The Specific Volume of Poly(tetrafluoroethylene) as a Function of Temperature (30°–372°C) and Pressure (0–2000 kg/cm²)

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Synopsis

Experimental data on the specific volume of a 50% crystalline sample of poly(tetrafluorethylene) are presented and discussed. Data points were taken along 22 isotherms spaced 5 to 30°C apart (up to 372°C) in pressure increments of 100 kg/cm² up to 2000 kg/cm². In addition to the melting transition and the first-order solid–solid transition near room temperature, a previously reported second-order transition near 140°C at $P = 0$ is observed. This transition shifts to higher temperatures with increasing pressure by about 0.015°C per kg/cm². The melt data are discussed in detail. They can be fitted to both the empirical Tait equation, with the usual exponential temperature dependence of the Tait parameter, and to the Simha-Somcynsky hole theory (with the reducing parameters V^* = 0.424 cm³/g, T^* = 7906°K, and P^* = 7100 kg/cm² = 6960 bars), thus providing a test for this theory at high reduced temperatures near $\tilde{T}$ = 0.08.

INTRODUCTION

Pressure-specific volume–temperature (PVT) data of polymers yield a wealth of information to the polymer scientist and the plastics engineer. To the engineer they are helpful in an analysis of forming operations, which almost always involve elevated temperatures and high pressures. But they also add to his knowledge of material properties at end use conditions. The polymer scientist needs PVT data for comparison with theoretical equations of state and for the study of melt, glass, and secondary transitions. This work on poly(tetrafluorethylene) (PTFE) was motivated both by the applied and fundamental aspects of PVT data, and it continues the series of reports[1–3] on PVT properties of polymers from our laboratory. Because PTFE is very stable at temperatures as high as 400°C, we hoped, in particular, to be able to test the Simha-Somcynsky hole theory of polymers[4] in a range of reduced temperatures never before reached. Previous work[5] had often shown noticeable systematic differences between theory and experiment at the highest temperatures reached, although it is not clear whether these deviations were caused by inadequacies in the theory or by experimental difficulties.

EXPERIMENTAL

The sample of PTFE used in this work was machined from a ran-extruded rod, made by Polyflon Resine S.p.A, Italy (trademark Lubriflon). Its density by hydrostatic weighing was found to be 2.151 g/cm³ at 25°C. This corresponds to a degree of crystallinity of about 51% or 52%, assuming zero void content.[6]

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The apparatus and evaluation procedure for obtaining PVT data have been described in detail.[1,2] The sample (in the case of PTFE about 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 2000 kg/cm² are applied with a hand pump,[7] using a stabilized 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, which is measured by a linear variable differential transducer, can be converted into a volume change of the sample, making use of the cross-sectional area of the bellows and the known PVT properties of the confining mercury. This apparatus is capable of measuring specific volumes of polymers in the range of 30 to 380°C and pressures of 2000 kg/cm². The accuracy is about 0.001 to 0.002 cm³/g up to 200°C and 0.002 to 0.004 cm³/g up to 380°C. The reduced accuracy at higher temperatures is caused by an uncertainty in the PVT properties of mercury above 200°C.

Measurements of PTFE were performed along 22 isotherms spaced 5° to 30°C apart, and at pressure increments of 100 kg/cm² up to 2000 kg/cm². Since mercury boils at 356°C at atmospheric pressure, the pressure was never lowered below 100 kg/cm² during the course of the measurements. Values of the specific volume at $P = 0$ are generated by extrapolation.

RESULTS AND DISCUSSION

Figure 1 presents some of the results in the form of isobars obtained by cross-plotting of the appropriate experimental isothermal data. Individual points are shown for the $P = 1500$ kg/cm² isobar only, in order to mark the measured isotherms and to give an idea of the scatter in the data. In addition,
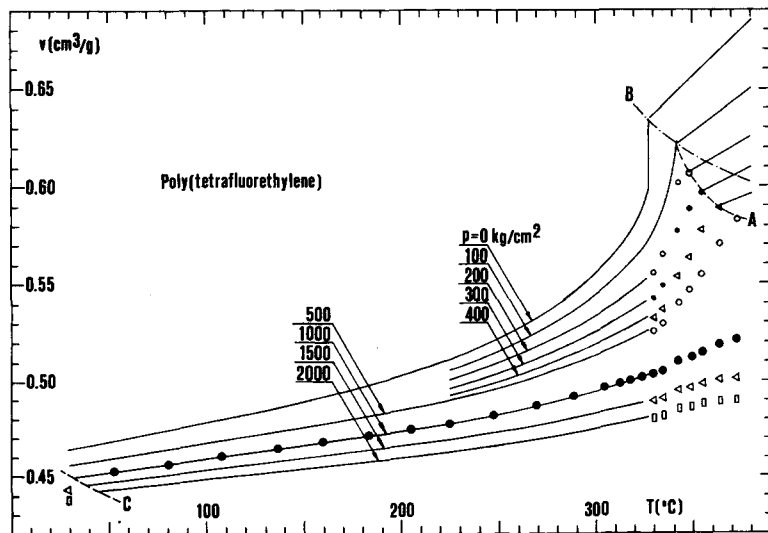

