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Determination of the thermophysical properties of polymers (PET) using photoacoustic spectroscopy

J. P. VALCÁRCEL M.
Universidad Surcolombiana, A.A. 385, Neiva, Colombia S.A.
J. PALACIOS A.
Facultad de Química, Universidad Nacional Autónoma de México, México D.F., 04510
J. J. ALVARADO-GIL
Departamento de Física Aplicada, CINVESTAV-IPN, Unidad Mérida, Yucatán, México, 97310
E-mail: jjag@kin.cieamer.conacyt.mx

Using photothermal techniques and the Open Photoacoustic Cell (OPC) we measure thermophysical properties, such as thermal diffusivity, thermal conductivity, and heat capacity per unit volume of 5 polymer foils, poly(ethylene terephthalate) PET, of different molecular weights. It is shown that the physical properties influence strongly the thermal ones, and that photoacoustics can be used as a monitoring technique in the application of polymers. © *1999 Kluwer Academic Publishers*

1. Introduction

Photoacoustic (PA) spectroscopy looks directly at the heat generated in a sample, due to non-radiative de-excitation processes, following the absorption of light [1]. The common element in all these processes is that "heat" is produced by interaction of the incident beam with a sample. The absorption of the beam and subsequent de-excitation-relaxation give rise to a heat source that may be distributed throughout a large region of the sample or confined to a small region such as the surface of an opaque solid; the source may be periodic, or pulsed, generating corresponding (periodic or pulsed) thermal and acoustic fields. Detection schemes may be sensitive to the thermal fields or to the acoustic field or both [1, 2]. The purpose of this work is to measure, using the photothermal techniques and the open photoacoustic cell (OPC) configuration, the thermal parameters of polymeric samples. The general term, thermal properties includes a wide range of properties and phenomena [2, 3, 4]. In this work the discussions are confined to find three of the most important thermal or thermophysical parameters such as thermal diffusivity, thermal conductivity, and heat capacity per unit volume, of five poly(ethylene terephthelate) (PET) materials mainly used as food or liquid containers.

2. Instrumentation and materials

The five PET samples under investigation, each having different physical-chemical properties such as crystallinity, chips per gram, and viscosity, were produced in the Laboratorio de Química Macromolecular-UNAM, and identified with the abbreviations M1, M2, M3, M4, and M5, respectively. This material was initially manufactured as tiny pellets and it was necessary to convert to films. To do this, we melted 7 of these pellets between two hot aluminum plates, and then, under a pressure of 10 kg, the final film thickness was 400 μm. Next, each sample was polished in a Buelher polisher/grinder machine using a 600 sandpaper. The films were finally cut, obtaining 350 μm thick 10×10 mm squares.

The experimental arrangement for the thermal diffusivity measurements using the OPC method is similar to the one described by Marquezini *et al.* [5] and Espinoza-Beltran *et al.* [6]. It consists on mounting the specimen directly onto a cylindrical microphone and using the front air chamber of the microphone itself as the usual gas chamber of conventional photoacoustics. In our case the light source used for optical excitation of the samples was a 20 mW He-Ne laser (Oriel Model 79312). A light chopper (SRS, Model SR540), was used to modulate the laser beam in the range from 15 to 300 Hz. The output signal of the photoacoustic cell, was further filtered through passage from an SR850 DSP model lock-in amplifier-band-pass filter. A PC was interfaced to the experimental setup with the aid of a Data Translation analog-digital converter, and the cross correlations were performed digitally.

3. Theory

We have monitored the thermal diffusivity (α) of our polymers using the OPC technique. Thermal diffusivity is the quantity that measures the rate of diffusion of heat in a material [7, 8]. Physically, the inverse of α is a measure of the time required to achieve thermal equilibrium in a given material. Apart from its own intrinsic importance, its determination provides the value of the thermal conductivity κ, if the density ρ, and the heat capacity at constant pressure C_p, are known $\kappa = \alpha\rho C_p$.

