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Ferroelectricity of Novel Liquid Crystals with Tetrafluoro-Phenylene and Biphenylene

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Ferroelectric properties were investigated by plotting hysteresis loops of spontaneous polarization versus field with sine waveform for 4′-[(*s*)-2-methylbutoxycarbonyl] phenyl 4″-[(4-*n*-heptyloxyl-2, 3, 5, 6-tetrafluorophenylene) ethynyl] benzoate and 4′-[(*s*)-2-methylbutoxycarbonyl] phenyl 4-(4′-*n*-heptyloxy-2, 3, 5, 6-tetrafluorobiphenyl-1-ethynyl) benzoate, respectively. The latter shows enantiotropic mesophases of crystal, chiral smectic C, smectic A, cholesteric and isotropic states. It also has a chiral smectic C temperature range of 97°C, a melting point of 61°C and a polarization of $5.5 \times 10^{-6}\,\mathrm{C/m^2}$ at temperature of 10°C below curie point.

Keywords: Smectic; chiral; ferroelectric; tilt; polarization; tetrafluorobiphenylene

INTRODUCTION

Considerable effort was made in synthesizing new ferroelectric liquid crystals with fluorinated molecular structure to find new materials with better characteristics for practical applications. It is found that the large electronegativity and the small size of the fluorine atom may play an important part in improving material physical properties. Recently, many works were carried out on synthesizing new compounds with the 2, 3, 5, 6-tetrafluoro-1, 4-phenylene or the 2, 3, 5, 6-tetrafluoro-1, 4′-biphenylene unit in the skeleton by J. Wen *et al.* [1, 2, 3]. They reported that the liquid crystals containing the tetrafluoro-phenylene or biphenylene unit favored the formation of the nematic phase as well as had the simplification of mesomorphic smectic types [1, 4, 5]. Explained by G. W. Gray [6], fluoro-substitutents usually have two opposing effects, that is, while the change in the molecular polarizability may increase the mesophase thermal stability, the decrease in the length/breadth ratio causes a decrease. In most cases, the decrease of the mesophase thermal stability is dominant.

The possibility of finding ferroelectricity in liquid crystals has long been a subject of interest from both the theoretical and applicative points of view. In this study we will aim to observe the chiral smectic mesophases of synthesized compounds with tetrafluorophenylene and tetrafluorobiphenylene.

Ferroelectricity is generally defined as material exhibiting a zero-field spontaneous polarization P_s, subject to reversal by an external electric field or showing the polarization versus field hysteresis.

In our work, an indirect observation of P_s was carried out by measuring the current of the electric displacement differential including the contribution of the polarization reversing with a sine waveform electric field. A rather wide temperature range of the chiral smectic C phase or the ferroelectric mesophase and a good phase sequence were shown in one compound. It should have potential as a new important ferroelectric liquid crystal for the actual use of switching display devices.

EXPERIMENTAL

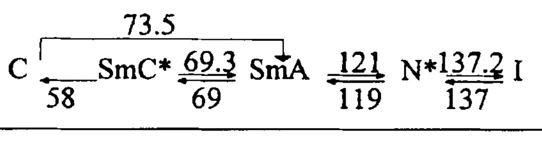
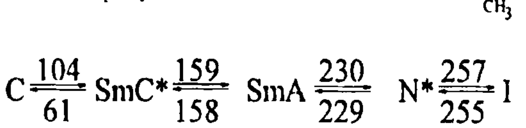
4′-[(*s*)-2-methylbutoxycarbonyl] phenyl 4″-[(4-*n*-heptyloxy-2, 3, 5, 6-tetrafluorophenylene) ethynyl] benzoate (8TFPEB) and 4′-[(*s*)-2-methylbutoxycarbonyl] phenyl 4-(4′-*n*-heptyloxy-2, 3, 5, 6-tetrafluorobiphenyl-1-ethynyl) benzoate (8TFBPEB) were synthesized by J. Wen *et al.* [1], and their ferroelectric properties were investigated in this study. Empty cells were prepared by standard photolithography techniques in Xinxiang No. 713 Factory, China. The cells that were made up of indium tin oxide coated glass had an electrode area of $5.0 \times 5.0\,\text{mm}^2$, a space gap of about $7.2\,\mu\text{m}$ and an aligning treatment of buffing two surfaces coated with polyimide in a parallel single direction. As 8TFPEB and 8TFBPEB filled in the empty cells, liquid crystal layers were formed perpendicular to the alignment direction in the mesomorphic transition from cholesteric to smectic A. After being cooled into the chiral smectic C phase (SmC*), homogeneous aligned cells were obtained.

