

CHAPTER 3

LOW POWER ULTRASOUND MEASUREMENTS

3.1 Decomposition Studies of Peroxodisulphate (PDS)

Potassium Peroxodisulphate (PDS), (E.Merck, Germany) was twice recrystallised in distilled water and its Purity was found to be 99.8% by the iodometry assay. A Stock solution was Prepared and estimated daily by iodometry. Sulphuric acid, Potassium iodide, Potassium dichromate and sodium thiosulphate were mostly of Analar quality (E.Merck, India) and were used as such without further Purification. Water was distilled over alkaline permanganate in all glass unit (M/s.Vensil, India). This doubly distilled water was used for the preparation of all the reagents and solutions. A typical procedure for the study is outline below:

PDS solution (0.02M) was prepared daily afresh and estimated by iodometry. Required volume of PDS solution was pipetted out into the reaction vessel to get the desired concentration and maintained at the predetermined constant experimental temperature using a constant temperature bath (M/s.Toshniwal brothers, Madras, India). The total reaction mixture volume was kept as 10mL. After the equilibration of this temperature, the constant frequency 1 MHz ultrasonic interferometer and a stop watch were switched on. This was taken as the starting time. At the end of the known reaction time(15min) a known volume (2mL)was pipetted out from the reaction vessel and poured into an iodine flask (250mL) containing 25ml each of distilled water, KI (10%) solution and Sulphuric acid (2N). The flask was stoppered tightly and kept in the dark for 30 minutes to complete the reaction between PDS and KI. The total iodine liberated by the reaction of KI was titrated against standardized thiosulphate solution using starch indicator. The PDS concentration thus determined at the reaction time (15min) was used for further calculations. Duplicate measurements showed that the results were reproducible with an error $\pm 3\%$.

The same procedure was repeated for sonication periods of 30, 45 and 90 minutes respectively. The experiment was performed for temperatures 30°C, 35°C, 40°C, 45°C and 50°C for the sonication periods of 15, 30, 45 and 90 minutes respectively. The results and discussion for this part is described in chapter 8.1.

3.2 Polymerization Kinetics Measurements of Methyl Acrylate (MA)

Potassium Peroxodisulphate (PDS), (E.Merck, Germany) was twice recrystallised in distilled water and its purity was found to be 99.8% by the iodometry assay. A stock solution was prepared and estimated daily by iodometry. PDS is used as the initiator. Methyl acrylate (MA) (E.Merck, India) of analar grade was used as the monomer stock solution was prepared and estimated daily by iodometry. Sulphuric acid, potassium iodide, potassium dichromate and sodium thiosulphate, were mostly of Analar quality (E.Merck, India) and were used as such without further purification. Water was distilled over alkaline permanganate in all glass units (M/s.Vensil, India). This doubly distilled water was used for the preparation of all the reagents and solutions. A typical procedure for the study is outlined below:

PDS solution (0.02M) was prepared daily afresh and estimated by iodometry, MA solution (0.4M) was prepared daily afresh and estimated by iodometry. The required amount and strength of the aqueous solution of MA was taken into the reaction vessel and maintained at a predetermined temperature using a constant temperature water bath (M/s.Toshniwal brothers, Madras, India). A pre-equilibrated solution of PDS was added into the reaction vessel and the time of passing the ultrasound was taken as the starting time for polymerization reaction was kept as 10 mL in all the experiments. The rate of polymerization, $R_p(-d[MA]dt)$ was determined by following the concentration of remaining monomer at the end of the polymerization time by bromometry to estimate the double bonds present in the monomer. The rate of decomposition of the initiator $(-d[PDS]dt)$ Was also determined following the same procedure. The above

procedure was repeated for four different constant temperatures. The results and the discussion for this part of the work as explained in chapter 8.

