

Pressure–Volume–Temperature Relationships of Solid and Molten Polypropylene and Poly(butene-1)

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Synopsis

Experimental data on the dependence of the specific volume on temperature and pressure (PVT data) to 2000 kg/cm² of isotactic polypropylene and isotactic poly(butene-1) are reported and discussed. The temperature range covered is 30–297°C for polypropylene and 30–246°C for poly(butene-1), thus encompassing the solid and molten states of both materials. An empirical equation of state based on the Tait equation can be fitted to the melt data of both materials. The coefficients reported reproduce the measured specific volumes with a standard deviation of less than 0.001 cm³/g.

INTRODUCTION

In this paper experimental data on the dependence of the specific volume on temperature and pressure (PVT data) of the two polyolefins polypropylene and poly(butene-1) are presented and discussed. Data were taken at pressures to 2000 kg/cm²,[†] and the temperature range extended from 30°C to well above the crystalline melting ranges of these two materials. While PVT data are certainly of inherent interest to the polymer scientist and engineer, the primary purpose of this work was to generate data for a comparison¹ with the Simha-Somcynsky² hole theory of polymeric liquids, together with data on other polyolefins, namely, linear^{3–5} and branched^{3–6} polyethylenes and poly(4-methylpentene-1).⁷

The author knows of no PVT data on poly(butene-1), whereas the available data on polypropylene are so limited that extensive new measurements using modern equipment seemed warranted. Foster et al.⁸ reported data on both solid and molten polypropylene to 618 atm and 250°C. Semjonow⁹ gives just a few isolated points in the melt to 1400 kg/cm², and Dupp¹⁰ graphically displays the PVT relations of two polypropylenes based on unpublished data by Knappe at the Deutsches Kunststoff Institut, Darmstadt, Germany. In a study of the melting of polypropylene under pressure, Baer and Kardos¹¹ have published three isobars at 320, 620, and 1000 atm. Their specific volumes are about 15% lower than those of the other investigators.

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[†]Pressures are reported in units of kg/cm² (kilogram-force per cm²). Other units may be obtained as follows: 1 kg/cm² = 9.80665 × 10⁴ N/m² = 9.80665 × 10⁴ Pa = 0.980665 bar = 0.967841 atm = 14.223 psi.

EXPERIMENTAL

Commercial samples of polypropylene (PP) and poly(butene-1) (PBT) made by Chemische Werke Hüls, Marl, Germany, were used in this work. The PP was Vestolen P 6200. It is a highly isotactic homopolymer of high molecular weight; according to the manufacturer, the viscosity-average molecular weight is 5.7×10^5 and the melt index is 0.35 g/10 min at 230°C and 2.16 kg load. Sample pellets were annealed at 150°C for 2 hr. The density after annealing was 0.906 g/cm³ at 23°C. The PBT was Vestolen BT 8000, also a highly isotactic polymer of high molecular weight (viscosity-average molecular weight about 1.8×10^6 , melt index 0.1 g/10 min at 190°C and 2.16 kg load). Its density after annealing at 110°C for 2 hr was 0.913 g/cm³ at 23°C. This density and DTA melting curves indicate that the crystalline portion of this PBT was essentially 100% form I (rhombohedral).

The apparatus used for this work has been described in detail.¹² It consists of a sample cell containing the sample and mercury as a confining liquid. A flexible bellows closes off one end of the sample cell. The linear motion of this bellows resulting from a pressure and/or temperature change is measured by a linear variable differential transformer, and this information is used to calculate changes in specific volume of the sample with respect to a standard state, at which the absolute sample specific volume is known. The absolute accuracy of specific volumes determined with this apparatus at pressures to 2000 kg/cm² is $1-2 \times 10^{-3}$ cm³/g up to 200°C and better than 4×10^{-3} cm³/g at temperatures to 380°C. Measurements were performed along 21 isotherms between 30 and 297°C for PP, and along 21 isotherms between 30 and 246°C for PBT. Data points were recorded in pressure increments of 100 kg/cm² up to 2000 kg/cm² along each isotherm.

