



Dielectric study of the segmental relaxation of low and high molecular weight polystyrenes under hydrostatic pressure

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Abstract

In this work we analyze by means of dielectric spectroscopy the dynamics of the α -relaxation process of low and high molecular weight polystyrene over a wide range of pressures and temperatures. The results are interpreted in terms of a recently proposed equation which describes the behavior of the structural relaxation time, $\tau(T, P)$, as a function of both pressure and temperature. This equation has been derived from the Adam–Gibbs (AG) theory by writing the configurational entropy, S_c , in terms of the excess thermal heat capacity and of the excess thermal expansion. Consequently, the molecular dynamic of glass-forming liquids can be linked to its thermodynamic properties. The pressure dependence of the segmental dynamics for both polymers is here measured and analyzed in the AG framework for the first time. $\tau(T, P)$ was found to be very well described using the extended AG equation. Additionally, the pressure dependence of the fragility and glass transition temperature (T_g) is analyzed and discussed in terms of the role of chain length and end groups.

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1. Introduction

The nature of the glass transition is an important open question in condensed matter physics and in polymer science in particular. In the last decades many theories have been proposed to elucidate the molecular dynamics in glass forming systems. Among them, the Adam–Gibbs (AG) theory [1], which relates the dynamics and thermodynamics behavior of the glass formers, has shown to be a very good approach to describe the molecular dynamics close (and above) T_g [2,3]. Moreover, an extension of the AG theory has been recently proposed to describe the component dynamics in miscible polymer blends [4]. Besides the success of these approaches in describing the segmental or

α -relaxation, the understanding of the molecular dynamics of glass forming systems is hardly possible using temperature as the single thermodynamic variable. By varying temperature both thermal energy and density change and therefore their specific contribution becomes indistinguishable. Recent progress in this sense has come from the routinely use of pressure as an experimental independent variable [5–12], and thus, the segmental dynamics has been measured as a function of both pressure and temperature in a wide variety of polymers. In this way the thermal and density contributions to the segmental dynamics can be decoupled. In particular, a pressure extension of the AG theory (PEAG) has been recently proposed to take into account the effects of pressure on the segmental dynamics. This approach has been applied with success to some polymers [6,10–12].

In this work, we have measured for the first time the dielectric dynamics of low and high molecular weight

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polystyrene over a broad range of frequency, temperature and pressure, and we have analyzed the data in terms of the PEAG model. By varying the molecular weight we were able to analyze the role of the chain length and end groups on the pressure dependence of T_g and fragility.

2. Theory

The Adam–Gibbs (AG) theory, which is based on the assumption of co-operative rearranging regions, gives an expression that relates the increase of structural relaxation time, τ , to the reduction of configurational entropy, S_c , by [1]

$$\tau = \tau_0 \exp(C/TS_c), \quad (1)$$

where τ_0 is the value of τ at very high temperature and C is a material constant. This quantity is here assumed independent of temperature and pressure. Since S_c is not experimentally accessible, it is usually identified with the excess entropy ($S_c \propto S_{ex} = S_{melt} - S_{crystal}$). Although the physical meaning of this assumption is still under debate and no general agreement has been achieved [13–15], some findings seem to suggest a general validity of the proportionality between S_{ex} and S_c . Thus, S_c at atmospheric pressure can be estimated as

$$S_c(T) = g_T S_{ex}(T) = g_T \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT', \quad (2)$$

where $\Delta C_P = C_P^{melt} - C_P^{crystal}$ is the excess heat capacity at atmospheric pressure and T_K is the Kauzmann temperature.

Recently, Casalini et al. [6,7] have proposed an extension of Eq. (2) for the configurational entropy (S_c), by adding a term related to the pressure change. Thus, S_c is given by

$$S_c(T, P) = g_T \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT' - g_P(T) \times \int_0^P \Delta \left(\frac{\partial V}{\partial T} \right)_P dP', \quad (3)$$

where $\Delta(\partial V/\partial T)_P = \Delta(\partial V/\partial T)_P^{melt} - \Delta(\partial V/\partial T)_P^{crystal}$ is the difference of the thermal expansivity of the melt and the glass; if g_P does not depend on temperature, then the thermal and volumetric contributions to the configurational entropy are fully decoupled.

