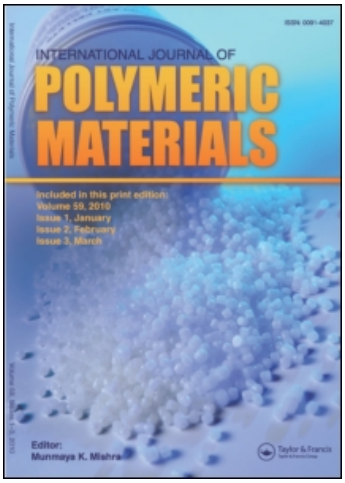

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Study of Heat Diffusion in Polyaniline by Open Photoacoustic Cell Technique

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Polyaniline in a powder form was chemically prepared and its thermal diffusivity was determined by photoacoustic method in the open cell configuration. The effect of acid doping on heat transport in polyaniline was investigated. The observed increase in thermal diffusivity of acid-doped samples points to a carrier contribution to heat diffusion.

Keywords: photoacoustic, polyaniline, thermal diffusivity

INTRODUCTION

Conducting polymers have been extensively studied during the last two decades because of their highly significant contributions in the fields of applied and basic science. A major breakthrough in the field of electrically conducting polymers occurred in 1977 with the discovery of conducting polyacetylene by Shirakawa et al. [1]. Since this Nobel

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Prize-winning discovery, much of the work has centered on synthesis and characterization of novel polymers with π-conjugated backbone due to their highly promising conducting properties. As the band gap of typical conjugated polymers is about 1.5 eV, the electrical conductivity is low and the material is an insulator or a semiconductor. The electrical conductivity can be considerably enhanced by the introduction of charge into these polymer chains by various methods like oxidation, reduction, and acid doping [2–5].

Polyaniline (PANI) is one of the typical conducting polymers of the first generation. Much of the work was focused on tailoring its electrical conductivity. Heat diffusion in this material remains practically unexplored. Its use in diverse fields such as molecular electronics and sensor technology makes proper thermal design of the devices employing conducting polymers essential [6–12]. Poor thermal management of devices employing conducting polymers may lead to device failure. An estimate of heat diffusion in a material can be obtained from its thermal diffusivity value. It is the ratio of thermal conductivity to the thermal capacity-per-unit volume, given by $\alpha = k/\rho C$; where k, ρ and C are the respective values of thermal conductivity, density and specific heat capacity of the material.

Of the various methods in use for the thermal characterization of a material, photothermal techniques enjoy the unique advantage of being noninvasive. Photoacoustic (PA) technique belongs to the class of photothermal methods and is one of the commonly used thermal wave methods for thermal characterization [13–17]. It is essentially a closed cavity detection of energy liberated by atoms or molecules through nonradiative de-excitation mechanism resulting from light absorption by a sample. The sample to be studied is placed in a closed cell in the PA method. For gases and liquids the sample generally fills the chamber. However in the case of solids, the sample fills only a portion of the chamber and the rest of the chamber is filled with a nonabsorbing gas. When the sample is irradiated with a modulated beam of radiation, absorption of intermittent radiation and subsequent nonradiative de-excitation taking place in the sample material produces an acoustic signal in the gas medium with which the sample surface is in contact within the cell. This acoustic signal is detected by a sensitive microphone kept inside the cell. The theoretical explanation to PA effect in condensed media was formulated by Rosencwaig and Gersho [18].

A modified form of PA technique, called the open photoacoustic cell (OPC) in the transmission detection configuration is used for the present study. OPC configuration is a simple and convenient form of the conventional PA cell. This technique has been successfully applied for the study of optical spectra of liquids and thermal and transport

properties of different materials [19–21]. The OPC theory was developed by Helander and was later modified by McQueen [22–24]. In the OPC configuration, the solid sample is mounted directly onto the top of microphone leaving a small volume of air in between the sample and the microphone. OPC detection has been widely employed in the thermal characterization of various samples. The periodic pressure variation in the air chamber can be explained using the Rosencwaig–Gersho theory. The sample is assumed to be optically opaque so that all the energy is absorbed at the sample surface itself and the heat flux into the surrounding air is negligible.

According to the 1-D heat flow model of Rosencwaig and Gersho, the expression for the PA signal is obtained as

$$\delta P = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi l_g T_0 k_s f \sin h(l_s \sigma_s)} \exp\left[j\left(\omega t - \frac{\pi}{2}\right)\right] \tag{1}$$

where γ is the specific heat ratio of air, P_0 and T_0 are the ambient pressure and temperature respectively, I_0 is the incident light intensity, f is the modulation frequency, l_i, k_i and α_i are the length, thermal conductivity and thermal diffusivity of material i respectively. Here the subscript i denotes the sample (s) and gas (g), and, $\sigma_s = (1+j)a_s$, with $a_s = (\pi f/\alpha_s)^{1/2}$ is the complex thermal diffusion coefficient of the sample.

