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# A study on the thermal properties of cinnamoyl chalcones

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## Abstract

Three cinnamoyl chalcones and two difurans are synthezised and their thermal diffusivities at room temperature are measured using photoacoustic (PA) technique. Thermal diffusivity is found to vary with the number of methoxy groups conjugated.

*Keywords:* Chalcone; Difuran; Thermal diffusivity; Methoxy group; Photoacoustics

## 1. Introduction

Chalcones (1,3-diphenyl-2-propen-1-ones) are biogenetic precursors [1] of flavonoids in higher plants and they display a wide variety of pharmacological effects, including cytotoxity towards cancer cell lines, antitumor, antimitotic, antimutagenic, and antitumor-promoting activities; antibacterial, antiviral, anti-inflammatory, antiulcerative and hepatoprotective activities. Chemically they consist of two aromatic rings with an unsaturated chain.

Various chalcone derivatives are notable materials for their second harmonic generation (SHG). Ravindrachary et al. [2] have synthesised a novel non-linear optical material 1-(4-methylphenyl)-3-(4-*N*,*N* dimethyl amino phenyl)-2-propen-1-one. This chalcone derivative has second harmonic generation efficiency of 0.8 times that of urea. Absence of absorption in the visible region and absorption in the UV region with a wide band gap of 2.4 eV in this single crystal extends its use in the non-linear optics application.

Wu et al. [3] have reported that 2-methoxy-3-methyl-4,6-dihydroxy-5-(3′-hydroxy) cinnamoylbenzaldehyde possesses potent anti-HIV activity and C-2 methoxy group in the chaclone skeletone may be critical for anti-HIV activity. Rao et al. [4] have sythesised ten structurally related 2′-oxygenated chalcone derivatives (2POCDs), bearing either hydroxy and/or methoxy substituents on the A and B rings to generate novel anticancer structure and they have noticed that the methoxy group at the carbon-2 atom greatly enhanced the ability of chalcone to inhibit cell growth.

Prior to the formulation of any drug into a dosage form it is of vital importance to ensure the physical stability of the drug and its compatibility with potential excipients. Changes of phase and degradation are accompanied by heat flow or a change in heat capacity. Therefore, thermal analysis plays a major part in the development of new drugs, formulations, and drug delivery systems [5]. Moreover, knowledge of thermal properties is essential in the efficient and economical design of all processing operations involving heat transfer.

Thermal diffusivity is an important heat transport property of material. Hence, we have determined the thermophysical parameter thermal diffusivity for three cinnamoyl chalcones and two difurans (Table 1) using photoacoustic (PA) technique. These difurans are found to be antifeedants.

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Table 1
IUPAC names of the chalcones studied

| Sample | IUPAC name | Molecular formula |
|---|---|---|
| $S_1$ | 2′,4′-Dihydroxy-5′-(4-methoxy) cinnamoyl-4-methoxychalcone | $C_{26}H_{22}O_6$ |
| $S_2$ | 2′,4′-Dihydroxy-5′-(4-methyl) cinnamoyl-4-methylchalcone | $C_{26}H_{22}O_4$ |
| $S_3$ | 2′,4′-Dihydroxy-5′-(3,4-dimethoxy) cimmamoyl-3,4-dimethoxychalcone | $C_{28}H_{26}O_8$ |
| $DS_1$ | 2,6-Diacetlyl-3,5-bis(4′-methylstyryl) benzo [1,2-b;5,4-b′]difuran | $C_{32}H_{26}O_4$ |
| $DS_2$ | 2,6-Diacetyl-3,5-bis(3′,4′-dimethoxystyryl) benzo [1,2-b;5,4-b′]difuran | $C_{34}H_{30}O_8$ |

## 2. Synthesis of cinnamoyl chalcones

The chalcones $S_1$, $S_2$, $S_3$ have the common basic skeletal structure but with different side chain (with different $R_1$ and $R_2$). The structure is shown in Fig. 1. For $S_1$, $R_1$ is H and $R_2$ is $OCH_3$ and for $S_2$, $R_1$ is H and $R_2$ is $CH_3$ and for $S_3$, $R_1$ and $R_2$ are $OCH_3$.

