

The Measurement of Thermal Diffusivity in Poly(methyl acrylate) by Photoacoustic Technique

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ABSTRACT: It is suggested that when a polymer is synthesized from a monomer and an added initiator in the presence of ultrasound, the process may produce polymers with predetermined structures and physical properties. An attempt is made to measure thermal diffusivity. Poly(methyl acrylate) (PMA) is synthesized using monomer methyl acrylate and an added initiator peroxydisulfate in the presence of ultrasound of frequency 35 kHz and power 100 W/cm² at 50°C for various known sonication periods. PMA is obtained as a colorless, semitransparent solid. The solid PMA is cut into thin wafers in a highly symmetric direction to have uniform sizes. PMA samples are synthesized for 11 different sonication periods. These PMA samples are used to study their thermal diffusivity (α) by photoacoustic (PA) technique. Thermal diffusivity is calculated by measuring the amplitude and phase of the PA signal separately. A plot of

the sonication period versus thermal diffusivity obtained from amplitude measurements of PMA indicates that there is an increase in thermal diffusivity from 2×10^{-6} to 4.7×10^{-6} m²/s when sonication period is increased from 30 to 330 min in steps of 30 min. The same trend is seen in a plot between sonication period and thermal diffusivity when the thermal diffusivity is calculated by PA phase measurements. There is a small difference in the experimental values obtained by the two measurements. Dependence of thermal diffusivity of PMA on ultrasonic sonication is discussed in detail. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3756–3760, 2006

Key words: synthesis; solid state polymerization; thermal properties; conducting polymers

INTRODUCTION

Viscoelastic properties, optical properties, and thermal properties of poly(methyl-methacrylate) (PMMA) synthesized by conventional methods have been reported in literature.^{1–5} Still a complete thermal study on poly(methyl acrylate) (PMA) for thermal diffusivity is sparse. So, here we report our measurements on the thermal property in view of the study on conducting polymers. The PA technique is the simplest NDT tool for studying the thermal diffusivity of the polymers. Thermal effusivity measurements are also possible with this technique.

The thermal diffusivity of the polymer PMA synthesized by the monomer methyl acrylate and potassium peroxydisulfate as initiator at different sonication periods, at moderately high power, is reported here.

EXPERIMENTAL

Preparation of poly (methyl acrylate)

Polymerization is carried out by keeping the experiment solution mixture in a 100-mL flat-bottom glass test tube immersed in a transonic digital ultrasonic water bath (Elma T490DH). The ultrasonic water bath, a rectangular metallic tub filled with water to three-fourth of its total capacity, gives out ultrasonic waves of fixed frequency 35 kHz, which can be varied for various powers starting from 20 to 140 W/cm² in steps of 20 W/cm². A frequency of 35 kHz and a power of 100 W/cm² at a constant temperature of 50°C are employed throughout our experiment. Methyl acrylate solution of strength 0.33M is mixed with a solution of potassium peroxydisulfate of strength 0.005M in a clean flat-bottom glass test tube to a total volume of 25 mL. A solution of methyl acrylate (20 mL) and potassium peroxydisulfate (5 mL) is used throughout our studies for synthesizing PMA. Ultrasound is passed for 30 min 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 (75 mL) of sulfuric acid of strength 2N is slowly and gently added to the reaction mixture and is allowed to settle down. After an interval of 48 h, we get a thin