If the sample is optically opaque and thermally thick, then Eq. (1) reduces to

$$\delta P = \frac{\gamma_0 P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi l_g T_0 k_s} \frac{\exp\left[-l_s (\pi f/\alpha_s)^{1/2}\right]}{f} \exp\left[j\left(\omega t - \frac{\pi}{2} - l_s a_s\right)\right] \tag{2}$$

where l_s and a_s are the thickness and thermal diffusion coefficient of the sample. Thus, according to Eq. 2 the phase of the PA signal varies with modulation frequency as $l_s(\pi f/\alpha_s)^{1/2}$. Hence, thermal diffusivity can be obtained from the phase data. The temperature gradient within the sample can cause thermoelastic bending in certain materials. In such a case the graph between the phase of the PA signal and $f^{1/2}$ is not a straight line [25–27]. Eq. (2) becomes

$$\delta P = \frac{3\alpha_T R^4 \gamma P_0 I_0 \alpha_s}{4\pi R_c^2 l_s^2 l_g k_s f} \left[\left(1 - \frac{1}{x}\right)^2 + \frac{1}{x^2}\right]^{1/2} e^{j(\omega t + \pi/2 + \Phi)}; \tag{3}$$

where $x = l_s(\pi f/\alpha_s)^{1/2}$, $\Phi = \tan^{-1}\left[\frac{1}{x-1}\right]$ and α_T is the thermal expansion coefficient of the sample. R and R_c are the radii of the front hole of the microphone and OPC air chamber, respectively. The thermal diffusivity of such materials can be obtained from the phase data by fitting the

following equation:

$$\phi = \phi_0 + \tan^{-1}\left\{[l_s(\pi f/\alpha_s)^{1/2} - 1]^{-1}\right\} \quad (4)$$

EXPERIMENTAL

Sample Preparation

Polyaniline in a powder form was prepared by chemical oxidative polymerization using ammonium persulphate as initiator in the presence of 1 M HCl at 0–5°C. The reaction was allowed to continue for 4 h. The polyaniline thus formed was vacuum-dried. Samples doped with 1 M sulphuric acid were also prepared. For this, polyaniline was first de-doped by treating it with ammonium hydroxide for 24 h, and then doped with 1 M sulphuric acid. Polyaniline samples in the three different forms—undoped, 1 M hydrochloric acid-doped and 1 M sulphuric acid-doped—were pelletized to form pellets of 1 cm diameter with a thickness of less than 1 mm.

Thermal Diffusivity Measurements

The experimental setup for PA measurements consists of an open photoacoustic cell, pump laser, mechanical chopper and a lock-in amplifier. The continuous wave laser emission at 488 nm from a 50 mW Argon ion laser (Linconix 5000) is intensity-modulated using a mechanical chopper. The beam is allowed to fall on the PANI pellet fixed on the OPC by a small amount of vacuum grease. The pressure variations resulting from the thermal waves produced are detected using a miniature microphone (Knowles FG 3329). The output from the microphone is fed to the lock-in amplifier (Stanford Research Systems SR830). The phase of the PA signal for different modulation frequencies is noted from the lock-in-amplifier. The observations were repeated, also, for the two samples doped with 1 M hydrochloric acid and 1 M sulphuric acid.

RESULTS AND DISCUSSION

The variation of phase of the PA phase with modulation frequency for undoped PANI is shown in Figure 1. The corresponding plots for samples doped with 1 M hydrochloric acid and 1 M sulphuric acid are shown in Figures 2 and 3. In all cases the variation is not linear and the effect of thermoelastic bending is evident. The thermal diffusivity

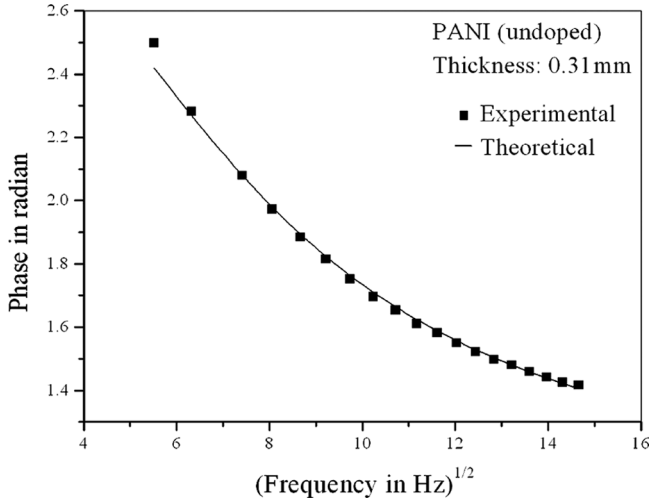

FIGURE 1 Variation of PA phase with modulation frequency for undoped PANI.

