Ultrasonic investigation of semicrystalline polymers: study of poly(ethylene terephthalate)

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Ultrasonic velocity and attenuation were measured as functions of temperature (20 to 320°C) and hydrostatic pressure up to 900 bar at acoustic frequencies varying from 1 to 6.33 MHz on semicrystalline poly(ethylene terephthalate). Melting, α-relaxation and glass transition temperatures and their dependence on pressure were determined from the variations of ultrasonic characteristics. Comparison with very low-frequency ($1–10^{-1}$ Hz) dynamic mechanical spectroscopy is done in the case of α-relaxation, which can be described in terms of a Vogel–Fulcher–Tammann relation. With simultaneous specific volume measurements, glass transition temperature is determined by different methods to validate ultrasonic results. In particular, data analysis through a physical model is described to improve the method in the case of semicrystalline polymers.

(Keywords: ultrasonic characterization; melting; α-relaxation; glass transition; poly(ethylene terephthalate))

INTRODUCTION

Studies on dynamic properties of polymers are usually carried out at low frequencies with different approaches in terms of rheology. These techniques are by no means unique, nor universal. Ultrasonic techniques have proven to be useful to study elastic solids or viscous fluids, but are not common practice for the study of polymers. Recent experiments[1,2] have been done essentially on amorphous polymers and the technique has been revealed to be powerful for characterization and determination of some thermodynamic parameters. In this paper, we present results concerning a semicrystalline polymer, poly(ethylene terephthalate), whose industrial importance is not to be demonstrated. Discussion will be focused on the glass transition region and the dependence of different physical parameters (glass transition temperature, melting temperature, α-relaxation) on the applied pressure.

EXPERIMENTAL TECHNIQUE

Ultrasonic characterization of materials is based essentially on the propagation of small-amplitude waves and the determination of the characteristics of propagation (velocity, attenuation, frequency of the wave). These data provide access to the storage and loss moduli of the material.

The complex modulus L^* corresponding to longitudinal waves is given by:

$$L^* = L' + \mathrm{i}L'' \qquad L' = v_L^2/V \qquad L'' = 2\alpha_L v_L^3/\omega V$$

where v_L, α_L, V and ω are respectively the velocity, the attenuation of the wave, the specific volume and the angular frequency ($\omega = 2\pi f$).

Experiments were carried out using an original device previously developed in this laboratory, which is described in detail elsewhere[3]. Ultrasonic waves issued from piezoelectric transducers are transmitted through the specimen using two buffer rods. Axial displacement of the rods in a jig placed under a hydraulic press allowed the application of a monitored pressure up to 2 kbar. The thickness of the sample is measured by an LVDT transducer, giving access to specific volume. A heating/cooling system allows measurements from −150 to 350°C with heating/cooling rates from 50 to 0.015°C min^{-1} and isothermal conditions of ±0.1°C in stability. The whole device is under computer control and all data concerning length of specimen, temperature, pressure and acoustic signal are collected every 10 s.

Poly(ethylene terephthalate) (PET) pellets, supplied by Rhone-Poulenc Films Industries ($\bar{M}_n = 20\,000$), were conditioned for 2 h at 50°C under vacuum before testing.

Experiments were done from the melt (15 min between 295 and 315°C depending on applied pressure as standard treatment) with heating/cooling rates of 2°C min^{-1} or under isothermal conditions. The pressure was applied in the melt state and maintained constant all through the experiment. The data presented here were obtained with longitudinal waves at a frequency $f = 2.5$ MHz and in a pressure range from 150 to 900 bar. Some other experiments were also done at different frequencies.

The crystallinities of samples were determined after cooling by d.s.c. and a density-gradient column and show no significant difference according to pressure for the same cooling rate.

