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Relaxation Studies of Poly(propylene glycol) under High Pressure

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ABSTRACT: The effect of pressure on the relaxation processes in poly(propylene glycol) of number-average molecular weights 400 and 4000 g mol^{-1} (PPG-400 and PPG-4000) has been investigated using dielectric spectroscopy as well as thermal conductivity and heat capacity measurements. The relaxations associated with segmental motions within the polymer chain (α relaxation) and whole chain motions (α′ relaxation) have been studied in the temperature range 200−400 K for pressures up to 2 GPa. The two processes display slightly different sensitivities to pressure, and as a consequence, are better separated at high pressures. As a result, high-pressure data exhibit the α′ relaxation also in PPG-400, whereas previous investigations at atmospheric pressure have detected it only in PPG of molecular weights above about 1000 g mol^{-1}. At atmospheric pressure, the values for $(\partial T/\partial p)_{\tau=1\mathrm{s}}$ of the α relaxation are, respectively, 140 and 192 K GPa^{-1} for PPG-400 and PPG-4000, where τ is the relaxation time. Because of the difference in $(\partial T/\partial p)_\tau$, the relaxation of the α motions and therefore the glass-transition temperature exhibits a more significant dependence on molecular weight at high pressures. At 295 K and 0.3 GPa, the activation volumes for the α and α′ processes of PPG-4000 are about the same (≈45 cm^3 mol^{-1}). At the same conditions, the activation volume for the α process of PPG-400 is about half of that for PPG-4000. An analysis of the α relaxation in terms of the strong-fragility classification shows that the degree of fragility of both PPG-400 and PPG-4000 increases slightly with increasing pressure.

Introduction

Poly(propylene glycol) (PPG) and poly(propylene oxide) (PPO) (PPG without the OH end groups) have been studied extensively in numerous relaxation studies at atmospheric pressure,[1−9] and in some cases also at elevated pressures.[10−13] In this work, we extend these studies to high pressures (2 GPa) and explore the glass-formation characteristics under high-pressure conditions. In particular, pressure effects on the relaxation spectrum and the strong−fragile behavior of PPG are investigated.

Experimental results for PPG and PPO coincide for properties which are determined by the polymer chain and not by the end groups. Moreover, all properties of high-molecular-weight samples of PPG and PPO should agree well since the importance of the end-group properties vanishes. It follows that previous results for PPO provide valuable information in a study of PPG.

As for most polymers, the relaxation spectrum of PPG (and PPO) is quite complex and PPG exhibits at least three distinctly different relaxation processes, which are normally denoted α, α′, and β. The α process is the most prominent one and is associated with the segmental motions within the polymer chains. The freeze-in of these motions is responsible for the glass-transition, which occurs at about 200 K at atmospheric pressure for molecular weights above 400 g mol^{-1}.[2,14] The α′ relaxation is attributed to the motions of the whole polymer chain and is therefore dependent on molecular weight. The α′ process moves toward higher frequencies with decreasing molecular weight and merges with the α process for molecular weights below about 1000 g mol^{-1}.[1,2] The α′ process is observed at lower probe frequencies than the α process and, as a consequence, it freezes in at a slightly higher temperature than the glass-transition temperature. The origin of the weak β process, which is observed in almost all types of glasses, is still not established. However, the successful mode-coupling theory as well as computer simulations indicate that it is associated with localized motions which involve only a few number of atoms.[3] In this work, we are not concerned with the β relaxation.

The glass-transition temperature T_g is generally determined by observing the abrupt increase in the heat capacity which accompanies the glass-transition on heating at a constant rate. The glass-transition temperature depends both on the employed heating rate and on the thermal history. That is, the measured value for T_g depends on the way the glassy state was formed and can therefore vary between different investigations despite that the same heating rate is used. We have used two dynamic methods to explore the relaxations of the α and α′ processes under pressure. As we show, both dielectric spectroscopy and measurements using the hot-wire method are useful in such studies. The former, or similar, methods, in which molecular motions present in the supercooled liquid state are forced out of equilibrium by a periodically varying perturbation, is commonly used to study relaxation phenomena. In such cases, the sample state is not dependent on the thermal history if the cooling or heating rate is slow in comparison with the relaxation time τ. The measured values for τ as a function of temperature provide an estimate for the calorimetrically determined value for T_g, which corresponds roughly to the temperature where τ is of order 10^3 s, but an exact comparison is not possible. We use T_α and $T_{\alpha'}$ to indicate the temperatures where the relaxations of the α and α′ processes occur in the time scale of our methods. Consequently, $T_\alpha(\tau = 10^3\ \mathrm{s})$ corresponds roughly to T_g. In this work, we study mainly the effect of pressure on the relaxation spectra, but we compare also the pressure influence on the relaxation of molecular motions as observed using the hot-wire method and that observed in bulk modulus measurements (that is, if the pressure change of the

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relaxation temperature observed in hot-wire measurements corresponds well with that for T_g).

In hot-wire measurements, values for thermal conductivity λ and heat capacity per unit volume ρc_p are obtained. Using this method, the sample is probed by a short heating pulse passed through a thin metal wire, which is immersed in the sample. It has been shown previously[15] that the method is sensitive to the kinetic character of the glass-transition and yields anomalous values when the sample relaxation time is of the same order as the heat pulse length. In particular, one observes a peak in λ and a dip in ρc_p which both are artifacts that arise due to the relaxation process, and the peak maximum in λ occurs at an average relaxation time of 0.3 s.[15] In a frequency domain measurement, this corresponds approximately to a relaxation maximum at 0.5 Hz ($=1/(2\pi\tau)$). Since τ is short at the temperature for the peak maximum in λ, this temperature is independent of thermal history for the employed heating and cooling rates of the sample (<0.5 K min^{-1}). The artifacts are useful signatures of a relaxation process and are here used to study the effect of pressure on the α and α' relaxations. It is important to point out that this method, as opposed to dielectric spectroscopy, is sensitive also to a relaxation process which is not associated with a dipole. Consequently, a relaxation process which is not, or only weakly, associated with a dipole can be observed in hot-wire measurements but remains undetected or weak in dielectric spectroscopy.

