Heat Transfer in Poly(methyl acrylate) by Photoacoustic Measurements

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ABSTRACT: The thermal properties (thermal diffusivity, thermal effusivity, thermal conductivity, and specific heat capacity) of poly(methyl acrylate), which was obtained by ultrasonochemical polymerization, were measured experimentally with photoacoustic and other techniques. In addition, the thermal expansion of poly(methyl acrylate) was measured experimentally with an indigenously modified Fizeau's apparatus and is reported here for the first time to an accuracy of 0.05%. The results were compared with the available literature values and examined. Sinclare's apparatus was used to determine the specific heat capacity and matched well with differential scanning calorimetry measurements. The method-of-mixtures technique was an alternative method of determining the specific heat capacity. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1071–1076, 2004

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INTRODUCTION

Knowledge of the thermal conductivity (κ) and thermal expansion of polymers aids in the selection of a candidate for engineering applications, such as computers and automobile engines. The ability to transfer heat away from hot parts and allow them to cool makes a candidate useful. Similarly, wear and tear can be minimized when a suitable polymer is chosen to draw heat away from friction-heated parts. Expanded polystyrene (Styrofoam) and polyacetal are used in many applications in which thermal insulation plays a vital role. Engineering polymers typically used as materials in engines are evaluated for their insulating or conducting properties. The thermal effusivity (e) is the property that dictates the initial interfacial temperature when two semi-infinite bodies come into contact.

When such polymers are synthesized, ultrasound can initiate and activate the process. For example, potassium peroxodisulfate (PDS) has been used as a mild oxidizing agent[1] and as an initiator for the polymerization of vinyl monomers. PDS is used as a lone initiator for the polymerization of acrylamide.[2,3] PDS has also been used in a redox couple for vinyl polymerization.[4] Radicals capable of initiating polymerization are usually produced by thermal or photochemical decomposition of either the pure monomer or the added initiator component. The possibility of using ultrasound to initiate polymerization has been explored for the formation of polyacrylonitrile in aqueous solutions,[5] and Price et al.[6] used ultrasound to initiate the polymerization of methyl methacrylate (MMA). These studies have shown that ultrasound is an alternative method of initiation for vinyl polymerization and offers a great deal of control over the process. Ultrasonic initiation may produce polymers with predetermined structures and properties, such as the molecular weight, polydispersity, and tacticity. In the presence of ultrasound, the polydispersity is altered because of the following combined effects: enhanced molecular motion and the possibility of initiation occurring evenly throughout the system through mixing and producing more chains at the same rate.[7] High-frequency, low-intensity ultrasound has been used for following the course of polymerization reactions[8] and for monitoring conformational changes in polymers.[9]

The viscoelastic properties, optical properties, and thermal properties of poly(methyl methacrylate) (PMMA) synthesized by conventional methods have been reported in the literature.[10–15] Still, a complete

thermal study on poly(methyl acrylate) (PMA), including the thermal diffusivity (α), κ, the specific heat capacity (C_p), and the thermal expansion is lacking. Therefore, we report here our measurements on the aforementioned properties for the study of electrically conducting polymers. The photoacoustic (PA) technique is the simplest tool for studying the electrical conductivity and κ values of polymers. Also, e measurements are possible with this technique, and such studies are in progress for vinyl monomers.

The heat-transfer properties of polymer PMA (synthesized with an added initiator and very low power ultrasound) are reported here.

EXPERIMENTAL

Preparation and characterization of PMA

A solution of methyl acrylate (MA) and initiator PDS was prepared and then was characterized by bromometry[16] and iodometry after the initial cleaning and purification of the materials and the apparatus.

