Polymeric ferroelectric liquid crystals with a 2-methylalkanoyl group-effect of substitution in the core benzene ring

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POLYMERIC FERROELECTRIC LIQUID CRYSTALS WITH A 2-METHYLALKANOYL GROUP–EFFECT OF SUBSTITUTION IN THE CORE BENZENE RING

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Polymeric ferroelectric liquid crystals with a 2-methylalkanoyl group in their mesogenic side chains exhibit large spontaneous polarization and are expected to respond quickly to an electric field. We prepared and examined novel polymeric liquid crystals. They contained a 2-methylbutanoyl or a 2-methyloctanoyl group, in which the ortho position to the alkanoyl group on the core was replaced by a fluorine atom, a hydroxy group, or a methyl group. We studied the effect of the substitutions on their properties and found that they lower the clearing points. The low spontaneous polarizaion of the polymer that underwent the fluorine substitution can be explained by the electronegativity of the fluorine atom. IR analysis verified that the substituted hydroxy group formed an intramolecular hydrogen bond with the adjacent alkanoyl carbonyl group. The steric hindrance introduced by the methyl substitution increased the tilt angle and slightly increased the intermolecular distance between the mesogens.
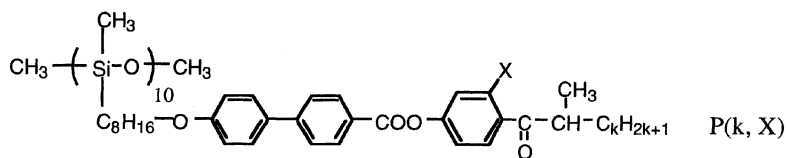
INTRODUCTION

Recently, a variety of polymeric ferroelectric liquid crystals (PFLCs) have been synthesized and characterized because of increasing interest in their unique properties [1]. PFLCs not only exhibit bistable modes like low-molecular-weight ferroelectric liquid crystals (FLCs) but also have high resistance to mechanical shock. However, their slow response to an electric field (100 to 1000 times slower than that of FLCs) is a major disadvantage. Furthermore, many requirements for liquid crystals must be satisfied in regard to their use in electronics applications such as a wide temperature range—including room temperature for chiral smectic C (SmC*)—an appropriate tilt angle, and a low voltage drive. Our approach to reducing the response time involves increasing the spontaneous polarization (Ps). We have previously reported a series of FLCs containing a chiral alkanoyl group, which exhibit a high Ps of up to $146 \, nC/cm^2$ at $10°C$ below the SmA-SmC* transition temperature [2a,2b]. We investigated the effect of substitution at the ortho position of the FLC core and reported that hydroxy group substitution was an effective way of increasing Ps. We prepared corresponding PFLCs, in which this type of FLC side chain was incorporated without substitution into the polysiloxane main chain, and obtained a Ps of $80 \, nC/cm^2$ at $10°C$ below the SmA-SmC* transition [3]. In this study, we prepared novel PFLCs that contained a chiral alkanoyl group in which we replaced the ortho position to the alkanoyl group on the core with a fluorine atom, hydroxy group, or methyl group. We discuss the effects of this substitution on phase transition and ferroelectric liquid crystal properties. We analyzed the PFLCs by X-ray diffraction and IR spectroscopy. We also discuss the molecular environments.

RESULTS AND DISCUSSIONS

The structures, number-average molecular weights (Mn), and molecular weight distributions (Mw/Mn) of PFLCs are shown in Table 1. The PFLC properties, such as phase transition temperature and Ps, depend on the polymerization degree but are almost constant when this value is more than 10 [2b]. We used polysiloxane with an average polymerization degree of 12 as a starting material. The molecular weights of the synthesized PFLCs were between 4,800 and 7,000, which means that the average polymerization degree values were 10 to 11 and the reaction sites were almost fully substituted. This suggests that the properties of these PFLCs can be compared without considering molecular weight effects.

TABLE 1 Structures, Molecular Weights, and Molecular Weight Distributions

	k	X	Mn	Mw/Mn
P(2, H)	2	H	5,300	1.5
P(2, F)	2	F	5,500	1.2
P(2, 0H)	2	OH	5,700	1.2
P(2, CH₃)	2	CH₃	4,800	1.2
P(6, H)	6	H	6,000	1.3
P(6, OH)	6	OH	7,000	1.3

$$CH_3-\left[Si-O\right]_{10}-CH_3 \quad C_8H_{16}-O- \bigcirc\!\!-\!\!\bigcirc -COO- \bigcirc\!\!\!^{X} -\overset{CH_3}{\underset{O}{C}}-CH-C_kH_{2k+1} \qquad P(k, X)$$

Phase Transition Temperatures

All the PFLCs exhibited smectic A (SmA), SmC*, and higher-order smectic phases (SmX). The temperature ranges of these liquid crystal phases are shown in Figure 1. Glass transition (Tg) occurred for all the PFLCs but no melting points were observed.
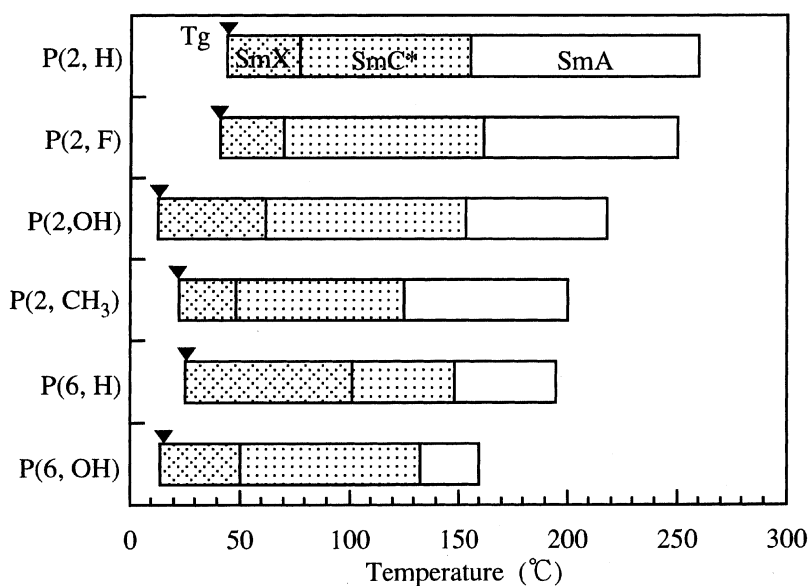
FIGURE 1 Phase transition temperatures.