Fig. 1. Selected isobars in the PVT diagram of PTFE, obtained by cross-plotting of experimental, isothermal data. Line A: marks the beginning of solidification on pressurizing the melt, starting from $P = 100$ kg/cm². Line B: approximate pressure dependence of the end of the melting interval in isobaric heating experiments, using data of McGeer and Duus.[8] Line C: pressure dependence of the solid–solid transition temperature according to Beecroft and Swenson.[12]

TABLE I
Measured Specific Volumes of PTFE Melt Versus Temperature and Pressure

T, °C	Specific volume, cm³/g				
	$P = 0^a$	100	200	300	400
330.4	0.637				
335.4	0.642				
342.8	0.648	0.621			
348.5	0.653	0.627	0.607		
355.0	0.661	0.632	0.612	0.597	
364.2	0.669	0.637	0.617	0.601	0.589
372.4	0.677	0.643	0.620	0.606	0.594

ᵃ Pressure, in kg/cm².

individual points, not connected by lines, are shown in the melt transition range. The lowest isobar plotted from directly measured data, $P = 100$ kg/cm², shows a sharp end of the melting interval at about 342°C. When the melt is pressurized above this temperature, starting from $P = 100$ kg/cm², it shows a beginning solidification when the pressure reaches line A. All points above line A therefore belong to the (possibly supercooled) melt. Experimental data for the melt are listed in Table I and will be discussed in detail below. The position of line A is noticeably dependent on the experimental time scale used. In these experiments the pressure was increased in increments of 100 kg/cm² in a few seconds, and the volume reading was taken after waiting for 1 min at each pressure. The relatively fast crystallization of PTFE contrasts sharply with the behavior of poly(4-methylpentene-1)[3] which showed no solidification (on a similar time scale) when pressurized to 2000 kg/cm² above its zero-pressure melting point.

McGeer and Duus[8] give $T_m = 324°C + (0.154°C/atm)$ for the pressure dependence of the melting point of PTFE in isobaric heating experiments for pressures to about 600 atm. However, their "melting point" does not correspond to the end of the melting interval, but rather to a somewhat lower temperature (compare their value of 324°C for $P = 0$ with the commonly accepted value of 327°C for the end of the melting interval,[9] which is also observed for this sample in DTA experiments). Assuming that the end of the melting interval shows the McGeer and Duus pressure coefficient of 0.154°C/atm, line B should represent the end of the melting interval in isobaric experiments. Line B intersects our extrapolated $P = 0$ isobar within one degree from 327°C, as it should, and it runs somewhat above line A for $P \geqslant 100$ kg/cm², showing the relatively small amount of supercooling in our isothermal experiments. The pressure dependence of the melting transition reported by Pistorius[10] (about 0.01°C/atm) is not in agreement with this work.

PTFE is known to show two solid–solid transitions between 19 and 30°C.[11–14] At higher pressures these transitions move to higher temperatures. Our data do not extend below 30°C and thus cannot be used to study these transitions in detail. However, the data points at 30°C and $P > 1000$ kg/cm² are clearly a little below the isobars drawn through the higher temperature points and thus indicate a transition. Line C in Figure 1 represents the pressure dependence of the solid–solid transition temperature according to Beecroft and Swenson.[12] This line is certainly in agreement with our data.

A second-order transition near 130°C (400°K) was reported at Araki[6] in precision zero-pressure dilatometry work. He interpreted it as the glass transition
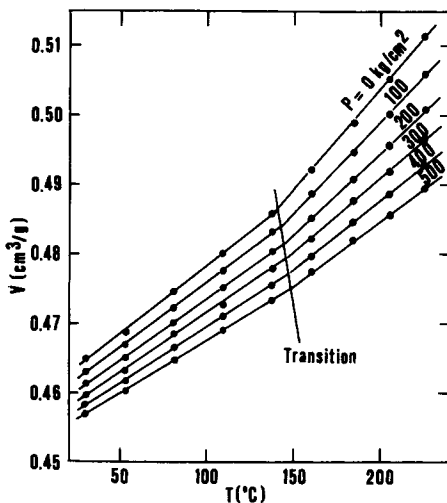
Fig. 2. Large-scale plot of PVT data between 30° and 225°C and $P \leqslant 500$ kg/cm², showing the second-order transition vs pressure. Solid dots: experimental points. Solid lines: linear least-squares fits to experimental data.

