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Thermal Conductivity of Amorphous Teflon (AF 1600) at High Pressure

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The thermal conductivity, λ, of amorphous Teflon AF 1600 [poly(1,3-dioxole-4,5-difluoro-2,2-bis(trifluoromethyl)-co-tetrafluoroethylene)] has been measured at pressures up to 2 GPa in the temperature range 93–392 K. At 295 K and atmospheric pressure we obtained $\lambda = 0.116\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The bulk modulus was measured up to 1.0 GPa in the temperature range 150–296 K and the combined data yielded the following values for $g = (\partial \ln \lambda / \partial \ln \rho)_T$: 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.

KEY WORDS: bulk modulus; equation of state; high pressure; poly(1,3-dioxole-4,5-difluoro-2,2-bis(trifluoromethyl)-co-tetrafluoroethylene); thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Teflon, poly(tetrafluoroethylene), is a well-known polymer with unusual properties. It does not absorb water, it is resistant to chemical attack, it has a low dielectric constant, and it can be used even at moderately high temperatures (558 K), while not being brittle at low temperatures (77 K). It is a semicrystalline polymer, useful in many electrical and chemical applications. In optical experiments, it is desirable to have transparent polymers which are also chemically inert. In 1989, Du Pont Company developed a new type of amorphous, hence transparent, polymer with the excellent chemical properties of poly(tetrafluoroethylene). This new family of amorphous fluoroplastics, known as Teflon AF, is amorphous copolymers of 1,3-dioxole-4,5-difluoro-2,2bis(trifluoromethyl) and tetrafluoroethylene (CAS:

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37626-13-4). Teflon AF 1600 contains 66 mol% 1,3-dioxole-4,5-difluoro-2,2-bis(trifluoromethyl) and has a glass transition temperature at 433 K.

Its thermal conductivity, λ, was unknown prior to this investigation. We have used the transient hot-wire method to measure λ under pressure over a wide range of temperatures.

Using auxiliary equation-of-state measurements, we transformed our data for $\lambda(p)$ to data for $\lambda(V)$ and expressed the volume dependence of λ by the Bridgman parameter, g, which is defined as $g = -[(\partial\lambda/\lambda)/(\partial V/V)]_T$. This parameter could be used to organize materials into groups. Glasses exhibit normally values for g less than 3 and liquids have values close to 3, whereas those of crystalline materials are in general larger than 4. However, there are exceptions such as phase Ih of ice ($g = -2.5$ at 248 K) or amorphous SiO_2 ($g = -1.5$ at 295 K), and from a theoretical point of view, the origin for these ranges for g is not fully understood. In the present work, we have determined g for Teflon AF and used it to transform data for isobaric $\lambda_p(T)$ to data for isochoric $\lambda_V(T)$. This is important when theoretical models for λ, which are indeed derived under isochoric conditions, are evaluated. The difference in conditions between experimental and theoretical work is quite commonly ignored. This might be justified at low temperatures, where thermal expansion normally is small. At high temperatures, however, the comparison between theory and experiment might be deceptive if the difference is not accounted for.

In order to make the described transformation of λ, it is necessary to know $g(T)$. In practice, we have previously commonly used a value for g at room temperature and assumed g to be temperature independent. There has been no previous systematic investigation to validate this assumption. In fact, there are very few data for g at all, which is due partly to the difficulties of measuring λ under high pressure. The main propose of this investigation was to determine temperature dependence of g for a polymer. Previously, we had measured g for poly(methyl methacrylate) (PMMA) [1], which yielded a value of 3.4 at 296 K.

2. EXPERIMENTS

The samples of Teflon AF 1600 which were studied in the present work were supplied as disks, 39 and 14 mm in diameter, by Du Pont Polymers, Delaware, U.S.A.