It is worth noting here that S_{ex} and $\Delta(\partial V/\partial T)_P$ are defined as the difference between the corresponding quantity of the melt with respect to that of the crystal. However, it is sometimes impossible in polymers to get the thermodynamic properties of the crystalline state. In these cases, it is usually assumed that the heat capacity and thermal expansion for the crystal are similar to those of the glass [16]. Thus, we have used for calculations and $\Delta C_P \cong C_P^{melt} - C_P^{glass}$ and $\Delta(\partial V/\partial T)_P \cong \Delta(\partial V/\partial T)_P^{melt} - \Delta(\partial V/\partial T)_P^{glass}$.

3. Experimental

3.1. Samples

Nearly monodisperse low ($M_w = 780$ g/mol) and high ($M_w = 70950$ g/mol) molecular weight (M_w) polystyrene (PS) was used in this work. The samples were dried in a vacuum oven above T_g for 24 h. The low M_w sample was prepared by putting the polymer between two gold-plated electrodes, 20 mm diameter, with a spacer of 0.1 mm thickness. Details about high M_w sample preparation are given in Ref. [17].

3.2. Dielectric measurements under pressure

Dielectric measurements were carried out in a pressure cell (0–300 MPa) supplied by Novocontrol GmbH. The cell, basically a stainless steel cylinder with a hermetic seal, is filled with a silicone fluid which transmits the pressure from the piston to the sample. The dielectric loss was measured with a broadband (10^{-2} – 10^6 Hz) alpha dielectric analyzer (Novocontrol GmbH). The measurements were performed by frequency sweeps at constant temperature, with stability better than ± 0.1 K, and constant pressure, with stability better than ± 2 MPa.

3.3. Calorimetric data

The temperature dependence of the heat capacity for both low and high M_w polystyrenes has been measured by us in a previous work [4] by means of a differential scanning calorimeter (DSC-Q1000) from TA-Instruments. Measurements were performed in the temperature modulated mode with an average heating rate of 0.1 K/min, amplitude of 0.5 K and an oscillation period of 100 s.

3.4. Pressure–volume–temperature data

The temperature dependence of the melt volume at different pressures for the high M_w PS has been measured by us using a Thermo Haake PVT/100 instrument. For the low M_w PS the corresponding data was taken from Ref. [18]. For the glassy state, no significant variation with molecular weight is reported in Ref. [18] and therefore we have performed an average among the available data on the literature below T_g .

4. Results and discussion

4.1. Dielectric relaxation times

Fig. 1 shows the dielectric loss of low M_w polystyrene as a function of frequency at constant temperature and several pressures as measured using the pressure cell. The spectra were fitted using the Havriliak–Negami (HN) equation

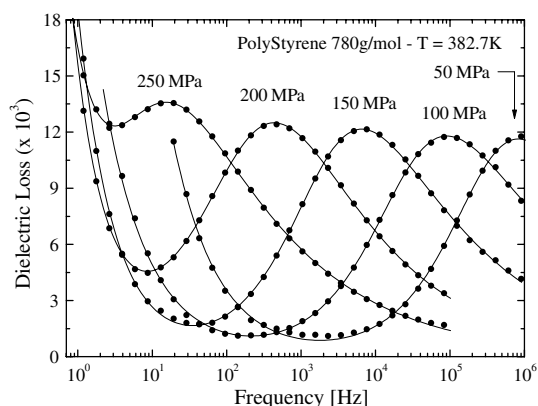


Fig. 1. Dielectric loss (ϵ'') vs. frequency for low M_w polystyrene at 382.7 K and several pressures.

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^{\alpha\beta}]}, \quad (4)$$

where $\Delta\epsilon$ is the relaxation strength, τ_{HN} is the relaxation time and α and β are shape parameters.

Figs. 2 and 3 show the Arrhenius plots for the segmental relaxation time of maximal loss $\tau_{Max} = \omega_{Max}^{-1} = 1/(2\pi f_{Max})$ as a function of temperature, at different pressures, for low and high M_w PS, respectively. Filled lines in Figs. 2 and 3 represent the corresponding fits to the PEAG equation as explained below.

