

Polymer Thermal and Acoustic Properties using Heterodyne Detected Transient Grating Technique

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Received 12 November 2010; revised 12 February 2011; accepted 15 February 2011; published online 14 March 2011

DOI: 10.1002/polb.22233

ABSTRACT: We investigated the acoustic and thermal features of a polymeric system by a heterodyne detected transient grating technique. We studied two polymers characterized by different molecular weights. Transient grating experiments could reveal a reliable series of information on sound velocity, acoustic damping time, and thermal diffusion of the polymers. The tempera-

ture and molecular weight dependence of the polymer acoustic and thermal properties are reported. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 49: 685–690, 2011

KEYWORDS: amorphous; glass transition; light scattering; thermal properties

INTRODUCTION Polymers have great importance in many fields of science and engineering,^{1–3} and also have very wide application in protecting layers,¹ substrates for electronic devices and optoelectronic industry.^{2–4}

Thermal and acoustical properties are physical properties of polymers that are of both fundamental and practical interest.^{5,6} For example, the development of heat during the application of electronic devices may cause large temperature gradients, which could lead to failure of the component. Estimation of these temperature gradients may then become important and requires knowledge of thermal diffusivity. Moreover, polymers are commonly used for noise insulation or protection so the knowledge of their physical properties and, in particular, acoustical properties, results relevant. In addition, both acoustical and thermal properties are sensitive to the variation of structural factors. Therefore, knowledge on these two properties improves our understanding of the fundamental aspect of polymers. Nowadays, several different techniques for the determination of the thermal^{7,8} and acoustical⁹ properties may be found in the literature, the photoacoustic spectroscopy (PA) and related photothermal techniques (PT),^{10–12} apart from providing direct optical absorption spectra,^{13,14} can also be used to perform depth profile analysis^{13,15} and characterization of thermal proper-

ties.^{16,17} In this work, we examine a single technique based on laser pulses to determine both PA and PT properties of polymers.

During the last decades, pulsed lasers have been largely utilized to improve both PA and PT techniques. In fact, short laser pulses can be used to generate impulsive heating and acoustic frequencies that are much higher than those achieved through conventional acoustic methods, permitting practical study of fundamental high-frequency dynamics in disordered systems (e.g., glass-forming liquids and amorphous solids).

The transient grating (TG)^{18–20} is a technique particularly interesting, because it is able to combine both PA and PT spectroscopy in a single experiment. In recent years, the introduction of heterodyne optical detection in the TG spectroscopy (HD-TG)²¹ has further improved the experimental sensitivity yielding extensive contributions to our understanding of complex relaxation in supercooled liquids.^{19,20} In these studies, HD-TG measurements have revealed detailed information concerning the temperature-dependent dynamics of structural relaxation, thermal diffusion,²² and molecular orientational dynamics.²³ Recently, the HD-TG has applied to the investigation of acoustic and flow dynamics in nanostructured and nanoconfined liquids.^{24,25}

