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*Relation between the spontaneous polarization and alkyl chain length was investigated in ferroelectric switching of N,N′-bis(3,4,5-trialkoxyphenyl)urea (***1-7***) possessing* n-C_4H_9, n-C_8H_{17}, n-C_9H_{19}, n-$C_{10}H_{21}$, n-$C_{11}H_{23}$, n-$C_{12}H_{25}$, *and* n-$C_{16}H_{33}$, *respectively. The phase behaviors were investigated by differential scanning calorimetry, polarized optical microscopy, and the column diameters were obtained by X-ray diffraction. Compound* **2-7** *exhibited rectangular and hexagonal columnar phases. All of the hexagonal columnar phases showed ferroelectric switching under a triangular wave voltage. From the plot of the spontaneous polarization against the carbon atom number of the alkyl chains, correlation between them were clarified and it was strongly suggested that the switching current peaks originated in switching of the polar columns, not in the movement of ionic impurities.*

Keywords Ferroelectric columnar phase; liquid crystal; polarity; switching; urea

Introduction

Realization of ferroelectric columnar liquid crystal phases with achiral molecules is an important scientific challenge and no one has achieved the columnar phases yet. To realize the columnar phases, molecules have to pack one-directionally for generation of polarity in the columns. So far, many shape-assisted approaches were performed. Bowlic and conical molecular shapes were effective for one-dimensional packing of molecules [1–11]. However, the polar columns of those molecules were organized in anti-parallel to cancel out their macroscopic polarities, and any switching behaviors were not observed on applying an electric field. In 2005, our group developed a hydrogen bond-assisted approach, and realized ferroelectrically switchable hexagonal columnar (Col_h) liquid crystal phases which indicated switching

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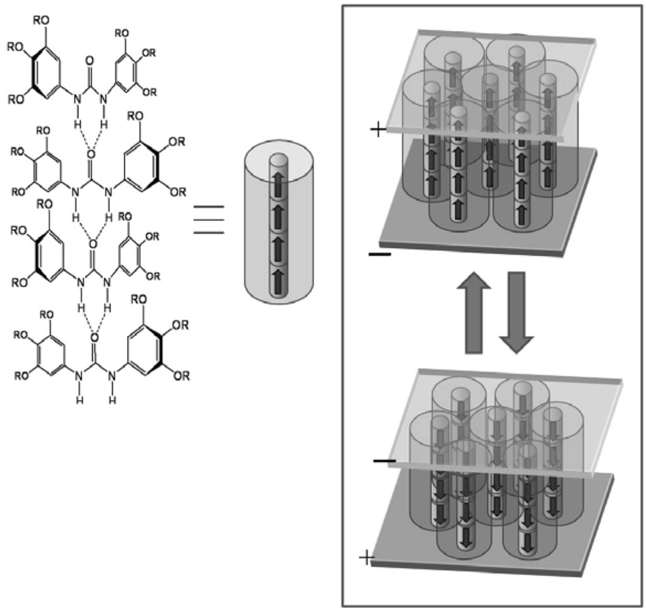
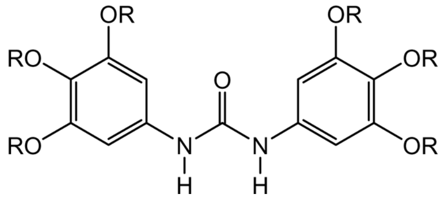


Figure 1. Molecular packing structure in the column and its switching behavior under applying an electric field.

behaviors under applying a triangular wave voltage (Fig. 1) [12,13]. The switching of the macroscopic polarities was confirmed by observation of their second harmonic generation [14–16]. The response time in the switching was very short (1 ms). The response time is much faster than that of ion movement in liquid crystal phases. However, some scientists claimed that the switching might originate in movement of ionic impurities. In order to clarify that the switching peaks came from the polar switching of the columns, in this paper, we investigated the relation between the spontaneous polarization and the alkyl chain length of the liquid crystalline ureas. If the peaks originated in the movement of some ionic impurities, the amount of the impurities of one sample was different from that of other sample and there would be no relation between the switching current peak area and the column diameters. On the other hand, if the switching current peaks originate in the polar switching of the columns, there would be some relation between the peak area and the column diameter. In this study, we prepared *N,N′*-bis(3,4,5-trialkoxyphenyl)ureas **1–7** (Fig. 2), respectively, and their column diameters and spontaneous polarizations (*Ps*) were investigated.