4.2. Adam–Gibbs approach

4.2.1. Thermal effects

According to previous results [4,11,12], the heat capacity can be well described by linear functions both above and below T_g . Thus, the excess heat capacity (ΔC_P) can be expressed according to the empirical linear equation $\Delta C_P = b - m_T T$. The fitting of the experimental data (see Ref. [4]) gives $b = (85.5 \pm 0.01) \text{ J K}^{-1} \text{ mol}^{-1}$, $m_T = (0.18 \pm 0.01) \text{ J K}^{-2} \text{ mol}^{-1}$ and $b = (99.0 \pm 0.01) \text{ J K}^{-1} \text{ mol}^{-1}$, $m_T = (0.171 \pm 0.002) \text{ J K}^{-2} \text{ mol}^{-1}$ for low and high M_w

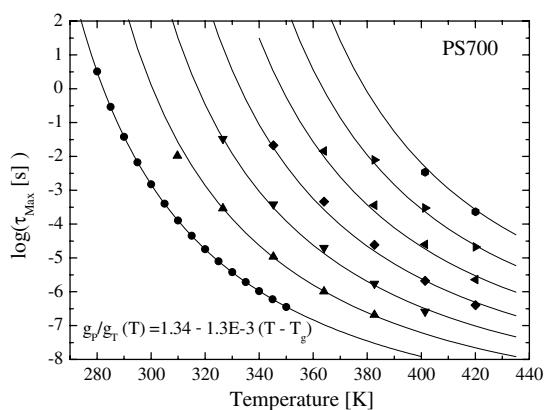


Fig. 2. Segmental relaxation time of low M_w polystyrene as a function of temperature at different pressures from bottom to top: atmospheric pressure (0.1, 50, 100, 150, 200, 250 and 300 MPa).

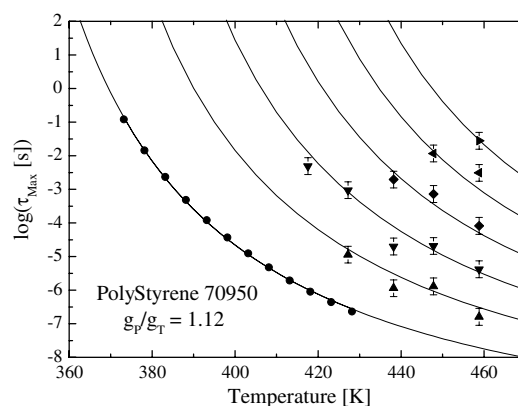


Fig. 3. Segmental relaxation time of high M_w polystyrene as a function of temperature at different pressures from bottom to top: atmospheric pressure (0.1, 50, 100, 150, 200 and 250 MPa).

PS, respectively. In this way, the thermal contribution to the configurational entropy result in

$$\begin{aligned} S_c(T, P \cong 0) &= g_T \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT' \\ &= g_T (b \ln(T/T_K) - m_T(T - T_K)). \end{aligned} \quad (5)$$

Thus, by introducing this result in Eq. (1), the temperature dependence of the relaxation time at atmospheric pressure would be given by

$$\tau(T, 0) = \tau_0 \exp \left[\frac{C/g_T}{T(b \ln(T/T_K) - m_T(T - T_K))} \right]. \quad (6)$$

By using Eq. (6) to fit the atmospheric pressure experimental data we got [4] $\log(\tau_0 [\text{s}]) = -12.5 \pm 0.1$, $C/g_T = (75.8 \pm 0.4) \text{ kJ mol}^{-1}$, $T_K = (223.8 \pm 0.2) \text{ K}$ and $\log(\tau_0 [\text{s}]) = -12.4 \pm 0.1$, $C/g_T = (60.7 \pm 0.3) \text{ kJ mol}^{-1}$, $T_K = (322.2 \pm 0.2) \text{ K}$ for low and high M_w PS, respectively. Lowest lines in Figs. 2 and 3 show the best fit to the experimental data by using Eq. (6).