of PTFE, based on the dependence of the strength of the transition on crystallinity and the ratio of the transition temperature to the melting point (400°K/600°K = 0.66). This interpretation was put in doubt by the analysis of Ohzawa and Wada,[15] who assigned a T_g of 208°–238°K. Haldon, Schell, and Simha[16] find a change in expansion coefficient near 238°K, while Boyer[17] reports a T_g of 223°K based on extrapolation of copolymer data. Moré specifically, Boyer[18] now assigns 223°K as $T_g(L)$, the lower of the two glass transitions found in many semicrystalline polymers,[19] while rejecting the 400°K transition as a possible $T_g(U)$, because it does not show the right crystallinity dependence in the work of Araki[6] and is too far removed from $T_g(L)$. This "400°K transition" is clearly visible in an enlarged plot of our data in the range of $30 < T < 225$°C and $0 < P < 500$ kg/cm² (Fig. 2). The transition temperature $T^\dagger$ at $P = 0$ is about 138°C (410°K), increasing by about 0.015° ± 0.01°C per kg/cm².

The transition temperature at each pressure was determined as the intersection of straight-line fits for each isobar above and below the transition. The transition temperatures so determined were then fitted linearly against pressure, yielding the pressure coefficient and the uncertainty quoted above. The rather large uncertainty in $dT^\dagger/dP$ is caused by the rather sliding intersections of the isobars, especially at the higher pressures. It seems clear, however, that the pressure dependence is smaller than the pressure dependence of T_g in wholly amorphous polymers[1,2,20,22] but similar to the pressure dependence of the glassy transition near 20°C in poly(4-methylpentene-1),[3] another semicrystalline polymer. This transition has been interpreted as $T_g(L)$ by Boyer.[19] The jump in the volume expansion coefficient at $T^\dagger$ ($P = 0$) is $\Delta\beta = \beta(T > T^\dagger) - \beta(T < T^\dagger) = 5.97 \times 10^{-4} - 3.98 \times 10^{-4} = 1.99 \times 10^{-4}$°C⁻¹, yielding $\Delta\beta T^\dagger = 0.082$. This value might be corrected for crystallinity by dividing by 0.5, yielding a value of 0.164, which would be high when compared to true glass transition in wholly amorphous polymers. However, this method of "correcting" for crystallinity is arbitrary (e.g., it would be wrong to apply this treatment to a $T_g(U)$[19]), and the meaning of the result is not clear at all. We have included it simply as numerical information.

We now turn to a discussion of the melt data, which are listed in Table I. Our values may be compared to little-known work by Lupton,[23] who measured PVT properties of PTFE up to a pressure of 600 bars by a simple piston displacement method. Lupton was able to fit his data to a modified Spencer-Gilmore equation of state:

$$(P + a) \cdot (V - b) = B(T - c) \tag{1}$$

with $a = 400$ atm $= 413$ kg/cm^2, $b = 0.5$ cm^3/g, $c = 417°$K, $B = 0.306$ cm^3 atm/g °K $= 0.316$ cm^3(kg/cm^2)/g °K. Recalculating specific volumes from this formula shows excellent agreement with our data. The difference in specific volume is always less than 1%, but Lupton's data show a smaller volume expansion coefficient for all pressures. For example, at $P = 0$ we obtain $\beta = 1.46 \times 10^{-3}$ °C^{-1}, and Lupton's data yield $\beta = 1.17 \times 10^{-3}$ °C^{-1}.

It is often useful to have a simple mathematical representation of PVT data for purposes of interpolation and data comparison. We use the Tait equation,

$$V(P,T) = V(0,T) \{1 - 0.0894 \ln[1 + P/B(T)]\} \tag{2}$$

to represent our melt data. This equation has been found to yield a good representation of the specific volumes along isotherms in a large number of polymeric melts and glasses.[2,3,20-22,24,25] The melt parameter $B(T)$ is usually found to have an exponential temperature dependence[2,20-22,24,25]

$$B(T) = B_1 \exp(-B_2 T) \tag{3}$$

Together with a suitable expression for $V(0,T)$, eqs. (2) and (3) represent a complete equation of state for a polymer melt. Least-squares fits for PTFE yielded

$$V(0,T) = 0.3200 + 9.5862 \times 10^{-4} T$$

(V in cm^3/g and T in °C) and

$$B(T) = 4336 \exp(-9.38 \times 10^{-3}T)$$

(B in kg/cm^2 and T in °C). These fits reproduce the data in Table I to better than 0.001 cm^3/g.