RESULTS

When a specimen is cooled from the melt to 20°C at a rate of 2°C min^{-1}, maintained for 10 min at this temperature and then heated at the same rate up to the molten state, propagation characteristics and specific volume

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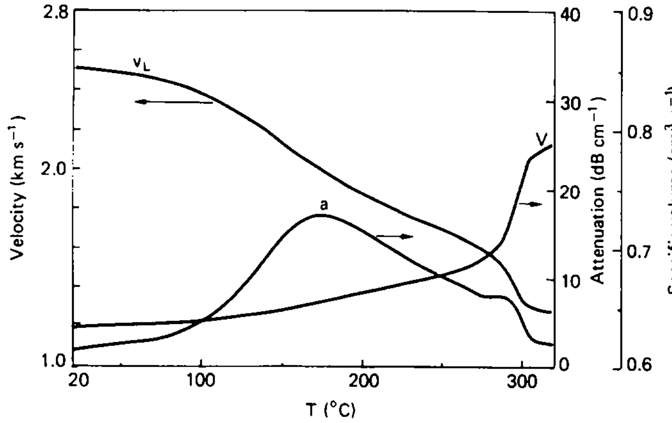

Figure 1 Simultaneous measurements of attenuation, velocity (longitudinal wave, $f = 2.5$ MHz) and specific volume. Cooling (from the melt) and heating rate = 2°C min^{-1}. Applied pressure = 900 bar

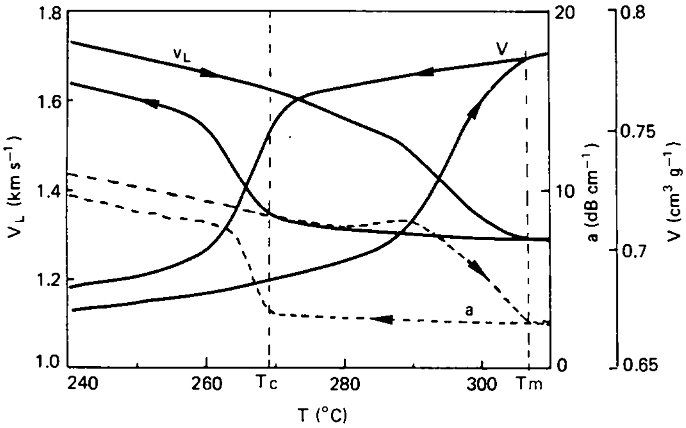

Figure 2 The crystallization/melting region. Pressure = 900 bar. Heating/cooling rate = 2°C min^{-1}

present variations as described in *Figure 1*. From these curves three typical regions can be distinguished. Starting at the higher temperatures they are as follows:

(i) The crystallization/melting region. This domain located in the high-temperature range is characterized by discontinuities in both ultrasonic parameters, i.e. velocity and attenuation. The specific volume presents abrupt changes in this zone. Characteristic temperatures of crystallization or melting (T_c, T_m respectively) can be determined (*Figure 2*).

(ii) The α-relaxation region. As temperature decreases, sound velocity increases, following an inverted S-shaped variation. At the same time, attenuation exhibits a strong maximum. Variations of both ultrasonic characteristics indicate a mechanical relaxation phenomenon, which can be identified with the α-relaxation observed at lower temperature in low-frequency experiments[4]. A characteristic temperature T_α of this relaxation can be determined as the peak temperature.

(iii) The glass transition region. At temperatures below the α-relaxation zone, velocity and specific volume present a break in their variations with temperature (*Figure 3*). The change in slope for the velocity is accompanied by a rapid variation in attenuation. The temperature corresponding to the break in specific volume variation can be defined as the glass transition temperature, T_g, according to the usual definition.

Results concerning these three regions will be discussed separately and in particular the dependence on pressure of the characteristic temperatures defined above.

The crystallization/melting region

The variations of ultrasonic characteristics in this region allow determination of melting temperatures under pressure. Usually determinations of melting under elevated pressures are made by detecting the change in volume at constant pressure and constant heating rate and require a specific device[5].

In our experiments, the volumetric change method can be compared with the ultrasonic characteristics variation method. In *Figure 4*, both determinations are shown. The ultrasonic method is in very good agreement with the classical determination. As in most semicrystalline polymers the melt transition is not very sharp; the error in both methods can be estimated to ±1°C.