In general, chalcone is prepared using the Claisen–Schimdt condensation of acetophenone with appropriate aromatic aldehyde in alkaline condition. Diacetyl resorcinol and aromatic aldehyde are used here in the preparation of chalcones $S_1$, $S_2$ and $S_3$. A mixture of 4,6-diacetyl resorcinol (1.94 g, 0.01 mol) and appropriate aromatic aldehyde (0.02 mol) in ethanol and 60% aqueous potassium hydroxide were kept at room temperature for 24 h. The reaction mixture was then treated with 1:1 hydrochloric acid (HCl) to get these three dichalcones. They were characterized by comparison with authentic sample (2′,4′-dihydroxy-5′-(2-methoxy) cinnamoyl-2-methoxychalcone) [6]. The infrared spectrum of chalcone $S_1$ taken using Perkin-Elmer 577 Grating Infrared Spectrophotometer revealed peaks at 1630, 1250, 795 and 985 $cm^{-1}$ which is characteristic of C=O, C–O, tetra substituted benzene and para substituted benzene functional groups, respectively. This spectrum is characteristic of chalcones.

## 3. Synthesis of difuran

The other chalcone compounds $DS_1$ and $DS_2$ have the common basic skeletal structure with different side chain (with different $R_1$ and $R_2$). The structure is shown in Fig. 2. For $DS_1$, $R_1$ is H and $R_2$ is $CH_3$ and for $DS_2$, $R_1$ and $R_2$ are $OCH_3$.

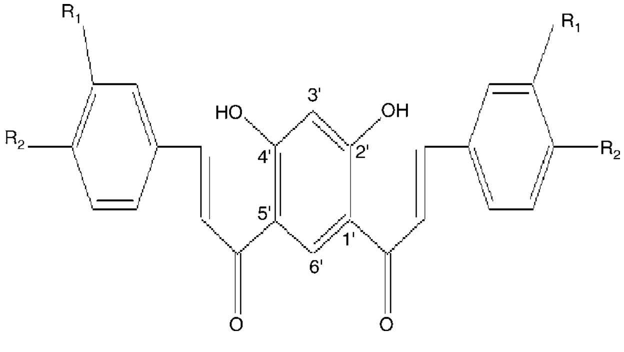

Fig. 1. Molecular structure of cinnamoyl chalcones.

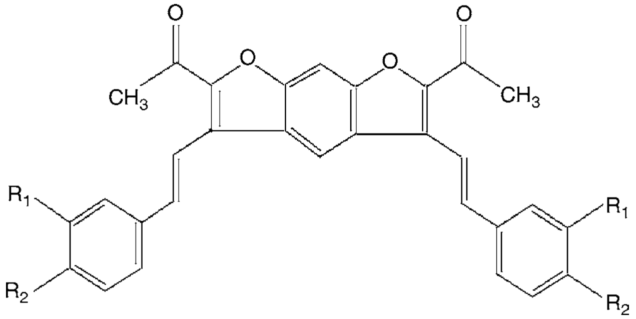

Fig. 2. Molecular structure of difurans.

To prepare these difurans, to a stirred solution of dichalcone ($S_2$ or $S_3$ (0.01 mol)) in benzene (60 ml) and 20% aqueous $K_2CO_3$ (60 ml), 125 mg of tetrabutyl ammonium hydrogen sulphate ($TBAHSO_4$), a phase transfer catalyst in benzene (10 ml) was added and vaporized for 20 min. To this emulsion, chloroacetone (0.02 mol) in benzene (30 ml) was added and vapourised over a period of 30 min. The mixture was stirred for 6 h at room temperature. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was then removed under diminished pressure and the residue was dried and crystallized from appropriate solvent to yield $DS_1$ and $DS_2$, respectively. The detailed characterisation for these chalcones is already given [7].