According to the Rosencwaig and Gersho theory applied in the case of the OPC [1], in the case of a sample of thickness l and thermal diffusivity α, the photoacoustic signal for an opaque sample follows the equation

$$S = \frac{A}{f}\exp(-af^{1/2}) \qquad (1)$$

for a thermally thick sample, that is to say the sample thickness (l) is much larger that the heat diffusion length (μ) given by $\mu = \sqrt{\alpha/(\pi f)}$. Where f is the modulation frequency of the incident beam, $a = (\pi l^2/\alpha)^{1/2}$ and A is a constant. We thus have two adjustable parameters A and a to describe the PA monitoring of the thermal diffusivity of the sample. In our case to make sure that the opaqueness condition implicit in Equation 1 is fulfilled, we attached a thin circle of aluminum foil (20 μm thick and 5 mm in diameter) to the front of the sample using a thin layer of thermal paste.

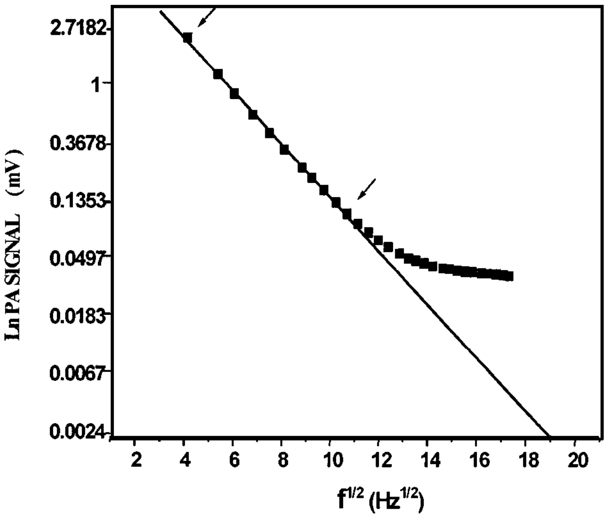

Figure 1 OPC amplitude as a function of the modulation frequency for M5 sample. The arrows show the frequency range where the sample is thermally thick, the continuous line represents the best fit of the experimental data to Equation 1.

Fig. 1 shows a typical plot of the Log of the amplitude of the PA signal vs. the square root of the modulation frequency. The continuous line represents the best fit of the experimental data to Equation 1, in the thermally thick regimen.

The heat capacity per unit volume, ρC_p, was measured using the temperature rise method, under continuous white-light illumination. This technique is based on the one used in [9] and is well described in [7]. In this method, both sample surfaces are sprayed with black paint in order to guarantee black body absorption and radiation conditions and to assure the same heat transfer coefficient for each side of the sample. The samples are then adiabatically suspended in a Dewar which is subsequently vacuum sealed. Under these conditions the main heat loss mechanism is by radiation. The Dewar has an entrance glass window through which the continuous white light is focused onto one of the sample surfaces. A thermocouple which is attached with thermal paste on the opposite surface of the sample monitors the temperature evolution of the back surface as a function of the time. Solving the one dimensional heat diffusion equation [10] it has been shown that the back surface temperature rise is given by

$$\Delta T = \left(\frac{I_o \alpha \tau}{l\kappa}\right)[1 - \exp(-t/\tau)] \qquad (2)$$

where I_o is the intensity of the incident light beam and $\tau = \frac{l\rho C_p}{2H}$ is the rise time. Here $H = 4\sigma T_o^3$, where σ is the Stefan-Bolztmann constant, T_o is the ambient temperature, and H is the radiation transfer coefficient. τ is determined by fitting the experimental results to Equation 2. The thermal conductivity κ is readily obtained from the previously determined value of α, using the relationship $\kappa = \alpha\rho C_p$.

In Fig. 2 we show the back surface temperature as a function of time for M5 polymer; the heating curve (a), corresponds to the case when the light is on, following Equation 2. The cooling curve (b) corresponds to the case when the light is off.

