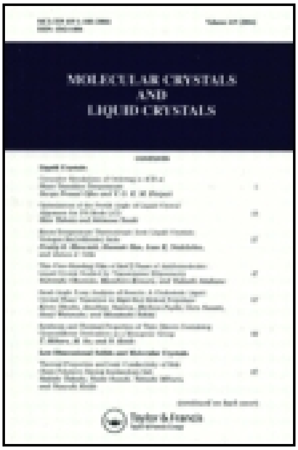

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Birefringence Induced by Ultrasonic Waves in the Isotropic Phase of PCB†

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We have studied the birefringence induced by ultrasound Δn in the isotropic phase of pentylcyanobiphenyl (PCB) as a function of temperature, frequency and acoustic intensity. We have found that Δn is proportional to the square root of the acoustic intensity P and that the ratio $\Delta n/\sqrt{P}$ decreases with increasing frequency indicating that our data are within the $\omega\tau \gtrsim 1$ regime, where τ denotes the orientational relaxation time. We have also measured in the same experiment the ultrasonic absorption coefficient α. From the comparison between the behavior of the induced birefringence and that of the ultrasonic absorption we have shown that the optical relaxation frequency (τ_{op}^{-1}) is smaller by a factor 6 to 8 than the acoustical relaxation frequency (τ_{ac}^{-1}). This result is explained by the fact that the absorption coefficient contains the contribution of all the fluctuation modes of the order parameter, while the induced birefringence is governed by the modes of longest wavelengths.

I INTRODUCTION

Some liquids, isotropic at rest, become birefringent when traversed by ultrasonic waves. This effect is dependent on the acoustic intensity and the frequency of the wave. Experimentally, the induced birefringence, Δn, is determined by measuring the angle δ by which the light polarization vector is rotated. Since Δn is dependent on the acoustic intensity P, it is in fact necessary, to obtain quantitative results, to measure δ and P simultaneously.

Although birefringence induced by ultrasound is a sensitive probe to study the dynamics of molecular orientation, the technique has not been widely used because of the experimental difficulties resulting from the low value of the induced birefringence and of the presence of parasitic effects, such as heating and streaming effects, related to the value of the acoustic intensity.[1-3]

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Recently we have made some improvements in the traditional technique which has allowed us to study the pretransitional effects which appear in *p*-azoxyanisole (PAA) near the nematic-isotropic transition temperature $T_c \simeq 135°\mathrm{C}$.[4] This study has shown that Δn is proportional to $\sqrt{P}$ as for pure liquids, and that the ratio $\Delta n/\sqrt{P}$ diverges as one approaches the transition.

We present here a study of the $\omega\tau \sim 1$ regime, which can be easily reached at ultrasonic frequencies by choosing a room-temperature liquid crystal such as pentylcyanobiphenyl (PCB).

Since our apparatus presents the advantage of simultaneously measuring the ratio $\Delta n/\sqrt{P}$ and the ultrasonic absorption α, it has been possible to compare, for identical experimental conditions, the relaxation time as measured by induced birefringence to the relaxation time as measured by ultrasonic absorption.

II EXPERIMENTAL

Experimental details of the set-up have been given in Ref. 4 so they will not be discussed further. We simply recall here the principles of the experiment.

In an experiment of birefringence induced by ultrasound the direction of propagation of the incident light is perpendicular to that of the ultrasonic wave and the light is polarized at an angle of 45° to the direction of sound propagation. In the absence of ultrasonic waves an analyzer is adjusted for a transmission null. When the medium becomes birefringent under the influence of ultrasonic waves, the light polarization vector is rotated through an angle δ and a small amount of light is transmitted through the analyzer. The change in light intensity I is detected by a photomultiplier and is recorded on an oscilloscope as a voltage. The phase angle δ is related to the change of intensity I by the formula

$$I = I_0 \sin^2 \frac{\delta}{2} \tag{1}$$

where I_0 is the intensity measured in the absence of the sound waves when the polarizer and analyzer are parallel. Therefore by measuring the ratio I/I_0 it is possible to deduce δ and thereby Δn which is related to δ by

$$\delta = \frac{2\pi l}{\lambda} \Delta n \tag{2}$$

where l is the optical path length in the medium and λ the optical wavelength in vacuo.

If the medium exhibits a sinusoidally varying birefringence, then the birefringence $\overline{\Delta n}$ found in this way is $\Delta_{\max}/\sqrt{2}$ (i.e. $\overline{\Delta n}$ is the r.m.s. value of Δn).

