

The Specific Volume of Poly(4-methylpentene-1) as a Function of Temperature (30°–320°C) and Pressure (0–2000 kg/cm²)

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Synopsis

The dependence of the specific volume of a commercial sample of poly(4-methylpentene-1) (Mitsui TPX, RT-20, abbr. PMP) on temperature (30°–320°C) and pressure (0–2000 kg/cm²) has been determined. Results are reported in tabular form and as approximate fits, making use of the Tait equation. The data show that the crystalline melting transition of this type of PMP is completed at 235°C under zero pressure and gives indication of a glass transition temperature T_g at about 20°C at $p = 0$. Its approximate pressure dependence is given by $dT_g/dp \approx 0.015^\circ\text{C kg}^{-1}\text{ cm}^2$. The zero pressure results on the melting and glass transitions are in agreement with DTA results. The p - v - T data, quenching experiments, and a determination of the crystalline unit cell (tetragonal, $a = b = 18.70 \text{ \AA}$, $c = 13.54 \text{ \AA}$) confirm earlier work indicating that the room-temperature crystalline specific volume of PMP is greater than the amorphous specific volume. This unusual density behavior persists to a temperature of 50–60°C at $p = 0$ and to temperatures as high as 230–240°C under a pressure of 2000 kg/cm².

INTRODUCTION

Hydrostatic pressure is known to have a profound influence on the physical properties of polymers. Two recent reviews^{1,2} have summarized the effects of hydrostatic pressure on the specific volume (equation of state), glass and melting transitions, crystallization, and mechanical properties of polymers. A thorough knowledge of these and other phenomena (e.g., the specific heat, thermal conductivity) at high pressures is necessary for our understanding of polymeric materials, both from the fundamental point of view of the polymer scientist and from the point of view of the plastics engineer, since polymers are almost always processed at high temperatures and pressures, and in use they are often subjected to states of stress possessing a strong hydrostatic component.

One of the most fundamental properties affected by hydrostatic pressure is the specific volume. Although the specific volume is one of the simplest properties to be measured at high pressures and temperatures, relatively little work has been reported using equipment which provides a truly hydrostatic state of stress even for samples in the solid state. The first apparatus to accomplish this was, to our knowledge, that of Parks and Richards,³ who used it to furnish data on low-density polyethylene (LDPE). Hellwege et al.⁴ have described an apparatus capable of pressures to 2000 bar and temperatures to 250°C. It was used to provide data⁴ on polystyrene (PS) to 250°C, poly(methyl methacrylate)

(PMMA) to 140°C, poly(vinyl chloride) (PVC) to 100°C, LDPE to 175°C, and high-density polyethylene (HDPE) to 203°C. Heydemann and Guicking⁵ reported measurements between -80° and 150°C and pressures to 1000 bar on plasticized PVC and on PMMA. While the pressure in these measurements was truly hydrostatic, the volume changes were calculated from the length changes of a molded sample, thereby assuming the sample to be isotropic. Reliable measurements on a melt do not seem to be possible with this type of apparatus because irreversible length changes (at constant volume) are easily possible in the melt. More recently, Quach and Simha⁶ have described equipment capable of very precise p - v - T measurements between 0° and 200°C and pressures to 2000 bar. It has been used to provide data on PS⁶ and poly(orthomethylstyrene),⁶ isotactic and atactic PMMA,⁷ several methacrylates,⁸ LDPE,⁸ HDPE,⁸ and PE of very high molecular weight.⁸ We have recently described an apparatus¹⁰ basically similar to the design of Quach and Simha,⁶ but having an extended temperature range to at least 380°C (revised upward from the 350°C given in ref. 10) at pressures to 2200 bar. We have already reported data on two polystyrenes.^{9,10} This work on poly(4-methylpentene-1) continues the reports on p - v - T properties from our laboratory.

EXPERIMENTAL

Samples

We used a commercial grade of poly(4-methylpentene-1) (PMP), manufactured by Mitsui Petrochemical Industries, Japan, and designated "TPX" RT-20. It is basically an extrusion grade but also used for some injection moldings. In its commercial form, PMP is a light (density ≈ 0.83 g/cm³), partially crystalline (isotactic) material with a crystalline melting point of about 240°C according to the manufacturer. Despite its crystallinity, it is completely transparent. Pellets were used after they had been thoroughly dried and annealed for about 4 hr at 150°C under a dry N₂ atmosphere.

