CHAPTER 4

HIGH POWER ULTRASOUND MEASUREMENTS

4.1 Photoacoustic Measurements

The principle of photoacoustic spectroscopy is that a fraction of incident-chopped optical radiation, when absorbed by the sample, raises the molecules of the sample from the ground electronic state to the excited electronic state and these excited molecules relax to the ground state through nonradiative de-excitation, i.e., periodic heat emission.

This periodic heat emission produced in the sample is diffused through an air medium in front of the sample. This temperature variation changes the pressure in the PA cell, which is detected as acoustic signal by a microphone. Many experiments and theoretical investigations are available for conducting polymers elsewhere[1]. The PA measurements for specific heat capacity and thermal conductivity for PMA of different molecular weights are of investigator's research interest. The present PA spectrometer for measurement of thermal diffusivity, is set up with a Xenon lamp (450W, SPEX), monochromator (100-1000nm, SPEX), electromechanical chopper (EG &G, model 601-1), an innovatively designed photoacoustic cell which is kept inside a vibration free metallic cylindrical vessel of length 45cm and diameter 21cm weighing nearly 40kg with slits and adjustable screws. A sensitive electret microphone, a lock-in amplifier (EG &G Model 7225) in which provisions are made to measure amplitude and phase difference between incident modulating light signal and emitted acoustic signal for different chopping frequencies are used in this work.

As the PMA sample is kept in the PA cell, the light absorbed by the sample would generate thermal waves and subsequently the sensitive electret microphone detects the acoustic waves. The weak signal is fed into the lock-in-amplifier for amplification. In the same setup provisions are made to note down the amplitude

and the phase of the photoacoustic signals. The frequency of the chopper can be varied from 0.1Hz to 999.9Hz.

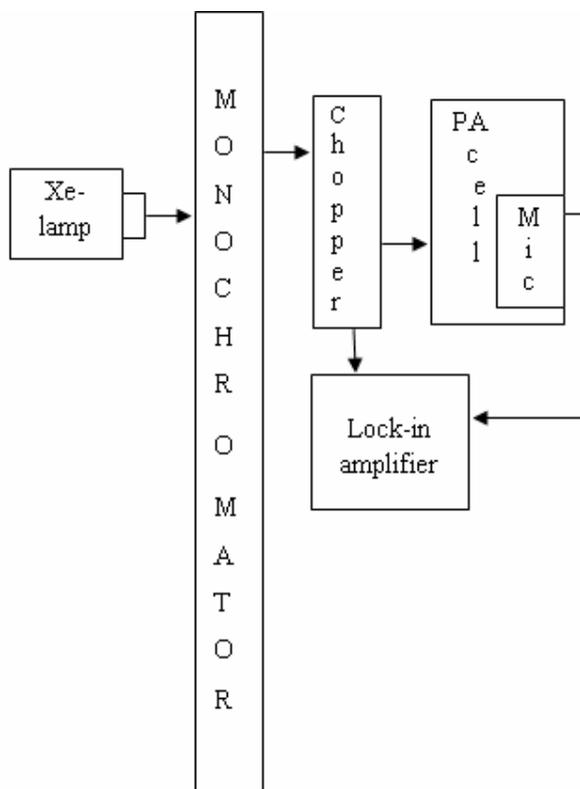The experimental setup is shown in Figure 4.1.

Figure 4.1: Photoacoustic Setup

4.2 Thermal Diffusivity by Photoacoustic Phase and Amplitude Measurements for PMA Synthesized Using High Power Ultrasound

Depth Profile Analysis

In this method the wavelength of the chopped optical radiation is fixed and the chopping frequency is varied. For every chopping frequency the phase and amplitude of the PA signal is recorded in the same lock-in amplifier setup. The

chopping frequency was started from 10Hz and stopped at 70Hz (in steps of 0.1Hz) as the signal became constant in amplitude above the said higher frequency. A graph is plotted between $\ln\sqrt{2\pi f}$ and $\ln(Phase)radian$ for phase measurements and ln (chopping Frequency) and ln (amplitude) for the amplitude measurements. From these curves the characteristic frequency, f_c of the sample is found out. This procedure is discussed in chapter 8. This frequency f_c is that point at which the PMA sample goes from thermally thin to thermally thick state i.e., the PA signal varies as 1/f with the chopping frequency after this point as required for a thermally thin sample.[1] The characteristic frequency for all the 11 samples is found out by following the above procedure. Thermal diffusivity (α) is calculated from amplitude using equation *E4-1* and from phase using equation *E 4-1a*

$$\alpha = l^2 f_c m^2 s^{-1} \qquad\qquad (E\ 4\text{-}1)$$

$$\alpha = \frac{l^2}{(slope)^2} X \frac{1}{2}\ (m^2 s^{-1}) \qquad\qquad (E\ 4\text{-}1a)$$

where l is the thickness of the sample.

