Anomalous Photoinduced Current Transients in Nematic Liquid Crystals

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Anomalous photoinduced current transients in the nematic phase are experimentally observed by illuminating a liquid-crystal sample with a xenon-flash-lamp pulse while applying a dc voltage. The response time is fast, of the order of a microsecond, and is independent of the magnitude of the applied voltage. The peak current is independent of the wavelength of the light and displays a critical response near the nematic-isotropic phase-transition temperature. Pyroelectricity in nematic liquid crystals is proposed as the physical origin of the phenomenon.

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The mechanism of electric conduction in nematic liquid crystals plays an important role in such photoinduced effects as the appearance of an electromotive force due to illumination with visible light[1] and of transient photocurrents caused by pulsed laser excitation.[2] These mechanisms are not well understood. However, it has been pointed out[1,2] that the molecular ordering in the cell, especially in the vicinity of the substrate surface, is closely related to the photoinduced effects. In this Letter, the transient behavior of an anomalous photoinduced current in nematic liquid crystals is described. To the best of our knowledge this type of anomalous current has not been previously reported.

The nematic liquid-crystal material was introduced between two pieces of glass with transparent In_2O_3 electrodes on their surfaces. Substrates without and with a polyimide thin layer (100-nm thickness) for homogeneous alignment of nematic molecules were used. The area of these cells was typically 2 cm^2. The thickness of the cell was 6.8 μm. Provisions were made for maintaining the cell at a constant temperature. The sample was illuminated by a depolarized xenon-flash-lamp pulse (energy 15 $\mu J/cm^2$, duration 10 μsec) perpendicular to the glass surface. The energy of light was monitored by use of an optometer (United Detector Technology Model 40X). Interference filters (λ_{max}=400, 500, 600, 700, 800, 900 nm) were used for the measurements of the spectral sensitivity. The flash lamp was situated in an electronically isolated box. Transient currents were observed through a series load resistor (1 kΩ) by means of a digital storage oscilloscope (Iwatsu DS-6612). A constant negative dc voltage was applied to the cell. The materials which we have investigated include 4-cyano-4′-5-alkyl-biphenyls (5CB; BDH Chemical Ltd., K15) having a positive dielectric anisotropy $\Delta\epsilon$=10, and a mixture of nematic azoxy compounds and a biphenyl ester (Merck Ltd., 997DSM Licristal) having $\Delta\epsilon = -0.6$.

The measurements were repeatedly carried out for three different samples prepared under the same conditions. A typical photoinduced current transient at an applied voltage of −30 V and at a constant temperature of 30 °C in 5CB is shown in Fig. 1. For these conditions, the dark current is −0.5 $\mu A/cm^2$, fairly small relative to the photoinduced current. If the voltage is reversed, the transient current also reverses. Illumination from the direction of the negative and positive electrodes yields the same results. The initial-peak current which is shown in the inset of Fig. 1 is an anomalous current in the direction opposite to the applied voltage in the nematic range. This was the main subject of our investigation. This singular current transient has not been previously reported to the best of our knowledge. The

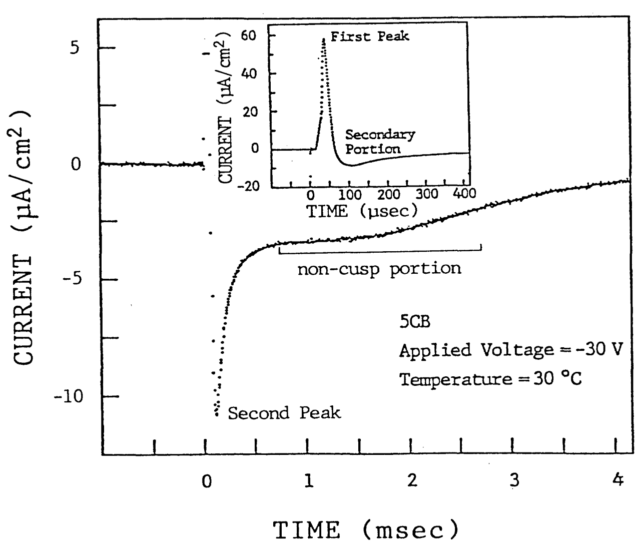

FIG. 1. Typical current transient, with inset showing the first peak. The time behavior of the current is shown for an applied voltage of −30 V at a constant temperature of 30 °C in 5CB.

secondary portion represents a current in the same direction as the applied voltage. This current is believed to be due to the generation (second peak) and transport (noncusp portion) of photoinduced carriers. However, we have not identified the origin of the charge carriers as either electrons or ions in our present experiments. Similar current transients are also observed for cells containing blocking layers for charge injection from the electrodes.