As mentioned above, the acoustic intensity P at the position where the birefringence is measured, must be known in an acoustically induced birefringence experiment. In our apparatus the birefringence is induced by pulse ultrasonic waves. This allowed us, not only to reduce heating and streaming effects, but also to measure the variations of the acoustic intensity P and of the ultrasonic absorption α as a function of temperature.

If Δ(dB) represents the number of decibels needed to maintain the received acoustic pulse at a fixed value when the temperature is varied from T_1 to T_2, then the relative variation of P is given by

$$P(T_2)/(P(T_1) = 10^{\Delta(\mathrm{dB})/20} \tag{3}$$

and that of α by

$$\alpha(T_2) - \alpha(T_1) = 0.115\,\frac{\Delta(\mathrm{dB})}{d} \tag{4}$$

Δ(dB) is directly read on a calibrated attenuator. d is the acoustical path length and the factor 0.115 converts α from decibels to nepers. In formula (3), it has been assumed that the induced birefringence is observed at the middle of the acoustical path.

The present study was made at frequencies of 8.2, 4.45 and 1.11 MHz. The acoustical path length d was 6.1 mm at 8.2 and 4.45 MHz, and 11.8 mm at 1.1 MHz. The length of the ultrasonic pulse was adjusted to the maximum value permitted without reflected sound, at the time of the observation was made. The ultrasonics were pulsed at a frequency of about 10 Hz. The optical path length submitted to ultrasound was 10 mm at 8.2 and 4.45 MHz, and 28 mm at 1.1 MHz. Values of the acoustic intensity on the emitting transducer were in the range of 10 mW/cm^2. The light source was a 5 mW He–Ne laser that could be attenuated using neutral density filters. The transmitted light was detected by a photodetector and recorded on a storage oscilloscope. Typical recorded traces showing the electric, acoustic and induced birefringence pulses were presented in Ref. 5. The cell was thermostated to ±0.01°C. PCB was obtained from Hoffman-La Roche and used as received. The transition temperature was $T_c \simeq 35.5$°C.

III RESULTS AND DISCUSSION

a) Behavior of the induced birefringence

With small molecules the induced birefringence Δn is due to the velocity gradient caused by the wave and varies sinusoidally.[6] Δn is related to flow birefringence and may be written as:

$$\overline{\Delta n} = \frac{\sqrt{P}}{\sqrt{\rho v^3}}\left(\frac{\delta n}{G}\right)\frac{\omega}{\sqrt{1+\omega^2\tau^2}} \tag{5}$$

where $\overline{\Delta n}$ is the r.m.s. value of Δn and $\delta n/G$ is the quantity measured in a flow birefringence experiment, v and ω are respectively the velocity and the frequency of the wave, and τ is a relaxation time.

According to the de Gennes' model[5] of the isotropic phase of liquid crystals, τ and $\delta n/G$ are proportional to $(T - T_c^*)^\gamma$. T_c^* is the virtual second order transition temperature which is less than the actual transition temperature T_c, and γ is an exponent that is unity in a mean field theory.

Therefore in the hydrodynamic regime ($\omega\tau \ll 1$)

