

Photoacoustic evaluation of the thermal effusivity in the isotropic phase of certain comb-shaped polymers

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Abstract

The thermal effusivity values in the isotropic phase of certain comb-shaped polymers have been evaluated for the first time using an open photoacoustic cell configuration. The compounds investigated have siloxane and acrylate backbone and they carry mesogenic groups in their side chain. The results indicate that the polymer chain length as well as the side chain length have pronounced influence on the thermal effusivity values in liquid crystalline polymers.

1. Introduction

The synthesis of polymer systems which successfully combine the unique properties of low molecular weight liquid crystals (LC) and high molecular weight polymers with their ability to form films, fibers, coatings etc offers great promise in the field of data storage and display technology. Comb-shaped polymers carrying mesogenic groups in their side chain are a class of materials that combine the properties of polymers with those of liquid crystals [1–6]. The phase transitions between the crystalline, smectic, nematic and isotropic phases in liquid crystalline polymers (LCPs) are similar to those occurring in low molecular weight LCs. In side chain LCPs the liquid crystal moieties are attached to the polymer backbone through a flexible spacer, which enable them to move freely and therefore behave like a classical low molecular weight LC in their optical, electrical and magnetic characteristics. The structure and length of the spacer as well as the structure of the mesogen and the type of backbone have a pronounced effect on the type of phase transition and the transition temperatures in these materials. The structural and physicochemical properties of comb-shaped polymers in dilute solutions, gels and in the solid phase have been extensively studied in the past decades [5].

One of the most recent and important applications of LCPs is in the field of optical data storage. The thermo-optic recording is achieved by incorporating a dye into the LCP, which on irradiation with laser beam absorbs the light energy and re-radiates it as heat. Consequently the LCP is locally heated into the isotropic phase and a change in the optical density takes place on

cooling [7]. Usually very thin films (5–10 μm) are required for the optical data storage. The speed at which the laser treated area cools back into the glassy or liquid crystalline phase is determined by a parameter called the thermal effusivity of the thin film. This quantity measures essentially the thermal impedance of the sample, which in other words, is the sample's ability to exchange heat with the environment [8]. The thermal effusivity, defined by the expression $e_s = (k\rho C)^{1/2}$, is an abstract thermal quantity with dimensions $\text{W s}^{1/2} \text{cm}^{-2} \text{K}^{-1}$, where k is the thermal conductivity, ρ is the density and C is the heat capacity at constant pressure. e_s is a relevant thermophysical parameter for surface heating or cooling processes as well as in quenching processes.

In recent years, the photoacoustic (PA) technique has been proven to be an innovative, reliable and convenient method for the thermal characterization of liquid crystals [9–13]. The PA effect basically relies on the absorption of modulated light by the sample and the subsequent liberation of thermal energy via nonradiative relaxation with consequent generation of acoustic signals. The exclusive dependence of the PA signal on the thermal as well as optical properties of the sample makes it a very promising tool for thermal characterization of liquid crystals. Even though the PA technique has been used for the study of a variety of liquid crystals, this method has not yet been employed in the characterization of liquid crystalline polymers.

In this paper, we report the thermal effusivity values measured in the isotropic phase of certain side chain LCPs using an open photoacoustic cell configuration. The materials investigated are poly(4-hexamethylenoxy-4'-3-methyl butyloxy carbonyl-benzyl benzoate) siloxane, poly(methyl siloxy, 4-cyano-4'-tetramethylenoxy-biphenyl-siloxane) and Poly (4-cyano-4'-propyloxy-biphenyl) acrylate. The trade names provided to these LCPs by the manufacturer are LCP1, LCP93 and LCP95, respectively and for the sake of convenience we will use these names in the rest of the text [14]. The chemical structure of these materials is shown in figure 1. LCP1 and LCP95 are homopolymers whereas LCP93 is a copolymer. LCP93 carries two different side chain groups of which only one is mesogenic. Since the first two LCPs are made of flexible polysiloxane backbone, the glass transition temperatures of these materials are very low, -10.9 and -9.3 $^{\circ}\text{C}$ respectively. But a stiffer polyacrylate backbone of LCP95 results in a very high glass transition temperature (49.5 $^{\circ}\text{C}$) in this material. The smecticC to isotropic transition temperature of LCP1 is 70.7 $^{\circ}\text{C}$ and smecticA to isotropic transition temperatures of LCP93 and LCP95 are 76.0 and 85.4 $^{\circ}\text{C}$ respectively [14]. LCP1 and LCP93 are white viscous materials at room temperature, which become fluid on heating to the isotropic phase. LCP95 is a white powder at room temperature, which on melting becomes fairly viscous liquid in the isotropic phase.