The tilt angle of the molecular long axis from the layer normal for the sample cells in SmC* was essentially decided by rotating the microscope stage when viewed between crossed polarizers after polarity inversions of the applied external electric field [7,8]. The angle is equal to half the rotation value between two positions corresponding to optical extinct states. The states are symmetrically disposed around the layer normal or the molecular long axis of the SmA phase, which is parallel to the buffing axis of the cell surfaces.

SmC* and other mesophases of 8TFPEB and 8TFBPEB were identified as shown in Table I by an electric method of plotting the polarization versus field hysteresis in conjunction with other general methods. The others are the observations of a differential scanning calorimeter, optical polarizing microscope textures and characteristic fringe patterns or an optical transmissivity undulation associated with the molecular tilting [8]. The apparatuses used are an Olympus BH2 polarizing microscope equipped with a Mettler FP52 hot stage (micro-furnace), a FP5 temperature control unit (Mettler Instrument Corp., Highstone/New Jersey), and a thermal analysis system of a DSC-50 Differential Scanning Calorimeter/TGA-50 Thermogravimetric Analyzer/TA-501 Thermal Analyzer with data station (Shimadzu, Japan).

Observations of the polarization hysteresis curves were indirectly carried out by integrating the current of the polarization differential dP_s/dt, which was calculated from the overall current versus field loops using the sine waveform. It is similar to the triangle waveform method [9], as shown in Figure 1. The sine external electric field was generated by a XD-7 low

TABLE I Structures and mesophases of 8TFPEB and 8TFBPEB where R is n-C_8H_{16}. SmC*, SmA, N*, I and C refer to the chiral smectic C, smectic A, chiral nematic, liquid and solid phases

8TFPEB	Structure	
	Mesophases (°C)	$$\begin{tikzcd} C \arrow[rr, bend left, "73.5"] & SmC^* \arrow[l, "58"'] \arrow[r, shift left, "69.3"] & SmA \arrow[l, shift left, "69"] \arrow[r, shift left, "121"] & N^* \arrow[l, shift left, "119"] \arrow[r, shift left, "137.2"] & I \arrow[l, shift left, "137"] \end{tikzcd}$$
8TFBPEB	Structure	
	Mesophases (°C)	$C \underset{61}{\overset{104}{\rightleftarrows}} SmC^* \underset{158}{\overset{159}{\rightleftarrows}} SmA \underset{229}{\overset{230}{\rightleftarrows}} N^* \underset{255}{\overset{257}{\rightleftarrows}} I$

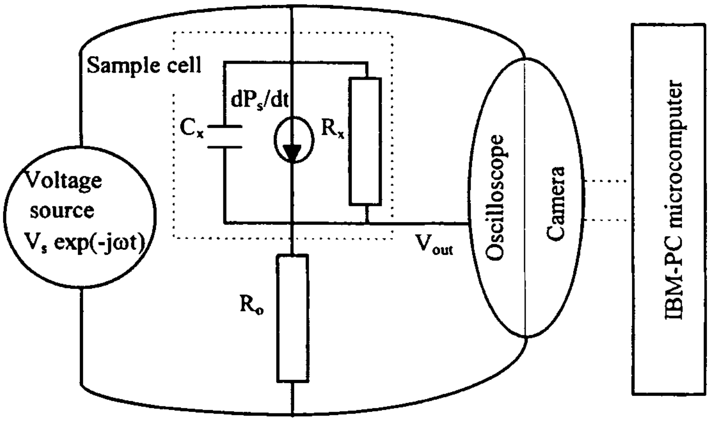


FIGURE 1 Schematic diagram of the spontaneous polarization measurement by applying a sine electric field.

frequency signal source with a power amplifier (Shanghai No. 26 Radio Factory, China). Hysteresis loops were displayed on a Xin-Jian 2235 100 MHz Oscilloscope (Shanghai No. 21 Radio Factory, China), saved on film by a camera (Cannon Autobody, Japan) and treated by an IBM personal computer.

RESULTS

Figures 2 and 3 show measurement results of the overall current dD/dt hysteresis versus the external applied sine electric field E with magnitudes E_0 of 5.6 and 10.5 MV/m at temperatures of $T_c - T = 1, 3, 8, 19, 39$°C and 0.3, 1, 2, 4.5, 8°C for 8TFBPEB and 8TFPEB, respectively. All these curves exhibit humps corresponding to the polarization P_s reversing on fields of 1.12, 1.19, 1.26, 1.54, 1.68 MV/m and 4.2, 4.73, 5.25, 6.22, 6.65 MV/m for two compounds. From the above results or the hysteresis of polarization versus field, the ferroelectricity of both liquid crystals was confirmed.