Polymerization was performed in a thermostable, double-walled metallic cell of an ultrasonic interferometer, which could provide ultrasound at a frequency of 1 MHz (with a measured power of 0.7 mW/cm^2) continuously to the reaction solution. MA (0.1M) was mixed with PDS (0.01M) in a ratio of 8:2 (the total volume was 10 mL) in a thermostable cell, and water was circulated through the outer jacket of the cell with a thermostat maintained at 30°C (with an accuracy of $\pm$ 0.1°C). The total volume of the reaction contents in the cell was 10 mL. Ultrasound of a predetermined frequency and intensity was continuously passed through the solution for a period of 45 min. Exactly at the end of 45 min, the reaction mixture was poured into pure methanol for precipitation. After a precipitation interval of 48 h, a semicrystalline, solid, semitransparent, nonconducting polymeric material (PMA) was obtained in the solution. The solid mass was filtered with a 0.45-μm filter and was washed with distilled water and dried under atmospheric air.

After the sample was prepared, the basic characterization was performed as follows.

Density (ρ) measurements

The ρ value of the PMA sample was determined by a floatation method with a mixture of p-xylene (ρ = 856 kg/m^3) and carbon tetrachloride (CCl$_4$; ρ = 1590 kg/m^3). p-xylene and CCl$_4$ were used because they are miscible and have very different ρ values. In a beaker, about 10 mL of CCl$_4$ was placed, and a PMA sample was added to this liquid; the mixture was stirred gently. The PMA sample was observed to determine if it completely sank or

floated on the surface. If ρ of the solution was equal to that of the sample, then it floated in the middle (level in the beaker) of the solution; that is, it neither sank nor floated. This liquid was placed in a specific gravity bottle for ρ measurements. Thus, ρ of the PMA sample was found to be 1187 kg/m^3.

Because the exact number of repeat monomer units of PMA is not known, this floatation method is ideal for ρ measurements.

Differential scanning calorimetry (DSC) measurements

Even though the specific heat of the PMA sample could be measured with the method of mixtures, an accurate way of the estimating specific heat was DSC. DSC measurements from 20 to 110°C are shown in Figure 1. At 47.33°C, there was a maximum heat flow of 1054 J/kg. The area enclosed by this graph of the flow of heat versus the temperature provided the enthalpy. Taking two such temperature intervals, T_1 and T_2, we could determine enthalpies H_1 and H_2 with the graph. The change in the enthalpy, at a constant pressure, provided the internal energy (U). From the DSC spectrum, C_p of the PMA sample was determined as follows:

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P \tag{1}$$

where T is the absolute temperature and p is constant pressure.

C_p was found to be 101.72 J kg^{-1} K^{-1}.

C_p of the PMA sample was also determined by the method of mixtures with Sinclare's apparatus, the maximum accuracy being obtained with Barton's radiation correction. The C_p value obtained with this method (101.92 J kg^{-1} K^{-1}) agreed well with the DSC measurement.

The purified PMA was sliced into thin wafers with a maximum size of 2 mm $\times$ 2 mm $\times$ 0.45 mm. The sample was then ready to be investigated by the PA technique.

