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Polarization switching in a columnar liquid crystalline urea as studied by optical second-harmonic generation interferometry

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The polar order and its switching characteristics have been investigated by means of optical second-harmonic generation interferometry in a compound N,N'-bis(3,4,5-trialkoxylphenyl)urea ($R=n$-$C_{16}H_{33}$) being connected by intermolecular hydrogen bondings to form a columnar liquid crystalline phase. The polar structure is formed along the column by applying an electric field and is cooperatively switched by reversing the field. The polar order is relaxed to a nonpolar state within a few milliseconds by terminating the field. No macroscopic polar order exists at least in a range of a visible wavelength scale in the absence of a field.

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The polar order in liquid crystalline phases becomes possible by reducing the symmetry to C_n or C_{nv}. It has simply been made by introducing chirality into the systems; the chiral smectic-*C* (SmC^*) phase, which has a C_2 symmetry, is the first ferroelectric phase in liquid crystals [1,2]. The ferroelectricity was also realized by introducing chirality even in the columnar liquid crystal phase consisting of disklike *chiral* molecules [3–9]. The molecules are tilted from the column axis in the rectangular phase, resulting in the polar order perpendicular to columns, and can switch by an electric field.

Recently, a polar order was successfully realized within a smectic layer by closely packing bent-core molecules [10]. The same concept is possibly used to form polar columns in the columnar phase. Actually many types of bowlic- [11–13], conical- [14–16], and shuttlecock-shaped [17,18] molecules have been designed and synthesized. They can organize one-dimensional molecular packing, resulting in strong polar order along the column. However, most of them are neither macroscopically polar nor induce macroscopic polar orders by an electric field. That is because their molecular structure may be too rigid to respond to a field. Recently two columnar phases have been reported as switchable polar columnar phases; i.e., urea derivatives linearly linked by hydrogen bonding [19] and bent-core polycatenar molecules [20]. In the latter system, the umbrellalike molecular assembly of bent-core molecules can respond to an electric field by the "softening" of the cone angle of the molecular assembly. The polar switching was observed in switching current measurements in both systems. However, this observation is not sufficient to conclude the ferroelectric switching. Actually, ionic current flow associated with the field application sometimes gives erroneous switching current peaks upon field reversal [21,22]. Here we report an unambiguous polar switching in the former molecular system by means of second-harmonic generation (SHG) interferometry. This technique provides us with a very powerful tool to prove not only polar orders but also the switching of polarization, which cannot be detected by linear optical techniques such as optical absorption.

The material used in this study was N,N'-bis(3,4,5-trialkoxylphenyl)urea [19] shown in Fig. 1(a). The molecule has a urea unit in the molecular center, forming intermolecular double hydrogen bonding and shows the phases with one-dimensional molecular stacking as indicated in Fig. 1(b). There are at least two columnar phases, the hexagonal (Col$_h$) and the rectangular (Col$_r$), as indicated in Fig. 1(c). Glass substrates that have a patterned indium tin oxide (ITO) area (5×4 mm^2) were spin coated with a surface alignment layer (AL1254) for homogeneous alignment but were not rubbed. After fabricating typical sandwich-type cells of about 5 μm thick, the compound was introduced into cells in the isotropic phase and cooled down to the Col$_h$ phase (160 °C) with a rate of −1.0 °C/min. Prior to SHG measurements, a triangular electric field (100 Vpp) was applied to the sample, aligning the columns normal to the substrate. Without using any surface treatment such as rubbing, perfect alignment was obtained, i.e., the cells were completely black under crossed polarizers irrespective of the cell rotation angles about the cell surface normal. The situation did not change after applying an electric field, indicating that the perfect column orientation was preserved during the polarization switching.

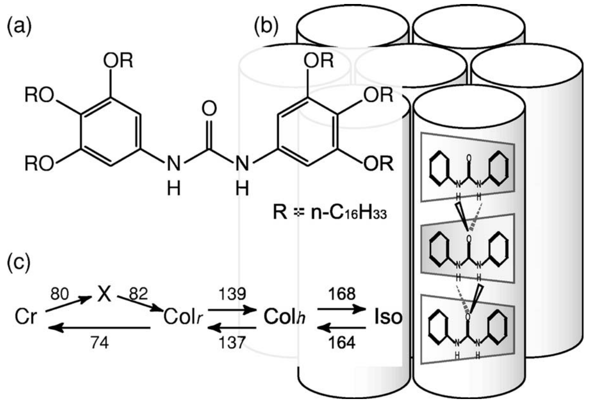


FIG. 1. (a) The molecular structure of N,N'-bis(3,4,5-trialkoxyphenyl)urea and (b) its molecular assembly of the columnar hexagonal phase. (c) The phase sequence and its transition temperatures of the urea compound determined by differential scanning calorimetry and x-ray diffraction measurement.

