

A Phenomenology Based Equation of State for Polymer Melts

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SYNOPSIS

An equation of state for polymer melts has been devised from observations on pressure–volume–temperature data for several thermoplastics. The final equation has the form $(P + \Pi - mT \ln(cV^*)) \ln(cV^*) = gT$, where P is pressure; T , absolute temperature, V^* , the volume normalized by van der Waal's volume; and Π , m , g , and c , parameters. Pertinent ancillary relationships include a "universal" bulk modulus vs. a normalized volume function and an observation that the thermal expansion coefficient is solely dependent on pressure. We find that the parameter " Π " is precisely the first derivative of internal energy with respect to volume and is evaluated from the thermal expansion coefficient and bulk modulus. It appears that " Π " is constant over a wide range of conditions. The parameters " m " and " g " are related through the bulk modulus relation. Finally, " c " has been found to be nearly a constant whose action is to change the volume reference state to the melt volume when extrapolated to absolute zero. The "universal" nature of the temperature-reduced bulk modulus and the constancy of Π suggest that the melt state is controlled by entropy rather than by potential energy. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

There are several equations of state available in the literature¹ that have been derived from conceptual models of polymer behavior. They typically utilize reduced temperature, pressure, and volume so that they involve a minimum of three independent, adjustable parameters and usually more. As a result, the best that can be expected of the extant equations is to reproduce pressure–volume–temperature (P–V–T) data once they have been obtained, although the reproduction is usually excellent.

An alternate approach to developing an equation of state is attempted in this article. Rather than trying to fit data to a conceptual model, we will attempt to develop an equation directly from observations on the data. In addition, we expect to extract physical meaning from the equation, as anticipated by Seitz.²

EXPERIMENTAL

P–V–T data were obtained in the same manner as previously reported.³ Five polymers have been investigated. The descriptions, abbreviations, and van der Waal's volumes of the materials studied are given in Table I.

All samples were dried in a vacuum oven for 4 h at 20 K below their glass transitions before measuring. Volume data were taken at 5 K and 10 MPa increments from 300 to about 550 K and 0–200 MPa, respectively.

EXPERIMENTAL

P–V–T data for all polymers are shown graphically in Figure 1(a)–(e), all showing the transition triangle in passing from the glass to the melt. From now on, we will only consider data that is unequivocally in the melt domain. Thus, we will ignore data in the transition region as well as the glass.

All derived quantities were obtained by taking differences directly from the data. Since we are