PA measurements

The principle of PA spectroscopy is that a fraction of incident chopped optical radiation, absorbed by a 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
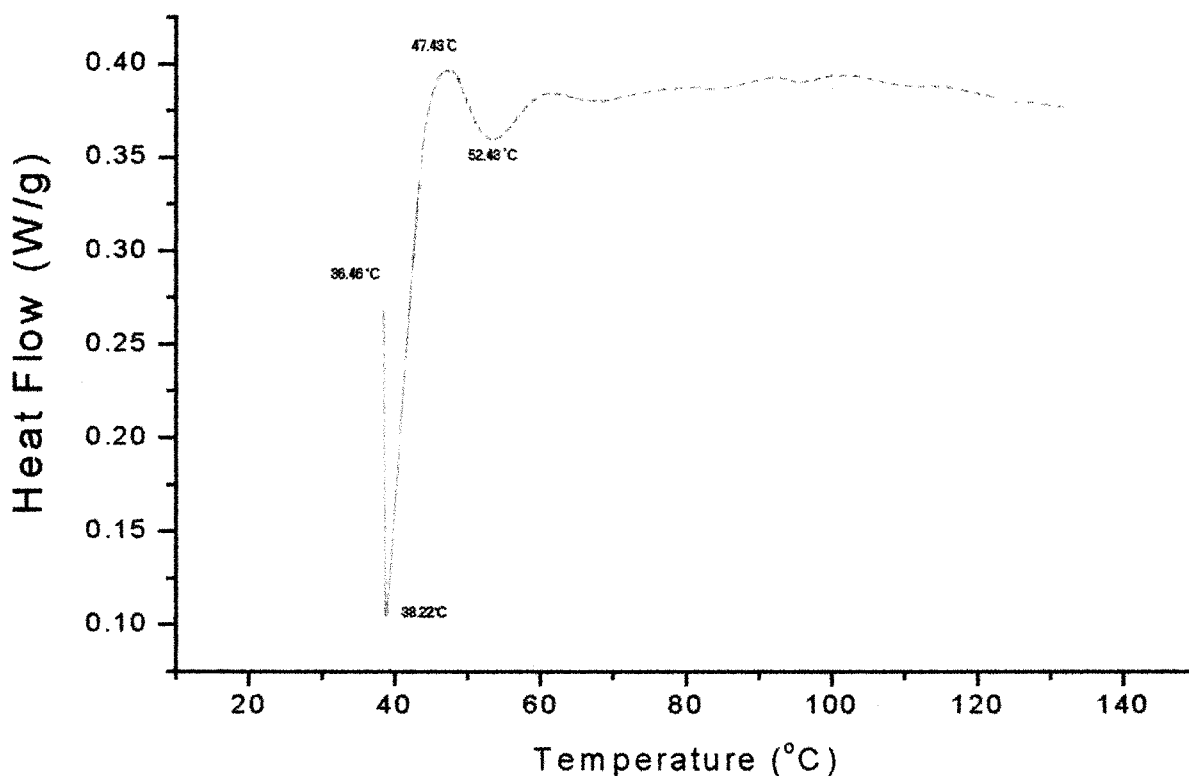
Figure 1 DSC spectrum of PMA.

theoretical and experimental studies,[17,18] particularly with respect to electrically conducting polymers. PA measurements for the determination of κ, 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, a PA cell (model 601-1, EG&G), a condenser microphone, a lock-in amplifier (model 7225, EG&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 wafer 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. This experimental setup is shown in Figure 2.

RESULTS AND DISCUSSION

The PA spectra of the PMA sample were recorded in the following two ways.

Depth profile analysis

The wavelength was fixed, and the chopping frequency was varied. The data are plotted in Figure 3.

Figure 3 shows that when the chopping frequency was varied for the opaque PMA sample, there was a peak around 20 Hz. This was the point at which the PMA sample changed from being thermally thin to being thermally thick; that is, the PA signal varied as the reciprocal of the frequency with the chopping frequency after this peak as required for a thermally thin sample.[19,20] This frequency is called the characteristic frequency (f_c), and we estimated it to be 20 Hz for this PMA sample.

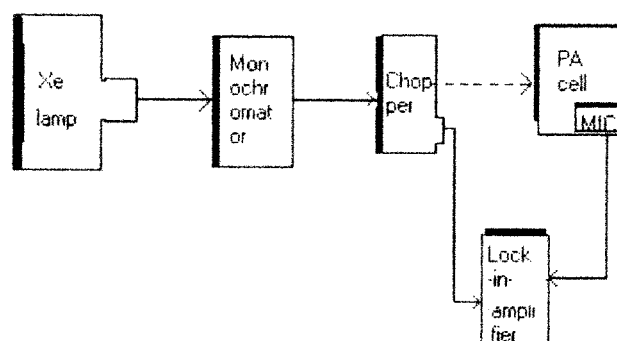Because the PA signal amplitude was measured through the tracing of the waveform obtained in the