Results for τ of the α relaxation as a function of temperature provide a useful way to characterize glass formers in terms of strong and fragile behavior.[16,17] If τ changes relatively slowly with temperature, following an Arrhenius behavior $\tau \propto \exp(B/T)$ in a wide temperature range, then glass formers are referred to as strong since their structures degrade slowly on heating, and a well-known example is SiO_2. The other extremes are referred to as fragile. In those cases, τ changes more rapidly near the calorimetric glass-transition temperature, and furthermore, the Vogel−Fulcher−Tamman−Hesse (VFTH) equation $\tau \propto \exp[B/(T - T_0)]$ must be employed to describe $\tau(T)$ in a wide temperature range.

PPG exhibits an intermediate behavior between the two extreme limits of strong and fragile behavior,[16] which is typical for polymers. One way to modify the behavior is to introduce cross-links between the chains. Here, we investigate if the strong−fragility behavior is also influenced by applying high pressure, and we show that it is changed slightly toward a higher degree of fragility at high pressures.

Experimental Section

Materials. The two samples of poly(propylene glycol) (PPG) were supplied by Polyscience Inc. The number-average molecular weights were 400 g mol^{-1} for PPG-400 and 4000 g mol^{-1} for PPG-4000. Since PPG is hygroscopic, the samples were prepared in a vacuum oven, which was heated to 360 K under a vacuum better than 10^{-3} Pa. The samples were kept under these conditions for 24 h and, subsequently, cooled to room temperature during 24 h. After this treatment the samples were assumed to be free from water and solvents.

Dielectric Spectroscopy. We used an unguarded parallel capacitor made of brass plates with Teflon spacers. The capacitor was placed within a Teflon cell which was mounted in a piston-cylinder device of an internal diameter of 45 mm. The arrangement has previously been described in detail.[18] To minimize external noise, the copper wires from the cylinder device were screened and connected to coaxial cables. The temperature was measured with an internal chromel alumel thermocouple. The temperature could be varied by cooling or heating the whole pressure cylinder. The pressure was determined from the press force per area using an empirically established correction for friction. The complex admittance, Y^*, of the cell capacitor was measured using a frequency response impedance analyzing system.[18] The system can operate in the frequency range 5 Hz to 13 MHz, with an oscillator voltage of 1.1 V. Since we are only interested in studying the dielectric loss maximum versus temperature and pressure, and a transformation to complex permittivity needs accurate calibration data, we choose not to transform our data. Instead, we present the data in the form of complex capacitance $C^* = Y^*/i\omega = C' - iC''$. The loss, C'', is defined as G/ω, where G is the parallel conductance and ω is the radian frequency of the applied electric field. We have also carried out a few measurements below 5 Hz. A detailed description of this measurement system has previously been given in ref 18.

Hot-Wire Method. The transient hot-wire method was used to measure simultaneously the thermal conductivity λ and the heat capacity per unit volume ρc_p, where c_p is the isobaric specific heat capacity and ρ is the mass density. The method has previously been described in detail.[19] The sensor was a nickel wire (0.1 mm in diameter) placed horizontally in a ring of constant radius within a Teflon cell. The hot wire was surrounded by the medium under investigation (PPG). The whole assembly was loaded into a piston-cylinder apparatus and the pressure was generated by a 5 MN hydraulic press. The hot-wire probe was heated by a 1.4-s pulse of nearly constant power and the wire resistance was measured versus time. The temperature rise of the wire could thus be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ and ρc_p. The inaccuracy was estimated as ±2% in λ and ±5% in ρc_p.[19]

The hot-wire method yields specific signatures for a glass-transition. Both isothermal measurements and isobaric measurements yield a peak in λ and dip in ρc_p near T_g. These are artifacts of the method and due to a time dependence in c_p near T_g.[15] Since this dependence is not accounted for in the analysis of the hot-wire temperature rise, this results in anomalous values for λ and ρc_p.

High-Pressure Equipment. Two types of high-pressure apparatuses were used during the investigations. In the temperature range 260−430 K, we used equipment which can operate up to 2 GPa. A general description of this equipment has previously been given.[20] At temperatures below 260 K, we used an apparatus which operates to 1.0 GPa.[21]

The temperature of the high-temperature vessel (260−430 K) was varied by either heating or cooling the whole pressure vessel. For this purpose, the vessel was equipped with both an electrical resistance heater and a cooling coil of a copper tube. Through the latter we could pass liquid nitrogen.

Below 260 K, we used a vessel specially designed for low temperatures. The vessel was continuously cooled by a closed cycle helium compressor (RW 500) with a cold head (RSG 120) from Leybold AG, which was clamped on the copper cylinder surrounding the pressure vessel. The temperature of the vessel could be controlled by varying the power to an electrical resistance heater placed on the cold head. The heat flow through the top and bottom pistons was reduced by copper braids connected between the cold head and the tool-steel anvils which transmit load to the pistons. The anvils were thermally insulated from the press by using plates of glass-fiber reinforced siloxane resin. The pressure vessel was kept in a vacuum chamber which was continuously pumped to yield a pressure of about 10 Pa.