The melting behaviour of PET under pressure is similar

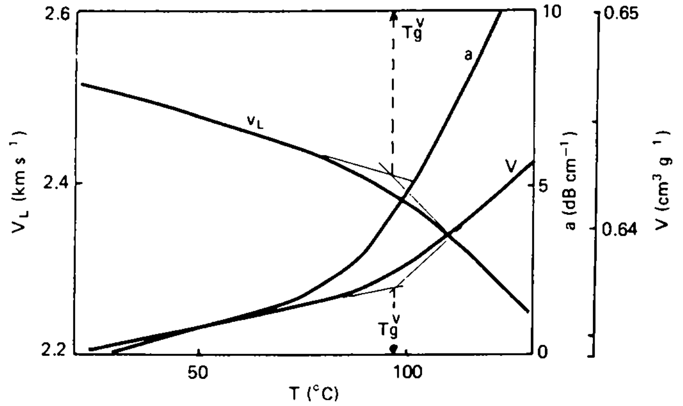

Figure 3 The glass transition region. Pressure = 900 bar. Heating rate = 2°C min^{-1}

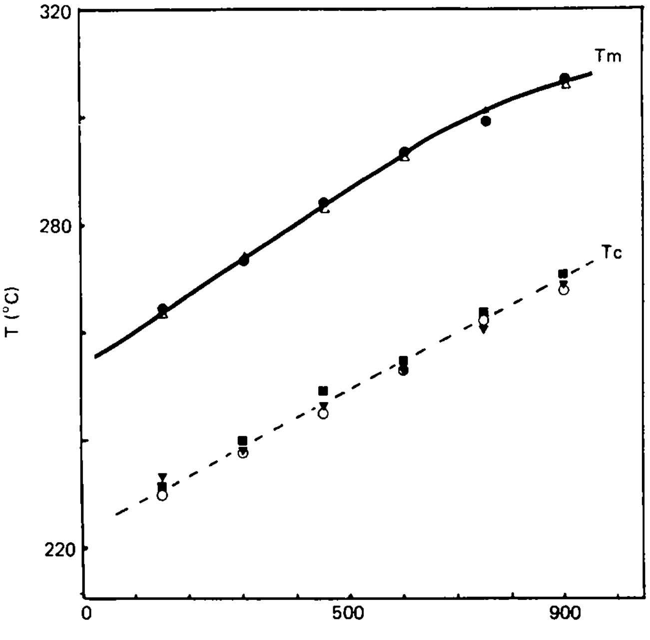

Figure 4 Variations of T_m and T_c with pressure. T_m and T_c are defined as in *Figure 2*. T_m: (●) specific volume method, (△) ultrasonic method. T_c: (■) specific volume method, (○) velocity changes, (▽) attenuation changes

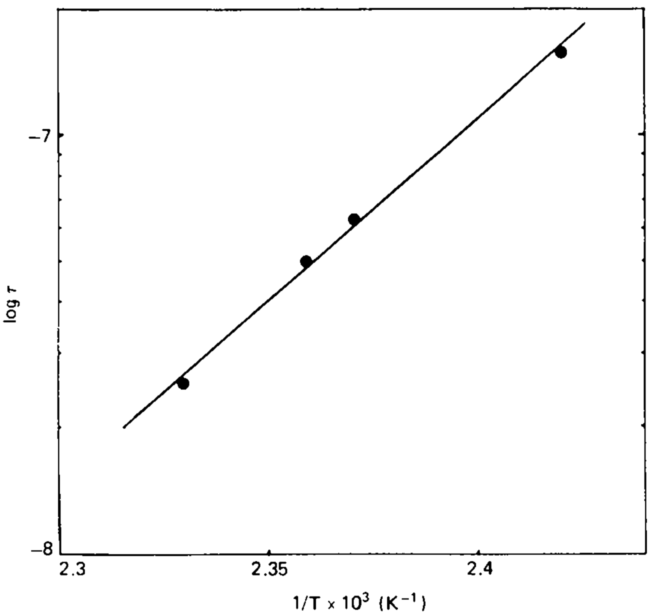

Figure 5 Log τ *versus* 1/T. Values of τ are obtained from experiments done at 300 bar

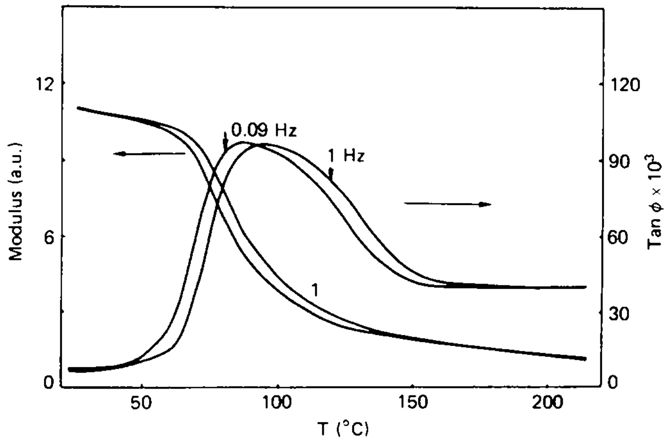

Figure 6 Low-frequency experiments (mechanical spectrometry). The specimen is the same as those giving results shown in *Figure 5*