2.1. Measurements of Thermal Conductivity

We used the transient hot-wire method [2] to measure the thermal conductivity λ. The method yields also data for heat capacity per unit volume ρc_p, where c_p is the isobaric specific heat capacity and ρ is the mass density. However, since these data can be calculated more accurately from previously measured data for ρ and c_p, they are not presented here. The sensor was a nickel wire (0.1 mm in diameter), installed as a circular loop between two solid Teflon AF 1600 plates (8 mm in thickness and 39 mm in diameter) in a poly(tetrafluoroethylene) cell. We must point out that we always use poly(tetrafluoroethylene) cells for hot-wire experiments under pressure and that it is, therefore, a coincidence that the sample is a similar polymer. The whole assembly was loaded into a piston-cylinder apparatus and 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 as a function of 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 [2] in λ was estimated as $\pm 2\%$.

We used two types of high-pressure apparatus during the investigations. In the temperature range 236–400 K, we used equipment which can operate up to 2 GPa. A general description of this equipment has been given in the literature [1, 3]. At temperatures below 236 K, we used an apparatus which operates to 1.0 GPa [4].

The temperature of the high-temperature vessel (236–400 K) was varied by heating or cooling the whole pressure vessel. For this purpose, the vessel was equipped with both an electrical resistance heater and a cooling coil (copper tube). Through the latter we could either circulate Freon from a refrigerating unit or pass liquid nitrogen.

Below 236 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 to 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 using plates of glass-fiber-reinforced siloxane resin. The pressure vessel was kept in a vacuum chamber, continuously pumped to yield a pressure of about 10 Pa.

The temperature T of the specimen was measured with an internal chromel–alumel thermocouple, which had been calibrated against a commercial diode sensor. The pressure p was determined from the load per area, with an empirical correction for friction established using the pressure dependence of a manganin wire. The inaccuracy in pressure was estimated to be ± 40 MPa at 1 GPa. Temperature and pressure were regulated using an adaptive controller (First Control System AB, Västerås, Sweden) [4]. 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 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 [5]. 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 [6]. The temperature was measured by a thermocouple and kept to within ±0.5 K (by the three-term control system). 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 in order 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 monotonically, in a series of steps of typically 35 MPa up to the final pressure of 1.4 GPa. Subsequently, we decreased the pressure using the same step size down to atmospheric pressure. After each pressure step, we waited approximately 20 min for the volume to stabilize. In order 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 isothermal bulk modulus, $B(p) \equiv -(\partial p/\partial \ln V)_T$, was calculated by fitting the Murnaghan equation [7] to these data. The inaccuracy in $B(p)$ was estimated as ±2%.

3. RESULTS

3.1. Thermal Conductivity

We performed isothermal measurements of thermal conductivity in three pressure ranges:

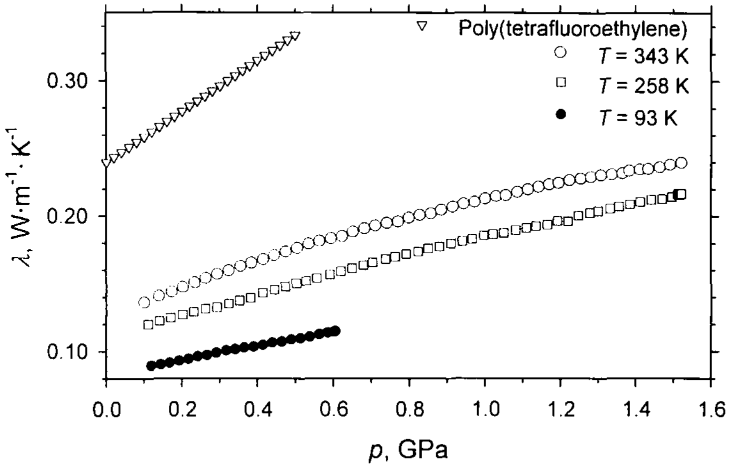

Fig. 1. Thermal conductivity, λ, plotted against pressure, *p*, for Teflon AF 1600 at temperatures of 93, 258, and 343 K.

- 0.1–2.0 GPa at 379.3, 367.3, 357.1, 338.2, and 323.0 K;
- 0.1–1.5 GPa at 342.8, 328.4, 315.9, 306.0, 297.0, 281.5, 273.1, 258.1, 245.1, and 235.7 K; and
- 0.1–0.6 GPa at 235.6, 200.7, 185.3, 170.2, 160.3, 150.2, 135.2, 120.1, and 93.3 K.