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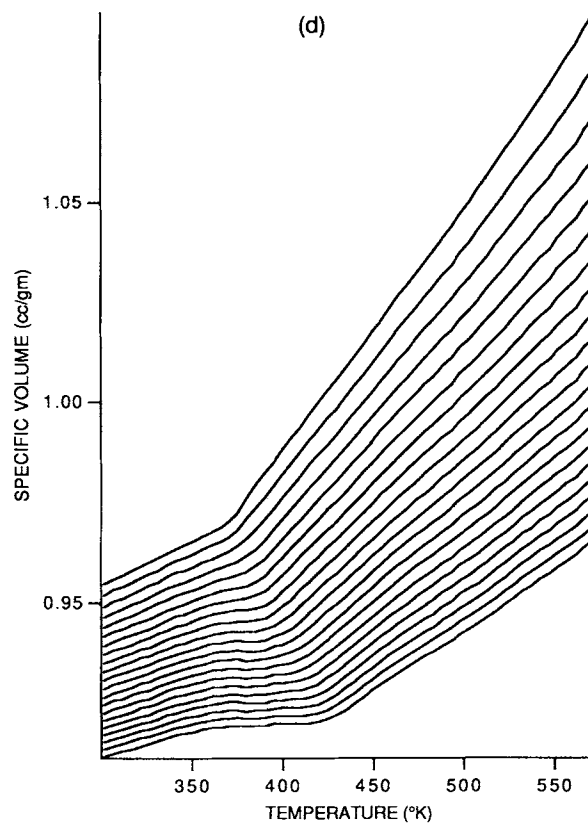
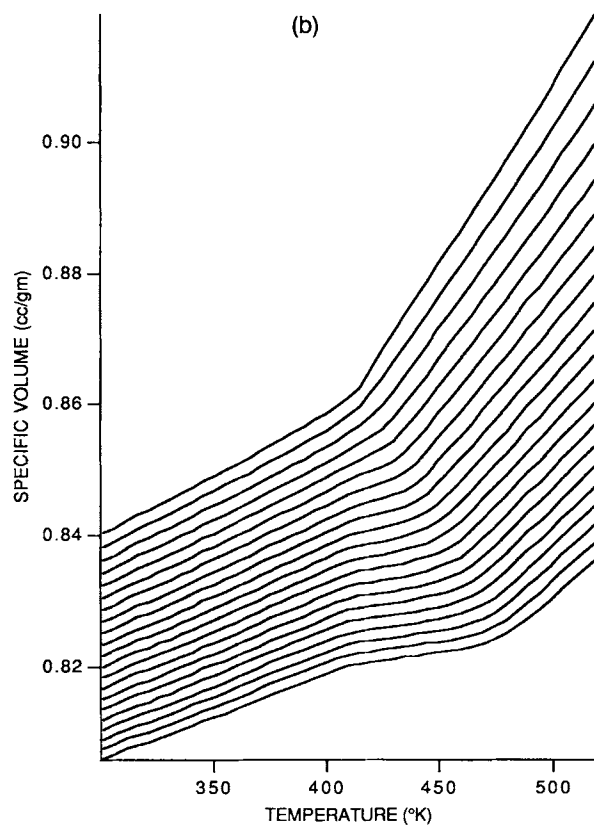
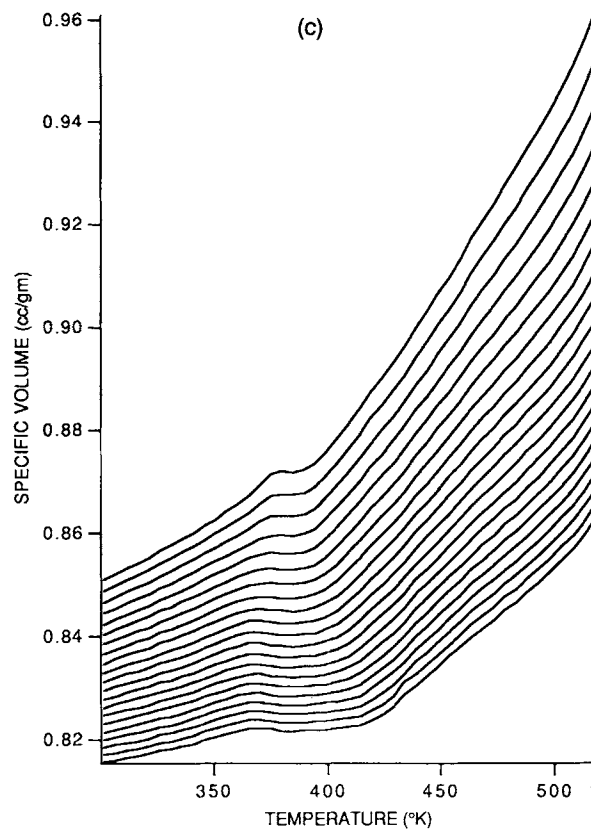
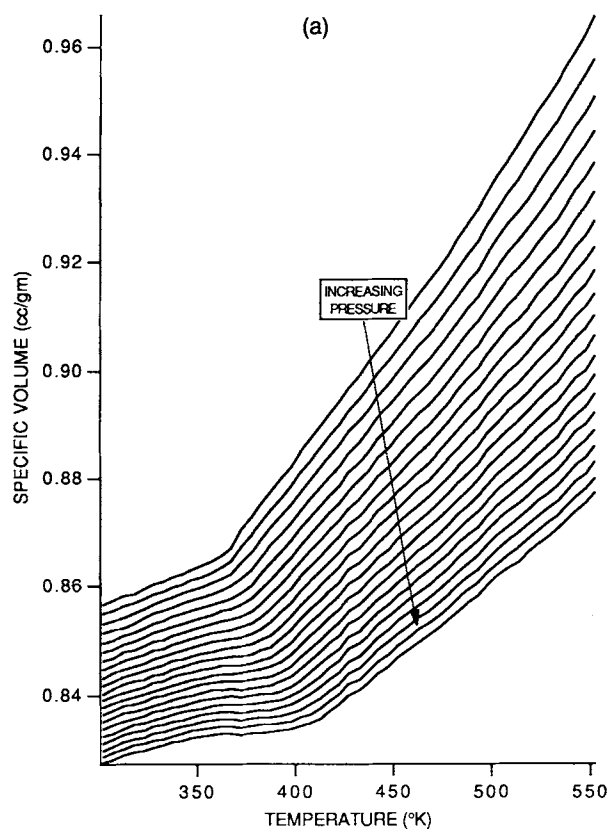


Figure 1 (a) P-V-T data for phenoxy resin (PHEN); (b) P-V-T data for polycarbonate (PC); (c) P-V-T data for poly(methyl methacrylate) (PMMA); (d) P-V-T data for polystyrene (PS); (e) P-V-T data for poly(styrene-*co*-acrylonitrile) (SAN).