2. Theory

The cross-sectional view of the open photoacoustic cell (OPC) is shown in figure 2. In a typical OPC the microphone compartment will be closed with the sample and its outer surface will be illuminated with a modulated optical radiation. To find the pressure fluctuation in the front air chamber of the OPC, we use the theoretical model proposed by Rosencwaig and Gersho [15]. According to this model, the periodic pressure fluctuation associated with the photoacoustic effect resulting from the light absorption is mainly due to the heat flow from the sample to the photoacoustic chamber. Assuming that the coupling fluid (usually air) in the photoacoustic chamber responds adiabatically, the pressure fluctuation in the OPC configuration is given by

$$\delta P = \frac{\gamma P_0}{T_0} \bar{\theta} \quad (1)$$

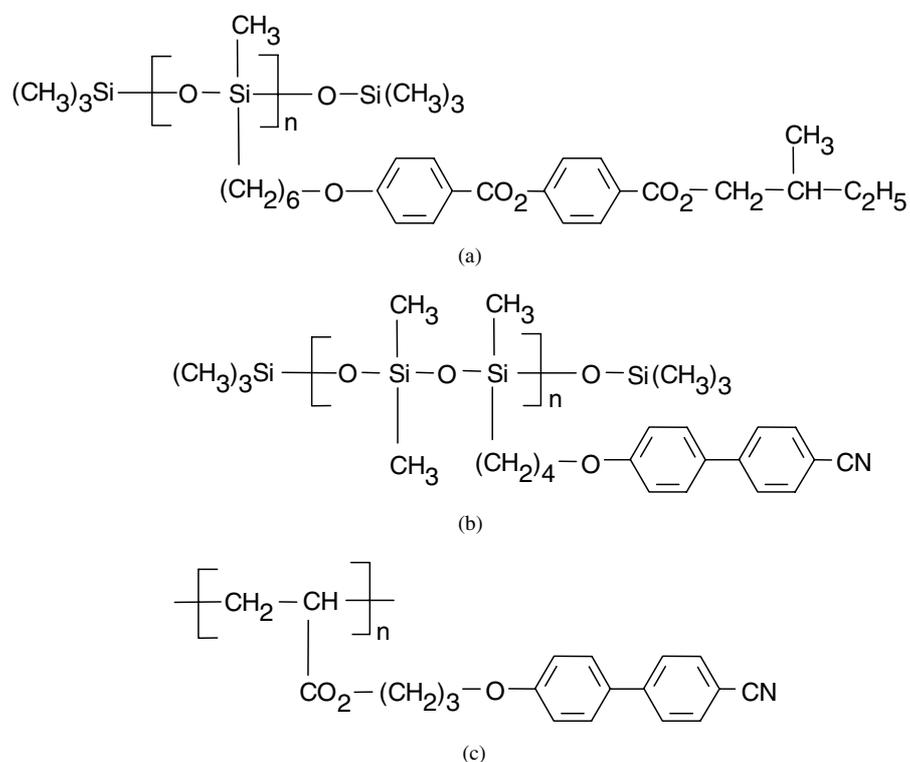


Figure 1. Structure of the liquid crystalline polymers. (a) LCP1, (b) LCP93 and (c) LCP95.

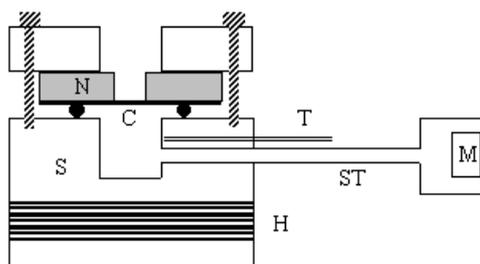


Figure 2. Cross-sectional view of the open photoacoustic cell. N is the nylon ring, C the copper foil, T the thermocouple, S the stainless steel body, H the heater coil, ST the stainless steel tube and M the microphone.

where P_0 and T_0 are the ambient pressure and temperature, γ is the ratio of heat capacities and $\bar{\theta}$ is the spatially averaged temperature fluctuation of the air in the PA chamber. This temperature fluctuation can be obtained by solving the thermal diffusion equation for the sample–air chamber system [15, 16].