P - v - T Measurements

The apparatus and evaluation procedure for obtaining pressure-volume-temperature (p - v - T) data have been described in detail.¹⁰ The sample (1-2 g) is contained in a rigid sample cell one end of which is closed by a flexible metal bellows. The space in the cell not taken up by the sample is filled with mercury under vacuum. This sample cell is mounted in a pressure vessel, and pressures to 2200 kg/cm²* are applied with a hand pump using silicon oil as the pressure-transmitting fluid. The pressure is transmitted to the contents of the sample cell by the flexible bellows, which expands until the pressure in the sample cell equals the applied pressure. The displacement of the bellows is measured by a linear variable differential transducer the coil of which is mounted outside the pressure vessel. This displacement can be converted into a volume change of the sample, making use of the cross-sectional area of the bellows and the (known)

* We use pressure in units of kg/cm² (kilograms-force per cm², abbreviated kp/cm² in the German literature). Other units may be obtained as follows: 1 kg/cm² = 9.80665 $\times 10^4$ N/m² = 0.980665 bar = 0.967841 atm = 14.223 psi.

p - v - T properties of the confining mercury. This apparatus is capable of measuring specific volumes of polymers between 30° and 380°C at pressures to 2200 kg/cm² with an accuracy of 0.001–0.002 cm³/g.

Measurements on PMP were performed along 22 isotherms (spaced 10° to 20°C apart) between 30° and 320°C and at pressure increments of 100 kg/cm² up to 2000 kg/cm². The lowest pressure at which measurements were taken was 100 kg/cm². The results quoted for $p = 0$ are therefore extrapolated. This procedure yields more reliable values for the specific volume at $p = 0$, because of some outgassing observed in most polymers at high temperatures.¹⁰

Determination of Sample Specific Volume

The absolute specific volume of the polymer at one temperature must be known for the evaluation of the data from the p - v - T apparatus.¹⁰ For PMP the room-temperature specific volume is determined as follows: Water and glycerol are mixed until the sample stays suspended in the liquid. The specific volume of this mixture is equal to the specific volume of the sample, and it is determined by weighing an accurately known volume. This procedure is believed to yield the specific volume to ± 0.0003 cm³/g, since a change in liquid density of this magnitude will cause the sample to rise or sink at an easily observable rate.

X-Ray Determination of Crystalline Density

Crystalline reflections from a compression-molded, annealed plate of PMP were scanned in a Philips counter diffractometer. Cu K_α radiation ($\lambda = 1.5418$ Å) was used in conjunction with a Ni filter and pulse-height discriminator. Both the scattering and the divergence slit were set at $\frac{1}{4}^\circ$. The scanning speed was $\frac{1}{4}^\circ/\text{min}$. The goniometer scale was calibrated by accurately setting the zero of the scale (to within 0.02°) and by setting the (111) reflection from a silicon calibration sample to an angle $2\theta = 28.47^\circ \pm 0.02^\circ$, corresponding to $d_{111} = 3.1354$ Å.

Differential Thermal Analysis (DTA)

All DTA determinations of the glass transition temperature, the melt temperature range, and the enthalpy of melting were performed on a Mettler TA 2000(B) quantitative thermal analysis system. A dry nitrogen blanket of 15 ml/min was used in all runs.

RESULTS AND DISCUSSION

The specific volume of PMP as a function of pressure and temperature is reported in Table I. The isobars at 0, 500, 1000, 1500, and 2000 kg/cm², obtained by crossplotting the appropriate data from Table I, are shown in Figure 1. Individual data points are shown for the 1000 kg/cm² isobar in order to indicate the temperatures at which measurements were taken and to give an idea of the scatter in the data.

We first turn the data at zero pressure. The specific volume at 22°C and $p = 0$ is 1.203 cm³/g. The specific volume-versus-temperature curve at zero