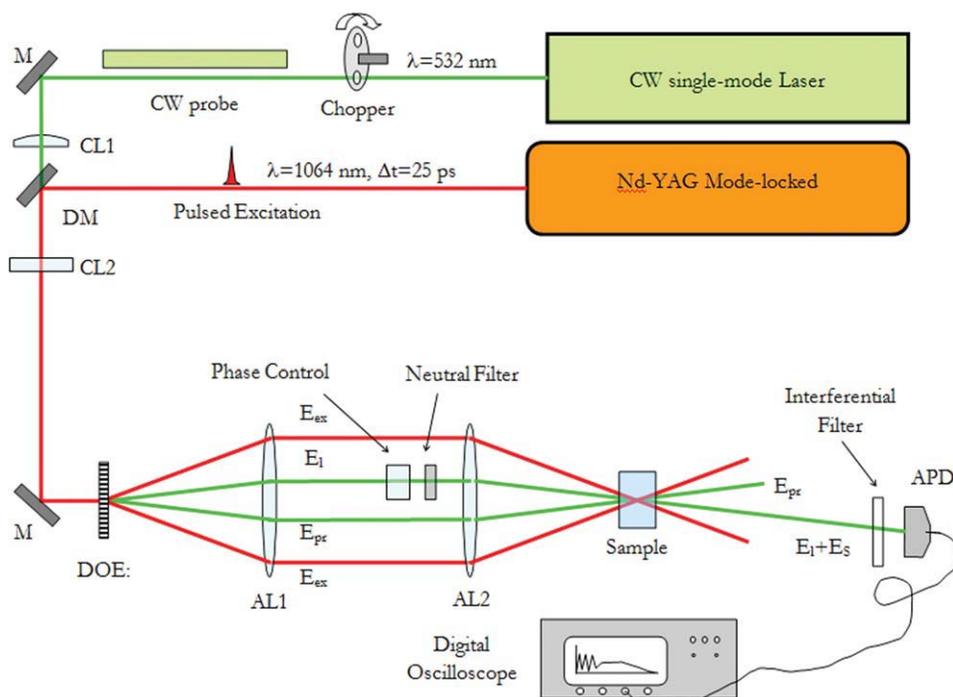


FIGURE 1 Optical set-up for a HD-TG experiment, CL, cylindrical lens; M, mirror; DM, dichroic mirror; DOE, diffractive optic element; AL, achromatic lens; ADP, avalanche photodiode; E_l , local field; E_{pr} probe field; and E_{ex} is excitation field.

Indeed, HD-TG experiments are highly sensitive, nondestructive probes that can be readily adapted to the polymer investigations. For example, the utilization of these techniques for optical generation and detection of high-frequency surface acoustic waves in films have proven to be particularly adapted to study the polymeric film properties.²⁶ As well, HD-TG experiments can be used to determine important information about the elastic and thermal properties of bulk polymeric materials. In our knowledge, there are no HD-TG studies on bulk glassy polymer and only one pioneering study, performed by “homodyne”-detected TG experiment, by Blanchard et al.²⁷ In this work, the experimental limitations does not enable the investigation of polymer thermal properties, and it was investigated only a polymer characterized by a single molecular weight.

We are reporting, here, the study of the acoustic and thermal properties of a polymer, poly-methyl-methacrylate (PMMA), in its glassy phase. The effect of two different molecular weights has been characterized. The heterodyne detection and the continuous wave probing, present in our experimental set-up, allowed us to follow the PT and PA phenomena over a very wide time windows with a unique high sensitivity and data quality. We compared the results of HD-TG experiment with the data from other techniques.

EXPERIMENTAL

In an impulsive TG experiment, two high-power pulses, obtained by dividing a single pulsed laser beam, interfere inside an absorbing sample to produce a spatially periodic variation of the optical material properties (e.g., refractive

index and the absorption coefficient) by standing-wave excitation of some of the material modes. Thermal expansion that follows heating, induced by these pulses launches acoustic and thermal responses characterized by a well-defined wave-vector whose magnitude is determined by the crossing angle, θ , and the wave-length, λ , of the excitation beams, $q = (4\pi/\lambda)\sin(\theta/2)$. The acoustic response consists of two counter propagating waves, which give rise to damped oscillations typically evolving on a nanosecond time scale. The thermal response gives rise to a quasi-steady state material response, which persists until thermal diffusion washes out the temperature grating on microsecond time scales. A schematic illustration of the experimental set-up is depicted in Figure 1. In this set-up, we used an optical heterodyne detection (HD) method that enables the detection of very low-level signal. A common experimental problem in light scattering spectroscopy is to detect extremely weak signal beams with good signal-to-noise ratios. When the diffraction efficiency is very small, the unavoidable background of diffuse light may be more intense than the signal light. In a homodyne detection, the detector detects the intensity of the scattered field, $E_s(t)$, corresponding to the time average over the optical period of the square of the field. In the heterodyne detection, we combine the signal field with a reference beam, called local oscillator (local field), whose magnitude and phase are known, so that the photodetector current is proportional to the scattering amplitude instead of the scattering intensity. HD is a well-established method for achieving both signal amplification and linearization. If the reference field has a high intensity, the homodyne contribution becomes negligible, and the time variation of the signal is

dominated by the heterodyne term, which is directly proportional to the signal field. Furthermore, to eliminate the homodyne contribution, we change the phase of reference field and subtract two different phases from each other. Comparison with the homodyne term reveals that there are two major advantages in using heterodyne. First, it improves substantially the signal to noise ratio in the time window, because of both signal increment and remove all spurious signals, which are not phase sensitive. Second, it enhances enormously the sensitivity, because the detector signal is directly proportional to signal field instead of being proportional to its square. Therefore, the HD allows us measuring the very long relaxation times, where the TG signals become very weak for any material.