RESULTS AND DISCUSSION

It would be impractical to list the nearly 900 data points recorded in these experiments. Instead, selected isobars obtained by cross-plotting the original (isothermal) data are displayed in Figure 1 for PP and in Figure 2 for PBT. In addition, mathematical fits will be presented, which reproduce the measured melt data to within experimental accuracy. A complete listing of all data, both solid and melt, may be obtained from the author. The polypropylene data of this work agree to within 1% with those of Knappe (as reported by Dupp¹⁰), and they are a maximum of 2.7% higher than those of Foster et al.⁸

The zero-pressure isobars show a distinct end of the zero-pressure melting interval (T_M) at 170°C for PP and at 133°C for PBT. The melting point of PBT is in complete agreement with results from DTA work and thermo-optical analysis (TOA). In the case of PP, both DTA and TOA yield a somewhat lower melting point of 167°C. This agreement is judged to be satisfactory. The zero-pressure isobars of both melts can be fitted to the following expression, representing a constant thermal expansivity $\alpha_0 = 1/V(\partial V/\partial T)_{P=0}$:

$$V(0, T) = V_0 \exp(\alpha_0 T) \quad (1)$$

Numerical values of V_0 and α_0 are given in Table I. Their use in eq. (1) reproduces the measured zero-pressure specific volumes of the melt with a standard deviation of less than 0.001 cm³/g. Figure 3 shows a comparison of the zero-

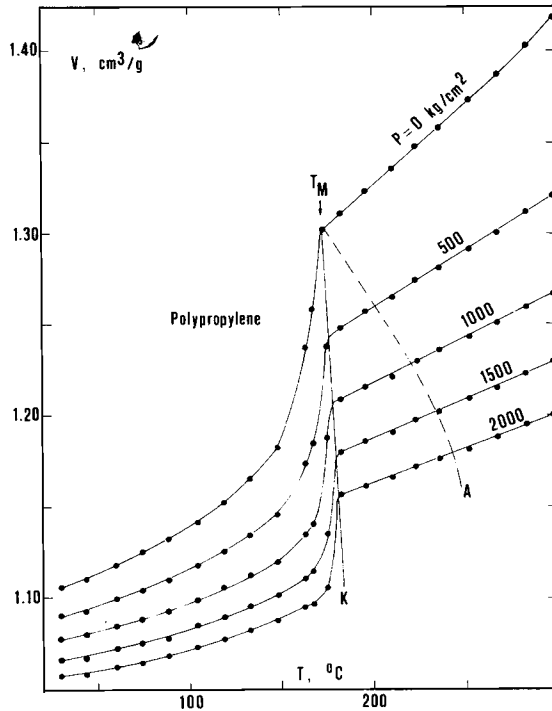


Fig. 1. Selected isobars in the PVT relationship of polypropylene.

TABLE I
Coefficients to be used in Eqs. (1) and (3), determined by Least-Squares Fitting

Coefficient	Polypropylene	Poly(butene-1)
$V_0, \text{cm}^3/\text{g}$	1.1606	1.1417
$\alpha_0, ^\circ\text{C}^{-1}$	6.700×10^{-4}	6.751×10^{-4}
$B_0, \text{kg}/\text{cm}^2$	1520	1708
$B_1, ^\circ\text{C}^{-1}$	4.177×10^{-3}	4.533×10^{-3}

pressure melt isobars of PP and PBT with those of a low-density polyethylene (LDPE)⁶ and poly(4-methylpentene-1) (PMP)⁷ reported previously by the author. It is obvious that all four materials have remarkably similar zero-pressure isobars: both the absolute values of $V(0, T)$ and the expansion coefficients are within 3% of each other for all four samples.

The pressure dependence of the end of the melting interval cannot be measured in the isothermal mode of experimentation employed in this work. When the melt is pressurized isothermally, starting from $P = 0$, the time scale of the experiment is the factor which decides whether crystallization occurs or not. At the pressurization rates of these experiments (about 15 min to reach 2000 kg/cm²), no crystallization is observed for PBT, while PP shows the beginning of crystallization roughly along line K of Figure 1. Also in Figure 1, the pressure dependence of the end of the melting interval reported by Baer and Kardos (isobaric heating experiments) is superimposed on the present data (line A).

