Thermal Conductivity and Heat Capacity per Unit Volume of Poly(methyl Methacrylate) Under High Pressure

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The thermal conductivity and heat capacity per unit volume of poly(methyl methacrylate) (25 and 350 kg · mol⁻¹ in molecular weight) have been measured in the temperature range 155–358 K at pressures up to 2 GPa using the transient hot-wire method. The bulk modulus has been measured up to 1.0 GPa at 294 K and yielded a constant value $g = 3.4 \pm 0.3$ for the Bridgman parameter. No dependence on molecular weight could be detected in the properties we measured.

KEY WORDS: bulk modulus; heat capacity; high-pressure poly(methyl methacrylate); thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Experimental results concerning the thermal properties of polymers versus both temperature T and pressure P are still rare. Most such results for poly(methyl methacrylate) (PMMA) concern the heat capacity and have been carried out using calorimetric methods at atmospheric pressure. However, conventional calorimetric methods are difficult to use at higher pressures. We have used the transient hot-wire method to measure simultaneously both the thermal conductivity and the heat capacity per unit volume.

With the aid of a subsidiary measurement of bulk modulus, together with literature data for thermal expansivity, we could transform our data for thermal conductivity to isochoric conditions.

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2. EXPERIMENTS

The two samples of poly(methyl methacrylate) (PMMA) which have been studied in the present work were supplied in bead form by Polysciences Inc. According to the Swedish supplier Labkemi, the average molecular weight was $25 \, kg \cdot mol^{-1}$ for PMMA sample A and $350 \, kg \cdot mol^{-1}$ for sample B. In order to suit the experiments, the polymer beads were pressed into solid form. This was done using a small piston-cylinder pressure vessel, together with a heating system and a hydraulic hand-press. The solids were formed at a pressure of 25 MPa and a temperature of 425 K.

2.1. Measurements of Thermal Conductivity and Heat Capacity per Unit Volume

We used the transient hot-wire method to measure simultaneously both 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 we used has previously been described [1]. An outline of the method is that the hot wire was a nickel wire (0.1-mm diameter), which was installed as a circular loop between two solid plates of specimen (8 mm thick and 39 mm in diameter) in a Teflon cell. 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-s) pulse of nearly constant power and the wire resistance was measured versus time, which enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ and ρc_P. The inaccuracy [1] was estimated as $\pm 2\%$ in λ and $\pm 5\%$ in ρc_P. The standard deviation in λ and ρc_P was an order of magnitude better than the inaccuracy.

The temperature of our experimental system was changed by heating or cooling the whole pressure vessel. For this purpose, the vessel was equipped externally with both an electrical resistance heater and a cooling coil of copper tubing. Though the latter, we could either circulate freon from a refrigerating unit or pass liquid nitrogen. The temperature T of the specimen was measured using an internal chromel vs. alumel thermocouple which had been calibrated against a commercially available silicon diode. The pressure P pertaining to the specimen was determined from measured hydraulic press load divided by pressure-vessel piston area, together with an emperical correction for friction which had been established using the pressure dependence of resistance of a manganin wire.

Both temperature and pressure were regulated using an adaptive microcontroller (First Control Systems AB, Västerås, Sweden). A general description of such a control system has been given elsewhere [2]. The

equipment was operated at temperatures in the overall range 150–400 K and control was typically within ±0.3 K. The pressure of the specimen up to 2 GPa could be controlled within ±5 MPa.

In previous experiments involving the type of pressure vessel which we have used here (e.g. in Ref. 3), the movable upper piston of the vessel was exposed to the air of the laboratory and, as a result, became covered with frost under cryogenic conditions. In this situation, there was a consequent added uncertainty in the extent to which friction between piston and vessel affected the pressure which was determined in the experiments. To eliminate this added uncertainty, we arranged in the present work for an airtight hollow cylindrical "drum" which was attached to the top surface of the vessel and which had the upper piston inside it. The upper component of this drum consisted mainly of a thin sheet of Teflon which allowed for movement of the upper piston. A slow flow of dry nitrogen gas was maintained inside the drum. With use of this arrangement, the upper piston of the pressure vessel was observed to remain free of frost under all conditions.

