

LASER INDUCED PHOTOACOUSTIC TECHNIQUE FOR THE DETECTION OF PHASE TRANSITIONS IN LIQUID CRYSTALS

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In this paper we report the use of a laser induced photoacoustic technique for the detection of multiple phase transitions in heptyl-oxy-cyanobiphenyl (7OCB) and octyl-oxy-cyanobiphenyl (8OCB) liquid crystals. The observed photoacoustic signal amplitude profile carries clear signatures of two first order transitions in 7OCB and two first order and a second order transitions in 8OCB. Analysis of the experimental data using Rosencwaig–Gersho theory shows that the sudden decrease in the photoacoustic (PA) signal amplitude during phase transitions is due to a sharp increase in the heat capacity of the samples near the transition temperatures.

Keywords: Photoacoustic technique; Heptyl-oxy-cyanobiphenyl; Rosencwaig–Gersho; Nematic transition

INTRODUCTION

Variation of thermal, optical and other physical parameters during phase transitions in liquid crystals has been a subject of extensive theoretical and experimental studies. In many of the earlier reported investigations a drastic change in these parameters has been noticed near the transition

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temperatures [1–5]. The phases well above and below the phase transformation are stable enough in the thermodynamic sense, but near to the phase transitions there exists some pre-transitional anomalies. Among the various phases exhibited by the liquid crystals, smecticA to nematic transition is one of the most widely studied one [6–8]. This is because the above transition may be second order or first order depending on the molecular packing and intermolecular interactions. A variety of characterization techniques such as X-ray scattering, NMR, calorimetry and optical methods are commonly used for detecting the phase transitions in liquid crystals [4,6–10]. Recently, Rajasree *et al.* have studied the phase transitions in certain liquid crystals using a laser beam deflection technique based on single beam mirage effect [11].

In the last two decades photoacoustic (PA) technique has been employed fairly extensively for studying the thermal and optical properties of materials [12,13]. The PA effect is the generation of acoustic signal when a sample placed in an airtight cavity is irradiated with intensity modulated optical radiation. In the gas–microphone configuration, the nonradiative de-excitation subsequent to the periodic absorption of light by the sample generates thermal waves within the sample, which diffuse into the coupling gas (usually air) causing a periodic pressure variation inside the sample compartment. A suitably placed sensitive microphone can be used to detect this periodic pressure variation. Since the PA signal is highly sensitive to thermal parameters of the sample, the most important of which are the thermal conductivity and heat capacity, many people have used this method to detect phase transitions in solids and to some extent in liquid crystals [14–16]. The PA technique is fully non-contact and non-destructive in nature and the experimental set up is very simple. Though the PA technique is essentially a photo-induced calorimetric method, it is free from many of the limitations of other optical and calorimetric methods since only the light absorbed by the sample contributes to the PA signal. Also, the use of modulated light beam together with a lock-in detection makes this technique highly sensitive with a very high signal to noise ratio. Fortuitously the PA method is applicable to both transparent and opaque samples. The advantage of PA technique over calorimetric methods is that it can be used for the simultaneous measurement of static and dynamic thermal parameters such as heat capacity, thermal conductivity, thermal diffusivity, etc. provided, the excitation wavelength should be selected in such a way that the material under investigation should be optically opaque

at this wavelength [17]. Moreover, the ac calorimetric method is highly time consuming and the experimental set up is more intricate in comparison with the PA technique. Also, since the major part of the PA signal is contributed by the light absorbed within the first thermal diffusion length of the sample, by changing the modulation frequency of the laser beam from a few Hz to few thousand Hz, one can easily vary the thermal diffusion length in the sample over a considerable range [18]. This can be made use in probing surface as well as bulk effects in liquid crystals.

In the present paper, we describe the use of PA technique for the detection of phase transitions in heptyl-oxy-cyanobiphenyl (7OCB) and octyl-oxy-cyanobiphenyl (8OCB) liquid crystals. The novelty of the present method is that the liquid crystal sample themselves do not absorb the pump beam. Consequently, optical absorption at this wavelength is achieved by mixing the sample with a trace amount of an organic dye, which absorbs the pump beam. Using Rosencwaig-Gersho (R-G) theory for photoacoustic effect, we have made a simple qualitative analysis of the heat capacity anomaly near the transition region [18]. A comparison of the present data with that available in the literature has also been made and the various aspects of the PA signal behaviour are discussed.