## 4. Photoacoustics

Photoacoustic technique is a simple and reliable non-destructive technique for the characterization of thermal, optical and structural properties of material. This technique has attracted considerable attention because of the ease with which optical spectra of substance normally difficult to examine by conventional spectroscopic method can be obtained. Photoacoustic spectroscopy is different from conventional techniques chiefly in that sample under analysis is examined not through the subsequent detection of photons but rather through a direct measure of the energy absorbed by the sample as a result of its interaction with a photon beam.

When a modulated light is absorbed by the sample located in a sealed cell (PA cell), the non-radiative de-excitation process of the absorbed light generates modulated transfer of heat to the surface of the sample. This modulated thermal gradient produces pressure waves in the gas inside the cell and the microphone coupled to the cell can detect such oscillations

[8]. The resulting PA signal depends not only on the amount of heat generated in the sample but also on how the heat diffuses through the sample. The quantity, which measures the rate of diffusion in a material, is the thermal diffusivity $\alpha$, which is defined as

$$\alpha = \frac{k}{\rho c}\,(\mathrm{m^2\,s^{-1}})$$

where $k$ is the thermal conductivity; $\rho$, the density; and $c$ is the heat capacity.

## 5. Experimental set-up

The present photoacoustic spectrometer consists of 450 W Xenon lamp (Jobin Yvon), an electromechanical chopper (Model number PAR 650), a lock in amplifier (Model Perkin Elmer 7225 DSP) and the PA cell made of stainless steel. The Xenon spectrum exhibits a charateristic peak around 467 nm. The experimental set-up is shown in Fig. 3. Chalcone is obtained in powder form after synthesis. Sample for photoacoustic measurement is prepared by packing 4 mg of chalcone powder inside a transparent plastic cover of dimension 5 mm × 4 mm. This is done because only solid sample can be placed in the present PA cell used. Plastic cover is used just to hold the sample. Pelletizing the powder can also be done for PA measurements, but the connectivity of the particles depends on the amount of pressure applied to pelletize the sample. So, uniqueness in results may not be expected. Hence, sample prepared in the above described manner is placed inside the PA cell. The experimental precaution when carrying PA measurement is necessary and it is dicussed in [9]. White light from the xenon lamp is chopped by an electromechanical chopper and the chopped beam falls on the sample inside the cell. The diameter of the light spot incident over the sample is around 0.3 cm. Light is absorbed on the surface of the sample. The photoacoustic signal generated is detected by the microphone in the PA cell. The microphone is placed behind the sample, so that only transmitted waves are detected. This is then fed to a lock-in amplifier where the readings are recorded.

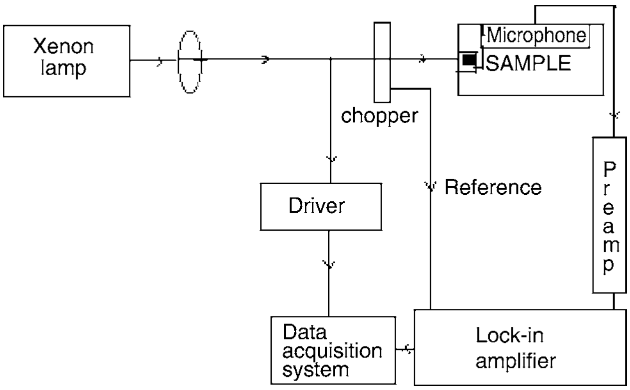

Fig. 3. Photoacoustic spectrometer.