In Figure 1, the sample cell is in series with a sampling resistor of R_0. The overall current dD/dt including the contribution of the polarization differential is directly monitored by R_0 to represent ferroelectric properties. Thus, P_s can be calculated from the theoretical equation and the results of Figures 2 and 3, which was shown in Figure 4 for 8TFBPEB.

P_s estimated is 0.83, 2.0, 5.2, 11.4, 18.5 × 10^{-6} C/m^2 and 1.6, 4.7, 8.3, 9.5, 10.3 × 10^{-6} C/m^2 at various temperatures for 8TFBPEB and 8TFPEB.

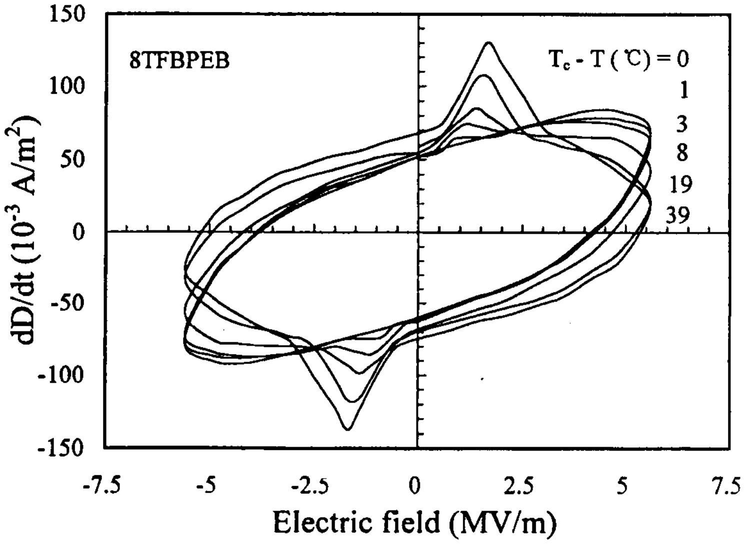


FIGURE 2 Ferroelectric hysteresis loops of the overall current dD/dt versus the electric field with magnitude of 5.6 MV/m at temperatures $T_c - T$ of 1, 3, 8, 19 and 39°C for 8TFBPEB.

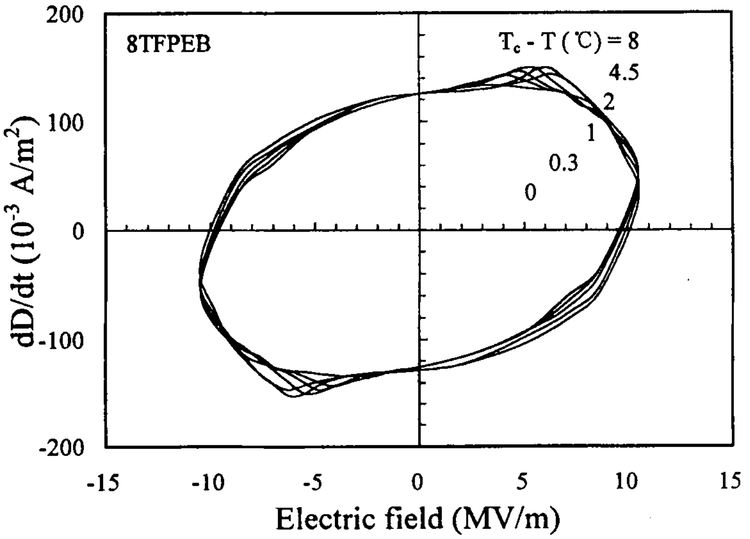


FIGURE 3 Ferroelectric hysteresis loops of the overall current dD/dt versus the electric field with magnitude of 10.5 MV/m at temperatures $T_c - T$ of 0.3, 1, 2, 4.5 and 8°C for 8TFPEB.

Figure 5 represents the polarization P_s as a function of temperature. P_s of 8TFBPEB decreases when the temperature T increases and reaches zero as T approaches 158°C (the transition temperature between SmA and SmC*). The curie point of 8TFPEB can also be observed in Figure 5. It is about 69°C where a hump of the hysteresis loop of dD/dt versus E appeared with the onset of the SmA/SmC* mesomorphic transition.

