Preface

The last few decades witnessed a surge in advanced techniques for material characterization with the availability of intense coherent sources of radiation. Photothermal science deals with a wide range of techniques and phenomena based on the conversion of absorbed optical energy into heat. Optical energy is absorbed and eventually converted into thermal energy by a variety of materials in the solid, liquid and gaseous states. Although the initial absorption process in many materials are selective, it is common for excited electronic states in atoms or molecules to give away its excitation energy by a series of non-radiative transitions that result in a general heating of the material. Photothermal heating can result in different effects which, in turn, provide various detection mechanisms. Photothermal heating can provide convenient and sensitive methods for detecting optical absorptions in matter. It can also provide information concerning various de-excitation mechanisms. Photothermal methods enjoy the advantage of being non-destructive. This optical diagnostic technique can provide information that is not obtainable by other conventional methods. Thus photothermal technique gained wide acceptance in the study of various optical and thermal parameters. Of the various photothermal methods in use, two techniques – the transverse probe beam deflection method and the open photoacoustic cell technique are employed for thermal characterization in the present work.

The discovery of highly conducting polyacetylene in 1977 by Shirakawa et. al has revolutionized the field of conducting polymers. The conductivity of this conjugated polymer could be increased by about fourteen orders by the process of doping. Since this Nobel Prize winning discovery, much of the work has been centered on synthesis and characterization of novel
polymers with $\pi$-conjugated backbone due to their highly promising optical, electrochemical and conducting properties. Conducting polymers are generally synthesized by chemical or electrochemical methods. Another technique used for obtaining polymer films is plasma polymerization. This technique makes use of molecules occurring in various plasma environments. Pin hole-free films with good adhesion to the substrate can be deposited using this method. The advantage of this technique lies in the easy control of polymerization reaction to any desired surface. The distinguishing feature of plasma deposited films is its highly cross-linked nature. On the other hand chemical synthesis produces polymers with an ordered structure. The electrical conductivity of these polymers can be tuned from the insulating regime to the highly conducting regime by suitable doping. The combination of conductivity and polymeric properties such as flexibility, processability and a reduction in weight and cost makes this class of polymers suitable for wide ranging applications.

In the present study, radio frequency plasma polymerization technique is used to prepare thin films of polyaniline, polypyrrole, poly N-methyl pyrrole and polythiophene. The thermal characterization of these films is carried out using transverse probe beam deflection method. Electrical conductivity and band gaps are also determined. The effect of iodine doping on electrical conductivity and the rate of heat diffusion is explored.

Bulk samples of poyaniline and polypyrrole in powder form are synthesized by chemical route. Open photoacoustic cell configuration is employed for the thermal characterization of these samples. The effect of acid doping on heat diffusion in these bulk samples of polyaniline is also investigated. The variation of electrical conductivity of doped polyaniline and polypyrrole with temperature is also studied for drawing conclusion on the
nature of conduction in these samples. In order to improve the processability of polyaniline and polypyrrole, these polymers are incorporated into a host matrix of poly vinyl chloride. Measurements of thermal diffusivity and electrical conductivity of these samples are carried out to investigate the variation of these quantities as a function of the content of polyvinyl chloride.

Chapter 1 is an introduction to the photothermal science. The various photothermal effects with the corresponding detection schemes are discussed in this chapter. A brief outline of the theory behind photothermal deflection and photoacoustic effect is also given.

An introduction to conducting polymers is presented in the first half of chapter 2. The second half explains the preparation techniques along with optical and electrical characterization of the conducting polymer samples used in this study. A brief description of the radio frequency plasma polymerization technique used for the preparation of polymer films is given. Methods adopted for chemical synthesis of polymer samples are outlined. Direct and indirect band gaps of pure and iodine doped films are obtained from the uv-vis-NIR measurements. The results of the electrical conductivity measurements of pure and iodine doped films are also presented.

An outline of the present experimental arrangement for transverse probe beam deflection configuration is presented in chapter 3. The observed variation of phase and amplitude of the photothermal signal with pump – probe offset is shown graphically for the four different thin film samples under investigation. The value of thermal diffusivity of each film is extracted from these plots. The effect of iodine doping on heat diffusion in these films is also investigated and the results are presented.

Chapter 4 describes the photoacoustic measurements on bulk samples. A brief theoretical outline and the details of our experimental setup of open
photoacoustic cell configuration are given. The variation of the phase of the photoacoustic signal with modulation frequency is represented graphically for each of the bulk polymer samples - chemically prepared polyaniline and polypyrrole. The effect of doping on heat diffusion in polyaniline is also investigated by carrying out photoacoustic measurements on polyaniline doped with hydrochloric acid, sulphuric acid and camphor sulphonlic acid. Thermal diffusivity is computed by theoretical fit taking into account the effect of thermo-elastic bending.

The photoacoustic determination of thermal diffusivity of conducting polymer composites is presented in chapter 5. The preparation techniques for two conducting polymer composites - polyaniline-poly vinyl chloride and polypyrrole-poly vinyl chloride - are outlined. Open photoacoustic cell method is used to determine the thermal diffusivity values for three different compositions. The room temperature electrical conductivity values for the same compositions are also determined as an attempt to obtain the correlation between electrical and heat transport processes.

The summary of the important findings of the present work and the conclusions arrived at based on the results obtained are presented in the last chapter.