

Equation of State for Polymer Liquids

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Synopsis

An empirical pressure–volume–temperature (PVT) equation of state is presented for polymers in the liquid state, i.e., above the melting point of a crystalline polymer or the glass transition of an amorphous polymer. In terms of reduced variables, the equation is given by $P\bar{V}^5 = T^{3/2} - \ln \bar{V}$. Values of the three reducing parameters are given for 23 polymers. Comparison of the predictions of this equation with experimental data are made for all of the polymers. The data are generally available up to a pressure of 2 kbar and a temperature 100°C above the melting or glass transition temperature. Measured and calculated volumes agree within about 0.001 cm³/g, which is the accuracy of the measurements. Detailed comparisons with the empirical Tait equation are made. Equations are also presented for isothermal bulk modulus, thermal expansion coefficient, and Gruneisen parameter.

INTRODUCTION

In this article, a new pressure–volume–temperature (PVT) equation of state for polymers is presented. The equation of state is compared with experimental measurements, from the literature, on thermoplastic polymers in the liquid state, i.e., above the melting point for crystalline polymers or above the glass transition for amorphous polymers. The pressure and temperature ranges of the experimental data generally cover the conditions used in forming polymers.

The new equation of state is derived by combining the theoretical temperature dependence of thermal pressure from Pastine and Warfield¹ with the zero pressure isobar of Simha and Somcynsky² and an empirical volume dependence of thermal pressure. Detailed comparisons are made with the empirical Tait equation.

It will be shown that the new equation of state is a simple, three-parameter equation in the form of a corresponding states relation (expressed in terms of reduced variables only). Volumes calculated with this equation agree with measured values within the accuracy of the measurements, typically 0.001 cm³/g. This accuracy is comparable to that found with the Tait equation but requires only three parameters while the Tait equation requires at least four and sometimes six.

EQUATION OF STATE

The total pressure P in a polymer can be written as the sum of the internal pressure P_0 and the thermal pressure P_T , where P_0 is the pressure along the $T = 0$ isotherm and is determined by the internal energy while P_T is the additional pressure, at any volume, resulting from thermal motion,

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$$P(V,T) = P_0(V) + P_T(V,T) \quad (1)$$

where V and T are specific volume and absolute temperature, respectively.

Pastine and Warfield¹ used a simple model of a polymer liquid based on a vibrating chain in a rigid cylinder. Their results were specifically applied to molten polyethylene, but the analysis is applicable to polymers in general. The primary result of this theory is that the thermal pressure is proportional to $T^{3/2}$,

$$P(V,T) = P_0(V) + A(V)T^{3/2} \quad (2)$$

where A is some function of volume. A limitation of the theory is that the internal pressure term used is only applicable above about 1 kbar.

One of the most successful equations of state for polymers was derived by Simha and Somcynsky² using cell theory. This equation is in good agreement with experiment but is somewhat unwieldy mathematically though a moderately accurate polynomial curve fit is available.³ At zero pressure, however, an extremely accurate representation of the theory is given by⁴

$$\ln V(O,T) = \ln V(O,O) + (T/T_0)^{3/2} \quad (3)$$

where we have chosen to define $V(O,O)$ and T_0 as the coefficients in eq. (3). For brevity, $V(O,O)$ will generally be denoted as V_0 .

Noting the common $T^{3/2}$ factor in the two theories and the complementary pressure regions in which they apply, a combination of Pastine-Warfield theory [eq. (2)] and Simha-Somcynsky theory [eq. (3)] was developed. Setting

$$A(V) = f(V)/T_0^{3/2} \quad (4)$$

it is straightforward to show that

$$P(V,T)/f(V) = (T/T_0)^{3/2} - \ln(V/V_0) \quad (5)$$

where $f(V)$ has dimensions of pressure. Pastine and Warfield expressed $f(V)$ as an inverse power law in volume. We have found empirically that the most accurate results are obtained when the fifth power of the volume is used

$$f(V) = B_0(V/V_0)^{-5} \quad (6)$$

where B_0 is a parameter with the dimensions of pressure. The new equation of state can then be written as

$$(P/B_0)(V/V_0)^5 = (T/T_0)^{3/2} - \ln(V/V_0) \quad (7)$$

Defining reduced variables $\bar{P} = P/B_0$, $\bar{V} = V/V_0$, and $\bar{T} = T/T_0$, eq. (7) can be written in the form

$$\bar{P}\bar{V}^5 = \bar{T}^{3/2} - \ln \bar{V} \quad (8)$$

Note that eq. (8) is in the form of a corresponding states relationship. All polymers follow the same equation in terms of reduced variables. All polymers compared at the same reduced pressure and temperature are in a corresponding state; they have the same reduced volume.