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When we substituted a fluorine atom, hydroxy group, or methyl group in the PFLCs there was a drop in the clearing point level. In a previous study of low-molecular-weight FLCs [2a] the lateral substitutions reduced the clearing point level and linear relationships were observed between the clearing point and the molecular breadth. In this study, we also examined these relationships for the PFLCs. We defined the molecular breadth as the distance between the end atom of the substituent and the hydrogen atom at the ortho position of the alkanoyl group, presuming the conformation shown in Figure 4. In comparison with the **P(2, X)** series, the bulkiness or size of the substituent has a considerable effect on the clearing point, as shown in Figure 2, where the clearing point level falls with increasing substituent bulkiness reaching its lowest level of 60°C with the methyl group. The substituent interferes with the interaction between the mesogen side chains in the PFLCs, increasing the breadth of the mesogens and hence reducing the interactive forces between them. The clearing point of **P(2, F)**, however, is slightly above the line connecting **P(2, H)**, **P(2, OH)**, and **P(2, CH₃)**. This can be attributed to the polarization of fluorine enhancing intermolecular cohesion.

Such a reduction in transition temperature is not clear in the SmA to SmC* transition except for **P(2, CH₃)**, where the SmA-SmC* transition temperature falls by 31°C (from that of **P(2, H)**) together with the 29°C drop in the SmC*-to-SmX transition temperature. The considerable
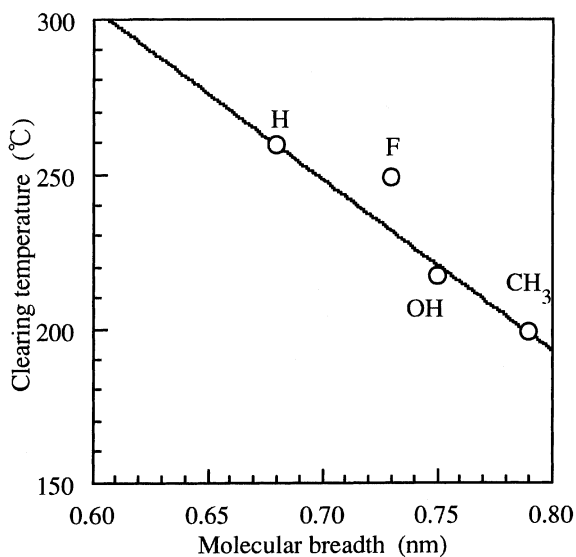

FIGURE 2 Molecular breadth and clearing temperature.

hindrance caused by the methyl group may also be responsible for this. Substitution by a hydroxy group (**P(2, OH)**) also lowers the SmC*-to-SmX transition temperature by 15°C while lowering the SmA-to-SmC* transition temperature by 2°C, thus extending the SmC* range. Similar characteristics were observed in **P(6, OH)**, where the SmC*-to-SmX transition temperature was reduced by 51°C. This feature is favorable for practical applications such as displays.

Ferroelectric Liquid Crystal Properties

The temperature dependence of Ps for PFLCs is shown in Figure 3. The PFLCs with the 2-methyloctanoyl group (**P(6, X)**) provide higher Ps than those with the 2-methylbutanoyl group (**P(2, X)**). The longer end alkyl chain is favorable in terms of increasing Ps. Such a tendency has been observed in ester-type FLCs [5] and in the corresponding FLCs [2b]. This tendency was considered to be due to damping of the chiral center motion. However, this effect leveled off for end alkyl chain lengths longer than 6 in the alkanoyl FLCs [2b], so no further increase is expected in Ps for the PFLCs.

The highest Ps value, $180 \, nC/cm^2$, was observed for **P(6, OH)**, which is 1.5 times larger than that for **P(6, H)**. The intramolecular hydrogen bond
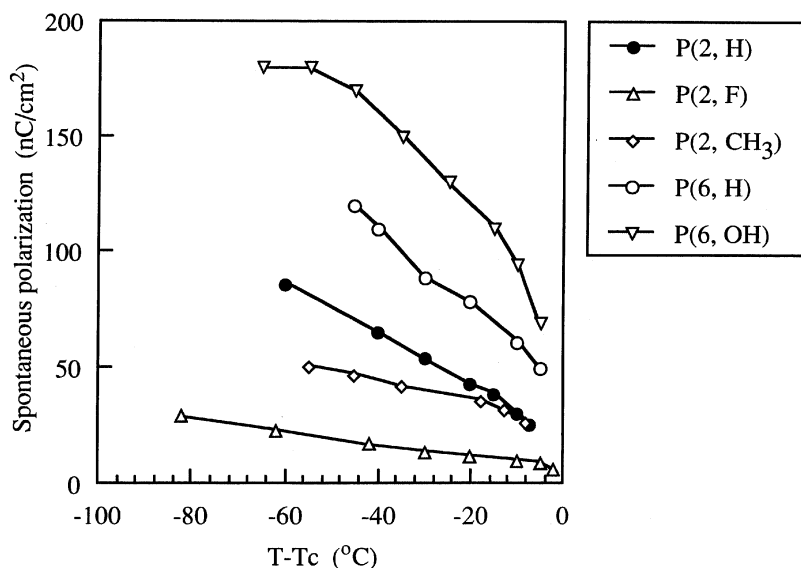
FIGURE 3 Temperature dependencies of spontaneous polarization.

shown in Figure 4 may be a factor causing the increase in Ps, as found in the corresponding FLCs [2a]. The conformations in Figure 4 were determined by MM calculation. For P(6, OH) the carbonyl group and hydroxyl groups are located on the same side of the molecular long axis because of the formation of an intramolecular hydrogen bond (Figure 4a). The increase in Ps with the introduction of a hydroxyl group is explained by the

(a)   P(2, OH)

(b)   P(2, CH$_3$)

