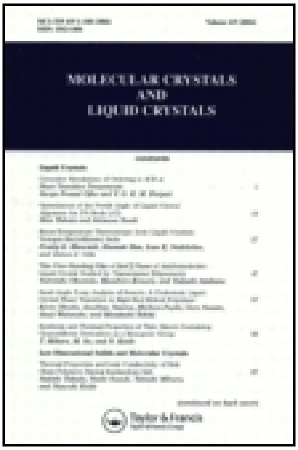

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Ferroelectrically Switchable Columnar Liquid Crystalline Ureas

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Ferroelectrically Switchable Columnar Liquid Crystalline Ureas

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*The phase behavior of N, N′-bis(3,4,5-trihexadecyloxyphenyl)urea (***1***) was investigated by differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction. It was found that* **1** *exhibited two columnar phases, rectangular columnar and hexagonal columnar phases. The switching current peak ($Ps \approx 600\,nC/cm^2$) was observed under applying a triangular voltage with maintaining the homeotropic (dark) texture, which suggested that the polarities of the columns were changed by the applied triangular voltage without changing the directions of the column axes. The mechanism for the ferroelectric switching behavior was explained by the conformational isomerization of the urea moiety.*

Keywords: ferroelectric columnar phase; liquid crystalline; polarity; switching; urea

INTRODUCTION

Realization of ferroelectric columnar phase with achiral molecules is still a scientific challenge in the chemistry and physics of liquid crystals. In a ferroelectric columnar phase, the direction of the macroscopic polarity can be switched by applying an electric field and can be kept after switching off the electric field as shown in Figure 1. Though it was attempted by using conical and bowlic molecular shapes [1–11], the switching behavior was not observed so far. Recently, two examples which indicated ferroelectrical switching behaviors are reported by Gorecka's and our groups [12]. In these cases, the macroscopic

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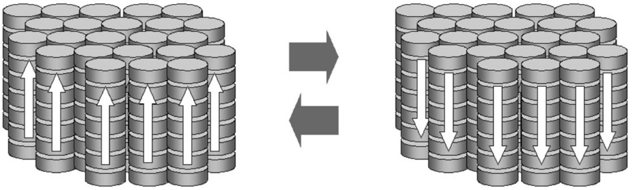


FIGURE 1 Switching of the polarity in ferroelectric columnar phases.

polarity disappeared after switching off the voltage. More recently, Tschierske's group reported a columnar phase which showed a switching peak while applying a triangular voltage [13]. However, in this case, it was found that the columnar phase changed to a smectic phase during the switching process. Accordingly, no one has performed ferroelectric columnar liquid crystal phases with achiral molecules.

If each column can change its polarity independently, high density memory devices can be realized by controlling their polarities with a usage of a small electrode such as a probe of a scanning tunnel microscope (STM) (Fig. 2).

In this article, we describe ferroelectrically switchable liquid crystalline urea and their properties and switching mechanism.

EXPERIMENTAL

Synthesis of 1

3,4,5-Trihexyloxyaniline (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 $MgSO_4$ and concentrated in vacuum. The products were separated by silica gel column

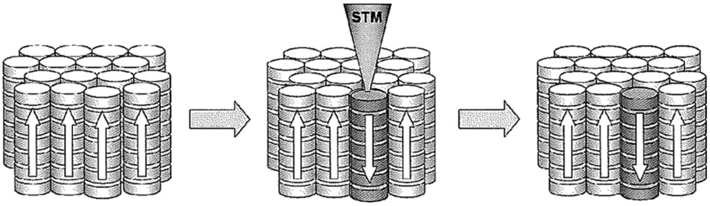


FIGURE 2 High density memory device using the ferroelectric columnar phase.

chromatography eluting with chloroform to give the corresponding urea as white crystalline powder[14].