2.2. Measurement of Isothermal Bulk Modulus

A piston-cylinder type of apparatus was used to measure the variation of specimen volume with pressure at room temperature. A full description of this equipment is intended [4] but has yet to appear, so a few instrumental and operational details will be given here. The pressure vessel in these experiments had an internal diameter of 15 mm. Volume change of the specimen was measured using two transducers. These transducers were situated on opposite sides of the pressure vessel and they made mechanical contact with each piston by means of a yoke. The signals from the two transducers were averaged so as to sompensate for any slight tilting of the pistons. Each displacement transducer was calibrated using a precision screw micrometer. The pressure was generated using a hydraulic press. The press force on the piston was measured to ±10% using a commercial load cell (Hottinger Baldwin Type C2, 50 ton). This force was regulated using a three-term control system so as to yield a variation of <1 MPa. The pressure range was up to 1.3 GPa. A Hewlett Packard 3457A multimeter was used for measuring and digitizing the various analogue signals. The multimeter was connected to a personal computer for data collection and handling. The sample was contained within an indium capsule which had a wall thickness of 0.5 mm. The length of specimen was about 23 mm.

In the course of the measurements, the pressure was changed in a series of steps. Each individual pressure step ΔP had a magnitude in the range from 30 to 40 MPa. For technical reasons, the change ΔP was made over a time interval of 70 s.

The pressure was changed monotonically, either increasing or decreasing. In order to take frictional effects into account, measured loads, for increasing and decreasing pressure, were averaged for each value of measured volume so as obtain data for volume vs pressure (adjusted for friction). In other words, it was assumed that frictional effects were symmetric with respect to increasing and decreasing pressure. The data for volume were also adjusted so to take several small corrections into account. These were (a) dilation (with pressure) of the bore of the vessel which was calculated [5] (and was <1% of the total specimen volume), (b) compression of the In capsule material using the results of subsidiary experiments in our laboratory which agreed with literature data [6], and (c) compression of the pistons which was measured directly in a subsidiary experiment. We then obtained finally our results for volume vs pressure (adjusted for friction), $V(P)$. Isothermal bulk modulus, $B(P)$, was calculated by fitting a Murnaghan equation [7] to these data for $V(P)$. The inaccuracy in B was estimated to be $\pm 2\%$ (for materials in the glass state).

3. RESULTS

3.1. Thermal Conductivity

Isothermal measurement of thermal conductivity has been carried out at temperatures of 155, 175, 212, 223, 237, 244, 294, 302, 313, 330, and 348 K for sample A and 247, 260, 275, 287, 295, 312, 330, 348, and 358 K for sample B.
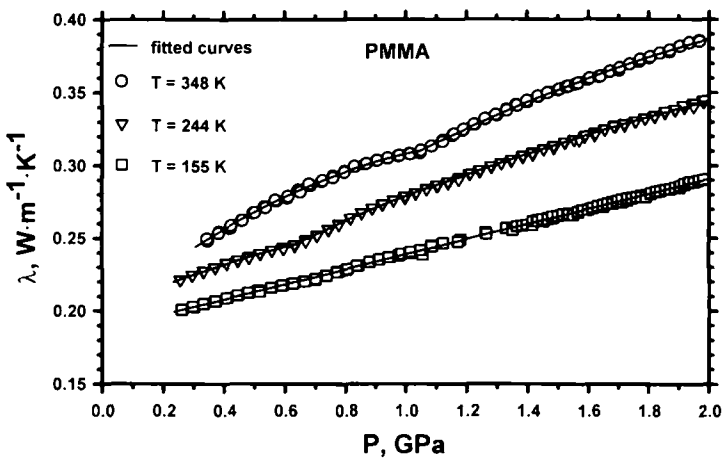

Fig. 1.   Thermal conductivity, λ, plotted against pressure P for temperatures 155, 244, and 348 K for PMMA of 25 kg·mol^{-1} in molecular weight.

