Photoacoustic studies of glassing processes of metacrylate polymers

D. Orzi, J. Tocho

► To cite this version:

D. Orzi, J. Tocho. Photoacoustic studies of glassing processes of metacrylate polymers. Journal de Physique IV Proceedings, 1994, 04 (C7), pp.C7-245-C7-248. 10.1051/jp4:1994758 . jpa-00253287

HAL Id: jpa-00253287

<https://hal.science/jpa-00253287>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Photoacoustic studies of glassing processes of metacrylate polymers

D. Orzi and J.O. Tocho

Centro de Investigaciones Opticas (CIC-CONICET), Dto. de Física, Universidad Nacional de La Plata, Casilla de Correo 124, 1900 La Plata, Argentina

Abstract: The glass transition in acrylate polymers was studied using photoacoustic signals induced by a Nd:YAG pulsed laser. The transition temperature was obtained by an analysis of the amplitude and time dependence of the signal.

1. INTRODUCTION

Thin films of organic polymers doped with dipolar molecules and poled by high electric field have shown interesting non linear optics properties.^[1] Efficient second harmonic generation results from a combination of a large second order polarisability of doping molecules and a non-centrosymmetric structure of the poled material. Poling can be performed at room temperature but poling at high temperature, close to glass-transition temperature, has several advantages for polymers.^[2] A rotation of guest molecules is then possible and a strong orientation is developed. In this field and others of more technological interest an easy determination of glass transition temperature is useful.

2. THEORY

2.1 Glass Transition

The glass transition is described as the temperature T_g , or region, on the temperature scale where the thermal expansion coefficient α undergoes a discontinuity. The discontinuity in α is accompanied by discontinuities in heat capacity and in compressibility. At temperatures high enough for a rapid Brownian motion, a lowering of temperature is accompanied by a collapse of the free volume as the molecular adjustments take place within the experimental time of cooling; this situation corresponds to temperatures above T_g . At lower temperatures the adjustments are slower and if crystallization does not occur first, a temperature is reached where the collapse can no longer occur within the experimental cooling times. Then the only

residual contraction is of a solid like character; this corresponds to temperatures below T_g .^[3]

2.2 Photoacoustic Signal

Laser induced photoacoustic signals provide information about thermoplastic properties in a very attractive way. The amplitude of the first cycle of the time-resolved photoacoustic signal (PAS), can be written:^[4]

$$\text{PAS} = K (\alpha v^{1/2} / C_p) (1-10^{-A}) E_0, \quad (1)$$

where E_0 is the pulse laser energy, A is the absorbance of the sample, α is the expansion coefficient, C_p is the specific heat at constant pressure, v is the acoustic velocity, and K is an instrumental constant including the response properties of the transducer. This expression is valid for short pulses excitation as discussed by Tam^[5]. PAS can be used for monitoring thermal anomalies in α , v and C_p .

3. EXPERIMENT

Nd:YAG pulsed laser ($t_p = 10$ ns) were used to excite $1 \text{ cm} \times 1 \text{ cm} \times 20 \text{ }\mu\text{m}$ samples of polymethylmetacrylate (PMMA) or polyethylmetacrylate (PEMA) on glass. The polymers were doped with a non fluorescent dye (Disperse Red 1) with a concentration up to $A=0.05$ at the laser wavelength. A programmable oven was used to change the temperature of the sample. The rate of heating and cooling used was $3\text{-}5 \text{ }^\circ\text{C}$ per minute. No thermal treatment was done to the samples previous to the measurements. The PAS and the time delay between the laser pulse and the arrival of the acoustic signal was measured with a digital oscilloscope and stored as a function of temperature.

Fig 1 (a) schematically shows the essential elements of the experiment. The glass plate used to connect the sample with the PZT can be seen in Fig. 1 (b); this allowed to maintain a constant temperature for the transducer outside the oven.

4. EXPERIMENTAL RESULTS

Experimental results for the time delay as a function of temperature can be seen in upper part Fig. 2. The change in the delay time measured in the bare glass was one order of magnitude less than the result obtained with the sample. This results allow us to calculate the change in sound velocity that is necessary to correct the photoacoustic amplitude for its $(v)^{1/2}$ dependence (c.f. eq. 1). Corrected PAS is shown in the lower part of the same figure. Changes observed for both samples clearly show the glass transitions.

Fig. 1. (a) Experimental set-up. PZT: piezoelectric transducer, A: amplifier, S: sample H: heater, TM: temperature meter, EM: energy meter, DO: digital oscilloscope. (b) Acoustic coupling between the sample (inside oven) and transducer (outside oven)

5. DISCUSSION AND CONCLUSIONS

It is well known that the temperature of glass transition can differ according to several experimental parameters, mainly from the use of different rates of heating and different purities of samples. The method used here depends on the rate of heating and on the initial state of the glass, since the shifts on α and C_p depend on its thermal history. The glass transition is not sharp and T_g is defined as the mid-point of the temperature interval over which the transition takes place. Therefore, from Fig. 2, glassing temperatures was determined as $T_g \approx 110^\circ\text{C}$ and $T_g \approx 90^\circ\text{C}$ for the PMMA and PEMA, respectively. Glassing temperature for PEMA obtained for this method was higher than the published values.^[6] The transition region for this material could be shifted to higher temperatures for the high heating and cooling rates used. It is well known that the measuring time scale can determine the transition temperature.^[7]

Fig. 2. Photoacoustic amplitude and delay time as a function of temperature for PMMA and PEMA. Upper part: time-delay between laser pulse and arrival of acoustic signal; lower part: PAS (corrected for velocity).

REFERENCES

- [1] Mohajerani, E., Gilbert, A. and Mitchell, G.R., *J. Phys. D: Appl. Phys.* **25** (1992) 1304-1309.
- [2] Mortazavi, M.A., Knoesen, A., Kowel, S.T., Higgins, B.G. and Dienes, A., *J. Opt. Soc. Am. B* **6** (1989) 733-741.
- [3] Ferry J.D., *Viscoelastic Properties of Polymers* (John Wiley & Sons, New York, 3rd edition, 1980) pp. 265-315.
- [4] Tocho, J.O., Ramírez, R. and Gonzalo, J.A., *Appl. Phys. Lett.* **59** (1991) 14-16.
- [5] Tam A.C., "Signal enhancement and noise suppression considerations in photothermal spectroscopy", 7th International Topical Meeting on Photoacoustic and Photothermal Phenomena, Doorwerth 26-30 August 1991, pp 114-145.
- [6] Aldrich Chemical Company, Inc., *Catalog Handbook of Fine Chemicals* (1992-1993) pp. 1034-1036.
- [7] Buchner, B. and Korpiun, P., *Appl. Phys. B* **43** (1987) 29-33.