The solid-state data cannot be fitted to the Tait equation. A point-by-point calculation of the Tait parameter leads to a B increasing along each isotherm by about 20%–30% between $P = 0$ and $P = 2000$ kg/cm^2. The same tendency has been observed in a less pronounced form in other semicrystalline polymers.[3,25]

COMPARISON OF MELT DATA TO THE SIMHA-SOMCYNSKY HOLE THEORY

The Simha-Somcynsky (S-S) hole theory[4] yields the following equation of state in reduced variables $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, $\tilde{P} = P/P^*$:

$$\tilde{P}\tilde{V}/\tilde{T} = [1 - 2^{-1/6} y(y\tilde{V})^{-1/3}]^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \tag{4}$$

The hole fraction $1 - y$ satisfies the following equilibrium condition:

$$(s/3c)[1 + y^{-1} \ln(1 - y)] =$$
$$(y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}]$$
$$+ [2^{-1/6}y(y\tilde{V})^{-1/3} - 1/3][1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} \quad (5)$$

Here, $3c/s$ is the "flexibility ratio," that is, the number of volume-dependent degrees of freedom per chain segment. Its value should be characteristic of the system. However, this ratio cannot be obtained from PVT data, since it has been shown[4] that the reduced equations of state for different values of $3c/s$ can be superimposed. Equations (4) and (5) are therefore commonly used by setting $3c/s = 1$. This will affect the values of the reducing parameters V^*, T^*, and P^* of a particular system, a fact which must be borne in mind when comparing the reducing parameters of different systems. From the definition of the starred reducing parameters, the following relation may be deduced:

$$(P^*V^*/T^*)M_0 = R(c/s) \quad (6)$$

where M_0 is the molecular weight of the segment and R is the gas constant; R has the numerical value 83.1 when P^* is expressed in bars, T^* in °K, and V^* in cm³/g. Equation (6) becomes $(P^*V^*/T^*) = R/3 = 27.7$ when $3c/s = 1$ is used; M_0 then appears as the molecular weight of a segment having exactly one external degree of freedom.

The reducing parameters for PTFE melt were determined as follows: A numerical solution of eqs. (4) and (5) for $\tilde{P} = 0$ yields values for the theoretical zero-pressure isobar $\tilde{V}_0 (\equiv \tilde{V}(0,\tilde{T}))$ vs $\tilde{T}$. This relation is plotted on a large scale as log $\tilde{V}_0$ versus log $\tilde{T}$. On this plot the experimental points are superimposed by shifting the experimental log V_0 versus log T curve parallel to the axes until a good superposition results. Figure 3 shows the results of this superposition for our melt data. We find $T^* = 7906°$K and $V^* = 0.424$ cm³/g from the shift factors. The range of reduced temperatures $\tilde{T}$ covered $(0.0763 < \tilde{T} \leq 0.0817)$ extends to much higher reduced temperatures than other work. (Previous high for polymers: $\tilde{T} = 0.0513$ in work on high molecular weight polyethylene.[5,25]) The ratio T_g/T^* has been discussed with the intent of checking out the possibility of T_g being a reduced temperature.[5,26] Values of T_g/T^* between 0.036 and 0.026 were found, the lower values being favored by low-T_g materials. For the second-order transition temperature $T^\dagger \approx 410°$k displayed in Figure 2 the ratio is
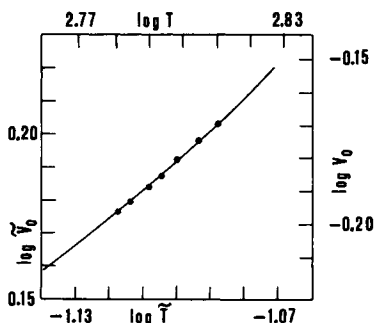

Fig. 3. Experimental zero pressure isobar (log V_0 vs log T) for PTFE melt (solid points), superimposed on theoretical zero pressure isobar (log $\tilde{V}_0$ vs log $\tilde{T}$) of Simha-Somcynsky hole theory (solid line). This superposition yields $V^* = V_0/\tilde{V}_0 = 0.424$ cm³/g and $T^* = T/\tilde{T} = 7906°$K.

$T^\dagger/T^* = 0.052$, again indicating that $T^\dagger$ is not the glass transition. On the other hand, a value of 0.028 is obtained for $T_g(L)/T^*$, using Boyer's value[18] of $T_g)l$) = 223°K, supporting the contention that the 223°K transition is indeed the glass transition.