The temperature T of the specimen was measured using an internal chromel alumel thermocouple, which had been calibrated against a commercial diode sensor. The pressure p was determined from the load/area, with an empirical correction for friction, which had been established using the pressure dependence of a manganin wire. The inaccuracy in pressure was estimated as ±40 MPa at 1 GPa. Temperature and pressure were regulated using an adaptive microcontroller (First Control System AB, Västerås, Sweden). A thyristor unit

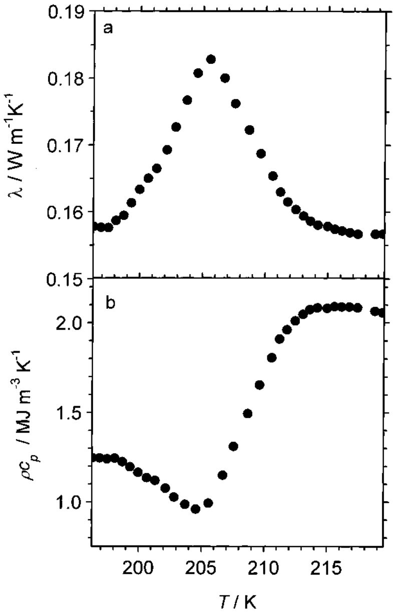

Figure 1. Hot-wire results for PPG-400 at a pressure of 0.1 MPa, which show (a) the anomalous peak in the thermal conductivity and (b) the anomalous dip and the step increase in the heat capacity per unit volume, which arise due to a relaxation process.

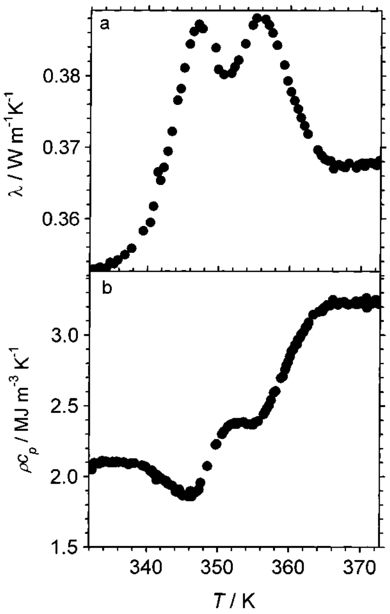

Figure 2. Hot-wire results for PPG-400 at a pressure of 2 GPa, which show (a) the anomalous peaks in the thermal conductivity and (b) the two-step increases in the heat capacity per unit volume, which are associated with the α and α′ processes.

provided the modulated power for the heaters. Using this procedure, the temperature could be kept to within ±0.5 K during isothermal measurements. The pressure fluctuation during isobaric measurements was less than ±1 MPa.

Results and Discussion

Figure 1a shows $\lambda(T)$ for PPG-400 at 0.1 MPa, and Figure 1b shows the corresponding results for $\rho c_p(T)$. The abrupt increase in ρc_p is associated with the glass-transition and signals that the motions of the α process become active on the time scale of the hot-wire method. The peak in $\lambda(T)$ and the dip in $\rho c_p(T)$ (Figure 1) are the artifacts that arise due to the relaxation, and the maximum in λ corresponds to a relaxation time of about 0.3 s.[15] The results for λ and ρc_p of PPG-4000 (not shown) are similar, but the step increase in ρc_p is shifted to a slightly higher temperature. As described in the Introduction, results for dielectric loss of PPG-4000 show two relaxation processes, the α and α′ relaxations. Despite this, we observe only one relaxation process in our data for λ and ρc_p at atmospheric pressure. This is due to the fact that the two relaxations merge at low probe frequencies. Our data for dielectric loss show that the loss maxima, associated with the two relaxations, differ by 40 K at a probe frequency of 10^5 Hz but only 15 K at 10^2 Hz. Since the onset of the peak in λ at the low-temperature side corresponds to $\tau \approx 10^2$ s ($\sim 10^{-3}$ Hz) and that of the high-temperature side to $\tau \approx 10^{-2}$ s ($\sim 10^1$ Hz),[15] it is reasonable to assume that the α and α′ relaxations combine to give a single peak in λ. At higher pressures, however, the two processes are well-separated in frequency (and temperature) so that two peaks appear in λ (Figure 2).

Figure 2 shows the results for $\lambda(T)$ and $\rho c_p(T)$ at 2.0 GPa for PPG-400. The two closely spaced peaks in λ and the two steps in ρc_p show that PPG-400 exhibits two relaxation processes at high pressure. The same results are observed in the data for PPG-4000. At pressures below about 0.65 GPa for PPG-400 (0.5 GPa for PPG-4000), we find only one relaxation process, which is the same result as that observed previously in data for dielectric loss of PPG-400 at atmospheric pressure.[1,2] Consequently, τ of the two processes must exhibit different $(\partial T/\partial p)_\tau$ so that they split up into two distinguishable processes at high pressures. Recent data for the two relaxations of PPG-4000 at high pressure corroborate our results.[11] These show that the two relaxations are better separated at high pressure. Furthermore, at $\tau = 0.3$ s, which corresponds to the peak maximum in λ, they should differ about 0.1 GPa at 250 K. This is in fair agreement with the result of the hot-wire method, where the maxima in λ occur near this temperature and are separated by about 0.05 GPa. Moreover, it seems reasonable that the α process which is associated with segmental motions within the polymer chains should be less sensitive to pressure changes than the α′ process where the whole molecular chain is involved and, as a consequence, that the two processes should become better separated in frequency (and temperature) at increasing pressure.

We can conclude that the two relaxation processes observed in the data for λ and ρc_p are probably associated with the α and α′ relaxations. Moreover, the latter occurs at a slightly higher temperature than the α relaxation, and the difference in temperature increases with increasing pressure. The α′ process can therefore be observed in the hot-wire results for PPG-400 at high pressures but merges with the α process at atmospheric pressure.