(c)   P(2, F)
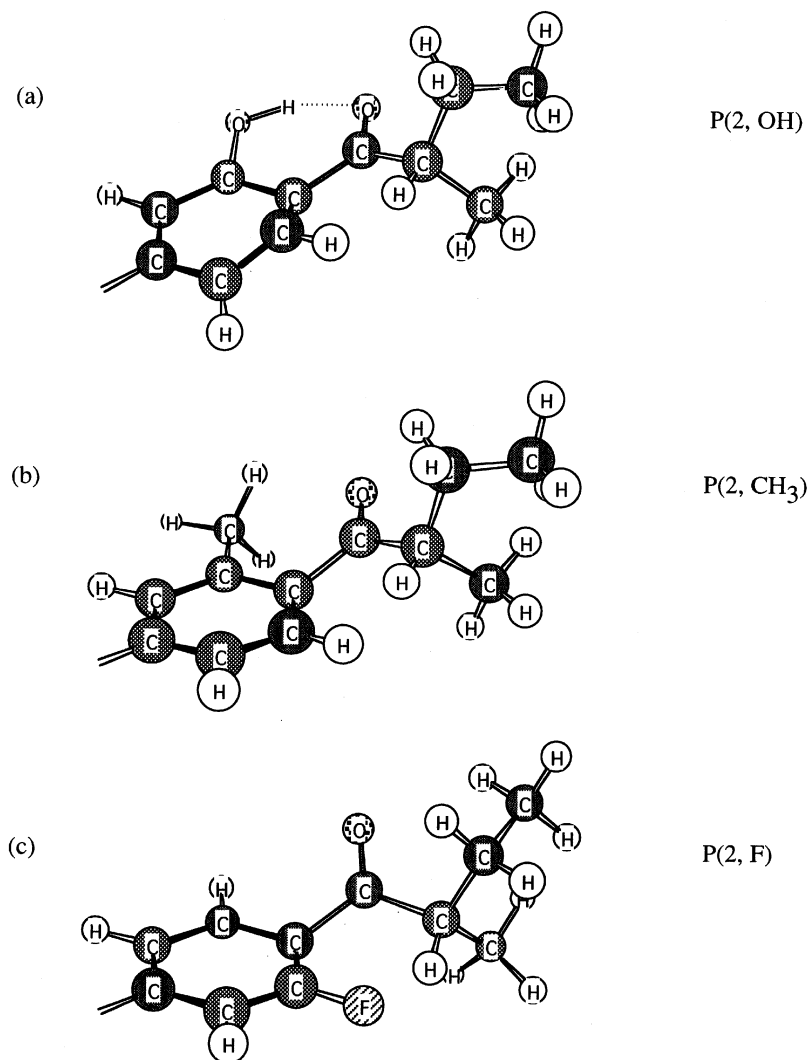
FIGURE 4 Presumed conformation for the lateral substitution groups.

increase in the dipole moment perpendicular to the long axis. By contrast, the Ps of **P(6, OH)** is $52 \, nC/cm^2$ smaller than that of the corresponding low-molecular-weight FLC at $10°C$ below the SmC*-SmA transition temperature. The polymer main chain dilutes the mesogen density, consequently reducing the Ps.

Substitution with a methyl group or fluorine atom reduces the Ps in the **P(2, X)** series. This phenomenon can be explained in the same way as for the corresponding FLCs [2a]. In the model of $P(2, CH_3)$, the carbonyl and methyl groups are on the same side because of the steric repulsion between the methyl group and the 2-methylbutyl group attached to the carbonyl group. The group moments of the methyl substituents reduce that of the carbonyl group and this reduces the total Ps. Furthermore, the strong electronegativity of the fluorine atom repels the carbonyl oxygen atom and causes the carbonyl group to face in the opposite direction (Figure 4c). This conformation explains the reduction in the Ps of $P(2, F)$.

The temperature dependence of the apparent optical tilt angles for **P(2, X)** is shown in Figure 5. The introduction of a methyl group increases the apparent optical tilt angle from that of **P(2, H)**. **P(2, CH₃)** shows the largest tilt angle, $32.5°$. The steric hindrance of the methyl group is thought to interfere with the intermolecular interactions and consequently change the molecular packing, resulting in an increase in the apparent tilt angle.
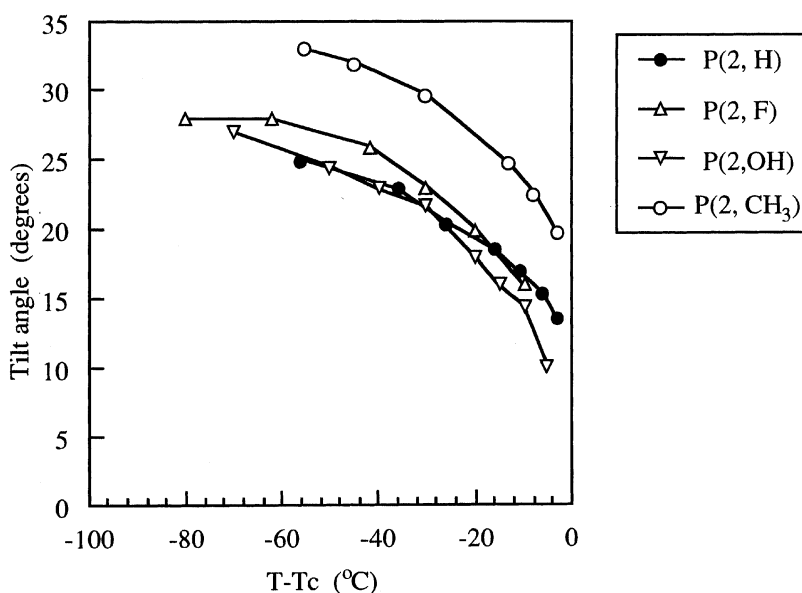

FIGURE 5 Temperature dependencies of tilt angles.

The apparent optical tilt angles of **P(2, OH)** and **P(2, F)** are almost the same as that of **P(2, H)**. Poths et al. reported that the introduction of a fluorine atom into the PFLC led to a large tilt angle [6], but in our PFLC system fluorine substitution in **P(2, F)** increased the apparent tilt angle to a maximum of only 3°.

X-ray Diffraction Analysis

Figure 6 shows the X-ray diffraction patterns of **P(2, X)**s at room temperature (298 K), with all the PFLCs in the SmX phase. The peaks around 20° are related to the intermolecular distance of the mesogens and are listed in Table 2. They are around the same degree, independent of the substitutions. Their widths, however, are different, which reflects their distributions. The lateral substitution causes an increase in the half peak widths, with **P(2, OH)**, showing the largest increase, followed by **P(2, CH₃)**, and **P(2, F)**. The packing state of the mesogens is disturbed by the steric hindrance of the lateral substituents for **P(2, F)** and **P(2, CH₃)**. The peak for **P(2, OH)** is very broad and the intermolecular distance is slightly smaller than that for **P(2, H)**. This can be thought to indicate that the packing state of the mesogens of **P(2, OH)** differs from that of **P(2, H)**.