The pressure-reducing parameter P^* is finally determined by calculating from the S-S theory for each data point the reduced pressure $\tilde{P}$ needed to reproduce the observed reduced volume $\tilde{V}$ (using V^* and T^* previously determined from the zero pressure isobar). Comparison of $\tilde{P}$ with the actual P yields P^* (= $P/\tilde{P}$). The values of P^* so determined are averaged. The result is $P^* = 7100$ kg/cm^2 = 6960 bar, with a standard deviation of 4% (14 data points). Figure 4 finally shows a direct comparison of the experimental data with the predictions of the S-S theory, using the above reducing parameters. The agreement is quite good, the maximum deviation in V being about 0.003 cm^3/g, which is about the same as the experimental uncertainty. Moreover, the deviations are not completely systematic.

P^*V^*/T^* for this system is 0.373 bar cm^3/g °K. Application of eq. (6) yields a value of 74.2 for M_0, the molecular weight of the effective segment (i.e., the segment having exactly one volume-dependent degree of freedom), and a value of 1.48 for the ratio M_0/M_r, where $M_r = 50$ is the molecular weight per carbon backbone unit.

Simha and co-workers[5] have found an empirical correlation between P^*V^*/T^* (or M_0) and T^* is a number of systems:

$$\ln (P^*V^*/T^*) = 1.319 - (3/2.01)(T^* \times 10^{-4}) \qquad (7)$$

or

$$10^{-4}T^* = \ln(M_0/7.4067)^{2.01/3}$$

(P^* in bars, V^* in cm^3/g, and T^* in °K.) Our data on PTFE do not fit into this scheme at all. For $T^* = 7906$°K, the predicted value of P^*T^*/T^* is 1.15, which is much higher than the experimental value of 0.373, and the predicted value of M_0 is 24.1, compared with the experimental value of 74.2. The predicted value of 24 for M_0 is, of course, very low. It is hard to imagine how the requirement
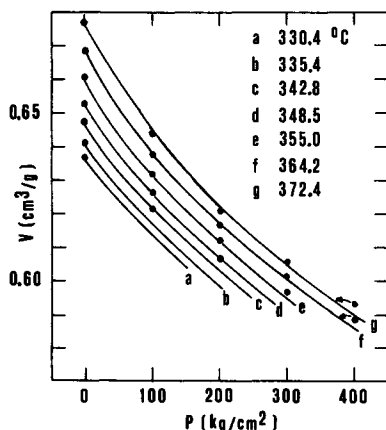

Fig. 4. Comparison of the experimental specific volume of PTFE melt (solid dots) with theoretical isotherms (solid lines) calculated from the Simha-Somcynsky hole theory, using $V^* = 0.424$ cm^3/g, $T^* = 7906$°K, $P^* = 7100$ kg/cm^2 = 6960 bars.

$3c/s = 1$ could be met in half a carbon backbone unit in such a simple structure. At any rate, eq. (7) should not be used in estimating P^* from zero pressure data (i.e., from T^* and V^*) in the case of PTFE, a method suggested by Olabisi and Simha.[5,27]

Another correlation displayed by Olabisi and Simha[5] is that between the molar segmental volume M_0V^* and T^*. Previously investigated systems fell on one of two lines:

$$10^{-4}T^* = \ln(M_0V^*/9.3)^{2.1/3} \qquad (8)$$

or

$$10^{-4}T^* = \ln(M_0V^*/7.4)^{2.2/3} \qquad (9)$$

(T^* in °K, V^* in cm³/g). With $T^* = 7906$°K, eq. (8) predicts $M_0V^* = 28.8$ and eq. (9) yields 21.7, compared with the experimental M_0V^* value of 31.5 cm³/mole. The agreement with eq. (8) is excellent.

For completeness we have also evaluated Lupton's results[23] in terms of the S-S theory. The results are $V^* = 0.461$ cm³/g, $T^* = 8730$°K, $P^* = 4470$ kg/cm² $= 4380$ bars. These parameters, especially P^*, are quite different from the ones deduced from our data, although Lupton's data do not differ more than 1% from ours. The different parameter values are caused mainly by the fact the Lupton's volume expansion coefficient is smaller than ours (see previous section). This illustrates the fact that small systematic differences in the data are magnified in the reducing parameters. In addition, we calculate $P^*V^*/T^* = 0.231$, $M_0 = 119.9$, $M_0/M_r = 2.40$, and $M_0V^* = 55.27$. Again the value of P^*V^*/T^* is much below the trendline, eq. (7). In addition, there is no agreement between the experimental value of M_0V^* and either of the two trendlines, eqs. (8) and (9).

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