EXPERIMENTAL

For the present investigation we have made use of a resonant photoacoustic cell with microphone detector. The cell is made of stainless steel and it has the provision to vary the temperature of the sample in the range of 77–450 K. The microphone with flat frequency response is kept at room temperature in a separate cavity and is acoustically coupled to the sample compartment by means of a thin walled stainless steel tube of inner diameter 1 mm. The light source used is an Argon ion laser (Liconix 5000 series) operating at 488 nm with a Gaussian profile. The laser beam at a power level of 20 mW is intensity modulated at a frequency of 344 Hz using an electromechanical chopper (Ithaco HMS 230). The sample is illuminated at its front surface and the PA signal is detected using an electret microphone. A single-phase analogue lock-in-amplifier (Stanford SR 510) is used to record the PA signal amplitude variation during the temperature scanning. The block diagram of the experimental set up is shown in Fig. 1. A temperature controller is used to vary the temperature of

the cell at the rate of $0.3^{\circ}\text{C}/\text{min}$, a nominal heating rate for PA measurements. During such a slow heating rate the leak in the microphone is sufficient to equalise the pressure inside the cell with the outside pressure. Also, the laser beam with a diameter of 1.2 mm is defocused so as to illuminate the entire surface of the sample (20 mm^2). This is done to reduce the local heating effect at the illuminating site and to ensure that the signal is contributed by the whole sample. The experimental set up is initially standardized using carbon black as the sample.

The liquid crystals 7OCB and 8OCB are obtained from Merck UK and are used without further purification. The samples are white powder in the crystalline state while in the smecticA and nematic phases they are white viscous fluids and finally in the isotropic phases they appear like an ordinary, colourless liquid. Similar to many other liquid crystals, 7OCB and 8OCB do not absorb optical radiation in the visible region. Hence, in order to generate PA signal, the liquid crystal samples are mixed with a trace amount (0.5% weight) of an organic dye, eosin, which has very good absorption at the excitation wavelength (488 nm). Good thermal and photo stability of eosin is taken into account while selecting it as the colouring substance. The liquid crystal confined in a small volume of the PA cell has a thickness of about 1.3 mm. The PA signal amplitude is recorded during heating of the sample starting from the crystalline phase. Great care is taken in the choice of the laser beam intensity as well as the heating rate to make sure that the PA signal profile is not affected by too high a laser intensity or by a high heating rate. This is because at elevated heating rates, sufficient

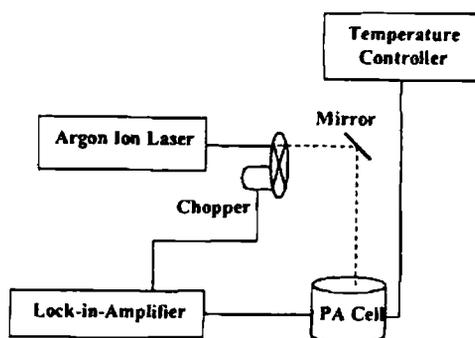


FIGURE 1 Schematic diagram of the experimental set up.

time will not be obtained to equalize the pressure inside the PA cell with that outside the cell, which will result in a continuously rising background PA signal since the signal amplitude is directly proportional to the pressure inside the cavity. This is observed when carbon black film is used as reference sample. Also, when unexpanded laser beam at very high intensities is used, a slight distortion in the PA signal profile is noticed. This could be due to the localised heating of the sample.