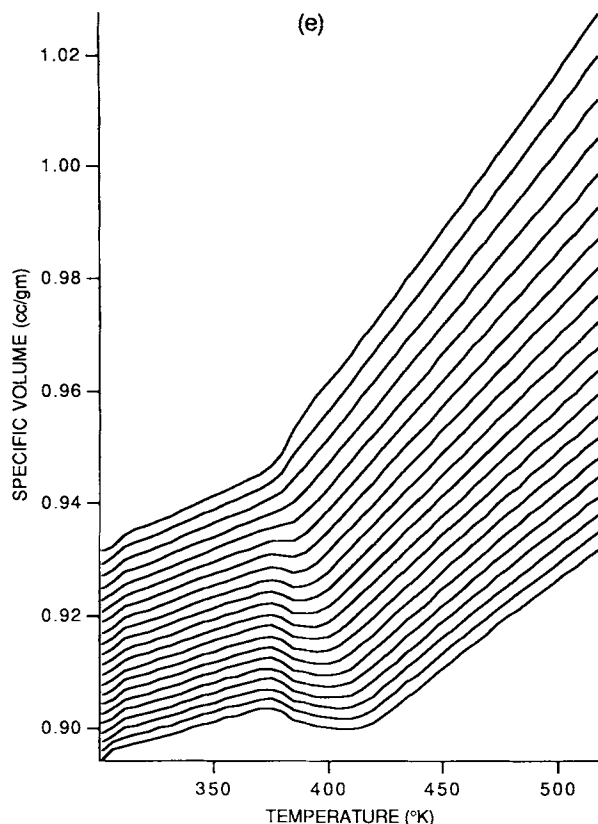


Figure 1 (Continued from the previous page)

dealing with small differences of large numbers, it is not surprising that there is a great deal of scatter in the values. It was felt that this method is preferable to using smoothed data as several attempts

Table I Van der Waal's Volumes and Abbreviations for the Polymers

Material Description	Abbreviation	Van der Waal's Volume (cc/g)
Polystyrene (Styron TM 685D)	PS	0.605
Polycarbonate (Calibre TM 300-10)	PC	0.536
Poly(methyl methacrylate) (Plexiglas TM)	PMMA	0.561
Phenoxy resin (PKCG TM)	PHEN	0.572
Poly(styrene-co-acrylonitrile) (Tyril TM 880-30 wt % AN)	SAN	0.606

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to do so generally introduced unacceptable artifacts, especially at the extremes of the volume data.

There are two primary observations made on the derived quantities. Figure 2 shows the thermal expansion (β) coefficients for polystyrene at several pressures. In spite of the scatter, this is a reasonable demonstration of sensitivity to pressure and insensitivity to volume and, by inference, to temperature also. Figure 3 shows the dependence of bulk modulus on volume as well as the reduction of bulk modulus by absolute temperature. Departures upward from the superimposed curves indicates the onset of the glass transition region. Notice that in both figures the abscissa is specific volume divided by specific van der Waal's volume. Values for van der Waal's volume were obtained from standard tables.⁴

We also found that the bulk modulus (B) behavior was very nearly the same for all polymers tested. This is shown in Figure 4. The volume spread is $\pm 2\%$, which opens the possibility that the curves are really identical. To demonstrate this possibility, the curves were proportioned to give equal volumes at one B/T (modulus over temperature) value. Figure

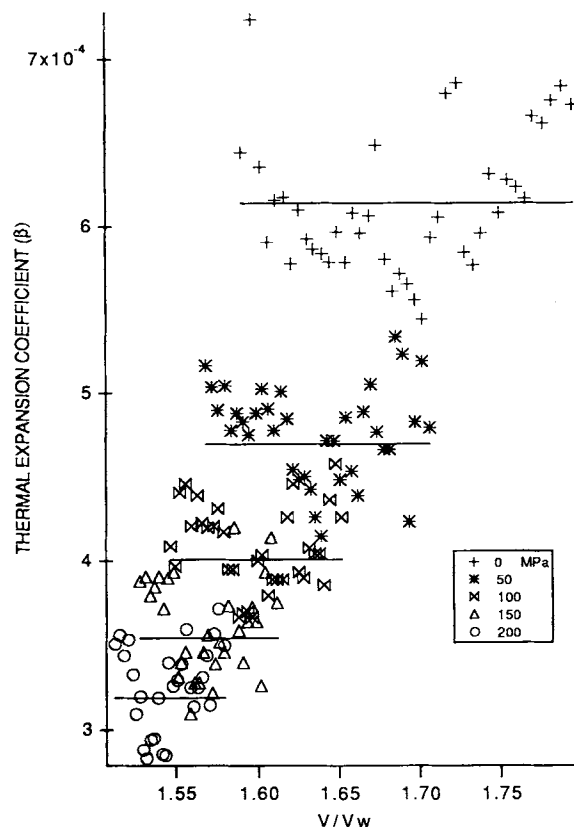


Figure 2 Thermal expansion coefficients for polystyrene (PS) at various applied pressures.