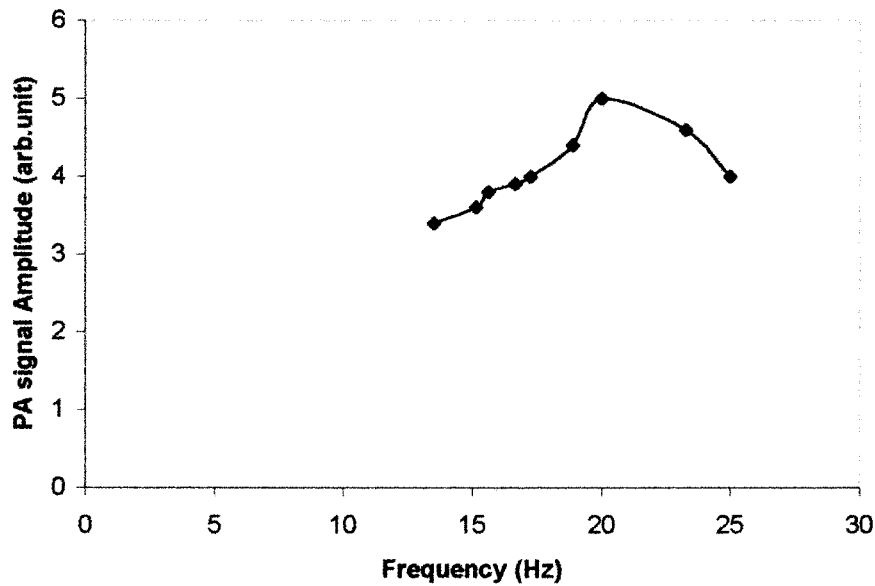**Figure 2** Schematic diagram of the PA experimental setup.

Figure 3 Dependence of the PA signal amplitude on the frequency.

DSO, the experimental error was ±2%, and so the peak was as shown in Figure 3.

α was then calculated as follows:

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

where l is the thickness of the sample.

Knowing C_p, ρ, and α of the sample, we could calculate κ and e as follows:

$$\kappa = \alpha \rho C_p (W \ m^{-1} \ K^{-1}) \qquad (3)$$

$$e = \sqrt{\kappa \rho C_p} (W \ s^{1/2} \ m^{-2} \ K^{-1}) \qquad (4)$$

where κ is thermal conductivity.

Wavelength scanning

The chopping frequency was fixed, and the wavelengths were varied. The spectrum is given in Figure 4. The nature of the curves confirms that PMA was a thermally nonconducting polymer.
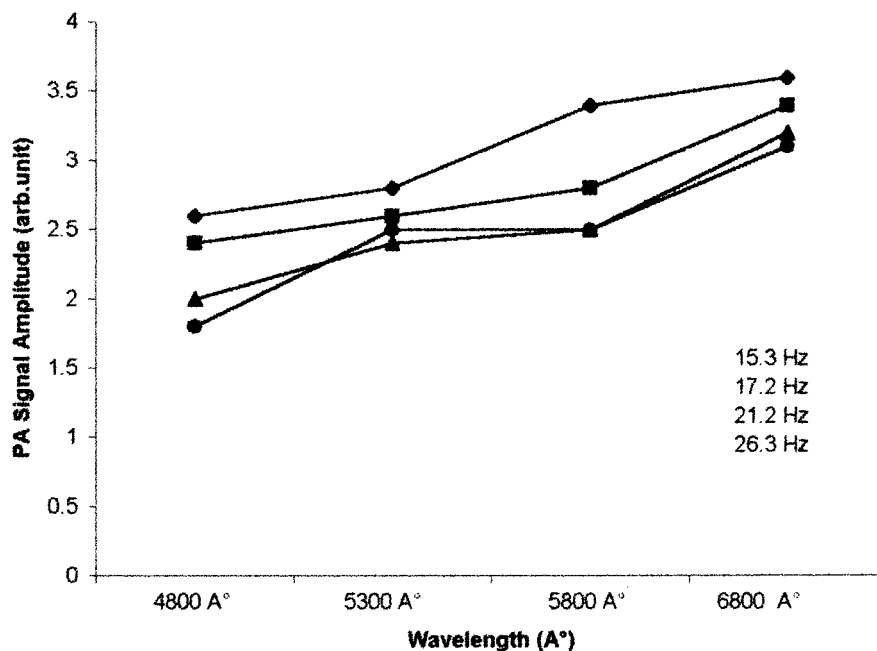

Figure 4 Dependence of the PA signal amplitude on the wavelength.

