Electro-optic Kerr effect in the isotropic phase above the columnar phase of a urea derivative

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The authors have measured the electro-optic Kerr effect in the isotropic phase of a urea derivative. Electric-field-induced birefringence Δn was observed in the isotropic phase even 30 °C above the isotropic-columnar phase transition temperature. The induced birefringence is inversely proportional to temperature, as predicted by the Landau–de Gennes theory. Two distinct regions are identified from the proportionality constants in the isotropic phase; optical second-harmonic generation (SHG) is easily observable in the low-temperature region on applying an electric field, whereas SHG activity does not emerge in the higher-temperature region. The structure of molecular assemblies is discussed based on these experimental results.

Liquid crystals have long-range orientational order, so that a small field is enough to align their director. The effect of an electric field is due to dielectric anisotropy and is widely used in liquid crystal displays. Even in the isotropic (Iso) phase in the vicinity of the phase transition to the nematic phase, birefringence Δn is easily induced by an electric field E. This phenomenon is known as the Kerr effect [1], and the induced Δn is proportional to E^2,

$$\Delta n = \lambda B E^2, \quad (1)$$

where λ is the wavelength of light in vacuum and B is the Kerr constant. Since the Kerr effect in the Iso phase of liquid crystalline materials originates from the field-induced reorientation of clusters with a local nematic order defined by the coherence length ζ, but not at the molecular level, the Kerr constant is larger than in conventional Kerr materials such as nitrobenzene by 1–2 orders of magnitude [2–11]. The Kerr constant in the Iso phase of nematogens diverges as the temperature approaches T_C^*, the critical temperature where ζ grows infinitely, and is typically 1 K lower than $T_{\text{N-I}}$, the nematic-Iso transition temperature. The strong temperature dependence of the Kerr constant of nematogens is theoretically described using the Landau–de Gennes theory [12–14] and is given by

$$B = K_B/(T - T_C^*) \quad (2)$$

with constant K_B.

There have been extensive studies of the Kerr effect in the Iso phase, but most of them were made just above the nematic phase except for one above a polymer-stabilized blue phase [15]. Here, we report the occurrence of the Kerr effect in the Iso phase above the columnar phase. During studies of polar switching in the columnar phase of a liquid crystalline urea derivative, we realized by means of switching current measurements [16], optical second-harmonic generation (SHG), and dielectric measurements [17] that polar order was easily induced by applying an electric field even in the Iso phase. Intermolecular hydrogen bonds were also confirmed even in the Iso phase, suggesting the existence of

columnar molecular assemblies. These findings motivated us to carry out electro-optic Kerr measurement in this material system. The result is interesting; two regimes with different Kerr constants were identified in the Iso phase. We will discuss the molecular assemblies in the Iso phase.

The liquid crystalline material used for the electro-optic Kerr measurement was N,N'-bis(3,4,5-trihexadecyloxyphenyl)urea [16], which shows the phase sequence Iso $\xrightarrow{164\,°C}$ Col$_h$ $\xrightarrow{137\,°C}$ Col$_r$ on cooling and Col$_r$ $\xrightarrow{139\,°C}$ Col$_h$ $\xrightarrow{168\,°C}$ Iso on heating (transition temperatures obtained by differential scanning calorimetry), where Iso, Col$_h$, and Col$_r$ stand for the isotropic, hexagonal columnar, and rectangular columnar phases, respectively. The molecule has a urea unit in the center and hence there are intermolecular double hydrogen bondings, resulting in a one-dimensional molecular assembly forming a column. Sample cells for the Kerr measurements (Kerr cells) were fabricated using two glass substrates, one of which had a pair of in-plane electrodes of indium tin oxide (ITO) of 7 mm in length and with a gap of 50 μm. The cell gap is 13 μm, so that the field is not uniform, as shown in Fig. 1. Because of this Kerr cell design, the observed Kerr constant must be a little smaller one than the true one. These substrates with and without the patterned ITO were coated with polyimide
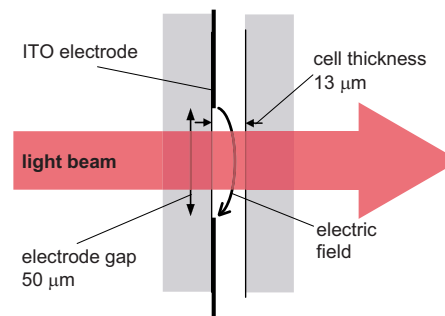

FIG. 1. (Color online) Design of the Kerr cell used in this study. The relation between the applied electric field and the incident beam is also depicted in the figure.

(AL1254, JSR) and were baked at 180 °C for 1.5 h for imidization to obtain homogeneous alignment. The liquid crystal material in the Iso phase was introduced into an empty cell 13 μm thick with bead spacers using capillary suction.