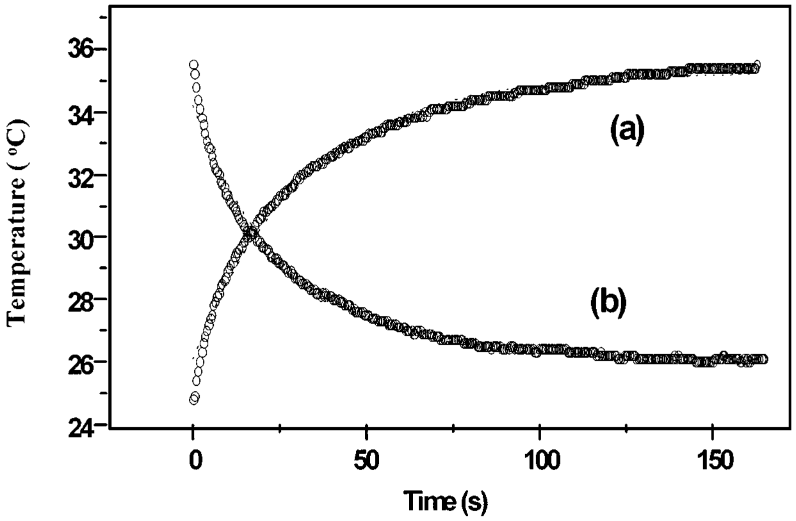

Figure 2 Back surface temperature evolution for a M5 polymer sample. Curve (a) corresponds to the situation when the light is on, and curve (b) when the light is off.

TABLE I Values of thermal and physical properties of polymers (PET) M-1, M-2, M-3, M-4, and M-5. % Deg represents the percent of residual monomers of ethylene glycol. The density in g/cm^3 is obtained by the Density Gradient method. Apparent density represents the weight in grams of chips of polymer in 1 cm^3. Chips/g is the number of solid particles per gram. % Powder is the percent of powder PET in a sample of chips

Parameter	M-1	M-2	M-3	M-4	M-5
Viscosity η (Ns m^{-2})	0.705	0.733	0.800	0.805	0.820
% Deg	1.75	2.8	1.41	2.80	1.70
Fusion point (°C)	252	251	251	251	252
Density (g/cm^3)	1.405	1.397	1.397	1.415	1.397
Apparent density (g/cm^3)	0.898	0.895	0.875	0.860	0.889
% Powder			0.08		0.005
Chips/g	44	40	52	34	79
Molecular weight × 10^4	2.84	2.99	3.38	3.4	3.49
Conductivity κ (J s^{-1} cm^{-1}K^{-1} · 10^{-4})	11.53	12.92	28.8	11.76	32.24
Crystallinity (%)	59	52	52	67	52
Diffusivity α (cm^2 s^{-1} · 10^{-4})	6.48	6.84	24	8.4	24.8
H.Cap/Vol ρC_p (J cm^{-3} K^{-1})	1.78	1.89	1.2	1.4	1.3

4. Results and discussion

Table I shows the values of the thermophysical parameters as well as some of the most important physical-chemical properties such as viscosity, chips per gram, molecular weight, etc., since the thermal behavior of each material depends on its corresponding physical properties. The values are tabulated in increasing order of the intrinsic viscosity. This was calculated from the Mark-Houwink-Sakurada equation: $[\eta] = KM_{\text{vis}}^{a}$. Other values of poly(ethylene terephthalate) PET are found under the name poly(oxyethileneoxyterephthaloyl) in reference [13].

To find the best correlation between the thermal parameters and the thermophysical characteristics of our samples, we plot the corresponding values of thermal conductivity, thermal diffusivity and heat capacity per unit volume with those of intrinsic viscosity, chips/g, and molecular weight.

In Fig. 3, we show the thermal conductivity κ as a function of the intrinsic viscosity $[\eta]$, for materials M1, M2, M3, M4, and M5. We can see in this figure that thermal conductivity increases as the viscosity increases. In particular, the M5 sample presents the largest value of thermal conductivity, $\kappa = 32.24 \cdot 10^{-4}$ Js^{-1} cm^{-1} K^{-1}.

In Fig. 4 we present the thermal conductivity against the number of chips per gram plotted for all the samples. As can be seen in this figure, as well that in the case of the viscosity, we observe an increase in thermal conductivity when chips number is increased. This is in accordance with the quantitative idea of heat transport phenomena, that is to say, the larger the number of particles, then the heat conduction is better.

In Fig. 5, we show that the thermal conductivity κ, of the polymers increases as the molecular weight of the sample increases.