## 6. Thermal diffusivity

Thermal diffusivity is the rate of periodic heating or transient heat propagation through a medium. To determine the thermal diffusivity of chalcones, photoacoustic signal is recorded as a function of chopping frequency. The chopping frequency is varied between 10 and 90 Hz as only for low chopping frequencies the thermal penetration into the sample will be up to the thermal diffusion length which is a unique parameter for any material. The information on thermal diffusion length ($\mu$) is necessary because the thickness of the sample ($l$) to be used is determined from this for thermally thin samples i.e. when $l < \mu$, this is thermally thin, otherwise (if $l > \mu$) it is thermally thick. As long as the samples are thermally thin, the analysis of PA depth profile is simpler. The variation of the amplitude (in μV) and the phase of the photoacoustic signal are measured as a function of modulation frequency for the different chalcones synthesized. Typical graphs for just one sample ($S_1$) are shown in Figs. 4 and 5. It is conventional to draw graph connecting PA amplitude (normalised) with chopping frequency. Normalisation is needed as the source of light will have its own spectral response. For this, generally before taking the actual measurements with the sample, carbon black will be used as the sample and the response with xenon lamp is observed. With this response normalization is done. The figures given in this paper are for normalised amplitude.

Thermal diffusivity is then calculated from the characteristic frequency of the sample (the characteristic frequency is defined as the frequency at which the sample goes from thermally thick region to thermally thin region where the slope changes and where $1/f$ variation is observed in the graph). If $f_c$ is the characteristic frequency then the thermal diffusivity [10] can be calculated from,

$$\alpha = f_c l^2\,(\mathrm{m^2\,s^{-1}})$$

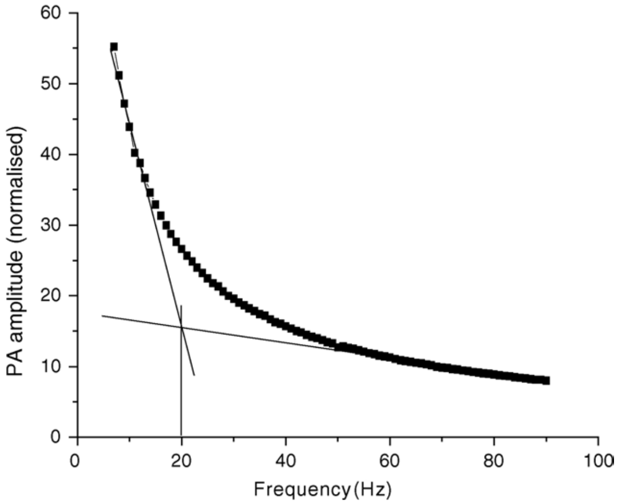

Fig. 4. Photoacoustic amplitude vs. chopping frequency $S_1$ (2′,4′-dihydroxy-5′-(4-methoxy) cinnamoyl-4-methoxychalcone).

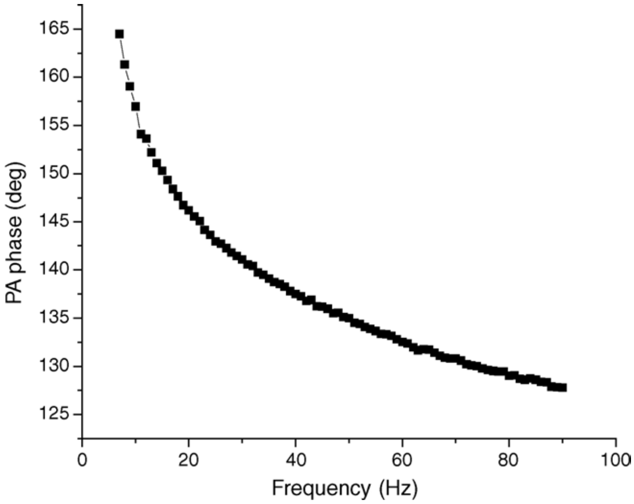

Fig. 5. Photoacoustic phase vs. chopping frequency $S_1$ (2′,4′-dihydroxy-5′-(4-methoxy) cinnamoyl-4-methoxychalcone).

where $l$ is the thickness of the sample. This equation is valid only for thermally thin sample. Thickness of the sample is measured using a high-resolution microscope and the error estimated in the thickness measurement is around 1%. So, now the thermal diffusivity of the sample along with plastic cover is measured.