RESULTS AND DISCUSSION

The liquid crystals 7OCB and 8OCB belong to the alkoxy-cyanobiphenyl family and are well known for their high chemical stability. The normalized PA signal amplitude variation during the heating of the liquid crystal 8OCB starting from the crystalline phase is shown in Fig. 2. From this plot it can be seen that there is a remarkable variation in the PA signal amplitude at three distinctly different temperatures. This anomalous behaviour of the PA signal is obviously due to the sudden changes in the thermal parameters like heat capacity, thermal conductivity etc of the sample under investigation. Such changes occur normally during the transition from one phase to another phase of the material. In the case of 8OCB, three minima are observed in PA signal profile and are located at 53.7, 67.3 and 80.2°C. These values are in good agreement with the earlier reported phase

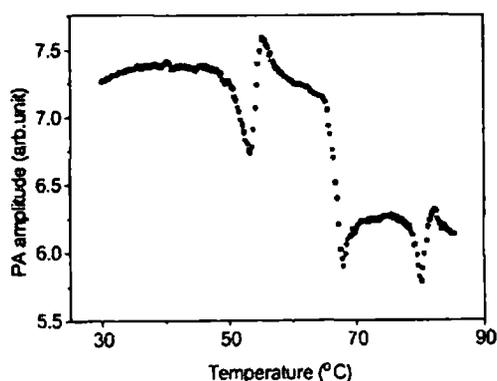


FIGURE 2 PA signal amplitude vs. temperature plot, starting from the crystalline phase of the liquid crystal 8OCB.

transition temperatures 54, 67.2 and 80.2°C of this particular liquid crystal [6–8,11,19,20]. These transition temperatures are assigned to crystalline to smecticA, smecticA to nematic and nematic to isotropic transitions, respectively. It is worthwhile to note here that in Fig. 2, the crystalline to smecticA and nematic to isotropic transitions are clearly marked by a dip in the PA signal profile followed by a small peak structure. This shape of the PA signal amplitude is consistent with the theoretical model developed by Korpiun *et al.* for the PA response during a first order phase transition [21]. On the other hand, during the smecticA to nematic transition, the dip in PA signal profile has smaller depth compared to the other two transitions. Also in this case, the PA signal profile does not carry any peak structure in the vicinity of transition temperature. Furthermore, in the case of smecticA to nematic transition, the sudden change in PA signal amplitude is restricted to a relatively small temperature range while for the other two transitions the change in the signal amplitude is visible over a much larger temperature range. These facts attribute a different nature for the smecticA to nematic transition in 8OCB, which is reported to be essentially a second order transition, whereas the other two transitions are clearly a first order one [6,20,22].

Similar results are obtained in the case of 7OCB also. The normalized PA signal variation with temperature for 7OCB is shown in Fig. 3. In this case, only two transitions are observed and the corresponding transition temperatures are 54.7 and 73.2°C. These values are also in good agreement

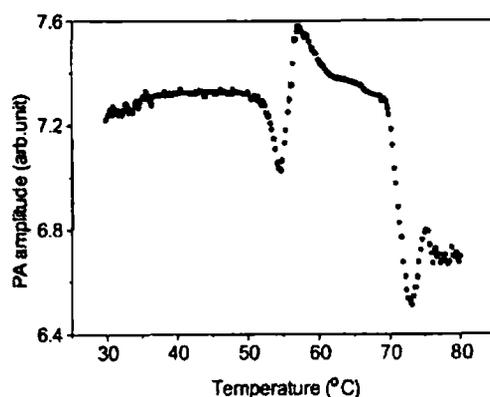


FIGURE 3 PA signal amplitude vs. temperature plot, starting from the crystalline phase of the liquid crystal 7OCB.

with the earlier reported values 55 and 73.5°C of the crystalline to nematic and nematic to isotropic liquid transitions, respectively,† [11,23]. Both the transitions are first order in nature and in this case also a large change in the PA signal amplitude similar to that during first order transitions in 8OCB is visible. In the case of both the liquid crystals, no major change in the transition temperatures is observed in comparison with the earlier reported values. This clearly indicates that the transition temperatures of 7OCB and 8OCB remain almost unaffected by the addition of a small amount of an organic dye.