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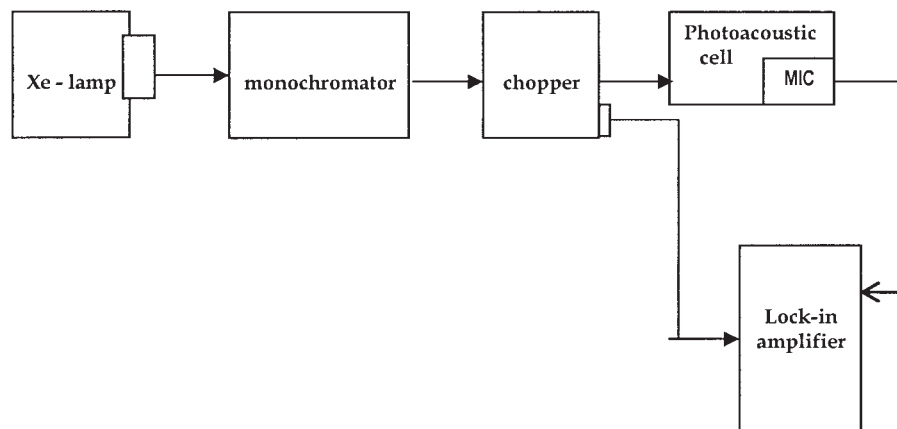


Figure 1 Schematic diagram of the photoacoustic setup.

solid layer of PMA settled at the bottom of the test tube. The remaining liquid mixture is poured out, and 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 layer is washed with distilled water and dried under atmospheric conditions. Thus we obtain PMA wafer, which is semitransparent and colorless. Using the same procedure as given earlier, we synthesize PMA by varying the period of sonication for 12 : 30, 60, 90, 120, 150, 180, 210, 240, 270, 300 and 330 min. Hence there are 11 PMA samples for 11 different sonication periods. The sample is cut in a highly symmetric direction to have uniform dimension of $4 \times 4 \times 0.35 \text{ mm}^3$.

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.⁶ Thermal diffusivity, specific heat capacity, and thermal conductivity for both vinyl and conducting polymers of different molecular weights are of research interest.

The present PA spectrometer, for measurement of thermal diffusivity, is set up with a Xenon lamp (450 W, SPEX); monochromator (100–1000 nm, SPEX); electromechanical chopper (EG and G, model 601-1); an innovatively designed photoacoustic (PA) cell which

is kept inside a vibration-free metallic cylindrical vessel of length 45 cm and diameter 21 cm weighing nearly 40 kg, with slits and adjustable screws; a sensitive electret microphone; and lock-in amplifier (EG and 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. The experimental setup is shown in Figure 1. Before carrying out the experiment with PMA sample, the PA setup is calibrated with air and also quartz glass for which α agrees well with the literature values. As the PMA sample is kept inside 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 and also for noting down the readings. The frequency of the chopper can be varied from 0.1 to 999.9 Hz.

RESULTS AND DISCUSSION

Now the PA spectra of one of the PMA samples prepared under a sonication period of 330 min is recorded in the following way.

Depth profile analysis

Here the wavelength is fixed and the chopping frequency is varied. For every chopping frequency the amplitude and the phase of the PA signal are recorded in the same lock-in amplifier setup. We started from 10 Hz and ended at 70 Hz, as the signal became constant in phase and amplitude above 70 Hz. A graph is plotted between \ln (amplitude of the PA signal) and \ln (chopping frequency). From this curve the characteristic frequency, f_c , of the sample is obtained. This procedure is shown in Figure 2. This frequency f_c is that point at which the PMA sample goes from ther-