The significance of the reducing parameters is as follows. V_0 is the polymer liquid volume extrapolated (without change of phase) to zero temperature and pressure. T_0 is defined implicitly from the relation $V(B_0, T_0) = V(O, O)$. It will be shown later that B_0 is the isothermal bulk modulus extrapolated to zero temperature and pressure.

Equation (8) is a simple, three-parameter equation of state. The question that remains is: How accurately do the predictions of eq. (8) agree with experiment?

EXPERIMENTAL COMPARISON

Experimental data for 11 crystalline and 12 amorphous polymers was examined. The data generally covers the range from 0 to 2 kbar and from the melting or glass transition to 100°C above the transition.

In some cases, the experimental data is given in tabular form but often the data is expressed in terms of the parameters of the Tait equation since this equation represents the data within the accuracy of the measurements. Experimental accuracies vary from values as low as 0.0005 cm³/g at low temperature to as much as 0.0040 cm³/g at high temperature.

The Tait equation for polymers is

$$V(P, T) = V(O, T) \{1 - 0.0894 \ln[1 + P/B(T)]\} \quad (9)$$

where the zero pressure isotherm is usually given by

$$V(O, T) = V_{0T} e^{\alpha T} \quad (10)$$

where α is the thermal expansion coefficient and we have added the subscript T (for Tait) on the preexponential factor to distinguish this parameter from the V_0 already defined. The Tait parameter B is usually given by

$$B(T) = B_{0T} e^{-B_1 T} \quad (11)$$

so that the Tait equation usually involves four parameters: V_{0T} , α , B_{0T} , and B_1 . In some cases, however, eqs. (10) and (11) do not fit the data accurately, and polynomial expressions are used:

$$V(O, T) = a_0 + a_1 T + a_2 T^2 \quad (12)$$

$$B(T) = b_0 + b_1 T + b_2 T^2 \quad (13)$$

When eqs. (12) and (13) are used, the Tait equation requires six parameters.

Note that the Tait equation [eq. (9)] is only a volume-pressure relation. To obtain a complete PVT equation of state, $V(O, T)$ must be determined separately. For the sake of brevity, we will follow the common terminology of referring to the resulting equation of state as the Tait equation.

To compare the new equation with experimental data, either in a table or as a Tait equation, the reducing parameters V_0 , T_0 , and B_0 must be determined. The first step is to evaluate V_0 and T_0 from the zero pressure data. From eq. (7) at $P = 0$,

$$\ln[V(O,T)/V(O,O)] = (T/T_0)^{3/2} \quad (14)$$

Thus a plot of $\ln V(O,T)$ vs. $T^{3/2}$ should be a straight line of slope $1/T_0^{3/2}$ and intercept $\ln V_0$. Typical data for four crystalline polymers is shown in Figure 1. The polyethylene points shown are taken from tabular data while the other data points were calculated, at evenly spaced intervals, from the Tait equation. In all cases, the data is represented very accurately with a straight line, yielding T_0 and V_0 .

The final parameter to be determined is B_0 . From eq. (7), a plot of P vs. $T^{3/2}$ at constant volume should be a straight line with a slope proportional to B_0 . The results for high density polyethylene, as an example, are shown in Figure 2. Once again, the linear relation fits the data⁵ very well, lending support to the simple model used to calculate this type of behavior.¹ It is worth pointing out that a plot such as Figure 2 cannot, as a rule, be made from tabular data since the data is not available at constant volume. With an analytic equation, in this case the Tait equation, one can interpolate to find the pressure and temperature along constant volume lines, as was done in Figure 2.