to that of other crystalline polymers, i.e. the melting point rises with increasing pressure and the rate of change with pressure dT_m/dP decreases when pressure increases. In our experiments dT_m/dP varies from 0.060 to 0.056 C bar^{-1} when pressure increases from 150 to 900 bar. This result is in agreement with classical volumetric studies[5,6].

It is also interesting to note that the beginning of velocity change coincides with the beginning of volume change, that is in fact the start of melting. On the other hand, the change in attenuation does not correspond to that and occurs at higher temperature. This seems to indicate that the parameter sound velocity is sensitive to melting of small crystallites whereas attenuation decreases only when larger crystalline entities begin to melt. The change in attenuation could be attributed to the collapse of the spherulitic structure.

When material is cooled from the melt, changes in ultrasonic characteristics also give access to dynamic crystallization temperature T_c. *Figure 4* shows the dependence of T_c on applied pressure.

The α-relaxation region

In this region, changes in attenuation and velocity or in storage and loss moduli present the characteristics of a classical mechanical relaxation. This relaxation is identified as the α or main mechanical relaxation related to the non-crystalline phase of the polymer. There have been numerous investigations of this type of relaxation in amorphous polymers[7]. On the contrary, in semicrystalline polymers the situation is not so simple and the crystalline phase introduces difficulties in the understanding of physical mechanisms[7,8]. In the case of crystalline PET, the main relaxation has been attributed to the amorphous phase[4] and its strength is sensitive to crystallinity. The whole material is then to be considered as a composite.

When measurements are made at low frequencies (≃1 Hz), the mechanical α-relaxation nearly coincides with the glass transition, and the temperature of the maximum of loss modulus T_α is often taken in an incorrect manner as the glass transition temperature[9]. On the contrary, when measurements are performed at higher frequencies, such as in ultrasonic investigations, the relaxation phenomena can be clearly distinguished from the glass transition since T_α is observed at higher temperature.

The loss modulus goes through a maximum for the condition $\omega\tau = 1$, so it is possible to obtain an apparent activation energy defined as $E = d \ln \tau / d(1/T)$ when experiments are done at different frequencies. On *Figure 5* we have plotted log τ vs. 1/T and in this domain of temperature (or frequency) the phenomenon shows an apparent activation energy = 1.7 eV. This value has to be compared with that obtained at lower frequencies (1–0.1 Hz) on the same specimen (*Figure 6*), at atmospheric pressure, which is as high as 6.2 eV. Through a large interval of temperature (*Figure 7*) it can be seen that the mechanical relaxation does not follow an Arrhenius law but rather a Vogel–Fulcher–Tammann relation. This behaviour above T_g is characteristic of the amorphous phase. The secondary relaxation[4] time plotted on the same figure from results at low frequency (1 Hz)

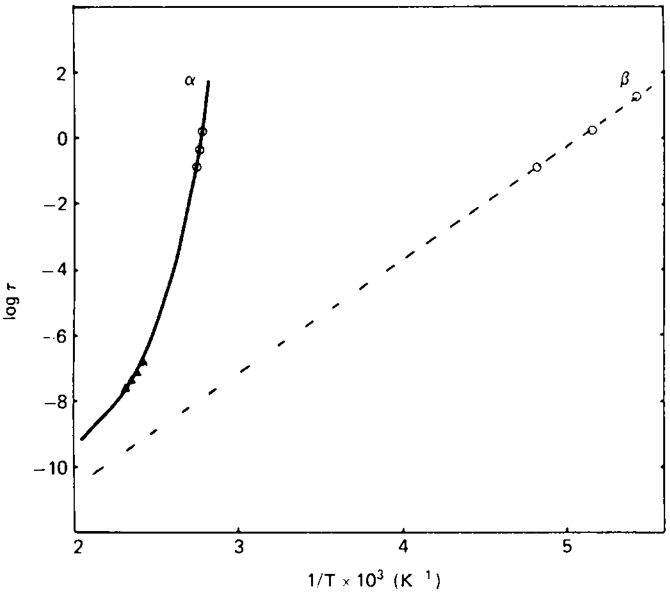

Figure 7 Log τ *versus* 1/T over a large range of temperature: circles, mechanical spectrometry; triangles, ultrasonic measurements