The peaks around 2.8° reflect the layer spacing distances (L_{obs}) we determined, which are also listed in Table 2. They are 2.99 to 3.27 nm. The peak for **P(2, OH)** is very sharp and strong, showing that the layer structure is different from the others.
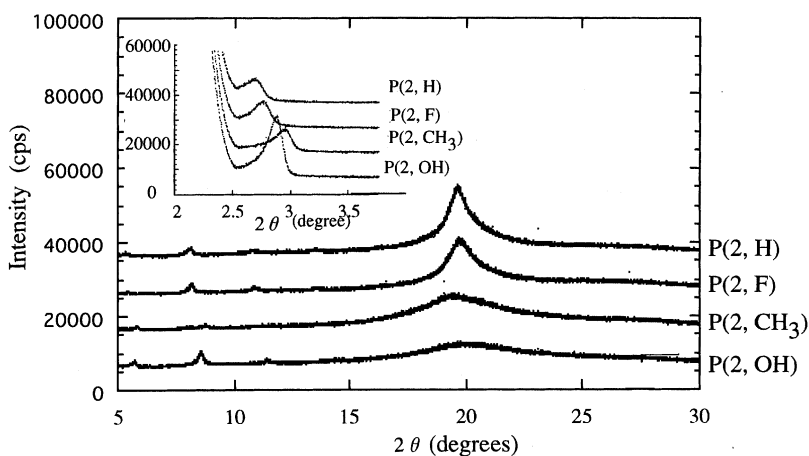
FIGURE 6 X-ray diffraction patterns.

TABLE 2 Layer Spacing and Intermolecular Distance

	Intermolecular Distance*		Layer Spacing (L_{obs})*		Tilt Angle* (degree)	Calculated Layer Spacing (L_{cal})** (nm)
	2θ (degree)	(nm)	2θ (degree)	(nm)		
P(2, H)	19.6	0.451	2.70	3.27	25	3.3
P(2, F)	19.7	0.450	2.77	3.19	28	2.8
P(2, OH)	19.9	0.446	2.88	3.06	28	2.9
P(2, CH₃)	19.3	0.459	2.95	2.99	33	2.6

*, Measured at room temperature. **, L_{cal} = molecular length × cos(tilt angle).

The layer spacing is calculated using the following equation:

$$L_{cal} = n \cdot \cos\theta,$$

where L_{cal} is calculated using the molecular length (n) based on the Boulder model [7] (Figure 7) and the tilt angle (θ). Here we assume that one molecular length is approximately equal to the layer spacing in SmA. As the tilt angles cannot be measured in the SmX, we adopted the saturated tilt angle in the SmC* range and assumed that the tilt angle of SmC* was maintained into the SmX phase. Table 2 compares the resulting calculated layer spacing (L_{cal}) with the experimentally obtained values (L_{obs}). L_{cal} agrees well with L_{obs} for all **P(2, X)**. This result demonstrates the validity of the assumptions stated above.

FT-IR Analysis

The IR spectra of the **P(2, X)**s in the SmC* phase (110°C) are shown in Figure 8. The absorption peaks of the stretching vibration for the ester C=O and benzene ring C=C appear around 1735 and 1600 cm^{-1}, respectively, for all the **P(2, X)**. A singular feature is found in the ketone C=O peaks, where the **P(2, OH)** peak shifted more than 45 cm^{-1} downward from those of the other **P(2, X)** found around 1680 cm^{-1}. This tendency remained in lower concentrations of the polymer. These results show the formation of intramolecular hydrogen bonds between the ketone C=O and the substituted hydroxy group, corresponding to the phenomenon observed in the FLCs [2a].

