In this work thermal lens spectrometry is applied to investigate the thermo-optical properties of polymers as a function of temperature. The method is applied in poly(vinyl chloride) as a testing sample. It is proposed that thermal lens spectrometry with minor change in its experimental configuration, could be adapted to develop a new tool, called differential thermal lens scanning, especially designed for the investigation of phase transition in polymers.

Keywords: Thermal lens method, glass transition, poly(vinyl chloride), thermo-optical properties, glass transition.

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In the last two decades we have witnessed the development of a number of techniques for non-destructive characterization of the thermal, optical and structural properties of materials based upon the photothermal techniques [1, 2]. Despite this growing interest and the importance of the applications of these techniques to the polymer area [3, 4], so far the photothermal measurements have been carried out mostly at near room temperature conditions. This apparent limitation is essentially dictated by the fact that most of the photothermal polymer measurements reported so far were based upon the use of the photoacoustic technique. The use of an electret microphone, in a conventional photoacoustic, is the main reason why applications to polymers have been restricted to near room temperatures.

In this work we discuss the use of an alternative photothermal technique for measurements of the thermo-optical properties of polymers as a function of temperature. The proposed technique is based upon the use of the thermal lens (TL) technique [5]. The room-temperature TL technique has been proved to be a valuable method for investigating not only the complete thermal and spectroscopic properties of transparent materials, such as, glasses [6-12], liquid crystals [13, 14] and polymers, but also for the sensitive monitoring of the kinetics of fast chemical reactions [15], percolation in microemulsions [16], and dynamics of water-surfactant interaction [17]. Since the TL technique is an intrinsically remote technique the measurements on a sample placed inside a harsh environment presents, in principle, no extra difficulty. It is precisely this aspect we take advantage of to carry on the thermal properties measurements of polymers as a function of temperature.

**Experimental**

In the two beam arrangement the TL effect is created when an excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the refractive index of the sample and therefore producing a lens-like element within the sample. The propagation of the probe beam laser through the TL results in either a defocusing (dn/dT < 0) or a focusing (dn/dT > 0) of the beam center. The theoretical treatment of the TL effect considers the aberration of the thermal lens as an optical path length change to the probe laser beam, which can be express as an additional phase shift on the probe beam wave front after its passing through the sample. The analytical expression for absolute determination of the thermo-optical properties of the sample is given by [6-14, 18]:

\[ I(t) = I(0) \left[ 1 - \frac{\theta}{2 \tan \omega T} \right] \left[ \frac{2mV}{(0+2m)^2 + V^2} V_{c} \right] \left[ \frac{n_c}{2} + 1 \right] \]

Where

\[ \theta = -\frac{P_e \omega_0}{2\pi} \left( \frac{\partial n}{\partial T} \right)_p \]

\[ V = \frac{Z_1}{Z_c} \]

\[ m = \left( \frac{\omega_p}{\omega_e} \right)^2 \]

\[ V_c = \frac{a_e^2}{4D} \]

In Eq. (1) I(t) is the temporal dependence of the probe laser beam at the detector, I(0) is the initial value of I(t), \( \theta \) is the thermally induced phase shift of the probe beam after its passing through the sample, \( \omega_p \) and \( \omega_e \) are the probe beam and excitation beam spot sizes at the sample, respectively, \( P_e \) is the excitation beam power, \( A_e \) is the optical absorption coefficient of the sample at the excitation beam wavelength (cm\(^{-1}\)), \( Z_c \) is the confocal distance of the probe beam, \( Z_1 \) is the distance from the probe beam waist to the sample, \( l_0 \) is the sample thickness, \( K \) is the thermal conductivity, \( \lambda_p \) is the probe beam temperature, \( \tau_c \) is the characteristic thermal lens time constant, and (ds/dT) is the temperature coefficient of the optical path length change at the probe beam wavelength, which can be rewritten as [6, 19]:

\[ \frac{ds}{dT} = (n-1)(1+\nu)\kappa_T + \frac{dn}{dT} \]

\( s \) is the probe beam waist, and \( \nu \) is the thermal expansion coefficient of the sample.
Where, $\alpha_0$ is the sample linear thermal expansion coefficient, $\nu$ is the Poisson ratio, and $dn/dT$ is the temperature coefficient of its refractive index.

The TL experiments have been performed with the mode mismatched configuration. The setup is shown in Fig. 1.

In the time resolved measurements, $\theta$ and $t_c$ are straightforwardly obtained from the fitting of the experimentally observed profile of the developing thermal lens to Eq.(1). Therefore, it can be observed that by having the experimental value of $\theta$, the thermal conductivity and optical absorption coefficient determined from complementary techniques, the absolute value of the parameter $ds/dT$ of the sample can be determined.

The TL experiments were performed in poly(vinyl chloride) (PVC) in the temperature range from 22 °C up to 70 °C. The testing sample used in this work consisted of 200 µm thick diameter disks of (PVC) films. The PVC films were prepared using a 20,000 molar weight PVC powder (Aldrich). The films were cast from a 6.5% (w/w)1,2-di-chloroethane solution, at room temperature, over a flat clean glass surface. In order to validate and evaluate the sensitivity of the proposed method we have also carried out complementary measurements of the samples specific heat, using the transient heat method [20], and differential scanning calorimetry (DSC) for the evaluation of the glass transition temperature.

Results and Discussion

In Fig. 2 we show a typical transient TL signal for the PVC sample for a pumping power of 75 mW at room temperature. The solid line correspond to the data fitting to Eq. (1).

To somewhat complex temperature dependence of both $D$ and $\theta/P$, we have also carried out DSC measurements. In Fig. 5 we present a typical DSC curve for our samples. This results indicates that the glass transition region of our PVC sample extents from 58 °C to roughly 67 °C with a peak at 62.5 °C. We note from Figs. 3 and 4 that both $D$ and $\theta/P$ exhibit a marked change in their temperature dependence in this glass transition region. Between 50 °C and 67 °C, the thermal diffusivity decreases roughly by a factor of 2 at the same time that $\theta/P$ experiences an increase of the order of 3.5.
maximum at 64 °C, as shown in the upper curve. The comparison between the two plots in Fig. 5 is such that the first peak in curve (a), occurring at 56 °C, correspond roughly to the inflexion point of the DSC curve in its rising portion after going through the minimum. The minimum of curve (a) occurring at 61 °C, in contrast, correspond to the glass transition temperature.

In conclusion, in this paper we discuss the use of the TL technique for investigating the thermal properties of polymers as a function of temperature. It is also discussed how the experimentally determined TL parameters can be used to locating the glass transition in polymers. The methodology is tested using solution casted films of PVC as a testing sample. A comparison with conventional differential scanning calorimetry data is made. It is proposed that the current transient thermal lens methodology, with minor changes in its experimental configuration, could be adapted to develop a new methodology, called differential thermal lens scanning, especially designed for the investigation of the phase transitions in polymers.

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