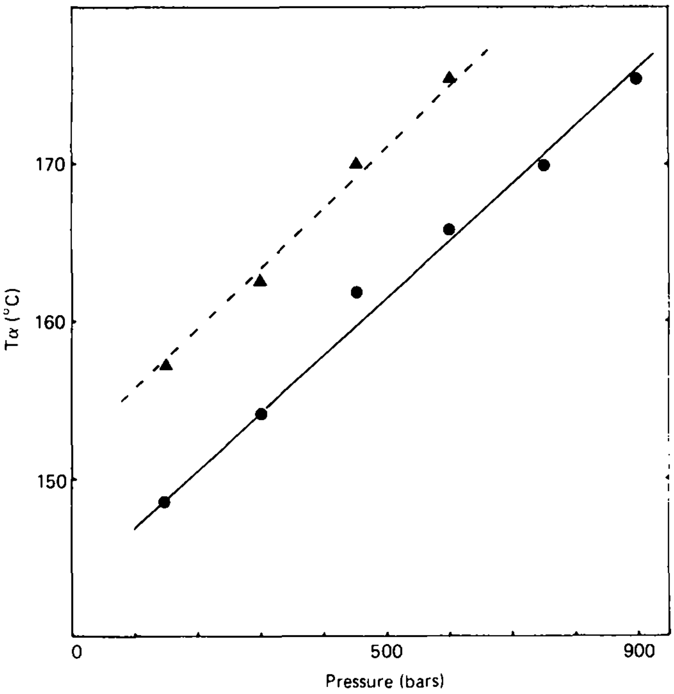

Figure 8 Variations of T_α with pressure. Heating rate = 2°C min^{-1}. Circles, 2.5 MHz; triangles, 6.33 MHz

is not observed in ultrasonic experiments according to the shift of the β-peak towards high temperature with frequency and the decrease of its amplitude with both crystallinity and temperature.

Another point of interest concerns the shift to higher temperature of T_α with increasing pressure. Values of T_α at different pressures are shown in *Figure 8* and exhibit a linear dependence on pressure, as $\mathrm{d}T_\alpha/\mathrm{d}P = 0.036$°C bar^{-1}. This dependence is of the same order as that of the glass transition temperature, as will be seen in the next subsection.

The glass transition region

In the liquid glass transition region, materials show a discontinuity in the change in specific volume, enthalpy and entropy with temperature. This is a manifestation of the slowing of molecular kinetics when the contribution from configurational changes in the structure of the supercooled liquid become vanishingly small.

When a polymer is partially crystalline, the increase in the expansivity is small and difficulties can arise in determining the glass transition temperature.

In our experiments, where we measure simultaneously the specific volume and the ultrasonic characteristics, a comparison is possible between the classical method (volumetric) and ultrasonic method, since the propagation characteristics present changes when approaching the glass transition temperature. So, two determinations of the glass transition temperature were used, as follows:

(i) Volumetric change. The break in the slope of specific volume gives access to the classical thermodynamic T_g^v value.

(ii) Sound velocity change. When temperature is approaching T_g, a break in the slope of v T curves can be seen, coinciding with the characteristic temperature T_g. For the same heating rate this value is independent of measurement frequency.

On *Figure 9* values of T_g obtained by these different methods are plotted *versus* pressure, and good agreement is obtained between volumetric and ultrasonic determinations. Of course in semicrystalline polymers the determination of break point in the curves is not so accurate as in the case of amorphous polymers[2] and some dispersion can occur in the results. To avoid this problem, another determination of T_g has been tested based on a physical description of glass transition previously developed by Perez *et al.*[10,11] and using the parameter[12]:

$$\mu = \mathrm{d} \ln \tan \phi/\mathrm{d}T$$

where:

$$\tan \phi = L''/L'$$

According to this model, the loss tangent can be calculated as:

$$\tan \phi = \frac{(\omega\tau)^{-K'} + \eta' \sin(K\theta)C^{-K}}{1 + \eta' \cos(K\theta)C^{-K}}$$