From Figs 3, 4 and 5 we can establish that the thermal conductivity depends strongly on the physical-chemical parameters of intrinsic viscosity, number of chips per gram, and molecular weight, showing in nearly all the cases an increase when the physical-chemical parameter increases.

Fig. 6 shows that the thermal diffusivity increases considerably, when the intrinsic viscosity is increased. A great difference between the values of α for the

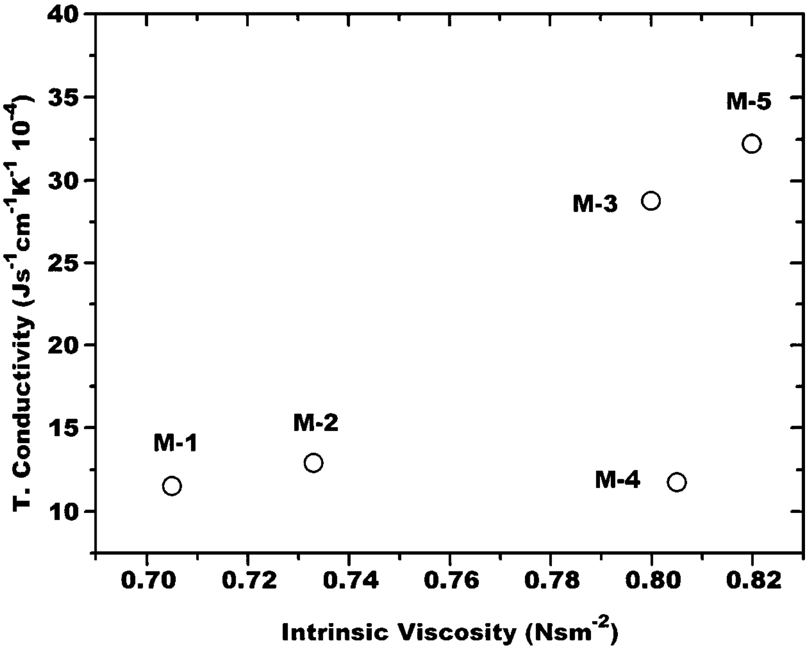

Figure 3 Thermal conductivity as a function of the viscosity for the five polymers.

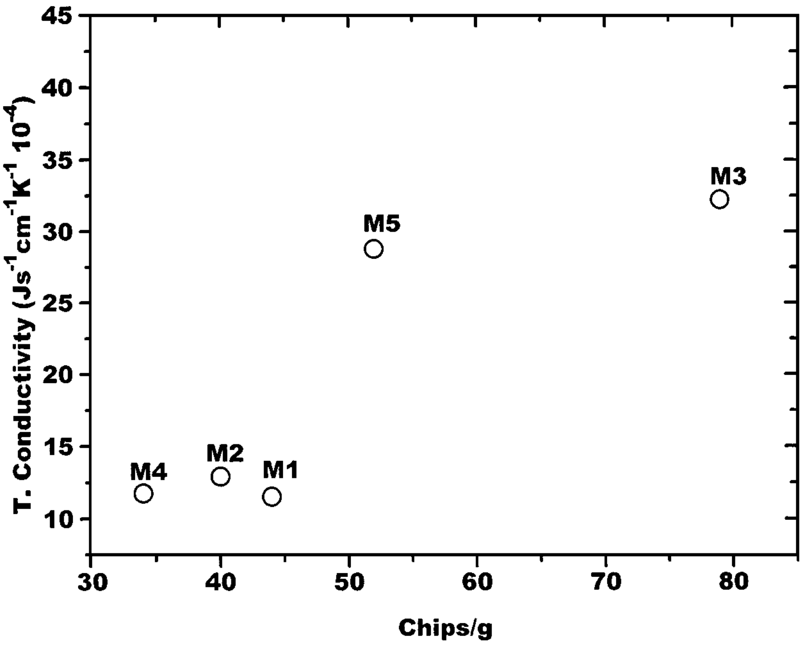

Figure 4 Thermal conductivity as a function of the number of chips per gram of the polymers.