Figure 2b shows that the step in ρc_p associated with the α′ process of PPG-400 at 2 GPa is somewhat bigger than that for the α process. Consequently, the motions associated with the whole molecule (α′ process) contribute slightly more to the heat capacity than those that are associated with the individual segmental motions within the chains (α process). For PPG-4000 at 2 GPa, the motions associated with the two-processes contribute to roughly the same extent to the heat capacity. That is, the two step changes in ρc_p are of about the same size. It is a bit surprising that the α′ relaxation is so

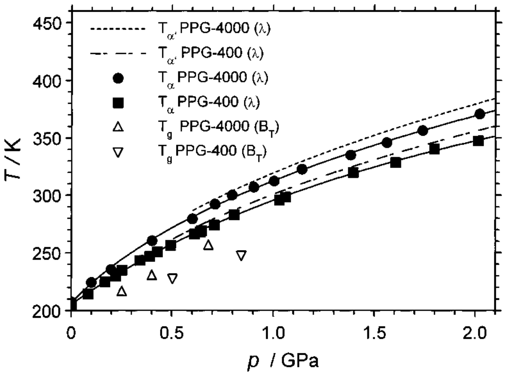

Figure 3. Relaxation temperatures for the α and α′ process as a function of pressure, for PPG-400 and PPG-4000, as probed by the hot-wire method. The solid and dash lines represent fits of eq 4. Triangles represent data for T_g from measurements of bulk modulus B_T.[23]

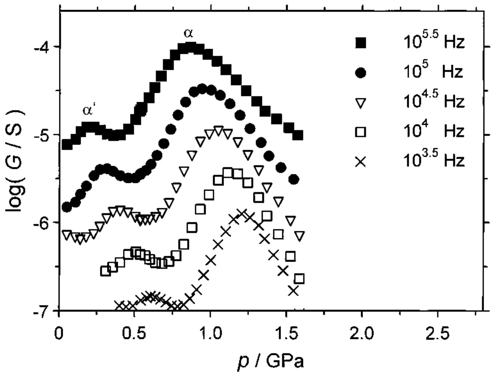

Figure 4. Conductance for PPG-4000 as a function of pressure at 345 K and for probe frequencies indicated in the figure.

pronounced in the data for ρc_p. However, the reason for the small effect of the α′ process in the dielectric data is due to a small associated dipole, whereas the result here for ρc_p shows that the motions associated with this process contribute significantly to the heat capacity.

Figure 3 shows the results for T_α and $T_{\alpha'}$ as a function of pressure for both PPG-400 and PPG-4000, where T_α and $T_{\alpha'}$ denote the relaxations of the α and α′ processes as observed using the hot-wire method. From these results, it is obvious that both T_α and $T_{\alpha'}$ become dependent on molecular weight at high pressures, but are roughly independent of molecular weight at atmospheric pressure. It is somewhat surprising that the α process shows a significant dependence of molecular weight at high pressure. The result indicates that the molecular weight of PPG-400 is not sufficiently high to ignore the effect of end groups on the segmental motions within the polymer chain at high pressures. A hypothesis is that the hydrogen bonds in PPG make T_α independent of molecular weights above about 400 g mol^{-1} at atmospheric pressure, but that the bonds are affected by high pressure so that T_α becomes dependent on molecular weight. That is, the apparent increase of chain lengths induced by the hydrogen bonds at atmospheric pressure is affected by high pressures. Figure 3 also shows that T_α differs from $T_{\alpha'}$ at high pressures but that they merge at low pressure for both PPG-400 and PPG-4000.

Results for the conductance of PPG-4000 as a function of pressure show that the two processes tend to merge as the relaxation time decreases (Figure 4). This is the same effect as that observed at decreasing temperature. In other words, when τ of the two processes decrease, they occur closer in temperature and pressure space. However, the results of λ and ρc_p show that they do not merge completely at high pressures for the frequency window investigated here. A linear extrapolation of the results shown in Figure 4 shows that the two processes should differ by 0.45 GPa at 320 K in the hot-wire results, whereas these show a difference of 0.15 GPa (Figure 3). Although there is a rather large disagreement in magnitude, the result of this rough estimate supports the finding from the hot-wire results that the processes are better separated at high pressures.

From the dielectric results for the temperature and pressure dependencies of τ, we obtain the activation energy E_a and activation volume $\Delta V^\#$, respectively. These are given by[22]

$$E_a = R(\partial \ln \tau / \partial T^{-1})_p \qquad (1)$$

$$\Delta V^\# = RT(\partial \ln \tau / \partial p)_T \qquad (2)$$

where R is the gas constant.

For PPG-4000 at 295 K and 0.3 GPa, $\Delta V^\#_\alpha = 43$ cm^3 mol^{-1} and $\Delta V^\#_{\alpha'} = 48$ cm^3 mol^{-1}. It is interesting to note that the activation volumes are the same to within experimental accuracy, despite the fact that the α′ process is associated with the motions of the whole chain whereas the α process is associated with segmental motions within the chains. Although the activation volume changes with temperatures (as well as with pressure), the values for $\Delta V^\#$ of the two processes are probably not very different from each other also at low temperatures. At least they exhibit similar temperature dependence of $\Delta V^\#$ within the range observed here (350−290 K), which is described well by second-order polynomials. An extrapolation using a fitted second-order polynomial yields $\Delta V^\#_\alpha = 92$ cm^3 mol^{-1} at 250 K, which is in excellent agreement with previous results obtained from dielectric[7] and photon correlation[11] spectroscopy ($\Delta V^\#_\alpha \approx 95$ cm^3 mol^{-1}).

The activation energy of PPG-4000 at atmospheric pressure is in the range of the values found previously using dielectric spectroscopy (32−52 kJ mol^{-1} at 295 K and 85−120 kJ mol^{-1} at 240 K), but disagree with those of other methods (17−23 kJ mol^{-1}).[9] At atmospheric pressure and 240 K, the two processes have about the same activation energy $E_{a,\alpha} = E_{a,\alpha'} = 90$ kJ mol^{-1}. At a further decrease of temperature, E_a of the α process becomes larger than that of the α′ process, which can account for its smaller value for $(\partial T/\partial p)_\tau$ $(=T\Delta V^\#/E_a)$.

