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Thermal Conductivity, Heat Capacity, and Compressibility of Atactic Poly(propylene) Under High Pressure

S. P. Andersson[1,2] **and O. Andersson**[1]

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The thermal conductivity λ and the heat capacity per unit volume of atactic poly(propylene) have been measured in the temperature range 90–420 K at pressures up to 1.5 GPa using the transient hot-wire method. The bulk modulus has been measured in the range 200–295 K and up to 0.7 GPa. These data were used to calculate the volume dependence of λ, $g = -[(\partial\lambda/\lambda)/(\partial V/V)]_T$, which yielded the following values for the glassy state ($T < 256$ K at atmospheric pressure): 3.80 ± 0.19 at 200 K, 3.74 ± 0.19 at 225 K, 3.90 ± 0.20 at 250 K, 3.77 ± 0.19 at 271 K, and 3.73 ± 0.19 at 297 K. The resultant value for g of the liquid state was 3.61 ± 0.15 at 297 K. Values for g which are calculated at 295 K, using theoretical models of $\lambda(T)$, agree to within 12% with the experimental value for the glassy state.

KEY WORDS: atactic poly(propylene); bulk modulus; equation of state; heat capacity; high-pressure; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Experimental results concerning the thermophysical properties of polymers under high pressure are still rare. The main purpose of this work is to determine the volume dependence of the thermal conductivity for atactic poly(propylene) (aPP) and, in particular, that for the glassy state of aPP. Atactic polymers have a random arrangement of side-groups. The volume dependence of thermal conductivity is described by the Bridgman parameter g, which is defined as $g = -[(\partial\lambda/\lambda)/(\partial V/V)]_T$.

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[1] Department of Experimental Physics, Umea University, S-90187 Umea, Sweden.

[2] To whom correspondence should be addressed.

We have previously investigated poly(methyl methacrylate) (PMMA) and Teflon AF 1600 (amorphous Teflon), which yielded $g = 3.4$ at 294 K for PMMA [1] and the following values of g for amorphous Teflon [2]: 2.8 ± 0.2 at 296 K, 3.0 ± 0.2 at 258 K, 3.0 ± 0.2 at 236 K, 3.4 ± 0.2 at 200 K, and 3.4 ± 0.2 at 150 K. In addition to these results, there are only a few other investigations of g for polymers. Slack [3] has calculated the Bridgman parameters at 303 K using literature data of $\lambda(p)$ and the bulk modulus for both amorphous (a) and semicrystalline (sc) polymers, which yielded poly(styrene) $g = 1.84$ (a), isotactic poly(propylene) $g = 1.85$ (sc), low-density poly(ethylene) $g = 2.16$ (sc), high density poly(ethylene) $g = 4.96$ (sc), poly(methyl methacrylate) $g = 2.43$ (a), and Teflon $g = 2.58$ (sc). Ross et al. [4] have calculated a value for g of poly(vinyl acetate) and obtained $g = 2.4$ (liquid state) at 360 K. Sandberg [5] has calculated the Bridgman parameter for the following polymers: poly(vinyl acetate) $g = 1.7$ (a) at 300 K and $g = 2.6$ (liquid state) at 360 K, poly(*cis*-1,4-isoprene) $g = 4.3$ (rubber state) at 300 K, poly(ethylene) $g = 2.2$ (liquid state) at 430 K, low-density ($\rho = 926\ \mathrm{kg \cdot m^{-3}}$) poly(ethylene) $g = 4.3$ (sc), and high-density ($\rho = 965\ \mathrm{kg \cdot m^{-3}}$) poly(ethylene) $g = 6.0$ (sc). It follows that amorphous polymers exhibit values for g in the range 1.5 to 4, which are close to those of other disordered states, e.g., g for liquids is about 3 [4]. Semicrystalline polymers, such as high-density poly(ethylene), can show values for g which are larger than 4, approaching those for simple crystals, e.g., KCl ($g = 5.7 \pm 0.5$) and NaCl ($g = 6.7 \pm 0.7$). Consequently, g has a tendency to increase with increasing degree of structural order. However, there are exceptions such as phase Ih of ice, which exhibits a negative value ($g = -2.5$ at 248 K), whereas g of amorphous ice must be positive since λ is increasing with increasing pressure [6]. The low values for g of isotactic poly(propylene) and poly(ethylene) [3] could also be exceptions but, as well, a result of combing data for the bulk modulus and $\lambda(p)$ for samples of different thermal histories. This could explain why Slack [3] observed a much smaller value for g of low-density poly(ethylene) compared with the value obtained by Sandberg [5]. The same reason might explain the difference between our value for g of PMMA [1] and that of Slack [3] ($\Delta g \approx 1$). It is our experience that accurate data for g of polymers can be obtained only by measuring both $\lambda(p)$ and the bulk modulus for samples subjected to identical thermal treatments.

During the 1960s and 1970s, the bulk modulus was determined for the most frequently used polymer materials. In general, these investigations concerned pressures up to about 0.3 GPa and the temperature range for the glassy and liquid states. In this investigation we have measured the bulk modulus up to 0.7 GPa for temperatures in the range 295–200 K. Since the glass transition temperature for aPP is 256 K at atmospheric pressure, we obtain results for both liquid and glassy states. However, the main part of the measurements is concerned with the glassy state. At low pressures ($p < 0.3$ GPa) and at temperatures well below the glass transition temperature, the bulk modulus is normally described well by a linear function of pressure. In this investigation, we can explore the extent to which this simple relation is valid also at high pressures. The Murnaghan equation of state, which is derived under the assumption that the bulk modulus B is a linear function of pressure ($B(p) = B_0 + B_1 p$), is fitted to data. The fitting parameters of the Murnaghan equation (B_0 and $(dB/dp) = B_1$) are compared with the bulk modulus calculated from the slope between consecutive pairs of data for p and ln V, i.e., as $B = -(\Delta p/\Delta \ln V)$.