TABLE I
Measured Specific Volumes Versus Temperature and Pressure.
Line A Separates Points Belonging to the (Possibly Supercooled) Melt

p	TEMP.(°C)										
	29.0	37.9	49.7	61.1	72.9	83.8	94.6	103.5	115.4	135.1	154.8
0	1.2080	1.2119	1.2182	1.2247	1.2325	1.2377	1.2462	1.2509	1.2595	1.2721	1.2858
100	1.2026	1.2057	1.2120	1.2185	1.2256	1.2308	1.2384	1.2431	1.2502	1.2621	1.2750
200	1.1972	1.1995	1.2056	1.2123	1.2186	1.2238	1.2303	1.2346	1.2417	1.2528	1.2642
300	1.1917	1.1941	1.1996	1.2061	1.2124	1.2169	1.2229	1.2277	1.2340	1.2452	1.2549
400	1.1871	1.1886	1.1942	1.2000	1.2063	1.2107	1.2168	1.2207	1.2271	1.2375	1.2465
500	1.1825	1.1840	1.1892	1.1946	1.2009	1.2046	1.2107	1.2146	1.2202	1.2299	1.2389
600	1.1779	1.1794	1.1842	1.1896	1.1956	1.1992	1.2045	1.2085	1.2141	1.2231	1.2321
700	1.1732	1.1748	1.1792	1.1846	1.1902	1.1939	1.1992	1.2028	1.2084	1.2170	1.2254
800	1.1694	1.1710	1.1750	1.1800	1.1852	1.1894	1.1939	1.1975	1.2027	1.2114	1.2194
900	1.1656	1.1664	1.1704	1.1755	1.1807	1.1840	1.1890	1.1926	1.1974	1.2058	1.2134
1000	1.1618	1.1626	1.1666	1.1709	1.1761	1.1795	1.1844	1.1872	1.1929	1.2006	1.2074
1100	1.1588	1.1596	1.1628	1.1667	1.1720	1.1749	1.1795	1.1827	1.1876	1.1953	1.2022
1200	1.1549	1.1558	1.1586	1.1625	1.1674	1.1704	1.1754	1.1782	1.1831	1.1909	1.1978
1300	1.1519	1.1528	1.1552	1.1588	1.1636	1.1666	1.1713	1.1737	1.1790	1.1865	1.1926
1400	1.1481	1.1489	1.1516	1.1556	1.1599	1.1629	1.1675	1.1700	1.1749	1.1817	1.1883
1500	1.1451	1.1459	1.1484	1.1516	1.1561	1.1584	1.1634	1.1659	1.1704	1.1777	1.1839
1600	1.1420	1.1429	1.1451	1.1482	1.1524	1.1546	1.1593	1.1618	1.1663	1.1733	1.1795
1700	1.1390	1.1399	1.1417	1.1445	1.1486	1.1509	1.1556	1.1581	1.1626	1.1696	1.1751
1800	1.1360	1.1369	1.1387	1.1415	1.1457	1.1479	1.1518	1.1544	1.1585	1.1652	1.1716
1900	1.1334	1.1339	1.1357	1.1385	1.1427	1.1446	1.1485	1.1515	1.1548	1.1616	1.1680
2000	1.1307	1.1309	1.1327	1.1356	1.1398	1.1413	1.1452	1.1478	1.1512	1.1580	1.1636

p	TEMP.(°C)										
	176.5	196.3	206.8	217.7	228.9	240.5	250.5	265.9	285.6	305.8	318.9
0	1.3023	1.3209	1.3323	1.3479	1.3675	1.3895	1.4003	1.4137	1.4323	1.4530	1.4738
100	1.2899	1.3061	1.3151	1.3275	1.3454	1.3679	1.3774	1.3881	1.4047	1.4222	1.4397
200	1.2783	1.2921	1.3004	1.3103	1.3256	1.3467	1.3554	1.3673	1.3819	1.3978	1.4129
300	1.2684	1.2806	1.2880	1.2964	1.3095	1.3295	1.3379	1.3485	1.3632	1.3767	1.3902
400	1.2592	1.2706	1.2773	1.2840	1.2955	1.3152	1.3219	1.3326	1.3469	1.3588	1.3707
500	1.2508	1.2615	1.2674	1.2737	1.2840	1.3016	1.3084	1.3183	1.3314	1.3425	1.3536
600	1.2433	1.2532	1.2587	1.2641	1.2724	1.2893	1.2961	1.3052	1.3175	1.3287	1.3399
700	1.2365	1.2456	1.2508	1.2558	1.2633	1.2786	1.2850	1.2937	1.3061	1.3164	1.3260
800	1.2298	1.2381	1.2433	1.2475	1.2550	1.2687	1.2747	1.2835	1.2946	1.3042	1.3138
900	1.2234	1.2314	1.2366	1.2404	1.2467	1.2596	1.2652	1.2732	1.2848	1.2940	1.3024
1000	1.2179	1.2247	1.2299	1.2333	1.2392	1.2513	1.2570	1.2649	1.2753	1.2846	1.2926
1100	1.2119	1.2186	1.2232	1.2274	1.2325	1.2439	1.2487	1.2559	1.2663	1.2756	1.2832
1200	1.2060	1.2137	1.2181	1.2215	1.2259	1.2356	1.2412	1.2484	1.2581	1.2666	1.2746
1300	1.2008	1.2078	1.2122	1.2156	1.2200	1.2289	1.2330	1.2410	1.2511	1.2592	1.2665
1400	1.1965	1.2027	1.2075	1.2105	1.2141	1.2222	1.2271	1.2336	1.2441	1.2518	1.2591
1500	1.1916	1.1976	1.2020	1.2054	1.2090	1.2156	1.2205	1.2269	1.2371	1.2445	1.2518
1600	1.1870	1.1933	1.1970	1.2003	1.2040	1.2101	1.2146	1.2211	1.2305	1.2379	1.2448
1700	1.1835	1.1890	1.1927	1.1952	1.1989	1.2047	1.2088	1.2153	1.2247	1.2313	1.2383
1800	1.1792	1.1847	1.1880	1.1910	1.1938	1.1992	1.2029	1.2095	1.2189	1.2256	1.2322
1900	1.1752	1.1804	1.1841	1.1863	1.1895	1.1937	1.1979	1.2045	1.2131	1.2198	1.2264
2000	1.1713	1.1769	1.1799	1.1824	1.1853	1.1895	1.1924	1.1994	1.2082	1.2141	1.2207