Methylacrylate solution of strength 0.33M is mixed with a solution of Polymerization is carried out by keeping the experiment solution mixtures in a flat bottom glass test tube of capacity 100ml immersed in a transonic digital ultrasonic water bath (Elma T490DH). The ultrasonic water bath, which is a rectangular metallic tub filled with water to three-fourth of its total capacity gives out ultrasonic waves of fixed frequency 40 KHz which can be varied for various powers starting from 20W/cm² to 140W/cm² in steps of 20W/cm². A frequency of 40 KHz and a power of 100W/cm² at a constant temperature of 50°C are employed throughout our experiment. Methylacrylate solution of strength 0.33M is mixed with a solution of potassium peroxodisulphate of strength 0.005M in a clean flat bottom glass test tube with the total volume as 25ml. A solution of Methylacrylate 20ml and potassium peroxodisulphate 5ml is used throughout our studies in synthesizing PMA. Ultrasound is passed for a period of 30 minutes continuously and stopped exactly at the end of the 30th minute. The reaction test tube is taken out from the ultrasonic bath and a fixed volume (75ml) of Sulphuric acid of strength 2N is slowly and gently added to the reaction mixture and is allowed to settle down. After an interval of 48 hours we get a thin solid layer of PMA settled at the bottom of the test tube. The remaining liquid mixture is poured out the thin layer of PMA is taken out gently from the test tube and placed over a filter paper, which absorbs all the liquid content and dries the thin layer of PMA. This thin layer is washed with distilled water and dried in atmosphere air conditions. Thus we obtain PMA wafer, which is semitransparent, and colorless. Using the same procedure as given above we synthesize PMA by varying the period of sonication for 30, 60, 90, 120, 150, 180, 210, 240, 270, 300 and 330 minutes. There are eleven PMA samples of thickness of 0.35mm for eleven different sonication periods are available for the further studies. The sample is cut to have uniform dimension of 4 x 4 x 0.35mm in a highly symmetric direction.

3.3 Thermal Diffusivity

Centuries before, Jean Fourier (1768-1830) derived a basic law defining the propagation of heat in a one-dimensional homogeneous solid as [1-3]

$$\frac{\partial Q}{\partial t} = -\kappa A \frac{\partial T}{\partial x} \quad (E 3-1)$$

The above equation is known as Fourier equation. *Equation (3-1)* implies that the quantity of heat dQ conducted in the x -direction of a uniform solid in time dt is equal to the product of the conducting area A normal to the flow path, the temperature gradient dT/dx along this path, and the thermal conductivity k of the conducting material.

Formal definition of thermal diffusivity arises when deriving an expression for a transient temperature field in a conducting solid from the Fourier equation. The equation describing the temperature field in a homogeneous, linear conducting solid with no internal heat source is

$$\nabla^2 T = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (E 3-2)$$

where the thermal diffusivity α is given by

$$\alpha = \frac{\kappa}{\rho C_p} \quad (E 3-3)$$

where k is the thermal conductivity, ρ is the density and C is the specific heat capacity of the material. The thermal diffusivity α is usually expressed in m^2s^{-1} . The thermal diffusivity is thus a derived quantity whose significance is evident from the above relationship. The reciprocal of thermal diffusivity, $1/\alpha$, expressed in sm^{-2} is a measure of the time required to heat-up a conducting material to some temperature level. Therefore, the ratio of heating times for two materials of the

same thickness will be inversely proportional to their respective thermal diffusivity values. Obviously, α is a significant thermophysical parameter that determines the heat diffusion in bulk as well as thin film samples.

3.4 Thermal Effusivity

The thermal effusivity, similar to thermal diffusivity, is a unique thermal property of a material [4]. The major difference between the two is that diffusivity is a bulk property of the sample whereas the effusivity is a surface property. The thermal effusivity is defined by:

$$e_s = \sqrt{\kappa\rho C_p} (Ws^{1/2}m^{-2}K^{-1}) \quad (E 3-4)$$

where k is the thermal conductivity, ρ is the density and C is the specific heat capacity. Though the thermal effusivity is an abstract thermal quantity and is a relevant thermophysical parameter for surface heating and cooling as well as in quenching processes, it is one of the least explored quantities in physics. Actually, the thermal effusivity is a measure of the sample's thermal impedance or it is a measure of the sample's ability to exchange heat with the environment. The thermal effusivity of liquid crystals has great importance when they are used as temperature sensors or in temperature sensitive devices/applications. For example, one of the most recently introduced and important applications of liquid crystalline polymers is in the field of optical data storage [5-8]. The thermo-optic recording is achieved by incorporating a dye into the sample, which on irradiation with laser beam absorbs the light energy and re-radiates it as heat. Consequently the sample is locally heated into the isotropic phase and a change in the optical density takes place on cooling. Usually very thin films (5-10 μm) are used for the optical data storage. Here, the speed with which the laser treated area cools back into the glassy or liquid crystalline phase is mainly determined by the thermal effusivity of the thin film.