Previous investigations of the thermal conductivity for polymers have concerned mainly the temperature dependence and, in a few cases, also the pressure dependence. In this work we make the picture more complete by introducing the volume dependence. The volume dependence is important because all the theoretical models of thermal conductivity versus temperature are derived under isochoric conditions, whereas experimental data normally are measured under isobaric conditions. This work makes it possible to investigate if these theories for temperature dependence can describe the volume dependence and, consequently, provides a further check of the theoretical models.

2. EXPERIMENTAL PROCEDURE

The sample of atactic poly(propylene) (aPP) was supplied by Scientific Polymer Products, Inc. The weight-average molecular weight was $2.0 \text{ kg} \cdot \text{mol}^{-1}$. The specimen material was initially heated to about 400 K to obtain the low-viscous liquid form and, subsequently, poured into the sample cells.

2.1. Measurements of Thermal Conductivity and Heat Capacity

We used the transient hot-wire method 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 [7]. 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 (aPP). 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 $\pm 2\%$ in λ and $\pm 5\%$ in ρc_p [7]. We have used two types of high-pressure apparatuses during the investigations. In the temperature range 270–430 K, we used equipment which can operate up to 2 GPa. A general description of this equipment has previously been given [8]. At temperatures below 270 K, we used an apparatus which operates to 1.0 GPa [9].

The temperature of the high-temperature vessel (270–430 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 either circulate Freon from a refrigerating unit or pass liquid nitrogen.

Below 270 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 a 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 load/area, with an empirical correction for friction 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, Västeras, Sweden). A thyristor unit 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 observed to be less than ± 1 MPa.

2.2. Equation-of-State Measurements

The equation-of-state $V(p, T)$ was measured in a piston-cylinder device with an internal diameter of 15 mm. A full description is given elsewhere [10]. The force on the piston was measured by a commercial load cell and was regulated by a three-term control system.

All the results were corrected for piston compression and mean area expansion, both calculated from measured data and theory [11]. The temperature was measured by a thermocouple and kept to within ±0.5 K by a three-term control system or by the microcontroller (First Control System AB). The specimen was enclosed in an indium capsule, 27 mm high with a wall thickness of 0.5 mm, to ensure low friction. The piston position was measured to a resolution of $\pm 0.1\ \mu m$ by a system of two displacement transducers, i.e., linear differential transformers with a maximum measuring range of ±10 mm. These transducers were situated on opposite sides of the pressure vessel and were fixed to each piston by means of symmetrical yokes. The signals from the two transducers were averaged to take any slight tilting of the pistons into account.

The pressure was calculated as force divided by cylinder area. When measuring the volume, we first increased the pressure at a constant rate (typically $0.175\ \mathrm{GPa \cdot hr^{-1}}$) to the maximum pressure of 1.4 GPa. Subsequently, we decreased the pressure using the same rate down to atmospheric pressure. During the ramps we measured the volume at certain pressure values. To take friction into account, the volume data were calculated as the average of values taken under increasing and decreasing pressure, yielding data for the volume versus pressure. The inaccuracy in $B(0)$ was estimated as ±2%.

3. RESULTS

3.1. Thermal Conductivity and Heat Capacity per Unit Volume

Figure 1 shows the results for $\lambda(p)$ of the liquid and glassy states for aPP. The abrupt change of $(\partial\lambda/\partial p)_T$ is associated with the glass transition in aPP. In the liquid state near the glass transition, $(\partial\lambda/\partial p)_T$ is 1.6 times larger than the value of the glassy state just above the glass transition. This is due to the fact that the liquid state is about 1.6 times as compressible as the glassy state. Consequently, the pressure dependence of λ reflects this volumetric effect, which is related to the glass transition. As can be seen in Fig. 1, the pressure dependence of λ is somewhat weaker at 90 K compared with that at 297 K. Since the compressibility decreases with temperature, the pressure dependence of λ appears to roughly follow this decrease.

Figure 2 shows the temperature dependence of the thermal conductivity. The peaks in λ and the dips in ρc_p (see Figs. 3 and 4) are associated with the glass transition and are explained in Section 3.3. The data for $\lambda(T)$ at low pressure (0.02 GPa) follow roughly the general behavior of amorphous polymers [12], that is, a weak increase in λ up to the temperature region of the glass transition, followed by an equally weak

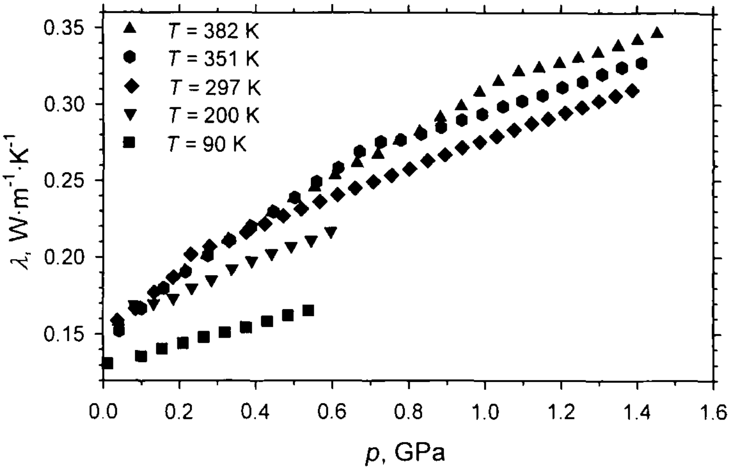

Fig. 1. Thermal conductivity versus pressure for aPP at temperatures of 90, 200, 297, 351, and 382 K.

decrease above this region. For higher pressures, however, the temperature dependence in glassy and liquid states are nearly equal and weakly positive (Fig. 2).