A helium-neon (He-Ne) laser was used as light source. The Kerr cell was located between crossed polarizers with the field direction at ±45° to the polarizer axes. When a sinusoidal electric field (1 kHz, 6.4 V/μm) was applied to the Kerr cell, the transmitted light was modulated. By inserting a Soleil-Babinet compensator between the polarizers, linear detection of the modulated component of the transmittance, I_{ac}, due to the induced Δn is possible, as well as of the dc component of the transmittance, I_{dc}, since the induced retardation is much smaller than the retardation by the compensator (optical bias Γ). The transmitted light was detected by a pin photodiode. The modulated light intensity I_{ac} and dc light intensity I_{dc} were respectively detected by a lock-in amplifier at 2 kHz (double the frequency, 2*f*, of the applied field frequency) and a digital voltmeter.

As a preliminary measurement, we checked the optical bias dependence of I_{ac} and I_{dc} and confirmed that the maximum I_{ac} is obtained when $\Gamma = \pi/2$. By choosing $\Gamma = \pi/2$, the ratio of the ac and dc components is given by

$$I_{ac}/I_{dc} = (2\pi l/\lambda)\Delta n \qquad (3)$$

where l is the sample length (cell thickness). We measured I_{ac}/I_{dc} by rotating the sample about the cell surface normal, and confirmed that the maximum ratio was obtained when the field direction was at ±45° with respect to the polarizer directions. Thus, every measurement was carried out in this condition.

Optical second-harmonic generation measurements were conducted using a conventional setup with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (2 mJ/pulse, 1.064 μm, 10 Hz repetition, 6 ns duration) as the light source. By normal incidence of the fundamental light linearly polarized parallel to the field on the same cell used for the Kerr measurements, SHG polarized parallel to the incident polarization was detected in the transmission direction under the application of an electric field. The signal was taken at a maximum field strength 6 V/μm of the applied triangular wave field of 10 Hz.

In order to confirm that the electro-optic response is due to the Kerr effect, the electric-field dependence of the modulated signal intensity was measured. The result at 155 °C is shown in Fig. 2. It is clear that I_{ac} is proportional to the square of the applied field. The result is consistent with Eqs. (1) and (3).

Next, the temperature dependence of I_{ac} was measured upon the application of a field of 3.2 V/μm to confirm the relationship given by Eq. (2). The sample was gradually cooled from 180 °C (well above the transition temperature between Iso and Col$_h$, $T_{I\text{-}Ch}$) to $T_{I\text{-}Ch}$. The measurements were carried out in the cooling process. The result is plotted in Fig. 3. It is noted that the Kerr signal is detected even 30 °C above $T_{I\text{-}Ch}$ and increases with decreasing temperature. The inverse of the estimated Δn obtained by Eq. (3) is also plotted in Fig. 3. Two temperature ranges are identified, as indicated by straight lines determined by the least-mean-
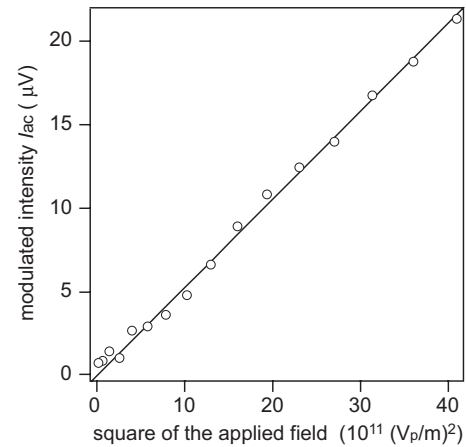

FIG. 2. Modulated signal intensity I_{ac} as a function of square of applied field. The solid curve is the best fit determined from the least-mean-squares method.

squares method. The temperature difference between the transition temperature between Iso and liquid crystal phases $I_{I\text{-}LC}$ and T_C^*, $\Delta T = T_{I\text{-}LC} - T_C^*$ and the Kerr constant B at the temperature (155 °C) showing the maximum modulated light intensity are listed in Table I. The results for some other liquid crystals are also shown for comparison. The Kerr constant in the urea derivative is 1.546×10^{-14} m/V^2, which is much smaller than that in the Iso phase of other nematogens.

One of the notable observations for Δn^{-1} in Fig. 3 is the two distinct temperature regions showing different slopes in the Iso phase. To further examine the behavior in these regions, we conducted SHG measurements. In the absence of an electric field, no SHG signal was detected, as expected. Surprisingly, however, a SHG signal emerges on applying an electric field even in the Iso phase, as shown in Fig. 4. These data were taken in a slow cooling process from 174 °C (Iso) to 130 °C (Col$_r$). The SHG signal started to emerge at 171 °C and gradually increased in the Iso phase with decreasing temperature. We confirmed that the transition to Col$_h$ occurred at about 155 °C, where a sharp increase in SHG is seen. After the peak, the signal began to decrease in the Col$_h$ phase with decreasing temperature and disappeared
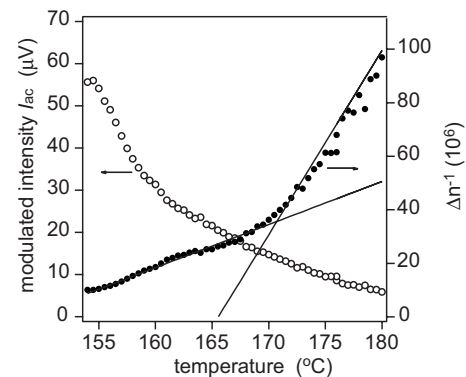

FIG. 3. Modulated signal intensity I_{ac} (open circles) and the inverse of the induced birefringence Δn^{-1} (closed circles) determined from Eqs. (1)–(3) as a function of temperature. Solid curves are the best fits to these results.