Table I. Isothermal Pressure Dependence of λ Fitted to Equation of Form $\lambda = AP^2 + BP + C$, where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and P in GPa

T (K)	P (GPa)	A^a	B^b	C^c	Sample
155	0.270–2.000	3.08	0.0512	0.187	A
175	0.270–1.200	3.36	0.0613	0.191	A
212	0.270–1.500	7.37	0.0661	0.198	A
223	0.270–0.651	−476	0.102	0.198	A
223	0.651–0.859	−333	0.145	0.164	A
223	0.859–2.000	−637	0.0801	0.200	A
237	0.270–0.801	−280	0.0942	0.199	A
237	0.801–1.076	−595	0.202	0.133	A
237	1.076–2.000	6.15	0.0650	0.211	A
244	0.270–0.660	−254	0.0867	0.201	A
244	0.660–0.887	−379	0.160	0.158	A
244	0.887–2.000	−81.7	0.0911	0.196	A
247	0.270–0.722	−243	0.0952	0.196	B
247	0.722–2.000	−167	0.116	0.177	B
260	0.270–0.669	−138	0.0921	0.196	B
260	0.669–2.000	−158	0.114	0.182	B
275	0.270–0.764	−202	0.0994	0.199	B
275	0.764–1.181	−1630	0.401	0.0514	B
275	1.181–2.000	−328	0.173	0.138	B
287	0.270–0.659	−96.4	0.105	0.193	B
287	0.659–1.219	−1250	0.310	0.109	B
287	1.219–1.295	−1980	0.628	−0.172	B
287	1.295–2.000	−361	0.189	0.126	B
294	0.270–0.856	−209	0.123	0.195	A
294	0.856–1.091	−197	0.0821	0.229	A
294	1.091–1.282	1500	−0.243	0.382	A
294	1.282–2.000	−218	0.139	0.174	A
295	0.270–1.042	−158	0.116	0.195	B
295	1.042–2.000	165	0.0660	0.229	B
302	0.270–0.831	−190	0.119	0.199	A
302	0.831–0.992	−972	0.206	0.181	A
302	0.992–1.254	95.0	0.0798	0.200	A
302	1.254–2.000	−165	0.124	0.185	A
312	0.270–0.772	−189	0.122	0.200	B
312	0.772–0.930	−1880	0.350	0.125	B
312	0.930–2.000	−186	0.135	0.177	B
313	0.270–0.837	−274	0.131	0.197	A
313	0.837–0.975	−232	0.0902	0.228	A
313	0.975–1.177	2570	−0.473	0.511	A
313	1.177–2.000	−222	0.148	0.167	A

Table I. *(Continued)*

T (K)	P (GPa)	A^a	B^b	C^c	Sample
330	0.270–0.535	−78.0	0.112	0.207	A
330	0.535–1.040	−966	0.231	0.169	A
330	1.040–1.114	1270	−0.199	0.374	A
330	1.114–2.000	−302	0.172	0.156	A
330	0.270–0.751	−356	0.143	0.198	B
330	0.751–0.997	−1120	0.243	0.166	B
330	0.997–2.000	−232	0.151	0.171	B
348	0.270–1.055	−590	0.170	0.198	A
348	1.055–1.339	24.3	0.0924	0.211	A
348	1.339–2.000	−90.1	0.104	0.216	A
348	0.270–1.036	−745	0.191	0.189	B
348	1.036–1.277	601	−0.0341	0.277	B
348	1.277–2.000	−168	0.131	0.192	B
358	0.270–0.800	−602	0.184	0.189	B
358	0.800–1.050	−1950	0.407	0.0964	B
358	1.050–2.000	−250	0.161	0.167	B

^{a} A is in $10^{-4}\,W \cdot m^{-1} \cdot K^{-1} \cdot GPa^{-2}$.
^{b} B is in $W \cdot m^{-1} \cdot K^{-1} \cdot GPa^{-1}$.
^{c} C is in $W \cdot m^{-1} \cdot K^{-1}$.

Figure 1 shows the pressure dependence of the thermal conductivity at three temperatures for sample A. It can be seen from the figure that the thermal conductivity increased with pressure at these temperatures. At the highest temperatures (244 and 348 K) a cusp can be detected on each curve. The cusp size is near, but probably outside the range of the experimental inaccuracy, so we infer that a real physical effect is involved. A possible interpretation is discussed later. The figure also indicates that the cusp moves to lower pressures as the temperature decreases, and no cusp was detectable for the curve corresponding to 155 K. Similar results (not shown) were obtained for the thermal conductivity of sample B. The difference in thermal conductivity between sample A and sample B, at the same value of T and P, is typically $\leqslant 1\%$, which is within the experimental inaccuracy. We therefore conclude that λ of our polymer material is not sensitive, at the percent level, to an order of magnitude change of average molecular weight.