Figure 3 shows the result for $\rho c_p(p)$ at the same five temperatures as in Fig. 1, and the abrupt increase in ρc_p (or c_p) reflects the onset of molecular motions at the glass transition. It can be seen from Fig. 3 (at 382

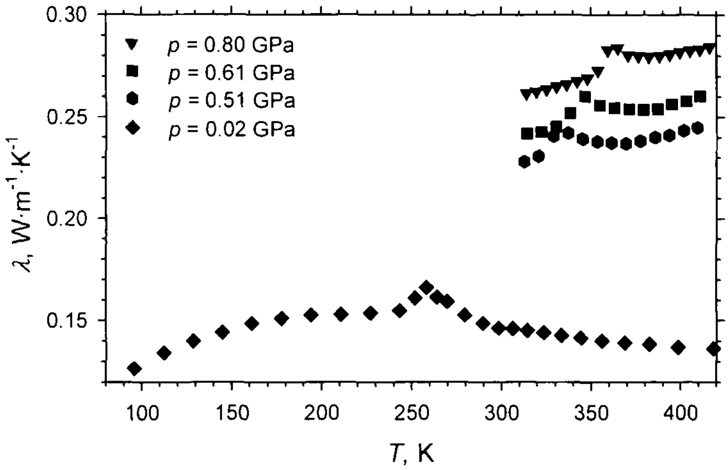

Fig. 2. Thermal conductivity versus temperature for aPP at pressures of 0.02, 0.51, 0.61, and 0.80 GPa.

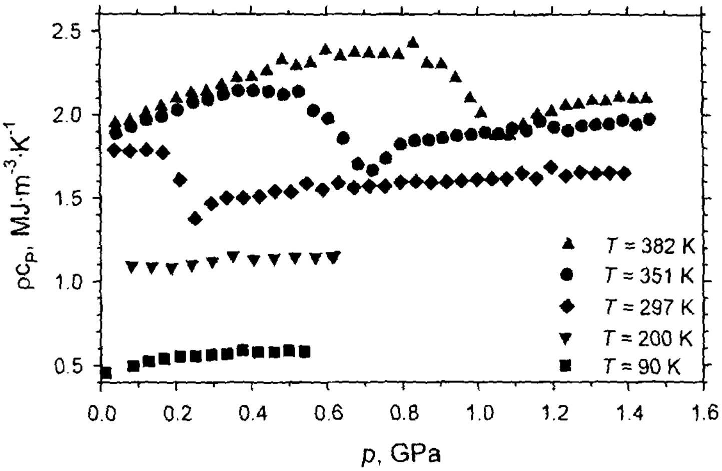

Fig. 3. Heat capacity per unit volume versus pressure for aPP at temperatures of 90, 200, 297, 351, and 382 K.

and 351 K) that the liquid state exhibits a somewhat larger pressure dependence for ρc_p than that of the glassy state, which is due mainly to the difference in the compressibility between the states. In the glassy state, c_p is almost constant with pressure (not shown in the figures), while for the liquid state the change in c_p with pressure is less than 4% per 1 GPa. At 90 K and for pressures higher than 0.2 GPa, the pressure dependence of ρc_p

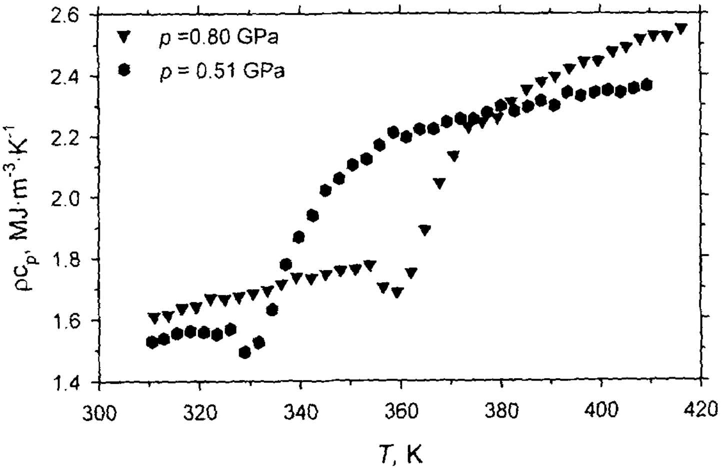

Fig. 4. Heat capacity per unit volume versus temperature for aPP at pressures of 0.51 and 0.80 GPa.

is rather weak (almost constant). This indicates that the increase in density with pressure is nearly equal to the decrease in heat capacity with pressure.

Figure 4 shows the temperature dependence for ρc_p of the glassy and liquid states. If we disregard the dip in ρc_p (explained in Section 3.3), the data follow the general temperature behavior of c_p for amorphous polymers. That is, in our temperature range, c_p increases almost linearly up to the glass transition temperature T_g, where the step change at T_g is followed by a weak increase in c_p with temperature. (The change in density with temperature is negligible compared to the change in c_p with temperature.)

3.2. Bulk Modulus

Isothermal measurements of volume versus pressure have been performed at 297, 272, 250, 225 and 200 K. The isothermal bulk modulus, $B(p) = -V(\partial p/\partial V)_T$, was calculated as the slope between consecutive pairs of data for p and $\ln V$, i.e., as $B = -(\Delta p/\Delta \ln V)$. Figure 5 shows the results at 297 K, where the change of slope in B corresponds to the glass transition. The solid lines in Fig. 5 are inserted to guide the eye. The data below and above the glass transition are described well by first- or second-order polynomials, and the coefficients are given in Table I. One of the most commonly employed functions to describe volume data is the Murnaghan