Optical tilt angles of both compounds were determined, shown in Figure 6. The tilt angle is zero in temperatures above 158 and 69°C due to liquid crystals of the sample cells being in the smectic A mesophase, and arises rapidly when the temperature depresses below and near the curie points. It has saturated values of 8.4 and 13.0 degrees for 8TFBPEB and 8TFPEB, respectively.

It is seen that detecting the hysteresis curve of dD/dt or P_s versus field will become effective to identify ferroelectric mesomorphic phases of liquid crystal materials. In this work, it is the method that was used to decide the SmC* phase of 8TFBPEB or 8TFPEB in conjunction with the observations of the tilt angle dependence on temperature and the optical transmissivity undulation due to the molecular tilting. The results were represented in Table I. 8TFBPEB shows an enantiotropic SmC* phase, but 8TFPEB has a monotropic one only, that is, the latter shows SmC* only in cooling. 8TFBPEB is a crystal below 61°C in cooling and 104°C in heating, chiral

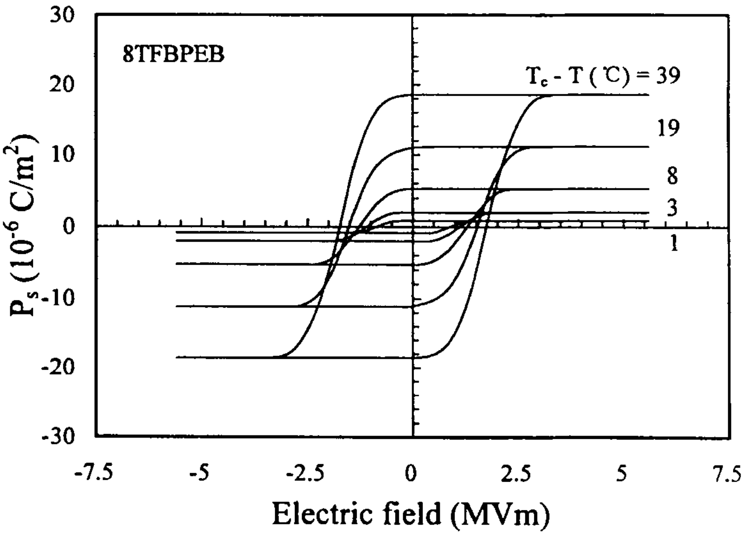


FIGURE 4 Ferroelectric hysteresis loops of the spontaneous polarization versus the electric field with magnitude of 5.6 MV/m at temperatures $T_c - T$ of 1, 3, 8, 19 and 39°C for 8TFBPEB.

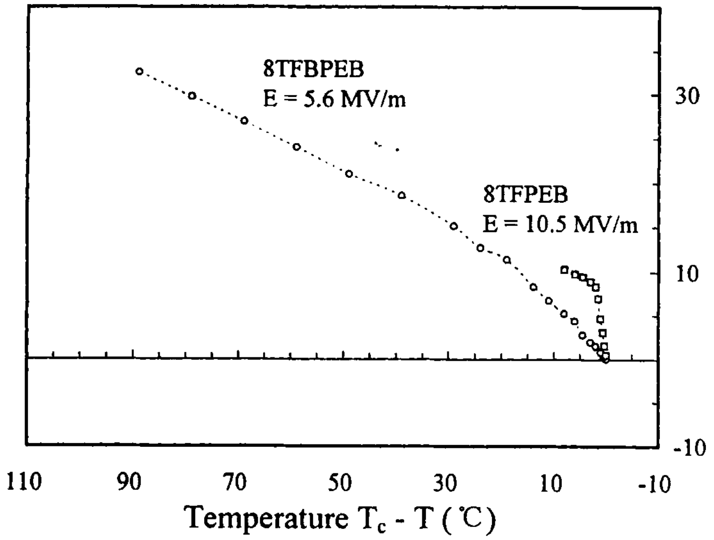


FIGURE 5 Temperature dependence of the polarization by applying the electric field with magnitudes of 5.6 and 10.5 MV/m for 8TFBPEB and 8TFPEB.