Consider an OPC geometry as shown in figure 3. When the OPC is closed with a composite sample consisting of a thermally thin absorbing layer and a non-absorbing liquid, and when it is irradiated with a modulated optical radiation, the periodic heat is generated at the interface of the two layers. In the present case we used a copper foil as the absorbing layer and the modulated light after passing through the transparent liquid is allowed to fall on it. The heat

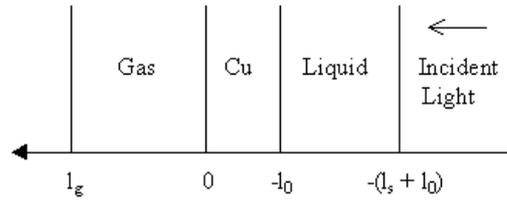


Figure 3. Schematic diagram of open photoacoustic cell geometry.

generated at $x = -l_0$ will diffuse through the thermally thin copper foil and the PA signal δP_1 produced in the chamber will depend on the thermal properties of the liquid as given by

$$\delta P_1 = \frac{\gamma P_0 \beta I_1 \alpha_g^{1/2} \alpha_s^{1/2}}{2\pi T_0 l_g k_s f} e^{j(\omega t - \pi/2)} \quad (2)$$

where I_1 is the incident light intensity on the Cu foil, β is the absorption coefficient of copper, α_g and α_s are the thermal diffusivities of air and the transparent liquid, l_g is the length of the gas column in the PA chamber and k_s is the thermal conductivity of the transparent liquid. From the above expression it can be seen that the PA signal varies as f^{-1} and is proportional to the ratio $(\sqrt{\alpha_s}/k_s) = e_s^{-1}$, the inverse of the thermal effusivity of the liquid sample.

In contrast, when there is no liquid layer in contact with the copper foil, it can be shown that the pressure fluctuation δP_2 inside the chamber is given by

$$\delta P_2 = \frac{\gamma P_0 \beta I_2 \alpha_g^{1/2} \alpha_0}{2\pi^{3/2} T_0 l_g l_0 k_0 f^{3/2}} e^{j(\omega t - 3\pi/4)}. \quad (3)$$

Thus the signal amplitude varies as $f^{-3/2}$ and is proportional to (α_0/k_0) , where α_0 and k_0 are the thermal diffusivity and thermal conductivity, respectively, of the copper foil. In the above expression, I_2 is the incident light intensity on the copper foil and l_0 is the thickness of the copper foil. It follows from expressions (2) and (3) that by measuring the PA signals from the empty sample holder and that from the liquid sample-filled sample holder as a function of the modulation frequency, one can measure the thermal effusivity of the transparent liquid.

3. Experiment

The experimental set-up used for the measurement of the thermal effusivity consists of an argon ion laser (Liconix 5000) operating at 488 nm and an open photoacoustic cell (OPC). The major difference of our multipurpose OPC from the conventional OPC is that the latter is usually a minimum volume cell with the microphone kept very close to the sample. However, in our case, since the liquid crystals have to be heated, we kept the microphone chamber away from the sample chamber and both of them were acoustically coupled through a thin-walled stainless steel tube of inner diameter 1 mm. A cross-sectional view of the OPC is shown in figure 2. The cell has an acoustic resonance peaked at 450 Hz. The sample chamber was heated using a heater coil wound over the chamber and the sample temperature was controlled to a stability of $\pm 0.13^\circ\text{C}$ using a chromel–alumel thermocouple connected to a temperature controller. The liquid crystal sample holder used for the present investigation is made of a nylon ring of thickness 3 mm and inner diameter 7 mm, the bottom of which is closed by a 60 μm copper foil. The liquid crystal is placed inside the ring and the entire sample holder is placed on the top of the air chamber. Owing to the comparatively large volume of the cell, we

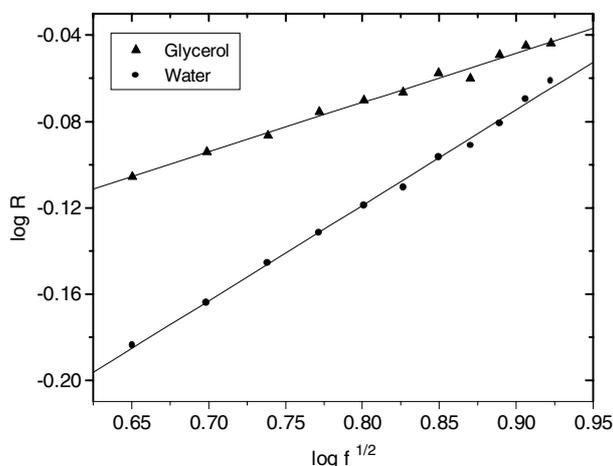


Figure 4. Logarithmic plot connecting the square root of frequency f and the amplitude ratio R for water and glycerol with the reference sample (Cu foil).

have used a laser power of 200 mW to ensure a high signal-to-noise ratio. The photoacoustic signal detected using an electret microphone (Knowles BT 1834) was processed using a lock-in amplifier (Stanford Research Systems SR 510). The signal amplitude was recorded as a function of modulation frequency of the laser beam for both the empty sample holder and for the sample holder filled with the liquid crystals.