3.5 PA Measurement of Thermal Diffusivity and Effusivity of PMA

The principle of PA spectroscopy is that a fraction of incident chopped optical radiation, absorbed by 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 produces a variation in the pressure in the sample, which is detected as an acoustic signal by a microphone. Although the effect has been known for over a decade, there has been increased interest in it recently both in theoretical and experimental studies, particularly with respect to electrically conducting polymers. PA measurements for the determination of k, α, c_p , and e for both vinyl and conducting polymers of different molecular weights are of interest to researchers.

The PA spectrometer for the thermal studies was set up with a xenon lamp (450 W; Spex, Brookhaven, Inc., New York, UK), a monochromator (100-1000 nm; Spex), an electromechanical chopper, PA cell (model 601-1, EG&G), a condenser microphone, a lock-in amplifier (model 7225, FG&G), and a digital storage oscilloscope (DSO; 20 MHz; Gould, Brookhaven, Inc.).

For our experiments, the PA cell was made from an airtight glass funnel with a stem diameter of 0.8 cm and a length of 3.0 cm with a perfect internal lamp black coating that prevented any leakage of the acoustic signal. The purified PMA water was placed inside this cell, and the condenser microphone was placed very close to the sample but was not touching it. The light absorbed by the PMA sample generated thermal waves, and then the sensitive condenser microphone detected the acoustic waves. The weak signal was fed into the lock-in amplifier for amplification and also into the DSO. The frequency of the chopper could be varied from 15 to 100 Hz.

3.6 Polymerization of monomers in the Presence of Ultrasound and Peroxodisulphate

Polymerization of vinyl monomers is well-known and interesting with peroxy salts – initiated polymerization. Iso-electronic peroxy salts namely peroxodisulphate and peroxomonosulphate were used for polymerization of vinyl monomers, acrylamide [9], and methacrylamide [10] in inert atmosphere. Ultrasound was used to decompose peroxodisulphate [11] and this provided a scope for polymerization under this atmosphere with a faster rate of production of primary radicals. Using this advantage, we have carried out vinyl polymerization with peroxodisulphate [12, 13] and peroxomonosulphate [14] in the presence of ultrasound of frequency 1MHz with 5.5 W/cm^2 as power output. In continuation of our polymerization studies on vinyl monomers we have now taken methyl acrylate, a methyl ester of acrylic acid, again a vinyl monomer and studied the polymerization reaction dynamics under the influence of ultrasound with a frequency of 1MHz and 5.5 W/cm^2 power output and analyzed.

Experimental

Peroxodisulphate of potassium salt (PDS) was a guaranteed reagent (E-Merck, India) and was used after recrystallization in water. The monomer methyl acrylate (MA) and initiator peroxodisulphate (PDS) were estimated by bromometry and iodometry. Water, doubly distilled over alkaline permanganate in an all glass apparatus was used for preparing all the solutions. All other reagents used were of Analar grade (E-Merck, India).

Ultrasonic interferometer that can impart a constant ultrasonic power of 5.5 W/cm² at 1 MHz frequency into the solution kept in a 12 mL thermostatic cell (M/S Mittal Enterprises, New Delhi, India) was used for the polymerization study. The required amount of the aqueous solution of MA was taken in the thermostatic cell and maintained at a predetermined temperature using a constant temperature water bath (M/S Toshniwal Brothers, Delhi, India). A pre-equilibrated PDS solution was added into the cell and the time of switching on the power supply of the ultrasonic interferometer was taken as the starting time for polymerization. The total volume for the polymerization reaction was kept as 10 mL in all experiments. The rate of monomer disappearance $(-d [MA]/dt) = R_p$ was determined by following the concentration of remaining monomer at the end of polymerization time by bromometry to estimate the double bonds present in the monomer and the rate of PDS disappearance $(-d[PDS]/dt)$ was followed for the polymerization conditions separately by estimating the concentration of the unreacted PDS by iodometry. Duplicate runs were performed and the results were obtained within experimental error ($\pm 3\%$).

3.7 Thermal Expansion of PMA

The thermal expansion coefficient for this PMA sample was also determined with Fizeau's method in the direction of higher symmetry. This method is an accurate ($\pm 0.05\%$ error) optical method for determining the linear thermal expansion coefficient for metals and alloys by forming interference fringes. This method was used here for the first time to measure the thermal expansion coefficient for a polymer. We used our PMA sample for the measurements. The experimental setup is shown in figure 3.1.