We used a pulse laser as pump, with a wavelength of 1064 nm, the pulse duration is 25 ps, and its repetition rate is 10 Hz that was produced by an amplified regenerated oscillator Nd-YAG (mod. PL2143 by EKSPLA). The output pulses can reach energy of 50 mJ. The probing beam, at 532-nm wavelength, is produced by a diode-pumped intracavity-doubled Nd:YVO (mod. Verdi by Coherent), which is a CW single-mode laser that is characterized by excellent intensity stability with a low and flat noise-intensity spectrum. To properly measure the natural damping of the induced acoustic oscillations, the pump and probe beams are focused on the DOE following a particular geometry (Fig. 1):²⁰ the pump is cylindrical focused by a cylindrical lens, to have on the sample an excitation grating very extended in the q -direction (in the present experiment, the grating Gaussian waist is 6 mm) while the probe beam is focused through two crossed cylindrical lenses to a circular spot (waist 0.5 mm). Without this excitation-probing geometry, the acoustic damping is affected also by the finite size of excited grating. In this experiment, the waist of our excited grating was enough wide to measure intrinsic acoustic damping up to 1 μ s.

We studied two different molecular weights (M_w) of PMMA. One with glass transition of $T_g = 96$ °C and molecular weight of $M_w = 120,000$ and another one with $T_g = 124$ °C and $M_w = 996,000$.

PMMA shows a weak absorption at 1064 nm (pump wavelength) due to the overtones and/or combination of the vibrational bands. Therefore, irradiation by the nonresonant excitation light gives rise to weak absorption into this vibrational overtone, resulting in mild heating. Typically, these excitations thermalize in a few picoseconds producing immediately a thermal grating.

We measured the relaxation processes of PMMA as a function of temperature and molecular weight for a wave vector of $q = 1 \mu\text{m}^{-1}$ in the polarization configuration of two pumps, probe and detection beams orthogonal to the scattering plane. The measurement has been carried out in the temperature range from 21 to 40 °C to avoid any complication due to glass transition and aging effect. The temperature has been kept well below T_g , so during the measurement the aging effect is ignorable. This can be verified by the inde-

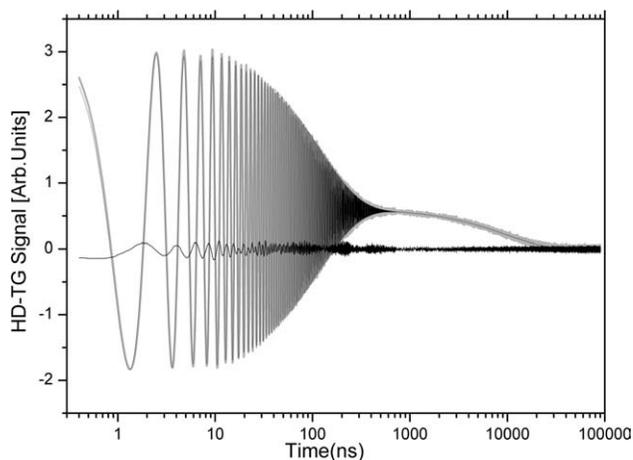


FIGURE 2 HD-TG data (gray line), fit (black line), and residues (lower lines) for PMMA ($M_w = 120,000$), at the $T = 24$ °C and at wave-vector $q = 1 \mu\text{m}^{-1}$.

pendence of the HD-TG signal from the waiting time, differently from what has been reported in ref. 27.

PMMA-measured signal spans over many decades in time, typically from 1 ns up to about 10 μ s. Hence, we recorded the data in a pseudologarithmic time scale. We used a fast time window (0–800 ns with a 50-ps time step) and a broader one (0–100 μ s with a 4-ns time step) and then both measurements are merged into a single data file, without any problems of overlapping. Each data is an average of 3000 recording (corresponding to 25min of acquisition time), and this is enough to produce an excellent signal-to-noise ratio.