1c: white solid; mp. 80.4°C; TLC ($CHC1_3$, Merck silica gel 60): $R_f = 0.47$; ^1H NMR (500.0 MHz, $CDCI_3$): $\delta 0.88$ (overlapped t, 18H), 1.23–1.33 (m, 144H), 1.41–1.49 (m, 12H), 1.73 (quint, $J = 7.4$ Hz, 4H), 1.78 (quint, $J = 7.3$ Hz, 8H), 3.90–3.95 (m, 12H), 6.32–6.40 (br, 2H), 6.55 (s, 4H); ^{13}C NMR (125.65 MHz, $CDCI_3$): δ 14.10, 22.69, 26.10, 26.15, 29.37, 29.45, 29.63, 29.66, 29.72, 29.75, 29.77, 30.32, 31.92, 69.22, 73.54, 100.91, 133.12, 135.34, 153.51; IR (KBr): 3310 cm^{-1}, 2919, 2850, 1644, 1602, 1504, 1226, 1121; Anal., calcd for $C_{109}H_{204}N_2O_7$(%): C, 79.11; H, 12.43; N, 1.69; found: C, 79.12; H, 12.63; N, 1.66.

Switching Experiment

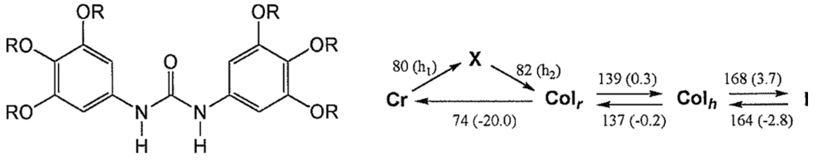
Compound **1** was sandwiched by two glass plates which was coated with indium tin oxide and polyimide films (made by E.H.C, cell gap: 5 μm). The cell was set on a hot stage (INSTEC) provided with a polarized light optical microscope (Nicon, Eclipse pol-400). The switching experiment was performed at 160°C with a triangular wave voltage (6 Hz, Vpp200 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 Superstructures

The urea (**1**) was synthesized from pyrogallol with four steps[14]. The phase behavior was investigated by differential scanning calorimetry (DSC) and their phases were identified by polarized optical microscopy (POM). Their superstructures were analyzed by X-ray diffraction (XRD). The phase behavior was shown in Figure 3. Compound **1** exhibited two columnar phases, rectangular columnar (Col_r) and hexagonal columnar (Col_h) phases, which showed typical textures of Col_r and Col_h phases in POM, respectively.

The XRD of **1** in the Col_r phase is shown in Figure 4, which shows a sharp peak at 28.8 Å and a peak at 22.6 Å which correspond to d200 and d110 peaks of the Col_r phase. The small peaks at 15.2, 12.4, and 11.2 Å correspond to d310, d020 and d220 peaks, respectively. The broad peak at 9.6 Å is observed as the d001 peak. The XRD of **1** in the Col_h phase is shown in Figure 5, which shows a sharp peak at 24.7 Å and a small peak at 12.4 Å which correspond to its d100 and d200 peaks, respectively. The small peaks, d110 and d210, are not observed clearly. The broad peak at 9.6 Å is observed again as the



1 (R = $(CH_2)_{15}CH_3$)

FIGURE 3 Molecular structure of **1** and its phase behavior. The transition temperatures (°C) and enthalpies (in parentheses, kcal/mol). *Cr*, *Col$_r$*, *Col$_h$*, I, and X indicate crystal, rectangular columnar, hexagonal columnar, isotropic, and unidentified phases. The transitions from Cr to X and from X to Col$_r$ were could not be distinguished ($h_1 + h_2 = 15.9$ kcal/mol).

*d*001 peak. In IR spectroscopy, these two phases had the N-H absorption peaks at 3319 and 3338 cm^{-1}, respectively, which indicated that the urea molecules had strong intermolecular hydrogen bonds. The wavenumbers are smaller than those of free N-H stretching of ureas (3427–3444 cm^{-1}) [15].

From the observation in the POM and XRD, the urea molecules in the *Col$_h$* phase have a linearly hydrogen-bonded network to generate the hexagonal columnar superstructure depicted in Figure 6. Then, we had a question about the superstructure. How are the polar columns packed in the *Col$_h$* phase?