Fizeau's Apparatus

AB and AF were two optically plane glass plates whose ends were tied together at one end A. Hence, these two glass plates formed an air wedge between themselves. The other end of the AF plate rested on a carbon rod RR. This carbon rod actually had two segments, RR' and, RR'' and between the segments, the sample was placed as shown in Figure 8.11. The PMA sample was heated to a steady temperature through the passage of an electric current through the coil of wire CC wound around carbon rod RR. The polymer expanded, increasing the angle of the air wedge, and so the fringe width (β) decreased. The linear expansivity of the polymer depended on the rise in the temperature:

$$\text{Linear expansivity} = \frac{\text{Increase in length}}{\text{Initial length} \times \text{Rise in temperature}} \quad (E\ 3-5)$$

With Fizeau's experimental technique, the increase in the length of the PMA sample was calculated from the original length (0.3 mm) of the PMA sample. The height of the air wedge (h) was calculated as follows:

$$h = \frac{L\lambda}{2\beta} \quad (E\ 3-6)$$

where L is the length of glass plate AB and λ is the wavelength of light. In the experimental setup, a 0.3 mm-high PMA sample with a 2 mm x 2 mm square base was used. The measurements are shown in Table II. The average thermal expansion coefficient at 45–75°C for the PMA sample was $75.61 \pm 0.03 \times 10^{-6}/^{\circ}\text{C}$. The literature value for the thermal expansion coefficient for PMMA was $70 \times 10^{-6}/^{\circ}\text{C}$ [15] Proper corrections for the expansion of the carbon rod were carried out.

FIZEAU'S APPARATUS

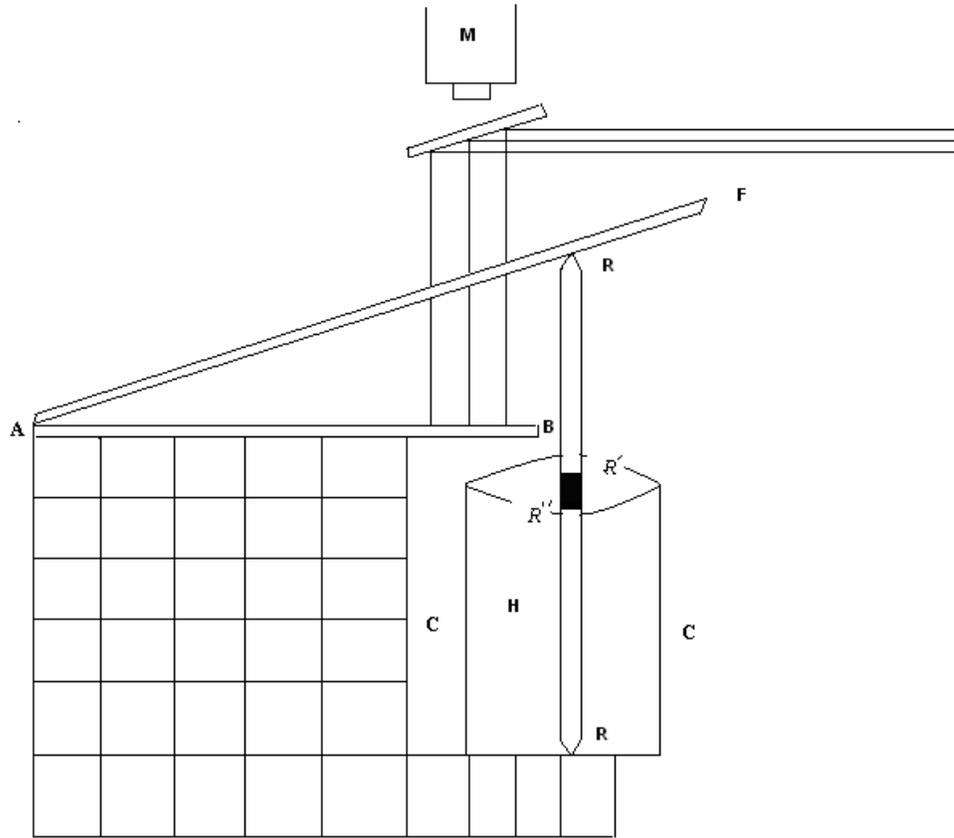


Figure 3.1 Fizeau's Apparatus

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