As mentioned earlier, the liquid crystals taken in the PA cell have a thickness of about 1.3 mm and are optically transparent at 488 nm. Also, the addition of a very small quantity of dye to the sample causes only a slight colouring of the material. Under these conditions and at a chopping frequency of 344 Hz, it is quite reasonable to assume that the sample under investigation is optically thin and thermally thick. In such a situation, the expression given by R-G theory for the periodic pressure variation inside the cavity reduces to a simple form,

$$Q \cong \frac{-i\gamma P_0 I_0 \beta \mu_s^2}{4\sqrt{2} T_0 l_g a_g k_s} \quad (1)$$

where γ is the ratio of heat capacities, P_0 and T_0 are the pressure and temperature inside the cavity, I_0 is the incident light intensity, l_g is the length of the gas column, β and μ_s are the optical absorption coefficient and thermal diffusion length, respectively, of the sample, k_s is the thermal conductivity of the sample and $a_g = 1/\mu_g$, the thermal diffusion coefficient of the gas inside the cavity. In this case, only the light absorbed within the first thermal diffusion length contributes to the signal, in spite of the fact that light is being absorbed throughout the length of the sample. Then the PA signal amplitude is given by

$$Q = K \left(\frac{\mu_g}{T_0} \right) \left(\frac{\mu_s^2}{k_s} \right) \quad (2)$$

where, the proportionality constant K includes all the constant terms. For air, (μ_g/T_0) is a slowly varying function of temperature, which can be evaluated from the thermal parameters of air. The term (μ_s^2/k_s) is equal to

Merck Liquid Crystals Data Sheet (Merck UK).

$(2/\omega\rho_s C_s)$ where ω is the chopping frequency, ρ_s and C_s are the density and heat capacity of the sample. Hence the PA signal amplitude will vary with the temperature as C_s^{-1} .

Hence, the quantity $[(1/\text{PA amplitude}) \times (\mu_g/T_0)]$ will be proportional to the specific heat capacity of the sample. Figure 4 shows the profile of this quantity for 7OCB and 8OCB which is derived from the PA signal amplitude and by using Eq. (2). It is clear from this plot that heat capacities (in arbitrary units) of both the liquid crystals exhibit a sharp peak structure within the transition region. From this figure, it can also be seen that change in heat capacity is occurring in a narrow temperature range during a second order smecticA to nematic transition while in the case of other first order transitions, heat capacity changes occur in a much broader temperature range. Also, the intensity of the peak in the heat capacity profile during smecticA to nematic transition of 8OCB is much less than that during nematic to isotropic transition. This observation is in good agreement with the earlier high-resolution ac calorimetric measurement on 8OCB by Garland *et al.* [6].

CONCLUSIONS

First order as well as second order phase transitions in two alkoxy-cyanobiphenyl liquid crystals, 7OCB and 8OCB, are studied using a laser

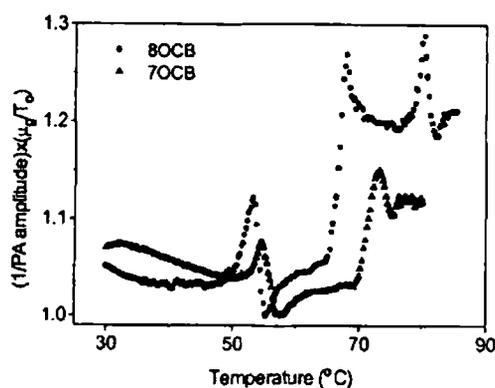


FIGURE 4 $(1/\text{PA signal}) \times (\mu_g/T_0)$ vs. temperature plot of 8OCB and 7OCB.

induced photoacoustic technique. The observed phase transition temperatures are found to be in good agreement with the earlier reported values. Also, we have noticed that the addition of a very small quantity of organic dye to the liquid crystals as a colouring substance has not affected the transition temperatures in any significant manner. Furthermore, we have observed a slight change in the PA signal profile during a second order transition in comparison with the first order transitions. The sudden decrease in signal amplitude during phase transitions is mainly due to the sharp increase in the heat capacity of the liquid crystals near the transition temperatures. Our investigations show that the PA technique is a powerful analytical tool for the study of variations in thermal parameters associated with phase transitions in liquid crystals.

Acknowledgements

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