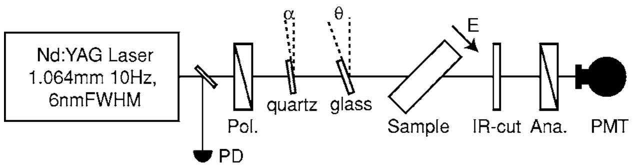


FIG. 2. Optical setup for SHG interferometry measurements. Polarizer (Pol.) and Analyzer (Ana.) were set in the p-in–p-out geometry. The fundamental light from a Nd:YAG laser was extinguished by an ir-cut filter (IR-cut) in front of a photomultiplier tube (PMT). The SHG signals from a sample cell and a quartz interfered with each other, and the phase difference was varied by rotating a glass plate.

Figure 2 shows an optical setup for SHG interferometry measurements. The fundamental light from a Nd:yttrium aluminum garnet (YAG) laser (Surelite I; SLI-10 1064 nm, 10 Hz, 2 mJ/pulse) was incident on a Y-cut quartz plate for a reference SH generator at an incidence angle α of about 8.6°, and impinged on the sample cell at an incidence angle of 45° after passing through a glass plate as a phase modulator. Most of the SHG measurements were performed by the incidence of p-polarized light to detect p-polarized SHG signals (p-in–p-out) from the transmitted direction. The phase between the SHG signals from the quartz and the sample cell was mutually shifted by the out-of-plane rotation of the glass plate due to the different optical path lengths (refractive indices) at the fundamental light and the SHG light wavelengths, producing an interference fringe in the SH signal intensity. The SHG relaxation measurement was carried out using a mode-locked Ti:Sapphire laser (Vitesse: Coherent; 800 nm, 80 MHz, 80 fs, 280 mW) instead of the Nd:YAG laser. The SHG signal was amplified by a current preamplifier (NF LI-76), and its intensity was monitored during and after applying a rectangular-reversing-pulsed field of 4 ms in duration. Dielectric measurements were performed with a Solartron 1296 dielectric interface and a 1255B frequency response analyzer. The capacitance of an empty cell was 35.6 pF and the oscillation strength was 3 Vrms without dc bias.

When the sample was slowly cooled from the isotropic phase without applying an electric field, negligible SHG was detected in all the phases. After the column reorientation by applying an electric field, the cell was not SHG active either, in the absence of a field. SHG activity arose only under an electric field in p-in–p-out and s-in–p-out polarization conditions with the intensity ratio of about 4.3. No SHG signal was detected in p-in–s-out and s-in–s-out polarization combinations. These preliminary SHG measurements supply two important pieces of information: (1) a polar order of at least a visible wavelength scale exists only under the application of an electric field and (2) the polar direction is parallel to the columns. Then next question is how the polarization switching occurs. The SHG interferometry unambiguously gives the answer.

Figure 3 shows the results of SHG interference measurement at 160 °C. The SHG signal was detected at the field maxima (closed circles for +15.44 V/μm and open circles for −15.44 V/μm) of a triangular-wave field as a function of the rotation angle θ of the glass plate. The fringe structures, which originate from the interference of the SHG signals from the quartz plate and the sample, are clearly observed and are out of phase to each other, obviously indicating the reversal of the polar direction. Thus, the polar order is formed along the field direction, which coincides with the column axis, by applying an electric field and is reversed when the applied field is reversed. This polar switching brings about a single switching current peak, as reported [19].