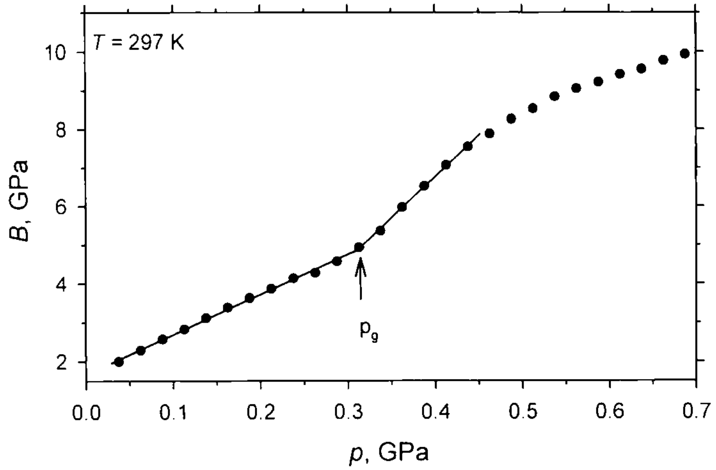

Fig. 5. Bulk modulus versus pressure for aPP at 297 K. The values shown were obtained directly from first differences, $B = -\Delta p/\Delta \ln V$, between consecutive pairs of data. The arrow indicates the glass transition pressure p_g.

Table I. Bulk Modulus for aPP[a]

T (K)	p range (GPa)	a (GPa)	b	c (GPa^{-1})	B_0 (GPa)	B_1
297	0.00–0.3020	1.68 ± 0.06	10.2 ± 1.0		1.76 ± 0.06	9.76 ± 1.0
297	0.5046–0.70	4.74 ± 0.10	7.56 ± 0.76			– –
271	0.00–0.1079	1.82 ± 0.06	11.3 ± 1.1		1.85 ± 0.06	10.9 ± 1.1
271	0.3244–0.70	4.76 ± 0.10	6.68 ± 0.69	–		
250	0.00	1.93 ± 0.06[b]	– –			– –
250	0.2080–0.70	4.29 ± 0.10	7.22 ± 0.72	–		–
225	0.00–0.700	4.52 ± 0.10	5.42 ± 0.54	2.45 ± 0.25	4.53 ± 0.10	6.36 ± 0.63
200	0.00–0.700	5.15 ± 0.10	4.15 ± 0.42	3.70 ± 0.37	5.05 ± 0.10	6.00 ± 0.60

[a] The bulk modulus was calculated from the definition $B = -(\Delta p/\Delta \ln V)$ and described by first- or second-order polynomials: $B(p) = a + bp + cp^2$. $B_0 = B(0)$ and $B_1 = dB/dp$ are the parameters in the Murnaghan equation (see text).

[b] Extrapolated value from high temperatures.

equation of state [13]. This equation is believed to provide a good description up to about 1 GPa [14] and is given by

$$\frac{V(p)}{V(p=0)} = \left(1 + \frac{B_1}{B_0} p\right)^{-1/B_1} \tag{1}$$

The Murnaghan equation was derived assuming that B is a linear function of pressure, i.e., $B(p) = B_0 + B_1 p$, with the constants B_0 and B_1 being defined by $B_0 = B(0)$ and $B_1 = dB/dp$. The results for the coefficients B_0 and B_1 are summarized in Table I. The fits at 200 and 225 K yielded results for B_0 in good agreement with those calculated from the derivative of p vs ln V. However, the results for B_1 did not agree well, which is of course because $B(p)$ is not a linear function of pressure. On the other hand, the Murnaghan equation gives a good description of volume data in small pressure ranges, such as those for the liquid state at 297 and 271 K. We can conclude that the Murnaghan equation of state provides a good description of volume data for aPP for pressure ranges less than about 0.5 GPa but is less useful for wider pressure ranges.

3.3. Glass Transition

The change of slope in the data for $\lambda(p)$ and the step changes in $\rho c_p(p)$, shown in Figs. 1 and 3, are associated with the glass transition. With increasing temperature or decreasing pressure, ρc_p increases discontinuously at the transition, and it is well-known that the position of the transition depends on the rate of temperature or pressure change. In addition to these signatures for the glass transition, the hot-wire method yields a local maximum in λ (Fig. 2) and a local minimum in ρc_p (Figs. 3 and 4) at the glass transition. In a detailed analysis of the isothermal data for λ shown in Fig. 1, it also possible to observe a weak local maximum in λ at the glass transition. These are artifacts of the method and can be ascribed to the 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 (see experiments), this results in anomalous values for λ and ρc_p.

The glass transition temperature corresponds to the point where the structural relaxation time τ is about equal to the characteristic experiment time. For hot-wire measurements there are two times scales to consider. The rates of pressure and temperature change (0.175 GPa $\cdot$ hr^{-1} and 12 K $\cdot$ hr^{-1}) correspond to a large relaxation time ($\tau \geqslant 10^3$), whereas the maximum of the peak in λ and the minimum of the dip in ρc_p correspond to a relaxation time of about 1 s, which is the duration of the hot-wire heat pulse. Consequently, the glass transition point detected by the hot-wire probe is associated with $\tau \approx 1$ s and should therefore be compared with results from methods using about the same time scale, e.g., dielectric measurements using a frequency of order 1 Hz. On the other hand, the glass transition detected by the bulk modulus measurements should be comparable with results obtained by, for example, differential scanning calorimetry.

The results for T_g are shown in Fig. 6. Values for T_g from data for both $B(p)$ and $\lambda(T)$ are included. Since the experimental time scale for the latter is much shorter, these give significantly higher values for T_g. To describe the pressure dependence for T_g, the data obtained from $\lambda(T)$ were chosen due to the larger number of values. The values for T_g were taken from the peak position in $\lambda(T)$ and these could be described to within 2 K by the expression

$$T_g = 616.95 - \frac{1}{2.768 \times 10^{-3} + 1.467 \times 10^{-3} p} \tag{2}$$

where T is in K and p is in GPa. This equation gives $T_g = 255.6$ K and $dT_g/dp = 191$ K $\cdot$ GPa^{-1} at atmospheric pressure. Passaglia and Martin [16] have reported the values $T_g = 243.6$ K and $dT_g/dp = 204$ K $\cdot$ GPa^{-1}. Consequently, the values for the pressure derivative of T_g are in reasonable agreement, and the significant difference in T_g is due to different experimental time scales. Passaglia and Martin [16] did not explicitly state the rate of the temperature change in their experiment. An additional complication for a comparison between the result is that T_g also depends on