The time occurrence of the first peak is independent of the reciprocal of the applied voltage in a range of 5–30 V and yields a constant time lag of 5 μsec from the occurrence of the light pulse peak. A similar plot of the noncusp portion yields a nearly straight line and the extrapolated line does not pass through the origin. Plots of the magnitude of the first-peak (shown in Fig. 2) and second-peak current as a function of the applied voltages typically yield the same relation of $I \propto V^n$, where the exponent n is about 2.0 for lower applied voltages and approaches 1.0 at higher voltages. The noncusp current is not due to the space-charge–limited current because of the experimental results described above and the noncusp shape. Although this subject is beyond the scope of this Letter, one possible interpretation of our results is based on the variation of the carrier mobility with the molecular orientation.[3] Molecular ordering affects the distance between hopping sites in the conduction of the charge carriers and/or the traveling of the impurity carrier ions in the bulk. In addition to these results, the magnitudes of both the first and second current peaks increase linearly with the intensity of illuminated light and saturate at higher intensity. Figure 3 shows the spectral sensitivity of the first- and second-peak currents normalized to the intensity spectrum of the flash lamp and the transmittance of each interference filter. The range of the wavelength of the light is 350–900 nm and is restricted by the spectrum of the xenon lamp. These plots show a noticeable difference in the origin of the first- and second-peak currents in our experiment. The first-peak current is almost independent of the wavelength in the range of our measurements. The spectrum of the second-peak current, however, varies quite strongly, corresponding approximately to the absorption spectrum of 5CB which is also shown in Fig. 3. A plot of the second-peak current versus the reciprocal of the temperature yields a straight line over the range of the nematic and isotropic phases. From these results, we estimated the activation energy to be 0.14 eV. On the other hand, the first-peak current displays a critical behavior in the vicinity of the nematic-isotropic phase transition temperature, T_c, and disappears abruptly above T_c as shown in Fig. 4. The second-peak current, which is not shown in Fig. 4, does not display this remarkable change and is small in comparison to the first-peak current.

What is the origin of the anomalous photoinduced current? Although the experiments described above do not yield definite conclusions, one possible interpretation for the anomalous photoinduced current is the pyroelectric effect. Because the anomalous current is opposite to the dark current, it is conceivable that an internal electric field is generated by the pyroelectric effect in 5CB. The critical behavior (shown in Fig. 4) in the vicinity of T_c corresponds to that of the specific heat associated

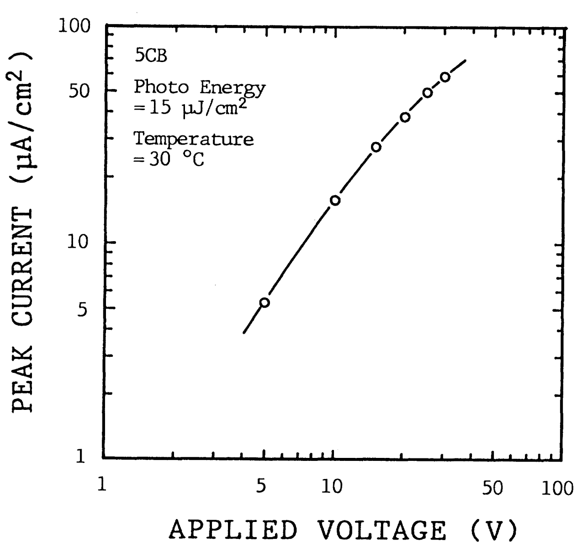

FIG. 2. Magnitude of the first-peak current as a function of the applied voltage at a constant temperature of 30 °C in 5CB.