Figure 1 shows the pressure dependence of the thermal conductivity at three selected temperatures. The thermal conductivity evidently increases monotonically with increasing pressure, which is the normal behavior. In a detailed analysis, it can be seen that the curve for the highest temperature (342.8 K) is not as linear as the other two curves. In addition, we found that other isotherms exhibit a weak dip at pressures between 1.4 and 1.7 GPa as illustrated in Fig. 2. The indentation on these curves is outside the experimental inaccuracy and can be a signature of a phase transition. However, in order to establish firmly the origin of these dips, it is necessary to have data for other physical properties.

The result for λ (in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$) can be represented by two equations. The first is

$$\begin{aligned}\lambda = {} & 7.1839 \times 10^{-2} + 1.7238 \times 10^{-4} T - 5.2534 \times 10^{-8} T^2 \\ & - 3.9656 \times 10^{-2} p + 6.8530 \times 10^{-2} p^2 + 9.7559 \times 10^{-4} Tp \\ & - 2.0287 \times 10^{-6} T^2 p - 6.4211 \times 10^{-4} Tp^2 + 1.3654 \times 10^{-6} T^2 p^2 \qquad (1)\end{aligned}$$

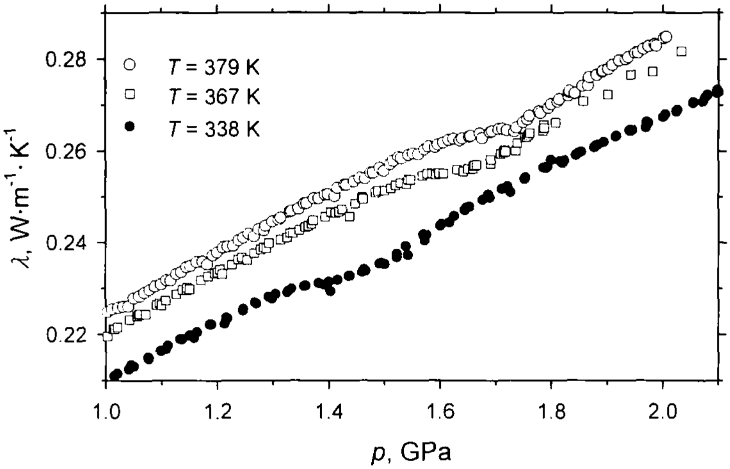

Fig. 2. Zoomed plot of thermal conductivity, λ, plotted against pressure, p, for Teflon AF 1600 at temperatures of 338, 367, and 379 K.

(valid for the pressure range 0–0.60 GPa and the temperature range 93–250 K), and the second is

$$\begin{aligned}\lambda = {} & 7.6900\times10^{-2} + 1.2800\times10^{-4}T + 4.8197\times10^{-8}T^2 \\ & + 8.9054\times10^{-2}p - 1.8060\times10^{-2}p^2 \\ & - 2.4828\times10^{-4}Tp + 0.81318\times10^{-6}T^2p \\ & + 1.3767\times10^{-4}Tp^2 - 0.37260\times10^{-6}T^2p^2 \end{aligned} \tag{2}$$

(valid for the pressure the range 0–1.5 GPa and the temperature range 250–380 K). These equations were obtained by fitting of the isothermal data for λ. In order to obtain a good description of the experimental data, it was necessary to divide the temperature range into two parts. As a consequence, the curves representing the data yield a discontinuous derivative at the joints and should therefore be used with caution in the vicinity of the joints. The maximum deviation from the data is only 1.9%, which is close to the estimated inaccuracy in λ.

3.2. Equation of State

Isothermal measurements of volume versus pressure were performed at 296, 258, 236, 200, and 150 K. Figure 3 shows the results at 296 and 150 K.