For PPG-400 at 295 K and 0.3 GPa, $\Delta V^\#_\alpha = 23$ cm^3 mol^{-1}, which is about half that of PPG-4000. Consequently, there is a significant difference and it seems reasonable to attribute it to the molecular-weight difference and the influence of the end groups. The activation energy, however, is only a few percent larger than that of PPG-4000, which is within experimental inaccuracy and agree with previous findings.[6]

It is not possible to detect the α′ process for PPG-400 in the results of dielectric spectroscopy. Isobaric measurements were performed at atmospheric pressure, 1, 1.2, 1.5, and 1.8 GPa. Despite the strong effect of the α′ process in the data for λ and ρc_p at 1 GPa and higher pressures, our dielectric results do not show the relaxation, which we attribute to a too weak dipole associated with the α′ process. For PPG-4000, the weak α′ process could be detected in isothermal runs at room tempera-

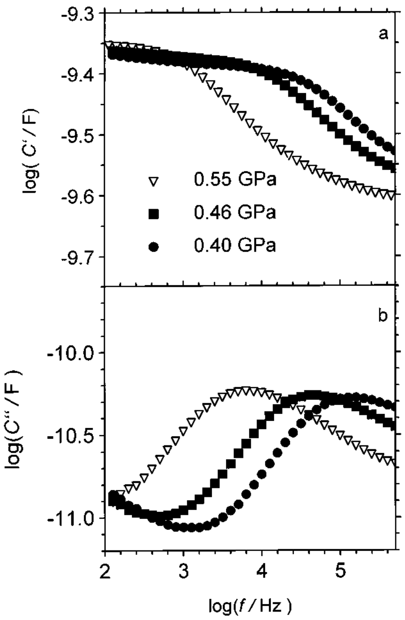

Figure 5. (a) Real part of capacitance and (b) imaginary part of capacitance as a function of frequency for PPG-4000 at pressures of 0.40, 0.46, and 0.55 GPa.

ture and at isobaric runs at atmospheric pressure. However, in data for isobaric runs at high pressures, it is not possible to distinguish the α′ process.

The relaxation spectra of both processes are broad, which for the α process (Figure 5) was quantified in terms of the Kohlrausch–Williams–Watts (KWW) relaxation function:

$$\phi \propto \exp(-(t/\tau_0)^{\beta_{\mathrm{KWW}}}) \tag{3}$$

where τ_0 is the characteristic relaxation time and the parameter β_{KWW} ($0 < \beta_{\mathrm{KWW}} \leq 1$) can be interpreted as a measure of the relaxation time distribution, where $\beta_{\mathrm{KWW}} = 1$ corresponds to a single relaxation time. Fits of the KWW function yield $\beta_{\mathrm{KWW}} = 0.51$, independent of molecular weight and pressure to within experimental inaccuracy. The value for β_{KWW} and its independence of molecular weight are in excellent agreement with previous results of Alper et al.[2] Furthermore, Williams[7] has shown that dielectric loss data of PPO as a function of temperature and pressure can be represented by a single master curve, which shows that the distribution of relaxation times, and therefore β_{KWW}, is independent of pressure.

Glass-Transition Temperature. Here we compare the results for T_α with those for T_g as well as with previous results for T_α. In particular, the pressure dependence of T_α and T_g as observed in measurements of the bulk modulus using a rate of pressure increase of 0.2 GPa h^{-1}.[23] The results for T_g were extracted from data obtained on increasing pressure and, consequently, going from the liquid to the glassy state. Our data for T_α (and $T_{\alpha'}$) were extracted from the hot-wire results which correspond to the lowest probe frequency used in this investigation (0.5 Hz) and should therefore agree best with data for T_g. The results show that the pressure dependencies of T_g obtained from a bulk modulus and thermal conductivity are the same to within experimental inaccuracy (Figure 3). Consequently, the curves for T_g and T_α versus pressure are almost parallel but shifted in temperature, which is mainly due to the different time scales of the methods. Williams[7] has shown that values for $(\partial T/\partial p)_\tau$ are dependent on τ and therefore on probe frequency, at least for frequencies above 100 Hz. Our results show that for a probe frequency of 0.5 Hz, the results for $(\partial T_\alpha/\partial p)_\tau$ of PPG provide a good measure of those for $\mathrm{d}T_g/\mathrm{d}p$.

Table 1. Expression: $T_{\alpha \text{ or } \alpha'}(p) = c(1+ b/ap)^{1/b}$ Fitted to Results for T_α ($T_{\alpha'}$) and p_α ($p_{\alpha'}$)[a]

polymer	relaxation	p-range (GPa)	a (GPa)	b	c (K)	ΔT[b] (K)
PPG-400	α	0.0–2.0	1.438	3.110	203.45	1.6
PPG-400	α′	0.4–2.0	1.161	3.305	200.14	1.8
PPG-4000	α	0.0–2.0	1.071	3.414	205.52	2.6
PPG-4000	α′	0.5–2.0	1.145	3.208	210.66	2.1

[a] The values for T_α and p_α were taken from the peak positions of λ. [b] Maximum deviation between experimental points and fitted curve

The results for the relaxations of both the α and α′ processes of PPG-400 and PPG-4000 are shown in Figure 3. The values were taken from the peak position in $\lambda(T)$ and $\lambda(p)$ and could be described to within 2.6 K by the following empirical equation:

$$T_{\alpha \text{ or } \alpha'}(p) = c\left(1 + \frac{b}{a}p\right)^{1/b} \tag{4}$$

where a, b, and c are fitting parameters (Table 1). The solid and dash lines in Figure 3 are fits of eq 4. We have $T_{\alpha \text{ or } \alpha'}(0) = c$ and $\mathrm{d}p/\mathrm{d}\ln T_{\alpha \text{ or } \alpha'} = a + bp$, which give $T_\alpha = 203.5$ K and $(\partial T_\alpha/\partial p)_\tau = 140$ K GPa^{-1} for PPG-400 at atmospheric pressure. The corresponding values for PPG-4000 are $T_\alpha = 205.5$ K and $(\partial T_\alpha/\partial p)_\tau = 192$ K GPa^{-1}. Using a heating rate of 20 K min^{-1} in differential scanning calorimetry, Johari et al.[14] obtained $T_g = 200.4$ and 203.8 K for PPG-400 and PPG-4000, respectively (where the values for T_g were taken at the onset of the step in C_p). Our values for T_α of the hot-wire method correspond to a probe frequency of about 0.5 Hz. Literature values of T_α at this frequency can be estimated using the VFTH equation, and data from ref 6 yield $T_\alpha = 203$ K for PPG-400 (extrapolated value). The same calculation for PPG-4000 yields $T_\alpha = 205.5$ K[5] and $T_\alpha = 206.4$ K.[12]

Williams[7] has reported $(\partial T_\alpha/\partial p)_{100\mathrm{Hz}} = 138$ K GPa^{-1} for PPO with an average molecular weight of 1.2×10^6 g mol^{-1}. Moreover, Fontanella et al.[12] have reported $\mathrm{d}T_g/\mathrm{d}p = 170$ K GPa^{-1} for PPO but the time scale and molecular weight were not given. We can conclude that our values for T_α and $\mathrm{d}T_\alpha/\mathrm{d}p$ are in fair agreement with previous results.