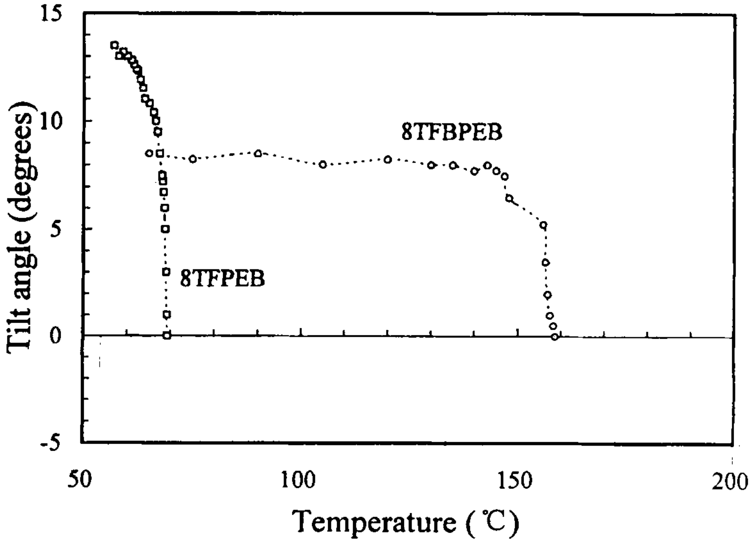


FIGURE 6 Temperature dependence of the tilt angle by applying the electric field with magnitudes of 5.6 and 10.5 MV/m for 8TFBPEB and 8TFPEB.

smecticC below 158°C, smecticA below 229°C, cholesteric below 255°C, and 8TFPEB is a crystal below 58°C in cooling and 73.5°C in heating, SmC* below 69°C in cooling, SmA below 119°C, Cholesteric below 137°C.

DISCUSSION

The polarization P_s can be measured by several methods. The standard in solid ferroelectrics is the Sawyer-Tower method and some indirect observations are to measure the overall current dD/dt or the current dP_s/dt induced by reversing the polarity of the applied external field [9]. In our study, the hysteresis loop of dD/dt (the electric displacement differential) versus field was plotted by directly monitoring the current which flowed through the sampling resistor $R_0(10^5\,\Omega)$ of the measurement circuit of Figure 1. It is well known that the liquid crystal cell can be regarded as a parallel circuit of a current source dP_s/dt, a resistor R_x and a capacitor C_x. Then dP_s/dt is obtained from dD/dt and the parameters of conductive and capacitive contributions (R_x and C_x).

$$dD/dt = dP_s/dt + E(1/R_x + j\omega C_x)/(1/R_0/R_x + j\omega C_x R_0) \qquad (1)$$

$$[j = (-1)^{1/2},\ \omega = 2\pi f,\ f = 100\,\text{Hz}]$$

where the sine-exciting electric field E has a magnitude of E_0 and a frequency of ω, that is, E equals $E_0 \exp(-j\omega t)$, and all other physical parameters are represented in complex. On the other hand, hysteresis curves only show real relations between dD/dt and field E, and so equation (1) must be expressed in reality. Because R_x and C_x are real constants of equivalent parameters to express the responsive physical properties of the liquid crystal cells (the ionic current and the charge accumulation), dD/dt becomes as follows:

$$\begin{aligned} dD/dt = dP_s/dt + [E/R_x + (E/R_0)(R_0{}^2/R_x{}^2 + R_0{}^2\omega^2 C_x{}^2) \\ + \omega C_x (E_0{}^2 - E^2)^{1/2} \operatorname{sign}(dE/dt)]/[(1 + R_0/R_x)^2 + R_0{}^2\omega^2 C_x{}^2]^{1/2} \qquad (2) \end{aligned}$$

where E is a real variable, sign(dE/dt) is a signal function of dE/dt when E is a real function, that is, the real part of $E_0\exp(-j\omega t)$. Supposing that dP_s/dt equals zero in electric field ranges of $E > 0$ in dD/dt holding less than zero and $E < 0$ in $dD/dt > 0$, constants of R_x and C_x could be decided by the computer calculating technique. In this study, R_x and C_x can be obtained directly due to conditions of $R_0 \ll R_x$ and $R_0 \ll 1/\omega C_x (R_0 = 10^5\,\Omega, R_x > 10^9\,\Omega, C_x < 10^{-9}\,\mathrm{F}$, and $f = \omega/2\pi = 100\,\mathrm{Hz})$, so dP_s/dt and P_s are calculated. P_s versus E curves of 8TFBPEB were plotted in Figure 4.

The temperature dependence of the spontaneous polarization P_s in Figure 5 and the tilt angle θ in Figure 6 shows that P_s is of $5.5 \times 10^{-6}\,\mathrm{C/m^2}$, θ of 8 degrees for 8TFBPEB, and P_s of $10.3 \times 10^{-6}\,\mathrm{C/m^2}$, θ of 13 degrees for 8TFPEB at $T_c - T$ of about 10°C. It is seen that the spontaneous polarization and the tilt angle of 8TFBPEB are smaller than those of 8TFPEB at the same temperature of $T_c - T$.