TABLE I. Collected values of Kerr constants B and temperature differences $\Delta T = T_{\text{I-LC}} - T_C^*$.

Material	B (10^{-12} m/V^2)	ΔT
EBAB [2]	175	3.0
5CB[a] [5]	127	1.3
E7 (BDH Chemicals) [10]	123	1.2
MBAB [2]	115	6.6
PCH-5 [7]	97.4	1.2
MBBA [2]	−9.5	0.6
EBBA [8]	−1.66	0.5
Polymer-stabilized blue phase [15]	1500–2000	2.2
Urea derivative	1.546×10^{-2}	9.5

[a]He-Cd laser (441.6 nm) instead of He-Ne laser (632.8 nm) for electro-optic measurement.

in the Col$_r$ phase. It is important to note that the temperature of the onset of SHG (171 °C) coincides with the inflection point in the temperature dependence of Δn^{-1}. These experimental observations strongly suggest two mechanisms of cluster formation in the Iso phase, which will be discussed in the following.

To discuss what is happening in the Iso phase, let us summarize the experimental facts so far observed in the lower-temperature region of the Iso region: (1) a switching current is observed on applying an electric field [16]; (2) a similar dielectric response to that in the Col$_h$ phase is observed at least just above $T_{\text{I-Ch}}$ [17]; (3) electric-field-induced SHG and Kerr effect are observed in the Iso phase. Based on these facts, we can conclude that *polar clusters* are easily formed on applying an electric field. According to the SHG dynamics experiments, polar switching is accomplished within 1 ms [17]. This fact means that the polarization, whose projection to the field direction is the same as the field direction, is first induced within columns (clusters) without changing the column direction, and reorientation of the polar clusters immediately follows. After randomization of the cluster orientation at zero field, the same polarization induction and reorientation occur in the opposite direction on applying the opposite field. Since both positive and negative fields induce the same Δn, the electro-optic response occurs at the double frequency $2f$. This is the pretransitional behavior to the polar columnar phase under an electric field.

In the higher-temperature Iso region (>171 °C), we can speculate that two species respond to the applied field: (1) simple individual polar molecules and (2) nonpolar assemblies. For the first case, we can expect a small Kerr constant obtained in the present experiment as in nitrobenzene mol-
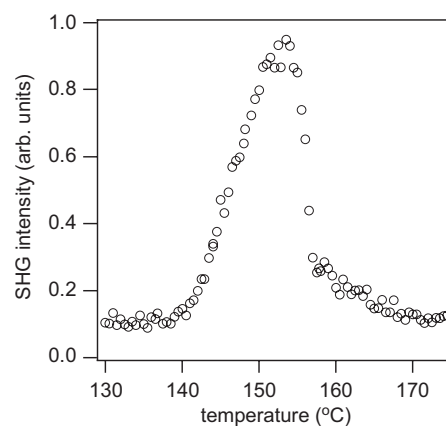

FIG. 4. SHG signal intensity as a function of temperature under the application of a triangular wave field of 6 V/μm.

ecules. However, such a large temperature dependence of Δn^{-1} is hard to explain, if individual molecules reorient due to the field application. For the second case, we can suspect the formation of a nematiclike domain with the coherent length ζ. The large temperature dependence can be explained by the temperature dependence of ζ. In other words, different types of clusters from those in the lower-temperature Iso region are formed. Polar order is not induced in the clusters judging from the lack of SHG activity, so that the Kerr response must be of dielectric origin, as usually observed in nematogens. The system proceeds toward the virtual phase with decreasing temperature but eventually changes to the other pretransitional state with polar order. We cannot draw conclusions about the virtual phase because of the lack of experimental results. However, the polarization must be canceled in this state. Because of the high temperature, the compound is not stable enough for us to pursue other experiments; it is easily degraded.

In conclusion, we have demonstrated the electro-optic Kerr effect in a liquid crystalline urea derivative in the Iso phase. The Kerr constant is much smaller than that of nematogens. The temperature dependence of the induced Δn obeys Landau–de Gennes theory, but two temperature regions were identified in the Iso phase; polar order is easily induced in the lower Iso region, and nonpolar order in the higher Iso region. Possible pretransitional model structures were discussed.

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