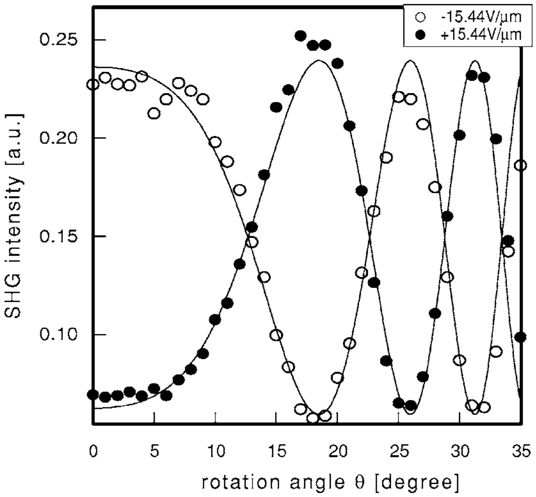
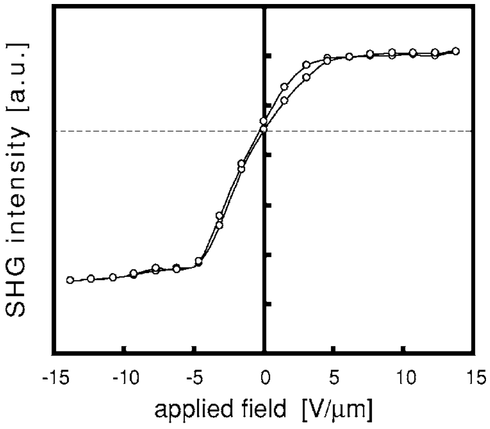


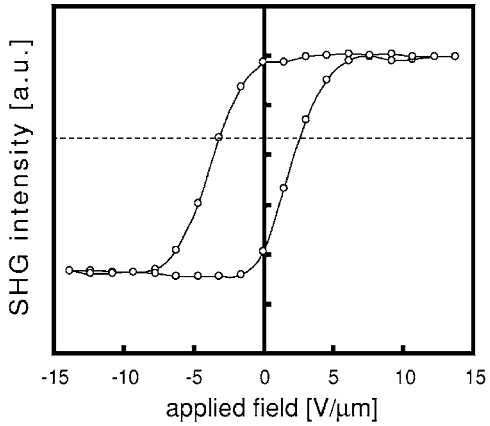
FIG. 3. SHG interferograms at 160 °C as a function of out-of-plane rotation of a glass plate. Closed and open circles show data points for +15.44 V/μm and −15.44 V/μm in a triangular applied field of 10 Hz. The solid curves are the theoretical best fits to the experimental SHG interferograms.

In order to examine the stability and relaxation of the polar structure, we measured the applied field dependence of SHG. The measurements were made in the interferometry geometry (Fig. 2) with a fixed glass plate at $\theta = 18°$ giving the optimal SHG signals in Fig. 3. The SHG signal was monitored during the application of a triangular-wave field with an amplitude of ±13.8 V/μm. The result was shown in Fig. 4 at (a) 1 Hz and (b) 10 Hz. Horizontal broken lines are the SHG intensity from the quartz plate, the same as the signal level after terminating a field. The SHG intensity variation exhibits hysteresis at 10 Hz (b), but the hysteresis is negligibly small at 1 Hz (a). The signal profile at 10 Hz [Fig. 4(b)] suggests a ferroelectric behavior with a finite polar order at 0 V. According to Fig. 4(a), however, the ferroelectric nature (the polar order at 0 V) is artificial because of a slow switching response. Actually we confirmed that the relaxation time of the polar order is of the order of a few milliseconds by the SHG relaxation measurement.

Figure 5 shows the result of the SHG relaxation measurement at 160 °C. A rectangular-reversing-pulsed field of an amplitude of 120 Vpp±(12.2 V/μm) was applied, as shown in Fig. 5. When the stepwise field was applied, SHG emerged and decayed after terminating the pulsed field within a few milliseconds. When the field was reversed, a dip in the SHG intensity appeared. This is caused by the switching of the polarization along the column according to the field reversal. We found that the rise time and dip position are dependent on the amplitude of the field, while the decay is almost in-



(a) 1Hz



(b) 10Hz

FIG. 4. Applied voltage dependence of SHG at 160 °C for (a) 1 Hz and (b) 10 Hz. The broken lines are the SHG intensity level from the quartz plate.

dependent of the amplitude. The details will be discussed in a separate paper.