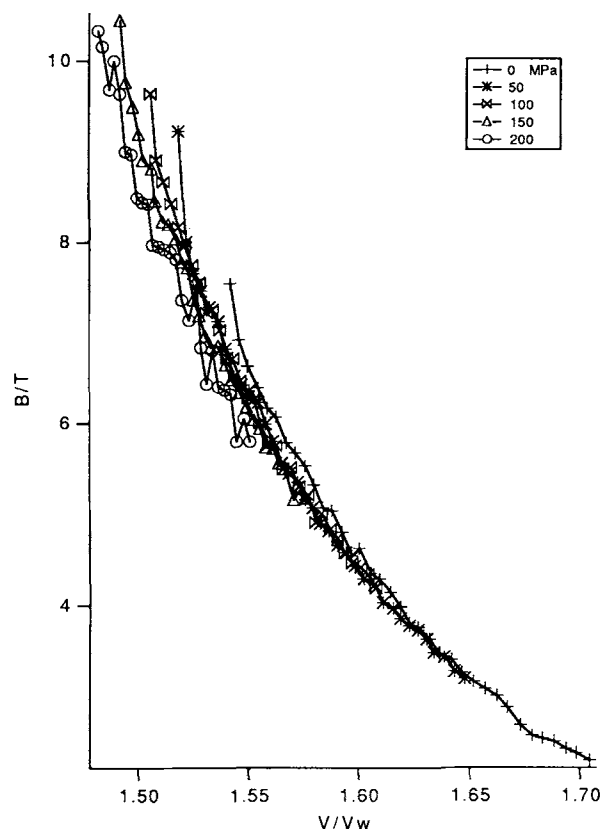


Figure 3 Temperature-corrected bulk moduli as a function of normalized specific volume for phenoxy resin.

5 shows the shape identity and thereby suggests that the spread in the curves is due to volume errors, either in the initial density measurements or in the values for van der Waal's volumes.

Derivation of the Equation of State

This derivation is based on the two observations presented in the previous section. The first observation is that the thermal expansion coefficient is a function of pressure only. The second observation is that B/T (bulk modulus divided by temperature) is a function of volume only, viz.:

$$\beta = \frac{1}{V} \left(\frac{\delta V}{\delta T} \right)_P = \left(\frac{\delta \ln V}{\delta T} \right)_P = f(P) \quad (1)$$

and

$$B/T = \frac{1}{T} \left(\frac{\delta P}{\delta \ln V} \right)_T = f \left(\frac{V}{V_w} \right) \quad (2)$$

We solve eq. (1) to give

$$\ln(cV^*) = Tf(P), \quad (3)$$

where V^* is V/V_w . Equation (3) is of the form presented by Tait⁵ except that the temperature multiplier is a function of pressure and not a constant. We next turn our attention to the pressure function associated with eq. (3). A useful choice is obtained from the equation of state given by Spencer and Gilmore,⁶ viz.:

$$(P + \Pi)(V - w) = R'(T - \tau) \quad (4)$$

where Π is an internal pressure term and R' is similar to the term n^*R in other equations of state (1) for which R is the gas constant and n is a molar concentration. Using Spencer and Gilmore's relationship, we obtain the following relation for the thermal expansion:

$$\left(\frac{\delta \ln V}{\delta T} \right)_P = \frac{R'}{V(P + \Pi)}$$

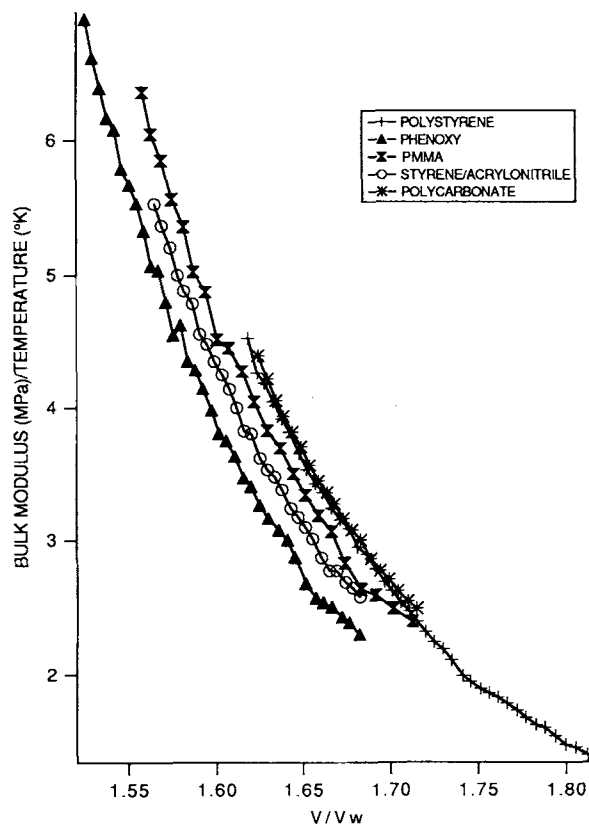


Figure 4 Temperature-corrected bulk moduli at atmospheric pressure as a function of normalized specific volume for all five polymers.