4.2.2. Volumetric effects

In order to calculate the volumetric contribution to the configurational entropy we need to estimate $\Delta(\partial V/\partial T)_P$. To do this we plotted the specific volume versus temperature, at different pressures and subtracted the slopes below and above T_g at each pressure. Fig. 4 shows the pressure dependence of $\Delta(\partial V/\partial T)_P$ so obtained and the best fits to an empirical exponential decay according to

$$\Delta(\partial V/\partial T)_P = \Delta(\partial V/\partial T)_{P=0} - A[1 - \exp(-P/P_0)], \quad (7)$$

with $A = (2.81 \pm 0.02)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$, $P_0 = (137 \pm 3) \text{ MPa}$, $\Delta(\partial V/\partial T)_{P=0} = (4.48 \pm 0.03)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ and $A = (1.98 \pm 0.21)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$, $P_0 = (122 \pm 4) \text{ MPa}$, $\Delta(\partial V/\partial T)_{P=0} = (3.54 \pm 0.10)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ for low and high M_w PS, respectively. Therefore the pressure contribution to the configurational entropy is

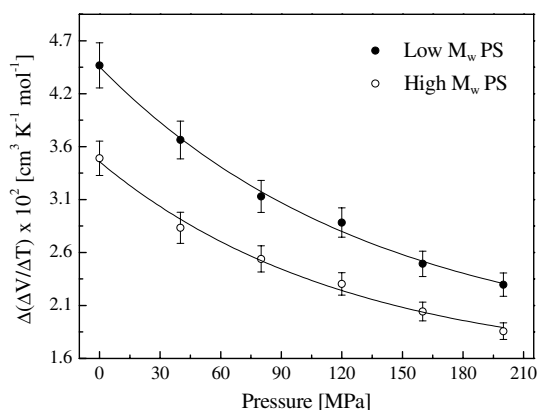


Fig. 4. Pressure dependence of $\Delta(\Delta V/\Delta T)$ for low and high molecular weight polystyrenes. Solid lines represent the best fit of the experimental data by means of Eq. (7).

$$g_P \int_0^P \Delta(\partial V/\partial T)_{P'} dP' = g_P P_0 \left[\Delta(\partial V/\partial T)_{P=0} \frac{P}{P_0} - A \left[\frac{P}{P_0} + \exp(-P/P_0) \right] \right]. \quad (8)$$

By using Eqs. (6) and (8) in (3) and then by replacing in Eq. (1) we have the following expression for the temperature–pressure dependence of the relaxation time

$$\tau(T, P) = \tau_0 \exp \left[\frac{C/g_T}{T \left\{ [b \ln(T/T_K) - m_T(T - T_K)] - \frac{g_P}{g_T} \left[\Delta(\frac{\partial V}{\partial T})_{P=0} P - A \left[P - P_0 \left(1 - \exp\left(-\frac{P}{P_0}\right) \right) \right] \right] \right\}} \right]. \quad (9)$$

It is worth to mention that most of the parameters of Eq. (9) have been obtained from DSC (b, m_T) and PVT ($A, P_0, \Delta(\partial V/\partial T)_{P=0}$) characterization and from the temperature dependence of the relaxation times at atmospheric pressure through Eq. (6) ($\log(\tau_0), C/g_T, T_K$). The only free parameter which has to be obtained from measurements of the relaxation time at higher pressures is g_P/g_T . We tried first to fit the experimental relaxation times for low M_w PS (Fig. 2), with a constant value of g_P/g_T , by minimizing the mean square deviation; however, a systematic deviation between the experimental and predicted points using Eq. (9) was observed in this case. However, as pointed out in the introduction, g_P could depend on temperature and therefore g_P/g_T could too. Thus, by assuming a linear dependence for g_P/g_T [19] with temperature, we can write $g_P/g_T(T) = (g_P/g_T)_{T_g} + m_g(T - T_g)$ and estimate $(g_P/g_T)_{T_g}$ and m_g by minimizing the mean square deviation as previously. The so obtained parameters for low M_w PS are $(g_P/g_T)_{T_g} = 1.34 \pm 0.02$ and $m_g = -(1.3 \pm 0.1)10^{-3} \text{ K}^{-1}$. Fig. 2 shows the excellent agreement between the experimental data and the calculated relaxation times through Eq. (9). For high M_w PS the higher uncertainties of the experimental data (due to experimental difficulties, see Ref. [17]) makes difficult to assume a linear dependence of g_P/g_T ; instead, a constant value of g_P/g_T was used in Eq.

(9) and a value of 1.12 ± 0.05 was obtained after fitting the experimental data. Fig. 3 shows the agreement between the experimental data and the relaxation times calculated with the PEAG equation (Eq. (9)). The obtained values of g_P/g_T are similar to those previously calculated for other polymers [11,12] and also for low molecular weight glass-formers [7].