RESULTS AND DISCUSSION

In the HD-TG experiment, a local heating produces a density change (also called impulsive stimulated thermal scattering) that often becomes the most important part of the HD-TG signal.^{18–20} Also, the pump fields create an instantaneous electrostrictive pressure, which is an additional density perturbation (impulsive stimulated Brillouin scattering). In Figure 2, we show in linear-log plot of typical HD-TG data on the polymer glass PMMA. It clearly shows the density dynamics of PMMA well below glass transition is characterized by two main dynamical processes, an acoustic phonon and a thermal relaxation. Heterodyne signal (S^{HD}), which is proportional to the change of dielectric constant, can be expressed by the following phenomenological equation:^{19–21}

$$S^{\text{HD}} \propto Ae^{-\Gamma_A t} \cos(\omega_A t) + Be^{-\Gamma_A t} \sin(\omega_A t) + Ce^{-\Gamma_H t} \quad (1)$$

The fitting parameters are the acoustic frequency and damping rate (ω_A and Γ_A), the thermal decay rate (Γ_H), and the amplitude constants (A , B , and C). From these parameters, we can obtain [20]: the sound velocity $c = \omega_A/q$, where $q = 1 \mu\text{m}^{-1}$ is experimentally fixed; the thermal relaxation time $\tau_H = 1/\Gamma_H$ and the acoustic damping time $\tau_A = 1/\Gamma_A$. Figure 2 shows that the HD-TG data were perfectly fitted by this equation. The results of fitting of the data for PMMA ($M_w = 120,000$) are displayed in Figures 3–5.

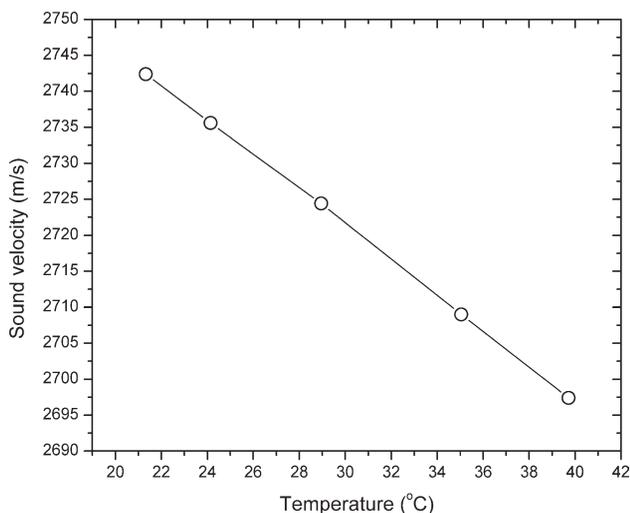


FIGURE 3 Sound velocity versus temperature for PMMA ($M_w = 120,000$).

In a nondispersive medium, the sound velocity is constant and does not depend on the exchanged q -vector, so the speed of the energy transport and the sound propagation are the same. In such medium, the velocity of sound is not depending on the frequency, but in a dispersive medium, the sound velocity is a function of its frequency. The spatial and temporal distribution of a propagating disturbance will continually change. Each frequency component propagates with its own phase speed, while the disturbance propagates at the group velocity. Amorphous polymers as PMMA are dispersive medium that means sound velocity changes by its frequency.²⁸ At decreasing of temperature, going from the liquid to the glassy state, the structural dynamic affects the sound propagation.^{20,21} At high temperatures, the velocity corresponds to the adiabatic zero frequency sound velocity, c_0 , while at low temperatures corresponds to the solid-like or “infinite” frequency sound velocity, c_∞ . In the transition