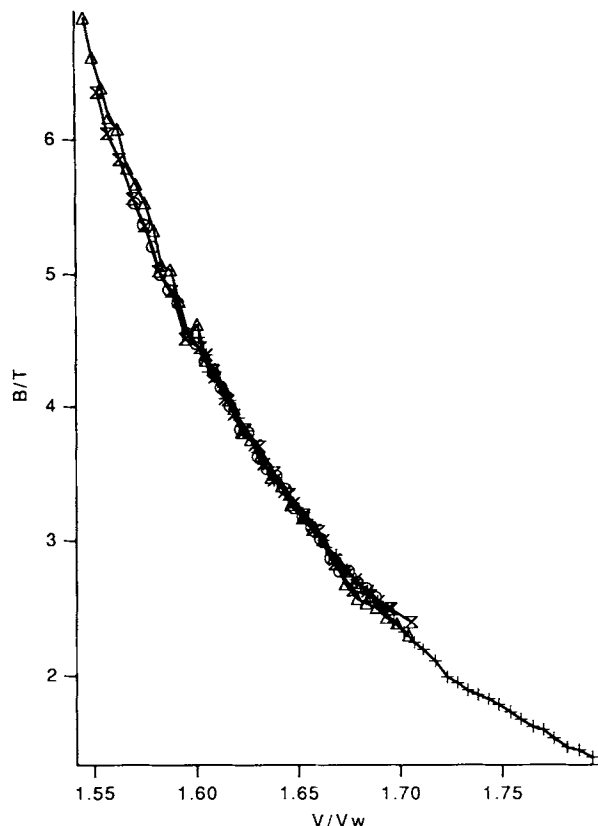


Figure 5 Temperature-corrected bulk moduli as a function of proportioned specific volumes. The data were proportioned so that a value for B/T of 3.75 occurred at a normalized specific volume of 1.627.

Since our primary assumption is that the thermal expansion coefficient is independent of V , we will simply absorb it into a parameter " g " along with R' . We get

$$f(P) = \frac{g}{P + \Pi} \quad (5)$$

We next combine eqs. (1), (3), and (5) and get

$$\frac{B}{T} = -\frac{1}{T} \left(\frac{\delta P}{\delta \ln(cV^*)} \right)_T = \frac{g}{[\ln(cV^*)]^2} \quad (6)$$

This equation gives a reasonable fit to the data in Figure 3 as shown in Figure 6. A much better representation is available if we include a term that reflects the volume sensitivity of internal pressure. This is done by simply adding a constant to eq. (6) and we obtain

$$-\frac{1}{T} \left(\frac{\delta P}{\delta \ln(cV^*)} \right)_T = \frac{g}{[\ln(cV^*)]^2} + m \quad (7)$$

The improvement in data representation is shown in Figure 7. We now arrive at our equation of state by solving eq. (7) to give

$$[P + \Pi - mT \ln(cV^*)] \ln(cV^*) = gT \quad (8)$$

RESULTS

We now have an equation with four adjustable parameters. This number can be reduced by applying eq. (7) one more time. The data in Figure 5 were proportioned to give a normalized volume of 1.627 at a value for the temperature-reduced bulk modulus of 3.75. When these values are inserted, we get

$$m = 19.69g - 3.75 \quad (9)$$

We can now determine a best fit with the remaining three parameters. This produces the results shown in Figure 8(a)–(e). The values for the parameters used are given in Table II.

Figure 8(a)–(e) each have five lines of data. Each line corresponds to a different applied pressure so

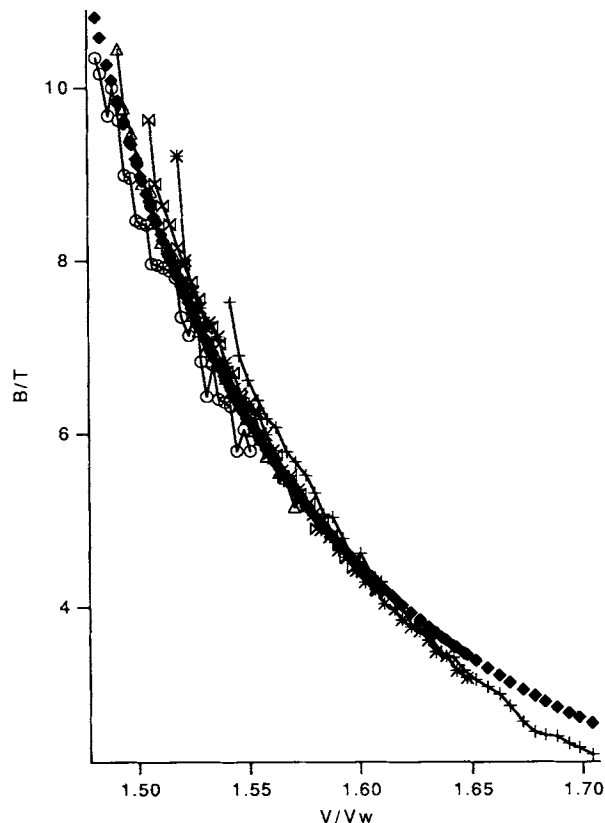


Figure 6 Equation (6) fit to the bulk moduli for phenoxy resin.