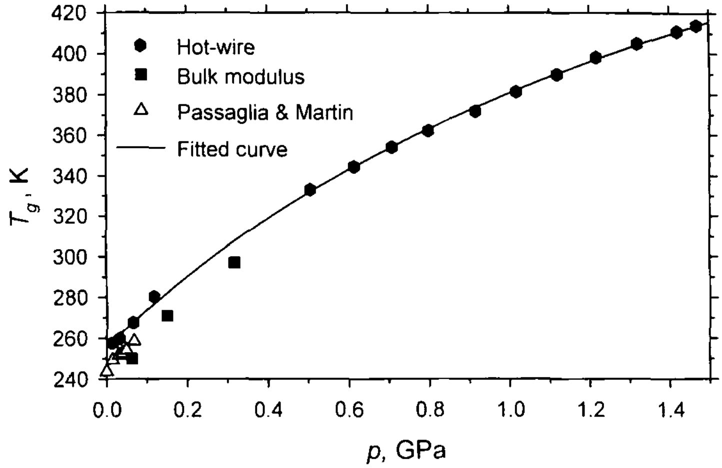

Fig. 6. Glass transition temperature versus pressure for aPP.

the molecular weight of aPP, which was larger for the sample of Passaglia and Martin [16] than for our sample. In general, T_g increases with increasing molecular weight but the exact relation (between T_g and weight average molecular weight) has not been determined for aPP. Consequently, additional data for T_g as function of molecular weight as well as experimental time scale are necessary for an accurate comparison of the results for T_g.

4. DISCUSSION

4.1. Thermal Conductivity

The relative value for thermal conductivity, $\lambda(p)/\lambda(0)$, of aPP under high pressure has been measured previously by Andersson and Sundqvist [17]. They used a cylindrical sample which was placed in a belt-type high-pressure apparatus. The sample was heated along its axis by a sinusoidally varying current. The thermal conductivity was determined from $\lambda = P_0 \ln(r_2/r_1)(1/2\pi l \Delta T)$, where P_0 is the average heating power, l is the length of the cylinder, and ΔT is the average temperature difference between two points at radii r_1 and r_2. The length of the sample, changes with pressure, which can be computed using $l\pi r^2 = V$, where r is the radius of the sample (approximately constant). However, at the time of these measurements compressibility data for aPP were not available. We have therefore corrected the data of Andersson and Sundqvist [17] using our data for the bulk modulus. Our result for the relative thermal conductivity

$\lambda(p, T)/\lambda(0, T)$ at 300 K and 1 GPa was 1.74, which is 12% larger than that of Andersson and Sundqvist [17]. Probably the reason for this deviation is that our data include both the glassy and the liquid states (different slopes of λ), while the data of Andersson and Sundqvist [17] did not show a glass transition, i.e., no change of slope for $\lambda(p)$. Their aPP was probably in (or near) the glassy state at atmospheric pressure due to high molecular weight (T_g increases with molecular weight). As a consequence, their data at 300 K correspond almost entirely to the glassy state. In fact, their pressure dependence of λ agrees fairly well with ours for the glassy state (our value for $(\partial\lambda/\lambda)/\partial p$ was approximately 3% larger than that calculated from the data of Andersson and Sundqvist [17]).

Our isobaric data for λ extrapolated to atmospheric pressure are 2–15% lower than those of Eiermann [18] in the temperature range 80–240 K. At temperatures below 130 K, our data are approximately parallel with those of Eiermann [18] and about 2% lower. At higher temperatures our $(\partial\lambda/\partial T)_p$ is much smaller than that of Eiermann [18]. For example, at 240 K we have $(\partial\lambda/\partial T)_p = 2.8 \times 10^{-5}\ \mathrm{W \cdot m^{-1} \cdot K^{-2}}$, while the corresponding value for the data of Eiermann [18] is $1.3 \times 10^{-4}\ \mathrm{W \cdot m^{-1} \cdot K^{-2}}$. The fairly large discrepancy between the results is difficult to explain, especially in view of the good agreement at lower temperatures. The data near 240 K are close to T_g and might therefore be affected by the glass transition, but for the difference in the temperature range 130–240 K, which is outside the experimental inaccuracy, we cannot find a convincing explanation.

4.2. Heat Capacity

We have not found any other result for ρc_p versus pressure with which our data can be directly compared. However, Andersson and Sundqvist [17] have reported data for relative specific heat capacity versus pressure. We can easily transform our results for $\rho c_p(p, T)$ to the specific heat capacity $c_p(p, T)$ by using our compressibility data, literature data for the linear thermal expansion in the range 80–240 K $\alpha = 10^{-6}(2.26 \times 10^{-4}T^2 + 0.14T + 39.5)\ \mathrm{K^{-1}}$ [19], and a value for the density at room temperature ($854.4\ \mathrm{kg \cdot m^{-3}}$). This yields data for the relative heat capacity $c_p(p, T)/c_p(0, T)$ versus pressure which do not agree well with those of Andersson and Sundqvist [17] at 300 K. However, as explained, their data probably correspond to the glassy state only, whereas we probe both the glassy and the liquid states. If we use our data for the glassy state ($p > 0.22$ GPa), we find an almost-constant value for $c_p(p)$. This should be compared with Andersson and Sundqvist [17], who reported a nearly linearly decreasing c_p with pressure. If we correct their data for the sample volume change assuming that the data correspond to the glassy state only (see Section 4.1), the result agrees to within 0.5% with our value for the glassy state of aPP.

Our results for ρc_p transformed to $c_p(T)$ in the temperature range 80–240 K agree to within 5% with calorimetric data [20], which is within the experimental inaccuracy.