1 (R = n-C_4H_9)
2 (R = n-C_8H_{17})
3 (R = n-C_9H_{19})
4 (R = n-$C_{10}H_{21}$)
5 (R = n-$C_{11}H_{21}$)
6 (R = n-$C_{12}H_{25}$)
7 (R = n-$C_{16}H_{33}$)

Figure 2. Molecular structures of **1–7**.

Experimental

Synthesis of 1–7

The liquid-crystalline ureas were synthesized by the following prodcedure [12]. 3,4,5-Trialkoxyaniline (4.91 mmol), *N,N′*-carbonyldiimidazole (4.00 mmol), and *N,N*-dimetylformamide (50 ml) were added into a 200 ml-three-necked round bottom flask. The solution was stirred under Ar atmosphere for 6 h at room temperature. Water (50 ml) was added and the solution was extracted with chloroform (50 ml × 3). The organic phase was dried over anhydrous $MgSO_4$

Table 1. Phase behaviors of **1–7**

Compound	Phase transilton (°C (kcal/mol))[a]
1 (R = n-C_4H_9)	$\mathrm{Cr}\ \underset{274.4\ (-7.3)}{\overset{274.4\ (11.0)}{\rightleftarrows}}\ \mathrm{Iso}$
2 (R = n-C_8H_{17})[b]	$\mathrm{Cr}\ \underset{159.5\ (-0.2)}{\overset{161.4\ (0.42)}{\rightleftarrows}}\ \mathrm{Col_r}\ \underset{163.3\ (-2.6)}{\overset{167.1\ (2.7)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{183.0\ (-2.2)}{\overset{187.9\ (2.4)}{\rightleftarrows}}\ \mathrm{Iso}$
3 (R = n-C_9H_{19})	$\mathrm{Cr}\ \underset{133.5\ (--0.3)}{\overset{135.1\ (0.5)}{\rightleftarrows}}\ \mathrm{Col_r}\ \underset{154.5\ (-1.5)}{\overset{157.5\ (1.6)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{180.0\ (-2.2)}{\overset{184.8\ (2.3)}{\rightleftarrows}}\ \mathrm{Iso}$
4 (R = n-$C_{10}H_{25}$)	$\mathrm{Cr_1} \xrightarrow{107.2\ (12.0)} \mathrm{Col_r}\ \underset{150.6\ (-1.0)}{\overset{153.1\ (1.0)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{178.0\ (-2.5)}{\overset{182.8\ (2.9)}{\rightleftarrows}}\ \mathrm{Iso}$ $\mathrm{Cr_1} \xleftarrow[90.7\ (-10.0)]{} \mathrm{Cr_2} \xleftarrow[98.7\ (-0.2)]{} \mathrm{Col_r}$
5 (R = n-$C_{11}H_{23}$)	$\mathrm{Cr}\ \underset{88.6\ (-13.0)}{\overset{111.9\ (14.0)}{\rightleftarrows}}\ \mathrm{Col_r}\ \underset{145.7\ (-0.7)}{\overset{148.3\ (0.8)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{174.6\ (-2.8)}{\overset{179.1\ (3.5)}{\rightleftarrows}}\ \mathrm{Iso}$
6 (R = n-$C_{12}H_{25}$)[b]	$\mathrm{Cr}\ \underset{91.9\ (-11.0)}{\overset{110.0\ (14.0)}{\rightleftarrows}}\ \mathrm{Col_r}\ \underset{146.6\ (-0.5)}{\overset{148.6\ (0.7)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{173.6\ (-3.0)}{\overset{178.3\ (3.5)}{\rightleftarrows}}\ \mathrm{Iso}$
7 (R = n-$C_{16}H_{33}$)[b]	$\mathrm{Cr_1} \xrightarrow{80.2\ (h_1)^{c}} \mathrm{Cr_2} \xrightarrow{82.8\ (h_2)^{c}} \mathrm{Col_r}\ \underset{137.2\ (-0.2)}{\overset{138.6(0.3)}{\rightleftarrows}}\ \mathrm{Col_h}\ \underset{163.8\ (-2.8)}{\overset{167.7\ (3.7)}{\rightleftarrows}}\ \mathrm{Iso}$ $\mathrm{Cr_1} \xleftarrow[74.0\ (-10.2)]{} \mathrm{Col_r}$