Switching Experiment of 1

We performed optoelectric experiment of **1** in the *Col$_h$* phase (160°C). Compound **1** was sandwiched with two glass plates coated with indium

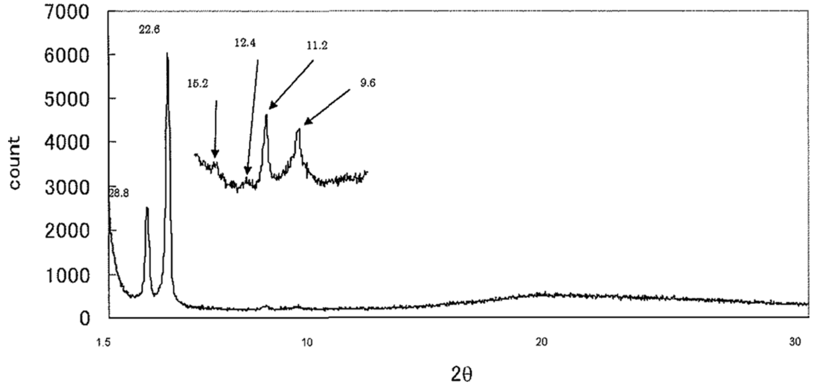


FIGURE 4 XRD of **1** in the *Col$_r$* phase (100°C).

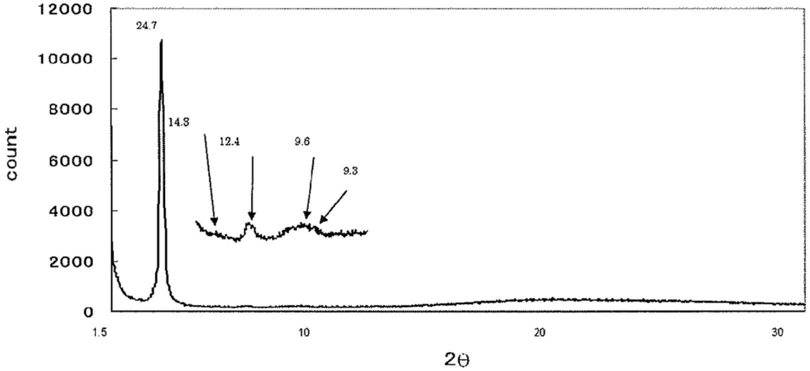


FIGURE 5 XRD of **1** in the *Col*$_h$ phase (145°C).

tin oxide (ITO) and polyimide compound (cell gap: 5 μm). As shown in Figure 3, the texture of the *Col*$_h$ phase was observed without applying a voltage. However, with applying a triangular voltage (6 Hz, Vpp200 V), the texture disappeared quickly (Fig. 7). The switching current peak ($Ps \approx 600\,\text{nC/cm}^2$) was observed under applying the triangular voltage, although the homeotropic (dark) texture was maintained. This suggested that the columns were organized homeotropically by applying the voltage and the polarities of the columns changed the directions repeatedly without changing their column

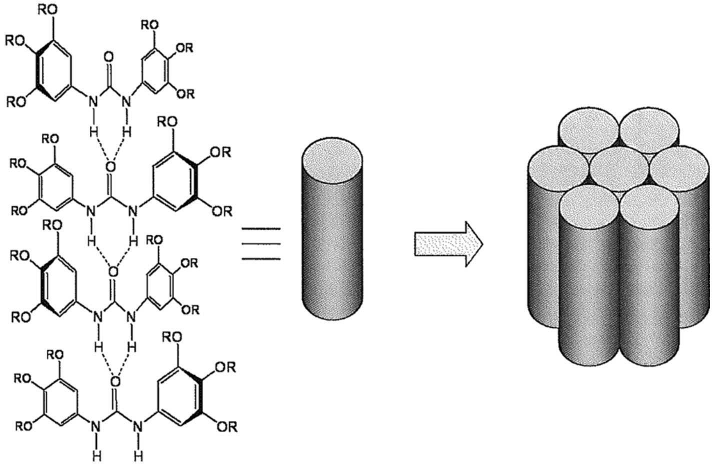


FIGURE 6 Models of the column of urea **1** and the hexagonal columnar phase.