4.3. Bulk Modulus

Our results for the atmospheric bulk modulus $B(0)$ of the liquid state are about 26% lower than those of Passaglia and Martin [16] (250–295 K), which is outside the experimental inaccuracy ($\pm 2\%$). In their work, B was calculated from a first-order polynomial fitted to the volume-versus-pressure data in the pressure range 0–0.08 GPa. If we instead recalculate the result of Passaglia and Martin [16] by employing the Murnaghan equation of state, we find, however, that the values for B agree to within 12%. Our values for $\partial B/\partial p$ are about 26 to 34% larger than those recalculated from the data of Passaglia and Martin [16]. We can conclude that the values for B depend strongly on the analysis method. Furthermore, differences in $B(0)$ and $\partial B/\partial p$ might be because the sample of Passaglia and Martin [16] was partly crystalline [since it contained 2 to 3% isotactic poly(propylene)]. Another difference which could influence the result is that the sample of Passaglia and Martin [16] had a viscosity average molecular weight of 15.7 kg · mol^{-1}, while our weight-average molecular weight is 2.0 kg · mol^{-1}.

Our extrapolated value for $B(0)$ of the glassy state at 253 K is 13% higher than that of Passaglia and Martin [16]. For the glassy state an additional complication besides those described for the liquid state is that B can be strongly dependent on thermal history, which therefore can yield differences in results. For poly(vinyl acetate) (PVAc) B changes more than 35% between glasses made under different conditions [21]. It is probable that B for the glassy state of aPP could vary in a similar way as for PVAc.

Furthermore, nonhydrostatic pressure conditions can arise for a solid state, which can cause shear flow and frictional forces inside the polymer. However, by assuming that the sum of *all frictional forces* including the internal ones are symmetric (in the sense that they have same magnitude but opposite directions with increasing and decreasing pressure, respectively), this problem is accounted for by our experimental procedure (see last paragraph under Experimental). It can also be important that our pressure range is 10 times larger than that of Passaglia and Martin [16]. During the first pressure cycle, the volume of solid materials changes irreversibly due to the elimination of internal voids. If this pressure range is small, then this elimination may be incomplete.

4.4. Volume Dependence of Thermal Conductivity

The volume dependence of λ was calculated from data for $\lambda(p)$ and $V(p)$. Figure 7 shows our results for $\log(\lambda)$ versus $\log(V/V(0))$ at 200 K, which yield $-g$ equal to the slope. Since these data are described well by a first-order polynomial, g is approximately independent of pressure, which is a result that was obtained at all temperatures. Figure 8 shows g versus temperature, and the result that g is constant or only weakly increasing with decreasing temperature is similar to that found for amorphous Teflon [2]. The difference in g between the glassy and the liquid states is insignificant.

As described in Section 1, crystalline phases normally show larger values for g than amorphous states. Consequently, one expects that g of aPP should be smaller than that for isotactic poly(propylene) ($g = 1.85$ [3]), since the latter is semicrystalline. The reverse result found here indicates that aPP is one of a few exceptions to this rule.

We can explore the extent to which theoretical models can predict values for g. A model for λ of glasses at "high" temperatures ($T > 50$ K) has been proposed by Cahill and co-workers [22]. In their model for disordered solids, heat is transported by random walk between localized excitations. The theory is based on the Einstein model for the Specific heat but

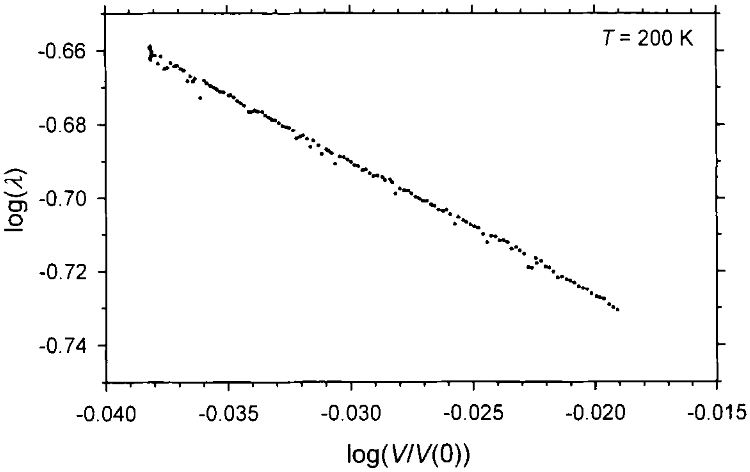

Fig. 7. Log of thermal conductivity versus log of relative volume for aPP at a temperature of 200 K.

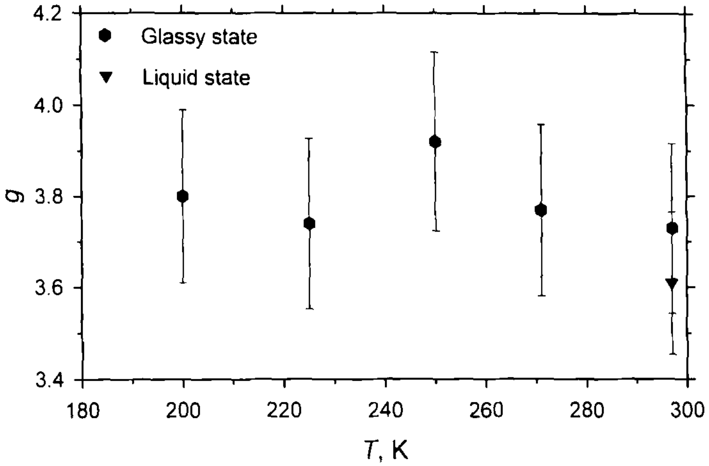

Fig. 8. Bridgman parameter versus temperature for aPP.