where θ, K, K' are numerical parameters (between 0 and 1 for K and K', and about some units for η'), $C = (1 + \omega^2\tau^2)^{1/2}$, $\theta = \arctan(\omega\tau)$ and τ is the mechanical relaxation time. When τ is large, i.e. at low temperature and/or at high frequencies:

$$\tan \phi = \eta' \sin(K\pi/2)(\omega\tau)^{-K} \simeq (\omega\tau)^{-K}$$

On the other hand, the model gives a value for τ:

$$\tau = (K\tau_\beta/t_0^{1-K})^{1/K}$$

τ_β is then the mechanical relaxation time for the β-process and t_0 the average time for the elemental correlated molecular movement. So:

$$\mu = \frac{\mathrm{d} \ln \tan \phi}{\mathrm{d}T} = \frac{U_\beta}{kT^2} - \frac{\mathrm{d}K}{\mathrm{d}\tau}\left(\ln(\omega t_0) + \frac{1}{K}\right)$$

assuming U_β is the activation energy of the β-process.

At temperatures below T_g, $\mathrm{d}K/\mathrm{d}T$ is zero since the

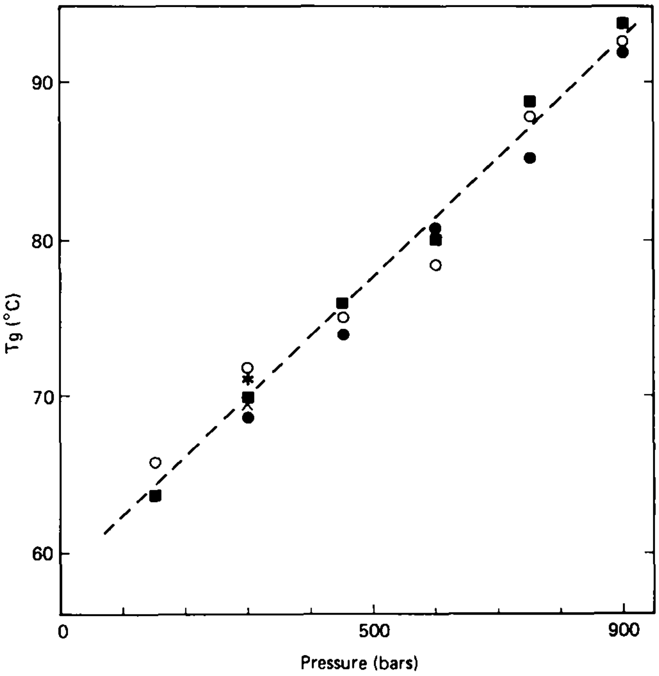

Figure 9 Variations of T_g with pressure: (○) volumetric method (T_g^v); (■, ∗, ×) velocity changes respectively at 2.5, 1, 6.33 MHz; (●) variation of $\mu = \mathrm{d} \ln \tan \phi/\mathrm{d}T$