The solid lines in Fig. 1 refer to second-order polynomials which represent the data and whose coefficients are given in Table I. The deviation between fitted curves and data was $<0.5\%$.
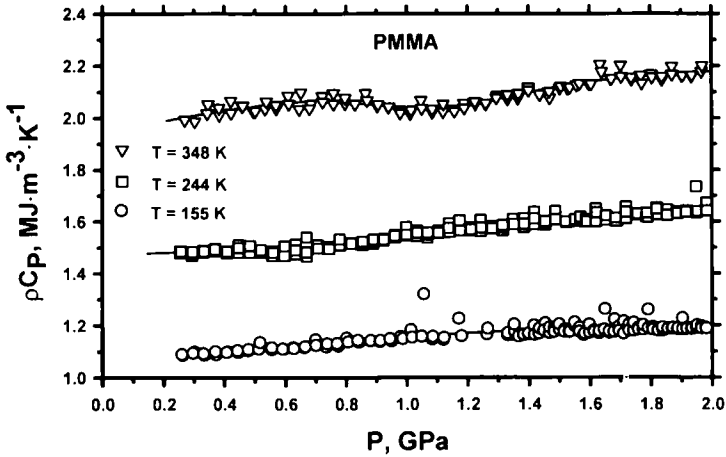
Fig. 2. Heat capacity per unit volume, ρc_P, plotted against pressure P for temperatures 155, 244, and 348 K for PMMA of 25 kg·mol^{-1} in molecular weight.

3.2. Heat Capacity per Unit Volume

Figure 2 shows the pressure dependence of the heat capacity per unit volume at the same three temperatures as in Fig. 1. It can be seen from the figure that the heat capacity per unit volume shows an overall increase with pressure at these temperatures. Figure 3, an expanded diagram of Fig. 2, shows the isotherm for 348 K. We can observe a similar cusp here as we
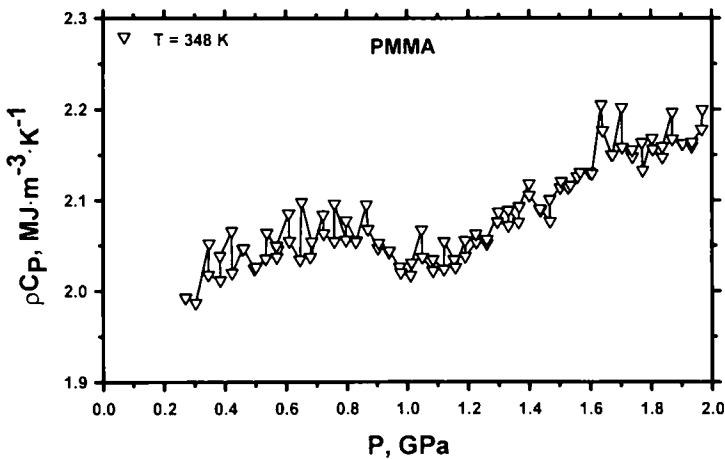

Fig. 3. Heat capacity per unit volume, ρc_P, plotted against pressure P at 348 K for PMMA of 25 kg·mol^{-1} in molecular weight.

Table II. Isothermal Pressure Dependence of ρc_P Fitted to Equation of Form $\rho c_P = EP^2 + FP + G$, Where ρc_P Is in $J \cdot m^{-3} \cdot K^{-1}$ and P in GPa