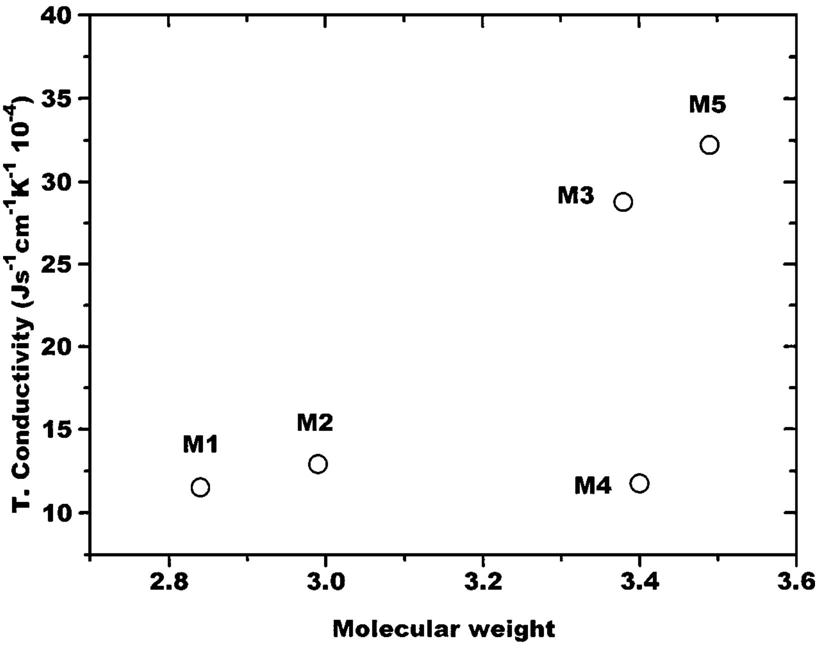

Figure 5 Thermal conductivity as a function of the molecular weight of the polymers.

samples M1, M2, M4, and the ones for M3 and M5 can be observed.

Fig. 7 shows the tendency of the thermal diffusivity of our polymeric samples to increase when the number of chips/g increases. This can be understood if we remark that the exposed area of the material is larger when we reduce the diameter of the particles, that is, when we increase the number of particles. In an analogous way, we show in Fig. 8, that the thermal difussivity is also increased when the molecular weight is increased.

From Figs 9, 10, and 11 we can see that these polymers have the tendency to reduce their ρC_p values as the intrinsic viscosity, number of chips/g, and their corresponding molecular weight, increase. These results are in good agreement with the theoretical predictions [8, 9, 10], given that the thermophysical properties depend directly on density, molecular weight, and other configuration factors of the polymer (i.e., the crystallinity).

We can see from Figs 10 and 11, that polymers M3 and M5 have lower values of ρC_p while their thermal conductivity and thermal diffusivity are larger, when compared to the reported in references [8, 12]. However the differences that could be found are a consequence of the differences in the physical characteristics such as molecular weight, degree of crystallinity, or orientation.

Comparing the thermophysical properties with those of physical properties of the polymers as viscosity,