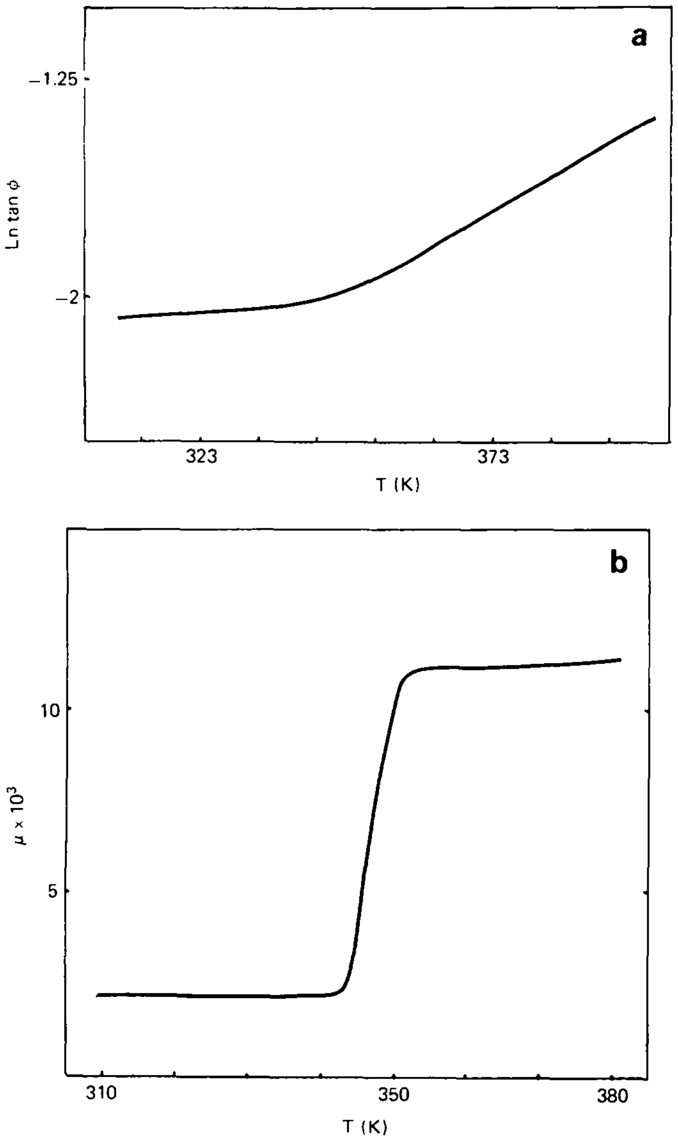

Figure 10 (a) Ln tan ϕ *versus* T ($f = 2.5$ MHz, $P = 450$ bar). (b) $\mu = \mathrm{d}\ \ln\tan\phi/\mathrm{d}T$ *versus* T for the same specimen

polymer is in an isoconfigurational state. But at $T > T_g$, K is temperature-dependent through the 'defect' concentration. Therefore a plot of μ against temperature for a fixed frequency would show an abrupt increase in the magnitude of μ at T near T_g.

Applying this method to our results gives another determination of T_g (*Figure 10*). Values of T_g obtained by this method are also plotted in *Figure 10*, showing good agreement with the two other determinations.

The dependence of T_g on pressure according to the whole data (by the three methods) is found to be $\mathrm{d}T_g/\mathrm{d}P = 0.039$°C bar^{-1}, within the limits of experimental error the same as the variation of T_α. A theoretical calculation of the dependence of T_g on pressure can be made using one of the Ehrenfest relations:

$$\mathrm{d}T^*/\mathrm{d}P = VT_g\,\Delta\alpha/\Delta C_p$$

The value of ΔC_p has been determined at atmospheric pressure on the densified material obtained at 900 bar by d.s.c. measurements and found to be equal to 13 J mol^{-1} K^{-1}. With values of V (molar volume), T_g and $\Delta\alpha$ determined at this pressure we obtain $\mathrm{d}T_g = \mathrm{d}P = 0.042$ K bar^{-1}, which shows a good correlation with our experimental determination.

From the physical model developed by Perez[9] another estimation of $\mathrm{d}T_g/\mathrm{d}P$ is possible according to relations:

$$\Delta\alpha = [N_A/(VkT^2)] \sum \Delta H_f(i)\,\Delta v_d(i) C(i)$$

$$\Delta C_p = (N_A/kT^2) \sum \Delta H_f(i)^2 C(i)$$

where N_A is Avogadro's number, $\Delta H_f(i)$ and $C(i)$ respectively are the enthalpy of formation and the concentration of quasi-defects of type (i) and $\Delta v_d(i)$ is the volume change associated with these defects.

Replacing these relations in the first Ehrenfest relation, as $\Delta v_d(i) = \alpha_g V\,\Delta H_f(i)/2R$, we obtain:

$$\mathrm{d}T_g/\mathrm{d}P = T_g\alpha_g V/2R$$

with our values a mean value of 0.041°C bar^{-1} is obtained.

CONCLUSIONS

Ultrasonic techniques giving access to wave propagation characteristics (velocity and attenuation) are found to be powerful in the characterization of polymers, in particular in the determination of important parameters such as glass transition temperature, α-relaxation temperature and, in the case of semicrystalline polymers, melting and crystallization temperatures. Comparisons with the classical volumetric method give very good agreement. In the glass transition determinations, the use of a simple parameter deduced from a physical model improves the ultrasonic method especially in the case of polymers with high rate of crystallinity. Moreover the combination of the acoustic parameters, volume and pressure and a well defined thermal history give access to all of the pertinent thermodynamic properties. Further work on analysing our data with respect to the thermodynamic state both in equilibrium and out of equilibrium is in progress.

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