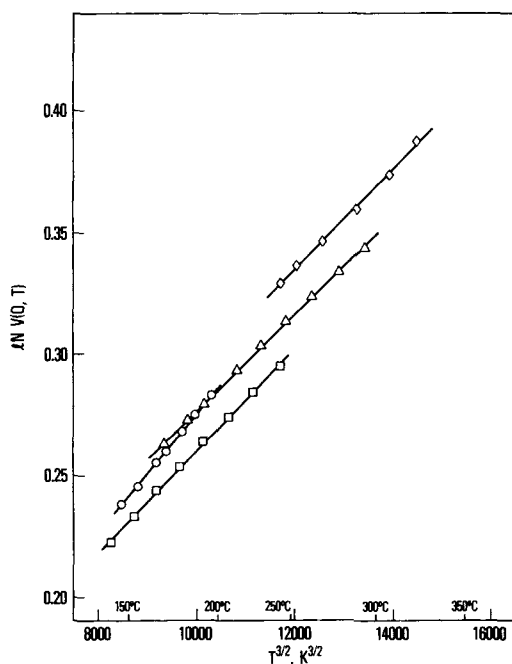


Fig. 1. Zero pressure log volume vs. $T^{3/2}$ for several crystalline polymers: (○) HDPE; (△) PP; (□) poly(butene-1); (▽) poly(4-methylpentene-1).

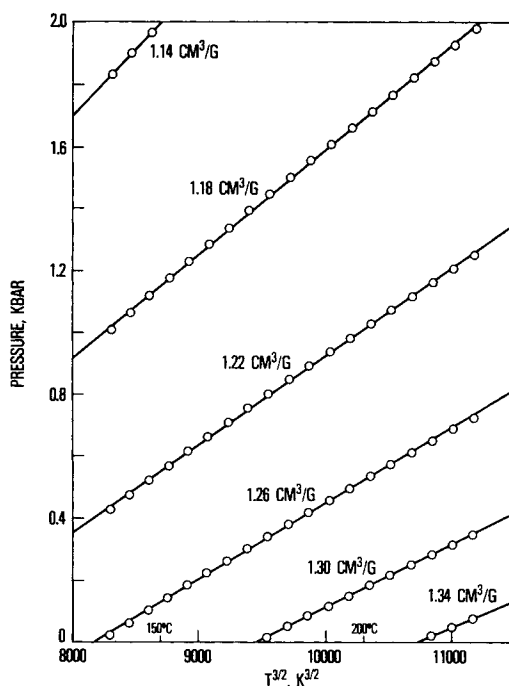


Fig. 2. Pressure vs. $T^{3/2}$ at constant volume for high density polyethylene: (O) experimental values; (—) this work.

Rather than determining V_0 and T_0 solely by fitting the $P = 0$ data, better overall agreement with experiment is obtained by fitting V_0 , T_0 , and B_0 simultaneously to all of the data. Using this procedure, values of V_0 , T_0 , and B_0 were determined for 23 polymers, both crystalline and amorphous. The necessary experimental data was taken from the literature. The results for crystalline polymers are given in Table I. The results for amorphous polymers are given in Table II. As can be seen, amorphous polymers tend to have smaller values of V_0 but larger values of B_0 than crystalline polymers. T_0 values are comparable.

Once the reducing parameters for a polymer have been determined, a comparison can be made between measured volumes and those calculated with eq. (8). Measured data is usually plotted in the form of isotherms or isobars rather than at constant volume as in Figure 2. For high density polyethylene liquid, a comparison of experimental⁵ and theoretical isotherms is shown in Figure 3. Within the scale of the figure, there is no discernable difference. Note that at 142.1°C, for example, the liquid phase only exists up to a relatively low pressure before solidification occurs. For the same polymer, a comparison of experimental and theoretical isobars is shown in Figure 4. Again, the agreement is seen to be good.

A quantitative comparison between theory and experiment was made in the following manner. For each polymer, a table of experimental volumes at various temperatures and pressures was prepared, from tabular data if available or equally spaced Tait equation values if not. A similar table of

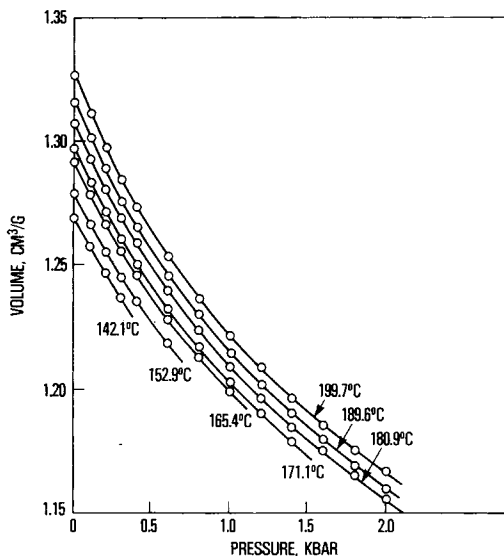


Fig. 3. Volume isotherms for high density polyethylene: (○) experimental values; (—) this work.