Pressure Dependence of Relaxation Times. Figure 6 shows the logarithm of frequency of the maximum dielectric loss $f_{\max}$ versus pressure for PPG-400 and PPG-4000 at room temperature. The pressure dependence of $f_{\max}$ or, equivalently, the relaxation time can be described by several models.[10,24] We have evaluated three models where the first one considered here is called the model of constant free volume compressibility.[10,24] This model is based on the assumption that the free volume decreases linearly with increasing pressure and yields the following expression:

$$\ln\left(\frac{f_{\max}}{f_{\max 0}}\right) = -\left(\frac{1}{\beta_{\mathrm{Tf}}(p_\infty - p)} - \frac{1}{F_0}\right) \tag{5}$$

where $f_{\max}$ and $f_{\max 0}$ are the frequencies of maximum loss at p and atmospheric pressure p_0, β_{Tf} is the isothermal free volume compressibility, F_0 is the frac-

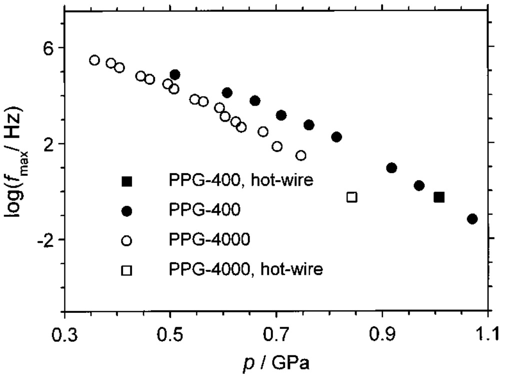

Figure 6. Frequency of maximum dielectric loss (α relaxation) as a function of pressure at 295 K for PPG-400 and PPG-4000. Data from hot-wire measurements are also included.

tional free volume at p_0, and p_∞ is the pressure for which the fractional free volume is equal to zero. The value for p_∞ was calculated from the relation[10] $p_\infty = p_0 + F_0/\beta_{Tf}$, where F_0 was calculated at 0.1 MPa. (If the value for F_0 is kept as a free parameter, the regression algorithm could not determine a unique set of parameters based on the experimental data.) Values for F_0 were determined from the Vogel equation[24] $F_0 = \alpha_f(T - T_\infty)$ using literature values for T_∞ and α_f,[24] where T_∞ is the temperature where the fractional free volume is equal to zero and α_f is the thermal expansivity of the fractional free volume. The following values for F_0 were obtained: 0.137 at 295 K, 0.155 at 311 K, 0.167 at 322 K, and 0.194 at 346 K. The value for the relaxation time at atmospheric pressure was calculated from $\tau_{00} = 1/(2\pi f_{max0})$. The results of the fitting are given in Table 2.

We have also considered a model which assumes a variable free volume compressibility. In analogy with the total isothermal compressibility, it has been suggested that the compressibility of the free volume must decrease with increasing pressure. A model which accounts for this yields a linear pressure dependence of f_{max} given by [10,24]

$$\ln\left(\frac{f_{max}}{f_{max0}}\right) = \Theta(p_0 - p) \tag{6}$$

where Θ is an empirical material-dependent parameter and f_{max} and f_{max0} are the frequencies of maximum loss at p and atmospheric pressure p_0. Values for Θ and τ_{00} obtained in the fitting procedure are given in Table 2.

The third model is based on an empirical model of Tait,[25] which has been successful in describing both volume and compressibility versus pressure for polymers in the liquid state. It has been suggested that the free volume should also follow this model.[26] This assumption yields

$$\ln\left(\frac{f_{max}}{f_{max0}}\right) = \ln\left(\left(1 + \frac{(p - p_0)}{B_{T,TAIT}}\right)^{-\Theta_C}\right) \tag{7}$$

where $B_{T,TAIT}$ is a fitting constant, which depends on the polymer but not on pressure and $p_0 = 0.1$ MPa, and Θ_C is given by

$$\Theta_C = C_{TAIT}/F_g^{\ 2} \tag{8}$$

The fractional free volume at the glass-transition temperature F_g is 0.027[24] and C_{TAIT} is 0.096 06. (The Tait equation was fitted to data for volume[23] versus pressure for PPG-400 and PPG-4000, which yielded C_{TAIT} =0.096 06.) The values for $B_{T,TAIT}$ and the relaxation time at atmospheric pressure τ_{00} (=$1/(2\pi f_{max0})$) obtained in the fitting procedure are given in Table 2. In addition, we have represented our data by a second-order polynomial for which the coefficients are given in Table 2.

We can conclude that the best representation of the α relaxation is provided by the linear model (eq 6) whereas the α′ relaxation is best described using the Tait model. However, the standard deviations obtained from the fits of the second-order polynomials are smaller than those of the three models, but then we need one more free parameter. Since the quadratic terms in the polynomials are significant, this shows that a linear model is not that useful to describe the pressure dependence of f_{max} for the whole pressure ranges.