The dielectric measurements also gave us the consistent results with the SHG relaxation measurement. The measurements were performed at every 5 °C from 160 °C during cooling from the isotropic phase. Before the measurement at 160 °C, a vertical electric field of 100 Vpp was applied to the sample to align the columns normal to the substrates. We confirmed the homeotropic alignment of the columns maintained below 155 °C by a microscope observation. Figure 6 shows the real and imaginary parts of the relative permittivity, $\epsilon^{*}=\epsilon'+i\epsilon''$. The relaxation frequencies obtained by the Cole-Cole plots of the results are in the range of 5–200 Hz depending on temperature, being consistent with the SHG relaxation experiment [23]. Hence, we can conclude that the present system is not truly ferroelectric, since there is no macroscopic polarization in the absence of a field. However, a macroscopic polar order along the column is easily induced by cooperative interaction between the polarization and an applied electric field, and is switchable by reversing a field.

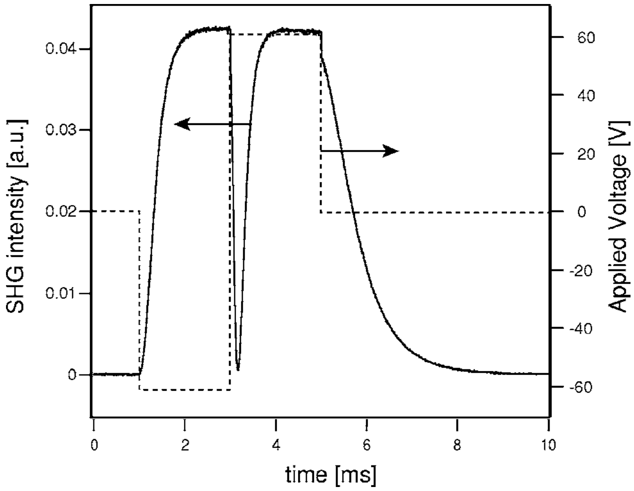


FIG. 5. Temporal change of the SHG intensity at 160 °C when a rectangular-reversing-pulsed field is applied.

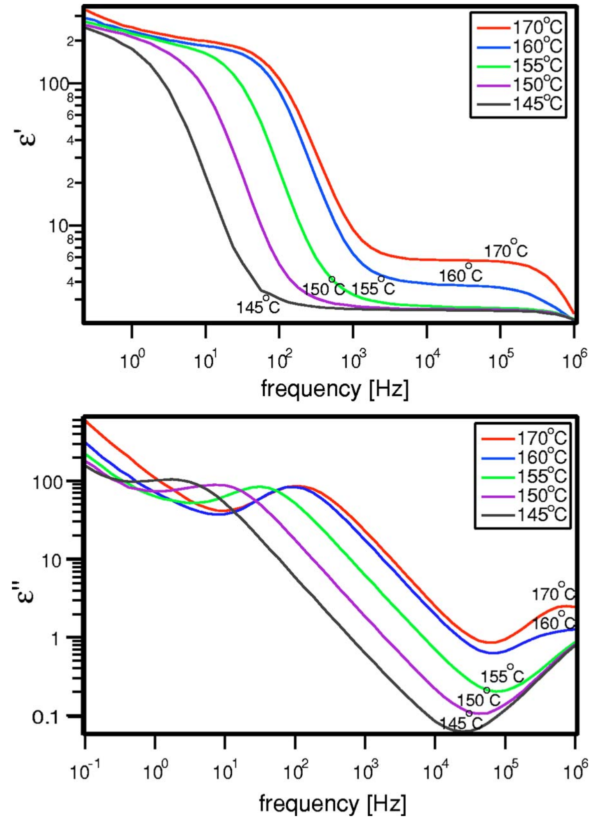


FIG. 6. (Color online) The dielectric dispersion of a liquid crystalline urea at various temperatures indicated in the figure.

In summary, we performed SHG interferometry measurements to investigate the polar structure in the columnar hexagonal Col_h phase of the liquid crystalline urea linearly linked by hydrogen bonds. The macroscopic polar order can cooperatively respond to an applied electric field. However, it relaxes within a few ms after the field termination.

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[23] The dielectric response in this frequency range is observed even at 170 °C, which is definitely in the isotropic phase. The polar domains possibly remain even in the isotropic phase. Actually spontaneous polarization is observed in the isotropic phase (see Ref. [19]). The details will be reported later.