theoretical volumes was then calculated. The average of the absolute value of the difference between the two tables, ΔV_{av} , is then an overall measure of the accuracy of the fit of the theory to the data. Values of ΔV_{av} are listed in the last columns of Tables I and II. In most cases, the fit accuracy is $0.0010 \text{ cm}^3/\text{g}$ or better and the worst fit is $0.0014 \text{ cm}^3/\text{g}$ for poly(4-methylpentene-1). For this polymer, a six-parameter Tait equation was needed to fit the data to within $0.0015 \text{ cm}^3/\text{g}$. The experimental accuracy is 0.0020

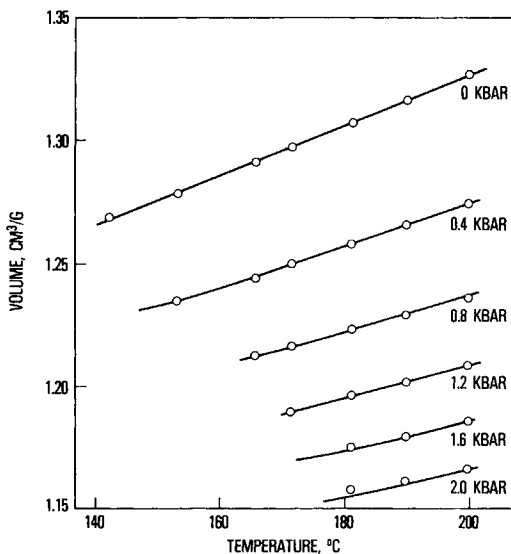


Fig. 4. Volume isobars for high density polyethylene: (○) experimental values; (—) this work.

TABLE I
Reducing Parameters and Fit Accuracy for Crystalline Polymers^a

Polymer	Source (Ref.)	V_0 (cm ³ /g)	T_0 (K)	B_0 (kbar)	ΔV_{av} (cm ³ /g)
1. Polytetrafluoroethylene	6	0.3592	875	36.4	0.0006
2. Poly(ethylene terephthalate)	7	0.6770	1464	41.4	0.0003
3. Polyethylene—high MW	5	1.0220	1122	32.4	0.0006
4. Polyethylene—linear	5	1.0362	1203	28.	0.0005
5. Polyethylene—branched	5	1.0591	1274	26.0	0.0010
6. Polyethylene—low density A	8	1.0726	1361	25.2	0.0010
7. Polyethylene—low density B	8	1.0801	1400	25.1	0.0010
8. Polyethylene—low density C	8	1.0747	1376	25.4	0.0009
9. Poly(butene-1)	9	1.0768	1426	21.0	0.0011
10. Polypropylene	9	1.0870	1394	20.5	0.0008
11. Poly(4-methyl pentene-1)	10	1.1178	1423	16.7	0.0014

^a These parameters are valid in the pressure range from 0 to 2 kbar and the temperature range from T_m to 100°C above T_m .

cm³/g. Thus the new equation fits the experimental data as well as the Tait equation, which is to say within the accuracy of the experimental measurements.

DERIVATIVES

Analytical equations of state are valuable not only for interpolation purposes such as to make a constant volume plot, but also for calculating derivatives. From the first derivatives of the volume, the bulk modulus and thermal expansion coefficient can be determined. The isothermal bulk modulus is given by