T (K)	P (GPa)	E^a	F^b	G^c	Sample
155	0.270–2.000	− 37.7	0.149	1.05	A
175	0.270–1.160	29.5	0.0594	1.17	A
212	0.270–2.000	− 10.7	0.111	1.32	A
223	0.270–0.679	− 383	0.350	1.36	A
223	0.679–0.741	− 1930	3.28	0.0679	A
223	0.741–2.000	− 48.3	0.220	1.30	A
237	0.270–0.759	− 69.9	0.0815	1.45	A
237	0.759–0.854	240	− 0.0781	1.39	A
237	0.854–2.000	− 33.3	0.190	1.36	A
244	0.270–0.602	− 144	0.144	1.45	A
244	0.602–2.000	− 28.3	0.190	1.38	A
247	0.270–0.673	− 243	0.307	1.36	B
247	0.673–2.000	− 43.3	0.274	1.30	B
260	0.270–0.497	− 861	0.744	1.31	B
260	0.497–2.000	− 56.1	0.316	1.32	B
275	0.270–1.016	214	− 0.0391	1.50	B
275	1.016–1.188	− 1280	2.60	0.353	B
275	1.188–2.000	− 154	0.688	1.04	B
287	0.270–0.884	− 5.722	0.322	1.44	B
287	0.884–1.123	− 395	0.724	1.39	B
287	1.123–2.000	− 66.9	0.373	1.37	B
294	0.270–0.765	− 46.7	0.257	1.62	A
294	0.765–1.087	− 635	0.977	1.42	A
294	1.087–1.293	− 2270	5.79	− 1.88	A
294	1.293–2.000	9.415	0.132	1.65	A
295	0.270–0.521	− 205	0.237	1.55	B
295	0.521–0.708	− 891	1.57	1.04	B
295	0.708–2.000	− 0.873	0.140	1.60	B
302	0.270–0.788	− 80.4	0.238	1.67	A
302	0.788–1.038	300	− 0.786	2.24	A
302	1.038–1.314	− 1220	3.14	− 1.99	A
302	1.314–2.000	− 33.8	0.218	1.60	A
312	0.270–0.631	− 41.2	0.327	1.60	B
312	0.631–0.928	58.3	− 0.174	1.88	B
312	0.928–2.000	− 78.4	0.415	1.45	B
313	0.270–0.842	29.2	0.194	1.72	A
313	0.842–1.061	0	− 0.419	2.25	A
313	1.061–1.359	0	0.331	1.46	A
313	1.359–2.000	− 62.9	0.290	1.63	A

Table II. (Continued)

T (K)	P (GPa)	E^a	F^b	G^c	Sample
330	0.270–0.857	−97.3	0.260	1.84	A
330	0.857–1.082	792	−1.79	2.94	A
330	1.082–2.000	−177	0.695	1.39	A
330	0.270–0.998	−405	0.626	1.62	B
330	0.998–2.000	−150	0.640	1.35	B
348	0.270–0.835	−184	0.323	1.93	A
348	0.835–1.084	0.00426	−0.197	2.23	A
348	1.084–2.000	−117	0.536	1.58	A
348	0.270–1.043	−468	0.797	1.62	B
348	1.043–2.000	−119	0.570	1.48	B
358	0.270–1.067	−615	1.06	1.56	B
358	1.067–2.000	−142	0.652	1.46	B

^{a} E is in 10^3 J · m^{-3} · K^{-1} · GPa^{-2}.
^{b} F is in 10^6 J · m^{-3} · K^{-1} · GPa^{-1}.
^{c} G is in 10^6 J · m^{-3} · K^{-1}.

observed in thermal conductivity data, at the same pressure. Further, we can see that the scattering of the data points for this isotherm are about 1 %, whereas the cusp has a magnitude of 2 %. This cusp is thus marginal, within the absolute inaccuracy but probably outside the imprecision. A possible interpretation is discussed later. At the lower temperature of 244 K, the cusp has moved to a lower pressure, which is the same as for the thermal conductivity data. We also see from Fig. 2 that the cusp is in fact very small at 244 K. At 155 K we could not detect a cusp (compare with λ in Fig. 1). The solid lines in Fig. 2 refer to second-order polynomials, which represent the data and whose coefficients are given in Table II. The deviation between fitted curves and data was < 1 %.

3.3. Bulk Modulus

The bulk modulus $B = -V(\partial P/\partial V)_T$ at 294 K was calculated by fitting the Murnaghan [7] equation of state

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

to the experimental volume-pressure data (not shown). The Murnaghan equation is derived by assuming that B is a linear function of P, i.e., that

$B(P) = B_0 + B_1 P$, with the constants B_0 and B_1 being defined by $B_0 \equiv B(0)$ and $B_1 \equiv dB/dP$. As a result of the fitting procedure

$$B_0 = 4.19 \pm 0.09 \text{ GPa}, \qquad B_1 = 9.2 \pm 0.2 \qquad \text{(sample A)}$$

$$B_0 = 4.30 \pm 0.09 \text{ GPa}, \qquad B_1 = 9.3 \pm 0.2 \qquad \text{(sample B)}$$

Thus, we could not detect, outside experimental inaccuracy, a dependence of isothermal bulk modulus on average molecular weight for our specimen materials.