The pressure data are best discussed in terms of the so-called Tait equation. This equation describes the volume along an isotherm in terms of the zero-pressure volume $V(0, T)$ and two adjustable temperature-dependent parameters $C(T)$ and $B(T)$, as follows:

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

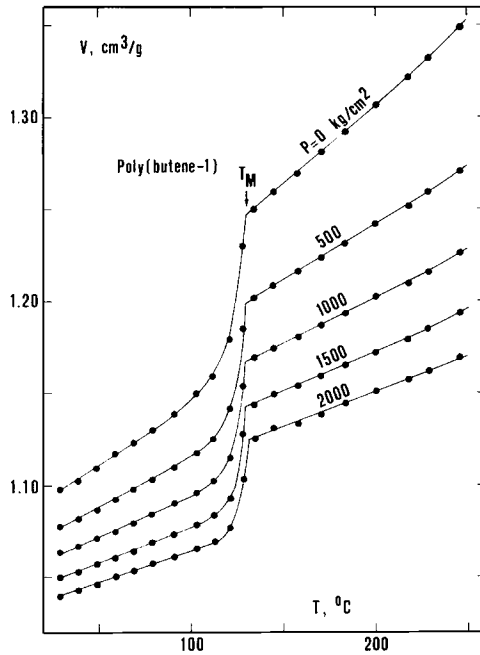


Fig. 2. Selected isobars in the PVT relationship of poly(butene-1).

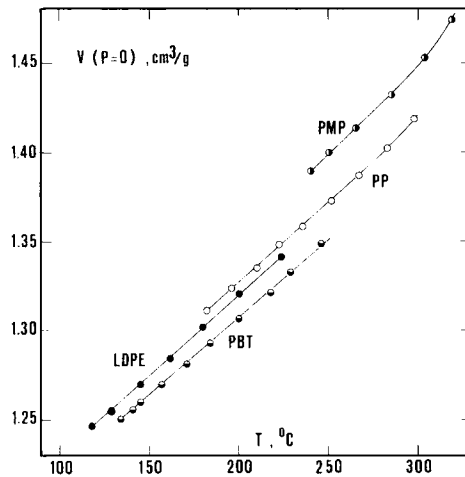


Fig. 3. Zero-pressure melt isobars of low-density polyethylene (LDPE),⁶ polypropylene (PP), poly(butene-1) (PBT), and poly(4-methylpentene-1) (PMP).⁷

This equation has been shown to represent very accurately the isothermal compressibility behavior of a large number of diverse liquids, including polymer melts, and also of polymer glasses (see refs. 4, 12, and 13). The Tait equation does not yield a good representation of the compressibility behavior of semi-crystalline polymers.^{4,6,7,15} This was also found to be the case for solid PP and PBT. For polymer melts, a good fit may normally be obtained using a "universal" value of $C = 0.0894$. The temperature dependence of B is exponential in most cases:

$$B(T) = B_0 \exp(-B_1 T) \quad (3)$$

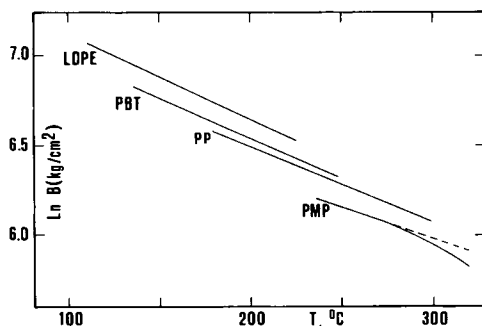


Fig. 4. Temperature dependence of the Tait parameter of polyolefin melts.

Equations (1)–(3) form a complete equation of state of polymer melts. Both PP and PBT melts are well represented by eqs. (1)–(3), with the universal of C . Values of B_0 and B_1 determined by least-squares fitting are listed in Table I. Use of these coefficients, together with the values for V_0 and α_0 also listed in Table I, will reproduce the measured melt specific volumes with a standard deviation of about $0.001 \text{ cm}^3/\text{g}$ for both materials over the whole experimental ranges of temperature and pressure.

Figure 4 shows the temperature dependence of the Tait parameter B of PP and PBT, and also of LDPE⁶ and PMP.⁷ The dashed line drawn for PMP is an estimate of the temperature dependence of B for PMP in the absence of degradation.⁷ In the series LDPE:PBT:PP:PMP we find a decrease in the values of B and also a smaller temperature dependence of B , i.e., smaller values of B_1 . A decrease in B also means an increase in the isothermal compressibility $\kappa = -1/V(\partial V/\partial P)_T$, since the following relations hold:

$$\kappa(P, T) = \{(P + B)[1/C - \ln(1 + P/B)]\}^{-1} \quad (4)$$

In particular at $P = 0$, $\kappa(0, T) = C/B(T)$.

The results on the PVT properties of PP and PBT, together with those of LDPE⁶ and PMP,⁷ have been discussed elsewhere¹ in terms of the Simha-Somcynsky hole theory.²

The author is grateful to Chemische Werke Hüls AG, Marl, Germany for a gift of the samples, and to Paul Schawalter for his competent assistance.

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Received October 5, 1977