Our fitting parameters at 311 K can be compared with previous results of Freeman et al.[10] They used the fluorescent lifetime of an intermolecular excimer-forming probe molecule dissolved in PPO to study the pressure dependence of the relaxation time. They obtained the following values for PPG-4000 (α relaxation): eq 5 yielded $\beta_{Tf} = 0.383$ GPa^{-1} and $\tau_{00} = 5.58$ ns, eq 6 yielded $\Theta = 21.5$ GPa^{-1} and $\tau_{00} = 5.10$ ns, and eq 7 yielded $B_{T,TAIT} = 6.58$ GPa and $\tau_{00} = 5.09$ ns. Moreover, they found that the linear model and the Tait model given by eqs 6 and 7, respectively, could describe the data satisfactory, while eq 5 was less useful in the pressure range 0−0.3 GPa. Our values for τ_{00} scatter much due to the fact that these values are extrapolated values and they are therefore uncertain. Our value for τ at 0.35 GPa obtained from the Tait model is in reasonable agreement with the extrapolated value from Freeman et al.[10] If we use a value for $\tau_{00} = 5$ ns obtained by Freeman et al.[10] at atmospheric pressure together with our experimental data, we find the following values: eq 5 yields $\beta_{Tf} = 0.116$ GPa^{-1}, $\tau_{00} = 10$ ns, and $S = 0.24$; eq 6 yields $\Theta = 15.0$ GPa^{-1}, $\tau_{00} = 0.72$ ns, and $S = 0.50$; eq 7 yields $B_{T,TAIT} = 3.46$ GPa, $\tau_{00} = 0.68$ ns, and $S = 0.57$; a second-order polynomial fit yields $a_1 = -5.801$ GPa^{-2}, $b_1 = -1.140$ GPa^{-1}, $\tau_{00} = 4.8$ ns, and $S = 0.048$. The large difference between our parameter values and those obtained by Freeman et al.[10] indicates that none of these models are useful to describe data in a wide pressure range, but they can be used for small pressure ranges, which in this case is about 0.2 GPa. For such small pressure ranges our results are described well by the linear model, which is consistent with results by Williams.[7]

Temperature Dependence of Relaxation Times. There are few investigations, if any, which have focused on the change of the strong−fragility behavior with pressure. Here, we consider our results for $\tau(T)$ of PPG and analyze those in term of strong−fragile behavior.

We have calculated our relaxation times from $\tau = 1/(2\pi f_{max})$, which yields an average relaxation time in the case of single-exponential relaxation ($\beta = 1$). However, since we have found that the distribution of relaxation times is independent of temperature and pressure, any type of mean relaxation time will differ by a constant factor from our values and these can therefore be used in the strong−fragile analysis.

Figure 7 shows our strong−fragility plot for PPG-400. Normally, the temperature in strong−fragility plots is scaled using the calorimetric glass-transition temperature or the relaxation temperature which corresponds

Table 2. Results for Logarithm of Frequency of Maximum Dielectric Loss as a Function of Pressure Described by Equations 5–7 and by the Polynomial log (f_{max}) = $a_1p^2 + b_1p$ + log (f_{max0})[a]

				β_{Tf} constant eq 5			linear model eq 6			Tait's model eq 7			second-order polynomial			
MW (g mol^{-1})	type[b]	T (K)	log f range	β_{Tf} (GPa^{-1})	τ_{00} (ns)	S	Θ (GPa^{-1})	τ_{00} (ns)	S	$B_{T,TAIT}$ (GPa)	τ_{00} (ns)	S	a_1 (GPa^{-2})	b_1 (GPa^{-1})	τ_{00} (ns)	S
400	α	295	6 to −1.2	0.092	68	0.39	23.0	0.016	0.36	1.82	0.002	0.46	−6.52	−0.63	673	0.08
4000	α	295	6 to −0.28	0.122	19	0.14	27.4	0.015	0.33	1.59	0.002	0.38	−16.1	5.31	303	0.16
4000	α′	295	5 to −0.28	*c*			19.5	430	0.06	2.63	343	0.04	0.981	−9.08	369	0.04
4000	α	311	6.5–2.0	0.115	12	0.22	19.7	0.029	0.12	2.29	0.007	0.16	−4.42	−2.94	1.35	0.04
4000	α′	311	5.5–3	*c*			16.3	180	0.05	3.28	161	0.04	1.82	−7.95	149	0.04
4000	α	322	6.5–2.5	0.113	7.0	0.18	17.1	0.019	0.13	2.65	0.005	0.15	−4.00	−1.73	1.52	0.06
4000	α′	322	5.5–2.5	*c*			14.3	96.5	0.11	3.62	77.2	0.09	2.99	−8.45	44.7	0.06
4000	α	346	6.5–2.5	0.100	6.5	0.21	13.3	0.006	0.12	3.33	0.001	0.15	−2.17	−1.45	0.66	0.07
4000	α′	346	6 to 3	*c*			11.4	49.5	0.03	4.63	42.7	0.03	0.234	−5.13	46.2	0.03

[a] The values for the relaxation times at atmospheric pressure were calculated from $\tau_{00} = 1/(2\pi f_{max0})$. The standard deviation and molecular weight are abbreviated *S* and MW, respectively. [b] Relaxation process. [c] Values for F_0 are not available for the α′ relaxation.

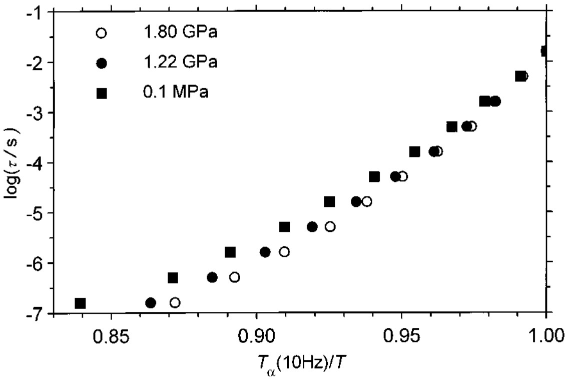

Figure 7. Relaxation time for PPG-400 as a function of scaled inverse temperature, where T_α at 10 Hz is used as a scaling parameter.

roughly to T_g, but we do not have access to such data at high pressure. We have therefore used T_α (10 Hz) as the scaling parameter, where T_α (10 Hz) is the relaxation temperature of the α process probed at a frequency of 10 Hz. Using this scaling procedure instead of that normally employed does not affect the interpretation of the result.