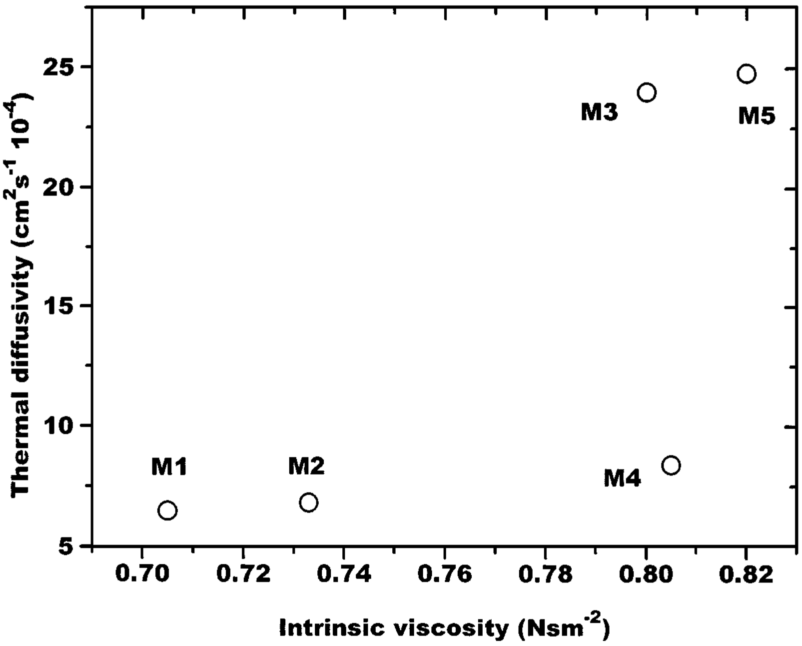

Figure 6 Thermal diffusivity as a function of the intrinsic viscosity of the polymers.

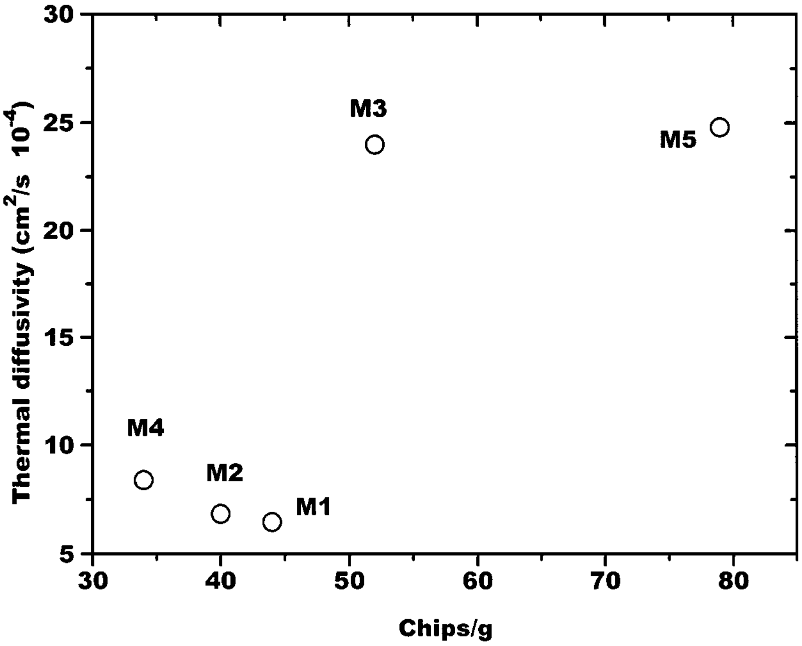

Figure 7 Thermal diffusivity as a function of the number of chips per gram of the polymers.

density, and crystallinity as can be seen in Table I, we can infer that: Samples M1, M2, and M4 have the following behavior:

(a) *As a function of their viscosity*: These materials have small thermal diffusivity and conductivity, while the heat capacities per unit volume (ρC_p) are higher. We observe a tendency for these values to diminish when the viscosity is decreasing.

(b) *As a function of their density*: These materials show small thermal diffusivity and conductivity, while their ρC_p is higher, with a tendency to decrease ρC_p when its density diminishes.

(c) *As a function of their crystallinity*: We also observe that thermal diffusivity and conductivity are small and that ρC_p is higher, with a tendency to decrease when the density decreases.

On the other hand, polymers M5 and M3 present the following behavior:

(a) *As a function of their viscosity*: These materials have a large thermal diffusivity conductivity, while ρC_p values are low, with a tendency to increase ρC_p when their viscosity raises.

(b) *As a function of their density*: These materials show a large thermal diffusivity and conductivity, while ρC_p has a low value, with a stable behavior of ρC_p when their density changes.

(c) *As a function of their crystallinity*: They have large thermal diffusivity and conductivity, while ρC_p has low values with a tendency to increase ρC_p as their crystallinity increases.