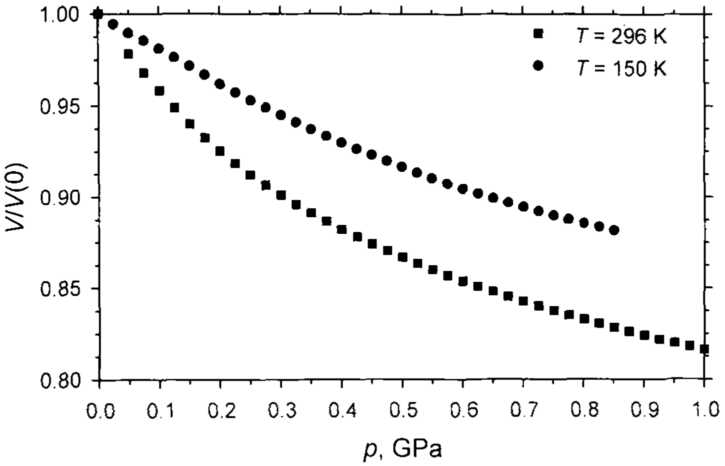

Fig. 3. Relative change of volume $V(p)/V(0)$ for Teflon AF 1600 at temperatures of 150 and 296 K.

The isothermal bulk modulus $B(p) = -V(\partial p/\partial V)_T$ was calculated by fitting the Murnaghan equation of state [7]

$$\frac{V(p)}{V(0)} = \left(1 + \frac{B_1}{B_0} p\right)^{-1/B_1} \tag{3}$$

to the experimental data of volume versus pressure. The Murnaghan equation is derived by assuming $B(p) = B_0 + B_1 p$, with the constants B_0 and B_1 being defined by $B_0 \equiv B(0)$ and $B_1 \equiv dB/dp$.

We found that both B_0 (in GPa) and B_1 could be described satisfactorily by a first-order polynomial function of temperature given by

$$B_0 = (7.45 - 0.0193T) \pm 0.08, \qquad 150 < T < 296 \text{ K} \tag{4}$$

$$B_1 = (2.92 + 0.0188T) \pm 0.2, \qquad 150 < T < 296 \text{ K} \tag{5}$$

In order to establish the complete equation of state, we need data for the thermal expansivity. One way to measure the thermal expansion is to measure volume versus temperature. However, in order to compare the data with literature data at atmospheric pressure, we have to account for the difference in pressure. This difference is fairly large (≈ 0.06 GPa) since we have to apply sufficiently large pressure to at least overcome the friction. In order to avoid this problem, we did instead measure the linear thermal expansion α. The indium capsule was removed and the four centered free-standing stapled plates, with a total length of 22 mm, were directly placed in the piston-cylinder device. The measurements were performed in the temperature range 180–270 K at a pressure of 0.22 MPa. The heating and cooling rates were approximately 0.05 K · min^{-1}. We obtained $\alpha = (73 \pm 2) \times 10^{-6}$ K^{-1}, which is in good agreement with the value supplied by Du Pont Polymers: $\alpha = 74 \times 10^{-6}$ K^{-1}.