[a] The transition temperatures (°C) and enthalpies (in parentheses, kcal/ mol) were determined by DSC (5°C/min) and are given above and below the arrows. Cr_1, Cr_2, and Cr indicate crystal phases, and Col_r, Col_h, and I indicate rectangular columnar, hexagonal columnar, and isotropic phases, respectively.

[b] Phase behaviors reported in Reference 12.

[c] The peaks could not be separated. $h_1 + h_2 = 15.9$ kcal/mol.

and concentrated in vacuum. The products were separated by silica gel column chromatography eluting with chloroform to give the corresponding urea as white crystalline powder.

Phase Identification and Measurement of Column Diameters

The phase identification and phase behavior were performed by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The intercolumnar distances in their Col_h phases were measured by X-ray diffractometer (XRD). Their column diameters were calculated from the $d(100)$ peaks, respectively.

Switching Experiment

The compounds were sandwiched by two glass plates which were coated with indium tin oxide and polyimide films (made by E.H.C, cell gap: 5 μm). The cell was set on a hot stage (INSTEC) provided with a polarized light optical microscope (Nikon, Eclipse POL400). The switching experiment was performed in the Col_h phase with a triangular wave voltage (6 Hz, *Vpp* 200 V). The current was monitored by measuring the voltage of the two terminal of a 1 kΩ resistance.

Results and Discussion

Investigation of the Phase Behavior and Measurement of Column Diameters

The phase behaviors of compounds **1–7** were shown in Table 1. Compound **1** exhibited no liquid crystal phase. Compounds **2–7** showed two kinds of columnar phases, rectangular columnar (Col_r) and Col_h phases, which showed typical textures of Col_r and Col_h phases in POM, respectively. Their superstructures were analyzed by XRD, and the column diameters were shown in Table 2. The column diameter increased with increase in the alkyl chain length. However, in the case of **6** ($R = n\text{-}C_{12}H_{25}$), the diameter was smaller than that of **5** ($R = n\text{-}C_{11}H_{23}$). Though the reason was not clear, it was assumed that the averaged repeat distance in the direction of the column axis might be longer than those of **2–5**, and **7**.

Table 2. Column diameters of the Col_h phases of **2–7**

Compound	Column diameter (Å)[a]
2 ($R = n\text{-}C_8H_{17}$)	21.9
3 ($R = n\text{-}C_9H_{19}$)	23.8
4 ($R = n\text{-}C_{10}H_{21}$)	24.4
5 ($R = n\text{-}C_{11}H_{23}$)	25.4
6 ($R = n\text{-}C_{12}H_{25}$)	24.3
7 ($R = n\text{-}C_{16}H_{33}$)	28.8

[a] The column diameters were calculated from $d(100)$ of the hexagonal columnar phases in XRD.

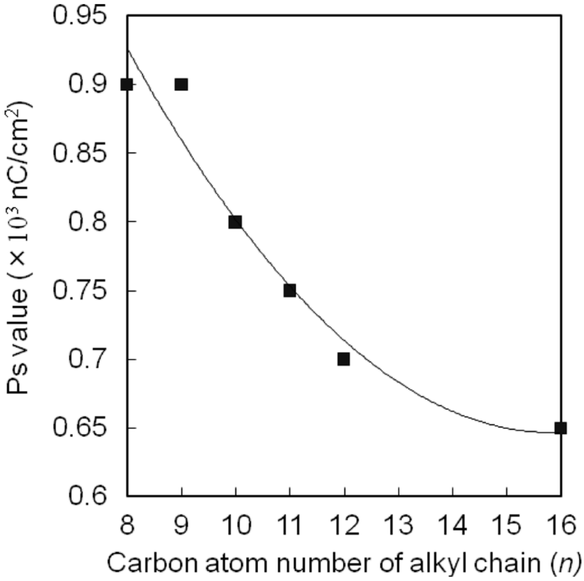


Figure 3. Plot of *Ps* value against the carbon atom number of alkyl chain (*n*). (The *Ps* values are plotted with filled squares. The solid line is an approximation curve in second order).