4. Results and discussion

Initially, the experimental set-up was calibrated using water and glycerol, the thermal properties of which are well established. The PA signals produced by the empty sample holder and that obtained after filling it with transparent liquids were measured as a function of the modulation frequency. Figure 4 shows the $\log f^{1/2}$ versus $\log R$ plot, where f is the chopping frequency and R is the ratio of the PA signal produced with liquid sample in the sample holder to that of an empty one. From a straight line fit to the ratio of the two signal amplitudes, the thermal effusivities were calculated using the expressions (2) and (3). The observed values of thermal effusivities of water and glycerol at 27 °C are $0.1545 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$ and $0.0933 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$ respectively. These values are in agreement with the literature values $0.1588 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$ and $0.0935 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$, respectively, for water and glycerol [17]. A slight deviation in the observed value of thermal effusivity of water may be due to the evaporation of water during the course of the experiment. For the above calculation, we have used $l_0 = 60 \text{ }\mu\text{m}$, $\rho_0 = 8.96 \text{ g cm}^{-3}$ and $C_0 = 0.385 \text{ J g}^{-1} \text{ K}^{-1}$ as the thickness, density and the heat capacity, respectively, of the copper foil [17].

The liquid crystal polymers LCP1, LCP93 and LCP95 were obtained from Merck Inc. UK and were used without further purification. Even though all these compounds are optically non-absorbers in the visible region, the highly viscous nature of the material in the isotropic phase reduces the optical transmission at 488 nm by a substantial amount. The percentage transmittance of LCP1, LCP93 and LCP95 at 90 °C were measured as 70%, 77% and 54% respectively. Figure 5 shows the $\log f^{1/2}$ versus $\log R$ plots of the liquid crystal polymers LCP1, LCP93 and LCP95. From a straight line fit to the experimental data the thermal effusivities were evaluated using the expressions (2) and (3). The thermal effusivities were calculated

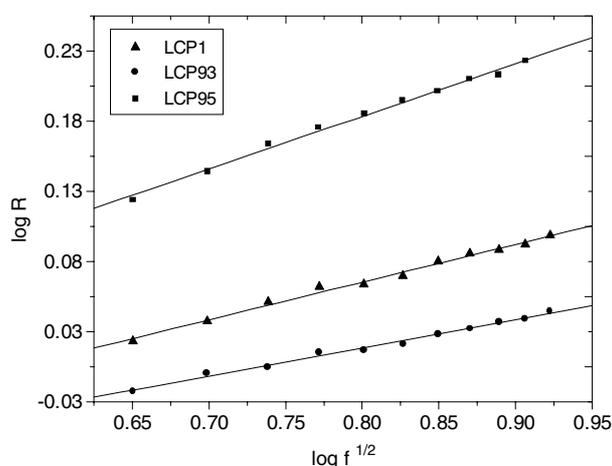


Figure 5. Logarithmic plot connecting the square root of frequency f and the amplitude ratio R for LCP1, LCP93 and LCP95 with the reference sample (Cu foil).

Table 1. The thermal effusivity of liquid crystalline polymers in the isotropic phase.

| Liquid crystal polymer | Thermal effusivity in $\text{W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$ |
|------------------------|--|
| LCP1 | 0.0741 |
| LCP93 | 0.0728 |
| LCP95 | 0.0687 |

from the y-intercept of the straight line. The estimated values of thermal effusivities at 90°C are summarized in table 1.

From the measured values of thermal effusivities, it can be seen that the thermal effusivity of LCP95 is much less than that of LCP1 and LCP93. The chain length of LCP1 is approximately 35 units while those of LCP93 and LCP95 are approximately 20 units and 12.5 units [14]. Hence, our observations confirm that an increase in chain length could result in an increased value of thermal effusivity. A reasonable argument for this observation is that the intramolecular thermal effusivity (contributed by the intramolecular thermal conductivity) is much greater than the intermolecular thermal effusivity (contributed by the intermolecular thermal conductivity) [18]. Even though the effective length of the main chain in LCP93 is slightly greater than that of LCP1, the latter possesses a slightly increased thermal effusivity over the former. This suggests that not only the main chain but the side chains also have some influence in the thermal effusivity value, as the side chain including the spacer of LCP1 is much longer than that of LCP93. Also the substantial decrease in the thermal effusivity value of LCP95 may be due to the decreased chain length of this compound. But the fact that this compound is made of a different polymer backbone should also be taken into account while comparing with LCP1 and LCP93. Hence, the generalization of the properties of comb-shaped LC polymers is rather difficult because the features of the structure of these materials together with the mutual effect of the individual structural elements of the macromolecules significantly complicates the identification of common properties in their physicochemical behaviour.

The present method is very simple, accurate and less time consuming for the thermal characterization of liquid crystals. A combination of the present method with the earlier

reported photoacoustic configurations can be used for the complete thermal characterization of liquid crystals and non-absorbing liquids.

Acknowledgments

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