4. DISCUSSION

4.1. Thermal Conductivity

We have not found any other results in the literature with which our data could be compared. However, we can compare our results with those for ordinary poly(tetrafluoroethylene) [8], which are given by $\lambda(T) = 4.86 \times 10^{-4} T + 0.120$ W · m^{-1} · K^{-1} (we have transformed the original equation to SI units) at atmospheric pressure and in the temperature range 298–598 K. This equation yields $\lambda = 0.274$ W · m^{-1} · K^{-1} at 316 K, which is approximately 2.3 times larger than the value we obtain at 316 K, by a short extrapolation to atmospheric pressure. Our data for Teflon AF 1600, extrapolated to atmospheric pressure, can be described by the equation $\lambda(T) = -5.73 \times 10^{-8} T^2 + 1.70 \times 10^{-4} T + 0.0733$ to within 1%. This yields a temperature derivative $(\partial\lambda/\partial T)_{p=0}$ of 4.86×10^{-4} W · m^{-1} · K^{-2} for poly(tetrafluoroethylene), which is more than 3.5 the value for Teflon AF 1600 at room temperature. Andersson and Bäckström [9] measured λ as a function of pressure of poly(tetrafluoroethylene) at room temperature. They reported a nearly linear pressure dependence, $\lambda = 0.24 + 0.188p$, with p in GPa. The curve is shown in Fig. 1 and the slope 0.188 W · m^{-1} · K^{-1} · GPa^{-1} is about twice the value we obtained at 297 K. If we instead consider the relative slopes of these quantities, we find, however, that $[(1/\lambda)(\partial\lambda/\partial T)]_T$ is 59% higher and $[(1/\lambda)(\partial\lambda/\partial p)]_T$ is only 3% higher for poly(tetrafluoroethylene). We can conclude that Teflon AF 1600 has a low thermal conductivity ($\lambda = 0.116$ W · m^{-1} · K^{-1}) at 295 K and atmospheric pressure and weak absolute pressure, and temperature dependencies comparable with those of poly(tetrafluoroethylene).

4.2. Volume Dependence of Thermal Conductivity

The volume dependence of λ can be calculated from data for $\lambda(p)$ and $V(p)$. Figure 4 shows our result at 200 K for $\log(\lambda)$ versus $\log(V/V(0))$, which yields $-g$ equal to the slope. Figure 5 shows g versus T for pressures less than 0.6 GPa. All values for g are approximately independent of pressure.

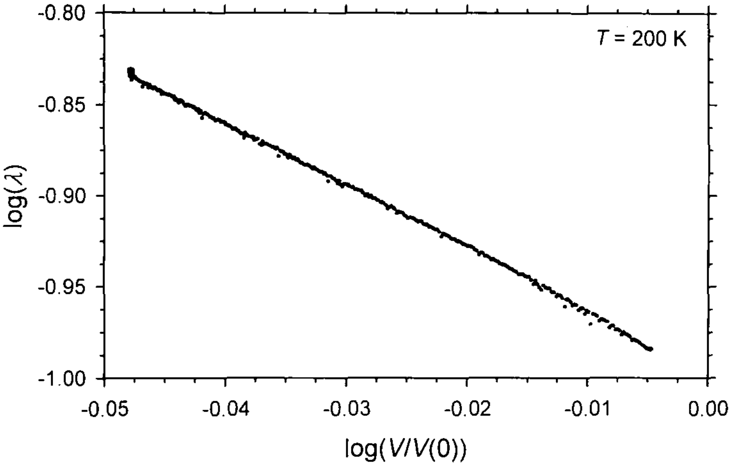

Fig. 4. The log of thermal conductivity, λ, plotted against the log of relative volume $V(p)/V(0)$ for Teflon AF 1600 at a temperature of 200 K.

Theoretical predictions of the temperature dependence of λ always refer to isochoric conditions, whereas measurements normally are done under isobaric conditions. In order to show the difference between the results, 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 Bridgman

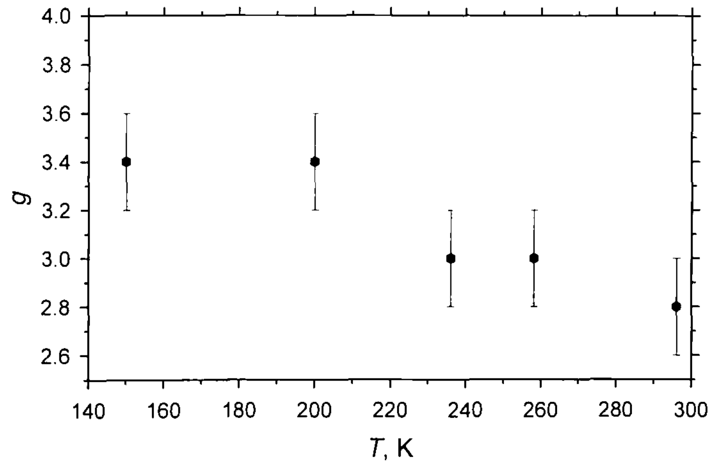

Fig. 5. The Bridgman parameter, g, plotted against T for Teflon AF 1600.