$$\frac{\overline{\Delta n}}{\sqrt{P}}\sqrt{\rho v^3} \sim (T - T_c^*)^{-1}$$

and for $\omega\tau \gg 1$

$$\frac{\overline{\Delta n}}{\sqrt{P}}\sqrt{\rho v^3} \sim \text{constant.}$$

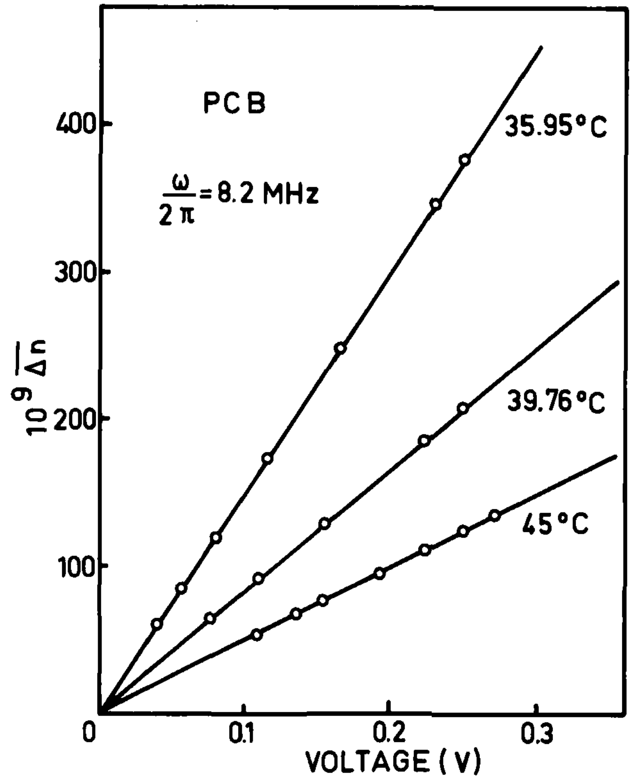

FIGURE 1 Variation of thr r.m.s. birefringence $\overline{\Delta n}$ with the voltage V at the receiving transducer. The linear variation shows that $\overline{\Delta n}$ is proportional to the square root of the acoustic intensity.

Figure 1 shows the variation of the r.m.s. birefringence $\overline{\Delta n}$ with the voltage V at the receiving transducer for various temperatures. As predicted by Eq. (5), $\overline{\Delta n}$ should be proportional to the square root of the acoustic intensity P, or to the voltage V, and the results in Figure 1 show that this is the case.

Figure 2 presents the temperature dependences of $\overline{\Delta n}$ (curve a and $\sqrt{P}$ (curve b) for one frequency ($\omega/2\pi = 8.2$ MHz). Also shown, as curve c, in Figure 2, is the temperature dependence of the ratio $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho v^3}$.[8] This ratio, which according to Eq. 5 is the relevant quantity, reveals no pretransitional increase, thus showing that the measurements near T_c are within the $\omega\tau \gg 1$ regime. The variation of this ratio, but measured at lower frequencies (4.45 and 1.1 MHz), is shown in Figure 3. One observes that this ratio increases with decreasing frequency, indicating that the system changes from the $\omega\tau \gg 1$ regime to the $\omega\tau \gtrsim 1$ regime. By fitting the data at 1.1 MHz with Eq. 5, $T_c^* \sim 35$°C and $\tau \sim 400\ 10^{-9}/\Delta T$ s are obtained. The value of τ is in satisfactory agreement with the value deduced from the optical Kerr experiments.[9]

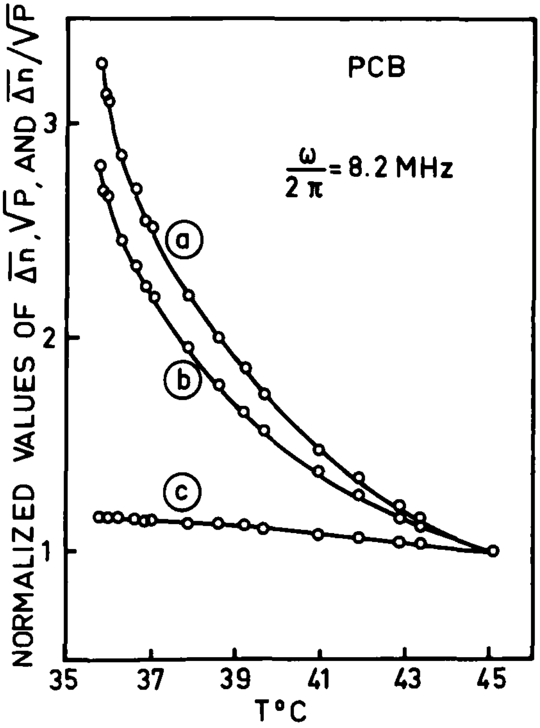

FIGURE 2 Temperature dependence of (a) the r.m.s. birefringence $\overline{\Delta n}$ (b) the square root of the acoustic intensity $\sqrt{P}$ at the middle of the acoustic path length where the induced birefringence was measured (c) the ratio $\overline{\Delta n}/\sqrt{P}$. The measurements were made for a fixed value of the acoustic receiving level as described in the text and the data have been normalized at $T = 45$°C.