Explanation for Correlation between the Ps and the Alkyl Chain Length

In Figure 3, the *Ps* value was plotted against the carbon atom number of the alkyl chain. A decrease in the *Ps* value was observed with increase of the carbon atom number of the alkyl chains. This was explained by the schematic representation shown in Figure 4. In each switching experiment, the electrode area and the cell gap were fixed (1.0 cm^2 and 5 μm). With increase in the column diameter, the number of the columns on the electrode area decrease. Accordingly, the *Ps* value decreased with increase of the carbon atom number of the alkyl chains. This strongly suggested that the switching current peaks under applying a triangular wave voltage originated in switching of the polar columns, not in movement of ionic impurities.

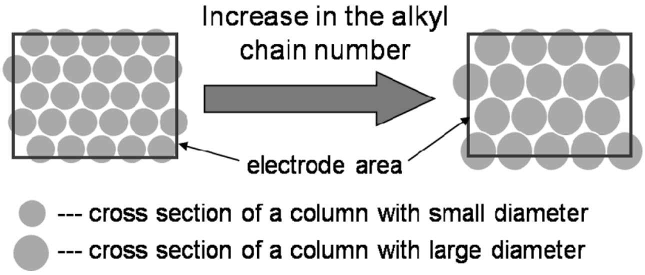


Figure 4. Schematic representation of small and large columns on the electrodes. With increase in carbon atom number of the alkyl chain number, the column diameter increases and the number of the columns on the electrode decreases.

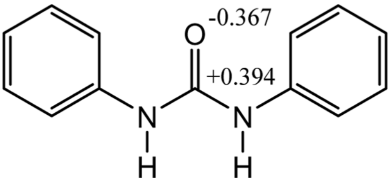


Figure 5. Structure of *N,N′*-diphenylurea and the net atomic charges of its carbonyl-oxygen and carbonyl-carbon atoms.

Estimation of Ps Value of One Column

Then, the *Ps* value of one column was estimated as follows. The column length was assumed to be 5 μm. The cross section (*S*) of the unit cell in the *Col$_h$* phase of **16** is $S = (28.8)^2 \times (\sqrt{3}/2) \times 10^{-16}$ (cm^2). The number (*N*) of the columns on the electrode is $N = 1/S$ on the 1 cm^2 electrode. Accordingly, the *Ps* value of one column is $Ps' = (650 \times 10^{-9})/N = (650 \times 10^{-9}) \times S = (650 \times 10^{-9}) \times (28.8)^2 \times (\sqrt{3}/2) \times 10^{-16} = 4.67 \times 10^{-20}$ (C). This value was 29.2% of the elementary electric charge $(=1.60 \times 10^{-19}$ C). Net atomic charges of *N,N′*-diphenylurea molecule (Fig. 5) were calculated by AM1. The atomic charges of the carbonyl-oxygen and carbony-carbon atoms were -0.367 and $+0.394$. In the urea column, negative and positive charges of molecules are canceled out by formation of the one-dimensional aggregates. However, atomic charges of the two terminal molecules of the column are not canceled out. Accordingly, the negative and positive atomic charges -0.367 and $+0.394$ remain at the two terminal molecules, respectively. The order of *Ps′* (= (elementaly electric charge) × 0.292) obtained by the switching experiment was reasonable as the *Ps* value of the polar column.

Conclusions

We investigated relation between the spontaneous polarization and the alkyl chain length in ferroelectrically switchable columnar phases, and it showed that they were correlated. The correlation indicated that each polar column had a certain amount of polarity, which did not depend on the column diameter. This also suggested strongly that switching behavior originated in the switching of the polar columns not in movement of ionic impurities. Further, the *Ps* value of one polar column (*Ps′*) estimated from this experiment was a reasonable value, which supported our switching mechanism.

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