parameter g and linear thermal expansivity α to make the transformation. The change in thermal conductivity due to thermal expansion alone is straightforward to calculate. We can start with $\ln(\lambda)$ and $\ln(V)$ and differentiate these functions with respect to T and p. We obtain

$$\begin{aligned} \partial \ln(\lambda) &= \left(\frac{\partial \ln(\lambda)}{\partial T}\right)_p dT + \left(\frac{\partial \ln(\lambda)}{\partial p}\right)_T dp \\ \partial \ln(V) &= \left(\frac{\partial \ln(V)}{\partial T}\right)_p dT + \left(\frac{\partial \ln(V)}{\partial p}\right)_T dp \end{aligned} \tag{6}$$

Isochoric condition $\partial \ln(V) = 0$ gives

$$(\partial \ln(\lambda))_V = \left(\frac{\partial \ln(\lambda)}{\partial T}\right)_p dT - \left(\frac{\partial \ln(\lambda)}{\partial p}\right)_T \left(\frac{\partial \ln(V)}{\partial T}\right)_p \left(\frac{\partial \ln(V)}{\partial p}\right)_T^{-1} dT \tag{7}$$

If we take the difference between isochoric and isobaric data, we obtain

$$(\partial \ln(\lambda))_V - (\partial \ln(\lambda))_p = -\left(\frac{\partial \ln(V)}{\partial T}\right)_p \left(\frac{\partial \ln \lambda}{\partial \ln V}\right)_T dT = \beta g\, dT \tag{8}$$

where β is the volume thermal expansivity.

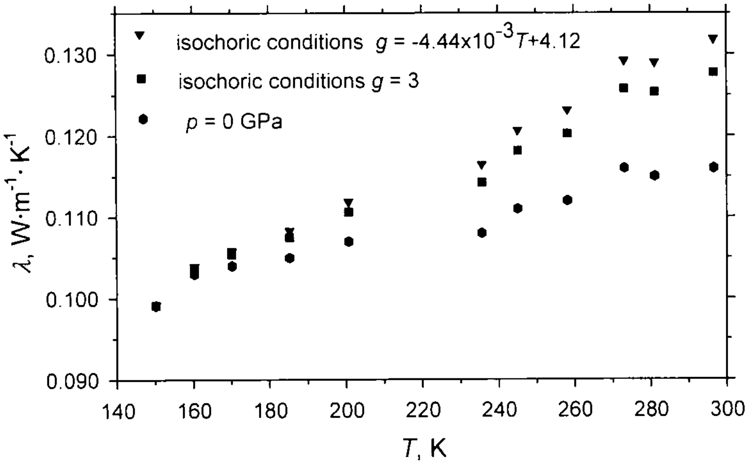

Fig. 6. Thermal conductivity, λ, plotted against T for Teflon AF 1600 under isobaric condition at pressure 0 GPa. Isochoric condition for density pertaining to $p_0 = 0$ GPa and $T_0 = 150$ K for measured g and constant $g = 3$.

In order to take the temperature dependence of g into account, we fitted a linear polynomial to $g(T)$, yielding $g(T) = -4.44 \times 10^{-3} T + 4.12$ and used the measured linear thermal expansivity. We assume further that volume expansivity can be determined as $\beta = 3\alpha$. Our isochoric results for the transformed isobar $p = 0$ (atmospheric pressure) are shown in Fig. 6 together with the isobar at 0. It is also interesting to compare our isochoric data with isochoric data which have been calculated using a constant g. This gives an estimate of the error in the transformation using such an assumption. As shown by the result in Fig. 6, a temperature-independent value is a reasonably good assumption. Many disordered states exhibit small values for g at room temperature. Glasses exhibit values for g in the range 1-3 [10], liquids close to 3, and plastic crystal phases in the range 3-6 [11]. It is a good possibility that the temperature dependence of g in these systems should not be much larger than that we found here for Teflon AF 1600 and we intend to test this hypothesis in future investigations.

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