4. DISCUSSION

4.1. Thermal Conductivity and Heat Capacity per Unit Volume

Our data for relative thermal conductivity $\lambda(P, T)/\lambda(0, T)$ at 294 K (not shown) agree within 2% with similar data from Andersson and Sundqvist [8] at a temperature of 300 K.

We have used our measured data for $\lambda(P)$ along isotherms to deduce results for $\lambda(T)$ along isobars and representative examples of the latter are shown in Fig. 4. The results in the figure include the isobar at zero pressure which we obtained by a short extrapolation in pressure. Our results for $\lambda(T)$ at zero pressure are approximately parallel with those of Eiermann
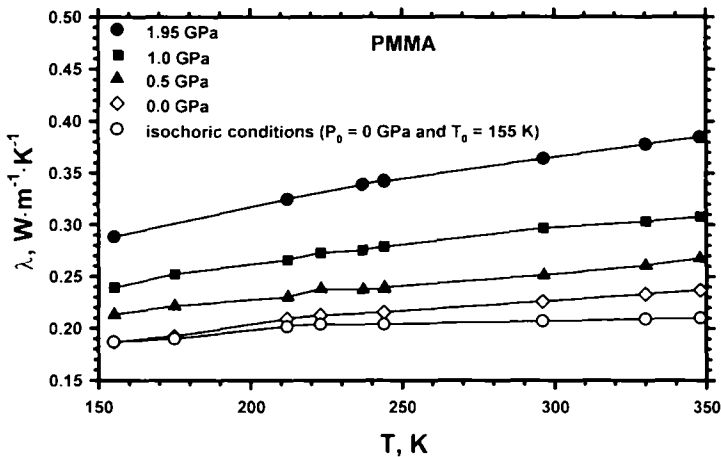

Fig. 4. Thermal conductivity, λ, plotted against temperature T for PMMA of 25 kg·mol^{-1} in molecular weight under isobaric conditions at pressure 0, 0.5, 1.0, and 1.95 GPa. Isochoric conditions for the density pertaining to $P_0 = 0$ GPa and $T_0 = 155$ K.

and Hellwege [9] and about 6% lower. Our results agree within 1–2% with those of Cahill and Pohl [10] at temperatures up to 240 K. At this temperature, Cahill and Pohl's result showed a discontinuous increase of about 6% which has not been observed by other workers. We conclude that the previous work which has just been described is in reasonable agreement with our results.

On the other hand, there is poor agreement with the results reported by Chen and Barker [11] and Barker et al. [12] in terms of both magnitude and pressure dependence of thermal conductivity. We infer that some serious experimental inaccuracy was affecting these results.

We now turn of a brief consideration of a cusp in $\lambda(P)$ along an isotherm which can be seen in Fig. 1. Barker et al. [12] observed a somewhat similar feature in $\lambda(T)$ which they attributed to a β transition in PMMA. The cusp they observed occured at about 220 K at zero pressure and the temperature at which it occurred increased with pressure. These observations are qualitatively consistent with the results in Fig. 1. There is thus some slight basis for associating the cusps shown in Fig. 1 with a β relaxation process occurring under high pressure. It is not, however, possible to make any meaningful connection with the result of other types of measurements from which the existence of a β process has been inferred. The results of Brillouin [13], dielectric [14], and dynamic loss [15] experiments all indicate a zero-pressue β transition temperature of about 320 K, i.e., about 100 K higher than suggested by Barker et al. [12]. However, it is well-known that the thermodynamic coordinates which will be observed for a relaxation type of transition will depend on the frequency window associated with the measurement probe. Thus, detailed comparison of a transition detected by thermal conductivity with that by other experiments is subjected to considerable uncertainty.

4.2. The Volume Dependence of Thermal Conductivity

The volume (V) dependence of the thermal conductivity can easily be calculated by using data for $\lambda(P)$ together with $V(P)$ data. Figure 5 shows our result for log λ vs log(V/V_0), where V_0 is the volume at zero pressure. The slope of the curve is the Bridgman parameter, g, which may be defined as

$$g = -\left(\frac{\partial \ln \lambda}{\partial \ln(V/V_0)}\right)_T = B\left(\frac{\partial \ln \lambda}{\partial P}\right)_T \tag{2}$$