According with our results, polymeric samples M1, M2, and M4 take longer periods of time to heat or cool,

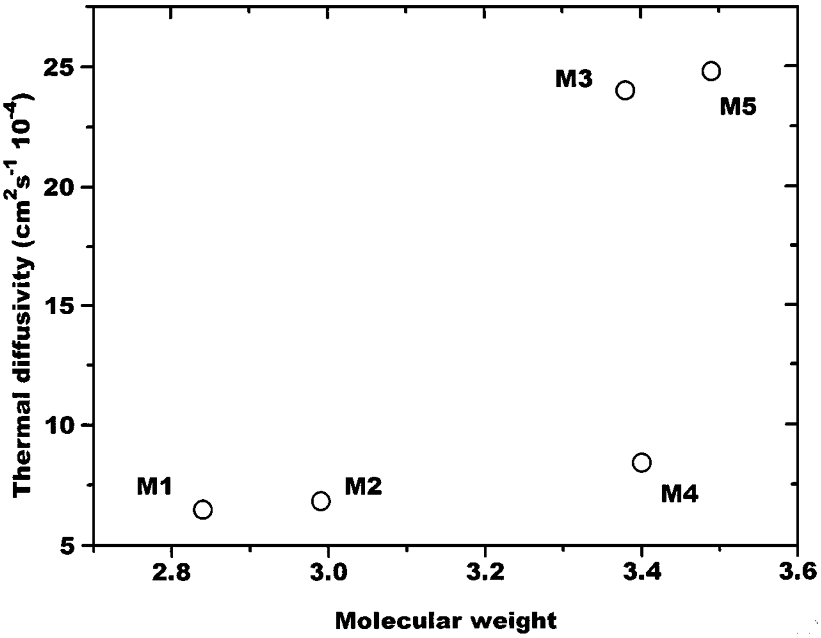

Figure 8 Thermal diffusivity as a function of the molecular weight of the polymers.

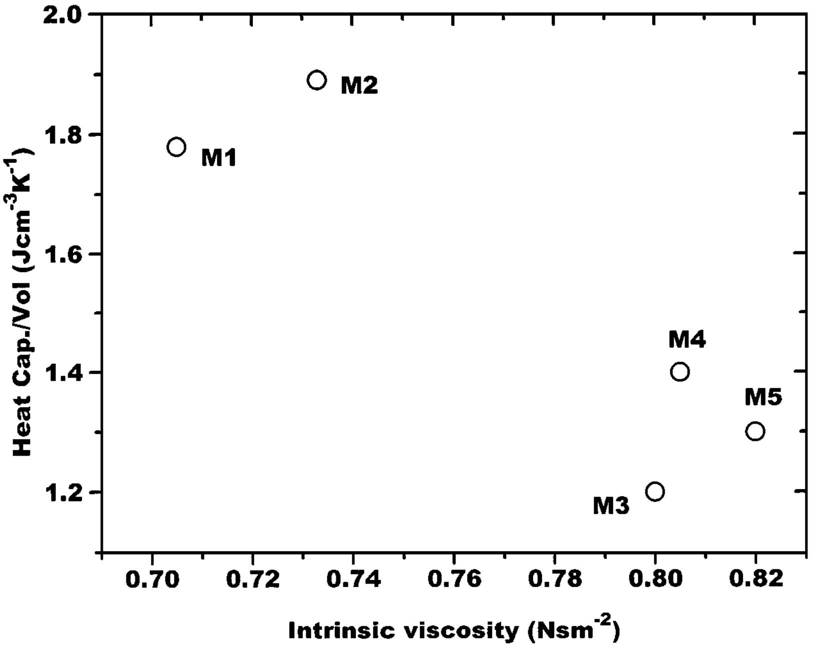

Figure 9 Heat capacity per unit volume as a function of the intrinsic viscosity of polymers.

but they remain hot for a longer period, whereas the polymers M3 and M5 heat up or cool down very fast. Materials like M3 and M5 diffuse the heat faster, so they could be good in applications where it is not necessary to maintain hot or cold conditions for a long time. These conclusions assure us, that if we need to keep any solid or liquid hot or cold for a long time, it is necessary to use containers made of M1, M2, or M4 materials.

Nevertheless, materials such as M3 and M5, that diffuse heat rapidly, would be appropriate for those manufacturing processes in which are important to consider reductions in energy consumption, costs, and time saving in melting huge quantities of these materials. This, of course, leads to save fuel, time, and energy to melt the polymers and obtain the desired final shape. That is to say, there is an important relationship among the thermal properties, and energy consumption in these processes, uses of the final products, equipment, and manufacturing techniques.