The ketone C=O peak wavenumbers are plotted as a function of temperature in Figure 9. The presence of methyl and fluorine substituents increases the wavenumber by 2 to 4 cm^{-1} compared with that of **P(2, H)**. The steric hindrance of the methyl group should prevent the ketone C=O group from taking a coplanar conformation with the benzene ring, in which
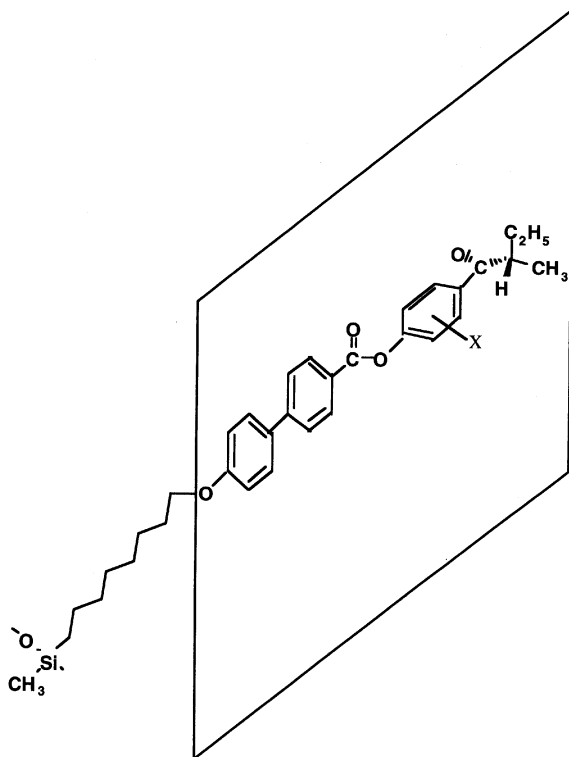
FIGURE 7 Model for the PFLCs.
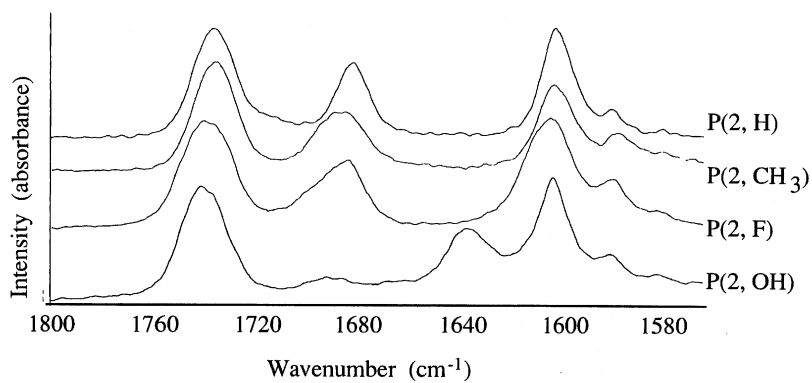
FIGURE 8 IR spectra.
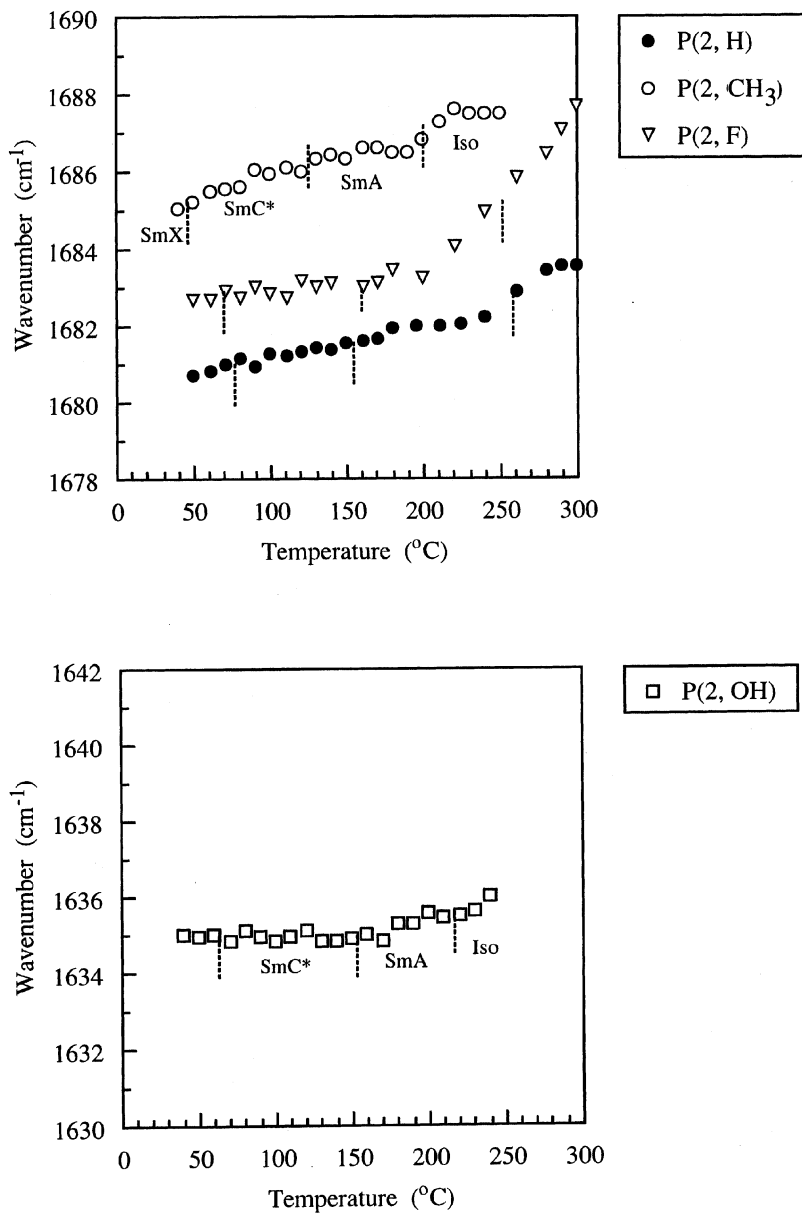
FIGURE 9 Temperature dependencies of wavenumbers for ketone C=O peaks.

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the electrons on the ketone C=O become less resonant with the benzene electrons. The electron-withdrawing effect of the fluorine atom can reduce the electron density of the ketone carbonyl carbon, thus enhancing the strength of the C=O bond. This inductive effect can cause a small increase in wavenumber; the steric effect is another possible cause. We observed the ketone C=O peak shift caused by the hydrogen bond over the entire measured range. The wavenumbers were almost the same in the isotropic liquid phase as in the smectic phases. The hydrogen bond was stable and influenced very little by the other molecules.

The peak wavenumbers versus temperature for the ester C=O group of **P(2, X)** are shown in Figure 10. For all **P(2, X)**, the wavenumber for the ester carbonyl group peak shifts lower as the temperature decreases. This is also observed with the other FLC systems [8]. This probably indicates that the intermolecular interaction between mesogens becomes stronger with decreasing temperature.

The wavenumber of the ester C=O absorption peak of **P(2, OH)** shifts $4 \, cm^{-1}$ higher in all the liquid crystal phases along with the isotropic phase, conforming the lack of hydrogen bonds between the ester carbonyl and the substituted hydroxy group in the liquid crystal phases. An increase in peak wavenumber is also observed in **P(2, F)**; it rises by 2.5 to $3 \, cm^{-1}$. The electron-withdrawing inductive effect of the hydroxy group or fluorine atom may be the cause of the wavenumber shift. The fact that the
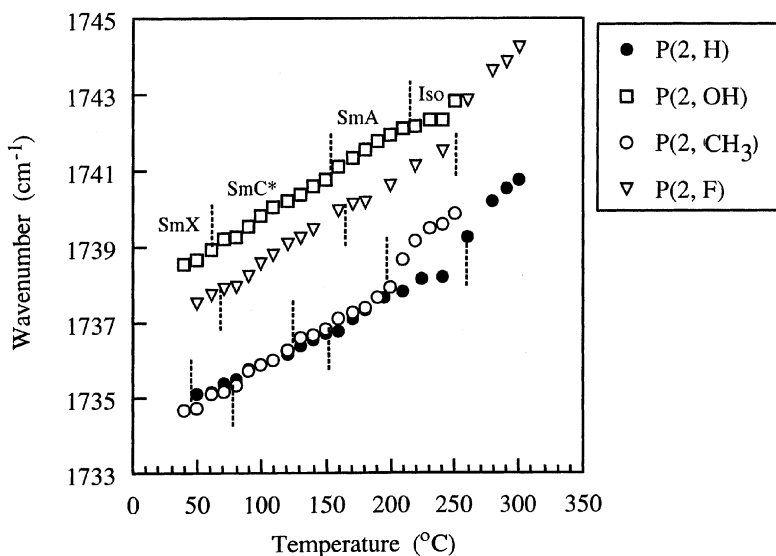
FIGURE 10 Temperature dependencies of wavenumbers for ester C=O peaks.

wavenumber of the ester C=O of **P(2, CH₃)** is similar to that of **P(2, H)** indicates that the steric hindrance of the methyl group, which is far from the substituted position, does not affect ester moiety.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) [KF-40-A7603] was obtained from Toshiba Silicon, Inc. and was used with no further purification. Benzene used in the hydrosilylation reaction for synthesis of PFLCs was purified in the usual way. Dicyclopentadienyl platinum (II) chloride catalyst was synthesized as previously reported [9]. The other starting materials were used with no further purification.