$$B_T = -V(\partial P/\partial V)_T \quad (15)$$

TABLE II
Reducing Parameters and Fit Accuracy for Amorphous Polymers^a

Polymer	Source (Ref.)	V_0 (cm ³ /g)	T_0 (K)	B_0 (kbar)	ΔV_{av} (cm ³ /g)
1. Polysulfone	11	0.7200	1585	39.7	0.0005
2. Poly(vinyl acetate)	4	0.7376	1156	38.2	0.0002
3. Polyarylate	12	0.7380	1590	37.1	0.0002
4. Polycarbonate	12	0.7436	1473	36.3	0.0005
5. Phenoxy	12	0.7763	1459	42.7	0.0009
6. Poly(dimethyl phenylene ether)	13	0.7840	1307	31.0	0.0003
7. Poly(methyl methacrylate)	5	0.7566	1453	38.4	0.0002
8. Poly(cyclohexyl methacrylate)	5	0.8162	1449	31.4	0.0009
9. Poly(<i>n</i> -butyl methacrylate)	5	0.8535	1284	31.0	0.0014
10. Polystyrene	14	0.8732	1581	29.7	0.0005
11. Polyorthomethylstyrene	14	0.8870	1590	31.1	0.0005
12. Polydimethylsiloxane	15	0.8782	999	18.5	0.0004

^a These parameters are valid in the pressure range from 0 to 2 kbar and the temperature range from T_g to 100°C above T_g .

From eq. (7)

$$B_T = B_0(V/V_0)^{-5} + 5P \quad (16)$$

At $T = 0$ and $P = 0$, $B_T(O,0) = B_0$. Thus, as stated earlier, B_0 is the value of the bulk modulus extrapolated to zero temperature and pressure. By comparison, from the Tait equation, eq. (9), it follows that

$$B_T(\text{Tait}) = [B(T) + P]\{11.19 - \ln[1 + P/B(T)]\} \quad (17)$$

For high density polyethylene, a comparison of the two bulk modulus equations, eqs. (16) and (17), is shown in Figure 5 as a function of pressure. The results are fairly close. In the absence of direct experimental evidence, there is little to choose between the two equations.

The thermal expansion coefficient,

$$\alpha = (1/V)(\partial V/\partial T)_P \quad (18)$$

from eq. (7), is given by

$$\alpha = (3T^{1/2}/2T_0^{3/2})[1 + (5P/B_0)(V/V_0)^5]^{-1} \quad (19)$$

Note that, at zero pressure,

$$\alpha(O,T) = 3T^{1/2}/2T_0^{3/2} \quad (20)$$

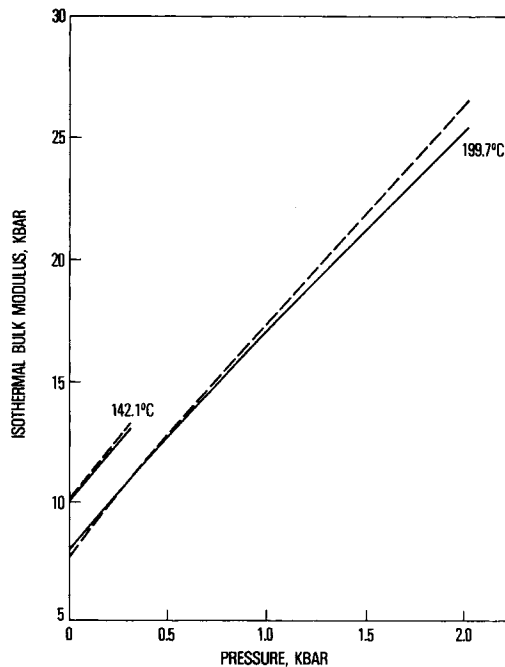


Fig. 5. Bulk modulus isotherms for high density polyethylene: (---) Tait; (—) this work.

a result which follows directly¹² from Simha-Somcynsky theory, eq. (3). By comparison, from eq. (9) it follows that

$$\alpha(\text{Tait}) = \alpha_0 + \frac{[P/B(T)](d \ln B/dT)}{[1 + P/B(T)]\{11.19 - \ln[1 + P/B(T)]\}} \quad (21)$$

For high density polyethylene, a comparison of the two thermal expansion equations, eqs. (19) and (21), is shown in Figure 6 as a function of temperature. Note that, from eq. (21) and as shown in Figure 6, the thermal expansion coefficient used in the Tait equation is a constant at $P = 0$ while eq. (19) predicts an increase with temperature. Also, at higher pressure, eq. (21) leads to a thermal expansion coefficient that decreases with temperature while eq. (19) predicts an increasing thermal expansion. In this regard, eq. (19) is probably more realistic than eq. (21).