Considering the relation between tilt angle and spontaneous polarization, a cell of unidirectional buffing treatment might give a smaller tilt angle than one of clean surfaces [8], especially in liquid crystals with a much greater helical pitch. So it is suggested that the surface treatment make the tilt angle become much smaller in 8TFBPEB due to the long main chain (the long helical pitch) than that in 8TFPEB because of the same type of the empty cell. Actually, a monodomain of 8TFBPEB cell could be obtained, but not for 8TFPEB. However it may be supposed that the smaller tilt angle produces a lower spontaneous polarization of 8TFBPEB than that of 8TFPEB at the same temperature of $T_c - T$.

From the results of Table I, 8TFBPEB exhibits enantiotropic mesophases of crystal, chiral smectic C, smectic A, cholesteric and isotropic states. But 8TFPEB has the same mesomorphic sequence only in the cooling procedure. Table I also shows that the SmC* temperature range reaches about 100°C and the melting point is near 60°C in 8TFBPEB with a good mesophase sequence. Such a wide SmC* temperature range and a low melting point are not commonly observed. To explain the unusual phenomenon, it is necessary to investigate the relation between the mesomorphic properties and the molecular structure.

Many liquid crystals were synthesized with a perfluorinated phenyl ring [10], and they exhibit the diminution of mesomorphic properties such as the disappearance of the reentrant nematic mesophase. Compounds 4′-*n*-alkoxy-2, 3, 5, 6-tetrafluorobiphenyl-4-carboxylic acids have only the nematic phase when one phenyl ring of the molecule is completely substituted by fluorine [11], whereas responding unsubstituted compounds show smectic as well as nematic mesophases [12].

One knows that the breadth increase of molecules and the coplanarity destruction of skeletons would be caused after the polyfluorinated substitution of one phenyl ring in the molecular structures of liquid crystals. The effects may lead to the lowering of the melting and clearing points, the depression of the mesomorphic thermal stability and the simplification of the mesomorphic types. For liquid crystals containing the tetrafluorobiphenyl unit in the structures of the four-phenyl-ring skeletons, the polyfluorinated substitution of one phenyl ring makes lateral internal intermolecular attractive forces diminish. However, as compared with materials containing three phenyl rings, the relative lateral and the ratio of the lateral to the terminal intermolecular attractive forces of compound molecules with four phenyl rings become greater due to the increase of the phenyl ring number. This may be consistent with the clearing point arising, the melting point not varying obviously, and the tendency forming the smectic mesophases. Finally, SmC* of the compound will be retained in a wider temperature range than that of the three-phenyl-ring series. For this reason, the melting point of 8TFPEB is near that 8TFBPEB, but the later exhibits rather worth properties from the applicative point of view with a good phase sequence, a SmC* temperature range of about 100°C and a low melting point near 60°C.

CONCLUSION

Ferroelectric properties were investigated by plotting hysteresis loops of spontaneous polarization versus electric field with sine waveform. Measured values of the polarization are of 5.5 and $10.3 \times 10^{-6}\,C/m^2$, and the tilt angles are of 8 and 13 degrees at temperature $T_c - T$ of about 10°C for 4'-[(*s*)-2-methylbutoxycarbonyl] phenyl 4-(4'-*n*-heptyloxy-2,3,5,6-tetrafluorobiphenyl-1-ethynyl) benzoate and 4'-[(*s*)-2-methylbutoxycarbonyl] phenyl 4"-[(4-*n*-heptyloxy-2,3,5,6-tetrafluorophenylene) ethynyl] benzoate, respectively. The former also exhibits enantiotropic mesophases of crystal, chiral smectic C, smectic A, cholesteric and isotropic states with a temperature range of chiral smectic C of about 100°C and a melting point near 60°C. The latter possesses the same mesomorphic phase sequence only in cooling and a ferroelectric mesophase temperature range of about 10°C.

The unusual phenomenon in the mesophase sequence and the ferroelectric chiral smectic C temperature range for two compounds is considered to be produced from their different molecular structures. That is, due to the polyfluorinated substitution of one phenyl ring in the four-phenyl-ring compound making the relative lateral internal intermolecular and the ratio of the lateral to the terminal intermolecular attractive forces become greater than those in the three-phenyl-ring compound.

Acknowledgements

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