TABLE I
Thermal Data Obtained for PMA by the PA Technique and from Other Sources

Sample	Thickness (μg/μm)	f_c Hz	α (m^2 s)	κ (W m^{-1} K^{-1})	e (W s$^{1/2}$ m^{-2} K^{-1})	Reference
PMA	300	20	1.8×10^{-6}	0.2173	161.98	This work
PMMA	0.40	—	—	0.16	—	21
Polymer–carbon fiber composites	175	—	25 $\times 10^{-6}$	—	—	22
Acetal resin homopolymer	5000	—	—	—	492	23
PMMA acrylic	—	—	—	0.17	—	24

The curves were analyzed for α, κ, and e, and the results are given in Table I.

As mentioned earlier, no such thermal measurements have been reported in the literature for PMA. To justify these PA measurements, we report here the available thermal measurements for PMMA, polymer/carbon-fiber composites, and an acetal resin homopolymer obtained by techniques other than the PA technique (Table I).

κ can be obtained as follows:

$$\kappa = \text{Specific heat capacity}$$
$$\times \text{Density} \times \text{Thermal diffusivity.}$$

In our measurements, ρ of the sample was of the same order as that of typical polymers, but C_p was one order lower in magnitude and α was one order higher in magnitude than those of typical polymers. However, κ

of the PMA sample was of the same order of magnitude as that of typical polymers.

The orders of magnitude for κ and e for the PMA sample were the same as those of PMMA and other similar polymers. This confirmed our measurements for PMA by the PA method.

Thermal expansion

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 5.
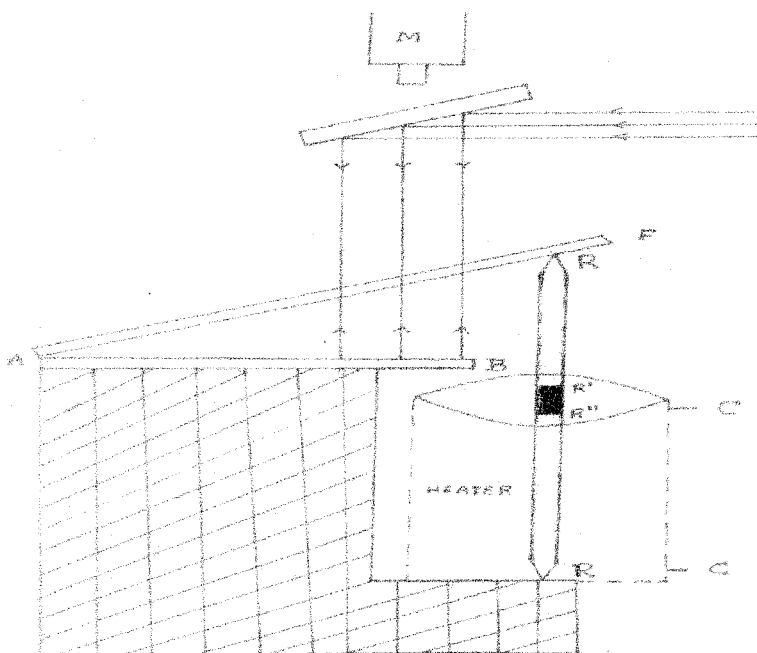

Figure 5 Fizeau's apparatus.

TABLE II
Evaluation of the Thermal Expansion Coefficient of PMA by Fizeau's Method

Trial	Temperature (°C)	Thermal expansion coefficient $\times 10^{-6}$ (°C)
1	45	72.31
2	55	77.38
3	65	73.23
4	75	79.53

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 5. 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:

Linear expansivity

$$= \frac{\text{Increase in length}}{\text{Initial length} \times \text{Rise in temperature}} \quad (5)$$

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:

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

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 $\times$ 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 $75.61 \pm 0.03 \times 10^{-6}$/°C. The literature value for the thermal expansion coefficient for PMMA was 70×10^{-6}/°C.[24] Proper corrections for the expansion of the carbon rod were carried out.