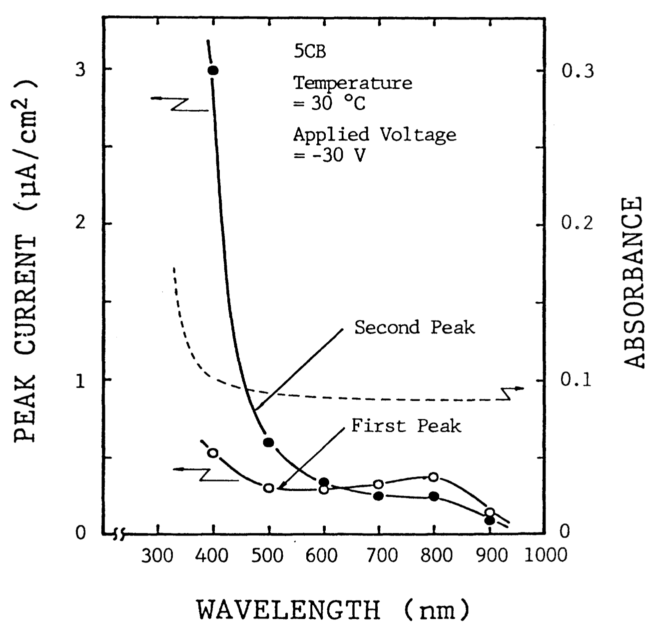

FIG. 3. Spectral sensitivity of the first- and second-peak currents at an applied voltage of −30 V and a constant temperature of 30 °C in 5CB. Dashed line shows the spectral absorbance of 5CB.

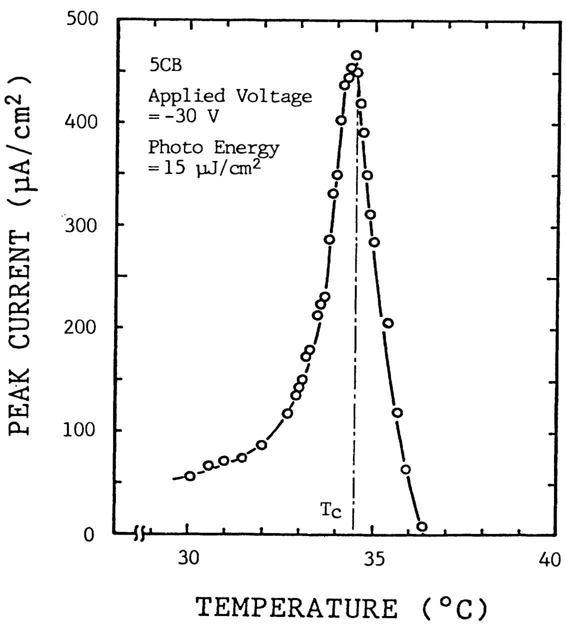

FIG. 4. Behavior of the first peak in the vicinity of the nematic-isotropic phase transition temperature T_c.

with an orientation order parameter.[4] The generation of the internal electric field based on this mechanism ends in a short time because of the small thermal diffusivity.[5] The transient nature of the behavior also received support from the interpretation that pyroelectric charges are instantaneously screened out by impurity conduction since 5CB is usually not a very good insulator. We must make special mention that the pyroelectric effect would originate in the vicinity of the substrate surface. In these regions there would occur dipole-dipole association[6] and/or selective adsorption of nematic molecules on the substrate. The characteristic of positive dielectric anisotropy of 5CB does not dominate the physical origin of the anomalous current, but yields the direction of the anomalous current and the director in the bulk. This interpretation is also supported by experimental results for the 997DSM substance with $\Delta\epsilon < 0$. In this case, the anomalous current appears in the same direction as that of the applied voltage, although electrohydrodynamic instabilities (dynamic scattering mode) are observed. However, it is not clear now why the direction of the anomalous current relative to the applied voltage changes with the sign of the dielectric anisotropy. It is not necessary for the origin of the anomalous current to consider the transport mechanism of photogenerated carriers in the bulk, because the time occurrence of the peak current is independent of the applied voltage. Similar anomalous currents are observed for samples containing different surfaces with and without polyimide layers. So the electrochemical effects in the vicinity of the substrate surface are not considered to be the origin. Also there is little contribution from screening effects of the dc electric field by photogenerated ions because the magnitude of the peak current is independent of the wavelength of light in the nematic range. These interpretations are supported by the experimental fact of the proportional relation between the magnitude of the peak current and the light intensity.

In summary, transient photocurrent measurements have been made on nematic liquid crystals. We observed the appearance of anomalous photoinduced current transients for the first time. Several features associated with anomalous current were observed. These phenomena will be useful for the photoelectronic-device applications of nematic liquid crystals. We propose the pyroelectric effect in nematic liquid crystals as the origin of the photoinduced anomalous current transient. We cannot interpret the physical relationship between the molecular ordering and the anomalous current at the present stage. However, it is clear that these are closely connected with each other. A theoretical treatment and further precise measurements are now in progress.

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