pressure shows a very distinct discontinuity in slope at about 235°C. This is the crystalline melting point of PMP, or, better, the end of the crystalline melting range, since no real discontinuity in specific volume is observed. DTA gives values of 235°–236°C for the end of the melting interval at heating rates of 1°, 5°, and 10°C/min in complete agreement with the p - v - T data. DTA also indi-

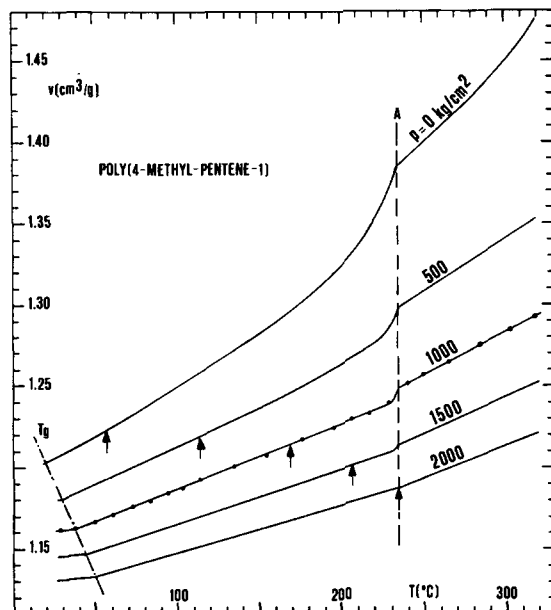


Fig. 1. Selected isobars, spaced 500 kg/cm^2 apart, in the p - v - T relationship of poly(4-methylpentene-1). The line marked T_g gives the approximate dependence of the glass transition temperature on pressure. The line marked A is an isotherm placed through the end of the zero-pressure melting interval. Arrows denote the approximate intersections of the melt isobars with the measured isobars of the sample, i.e., the points in the p - v - T diagram at which crystalline and amorphous regions have the same specific volume.

icates that melting starts at about $170^\circ\text{--}180^\circ\text{C}$. The melting enthalpy is about $5.5\text{--}6 \text{ cal/g}$, the uncertainty resulting from different ways of placing the DTA baseline.

If the $p = 0$ isobar of the melt is extrapolated to lower temperatures in order to get an estimate for the amorphous specific volume at room temperature, one gets the unusual result that this extrapolated melt isobar intersects the measured isobar of the sample between 50° and 60°C . If this extrapolation is meaningful, this means that the crystalline specific volume at room temperature is greater than the amorphous specific volume, and it also means that at 50° to 60°C the amorphous and crystalline specific volumes are equal and equal to the specific volume of the sample. This unusual behavior of the specific volume has already been reported on noncommercial PMP samples.¹¹⁻¹³ In order to check this result further, we determined the specific volume of quenched samples. There was a small but definite decrease in specific volume for samples quenched into ice water or liquid nitrogen: annealed samples had a specific volume of $1.203 \text{ cm}^3/\text{g}$, and the quenched samples gave values between 1.200 and $1.197 \text{ cm}^3/\text{g}$. The quenched samples still showed very definite x-ray crystallinity. The amorphous specific volume at 22°C therefore must be lower than $1.197 \text{ cm}^3/\text{g}$.