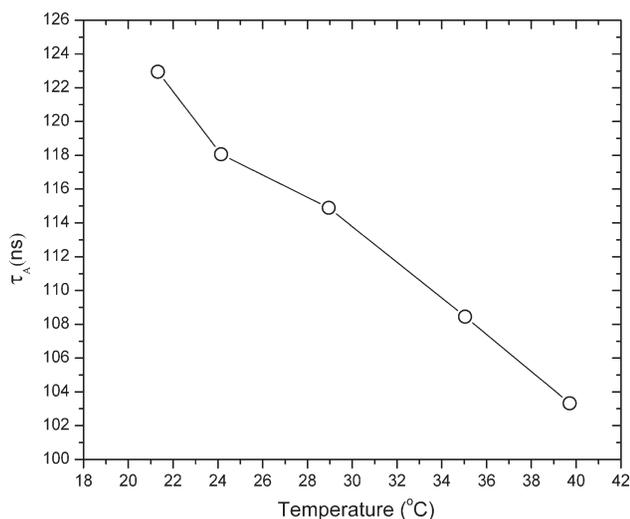


FIGURE 4 τ_A versus temperature for PMMA with $M_w = 120,000$.

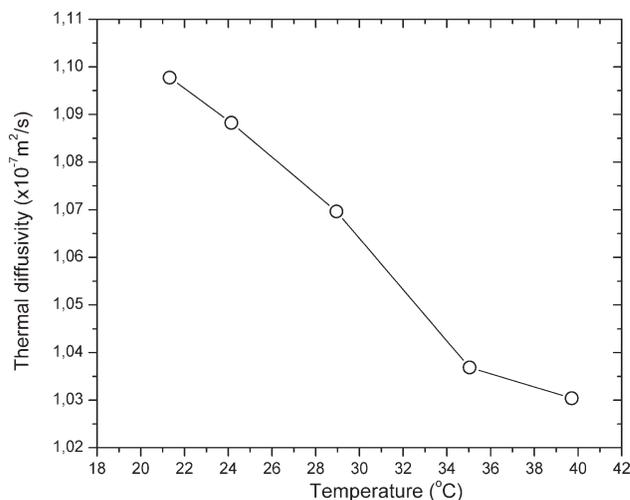


FIGURE 5 Thermal diffusivity versus temperature for PMMA ($M_w = 120,000$).

region, we have the maximum dispersive effect due to the strong coupling between structural relaxation and acoustic oscillation times, which become comparable. In our temperature range, being below the glass transition, we always measure the c_∞ sound velocity.

The measured value of PMMA sound velocity (Fig. 3) is comparable with the longitudinal sound velocity determined by other techniques such as Brillouin light scattering, which is around $c = 2750 \text{ m s}^{-1}$.^{29,30}

The velocity of sound can be expressed by the following relation:

$$c^2 = M/\rho \quad (2)$$

where M is the infinity frequency longitudinal modulus and ρ the density of the medium.

Increase in temperature causes a decrease in the density and a decrease in modulus of the medium. Figure 3 shows the sound velocity measured by the HD-TG experiment as a function of temperature. It is clear by increasing the temperature, the sound velocity decreases, so the change in density is less effective than the alteration in modulus. This finding is in agreement with the rate of change in the compressibility and density, which are around 1.13 and 0.0004.^{31,32} The linear relation of sound speed with temperature at these temperatures corresponds to the solid-like or “infinite” frequency sound velocity, c_∞ , described before. The acoustic damping time in the most amorphous material reduces by increasing the temperature (Fig. 4) that is corresponded to the solid-like regime.

Thermal diffusivity of PMMA measured by our HD-TG experiment is shown in Figure 5. Thermal diffusivity is the quantity that measures the change in temperature produced in unit volume of the material by the amount of heat that flows in unit time through a unit area of a layer of unit thickness with a unit temperature difference between its faces. The

HD-TG is also able to measure thermal diffusivity directly that can be calculated by following equation:

$$\chi = \frac{1}{\tau_H q^2} \quad (3)$$

Our data shows that the thermal diffusivity decreases as the temperature rise, as displayed by Figure 5. Santos et al.^{7,8} determine thermal diffusivity of the PMMA by laser flash technique and hot wire technique. For example, at 25 °C, they found thermal diffusivity is 1.054 for laser flash technique and 1.155 for hot wire.^{7,8} Our finding for thermal diffusivity is very close to those, which are measured by laser flash technique.