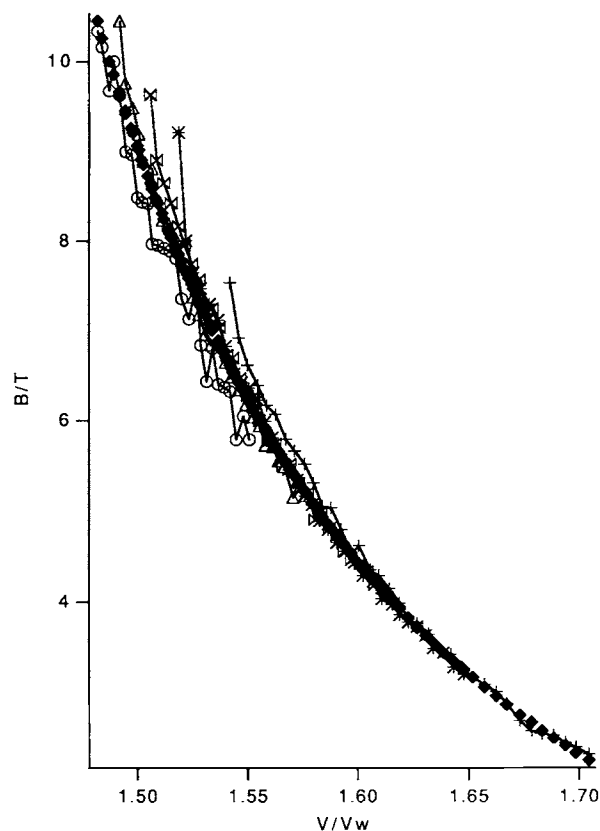


Figure 7 Equation (7) fit to the bulk moduli for phenoxy resin.

that the equation is shown to reproduce the full range of data up to 200 MPa within 0.4%.

DISCUSSION

First note that the values for “*c*” are nearly the same for the five polymers. The average value is 0.774. In a previous article,³ it was shown that the proper reference volume for polymer glasses is the volume at absolute zero. Seitz² found that the melt

Table II Parameter Values Used for Figure 8(a)–(e)

Material	Π (MPa)	c	g (MPa/K)
PS	320.6	0.7672	0.1867
PC	430	0.7621	0.2031
PMMA	501	0.7853	0.2258
PHEN	458	0.7809	0.2050
SAN	377	0.7747	0.1934

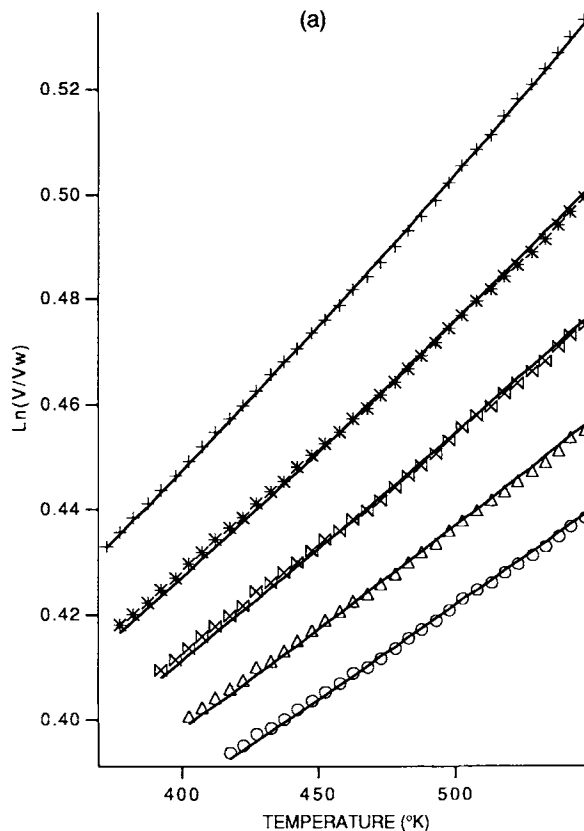


Figure 8 (a) Equation (8) fit to P–V–T data for PHEN. (b) Equation (8) fit to P–V–T data for PS. (c) Equation (8) fit to P–V–T data for PC. (d) Equation (8) fit to P–V–T data for PMMA. (e) Equation (8) fit to P–V–T data for SAN.

volume extrapolated to absolute zero is 1.27 times van der Waal's volume. The reciprocal is 0.787, which is acceptably close to the average value found for “*c*.” The constant “*c*” may also be interpreted in terms of a hard-sphere limitation such as suggested by Flory et al.⁷ Thus, we arrive at the suggestion that the proper reference state for polymer melts is the volume that the polymer would have at absolute zero if it were a melt all the way down. It would be helpful if we could say that “*c*” is definitely a universal constant, but this may or may not be true. There is uncertainty about precision in the values for van der Waal's volumes, and since there may well be some inaccuracy as well, I did not treat “*c*” as a universal constant. Its value was allowed to float.