Measurements

^{1}H-NMR spectra were measured on a Brucker MSL-400 NMR spectrometer. Specimens were dissolved in CDCl$_3$ with TMS as an internal standard. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine transition temperatures. A Nikon XTP-II optical polarized microscope equipped with a Mettler FP-80 hot stage was used to identify the liquid crystal phases. Spontaneous polarizations were measured by the triangular wave method, and tilt angles were determined on a Nikon XTP-II optical polarized microscope. FT-IR spectra were measured at decreasing temperatures using a JEOL FT-IR-3510 spectrophotometer equipped with a Mettler FP-80 hot stage, with specimens placed between CaF$_2$ plates. The wavenumber resolution was $0.5\,\mathrm{cm}^{-1}$ as determined by curve fitting. X-ray diffraction patterns were obtained with powder samples on a Rigaku RU-200 X-ray diffractometer using the Cu-Kα line.

Synthesis

The synthesis schemes for **P(k, X)**, where X is Me or F or H, and **P(k, OH)** are outlined in **Schemes 1** and **2**.

The PFLCs were synthesized by the hydrosilylation reaction of a vinyl monomer with poly(methylhydrosiloxane) [10]. Products were identified using ^{1}H-NMR and IR spectroscopy. Molecular weights were determined by gel permeation chromatography, using tetrahydrofuran as an eluent.

(S)-3-Methyl-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1, 1′-biphenyl-4-carboxylate (M(2, CH₃))

A 5.5 g measure of m-methylanisole was reacted with 5.3 g of (S)-2-methylbutyric acid chloride by the same method as described in a previous
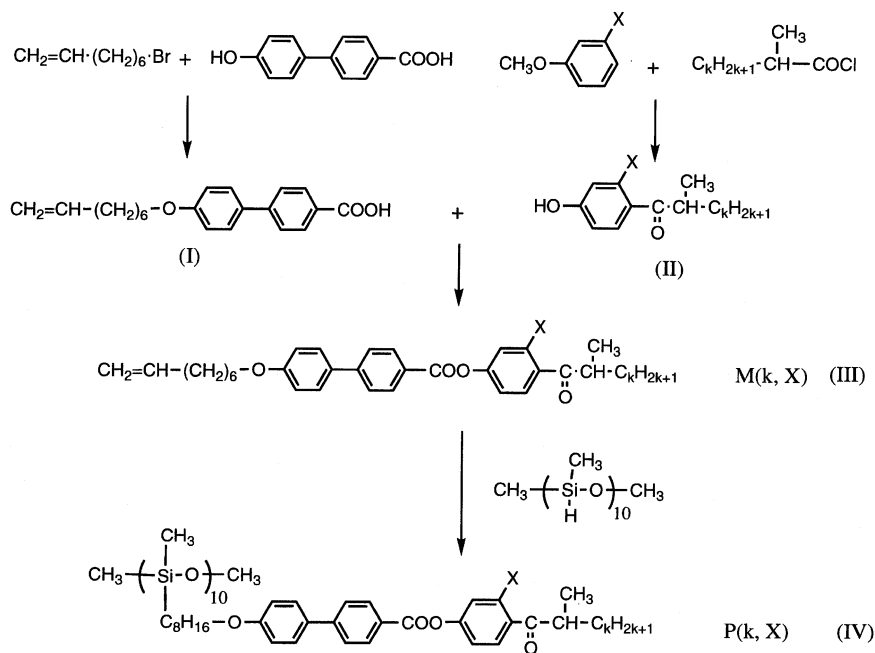
SCHEME 1 Synthesis of the polymers.

article [2a] to produce 2.1 g of (S)-3-methyl 4-(2-methylbutanoyl) phenol (a viscous liquid with a yield of 25%).

Next, 30 g of 8-bromooctene-1 was added to a 450 ml ethanol solution of 4-hydroxy-1,1′-biphenyl-4′-carboxylic acid (33.6 g) and potassium hydroxide (22.4 g) and the solution was refluxed for 5 h. The mixture was then neutralized with 1N-hydrochloric acid and poured into 1 l of water.

The precipitate was collected by filtration and then dispersed in 200 ml of N,N-dimethylformamide. 20 ml of 1N-hydrochloric acid was added to the dispersion and the mixture was stirred at 80°C. The reaction mixture was then neutralized with sodium hydroxide solution (1 N) and poured into 1 l of water. The precipitate was filtered out and the solution was washed with water. The solvent was then distilled off and the product was reprecipitated from ethanol to obtain 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid (white solid: 29.0 g, yield 82%).