It is important to note that the value of g_P/g_T for the low M_w PS equals 1.12 ± 0.05 (the value for the high M_w PS) in the temperature range 380–460 K, where the dynamics of the high M_w PS is observed. This fact makes to think that the function $g_P/g_T(T)$ does not depend on the molecular weight. This means that chain length or end groups do not determine the relative composition of the excess entropy. However, this relative composition depends on temperature; around T_g the volumetric contribution would be more important whereas at higher temperatures the thermal contribution to the excess entropy would be larger. Whether this is a general trend for other polymers is something which needs to be tested.

As aforementioned, the dielectric response of PS at high pressures is here presented for the first time and therefore we cannot compare our results with other previously published. However, it is possible from these results to get the pressure dependence of the dielectric T_g (i.e., $T(\tau = 10^2 \text{ s})$)

and the isobaric fragility (m) which have been previously measured by other techniques. The isobaric fragility (m) is defined as the slope of the curve $\log(\tau_{\text{Max}})$ vs. T_g/T at $T = T_g$, i.e., $m = d \log(\tau_{\text{Max}})/d(T_g/T)|_{T=T_g}$. From Figs. 2 and 3 we can calculate the dielectric T_g and m as a function of the pressure; the results are shown in Fig. 5. We found that the pressure dependence of the dielectric T_g for high

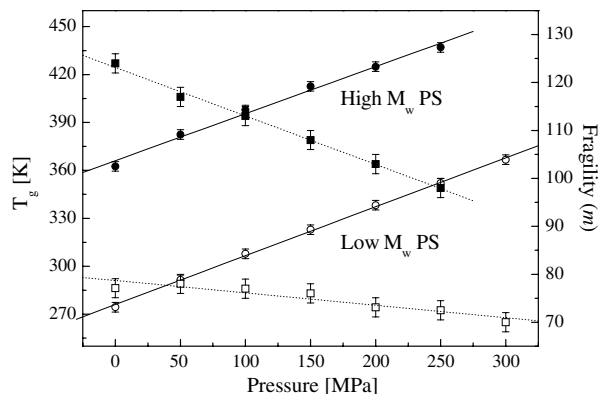


Fig. 5. Pressure dependence of T_g (circles) and fragility (squares) for low (open symbols) and high (filled symbols) molecular weight polystyrenes. Solid (T_g) and dashed (m) lines represent the best linear fit of the experimental data.

M_w PS is $dT_g/dP = 294 \pm 17$ K/GPa in good agreement with previous calculated value [20] (303 K/GPa by means of DTA measurements); whereas for low M_w PS we found $dT_g/dP = 306 \pm 12$ K/GPa, which is rather similar to the high M_w value. However, when normalized by $T_g(1/T_g dT_g/dP)$ we obtain 1.13 and 0.81 GPa^{-1} for low and high M_w , respectively, which gives a relative important chain length dependence. The higher normalized pressure dependence of T_g in low M_w PS is probably due to the higher density of end groups which are expected to be more sensitive to pressure changes.

The isobaric fragility obtained at atmospheric pressure for high M_w PS (124 ± 2) is rather similar to the previously published value of 116 [21]; whereas for low M_w PS we found 77 ± 2 which agrees with the published value of 80 [22]. Concerning to the pressure dependence of the isobaric fragility, this value is rather dependent of the pressure interval as well as of the experimental technique used to calculate it. For the whole pressure range we got for high M_w PS $dm/dP = -101 \pm 12$ GPa^{-1} which is smaller (probably due to differences in the M_w) than that one (-160 GPa^{-1}) calculated by Huang et al. [23] from photon correlation data. Noticeably, for low M_w PS the pressure dependence of the fragility is rather smaller $dm/dP = -26 \pm 4$ GPa^{-1} ; since fragility correlates with many glass former properties, these results are worth to be deeper investigated in future works.

5. Conclusions

We have presented in this work new experimental data concerning to the temperature–pressure dependence of the segmental relaxation time of low and high molecular weight polystyrene. The experimental data have been analyzed in terms of the pressure extended AG equation which has shown to give an excellent description of the relaxation times as a function of both pressure and temperature. These results support the validity of the AG frame. We have found that the function $g_P/g_T(T)$ would not depend on molecular weight. Additionally, the pressure dependence of T_g and fragility for the here studied polymers has been analyzed in terms of different chain lengths and compared with previous results.

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