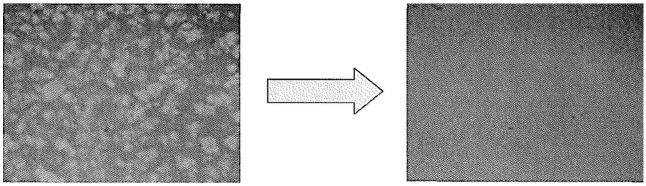


FIGURE 7 Microphotographs of **1** in the hexagonal columnar phase (160°C) (a) under applying no voltage and (b) under applying a triangular voltage (6 Hz, Vpp200 V) (the liquid crystalline compound was sandwiched with two glass plates coated with indium tin oxide and polyimide compound, cell gap: 5 μm).

axes. After switching off, the homeotropic texture was maintained. Accordingly, the polarities of the columns easily change their directions with applying an electric field. Further, from measurement of the second harmonic generation of **1** by Takezoe's group, it was found that the macroscopic polarity disappeared after the switching off [16,17]. Their experiment suggests that the length of the linearly hydrogen-bonded ureas decrease to the shorter length than the light wave-length (Nd:YAG laser: 1.064 μm) after the switching off, and the short supramolecular urea polymers align in parallel with canceling their polarities at 0 V.

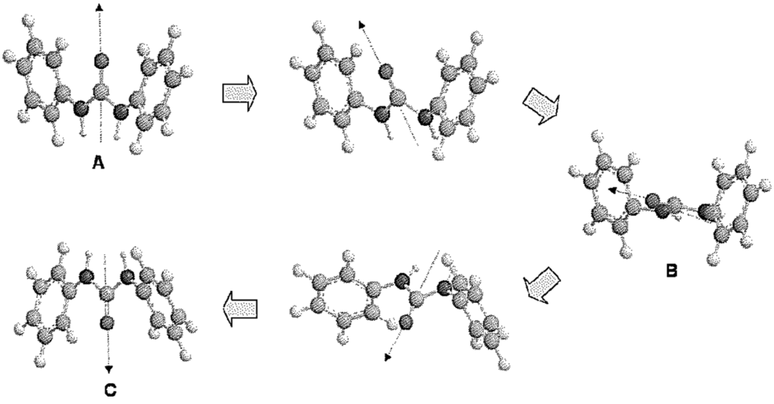


FIGURE 8 Proposed conformational isomerization of N,N'-diphenylurea. The carbonyl group changes its directions without changing the positions of the two phenyl groups. Conformer **B** is 6 kcal/mol less stable than conformer **A (C)**.

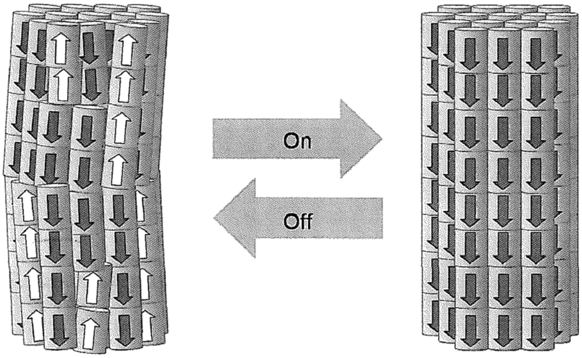


FIGURE 9 Proposed non-polar organization (left, under applying no electric field) and polar organization (right, under applying an electric field) in the hexagonal columnar phase.

Mechanism for the Switching Behavior

We proposed the following mechanism for the change of the polarities in the columns as shown in Figure 8. The urea molecules can change their conformations without changing the positions of the phenyl groups. Conformer **B** is 6 kcal/mol less stable than conformer **A (C)**, which was calculated by AM1. With the low conformational barrier, each of the carbonyl group can change the directions from one direction to the opposite direction. This molecular movement should occur easily in each of the columns at the temperature range of the Col_h phase. Accordingly, the macroscopic polarity is changed by applying the triangular wave voltage without changing the homeotropic alignments of the columns. Without applying an electric field, each column has many short polar molecular aggregates in it, and the aggregates cancel their polarities to have antiparallel association with the adjacent columns (Fig. 9). The broad small peaks of $d110$, $d200$, and $d210$ in the Col_h phase suggested the disorder in the intercolumnar distances.

CONCLUSIONS

We could demonstrate that the liquid crystalline urea exhibited a ferroelectrically switchable columnar phase. The switching behavior was explained by the conformational isomerization of the urea moiety. However, the energy barrier in the isomerization is too small to maintain the molecular conformation in the columns. To maintain the polar molecular packing, the conformational barrier should be increased or/and the strength of the hydrogen-bonds between molecules should be increased.

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