The quantity g for both PMMA samples was calculated to be 3.4 ± 0.3 in the pressure range 0 to 1 GPa at a temperature of 294 K. No pressure dependence of g could be detected in the experiments.
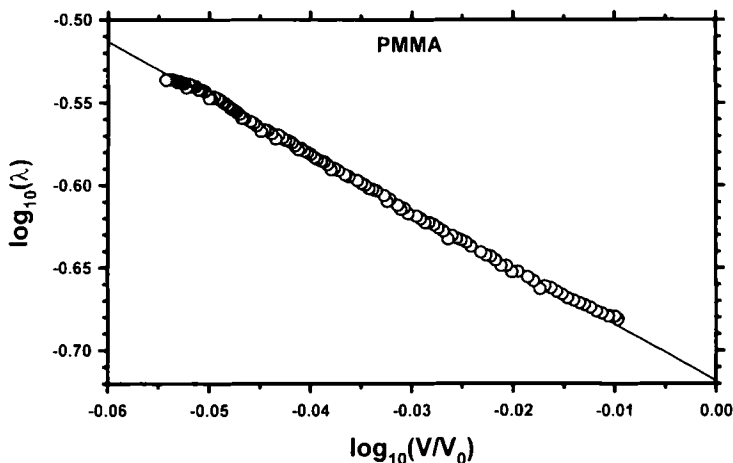
Fig. 5. The log of thermal conductivity λ plotted against the log of relative volume V/V_0 at 294 K for PMMA of 25 kg · mol^{-1} in molecular weight.

Theoretical prediction of the temperature dependence of λ refers to isochoric conditions, since no theory of $\lambda(T)$ take thermal expansion into account. We therefore used our data to determine the isochoric temperature behavior of the thermal conductivity. As discussed above, we transformed our isothermal data to isobaric by using at each pressure the data points (T and λ) corresponding to the measured isotherms. We have transformed the isobaric data to isochoric conditions by using our measured value of g and literature data for the thermal expansivity α [16]. The change of thermal conductivity due to thermal expansion alone is given by

$$\left(\frac{\partial \ln \lambda}{\partial T}\right)_P - \left(\frac{\partial \ln \lambda}{\partial T}\right)_V = -g\alpha \tag{3}$$

We must ignore any possible temperature dependence of g since we have $V(P)$ data only at room temperature. Our isochoric results for the transformed isobar $P = 0$ GPa are shown in Fig. 4 together with isobars at 0, 0.5, 1.0 and 1.95 GPa. Comparison between isobaric and isochoric curves in Fig. 4 shows that thermal expansion yields a 10% increase in thermal conductivity per 100 K.

4.3. Heat Capacity

We have not found any other results for heat capacity per unit volume versus pressure with which our data can be directly compared. However,

Anderson and Sundqvist [8] have reported the relative specific heat capacity versus pressure. We can easily transform our result for heat capacity per unit volume to specific heat capacity using our results $V(P)$. The mass density at 294 K and atmospheric pressure was measured and found to be 1180 kg·m^{-3} for both samples. Our atmospheric pressure extrapolated value of c_P was calculated to be 1.38 kJ·kg^{-1}·K^{-1} and this value is within about 2% of the result obtained by calorimetric methods [16]. For the pressure dependence of c_P, we found in general that this quantity follows the Andersson and Sundqvist data. However, our result for $c_p(P)$ were not linear with pressure as was the case for Andersson and Sunqvist [8]. The maximum difference between the two sets of data was 5% at 0.7 GPa. The inaccuracy in the result of Andersson and Sundqvist was around 5%, so these is agreement within experimental inaccuracy.

5. CONCLUSIONS

Our result for $\lambda(P, T)$ and $\rho c_P(P, T)$ were in reasonable agreement with previous work. Along isotherms for $T > 220$ K, we could detect a weak cusp in data for both λ and ρc_P, in each instance at identical P–T coordinates for the two properties. Such behavior could be associated with a β transition in PMMA but, if so, is difficult to relate to the corresponding transition as detected by measurement of other physical properties. By employing in addition our measurements of bulk modulus at 294 K we obtained a value 3.4 ± 0.3 for the Bridgman parameter g, with no pressure dependence of this quantity being detectable over the pressure range 0–1 GPa. For all properties which we measured, we obtained the same results, within experimental inaccuracy, for PMMA samples of molecular weights 25 and 350 kg·mol^{-1}.

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