Now the thermal effusivity (e) can be calculated from

$$e = \rho C_p \sqrt{\alpha}\, Ws^{1/2} m^{-2} K^{-1} \qquad\qquad (E\ 4\text{-}2)$$

where ρ is the density of the sample and C_p is the specific heat capacity of the samples

Density Measurements

The densities of the PMA samples were found out by floatation method using p-Xylene (density = 856 kg /m^3) and Carbon tetrachloride (density= 1590 kg/m^3) mixture. Since p-Xylene and Carbon tetrachloride are highly miscible and having large differences in densities, they are used for density measurements. Here, in a beaker of 50ml capacity 10 ml of carbon tetrachloride is taken and one

of the PMA samples is put in this liquid. The sample floats on the surface of the liquid. Then, slowly p-Xylene is added to this liquid little by little and stirred gently. Every time the PMA sample is observed whether it completely sinks or floats on the surface. If the density of the solution is equal to the sample, it will float in the middle (level in the beaker) of the solution i.e., it neither sinks nor floats. Then this liquid is taken in a 10 ml specific gravity bottle for density measurements. Following the same procedure density of all the eleven PMA samples is found out. The density ranges from 1051 kg/m^3 for the thirty minutes ultrasonicated samples to 1325 kg/m^3 for 330 minutes ultrasonicated PMA sample. Every density value is taken as the average of five density measurement trials with an experimental error ranging from 0.5 % to 1% for the entire measurements.

4.3 Specific Heat Capacity Measurements (using Sinclair's Apparatus)

The specific heat capacity (C_p) of the PMA samples was determined by the method of mixtures technique using Sinclair's apparatus, with maximum accuracy applying Barton's radiation correction. The Cp ranges from 101 Jkg^{-1}K^{-1} for the 30 minutes ultrasonicated PMA sample to 103 Jkg^{-1}K^{-1} for the 330 minutes ultrasonicated PMA sample. From these measurements one could infer that the specific heat capacity of the PMA samples did not vary with the change in ultrasonication period. Thus C_P is independent of the ultrasonication period for the PMA samples. Hence the mean constant value of 102 Jkg^{-1}K^{-1} is taken as C_P value for PMA for further calculation. This C_P is also in close agreement with the value of C_P for PMA sample by the same authors [2]. The experimental error in C_P measurement was $\pm$ 2%.

4.4 Determination of Thermal Diffusion Co-efficient and Thermal Diffusion Length

The thermal diffusion co-efficient, a is determined using the formula

$$a = \left(\omega/2\alpha\right)^{1/2} m^{-1} \qquad\qquad (E\ 4\text{-}3)$$

and the thermal diffusion length μ is determined using the relation

$$\mu = \left(2\alpha/\omega\right)^{1/2} m \qquad\qquad (E\ 4\text{-}4)$$

where ω is the angular characteristic frequency of the sample. In this study the thermal diffusion co-efficient is calculated at the characteristic frequency and also at frequencies less and greater than 2Hz of the characteristic frequency. A plot is drawn between thermal diffusion co-efficient and sonication periods are reported in chapter 8

An analysis of Figure 4 reveals that the thermal diffusion length is constant at the characteristic frequency for various sonication periods. The phase transition from thermally thin region to thermally thick region based on the characteristic frequency is clearly seen from the diagram.

4.5 TGA, DTA Studies on High Power PMA

The TGA, DTA are one of the best tools in studying the degradation process of chemical substances. The kinetics of the thermal degradation process can be effectively studied.[2] The Differential Scanning Calorimetric (DSC) can be used to study melting temperature, phase transitions, exothermic reactions, endothermic reactions, crystallization temperature, glass transition temperature and specific heat capacity. The researcher has used all these techniques to characterizes PMA. Govindaraj and Mariappan have characterized NASICON type glasses by DSC techniques [3]

4.6 X-Ray Photoelectron Spectroscopy Measurement

In X-Ray Photoelectron Spectroscopy (XPS), the sample is illuminated with X-rays from a Alkyd' source photoelectrons are emitted from the surface as a result of X-rays excitation whose kinetic energy is characteristic of the elements present. Surface elemental analysis is determined from the position of the peaks in the XPS SPECTRUM. Since the chemical state of the atom in the surface alters the electron binding energy, chemical shifts of up to 10ev can occur in the kinetic

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energy of the photoelectrons. This enables chemical bonding information to be derived from the precise positions and shapes of the XPS peaks. In addition XPS is amenable to the widest range of surfaces since X-rays do not normally cause charging problems or beam damage. Hence the technique may be used for all materials and is particularly useful for delicate surfaces such as polymers, catalysts, natural and synthetic fibers. In this work XPS has been used to characterize the carbon and oxygen auger peaks and binding energies. The instrument is pictured in chapter 2.

4.7 Atomic Force Microscopy Measurements

Atomic force microscopy (AFM) and its related techniques have proliferated successfully into many fields. Today this method is used to obtain the high-resolution static and dynamics images in investigation of the physical and mechanical properties of the thin film molecules and biological molecules. The researcher has used this technique to find the morphology of PMA which has given an insight on the electrical semiconducting nature of PMA.

4.8 X-Ray Diffraction Measurements

The X-ray diffraction measurements is one of the powerful tool to study the amorphous and crystalline nature of materials. In this work the experimenter has used XRD to find the amorphous, semi crystalline nature of PMA at different 2θ value.

References

[1]. Govorkov et al., 1997; Dias et al., (2003).

[2]. Bing Zhang and Frank D. Blum, *Polymer Preprints*, **42(2) XXXX**

[3]. G. Govindaraj and C.R.Marriappan , Solid State Ionics, **147** (2002) 49.