X-Ray diffraction data were found to be consistent with a tetragonal unit cell with $a = b = 18.70 \pm 0.06 \text{ \AA}$ and $c = 13.54 \pm 0.04 \text{ \AA}$. Assuming that the unit cell contains 28 repeat units,¹¹ the crystalline specific volume is $1.209 \pm 0.01 \text{ cm}^3/\text{g}$, a value which is indeed slightly higher than our sample specific volume. Table II gives the details of the evaluation of the x-ray pattern. Table III compares

TABLE II
 Evaluation of X-Ray Diffraction Data of PMP

Obs. angle 2θ	Index	Obs. spac., ^a Å	Calc. spac., ^{a,b} Å
9.50	200	9.31	9.35
12.43	211	7.12	7.12
13.42	220	6.60	6.61
16.37	311	5.41	5.42
16.80	212	5.28	5.26
18.32	321	4.84	4.84
20.65	411	4.30	4.30
21.30	420	4.17	4.18
21.65	322	4.10	4.12

^a Using $\lambda = 1.5418$ Å.

^b For tetragonal unit cell with $a = b = 18.70$ Å, $c = 13.54$ Å.

 TABLE III
 Structural and Other Data of PMP Samples Used in Different Investigations

Reference	$a = b$, Å	c , Å	Cryst. density, g/cm ³	Sample density, g/cm ³	Melt. point, ^a °C
Natta et al. ¹⁴		13.85		0.831	200–205
Frank et al. ¹¹	18.66	13.80	0.813	0.847	202–206
Griffith and Ranby ¹²			0.828	0.830–0.838	247–250
Litt ¹³	18.50	13.76	0.832		
This work	18.70	13.54	0.827	0.831	235–236

^a Other workers have reported melting points of 228°C¹⁵ and 235°C.¹⁶

our structural data with that of several laboratory-made samples.^{11–14} It is found that our value of a is somewhat larger than that of the other investigations, the value of c somewhat smaller. Note, however, that the samples of the other investigations also showed different melting points. Altogether, we may safely conclude that the crystalline specific volume of this commercial PMP is indeed higher than the amorphous specific volume.

The specific volume $v(0, T)$ at zero pressure can be fitted to polynomials of the form

$$v(0, T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 + \dots \quad (1)$$

The following coefficients, obtained by least-squares fitting, reproduce the data in Table I to better than 0.001 cm³/g over the temperature ranges indicated: For $T < 235$ °C, i.e., for the partially crystalline material, including all of the melting interval, $A_0 = 1.2044$ cm³ g⁻¹, $A_1 = -1.430 \times 10^{-4}$ cm³ g⁻¹ °C⁻¹, $A_2 = 1.154 \times 10^{-5}$ cm³ g⁻¹ °C⁻², $A_3 = -7.315 \times 10^{-8}$ cm³ g⁻¹ °C⁻³, and $A_4 = 1.705 \times 10^{-10}$ cm³ g⁻¹ °C⁻⁴. For $T > 235$ °C, i.e., for the melt, $A_0 = 1.4075$ cm³ g⁻¹, $A_1 = -9.095 \times 10^{-4}$ cm³ g⁻¹ °C⁻¹, and $A_2 = 3.497 \times 10^{-6}$ cm³ g⁻¹ °C⁻².

Turning now to the pressure results, we first note that the $p \neq 0$ isobars extrapolated from the melt again intersect the measured isobars of the solid sample. The intersections are marked with an arrow in Figure 1. At these intersections, the crystalline and amorphous specific volumes are again equal (and equal to

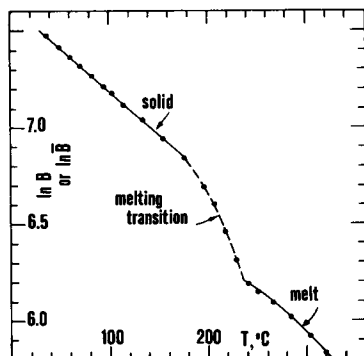


Fig. 2. Temperature dependence of the Tait parameter of PMP. For the solid state and the melting transition, the plot gives $\ln \bar{B}$, i.e., the average of the Tait parameter along an isotherm.

the specific volume of the sample), and the points marked with an arrow therefore represent a few isolated points of the p - v - T relations of completely amorphous or completely crystalline PMP. We also note that there is a break in the $p > 1000$ kg/cm² isobars at low temperatures. This break marks the glass transition under pressure.