Next, 1.8 g of 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid and 1.0 g of (S)-3-methyl-4-(2-methylbutanoyl)phenol were dissolved in 100 ml of dichloromethane. After that, 1.1 g of dicyclohexylcarbodiimide (DCC) was added to the solution, which was stirred for 20 hs at room temperature. After the solution had been filtered and the solvent evaporated, the
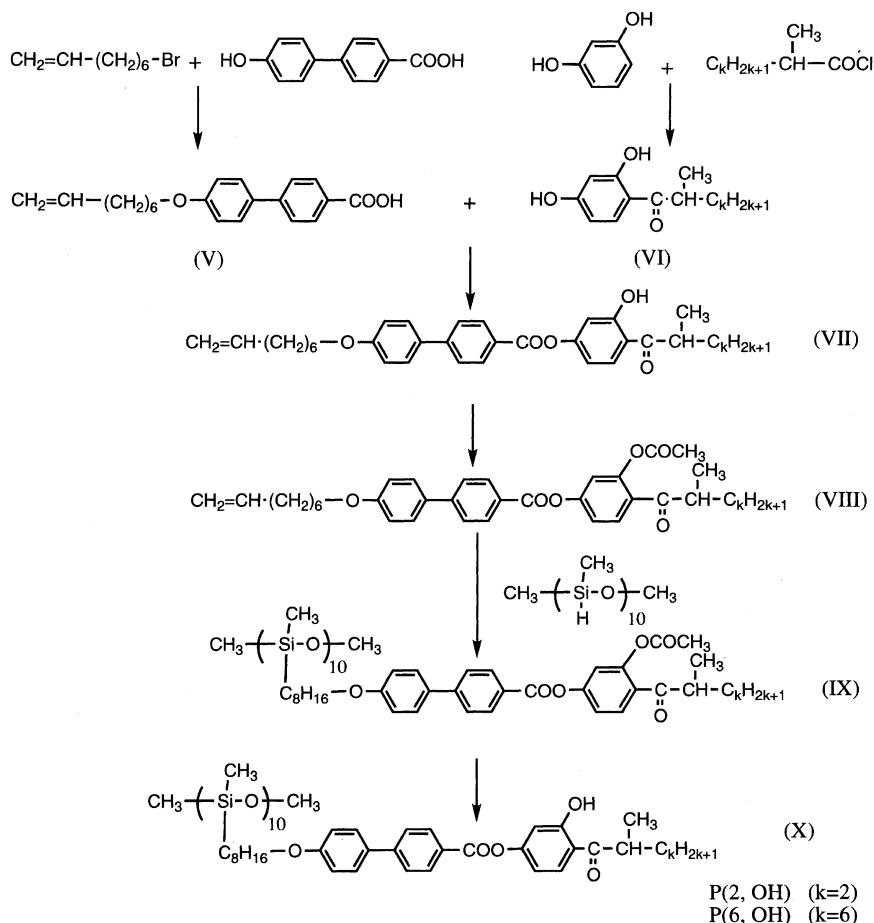
SCHEME 2 Synthesis of the polymers with hydroxy group.

residual product was purified by column chromatography, using silica gel with ethylacetate/n-hexane mixture as an eluent. Finally, 1.4 g of (S)-3-methyl-4-(2-methylbutanoyl)phenyl 7-octenyloxy-1,1′-biphenyl-4-carboxylate was obtained as a white solid (yield 54%).

(S)-3-fluoro-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1, 1′ H biphenyl-4-carboxylate (M(2, F))

Here, 4.1 g of m-fluoroanisole was reacted with 4.0 g of (S)-2-methylbutyric acid chloride using the method described in a previous paper [2a], to produce 2.6 g of (S)-3-fluoro 4-(2-methyl butanoyl)phenol (a viscous liquid with a yield of 40%).

Then 1.8 g of 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid was reacted with 1.0 g of (S)-3-fluoro 4-(2-methyl butanoyl)phenol, using a DCC catalyst. The crude product was purified in the manner described in the section on **M(2, CH₃)**, and 1.7 g of (S)-3-fluoro-4-(2-methylbuta-noyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate was obtained as a white solid (yield 66%).

(S)-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (M(2, H))

Anisole (8.25 g) and (S)-2-methylbutanoyl chloride (9.2 g) were reacted using the method described in a previous paper [2a] to produce 8.4 g of (S)-4-(2-methylbutanoyl)phenol as a white solid (62%).

Then 1.8 g of 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid was reacted with 0.93 g of (S)-4-(2-methylbutanoyl)phenol with DCC catalyst, and the resultant product was purified in the way described in the **M(2, CH₃)** section. Consequently, 1.5 g of (S)-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate was obtained as a white solid (yield 60%).

(S)-4-(2-methyloctanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (M(6, H))

First, 13 g of anisole was reacted with 21 g of (S)-2-methyloctanoyl chloride using the method described above to produce 14 g of (S)-4-(2-methyloctanoyl)phenol as a viscous liquid (yield 49%).

After this, 1.2 g of (S)-4-(2-methyloctanoyl)phenol was reacted with 1.8 g of 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid with DCC cata-lyst, and the crude product was purified in the way employed with **M(2, CH₃)**. Thus 1.6 g of (S)-4-(2-methyloctanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate was obtained as a white solid (yield 58%).

Synthesis of Polymeric Gerroelectric Liquid Crystals (P(2, CH₃), P(2, F), P(2, H) and P(6, H))

The polymeric FLCs were prepared from **M(2, CH₃)**, **M(2, F)**, **M(2, H)**, and **M(6, H)** by hydrosilylation with poly(methylhydrosiloxane). The procedure is described in detail below.

1.1 mmol of **M(k, X)** was dissolved in 50 ml of dry benzene together with poly(methylhydrosiloxane), where the **M(k, X)** was 10% more in terms of molarity than the corresponding Si-H group of the polymer. Then 1 ml of dicyclopentadienyl platinum (II) chloride catalyst/methylene chloride solution (1 mg/ml) was added to the reaction solution and the solution was heated at 70°C in a nitrogen atmosphere for 20 h. The solution was then cooled to room temperature and washed with water. The organic solvent layer was dried over anhydrous sodium sulfate and the solvent was then

evaporated off. The residue was purified by gel permeation column chromatography (Sephadex-LH60, manufactured by Pharmacia LKB Biotechnology Group), with chloroform as an eluent.

The synthesized polymers were identified by IR and ^{1}H-NMR analyses. The identification data are shown below.

P(2, CH₃): IR (KBr, cm^{-1}): 2924, 1734, 1684, 1604, 1262, 1192, 1072. ^{1}H-NMR δ (CDCl₃, ppm): 0.0–0.4 (3H, m, SiH₃), 0.4–0.7 (2H, m, Si-CH₂), 0.7–2.0 (20H, m, -CH₂-/-CH3), 2.3–2.7 (3H, m, CH₃), 3.1–3.4 (1H, m, C*H), 3.8–4.1 (2H, m, -CH₂O-), 6.8–8.4 (11H, m, benzene).

P(2, F):   IR (KBr, cm^{-1}): 2924, 1734, 1606, 1256, 1194, 1066. ^{1}H-NMR δ (CDCl₃, ppm): 0.0–0.4 (3H, m, SiH₃), 0.4–0.7 (2H, m, Si-CH₂), 0.8–2.0 (20H, m, -CH₂-/-CH₃), 3.1–3.4 (1H, m, C*H), 3.8–4.1 (2H, m, -CH₂O-), 6.8–8.4 (11H, m, benzene).