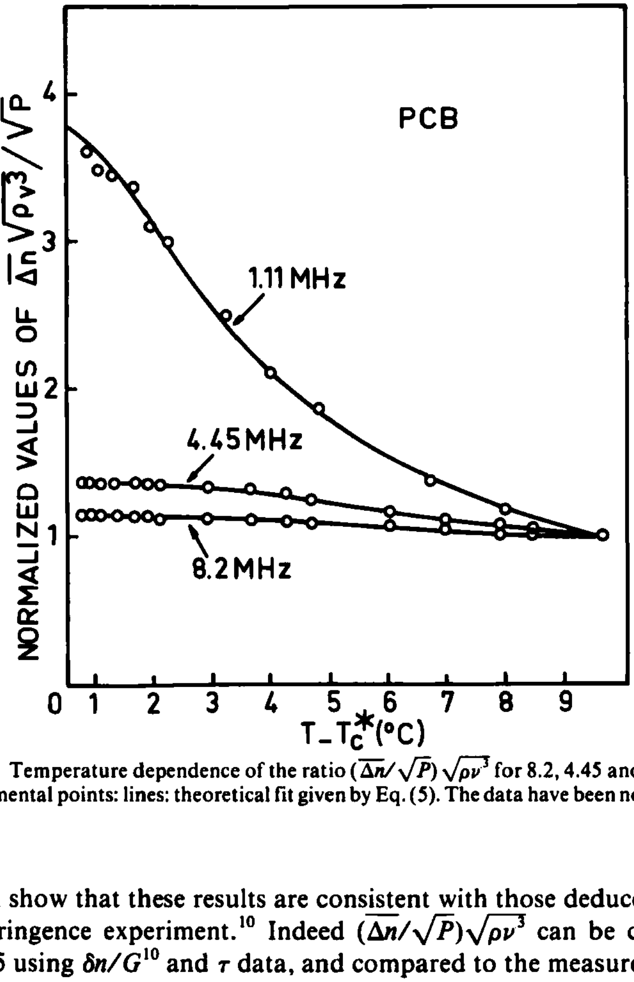

FIGURE 3 Temperature dependence of the ratio $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho\nu^3}$ for 8.2, 4.45 and 1.11 MHz. Dots: experimental points: lines: theoretical fit given by Eq. (5). The data have been normalized at $T = 45°\text{C}$.

One can show that these results are consistent with those deduced from a flow birefringence experiment.[10] Indeed $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho\nu^3}$ can be calculated from Eq. 5 using $\delta n/G$[10] and τ data, and compared to the measured values. Figure 4 shows that the agreement between calculated and measured values of $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho\nu^3}$ is good except near T_c. However, it is difficult to say if the small discrepancy which appears near T_c is due to a physical effect. Indeed this discrepancy could result from differences in the samples which came from different sources and/or from the errors made, for each experiment, in the determination of T_c^*.

Now concerning the values of the acoustic intensity P, as already mentioned in part II, only the relative variation of P as a function of temperature is known in the present experiment. Absolute values of P can be obtained by making experimental and calculated values of $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho\nu^3}$ equal at a given temperature (for example at $T - T_c^* = 10°\text{C}$ as done in Figure 4). The values of P are small (4, 8 and 45 mW/cm^2 at the emetting transducer at $T \sim T_c$ for

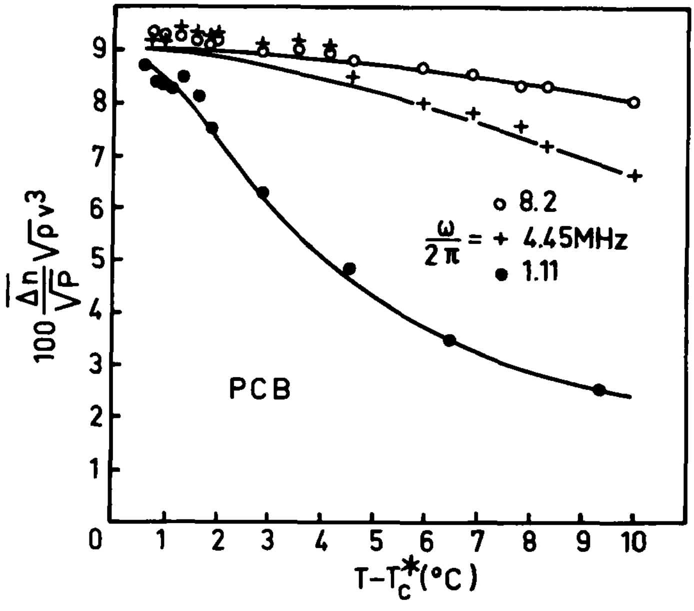

FIGURE 4 Comparison between measured values of $(\Delta n/\sqrt{P})\sqrt{\rho v^3}$ and those (the lines) deduced from Eq. 5 using $\delta n/G$, τ and v data.