Extrapolating back to $p = 0$, one obtains a zero-pressure glass transition temperature of about 20°C, in essential agreement with DTA work, which shows a glass transition between 15° and 25°C at a scanning rate of 5°C/min. The approximate pressure dependence of T_g is given by $dT_g/dp \approx 0.015^\circ\text{C}/\text{kg}/\text{cm}^2$. This pressure dependence, while quite uncertain due to the small number of data points below the glass transition line, is much smaller than that found for polystyrene glasses.^{4,6,9,10} A pressure dependence of the melting temperature cannot be obtained from these measurements: when the melt is pressurized, no solidification is effected in the time interval required for completion of the measurements along one isotherm (about 10 min). This must be due to the very slow crystallization rate at high temperatures and pressures. All data points to the right of isotherm A placed through the zero-pressure melting point, therefore, belong to the (possibly supercooled) melt.

For mathematical convenience, we have tried to represent our data by a mathematical expression. The so-called Tait equation has been found to yield a good representation of the volume changes along an isotherm for a number of polymers in the glassy state or in the melt.^{6,8,9} It is generally written as

$$v(p, T) = v(0, T)\{1 - 0.0894 \ln [1 + p/B(T)]\} \quad (2)$$

where $B(T)$ is the temperature-dependent Tait parameter, and it is determined from each data point along an isotherm, using the zero-pressure specific volume for that isotherm. A value of $B(T)$ independent of pressure indicates that the Tait equation is a good fit to the data. In the solid state of PMP, i.e., up to about 175°C, where melting begins according to the DTA results, and in the melting range itself (175° to 235°C), the Tait parameter is not a constant, but rather increases slowly with pressure (maximum change along an isotherm, about 5%). This observation has also been made on different polyethylenes,⁸ which are the only partially crystalline materials studied in terms of the Tait equation. For the melt ($T > 253^\circ\text{C}$), the Tait parameter is constant along an isotherm. $B(T)$ is usually found to be an exponentially decreasing function of temperature:^{8,9}

$$B(T) = B_1 \exp(-B_2 T) \quad (3)$$

In Figure 2, we give a plot of $\ln B$ versus T . Below 235°C, we have plotted \bar{B} , i.e., the natural logarithm of the average value of B along each isotherm. It can be seen that the average value of B follows an exponential temperature dependence up to 170° or 180°C, indicating once again that melting starts about here. In the melting range itself, the average value of B drops more steeply until a very distinctive break occurs at 235°C, the end of the melting range. Contrary to expectation, the temperature dependence is not exponential in the melt. A possible explanation for this might be the onset of thermal degradation at 270° or 280°C. The following least-squares fits represent the data in Figure 2:

(a) Solid state (30°–175°C):

$$\bar{B}(T) = 2087 \exp(-4.533 \times 10^{-3} T)$$

(b) Melting range (175°–235°):

$$\bar{B}(T) = 1093 + 4.130T - 2.8447 \times 10^{-2} T^2$$

(c) Melt (235°–320°C):

$$B(T) = 377 + 2.176T - 7.1834 \times 10^{-3} T^2$$

where T is in °C, B and \bar{B} in kg/cm². These coefficients substituted into eq. (2), together with the coefficients of the fits for the zero-pressure specific volume given above, reproduce the data of Table I to better than 0.0015 cm³/g in the melt, to better than 0.003 cm³/g in the solid state and to better than 0.005 cm³/g in the melting range.

A comment might be added about the absolute value of $B(T)$ in the melt. The values drop from about 490–340 kg/cm² in the temperature range covered, which includes the melt-processing temperature range. These values are considerably lower than those of polystyrene^{6,9} or polyethylene⁸ in their respective processing ranges, which means that PMP melt, under typical processing conditions, is much more compressible than PS or PE melts. This follows immediately from the fact that the (isothermal) compressibility K may be expressed through the pressure independent Tait parameter B as follows:

$$K(p, T) = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{0.0894}{\{1 - 0.0894 \ln[1 + p/B(T)]\} \cdot [p + B(T)]} \quad (4)$$

In particular at $p = 0$,

$$K(0, T) = \frac{0.0894}{B(T)} \quad (5)$$

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