P(2, H):   IR (KBr, cm^{-1}): 2925, 1734, 1682, 1604, 1274, 1192, 828, 766. ^{1}H-NMR δ (CDCl₃, ppm): 0.0–0.4 (3H, m, SiH₃), 0.4–0.7 (2H, m, Si-CH₂), 0.8–2.0 (20H, m, -CH₂-/-CH₃), 3.2–3.5 (1H, m, C*H), 3.8–4.1 (2H, m, -CH₂O-), 6.4–8.3 (12H, m, benzene).

P(6, H):   IR (KBr, cm^{-1}): 2927, 2854, 1736, 1681, 1602, 1261, 1190, 830, 764. ^{1}H-NMR δ (CDCl₃, ppm): 0.0–0.4 (3H, m, SiH₃), 0.4–0.7 (2H, m, Si-CH₂), 0.8–2.0 (28H, m, -CH₂-/-CH₃), 3.3–3.6 (1H, m, C*H), 3.8–4.1 (2H, m, -CH₂O-), 6.8–8.3 (12H, m, benzene).

P(k, OH) was prepared according to Scheme 2. The synthesis procedure for the side chain precursors (mesogens: **M(k, OH)**; polymers: **P(k, OH)**) is detailed in the following sections.

(S)-3-hydroxy-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (M(2, OH)) and its Polymeric Derivative P(2, OH)

First, 6.2 g of resorcinol was reacted with 9.8 g of (S)-2-methylbutanoyl chloride in the presence of zinc chloride as described in a previous paper [2a] to produce (S)-3-hydroxy 4-(2-methyl butanoyl)phenol as a yellow viscous liquid (VI; k = 2, yield: 38%).

Next, 3.3 g of 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylic acid (V) was reacted with 2.0 g of (S)-3-hydroxy 4-(2-methylbutanoyl)phenol (VI) with DCC catalyst. The product was purified in the same way as that used for **M(2, CH₃)**, except that the eluent for column chromatography was an ethyl acetate/n-hexane mixture (5/95 volume ratio), resulting in 3.88 g of (S)-3-hydroxy-4-(2-methylbutanoyl)pheny 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (VII; k = 2, yield: 78%).

Then 1.0 g of acetyl chloride and 5 ml of pyridine were added to 50 ml of anhydrous methylenechloride solution containing 3.9 g of (S)-3-hydroxy-4-(2-methylbutanoyl)phenyl 4′(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (VII). After the reaction mixture was stirred for 6 h at room temperature, the solution was washed with diluted hydrochloric acid and then with water. After removal of the solvent, the crude product was purified by column chromatography on silica gel with chloroform eluent and 2.5 g of (S)-3-acetoxyl-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate was obtained (VIII; k = 2, yield: 60%).

1.0 g of (S)-3-acetoxyl-4-(2-methylbutanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (VIII) and 0.1 g of poly(methylhydrosiloxane) (KF40-A7603) were dissolved in 50 ml of freshly distilled dry benzene. Then 2 ml of dicyclopentadienyl platinum(II) chloride catalyst/methylene chloride solution (1 mg/ml) was added to the reaction mixture and the reaction mixture was stirred at 60°C in a nitrogen atmosphere for 20 h. After being cooled to room temperature, the reaction mixture was washed with water, and the organic solvent layer was dried over anhydrous sodium sulfate. After the solvent was evaporated off, the residue was purified by gel permeation column chromatography (Sephadex-LH60) using chloroform as an eluent, producing 0.9 g of yellow-reddish intermediate polymeric product (IX; k = 2). The intermediate polymer (0.9 g) was dissolved in 90 ml of chloroform together with 0.1 g of propylamine and the solution was stirred for 3 days at room temperature. After the reaction, the mixture was washed with diluted hydrochloric acid and then with water, and then dried over anhydrous sodium sulfate. The solvent was then evaporated off, and the crude product was purified by gel permeation column chromatography (Sephadex-LH60; chloroform eluent). The polymer was then dissolved in chloroform and purified using active carbon. Finally 0.7 g of white polymer product (X; k = 2, **P(2, OH)**), was obtained.

IR (KBr, cm^{-1}): 2926, 2855, 1737, 1636, 1604, 1255, 1190. ^{1}H-NMR δ (CDCl$_3$, ppm): 0.0–0.4 (3H, m, SiH$_3$), 0.4–0.7 (2H, m, Si-CH$_2$), 0.7–2.0 (20H, m, -CH$_2$-/-CH$_3$), 3.3–3.6 (1H, m, C*H), 3.8–4.1 (2H, m, -CH$_2$O-), 6.6–8.3 (11H, m, benzene), 12.82 (1H, s, OH).

(S)-3-hydroxy-4-(2-methyloctanoyl)phenyl 4′-(7-octenyloxy)-1,1′-biphenyl-4-carboxylate (M(6, OH)) and its Polymeric Derivative P(6, OH)

P(6, OH) was synthesized from the polymeric intermediate (IX; k = 6) in the same way as for **P(2, OH)**.

IR (KBr, cm^{-1}): 2925, 2854, 1740, 1636, 1604, 1257, 1191. ^{1}H-NMR δ (CDCl$_3$, ppm): 0.0–0.4 (3H, m, SiCH$_3$), 0.4–0.7 (2H, m, Si-CH$_2$), 0.7–2.0 (32H, m, -CH$_2$-/-CH$_3$), 3.3–3.5 (1H, m, C*H), 3.8–4.1 (2H, m, -CH$_2$O-), 6.7–8.4 (11H, m, benzene), 12.80 (1H, s, OH).

CONCLUSIONS

We prepared polymeric ferroelectric liquid crystals (PFLCs) containing a 2-methylalkanoyl group in their mesogenic side chains. The ortho position on the core to the alkanoyl group was replaced by a fluorine atom, hydroxy group, or methyl group. The phase transition temperatures, spontaneous polarizations (Ps), and tilt angles were changed by the substitution. The substitutions reduced clearing points. The hydroxy substituent increased the Ps 1.5 times. The other substituents decreased the Ps. The methyl substitution increased the tilt angle but the other substitutions hardly changed the tilt angle at all. These changes are considered to result from the conformation change caused by introducing the substitutions. The layer spacing change derived from X-ray analysis and the temperature dependence of the IR peaks support this consideration.

For practical use the SmC* temperature range needs to be further extended to include room temperature, and the response time should be improved. This is expected to be achieved by mixing or by copolymerizing with other liquid crystal components. Such work will be reported later.

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