the localized excitations include also larger entities than a single atom. To determine the oscillator frequency they adopted the Debye model for lattice vibrations. The expression for λ is then given by

$$\lambda = \left(\frac{\pi}{6}\right)^{1/3} k n_{\mathrm{E}}^{2/3} \sum_i v_i \left(\frac{T}{\Theta_{\mathrm{E},i}}\right)^2 \int_0^{\Theta_{\mathrm{E},i}/T} \frac{x^3 \exp(x)}{(\exp(x)-1)^2}\,dx \tag{4}$$

where v_i is the sound velocity of the ith mode and $x = h\omega/kT$. The sum is taken over the three modes (two transverse and one longitudinal), where $\Theta_{\mathrm{E},i}$ is given by

$$\Theta_{\mathrm{E},i} = \left(\frac{v_i h}{k}\right)(6\pi^2 n_{\mathrm{E}})^{1/3} \tag{5}$$

where n_{E} is the number density of atoms. In the model of Cahill and Pohl [22], n_{E} and $v_i(\Theta_{\mathrm{E},i})$ are the only volume-dependent parameters, which yields the following expression for g:

$$g = \frac{\displaystyle\sum_i \left(\frac{v_i \dfrac{\partial}{\partial \ln V} \displaystyle\int_0^{\Theta_{\mathrm{E},i}/T} \frac{x^3 \exp(x)}{(\exp(x)-1)^2}\,dx - \displaystyle\int_0^{\Theta_{\mathrm{E},i}/T} \frac{x^3 \exp(x)}{(\exp(x)-1)^2}\,dx \,\dfrac{\partial v_i}{\partial \ln V}}{v_i^2} \right)}{\displaystyle\sum_i \left(\frac{\displaystyle\int_0^{\Theta_{\mathrm{E},i}/T} \frac{x^3 \exp(x)}{(\exp(x)-1)^2}\,dx}{v_i} \right)} \tag{6}$$

The longitudinal and transverse sound velocities in an isotropic medium are given by [23]

$$v_{\mathrm{L}}=\left(\frac{B_{\mathrm{S}}+\frac{4}{3}G_{\mathrm{S}}}{\rho}\right)^{1/2} \tag{7}$$

and

$$v_{\mathrm{T}}=\left(\frac{G_{\mathrm{S}}}{\rho}\right)^{1/2} \tag{8}$$

where B_{S} and G_{S} are the adiabatic bulk and shear modulus and ρ is the mass density. The relation between the adiabatic bulk modulus B_{S} and the isothermal bulk modulus B is given by [24]

$$\frac{1}{B}-\frac{1}{B_{\mathrm{S}}}=\frac{T\beta^2}{\rho c_{\mathrm{p}}} \tag{9}$$

where β is the volume thermal expansivity. At 295 K and atmospheric pressure the ratio B/B_{S} is larger than 0.99. Thus, the isothermal value for B is a good approximation of B_{S}.

From Eqs. (7) and (8) we obtain

$$\frac{\partial v_{\mathrm{L}}}{\partial \ln V}=\frac{1}{2}\left(-B\frac{(\partial B/\partial p)+\frac{4}{3}(\partial G/\partial p)}{B+\frac{4}{3}G}+1\right)\left(\frac{B+\frac{4}{3}G}{\rho}\right)^{1/2} \tag{10}$$

$$\frac{\partial v_{\mathrm{T}}}{\partial \ln V}=\frac{1}{2}\left(-\frac{B}{G}\frac{\partial G}{\partial p}+1\right)\left(\frac{G}{\rho}\right)^{1/2} \tag{11}$$

and for the derivative of the integral, we get

$$\frac{\partial}{\partial \ln V}\int_0^{\Theta_{\mathrm{E},i}/T}\left(\frac{x^3\exp(x)}{(\exp(x)-1)^2}\right)dx$$
$$=\left(\frac{\left(\frac{\Theta_{\mathrm{E},i}}{T}\right)^3\exp\left(\frac{\Theta_{\mathrm{E},i}}{T}\right)}{\left(\exp\left(\frac{\Theta_{\mathrm{E},i}}{T}\right)-1\right)^2}\right)\left(\frac{h(6\pi^2 n_{\mathrm{E}})^{1/3}}{kT}\left(\frac{\partial v_i}{\partial \ln V}-\frac{v_i}{3}\right)\right) \tag{12}$$

The number density of atoms, n_{E}, was calculated through a procedure proposed by Cahill and Pohl [25]. For aPP the following groups of atoms were treated as a single "atom" CH, CH_2, and CH_3, which gives $n_E = 3.68 \times 10^{28}$ m^{-3}. Using literature data for the shear modulus of aPP [26] yields $g = 6.3$ for the liquid state and $g = 3.3$ for the glassy state.

We can also estimate g by employing the simple Debye formula given by [27]

$$\lambda = \tfrac{1}{3}\rho c_V v_{ave} l \tag{13}$$

where c_V is the heat capacity at constant volume, which is associated with the transport process, v_{ave} is the average phonon velocity, and l is the phonon mean free path. In this model, the phonon mean free path of glasses and liquids is of the order of the intermolecular spacing due to the disordered structure. Thus, $l \propto V^{1/3}$ and c_V is approximately independent of density. This yields at high temperatures (classical limit)

$$g = \left(\frac{\partial \ln \lambda}{\partial \ln \rho}\right)_T = 1 + \left(\frac{\partial \ln v_{ave}}{\partial \ln \rho}\right)_T + \left(\frac{\partial \ln l}{\partial \ln \rho}\right)_T = \frac{2}{3} - \left(\frac{\partial \ln v_{ave}}{\partial \ln V}\right)_T \tag{14}$$

where the average phonon velocity can be estimated from the sound velocity by the relation [28]

$$\rho v_{ave}^2 = \tfrac{1}{3}\rho(v_L^2 + 2v_T^2) = \tfrac{1}{3}(B_S + \tfrac{10}{3}G_S) \tag{15}$$

The logarithmic volume derivative of the average velocity is

$$\left(\frac{\partial \ln v_{ave}}{\partial \ln V}\right) = \frac{1}{2}\left(\frac{\partial \ln v_{ave}^2}{\partial \ln V}\right) = -\frac{B}{2}\left(\frac{(\partial B/\partial p) + \frac{10}{3}(\partial G/\partial p)}{(B + \frac{10}{3}G}\right)\right) + \frac{1}{2} \tag{16}$$

Using our own isothermal bulk modulus and a literature value for the shear modulus [26] yields $g = 6.1$ for the liquid state and $g = 3.6$ for the glassy state.