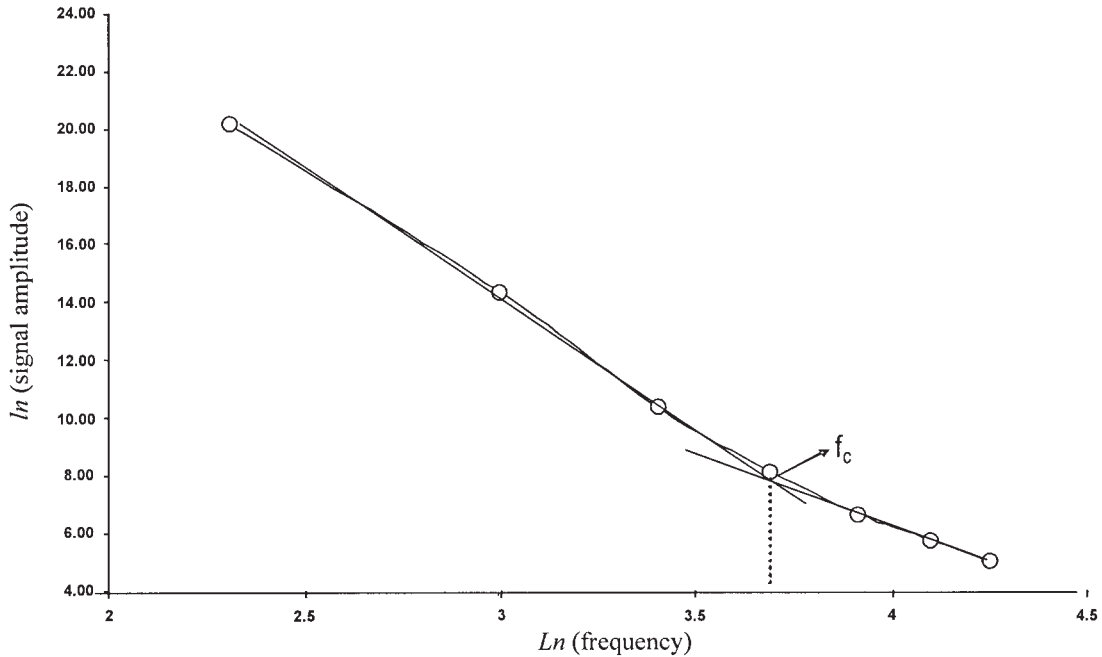


Figure 2 Finding f_c by plotting $\ln(\text{frequency})$ and $\ln(\text{signal amplitude})$.

mally 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.⁷ The characteristic frequency for all the 11 samples is found out by following the earlier procedure.

Now thermal diffusivity (α) is calculated from

$$\alpha = l^2 f_c \text{ m}^2/\text{s}^{-1} \tag{1}$$

Thermal diffusivity can also be calculated by measuring the phase of the PA signal for various chopping

frequencies. A graph is drawn between $\ln(\sqrt{2\pi f})$ and $\ln(\text{phase})$. The slope of this curve is related to thermal diffusivity as

$$\alpha = \frac{l^2}{(\text{slope})^2} \times \frac{1}{2} \text{ m}^2/\text{s}^{-1} \tag{2}$$

where l is the thickness of the sample. The method of finding α from amplitude measurements is shown in Figure 2 and the method of finding α from phase

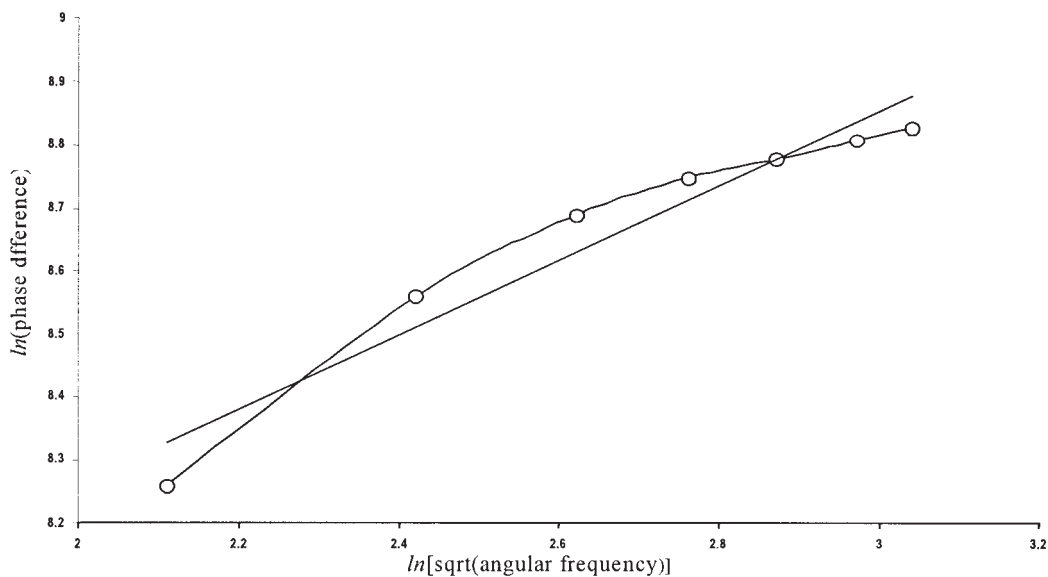


Figure 3 Finding slope by plotting $\ln[(\text{angular frequency})]$ and $\ln(\text{phase difference})$.