## 7. Two-layer model

Schematic representation of the sample along with plastic cover is shown in Fig. 6. $l$ is the total thickness of the sample and plastic cover. $l_1$ is the thickness of sample alone and $l_2$ ($2a$) is the thickness of plastic cover alone. Since the thermal properties of chalcones alone are important, this is deduced by deconvoluting the effective value (of chalcone powder and the plastic cover) by following the two-layer model. For a two-layer system consisting of material 1 of thickness $l_1$ and material 2 of thickness $l_2$ both having the same cross section, $\alpha$ the thermal diffusivity is calculated from [11]

$$\frac{l}{\sqrt{\alpha}} = \frac{l_1}{\sqrt{\alpha_1}} + \frac{l_2}{\sqrt{\alpha_2}}$$

$l = l_1 + l_2$ denotes the total thickness of the two layers. Thermal diffusivity thus calculated from the above analysis is given in Table 2 along with other literature values. The total error in estimated thermal diffusivities is around 5%. Then from the thermal diffusivity, thermal diffusion length ($\mu$) is calculated from the formula

$$\mu = \left(\frac{2\alpha}{\omega}\right)^{1/2} \text{(m)}$$

where $\omega$ is the chopping frequency. Here, thermal diffusion length is determined for all samples at their characteristic frequency.

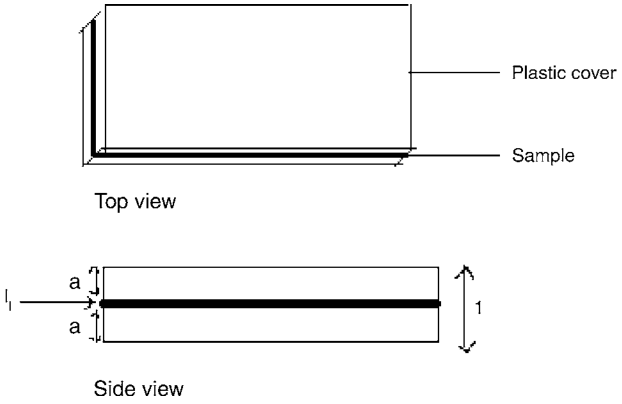

Fig. 6. Schematic representation of sample used for PA measurement.

Table 2
Thermal diffusivity of organic compounds reported in the literature

| Number | Compound | Thermal diffusivity ($\times 10^{-6}$ m$^2$ s$^{-1}$) | Reference |
|---|---|---|---|
| 1 | Benzophenone | 0.18 | [15] |
| 2 | Amylopectin | 0.13 | [14] |
| 3 | Amylose | 0.15 | |
| 4 | Amylose and amylopectin mixture | 0.14 | |
| 5 | Starch | 0.20 | |

## 8. Density measurement

Floatation method (called ‘sink’ or ‘swim’ method) is adopted to measure the density of the organic compounds and the measured values are given in Table 3. Xylene and carbon tetrachloride solutions were used in this method. Ten millilitre of these two solutions are taken in a container and mixed. Then the sample (with the cover) is put in this solution. If the sample is floating on the surface of the liquid, xylene is added or if it floats at the bottom of the liquid container, then $CCl_4$ is added. When the density of the sample equals the density of the solution then the sample will partly sink and partly float i.e. the sample will float in the middle of the solution. This is repeated for the plastic cover separately; then the density of the sample (chalcone) is found out.

Table 3
Density and thermal diffusivity of chalcones

| Sample | Density (kg m$^{-3}$) | $f_c$ (Hz) | Thermal diffusivity ($\times 10^{-6}$ m$^2$ s$^{-1}$) | Thermal diffusion length ($\times 10^{-6}$ m) |
|---|---|---|---|---|
| $S_1$ | 1007.6 | 20 | 0.24 | 0.62 |
| $S_2$ | 1144 | 24.47 | 0.26 | 0.58 |
| $S_3$ | 1117.69 | 21.11 | 0.37 | 0.71 |
| $DS_1$ | 1368.04 | 25.26 | 0.33 | 0.68 |
| $DS_2$ | 1133 | 26.66 | 0.81 | 0.98 |