The parameter “ Π ,” as expressed in eq. (8), can be shown to equal $(T\beta B - P)$. We recall the thermodynamic definition of pressure,⁸ viz.:

$$P = T\beta B - \left(\frac{\delta U}{\delta V} \right)_T$$

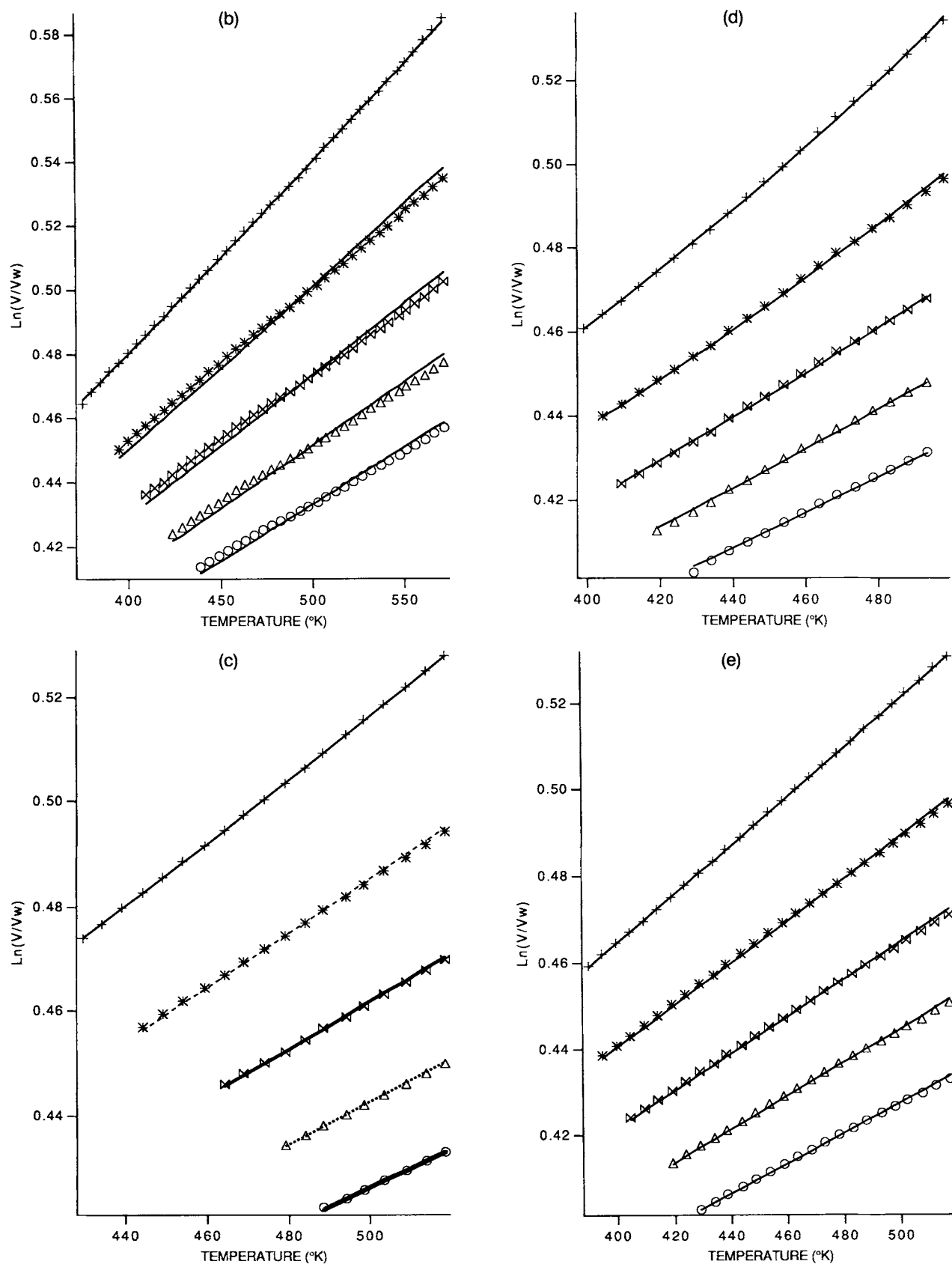


Figure 8 (Continued from the previous page)

