyltrisiloxypropyloxy)-4-biphenyl 4-(1-methylheptyloxybenzoate (TSiPPOB) was obtained. δ_{H} ((CH$_3$)$_2$CO): 0·6–2·0 (20 H, m), 3·9 (2 H, t), 4·2–4·5 (1 H, m), 6·7–8·3 ppm (12 H, m).

4.5. *Preparation of 4'-allyloxy-4-hydroxybiphenyl (5)*
4'-Allyloxy-4-hydroxybiphenyl was synthesized from allyl bromide and 4,4-dihydroxybiphenyl using the same method as for 4-allyloxyphenol.

4.6. *Preparation of (R)-4-(1-methylheptyloxy)benzoic acid*
(R)-4-(1-Methylheptyloxy)benzoic acid was synthesized from (S)-1-methylheptyl 4-toluenesulphonate and 4-hydroxybenzoic acid using the same method as for (R)-4'-(1-methylheptyloxy)-4-biphenyl-carboxylic acid.

4.7. *Preparation of (R)-4'-allyloxy-4-biphenyl 4-(1-methylheptyloxy)benzoate (8)*
(R)-4'-Allyloxy-4-biphenyl 4-(1-methylheptyloxy)benzoate was synthesized from 4'-allyloxy-4-hydroxybiphenyl and (R)-4-(1-methylheptyloxy)benzoic acid using the same method as for (R)-4-allyloxyphenyl 4'-(1-methylheptyloxy)-4-biphenylcarboxylate.

4.8. *Preparation of (R)-4-(3-heptylmethyltrisiloxypropyloxy)phenyl 4'-(1-methylheptyloxy)-4-biphenylcarboxylate (TSiPBOP)*
(R)-4-(3-Heptylmethyltrisiloxypropyloxy)phenyl 4'-(1-methylheptyloxy)-4-biphenylcarboxylate (TSiPBOP) was synthesized from (R)-4'-allyloxy-4-biphenyl 4-(1-methylheptyloxy)benzoate and heptamethyltrisiloxane using the same method as for (R)-4'-(3-heptylmethyltrisiloxypropyloxy)-4-biphenyl 4-(1-methylheptyloxy)-benzoate (TSiPPOB).

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