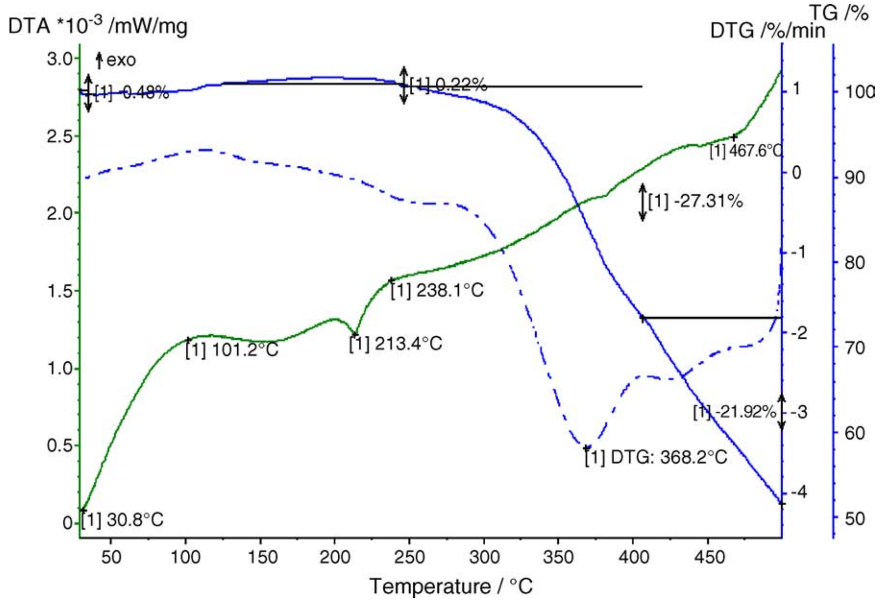

Fig. 7. DTA/TG curve for $S_2$ (2′,4′-dihydroxy-5′-(4-methoxy) cinnamoyl-4-methyl chalcone).

## 9. TG/DTA

TG/DTA measurements are made for these chalcones from ambient to 500 °C using the instrument STA 409C NETZCH-Geratebau GmbH thermal analyzer with alumina as the reference material as any phase transition in organic material can be seen in this range. A typical data on a particular chalcone $S_2$ is given in Fig. 7. The melting point is around 368.2 °C. Interesting phases are also observed. For example, at about 213.4 °C there should be a phase change, which should be probed in depth.

The melting of $S_1$ and $S_3$ are in the range of $S_2$. This is expected, as positional changes in the chalcones will not affect very much the bulk properties like melting point. But it is quite possible to affect the microscopic physical properties and so only the measurements of thermal diffusivity on these are considered in this work.

## 10. Results and discussion

The present investigation on five of the chalcone derivatives by photoacoustics shows a systematic trend for thermal diffusivity and this variation seems to be characteristic of the molecular structure.

$S_1$ has two methoxy groups and two hydrogen atoms whereas $S_3$ has four methoxy groups and so there is a considerable change in the molecular structure. Now the thermal diffusivity of $S_3$ is at least one and a half times the value of $S_1$. So the increase in thermal diffusivity by one and a half times is essentially due to the methoxy groups added which are properly conjugated.

Now when we compare $S_1$ and $S_2$ (or $S_2$ and $S_3$), $S_2$ has no methoxy groups ($CH_3O$) even though two methyl ($CH_3$) groups are there. When there is no oxygen present in the $S_2$, charge compensation is required for the stability compared to $S_1$ or $S_3$. When this methyl group is assumed as a substitutional defect in $S_3$ which is essentially $S_2$ replacing the methoxy group, then there will be more collisions between the host atoms and the defect atoms during the heat diffusion and so the mean free path will get reduced. This is the reason for the reduction in the thermal diffusivity in $S_2$ ($0.26 \times 10^{-6}\,m^2\,s^{-1}$) compared to $S_3$ ($0.37 \times 10^{-6}\,m^2\,s^{-1}$).