CONCLUSIONS

To the best of our knowledge, PA measurements for PMA (obtained by ultrasonochemical polymerization)

with respect to its thermal properties have been reported here for the first time. To check the correctness of the C_p value measured by DSC, we adopted the method-of-mixtures technique, and the two values agreed well. The thermal expansion coefficient for the PMA sample was determined with Fizeau's method to an accuracy of $\pm 0.05\%$ and has been reported here for the first time. The calculated thermal expansion coefficient for the PMA sample was of the same order as the already reported value for PMMA. These results for PMA are the first in the literature. We are also continuing our efforts in reporting similar results for other nonconducting polymers.

References

1. Ponnuraj, V.; Ramachandran, M. S.; Vivekanadam, T. S.; Chandra Singh, U. Bull Chem Soc Japan 1978, 51, 460.
2. Riggs, J. P. Am Chem Soc Div Polym Chem 1956, 6, 207.
3. Riggs, J. P.; Rodrigues, F. J Polym Sci 1967, 5, 3151.
4. Gopalan, A.; Paulrajan, S.; Subbaratnam, N. R. Venkatrao, K. J Polym Sci Polym Chem Ed 1985, 23, 1861.
5. Heglein, A. Makromol Chem 1954, 14, 14.
6. Price, G. J.; Norris, D. J.; West, P. J. Macromolecules 1992, 32, 6447.
7. Price, G. J.; Hearn, M. P.; Wallace, E. N. K. Polymer 1996, 37, 2303.
8. Pethrick, R. A. J Macromol Sci Rev Macromol Chem 1973, 9, 91.
9. Zana, R. J. J Macromol Sci Rev Macromol Chem 1975, 12, 165.
10. Mckenna, G. B.; Zapas, L. J. J Rheol 1979, 23, 151.
11. Fahrlander, M.; Bruch, M.; Menke, T.; Mulhaupt, R.; Friedrich, C. Rheol Acta 2001, 40, 1464.
12. Radhakrishnan, E.-S. Opt Fibre Technol 1996, 2, 114.
13. Berghmans, F.; Nasilowski, T. J Lightwave Technol 1998, 16.
14. Cahill, D.; Pohl, P. O. Phys Rev B 1987, 35, 4067.
15. Govorkov, S.; Ruderman, W.; Horn, M. W.; Goodman, R. B.; Rothschild, M. Rev Sci Instrum 1997, 68, 3828.
16. Mino, G.; Kaizermann, S.; Rausmussen, E. J Polym Sci 1959, 38, 393.
17. Reosencwaig, A.; Gersho, A. J Appl Phys 1976, 47, 64.
18. Dias, D. T; Medina, A. N.; Baesso, M. L.; Bento, A. C.; Porto, M. F.; Muniz, E. C.; Rubira, A. F. Rev Sci Instrum 2003, 74, 325.
19. Ganguly, P.; Rao, C. N. R. Proc Indian Acad Sci (Chem Sci) 1981, 90, 164.
20. Rosencwaig, A. J Appl Phys A 1978, 49, 2905.
21. Chu, D.; Touzelbaev, M.; Goodson, K. E.; Babin, S.; Pease, F. R. J Vac Sci Technol B 2001, 19, 2874.
22. Salazav, A.; Sanchez-Lavega, A. Presented at the 13th Symposium on Thermophysical Properties, Boulder, CO, June 22–27, 1997.
23. Riga, A.; Chandler, C.; Mathis, N. Heart Transfer Properties of Engineering Plastics by Effusivity Measurements; Mathis Instruments: Fredericton, Canada, 1998.
24. http://www.goodfellow.com/Technical Data/Thermal Properties, PMMA, Acrylic; For additional information: info@goodfellow.com; Materials, Cambridge Science Park, Cambridge CB4 4DJ, UK.