in each case was determined by curve fitting. The values of the obtained thermal diffusivity are shown in Table 1. In the present study, acid-doped samples show a higher value of thermal diffusivity than the undoped case. Thus it is observed that doping with acids like

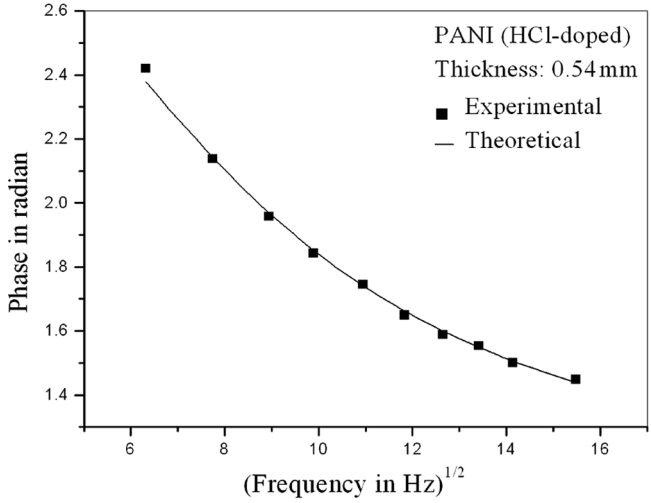

FIGURE 2 Variation of PA phase with modulation frequency for HCl-doped PANI.

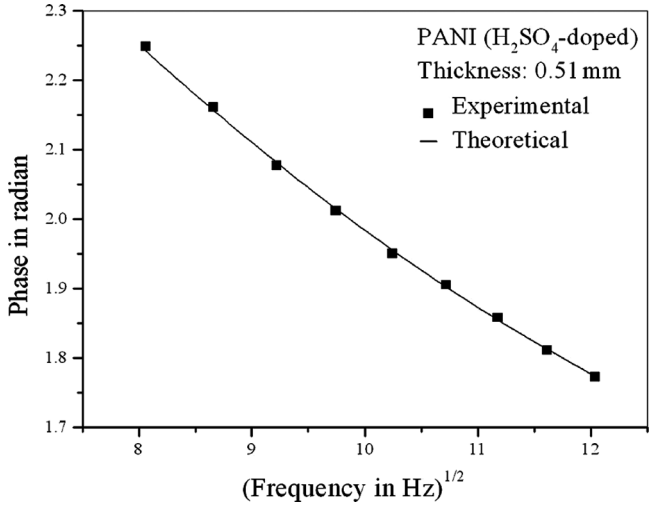

FIGURE 3 Variation of PA phase with modulation frequency for H_2SO_4-doped PANI.

hydrochloric acid and sulphuric acid enhances the heat diffusion in the specimen. This situation is to be compared with the electrical conductivity of acid-doped PANI. It is known that acid doping enhances the electrical conduction by several orders. In the case of doped PANI, there is a carrier contribution in addition to phonon-assisted heat transport. As a result of this carrier contribution to heat transport, the thermal diffusivity of doped samples increases. The values obtained fall in the range of the diffusivity for semiconductors. It is to be noted that there is not much difference between the values of diffusivity of PANI doped with the two different acids. This value, although smaller, is of the order of the thermal diffusivity of camphor sulphonic acid-doped polyaniline [28].

TABLE 1 Thermal Diffusivity Values for Undoped and Doped PANI

Sample	Thickness (mm)	Thermal diffusivity ($\times 10^{-5}$m^{2}s^{-1})
PANI	0.31	0.844 ± 0.008
PANI (HCl-doped)	0.54	3.031 ± 0.013
PANI (H_2SO_4-doped)	0.51	3.347 ± 0.010

CONCLUSION

PANI is known to possess a conjugated structure and samples obtained by chemical synthesis do not show any crosslinking or side reactions. The local order in such a sample will be relatively high. This can lead to reduced scattering of phonons in a chemically synthesized sample. By acid doping, a three-fold increase in the value of thermal diffusivity is observed. This increase can be related to the increase in carrier concentration upon doping. In the undoped state there is a phonon-assisted heat transport. In doped samples there is a carrier contribution to heat transport and a consequent higher diffusivity.

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