The above results clearly indicate that the thermal diffusion in these cinnamoyl chalcone derivatives are mostly governed by methoxy groups.

This is further supported by the PA measurements on difuran derivatives. For example, $DS_2$ has four methoxy groups conjugated where the thermal diffusivity is $0.81 \times 10^{-6}\,m^2\,s^{-1}$ whereas in $DS_1$ only methyl groups are present and so the thermal diffusivity is $0.33 \times 10^{-6}\,m^2\,s^{-1}$, nearly two and a half times smaller. Such a drastic reduction compared to chalcone derivatives is due to the molecular structure i.e. different molecular structures will have different thermal diffusivities. This property has already been tested for other materials like membranes and polymers.

George [12] has determined the thermal diffusivity of two liquid crystalline polymers (LCP1 and LCP93) using open cell photoacoustic technique. Both the two side-chain liquid crystalline polymers are made of flexible polysiloxane backbone but LCP1 is a homopolymer whereas LCP93 is copolymer which carries two different side-chain groups, of which only one is mesogenic. The difference in the estimated thermal diffusivity values (LCP1, $-7.93 \times 10^{-6}\,m^2\,s^{-1}$; LCP93, $5.26 \times 10^{-6}\,m^2\,s^{-1}$) of the two samples is characterised by their molecular structure. The total length of the two samples are almost the same but the length of the side chain of LCP1 is much greater than that of LCP93 and both the compounds are in two different smectic phases which may influence the thermal diffusivity values of these hybrids.

Barbu et al. [13] have determined the thermal diffusivity for symmetric (S) and asymmetric types (AS) of brominated polyphenylene oxide membrane (PPOBr) with Br atom in different position lateral catena (C) or aromatic ring (R) using photoacoustic technique. They have observed that for asymmetric ones, thermal diffusivity is higher when bromine atom is placed in lateral catena than in aromatic ring and hence they have concluded that thermal diffusivity is dependent on polymer structure.

It is to be noted that no reports on thermal properties for these cinnamoyl chalcones and difurans are available in literature and since this being the first report we have compared our results with other organic compounds, as for the order of the thermal diffusivity is considered.

TG/DTA measurements on these samples reveal the melting point of all to be in the order of 300 °C, but the changes in the thermal diffusivities are appreciable than the melting point. Phase transition in these systems will be probed in future. Rodriguez et al. [14] have determined the thermal conductivity and thermal diffusivity of amylose, amylopectin, starch and for a mixture of amylose and amylopectin obtained by the milling wet process using open photoacoustic cell technique. Bonno et al. [15] have measured the amplitude of photoacoustic signal as a function of chopping frequency for the benzophenone polycrystalline samples in the temperature 100–300 K and found thermal diffusivity at room temperature as $0.18 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$ and the present investigations on the chalcones listed in Table 2 are also in the same order. Similar agreement is seen with the thermal diffusivity of food solids measured by Rodriguez et al. [14].

So, when the PA measurements on the cinnamoyl chalcones and difurans are compared, it can be concluded that the thermal difusion in these materials is mainly due to methoxy groups. This supports the works of Rao et al. [4] where it has been proved that methoxy groups enhanced the ability of chalcone to inhibit the cell growth i.e. present work has some direct bearings on the biological activities. By this way one can correlate the physical measurements with biological activities, even though there is no one to one correspondence.

It is true that different sizes and different packing density of the powder would give rise to differences in photoacoustic behaviour. But in our present work we have used directly the powders just after synthesis for photoacoustic measurement without converting into pellet form. So the observed difference in thermal diffusivity of five chalcone derivatives cannot be due to packing density or connectivity of particles.

Since most of the chalcones are useful as drug materials, the decompostion and stability against optical absorption and thermal diffusion become important and the present study is aimed at this. Since these chalcone derivatives are not extensively reported in literature, this study will be useful for further investigation on these samples.

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