TABLE I
Thermal Diffusivity for Various Sonication Periods

| Power of sonication (W/cm^2) | Temperature ($^{\circ}C$) | Period of sonication (min) | Thickness of the sample (mm) | Characteristic frequency (Hz) | Thermal diffusivity (amplitude; $10^{-6} m^2 s^{-1}$) | Thermal diffusivity (phase; $10^{-6} m^2 s^{-1}$) |
|----------------------------------|-----------------------------|----------------------------|------------------------------|-------------------------------|--|--|
| 100 | 50 | 30 | 0.35 | 18.17 | 2.23 | 2.510 |
| 100 | 50 | 60 | 0.35 | 22.63 | 2.78 | 2.647 |
| 100 | 50 | 90 | 0.35 | 24.50 | 3.01 | 2.647 |
| 100 | 50 | 120 | 0.35 | 24.77 | 3.05 | 2.647 |
| 100 | 50 | 150 | 0.35 | 25.01 | 3.08 | 2.761 |
| 100 | 50 | 180 | 0.35 | 25.79 | 3.17 | 2.761 |
| 100 | 50 | 210 | 0.35 | 27.10 | 3.33 | 2.833 |
| 100 | 50 | 240 | 0.35 | 29.94 | 3.68 | 2.870 |
| 100 | 50 | 270 | 0.35 | 31.48 | 3.87 | 2.998 |
| 100 | 50 | 300 | 0.35 | 38.45 | 4.73 | 3.423 |
| 100 | 50 | 330 | 0.35 | 38.84 | 4.78 | 3.790 |

measurements is shown in Figure 3. The results are shown in Table I.

A graph is plotted between thermal diffusivity (physical property) and sonication period. This is shown in Figure 4. An analysis of the graph shows that the period of sonication from 45 to 200 min is the optimum period for the preparation of PMA since in this region thermal diffusivity of PMA seems to be stable which is of practical importance in rheology. The graph can be divided into three parts, the first from 5 to 45 min, second from 46 to 200 min, and third from 201 to 330 min.

The first may be due to the increase in molecular weight of the polymer since the rate of polymerization increases as sonication period is increased and then drops in general. Such a gradual increase in thermal diffusivity may be due to the changes in molecular weight.

During the sonication period (46–200 min) the change in molecular weight of the polymer formed may be slow and hence thermal diffusivity almost remains constant for this time interval and the addition of monomer units or depletion of monomer units may be in the same order.

For further period of sonication (above 200 min) if any depolymerization occurs, the monomer radical will be formed. This monomer radical may combine with the monomers present in excess to form a polymer of different kind, due to side reactions or crosslinking. Such a side reaction/crosslinking will definitely alter the molecular size, viscosity, thermal diffusivity etc., like any other physical property.

Such a crosslinking and chain reaction may occur and this may cause the changing trend in the physical property as in the case of PMMA and PS.⁸