Our results are in agreement with those thermophysical characteristics obtained for M3 and M5 polymers, noticing that their high thermal conductivity and diffusivity are consequent with their molecular weight, grade of crystallinity, and viscosity.

In conclusion we have shown that photothermal techniques are very useful and reliable to characterize the thermal properties of polymer samples. These results are particularly important in the practical applications such as the manufacture of drink containers or bottles.

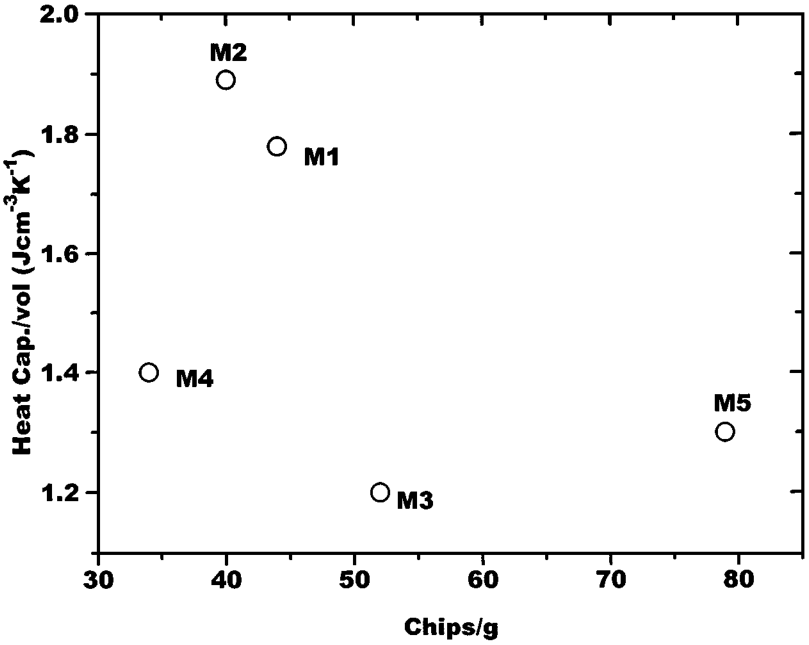

Figure 10 Heat capacity per unit volume as a function of the number of chips per gram of polymers.

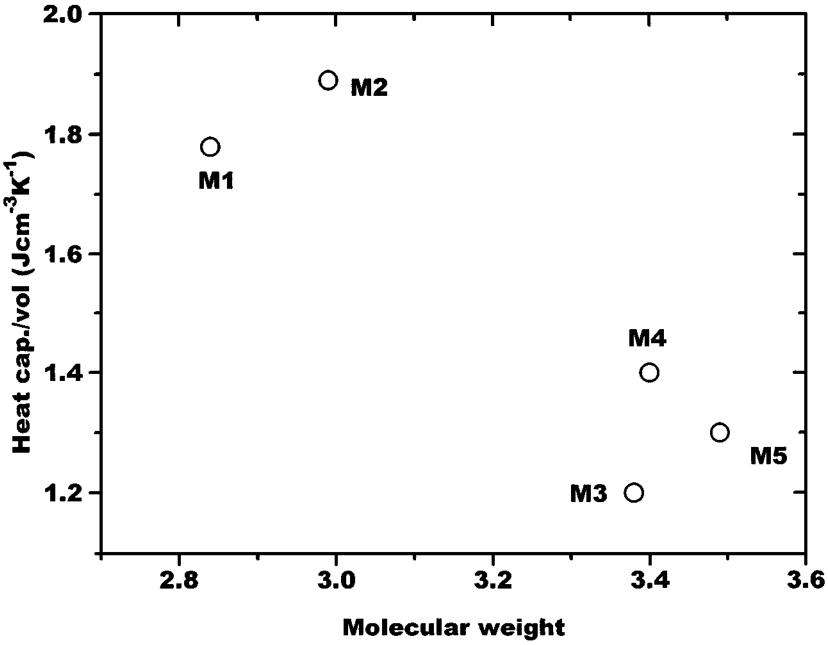

Figure 11 Heat capacity per unit volume as a function of the molecular weight of polymers.

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