Since our results for f_{max} versus temperature at atmospheric pressure agree fairly well with previous results for PPG-400 and PPG-4000,[6,8] our results for the degree of fragility at atmospheric pressure also agree with those of these investigations. At atmospheric pressure, PPG shows an intermediate behavior between the two extremes of strong and fragile, and our results show that this is also the case at high pressures. However, as shown in Figure 7, PPG-400 exhibits a small change toward a higher degree of fragility with increasing pressure. The same result was observed for PPG-4000. Although the changes toward a higher degree of fragility are small, they are outside the experimental inaccuracy. These results indicate that the character of the bonds which are relevant in the α process of PPG changes slightly with increasing pressure. A more detailed interpretation of these results requires more results on the effect of pressure on strong–fragility behavior and, especially, how different types of intermolecular bonds influence the results. In this case of PPG, it could be rewarding to study for example poly(propylene oxide) dimethyl ether, which cannot form hydrogen bonds. Consequently, such results would indicate if the hydrogen bonds are important for the results of PPG.

To summarize our results for the temperature dependence of f_{max}, we have fitted the VFTH equation to the results. The form of the VFTH equation used here is given by

$$\log(f_{max}) = \log(A) - D/(T - T_0) \qquad (9)$$

where *A*, *D*, and T_0 are fitting constants (Table 3). The parameters at different pressures are given in Table 3, and those at atmospheric pressure are in fair agreement with previous results.[6,8]

Conclusions

We have detected that both PPG-400 and PPG-4000 exhibit two major relaxation processes at high pressures. These are probably the α and α′ relaxations, which are associated with segmental motions within the polymer chains and whole chain motions, respectively. If these are probed at constant frequency, the relaxation temperature of the α′ process increases slightly more with increasing pressure than that for the α process. At atmospheric pressure and just above the glass-transition temperature, the activation energy of the α process is larger than that of the α′ process, which can account for the slight difference in $(\partial T_{relaxation}/\partial p)_\tau$ between the two processes.

The relaxation temperatures for the two processes become more dependent on molecular weight with increasing pressure. This is a bit surprising in the case

Table 3. The VFTH Expression (eq 9) Fitted to the Results of log (f_{max}) vs Temperature at Different Pressures for PPG-400 and PPG-4000

polymer	relaxation process	p (GPa)	log(f) range	log(A)	D (K)	T_0 (K)	standard deviation
PPG-400	α	10^{-4}	−0.275–6.0	12.65	599.73	157.6	0.096
PPG-400	α	1.00	1.0–6.0	10.94	470.37	246.8	0.033
PPG-400	α	1.22	1.0–6.0	11.58	574.50	253.1	0.022
PPG-400	α	1.51	1.0–6.0	11.74	599.12	267.2	0.021
PPG-400	α	1.80	1.0–6.0	12.02	652.90	278.7	0.028
PPG-4000	α	10^{-4}	1.25–6.0	12.06	471.25	166.5	0.036
PPG-4000	α′	10^{-4}	1.75–6.1	10.25	665.88	149.6	0.032
PPG-4000	α	1.20	1.5–6.25	11.68	662.32	264.6	0.044
PPG-4000	α	1.66	1.6–6.5	11.15	589.43	296.6	0.041

of the α process since the segmental motions in a high-molecular-weight polymer should not be affected by the properties of the end groups, which is the result observed at atmospheric pressure where the glass-transition is almost independent of molecular weight above about 400 g mol^{-1}. However, we can conclude that PPG-400, with the possibility of strong intermolecular hydrogen bonds, is not of sufficiently high molecular weight to ignore the effect of end groups on the α relaxation at high pressures. The reason for this result might be that the hydrogen bonds are affected by high pressure and, therefore, that the apparent molecular weight decreases. As a consequence, the glass-transition temperature of PPG at high pressure depends on molecular weight even above 400 g mol^{-1}.

At 295 K and 0.3 GPa, the activation volumes of the two processes for PPG-4000 are about the same, despite the fact that they are associated with whole chain motions and segmental motions within the chains, respectively. At the same conditions, the activation volume for the α process of PPG-400 is about half that for PPG-4000, which shows that the motions associated with the process are dependent on molecular weight.

The relaxation temperatures of the α process at atmospheric pressure using a probe frequency of 0.5 Hz are, respectively, 203.5 and 205.5 K for PPG-400 and PPG-4000, which agree well with previous results. The pressure dependencies of these relaxation temperatures are, respectively, 140 and 192 K GPa^{-1} for PPG-400 and PPG-4000, which are in fair agreement with those for the glass-transition temperature.

The Vogel–Fulcher–Tamman–Hesse equation was fitted to data for frequencies of maximum dielectric loss versus temperature for PPG-400 and PPG-4000, which yielded results in fair agreement with previous finding.

The results for the heat capacity show that the motions of the two processes contribute to about the same degree to the heat capacity. As a consequence, the α′ relaxation is clearly observed in the hot-wire results. This is quite different from the result of dielectric spectroscopy where the α′ process appears much weaker than the α process, which is due to a weak dipole associated with the α′ process.

The strong–fragility analyses show that both PPG-400 and PPG-4000 exhibit a slight increase of fragility with increasing pressure, which indicates that the intramolecular and intermolecular forces involved in the α process are affected by high pressure. The result corroborates that from the analysis of the relaxations of the α process, which also indicated a change in the bonding character with pressure since the relaxations become more dependent on molecular weight with increasing pressure. However, more high-pressure investigations which focus on the strong–fragility behavior are necessary before a detailed interpretation of the results is possible. In particular, high-pressure results for glass formers which exhibit different types of intermolecular bonds would be helpful.

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