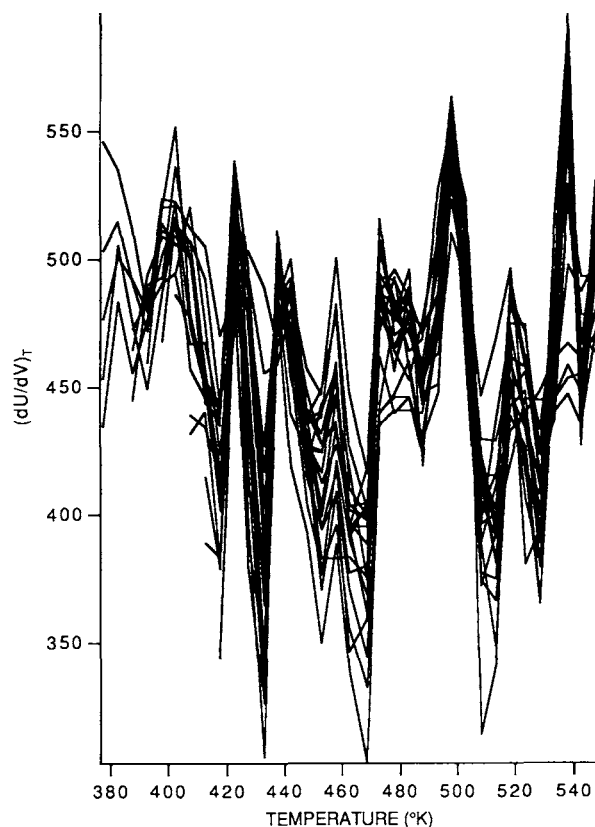


Figure 9 First derivative of internal energy with respect to volume $[(\delta U/\delta V)_T]$ for phenoxy resin.

where U is the internal energy of the system, and find that

$$\left(\frac{\delta U}{\delta V}\right)_T = \Pi \quad (10)$$

Values for the energy derivative are shown in Figure 9. There is a great deal of scatter, but the values are sufficiently well clustered that they may well be constant. This is especially valuable when we realize that " Π " can be evaluated directly from the data without a parametric fit. Actually, the values for " Π " in Table II were obtained by averaging the values derived from the data and not from allowing the value to float.

If " Π " is truly constant, then from the definition the thermodynamic equation of state⁸ we find that the bulk modulus for polymer melts is entropy-controlled rather than energy-controlled, viz.:

$$B = V\left(\frac{\delta^2 U}{\delta V^2}\right)_T - VT\left(\frac{\delta^2 S}{\delta V^2}\right)_T \quad (11)$$

and from eq. (10) above, we get

$$\left(\frac{\delta^2 U}{\delta V^2}\right)_T = 0$$

so that

$$B = -VT\left(\frac{\delta^2 S}{\delta V^2}\right)_T$$

There is some consistency in this observation since the distortional moduli (shear and tensile) are entropy-controlled in the melt or rubbery state.⁹

We finally note that the parameter " g " varies in a manner similar to " Π ." A preliminary trial that related " g " to " Π " gave a fair reproduction of the data, but not as good as allowing it to float also. So, we have the scenario that the parameters in eq. (8) may well boil down to one independent, material-specific parameter " Π ," which might be evaluated by measuring thermal expansion coefficients and bulk moduli via other techniques. To prove or disprove this contention will require more accurate, more precise data than are currently available.

Several of the observations made in this article are similar to those already published. As an example, eq. (6) above is similar in form to that given by Hartmann and Hague.¹⁰ In addition, the work of Dee and Walsh¹¹ anticipates an analogous relationship between " Π " and " g ." These latter two references base their volume functions on the Lennard-Jones 6-12 potential. If, as asserted above, the bulk modulus is controlled by entropy, it suggests that even though the operative relationship may have the Lennard-Jones form, it cannot have the classical Lennard-Jones interpretation. Consider that the abscissa in Figures 3-6 is simply the relative unoccupied volume of the polymer plus one. This says that these polymer melts are nearly identical when compared on a free-volume basis. In addition, it says that the energy parameter in the Lennard-Jones function is either the same for all polymers or we must look for an interpretation based on kinetic rather than potential energy.

CONCLUSIONS

A new equation of state has been devised from observations on pressure-volume-temperature (P-V-T) data for five thermoplastic polymers. The equation involves van der Waal's volumes plus four additional parameters. Of these four, two have been

related to each other via a "universal" relationship between bulk modulus and relative free volume. The other three parameters have been analyzed as follows:

The parameter " c " transforms the volume reference state from a normalized specific volume to the extrapolated melt volume at absolute zero. It may be a universal constant, but we will need more accurate values for the various types of volume to be sure.

The parameter " g " is similar to the parameter " nR " in several other equations of state. It may also relate to the parameter " Π ."

If the other two parameters have the relationships expressed above, then " Π " will be the only independent parameter in the equation. " Π " can be evaluated directly from P-V-T data or it might be evaluated from simpler measurements. The value for " Π " has been equated with $(\delta U/\delta V)_T$ and is constant within the accuracy of these experiments.

There is the inference in this work that the polymeric melt state is controlled by entropy alone. Thus, the volumetric function that describes the polymeric melt state should be based on kinetic rather than on potential energy considerations.

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cisive discussions. Special thanks go to E. Eidsmoe who wrote a computer code for converting P-V-T data into the derived values that were used in this work.

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