We also examined the effect of molecular weight on sound velocity and thermal diffusivity. The number of chain ends plays an important role for the physical properties in polymeric systems. The higher degree of polymerization causes the lower number of end chain and free volume.^{33,34} Nevertheless, in the literature, for high molecular weight polymer, it has not been reported any difference between sound velocities of polymers with different molecular weights very below T_g .³⁵ The acoustic measurements by HD-TG are typically affected by very small errors (e.g., for sound velocities around 0.001%), and they enable the detection variation induced by different molecular weights of the PMMA. Figures 6 and 7 illustrate how sound velocity and acoustic damping time are changed by varying the molecular weight. Figure 6 reveals that the difference in the sound velocity is very small. However, as it is clear for all investigated temperatures, the sound velocity of the higher molecular weight is systematically bigger than lower molecular weight. The acoustic damping time shows a clear difference around 5–9% between the two different molecular weights. Acoustic wave damped faster for lower molecular weight, because it is more compressible and less stiff compare to higher molecular weight.³⁶

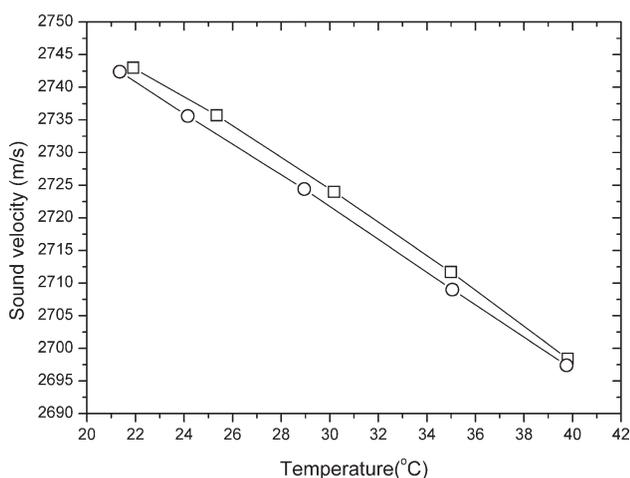


FIGURE 6 Sound velocity versus temperature for PMMA ($M_w = 120,000$, circle) and PMMA ($M_w = 996,000$, square).

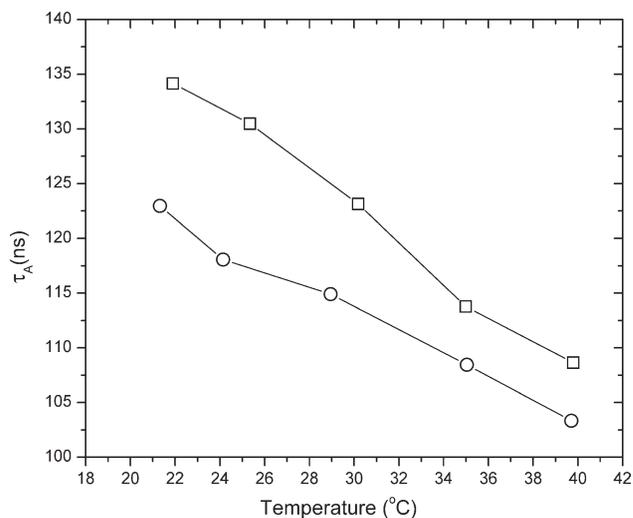


FIGURE 7 Acoustic damping time versus temperature for PMMA ($M_w = 120,000$, circle) and PMMA ($M_w = 996,000$, square).

We could not find any significant trend for the thermal diffusivity of the two samples, which is in agreement with the finding of Change et al., for high molecular weight polymers.³⁷

CONCLUSIONS

We studied acoustical and thermal behavior of polymers by HD-TG. Our results show that HD-TG experiment can reveal reliable information such as thermal diffusivity, sound velocity, and acoustic damping of polymers. The results of thermal diffusivity and sound velocity were comparable with the results of flash laser and Brillouin technique.

The sound velocities and damping acoustic times decrease with increasing temperature and both follow a linear relation in the investigated range. These results suggest that sound velocity is affected by compressibility more than density. The thermal diffusivity exhibits a decrease with increasing temperature.

We have also studied the effect of the molecular weight on the physical properties of PMMA for temperatures below T_g . The HD-TG experiment detects a difference on the PMMA acoustical properties due to the molecular weight, whereas no variation has been found on the thermal diffusivity. Higher molecular weight yields to slightly larger values of the sound velocity and clearly bigger acoustic damping times.

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