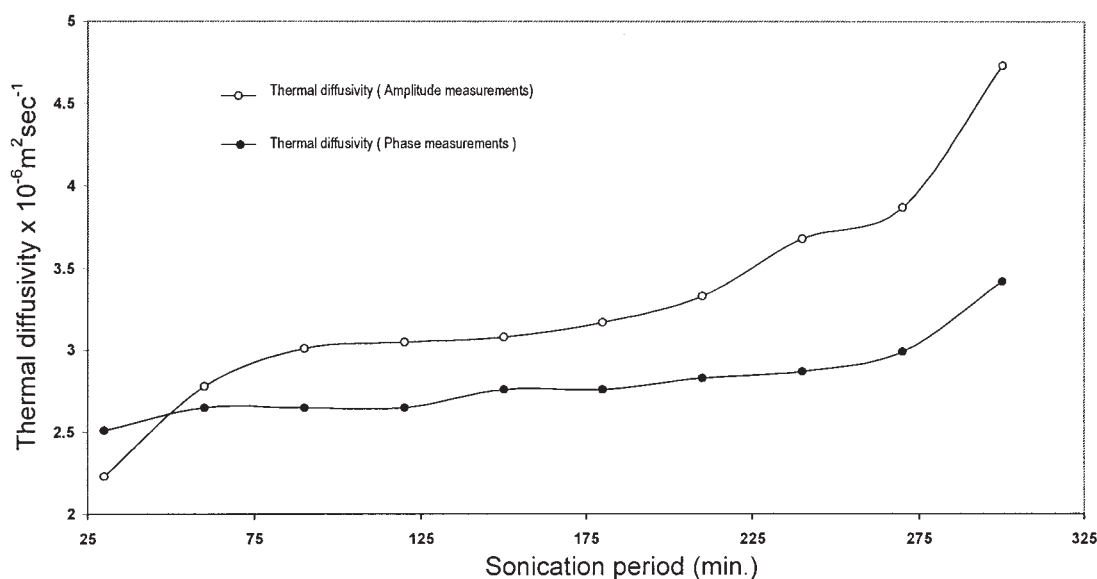


Figure 4 Variation of thermal diffusivity with sonication period.

TABLE II
Thermal Diffusivity from Other References

| Polymer | Process | Thermal diffusivity (m ² s ⁻¹) | Reference |
|---------------------------------------|-------------------------------|--|-----------|
| Polymer-carbon fiber composites | Modulated photothermal device | 6.0×10^{-6} | 9 |
| High-density polyethylene | Unsteady state technique | 2.05×10^{-7} | 10 |
| Polyvinylacetate/polyaniline solution | Thermal lens measurements | 1.05×10^{-7} | 11 |

The different monomer units from PMMA are involved and hence there is a change in the relative viscosity. Such a trend may also be possible here in our system, e.g., PMA generates methyl acrylate and/or macromonomer radical of different size, which will combine to give the polymer of different molecular size having different thermal diffusivity. This latter process may increase the rate of thermal diffusivity and hence the properties of the polymer.

The same trend is obtained in the graph between sonication period and thermal diffusivity when thermal diffusivity was calculated by PA phase measurements.

The thermal diffusivities calculated using amplitude (Fig. 4) and phase (Fig. 4) of the PA signal is given in Table I. The values of thermal diffusivity differs slightly because of the reason that in the graph of phase measurements is fitted to a straight line (Fig. 3) by least square fit and the best fit slope is taken for estimation of thermal diffusivity. The nonlinearity of the phase of the PA signal may be due to the frequency-dependent response of the microphone.

For the thermal conductivity κ is given by the formula

$\kappa = \text{specific heat capacity} \times \text{density} \times \text{thermal diffusivity}$.

In our measurements the density of the sample is of the same order of typical polymers, however, specific heat capacity is one order lower in magnitude but thermal diffusivity is one order higher in magnitude for typical polymers. But the thermal conductivity of the PMA sample is of the same order of magnitude for typical polymers. To justify the present PA measurement we report here the recently available thermal

diffusivity measurements for polymer-carbon composites,⁹ high density polyethylene,¹⁰ and poly vinyl acetate/poly aniline solution,¹¹ in Table II.

CONCLUSIONS

The PA measurement on thermal diffusivity of PMA is one of the nondestructive testing and evaluation methods complementary to the optical measurements. The results are encouraging and hence it is intended to study the thermal diffusivity of many polymers using the PA technique.

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