A fundamental parameter in equation of state studies is the Gruneisen parameter¹⁶ γ , which is related to the first derivative of the bulk modulus (i.e., second derivative of the volume). If the bulk modulus is a function only of volume,

$$2\gamma = -d \ln B_T / d \ln V \quad (22)$$

The volume can be varied by changing either the temperature or the pressure. In the first case

$$2\gamma_T = -\left(\frac{\partial \ln B_T}{\partial T}\right)_P \left/ \left(\frac{\partial \ln V}{\partial T}\right)_P = -\frac{1}{\alpha} \left(\frac{\partial \ln B_T}{\partial T}\right)_P \quad (23)$$

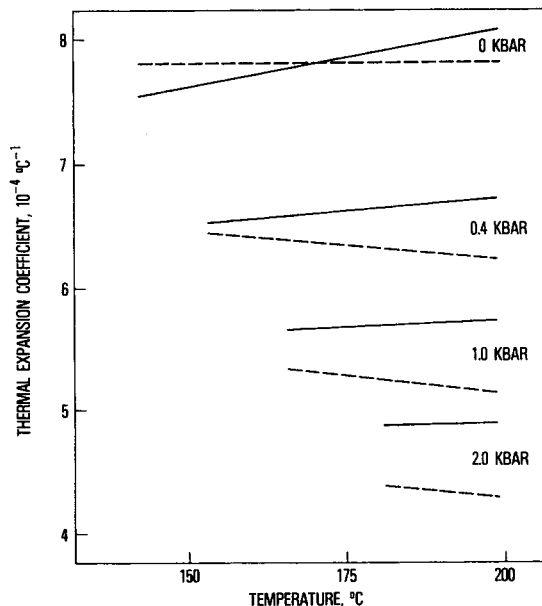


Fig. 6. Thermal expansion coefficient isobars for high density polyethylene: (—) Tait; (---) this work.

In the second case

$$2\gamma_P = -\left(\frac{\partial \ln B_T}{\partial P}\right)_T \left/ \left(\frac{\partial \ln V}{\partial P}\right)_T = \left(\frac{\partial B_T}{\partial P}\right)_T \right. \quad (24)$$

If B_T depends only on volume, $\gamma_T = \gamma_P$.

The Gruneisen parameter determined from the pressure dependence of the bulk modulus using eqs. (24) and (16) is given by

$$2\gamma_P = \frac{5B_0(V/V_0)^{-5}}{B_0(V/V_0)^{-5} + 5P} + 5 \quad (25)$$

At $P = 0$, $\gamma_P = 5$ compared with a value of 5.1 for the Tait equation at all pressures. Thus the pressure dependence in the two cases is very close, as can also be seen in Figure 5.

The Gruneisen parameter determined from the temperature dependence of the bulk modulus using eqs. (23) and (16) is given by

$$2\gamma_T = \frac{5B_0(V/V_0)^{-5}}{B_0(V/V_0)^{-5} + 5P} \quad (26)$$

At $P = 0$, $\gamma_T = 2.5$ compared with a value of b_1/α for the Tait equation, which for high density polyethylene gives a value of 3, not as close to the new equation as was the pressure derivative.

Note that in general for the new equation $\gamma_T \neq \gamma_P$ (specifically $\gamma_P - \gamma_T = 2.5$). This result follows from eq. (16), where B_T is shown to be not a function only of volume.

SUMMARY AND CONCLUSIONS

An empirical PVT equation of state has been presented for polymers in the liquid state. In terms of reduced variables, the equation of state is given by

$$\overline{PV}^5 = \overline{T}^{3/2} - \ln \overline{V} \quad (27)$$

For both crystalline polymers above T_m and amorphous polymers above T_g , calculated volumes agree with measured volumes within the accuracy of the measurements, typically 0.001 cm³/g. These results are comparable to the accuracy of the Tait equation but are obtained using fewer adjustable parameters.

The experimental data used to verify the equation of state is generally available under the conditions used in forming thermoplastics: a maximum pressure of 2 kbar and a maximum temperature 100°C above the T_m or T_g . Comparisons between theory and experiment were made for 23 polymers. The three reducing parameters for all of these polymers are given in Tables I and II.

In addition to the results for volume, equations are presented for the

isothermal bulk modulus, the thermal expansion coefficient, and the Gruisen parameter. For comparison, similar results for the Tait equation are also presented.

It is concluded that eq. (27) is a simple, accurate equation of state for polymer liquids under forming conditions.

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