We may also estimate g using a theory for λ of liquids. We have chosen to use the simple theory by Horrocks and McLaughlin [29]. They assumed that liquids could be treated as a cubic quasilattice structure in which the nearest-neighbor distance is a and found

$$\lambda = \sqrt{2}\,\tilde{c}_V \bar{\omega} a^{-1} \tag{17}$$

where $\bar{\omega}$ is the mean intermolecular vibrational frequency of the lattice and $\tilde{c}_V$ is the heat capacity per molecule which is associated with the transport process. Assuming that $\tilde{c}_V$ is independent of volume and temperature yields $\lambda \propto \bar{\omega} p^{1/3}$. The Bridgman parameter for liquids can then be expressed as

$$g_{\text{liq}} = \left(\frac{\partial \ln \bar{\omega}}{\partial \ln \rho}\right)_T + \frac{1}{3} = \gamma_{\text{L}} + \frac{1}{3} \tag{18}$$

where γ_{L} is the lattice Grüneisen parameter of a liquid. This parameter can be calculated from the relation [30]

$$\gamma_{\text{L}} = \frac{1}{2}\left(\frac{\partial B}{\partial p}\right)_T \tag{19}$$

assuming that the Poisson ratio is independent of pressure. Using our own value of $(\partial B/\partial P)_T$ yields $g = 5.1$ and $g = 3.9$ for the liquid and glassy states, respectively. Thus, we can conclude that the g value for the glassy state of aPP is well predicted by these models. However, for the liquid state there is poor agreement between theory and experiment. If we instead use half the value of $\partial G/\partial p$ given in Ref. 26, we get good agreement also for the liquid state. It could very well be the case that the value for $\partial G/\partial p$ of the liquid state [26] is too large due to influences of the glass transition. Consequently, the theories might provide a good prediction also for the liquid state.

All the models described above provide theoretical predictions of the temperature dependence of λ under isochoric conditions. However, measurements are normally done under isobaric conditions. To investigate if this difference is important for aPP, we transformed our experimental data to isochoric conditions. First, we calculated $\lambda(T)$ at atmospheric pressure using short extrapolations of our data for $\lambda(p)$. Subsequently, we used our measured values for g together with literature data for the volume thermal expansivity β to make the transformation. The change of λ due to thermal expansion alone is straightforward to calculate and is given by [2]

$$\partial \ln \lambda_{\text{V}} - \partial \ln \lambda_{\text{p}} = \beta g \, \partial T \tag{20}$$

To take the temperature dependence of g into account, we fitted a first-order linear polynomial function to our data for g in the temperature range 200–297 K, which yielded $g(T) = 3.90 - 4.29 \times 10^{-4} T$. Literature data for the linear thermal expansivity [19] can be represented by a second-order polynomial $\alpha = 10^{-6}(2.26 \times 10^{-4} T^2 + 0.14T + 39.5)$. We assume further that the volume expansivity can be determined as $\beta = 3\alpha$. For a temperature change of 50 K, the calculated isochoric data are 2.5% larger than corresponding isobaric values. We can conclude that this transformation is not important for aPP, at least not for temperature ranges of less than about 100 K.

4.5. Prediction of the Pressure Dependence of the Glass Transition

The pressure dependence of T_g may be predicted by the Ehrenfest equations [31]:

$$\frac{dT_g}{dp}=\frac{\Delta(1/B)}{\Delta\beta} \tag{21}$$

$$\frac{dT_g}{dp}=\frac{T_g\,\Delta\beta}{\rho\,\Delta c_P} \tag{22}$$

where $\Delta\beta$, $\Delta(1/B)$, and Δc_P are the changes at the transition in volume thermal expansion, inverse bulk modulus, and specific heat, respectively. Passaglia and Martin [16] obtained $dT_g/dp = 214\ \mathrm{K \cdot GPa^{-1}}$ and $244\ \mathrm{K \cdot GPa^{-1}}$ from Eqs. (21) and (22), respectively. This should be compared with our value of $191\ \mathrm{K \cdot GPa^{-1}}$ and we can conclude that Eqs. (21) and (22) yield rough estimates of dT_g/dp.

5. CONCLUSIONS

The Bridgman parameters for the glassy and the liquid states of aPP have nearly the same magnitude ($g \approx 3.7$) and are both almost independent of pressure and temperature. The Debye formula [27] and the models of Horrocks and MacLaughlin [29] and Cahill and Pohl [22] predict the Bridgman parameter for the glassy state to within 12% at 295 K, whereas that of the liquid state is overestimated by almost a factor of 2. However, the latter is probably because the measured value for $\partial G/\partial p$ of the liquid state is affected by the glass transition and therefore is too large. Our results for $\lambda(p, T)$, and $\rho c_P(p, T)$ were in reasonable agreement with previous work, but $B(p)$ differed significantly from literature data for both the liquid and the glassy states [16]. In the latter, the discrepancy can be due to different thermal histories. Furthermore, the results for both states can be affected by the difference in average molecular weight between our sample and that used in Ref. 16 and that the sample used in Ref. 16 contained 2–3% isotactic poly(propylene). In the case of aPP, the Murnaghan equation of state can represent volume data in pressure ranges of less than about 0.5 GPa but is less useful in wider pressure ranges. The Ehrenfest relations predict the pressure dependence of T_g to within 12–28%.

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