1.11, 4.45, and 8.2 MHz) and consistent with the values estimated in part II of this paper.

b) Comparison between the behavior of the induced birefringence and that of the ultrasonic absorption.

In Figure 5 we present the relative variations of $(\Delta n/\sqrt{P})\sqrt{\rho v^3}$ and of α/f^2 at $f = 4.45$ MHz. It is observed that $(\Delta n/\sqrt{P})\sqrt{\rho v^3}$ stays constant, while α/f^2 increases, as the temperature decreases to T_c. This result shows that the relaxation times involved in each of these two measurements are different. This is explained by the fact that the ultrasonic absorption is due to the coupling of the wave with all the modes of the system, and is expressed in the form of integral over wavelength, whereas the induced birefringence is governed by the longest mode. It follows that the variation with the frequency of these two quantities is different. The expression of the induced birefringence is given by Eq. 5, and that of the ultrasonic absorption by:[11,12]

$$\alpha/f^2 = B(T - T_c^*)^{-3/2}F(\omega^*) \qquad (6)$$

where B is a weakly temperature dependent coefficient and $F(\omega^*)$ the function which provides the frequency-dependence of α/f^2.[13]

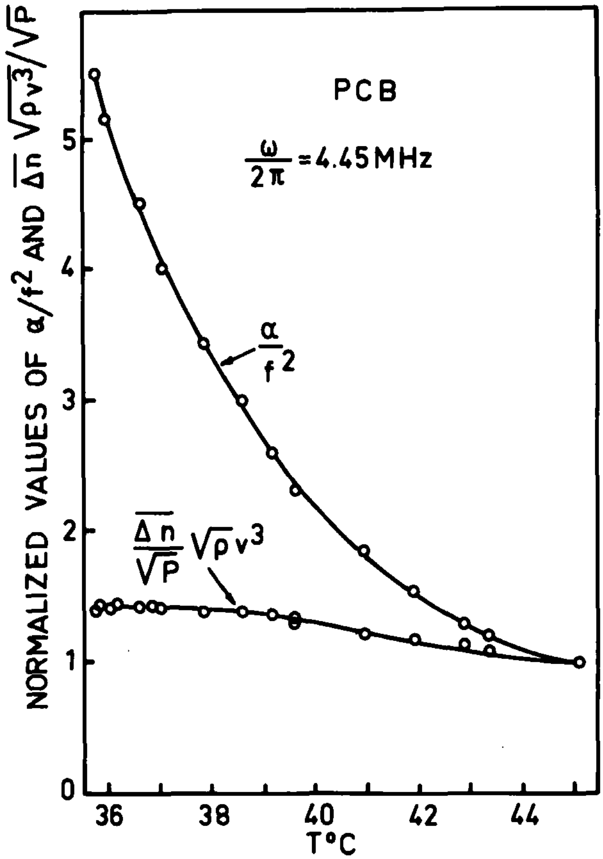

FIGURE 5 Relative behavior of $(\overline{\Delta n}/\sqrt{P})\sqrt{\rho v^3}$ and α/f^2 as a function of temperature for 4.45 MHz. The data show that the acoustical relaxation frequency is higher than the optical one.

$F(\omega^*)$ is written as

$$F(\omega^*) = \omega^{*-2}\left[|1 + (1 + \omega^{*-2})^{1/2}|^{1/2} - 2^{1/2}\right]$$

where ω^* is a reduced frequency equal to ω/ω_0, ω_0 being the characteristic frequency of the longest mode.

By analyzing our birefringence and absorption data at 1 MHz using Eqs. (5) and (6) we find that there is a factor of 6 to 8 between the ultrasonic relaxation time and the optical relaxation time.

In conclusion, this study has shown two different aspects of the coupling between the molecules and the ultrasonic wave. The first concerns the fluctuations in molecular orientation, which are coupled to fluctuating acoustic modes, and the second involves the orientational ordering which is effected by the mechanical interaction of the wave with the molecules. We have only determined the root mean square value of Δn. Maximum information could be obtained by measuring the phase lag between the induced birefringence and the wave at the acoustic frequency. This would allow a direct measurement of the relaxation time τ_{op}. This experiment is currently under way.

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